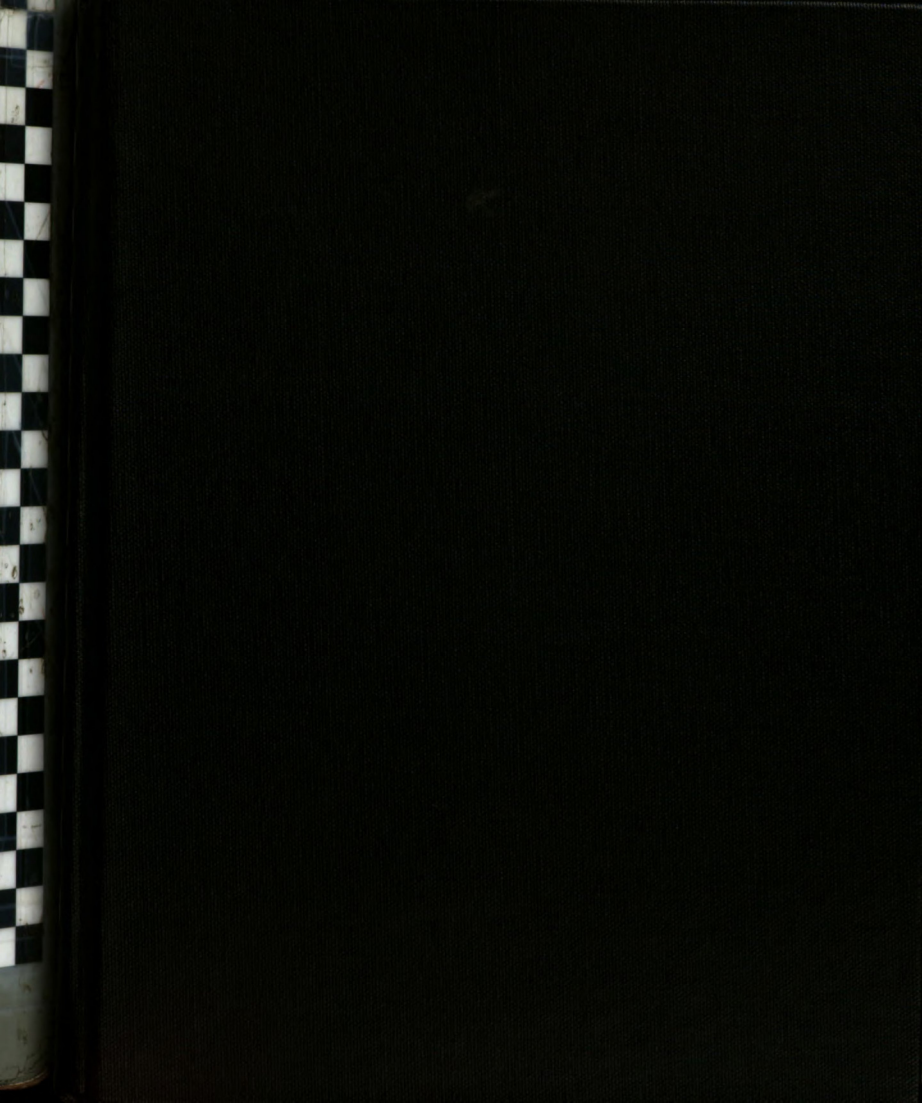






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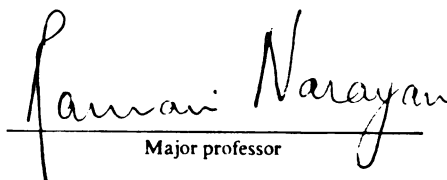
**INTRODUCTION TO PROPERTIES, ENGINEERING,
AND PROSPECTS OF POLYLACTIDE POLYMERS**

presented by

David R. Witzke

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemical Engineering.


Major professor

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**INTRODUCTION TO PROPERTIES, ENGINEERING, AND PROSPECTS OF
POLYLACTIDE POLYMERS**

VOLUME I

By

David R. Witzke

A DISSERTATION

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for degree of**

DOCTOR OF PHILOSOPHY

Department of Chemical Engineering

1997

ABSTRACT

INTRODUCTION TO PROPERTIES, ENGINEERING, AND PROSPECTS OF POLYLACTIDE POLYMERS

By

David R. Witzke

The physical and reaction properties of polylactides were characterized from a bulk production perspective. Emphases were placed on determining how initial *meso*-lactide (major racemization product) affects polylactide (PLA) properties and elucidating the role of the polymerization catalyst in the various bulk reactions. These physical and reaction property results were then combined with pilot plant engineering data to draw inferences about engineering design and resin processing.

The thermal, mechanical, and rheological properties of high molecular weight copolymers of L- and *meso*-lactide were characterized. These include the determination of transition temperatures, heat capacities, thermal decomposition behavior, solid and liquid volumetric properties, linear viscoelastic properties, an empirical rheological constitutive equation, and a lactide-PLA mixture viscosity relationship. In addition, PLA physical aging, lactide-PLA vapor-liquid equilibrium, and lactide properties are discussed in detail.

The major bulk PLA reactions are metal-catalyzed esterification type reactions that include reversible polymerization, initiation of PLA chains by transesterification of hydroxy acid impurities and water with lactide, transesterification among polymer chains (interchange reactions), and hydrolysis of PLA. Undesirable side reactions during

polymerization include racemization, color formation, and non-hydrolytic chain homolysis. The kinetics of reversible lactide polymerization, transesterification, melt hydrolysis, non-hydrolytic degradation, and racemization during polymerization have been determined and characterized mathematically for the stannous ethylhexanoate system.

A pilot plant was designed for continuous lactide polymerization based on the application of the reversible model to the ideal reactor design equations for two CSTRs in series. The reversible polymerization kinetics developed for stannous ethylhexanoate were verified in continuous operation at both pilot and commercial scale. Continuous devolatilization experiments were conducted with a pilot-scale twin screw extruder. Important devolatilization issues include low monomer vapor pressure at process conditions and the competition of melt depolymerization to reform lactide. PLA resin processing degradation was investigated with injection molding tests. Melt degradation was consistent with the developed kinetic model for stannous ethylhexanoate catalyzed melt hydrolysis at process conditions.

Three technical requirements were identified to facilitate PLA application: (1) melt deactivation of catalyst; (2) a manufacturing process having complete stereochemical control; (3) modification of the base thermal, mechanical, and rheological properties of PLA.

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ACKNOWLEDGMENTS

Certainly a dissertation of this scope is not accomplished without a wealth of support. I must first thank my major professor Dr. Ramani Narayan whose guidance and support was invaluable. I thank my committee members: Prof. Krishnamurthy Jayaraman, Prof. Dennis Miller, Prof. James Jackson, Prof. Eric Grulke, Dr. Jeff Kolstad, and Dr. Pat Gruber. Special thanks are due Prof. Grulke and Dr. Kolstad whose suggestions, constructive criticisms, and careful review helped shape and improve this dissertation.

I am thankful for the financial support provided by the MSU Department of Chemical Engineering and the Michigan Biotechnology Institute (first year), the Michigan Polymer Consortium Fellowship (second and third years), and Cargill Inc. (remaining three years part-time). I am indebted to the MSU Composite Materials and Structures Center, the Michigan Biotechnology Institute, and Cargill Inc. for providing laboratory space and equipment. I thank Prof. Dale J. Meier of the Michigan Molecular Institute for providing capillary viscometry equipment that I used to produce data for part of the rheological characterization work presented in Section 2.5.3.

I appreciate the patience and encouragement granted by my Cargill superiors while I finished my dissertation during evenings and nights after work, weekends, and holidays: Mr. Paul McWilliams, Mr. Pete Hawthorne, Dr. Rod Fisher, Dr. Jeff Kolstad and Dr. Pat Gruber. I thank current and former MBI/MSU polymer scientists in Prof.

Narayan's group for their help in various ways: Dr. Lie Nie, Mr. Amit Lathia, Mr. Mohan Krishnan, Mr. Dimitri Argyropoulos, Dr. Steven Bloembergen, and Dr. Zhongxiao Chen. I am especially grateful to Mr. Mike Rich, the MSU CMSC professional lab manager, for making time to answer my numerous polymer analysis questions and providing access and expert support to state-of-the-art polymer analysis and processing equipment. I am grateful to the following Cargill colleagues for their varied assistance: Dr. Robin Eichen-Conn, Mrs. Terri Dainsburg, Mr. Karl Luedescher, Mr. Randy Mazzocchi, Mr. Donavon Kirschbaum, and Mr. Mark Hartmann. I wish to thank former MBI colleagues Dr. Dave Glassner, Mr. Tom Nelson, and Mr. Todd Ireland. I thank the Cargill PLA operations team under the direction of Mr. Ron Borchardt for their assistance in implementing the experimental designs I established to produce the data in Sect. 4.2-4.3.

I am extremely grateful to the following who contributed directly to this work by performing experiments and providing data that were analyzed in this dissertation: Mrs. Beth Pumpllin, Ms. Kris Butts, and Mr. Steve Morse of MBI; Mrs. Nancy Buehler, and Mr. Eric Hall of Cargill. I was fortunate to acquire funding to briefly acquire the services of MSU students Beth, Kris, and Steve to assist in my work. Kris and Steve were instrumental in obtaining the PLA volumetric property data presented in Sect. 2.3. Beth made numerous contributions including characterizing PLA processing behavior, and performing thermal and mechanical property analyses (data in Sect. 2.2.1, 2.2.4, and 2.4). Nancy Buehler polymerized the PLA samples that I processed to determine the linear viscoelastic properties in Sect. 2.5.1. Nancy also performed capillary viscometry that contributed viscosity data and PLA melt hydrolysis data reported in Sect. 2.5.2 and 3.5.

Both Nancy Buehler and Eric Hall performed experiments that provided PLA water sorption data that I used to produce the PLA-water phase equilibrium curve presented in Sect. 1.2.3. I greatly appreciate the generous laboratory assistance Eric Hall provided. In particular, Eric helped me develop the vial polymerization technique that I used to generate reaction kinetics in Chapter 3.

I wish to express my gratitude towards my parents, grandparents, and brother for their understanding and support during these six hectic years that saw me change residences 8 times (4 interstate moves). I thank my future wife Floriza Mangahas (*buhay ng aking buhay*) for her loving support and encouragement.

David R. Witzke

Oskaloosa, IA
July, 1996

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Chapter 1 Introduction To Polylactides

1.1 Biodegradable Polymers as Commodity Thermoplastics

A growing environmental awareness and new environmental regulations in the United States, Europe, and Japan have created a substantial driving force for the incorporation of biodegradable plastics into our waste management programs. However, current performance and cost barriers must be overcome before biodegradable plastics become commonplace in our society.

1.1.1 Potential Role of Biodegradable Plastics in Solid Waste Management

Waste disposal pressures are felt greatest in Japan and Western Europe where the population density is over ten times that of the US: (in persons per square mile) Japan, 859; Germany, 595; Netherlands, 938; England, 961; and US, 70.¹ In the United States approximately 80% (volume basis) of municipal solid waste (MSW) is landfilled, 10% MSW is recycled or composted, and 10% MSW is incinerated.² By contrast, Japan incinerates 70% of its general waste.³ Plastics account for approximately 20%, by volume, of the US MSW.²

Landfilling retards biodegradation by entombing waste in a moisture-free anaerobic system² and is a poor choice for the disposal of such items as yard waste, food

waste, paper, and biodegradable plastics. The use of incineration in the US and EC as a waste disposal means has been limited by both cost and safety concerns over emissions and ash disposal.^{2,4} Recycling is an important component of any ecologically sound waste management strategy. However, recycling is limited to materials such as glass, metals, and some plastics and paper that are easily collected and separated into relatively homogeneous components. For example, a significant quantity of paper products are coated with polymers to improve barrier properties and are not amenable to recycling. In addition, the separation of plastics is often difficult, and in many cases recycling leads to plastics that have inferior properties. The composting of biodegradable materials that are not easily recycled, such as yard waste, food waste, some paper products, and single-use biodegradable plastics, is a necessary alternative to landfilling.

Single-use disposable polymer articles represent about 30% of the US polymers market (61 billion lb/yr)⁵ and are a natural target for biodegradable plastics;² the potential US market for biodegradable plastics is estimated at 20 billion lb/yr.⁶ This includes single-use disposable packaging materials, nonwovens (e.g., diapers), consumer goods (e.g., cutlery, cups, plates, razor handles), and paper coatings. With a current US market of 13.7 billion lb/yr, disposable packaging represents the largest portion of the potential biodegradable plastics market and is currently comprised of the following plastics (in billion lb/yr):⁷ high density polyethylene (HDPE), 4.4; low density polyethylene (LDPE), 4.1; polystyrene (PS), 1.6; polypropylene (PP), 1.5; polyethyleneterephthalate (PET), 1.4; and polyvinylchloride (PVC), 0.7.

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Examples of where biodegradable plastics could make immediate impact include applications where biodegradable materials such as paper, food waste, and yard waste are in contact with bioresistant polymers. This waste currently requires separation from the plastic component prior to composting or it is simply sent to landfill instead. The replacement of polyethylene coated paper and PE yard and food waste bags with biodegradable polymers would allow for direct hassle-free composting. Another seemingly ideal market is in agricultural mulch films⁷ where 0.2 billion lb/yr of LDPE are used in the US. The replacement with a biodegradable mulch film would save the farmer from having to collect the non-degradable film from the field.⁷

Biodegradable polymers are of little increased value unless composting infrastructures are developed. The US and Japan are considerably behind Western Europe in the development of a large-scale composting infrastructure.⁸ However, the composting infrastructure in the US is growing as evidenced by the increase in yard waste composting facilities from 651 in 1988, to approximately 2500 in 1992.⁶ Composting is defined as the "accelerated degradation of heterogeneous organic matter by a mixed microbial population in a moist, warm, aerobic environment under controlled conditions".⁶ In the compost environment, biodegradable polymers completely degrade to give carbon dioxide, water, and biomass (humic material and cell mass).⁹ The carbon-rich compost has value as a soil enricher.

The polymeric materials of today are synthetically derived from petroleum (oil). These are primarily hydrocarbon polymers that are intrinsically bioresistant and thus do

not partake in the ecosystem's natural carbon cycle. Their development was based on article performance and cost. However, it is becoming clear that tomorrow's polymeric materials must in addition be designed for their ultimate disposal as well as with consideration for conservation and resource utilization.⁶

Biodegradable polymers can be made from either petroleum (non-renewable) or agricultural feedstocks (renewable; generally in surplus in the US). However, only plastics derived from agricultural resources participate in the ecosystem's biological carbon cycle. The biological carbon cycle is the means by which organic carbon is cycled between atmosphere, plant and animal life, soil, and micro and macroorganisms.⁹ Although important as a solid waste means, biodegradation is in itself not sufficient to assure an ecologically sound use of organic carbon – annually renewable feedstocks must be used as well.

In Figure 1-1 we present a simplified cartoon illustrating the ideal participation of annually renewable resources (corn), biodegradable plastics, and composting in the ecosystem's biological carbon cycle. The cycle starts with the photosynthetic consumption of carbon dioxide and water to produce starch in corn. On maturation the corn is harvested, stored, transported, and finally processed into its basic constituents, including starch, at a corn wet-milling facility. The starch can then be used directly in starch thermoplastics or instead be enzymatically converted to D-glucose (dextrose) to be fermented into bacterial polyhydroxyalkanoates or lactic acid that is further converted to poly(lactic acid). After their intended use the plastics must then be collected and sent to composting facilities along with other biodegradable materials such as paper, yard and

food waste. Composting yields water, heat, carbon dioxide, and compost. The carbon dioxide is recycled to the atmosphere and the compost is plowed into fields for soil enrichment – completing the cycle. In this manner, biodegradable plastics derived from annually renewable agricultural feedstocks become part of "Nature's Recycling System".

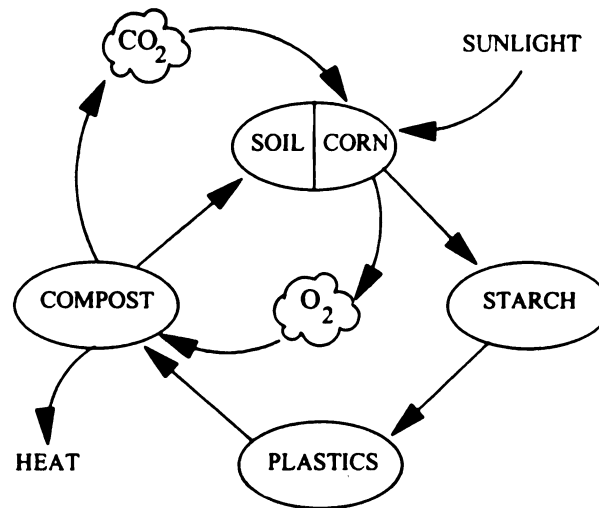


Figure 1-1. The borrowing and recycling back to nature of organic carbon for the production of single-use disposable biodegradable plastics from annually renewable resources, such as corn.

Depending on the duration of corn storage, plastic resin storage, and article use life, the total residence time of organic carbon in the process depicted in Figure 1-1 can be on the order of several years. Thus, we are borrowing organic carbon from the ecosystem to be returned in good condition on a period that is short compared to our lifetime. This is in direct contrast to the taking, and not returning in a useful form, of organic carbon from petroleum resources that developed over millions of years from the conditioning of dead plant and animal decomposition products. Both landfilling and the

use of petrochemical based polymers result in the foreclosure of borrowed organic carbon.

1.1.2 Types of Biodegradable Polymers

There are currently five major types of commercial biodegradable plastics on the market, Table 1-1. All but the starch thermoplastics are polyesters. Three are based on annually renewable resources; two are from petrochemicals. All are fully compostable. Not included are commercial water soluble biodegradable polymers such as polyvinyl alcohol (PVOH) and polyoxyethylene blends (both from petrochemicals).

Table 1-1 Current Commercial Biodegradable Polymers

Polymer	Feedstock
Polylactides (PLA)	Agricultural
Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV)	Agricultural
Starch-based thermoplastics	Agricultural
Polycaprolactone (PCL)	Petrochemical
Poly(1,4-butanediol-co-succinic acid) (Bionolle™)	Petrochemical

The starch thermoplastics generally are difficult to process, have poor water resistance, and are translucent. Despite these limitations starch-based biodegradable

thermoplastics were the first to market and thus far have been the most important commercial biodegradable plastic. Starch-based thermoplastics accounted for the largest share of 1993's 25 million lb/yr biodegradable plastics market in the US, Western Europe, and Japan.⁸ Starch-PCL blends are used for biodegradable bag applications. The PCL imparts greater flexibility and processability to this agricultural/petrochemical blend. Modified starch-based thermoplastics have been developed to improve water resistance and mechanical performance. Such a polymer is being currently marketed by the joint venture between Japan Corn Starch Ltd and the Michigan Biotechnology Institute/GRT under the trade name EverCorn™.

Polycaprolactone (PCL) is the most fully developed biodegradable polymer and is sold by several companies including Union Carbide. PCL is a flexible, translucent, semi-crystalline polymer having somewhat similar mechanical properties as that of polyethylene. However, its utilization as a homopolymer may be limited by its low use temperature owing to its 60°C melting point. This polymer has not been heavily marketed.

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV, has been sold under the trade name Biopol for several years by Zeneca (UK), formerly of ICI and recently purchased by Monsanto (4/96). The valerate provides a below-room temperature glass transition component that imparts toughness to the otherwise brittle PHB polymer. This gives PHBV mechanical properties that more resemble polypropylene than polystyrene. The use of this polymer is limited by its high cost of about \$4/lb (1996). Although currently PHBV is made from bacterial fermentation, Monsanto hopes to use PHBV

technology to express polyhydroxyalkanoates in soybeans and canola.¹⁰ This plastic would literally be harvested and could lower the cost of a PHBV type material.

Bionolle™ is a petrochemical-based biodegradable plastic manufactured by Showa Highpolymer Co, Japan (1994 capacity: 7 million lb/yr).¹¹ Bionolle™ is produced by the metal-catalyzed condensation polymerization of a glycol and a dicarboxylic acid, such as 1,4-butanediol and succinic acid. Diisocyanate is used as a chain extender to achieve high molecular weights. Bionolle™ is a flexible, translucent, semi-crystalline polymer that has properties similar to polyethylene. Having a melting temperature of about 120°C,¹¹ Bionolle has an upper use temperature that is superior to PCL.

Poly lactide or poly(lactic acid) polymers are stiff, brittle, and strong plastics that have mechanical properties and clarity that very closely resemble polystyrene. Unlike the other polymers listed in Table 1-1, polylactides can be transparent and do not support mold growth.³ Both amorphous and semi-crystalline polylactides can be produced from the same feedstock, catalyst, and process. Polylactides are currently being developed by numerous companies including Cargill Inc (US) and Mitsui Toatsu (Japan). Cargill currently operates the worlds largest polylactide facility in Savage, MN (capacity: 10 million lb/yr).

Although still in development stages, the polylactide and Bionolle™ type resins probably represent the greatest long-term potential of any of the biodegradable polymers listed in Table 1-1. The attractiveness of Bionolle™ as a single-use disposable polyethylene replacement would be furthered if it were derived from annually renewable resources instead of petrochemicals; both the glycol and succinic acid monomers can be

produced from agricultural resources. However, the increased value of renewability in addition to biodegradability has yet to be established in the marketplace.

Starch is the chief source of carbohydrate for humans and may be the preferred agricultural feedstock for all of the agriculturally derived polymers in Table 1-1. PHBV and L-lactic acid are produced by the fermentation of D-glucose, which is the hydrolysis product of starch. Although starch is certainly the most important agricultural feedstock for biodegradable polymer production, other potentially important agricultural feedstocks for polymers include: cellulose and lignocellulose (e.g., wood), natural fibers (e.g., kenaf), other polysaccharides (e.g., pectin, chitin), fats and oils (e.g., soybean oil), and proteins (e.g., zein, soy).⁷ Both soy and zein protein based polymers have received considerable research attention by Iowa State University and the Michigan Biotechnology Institute, respectively, but so far there has been no significant commercial developments.

Obviously biodegradable polymers must perform satisfactorily before widespread application can be realized. In addition, their production costs must decrease to become competitive with today's plastics. The acceptable premium that can be charged for attributes such as biodegradability and renewability has yet to be determined. The first large scale test with good performing biodegradable plastics should occur by the turn of the century. Just as the 20th Century marks the development and application of hydrocarbon based polymeric materials, the 21st Century may see the promotion to commodity status of oxygenated biodegradable polymers based on renewable resources.

1.2 Polylactides

1.2.1 Introduction

Possessing both hydroxyl and carboxyl groups, α -hydroxy acids such as lactic acid can be directly converted to polyesters by condensation polymerization. Poly(lactic acid) is prepared by the condensation polymerization of lactic acid. However, the degree of polymerization achieved by the direct condensation polymerization route is insufficient to achieve the good physical properties required for plastics applications. This is because of the low equilibrium constant of lactic acid esterification and the difficulty of water by-product removal in the increasingly viscous reaction mixture. Molecular weights by the direct condensation polymerization of lactic acid are generally less than 10,000 g/mol.

Lactide (144 g/mol) is the dilactone of lactic acid (90 g/mol) produced by the metal-catalyzed intramolecular transesterification of poly(lactic acid). By adding a metal catalyst after the condensation polymerization of lactic acid, the PLA repeat units can be separated in the form of the six-membered ring dimer of poly(lactic acid). Lacking hydroxyl and carboxyl end groups, lactide does not undergo esterification to yield water. Lactide is more volatile than poly(lactic acid) and is collected in high yield by vacuum distillation of the reaction mixture. Lactide is readily converted to high molecular weight polylactide by metal-catalyzed ring-opening polymerization.

The preparation of high molecular weight polylactide is summarized in Figure 1-2. First, lactic acid is heated under vacuum in a high surface area-to-volume process to remove free water and condensation water. After a degree of polymerization of between 2-25 is achieved, a metal catalyst is added and lactide is collected by vacuum distillation.

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After purification of lactide, polylactide is prepared by metal-catalyzed anionic ring-opening polymerization.

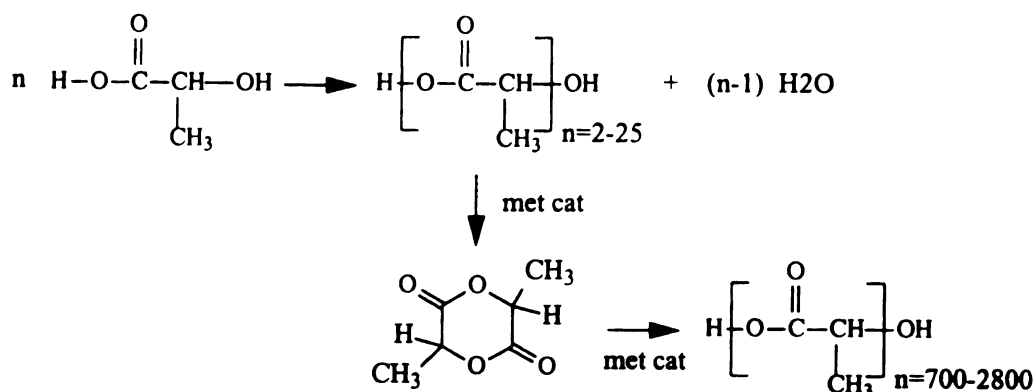


Figure 1-2. Preparation of polylactide from lactic acid.

In concept, high molecular weight PLA is obtained by the separation of lactic acid's alcohol and acid end groups from the 72 g/mol repeat unit. The lactide route presented in Figure 1-2 is basically a two-stage exploitation of LeChatelier's principle: first, the end groups are removed from the repeat units and reaction mixture in the form of intermolecular water until some intermediate end group conversion is achieved (e.g., $n = 10$ (738 g/mol), 90% -OH conversion); second, a catalyst is added and now the repeat units are removed from the end groups and reaction mixture in the form of cyclic dimers that can be easily polymerized (> 99.8% final -OH conversion).

Lactic acid is one of the simplest chiral molecules and exists as two stereoisomers, (*S*) L-lactic acid, and (*R*) D-lactic acid. The small-cap notation (e.g., L) is most common and is based on glyceraldehyde configurational notation. However, L-lactic acid rotates

the plane of polarized light in the opposite direction of L-glyceraldehyde. For lactic acid:

$S = L = (+) = (d)$ dextrorotatory; $R = D = (-) = (l)$ levorotatory.

Having two stereocenters, lactide has four possible stereometric scenarios, RR , SS , RS , and SR . However, RS and SR are achiral superimposable mirror images, and lactide has only three unique isomers: (SS) L-lactide, (RR) D-lactide, and (RS) *meso*-lactide.

L-Lactide and D-lactide are chiral enantiomers and have a diastereomeric relationship with the achiral isomer, *meso*-lactide. The direction of polarized light rotation is opposite for the esters of lactic acid (e.g., (SS) L-lactide and (SS) poly(L-lactide) are $(-)$ levorotatory).

High molecular weight polylactides can be made from any combination of the lactide isomers and are random copolymers. Depending on the isomer makeup, polylactides can either be semi-crystalline or amorphous. By adjusting the initial distribution of lactides, PLA resins are produced that have different end-use properties. The molecular architecture of the various polylactides are investigated in Section 1.2.4.

Polylactide polymers have the following attributes:

- Biodegradable, compostable
- From annually renewable resources
- PLA is generally recognized as safe (GRAS), Conn et al.;¹² important for food contact
- Biocompatible; hydrolyzes to lactic acid and water
- Incinerates clean (unlike many plastics)¹³ with less than half the heat of combustion³
- Amorphous and crystalline grades made from the same feedstock, catalyst, and process.

- Thermoplastic
- High strength, high modulus plastic
- Transparent
- Makes good quality amorphous and crystalline fibers, fabrics
- Although hydrolytically unstable in long time, PLA has much better water resistance than starch-based plastics.
- Excellent grease resistance, better than conventional plastics
- Unlike many biodegradables, PLA does not support mold growth.
- Good paper adhesion and gloss
- Good printability

However alluring, the physical and chemical properties of polylactides present numerous engineering and application obstacles that must be overcome prior to widespread PLA service. The classification of the current limitations and future prospects of polylactides are a focus of this dissertation.

1.2.2 History and Commercial Development

Although hypothesized and attempted by Bischoff and Walden in 1894, the polymerization of lactide to low molecular weight polylactide was first demonstrated in 1932 by Carothers, Dorough, and van Natta.¹⁴ High molecular weight polylactides were obtained through improved lactide purification¹³ which was patented by DuPont in

1954.¹⁵ However, in lieu of more durable polymers, DuPont shelved polylactides which were unfortunately found to be slowly degradable by moisture.¹³

The first commercial applications of polylactides were biomedical. In 1972, Ethicon Inc. developed medical sutures made of L-lactide and glycolide copolymer fibers that are sold under the trade names Vicryl and Galactin.¹³ These high-strength, resorbable, biocompatible fibers slowly hydrolyze to lactic and glycolic acid. Polylactides have also found use in prosthetic devices (implants) and in controlled-drug-release applications.

The recent explosion in polylactide interest is shown in Figure 1-3 by a plot of the number of published documents versus year of publication since 1966. This curve is further broken down into the number of journal articles and patent activity which sum to make the total. These data are based on a 5/96 Chemical Abstracts Search (ACS) on STN International using 14 CAS registry numbers and 96 synonyms for polylactides. The patent articles include both granted and applied for patents as normally published by the 23 patent offices followed by Chemical Abstracts (e.g., US Pat Office, Eur. Pat Office, Japan Patent Office, World Intellectual Property Org., WO).

Since 1966 there have been 2525 polylactide publications consisting of 1540 journal articles and 985 patents. The period between 1/90-5/96 accounts for nearly 70% of all polylactide publications since 1966. The level of polylactide journal publications began a sharp increase in 1982. Since then, the number of new articles has increased every year except between 1988-1989 where the number remained about the same. The

US has been the biggest contributor to journal articles with 470 and is followed by Japan (239), Netherlands (125), France (124) and the UK (96).

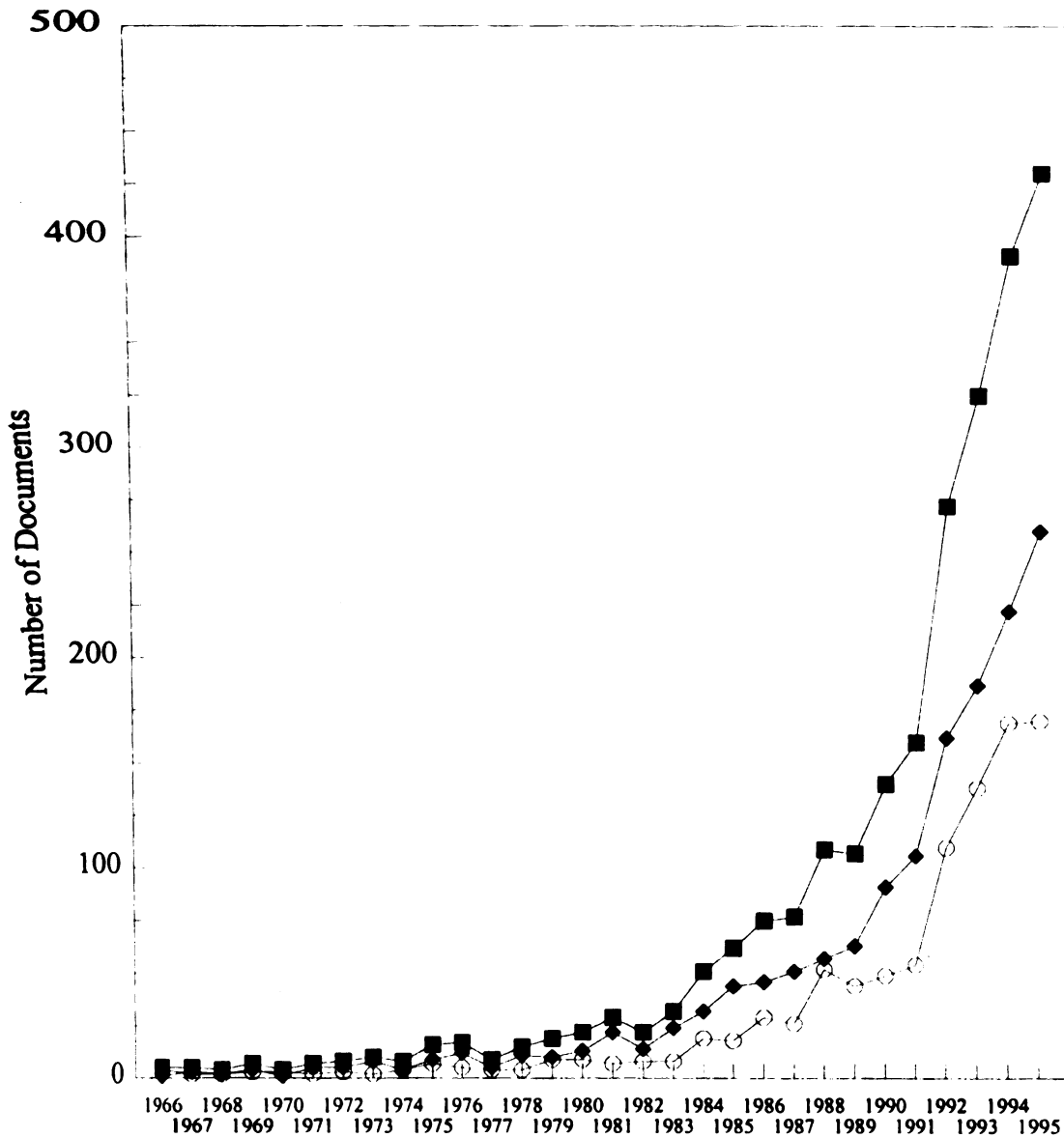


Figure 1-3. Number of polylactide publications versus year of publication (i.e., not cumulative): total publications (■), journal articles (◆), and patent publications (○).

Heavy patent activity began in 1991 and now nearly 200 new patents are published each year. The following patent offices have the most polylactide patent

publications (country of original application): Japan (295), WO (232), EP (167), US (128) and DE (Germany) (93). Japan accounts for 30% of all polylactide patent publications since 1966.

There are at least five companies aggressively developing polylactides for commercial application, Table 1-2.

Table 1-2 Companies Developing Polylactides

company	PLA production ^a capacity (million lb/yr)	patent ^b activity	integrated through feedstock
Cargill (US)	10	10	yes, corn
Mitsui Toatsu (Japan)	2-20 planned (1995)	97	no
Neste OY (Europe)	na	1	na
Shimadzu (Japan)	0.2 (1995)	22	na
Chronopol (US)	2 planned (1996)	56 ^c	na

^aproduction capacity values based on published news reports.

^bpatent activity based on Chemical Abstracts Search (5/96), ACS. Includes both granted and applied for patents as normally published by the 23 patent offices followed by Chemical Abstracts including: US Pat Office, Eur. Pat Office, Japan Patent Office, World Intellectual Property Org.

^cChronopol patents are assumed to include those assigned to Battelle, Ecochem, Ecopol, and DuPont.

Cargill Inc. currently operates the largest PLA facility. With over 50 billion in annual sales, Cargill is the largest private company in the US; including public US companies Cargill ranks 7th. To our knowledge, Cargill is the only PLA company that is

back-integrated through feedstock, corn. L-Lactic acid is produced by the bacterial fermentation of corn sugar (D-glucose): $C_6H_{12}O_6 \rightarrow 2C_3H_6O_3$, $\Delta G^\circ(25^\circ C, pH\ 7.0) = -136$ kJ/mol.¹⁶ We estimate that from corn to polylactide there are over 50 basic unit operations including mechanical separations, enzymatic conversions, purifications, fermentations, acidulations, evaporations, condensation, chemical separations, polymerization, devolatilization and drying operations. Cargill and Purac Biochem BV (division of CSM) recently announced (5/96) a 50-50 joint venture to build and operate a 70 million lb/yr lactic acid facility in the US (startup in 1998); the current US consumption of lactic acid is 55 million lb/yr. Purac currently produces an estimated 80% of the world's lactic acid. Cargill is well known for building and operating safe, low cost plants and has considerable separations expertise. This seemingly synergistic alliance of a specialty chemicals company with a commodities company links the worlds lactic acid experts with one of the worlds biggest corn wet milling biotechnology companies. Cargill is confident that their EcoPLA resins will sell for less than or equal to \$1/lb at large scale.¹⁷

Mitsui Toatsu produces polypropylene, polystyrene, and poly(vinyl chloride) and manufactures poly(glycolic acid) and glycolic-lactic acid copolymers for medical applications.¹⁸ They plan to become a raw-material supplier in biodegradable plastics and are said to be building a new poly(lactic acid) pilot plant.¹⁹ Although patent activity can sometimes be a poor indication of overall patent strength, Mitsui Toatsu has clearly been the most aggressive PLA company in patent applications.

Neste OY is a Finnish company that is known to be developing PLA applications. Very little has been published on their plans.

Shimadzu of Japan has been producing PLA in a 100 ton/yr pilot plant and has plans for future scale-up. They have developed a lactic acid fermentation process and have plans to be a PLA resin supplier. They are collaborating with Mitsubishi Plastics to develop PLA.¹⁸

Chronopol is a subsidiary of Golden Technologies which is the R&D division of ACX Technologies, a spin-off company of Adolph Coors.¹⁹ Chronopol and Ecochem entered into a 50-50 joint venture in 1995 named EcoPol. Ecochem is in turn a joint venture between DuPont and ConAgra. Ecochem had a short-lived (7/92 to fall/94)²⁰ lactic acid business using technology developed by ConAgra and the University of Wisconsin that was dissolved as a result of technical difficulties and falling lactic acid prices. Chronopol has announced a 2 million lb/yr PLA facility scheduled to start-up in late 1996 at a GTC Nutrition Company corn wet milling plant. Through EcoPol and its previous relationship with Battelle, Chronopol may have access to 56 patents including those assigned to DuPont.

Other companies that have expressed interest in developing polylactides include Dai Nippon (Japan) and Hycail (Netherlands, relationship with the University of Groningen). Hycail has considerable polylactide modification technology as evidenced by their authors' journal articles on the subject (e.g., Grijpma et al.).

Although there has been no such information so far, major US corn wet millers such as Archer Daniels Midland Co (ADM) and A.E. Staley (subsidiary of Tate & Lyle

PLC) should be considered as potential PLA resin suppliers. ADM has numerous biotechnology businesses based on corn including a 10-15 million lb/yr lactic acid business that it plans to double by the end of this year.²¹ A.E. Staley has announced (5/96) that they will be entering the lactic acid market in early 1997.²¹ However, there exists considerable technical obstacles to producing and developing useful polylactide resins. It is not simply a matter of waiting for a biodegradable plastics market to develop. The technical barrier to entry is probably a minimum of 5 years aggressive development.

Previously lactic acid and its derivatives have been a specialty chemical and food additive market. However, the success of polylactides will require commodity L-lactic acid supply. This should lower the cost of L-lactic acid which will increase demand in current applications and possibly spawn new uses for lactic. Examples include: "green" solvents such as ethyl lactate and butyl lactate to replace toxic aromatic solvents¹⁴ in paints and lacquers, and the production of acrylic acid and propylene glycol.¹³ In addition, lactic acid could find demand as a low cost chiral intermediate.

A racemic mixture of D- and L-lactic acid (D,L-lactic acid) has been manufactured from petrochemical resources. However, the largest synthetic manufacturer, Sterling Chemicals Inc (US), recently announced its exit from the lactic acid market (1996). This leaves Musashino (Japan) as the world's sole producer of synthetic D,L-lactic acid.²¹ In the absence of a large-scale lactate chiral separation, which has yet to be developed, D,L-lactic acid is only suitable for the production of amorphous polylactides.

There have been two major polylactide process breakthroughs since 1992: one each by Cargill and Mitsui Toatsu. Both are patented.

From a cost standpoint the most important breakthrough was the development of a solvent-free lactide purification process by Cargill, Gruber et al.²² This process incorporates distillation technology and provides a very pure liquid monomer at low cost. Previous technologies relied on solvent or melt crystallization for lactide purification.

Mitsui Toatsu has patented a lactic acid solvent polymerization process.²³ In this process they use a high boiling (200-250°C) hydrocarbon solvent in which both lactic acid and PLA are soluble but water is not. They report that PLA with up to 300,000 g/mol can be produced by this polycondensation process. This technology is very interesting from a copolymer standpoint. Instead of being limited to ring-opening comonomers that can be polymerized with the same lactide catalyst, the condensation route allows for many solvent miscible alcohol and acid monomers to be copolymerized with lactic acid.

1.2.3 Role of Water

Regardless of polymerization mode PLA contains backbone functionality, one ester per repeat unit, and is classified as a condensation polymer. The ester bonds are susceptible to hydroxyl initiated transesterification reactions and hydrolysis. The kinetics of these reactions are determined in Chapter 3. In this section we determine the equilibrium relationship between water, lactic acid, and the distribution of polylactic acid chains. In doing so we gain insight into the nature of polylactide's instability and finite shelf life.

Bezzi, Riccoboni, and Sullam¹⁴ proposed that the description of equilibrium between lactic acid and lactoyllactic acid is unsatisfactory unless higher lactic acid oligomers are taken into account. In such an analysis the authors determined the equilibrium constant of lactoyllactic acid hydrolysis to be 4.8. Assuming equal reactivity of functional groups, we can extend this information to high polymer and determine the equilibrium concentration of water as a function of PLA average molecular size.

Using data from Bezzi, Riccoboni, and Sullam tabulated in Holten,¹⁴ we plot the weight percentages of lactic acid and poly(lactic acid) versus percent water in Figure 1-4. At 80% water there is already a small amount of poly(lactic acid). This demonstrates a non-zero water equilibrium concentration. This also indicates that intermolecular water is removed prior to the removal of all of the free water in a lactic acid polycondensation process. The percent lactic acid goes through a maximum at 60 where both water and poly(lactic acid) cross at 20%. These data are reduced to a ternary composition plot in Figure 1-5.

With acid titration data the authors were able to determine the average degree of polymerization, $\bar{X}_n$, at each concentration. The degree of polymerization is the ratio of the potential acid endgroup concentration on complete hydrolysis (total concentration of repeat units), $[COOH]_0$, divided by the concentration of acid endgroups at equilibrium, $[COOH]$,

$$\bar{X}_n = \frac{M_n - 18}{72} = \frac{[COOH]_0}{[COOH]} \quad (1-1)$$

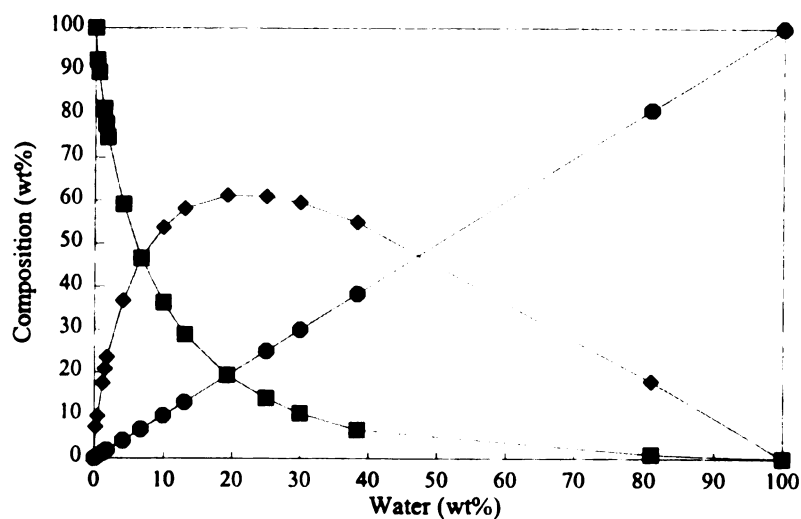


Figure 1-4. Chemical equilibrium in lactic acid solutions; percent poly(lactic acid) (■), water (●), and lactic acid (◆) versus percent water. Data from Bezzi, Riccoboni, and Sullam.¹⁴

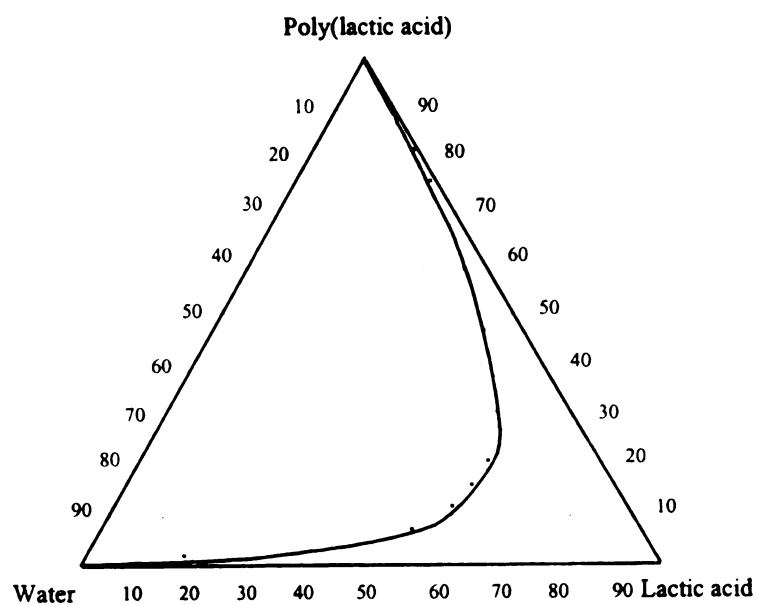


Figure 1-5. Ternary diagram of chemical equilibrium in lactic acid solutions. All data are in weight percent.

The number average molecular weight, M_n , is the product of the repeat unit molecular weight (72) and the degree of polymerization, plus a value of 18 g/mol for the endgroups.

A plot of the degree of polymerization versus percent water is presented in Figure 1-6.

The average degree of polymerization increases from a value of one (lactic acid = DP1) at high water concentration to a value of two (lactoyllactic acid = DP2) at 3 wt% water.

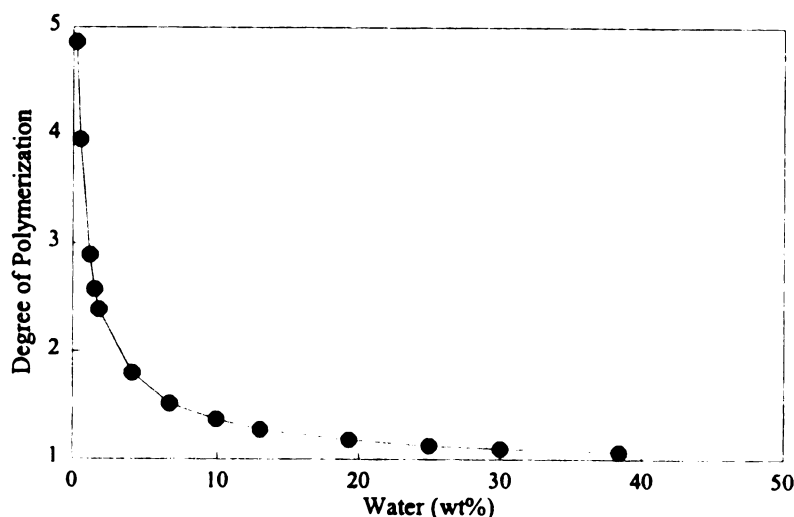


Figure 1-6. The average degree of lactic acid polymerization as a function of percent water in lactic acid solutions.

With this low molecular weight poly(lactic-acid)-water equilibrium data we now have all of the information required to determine the equilibrium constant of condensation (or its inverse, hydrolysis).

Lactic acid can condense with another lactic acid or poly(lactic-acid) to give water and the resulting poly(lactic-acid),



where L_1 and L_i are the molar concentrations of lactic acid and a poly(lactic-acid) with i 72g/mol repeat units. The rate of lactic acid condensation is proportional to the product of its molar concentration and the molar concentration of all hydroxyl endgroup species (i.e., PLA + lactic acid). The rate of PLA hydrolysis to produce lactic acid (reverse reaction) is proportional to the product of the water concentration and the concentration of all hydroxyl molecules larger than lactic acid. Therefore, the rate of lactic acid consumption is given by,

$$\frac{-dL_1}{dt} = k_f L_1 \sum_{i=1}^{\infty} L_i - k_r [H_2O] \sum_{j=2}^{\infty} L_j \quad (1-3)$$

where k_f and k_r are the condensation and hydrolysis rate constants, respectively. Hence, at equilibrium,

$$K_1 = \frac{[H_2O] \sum_{j=2}^{\infty} L_j}{L_1 \sum_{i=1}^{\infty} L_i} \quad (1-4)$$

where K_1 is the equilibrium constant of lactic acid condensation. Generally, any lactic acid or PLA species of size n can condense with any other lactic acid or PLA molecule:

$$K_n = \frac{[H_2O] \sum_{j=n+1}^{\infty} L_j}{L_n \sum_{i=1}^{\infty} L_i} \quad (1-5)$$

Therefore, in order to calculate the equilibrium constant of lactoyllactic acid condensation, for example, we need the molar concentrations of water, lactic acid + poly(lactic acid), and all PLA species of size greater than 2. Although this information is not directly obtained from the literature data used in Figure 1-4, we can determine the molar concentration of any L species using the average degree of polymerization or the acid end group fractional conversion, $p = \{[COOH]_0 - [COOH]\}/[COOH]_0$,

$$L_n = [COOH](1 - p)p^{n-1} \quad (1-6)$$

This is the Flory-Schulz distribution (Most Probable Distribution) which assumes an equal reactivity of functional groups and equates the molar concentration L_n at equilibrium to the probability that a randomly selected species L is exactly of size n . Combining equations (1-5) and (1-6), the equilibrium constant is independent of chain length and equivalent to

$$K_1 = K_2 = \dots = K_n = K = \frac{p[H_2O]}{[COOH]_0(1 - p)^2} \quad (1-7)$$

This is a general relationship found for step polymerization systems which relates the polycondensation equilibrium constant to the end group fractional conversion, water concentration, and total number of repeat units. Alternatively we could use the following

relationship, based on equation (1-4), with the data presented in Figure 1-4 to determine the equilibrium constant of lactic acid condensation:

$$K = \frac{[H_2O]([COOH] - L_1)}{L_1[COOH]} \quad (1-8)$$

To determine the equilibrium constant of PLA condensation we first converted the weight percent data to molar concentrations and corrected for density changes using the following relationship (ideal volume mixture equation, which is a decent representation of this system), where w_L is the total weight fraction of lactic acid and poly(lactic acid),

$$\frac{1}{\rho_{mix}} = \frac{w_L}{1.24} + (1 - w_L) \quad (1-9)$$

Consistent with the Most Probable Distribution assumption of equal reactivity of functional groups, the calculated equilibrium constants using equation (1-7) are fairly independent of molecular size. The results are summarized in Table 1-3. The lactic acid condensation equilibrium constant of 0.22 is in accord with the analysis by Bezzi, Riccoboni, and Sullam¹⁴ using this same data. The equilibrium constant for poly(lactic acid) condensation is determined to be about 0.25 for $X_n < 5$.

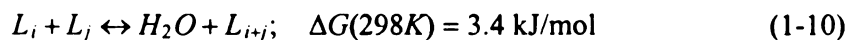


Table 1-3 Equilibrium Constant for PLA Condensation

Water (wt%)	Water (mol/L)	$[COOH]_0$ (mol/L)	p	X_n	K
38.36	24.20	7.88	0.06	1.07	0.22
30.01	19.28	9.16	0.09	1.10	0.22
25.00	16.25	9.97	0.11	1.13	0.23
19.31	12.71	10.96	0.15	1.18	0.24
13.06	8.72	12.13	0.21	1.27	0.25
9.91	6.67	12.82	0.27	1.37	0.26
6.68	4.53	13.58	0.34	1.51	0.26
4.10	2.80	14.36	0.44	1.80	0.28
1.84	1.26	15.24	0.58	2.39	0.27
1.53	1.05	15.40	0.61	2.57	0.28
1.22	0.84	15.61	0.65	2.89	0.29
0.53	0.36	16.09	0.75	3.96	0.27
0.26	0.18	16.33	0.79	4.86	0.21

The polycondensation equilibrium constant can be used along with the Most Probable Distribution to determine the entire distribution of molecular species in the lactic acid system as a function of the average degree of polymerization, $X_n = 1/(1-p)$. The equilibrium water concentration and acid endgroup concentration at a given conversion, p , are determined by simultaneously solving the equilibrium and mass balance equations ($\rho \approx 1.24$ g/ml):

$$0 = 0.25[COOH]\frac{(1-p)}{p} - [H_2O] \quad (1-11)$$

$$0 = 18[H_2O] + \left(\frac{72}{1-p} + 18 \right) [COOH] - 1000\rho(\text{g/ml}) \quad (1-12)$$

The lactic acid and individual PLA species concentrations are determined using equation (1-6). The weight fractions of the PLA chains are easily derived from equation (1-6)

$$w_n = \frac{L_n(72n + 18)}{1000\rho(\text{g/cm}^3)} = \frac{[\text{COOH}](72n + 18)(1 - p)p^{n-1}}{1000\rho} \quad (1-13)$$

Figure 1-7 presents the calculated PLA mole and weight fractions for a lactic acid solution containing 10 wt% water, $p = 0.27$. The water and lactic acid are equimolar. DP2, DP3, DP4, and DP5 account for 11%, 3%, 0.8% and 0.2% of all molecules, respectively. Lactic acid represents 50% of the solution by weight.

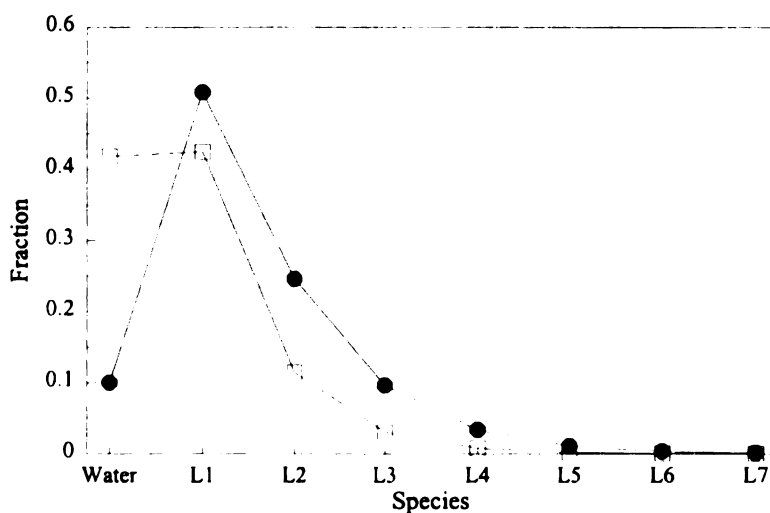


Figure 1-7. Distribution of molecular species in a lactic acid solution containing 10 wt% water ($p = 0.27$, $X_n = 1.37$); mole fractions (□), weight fractions (●).

Assuming equal reactivity of functional groups, we can use this same procedure to calculate the water equilibrium in higher molecular weight PLA, Figure 1-8. At 2,000 M_n

there is a calculated 100 ppm equilibrium water, and at 20,000 M_n there is about 1 ppm equilibrium water. For a 150,000 M_n poly(lactic acid), approximately the reported value for the Mitsui Toatsu type solvent polycondensation process (300,000 $M_w/2$ PDI),³ we calculate that there is about 0.015 ppm water in equilibrium with PLA. However, in the solvent phase condensation polymerization the equilibrium water content to achieve a given molecular weight PLA, in the absence of coupling agents, is proportional to the water content required for an equivalent molecular weight PLA from the initially aqueous phase. The proportionality constant depends on both the ratio of water activity coefficients and the exponential of the difference in standard state water chemical potentials of aqueous and solvent phases. Hence, the solvent choice in part determines the permissible water content to achieve a given molecular weight PLA.

For high molecular weight PLA the water equilibrium concentration is negligible and hydrolysis is essentially irreversible. This forms the basis for the melt hydrolysis kinetic model developed in Section 3.5.

In Section 4.4 we determine the equilibrium moisture adsorption curve for high molecular weight amorphous PLA at 25°C, $M_n = 50,000 - 100,000$. We present this PLA-water phase equilibrium curve in Figure 1-9 to compare to the PLA-water chemical equilibrium calculations in Figure 1-8.

Equilibrium water adsorption in PLA pellets occurs in less than 24 h. At 45% relative humidity PLA contains 2000 ppm water. This is a typical relative humidity of our air-conditioned laboratory in the summer. At this water concentration chemical

equilibrium dictates a polymer equilibrium average molecular weight of 450 g/mol ($X_n = 6$). This is the driving force for the hydrolyzation of high molecular weight (e.g., 50,000 M_n) PLA. With air as an infinite water reservoir PLA slowly but completely hydrolyzes to lactic acid.

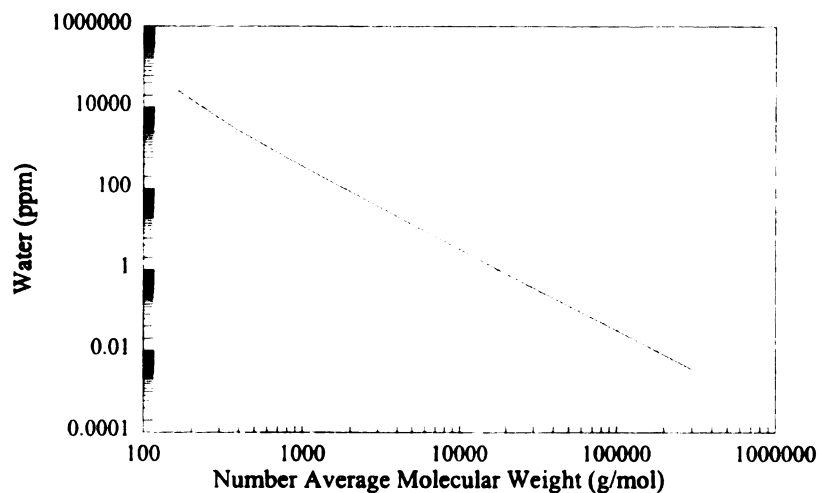


Figure 1-8. Chemical equilibrium between water and PLA as a function of molecular weight at 25°C .

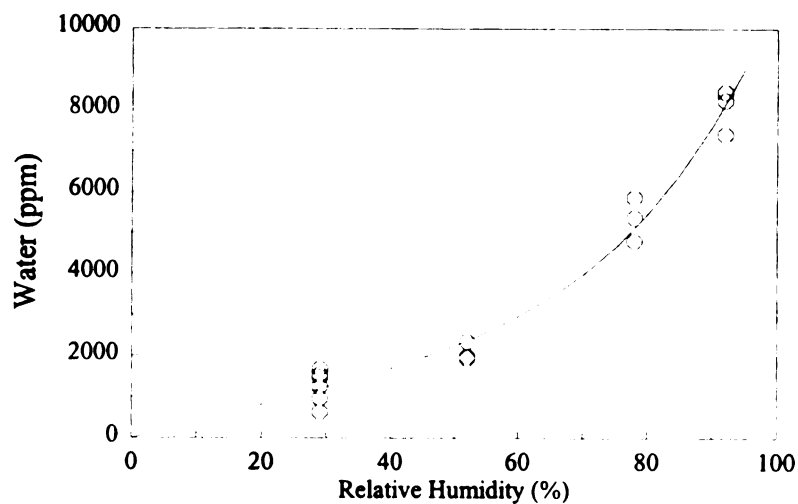


Figure 1-9. Phase equilibrium between water and high molecular weight PLA pellets (50,000-100,000 M_n) as a function of percent relative humidity at 25°C.

Poly lactides have considerably less water adsorption than do starch polymers or polyamides. However, ester bonds hydrolyze more readily than amide bonds.

Poly lactides have decent water barrier properties (not hygroscopic) but are unstable to hydrolysis in long time. Having 33% acyl ester bonds in their backbone, poly lactides have a much higher concentration of ester bonds than do commercial polyesters. Ester bonds are very stiff and give PLA a very high glass-transition temperature for an aliphatic polyester. However, the high concentration of ester bonds also makes them much more susceptible to hydrolysis.

In our moisture-rich environment polylactide articles of high molecular mass are thermodynamically unstable. Although phase equilibrium between water and polymer is rapid (water adsorption from air), the approach toward chemical equilibrium (hydrolysis) is sufficiently slow such that a shelf life can be defined. For these reasons the PLA part thickness is relatively unimportant for shelf life. In ambient on-the-shelf conditions, polylactide materials have been reported to retain their physical properties for about one year.¹³ *In vivo*, these materials lose their strength in about 3-6 weeks depending on their molecular weight and degree of crystallinity.¹³ PLA owes its instability to a polycondensation equilibrium constant of about 0.25 and its 33% backbone concentration of ester bonds.

1.2.4 Molecular Architecture

Unmodified polylactides are linear macromolecules having a molecular architecture that is determined by its stereochemical makeup. Each 72 g/mol repeat unit

contains one stereocenter that is either L (*S*) or D (*R*) in configuration. The repeat units are either added in dimers during ring-opening lactide polymerization or are added to the final polymer as lactic monomers via the direct condensation polymerization route (e.g., Mitsui Toatsu process). Both mechanisms involve acyl cleavage of the ester bond with retention of chirality.

The stereoisomers of lactic acid and lactide are depicted in Figure 1-10.

Meso-lactide possesses a two-fold axis of improper rotation and is therefore optically inactive.

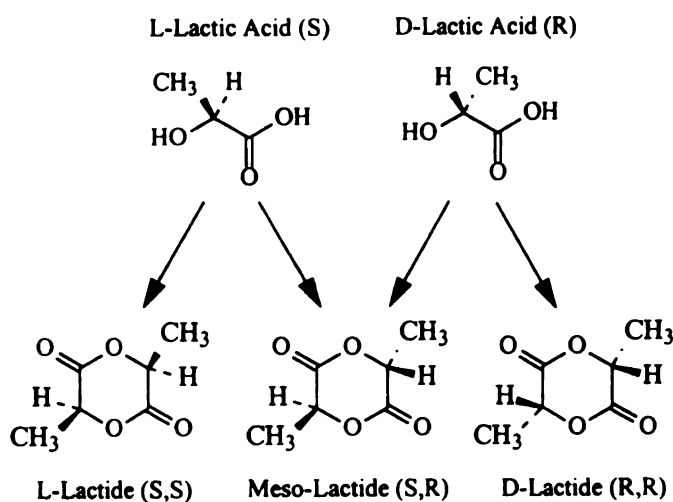


Figure 1-10. Stereoisomers of lactic acid and lactide.

The lactide isomers are produced from the depolymerization of low molecular weight poly(lactic acid) in proportions close to statistical expectation from the initial lactic acid isomers (equal reactivity),

$$w_{\text{L-Lactide}} = S^2; \quad w_{\text{D-Lactide}} = R^2; \quad w_{\text{Meso-Lactide}} = 2RS \quad (1-14)$$

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where S and R are the original fractions of L-lactic acid and D-lactic acid, respectively. For example, with 10% D-lactic acid and 90% L-lactic acid the subsequent fractions of L-, D-, and *meso*-lactide are 0.81, 0.01, and 0.18, respectively, based on the equal reactivity assumption. Figure 1-11 summarizes the ideal lactide isomeric distribution with varying initial L-lactic acid composition, 50-100% (the full range possible from an L-lactic acid source). With decreasing initial L-lactic acid, *meso*-lactide production becomes increasingly important. D-Lactide is always the minor component. Assuming equal reactivities the lactide mixture at stereochemical equilibrium contains 50% *meso*-, and 25% each of L- and D-lactide. However, in practice *meso*-lactide has a somewhat greater tendency to polymerize and the equal reactivity assumption is only approximate.

The initial distribution of lactide isomers determines the potential for polylactide crystallization. PLA derived from greater than 93% L-lactic acid can be semicrystalline; PLA from between 50-93% L-lactic acid is strictly amorphous. Both *meso*- and D- lactide form kinks in the otherwise very regular poly(L-lactide) molecular architecture. These molecular imperfections decrease both the rate and extent of poly(L-lactide) crystallization. In Figure 1-12 we show a ternary lactide composition diagram referenced to the initial percent L-lactic acid. At the potential crystalline and strictly amorphous composition transition there is approximately 0.5% D-, 13% *meso*-, and 86.5% L-lactide.

Figures 1-11 and 1-12 represent the subsequent PLA makeup for only bulk lactide purification processes where *meso* is not separated from the lactide enantiomers. Conventional lactide purification involves solvent recrystallization which precipitates the lactide enantiomers but leaves *meso*-lactide with the impurities. Essentially all of the PLA

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literature involves L- and D,L-lactide (racemate of L- and D-lactide) copolymers. However, from an industrial perspective solvent recrystallization is not cost-effective and *meso*-lactide is the most important L-lactide comonomer in bulk purification processes

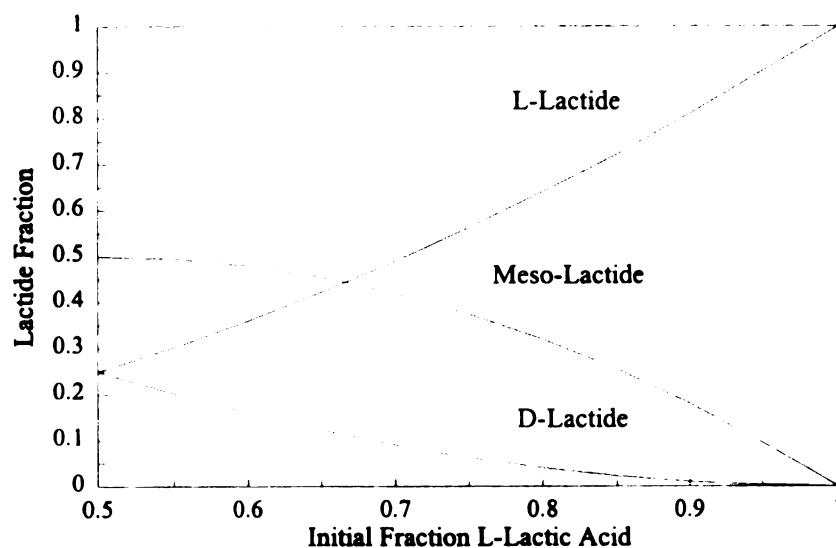


Figure 1-11. Lactide isomeric distribution versus initial L-lactic acid composition based on an equal reactivity assumption.

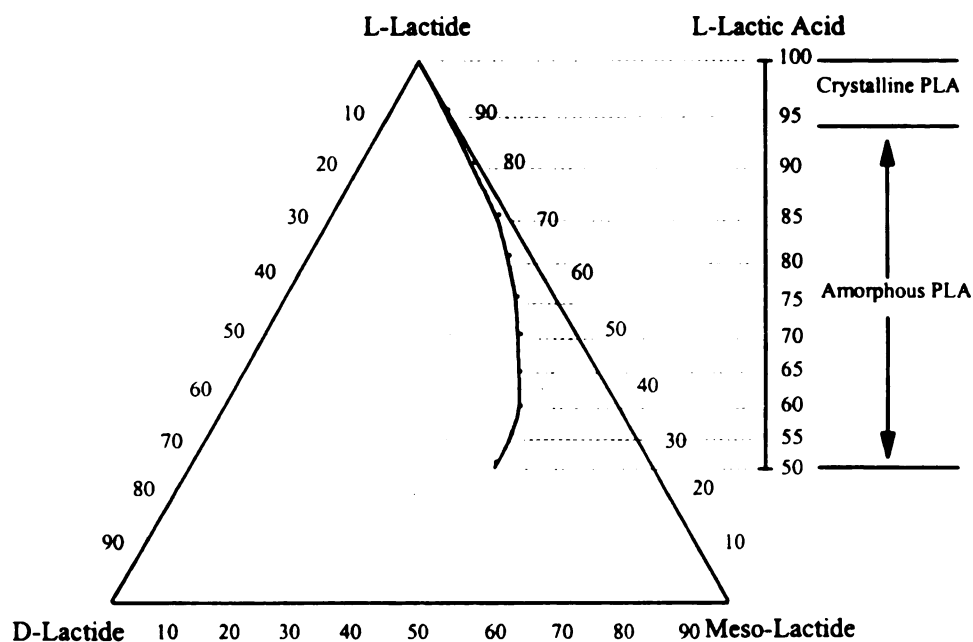


Figure 1-12. Ternary diagram for the distribution of lactide isomers referenced to the initial isomeric contribution of L-lactic acid.

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such as distillation (e.g., Cargill process). A major focus of this dissertation is to characterize the effects of *meso*-lactide on PLA properties.

At stereochemical equilibrium L- and D-lactic acid are equally represented, 50/50. A 20 wt% L-lactic acid solution will fully racemize to D,L-lactic acid after about 500 hr at 200°C (Witzke unpublished lactic acid racemization rate model). Although some microorganisms ferment D-lactic acid in high yield, there is currently no major source of D-lactic acid, and lactic acid containing less than 50% L-lactic acid is generally not available. In concept a 100% D-PLA will have identical physical properties as a 100% L-PLA (save for the direction of polarized light rotation). It is known that poly(L-lactide) and poly(D-lactide) form an equimolar stereocomplex crystalline structure (racemate compound) having a significantly higher melting temperature (230°C) than the homopolymers.^{24,25}

Through controlled racemization both crystalline and amorphous polylactides can be produced from a L-lactic acid source. However, synthetic D,L-lactic acid derived from petroleum resources is already fully "racemized" and only amorphous PLA can be produced. In concept, the development of large scale chiral separations could provide for crystalline PLA from a D,L-lactic acid source.

Dimeric polymerization imparts some order to the otherwise random distribution of L- and D- stereocenters in PLA chains. For this reason the direct polycondensation process and lactide ring-opening process give fundamentally different molecular architecture for PLA polymers derived from lactic isomeric mixtures other than 100% L-

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and 50/50 D,L-lactic acid. This can be demonstrated by NMR measurements. Both racemization and transesterification act to slowly decrease this increased order conferred by dimeric polymerization. High molecular weight bulk lactide polymerization often must be conducted at high temperatures (e.g., 190-200°C) for viscosity reasons. At these temperatures racemization can become an important side reaction. Inter- and intramolecular transesterification reactions randomly redistribute the repeat units. Using stannous ethylhexanoate (common PLA catalyst used throughout this dissertation) the effect of transesterification on randomizing the dimeric contributions is slow, but measurable, at 180°C.²⁶ Regardless, any bulk property differences attributed solely to molecular architecture differences between dimeric and monomeric lactic polymerization are most likely subtle (no change in mechanical properties, etc.).

Although of the same order of magnitude, the reactivity among lactide isomers is not exactly the same. *Meso*-lactide has a somewhat higher rate of hydrolysis and greater tendency to polymerize. The L- and D- enantiomers have identical rates. The rate differences between *meso*- and L- lactide must be a result of their configurational and conformational differences. We performed lactide energy minimizations using BIOSYM and found *meso*- to prefer a chair conformation, whereas L-lactide preferred a boat conformation, Figure 1-13. The respective melting points for *meso*- and L-lactide are 53 and 99°C (Section 2.8) indicating that the L-lactide structure can more easily fit into a crystalline lattice. The conformations of *meso*-lactide and L-lactide are shown as Newman Projections in Figure 1-14.

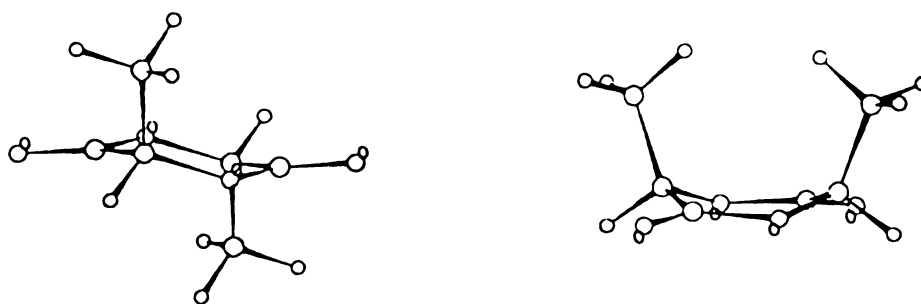


Figure 1-13. Minimum energy conformations for *meso*-lactide (chair) and L-lactide (boat).



Figure 1-14. Newman Projections through the carbon-carbon ring bonds of L-lactide and *meso*-lactide.

These preliminary energy minimization results suggest that *meso*-lactide is about 1.7 kcal/mol more stable than L-lactide. The major difference was the increased torsional energy for L-lactide (3 kcal/mol). *Meso*-lactide and L-lactide are the trans and cis analogs to the six-membered cycloalkane, 1,4-dimethylcyclohexane. However, the conformational energies differ considerably in part because of the SP² nonbonding electron pairs of the carbonyl oxygens.

Although not perfect, the assumption of equal reactivities for lactide production and polymerization is still decent and results in only a relatively small error in final composition estimations. However, the configurational and conformational differences

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between *meso*- and L-lactide result in different physical properties, such as melting point, solubility, and relative volatility, which are important for lactide production processes.

The most important role of *meso*-lactide is to provide amorphous polylactide through its copolymerization with L-lactide. We investigated the molecular architecture of various lactide stereocopolymers using POLYGRAFTTM molecular simulation software on a Silicon Graphics IRISTM. This allows us to better understand the effect of *meso*- and D-lactide on the structure and potential for crystallization of poly(L-lactide).

The tacticity of poly(L-lactide) is depicted in Figure 1-15. Although poly(L-lactide) is effectively syndiotactic, the literature refers to its structure as isotactic; this is probably because the lactide dimers are arranged in an isotactic fashion (isotactic in dimers). However, from a functional perspective we believe that syndiotactic is a more appropriate characterization of poly(L-lactide).

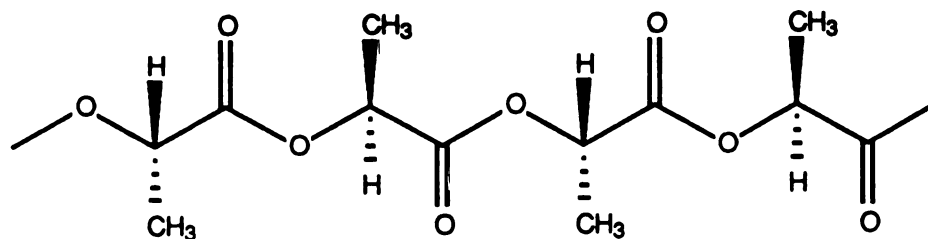


Figure 1-15. Structure of poly(L-lactide); syndiotactic in monomers (72 g/mol).

There is conflicting data regarding the stereospecificity of *meso*-lactide polymerization. The ¹H-NMR spectrum of Sn(II) octoate catalyzed poly(*meso*-lactide) is reported by Schindler²⁷ to be stereoregular with propagation occurring among *like*

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configurational repeat units (i.e., $(RS)-(SR)-(RS)-(SR)$). This structure is syndiotactic in dimers and is shown in Figure 1-16. However, the ^1H - and ^{13}C -NMR results of Thakur²⁸ support that Sn(II) octoate catalyzed poly(*meso*-lactide) tends toward propagation among *unlike* configurational repeat units (i.e., $(RS)-(RS)-(RS)-(RS)$). This ideal structure is isotactic in monomers and is presented in Figure 1-17. Kricheldorf et al.²⁹⁻³¹ polymerized *meso*-lactide with various catalysts and found no significant stereospecificity using ^1H - and ^{13}C -NMR spectroscopy.

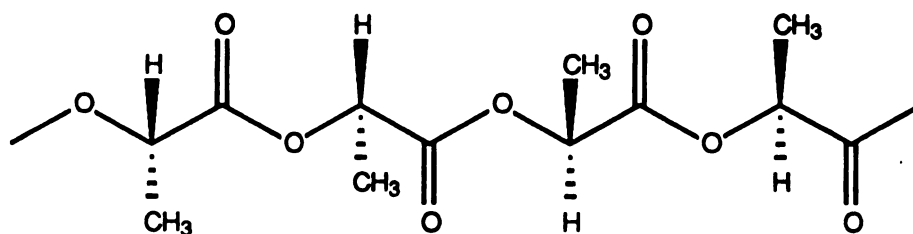


Figure 1-16. Ideal $(RS)-(SR)-(RS)-(SR)$ structure of poly(*meso*-lactide); syndiotactic in dimers.

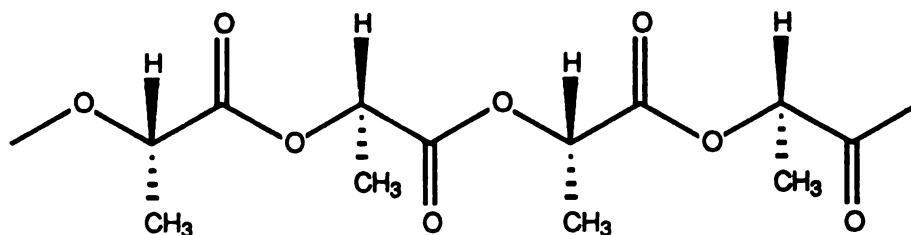


Figure 1-17. Ideal $(RS)-(RS)-(RS)-(RS)$ structure of poly(*meso*-lactide); isotactic in monomers.

The POLYGRAFTM polymer builder was used to simulate the basic molecular architecture of the following polylactides: poly(L-lactide), Figure 1-18; ideally regular poly(*meso*-lactide) (i.e., $RSRS$), Figure 1-19; poly(3-*meso*-co-37-L-lactide) (i.e., 7.5% *meso*), Figure 1-20; and poly(D-co-L-lactide), Figure 1-21. All of the polymers contained

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40 repeat units (72 g/mol) except poly(3-*meso*-co-37-L-lactide) which was simulated with 80 repeat units.

The poly(L-lactide) model, Figure 1-18, is depicted in both spherical and vector visualizations. The axial view suggests a highly ordered helical structure where the methyl groups are placed in a regular sequence of 8 lactide units per three turns: 8₃ helix. However, poly(L-lactide) has been determined to have a predominately 10₃ helical structure (α -structure) from WAXS patterns.³² The tighter 10₃ helix may be attributed to increased hydrogen bonding.

In Figure 1-19 stereoregular poly(*meso*-lactide) (*RSRS*) is found to have a looser helical structure, about a 6₁ helix. Interestingly, the methyl groups were not ordered in a regular pattern as seen in the axial view, and all of the oxygen atoms are located at the center of the helix. Stereoregular poly(*meso*-lactide) (*RSRS*), if it exists, probably lacks the regular placement of atoms relative to each other required for crystallization.

Poly(*meso*-lactide) is known to be amorphous.

The 3-*meso*-co-37-L-lactide polymer structure depicted in Figure 1-20 demonstrates the dramatic effect that *meso* segments have on the otherwise very regular poly(L-lactide) chain.

The random D-co-L-lactide molecular model, Figure 1-21, clearly presents the irregular nature and obvious amorphous behavior of this well-known racemic lactic acid copolymer.

For more detailed studies of the molecular architecture and stereochemistry of PLA, the reader is referred to several works concerning the molecular conformation and

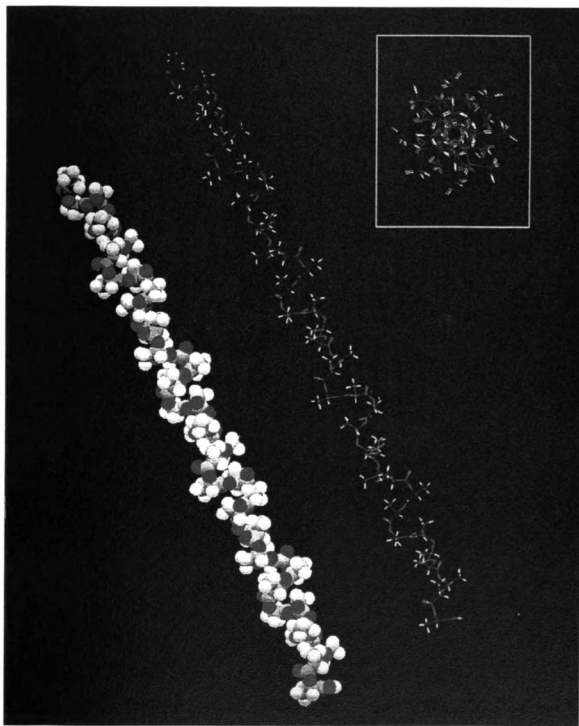


Figure 1-18. Molecular simulation of poly(L-lactide); spherical and vector visualization, $n = 40$.

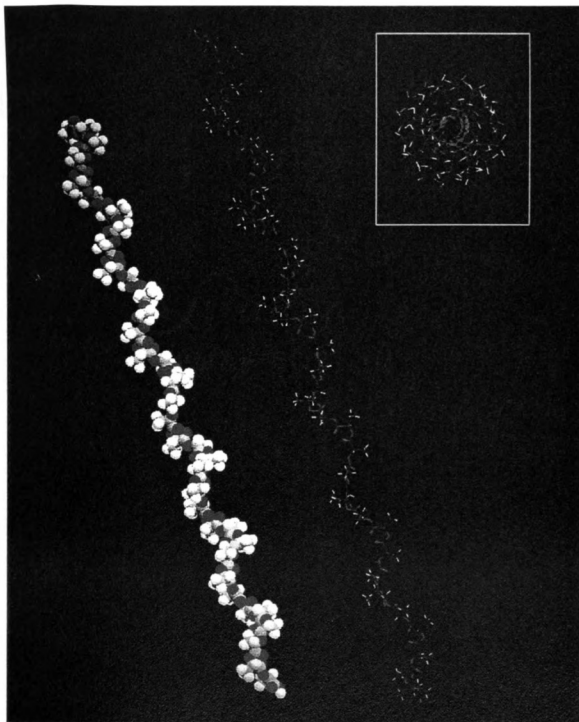


Figure 1-19. Molecular simulation of ideally regular poly(*meso*-lactide) (*RSRS*); spherical and vector visualization, $n = 40$.

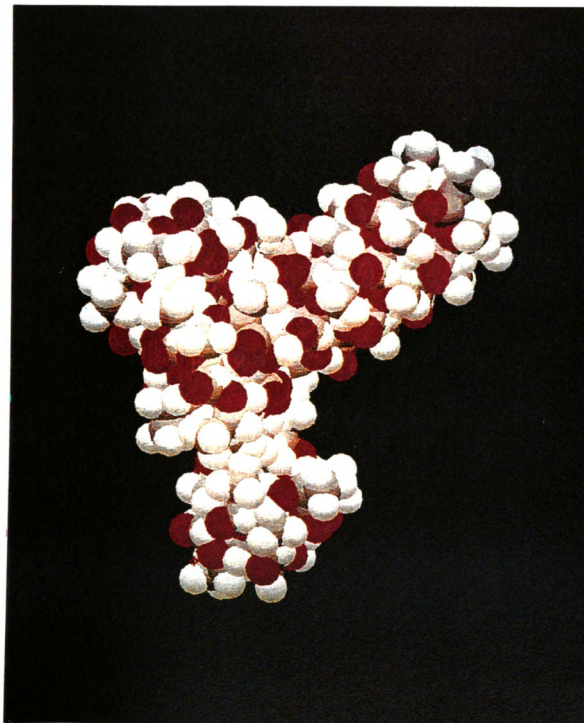


Figure 1-20. Molecular simulation of poly(3-*meso*-co-37-L-lactide) (i.e., 7.5% *meso*); $n = 80$.

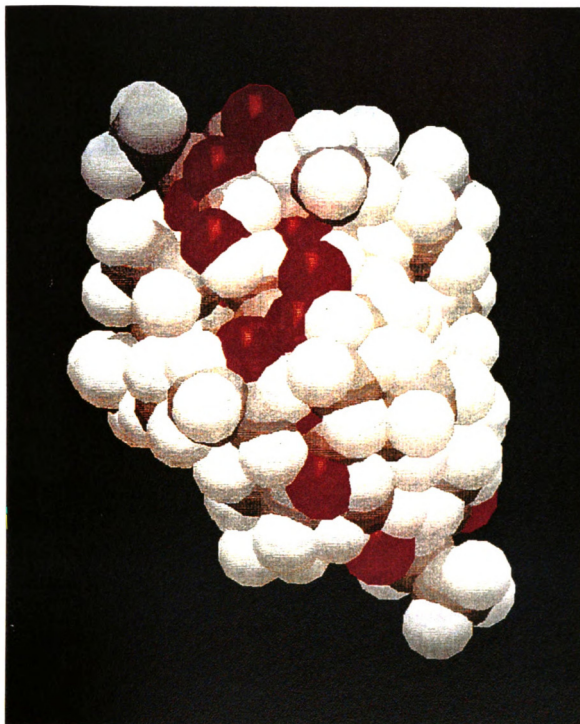


Figure 1-21. Molecular simulation of poly(D-co-L-lactide); $n = 40$.

configuration of PLA³⁸⁻⁴³ and papers involving the elucidation (mainly through NMR techniques) of the stereosequence distribution of PLA polymers.^{28,29,44-49}

Although there is limited literature information on *meso*- and L-lactide copolymers, *meso*-lactide plays an important role in the ability to produce both amorphous and crystalline polylactides through low cost bulk processing from an L-lactic acid source. Additionally, the characterization of racemization and transesterification rates is necessary for complete control over PLA stereochemistry in bulk production.

1.3 Dissertation Objective

The objective of this work is to characterize the physical and reaction properties of polylactides from a bulk production perspective and to use these results along with pilot engineering data to make inferences about engineering design, applications, critical technical barriers, and prospects for commodity PLA application. We have incorporated acquired knowledge from a literature survey along with results from experimental and theoretical methodologies to solve practical engineering problems. In doing so we provide an introduction to the properties, engineering, and prospects of polylactide polymers.

To our knowledge this is the first report on the properties and application of polylactides produced through the bulk lactide purification and polymerization processes required for low cost PLA manufacture. Two major differences exist between PLA produced for commodity and biomedical applications.

In bulk lactide processing *meso*-lactide derived from racemization is the most important L-lactide comonomer and is both a nuisance for the development of a useful crystalline PLA, and a means to produce amorphous PLA. In conventional polylactide preparations D-lactide, from the D,L-lactide racemate, is the major L-lactide comonomer. Hence, the current literature has been concerned with determining the properties for L- and D,L-lactide copolymers.

The second major difference between the two PLA preparations is the potential effect of the polymerization catalyst on other important PLA bulk reactions such as depolymerization, transesterification, and hydrolysis. In biomedical applications the catalyst is generally removed during PLA purification, whereas in bulk PLA processes melt devolatilization is used to remove unreacted monomer and the catalyst is not necessarily removed. In the absence of catalyst the -OH and -COOH end group concentrations determine reaction rates. However, when not removed the polymerization catalyst plays the dominate role in the rates of these other esterification type reactions.

This dissertation is largely concerned with the determination of *meso*- and L-lactide copolymer properties and the elucidation of the role of the polymerization catalyst in other bulk PLA reactions.

Dissertation Survey

In Chapter 2 we determine many of the thermal, volumetric, mechanical, and rheological properties of polylactides based on L-, *meso*-, and D,L-lactide monomers. Next, group contribution methods are used to estimate both PLA's thermal conductivity

as a function of temperature, and its solubility parameter. A lactide-poly lactide vapor-liquid activity model is developed and applied later in melt devolatilization calculations and data interpretation. We conclude Chapter 2 with a listing of measured and estimated lactide properties.

The bulk reaction properties of polylactides are determined in Chapter 3 using experimental data regressed to mathematical rate models. We develop a thermodynamically consistent reversible polymerization model using stannous ethylhexanoate as the catalyst. This model is used to predict both polymerization and depolymerization rates as a function of catalyst concentration, temperature, and initial monomer concentration. Next, hydroxyl chain initiation and transesterification (polymer interchange) rate forms are developed mathematically to predict the dynamics of the polymer molecular weight distribution during stannous ethylhexanoate catalyzed lactide polymerization for input values of temperature, catalyst concentration, and initial hydroxyl impurity concentration. In Section 3.5, PLA melt degradation is determined during processing at various moisture concentrations, temperatures, catalyst concentrations, and time. We conclude this chapter by developing a racemization rate equation from data collected during polymerization.

In Chapter 4 we apply the results of Chapters 2-3 to discuss and introduce basic process design and PLA engineering concepts. Specifically presented are basic engineering design equations for polymerization reactors and devolatilization. The importance of resin drying is discussed in relation to a determined moisture-PLA phase equilibrium diagram. The consequences of imperfect drying, which is inevitable, are

shown experimentally with injection molding tests. We conclude by estimating the extent of molecular weight degradation and lactide depolymerization at various processing conditions using the mathematical models developed in Chapter 3.

Chapter 5 summarizes some of the technical barriers to producing useful PLA based on the results of Chapters 2-4. The dissertation is concluded with a brief conceptual discussion of PLA chemical modification and lactide copolymerization with other biodegradable monomers, in reference to its potential to further the prospects of commodity PLA application.

Molecular Weight Note

Molecular weights were determined by gel permeation chromatography and are reported in direct reference to polystyrene standards in chloroform at 35°C. These values have not been corrected to a universal calibration. The universal correction was avoided because each of the various lactide copolymers would require the determination of its own Mark-Houwink constants. It was simply not practical and of little added value to determine the exact PLA molecular weights for all of the various lactide copolymers used in this dissertation. If desired, the polystyrene Mark-Houwink constants determined in Section 3.2 may be used with published Mark-Houwink constants in chloroform for poly(D,L-lactide)³³⁻³⁵ and poly(L-lactide)^{33,36,37} to correct the reported molecular weights for these particular polymers. However, no such information is available for the *meso*-lactide copolymers used throughout this dissertation.

Based on the hydrodynamic volumes of polystyrene and an average lactide copolymer we estimate that the true molecular weights are about 80% of the reported values, for the range of PLA molecular weights found in this dissertation. Therefore, the reported molecular weight values are precise but not accurate. However, no loss of usefulness is incurred by this approach and the reported molecular weight averages remain as useful predictors in the various correlations developed throughout this dissertation.

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Chapter 2 Physical Properties of Polylactides

2.1 Introduction

The physical properties of a polylactide are determined by: the chemical nature of the $(\text{CH}(\text{CH}_3)\text{COO})_x$ repeat units and the -OH and -H end groups to a lesser extent, the molecular architecture (stereochemistry and arrangement, e.g., linear, branched, cross-linked), and molecular mass distribution.

The qualitative understanding and quantitative modeling of polymer processes require knowledge about the temperature dependence of the following properties: density, specific heat capacity, viscosity, thermal conductivity, and reaction kinetics. Once constitutive equations relating these properties to temperature and other important parameters such as pressure and deformation rate are defined, transport and design equations may be utilized to make well-informed engineering decisions, such as choosing process conditions or designing equipment.

In a high molecular weight polylactide¹ the transition temperatures to a large extent determine (correlate with) the density, heat capacity, mechanical and rheological properties, and heat and mass transport in the polymer. Depending on the stereochemistry and thermal history, polylactides are either amorphous or semicrystalline at room temperature. In amorphous polymers the glass transition temperature, T_g , is the most

important determinant of physical properties. In semicrystalline polymers both T_g and the crystalline melting temperature, T_m , are important predictors. The dramatic changes in the motion of polymer chains that occur at these transition temperatures lead to changes in nearly all the polymer's physical properties including density, heat capacity, gas and liquid mass transfer rates, viscosity, mechanical modulus and mechanical energy absorption.² The transition temperatures largely determine the technical suitability of polylactides in various commercial applications.

The typical states of high molecular weight amorphous polylactides are shown in Figure 2-1. The glass transition temperature divides solid and rubbery liquid behavior and defines the upper use temperature for amorphous thermoplastic articles. The β -relaxation, T_β , defines the temperature below which polylactide exhibits only brittle fracture. Between T_β and T_g , amorphous polylactide undergoes physical aging (densification). Although normally brittle, amorphous polylactide can exhibit either ductile or brittle failure in the aging temperature region. Aging brings about a greater tendency for brittle fracture by increasing the temperature, between T_β and T_g , above which ductile fracture will occur for a given deformation rate. There is a broad temperature transition range, about 110-150°C, where amorphous polylactide changes from a rubbery to viscous liquid depending on the shear stress and average molecular weight of the polymer. Thermal decomposition becomes important between 215-285°C. Below this decomposition temperature molecular weight degradation of polylactides occurs primarily by hydrolysis (Section 3.5). Depending on the application, the processing temperature range for amorphous polylactide is between just above T_g and the decomposition temperature.

Mechanical and creep properties of a high molecular weight amorphous polylactide depend in part on how far below T_g the article is used or stored. Rheological properties, such as shear viscosity, correlate with the increase in processing temperature above T_g . Likewise, mass transfer of lactide, water, oxygen, oil, and other molecules through solid or liquid polylactide increases with temperature and correlates with the difference between use temperature and T_g .

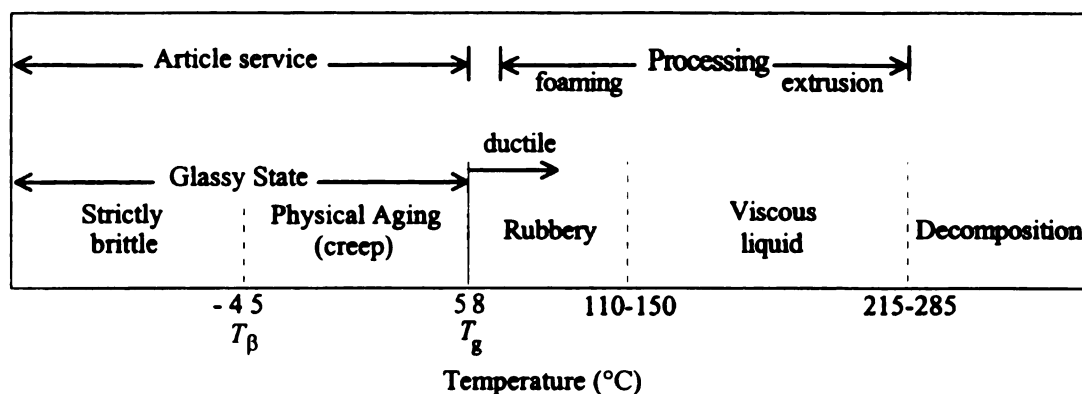


Figure 2-1. Metastable states of high molecular weight amorphous polylactide.

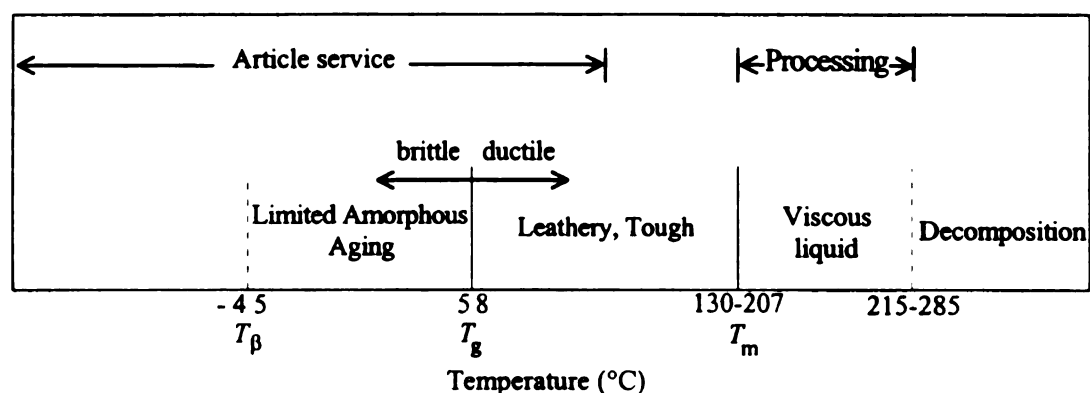


Figure 2-2. Metastable states of high molecular weight semicrystalline polylactide.

Figure 2-2 depicts the typical states for high molecular weight semicrystalline polylactides. The crystalline melting temperature, T_m , depends on both the processing conditions and stereochemistry of the polymer, and varies between 130-207°C. T_m divides tough "leathery" solid and viscous liquid behavior. The heat distortion temperature, HDT, of a semicrystalline polylactide corresponds to the upper use temperature of the article. The HDT increases with the extent of crystallinity and is bounded by T_g and T_m . The processing window is between the temperature where all the crystalline regions melt (slightly above T_m) and the decomposition temperature. For high T_m polylactides the processing window is quite narrow.

In semicrystalline polylactides T_g marks the transition from normally brittle to ductile fracture. Between T_g and the upper use temperature (HDT) the semicrystalline polylactide is very tough; the rubbery amorphous domains anchored by the rigid semicrystalline domains are able to absorb a considerable amount of energy before ductile failure results.

Mechanical properties of high molecular weight semicrystalline polylactides are affected by the extent of crystallization and the deviation in temperature from T_g . Heat and mass transfer in polylactides decrease with the extent of crystallization. Above T_m , the rheological properties and heat and mass transfer properties depend on the temperature difference with T_g , as they would for an amorphous polymer.

2.2 Thermal Properties

2.2.1 Transition Temperatures and Crystallization

The initial combination of lactide isomers before polymerization and average polylactide molecular weight influence the observed glass and crystalline melting transition temperatures. In addition, the extent and rate of polylactide crystallization is strongly affected by the concentrations of *meso*- and D-lactides prior to polymerization.

To investigate these effects, we characterized polylactides from six different lactide isomer mixtures by differential scanning calorimetry, DSC. In addition, to elucidate the effect of molecular weight on the glass transition temperature we performed DSC on four amorphous polylactides having number average molecular weights between 15,000 - 190,000 g/mol. Finally, nine poly(*meso*-co-L-lactide)s were studied to determine the effect of initial *meso* isomer content on the extent and rate of crystallization.

Experimental

Polymer. Six polylactides were supplied by Cargill Inc.: poly(6% L-co-6% D-co-88% *meso*-lactide), poly(28% L-co-28% D-co-44% *meso*-lactide), poly(50% L-co-50% D-lactide), poly(78.5% L-co-4% D-co-17.5% *meso*-lactide), poly(90.5% L-co-0.5% D-co-9% *meso*-lactide), and homopolymer poly(L-lactide). The random copolymers were produced from mixtures of three monomer batches: 100% L-lactide, 100% D,L-lactide, and 88% *meso*-lactide with 12% D,L-lactide. D,L-Lactide is the racemate of D and L-lactide at $T \leq 127^\circ\text{C}$ (e.g., at room temperature), and the racemic mixture of D and L-lactide at $T > 127^\circ\text{C}$ (e.g., at bulk polymerization temperatures). All

percentages are rounded to the nearest 0.5%. The amount of *meso*-lactide in the monomer batches was determined by gas chromatography (see Section 3.2 for analytical procedure).

Poly lactide molecular weights were determined by gel permeation chromatography, GPC (Section 3.2 for analytical setup and procedure). Molecular weights are reported relative to polystyrene standards.

Purification. To remove unreacted monomer we dissolved the polylactide samples in chloroform and separated the polymer from solution by precipitation in methanol. The white polymer precipitates were dried and annealed under vacuum at 85°C. The precipitates varied in structure from fibrous, poly(L-lactide); to stiff cake, poly(90.5% L-co-0.5% D-co-9% *meso*-lactide); to powdery, four remaining polylactides. The polylactides as received were not melt devolatilized and contained about 5% unreacted monomer.

Differential Scanning Calorimetry. The glass transition temperature, specific heat capacity increase at the glass transition, crystalline melting temperature, and heat of melting were determined by differential scanning calorimetry, DSC. A DuPont 910 DSC with DuPont 9900 General V2.2A software was used. The DSC was purged with 50 ml/min nitrogen passed through an oxygen and water adsorption bed. The DSC is maintained and calibrated on a scheduled basis in a professionally operated lab

(Composite Materials and Structures Center, Michigan State University College of Engineering, East Lansing, MI).

The following DSC algorithm was used: (1) heat to 200°C at 10°C/min (hereafter referred to as the first thermogram), (2) isothermal hold at 200°C for 5 min, (3) cool to 0°C at 5°C/min (4) heat to 200°C at 10°C/min (second thermogram).

The glass transition temperature is reported as the inflection point of the heat flow versus temperature curve. The reported crystalline melting temperature corresponds to the temperature at which the melting endotherm maximum occurs.

Results

Figures 2-3 and 2-4 present the first DSC thermograms for the six polylactides, after annealing at 85°C, in order of increasing initial L-lactide content. The poly(L-lactide) and poly(90.5% L-co-0.5% D-co-9% *meso*-lactide) thermograms exhibit crystalline melting endotherms with maxima at 179 and 145°C. Based on the heats of melting,³ these samples were approximately 56 and 41% crystalline, respectively.

The four polylactides having less initial L-lactide were entirely amorphous. These thermograms have significant enthalpy relaxation endotherms, 1-3 J/g, at the glass-rubber transition. This is not a cooling/heating hysteresis but rather the result of physical aging in the glassy state (Section 2.2.2). The absence of a relaxation endotherm in the poly(L-lactide) and poly(90.5% L-co-0.5% D-co-9% *meso*-lactide) samples is indicative of the increased dimensional stability associated with semicrystalline polymer morphology.

It is notable that the more crystalline poly(L-lactide) thermogram displays no apparent glass transition (Figure 2-4).

The second DSC thermograms are shown in Figures 2-5 and 2-6. Although both the poly(L-lactide) and poly(90.5% L-co-0.5% D-co-9% *meso*-lactide) samples were semicrystalline before the first temperature ramp, only the poly(L-lactide) sample regained crystallinity prior to the second heating. As evidenced by the exotherm in the cooling portion of the first poly(L-lactide) thermogram (Figure 2-4), crystallization occurred between 120 and 100°C during cooling at 5°C/min. To visually compare the areas of the crystallization exotherm and melting endotherm in the heat flow versus temperature plot (Figure 2-4), the crystallization area should be doubled because the cooling rate was exactly one half the heating rate.

The enthalpy relaxation endotherm observed in the first thermograms (Figure 2-3) for the four initially amorphous polylactides is reduced considerably in the second thermograms (Figure 2-5). The five-minute hold at 200°C, after the initial temperature ramp, ensures sufficient molecular relaxation (equilibration) to "erase" the "memory" of – or heat flow response to – sample stresses associated with the prior thermal history in subsequent calorimetry.

After cooling and reheating, the poly(L-lactide) glass transition became apparent in the second thermogram (Figure 2-6): $\Delta C_p = 0.19 \text{ J/g-}^\circ\text{C}$ at $T_g = 64^\circ\text{C}$. However, this T_g was affected by the crystallinity of the sample. Instead of a glass-rubber transition, this T_g reflects more of a glass-"leathery" (tough) transition because of the rubber-crystalline

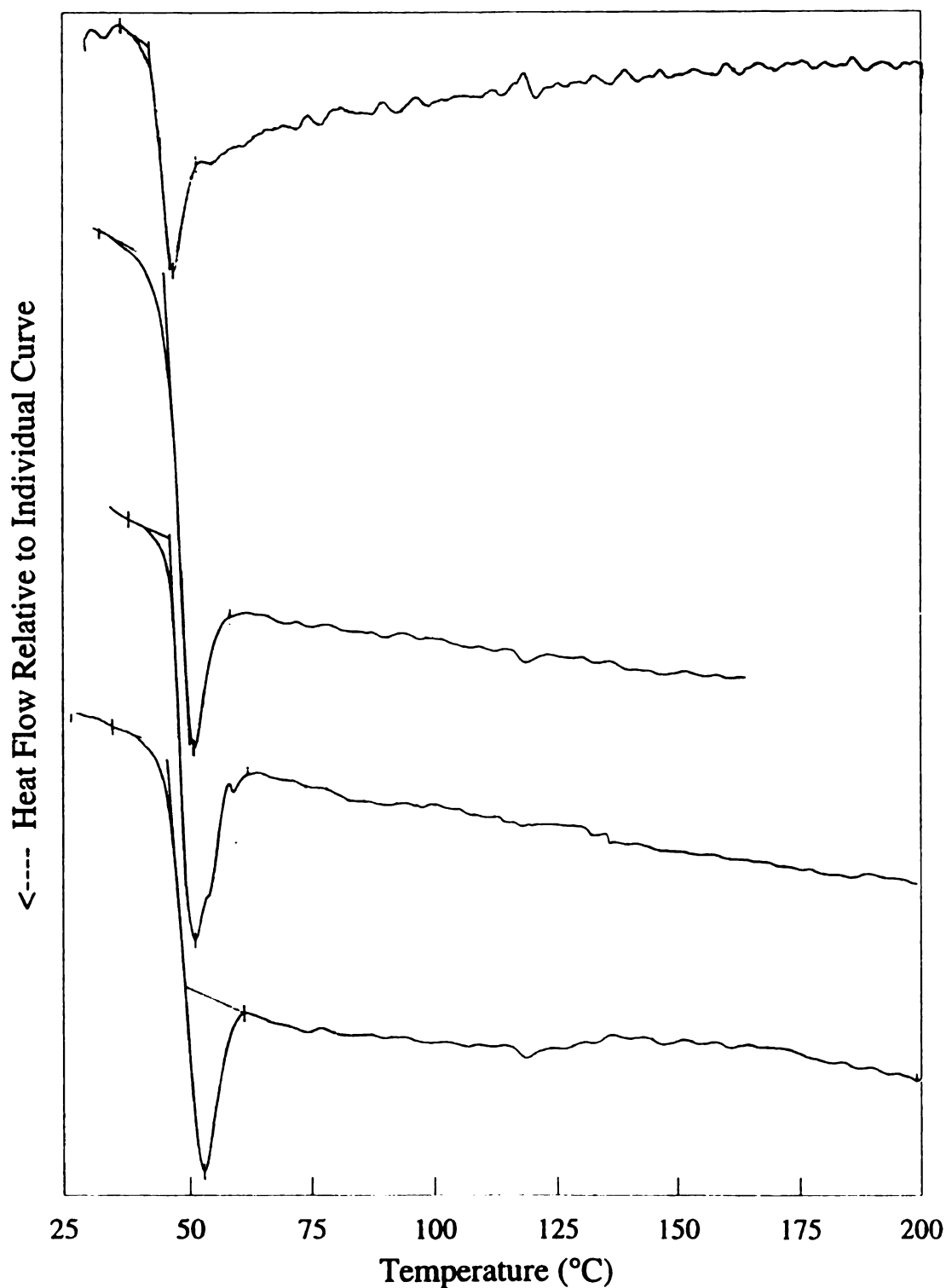


Figure 2-3. First thermograms of the four amorphous PLA's in order of increasing L-content (top to bottom): poly(6% L-co-6% D-co-88% *meso*-lactide), poly(28% L-co-28% D-co-44% *meso*-lactide), poly(50% L-co-50% D-lactide), poly(78.5% L-co-4% D-co-17.5% *meso*-lactide). The measured T_g 's are 44.3, 49.9, 50.2, and 50.6°C, respectively. The enthalpy relaxation endotherms immediately following T_g are between 1-3 J/g.

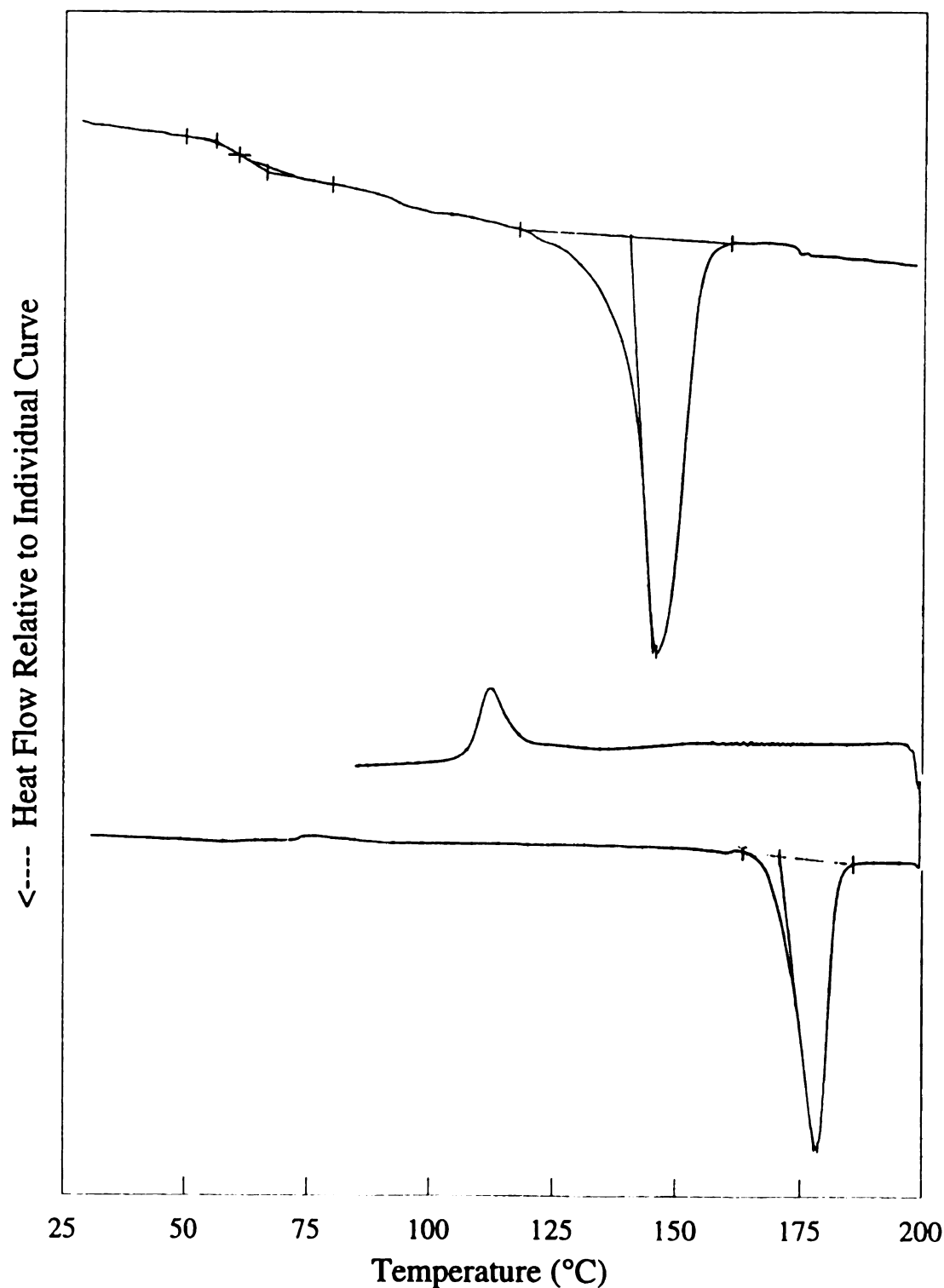


Figure 2-4. First thermograms of the two semicrystalline PLA's in order of increasing L-content (top to bottom): poly(90.5% L-co-0.5% D-co-9% *meso*-lactide), $T_g = 57.7^\circ\text{C}$, $T_m = 145^\circ\text{C}$, $\Delta H_m = 38.2 \text{ J/g}$; poly(L-lactide), no apparent T_g , $T_m = 179^\circ\text{C}$, $\Delta H_m = 52.5 \text{ J/g}$. Neither polymer exhibits an enthalpy relaxation endotherm. The poly(L-lactide) sample crystallized during the cooling following the initial heating (cooling rate, 5°C/min , is one half the heating rate; thus, the exotherm size appears 50% smaller).

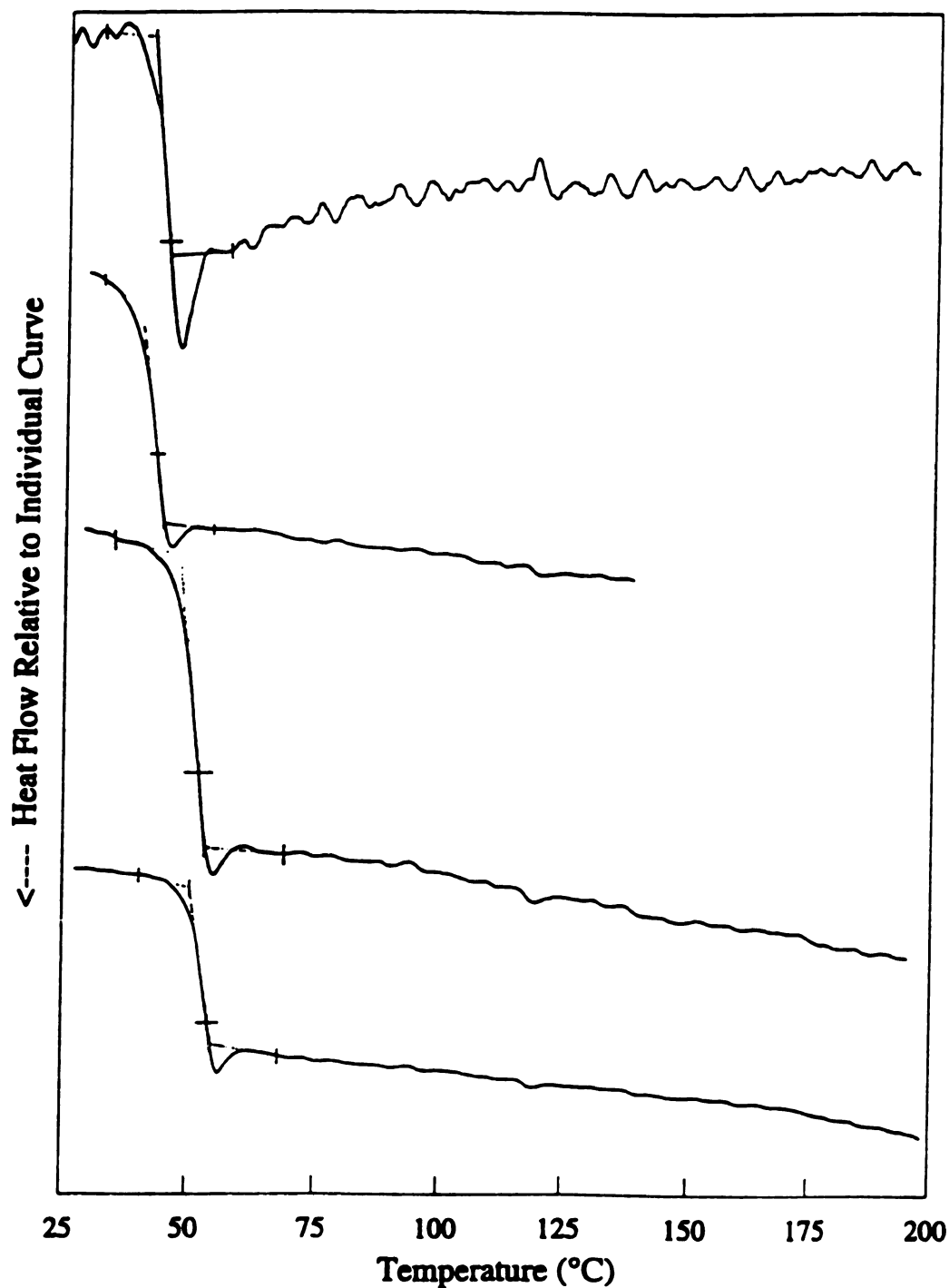


Figure 2-5. Second thermograms of the four initially amorphous PLA's in order of increasing L-content (top to bottom): poly(6% L-co-6% D-co-88% *meso*-lactide), poly(28% L-co-28% D-co-44% *meso*-lactide), poly(50% L-co-50% D-lactide), poly(78.5% L-co-4% D-co-17.5% *meso*-lactide). The measured T_g 's are 44.5, 42.9, 52.9, and 54.7°C, respectively. The ΔC_p 's are NA, 0.57, 0.58, and 0.55 J/g-°C, respectively. The enthalpy relaxation endotherms were either eliminated or significantly reduced from the first thermograms.

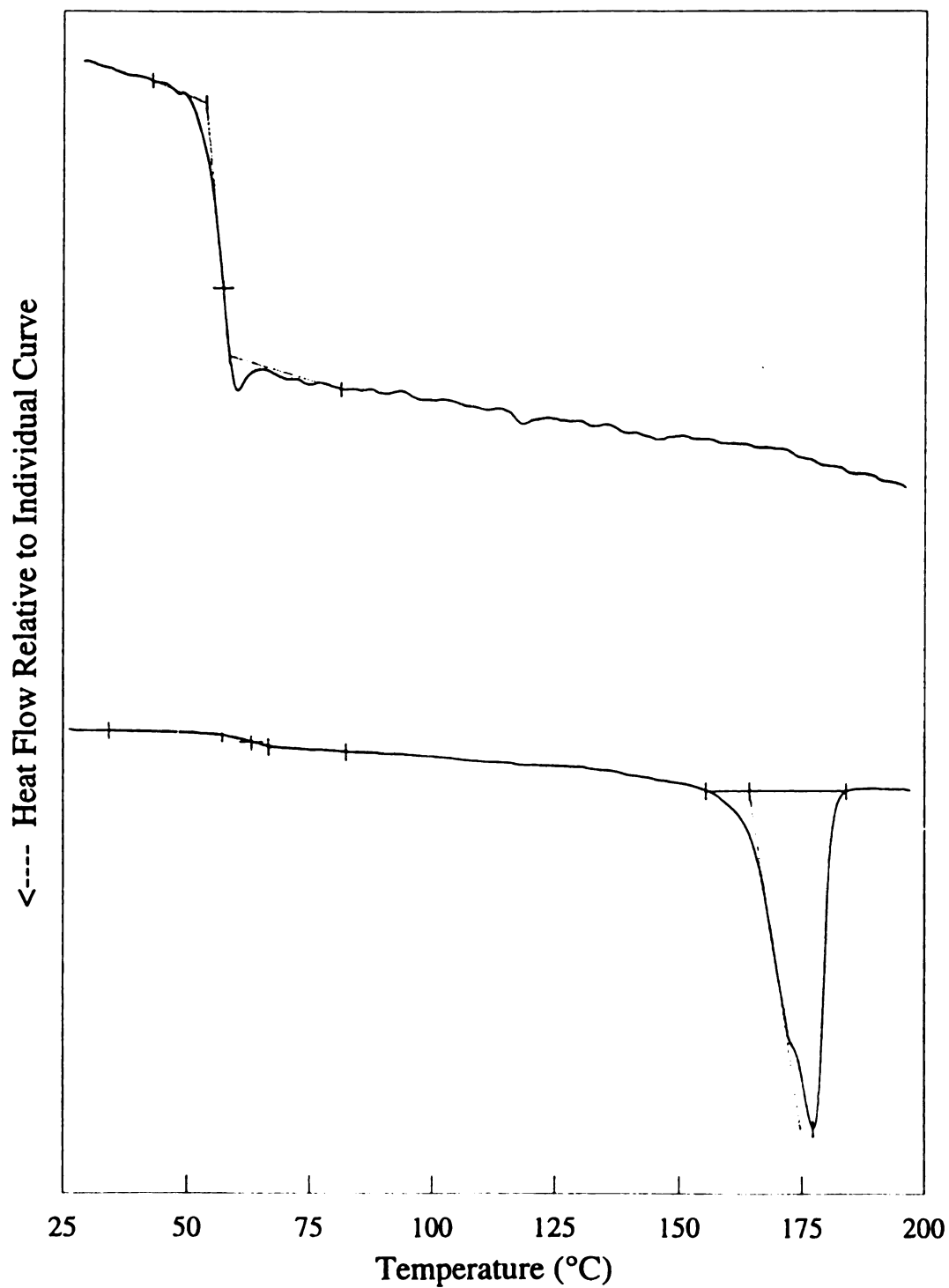


Figure 2-6. Second thermograms of the two initially semicrystalline PLA's in order of increasing L-content (top to bottom): poly(90.5% L-co-0.5% D-co-9% *meso*-lactide), $T_g = 57.7^\circ\text{C}$, no apparent T_m , $\Delta C_p = 0.55 \text{ J/g}\cdot^\circ\text{C}$; and poly(L-lactide), $T_g = 64.1^\circ\text{C}$, $T_m = 178^\circ\text{C}$, $\Delta H_m = 51.7 \text{ J/g}$, $\Delta C_p = 0.19 \text{ J/g}\cdot^\circ\text{C}$.

composite morphology. In the other polylactides the glass transitions in the second thermograms were generally within 3°C of their values in the first thermograms.

Table 2-1 summarizes the thermal transitions of the six polylactides from the calorimetry results presented in Figures 2-3 through 2-6. The glass transition temperatures are from the second DSC thermograms where all six polylactides exhibit a T_g . The crystalline melting temperatures, T_m , and heats of melting, ΔH_m , are taken from the first thermograms. Because of the noise in the poly(6% L-co-6% D-co-88% *meso*-lactide) baseline, the increase in specific heat capacity at the glass transition, ΔC_p , is not reported for this sample. The polydispersity index, $PDI = M_w/M_n$, was between 1.44-1.63 for all samples. These values are typical of batch lactide polymerizations conducted at about 130°C.⁴

Discussion: Glass Transition

By differential scanning calorimetry the glass transition is characterized by an increase in the specific heat capacity when progressing from the glassy state to the rubbery liquid state. In Table 2-1 the ΔC_p for poly(L-lactide) is lower than that for the other polylactides. This is because some of the sample crystallized during cooling before the second heating. Because the glass transition is exclusive to the amorphous phase, the increase in specific heat at T_g is sensitive to the fraction of sample that is amorphous. When poly(L-lactide) is cooled rapidly and not permitted to crystallize, ΔC_p is normally about 0.56 J/g-°C. For polylactides the change in specific heat capacity at the glass transition is 0.55-0.58 J/g-°C and is independent of the initial lactide isomer distribution.

**Table 2-1 Thermal Transitions of Lactide Copolymers
by Differential Scanning Calorimetry**

initial monomer composition (%)	sample mass (mg)	M_n (g/mol)	PDI	T_g^a (°C)	ΔC_p^a (J/g-°C)	T_m^b (°C)	ΔH_m^b (J/g)
6L/6D/88 <i>meso</i>	9.4	108,500	1.63	44.5	NA	-	-
28L/28D/44 <i>meso</i>	16.0	153,700	1.55	42.9	0.57	-	-
50L/50D	15.1	221,300	1.56	52.9	0.58	-	-
78.5L/4D/17.5 <i>meso</i>	8.2	56,600	1.44	54.7	0.55	-	-
90.5L/0.5D/9 <i>meso</i>	9.1	54,200	1.55	57.7	0.55	145	38.2
100L	7.1	57,400	1.51	64.1	0.19	179	52.5

^adata from second DSC thermogram; after DSC conditioning.

^bdata from first DSC thermogram; prior to DSC conditioning.

The T_g values in Table 2-1 appear to depend on the initial lactide isomer distribution. In addition, T_g is known to depend on the polymer number average molecular weight (important below some practical M_n). In order to elucidate the effect of polymer stereochemistry on T_g we determined the effect of M_n on T_g in a separate experiment.

Experimental. Four additional amorphous polylactides (15% D-lactide, 85% L-lactide) of different molecular weights were prepared by vial polymerization (Section 3.2 for procedure) using lactic acid to control the molecular weight (Section 3.3). The polymers were characterized by DSC and GPC. The results are summarized in Table 2-2.

Table 2-2 Effect of M_n on the T_g of Amorphous Poly(15% D-co-85% L-lactide)

M_n (g/mol)	M_w (g/mol)	PDI	T_g (°C)
12,000	15,400	1.28	43.6
29,000	50,750	1.75	51.0
40,200	96,600	2.40	52.4
78,800	189,000	2.40	55.0

Based on free volume theory the following equation is commonly used to relate T_g and M_n ,⁵

$$T_g(M_n) = T_g(\infty) - K/M_n \quad (2-1)$$

where $T_g(\infty)$, glass transition temperature at infinite molecular weight, and K are constants that depend on the particular polymer. In Figure 2-7 a plot of T_g versus $1,000,000/M_n$ (mmol polymer/kg), or specific zeroth moment of the molecular weight distribution, is indeed linear for polylactide. $T_g(\infty)$ and K were determined to be 56.6 °C and 157,000 °C-g/mol, respectively, by linear regression. Thus, a polylactide with $M_n = 50,000$ has a T_g that is about 3°C lower than that for an infinite molecular weight polylactide.

In Table 2-3 we combine the data in the preceding two tables to make a set of T_g data that is fairly well-balanced in M_n , initial *meso*-lactide isomer fraction, and effective initial L-mer fraction. L-Mer is the 72 g/mol polylactide repeat unit derived from L-lactic acid (L-Mer (%) = L-lactide (%) + 1/2 *meso*-lactide (%)); for example, *meso*-lactide

contains one L-mer and one D-mer, D-lactide contains two D-mer. The poly(D,L-lactide) datum ($T_g = 52.9^\circ\text{C}$) was omitted to make the data set better balanced in L-mer and *meso*. The 100% L-lactide polymer data in Table 2-1 has been excluded from Table 2-3 because the sample was semicrystalline during the measurement of T_g ; crystallinity affects T_g in a complicated way. All T_g data in Table 2-3 are from samples that were completely amorphous prior to the T_g measurement.

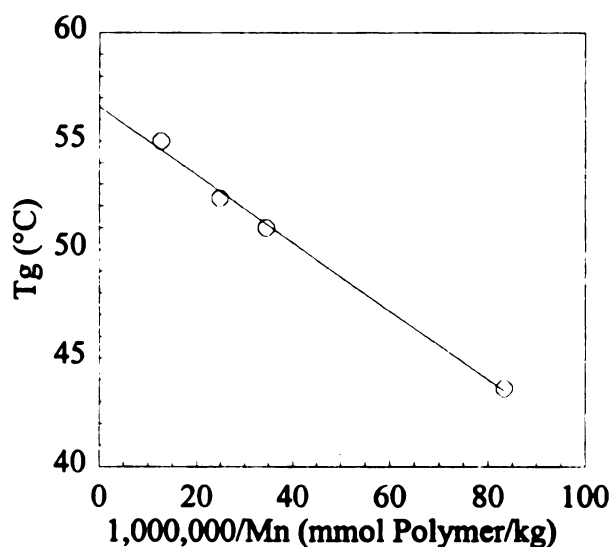


Figure 2-7. Linear relationship between T_g and $1E6/M_n$ in amorphous polylactide. The solid line is the linear model $T_g = 56.6 - 157,000/M_n$; $R^2 = 0.996$, $n = 4$.

A three-factor analysis of variance was performed to determine the importance of M_n , initial *meso*-lactide isomer fraction, and effective initial L-mer fraction on the observed T_g . Because T_g has a linear relationship with the inverse of M_n the chosen predictor was $1E6/M_n$ (mmol polymer/kg). By choosing the initial *meso*-isomer and initial L-mer fractions as independent predictors the stereochemistry at the start of the lactide

copolymerization is completely specified. A first order multiple linear regression model was used.

Table 2-3 Glass Transition Temperature of Various Amorphous Polylactides

T_g (°C)	M_n (g/mol)	$1E6/M_n$ (mmol/kg)	L-mer (%)	<i>meso</i> (%)
44.5	108,500	9.22	50	88
42.9	153,700	6.51	50	44
54.7	56,600	17.7	87.25	17.5
57.7	54,200	18.5	95	9
43.6	12,000	83.3	85	0
51.0	29,000	34.5	85	0
52.4	40,200	24.9	85	0
55.0	78,800	12.7	85	0

All three effects were statistically significant accounting for 95% of the variance in T_g . The glass transition temperature increases with M_n and L-mer content, and decreases with *meso* content. The following linear model can be used to estimate T_g ,

$$T_g = 45 - 180,000/M_n + 16w_{L\text{-mer}} - 7w_{\text{meso}}; \quad w_{L\text{-mer}} \geq 0.5 \quad (2-2)$$

where $w_{L\text{-mer}}$ and w_{meso} are the initial effective L-mer and *meso* fractions. This equation has a root-mean-square error of 1.5°C and is valid for an effective L-mer content $\geq 50\%$ (e.g., polylactides originating from combinations of L-lactic and racemic D,L-lactic acid). Using equation (2-2) we estimate the infinite molecular weight glass transition temperatures for poly(L-lactide), poly(*meso*-lactide), and poly(D,L-lactide) to be 61, 46, and 53°C,

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respectively. The significantly lower T_g for poly(*meso*-lactide) is practically important in applications that require plasticization of amorphous PLA segments.

Jamshidi et al.⁶ report $T_g(\infty)$ values of 58 and 57°C for poly(L-lactide) and poly(D,L-lactide), respectively. However, reported values for poly(L-lactide) are often several degrees higher. Joziassse et al.⁷ report T_g values of 63 and 54°C for poly(L-lactide) and poly(D,L-lactide), respectively. Their values are in accord with our findings.

Discussion: Crystalline Melting Transition

The rate and extent of high molecular weight polylactide crystallization during cooling or annealing in the melt, bulk crystallization, depends on the initial lactide isomer distribution. Only polylactides having a high degree of structural regularity can crystallize from the melt. This holds true for other modes of crystallization such as pressure and strain-induced crystallization.

In Table 2-1 the four polylactides containing less than 80% initial L-lactide content were amorphous after annealing (Figure 2-3). The crystalline melting temperature, T_m , and heat of melting, ΔH_m , of the two crystalline polylactides decreased with the initial *meso*-lactide fraction. The poly(L-lactide) was considerably more crystalline than the poly(90.5% L-co-0.5% D-co-9% *meso*-lactide) sample and would have a higher upper use temperature and a narrower processing window above T_m . In general, the heat distortion temperature for semicrystalline polymers correlates with the thermal transitions T_g and T_m , the degree of crystallization, and the thermal history.

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Both D-lactide and *meso*-lactide affect the crystallization of polylactide derived from L-lactic acid. However, *meso*-lactide is the main concern because the majority of D-mer produced by L-mer racemization contributes to *meso*-lactide rather than D-lactide before polymerization (Section 1.2.4).

Experimental. Nine random *meso*- and L-lactide copolymers were produced by Cargill. The polylactides were prepared in vials and had $M_w > 100,000$ g/mol. The initial *meso*- isomer content varied from 0-18%. DSC was performed⁸ with a Mettler DSC 30 using the following algorithm: 1) heat at 20°C/min to 200°C, hold for 2 min, rapidly quench, 2) isothermal hold at 110°C for 2 h, slow cool, 3) heat at 20°C/min to 200°C.

Table 2-4 summarizes the effect of initial *meso*-lactide on the average melting temperature and extent of crystallization after 2 hours of annealing at 110°C. The extent of crystallization, observed as ΔH_m , is plotted versus initial *meso*-lactide in Figure 2-8. Although crystallinity was found in annealed samples having as much as 18% *meso*-lactide, crystallization was not practically important in polylactide containing greater than 12% *meso*-lactide.

The equilibrium melting point depression by a noncrystallizable monomer in random copolymers is given by Flory⁹

$$\frac{1}{T_{m,eq}} - \frac{1}{T_{m,eq}^0} = \frac{-R}{\Delta H_u} \ln x_A \quad (2-3)$$

Table 2-4 Effect of *Meso*-Lactide on the Melting Temperature and Enthalpy

initial monomer composition (%)	T_m^b (°C)	ΔH_m^b (J/g)
100L	174.9	37.5
97L/3 <i>meso</i>	158.9	40.7
94L/6 <i>meso</i>	147.0	35.5
91L/9 <i>meso</i>	144.8	35.3
91L/9 <i>meso</i>	145.7	38.8
88L/12 <i>meso</i>	nd	0.0
85L/15 <i>meso</i>	nd	0.0
82L/18 <i>meso</i>	126.3	3.2
82L/18 <i>meso</i>	114.3	0.7

nd = none detected

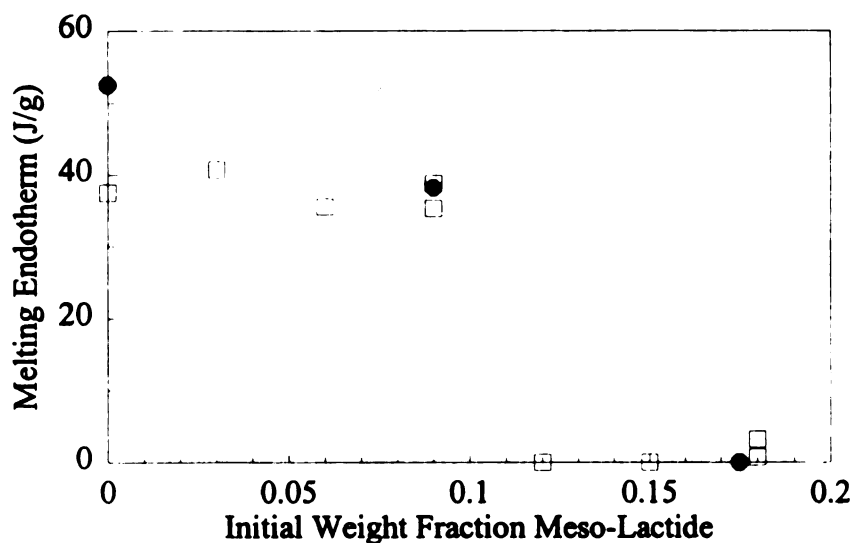


Figure 2-8. Effect of *meso*-lactide on the crystallization melting endotherm of polylactide by DSC. The presented data from Table 2-4 (□) are after 2 h annealing at 110°C; the data from Table 2-1(●) are after annealing at 85°C.

where $T_{m,eq}$, $T_{m,eq}^0$, R , ΔH_u , and x_A are the equilibrium melting point, equilibrium melting point without noncrystallizable comonomer, ideal gas constant, heat of melting per mole of repeat unit, and mole fraction of crystallizable monomer, respectively.

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Vasanthakumari and Pennings¹⁰ estimated the equilibrium melting temperature for poly(L-lactide) to be 207°C by extrapolating observed T_m versus crystallization temperature data. Fischer et al.¹¹ determined the heat of melting for purely crystalline poly(L-lactide) to be 93 J/g (6700 J/mol). Substituting these values into equation (2-3), the effect of *meso*-lactide on the theoretical equilibrium melting temperature is estimated by the dashed line in Figure 2-9. The actual T_m data from Tables 2-1 and 2-4 are fit to the solid line. Although the slopes of both melting temperature curves are similar, 3°C/%*meso*, the observed T_m are 30-43°C below $T_{m,eq}^0$. In general, this is a result of practical polylactide crystallization at temperatures between 85 -130°C and with crystallization times < 4 h.

The equilibrium melting curve in Figure 2-9 is effectively linear in *meso* weight fraction, w_{meso} , and Equation (2-3) can be simply expressed as

$$T_{m,eq}(^{\circ}\text{C}) = \frac{1}{\frac{1}{T_{m,eq}^0} - \frac{R}{\Delta H_u} \ln w_{L\text{-lactide}}} \cong 207^{\circ}\text{C} - 282w_{meso}; \quad w_{meso} \leq 0.18 \quad (2-4)$$

The observed melting temperature for practical polylactide crystallization is approximately

$$T_m(^{\circ}\text{C}) \approx 175^{\circ}\text{C} - 300w_{meso}; \quad w_{meso} \leq 0.18 \quad (2-5)$$

Combining Equations 2-2 and 2-5, Figure 2-10 presents typical T_g and T_m as a function of initial *meso*-lactide for random *meso*- and L-lactide copolymers.

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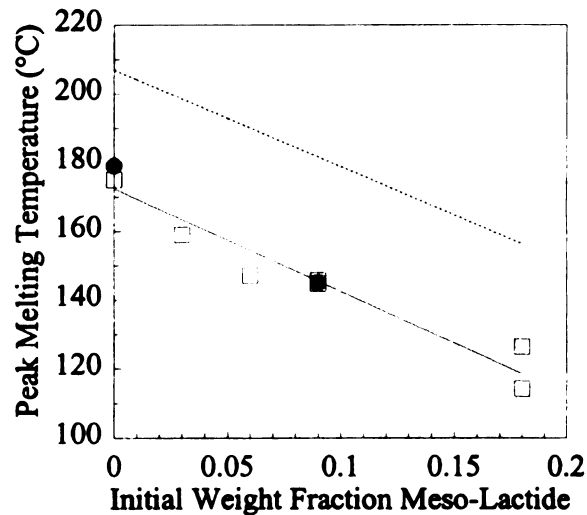


Figure 2-9. Effect of initial *meso*-lactide weight fraction on polylactide equilibrium melting temperature: dashed line based on equation (2-4). Observed melting temperature data from Table 2-1 (●), and data from Table 2-4 (□).

The melting point depression by *meso*-lactide is practically important. A lower melting point increases the processing window allowing a greater flexibility in processing conditions (i.e., higher viscosities and greater melt elasticity). In addition, processing at lower temperatures significantly lowers the rate of hydrolytic degradation which is the main source of polylactide degradation during processing (Section 3.5). The rate and extent of lactide reformation after devolatilizing below the equilibrium monomer concentration, a necessary step prior to resin processing (Sections 3.2 and 4.3), is also decreased by a lower processing temperature.

Annealing a semicrystalline polylactide between T_g and T_m will slowly increase the degree of crystallinity and the observed melting temperature toward their equilibrium values. For example, data in Table 3-3 (Section 3.2.2) show an increase in a poly(L-lactide) melting temperature from 184 to 198°C in 100 hours at 130°C. There is an

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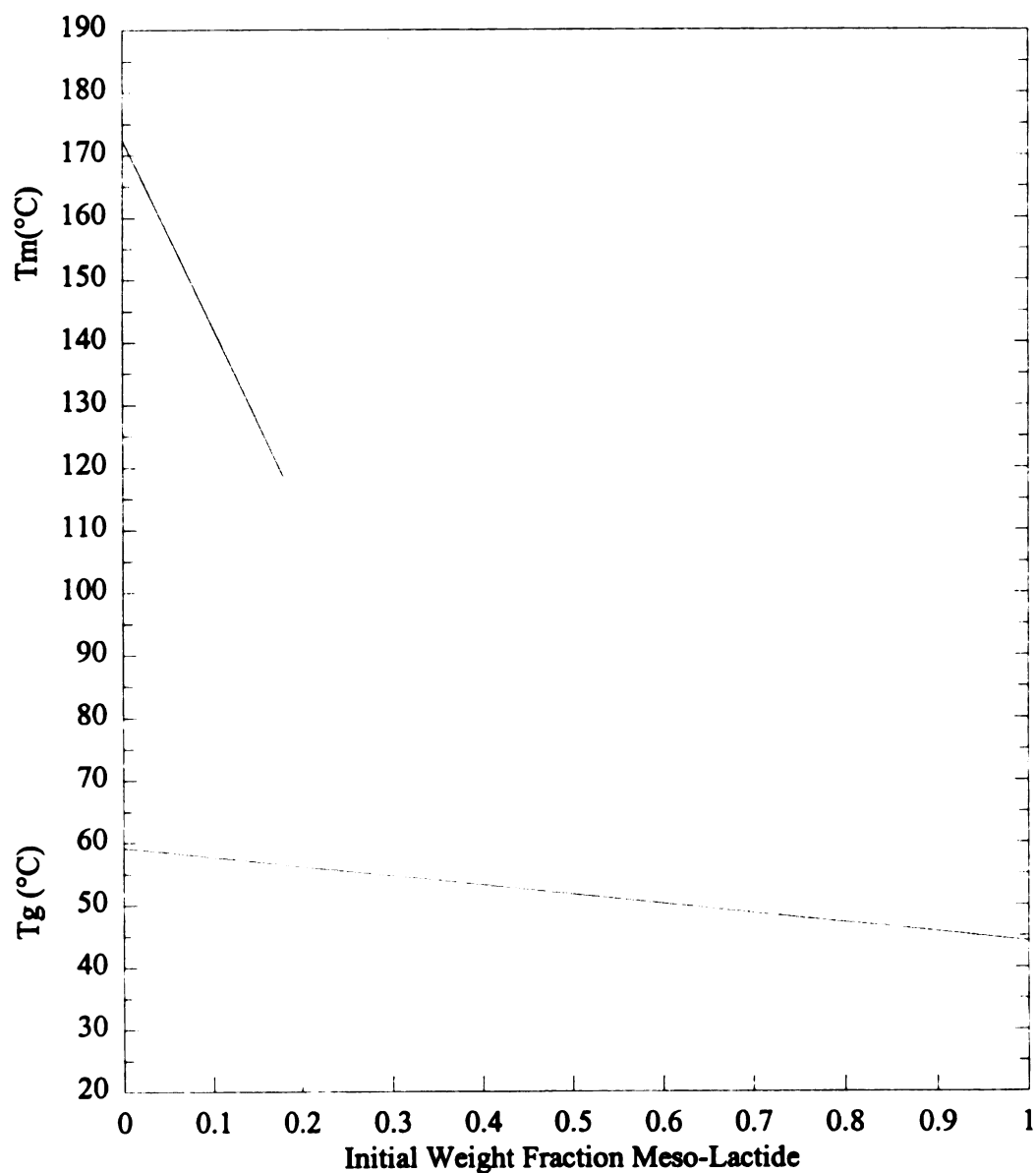


Figure 2-10. Typical melting and glass transition temperatures for random copolymers of *meso*- and L-lactide.

increase in T_m during annealing because polymer crystallization does not occur at equilibrium. This is in contrast to the crystallization of small molecules which tend to crystallize and melt at the equilibrium melting temperature. This high melting

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polylactide sample was approximately 89% crystalline, $\Delta H_m = 84$ J/g. Although such a polymer has enhanced tensile strength, tensile modulus, and heat distortion temperature (in excess of 180°C), it would be difficult to process in some applications because of the low viscosity and high degradation rate at its minimum processing temperature of about 215°C. Likewise, the annealing of a previously molded article from low to high crystallinity would be impractical for most commodity applications because of the required long annealing time at 90-130°C.

In addition to depressing the melting temperature and heat of melting, the initial *meso* content also decreases the rate of crystallization. This is apparent from the thermograms in Figures 2-4 and 2-6. Although initially crystalline, the 9% *meso* polylactide was not crystalline in the second thermogram, after cooling at 5°C/min from the melt and reheating at 10°C/min. However, the poly(L-lactide) sample recrystallized during the cooling step after the initial melting (Figure 2-4). This rate decrease in the *meso* containing sample is in part a result of the structural irregularities of the polylactide chains (kinks) imparted by the D-mer units which do not participate in crystallization. The polymer chains thus have a higher entropy because of these structural irregularities and require a longer period for ordering the L-segments into a regular conformation for crystallization.

Figure 2-11 shows a 10°C/min DSC thermogram for the same poly(L-lactide) in Figure 2-6 after a rapid quench instead of a slow cool from the melt. As evident by the symmetrical exotherm, 40 J/g, crystallization occurred during heating and developed an average melting temperature of 172°C and a melting enthalpy of 41 J/g. The onset and

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conclusion of main crystallization were 98 and 123°C, respectively; these values were determined by the intersection of the heat flow baseline with straight lines fit to the increasing and decreasing portions of the exotherm. The temperature at the crystallization peak was 110°C which falls exactly between the onset and conclusion of main crystallization. This peak temperature is close to the estimated temperature of maximum crystallization rate $T_{\text{cryst,max}}$ by the following rule of thumb¹²

$$T_{\text{cryst,max}} \approx \frac{(T_g + T_m)}{2} = 114^\circ\text{C} \quad (2-6)$$

where T_g and T_m are 57 and 172°C (Figure 2-11).

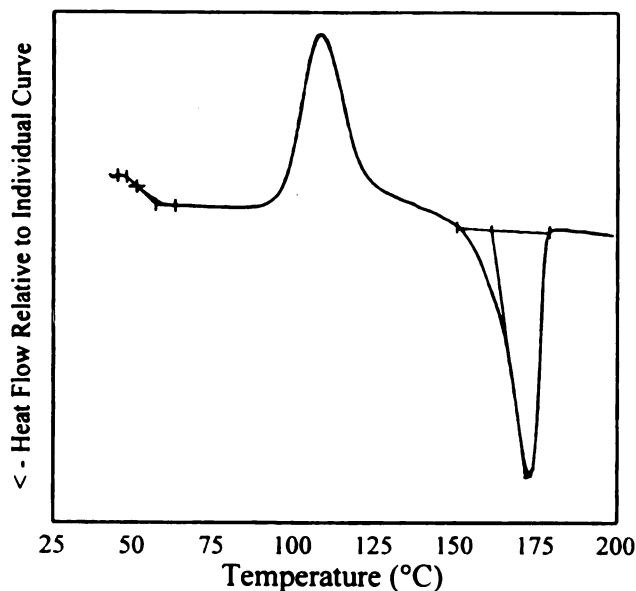


Figure 2-11. DSC thermogram of poly(L-lactide) after rapid cooling from the melt. The measured glass transition temperature, average melting temperature, crystallization exotherm, and melting endotherm were 57°C, 172°C, 40 J/g, and 41 J/g, respectively.

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The temperature of maximum poly(L-lactide) crystallization rate was determined in two separate studies to be 110°C, von Oepen et al.,¹³ and 130°C, Vasanthakumari et al.¹⁰ Because the rate of crystallization correlates with both T_g and T_m , we expect the temperature of maximum crystallization to decrease with *meso* content because of its depression of both T_g and T_m . For the 9% *meso* sample in Table 2-1 we estimate the temperature of maximum crystallization to be $(58+145)/2 = 101^\circ\text{C}$. This result is in good agreement with data by Kolstad.¹⁴

The time of poly(L-lactide) crystallization during heating in Figure 2-11 is calculated to be 2.5 min from the ratio of the temperature span, 25°C, and the heating rate, 10°C/min. This is about the same annealing time at 90-130°C required to achieve enough crystallinity to release an injection molded poly(L-lactide) part and obtain the desired increase in heat distortion temperature for most applications. Since injection molding cycle times for commodity plastics strongly affect part costs and are desired to be about 10-20 seconds for small parts (e.g., cutlery) it is clear that the crystallization rate of poly(L-lactide) without nucleating agents is unacceptable.

Kolstad¹⁴ tested a variety of nucleating agents and found talc to be the most effective in reducing the crystallization half-time of poly(L-lactide). He found that the addition of 6% talc reduced the crystallization half-time at 110°C from 3 minutes to 30 seconds for poly(L-lactide), and from 7 minutes to 80 seconds for 3% *meso* polylactide. It is apparent that the use of talc significantly improves the rate of polylactide crystallization. However, considering that some *meso*-lactide is inevitable in a

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commercial process, it is clear that further improvements are needed to achieve the cycle times desired in commercial processing lines.

There have been numerous investigations into the crystallization behavior of poly(L-lactide).^{10,11,13-20,21-32} However, only Kolstad¹⁴ and Huang et al.²⁸ have studied the effect of initial *meso*-lactide on poly(L-lactide) crystallization. As is normal for polymer bulk crystallization,² the morphology of poly(L-lactide) crystallites is found to be spherulitic.^{20,10,15,18,28-30} The predominately 10₃ helical structure (α -form) of poly(L-lactide) has been determined by DeSantis and Kovacs,²¹ Hoogsteen et al.²² and Okihara et al.²³ In addition, there have been numerous studies regarding the equimolar stereocomplex cocrystallization of pure poly(L-lactide) and poly(D-lactide).^{23,33-43} This PLA stereocomplex has a substantially increased average melting temperature of 230°C and enhanced mechanical strength.

Although both amorphous and semicrystalline PLA are generally brittle plastics, semicrystalline PLA is advantageous in applications where an upper use temperature greater than 60°C is required (e.g., hot food and beverage service ware, or where increased barrier properties are needed, such as in some bottle and plasticized film applications). In addition, crystallinity alleviates the problem of amorphous polylactide articles fusing together or "blocking" at extreme transportation or storage temperatures.

However alluring, the development of a commercially useful crystalline polylactide presents a daunting challenge to engineers and scientists. This is partially because of the inherently slow crystallization rate in the high molecular weight polylactide viscous melt. It is also a significant task to produce a polylactide containing a

very low content of *meso*-lactide in order to minimize its undesirable affect on crystallization rate. Thermal racemization can occur at any production step: lactic acid, lactide, and polylactide. Therefore, thorough understanding of how residence time, temperature, and catalysts affect racemization is critical for the successful production of low *meso* polylactide.

The development of a highly effective nucleating agent is essential to produce useful semicrystalline polylactide articles. Alternatively, fully biodegradable high T_g ($>100^\circ\text{C}$) amorphous lactide copolymers (with non-lactic comonomers such as alanine) could be developed to produce thermoplastics having increased service temperature and enhanced barrier properties (Section 5.2).

Conclusions: Thermal Transitions and Crystallization

1. Polylactide T_g increases with M_n and initial L-mer fraction, and decreases with initial *meso* fraction according to the relationship described in equation (2-2). The infinite molecular weight glass transition temperatures for poly(L-lactide), poly(*meso*-lactide), and poly(D,L-lactide) are estimated to be 61, 46, and 53°C, respectively.
2. The change in polylactide specific heat capacity at the glass transition was determined to be 0.55-0.58 J/g·°C and is independent of the initial lactide isomer distribution.

3. The degree of crystallization, observed by ΔH_m , decreases with increasing initial *meso*-lactide content. Crystallinity was not observed in polylactides containing less than 82% initial L-lactide.
4. Polylactide T_m decreases 3°C for every 1% initial *meso*-lactide.
5. The initial *meso*-lactide fraction decreases the rate of polylactide crystallization.
6. The temperature of maximum crystallization rate is about 114°C for poly(L-lactide).

2.2.2 Physical Aging

Several years ago a Cargill EcoPLA™ applications engineer⁴⁴ made an observation that, to us, was initially quite surprising. After routinely injection molding amorphous polylactide (17% *meso*-lactide, remainder L-lactide; $M_n = 89,100$, $M_w = 198,000$) tensile bars, the engineer stored the molded specimens in his truck for tensile testing the next day at another location. The tensile bars were stored in the vehicle during a period of extreme winter cold in Minneapolis (below -25°C). The specimens were returned to room temperature prior to testing. Contrary to normal tensile testing results that show failure at low percentage elongation, these specimens all exhibited over 100% elongation and did not fail (cold drawing). After testing, the samples retained the extended shapes developed during loading. However, when placed in a hot glass of water the samples rapidly returned to their initial unextended shape before testing.

In our injection molding and tensile testing experiments at Michigan State University the polylactide samples always failed with an elongation at break between

0-5%, depending on the molecular weight. Thus, we generally expect a polylactide tested at room temperature, 35°C below T_g , to behave as a brittle plastic rather than a tough yielding plastic. Cargill later found that when cold stored specimens sat at room temperature for a number of hours before testing (3-8 h), the specimens became brittle and would fail with a percentage elongation less than 5%.

So in a matter of hours the same polylactide specimen is transformed from a tough yielding plastic, able to absorb a considerable amount of applied energy before failure, to a brittle rigid plastic resembling polystyrene. We soon ascertained that this dramatic change in 17% *meso* polylactide article properties is a result of physical aging in the glassy state. Our introduction to the significance of polylactide aging exemplifies the importance of polylactide stereochemistry (specifically *meso* content), aging temperature below T_g (rate of aging), and prior thermal history (processing parameters) on the rate and extent of physical aging during storage.

Physical aging occurs in all glasses² (inorganic, organic, polymeric, monomeric) and is the gradual volume relaxation toward the equilibrium amorphous state.^{45,46} Accompanying this time-dependent return to equilibrium are changes in nearly all the glassy state physical properties.⁴⁶ Important polymer physical property changes during aging include^{45,47-50} increasing density, elastic modulus, and yield stress; decreasing creep rate, impact energy to break, and mass transfer rates of gasses and liquids. The progressive stiffening and dimensional changes characteristic of polymers that exhibit

strong aging at storage or service temperatures pose significant challenges in the design, manufacturing, and use of such materials.

Essentially all aspects of physical aging are qualitatively explained by the time-dependent change in free-volume.⁴⁵ The free-volume concept states that the mobility of atoms and molecules depend on their packing density;^{2,45} that is, as free-volume decreases relaxation times increase. Stress relaxation and creep are consequences of the volume relaxation that occurs during aging of glasses. Stress relaxation is the dynamic stress (force/area) decay after an instantaneous and constant deformation is imposed. Creep is the time-dependent dimensional changes that occur in glass articles subjected to a constant stress. A common example of creep is the observed dimensional changes of old windows; owing to gravitational force, the bottoms of old windows are measurably thicker than their tops.

Struik⁴⁵ studied the small-strain, linear viscoelastic range, creep compliance of over forty polymer systems and found that all polymers age in the same way; namely, relaxation times increase proportionally to the aging time. Using Time-Temperature Superposition, Struik developed a master creep curve for all amorphous polymers that is described by a single universal formula. Unlike chemical aging, physical aging is a thermoreversible process. When an amorphous polymer is heated above T_g the effects of aging are erased. Struik determined that physical aging increases with temperature and is bounded by the "secondary" transitions T_β and T_g . The aging rate correlates with how far below T_g the polymer is stored. The β -relaxation, T_β , represents the start of free movements of short segments on the polymer chain. Polymers that age at room

temperature (i.e., $T_{\beta} < T_{\text{room}} < T_g$) include polystyrene, poly(ethylene terephthalate), poly(vinyl chloride), and polycarbonate.

Starkweather et al.⁵¹ determined the T_{β} of polylactide (~95% L-lactide) to be -45°C at 1 kHz by dynamic mechanical analysis and dielectric relaxation measurements. They found the β -relaxation activation energy to be independent of temperature and attribute polylactide T_{β} to main chain noncooperative local motions. In addition, Starkweather et al. found a lower relaxation at -258°C which they attribute to motions of the methyl side groups; this relaxation was not observed in polyglycolide, $(\text{CH}_2\text{COO})_x$. Therefore, we expect polylactides to have about a 100°C aging window, -45 to 58°C (T_{β} to T_g).

Figure 2-12 illustrates the origin of polylactide aging with a specific volume vs. temperature (V - T) chart. When a polylactide melt is cooled through T_g (points a to b) the V - T path deviates sharply from equilibrium (b to c). This is because the abrupt decrease in molecular motion at T_g slows the rate of molecular packing such that it can no longer "keep up" with the cooling rate and maintain thermodynamic V - T equilibrium. Thus, the polymer glass is not in thermodynamic equilibrium and is supercooled having a volume, entropy, and enthalpy in excess of the equilibrium amorphous state; hence, the driving force for relaxation. The dashed equilibrium line is extrapolated from polylactide melt density data using the thermal coefficient of expansion, $7.391 \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$, determined in Section 2.3. The slope of the V - T cooling curve (b to c) depends on the cooling rate. Following cooling to a temperature between T_g and T_{β} , room temperature in this illustration, the supercooled glass experiences a gradual isothermal volume relaxation (c to d), during which the specific volume approaches the equilibrium specific volume.

After a period of aging, the polylactide glass when heated (*d* to *e*) follows a similarly sloped but lower V - T curve than during the previous cooling and becomes superheated relative to the equilibrium amorphous state. When the temperature reaches T_g the onset of large scale segmental motions permits an endothermic volume expansion, ΔV_{rel} , bringing the polymer back to V - T equilibrium (*e* to *b*). Equilibrium is followed upon continued heating of the melt (*b* to *a*).

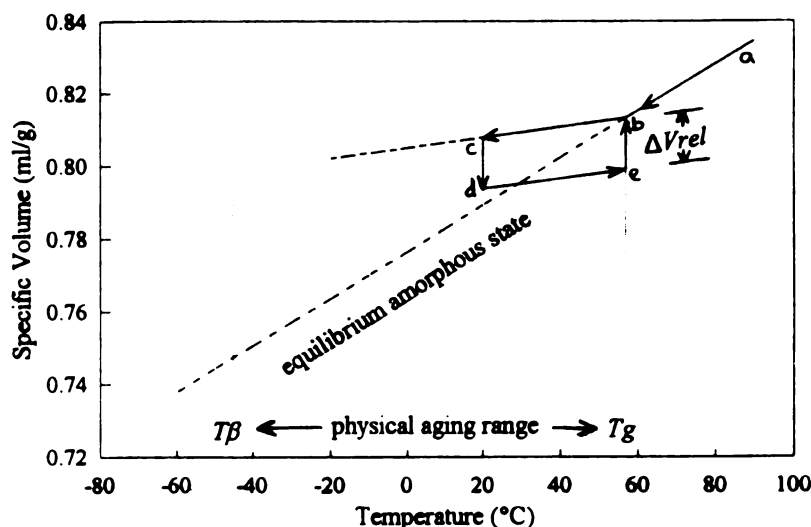


Figure 2-12. Source of amorphous polylactide aging. Specific volume vs. temperature during cooling from the melt through T_g (*abc*), aging in the glassy state during storage at room temperature (*cd*), and heating back through T_g (*deba*). During heating, an aged polylactide exhibits a sudden endothermic volume expansion (*eb*), ΔV_{rel} , at T_g .

In Figure 2-12 the V - T cooling curve (*abc*) through T_g resembles a secondary thermodynamic phase transition having a discontinuous first derivative of volume with respect to temperature. However, the heating curve after aging (*deba*) is nearly discontinuous at T_g and more closely resembles a primary phase transition. Regardless of V - T shape, the glass-rubber transition is believed not to be a thermodynamic phase

transition but rather a kinetic event.^{52,2,5} This is presumed in Figure 2-12: V - T equilibrium is unaffected by T_g .

The measurements of T_g and T_b are influenced by the time scale of the experiment (kinetically controlled); for example, T_g by DSC is reported in reference to the heating rate and prior cooling rate, and T_b by DMA is referenced to the frequency and heating rate. Above T_g the amorphous polymer has a relaxation time that is less than our normal observation time, and the material is ductile (rubbery or viscous liquid). The ratio of relaxation time to observation time, Deborah number,² is zero for ideal fluids, unity at T_g , and infinite for ideal solids. Below T_b the polymer behaves as an ideal solid and is strictly brittle.

In the aging temperature region between T_b and T_g either ductile or brittle failure may occur. The ratio of relaxation time to deformation time largely determines whether an amorphous glass will undergo ductile or brittle fracture. The characteristic relaxation time depends on the temperature and free volume (extent of aging). As the polymer glass ages the relaxation time increases with the decreasing free volume, and the temperature required for ductile fracture (brittle-ductile temperature or brittleness temperature) increases for a given deformation rate. Likewise, the mode of failure at a given temperature can be sensitive to the deformation rate. This is partly the reason why some polymers that exhibit tough ductile behavior during tensile testing (slow deformation rate) are brittle during Izod impact testing (fast deformation rate). A linear decrease in temperature affects the brittle-ductile transition equivalently to a logarithmic increase in straining rate.¹²

Not only does T_g divide liquid and solid behavior and thus define the upper use temperature for amorphous articles, but it also marks the temperature where the observed thermodynamic properties (V-T-H) change from age dependent (kinetically controlled) properties in the glassy state to equilibrium controlled properties in the melt. T_b represents a temperature below which only brittle fracture behavior exists. Although somewhat sensitive to time scale, T_b and T_g can be considered practical temperatures characteristic for each individual polymer. The T_b and T_g transitions define three metastable states for amorphous polymers: ideal solid showing only brittle fracture, aging glass which may exhibit either ductile or brittle fracture, rubbery or viscous melt which will flow under a sufficient applied load.

Similar to primary thermodynamic phase transitions, a change in enthalpy accompanies the change in volume at T_g that is observed upon heating an aged polymer glass. This endothermic enthalpy relaxation, ΔH_{rel} , is conveniently measured by DSC and is evidence of the free volume relaxation characteristic of aging. Muller and Wendorf⁵³ correlated the enthalpy relaxation with the volume relaxation at T_g in aged amorphous polycarbonate samples. In another study, Matsuoka⁵⁴ mathematically related the free volume to the excess enthalpy and entropy in the glassy state. The significance of associating the enthalpy relaxation with aging is that DSC can be used as a convenient analytical method to correlate the time dependent physical property changes during polymer aging with ΔH_{rel} .

When a polylactide sample is rapidly quenched through T_g and immediately reheated there is no enthalpy relaxation at T_g (no aging occurs). The enthalpy relaxation is

observed after glassy state aging for several hours and subsequent heating through T_g .

Figure 2-13 shows a typical DSC thermogram for an injection molded (MSU composite center) amorphous polylactide (88% L-lactide) tensile coupon following two months aging. The enthalpy relaxation is also evident in the amorphous DSC thermograms presented in Figure 2-3.

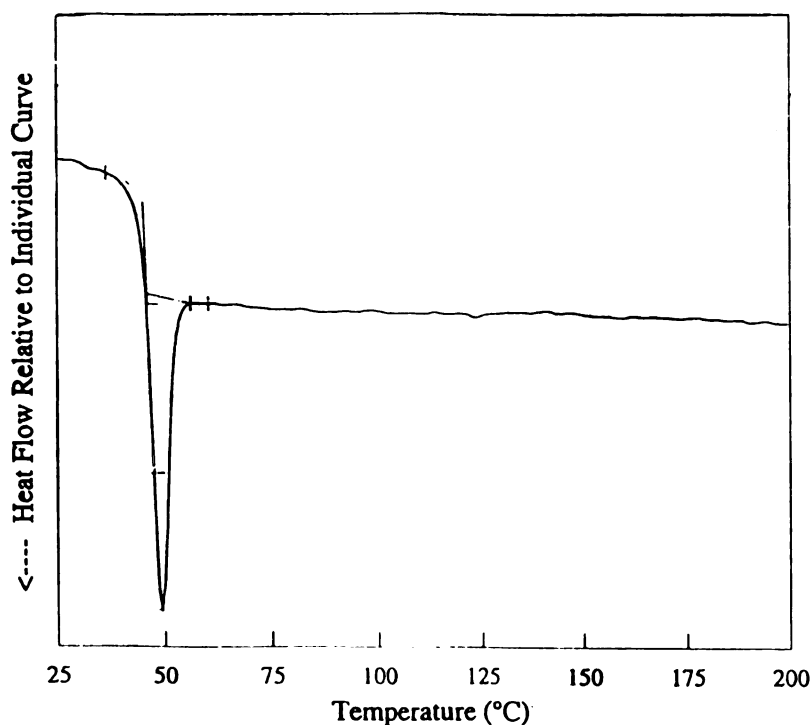


Figure 2-13. DSC thermogram of an amorphous polylactide injection molded coupon after aging at room temperature for two months. A sharp enthalpy relaxation after T_g , 6.7 J/g, is observed and is characteristic of an aged polylactide article.

Table 2-5 shows the DSC results of an amorphous polylactide aging study.⁵⁵

Polylactide pellets (about 17% initial *meso*-lactide, $M_w = 200,000$) which had been stored at room temperature for 1/2 year exhibited an enthalpy relaxation of 6.9 J/g by DSC. Ten samples of this polymer batch were heated in an oven to 200°C for 30 minutes, to erase the effects of aging, and then rapidly quenched through T_g . Immediately following the

quench a DSC was performed on one sample and no enthalpy relaxation was observed. The remaining samples were stored at room temperature (20°C) and tested by DSC at periodic intervals. The relaxation enthalpy was determined with a Mettler DSC 30 using a heating rate of 20°C/min. ΔH_{rel} was calculated from the endotherm area after T_g using the developed heatflow baseline after T_g and ΔH_{rel} . The peak temperature of the enthalpy endotherm, T_{peak} , increased over 3°C during aging. This increase is a result of the increase in T_g that occurs during densification. Similar increases in T_g on aging have been found in PET (3°C in 65 days),⁵⁶ polycarbonate, polystyrene,⁵⁷ and polyvinyl chloride.⁵⁸

Table 2-5 Development of ΔH_{rel} by DSC During Amorphous Polylactide Aging at $T_g - 38^\circ\text{C}$

time (days)	ΔH_{rel} (J/g)	T_{peak} (°C)
aged pellets	6.9	62.0
0	0	-
3	2.4	58.4
7	3.3	59.3
14	5.2	61.3
21	4.4	61.3
28	5.2	62.0
35	5.3	61.0
42	5.8	62.0
49	5.3	61.8
56	5.4	60.9

Based upon the W.L.F. equation the glassy state equilibration time is estimated to be over 10^6 years at $T_g - 38^\circ\text{C}$.⁴⁵ Because of the linear relationship between volume

relaxation at T_g and logarithmic time,⁵ we expect a linear relationship between ΔH_{rel} and logarithmic time. This linear relationship was demonstrated by Celli and Scandola⁵⁹ with poly(L-lactide) that had been melt quenched to inhibit crystallization. A plot of ΔH_{rel} versus $\ln(t)$ using the data in Table 2-5 is shown in Figure 2-14. An extrapolation of the data estimates that this polymer would obtain an ΔH_{rel} of 6.9 J/g in 160 days and a value of 10 J/g in 7 years.

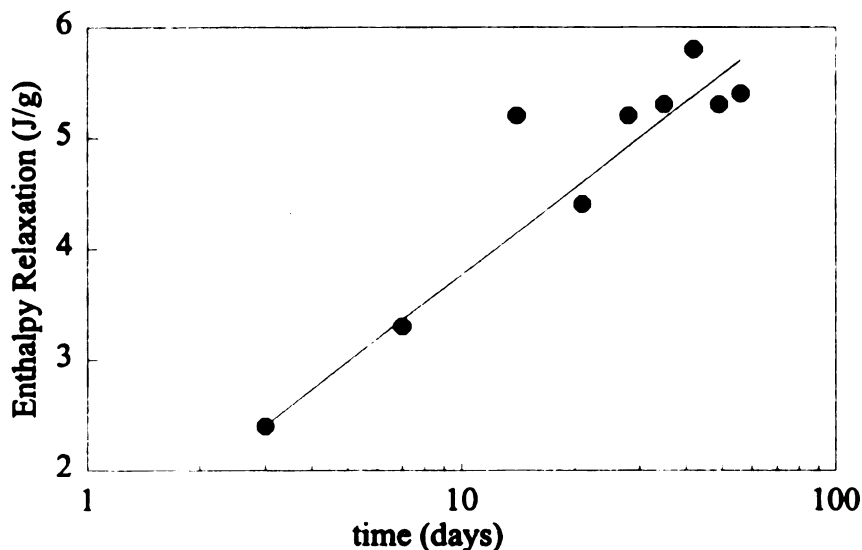


Figure 2-14. Aging of amorphous polylactide at T_g -38°C. The solid line is the linear relationship between enthalpy relaxation at T_g and logarithmic time. The 14 day sample was flagged as a possible outlier and omitted from the regression.

Jabarin and Lofgren⁶⁰ determined a critical ΔH_{rel} brittleness value for amorphous PET tensile coupons tested at room temperature. They found that PET tensile coupons that exhibit an enthalpy relaxation less than 3 J/g (measured by DSC) are ductile during tensile testing. However, as the same PET samples age they become brittle upon developing an ΔH_{rel} greater than 3 J/g. In another aging study Mukherjee and Jabarin⁵⁶ determined that crystalline oriented PET has the same critical ΔH_{rel} brittleness value as

amorphous PET, 3 J/g. They calculate that it takes unoriented PET several years at room temperature (T_g -58°C) for the ductile-brittle transition to occur.

Apparently for amorphous polylactide this ductile-brittle transition takes place after several hours of room temperature (T_g -38°C) storage. From the ΔH_{rel} data in Table 2-5 and the observation that tensile bars become brittle in less than one day of storage, we suspect that the ductile-brittle transition for amorphous polylactide occurs with an ΔH_{rel} of about 1-2 J/g, as measured by DSC heating through T_g .

Celli and Scandola⁵⁹ measured the development of ΔH_{rel} versus time in rapidly melt quenched (to inhibit crystallinity) poly(L-lactide) at 30°C (T_g -28°C), 40°C (T_g -18°C), and 48°C (T_g -10°C). As expected the development of ΔH_{rel} with time increased with temperature. For example, after 22 h. of aging the reported ΔH_{rel} values at 30, 40, and 48°C were 2.0, 2.9, and 3.8 J/g, respectively. Celli and Scandola also determined that ΔH_{rel} development increases with decreasing molecular weight. This same observation has been made with atactic polystyrene.⁶¹ The findings that the rate of ΔH_{rel} development increases with both a decreasing degree of subcooling, $T_g - T$, and decreasing molecular weight are consistent with the fact that increasing temperature and decreasing molecular weight act to lower a polymer's characteristic relaxation time.

Polymer physical aging below T_g is exclusive to the amorphous phase. Crystallization affects aging by (1) reducing the amorphous content available for aging and (2) providing physical crosslinks that stabilize and retard aging in the amorphous phase. Recalling the six polylactide DSC thermograms after melt quenching and room temperature storage in Figures 2-3 and 2-4, we found that the two semicrystalline

polylactide samples did not exhibit a relaxation endotherm whereas the four amorphous samples had ΔH_{rel} values of 1-3 J/g. This result is characteristic of the decreasing significance of polymer aging with crystallinity. Another example is provided by Tant and Wilkes⁶² who investigated the decreasing extent and rate of PET aging associated with increasing crystallinity.

Mukherjee et al.⁵⁶ studied the effect of orientation on the aging of semicrystalline PET. They found that orientation significantly reduces physical aging and the observed ΔH_{rel} during storage below T_g . They also found that highly oriented samples exhibited no change in density with storage below T_g , whereas samples with low levels of orientation experienced a density increase during aging. Orientation is a technique that could prove very useful for some polylactide applications. Not only will orientation increase dimensional stability by decreasing the affects of physical aging, but orientation at temperatures close to T_g may produce sustained ductile polylactide articles through the creation of new free volume. High stresses and deformations (e.g., cold drawing) cause formation of new free volume which counteract the effects of physical aging (densification). This is why the cold draw polylactide tensile bars remain flexible for some time until heating near or above T_g where the new volume is quickly reduced and the polymer relaxes to its original dimensions.

Prior processing conditions also affect the aging of polylactide articles. In injection molding, for example, physical aging of a stored sample below T_g depends on process conditions such as mold temperature, hydrostatic pressure, deformation history during molding, and cooling rate after molding.⁴⁶

In summary, the glassy state aging of polylactides depends on: aging temperature below T_g , degree of crystallization (*meso*- and *D*-lactide content, thermal history), degree of amorphous orientation, molecular weight distribution, and prior processing conditions.

The example cited at the beginning of this section describing the ductile polylactide tensile coupons after cold temperature storage is explained by the fast cooling rate from the melt, the polymer stereochemistry, and the aging temperature below T_g . The 17% initial *meso*-lactide ensured that the tensile coupons were entirely amorphous. On rapidly cooling the molded polymer through T_g the tensile coupons became supercooled, having a free volume in excess of the equilibrium volume (amorphous state). The tensile coupons were then stored at a very low temperature and the rate of aging was greatly reduced. When the coupons were brought back to room temperature for testing at a later time the extent of aging was small. Having a free volume in excess of some critical value, the samples were ductile exhibiting over 100% elongation (cold drawing). However, when the same coupons were aged at room temperature for between 3-8 h. the samples became brittle. This ductile-brittle transition is also observed in amorphous polylactide tensile bars that have not been cold stored by performing tensile tests every hour, immediately following injection molding, until the transition is observed. Because there is normally a considerable amount of time between injection molding and tensile testing, polylactide tensile coupons are generally brittle.

Conclusions: Physical Aging

1. Physical aging occurs in amorphous polylactides between -45 and 58°C (T_g to T_g). The free volume reduction that is characteristic of aging is evidenced in differential scanning calorimetry by an endothermic volume expansion (enthalpy relaxation) after T_g .
2. Crystallization reduces the rate and extent of polylactide aging. The initial *meso*- and D-lactide comonomer concentration affect polylactide aging by reducing the extent of crystallization during processing. The rate of aging increases with increasing temperature ($T < T_g$), decreasing molecular weight, and decreasing degree of orientation.
3. The ductile-brittle transition for amorphous polylactide tensile coupons apparently occurs within 8 h. of room temperature aging. For this reason, unmodified polylactides are generally brittle plastics like polystyrene. The rate and extent of polylactide physical aging are important for understanding and modifying the dimensional stability of polylactide articles (e.g., molded articles, fibers). Further work is needed to more fully understand polylactide aging and its consequences.

2.2.3 Specific Heat Capacity

The determination of PLA heat capacity at constant pressure, C_p , is essential for performing energy balances required in reactor design and resin processing. In this section we determine C_p as a function of temperature for polylactides from six different lactide isomer mixtures.

Differential scanning calorimetry, DSC, was used to determine $C_p(T)$ between 40-200°C for the same six polylactides studied in Section 2.2.1. The polylactide specific heat capacities were determined by comparing its heat flow response during a 10°C/min temperature ramp to that of an α -aluminum oxide (synthetic sapphire) standard having a heat capacity known to five significant figures.⁶³ The methodology and merits of using DSC for specific heat capacity determination are reported by O'Neill.⁶³

Experimental

Polymer. Heat capacities were determined for the following six polylactides: poly(6% L-co-6% D-co-88% *meso*-lactide), poly(28% L-co-28% D-co-44% *meso*-lactide), poly(50% L-co-50% D-lactide), poly(78.5% L-co-4% D-co-17.5% *meso*-lactide), poly(90.5% L-co-0.5% D-co-9% *meso*-lactide), and poly(L-lactide). The poly(L-lactide) sample was semicrystalline exhibiting a heat of melting of 48 J/g by DSC. The other five polylactides were amorphous. The thermal transitions and molecular weights of these polymers were reported in Section 2.2.1.

DSC Methodology. A regularly calibrated DuPont 910 DSC with DuPont 9900 General V2.2A software was used (CMSC, Michigan State University). The DSC was purged with 50 ml/min nitrogen passed through an oxygen and water adsorption bed.

The heat capacity characterization of each polylactide involved three DSC runs: empty DSC sample pan, α -aluminum oxide standard (supplied with the DuPont 910 DSC), and polylactide sample. The heat flow data for all three runs were determined against the same reference pan. First, the empty DSC pan was used to determine the heat

flow baseline at 10°C/min. Next, the α -aluminum oxide was added to this same DSC pan and accurately weighed to the nearest 0.1 mg. After recording the α -aluminum oxide heat flow data the loose powder was easily removed. The DSC pan was weighed again to ensure that all of the standard had been removed. Finally, the polylactide sample was added to the pan, weighed, and its heat flow response determined.

The following algorithm was used for all DSC runs: (1) set sample interval to 5.0 seconds, (2) equilibrate sample at 40.00°C, (3) isothermal hold at 40.00°C for 5 minutes, (4) temperature ramp of 10°C/min to 200.00°C. Sample sizes varied between 7.8-11.4 mg.

Specific Heat Capacity Determination

During a DSC run the heat flow rate, dH/dt , into the sample is proportional to its instantaneous specific heat

$$\frac{dH}{dt} = mC_p \frac{dT}{dt} \quad (2-7)$$

where m is the sample mass and the temperature ramp, dT/dt , is 10°C/min. It follows that the ratio of polylactide and α -aluminum oxide heat flow rates, referenced to the baseline heat flow rate, is equivalent to the ratio of their heat capacities, mC_p . The heat capacity data for the six polylactides were calculated with the following equation

$$C_p^{\text{PLA}} = C_p^{\alpha\text{-AlO}} \frac{m^{\alpha\text{-AlO}}}{m^{\text{PLA}}} \frac{(dH^{\text{PLA}}/dt - dH^{\text{ref}}/dt)}{(dH^{\alpha\text{-AlO}}/dt - dH^{\text{ref}}/dt)} \quad (2-8)$$

The α -aluminum oxide C_p data were provided in the DuPont 9900 reference book and can be found elsewhere.⁶⁴

O'Neill⁶³ reports that the ultimate precision of using DSC to determine C_p is 0.3% or better. This approaches the precision of an adiabatic calorimeter. However, in the absence of replication the precision will be limited by the ability to measure sample mass. For example, a 0.1 mg error in a sample mass of 10.0 mg gives a 1% loss in C_p precision.

Results and Discussion

The polylactide specific heat capacities are plotted versus temperature in Figure 2-15. Using the same polymers in Section 2.2.1 the amorphous heat capacity increase at the glass transition was determined to be 0.55-0.58 J/g-°C and independent of initial lactide isomer distribution. In Figure 2-15, this ΔC_p increase is observed between 40-60°C for the five amorphous polylactides. A smaller ΔC_p , 0.2 J/g-°C, is observed for the semicrystalline poly(L-lactide) beginning at 60°C. After the heat capacity increase at T_g , C_p for the five amorphous polylactides increases an average of 0.13 J/g-°C between 60 and 200°C. The crystalline phase of the poly(L-lactide) sample is not in strict equilibrium and its enthalpy change on melting, 48 J/g, occurs over a temperature range. This results in a broad first-order phase transition as depicted by the increase in C_p at T_m .

Specific heat capacity values at 60, 130, and 200°C are listed in Table 2-6. The four lowest initial L-lactide polylactides had nearly identical $C_p(T)$ between 60-200°C. However, poly(90.5L/0.5D/9*meso*-lactide) had $C_p(T)$ that were approximately 0.25 J/g-°C higher. Surprisingly, the semicrystalline poly(L-lactide) had the same C_p at 60°C as the

amorphous polylactides. Between T_g and T_m a semicrystalline polymer has a lower C_p than if it were amorphous. This is demonstrated by the increase in poly(L-lactide) C_p after melting. This data suggests that the inherent polylactide C_p increases with a high amount of initial L-lactide, > 90%. This result is unexpected and more data is required to confirm this finding.

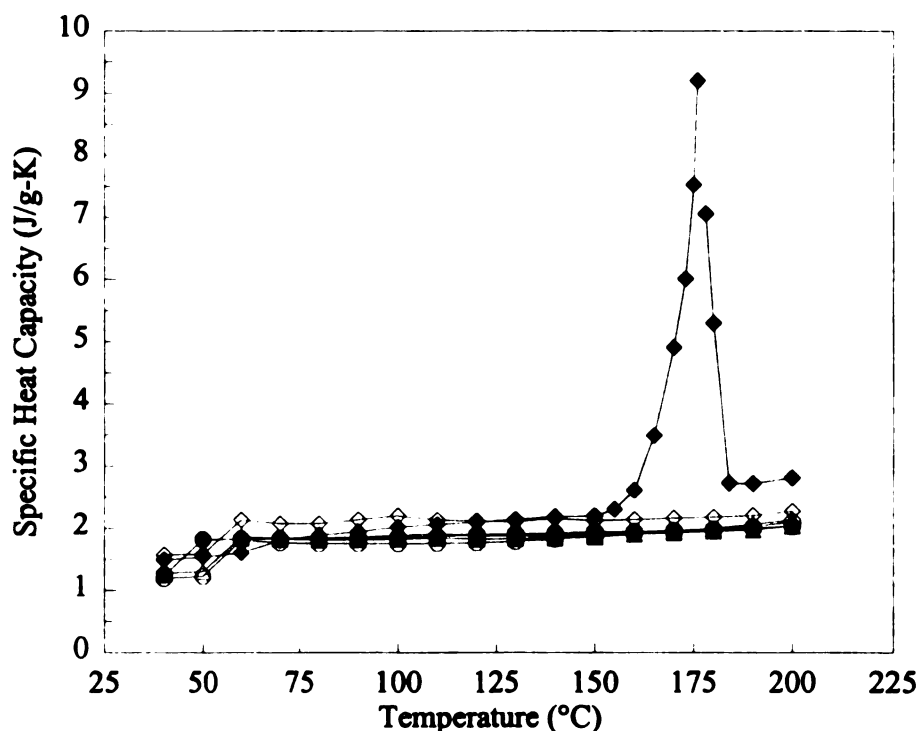


Figure 2-15. Specific heat capacities of six polylactides of varying isomer content: poly(6% L-co-6% D-co-88% *meso*-lactide), (▲); poly(28% L-co-28% D-co-44% *meso*-lactide), (●); poly(50% L-co-50% D-lactide), (○); poly(78.5% L-co-4% D-co-17.5% *meso*-lactide), (△); poly(90.5% L-co-0.5% D-co-9% *meso*-lactide), (◇); and poly(L-lactide), (◆).

For liquid polymers (melt) the increase in heat capacity with temperature is approximately linear.² The best-fit slope of the $C_p(T)$ versus T data in Figure 2-15 for the four lowest initial L-lactide polylactides is 0.00147 J/g-°C². With an RMSE of 0.04

Table 2-6 Specific Heat Capacity of Polylactides

initial monomer composition (%)	$C_p(T = 60^\circ\text{C})$ J/g-°C	$C_p(T = 130^\circ\text{C})$ J/g-°C	$C_p(T = 200^\circ\text{C})$ J/g-°C
6L/6D/88 <i>meso</i>	1.84	1.84	1.99
28L/28D/44 <i>meso</i>	1.83	1.91	1.97
50L/50D	1.81	1.79	1.98
78.5L/4D/17.5 <i>meso</i>	1.86	1.88	1.96
90.5L/0.5D/9 <i>meso</i>	2.14	2.11	2.21
100L	1.80 ^a	2.14 ^a	2.81

^asemicrystalline heat capacity data

J/g-°C, the following equation can be used to calculate $C_p(T)$ for amorphous polylactides between 60-200°C

$$C_p^l(T) = 1.71 + 0.00147 T(^{\circ}\text{C}) \quad (2-9)$$

Using this relationship the amorphous polylactide liquid state specific heat capacity is extrapolated to 25°C

$$C_p^l(25^\circ\text{C}) = 1.75 \text{ J/g-}^\circ\text{C} \quad (2-10)$$

From this result and the measured ΔC_p at T_g , the amorphous polylactide solid state specific heat capacity at 25°C is approximately

$$C_p^s(25^\circ\text{C}) = 1.2 \text{ J/g-}^\circ\text{C} \quad (2-11)$$

The calorimetric function, $1/C_p^l(25^\circ\text{C}) \, dC_p^l/dT$, is approximately constant for all liquid polymers, $1.2 \times 10^{-3} \, ^\circ\text{C}^{-1}$, with a mean deviation of 30%.² Based on Equations (2-9) and (2-10) the amorphous polylactide value for this expression is 30% lower

$$\frac{1}{C_p^l(25^\circ\text{C})} \frac{dC_p^l}{dT} = 0.84 \times 10^{-3} \, ^\circ\text{C}^{-1} \quad (2-12)$$

In Table 2-7 the solid and liquid state polylactide specific heat capacities at 25°C are calculated by the group contribution methods of Satoh and Shaw.² The group contribution estimations are in good agreement with the experimentally based amorphous polylactide $C_p(25^\circ\text{C})$ values in Equations (2-10) and (2-11). Van Krevelen² compared experimental $C_p(25^\circ\text{C})$ data for over 30 polymers to $C_p(25^\circ\text{C})$ estimations by the Satoh and Shaw methods and found mean deviations of 2% and 3.5%, respectively.

**Table 2-7 Group Contribution Calculations
of Solid and Liquid Polylactide Specific
Heat Capacities at 25°C**

group	(Satoh) $C_p^s(25^\circ\text{C})$ (J/mol- $^\circ\text{C}$)	(Shaw) $C_p^l(25^\circ\text{C})$ (J/mol- $^\circ\text{C}$)
-CH ₃	30.9	36.9
-CH-	15.6	20.95
-COO-	46	65
72 g/mol	92.5	122.85

$$C_p^s(25^\circ\text{C}) = 92.5/72 = 1.28 \, \text{J/g-}^\circ\text{C}$$

$$C_p^l(25^\circ\text{C}) = 122.85/72 = 1.71 \, \text{J/g-}^\circ\text{C}$$

Kulagina et al.⁶⁵ determined $C_p(T)$ for poly(D-co-L-lactide) at low temperatures using adiabatic and isothermal calorimetry. They measured C_p^s between -268°C and 4°C; and C_p^l between 4°C and 87°C. They report the following: $C_p^s(4^\circ\text{C}) = 1.25 \text{ J/g}^\circ\text{C}$; $C_p^l(25^\circ\text{C}) = 1.84 \text{ J/g}^\circ\text{C}$, $C_p^l(87^\circ\text{C}) = 1.95 \text{ J/g}^\circ\text{C}$. These values are 5-6% higher than the heat capacities we report here for amorphous polylactide.

The amorphous polylactide specific heat capacities are compared to those of commercial polymers in Table 2-8. The heat capacity of liquid polylactide is lower than those of PE and PP, indicating that less heat is required to increase polylactide's melt temperature. The $C_p(25^\circ\text{C})$ of polylactide and polystyrene are similar.

Table 2-8 Comparison of Specific Heat Capacities for Commercial Polymers

Polymer	$C_p^s(25^\circ\text{C})$ (J/g-°C)	$C_p^l(25^\circ\text{C})$ (J/g-°C)	$1/C_p^l(25^\circ\text{C}) dC_p^l/dT$ (°C ⁻¹)
PE ^a	1.55-1.76	2.26	1.0×10^{-3}
PP ^a	1.63-1.76	2.14	-
PS ^a	1.22	1.72	1.2×10^{-3}
PET ^a	1.13	1.55	-
PC ^a	1.17	1.59	1.4×10^{-3}
Nylon 6,6 ^a	1.47	-	0.5×10^{-3}
Amorphous PLA	1.2	1.75	0.84×10^{-3}

^adata from Van Krevelen²

Conclusions

1. The specific heat capacity of amorphous polylactide in the melt can be estimated from the following equation: $C_p^l(\text{J/g-}^\circ\text{C}) = 1.71 + 0.00147 T(^\circ\text{C})$.

2. The solid and liquid amorphous polylactide specific heat capacities at 25°C are 1.2 J/g-°C and 1.75 J/g-°C, respectively. These data are in accord with group contribution calculations and the data of Kulagina et al.⁶⁵

2.2.4 Thermal Decomposition

In the absence of moisture, the onset of significant thermal decomposition marks the upper processing temperature of polylactides. In this section we characterize the thermal decomposition of polylactides by thermogravimetric analysis, TGA. In addition, we attempt to demystify the thermal degradation behavior of polylactides by classifying the main types of PLA degradation and identifying the systems in which they dominate. Furthermore, we draw inferences about the roles of the following in PLA thermal degradation: water, polymerization catalyst, temperature, free radicals, hydroxyl PLA end groups, and oxygen.

We must be careful to distinguish between hydrolytic degradation and thermal decomposition. In the latter process it is also necessary to distinguish between degradation in an open and closed system.

Polylactide hydrolysis is the reverse of the condensation polymerization (esterification) of lactic acid. Because of the low equilibrium constant of lactic acid esterification and the relatively fast rate of ester hydrolysis, polylactide hydrolysis is important for articles stored in air at room temperature (shelf life) and for PLA melts at the moisture levels, temperatures, and times common for resin processing. In Section 3.5 we show that catalyzed hydrolysis accounts for the observed polylactide molecular

weight degradation during resin processing. This is because water at 100 ppm or greater remains in polylactide pellets after drying (Section 4.4). Thorough resin drying and eliminating or lowering the polymerization catalyst increases the molecular weight stability during processing. In Section 3.5 a melt hydrolysis kinetic model is developed to predict molecular weight degradation with time as a function of catalyst concentration, initial water concentration, initial molecular weight, and temperature.

Thermal decomposition occurs without water and becomes important during resin processing at relatively high temperatures ($> 215^{\circ}\text{C}$, Section 3.5). During the heating of polylactides both random degradation and depolymerization occur simultaneously. In random degradation, initiation of chain scission occurs randomly along the polymer chain (typically one site per repeat unit). In polyesters homolysis can occur by either alkyl or acyl cleavage. Depolymerization is the reverse of addition polymerization: lactide is reformed from polylactide. The monomer equilibrium concentration in polylactide increases with temperature; for example, 1.3% at 130°C and 4.7% at 220°C (Section 3.2). When a polylactide is heated to a higher temperature in a *closed system*, the lactide concentration increases with time until the rate of polymerization and depolymerization become equal and lactide-polylactide equilibrium is realized. Both the forward and reverse reaction are first order in catalyst and the rate at which equilibrium is achieved depends on the catalyst concentration. In Section 3.2 we develop a reversible lactide polymerization- depolymerization model that describes the lactide concentration with time as a function of catalyst concentration, temperature, and initial monomer concentration.

In a closed system the greatest a previously devolatilized polylactide will degrade by depolymerization is its monomer equilibrium concentration at the degradation temperature (e.g., < 5% molecular weight loss at 220°C). However, in an *open system* the observed degradation owing to depolymerization is unbounded. This is because in an air, nitrogen, or vacuum environment, lactide will diffuse into the vapor space in an attempt to establish lactide vapor-liquid phase equilibrium (an approximate lactide vapor-liquid equilibrium model is presented in Section 2.7). In an open system of large vapor space, a vacuum system, or a system where air or nitrogen is continuously swept, the lactide vapor activity remains near zero. As mass transfer of lactide from liquid to vapor occurs, lactide will further depolymerize to maintain chemical equilibrium in the liquid phase. Therefore, in concept polylactide can completely degrade by depolymerization in an open system. This is in fact the exact same process whereby lactide is made in high yield from low molecular weight poly(lactic-acid).

One way to determine the relative importance of depolymerization and random degradation is to compare the decrease in polymer molecular weight to the decrease in weight loss during TGA of dry PLA. Characteristic of depolymerization is a rapid decrease in polymer mass with a slow decrease in molecular weight. Typical polymers that decompose in this manner are 1,1-disubstituted vinyl polymers and certain reversible ring opening polymers (e.g., PLA). In random degradation there is a slow loss of polymer mass with an exponential decrease in molecular weight. This type of degradation is typical of condensation polymers (e.g., PLA) and mono- or non-substituted vinyl polymers. Because PLA degrades by both processes in an open system, we expect the

relative importance of the two methods to depend on the surface area-to-volume ratio of the melt and the catalyst concentration in the polymer. The observed depolymerization is increased with a high surface area-to-volume ratio (LeChatelier's principle owing to increased mass transfer) and a high catalyst concentration. In a TGA pan the 5-20 mg sample forms a relatively thin melt on the concave surface and the nitrogen sweep maintains a very low lactide vapor concentration. For these reasons TGA often leads to thermal decomposition behavior where depolymerization is the dominant process. This is easily observed by weight loss versus molecular weight data. However, as will be shown later in this section, random degradation is still important at these conditions and neither an accurate depolymerization rate nor random degradation rate can be easily determined from TGA data; these rates are determined in separate experiments in Sections 3.2 and 3.5, respectively. Because of the sensitivity of the results to sample size (surface area/volume), catalyst concentration, and geometry of the pliable TGA pans, published single data on PLA thermal decomposition rates by TGA should be regarded with some suspicion.

Despite these limitations and the fact that most PLA processes better represent closed or low surface area-to-volume systems, the characterization of PLA by TGA is still a convenient and useful method to compare its relative thermal stability to those of commercial polymers. However, it must be stressed that such data is of limited value for estimating process degradation behavior of polylactides.

In this section we use TGA to investigate the thermal decomposition of six polylactides varying in initial lactide isomer distribution. These are the same six

polylactides studied in Sections 2.2.1 and 2.2.3. The following parameters were determined for the six polylactides: initial decomposition temperature, half decomposition temperature, rate constants of weight loss at 186, 206, and 257°C, and activation energy of weight loss.

Experimental

Polymer. Thermal decomposition behavior was determined by thermogravimetric analysis on the following six polylactides: poly(6% L-co-6% D-co-88% *meso*-lactide), poly(28% L-co-28% D-co-44% *meso*-lactide), poly(50% L-co-50% D-lactide), poly(78.5% L-co-4% D-co-17.5% *meso*-lactide), poly(90.5% L-co-0.5% D-co-9% *meso*-lactide), and poly(L-lactide). The polymers were thoroughly dried and were not precipitated to remove lactide and contained about 5% lactide. The thermal transitions and molecular weights of these polymers are reported in Table 2-1. The 2-ethylhexanoic acid tin(II) salt catalyst levels in all polymers were 5,000 mol lactide/mol catalyst.

TGA Methodology. A regularly calibrated DuPont 951TGA with DuPont 9900 General V2.2A software was used. The TGA was purged with 50 ml/min nitrogen passed through an oxygen and water adsorption bed. Platinum TGA pans were used.

The weight loss versus temperature behavior of the six polylactides were determined at 10°C/min. Isothermal weight loss kinetics experiments were conducted at 186, 206, and 207°C. Sample sizes varied between 5-20 mg.

Results

Figure 2-16 shows a weight loss versus temperature TGA curve for poly(28% L-co-28% D-co-44% *meso*-lactide). The onset of weight loss, $T_{d,0}$, is 220-240°C. However, this value is somewhat misleading (low) because of the polymer's initial 5% residual monomer. The weight loss versus temperature behavior for the other five polylactides was nearly identical. Their decomposition temperatures are summarized in Table 2-9.

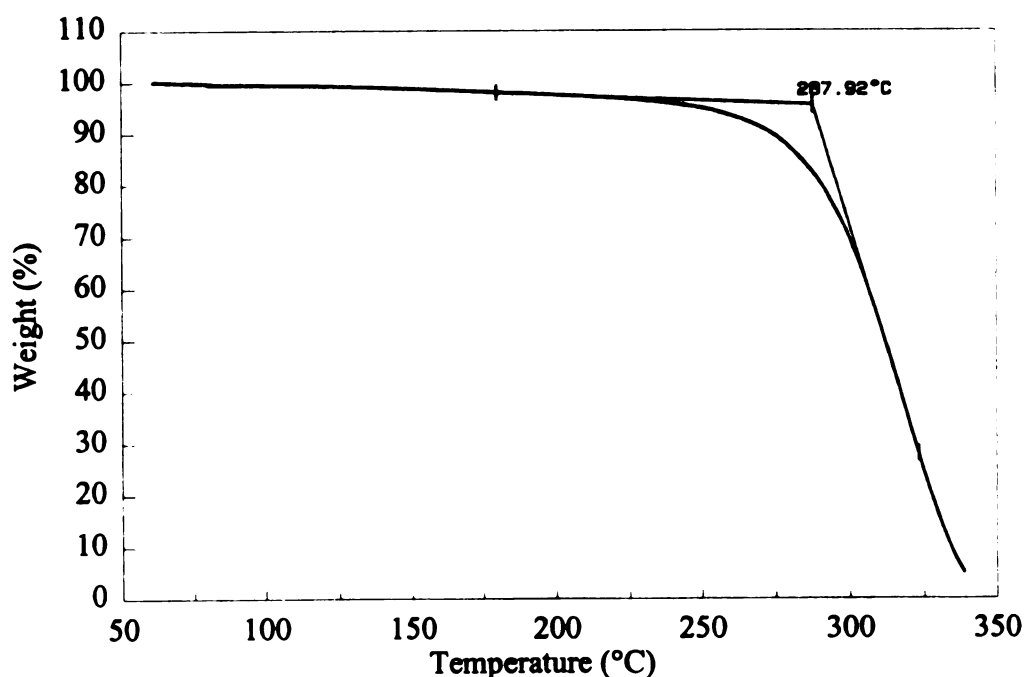


Figure 2-16. Weight loss versus temperature TGA curve for poly(28% L-co-28% D-co-44% *meso*-lactide).

The weight loss kinetics at 186, 206, and 257°C were determined by isothermal TGA experiments. In Figure 2-17 we show the effect of temperature on the weight loss kinetics of poly(L-lactide). At 186°C less than 5% of the sample is volatilized after one hour. This amount corresponds to the initial 5% residual lactide and suggests that

polylactide decomposition, as measured by weight loss, is unimportant at 186°C.

However, decomposition at 257°C is nearly complete after one hour. Between 0.5-5% solid residue remains after polylactide decomposition at 257°C.

Table 2-9 Summary and Comparison of Thermal Decomposition for Various Polylactides and Commodity Plastics

Polymer	$T_{d,0}$ (°C)	$T_{d,1/2}$ (°C)	E_a (kJ/mol)	k_{186C} (%/min)	k_{206C} (%/min)	k_{257C} (%/min)	k_{350C} (%/min)
6L/6D/88 <i>meso</i>	220-240	310	-	-	0.19	3.24, 4.57	-
28L/28D/44 <i>m</i>	220-240	312	-	-	-	2.60, 3.51	-
50L/50D	220-240	309	-	-	0.15	1.77, 3.97	-
78.5L/4D/17.5 <i>m</i>	220-240	311	-	-	-	3.52	-
90.5L/0.5D/9 <i>m</i>	220-240	312	-	-	-	2.84	-
100L	220-240	308	139	0.010	0.050	1.31, 2.10	190
PVC	170	270	134	-	-	1.64	170
PS	327	364	230	-	-	9×10^{-5}	0.25
PP	320	387	243	-	-	2×10^{-5}	0.071
PE	380	404	264	-	-	9×10^{-7}	0.0081
PET	380	450	-	-	-	-	-

data (non-italics) for PVC, PS, PP, PE, PET from Van Krevelen²

italics indicate extrapolated rate constants (based on E_a)

A summary of polylactides' isothermal weight loss kinetics are found in Table 2-9. The rate constants, k , were fit to zeroth-order kinetics which give a proportional relationship between percent weight loss, $100 - w(t)$, and time,

$$w(t) = 100 - kt \quad (2-13)$$

where $w(t)$ is the percent of initial mass. Zeroth-order kinetics are consistent with a process, such as depolymerization, where the number of polymer chains remain constant during weight loss. These kinetics were generally valid until 40-80% volatilization, whereafter first order kinetics became apparent,

$$w(t) = w_0 \exp(-kt) \quad (2-14)$$

Approximately 20% of the samples tested at 257°C followed first order kinetics from the start. With repeat TGA experiments we found no correlation between decomposition rate behavior and initial isomer composition.

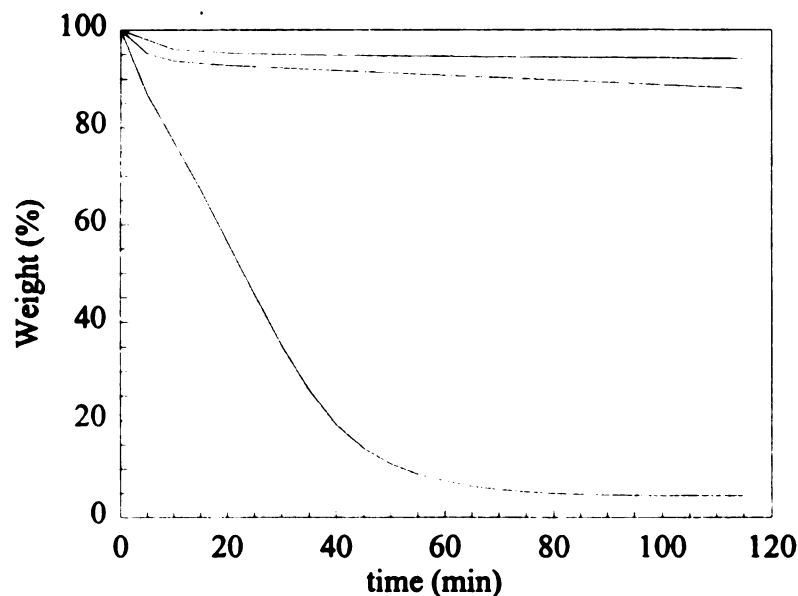


Figure 2-17. Kinetics of poly(L-lactide) weight loss by TGA at 186 (top), 206 (middle), and 257°C (bottom).

The zeroth-order rate constant values were similar for the various polylactides. At 257°C the 88% *meso* polylactide had a weight loss rate constant that was approximately

twice that of the poly(L-lactide) sample. The polylactide rate constants in Table 2-9 should be considered worst case values for dry polylactide. This is because of the high catalyst concentration, 5,000 mol lactide/mol catalyst, and the relatively high surface area-to-volume ratio of the TGA melt; both of these promote depolymerization in reversible polymers.

In Figure 2-18 we show an Arrhenius plot of $\ln(k)$ versus inverse absolute temperature,

$$\ln k = \ln k_0 - \frac{E_a}{R} \frac{1}{T(K)} \quad (2-15)$$

where k_0 , E_a , and R are the pre-exponential constant, activation energy of weight loss, and ideal gas constant, respectively. The activation energy of polylactide weight loss by TGA is 139 kJ/mol, between 186-257°C. In Section 3.2 we determine lactide's heat of polymerization, activation energy of polymerization, and activation energy of depolymerization to be -23.3 kJ/mol, 70.9 kJ/mol, and 94.2 kJ/mol, respectively.

Therefore, depolymerization alone can not account for the observed activation energy of weight loss during TGA – random degradation must be important as well. In Section 3.2 we also determine a 790°C ceiling temperature, $T_c = \Delta H_{rxn}/\Delta S_{rxn}$ ($\Delta G_{rxn} = 0$), for reversible lactide polymerization. However, because this value lies well above non-depolymerization degradation temperatures, a polylactide ceiling temperature based solely on lactide-polylactide equilibrium is strictly hypothetical.

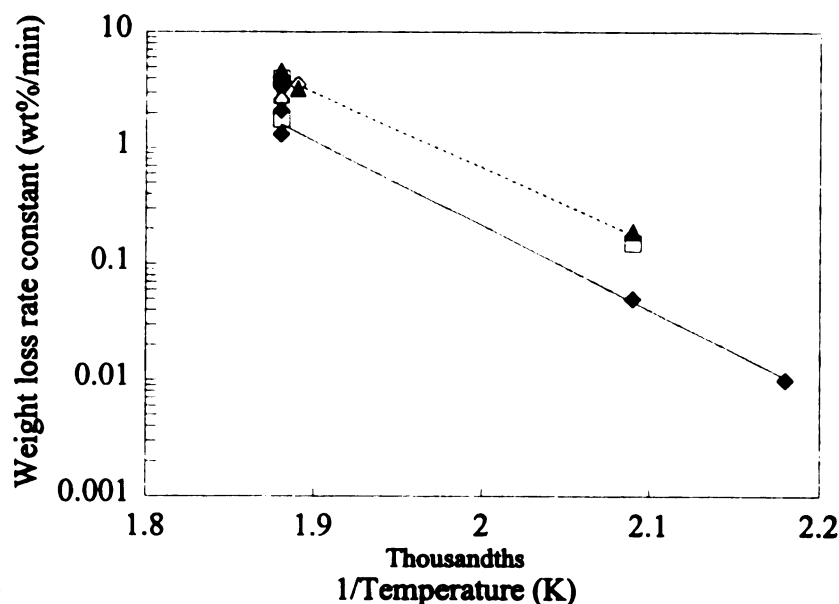


Figure 2-18. Arrhenius temperature dependence of the weight loss decomposition of polylactides. The activation energy of weight loss is 139 kJ/mol. The dashed and solid lines represent linear regressions for the 88% *meso* and poly(L-lactide) data, respectively. The TGA weight loss rate constants for the six polylactides are indicated as follows: poly(6% L-co-6% D-co-88% *meso*-lactide), (▲); poly(28% L-co-28% D-co-44% *meso*-lactide), (◇); poly(50% L-co-50% D-lactide), (□); poly(78.5% L-co-4% D-co-17.5% *meso*-lactide), (●); poly(90.5% L-co-0.5% D-co-9% *meso*-lactide), (△); and poly(L-lactide), (◆).

The relative thermal stability of polylactides are compared to some commodity thermoplastics in Table 2-9. The half decomposition temperature, $T_{d,1/2}$, is a good indicator of relative thermal stability and can be estimated from chemical structure based on group contribution methods.² $T_{d,1/2}$ is the temperature at which half of the polymer has been volatilized during a constant rate of temperature increase (typically about 3°C/min).² The following is the order of increasing thermal stability, based on $T_{d,1/2}$ values, for the polymers listed in Table 2-9: PVC < PLA < PS < PP < PE < PET. For the purpose of comparison, the weight loss rate constants for the listed commodity polymers were extrapolated to 257°C using their published E_a and $k_{350^\circ\text{C}}$ values. The rate of weight loss at

257°C is similar for PVC and polylactide, 1-4 %/min. PS, PP, PE, and PET have negligible weight loss at this temperature.

Van Krevelen² found a general correlation between a polymer's $T_{d,1/2}$ and the bond dissociation energy of its weakest bond. In addition, Van Krevelen developed an additive group contribution method to predict $T_{d,1/2}$ based on chemical structure. The following is a calculation of $T_{d,1/2}$ for polylactide using published² additive molar functions for thermal decomposition: $T_{d,1/2} = [Y(-\text{COO}-) + Y(\text{CH}(\text{CH}_3))]/72 \text{ g/mol} = (25000 + 18500 \text{ K-g/mol})/72 \text{ g/mol} = 604\text{K} = 331^\circ\text{C}$. The result is in reasonable agreement with experimental data, which is likely somewhat low owing to the high catalyst concentration. Van Krevelen determined the following general relationship between the activation energy of weight loss and $T_{d,1/2}$: $E_a \text{ (kJ/mol)} = T_{d,1/2} \text{ (}^\circ\text{C)} - 150^\circ\text{C}$. This correlation is shown in Figure 2-19 using data in Table 2-9.

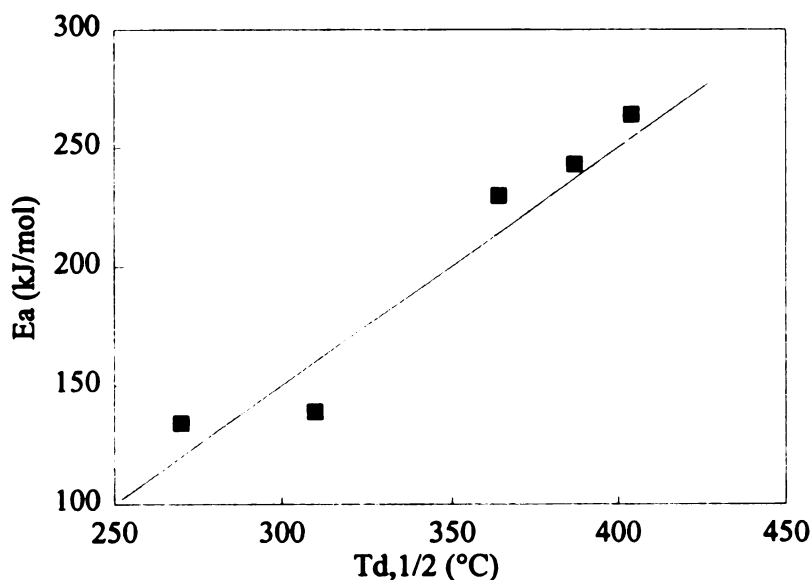


Figure 2-19. Correlation between the activation energy of weight loss and the half decomposition temperature for various polymers: PVC, PLA, PS, PP, and PE (in order of increasing $T_{d,1/2}$). The solid line is based on a relationship published by Van Krevelen:² $E_a = T_{d,1/2} - 150^\circ\text{C}$.

Discussion

McNeill and Leiper^{66,67} studied the thermal decomposition of polylactides at 230, 277, 322, 362, and 440°C using thermal volatilization analysis, TVA, mass spectrometry, infrared spectrometry, and NMR. In an open system, they determined the major products of PLA degradation to be cyclic oligomers (main product, about 50%), lactide, acetaldehyde, and carbon monoxide. Carbon dioxide and methyl ketene became significant products at 277 and 322°C, respectively. In addition, water, methane, and an unidentified yellow liquid were collected as minor products at all temperatures. Although carbon monoxide was detected at 230°C, the rate of CO production was low at temperatures < 370°C.

The open system degradation of polylactide in a mass spectrometer gave three series of peaks containing the polylactide repeat unit of 72 g/mol:⁶⁷

$$56 + 72n; \quad n = 0-10$$

$$72n; \quad n = 1-8$$

$$100 + 72n; \quad n = 0-2$$

The 56 g/mol peak was the strongest and is attributed to methyl ketene. The 100 g/mol peak was the second largest and is attributed to $\text{CH}_3\text{CHCOOCHCH}_3$ (lactone). These molecular weight peaks all lack contributions of -H and -OH endgroups indicating cyclic rather than linear PLA oligomers; this result was confirmed by NMR. Using infrared spectrometry, McNeill and Leiper found no evidence of changes in the structure of the

polylactide oligomers and concluded that no reactions take place during degradation that lead to a modification of the repeat unit structure.

Luderwald⁶⁸ obtained a similar mass spectra for polylactide degradation having peaks at $72n$, $56 + 72n$, and 100 g/mol. He concluded that polylactides and polyglycolides degrade thermally into cyclic oligomers and ω -hydroxy ketenes by cleavage of the ester bond. Garozzo et al.⁶⁹ investigated the thermal decomposition of polylactide by chemical ionization mass spectrometry. They obtained a similar mass spectra and attributed the cyclic oligomers to intramolecular exchange reactions.

The intramolecular transesterification reactions that produce the cyclic polylactide oligomers are a broad form of the reverse ring-opening polymerization reaction (depolymerization). Instead of yielding only lactide, oligomers of up to 8 repeat units (576 g/mol) are produced. In accord with the Principle of Microscopic Reversibility, depolymerization is shown to be first order in polymerization catalyst concentration in Section 3.2. In the GPC of polylactides produced at 180 - 200°C we observe a 3 wt% molecular weight population just above the lactide peak. Because these oligomers do not readily transesterify into the polymer population we believe they lack -OH end groups and are cyclic. At these temperatures the lactide equilibrium amount is 2.9-3.8% indicating that roughly one-half of the cyclic molecules are lactide. At the considerably higher temperatures of the McNeill and Leiper⁶⁷ study, lactide accounts for a substantially smaller fraction of the cyclic molecules. This is likely a result of the increased importance of homolysis to give ketene terminated oligomers. As a result of the exothermic nature of lactide polymerization, the equilibrium concentration of the individual cyclic oligomers

in polylactide will increase with temperature, corresponding to a decrease in the reaction equilibrium constant.

Figure 2-20 depicts the hydroxyl end-initiated intramolecular transesterification mechanism (backbiting) to give a cyclic polylactide oligomer and the corresponding linear polylactide of lower molecular weight. The resulting linear polylactide maintains the -OH end group. McNeill and Leiper⁶⁶ found that acetylation of the -OH end groups using acetic anhydride decreases the rate of polylactide decomposition (open system). This supports the concept that hydroxyl end-initiation plays an important role in polylactide decomposition.

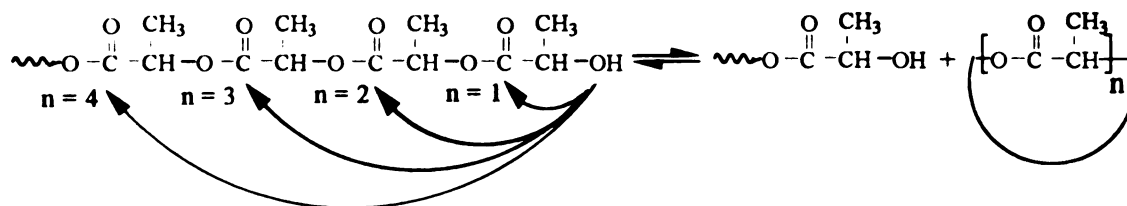


Figure 2-20. Hydroxyl end-initiated intramolecular transesterification to yield cyclic polylactide oligomers having a 72 g/mol repeat unit.

Along with intramolecular transesterification reactions that yield cyclic polylactide oligomers, McNeill and Leiper⁶⁷ propose homolysis mechanisms to account for the observed decomposition products. Through acyl-oxygen homolysis CO₂ and acetaldehyde, CH₃CHO, are produced along with the polylactide oligomers. In addition, alkyl-oxygen cleavage results in CO, CH₃CHO, and polylactide oligomers. With increasing temperature lactide and acetaldehyde further decompose to give CO and methane, CH₄: lactide = 2CO + 2CH₃CHO; CH₃CHO = CH₄ + CO. Based on their data

it is apparent that decomposition by homolysis (random degradation) becomes important somewhere between 230 and 277°C.

McNeill and Leiper⁶⁷ incorporated 1% of the free radical inhibitor diaminoanthraquinone into polylactide to test for degradation inhibition. This concentration of inhibitor amounts to about 1 mol inhibitor/mol polylactide. Degradation was studied by thermogravimetric analysis under vacuum at 230°C. They found a marked inhibiting effect of diaminoanthraquinone on the extent of weight loss between 1 h and 9 h, the conclusion of the test. This indicates that a free radical chain process is involved in polylactide degradation. It is notable that the initial slopes of weight loss versus time curves, < 1 h, were the same for the diaminoanthraquinone containing sample and the polylactide control. Although no explanation was given, this suggests to us that the rate of depolymerization was probably not affected and the free radical scavenger acts to stabilize homolytic random degradation.

Although homolysis is important, other non-free radical random degradation mechanisms such as thermal syn elimination (*cis*-elimination⁶⁸) of the ester bond may be important as well. Syn elimination occurs in esters at about 300-500°C⁷⁰ and involves the elimination of the ester bond to produce COOH and alkene end groups.

By thermogravimetric analysis McNeill and Leiper⁶⁶ found identical rates of decomposition for polylactide in vacuum, nitrogen, and air environments. This suggests that oxygen does not play a major role in the decomposition process. However, our experience with vial polymerizations indicates that oxygen is an important precursor to color formation (yellow) in polylactides. When a lactide is polymerized at 180°C with a

nitrogen head space, no color develops. However, when exposed to a dry air head space, a yellow color is observed at the air reaction mixture interface. During the polymerization the yellow color slowly moves down the vial until at the completion of the reaction the polymer is a uniform dark yellow. On dissolving and precipitating this polylactide the color is removed. This suggests that the color bodies are small molecules, and the color is not incorporated into the polymer chains. Because color formation in polylactides is aesthetically undesirable, oxygen must be eliminated during bulk lactide polymerization.

In the closed system degradation of polylactide in sealed tubes at 230, 277, 322, 362, and 440°C, McNeill and Leiper⁶⁷ found considerable differences in the gaseous products. Acetaldehyde (major product), water, and small amounts of CO₂, CO, and methane were found. More notably was the complete absence of methyl ketene and the formation of the following new products: ethylene, propylene, and butane-2,3-dione. Butane-2,3-dione was observed as a minor product at all temperatures while ethylene and propylene were only observed at the 362 and 440°C test conditions. The authors found acetaldehyde to decrease significantly with temperature accompanying an increase in methane production. They attribute this to acetaldehyde decomposition. The authors propose that ethylene and propylene production is a result of methyl ketene decomposition.

The results of this closed system polylactide degradation experiment are an important contribution to the understanding of the various mechanisms and end products of PLA decomposition. However, the authors stopped short of discussing the fundamental

differences between open system and closed system PLA degradation behavior. That is, how the contribution of depolymerization to decomposition is affected by the activity of lactide in the vapor phase (mass transfer driving force), the surface area-to-volume ratio of the melt (rate of mass transfer), and the polymer catalyst concentration (rate of depolymerization). Although this closed system degradation study⁶⁷ did not include a measurement of cyclic oligomers, we believe that the amount of cyclic oligomers is decreased substantially in this environment. In a closed system of limited head space the vapor-liquid equilibrium of lactide and cyclic oligomers should be quickly realized. Thus, their equilibrium concentrations in the liquid phase will be maintained, in the absence of their subsequent decomposition, and depolymerization will not be driven. This is in sharp contrast to an open process of high surface area-to-volume where removal of cyclic oligomers from both the liquid and vapor phases drives melt depolymerization.

In Table 2-10 we classify the main types of polylactide degradation, identify the systems in which they dominate, and make recommendations on how to decrease degradation rates and enhance thermal stability. This table is based on our melt hydrolysis rate studies in Section 3.5, depolymerization rate experiments in Section 3.2, decomposition results of this section; and polylactide degradation results found in the literature (particularly those of McNeill and Leiper).

Although many resin processes such as extrusion and injection molding are essentially closed processes, others like fiber spinning, sheet extrusion, and paper coating better mimic an open system. In these processes lactide can depolymerize back toward its

equilibrium concentration (post-devolatilization) during the initial heating of the resin and then diffuse out of the melt in the open system and coat the equipment with lactide crystals. This is a serious problem and renders these applications economically unattractive owing to increased production costs for down-time equipment cleaning (e.g., once per shift!). Therefore, complete command over the depolymerization of polylactide (Section 4.5) is essential for the viability of open system PLA applications.

Table 2-10 Summary of Important Polylactide Degradation Mechanisms

	Melt Hydrolysis Ea = 33.4 kJ/mol Chapter 3.5	Depolymerization Ea = 94.2 kJ/mol Chapter 3.2	Random Degradation Ea = 126 kJ/mol Chapter 3.5
conditions in which this mechanism is an important mode of decomposition	all temperatures where water > 100 ppm	open systems with high surface area-to-volume, T > 215°C	temperatures greater than about 215-250°C
major degradation products	lowers polylactide molecular weight	cyclic oligomers and lactide	acetaldehyde, CO, CO ₂ , and methyl ketene (open system only)
approaches to stabilization (in addition to minimizing time-temp severity)	thoroughly dry PLA resin; decrease, deactivate, or remove polymerization catalyst	decrease, deactivate, or remove polymerization catalyst; end-capping	add free radical scavengers

Later in this dissertation we clearly show that melt hydrolysis and depolymerization are first order in polymerization catalyst. There has been debate in the literature and among the biodegradable polymer community concerning the relative melt

stability between PLA produced from the catalyzed ring-opening polymerization of lactide (e.g., Cargill patents) and that which is produced by the direct condensation of lactic acid with the aid of high boiling solvents (e.g., Mitsui Toatsu patents). The relative stability of the ring-opening polylactide depends on the amount of polymerization catalyst remaining in the resin. However, by polymerization with very low levels of catalyst (e.g., $> 80,000$ mol lactide/ mol $\text{Sn}(2+)$) as shown in Section 3.2) or by deactivating the catalyst in the melt using off-the-shelf additives, the thermal stability between the two types of PLA become equivalent.

Conclusions

1. The onset of significant polylactide thermal decomposition is about 215°C (Section 3.5). Random decomposition mechanisms at temperatures between 220 - 285°C render the ceiling temperature for lactide polymerization (790°C , Section 3.2) without practical significance. The ceiling temperature is the highest temperature where polymerization is favorable based on monomer-polymer equilibrium.
2. Thermal decomposition is virtually independent of the initial lactide isomer distribution.
3. The activation energy of PLA weight loss is 139 kJ/mol, as determined by isothermal TGA between 186 - 257°C . The relative thermal stability of polylactide is accurately predicted from its chemical structure using an additive molar group

contribution method. Polylactide has similar thermal stability to PVC but is considerably less stable than PS, PP, PE, and PET.

4. Despite some excellent work to identify the products and conditions of polylactide degradation, the literature is plagued with ambiguity concerning the mechanisms of PLA degradation and the role of water, polymerization catalyst, temperature, free radicals, hydroxyl PLA end groups, and oxygen. In this section we sought to simplify and summarize polylactide degradation behavior based on the results presented in this dissertation and our interpretation of literature data. A summary of our findings are found in Table 2-10.

2.3 Volumetric Properties

Knowledge of polylactide's specific volume (or its reciprocal, density) as a function of temperature is important for engineering and application design. Examples include: sizing of production equipment, performing mass balances across equipment, understanding how resin processing conditions affect the final product (e.g., mold shrinkage) and designing polylactide part dimensions (e.g., wall thickness) to meet the load bearing requirements of the article.

2.3.1 Liquid Densities and Thermal Coefficient of Expansion

In this section we determine liquid densities as a function of temperature for the lactide isomers and amorphous polylactide.

Experimental

Monomers and Polymer. L-lactide was purchased from Boehringer Ingelheim. *Meso*-lactide was a gift from Cargill. The L- and *meso*-lactides had melting points of 99 and 53°C, respectively, by differential scanning calorimetry. The amorphous polymer was obtained from Cargill and was synthesized from 90% L-lactide and 10% *meso*-lactide. The polymer was devolatilized to remove unreacted lactide.

Specific Gravity Measurements. The specific gravity of *meso*-lactide and L-lactide were measured in various Precision hydrometers between 68-150°C and 110-172°C, respectively. The calibration of the hydrometers was verified with a Dow Corning oil of well-known density. The temperature was controlled using a mineral oil bath consisting of a four liter beaker insulated with glass wool. The oil bath was heated with a hot plate and continuously mixed with a magnetic stirrer. Upon reaching the desired temperature, a 300 ml glass cylinder was filled with a weighed quantity of lactide and emersed up to its top in the oil bath. After the lactide and oil bath obtained thermal equilibrium, determined by separate mercury thermometers, the hydrometer was placed in the lactide and the specific gravity was recorded following the reestablishment of thermal equilibrium. The density of the lactide was determined by multiplying the specific gravity by the density of water at 60°F (calibration standard for the hydrometers).

The density of the amorphous polylactide was measured between 150 and 210°C using a capillary viscometer. Random, triplicate density determinations were

made by measuring the weight of a displacement of polymer from a Haake Rosand RH7-2 capillary viscometer. The minor importance of the extensional flow components of polylactide allows for valid density estimations with this technique.

Results and Discussion

The density results for the lactide isomers and amorphous polylactide are shown in Table 2-11. No statistical difference was found between the liquid densities of *meso*-lactide, *L*-lactide, and amorphous polylactide at these temperatures. Figure 2-21 presents the density versus temperature data.

Table 2-11 Liquid Densities of Lactide Isomers and Amorphous Polylactide

<i>Meso</i> -Lactide		<i>L</i> -Lactide		Amorphous Polylactide	
Temperature (°C)	Density (g/cm ³)	Temperature (°C)	Density (g/cm ³)	Temperature (°C)	Density (g/cm ³)
68	1.22	110	1.176	150	1.134
78	1.21	116	1.172	150	1.127
88	1.20	121	1.165	150	1.153
108	1.182	122	1.168	170	1.126
118	1.173	131	1.159	170	1.121
131	1.162	134	1.162	170	1.123
140	1.154	139	1.151	190	1.113
150	1.145	142	1.155	190	1.084
		149	1.147	190	1.128
		150	1.147	210	1.095
		160	1.138	210	1.081
		161	1.138	210	1.103
		166	1.132		
		172	1.126		

The liquid thermal coefficient of expansion, α_l , was determined to be $7.4 \times 10^{-4} \text{ }^\circ\text{C}^{-1} \pm 0.17 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ by nonlinear regression of the L- and *meso*-lactide density data using a two parameter model referenced to 150°C , equation (2-16). The α_l values for other polymers are generally within 25% of this value.² The following equation describes the density of L-lactide, *meso*-lactide, and amorphous polylactide,

$$\rho(\text{g/cm}^3) = \frac{\rho_{150\text{C}}}{1 + \alpha_l(T(^\circ\text{C}) - 150)} = \frac{1.1452}{1 + 0.00074(T(^\circ\text{C}) - 150)} \quad (2-16)$$

This equation is represented by the solid line in Figure 2-21. The liquid thermal coefficient of expansion is constant between transition temperatures and equation (2-16) should be valid for extrapolation to the solid state (i.e., T_g for amorphous polylactide and T_m for the lactides), as well as extrapolation up to the next phase transition (i.e., decomposition temperature for polylactide, $220\text{--}285^\circ\text{C}$, and boiling temperatures for the lactides, 256°C (Section 2.8)). This equation is equally valid for D-lactide which has the same volumetric properties as its enantiomer L-lactide. On the basis of chemical similarity, we expect mixtures of the three lactides to also follow this relationship.

The assumption of incompressibility is good for most polymer processing operations. However, for high pressure processes, knowledge of how the specific volume changes with pressure is required to complete the equation of state, $V(T,P)$. The affect of pressure on density for amorphous polylactide can be estimated using the empirical Tait equation of state along with pressure dependence terms estimated in Van Krevelen.²

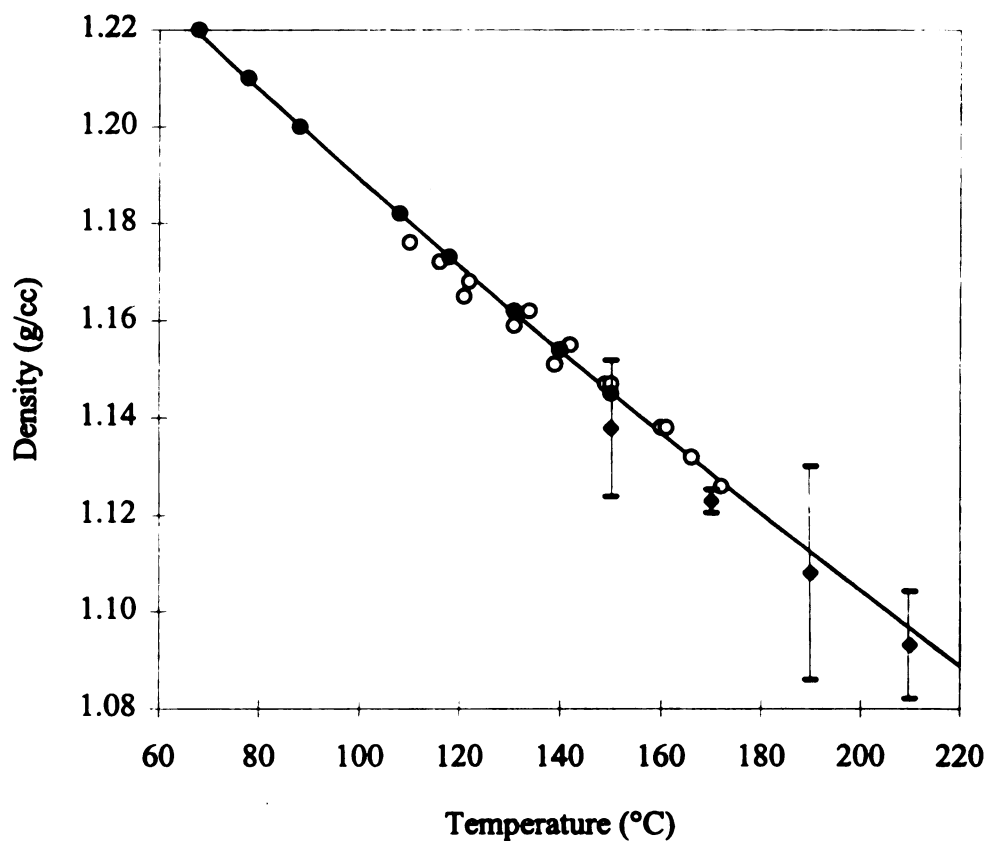


Figure 2-21. Liquid density versus temperature for *meso*-lactide (●), L-lactide (○), and amorphous polylactide (◆). The solid line is the density model, equation (2-16), based on a thermal expansion coefficient of $7.4 \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$.

Conclusions

1. The liquid densities as a function of temperature for the lactide isomers and amorphous polylactide (derived from 90% L- and 10% *meso*-lactide) were found to be the same and are described by equation 2-16.
2. The liquid thermal coefficient of expansion for the lactide isomers and amorphous polylactide is $7.4 \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$.

2.3.2 Solid Densities

The solid densities at 24°C, room temperature, were determined for the lactide isomers, and for amorphous and semi-crystalline polylactide. Based on the degree of crystallinity the density for purely crystalline polylactide is estimated and compared to literature values.

Experimental

Monomers and Polymer. L-lactide, *meso*-lactide, and amorphous polylactide were the same materials used in the previous section (Section 2.3.1). The semi-crystalline poly(L-lactide) was purchased from Boehringer Ingelheim. The polylactide had a melting point (peak of endotherm) and heat of melting of 181°C and 46.9 J/g, respectively, by differential scanning calorimetry (Section 2.2.1 for DSC setup). There was no apparent crystallization exotherm on heating indicating that no additional crystallization occurred during the calorimetry. The lactide monomers were crystalline; the amorphous and semi-crystalline polylactides were in pellet form.

Density Measurements. Solid density measurements were obtained by the displacement of a sample of determined mass into freshly boiled distilled water cooled to 24°C in a 25 ml pycnometer. The mass of the empty pycnometer was accurately measured with an analytical balance. The pycnometer was then partially filled with water and weighed. Next, a sample was added to the pycnometer which was then weighed and the sample mass determined by difference. Finally, the pycnometer was filled with water to the 25 ml marking and weighed. The density of the sample was then determined by the

ratio of its sample mass to its volume contribution in the pycnometer calculated from the density of water at 24°C, 0.997 g/cm³.

In addition, the skeletal density of the amorphous polylactide pellets were determined by mercury porosimetry (Micromeritics Instrument Corporation). The evacuation pressure was 50 µmHg with an evacuation time of 5 min and a mercury filling pressure of 1.5311 psia. The low and high pressure equilibration times were 10 s.

Results and Discussion

The results of the solid density measurements are summarized in Table 2-12. The average displacement densities for L- and *meso*-lactide were 1.36 and 1.33 g/cm³, respectively. As expected, the amorphous and semi-crystalline polylactides had significantly different densities, 1.25 and 1.36 g/cm³, respectively. By mercury porosimetry the amorphous polylactide pellets were determined to have a porosity of 8.24%, with a total pore area of 36.8 m²/g, and an average pore diameter of 0.0072 µm. The apparent density (with pores, but excludes volume between pellets) was determined to be 1.242 which is in agreement with the displacement density measurements. The skeletal density (without pores) was determined to be 1.354 which equals the lactide displacement densities.

The semi-crystalline polylactide was approximately 50% crystalline based on the heat of melting, 46.9 J/g, and the calculated heat of melting for polylactide crystals,¹¹ 93 J/g. From the degree of crystallinity, w_c , and the amorphous density, ρ_a , we can estimate

Table 2-12 Solid Densities of Lactide Isomers, and Amorphous and Semi-crystalline Polylactide at 24°C

Method	L-Lactide (g/cm ³)	Meso-Lactide (g/cm ³)	Crystalline Polylactide (g/cm ³)	Amorphous Polylactide (g/cm ³)
<i>Displacement</i>				
test 1	1.380	1.321	1.343	1.244
test 2	1.344	1.342	1.380	1.256
<i>average</i>	<i>1.36</i>	<i>1.33</i>	<i>1.36</i>	<i>1.25</i>
<i>Mercury Porosimetry</i>				
apparent density (with pores)				1.242
skeletal density (without pores)				1.354

the purely crystalline polylactide density, ρ_c , based on the ideal specific volume mixture equation:

$$\rho_c(\text{g/cm}^3) \cong \frac{w_c}{1/\rho - (1 - w_c)/\rho_a} = \frac{0.50}{1/1.36 - (1 - 0.50)/1.25} = 1.49 \quad (2-17)$$

From this we estimate the density ratio of purely crystalline to purely amorphous polylactide,

$$\frac{\rho_c}{\rho_a} \cong 1.19 \quad (2-18)$$

This estimate assumes ρ_a does not change for semicrystalline pellets. However, ρ_a is a function of pore volume which could decrease upon annealing. If pores fully collapse, ρ_a

= 1.35, then the purely crystalline density is estimated, using equation (2-18), to be 1.37 g/cm³, and $\rho_c/\rho_a = 1.10$.

Van Krevelen² compared the ratio of purely crystalline to purely amorphous densities for 27 polymer systems and found that $\rho_c/\rho_a = 1.13 \pm 0.08$. Furthermore, Van Krevelen found that highly crystalline polymers [such as poly(L-lactide)] had a density ratio of about 1.2; whereas, for low crystallinity polymers the ratio was less than 1.1.

In accord with our amorphous polylactide density measurements, Fischer et al.¹¹ measured the room temperature density of poly(D-co-L-lactide) as 1.248 g/cm³. However, they estimated the purely crystalline poly(L-lactide) density to be 1.290 g/cm³ based on the crystalline unit cell dimensions at 30°C. This density value is considerably lower than our measured value of 1.36 g/cm³ at 46.9 J/g.

In Table 2-13 we calculate the solid densities of amorphous and purely crystalline polylactide using the additive molar volume group contributions of Van Krevelen.²

Table 2-13 Solid Density Calculation of Amorphous and Purely Crystalline Polylactide Using Additive Molar Volume Group Contributions²

Structural Group	V _a (25°C) (cm ³ /mol)	V _c (25°C) (cm ³ /mol)
-CH(CH ₃)-	32.72	29.35
-COO-	23	21.5
<i>Density Calculation (g/cm³)</i>		
$\rho_a = (72.06 \text{ g/mol})/(32.72+23) = 1.293$		
$\rho_c = (72.06 \text{ g/mol})/(29.35+21.5) = 1.417$		

The group contribution density results are within 5% of our amorphous polylactide and purely crystalline polylactide density determinations of 1.25 and 1.49 g/cm³, respectively.

The above unity density of polylactide has significance in marine-based applications where polylactide articles will sink rather than float. Polylactides will eventually completely hydrolyze to lactic acid at a rate that depends on the water temperature and degree of crystallinity of the article. Polylactide articles could help alleviate the pollution problem of routine marine disposal of single use plastics by naval ships.

Conclusions

1. The solid room temperature displacement densities of L- and *meso*-lactide are 1.32-1.38 g/cm³.
2. The solid amorphous polylactide displacement density is 1.25 g/cm³. The skeletal density (absence of pores) of amorphous polylactide pellets was determined to be 1.35 g/cm³ by mercury porosimetry.
3. The purely crystalline poly(L-lactide) density is estimated to be 1.37-1.49 g/cm³.

2.4 Mechanical Properties

The room temperature mechanical properties of high molecular weight thermoplastics largely depend on the location of their thermal transitions (i.e., T_g , T_m) relative to room temperature, and the extent of crystallization. The determination of the

mechanical behavior of various lactide copolymers allows us to judge their suitability for various applications.

In this section we determine the basic mechanical properties for six high molecular weight amorphous polylactides containing various amounts of initial *meso*-lactide, 10-40%. The tensile, flexural, and Izod impact properties were determined according to ASTM standards. In addition, the mechanical properties of a high-flow unmodified polystyrene were measured for comparison and reference. Finally, we compare the measured polylactide mechanical properties to literature values of commodity thermoplastics.

It should be noted that all polylactide specimens were conditioned at room temperature for an extended period prior to testing and exhibited brittle fracture during loading. In Section 2.2.2 we discussed the importance of physical aging on the ductile to brittle transition in amorphous polylactides. This transition in mechanical behavior was found to occur after several hours of room temperature storage and correlates with the development of an enthalpy relaxation at T_g during heating, as observed by DSC. This endothermic enthalpy relaxation is evidence of the prior volume reduction that is characteristic of physical aging.

Experimental

Materials. Six unmodified polylactides of varying initial L-lactide and *meso*-lactide content were obtained from Cargill: 60% L-co-40% *meso*-, 66% L-co-34% *meso*-, 78% L-co-22% *meso*-, 80% L-co-20% *meso*-, 88% L-co-12% *meso*-, and 90%

L-co-10% *meso*-lactide. The *meso*-lactide was originally obtained from Henley. The initial ratio of L-lactide to *meso*-lactide in the monomer mixture prior to polymerization was determined by gas chromatography (Section 3.2 for GC setup and determination). All polymers contained a 10,000 mol/mol ratio of lactide to 2-ethylhexanoic acid tin(II) salt, polymerization catalyst.

The high flow polystyrene grade was obtained from Dow (PS-4).

Molecular Weight Determination. Polylactide molecular weights were determined using a Waters GPC calibrated against polystyrene standards. The analyses were performed at 35°C using chloroform as eluent at a flow rate of 1 ml/min. Polylactide molecular weights are reported relative to polystyrene standards and have not been corrected to an absolute basis using a universal calibration. The Mark-Houwink constants for polystyrene in chloroform at 35°C were determined to be $K = 1.67 \times 10^{-4}$ dl/g and $a = 0.692$.

Differential Scanning Calorimetry. The glass transition temperature was determined by differential scanning calorimetry at a heating rate of 10°C/min. A DuPont 910 DSC with DuPont 9900 General V2.2A software was used. The DSC was purged with 50 ml/min nitrogen passed through an oxygen and water adsorption bed. The DSC is maintained and calibrated on a scheduled basis by the Composite Materials and Structures Center, Michigan State University.

Injection Molding. Prior to molding, the polylactide pellets were dried at 50°C under vacuum for at least two hours and then stored in sealed containers with desiccant bags. A New Britian 75 injection molding machine (CMSC, Michigan State University)

was used. The temperature settings for zone 1, zone 2, and the nozzle were 149, 177, and 177°C, respectively. The chill time was 30 seconds and the total residence time of the polymer was about 8 min.

Tensile Testing. Tensile testing was performed in accord with ASTM D638 using the Michigan State University CMSC UTS equipment. All specimens were conditioned according to ASTM standards. For each material the average and standard deviation property values are reported based on the testing of five specimens. The specimens' widths and thickness varied between 0.4995-0.5025" and 0.1230-0.1250", respectively.

Flexural Testing. Flexural testing was performed in accord with ASTM D790 using the same UTS equipment (CMSC, Michigan State University). For each material the average and standard deviation property values are reported based on the testing of five specimens.

Izod Impact Testing. Notched Izod impact testing was performed in accord with ASTM D256 using TMI 400 testing equipment (CMSC, Michigan State University). All tests were performed at 25°C. A pendulum capacity of 1 ft-lb was used. All specimens had total and notched widths of 0.500" and 0.125", respectively. The reported average and standard deviation results for each material are based on seven specimens.

Results and Discussion

A summary of the mechanical property results for the six polylactides and polystyrene reference is presented in Table 2-14. The glass transition temperatures and

molecular weights are reported after molding. The nominal stress (force per initial cross-sectional area) and nominal strain (i.e., engineering strain = change in length per initial length) definitions were used in reported tensile and flexural testing results. The tensile modulus and flexural modulus are reported as the initial stress-strain slope near zero strain (initial modulus). The notched Izod impact results are reported in units of energy per width of notch.

The distinction between the general mechanical behavior of different polymers is most easily made by comparing tensile stress-strain curves. The initial modulus or slope is perhaps the most important indicator of mechanical behavior. A high modulus indicates a stiff material whereas a low modulus denotes flexibility. The tensile yield strength indicates whether the material is strong or weak. Before yielding, the stress-strain curve is generally linear and the deformation is recoverable and nearly linear-elastic. At strains beyond the yield stress, tough plastics will absorb a significant amount of the applied energy and yield (plastic deformation) – the sample will not break until a considerable amount of elongation has occurred without much change in the applied load. In contrast, a brittle plastic will fracture at a low percentage elongation (near the yield stress). The area under a stress-strain curve is the work to rupture and is a general measure of toughness.

Although quite different in test rate and direction of deformation, the Izod impact test is another measure of a material's toughness. In this test a pendulum of certain weight is used to strike and fracture notched molded specimens to determine the energy of fracture.

Table 2-14 Mechanical Properties for Unmodified Amorphous Poly(L-co-meso-lactide)s and Polystyrene

Polymer	T_g (°C)	M_n (g/mol)	PDI	Tensile Modulus (psi)			Tensile Yield Str. (psi)			Tensile Str. at Break (psi)			Elongation at Break (%)			Flexural Modulus (psi)			Flexural Strength (psi)			Notched Izod Impact (ft-lb/in)		
				AVE	SD		AVE	SD		AVE	SD		AVE	SD		AVE	SD		AVE	SD		AVE	SD	
90L/10m	57.4	63,700	1.91	549,000	13,000		7,730	201		7,620	183		3.4	0.2		532,000	9,600		12,400	150		0.47	0.03	
88L/12m	56.1	54,000	1.89	556,000	26,000		7,790	109		7,790	101		3.5	0.1		535,000	5,400		12,500	270		0.46	0.02	
80L/20m	55.2	71,300	2.11	566,000	8,000		7,420	178		7,240	362		3.3	0.3		505,000	7,300		12,400	70		0.45	0.05	
78L/22m	55.2	59,300	1.85	556,000	7,000		7,630	19		6,990	397		3.9	0.5		528,000	3,400		12,500	220		0.32	0.05	
66L/34m	52.5	41,000	2.24	549,000	9,700		6,580	72		6,190	334		3.3	0.3		531,000	5,600		11,300	80		0.39	0.05	
60L/40m	51.5	68,400	2.05	587,000	28,000		6,750	18		6,200	359		3.1	0.3		524,000	8,000		10,600	110		0.42	0.09	
PS	100			490,000	20,000		7,300	40		7,270	61		4.6	0.3		459,000	2,800		13,000	210		0.32	0.04	

The effects of the number average molecular weight and initial *meso*-lactide fraction on the mechanical properties were examined by performing an analysis of variance with a two-factor, first order multiple linear regression model. Because the molecular weights were fairly high and did not vary much, only the tensile modulus was found to be sensitive to molecular weight.

The tensile modulus for amorphous poly(L-co-*meso*-lactide) increases with the initial *meso*-lactide fraction and the number average molecular weight. Both predictors were significant at a 94% confidence level. With this model, 84% of the variance in the tensile modulus data was accounted for by changes in the initial *meso*-lactide fraction and M_n . However, more data is required to obtain a higher confidence in the initial *meso*-lactide effect.

Both the tensile yield strength and tensile break strength decrease with initial *meso* fraction, 99% confidence, and accounted for 86% and 95% of the variance, respectively. The flexural strength also decreases with initial *meso* fraction; 99% confidence, 83% of variance. The ratio of tensile yield strength to flexural strength for poly(L-co-*meso*-lactide) varied between 1.57-1.72 with an average value of 1.6. This strength ratio of 1.6 is common for polymers.²

Over the range in which the independent variables changed, the elongation at break (3.1-3.9%), flexural modulus (505-535 kpsi), and Izod impact strength (0.32-0.47 ft-lb/in) were all independent of both initial *meso*-lactide fraction and M_n .

In appearance the injection molded amorphous polylactide specimens were identical to the molded polystyrene specimens; they were both transparent and stiff.

However, the different specimens were easily distinguished by weighing; the densities of polylactide and polystyrene are 1.25 and 1.05 g/cm³, respectively. The amorphous polylactides were found to have very similar mechanical properties to polystyrene, Table 2-14. They are both stiff, brittle, and strong plastics having a tensile yield strength greater than 7,000 psi, elongation at break values less than 5%, and Izod impact values less than 0.5 ft-lb/in. The amorphous polylactides have tensile and flexural moduli that are about 15% greater than values for polystyrene. However, on a per-mass or specific-basis the moduli are about the same for PS and PLA.

Table 2-15 compares measured amorphous polylactide mechanical properties to literature values of unmodified commodity plastics. Polylactide specimens are very stiff and have higher tensile and flexural moduli than current commodity polymers: PS, LDPE, HDPE, PP, PVC, PET, PC, and Nylon 66. The polymers with glass transitions above room temperature (PLA, PS, PVC, PET, PC, Nylon 66) are all strong, having tensile strengths in excess of 7,000 psi. The polymers with glass transitions below room temperature (LDPE, HDPE, PP) are weak but flexible, having elongations at break in excess of 400%.

With elongations at break less than 5% and notched Izod impact values less than 0.5 ft-lb/in, polylactide and polystyrene are the only brittle polymers listed in Table 2-15. The polyethylene and polypropylene polymers are semi-crystalline and have glass transition temperatures below room temperature. Their toughness and high flexibility are a result of the configurational mobility of their polymer backbones in the amorphous regions (above T_g). The extent of crystallinity decreases the toughness and flexibility of

these polymers by decreasing the fraction of amorphous rubbery regions. This is in part the reason why LDPE is tougher than HDPE. In addition, viscoelastic behavior is sensitive to molecular architecture (e.g., branching in LDPE) when the amorphous regions are above T_g .

Table 2-15 Comparison of Amorphous Polylactide Mechanical Properties to Literature Values for Unmodified Commodity Polymers

	Tensile Modulus (psi)	Tensile Yield Str. (psi)	Tensile Str. at Break (psi)	Elongation at Break (%)	Flexural Modulus (psi)	Flexural Strength (psi)	Notched Izod Impact (ft-lb/in)
PLA (88L/12m)	556,000	7,790	7,790	3.5	535,000	12,500	0.46
LDPE	29,000	1,200	1,500	800			13
HDPE	145,000	4,400	4,400	600	116,000	6,500	2.4
PP	203,000	4,600	4,800	400	218,000	7,100	1.5
PS	493,000		7,300	2.5	479,000	12,000	0.52
PVC	377,000	7,000	7,300	30	508,000	13,000	0.81
PET	435,000		7,800	275	421,000		1.3
PC	363,000	9,400	8,700	125	363,000	13,000	15
Nylon 66	290,000	8,300	11,600	200	334,000		2.1

Literature values (non-PLA) from Van Krevelen²

PET, Nylon 66, and PC have glass transitions above room temperature but are still considerably tougher than polylactide. In Section 2.2.2 we found that while PET aging is slow, the rate of polylactide embrittlement was very fast. Therefore, PET owes its higher toughness to excess free volume which allows it to absorb increased energy before breakage. Nylon 66 has strong hydrogen bonding and its toughness is explained by its strongly developed crystallinity.² Polycarbonate has a pronounced main chain relaxation that occurs at a very low temperature, $T_g = -120^\circ\text{C}$.² The increase in Izod impact has been

correlated with a decreasing T_g and explains the tough nature and high impact resistance of PC.²

Therefore, based on mechanical properties we find that unmodified amorphous polylactide is a natural fit for the replacement of moderate temperature polystyrene applications. The connection of mechanical and rheological properties with T_g , T_g , T_m , and molecular architecture (i.e., structure property relationships) provides the basis of Section 5.2 which discusses approaches to modifying polylactide's mechanical behavior through copolymerization and chemical modification. In this manner, PLA-based biodegradable polymers can achieve greater utilization and achieve suitability for both high temperature PS applications (e.g., foam coffee cups, hot sandwich containers), and for applications where flexibility and toughness are required.

The effect of temperature on the mechanical properties of amorphous polylactide has not been studied here. However, like all other amorphous plastics the tensile modulus will drop by a factor greater than 1,000 at T_g . In amorphous polymers the heat distortion temperature is nearly the same as T_g and defines the upper use temperature for the material, (e.g., about 53-57°C for amorphous polylactide; 100°C for polystyrene).

Semi-crystalline polylactides can have upper use temperatures considerably greater than that of polystyrene. However, the development of commercially useful (commodity) crystalline polylactides is technically difficult (Section 2.2.1). The mechanical properties of semi-crystalline polylactides are not studied here.

Sinclair^{71,72} investigated the mechanical properties of poly(L-co-D-lactide)s as a function of D-lactide content up to 50%. Similar to our findings with initial *meso*-lactide,

the tensile strength increased with increasing L-lactide content. The tensile strength of the 95% initial L-lactide polymer approached 10,000 psi. Perego et al.⁷³ investigated the effects of crystallinity and molecular weight on the mechanical properties of PLA. They used D-lactide to control the crystallinity. They found that annealed semi-crystalline PLA possesses a higher tensional and flexural modulus, as well as somewhat enhanced impact strength. In addition, they found that the mechanical properties increase substantially up to molecular weight averages of 35,000 and 55,000 M_v for poly(D-lactide) and poly(L-lactide), respectively.

Conclusions

1. Unmodified amorphous poly(L-co-*meso*-lactide) is a stiff, brittle, and strong plastic that has mechanical properties and clarity that very closely resemble polystyrene. Amorphous polylactides are natural replacements for moderate temperature polystyrene applications. Polylactide's higher density and strength may allow for downgauging of some articles.
2. The tensile modulus for amorphous poly(L-co-*meso*-lactide) is among 549-587 kpsi and increases with molecular weight. Preliminary data suggests that the tensile modulus increases with the initial *meso* fraction as well. The modulus for amorphous poly(L-co-*meso*-lactide) is significantly higher than that of other unmodified commercial plastics (PS, LLDPE, LDPE, HDPE, PP, PVC, PET, PC, Nylon 66).

3. Tensile yield strength for amorphous poly(L-co-*meso*-lactide) decreases with initial *meso*-lactide fraction: 7700-7800 psi for 10% *meso*-, and 6600-6800 psi for 34-40% *meso*-lactide. Flexural strength decreases with increasing *meso* fraction as well: 12,500 psi for $\leq 22\%$ *meso*, and around 11,000 for 34-40% initial *meso* fraction.
4. Flexural modulus (505-535 kpsi), elongation at break (3.1-3.9%), and notched Izod impact strength (0.32-0.47 ft-lb/in) for amorphous poly(L-co-*meso*-lactide) were independent of initial *meso* fraction.

2.5 Rheological Properties

In this section we characterize the deformation and flow of unmodified polylactides of various initial isomer composition, molecular weight, and monomer concentration, at various conditions: strain, shear rate, temperature. This section is divided up into three subsections concerning linear viscoelastic properties, the development of a rheological constitutive equation, and lactide-polylactide mixture viscosities occurring during polymerization. The first subsection falls within the polymer science aspect of rheology whereas the latter two are more concerned with polymer engineering applications.

The extensional flows of polylactide are not investigated here. However, the time-dependent extensional viscosity is very important in many polymer processing applications including: film extrusion paper coating, blow molding, fiber melt spinning, and sheet formation. Unmodified polylactides have almost no die swell, even in capillary

viscometry with "zero" length dies. It is our experience that die swell can be roughly correlated with "melt strength" which is a desirable characteristic in the above mentioned applications. For example, a polymer with good melt strength, such as polyethylene, shows little neck-in during extrusion curtain coating of paper. A polymer with poor melt strength (e.g., unmodified polylactide) will have considerable neck-in and only cover a fraction of the paper on drawing. Although we do not quantify polylactide time-dependent extensional viscosities in this section, we briefly discuss the general approaches to improving polylactides melt strength through modification in Section 5.2.

The influence of pressure on PLA viscosity is also not investigated here. Very high hydrostatic pressure will significantly increase a polymer's melt viscosity by reducing its free volume. In high pressure molding applications the effect of pressure may become important. However, at the moderate pressures involved in most polymer applications the influence of pressure is not important. The change in PLA viscosity with pressure can be estimated from the coefficient of thermal expansion (Section 2.3.1) and the influence of temperature on viscosity by using equations published by Van Krevelen.² Using an approximate general equation² relating the effect of pressure on viscosity to the effect of temperature on viscosity, we calculate that with a hydrostatic pressure of 4,000 psig the increase in a polymer's viscosity would be equivalent to its increase with a 10°C temperature decrease.

2.5.1 Linear Viscoelastic Properties

Linear viscoelastic properties are used for characterization and quality control. The determination of these properties are particularly useful in the development of modified molecular architecture polymers (e.g., branching, cross-links). In addition, these properties are directly relevant to a limited number of polymer processing applications, such as the foaming of amorphous melts.

In this section we characterize the low strain viscoelastic properties of amorphous polylactides by dynamic parallel plate rheology at temperatures between 68-151°C and frequencies between 0.01-100 rad/sec. The tested polylactides varied in molecular weight and monomeric composition (L-, *meso*-, and D-lactide). The determined shear flow properties include: dynamic shear moduli and viscosity as a function of frequency, steady state zero-shear viscosity, steady state recoverable shear compliance, average relaxation time, plateau modulus, and time-temperature superposition shift factor.

Experimental

Polymers. Ten unmodified amorphous polylactides of varying initial L-, *meso*-, and D-lactide were used in this study. Four 85% L-co-15% D-lactide polymers of varying molecular weights were produced in vials according to the procedure outlined in Section 3.2. Crystalline L-lactic acid was used to target weight average molecular weights between 15,000-190,000 g/mol. Five *meso* containing copolymers were obtained from Cargill: 60% L-co-40% *meso*-, 66% L-co-34% *meso*-, 78% L-co-22% *meso*-, 80% L-co-20% *meso*-, and 90% L-co-10% *meso*-lactide. These same polymers were used in the

mechanical properties study and are described in greater detail in Section 2.4.

Poly(D-co-L-lactide) was purchased from CCA Biochem B.V. All ten polylactides were obtained from batch polymerizations.

Molecular Weight Determinations. Polylactide molecular weights were determined using a Waters GPC and are referenced directly to polystyrene standards. A discussion of the analytical setup is found in Sections 2.4 and 3.2.

Differential Scanning Calorimetry. The glass transition temperatures of the polylactides were determined using a DuPont 910 DSC. The analytical setup is described in Section 2.4. All polylactides (pellets and molded coupons) were tested and verified to be amorphous by DSC.

Compression Molding. Polylactide pellets were compression molded with a Carver Press (CMSC, Michigan State University) into rectangular parts of thickness 1-2 mm. The general procedure is as follows: between 30-35 g of polymer is placed in a pre-heated rectangular mold at 150°C and allowed 10 min to reach thermal equilibrium. Next a load required to assert 300 psig was applied for 20 min. Cooling water is then circulated through the platens to cool the part (25 min). Six 12.5 mm circular coupons were punched from each molded part for testing. All coupons were transparent.

Parallel Plate Rheology. An RMS 800 Rheometric Mechanical Spectrometer (CMSC, Michigan State University) was used. Before testing, the dimensions of each coupon were accurately measured with a micrometer. It was found that the dynamic moduli of the polylactide samples remained linear with percent strain up to about 20%. The testing conditions of temperature (68-151°C) and percent strain (< 20%) were chosen

to maintain an acceptable torque on the load cell (2-2,000 g-cm) to achieve accurate data. Dynamic parallel-disk frequency sweeps were performed on each sample (0.01-100 rad/sec or 0.1-100 rad/s). Temperature intervals of 15°C were used to ensure time-temperature superposition data overlap. To avoid degradation, a new sample was used for each change in temperature.

Results

Oscillatory shear experiments are the most common methods of determining the viscoelastic properties of amorphous melts.⁷⁴ The dynamic linear viscoelastic properties of the shear oscillatory experiment are directly related to stress relaxation and creep experiments through the Boltzmann Superposition Principle; that is, the dynamic moduli, $G'(\omega)$ and $G''(\omega)$, are directly related to the time dependent shear modulus, $G(t)$.

In a creep experiment above T_g the viscoelastic material is subjected to a constant stress, σ_0 , and the strain as a function of time, $\gamma(t)$, is monitored. After the stress is removed some of the deformation is recovered (recoil). The shear compliance, $J(t)$, is the ratio of strain to stress and prior to stress removal (long time portion of creep experiment) may be written as

$$J(t) = \frac{\gamma(t)}{\sigma_0} = J_e^0 + \frac{t}{\eta_0} \quad (2-19)$$

The recoverable shear compliance, J_e^0 , component of $J(t)$ is a measure of the elastic-like character of the shear flow.⁷⁴ All fluids have a non-zero viscosity but only viscoelastic

fluids have non-zero J_e^0 . Both the zero-shear viscosity, η_0 , and recoverable shear compliance are important constants that help characterize viscoelastic shear flow.

From dynamic experiments the zero-shear viscosity and recoverable shear compliance are determined from the dynamic moduli in the limit of low frequency⁷⁴

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''(\omega)}{\omega} \quad (2-20)$$

$$J_e^0 = \frac{1}{\eta_0^2} \lim_{\omega \rightarrow 0} \frac{G'(\omega)}{\omega^2} \quad (2-21)$$

The product of the zero-shear viscosity and recoverable shear compliance is the average relaxation time required for final stress equilibration in the liquid⁷⁴

$$\tau_0 = \eta_0 J_e^0 \quad (2-22)$$

Table 2-16 summarizes the η_0 , J_e^0 , and τ_0 parallel plate rheology results for the tested amorphous polylactides.

To a good approximation, the polymer's viscosity as a function of shear rate, $\dot{\gamma}$, is equivalent to the complex viscosity as a function of frequency, ω , at $\omega = \dot{\gamma}$ (Cox-Merz rule):⁷⁵

$$\eta(\dot{\gamma}) = |\eta^*(\omega)|_{\omega=\dot{\gamma}} = \left[\frac{1}{\omega} \sqrt{(G')^2 + (G'')^2} \right]_{\omega=\dot{\gamma}} \quad (2-23)$$

The viscosity-frequency curves depend strongly on the polymer's weight average molecular weight and the temperature of the experiment. The effect of temperature on the

Table 2-16 Summary of Viscoelastic Properties of Amorphous Polylactides

Polymer	M_n (g/mol)	M_w (g/mol)	T_g (°C)	T (°C)	η_0 (Pa·s)	J_e^0 (Pa ⁻¹)	τ_0 (sec)
85L/15D	12,000	15,400	43.6	68.4	7.10E+04	8.45E-06	0.600
				83.8	2.38E+03	1.00E-05	0.0238
85L/15D	29,000	50,750	51.0	84.1	8.50E+04	1.12E-05	0.952
				99.5	8.30E+03	1.15E-05	0.0954
85L/15D	40,200	96,600	52.4	84.5	1.00E+06	9.51E-06	9.51
				99.8	6.80E+04	1.40E-05	0.952
				114.7	8.70E+03	1.73E-05	0.151
85L/15D	78,800	189,000	55.0	83.1	1.60E+07	3.00E-05	480
				98.4	9.20E+05	2.60E-05	23.9
				115.0	9.40E+04	4.03E-05	3.79
50L/50D	38,300	76,600	48.3	90.2	1.30E+05	2.31E-05	3.00
				105.0	6.90E+03	3.46E-05	0.239
				125.0	8.45E+02	4.48E-05	0.0379
90L/10meso	63,700	121,700	57.4	120.8	2.30E+04	5.20E-05	1.20
				135.5	3.02E+03	2.50E-05	0.0755
				150.6	8.13E+02	2.33E-05	0.0189
80L/20meso	71,300	150,400	55.2	105.1	1.40E+05	2.70E-05	3.78
				119.9	3.00E+04	2.52E-05	0.756
				135.0	7.60E+03	2.50E-05	0.190
				150.3	2.40E+03	2.50E-05	0.0600
78L/22meso	59,300	109,700	55.2	89.8	3.10E+05	1.22E-05	3.78
				105.1	2.35E+04	1.61E-05	0.378
				120.1	4.23E+03	1.42E-05	0.0601
66L/34meso	41,000	91,800	52.5	89.7	1.70E+05	1.77E-05	3.01
				105.0	1.35E+04	1.77E-05	0.239
				119.9	2.85E+03	2.11E-05	0.0601
60L/40meso	68,400	140,200	51.5	90.6	2.00E+05	3.00E-05	6.00
				105.4	3.25E+04	1.85E-05	0.600
				121.0	4.80E+03	1.98E-05	0.0950
				134.4	1.40E+03	2.15E-05	0.0301

complex viscosity-frequency plot for poly(80% L-co-20% *meso*-lactide) is shown in Figure 2-22. In Figure 2-23 we present the effect of weight average molecular weight on the complex viscosity curve for poly(85% L-co-15% D-lactide). The dependence of viscosity on temperature and molecular weight is largest where viscosity is independent of frequency, zero-shear viscosity.

A plot of η_0 versus M_w for poly(85% L-co-15% D-lactide) at 70, 85, 100, and 115°C is presented in Figure 2-24. The data was fit to the following three parameter model where R is the gas constant:

$$\eta_0 = \eta_{0,\text{ref}} \left(\frac{M_w}{100,000} \right)^a \exp \left(\frac{E_a}{R} \left(\frac{1}{T(K)} - \frac{1}{373} \right) \right) \quad (2-24)$$

The weight average molecular weight exponent, a , was determined by regression to be 3.38 ± 0.13 . This value is in accord with the experimentally determined value of 3.4 for numerous polymer systems. The activation energy of flow, E_a , for this temperature range is 190 kJ/mol. The reference zero-shear viscosity, $\eta_0(M_w = 100,000, T = 100^\circ\text{C})$, was determined to be $89,400 \pm 9300$ Pa-s. The solid lines in Figure 2-24 represent this η_0 model. A good fit between data and model is observed.

The remainder of the η_0 data in Table 2-16 was taken over a wider temperature range, up to 150°C. To check if an Arrhenius η_0 temperature dependency is still valid over these temperatures a plot of the natural log of the ratio of η_0 to $89,400(M_w/100,000)^{3.38}$ versus the reciprocal of absolute temperature was prepared, Figure 2-25,

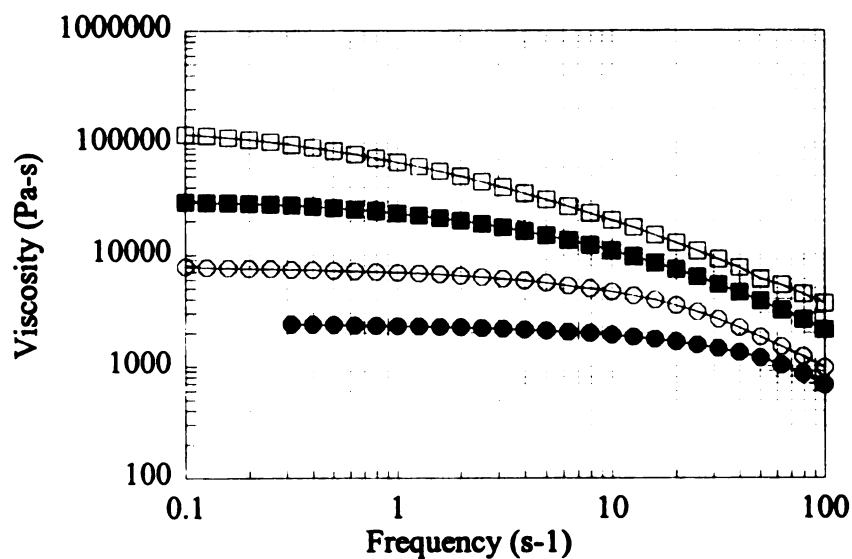


Figure 2-22. Viscosity versus frequency at 105 (□), 120 (■), 135 (○), and 150°C (●) for poly(80% L-co-20% *meso*-lactide), $M_w = 150,400$.

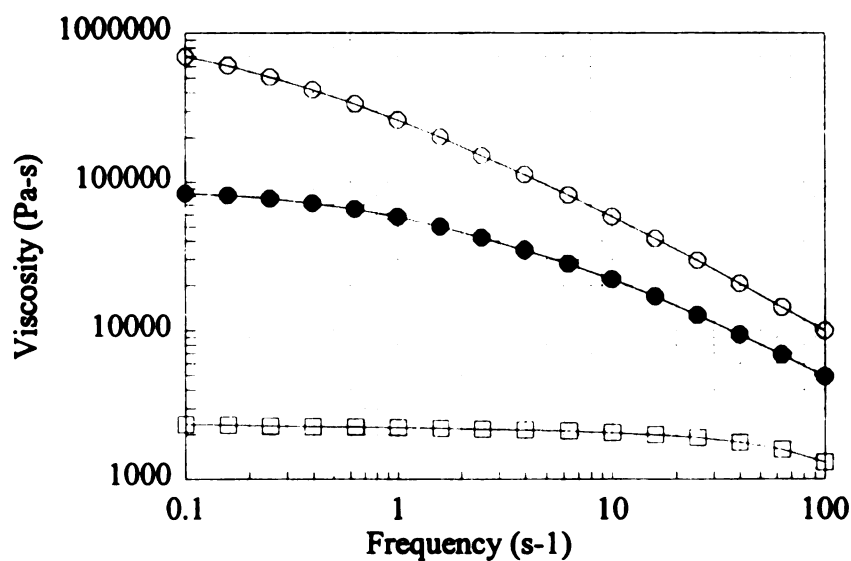


Figure 2-23. Viscosity versus frequency at 85°C for poly(85% L-co-15% D-lactide)s of different molecular weights: $M_w = 15,400$ (□); 50,750 (●); and 96,600 (○).

$$\ln \left(\frac{\eta_0}{89400(M_w/1E5)^{3.38}} \right) = \frac{E_a}{R} \frac{1}{T(K)} - \frac{E_a}{R} \frac{1}{T_{ref}} \quad (2-25)$$

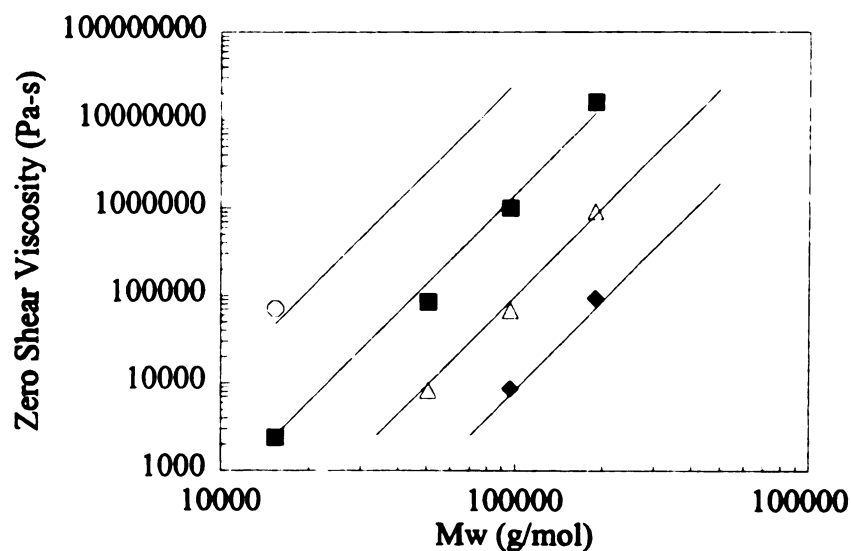


Figure 2-24. Zero-shear viscosity versus M_w for four poly(85% L-co-15% D-lactide)s at 70°C, (○); 85°C, (■); 100°C, (△); and 115°C, (◆). The three parameter η_0 model, equation 2-24, is represented by the solid lines.

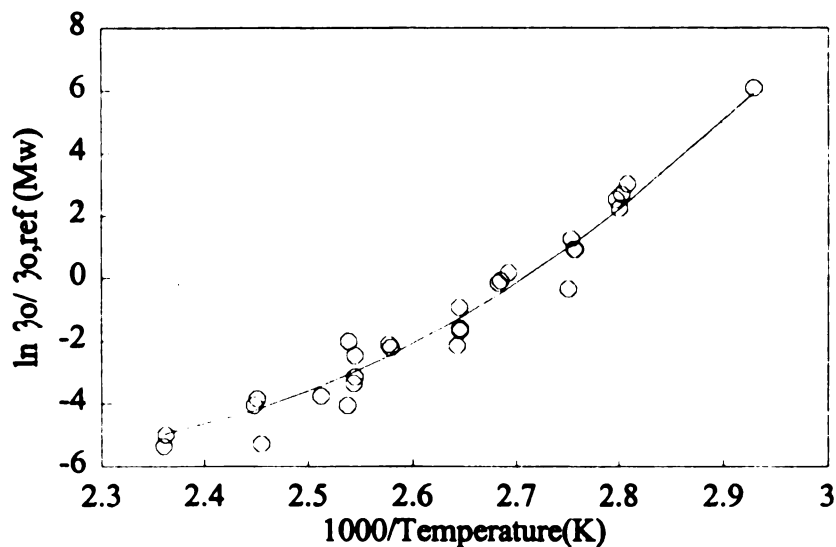


Figure 2-25. Sensitivity of the Arrhenius activation energy of flow (slope) to temperature for amorphous polylactide between 68-151°C.

The activation energy, product of the slope and R , was found to decrease with increasing temperature. This temperature dependency of E_a is typical of amorphous polymers processed between T_g and $T_g + 100^\circ\text{C}$. At these temperatures the WLF equation is a more

appropriate model choice and has been found to be valid for a number of polymers between $T_g - (T_g + 100^\circ\text{C})$.^{76,77}

Analysis of the data indicates that η_0 depends on the stereochemistry of the lactide copolymers. The zero-shear viscosity is found to increase with the initial amount of L-mer (72 g/mol) and decrease with the amount of *meso*-lactide. The following five parameter model with WLF temperature dependency was used to fit all of the η_0 data in Table 2-16,

$$\eta_0 = (a_1 + a_2 w_{\text{meso}} + a_3 w_{\text{L-mer}}) \left(\frac{M_w}{100,000} \right)^{3.38} \exp \left(\frac{-c_1(T(C) - 100)}{c_2 + (T(C) - 100)} \right) \quad (2-26)$$

where w_{meso} and $w_{\text{L-mer}}$ are the initial weight fractions of *meso*-lactide and L-mer. Because of the homogeneity of error in $\ln(\eta_0)$ with varying test conditions, the natural logarithm of both sides of equation (2-26) was taken prior to regression analysis. Both w_{meso} and $w_{\text{L-mer}}$ were found to be statistically significant: $a_1 = -13,000$, $a_2 = -142,000$, $a_3 = 112,000$. The WLF parameters had the following values: $c_1 = 15.6 \pm 1.6$, $c_2 = 110 \pm 11^\circ\text{C}$. The model root-mean-square-error (RMSE) was $\ln(\eta_0(\text{Pa-s})) = 0.30$.

Six diagnostic plots were prepared to evaluate $\ln(\eta_0)$ model aptness. Figure 2-26 presents the η_0 model predictions versus the actual experimentally determined values. The data appear randomly distributed about the 45° line and exhibit no distinct pattern. Model error versus actual η_0 is presented in Figure 2-27. There are no apparent trends, and error appears evenly distributed among the range of viscosity values. Figures 2-28 to 2-31 plot model error versus the four model independent variables: temperature, weight average molecular weight, and initial *meso*-lactide and L-mer weight fractions. Again,

there are no apparent error trends in the data. Equation 2-26, with the regressed parameter values, may be used to estimate the zero-shear viscosity of amorphous polylactides ($L_{mer} \geq 50\%$) between 55 -155°C.

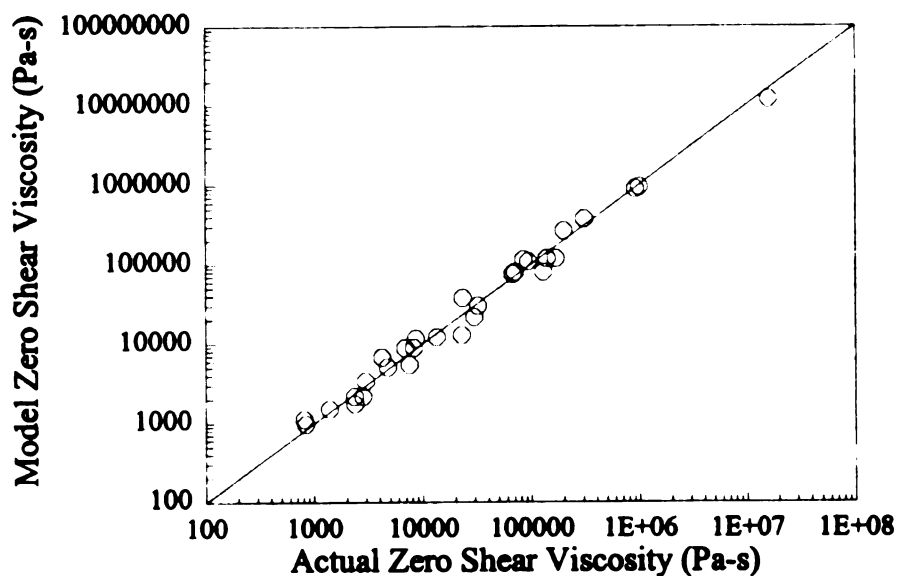


Figure 2-26. Predicted versus actual η_0 diagnostic plot.

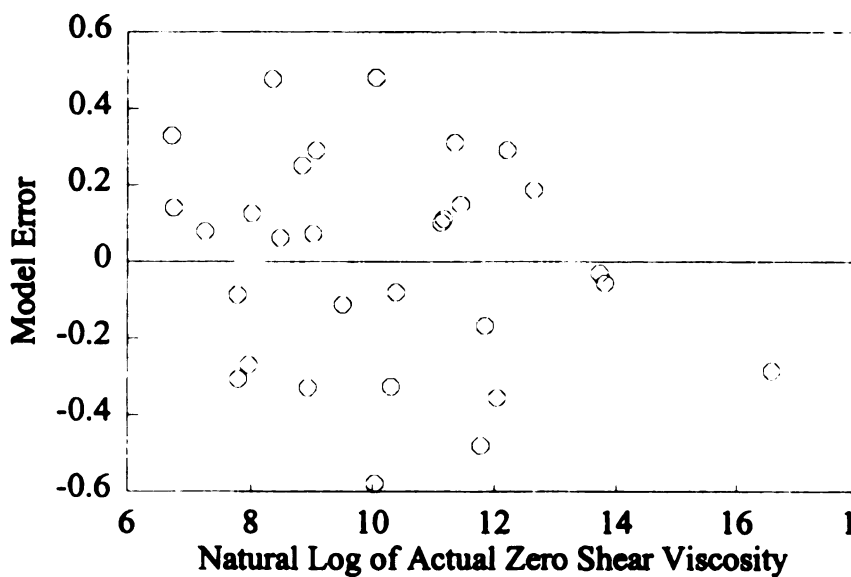


Figure 2-27. Residuals versus dependent variable, η_0 data.

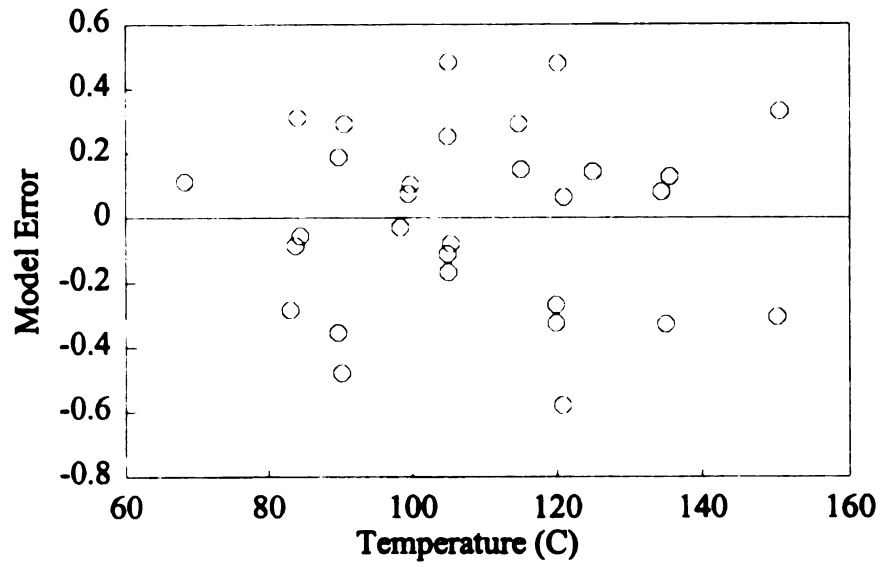


Figure 2-28. Model residuals versus temperature.

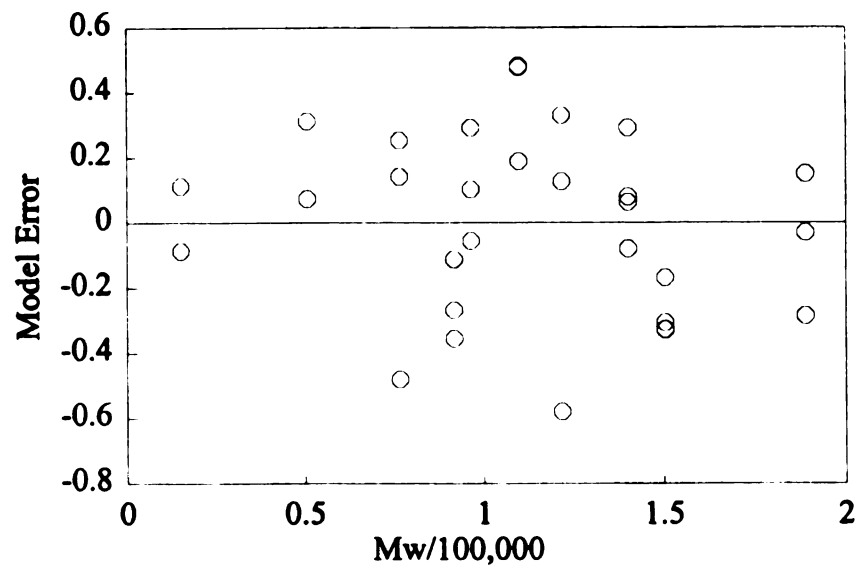


Figure 2-29. Model residuals versus $M_w/1E5$.

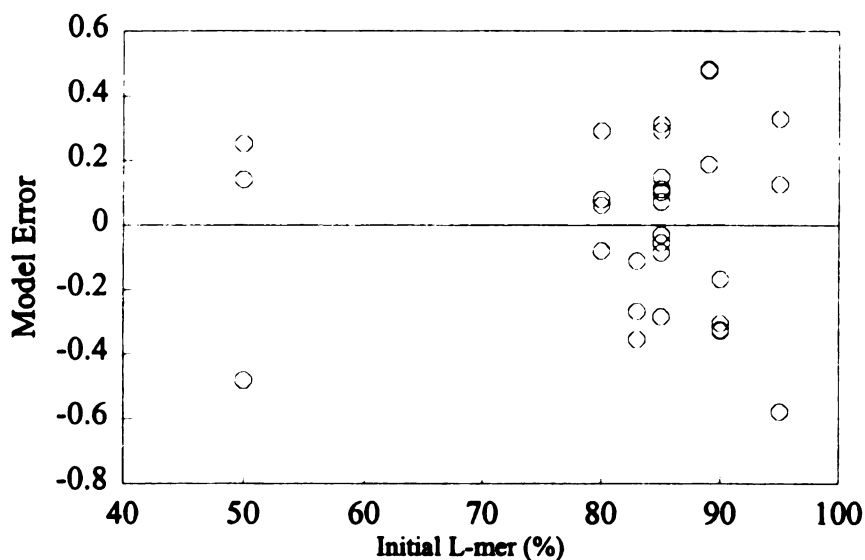


Figure 2-30. Model residuals versus percent initial L-mer.

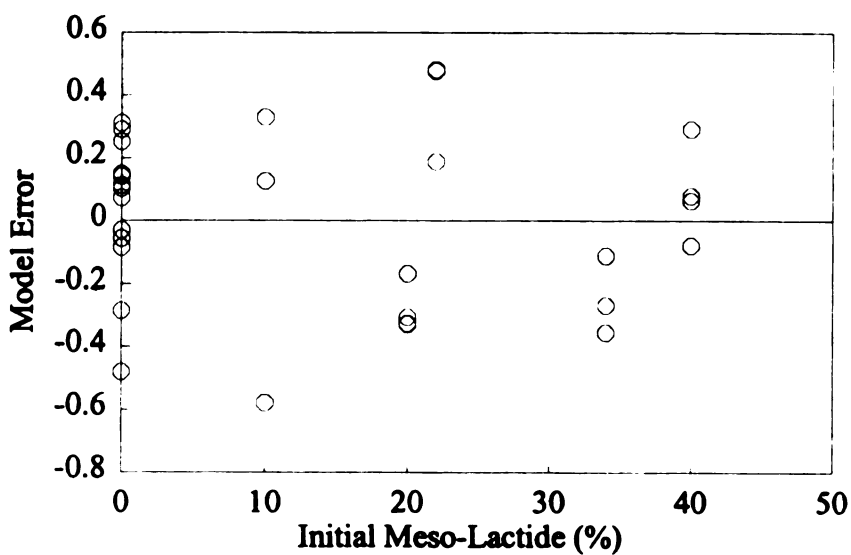


Figure 2-31. Model residuals versus percent initial *meso*-lactide.

The regressed WLF parameters are based on the natural log of the shift factor referenced to 100°C, or $T_g + 45^\circ\text{C}$. To compare to the universal WLF parameters, referenced at T_g with a log base ten shift factor, we use the following easily derived relationships to convert the regressed values to a reference temperature of $T_g = 55^\circ\text{C}$,

$$c_2(T_0 = T_g) = c_2(T_0 = T_g + 45) - (T_g + 45 - T_g) = 65.0^\circ\text{C} \quad (2-27)$$

$$c_1(T_0 = T_g) = \frac{c_1(T_0 = T_g + 45)}{2.3026} \left(1 + \frac{(T_g + 45 - T_g)}{c_2(T_0 = T_g)} \right) = 11.5 \quad (2-28)$$

These WLF parameters are compared to those of other polymers⁷⁷ and the universal constants in Table 2-17. Although c_2 for polylactide is within a normal deviation from the universal value, the deviation of c_1 from the universal value is larger than is normally found with other amorphous polymers.

Table 2-17 WLF Parameters Referenced to T_g

Polymer	c_1	c_2 (°C)	T_g (°C)
Polylactide	11.5	65.0	55
Polystyrene	14.5	50.4	100
Natural Rubber	16.7	53.6	-73
Poly(ethyl methacrylate)	17.6	65.5	62
Polyisobutylene	16.6	104	-71
"Universal Constants"	17.4	51.6	

The recoverable shear compliance, J_e^0 , data is determined from the dynamic oscillatory experiments using equation 2-21. However, in many cases the ratio of the dynamic storage modulus to the square of the frequency did not converge with decreasing frequency in the range tested. The experiments that did yield good J_e^0 values were in accord with the Graessley⁷⁴ finding that

$$\gamma_0 \eta_0 J_e^0 = 0.6 \pm 0.2 \quad (2-29)$$

where the characteristic shear rate $\dot{\gamma}_0$ (taken as ω_0 in this work) is the shear rate at $\eta = 0.8 \eta_0$. The remainder of the J_e^0 data were calculated using the following formula,

$$J_e^0 = \frac{0.6}{\eta_0 \omega (\eta = 0.8 \eta_0)} \quad (2-30)$$

The estimated J_e^0 values using this method gave results that seem reasonable with extrapolated G'/ω^2 data.

The poly(85% L-co-15% D-lactide) data provides a good range of M_w and T , and a two-factor analysis of variance was performed using a first order linear model to determine if these two variables affect J_e^0 . The regression results found M_w to be significant at 99% confidence and temperature to be insignificant. J_e^0 increases with M_w (and PDI) over this range of molecular weights. These results agree with both practice and theory.⁷⁶ Because J_e^0 is sensitive to the polydispersity index, PDI, we were unable to draw any inferences about the effect of PLA stereochemistry. The average recoverable shear compliance for high molecular weight amorphous polylactide is

$$J_e^0 = 2.3 \times 10^{-5} \text{Pa}^{-1}; \quad PDI \sim 2; \quad M_w > 50,000 \quad (2-31)$$

A single master viscosity curve of η/η_0 versus $\dot{\gamma}\tau_0$ is found to represent linear amorphous polymers having a similar PDI. With this knowledge we model the PLA $\eta(\omega)$ as a product of η_0 and a frequency function,

$$\eta = \eta_0(T, M_w, w_{\text{L-mer}}, w_{\text{meso}})f(\omega\tau_0) \quad (2-32)$$

where η_0 is determined from equation (2-26) and the average relaxation time, τ_0 , is $\eta_0 J_e^0$. A modified Eyring model was found to give a good representation of $f(\omega\tau_0)$ for the amorphous polylactide viscosity data,

$$\frac{\eta}{\eta_0} = \left[\frac{\sinh^{-1}(k\omega\tau_0)}{k\omega\tau_0} \right]^b \quad (2-33)$$

All 30 amorphous PLA $\eta(\omega)$ data sets were fit to this model and the two parameters were determined by nonlinear regression: $k = 1.25$, $b = 0.92$. The model (solid line) and data are presented in Figure 2-32. This curve is in good agreement with a general η/η_0 versus $\dot{\gamma}\tau_0$ curve published for polymers having a PDI of 2.0.²

Therefore, we can now estimate viscosity as a function of frequency (or shear rate, Cox-Merz rule) for amorphous polylactides using equations (2-26), (2-31), and (2-33) to calculate η_0 , J_e^0 , and finally $\eta(\omega)$. This estimation should be valid for all unmodified PLA random copolymers (L-mer > 50%), between T_g and $T_g + 100^\circ\text{C}$ (i.e., 55-155°C), and for all M_w (referenced to PS) where PDI is about 2.

Next we use time-temperature superposition to characterize the dynamic moduli of amorphous polylactides. Time-temperature superposition can be expressed mathematically for η_0 , G' , and G'' as

$$\eta_0(T) = \eta_0(T_{ref}) a_T \quad (2-34)$$

$$G'(\omega, T) = G'(a_T\omega, T_{ref}) \quad (2-35)$$

$$G''(\omega, T) = G''(a_T\omega, T_{ref}) \quad (2-36)$$

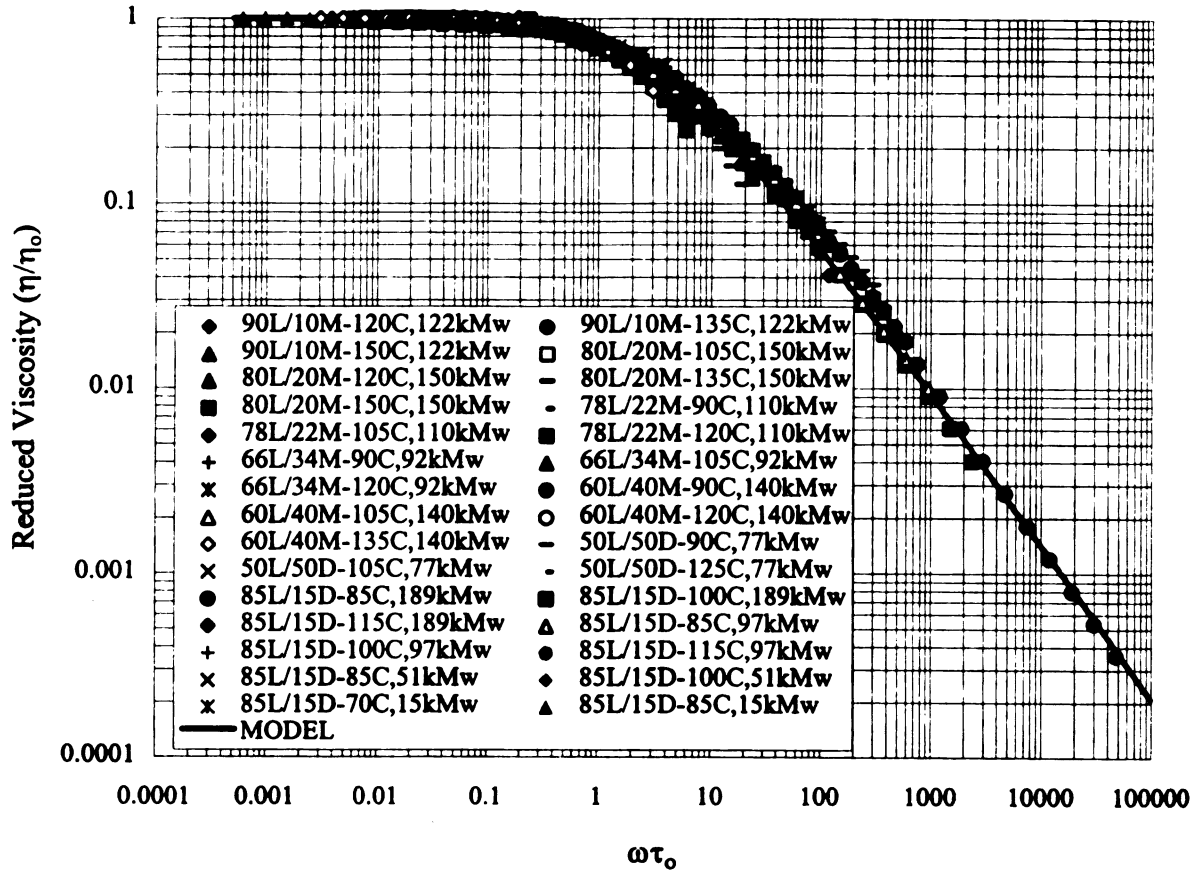


Figure 2-32. Master reduced viscosity curve for amorphous polylactides of various stereoisomer content and molecular weight, at temperatures between 55-155°C. The solid line represents the viscosity model.

The shift factor, a_T , is equivalent to the amount of frequency the viscoelastic property curve at T_{ref} needs to be shifted in order to match the viscoelastic property curve at T . We have already determined the a_T relationship for amorphous polylactides in the WLF based zero-shear viscosity model referenced to 100°C, equation (2-26),

$$a_T = \frac{\eta_0}{(a_1 + a_2 w_{meso} + a_3 w_{L-mer}) \left(\frac{M_w}{1ES} \right)^{3.38}} = \exp \left(\frac{-c_1 (T(C) - 100)}{c_2 + (T(C) - 100)} \right) \quad (2-37)$$

where c_1 and c_2 were determined to be 15.6 and 110°C.

In Figures 2-33 and 2-34 we present the dynamic storage and loss moduli for poly(80% L-co-20% *meso*-lactide) as a function of frequency at 105, 120, 135, and 150°C. Next we shift these curves horizontally by a factor of a_T , equation (2-37), referenced to 100°C. These master curves for G' and G'' are presented in Figures 2-35. The crossover frequency for the 150,000 M_w poly(80% L-co-20% *meso*-lactide) sample was 2 s^{-1} , referenced to 100°C. The crossover frequency (reciprocal time units) represents the change from elastic dominated mechanical behavior to a viscous dominated response. For a perfectly elastic solid $G'' = 0$ and $G' = G$, the shear modulus. For a perfectly viscous liquid $G' = 0$, $G'' = \eta\omega$. With increased time (decreased ω), the dynamic moduli enter the terminal flow region and have the following frequency relationships at long time, $\frac{d \ln(G')}{d \ln(\omega)} = 2$; $\frac{d \ln(G'')}{d \ln(\omega)} = 1$. The respective values achieved in the frequency limits of our experiments were about 1.6 and 1.0.

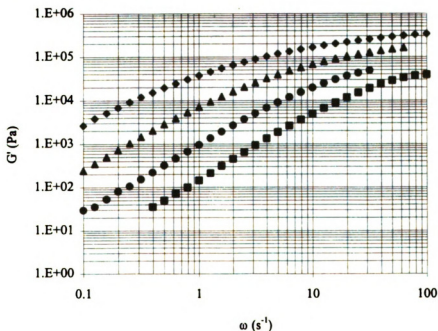


Figure 2-33. The dynamic storage modulus versus frequency for a 150,000 M_w poly(80% L-co-20% *meso*-lactide) sample at 105 (◆), 120 (▲), 135 (●), and 150°C (■).

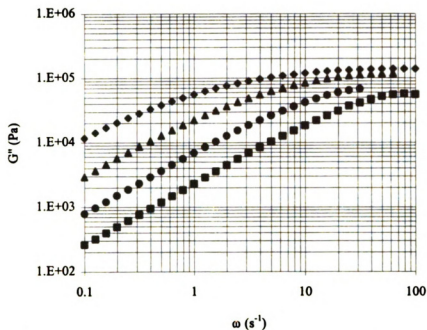


Figure 2-34. The dynamic loss modulus versus frequency for a 150,000 M_w poly(80% L-co-20% *meso*-lactide) sample at 105 (◆), 120 (▲), 135 (●), and 150°C (■).

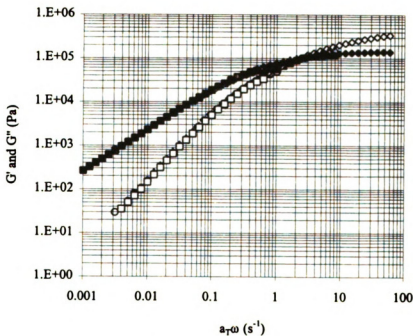


Figure 2-35. Master dynamic moduli curves for a 150,000 M_w poly(80% L-co-20% *meso*-lactide) sample with shift factor a_T referenced to 100°C. The storage modulus, G' , and loss modulus, G'' , are represented by the unfilled and filled markings, respectively.

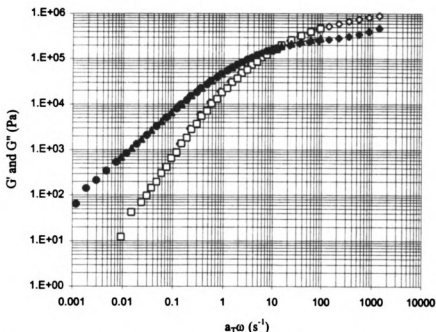


Figure 2-36. Master dynamic moduli curves for a 96,600 M_w poly(85% L-co-15% D-lactide) sample with shift factor a_T referenced to 100°C. The storage modulus, G' , and loss modulus, G'' , are represented by the unfilled and filled markings, respectively.

Master dynamic moduli curves were prepared for all 10 amorphous polylactide samples. Time temperature-superposition was observed in all samples and vertical shifts were not required. The crossover frequency was found to increase with decreasing molecular weight. This is shown with the 96,600 M_w poly(85% L-co-15% D-lactide) sample in the master dynamic moduli curves in Figure 2-36. In this sample a crossover frequency of $\omega a_T = 10 \text{ s}^{-1}$ was achieved. A plot of crossover frequency versus M_w is presented in Figure 2-37.

To better illustrate the effect of M_w on extending the elastic response and plateau modulus we plot the dynamic moduli versus $a_T \omega$ for the various M_w poly(85% L-co-15%

D-lactide)s in Figures 2-38 and 2-39. About four decades of frequency separate the 15,400 and 189,000 M_w samples at constant modulus.

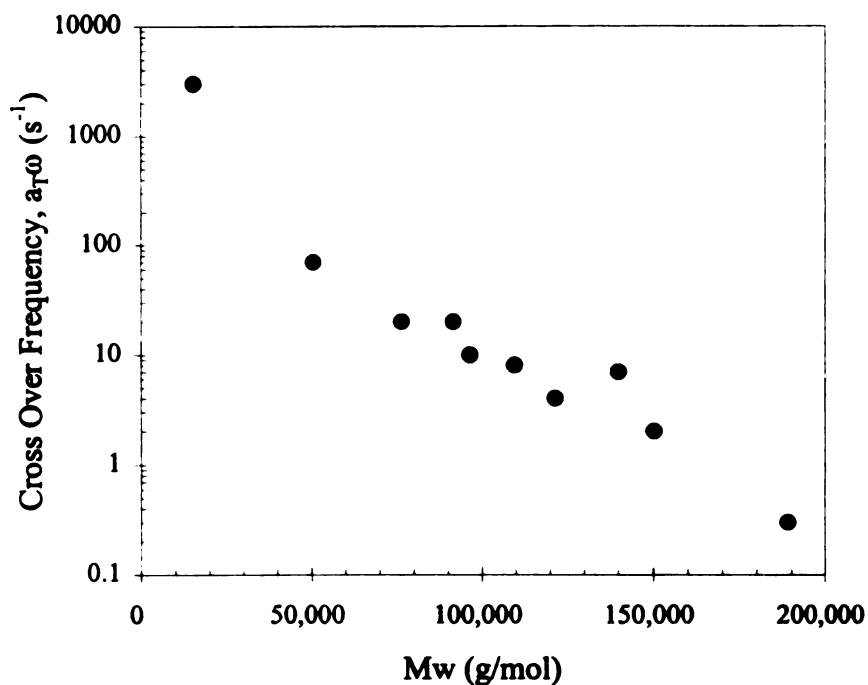


Figure 2-37. Crossover frequency versus M_w for 10 different amorphous polylactide samples, with shift factor a_T referenced to 100°C.

The plateau modulus is approximately equal to the storage modulus, $G_N^0 \cong G'$, in the region where G' is insensitive to ω . The entanglement molecular weight, M_e , is the apparent molecular weight of chains in the entanglement network which dominate the flow of viscoelastic polymers.⁷⁴ This characteristic molecular weight is determined from the plateau modulus,

$$M_e = \frac{\rho RT}{G_N^0} \quad (2-38)$$

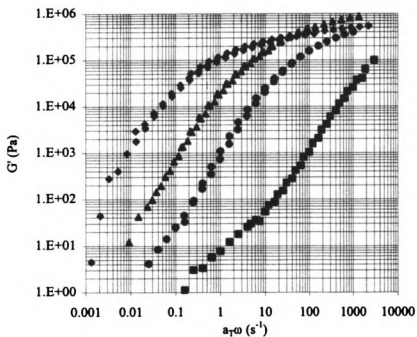


Figure 2-38. Master dynamic storage modulus curves for various M_w poly(85% L-co-15% D-lactide)s with shift factor a_T referenced to 100°C; M_w = 15,400 (■), 50,750 (●), 96,600 (▲), 189,000 (◆).

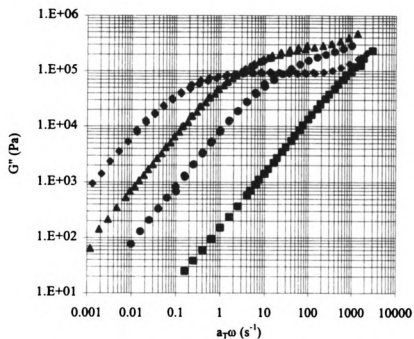


Figure 2-39. Master dynamic loss modulus curves for various M_w poly(85% L-co-15% D-lactide)s with shift factor a_T referenced to 100°C; M_w = 15,400 (■), 50,750 (●), 96,600 (▲), 189,000 (◆).

The G_N^0 and M_e values for the eight amorphous polylactides that exhibited a plateau region at test conditions (two lowest M_w PLAs did not) are summarized in Table 2-18 and compared to literature values for some commercial polymers.⁷⁴

Table 2-18 Plateau Modulus and Entanglement Molecular Weight for Amorphous Polylactides

Polymer	M_w (g/mol)	$G_N^0 \times 10^{-5}$ (Pa)	M_e (100°C) (g/mol)
85L/15D	96,600	10	3,650
85L/15D	189,000	5	7,300
50L/50D	76,600	5	7,300
90L/10 <i>meso</i>	121,700	1	36,500
80L/20 <i>meso</i>	150,400	4	9,130
78L/22 <i>meso</i>	109,700	9	4,060
66L/34 <i>meso</i>	91,800	5	7,300
60L/40 <i>meso</i>	140,200	4	9,130
PE (150°C)		22.0	1,100
PP (atactic, 75°C)		8.5	2,800
PS (190°C)		2.0	18,700

Literature values for PE, PP, and PS from Fetters in Graessley⁷⁴

The average plateau modulus for amorphous polylactide is determined to be 5×10^5 Pa.

The corresponding entanglement molecular weight is 7,300 g/mol at 100°C. This result is in good agreement with the value of 8,900 g/mol M_e determined by Grijpma et al.⁷⁸ using swelling measurements of poly(85% L-co-15% D-lactide) in chloroform.

Consistent with a higher glassy state modulus (determined in Section 2.4), polylactide's plateau modulus is somewhat higher than that of polystyrene. The change in PLA's modulus between the glassy and plateau regions is nearly four orders of magnitude, 3.9×10^9 to 5×10^5 Pa.

The entanglement molecular weight is also a qualitative measure of melt toughness. Low M_e polymers such as PE have high melt toughness. The following is the order of increasing toughness based on the values in Table 2-18: PS < PLA < PP < PE.

It is interesting to compare the product of J_e^0 and G_N^0 to the value observed for monodisperse polymers, $J_e^0 G_N^0 = 2.0$.⁷⁴ For amorphous polylactides with PDI = 2, $J_e^0 G_N^0 \cong 17$. The difference is explained by the sensitivity of J_e^0 to PDI. This suggests an increase in the elastic nature of the melt with increasing PDI.

Conclusions

The linear viscoelastic behavior of various amorphous polylactides has been characterized between 68-151°C by dynamic parallel plate oscillatory experiments. The following conclusions are made:

1. The zero-shear viscosity of amorphous polylactide depends on its isomeric makeup, weight average molecular weight, and temperature between T_g and $T_g + 100^\circ\text{C}$, according to equation (2-26). Specifically, the zero-shear viscosity was found to increase to a power of 3.38 with M_w and vary with temperature according

to the WLF equation referenced to 100°C ($T_g + 45^\circ\text{C}$) with constants $c_1 = 15.6$, and $c_2 = 110^\circ\text{C}$.

2. The recoverable shear compliance was determined to be $2.3 \times 10^{-5} \text{ Pa}^{-1}$ for amorphous polylactide having a $M_w > 50,000$ and a PDI of about 2.
3. The viscosity of all amorphous polylactides ($T, M_w, w_{\text{meso}}, w_{\text{L-mer}}$) with PDI ~ 2 follows a master curve of η/η_0 versus $\omega\tau_0$ fit to a modified Eyring model according to equation (2-33). This curve is in good agreement with a master curve for all amorphous polymers of PDI ~ 2 .
4. All of the tested amorphous polylactides were found to obey the principle of time-temperature superposition. The shift factor defined by equation (2-37) can be used to determine PLA viscoelastic properties at conditions that are experimentally inaccessible.
5. The plateau modulus for amorphous polylactide is $5 \times 10^5 \text{ Pa}$. PLA's characteristic entanglement molecular weight was calculated to be 7,300 g/mol. The modulus for amorphous PLA decreases from 3.9×10^9 to $5 \times 10^5 \text{ Pa}$ between the glassy and rubbery states.

2.5.2 Rheological Constitutive Equation

In this section we develop a simple empirical rheological constitutive equation for unmodified polylactides. This equation is used to predict the melt viscosity as a function of weight average molecular weight, temperature, and shear rate. This model may be substituted into the equations of change to solve for polylactide's flow behavior in a given

geometry (e.g., velocity profiles, volumetric flow, pressure drop, torque). In addition, the viscosity prediction can be directly substituted into the many developed polymer processing calculations and computer programs (e.g., melt conveying, viscous heat generation, optimization of extrusion conditions, mold and equipment design).

In Section 2.4 we used modulus as the most important practical measure to characterize a material's mechanical behavior. Similarly, we use viscosity as the most important practical measure to characterize flow behavior. These solid and liquid material functions are highly related: modulus is $\text{stress}(F/A)/\text{strain}$ and viscosity is $\text{stress}(F/A)/\text{strain rate (shear rate)}$.

The viscosity of polymer melts is of great importance in polymer processing applications. However, at the high strain and shear rates experienced in resin processing equipment the linear viscoelastic relationships developed in Section 2.5.1 are not applicable. Typical shear rates encountered in extrusion and injection molding are 10 - 10^4 and 10^3 - 10^5 s^{-1} , respectively. The effect of high strain on amorphous PLA viscosity at a constant shear rate is presented in Figure 2-40 using parallel plate rheological data. Above about 20% strain the viscosity of polylactide becomes nonlinear. Empirical viscosity relationships are often employed to model nonlinear behavior.

Experimental

Polymers. Four amorphous polylactides (~17% *meso*) with weight average molecular weights between 75,000-400,000 were obtained from Cargill. In addition, Cargill provided seven amorphous polylactides with varying initial *meso*-lactide, 10-40%.

All polylactides were melt devolatilized and contained about 1% residual lactide. All polymers were thoroughly dried prior to testing.

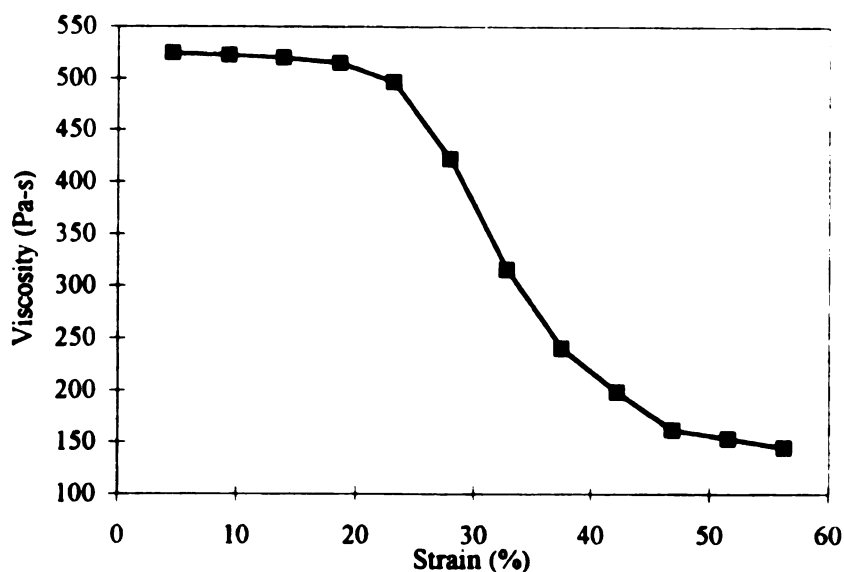


Figure 2-40. Viscosity versus percent strain at constant shear rate, 100s^{-1} , and 135°C for an amorphous polylactide.

Molecular Weight Determinations. Polylactide molecular weights were determined using a Waters GPC and are referenced directly to polystyrene standards. A discussion of the analytical setup is found in Sections 2.4 and 3.2.

Capillary Viscometry. Two capillary viscometers were used: Instron 3210 (Michigan Molecular Institute), Haake Rosand RH7-2 (Cargill). Various length, 0.25-16 mm, 1 mm diameter capillary dies were used. Apparent viscosity was calculated with the standard equations published in ASTM D3835-90. All reported data has been Rabinowitsch corrected. Bagley end effect corrections were not necessary. This was confirmed by comparing viscosity measurements on long and short (0.25 mm "zero

length") capillary dies; these measurements were found to be in good agreement. The unmodified PLA melts exhibited no die swell.

Results

The viscosity-shear rate behavior of four amorphous polylactides with M_w between 75,000–400,000 were determined by capillary viscometry at 150, 175, and 200°C. Figures 2-41, 2-42, and 2-43 show these data. The 400,000 and 75,000 M_w polymers have an order-of-magnitude viscosity difference at 175°C and 200s⁻¹. The two closest M_w polymers, 150,000 and 200,000, have similar viscosities. These temperatures and shear rates represent typical processing conditions for amorphous polylactides of this molecular weight range.

In developing a model for the viscosity of PLA at processing conditions we expect an Arrhenius temperature dependence at these higher temperatures. In addition, we expect lower extrapolated zero-shear viscosities, η_0 , having a lesser dependency on M_w than is found in linear viscoelastic behavior (e.g., equation (2-26)). However, we still expect similar model functionality,

$$\eta = \frac{\sinh^{-1}(\eta_0 \dot{\gamma} B)}{\dot{\gamma} B} \quad (2-39)$$

where $\dot{\gamma}$ is shear rate and B is a model parameter. Here we have essentially replaced $\eta_0 k J_e^0$ from equation (2-33) with $\eta_0 B$. Since k is of order unity we expect B to assume the order

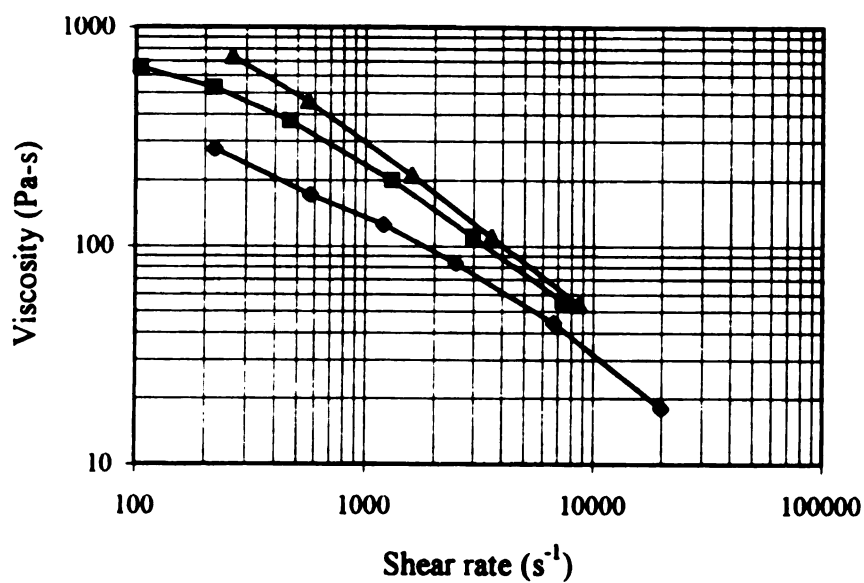


Figure 2-41. Viscosity-shear rate behavior at 150°C for amorphous polylactides of various weight average molecular weights: 200,000 g/mol, (▲); 150,000, (■); 75,000, (◆).

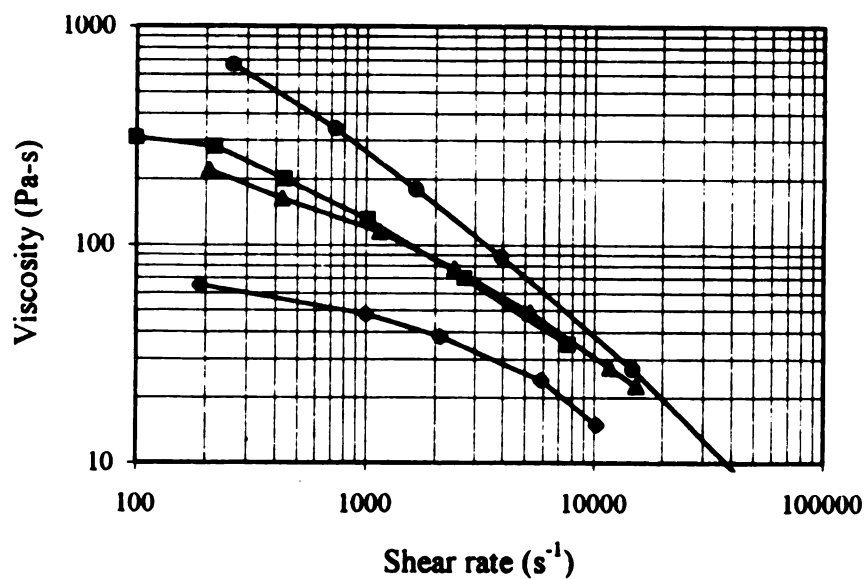


Figure 2-42. Viscosity-shear rate behavior at 175°C for amorphous polylactides of various weight average molecular weights: 400,000 g/mol, (●); 200,000, (▲); 150,000, (■); 75,000, (◆).

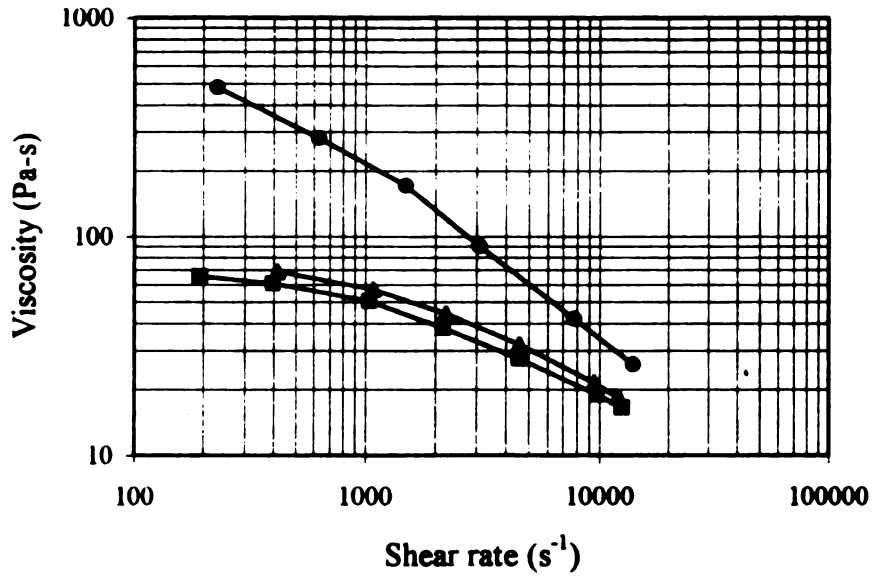


Figure 2-43. Viscosity-shear rate behavior at 200°C for amorphous polylactides of various weight average molecular weights: 400,000 g/mol, (●); 200,000, (▲); 150,000, (■).

of magnitude of J_e^0 and be independent of M_w and T . This is very useful as it allows us to take care of M_w and T effects through η_0 ,

$$\eta_0 = \eta_{0,\text{ref}} \left(\frac{M_w}{100,000} \right)^a \exp \left(\frac{E_a}{R} \left(\frac{1}{T(K)} - \frac{1}{448} \right) \right) \quad (2-40)$$

where the referenced parameter $\eta_{0,\text{ref}}$ is $\eta_0(M_w = 100,000, T = 175^\circ\text{C})$.

Equation (2-39) was used to regress the data presented in Figures 2-41, 2-42, and 2-43. To minimize transformation error, the natural logarithm of both sides of the equation was taken prior to regression analysis. Very good fits were obtained with all 10 data sets. As expected, the parameter B was found to be independent of M_w and T , and averaged $1.67 \times 10^{-5} \text{ Pa}^{-1}$. With B taken at this constant value, the zero-shear viscosities

were regressed again using equation (2-39). The regression results for B and η_0 are presented in Table 2-19.

**Table 2-19 Viscosity Model
Parameters for Amorphous PLA
Capillary Viscometry Data**

M_w (g/mol)	T (°C)	η_0 (Pa-s)	B (Pa ⁻¹)
75,000	150	330	1.67E-05
75,000	175	55	2.34E-05
150,000	150	1,000	1.20E-05
150,000	175	322	1.76E-05
150,000	200	59	1.85E-05
200,000	150	2,830	1.33E-05
200,000	175	238	1.55E-05
200,000	200	71	1.47E-05
400,000	175	2,100	2.00E-05
400,000	200	800	1.57E-05

Next, the η_0 values were regressed to the logarithm of equation (2-40). The following parameters were determined: $\eta_{0,\text{ref}} = 97 \pm 18$ Pa-s, $a = 2.24 \pm 0.25$, $E_a = 104 \pm 13$ kJ/mol. The viscosity of various molecular weight amorphous polylactides can be estimated at various processing conditions ($T, \dot{\gamma}$) using this four parameter model, equations (2-39) and (2-40). This model accounts for 97.5% of the variance in the $\ln(\eta)$ data. The total model root-mean-square-error is $\ln(\eta(\text{Pa-s})) = 0.18$.

The actual data from the previous figures are plotted with the model predictions in Figures (2-44), (2-45), and (2-46). The results are reasonable and the viscosity model

described by equations (2-39) and (2-40) should be appropriate for unmodified PLA engineering calculations.

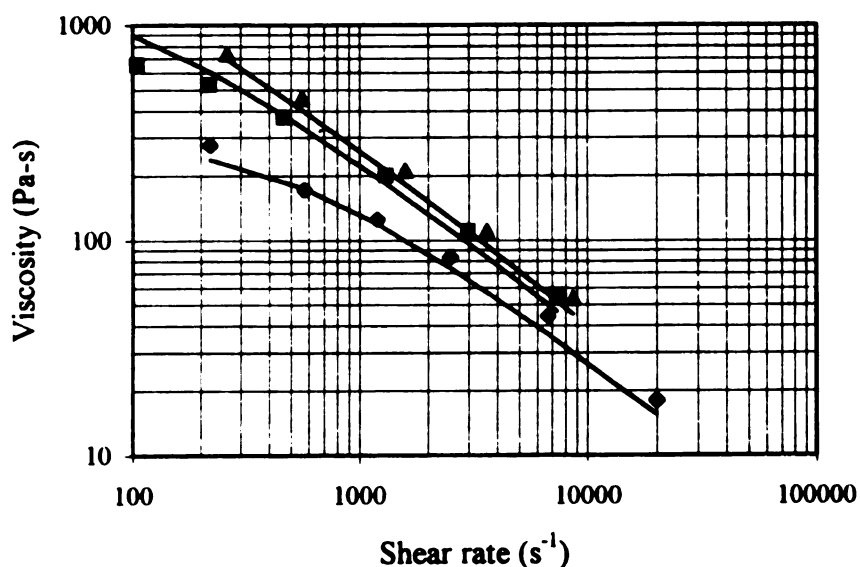


Figure 2-44. Comparison of viscosity model (solid line) to viscosity-shear rate data at 150°C with various M_w PLA: 200,000 g/mol, (Δ); 150,000, ($\blacksquare$); 75,000, ($\blacklozenge$).

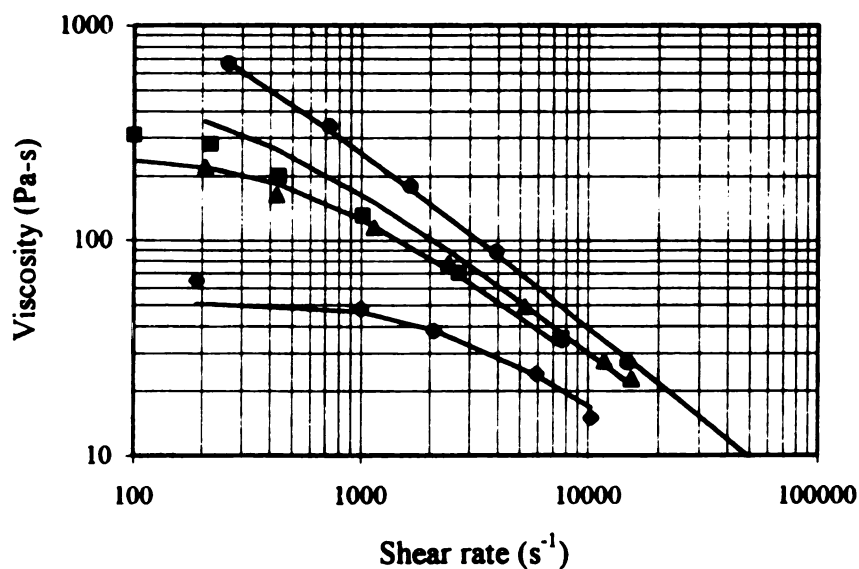


Figure 2-45. Comparison of viscosity model (solid line) to viscosity-shear rate data at 175°C with various M_w PLA: 400,000 g/mol, ($\bullet$); 200,000, (Δ); 150,000, ($\blacksquare$); 75,000, ($\blacklozenge$).

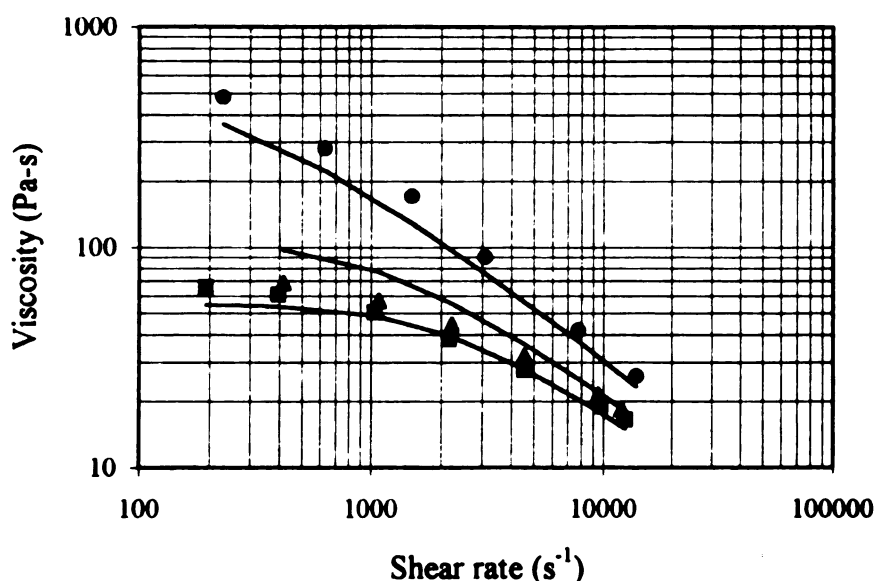


Figure 2-46. Comparison of viscosity model (solid line) to viscosity-shear rate data at 200°C with various M_w PLA: 400,000 g/mol, (●); 200,000, (▲); 150,000, (■).

The effect of initial *meso*-lactide on the viscosity of amorphous polylactides at processing conditions (nonlinear viscoelastic region) was investigated by capillary viscometry. The viscosities of amorphous polylactides with 10–40% initial *meso*-lactide and M_w between 92,000–165,000 g/mol were determined at 150–200°C. However, no effect of initial *meso*-lactide on $\eta(\dot{\gamma})$ could be determined and the data are not presented here. The effects of M_w and T dominate the viscosity of amorphous polylactides at these high shear rate conditions. This most likely renders any viscosity effects of PLA stereochemistry unimportant, if not immeasurable.

Conclusions

1. An empirical constitutive viscosity equation was determined for amorphous polylactides at typical processing conditions, equations (2-39) and (2-40). This relationship may be used to predict the viscosity of amorphous PLA for a wide

range of M_w (75,000–400,000), temperatures (150–220°C), and shear rates (100–20,000 s⁻¹).

2. The effect of initial *meso*-lactide, between 10–40%, on amorphous PLA viscosity is insignificant in the nonlinear viscoelastic region.

2.5.3 Reaction Viscosity; Mixture Viscosity Equation

During bulk lactide polymerization the viscosity changes by six decades in magnitude and the quantification of the rapidly rising viscosity with conversion is important for properly designing the polymerization process. Because the polymerization kinetics are first order in monomer (Section 3.2) multiple polymerization stages are required to reduce the mean residence time and its distribution for a given monomer conversion. Therefore, the pumping and agitation requirements change with viscosity from stage to stage. The knowledge of the reaction viscosity is also important in designing copolymerization systems. It is often preferable to add comonomers or other additives somewhere along the reaction train where the mixing behavior or extent of prior polymer growth is right for the desired polymer modification.

In addition to polymerization, the lactide-poly(lactide) mixture viscosities are also very sensitive to monomer concentration in the devolatilization process. It is advantageous to remove and recycle monomer from the reaction mixture prior to the diminishing returns of monomer conversion with time (volume), owing to the reversible reaction and significant monomer equilibrium concentration. In devolatilization the initial

monomer concentration could be as high as 15%, and the shear rates could vary from low (e.g., high viscosity wiped film evaporator) to high (e.g., twin screw extruder).

In this section we determine the mixture viscosity as a function of monomer concentration, temperature, molecular weight, and shear rate. Combining the mixture viscosity equation with polymerization kinetics gives the reaction viscosity as a function of conversion.

Experimental

Polymer. An amorphous polylactide (~17% *meso*) with a weight average molecular weight of 90,000 was obtained from Cargill. The polymer was powderized prior to dry mixing with crystalline L-lactide. Monomer concentrations were determined from the capillary extrudate by GPC. All monomer-polymer mixtures were miscible.

Capillary Viscometry. An Instron 3210 (Michigan Molecular Institute) capillary viscometer was used for the mixture viscosity experiments (see Section 2.5.2 for details).

Results

Figures 2-47, 2-48, and 2-49 present the viscosity-shear rate relationships for an amorphous polylactide containing 2.2%, 10.0%, 17.3%, and 33.7% L-lactide at 154, 174, and 198°C. The effect of monomer concentration on the mixture viscosity is considerable. The mixture viscosities with 33.7% monomer are less than that of honey at room temperature (about 10 Pa-s).

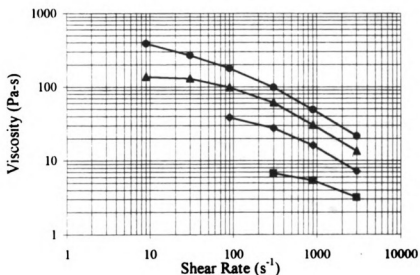


Figure 2-47. Viscosity-shear rate curves at 154°C for lactide-PLA mixtures containing lactide in amounts of 2%, 10%, 17%, and 34%.

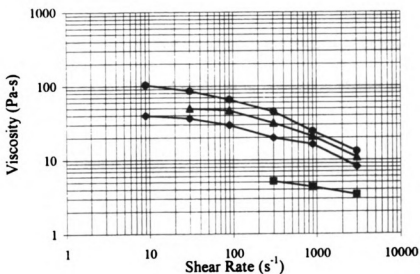


Figure 2-48. Viscosity-shear rate curves at 174°C for lactide-PLA mixtures containing lactide in amounts of 2%, 10%, 17%, and 34%.

We attempt to model this system by determining the extrapolated zero-shear viscosities as a function of temperature, M_w , and polymer weight fraction w_p . Equation (2-39) was used to determine η_0 for each of the data sets. In general, equation (2-39) fits the data very well. The results of the regressed η_0 are summarized in Table 2-20.

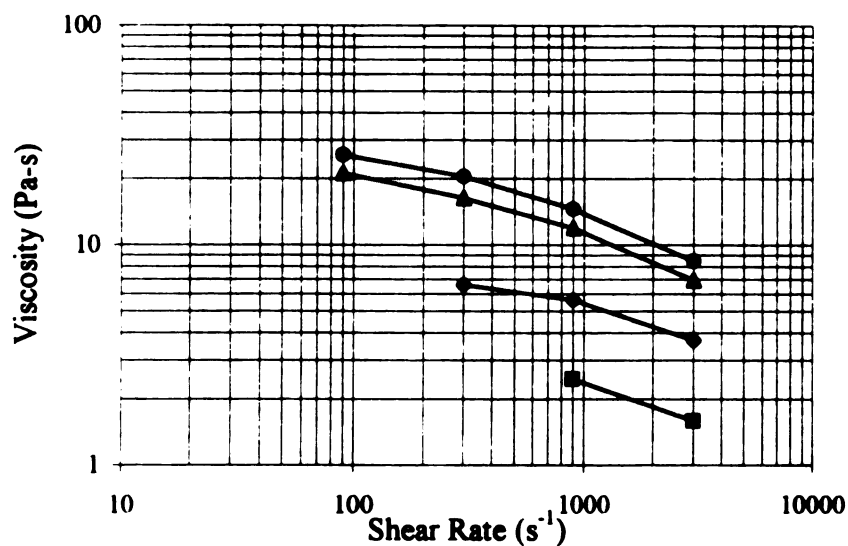


Figure 2-49. Viscosity-shear rate curves at 198°C for lactide-PLA mixtures containing lactide in amounts of 2%, 10%, 17%, and 34%.

Analysis of the data indicates that $\ln(\eta_0)$ is linear with $\ln(w_p)$. This relationship is presented in Figure 2-50. Accordingly, we edit our η_0 equation to include w_p ,

$$\eta_0 = \eta_{0,\text{ref}} w_p^n \left(\frac{Mw}{100,000} \right)^a \exp \left(\frac{Ea}{R} \left(\frac{1}{T(K)} - \frac{1}{448} \right) \right) \quad (2-41)$$

By regression with equation (2-41) the polymer weight fraction exponent was determined to be $n = 8.0 \pm 0.8$. Combining equation (2-41) with equation (2-39) we are able to estimate the viscosity of a lactide-poly lactide mixture as a function of M_w , T , $\dot{\gamma}$, and w_p . Figure 2-51 presents the predicted results versus actual data for the 175°C condition. The model's representation of the data is satisfactory.

**Table 2-20. Zero-Shear Viscosities
for Lactide-PLA Mixtures**

T (°C)	Lactide (%)	w_p	η_0 (Pa-s)
154	0.02	0.98	304
154	0.1	0.9	100
154	0.17	0.83	35
154	0.34	0.66	6
174	0.02	0.98	82
174	0.1	0.9	45
174	0.17	0.83	28
174	0.34	0.66	5
198	0.02	0.98	22
198	0.1	0.9	18
198	0.17	0.83	6
198	0.34	0.66	2

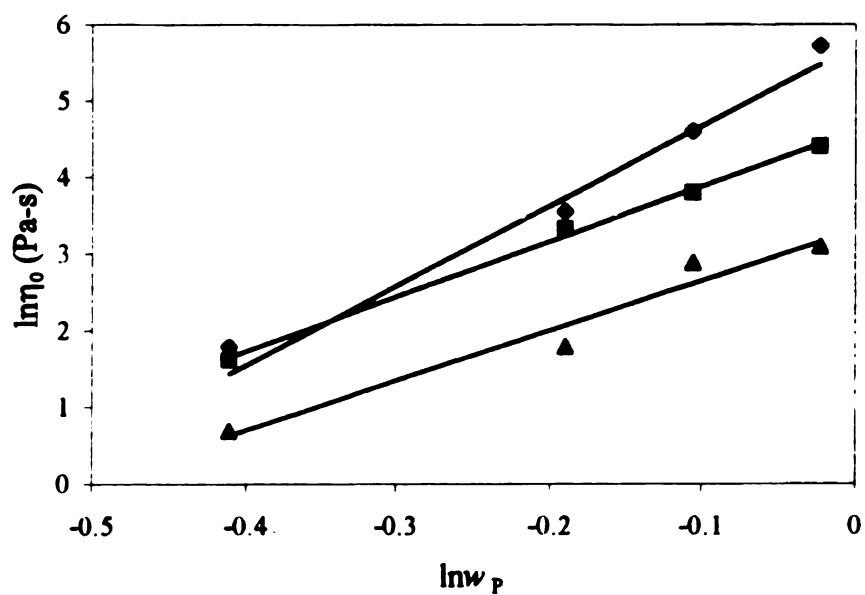


Figure 2-50. Linear relationship between the natural logarithms of viscosity and polymer weight fraction; 154°C (◆), 174°C (■), 198°C (▲).

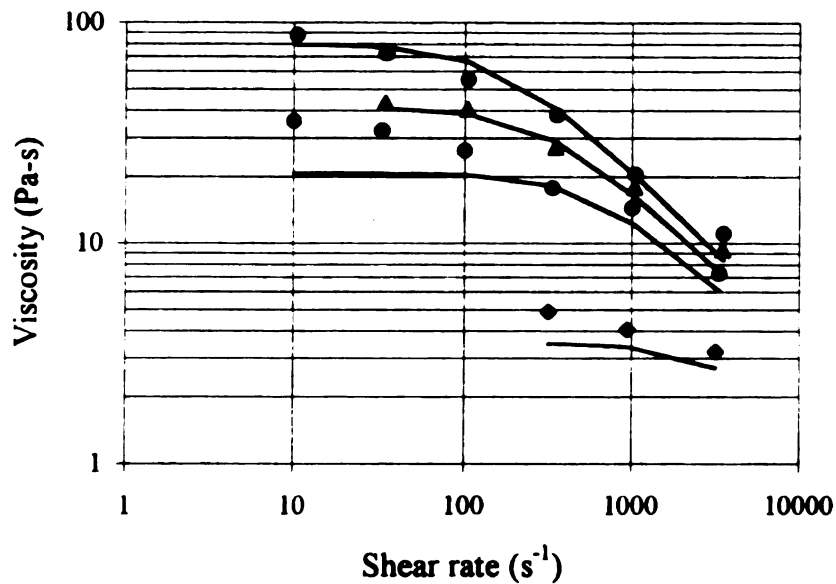


Figure 2-51. Comparison of the mixture viscosity model to the viscosity-shear rate data at 174°C. The lactide-PLA mixtures contain lactide in amounts of 2%, 10%, 17%, and 34%.

Conclusions

A lactide-poly lactide mixture viscosity equation was obtained from the regression of experimental data by including a polymer concentration term in the zero-shear viscosity equation. Equations (2-39) and (2-41) can be used to estimate the mixture viscosity over a wide range of temperatures, molecular weights, shear rates, and polymer concentration.

2.6 Transport of Thermal Energy

Knowledge of polylactide's thermal conductivity and its temperature dependence is important for calculating heating and cooling rates in amorphous and semi-crystalline solids (articles) and in the melt (resin processing). For the purpose of approximate engineering calculations we estimate the thermal conductivity as a function of

temperature for amorphous PLA in the glassy and liquid states. Based on these results we estimate the thermal conductivity of semi-crystalline PLA at room temperature.

The thermal conductivity, k , of an amorphous polymer is approximately proportional to the product of its heat capacity, C_p , density, ρ , and sound velocity through the material.² In other words, the thermal diffusivity, α , is proportional to the sound velocity. The thermal diffusivity at 25°C for an amorphous polymer can be estimated by the following²

$$\alpha(\text{m}^2/\text{s}) = \frac{k}{\rho C_p} \approx 5.25 \times 10^{-11} \left(\frac{U_R}{V} \right)^3 \quad (2-42)$$

where U_R and V are the polymer's Rao function, $(\text{cm}^3/\text{mol})(\text{cm/s})^{1/3}$, and molar volume, respectively. The Rao function is calculated by additive group contributions:²

$$U_R = U_{R,-\text{COO}-} + U_{R,-\text{CH}(\text{CH}_3)-} = 1225 + 1875 = 3100 \quad (2-43)$$

and the molar volume is $57.65 \text{ cm}^3/\text{mol}$ based on a density of 1.25 g/cm^3 (Section 2.3.2).

The values of both functions are based on the lactic mer unit of 72.06 g/mol . Substituting these values into Equation (2-42) we estimate the amorphous polylactide thermal diffusivity at 25°C to be $8.2 \times 10^{-8} \text{ m}^2/\text{s}$. This value is 14% lower than that of polypropylene and 26% lower than the thermal diffusivity of polystyrene.²

The amorphous polylactide thermal conductivity is the product of the thermal diffusivity, the density, and the heat capacity (1.20 J/g-K , Section 2.2.3) at 25°C,

$$k(\text{J/m-K-s}) \approx \alpha \rho C_p \approx 0.13 \quad (2-44)$$

This value is a bit lower than the value for polystyrene, 0.142 J/m-K-s, suggesting that the thermal insulating properties of PLA might be as good or slightly better than that of PS.

A plot of $k(T)/k(T_g)$ versus T/T_g is approximately the same for amorphous polymers.² From this generalized curve and the known heat capacity at 25°C the PLA thermal conductivity as a function of temperature is estimated in Table 2-21.

Table 2-21 Estimated Amorphous Polylactide Thermal Conductivity

T/T_g (K/K)	$k(T)/k(T_g)$ (J/m-K-s)	T (°C)	$k(T)$ (J/m-K-s)
0.2	0.72	-207	0.094
0.4	0.83	-141	0.109
0.6	0.92	-74	0.121
0.8	0.97	-8	0.127
1.0	1.00	58	0.131
1.2	0.96	124	0.126
1.4	0.92	190	0.121
1.6	0.88	257	0.115

The data is graphically shown in Figure 2-52. The estimated thermal conductivity passes through a maximum at T_g , 0.13 J/m-K-s, and then decreases by 8×10^{-5} (J/m-K-s)/°C up to the onset of thermal decomposition, 215-285°C.

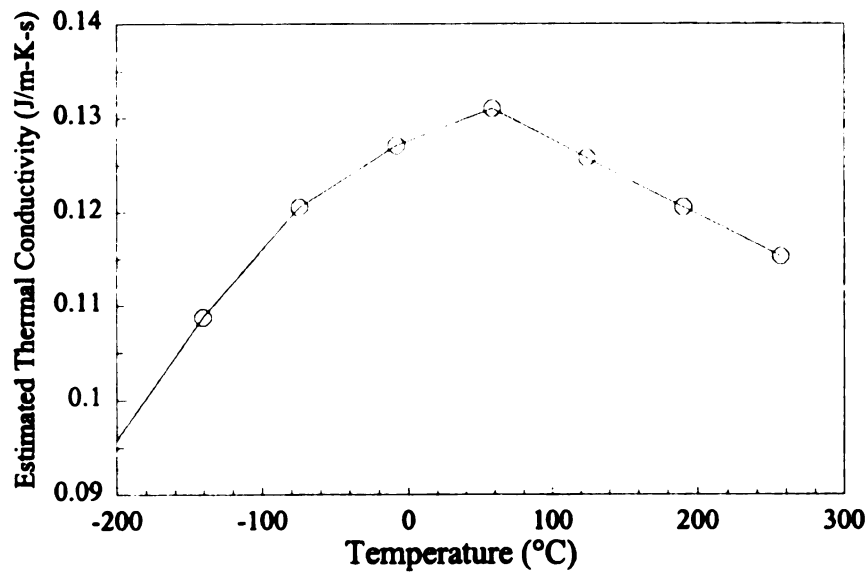


Figure 2-52. Estimated thermal conductivity of amorphous polylactide.

The thermal conductivity of crystalline PLA will be higher than that of amorphous PLA. Using a relationship developed by Eiermann, shown graphically in Van Krevelen², we estimate the room temperature thermal conductivity of semi-crystalline polylactide. The semi-crystalline thermal conductivity is based on the k value of amorphous and purely crystalline polylactides. The thermal conductivity for purely crystalline polylactide can be estimated from another Eiermann relationship²

$$k_c(\text{J/m-K-s}) = k_a \left(1 + 5.8 \left(\frac{\rho_c}{\rho_a} - 1 \right) \right) = 0.27 \quad (2-45)$$

where the density ratio was calculated to be 1.18 in Section 2.3.2. Using this result and Eiermann's graphical relationship between thermal conductivity and the degree of crystallization, the thermal conductivity for partially crystalline polylactide is estimated

in Table 2-22. These results are only rough estimates and depend on the accuracy of the amorphous polylactide thermal conductivity estimation.

Table 2-22 Estimated Thermal Conductivity of Semi-Crystalline Polylactide at 25°C

Degree of Crystallinity	$(k-k_a)/(k_c-k_a)$	$k(25^\circ\text{C})$ (J/m-K-s)
0	0	0.13
0.25	0.18	0.16
0.5	0.42	0.19

Conclusions

1. Based on a group contribution method, the thermal conductivity for amorphous polylactide at 25°C is estimated to be 0.13 J/m-K-s. The dependence of thermal conductivity on temperature is estimated in Figure 2-52. These estimates are intended for approximate engineering calculations.
2. The thermal conductivity for semi-crystalline polylactide is estimated in Table 2-22. These values should also be considered as estimates.

2.7 Phase Equilibrium

2.7.1 Lactide-Polylactide Vapor-Liquid Activity Coefficient Model

The modeling of lactide vapor-liquid equilibrium in polylactide is important for engineering calculations. Most important is the determination of the thermodynamic pressure requirement to achieve a desired lactide concentration in polylactide during melt

devolatilization at a given temperature (Section 4.3). Competing with lactide vapor-liquid phase equilibrium is lactide-poly lactide reversible polymerization equilibrium. The lactide equilibrium concentration in polylactide increases with temperature (e.g., 2% at 160°C, 5% at 220°C; Section 3.2).

Together, vapor-liquid lactide phase equilibrium and lactide-poly lactide reaction equilibrium define the thermodynamics of the lactide-poly lactide system at a given temperature. However, the rates at which vapor-liquid equilibrium and reaction equilibrium are established are quite different. At a given temperature, the observed lactide concentration in the PLA melt depends on the balance of liquid-to-vapor mass transfer and the rate of depropagation to maintain chemical equilibrium. The liquid-to-vapor mass transfer is enhanced by a low activity of lactide in the vapor phase (e.g., low pressure), a high temperature, and high surface area-to-volume ratio. The rate of approach toward lactide-poly lactide reaction equilibrium is enhanced by high catalyst level and temperature. For example, melt devolatilization is required to lower the lactide level in polylactide below its equilibrium conversion to obtain good processing characteristics and polymer properties. In melt devolatilization a very high surface area-to-volume ratio is used at high temperature and low pressure to remove most of the lactide. The polymer melt is then quickly quenched before depolymerization can increase the lactide concentration back toward its equilibrium value. During melt devolatilization chemical equilibrium is not obtained but a transient vapor-liquid lactide equilibrium is approached.

The vapor pressure of lactide above a lactide-poly lactide melt depends on the concentration of lactide in the polymer and the temperature of the system. At vapor-liquid phase equilibrium the fugacity of lactide in the vapor and liquid phases are equal:

$$f_1^{vap}(T, P) = f_1^{liq}(T, P) \quad (2-46)$$

The vapor phase lactide fugacity is approximately equivalent to its partial pressure, P_1 , and the liquid phase lactide fugacity is approximately equal to the product of its activity and its pure component saturated vapor pressure.⁷⁹

$$P_1 = a_1 P_1^{sat} \quad (2-47)$$

The activity is calculated from the ratio of lactide partial pressure to its pure component saturated vapor pressure (determined in Section 2.8),

$$a_1 = \frac{P_1}{\exp(21.0 - 7600/T(K))} \quad (2-48)$$

The Flory-Huggins activity model is commonly used for polymers and relates the activity of the volatile component to its concentration in the polymer and the polymers molecular weight. For polymers having a degree of polymerization greater than 100 the molecular weight term becomes insignificant and the activity model can be expressed as⁸⁰

$$\ln a_1 = \ln \phi_1 + (1 - \phi_1) + \chi(1 - \phi_1)^2 \quad (2-49)$$

where ϕ_1 , a_1 , and χ are the lactide liquid phase volume fraction (equivalent to mass fraction; equal densities), lactide activity, and Flory interaction parameter, respectively. The Flory-Huggins theory criterion for complete liquid phase miscibility over the entire composition range is $\chi < 0.5$. Although we were unable to find lactide-PLA χ data in the literature, we have observed complete lactide-amorphous polylactide miscibility during polymerizations between 130-220°C, and during lactide-PLA mixture viscosity expts. Therefore, we are certain that $\chi < 0.5$ for the lactide-PLA system. In the following calculations we will ignore any concentration dependence of χ (valid assumption for good solvents⁸⁰).

Predictions of lactide vapor pressure as a function of temperature and lactide melt concentration using equation (2-49) with $\chi = 0.3$ are shown graphically in Figure 2-53. At 220°C the lactide partial pressure requirement to achieve 1% lactide in the melt at phase equilibrium is 10 mmHg. The actual choice of χ matters little for such calculations at $\chi < 0.5$. For χ values of 0.1 and 0.5 the resulting pressure requirements at 220°C and 1% lactide are 8 and 12 mmHg, respectively. This degree of sensitivity is acceptable for preliminary engineering calculations. Equations (2-48) and (2-49) may be used for estimations of lactide vapor pressure over the entire lactide concentration range at melt temperatures.

For nonpolar polymer systems the Flory interaction parameter can be predicted from the solubility parameters of the solvent and polymer. These can be calculated by additive group contributions based on chemical structure. Thus a predictive activity model can be developed in the absence of experimental data. However, this relationship

between χ and the solubility parameters is not valid for polar systems. This is because of its basis on regular solution theory where the geometric mean assumption of solubility parameters,⁸⁰ and the assumption of zero excess molar free volume and entropy⁷⁹ are not applicable to polar systems. In addition, this relationship is not valid in systems where solvent reacts with polymer.^{80,81}

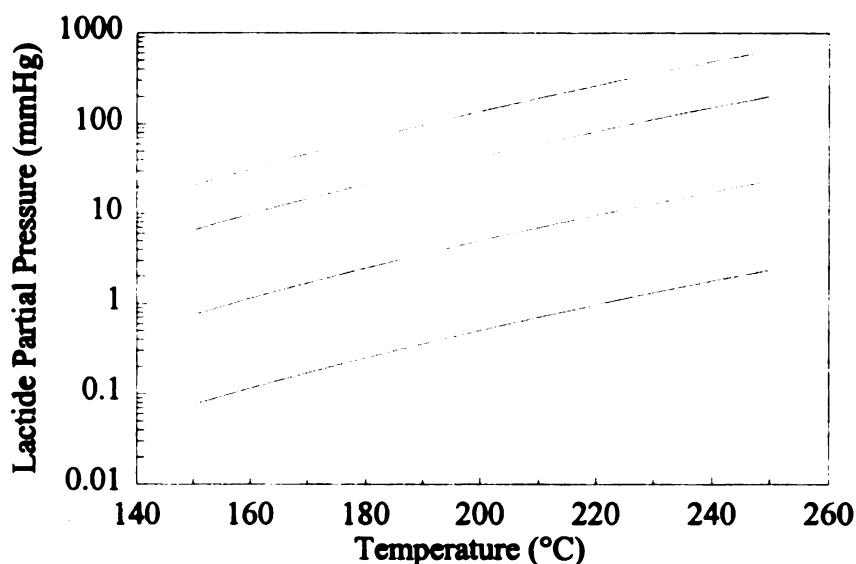


Figure 2-53. Estimation of lactide partial pressure in a lactide-poly lactide liquid mixture for $\phi_1 = 1$ (top curve), 0.1, 0.01, and 0.001.

Predictions of lactide-poly lactide vapor-liquid equilibrium, based on equations (2-48) and (2-49) and $\chi = 0.3$, appear quite reasonable at low pressures based on devolatilization experimental data presented in Section 4.3. However, this relationship should only be used for approximate engineering calculations. In general, the lactide-poly lactide system is quite complicated – polar, moderately hydrogen bonding, chemical reaction equilibria – and the development of a highly accurate activity model would require a considerable amount of $\chi(\phi_1, T)$ data at very low catalyst concentration.

2.7.2 Solubility Parameter

Blends of PLA with other polymers and plasticizers are a relatively simple way to change the mechanical properties of the material. The development time has been estimated at 7-10 years for a new polymer and 2-4 years for a new polymer blend.⁸² Although there is no fool-proof method to determine miscibility a priori, the similarity between the components' solubility parameters and hydrogen bonding characteristics gives us insight into the potential for liquid-liquid miscibility. For this purpose, the comparison of solubility parameters can be used as a screening test to eliminate the otherwise attractive blend candidates that would make immiscible PLA blends. This is not to say, however, that immiscible systems are strictly undesirable.

The thermodynamic criterion for miscibility is that the change in the Gibbs free energy is negative on mixing; namely, $\Delta G_m = \Delta H_m - T\Delta S_m < 0$. The entropy component, ΔS_m , is related to the inverse of molecular weight (Flory-Huggins),^{81,82}

$$\Delta S_m = -R\bar{V}\left[\frac{\rho_1}{M_{n,1}}\phi_1\ln\phi_1 + \frac{\rho_2}{M_{n,2}}\phi_2\ln\phi_2\right],$$

and the entropy contribution to ΔG_m is minimal for the mixing of two high molecular weight polymers. Therefore, the enthalpy of mixing must be close to zero or be negative in order for miscibility to occur: $\Delta H_m \leq 0$. The Hildebrand and Scott (1959) and Scatchard (1949) relationship between the heat of mixing and the square of the difference in solubility parameters, $\Delta H_m = V\phi_1\phi_2(\delta_1 - \delta_2)^2$, always predicts $\Delta H_m > 0$. However, this relationship is only valid for nonpolar, nonassociating systems,^{80,82} and is less useful for predicting PLA miscibility with other polymers. Nonetheless, the comparison of solubility parameters and hydrogen bonding

strength can be an important step in selecting polymers that might be miscible with PLA at certain concentrations and temperatures.

Polymer-polymer systems are typically incompatible and the few systems that are miscible have specific interactions between the polymers, such as hydrogen bonding and acid-base equilibria, which make the heat of mixing exothermic. For example, poly(ϵ -caprolactone), a biodegradable flexible ring-opening polylactone: $((\text{CH}_2)_5\text{-COO})_x$, has been found to be miscible with several other polymers including PVC, nitrocellulose, SAN, and ABS (although not with high M_w PLA). A reason for its miscibility is that the methylene subunits are not very compatible with the ester subunit in the same repeat unit, and the addition of another polymer that is more compatible with the methylene subunits can "dilute" the unfavorable interactions providing for an exothermic heat of mixing.

Using seven different solvents with known solubility parameters, Siemann⁸³ determined the Hildebrand solubility parameter of poly(L-co-D-lactide) to be 20.5-21.1 (MPa)^{0.5} by means of both density and limiting viscosity methods.

Chloroform (poor hydrogen bonding) and dioxane (moderate hydrogen bonding) are two of the better solvents for polylactide and have solubility parameters of 19.0 and 20.3 (MPa)^{0.5}, respectively.⁸¹ These values are in accord with the PLA solubility parameter as measured by Siemann. In addition, it is useful to see how the measured solubility parameters compare with those calculated by group contribution methods. In Table 2-23 we calculate the solubility parameters of polylactide by the methods of Small, Van Krevelen, and Hoy.⁸¹ We also estimate the solubility parameter of lactide based on

an additional six-membered ring contribution. All calculations are based on a density of 1.25 g/cm³ (Section 2.3).

Table 2-23 Solubility Parameter Calculations by Group Contribution Methods

Cohesive Energy Density Contributions F [(MPa) ^{0.5} cm ³ mol ⁻¹]			
Group	Small	Van Krevelen	Hoy
-CH(CH ₃)-	495	560	479
-COO-	634	511	688
ring - 6	204		-48
Solubility Parameter Calculations δ (MPa ^{0.5}) = F / 115(cm ³ /mol)			
polylactide	19.6	18.6	20.3
lactide	21.4		19.9

Although slightly lower, the calculated solubility parameters in Table 2-23 all lie within 9% of the values determined by Siemann. The Small method predicts a positive δ contribution for lactide's six-membered ring whereas the method of Hoy predicts a negative contribution. In either case the differences are not large.

In summary, the polylactide solubility parameter determination by Siemann is consistent with expected values and may be used to select other polymers having similar solubility parameters and hydrogen bonding characteristics as miscible blend candidates.

2.8 Monomer Properties

The properties of the lactide stereoisomers are not generally found in chemistry and engineering handbooks. However, limited data on lactide properties can be found scattered throughout the patent literature, biomedical journals, and at various universities and corporations involved in polylactide research. We have investigated the properties of lactides and summarize the results of our experimental findings, calculations, and literature review in the discussions that follow.

The stereochemistry of the lactide isomers were reviewed in Section 1.2.4. There exists three unique lactides having a molecular weight of 144.13 g/mol: L-lactide (S,S), D-lactide (R,R), and *meso*-lactide (RS = SR; achiral). Except for the direction of polarized light rotation, the physical properties of the L- and D-lactide enantiomers are identical. DL-Lactide exists as a cocrystalline racemate compound and has crystalline properties which are different than L-lactide, e.g., melting point. On melting, the D- and L-lactide racemic mixture vapor pressure and density properties are identical to that of L-lactide. Based on similarity of chemical structure (e.g., no change in volume or enthalpy on mixing) other liquid and gas racemic lactide properties are likely similar to L-lactide as well. All three isomers have an estimated dipole moment of about 0.75 debyes based on 3-D atomic partial point charges of low energy conformations (Molecular Modeling Pro™ 1.4 software). Higher energy conformations have significantly higher dipole moments (e.g., 1-2 debyes). L- and D-Lactide exhibit a strong rotation of polarized light. Jungfleisch and Godchot⁸⁴ report the sodium light specific rotation of L-lactide in benzene to be -298° at 18°C. This is in agreement with product literature by PURAC which report 25°C

specific rotation values in benzene of -294° (max) and $+290^{\circ}$ (min) for L- and D-lactide, respectively.

Density

The liquid and solid lactide densities were determined in Section 2.3. The liquid densities of the lactide isomers were found to be the same and are accurately described as a function of temperature by the following equation

$$\rho(\text{g/cm}^3) = \frac{1.1452}{1 + 0.00074(T(^{\circ}\text{C}) - 150)} \quad (2-16)$$

The solid displacement densities at 24°C were determined to be 1.32-1.38 g/cm^3 for L- and *meso*-lactide. This corresponds to an average lactide molar volume of 107 cm^3/mol .

Melting Point and Heat of Melting

The melting temperature and heat of melting for L-, *meso*-, and DL-lactide were determined by differential scanning calorimetry, DSC.

Materials. L- and DL-Lactide were purchased from CCA Biochem. B.V., Holland. *Meso*-lactide was obtained from Henley. Two lactide mixtures were obtained from Cargill Inc.: 12% *meso*- 88% L-lactide mixture (less than 0.5% D-lactide); and 95% *meso*- 5% L-lactide.

Experimental. A DuPont 910 DSC with DuPont 9900 General V2.2A software was used (Composite Materials and Structures Center, Michigan State University). The

heating rate was 10°C/min. The DSC was purged with 50 ml/min nitrogen passed through an oxygen and water adsorption bed. The melting temperature is reported as the onset of melting determined by the intersection of the linear portion of the melting endotherm with the heat flow baseline prior to melting. The peak melting temperature refers to the temperature at which the maximum in the melting endotherm occurs. The heat of melting is determined by the integration of the melting endotherm.

Figure 2-54 presents the DSC thermograms. The melting temperatures of *meso*-, L-, and DL-lactide were 53, 96, and 125°C, respectively. The peak melting temperatures were 3°C higher than the onset of melting for all three samples. The heats of melting for the *meso*-, L-, and DL-lactide samples were 118, 146, and 185 J/g, respectively. However, observed melting endotherm values are sensitive to prior crystallization conditions.

The measured melting temperatures for L- and DL-lactide agree well with literature values.⁸⁴⁻⁸⁶ The measured melting temperature for *meso*-lactide is in accord with the value of 53°C reported in a Boehringer Ingelheim patent⁸⁷ for a lactide consisting of 99.8% *meso*-lactide and 0.2% DL-lactide, determined by gas chromatography. The reported heat of melting for the Boehringer Ingelheim *meso*-lactide is 128 J/g.⁸⁷

Figure 2-55 presents the DSC thermograms for the two lactide mixtures: 12% *meso*- 88% L-lactide mixture, and 95% *meso*- 5% L-lactide. Both *meso*- and L-lactide melting temperatures are apparent in the thermograms. This indicates the existence of at least two solid phases below the *meso*- melting temperature, and a two phase (liquid *meso*-lactide and solid L-lactide) region between the *meso* and L-lactide melting temperatures. The *meso*-lactide melting point is depressed by the presence of L-lactide.

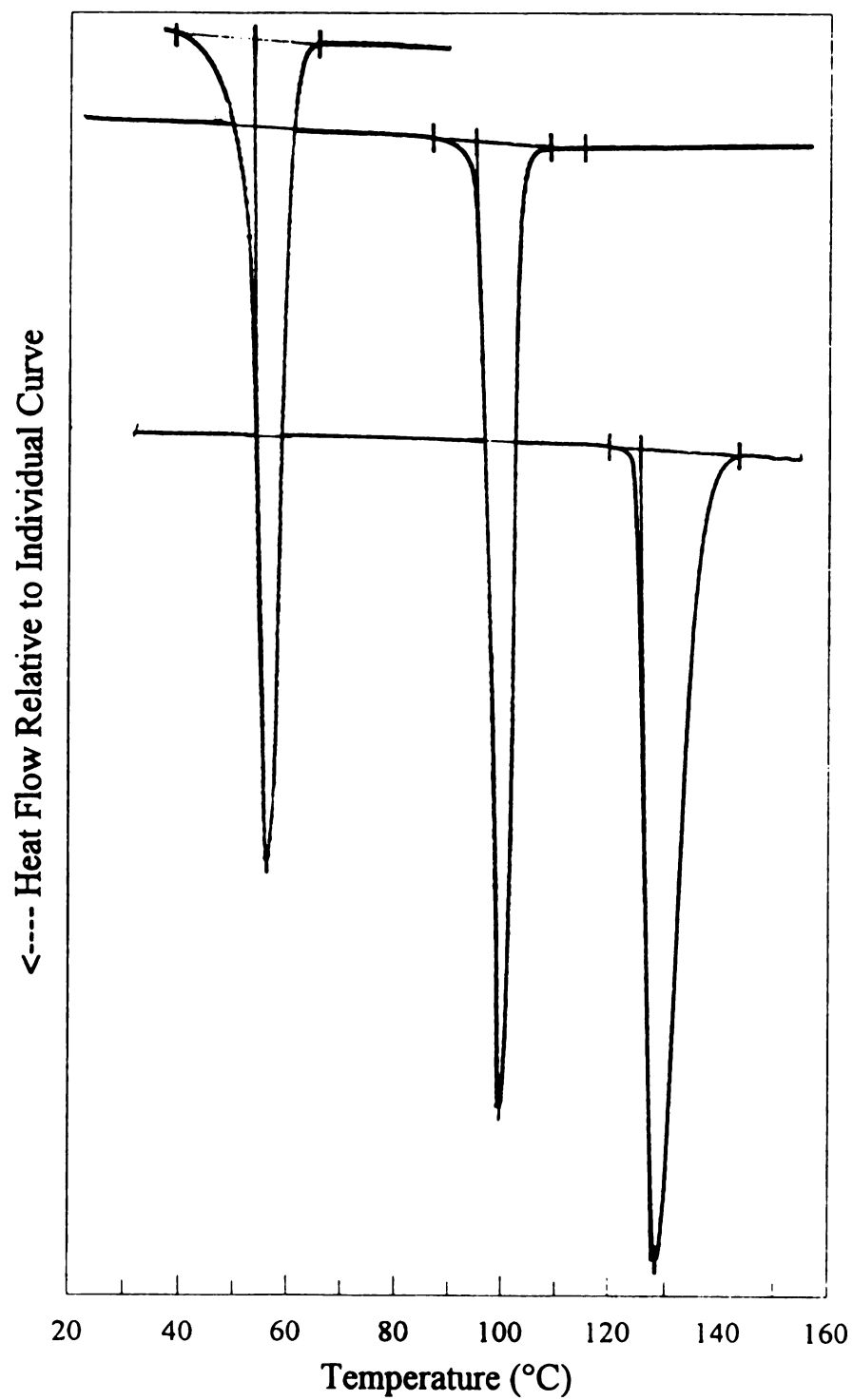


Figure 2-54. Melting temperature and heat of melting for *meso*-lactide (53°C, 118 J/g); L-lactide (96°C, 146 J/g); and D,L-lactide (125°C, 185 J/g).

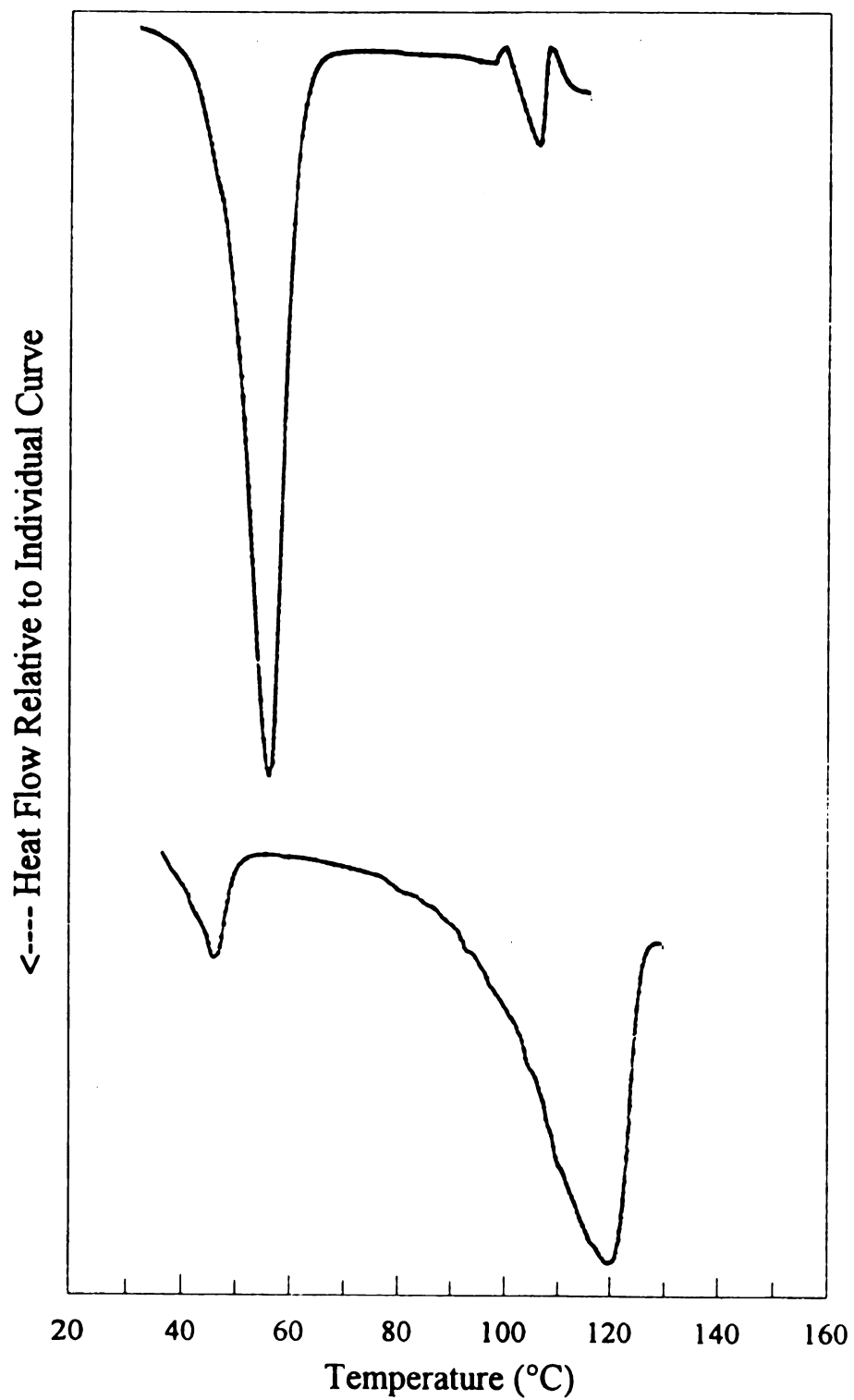


Figure 2-55. DSC thermograms for two lactide mixtures: 95% *meso*- 5% L-lactide (top), and 12% *meso*- 88% L-lactide (bottom).

The 12% *meso*- sample had a melting temperature of 42.3°C, and the 95% *meso*- sample had an onset of melting of 47.4°C. Their peak melting temperatures were 46.7 and 56.0°C, respectively. The onset of L-lactide melting for both samples was 100°C. However, the 12% *meso*- sample had a broader melting endotherm with a peak melting temperature of 118°C, compared to a temperature of 105°C for the 95% *meso*-lactide.

The crystalline solid phase diagram for the various lactide isomers is interesting. The fact that D,L-lactide has a melting point that is higher than the pure enantiomers indicates that it is a racemate compound and has at least two eutectics: each at equal distances from the 50% D-lactide composition in a temperature versus D-lactide plot. The D- and L-lactide eutectic points were determined by Kleine and Kleine:⁸⁸ 20% and 80% D-lactide with melting points of 94°C. Likewise, the observation that the addition of *meso*- to L-lactide broadens the L-lactide melting endotherm suggests that the two lactides may not simply be a mixture of two crystalline components. Furthermore, the inability to purify *meso*-lactide beyond a certain D,L-lactide composition by solvent crystallization suggests a eutectic composition between 5-20% D,L-lactide. The Boehringer Ingelheim patent⁸⁷ incorporates the use of distillation to obtain very pure *meso*-lactide (from an initial racemic lactic acid source) having a melting temperature of 53°C. *Meso*-lactide purification by crystallization (from an initial racemic lactic acid source; approximately 50% *meso*-, 25% D-, and 25% L-lactide) results in a melting temperature of 41-45°C, suggesting that significant amounts of DL-lactide remain. We also have investigated *meso*-lactide purification by distillation.⁸⁹ In agreement with the results of Boehringer Ingelheim we found that distillation (high reflux ratio) yields very pure *meso*-lactide.

The solid phase diagram for lactide isomer mixtures appears to be complex and is not further investigated here.

Vapor Pressure

Using vapor pressure data found in a Boehringer Ingelheim patent⁸⁷ and from data made available by Cargill we have developed vapor pressure models for *meso*- and L-lactide (or D-lactide). The vapor pressure for DL-lactide is found to be identical to that of L-lactide.

Figure 2-56 presents vapor pressure versus temperature data for *meso*-lactide. The *meso*-lactide data from Boehringer Ingelheim and Cargill are similar. Both data sets were included in the model determination. The multiple parameter Reidel equation was initially regressed and insignificant parameters were removed resulting in a two parameter *meso*-lactide vapor pressure model. This two parameter model is equivalent to the Clausius-Clapeyron equation where the enthalpy of vaporization is assumed to be independent of temperature. The model is depicted in Figure 2-56 as a solid line and is described by the following equation:

$$\ln P_{\text{meso}}(\text{mmHg}) = 19.2 - \frac{6700}{T(\text{K})} \quad (2-50)$$

Figure 2-57 presents the L- and DL-lactide vapor pressure data. The L- and DL-lactide data were not statistically different. A two parameter L- and DL-lactide vapor

pressure model is presented in equation (2-51); again, only two parameters could be justified.

$$\ln P_L(\text{mmHg}) = 21.0 - \frac{7600}{T(\text{K})} \quad (2-51)$$

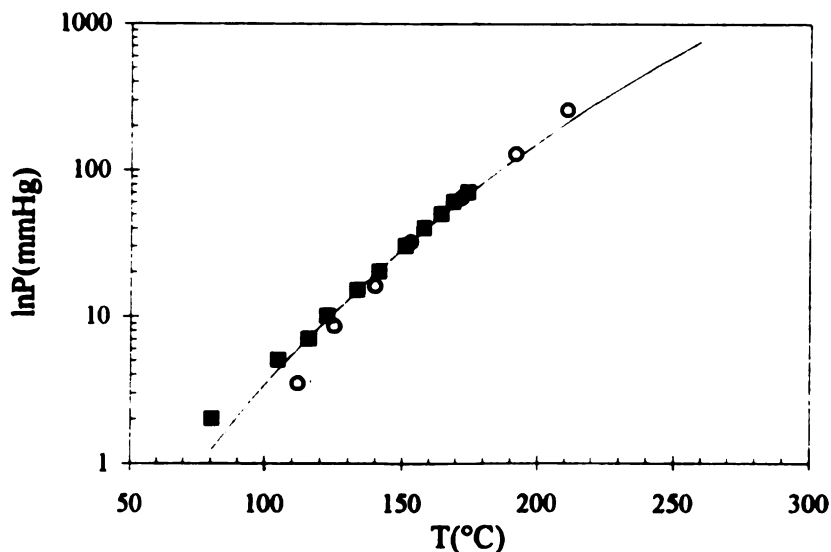


Figure 2-56. Vapor pressure of *meso*-lactide: data from Cargill (O), Boehringer Ingelheim (■). Equation (2-50) is represented by the solid line.

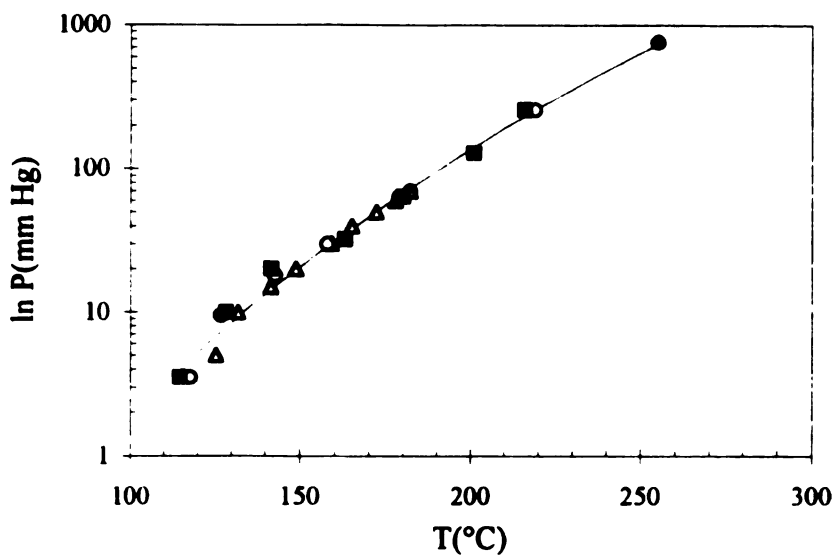


Figure 2-57. Vapor pressure of L- and D,L-lactide: L-lactide data from Cargill (O); D,L-lactide data from Cargill (■), Boehringer Ingelheim (Δ), CRC Chemistry and Physics Handbook (●). Equation (2-51) is represented by the solid line.

The relative volatility of *meso*- to L-lactide, P_{meso}/P_L , is important for the separation of *meso*- and L-lactide by distillation. Figure 2-58 presents the relative volatility as a function of temperature based on equations (2-50) and (2-51). It is apparent that the separation of *meso*- from L-lactide by distillation is more favorable at lower temperatures, (i.e., reduced distillation pressure).

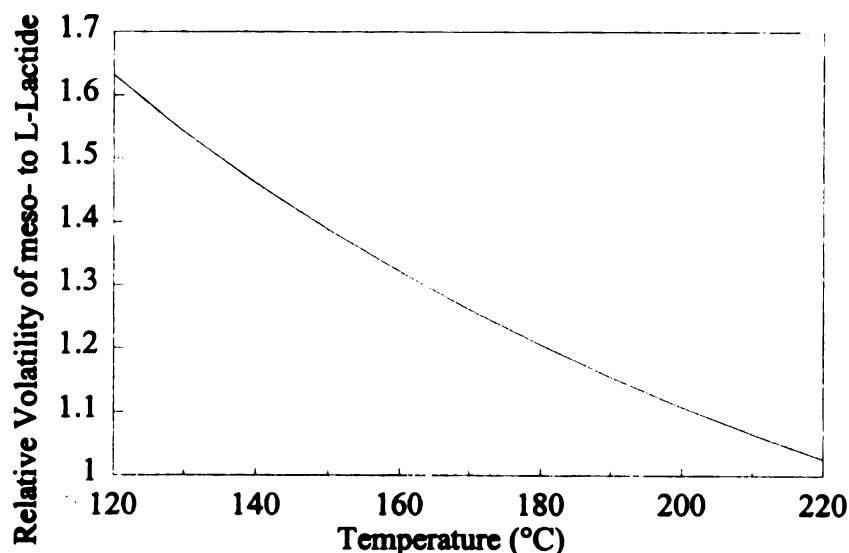


Figure 2-58. Relative volatility of *meso*- to L-lactide as a function of temperature.

Boiling Point, Heat of Vaporization, and Solubility Parameter

The normal boiling point of *meso*- and L-lactide is determined by setting the pressure term in equations (2-50) and (2-51) equal to 760 mmHg and solving for the temperature. Based on these equations the normal boiling points for all lactides are among 256-260°C. A boiling point of 255°C at 757 mmHg is reported for DL-lactide in the CRC Chemistry and Physics Handbook. The *meso*-lactide boiling temperature value of 260°C, based on the Clausius-Clapeyron regression, is from extrapolated data.

Analyzing the Cargill portion of the data in Figure (2-56) yields a normal boiling point of 245°C.

The heats of vaporization are determined from equations (2-50) and (2-51). The constant above the temperature term is equivalent to the ratio of the heat of vaporization and the ideal gas constant. The heats of vaporization for *meso*- and L-lactide are determined to be 56 and 63 kJ/mol, respectively. Using only the Cargill data gives a *meso*-lactide heat of vaporization of 66 kJ/mol.

The solubility parameter of lactide is related to its heat of vaporization⁸¹ and was estimated in Section 2.7.2 to be 19.9-21.4 MPa^{0.5}.

Enthalpy and Entropy of Polymerization

The enthalpy and entropy of L-lactide polymerization is determined in Section 3.2 to be -23.3 ± 1.5 kJ/mol and -22.0 ± 3.2 J/mol-K.

Viscosity

A relationship for lactide viscosity as a function of temperature was determined from raw data provided by Cargill: $\mu(\text{cp}) = 2.71, 2.23, 1.88$ at $T(^{\circ}\text{C}) = 109.7, 120.0, 130.2$, respectively. The following two parameter model⁹⁰ is used to regress viscosity as a function of temperature

$$\ln \mu(\text{cp}) = A + \frac{B}{T(\text{K}) + 17.71 - 0.19T_b} \quad (2-52)$$

where T_b is the normal boiling point, 529K. A plot of $\ln(\mu)$ versus $1/(T(K)-83)$ is linear and the following equation can be used to calculate the viscosity of lactide as a function of temperature:

$$\mu(\text{cp}) = \exp\left(-4.718 + \frac{1710}{T(K) - 83}\right) \quad (2-53)$$

2.9 References and Notes

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**INTRODUCTION TO PROPERTIES, ENGINEERING, AND PROSPECTS OF
POLYLACTIDE POLYMERS**

VOLUME II

By

David R. Witzke

A DISSERTATION

**Submitted to
Michigan State University
in partial fulfillment of the requirements
for degree of**

DOCTOR OF PHILOSOPHY

Department of Chemical Engineering

1997

Chapter 3 Reaction Properties of Polylactides

3.1 Introduction

In this chapter we investigate the bulk reaction properties of polylactides. There are six types of reactions that we consider: (1) reversible polymerization using stannous ethylhexanoate, (2) hydroxyl chain initiation, (3) transesterification among polymer chains, (4) melt hydrolysis, (5) non-hydrolytic chain cleavage, and (6) racemization.

3.2 Reversible Polymerization Kinetics and Thermodynamics

A preferred catalyst for lactide polymerization is 2-ethylhexanoic acid tin(II) salt. This catalyst is known for its fast rate of polymerization,^{1,2} low degree of racemization at high temperature,^{3,4} and acceptance by the FDA as a food additive.² The optimum catalyst level depends on the residence time of polymerization and the melt stability of the resin.

High temperatures (170-220°C) permit rapid polymerization with subsequent devolatilization and extrusion in the melt. However, at these temperatures the lactide equilibrium concentration in polymer is important and an irreversible kinetics model does not adequately describe the rate of polymerization. The devolatilization operation is critical after bulk polymerization where at least 3-5% lactide remains in the polymer. At these levels, the accumulation of lactide on resin processing equipment is a problem.

Such high lactide levels would pose further problems in food contact applications where the extraction of lactide into food is a concern. Of additional importance is the quantification of the rate of depolymerization. This is important in post-devolatilization resin processing.

Although considerable work has been done on the mechanism of lactide polymerization with various catalysts,^{2,4-19} only a few papers discuss the kinetics of lactide polymerization.^{1,9,17,19} Of these, none address the reversible aspect of the polymerization. Using various catalysts and low temperatures, Dittrich and Schulz established that the rate of lactide conversion is first order in monomer and catalyst concentration.¹⁷ Recent studies using aluminum alkoxide catalysts concur.^{9,19} Eenink studied the kinetics of L-lactide bulk polymerization with tin(II) ethylhexanoate over a narrow temperature range, 103-130°C.¹ He determined an activation energy for the propagation rate constant using an irreversible model that is first order in catalyst and monomer concentration.

We found few papers that addressed the thermodynamics of lactide polymerization. By measuring heat capacities and enthalpies of combustion, Kulagina et al. estimated the thermodynamic parameters of D,L-lactide copolymerization.²⁰ Duda and Penzek determined the thermodynamic parameters for L-lactide polymerization in dioxane, 80-133°C, by measuring monomer equilibrium concentrations.²¹ By extrapolation from solution data, they arrived at thermodynamic parameters for bulk polymerization.

In this study, kinetic experiments of L-lactide polymerization with tin(II) ethylhexanoate were performed over a wide range of temperatures (130-220°C) and

monomer-to-initiator molar ratios (1,000-80,000). Depolymerization kinetics was also determined at these conditions using bulk devolatilized polymer. A monomer equilibrium curve was established, and the thermodynamics of L-lactide polymerization were quantified. These data were used to develop a reversible kinetic model for L-lactide polymerization with tin(II) ethylhexanoate that adequately predicts the rate of polymerization and depolymerization, over temperatures and catalyst concentrations of industrial interest. The effect of crystallization on the rate and extent of L-lactide polymerization was also quantitatively determined.

Experimental Section

Monomers. L and D,L-lactide (racemate of D and L-lactide) were purchased from Boehringer Ingelheim. Monomers were dried under vacuum for 12 h at 50°C before polymerization. Gas chromatography, GC, was used to determine monomer purity. A Hewlett Packard 5890 GC was used: DB-17 capillary column (J & W), 30 m x 0.25 mm, 0.25 μ m film thickness, injector (split, 100:1) at 200°C, detector at 260°C. Temperature program: 10 min at 100°C, 10°C/min to 250°C, 3 min at 250°C. Retention times: *meso*-lactide, 13.4 min, L-lactide and D-lactide, 14.6 min. Polylactide samples, along with internal standards, were dissolved in acetonitrile and reacted with a silane-based derivatizing reagent (N-methyl-N-(*t*-butyldimethylsilyl)-trifluoroacetamide with 1% *t*-butyl-dimethylchlorosilane; Regis Chemical Company) to enable the detection of acidic components. The L-lactide was 99.67% pure, with 0.24% *meso*-lactide, 0.072% lactoyllactic acid (DP2), 0.008% lactic acid, 0.008% DP3, and < 0.005% DP4. The

D,L-lactide was 99.71% pure, with 0.23% *meso*-lactide, 0.06% DP2, < 0.005% lactic acid, and < 0.005% DP3 plus DP4.

Catalyst. 2-Ethylhexanoic acid tin(II) salt (a.k.a. tin(II) ethylhexanoate, stannous octoate), 405.11 g/mol, was purchased from Aldrich. Reported purity is 95%, with 4.6% ethylhexanoic acid, 0.3-0.5% water, and less than 0.05% *tert*-butylcatechol (stabilizer). For transfer purposes, catalyst solutions (4-13% by weight) were prepared in anhydrous toluene (Aldrich). The catalyst solutions were prepared fresh for each polymerization.

Monomer Conversion Analysis. For conversions less than 90%, lactide concentration was determined by gel permeation chromatography, GPC. A Waters apparatus equipped with a 410 RI detector, 510 pump, equipped with three Ultrastyrigel columns (in the order 10^5 , 10^4 , and 500-Å pore size), attached in series, was used. The analyses were performed at 35°C using chloroform as eluent at a flow rate of 1 ml/min.

For conversions greater than 90%, extraction of lactide into cyclohexane with subsequent gas chromatography was used to determine monomer concentration. GC is preferred at high conversion because low molecular weight degradation products become significant, in the time required to achieve high conversion, and coelute with the monomer during GPC. The polymer samples were dissolved into chloroform and further diluted with a larger volume of cyclohexane. The lactide isomers remain in solution while the polymer precipitates out and is removed by filtration. Internal standards were used with each run to verify the results. The same GC columns and temperature profile were used as with the monomer purity analysis. This GC lactide conversion method has

an experimentally determined standard deviation of 0.012% lactide. Lactide levels as low as 0.005% are quantified.

Both the GPC and GC techniques for the determination of lactide concentration in polylactide have been extensively studied and verified by Cargill in a stringent safety assessment.²²

Molecular Weight Determinations. Polylactide molecular weights were determined using the Waters GPC, calibrated against polystyrene standards. Polylactide molecular weights are reported relative to polystyrene standards and have not been corrected to an absolute basis using a universal calibration. The Mark-Houwink constants for polystyrene in chloroform at 35°C were determined to be $K = 1.67 \times 10^{-4}$ dl/g and $a = 0.692$.

Water Analysis. A 684 KF coulometer by Brinkmann was used for the determination of water concentration in monomer before polymerization.

Degree of Crystallization. The crystalline melting temperature and heat of melting of the lactide polymers were determined by differential scanning calorimetry. A Mettler DSC 30 was used with a heating rate of 10°C/min and sample sizes between 5-10 mg. The reported crystalline melting temperature corresponds to the temperature at which the maximum in the melting endotherm occurred. The heat of melting is reported as the integral of the melting endotherm. None of the tested samples crystallized during DSC operation, as noted by the absence of an exotherm in the DSC thermograms.

Density Measurements. The specific gravities of *meso*-lactide and L-lactide were measured in various hydrometers between 68-150°C and 110-172°C respectively. The

calibration of the hydrometers was verified with a Dow Corning oil having a well-known density. The density of a devolatilized amorphous polylactide polymer was estimated between 150 and 210°C using a capillary viscometer. Random, triplicate density estimations were made by measuring the weight of a displacement of polymer from a Haake Rosand RH7-2 capillary viscometer. The minor importance of the extensional flow components of polylactide allows for valid density values with this technique. The amorphous polymer was synthesized from 90% L-lactide and 10% *meso*-lactide.

Polymerization Procedure. Polymerizations were performed in the bulk in oven dried, silanized, 8 and 40 ml vials. The polymer in the 40 ml vials was used for the depolymerization experiments. To obtain a uniform catalyst concentration in the vials, a mother flask was used to melt the monomer and add and mix the catalyst before transfer to the vials. Using a mineral oil bubbler, the flask was maintained under a slight pressure of dry nitrogen, passed through a molecular sieve indicating moisture and oxygen trap. The flask was evacuated and flushed with nitrogen several times with the use of a Firestone valve prior to monomer addition in a nitrogen purged glove bag. Before catalyst addition, samples were taken for water and acidic impurity analysis. The catalyst solution was added through a septum inlet adapter by syringe. Once the catalyst was thoroughly mixed, the vessel was further pressurized with dry nitrogen and the screw top vials were filled through a 1/4" stainless steel sampling port under nitrogen flush.

The vials were then transferred to an adjacent silicon oil bath and immersed up to their caps with the use of a test tube rack to ensure isothermal polymerization.

Temperature was controlled to within $\pm 1^\circ\text{C}$ using auto-tuning PID controllers. Vials

were pulled from the reaction bath at predetermined intervals and the reactions were quenched by immersing the vials in liquid nitrogen. Molecular weight variability across a vial was determined by performing GPC on two vials sampled at four points each. The number average molecular weight deviation was among 2-6% across each vial, which is comparable to the deviation for a single sample with repeat injection. We conclude that with this polymerization procedure there is no significant vial inhomogeneity.

Polymerization samples at times less than 30 min were taken directly from the mother flask and transferred under nitrogen flush into 40 ml vials of chloroform, using 10 ml broken tip pipettes.

Depolymerization Procedure. Residual lactide was removed from the polymers by reactive devolatilization. The polymer was ground to a powder and placed in aluminum trays at 1/4 in. depth and dried under vacuum for four hours at 70°C. The samples were heated to 160°C and cooled under nitrogen purge to 125°C. The nitrogen line was closed and the samples were exposed to 0.5 mm Hg vacuum for 12 hr. Typical lactide levels after devolatilization were 0.01%. Devolatilized polymer samples were vacuum sealed with a propane torch in silanized 5 ml long-stem vacule ampules. Monomer reformation experiments were performed in insulated silicon oil baths with auto-tuning PID temperature controllers. At predetermined intervals, the vials were removed and quenched in liquid nitrogen for molecular weight and lactide concentration analyses.

3.2.1. Reversible Polymerization Model

Lactide polymerization data suggest a reversible rate form with a propagation term that is first order in monomer and catalyst. Figures 3-1 and 3-2 show representative curves of the change in number average molecular weight with time and conversion. In agreement with Eenink,¹ and Nijenhuis et al,¹⁸ initiation is fast compared to propagation. This was found at all polymerization conditions in this study. The linear dependence of molecular weight on conversion is consistent with a mechanism where initiation is fast, monomer does not react with monomer, and there is no termination of reaction centers. This type of molecular weight dependence is characteristic of living polymers and is typical with polymers from monomers possessing carboxyl electron-withdrawing groups. Although the kinetics resemble anionic chain polymerization, the polymerization of lactide with tin(II) ethylhexanoate proceeds presumably through a coordination insertion mechanism.^{2,4,6-14,19} Regardless of the mechanism, a general reversible rate form assuming fast initiation is proposed:



where lactide, M , is polymerized as lactic dimers on initiated polymer chains, R^* . With the fairly well established assumption of equal reactivity among functional groups, and assuming that the total number of reaction centers is equivalent to the initial number of catalyst molecules, $I = \sum_{n=2}^{\infty} R_n^*$, the rate of polymerization is expressed as

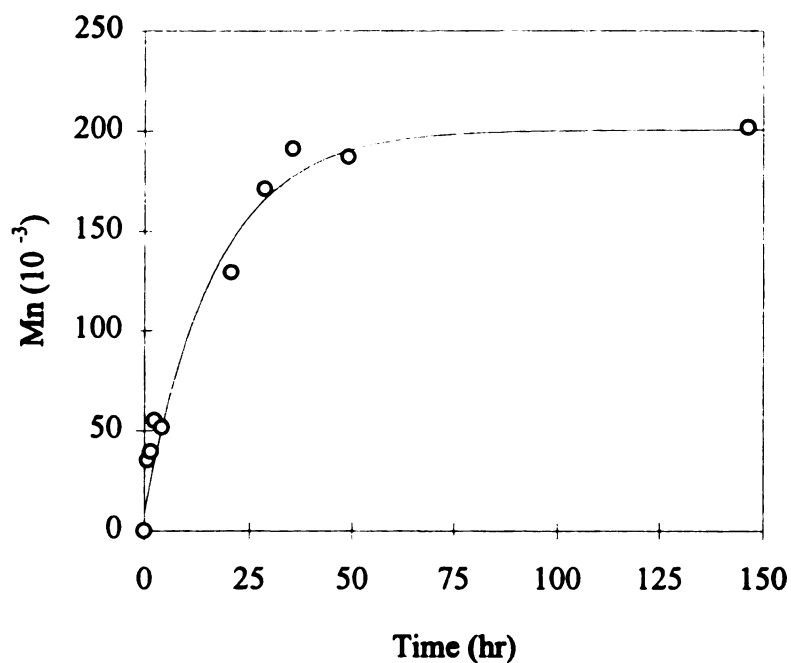


Figure 3-1. PLLA number average molecular weight versus time. Polymerization conditions: 130°C with a monomer-to-initiator ratio of 10,000.

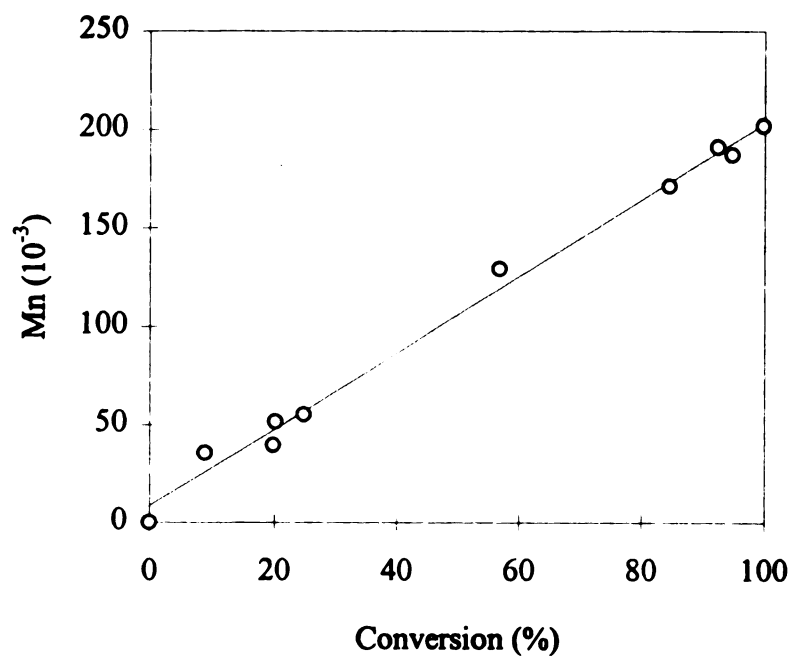


Figure 3-2. PLLA number average molecular weight versus conversion. Polymerization conditions: 130°C with a monomer-to-initiator ratio of 10,000.

$$\frac{-dM}{dt} = k_p MI - k_d I = k_p I(M - M_{eq}) \quad (3-2)$$

The monomer equilibrium concentration, M_{eq} , is conveniently obtained from equilibrium experiments and is a function of temperature:

$$M_{eq} = \frac{k_d}{k_p} = \frac{1}{K_{eq}} = \exp\left(\frac{\Delta H_{lc}}{RT} - \frac{\Delta S_{lc}}{R}\right) \quad (3-3)$$

where ΔH_{lc} , ΔS_{lc} , and R , are the heat of polymerization, entropy of polymerization, and gas constant, respectively. The subscripts in ΔH_{lc} and ΔS_{lc} refer to equilibrium between pure monomer liquid, l , and condensed amorphous polymer, c , as per the notation of Dainton and Ivin.²⁴ A complete thermodynamic description of reversible ring-opening polymerization is found elsewhere.²³⁻²⁵ The propagation rate constant, k_p , depends on temperature and is described by an Arrhenius equation, where E_a is the activation energy and A_{448} is the preexponential constant referenced to 448K,

$$k_p = A_{448} \exp\left(\frac{-E_a}{R} \left(\frac{1}{T(K)} - \frac{1}{448K}\right)\right) \quad (3-4)$$

Integrating equation (3-2) with an initial monomer concentration, M_o , gives the monomer concentration and conversion as a function of time:

$$M(t) = M_{eq} + (M_o - M_{eq})\exp(-k_p I t) \quad (3-5)$$

$$X_{mon}(t) = (1 - M_{eq}/M_o)(1 - \exp(-k_p I t)) \quad (3-6)$$

The four parameter model defined by equations (3-3), (3-4), and (3-6), simulates the extent of lactide polymerization and depolymerization as a function of time, temperature, catalyst concentration, and initial monomer concentration.

In the definition of the rate of lactide polymerization (equation 3-2) no account is taken for the volume change on reaction, i.e., $\frac{-dM}{dt} = \left(\frac{-dM}{dt} \right)_v$. Density data is presented in Figure 3-3. No statistical differences were found among the liquid densities of *meso*-lactide, L-lactide, and amorphous polylactide at polymerization temperatures. Their densities were fit to a single parameter model using a reference temperature of 150°C, with a density of 1.145 g-cm⁻³. Between 68°C and 172°C, the thermal coefficient of expansion was determined to be 7.391x10⁻⁴°C⁻¹. The melt densities, ρ , of lactide and amorphous polylactide are calculated using the following expression,

$$\rho(\text{gcm}^{-3}) = \frac{1.145}{1 + 0.0007391(T(C) - 150)} \quad (3-7)$$

The data suggest that the kinetic effect of the volume change on reaction is not significant.

In bulk ring-opening polymerizations where the change in volume on reaction can be neglected, it is appropriate to express equilibrium and non first-order rate constants in terms of weight fractions. This is consistent with the fundamental correctness of using mole fractions to describe equilibrium constants in liquids.²⁶ Furthermore, weight

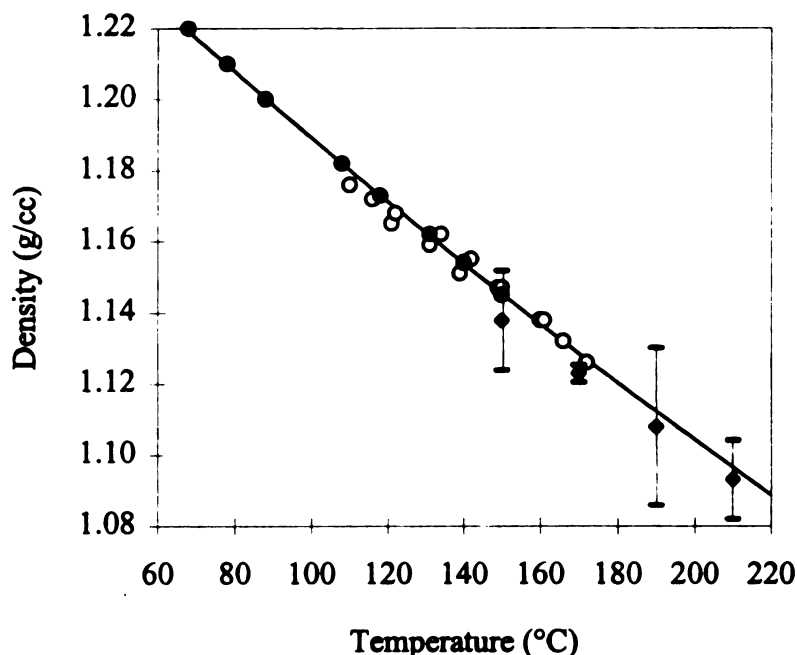


Figure 3-3. Liquid density versus temperature for *meso*-lactide (●), *L*-lactide (○), and amorphous polylactide (◆). The solid line is the density model defined by equation (3-7).

fractions are common response variables for analytical measurements of monomer concentration in polymer, such as in GPC and GC. However, equilibrium constants for bulk ring-opening polymerizations are commonly expressed with units of concentration (molarity). Implicit in such data is an assumption of density and its temperature dependence, which makes it difficult to use published equilibrium data when good density data is unavailable at polymerization temperatures. In this work, weight fractions are used instead of concentrations, time is expressed in h, and catalyst, I , is taken as initial mole percentage. Expressed in this manner, the propagation rate constant has a magnitude of at least order unity with the dimensions $\text{hr}^{-1}\text{-catalyst mol}\%^{-1}$. Equation (3-7) can be used to convert the equilibrium constant from a weight fraction to one having units of concentration.

Reversible model data analysis. Using the reversible polymerization model, nonlinear regression analyses were performed on the polymerization and depolymerization kinetic data to determine the validity of the fitted model. Next, inferences about the effects of temperature and catalyst level are made. Finally, an analysis of predicted against observed conversion was performed to determine the accuracy of the model among the temperatures and catalyst levels studied.

L-lactide polymerization data at 220°C, with molar ratios of monomer-to-initiator, M/I , varying between 10,000 and 80,000, are presented with the fitted model in Figure 3-4. Graphical analyses of the residuals confirmed that the propagation rate is first order in monomer. Figure 3-5 gives a visual assessment of the model's effectiveness at low temperature, 130°C, and higher catalyst levels, $M/I = 1,000$ to 20,000. The data are well represented by the model.

As a result of the reversibility of lactide polymerization, we can gain additional kinetic and thermodynamic information from depolymerization experiments. The regression of equation (3-6), with the appropriate value of M_o for devolatilized polymer, gives a direct solution for k_p and M_{eq} . The propagation rate constant, k_p and depropagation rate constant, k_d , are related through the equilibrium constant by the principle of microscopic reversibility (i.e., $M_{eq} = k_d/k_p$). It follows that catalysts that enable rapid polymerization should also give comparatively fast depolymerization. In this regard, it is not surprising that transesterification and hydrolysis are also catalyzed by lactide polymerization catalysts.^{2,3,7,27}

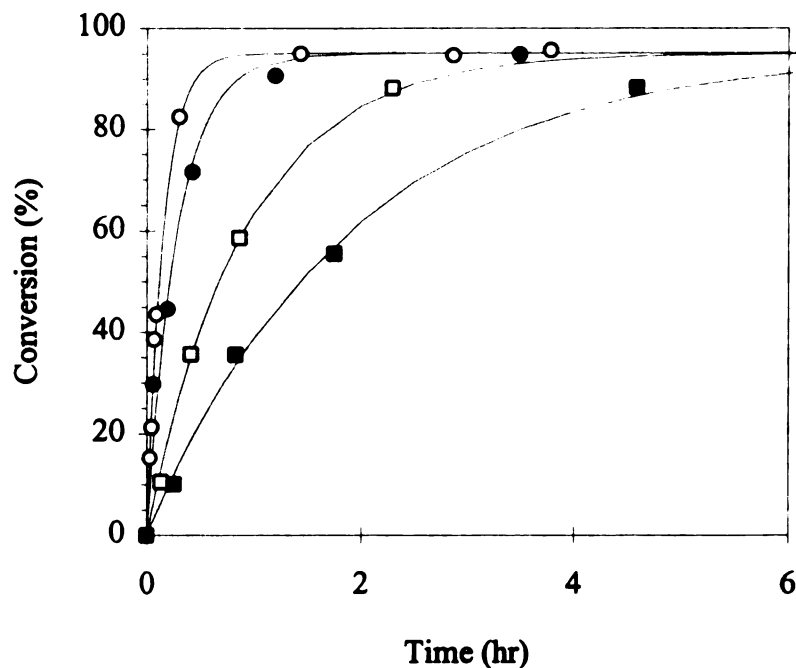


Figure 3-4. Effect of catalyst level on the kinetics of L-lactide polymerization at 220°C. The solid lines are the reversible model fits for the respective monomer-to-initiator ratios: 10,100 (○); 20,000 (●); 39,600 (□); 79,300 (■).

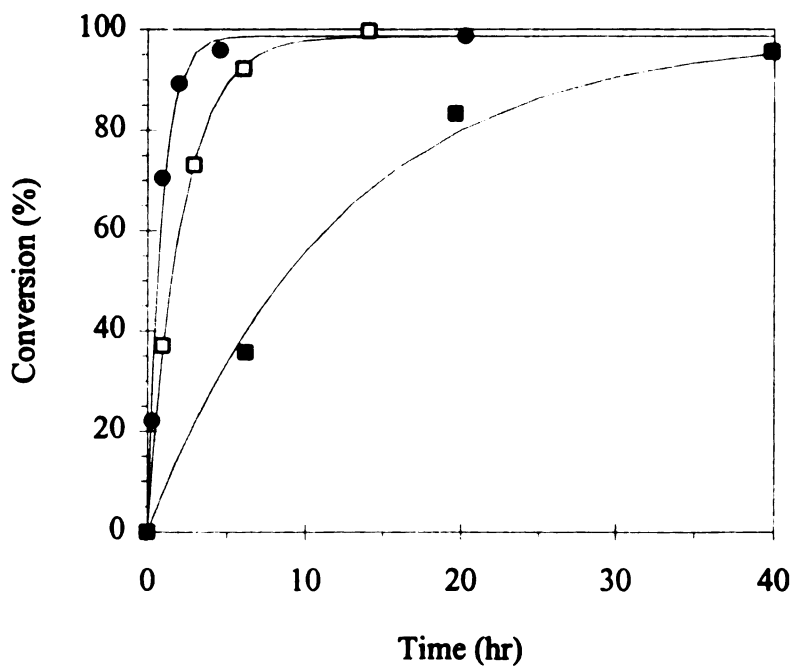


Figure 3-5. Effect of catalyst level on the kinetics of L-lactide polymerization at 130°C. The solid lines are the reversible model fits for the respective monomer-to-initiator ratios: 1,000 (●); 2,940 (□); 19,200 (■).

The results of the depolymerization experiments at 190 and 220°C are shown in Figures 3-6 and 3-7. Although scatter in the data is apparent, the data clearly show that the rate of depolymerization is dependent on catalyst concentration. As expected, there is no distinct trend between monomer equilibrium and catalyst level. Combining both polymerization and depolymerization data, Figures 3-8 and 3-9 show the approach towards chemical equilibrium. The reversible model fits the observed polymerization and depolymerization data well.

Racemization was found to be a significant side reaction during the 130-220°C polymerization and depolymerization experiments. At conversions greater than 90%, the total lactide determined by GC contained between 2-20% *meso*-lactide. The initial *meso*-lactide amount before the polymerizations was 0.24%. The *meso*-lactide concentration in unreacted monomer increased with time and temperature. Monomer equilibrium concentrations are reported as the sum of lactide isomers.

The effect of temperature on polymerization is presented in Figure 3-10. At each temperature the propagation rate constant, k_p , and monomer equilibrium concentration, M_{eq} , were determined by nonlinear regression of equation (3-6). Likewise, k_p and M_{eq} values were determined for the depolymerization experiments. Direct nonlinear regression is preferred over linear regression because of the observed homogeneity of error in conversion versus time. A linear transformation of the conversion expression (equation 3-6) gives biased estimators upon regression, and an inferior fit is observed. The data from the polymerization and depolymerization experiments yielded consistent

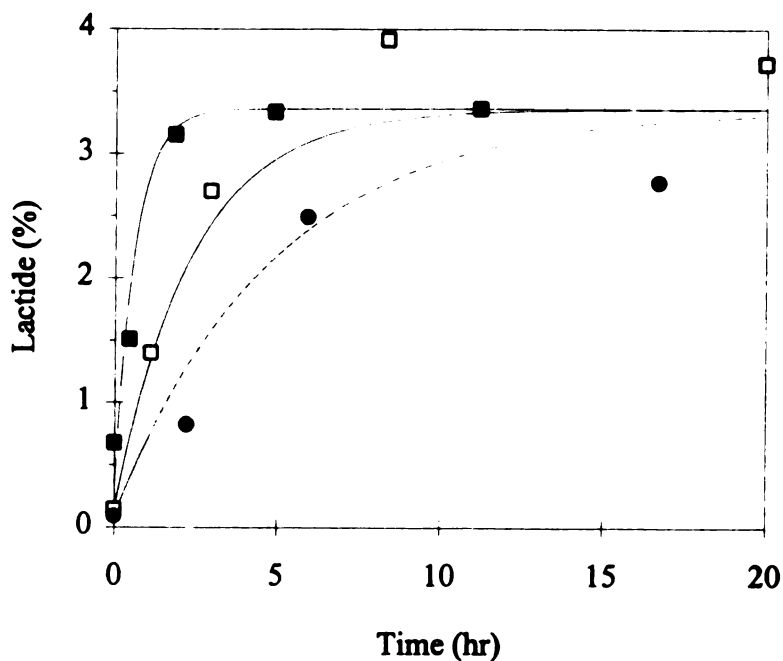


Figure 3-6. Effect of catalyst level on depolymerization of PLLA at 190°C. The lines are the reversible model for the respective monomer-to-initiator ratios: (— - —) for 10,300 (■); (—) for 39,200 (□); (-----) for 80,600 (●).

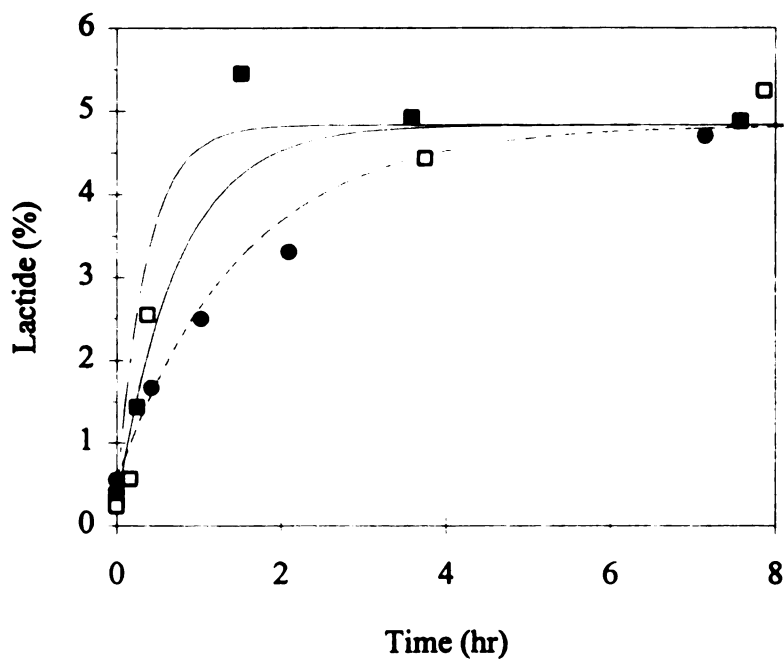


Figure 3-7. Effect of catalyst level on depolymerization of PLLA at 220°C. The lines are the reversible model for the respective monomer-to-initiator ratios: (— - —) for 19,200 (■); (—) for 39,200 (□); (-----) for 80,600 (●).

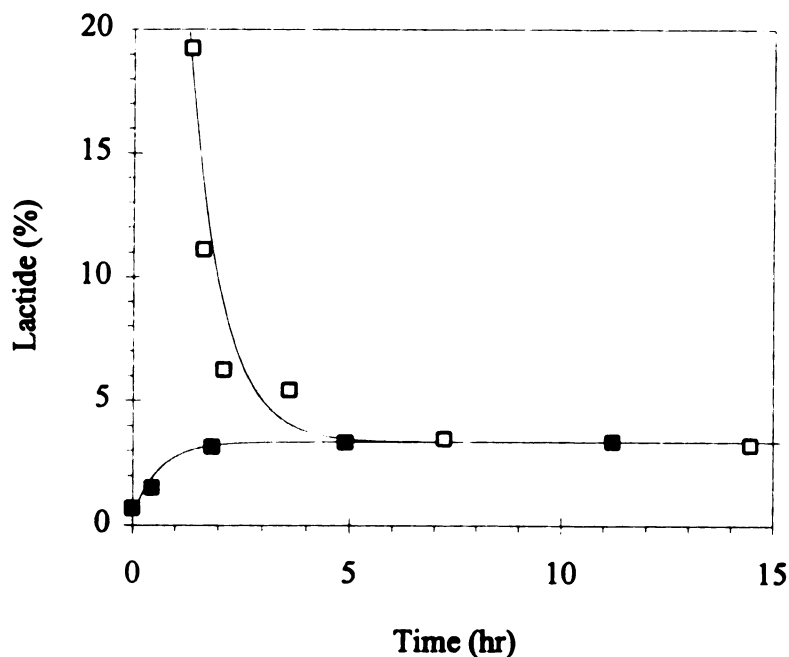


Figure 3-8. Approach toward chemical equilibrium at 190°C. The solid line is the reversible model for the superimposed polymerization ((□): $M_o = 1$, $M/I = 10,000$) and depolymerization ((■): $M_o = 0.0068$, $M/I = 10,300$) data.

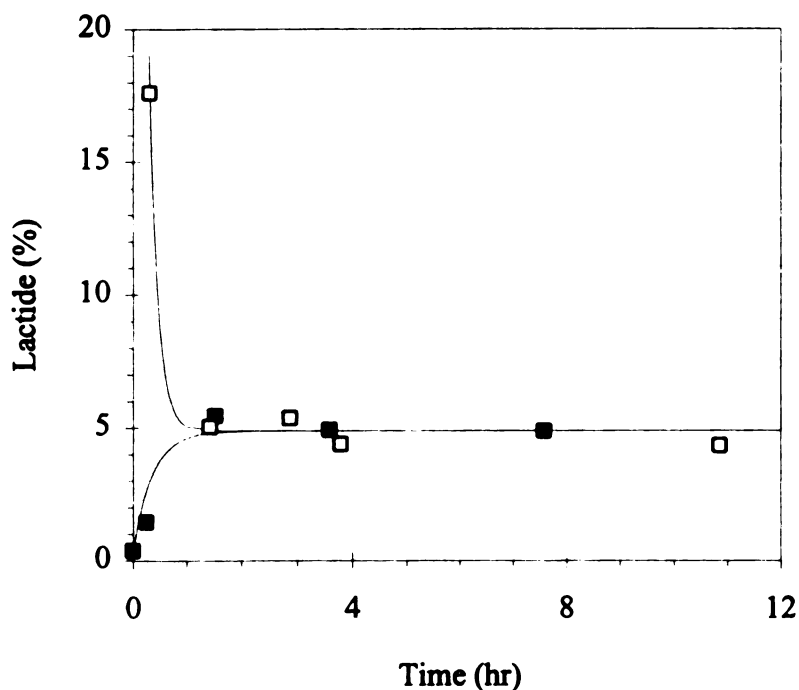


Figure 3-9. Approach toward chemical equilibrium at 220°C. The solid line is the reversible model for the superimposed polymerization ((□): $M_o = 1$, $M/I = 20,000$) and depolymerization ((■): $M_o = 0.0038$, $M/I = 19,200$) data.

rate constant and equilibrium concentration estimates. However, the most precise estimates of k_p were obtained from polymerization data and the most precise estimates of M_{eq} were obtained from depolymerization data. This is because more data were taken in the kinetically controlled portion of the curve for the polymerizations, while the depolymerization experiments tended to have more points in the equilibrium sensitive portion of the curve.

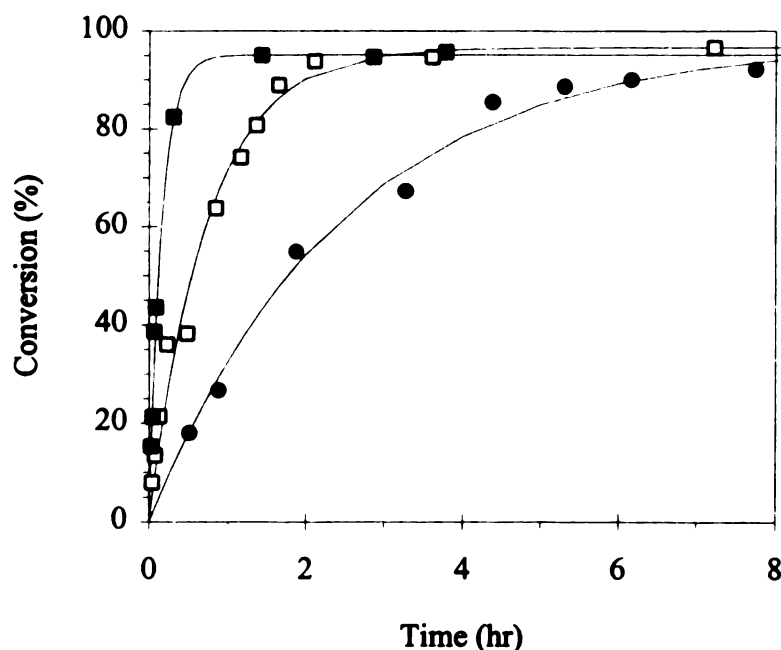


Figure 3-10. Effect of temperature on the kinetics of L-lactide polymerization with a monomer-to-initiator ratio of 10,000. The solid line is the reversible model for the respective temperatures: 220°C (■), 190°C (□), 160°C (●).

An equilibrium curve of L-lactide in amorphous PLLA is shown in Figure 3-11.

The monomer equilibrium values at 190 and 220°C were determined from the depolymerization experiments. At 130 and 160°C the M_{eq} were obtained from amorphous equilibrium data presented later, in Table 3-2. With a root-mean-square error of 0.33%

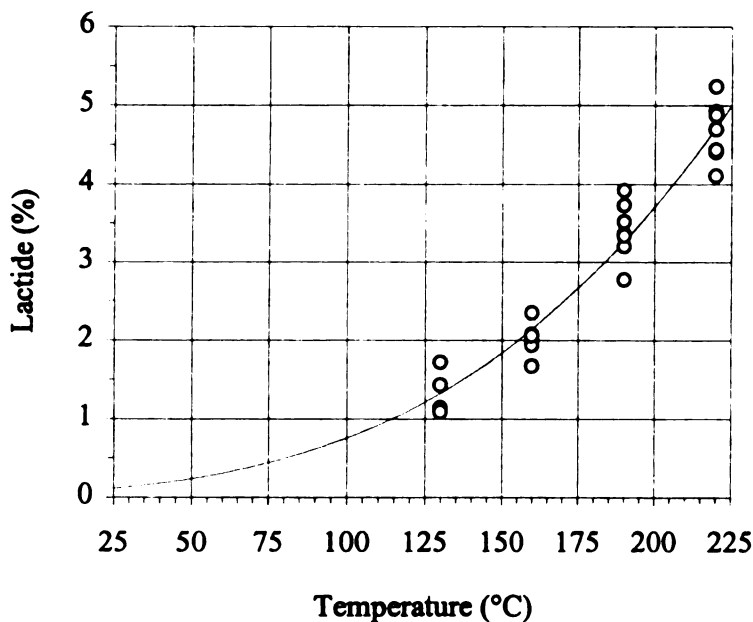


Figure 3-11. Monomer equilibrium curve for L-lactide polymerization (amorphous phase). The solid line is the equilibrium model defined in equation (3-3): $\Delta H_{lc} = -23.3$ kJ·mol⁻¹, $\Delta S_{lc} = -22.0$ J·mol⁻¹K⁻¹.

lactide, the equilibrium lactide amounts at 130, 160, 190, and 220°C were found to be 1.32, 2.15, 3.27, and 4.72 wt% respectively. The heat and entropy of polymerization were determined by nonlinear regression of equation (3-3): $\Delta H_{lc} = -23.3 \pm 1.5$ kJ mol⁻¹, $\Delta S_{lc} = -22.0 \pm 3.2$ J mol⁻¹ K⁻¹, from which, the ceiling temperature of polymerization ($\Delta G_{lc} = 0$) is estimated:

$$T_c = \frac{\Delta H_{lc}}{\Delta S_{lc}} = 786 \pm 87^\circ\text{C} \quad (3-8)$$

The calculated value of T_c is sensitive to the specified standard states: 'pure' liquid monomer, amorphous polymer, 1 atm. The regression was performed using M_{eq} expressed in weight fractions; thus, the standard state $M = 1$ corresponds to pure liquid

monomer. For bulk polymerization of L-lactide we believe T_c to be among 650-1038°C (95% confidence limits). However, because the ceiling temperature lies well above nondepolymerization degradation temperatures,²⁸⁻³² T_c for lactide polymerization is hypothetical.

Thermodynamic parameters for the copolymerization of D,L-lactide were calculated from calorimetry data by Kulagina et al.²⁰ On the basis of comparable monomer equilibrium, we expect similar ΔH_{lc} and ΔS_{lc} values between polymers of L- and D,L-lactide. At 400K Kulagina et al. estimated ΔH_{lc} and ΔS_{lc} at -27.0 kJ mol⁻¹ and -13.0 J mol⁻¹ K⁻¹, respectively. Although the enthalpies of polymerization are similar, the entropies differ significantly. Their values are referenced to a standard state of zero entropy for crystalline D,L lactide at 0K.

Duda and Penczek²¹ reported thermodynamic parameters for L-lactide polymerization in 1,4-dioxane at temperatures from 80 to 133°C. By extrapolating equilibrium data from solution to bulk concentrations, they arrived at the following parameters: $\Delta H_{lc} = -22.9$ kJ mol⁻¹, $\Delta S_{lc} = -25.03$ J mol⁻¹ K⁻¹ ($T_c = 641^\circ\text{C}$). Although their equilibrium data were determined in solution at low temperatures, the thermodynamic parameters lie within the standard error of our estimates. In accordance with the data of Duda and Penczek, we feel our thermodynamic parameters accurately describe the chemical equilibrium between L-lactide and amorphous PLLA.

After establishing the equilibrium relationship, propagation rate constants were regressed from the polymerization data using the reversible model. A summary of the results is presented in Table 3-1. Although crystallization accompanied polymerization at

130°C, the propagation rate constants reported in Table 3-1 are independent of the influence of crystallization on the polymerization rate. The rate constants at 130°C were regressed using the reversible model at the predetermined amorphous monomer equilibrium amount of 1.32%. Good model fits were obtained for the 130°C rate data at conversions less than 50%. These k_p are in good agreement with k_p determined from the irreversible model using rate data at less than 50% conversion. A discussion and model of the effect of crystallization on the rate of polymerization are presented later in this paper.

Table 3-1 Propagation Rate Constant Summary

T (°C)	M/I (mol/mol)	I (mol%)	k_p (hr ⁻¹ cat.mol% ⁻¹)
130	1,000	0.0999	11.3
130	2,940	0.0340	13.8
130	9,460	0.0106	6.1
130	19,200	0.00522	16.0
160	9,890	0.0101	40.1
190	10,000	0.0100	136
220	10,100	0.00993	639
220	20,000	0.00500	687
220	39,600	0.00253	435
220	79,300	0.00126	416

The rate equation assumption of first order dependence on I was verified by fitting the data to a power law rate form: $k_{eff} = kI^a$, where $k_{eff} = k_p I$. Regression of the 220°C data gave $a = 1.10 \pm 0.14$. A similar analysis was performed on the 220°C depolymerization data, Figure 3-7, yielding $a = 0.76$. However, because of variance in the

depolymerization data, the 95% confidence limits on a are 0.26 and 1.50. Therefore, the rates of lactide propagation and depropagation with tin(II) ethylhexanoate are indeed first order in catalyst.

The temperature dependence of k_p is depicted with an Arrhenius plot in Figure 3-12. Using all the polymerization data, the activation energy and preexponential constant were determined by nonlinear regression with equations (3-4) and (3-6): $E_a = 70.9 \pm 1.5 \text{ kJ mol}^{-1}$, $A_{448} = 86.0 \pm 3.0 \text{ hr}^{-1} \text{ cat mol}\%^{-1}$. Thus, the propagation rate constant can be estimated over a large temperature range using equation (3-4).

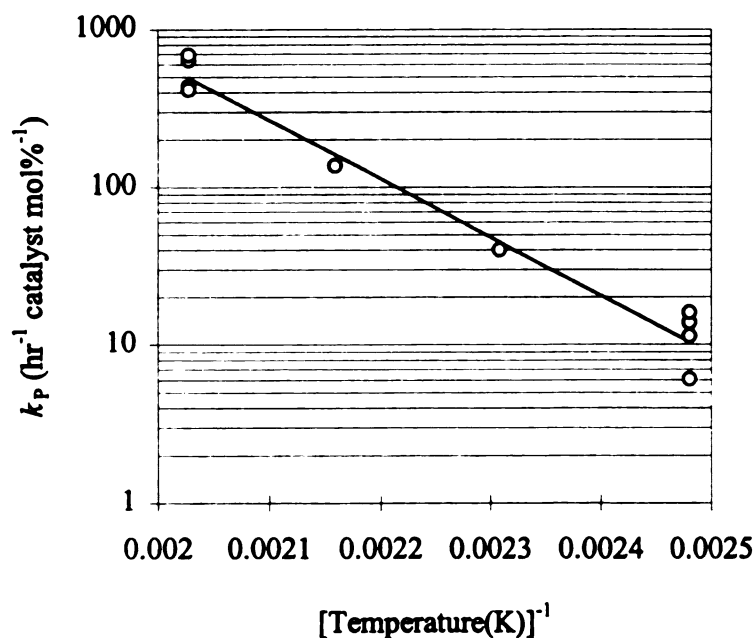


Figure 3-12. The temperature dependence of the propagation rate constant of L-lactide with tin(II) ethylhexanoate. The solid line is the Arrhenius model defined in equation (3-4): $E_a = 70.9 \text{ kJ mol}^{-1}$, $A_{448} = 86.0 \text{ hr}^{-1} \text{ cat mol}\%^{-1}$.

Eenink¹ calculated an activation energy of 80.6 kJ mol^{-1} for L-lactide polymerization with tin(II) ethylhexanoate, $M/I=10,000$, from $103\text{-}130^\circ\text{C}$, using an

irreversible rate model that is first order in catalyst and monomer. Eenink regressed his data at conversions far from equilibrium [less than 85%], and any error in his calculated rate constants attributed to the irreversibility of the model is small. The minor discrepancy in activation energy may be attributed to the increased variance in E_a with the narrow temperature range.

The effect of model choice on the rate constant is described in Figure 3-13. From equation (3-5), a plot of $-\ln((M-M_{eq})/(M_o-M_{eq}))=kIt$ versus time should be linear. The equivalent expression for the irreversible model is $-\ln(M/M_o)=kIt$. Thus, the slope of these curves is the propagation rate constant for the respective model. At low temperatures, such as those used in the Eenink study, the rate constant is fairly insensitive to time at conversions less than 85%. At higher conversions the apparent rate constant decreases until a value of zero is arrived at equilibrium. At industrial temperatures ($> 180^\circ\text{C}$) the effect of equilibrium on the apparent rate constant becomes more dramatic at lower conversions, and the irreversible model is less adequate. With our data, plots of $-\ln((M-M_{eq})/(M_o-M_{eq}))$ versus time yield straight lines over all conversion.

On account of decreasing polymerization rates, Eenink¹ found the irreversible fit poor for conversions greater than 85%. In a similar finding, Nijenhuis et al.¹⁸ suggested that L-lactide polymerized with tin(II) ethylhexanoate becomes diffusion controlled at conversions greater than 80%. The polymerizations in both contributions were performed at temperatures where crystallization accompanied polymerization. However, this same result was also reported for amorphous poly(D,L-lactide) by Lyudvig et al.,^{33,34} who attributed the decreasing rates to a "gel-effect" resulting from hydrogen bonding.³³ Based

on the thermodynamic calculations of Kulagina et al.,²⁰ which infer from free energy calculations that at $T < 200^\circ\text{C}$ the monomer equilibrium amount is less than 0.5%, Eerink discounted the influence of equilibrium on the rates. However, direct measurements in our work conclude that monomer equilibrium is of greater consequence, and suggest that some of the decreases found in polymerization rates at high conversion may be attributed to chemical equilibrium.

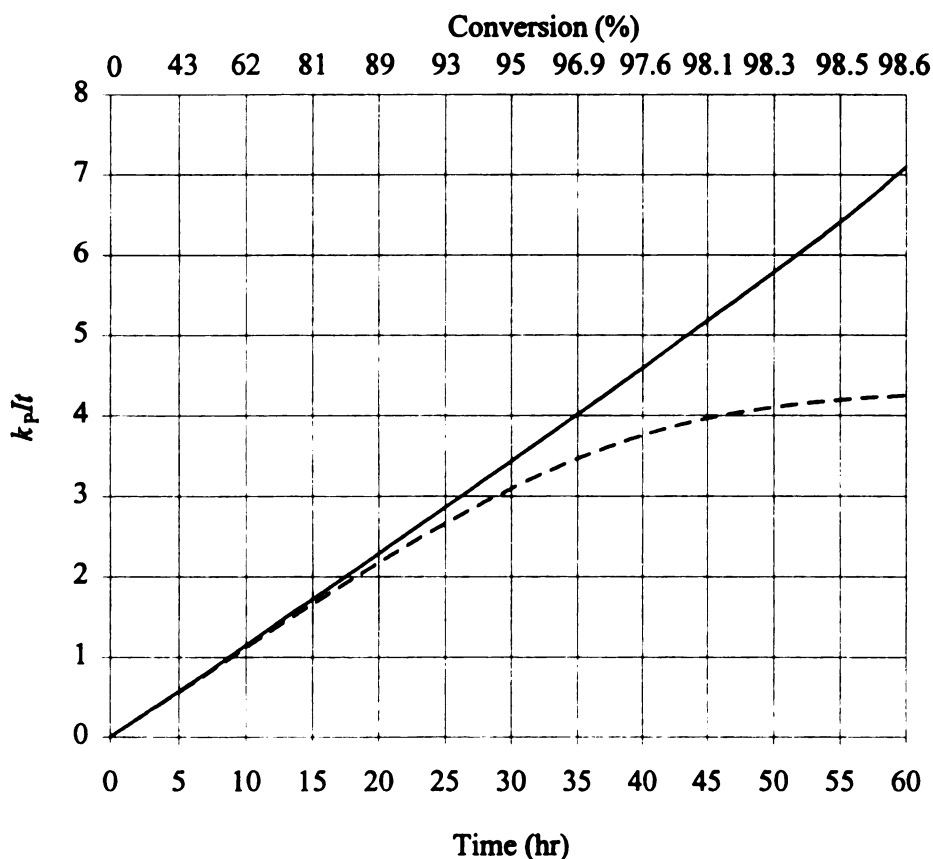


Figure 3-13. The effect of model choice on the observed L-lactide polymerization rate constant at 130°C and $M/I = 10,000$. The slopes of these lines are the respective rate constants. The solid line is the reversible model whereas the dashed line represents the irreversible model.

The reversible model accurately predicts the kinetics of the reversible polymerization of L-lactide with tin(II) ethylhexanoate among 130-220°C with $M/I = 1,000$ -80,000, over a full range of conversion. The incorporation of temperature transforms the model from one that has two parameters, k_p and M_{eq} , into one that has four: A , E_p/R , $\Delta H_p/R$ and $\Delta S_p/R$. A diagnostic plot of predicted lactide amounts versus observed amounts for the polymerization data is presented in Figure 3-14. The plot yields points that appear randomly distributed about the 45° line and exhibit no distinct pattern. At conversions less than 85%, the root-mean-square error of the model, RMSE, is 5.7% lactide. Above 85% conversion and at equilibrium the RMSE's are 1.5% and 0.33% lactide respectively. Figure 3-15 shows the effectiveness of the model for predicting depolymerization. The model predicts the depolymerization data with a RMSE of 0.38% lactide. In summary, the plots confirm the appropriateness of the reversible model and the fit of the kinetic data.

3.2.2. Effect of Crystallization on Polymerization Kinetics

Crystallization accompanies the bulk polymerization of L-lactide at temperatures between 100°C and 145°C. From our 130°C polymerization and depolymerization data, we found that crystallization increases the polymerization rate and decreases the total amount of monomer at reaction equilibrium. These results are in accord with the data of Nijenhuis et al.¹⁸ To quantify the effects of crystallization, we assume that only functional groups in the amorphous phase remain available for reaction and that catalyst and lactide monomer are rejected from the polymer crystalline phase.

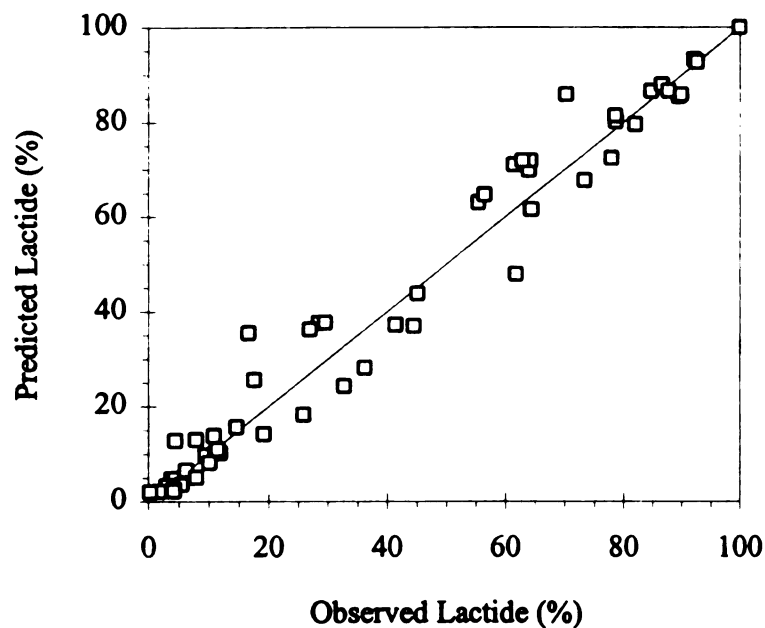


Figure 3-14. Reversible model performance for the L-lactide polymerization data. Polymerization conditions: 130-220°C, $M/I = 1,000-80,000$. The root-mean-square error of the model is 5.7% lactide.

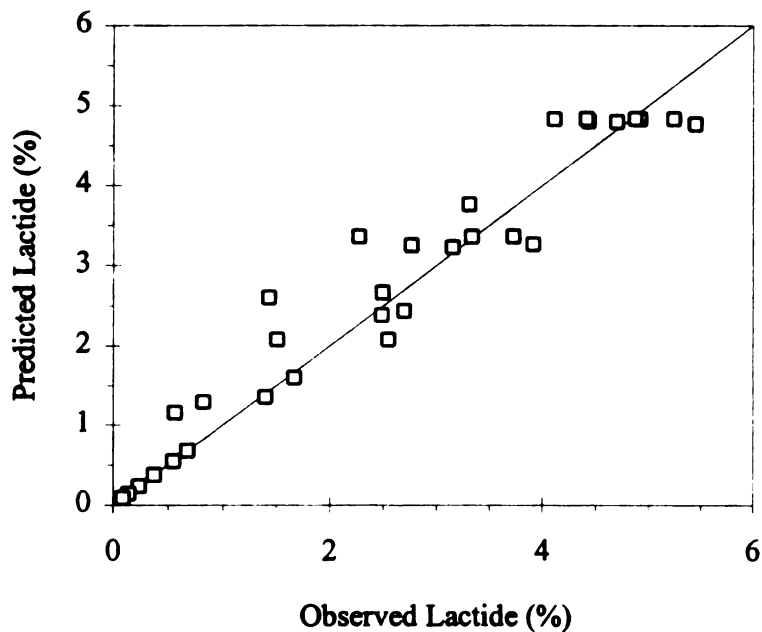


Figure 3-15. Reversible model performance for the L-lactide depolymerization data. Depolymerization conditions: 190-220°C, $M/I = 10,000-80,000$. The root-mean-square error of the model is 0.38% lactide.

Depolymerization experiments at 130 and 160°C with highly crystalline poly(L-lactide), PLLA, yielded equilibrium lactide concentrations that were lower than expected based on the 190 and 220°C results. During these experiments the PLLA melting temperature was above the test temperature, and the samples remained as loose powders. Thus, the depolymerization reaction appears to be excluded from the crystalline phase; consequently, the total lactide concentration in the polymer is suppressed.

This hypothesis, based on depolymerization data, was confirmed through polymerization tests. According to the hypothesis, a noncrystallizable random copolymer of L and D-lactide should retain a higher lactide concentration than a crystalline polylactide. Table 3-2 presents the equilibrium lactide values for long time polymerizations at 130°C (24 h) and 160°C (5 h), $M/I=1,000$, with three isomer compositions: 50%, 85%, and 100% L-lactide (with D-lactide as the balance). Lactic acid was used to stoichiometrically control the number average molecular weights at 85,000. At 160°C all the polymerizations proceeded in the absence of crystallization, and no statistical differences in monomer equilibrium were found among the three isomer compositions. However, at 130°C the 100% L- polymers crystallized during polymerization, and the total amounts of lactide in these semicrystalline samples were substantially reduced. Therefore, crystallization reduces the apparent equilibrium monomer concentration in polylactide.

Table 3-2 Monomer Equilibrium at 160°C and 130°C

composition ^a	<i>T</i> (°C)	lactide (%)	<i>M_n</i>
50L	160	1.99	84,600
50L	160	2.08	107,800
85L	160	1.94	78,700
85L	160	1.67	85,200
100L	160	2.35	76,800
100L	160	2.06	70,500
50L	130	1.43	99,600
50L	130	1.72	122,800
85L	130	1.14	87,600
85L	130	1.09	94,700
100L	130	0.16 ^b	88,400
100L	130	0.43 ^b	88,900

^a remainder D-lactide^b semicrystalline

Along with the lactide equilibrium effect, crystallization also affects lactide polymerization kinetics. With our 130°C L-lactide polymerization data, plots of $-\ln((M-M_{eq})/(M_o-M_{eq}))$ versus time yield a propagation rate constant (the slope) that increases with time. Thus, the reversible model is no longer valid when crystallization accompanies polymerization.

Table 3-3 presents a summary of the 130°C polymerization data with $M/I = 9,500$. Polymer crystallinity was found in quenched samples with conversions greater than 20%. Somewhere between 20 and 60% conversion the polymer began to crystallize and precipitate out of solution. This corresponds to the point where the melting temperature,

T_m , exceeded the polymerization temperature. Differential scanning calorimetry was used to determine T_m and heat of melting, ΔH_m . The crystalline weight fractions, ω , were obtained by dividing the heats of melting by 93.7 J/g: the approximate heat of melting at 100% crystallinity determined by Fischer et al.³⁵ from single crystals of PLLA.

Table 3-3 Crystallization of Poly(L-lactide) During Polymerization at 130°C, M/I = 9500

time (hr)	conversion (%)	ΔH_m (J/g)	ω	T_m (°C)
2.37	13.3	0	0	-
4.23	20.0	20	0.21	125.0
8.82	39.2	a	a	a
15.4	64.0	26.5	0.28	138.2
24.1	81.0	46.9	0.50	156.0
28.8	90.5	b	b	173.7
45.5	97.75	82.9	0.88	184.0
49.5	98.30	79.1	0.84	186.3
146	99.79	83.7	0.89	197.6

^a not determined

^b poor DSC thermogram, allowed detection of T_m only

The melting point and heat of melting were found to increase with time. The final sample had a heat of melting of 83.7 J/g and a T_m of 197.6°C. The 14°C increase in melting point observed over the last 2% conversion is likely because of an annealing process, 100 h at 130°C.

It is noteworthy that Nijenhuis et al.¹⁸ obtained an as polymerized PLLA heat of melting of 100 J/g, T_m = 207°C, using a zinc catalyst. From observed T_m versus

crystallization temperature data, Vasanthakumari and Pennings³⁶ extrapolated a theoretical PLLA melting temperature of 207°C.

The instantaneous monomer and catalyst concentrations in the amorphous phase increase when polymer crystallizes and precipitates out of solution. Thus, if both catalyst and monomer are excluded from the crystalline phase, it follows that the rate of polymerization should subsequently increase. With these assumptions the open system mass balance on monomer weight fraction in the amorphous phase, M , is

$$dM = -k_p I M dt + k_d I dt - M \frac{dV}{V} \quad (3-9)$$

where V is the volume in the amorphous phase, and I , k_p , and k_d are the mole percentage catalyst, propagation constant, and depropagation constant, respectively.

The assumption of catalyst exclusion from the crystalline phase is justified by assuming that the catalyst concentration in the amorphous phase remains constant during crystallization (incorporation into the crystals without differentiation). For instantaneous crystallization of formed polymer, $M=1$ and $dM = 0$, equation (3-9) gives a polymerization rate that is not significantly different from the reversible model at 130°C, equation (3-5); this solution is identical to equation (3-5) when $M_{eq} = 0$ (irreversible). Thus, if the catalyst concentration remains constant, crystallization does not affect the apparent rate of monomer conversion. From our polymerization data, which clearly show that crystallization increases the rate of polymerization, we conclude that the catalyst must be excluded from the crystalline phase: $I(t) = \frac{V_0}{V(t)} I_0$.

The following equation relates the volume in the amorphous phase, the weight fraction of the crystalline phase, ω , and the ratio of the apparent (measured) monomer weight fraction to the amorphous phase monomer weight fraction:

$$\frac{V(t)}{V_0} = 1 - \omega(t) = \frac{M(t)_{\text{apparent}}}{M(t)} \quad (3-10)$$

Using equation (3-10), the chain rule, $dM_{\text{apparent}} = \frac{V}{V_0} dM + \frac{M}{V_0} dV$, and equation (3-9) incorporating the definition for $I(t)$, the mass balance for the apparent monomer weight fraction is

$$dM_{\text{apparent}} = (M_{\text{eq}} - M)k_p I_0 dt \quad (3-11)$$

where M_{eq} is the equilibrium monomer weight fraction in the amorphous phase (equation 3-3).

Equation (3-11) can only be solved if we know how M_{apparent} changes with respect to M (i.e., we have crystallization kinetics). However, we can directly solve for the lower bound of $M(t)_{\text{apparent}}$ by assuming instantaneous crystallization of polymer, $M=1$.

Integrating between $M_{0,\text{apparent}}$ and $M(t)_{\text{apparent}}$ we find that with instantaneous crystallization the apparent monomer weight fraction is a linear function of time,

$$M(t)_{\text{apparent}} = M_{0,\text{apparent}} + (M_{\text{eq}} - 1)k_p I_0 t \quad (3-12)$$

For unknown crystallization kinetics we assume an empirical relationship between M_{apparent} and M to solve equation (3-11). A well behaved family of curves is obtained by using the following relationship

$$M = M_{\text{apparent}}^{(1-\alpha)} \quad (3-13)$$

where $0 \leq \alpha \leq 1$. When $\alpha = 0$, polymerization proceeds in the absence of crystallization and the solution to equation (3-11) is equivalent to the reversible model, $M_{\text{apparent}} = M$. When $\alpha = 1$, the solution of equation (3-11) yields the instantaneous crystallization solution, equation (3-12). The analytical solution to equation (3-11) is simplified by assuming irreversible kinetics, $M_{\text{eq}} = 0$. The error in doing this is negligible, except at apparent conversions near 100% where the relative error becomes large.

$$M(t)_{\text{apparent}} = (M_{0,\text{apparent}}^\alpha - \alpha k_p I_0 t)^{1/\alpha} \quad (3-14)$$

The family of curves for different α are presented in Figure 3-16 along with the observed 130°C polymerization data. With $\alpha = 0.4$ an adequate fit of the kinetic data is observed.

The α parameter can be directly obtained from crystallization and conversion data;

$$M(t)_{\text{apparent}} = (1 - \omega(t))^{1/\alpha} \quad . \quad \text{A value of } \alpha = 0.4 \text{ also adequately fits the crystallinity data.}$$

The effect of crystallinity on the depolymerization of L-lactide at 160°C, $M/I = 9,500$, is shown in Figure 3-17. In 16 h the monomer in the highly crystalline sample, $\omega = 0.89$, increased from 0.004% to only 0.26%. In contrast, the reversible model predicts that amorphous polylactide would obtain a M_{eq} of 2.15%. This is consistent with the

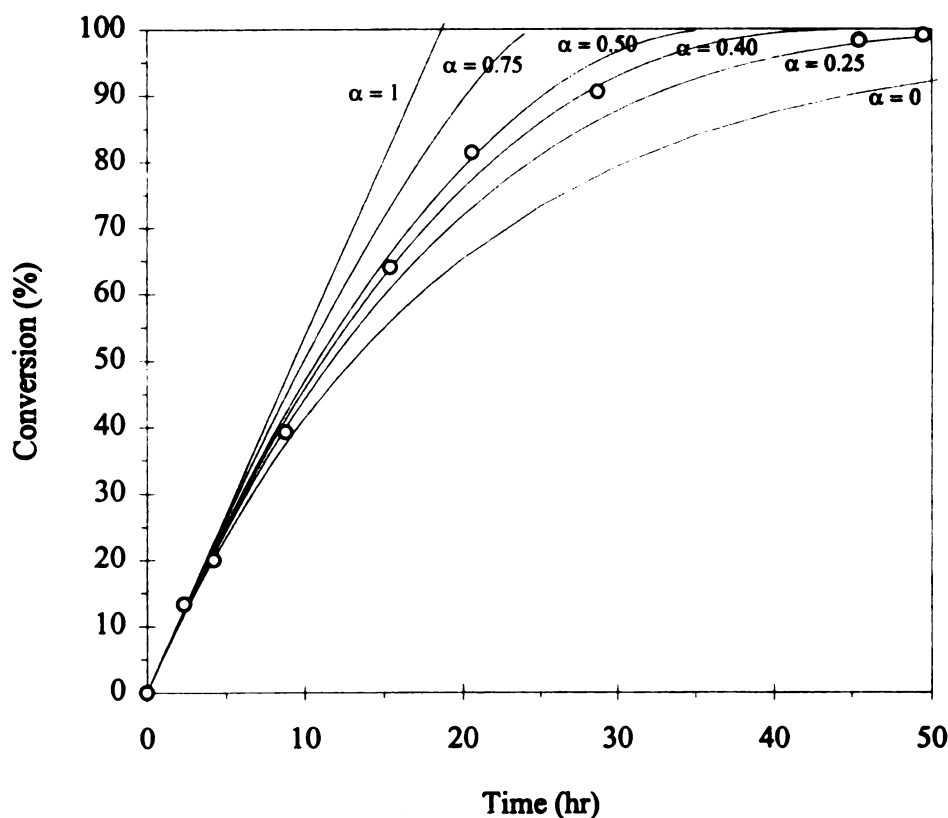


Figure 3-16. Effect of crystallization on the kinetics of L-lactide polymerization at 130°C with $M/I = 9,500$. The solid lines are the family of curves defined by equation (3-14) for various α . The observed data is represented with (O). For $\alpha = 0$, no crystallization, the curve is equivalent to the reversible model, equation (3-6). For $\alpha = 1$, instantaneous crystallization of polymer, the curve is equivalent to the analytical solution presented in equation (3-12).

measured value of 0.26% if all the lactide is in the amorphous phase. The apparent monomer concentration at reaction equilibrium can be determined from the product of the amorphous weight fraction and the known equilibrium concentration in the amorphous phase (equation 3-3),

$$M_{eq,apparent} = (1 - \omega)M_{eq} \quad (3-15)$$

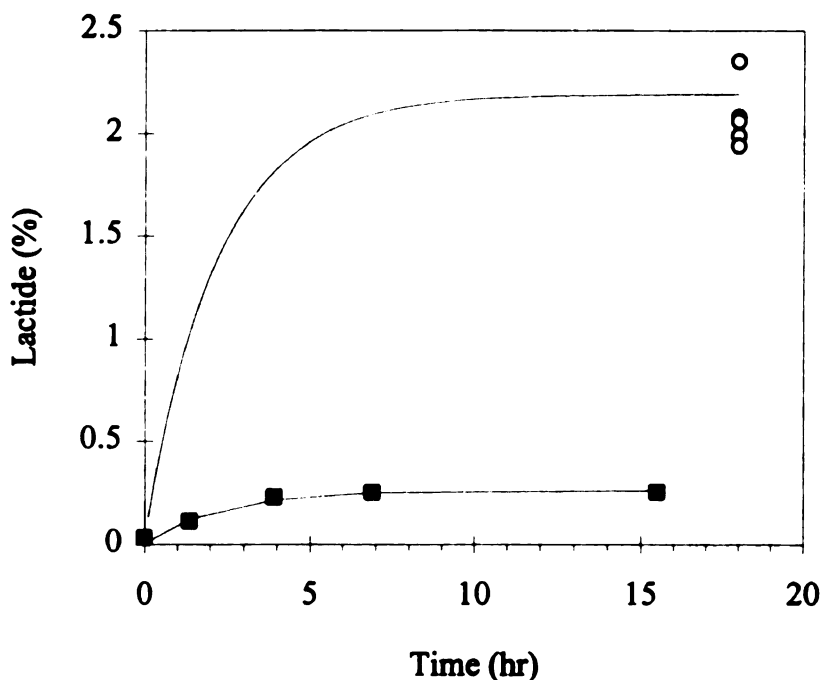


Figure 3-17. Effect of crystallization on the depolymerization kinetics of PLLA (■) at 160°C with $M/I = 10,000$. The sample had a heat of melting of 83.7 J/g, $\omega = 0.89$. The upper solid line is the reversible model. Equilibrium L-lactide polymerization data at 160°C (amorphous) is presented for reference, (○).

We conclude that crystallization increases the rate of polymerization and decreases the apparent monomer equilibrium concentration in proportion to the degree of crystallinity. Furthermore, polymerization and depolymerization rate data are consistent with a process where reaction only occurs in the amorphous phase, and catalyst and lactide monomer are excluded from the crystalline phase.

Conclusions

The reversible kinetics of L-lactide bulk polymerization with tin(II) ethylhexanoate was determined over a wide range of temperatures, 130-220°C, and monomer-to-initiator molar ratios, 1,000-80,000. Both polymerization and

depolymerization are accurately described by a reversible model with a propagation term that is first order in monomer and catalyst. The activation energy of propagation is $70.9 \pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$. The enthalpy, entropy, and ceiling temperature of polymerization are $-23.3 \pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$, $-22.0 \pm 3.2 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$, and $786 \pm 87^\circ\text{C}$, respectively. Crystallization increases the propagation rate and decreases the apparent monomer equilibrium in proportion to the degree of crystallinity.

3.3 Hydroxyl Initiation

Natural impurities in lactide include lactic acid, lactoyllactic acid (DP2), DP3, DP4 and water. Oligomers larger than DP4 are not detectable with our GC protocol (less than 0.005%) in the reaction mixture prior to polymerization. It is known that hydroxyl impurities stoichiometrically control the number average molecular weight of polylactide.^{4,7,18,37-41}

In the PLA-stannous ethylhexanoate system, the number of PLA chains is independent of both catalyst concentration and temperature (below thermal decomposition temperatures). Each of the hydroxyacid impurities or water, which serve to initiate a polymer chain, is expected to form a polymer chain with one hydroxyl end group and one acid end group (one-to-one correspondence between hydroxyl impurities and polymer chains). Both water and hydroxyl impurities initiate polymer chains by nucleophilic attack on the carboxyl groups in lactide and polymer. When water or lactic acid reacts with lactide the hydroxy acid dimer and trimer (DP2 and DP3) are formed, respectively, and they in turn will react with carboxyl groups in the reaction mixture. The

total amount of hydroxyl end groups is conserved throughout the polymerization; thus, the initial hydroxyl impurities determine the number density of polymer chains (i.e., M_n). The linearity of a plot of M_n versus lactide conversion (Figure 3-2) indicates that chain initiation is fast using stannous ethylhexanoate at bulk polymerization temperatures.

In Table 3-4 we present data demonstrating the use of hydroxyl additives (in this case crystalline lactic acid) to target final M_n during lactide polymerization with stannous ethylhexanoate. These data were obtained from the preparation of controlled M_n PLA samples used to characterize PLA viscoelasticity in Section 2.5.1.

Table 3-4 Control of PLA M_n Using Crystalline Lactic Acid

Total mmol OH/kg	Target M_n	Observed M_n
100	10,000	12,000
50	20,000	29,000
25	40,000	40,200
12.5	80,000	78,800

Typically, well stored lactide contains about 2-5 mmol OH/kg. The water and lactic acid oligomers are determined by Karl-Fisher titration and GC, respectively. The amount of additional OH impurities required (mmol/kg) for a given target M_n is simply the ratio $1E6/M_n$ less the starting amount of OH.

The number average molecular weight is predicted during polymerization from the fractional monomer conversion, X_m , (equation 3-6) and the initial molar ratio of monomer to total OH impurities M/OH ,

$$M_n = 144.13 \left(\frac{M}{OH_{total}} \right) X_m \quad (3-16)$$

Below thermal degradation temperatures, the effect of temperature on final M_n at equilibrium monomer conversion is slight ($X_{m,eq} = 0.979$ and 0.967 at 160 and 190°C , respectively).

In the reversible polymerization kinetics study in the previous section, the number average molecular weights were usually controlled to less than 95,000 to facilitate grinding of the polymer. Our experience using lactic acid to control molecular weight is that natural impurities do not significantly affect the rate of polymerization to high polymer. For example, at 130°C and $M/I = 10,000$, we used lactic acid to target molecular weights between 87,000 and 201,000 in three polymerizations. Analyses of the kinetic data gave propagation rate constants that were not statistically different. With the depolymerization rate data we also found no correlation between monomer equilibrium and molecular weight. These two observations suggest that the concentration of end groups are relatively unimportant in determining propagation and depropagation rates.

It is conceivable, however, that at low molecular weights (i.e., high level of impurities) the rates of propagation and depropagation are influenced by the higher

concentration of hydroxyl end groups. Therefore, we can not conclude from our data that natural hydroxyl impurities do not mechanistically influence the polymerization kinetics of lactide with tin(II) ethylhexanoate. However, it is clear that in the polymerization to high polymer, the relative importance of catalyst concentration and temperature render any kinetic effects of natural impurities insignificant.

It is notable that alcohols (unnatural impurities) are found to increase the rate of polymerization while carboxylic acids decrease the rate of polymerization but do not affect molecular weight.⁴⁰ This is in agreement with our findings. Therefore, it may be the bifunctionality of hydroxyacid and water natural impurities that nets a nearly neutral effect on the rate of high molecular weight polymerization.

Intermolecular transesterification among polymer chains (interchange reactions) yields a polymer molecular mass that approaches the most probable distribution (Flory-Schulz distribution) result for condensation polymers. Intramolecular transesterification gives cyclic oligomers and lactide (depropagation). In the vial polymerization work presented in the previous section we found that with high polymerization temperatures, $\geq 160^{\circ}\text{C}$, a polydispersity index, $PDI = M_w/M_n$, of 2.0 is achieved at long time. The approach of PDI towards 2.0 at 190°C and $M/I = 10,000$ lactide/Sn(II) (mol/mol) is presented in Figure 3-18. However, with the 130°C data we found transesterification to be "incomplete" at equilibrium conversion, $PDI = 1.5\text{-}1.6$. This is in accord with Eleni:¹ $PDI = 1.6$ at 130°C . In Section 3.4 we show that this is a result of reduced transesterification kinetics owing to crystallization that accompanies polymerization at temperatures $< 160^{\circ}\text{C}$.

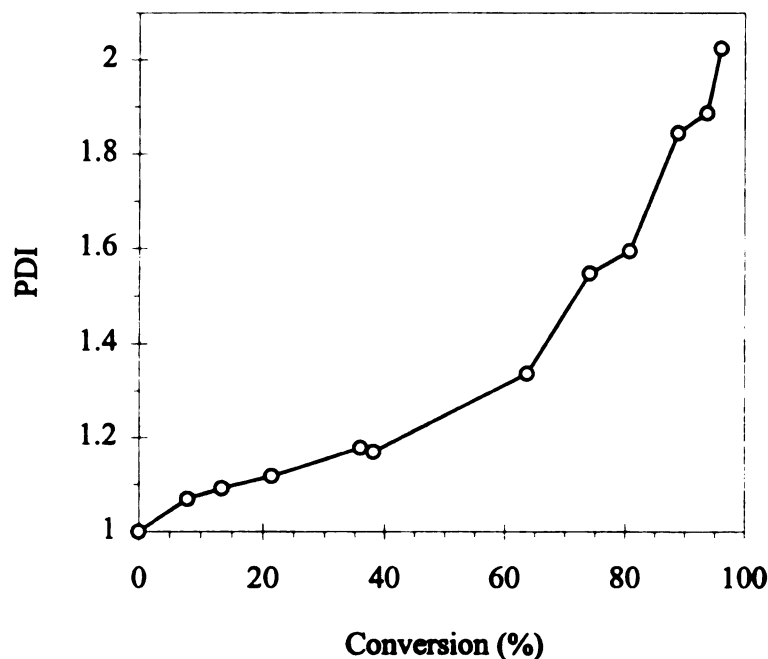


Figure 3-18. Plot of polydispersity index versus L-lactide conversion at 190°C and $M/I = 10,000$. Transesterification reactions are responsible for the approach of PDI towards 2.0 (most probable distribution).

***Semiliving* Polymerization Hypothesis**

To explain the observed living polymerization kinetics with a polydispersity that is not narrow and approaches the most probable distribution we suggest that (1) transesterification reactions are important and broaden the MWD, and (2) this system may be described as *semiliving* having both dormant and living chains that "exchange" status throughout the polymerization.

The kinetic rate form for lactide polymerization is consistent with a living polymerization. However, the molecular weight distribution does not follow the Poisson distribution for living polymers and is not narrow. This is a result of polylactide being both an anionic (or coordination-insertion) ring opening polymer (thus the rate form) and a condensation polymer susceptible to transesterification reactions. The polymerization catalyst facilitates lactide addition and determines the rate of polymerization. The

hydroxyl impurities determine the number of polymer chains and define the molecular weight at equilibrium conversion. In this system the catalyst and initiators are different molecules (Sn(II) and R-OH) since the catalyst lacks the nucleophilicity required to initiate polymer chains. Kricheldorf et al.¹⁵ found that initiators of high nucleophilicity are required to initiate lactide via anionic polymerization. The catalyst must either facilitate addition between lactide and OH end groups or swap the ethylhexanoate substitution for a stronger nucleophile such as water or an alkoxide lactic ligand (i.e., -Sn-OH or -Sn-OC(CH₃)COOH). We hypothesize that this system can be described as *semiliving*, where PLA chains alternate between dormant and living (active to propagation/depropagation) through exchange of the reaction centers. Unlike chain transfer reactions, exchange reactions result in dormant rather than dead polymer chains.

For a 100,000 M_n polymer ($M/OH = 700$) polymerized at an initial molar ratio of monomer to catalyst of $M/I = 10,000$, there are nearly 15 times as many polymer chain initiating molecules than catalyst molecules. We propose that the number of living chains at any one time is equivalent to the number of catalyst molecules and that the number of dormant chains are equivalent to the difference of catalyst and OH molecules, $OH - I$. The fraction of living and dormant chains are:

$$x_{\text{living}} = \frac{I}{OH} = \frac{M/OH}{M/I},$$

$$x_{\text{dormant}} = \frac{OH - I}{OH} = \frac{M}{OH} \left(\frac{1}{M/OH} - \frac{1}{M/I} \right) \quad (3-17)$$

Therefore, for the polymer described above, the percentage of living chains at any one time is 7%.

Through this hypothesis the polymer chains exist in a state of dynamic equilibria where reactions (transesterification? or alkoxide-carboxylate?) swap reactive centers among chains and dormant chains become live and vice versa. We assume that there is no termination of reaction centers. This being true, the *semiliving* system would achieve an increase in molecular weight if fresh monomer with a lower concentration of hydroxyl impurities is added to a polymer at equilibrium conversion which initially had a greater concentration of hydroxyl impurities. This is an easy experiment and has been verified in our lab. For example, with the melt addition of 10 g lactide containing 10 mmol/kg OH ($M/OH = 700$) to 10 g PLA that was originally polymerized with 50 mmol/kg OH ($M/OH = 140$, $M_n = 20,000$), the final PLA after the polymerization of fresh lactide will have $M_n = 33,000$ (30 mmol/kg OH, $M/OH = 230$).

There are numerous mechanistic interpretations of the role of OH + Sn(II) in lactide polymerization.^{2,18,40-43} Proposed mechanisms involve stannous ethylhexanoate hydrolysis to more active species (e.g., alkoxides) and complexation between Sn(II) and ROH groups.

Aluminum alkoxide catalyzed lactide polymerization is believed to proceed through a coordination-insertion mechanism.^{9,11,12,14,36,37} In anhydrous toluene at 70°C, the aluminum alkoxide-lactide polymerization has been shown to be a living system (at least at low conversion) having the characteristic narrow molecular weight distribution and M_n

$= M/I$ (DuBois, Jerome, Teyssie). However, it was found that at high conversion the molecular weight distribution broadened. Initiation was found to be slow in toluene at this temperature.

Unlike tin(II) ethylhexanoate, the aluminum alkoxide catalyst contains a good nucleophile, the alkoxide group. We believe that the literature results indicate that the alkoxide group more quickly reacts to initiate polymer chains than does the hydroxy impurities from the lactide source. Therefore during the early course of polymerization the number of initiating groups equal the number of catalyst molecules ($OR = I$) and all of the polymer chains are living. In addition, aluminum alkoxide catalysts having p alkoxide groups per aluminum are reported to follow $M_n = M/(p \cdot I)$. As found in the Sn(II) ethylhexanoate system, the rate of polymerization depends on the concentration of metal catalyst and the molecular weight depends on the number of good nucleophiles for initiation. The main difference is that with the aluminum alkoxide solution polymerization the number of reactive initiators was initially equivalent to the number of catalyst molecules (where $p = 1$). Later in the course of polymerization transesterification reactions may have become important and broadened the MWD. In concept, the *semiliving* Sn(II) system should reduce to a living system when $Sn(II) = OH$ and polymerization conditions are such that interchange reactions are unimportant in the time of lactide polymerization.

Conclusions

We conclude that natural hydroxyl impurities (water, lactic acid, lactic oligomers) are not kinetically limiting in the propagation step and suggest that they do not participate in termination reactions. For these reasons, the kinetic rate form of polymerization is consistent with a living polymerization. However, the hydroxyl impurities do participate in transesterification reactions that stoichiometrically define the number average molecular weight. A *semiliving* model is proposed where a fraction of chains, defined by the catalyst concentration, is living and the remainder of chains (*OH-I*) are dormant. Polymer interchange reactions broaden the molecular mass towards the most probable distribution result.

3.4 Transesterification

In the prior two sections we found that although chain initiation is fast compared to propagation in the lactide-Sn(II) system, transesterification is relatively slow as evidenced by the gradual approach towards the most probable MWD during batch polymerization. Considerably higher *PDI* than 2 can be achieved in nonideally mixed continuous stirred tank reactors, CSTRs. For many applications a broader MWD is desired (e.g., increased melt elasticity). In order to optimize the lactide polymerization reactor cascade, information about how the transesterification kinetics affect the MWD and change with catalyst concentration, temperature, hydroxyl impurities concentration, and time is required. The transesterification model can be integrated with the reactor design equations to provide an operations tool to target a specific MWD required for a

certain application. An introduction to the reaction engineering of PLA is presented in Section 4.2.

The elucidation of the role of catalyst in the polymer interchange reaction is key to developing a useful rate model. Because of the high activation energies of lactide propagation (71 kJ/mol with tin(II) ethylhexanoate) and depropagation (94 kJ/mol with tin(II) ethylhexanoate: $E_{a,d} = -\Delta H_k + E_{a,p}$) we know that a good catalyst is required for polymerization or depolymerization to occur to any appreciable extent. However, the condensation of lactic acid to low molecular weight poly(lactic acid) is self-catalyzed by the acid end groups and occurs in the absence of a metal catalyst. The activation energy of intermolecular transesterification at the acid end group (condensation) is obviously much lower than that of ring-opening and ring-closing intramolecular transesterification reactions. For the transesterification rate model we must determine both the activation energy of polymer interchange and the importance of the polymerization catalyst.

In Section 3.4.1 we make inferences concerning the importance of catalyst, temperature, and polymerization reversibility on $MWD(t)$ during lactide polymerization. In Section 3.4.2 we present alternative transesterification kinetic schemes that provide mechanistic insight into the role of catalyst and form the basis for a rigorous $MWD(t)$ kinetic model for lactide polymerization.

3.4.1 Interchange Reactions During Polymerization

The change in MWD with time during polymerization at 130°C and $M/I = 10,300$ lactide/Sn(II) (mol/mol) is depicted in a GPC chromatogram in Figure 3-19. The GPC

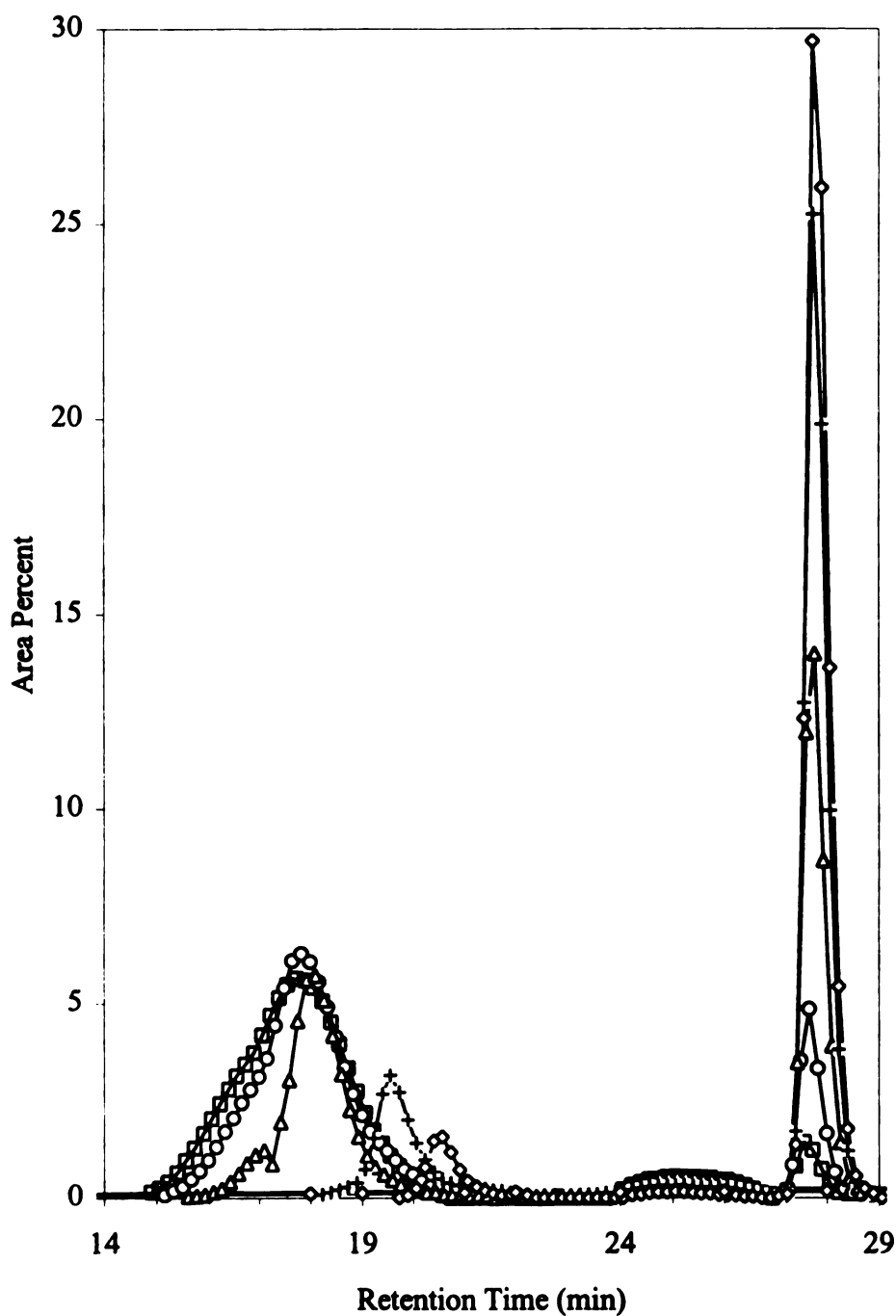


Figure 3-19. GPC chromatogram depicting the change in MWD during polymerization at 130°C and $M/I = 10,300$ lactide/Sn(II) (mol/mol). In this chromatogram polymer elutes at < 20 min and lactide elutes at 27-28.5 min. Polymerization sample times are: 0.75 hr (♦), 2.4 hr (+), 8.75 hr (Δ), 28.7 hr, (○), and 49 hr (□).

analytical setup is described in Section 3.2. Conversion and molecular weight data are presented in Table 3-5. In this chromatogram the polymer elutes at < 20 min (after 0.75 hr polymerization time) and lactide elutes at > 27 min. The broad low peak at 24–27 min is most likely cyclic oligomers that will eventually reach an equilibrium relationship with high polymer (similar to lactide/PLA equilibrium). At high conversion the peak molecular weight does not change appreciably with polymerization time but the distribution continues to broaden. This broadening represents the production by interchange reactions of very high molecular weight chains. This is apparent in Figure 3-20 which presents a plot of weight percent of total sample (including monomer) versus molecular weight. The ordinate values are the total percent of repeat units in polymer chains of that particular MW slice (discrete). The sum of all discrete ordinate values is the first moment (total percent of repeat units that reside in polymer). After 146 hr the M_n and PDI reach values of 171,000 and 1.64, and 2% of the repeat units reside in chains having a molecular weight greater than 800,000. It is notable that although crystallization accompanies polymerization after 8 hr, transesterification still proceeds even at very high degrees of crystallization (> 85%). This suggests that the OH initiating species and catalyst (if catalyzed) remain in the amorphous phase. The number of polymer chains per mass, $\mu_0(\text{mmol/kg}) = X_{\text{mon}} * 1\text{E6}/M_n$, remain constant at long time indicating that degradation reactions are unimportant at 130°C.

Table 3-5 Change in Polydispersity During Polymerization at 130°C and $M/I = 10,300$ lactide/Sn(II) (mol/mol)

time (hr)	conversion (%)	M_n (g/mol)	PDI	μ_0 (mmol/kg)	semicrystalline
0.75	8.9	25,900	1.08	3.4	no
2.4	24.8	41,900	1.26	5.9	no
8.75	55.5	126,000	1.30	4.4	yes
28.7	84.6	143,000	1.43	5.9	yes
49	94.8	157,000	1.51	6.0	yes
146	99.8	171,000	1.64	5.8	yes

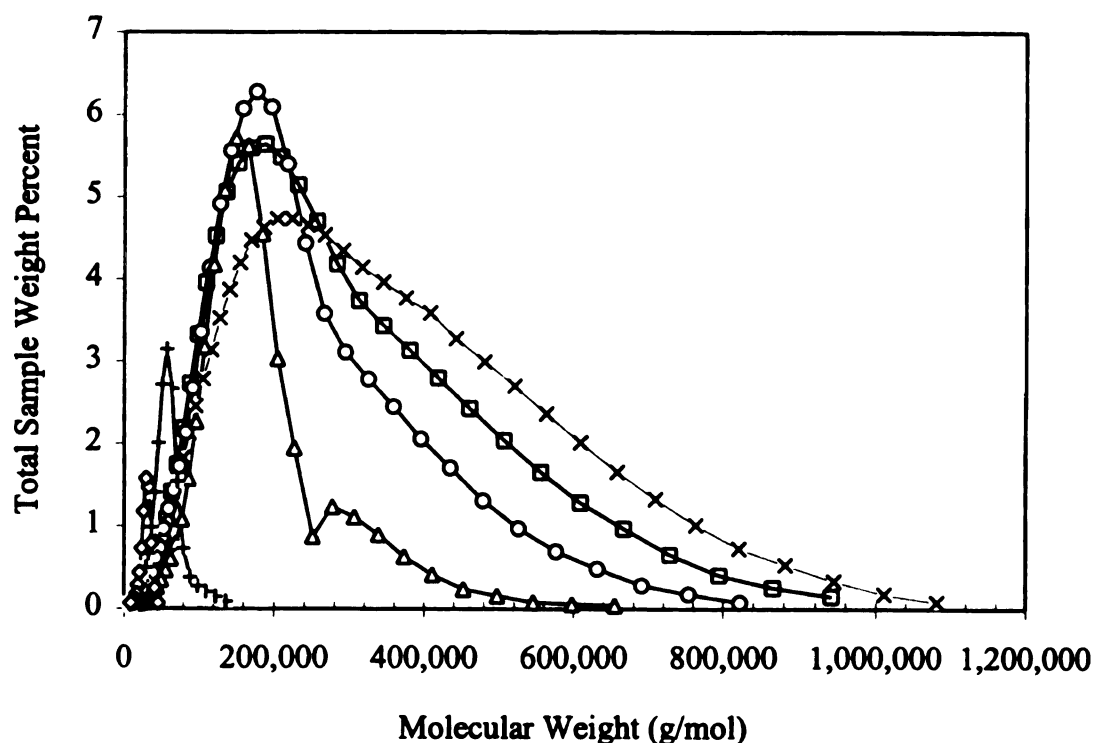
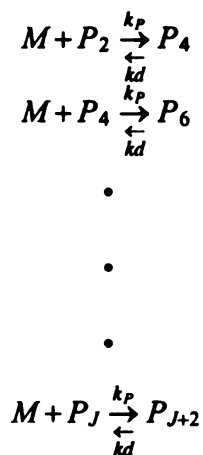


Figure 3-20. Change in MWD during polymerization at 130°C and $M/I = 10,300$ lactide/Sn(II) (mol/mol). Polymer interchange reactions producing polymer chains of high molecular mass broaden the molecular weight distribution. Polymerization sample times are: 0.75 hr ($\diamond$), 2.4 hr (+), 8.75 hr (Δ), 28.7 hr (O), 49 hr ($\square$), and 146 hr (x).

Effect of Polymerization Reversibility on MWD

A few literature references have suggested that the reversibility of lactide polymerization contributes to a broadening of the MWD. In concept, depropagation will slowly act to randomize the MWD. However, because the monomer equilibrium amount is less than 5 wt% at lactide polymerization temperatures, the rate of depropagation is less than 1/20th that of propagation. Therefore, the effect of reversibility on the MWD may not be important in the time of practical polymerization. To determine the importance of reversibility on the MWD during batch lactide polymerization of known kinetics we simulate the chain population dynamics in the absence of transesterification. A FORTRAN program was written to solve for the dynamic chain populations during lactide polymerization according to the following kinetic scheme:



The following initial conditions were used for input values of $M/I = M/OH$: $P_2 = I$, $P_3 = P_4 = \dots = P_n = 0$. A simple Euler algorithm was used to numerically solve the population differential equations with a step size appropriate to the choice of M/I . In all simulations

the output lactide conversion with time was in accord with the analytical solution (Section 3.2), and the total number of chains remained constant with time (consistency checks). The FORTRAN code is presented in Section 3.4.3.

The simulated *PDI* vs. t/θ results for $M/I = 10$ at 220°C is presented in Figure 3-21. The characteristic polymerization time is $\theta = 1/(k_p I)$. 3θ is the time required to achieve 95% of equilibrium and represents the time limit for practical lactide polymerization. The simulation results indicate that over 500θ are required for the *PDI* to approach the most probable distribution result, $PDI = 2 - 1/(M/OH^*(1 - M_{eq})) = 1.895$, for reversible lactide polymerization in the absence of transesterification. In Figure 3-22 we present *PDI*(t) for $M/I = 1,000$ up to 5θ for both reversible and irreversible ($M_{eq} = 0$) lactide polymerization. The initial spike from $PDI = 1$ to 1.01 is a result of the initial condition $P_2 = I$ and decreases with decreasing I . The resulting *PDI* for reversible and irreversible lactide polymerization up to 5θ are nearly indistinguishable. The *PDI* results for reversible lactide polymerization ($t < 5\theta$) in the absence of transesterification are in accord with the Poisson distribution result for living polymerization, $PDI = 1 + 1/X_n = 1 + 1/(M/OH^*(1 - M_{eq})) = 1.001$. Based on the known lactide polymerization kinetics and presented kinetic scheme for dimeric ring-opening polymerization, we conclude that the effect of the reversible aspect of lactide polymerization on the MWD is unimportant during practical polymerization times. Therefore, intermolecular polymer interchange reactions during lactide polymerization must be entirely responsible for the approach of the MWD toward the most probable distribution.

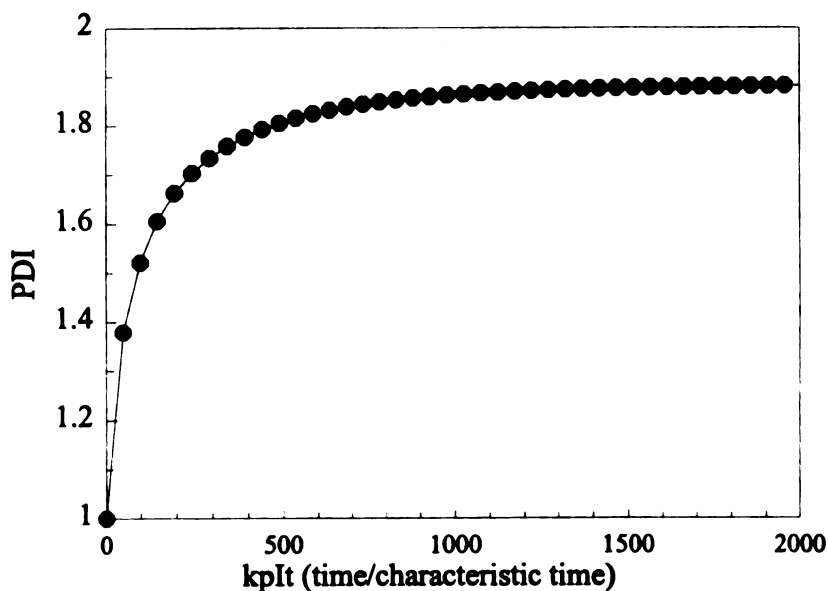


Figure 3-21. $PDI(t)$ simulation results for reversible lactide polymerization in the absence of transesterification. The characteristic polymerization time is $\theta = 1/(k_p I)$. Although the most probable distribution result is approached after 5000, only 30 are required to practically complete lactide polymerization.

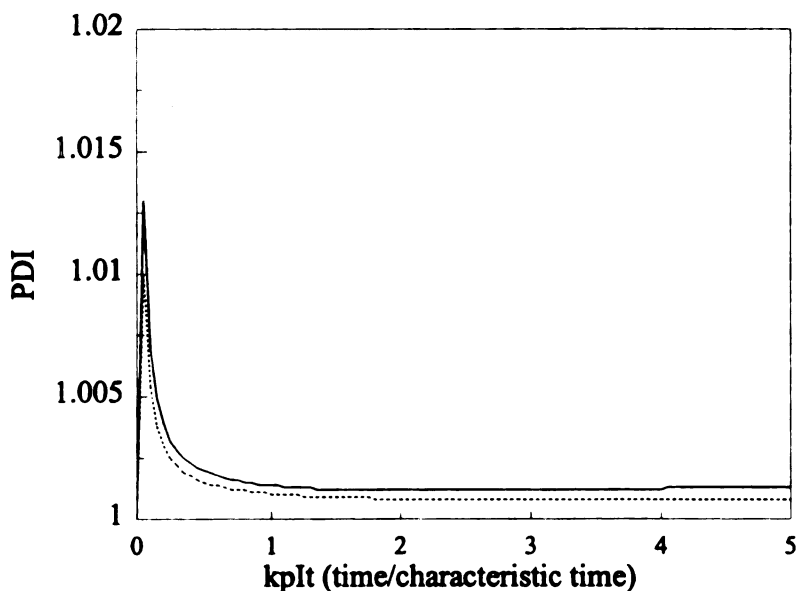


Figure 3-22. $PDI(t)$ simulation results for both reversible (solid line) and irreversible (dashed line) lactide polymerization in the absence of transesterification. In normal polymerization times the contribution of reversibility to the MWD is insignificant.

Effect of Temperature on MWD During Polymerization

Figure 3-23 presents *PDI* versus time data taken during lactide polymerizations at 130, 160, 190, and 220°C ($M/I = 10,000$ mol/mol). Experimental procedures and rate data for these polymerizations were presented in Section 3.2. Each datum is a separate vial polymerization and each curve represents numerous vial polymerizations taken from the same temperature bath. This procedure enhances confidence in the results (averaging) but adds scatter to the data curves. The rise in $PDI(t)$ towards the most probable value of 2 increases with temperature. To compare these data at a constant extent of lactide polymerization, Figure 3-24 presents a plot of *PDI* versus $k_p I t = t/\theta$. These results indicate that the *PDI* development is reduced with increased temperature at a constant extent of polymerization. Therefore, we find that polymerization has a greater temperature sensitivity (activation energy) than transesterification as measured by *PDI*.

Figure 3-25 is a plot of *PDI* versus $k_p I t$ up to a time of 50. The 130°C *PDI* data is initially the highest (low t/θ) but lags behind the *PDI* of higher temperature polymerizations at high conversion where a final value of $PDI = 1.64$ is achieved at 8.70 (Table 3-5). The apparent decrease in transesterification rate at 130°C is a result of crystallization accompanying polymerization at this low temperature. This is interesting because we found that crystallization increases the polymerization rate (Section 3.2). The main difference is that lactide is excluded from crystalline domains whereas the chain repeat units participate in the crystalline domains.

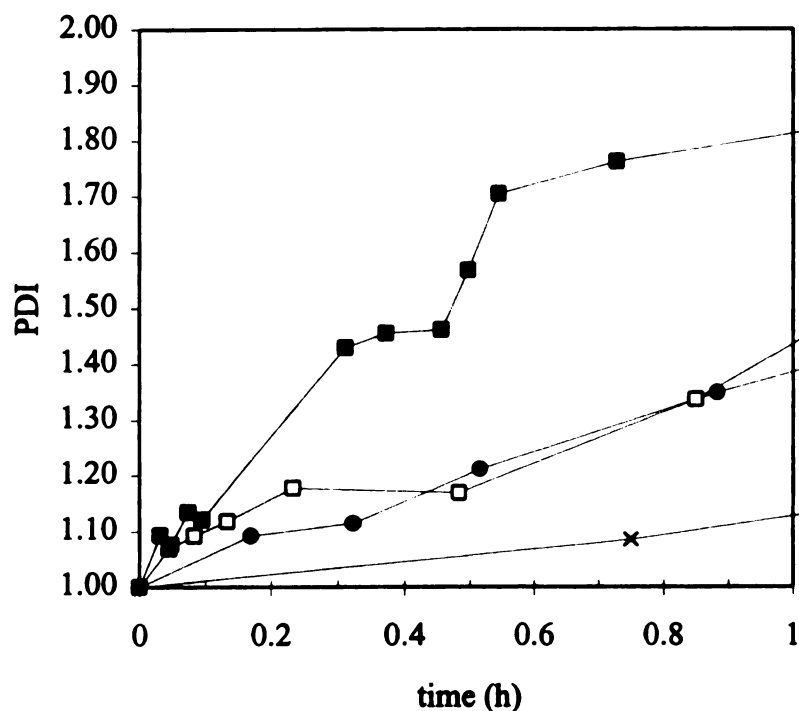


Figure 3-23. *PDI* versus time curves for lactide polymerization ($M/I = 10,000$) at 130°C (x), 160°C (●), 190°C (□), and 220°C (■).

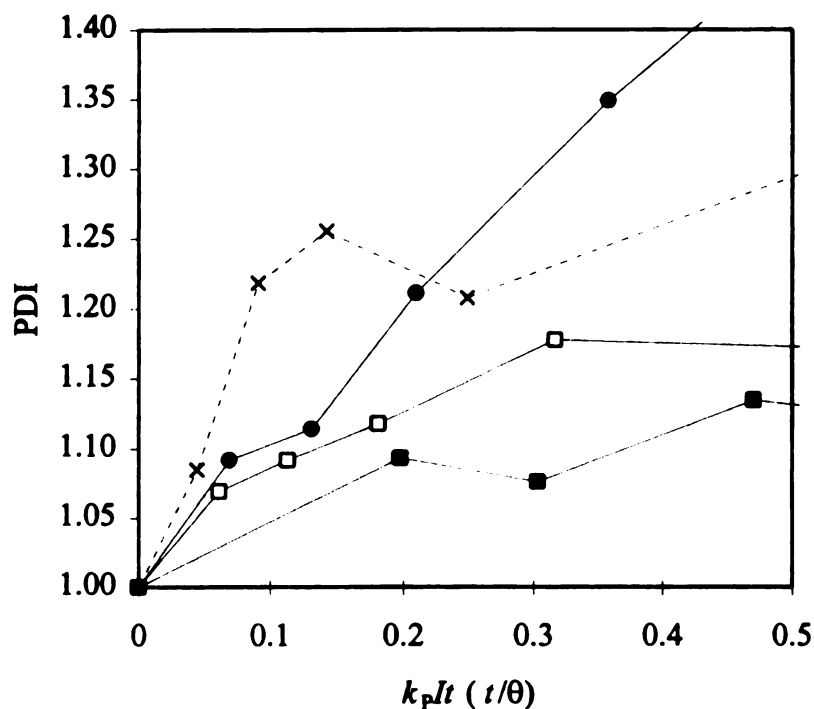


Figure 3-24. *PDI* versus $k_p I t = t/\theta$ curves for lactide polymerization ($M/I = 10,000$) at 130°C (x), 160°C (●), 190°C (□), and 220°C (■). The *PDI* values at constant extent of polymerization are lower for higher temperature polymerizations. This indicates that the rate increase with temperature is greater for polymerization than for transesterification as measured by *PDI*.

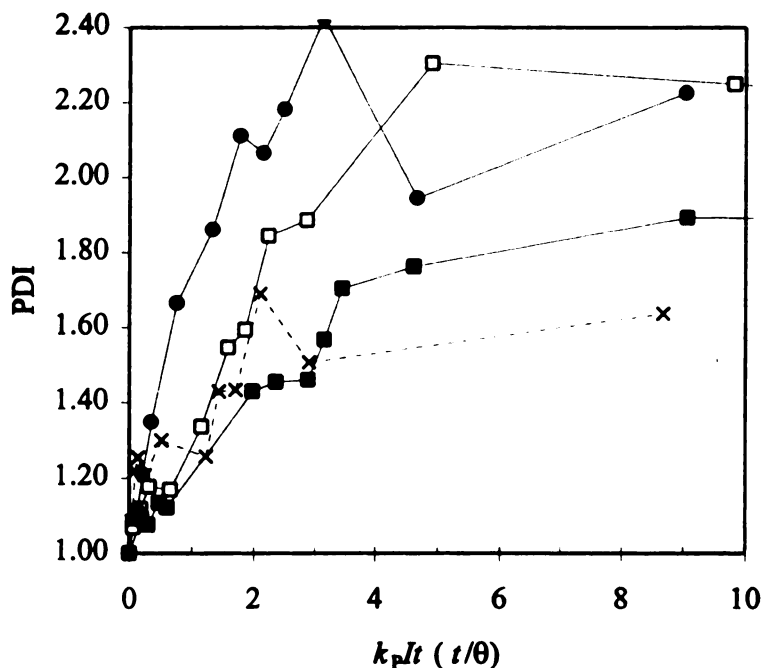


Figure 3-25. *PDI* versus $k_p I t = t/\theta$ curves up to a time of 10 θ for lactide polymerization ($M/I = 10,000$) at 130°C (x), 160°C (●), 190°C (□), and 220°C (■). Crystallization accompanies polymerization at 130°C and is responsible for the decreasing transesterification rate.

Effect of Catalyst Level on MWD

The influence of catalyst concentration on $PDI(t)$ at 130°C and 220°C is depicted in Figures 3-26 and 3-27. At both polymerization temperatures the rise of $PDI(t)$ increases with catalyst concentration. In Figures 3-28 and 3-29 we plot this same PDI data versus $k_p I t$ to compare the importance of catalyst concentration on PDI development to its first-order influence on polymerization. At 130°C the PDI versus $k_p I t$ curves at $M/I = 1000$, 3000, and 20,000 are equivalent. At 220°C the $M/I = 20,000$ PDI data is somewhat higher than the others (note its $PDI(t)$ rise was similar to that of $M/I = 10,000$ in Figure 3-27) but there is no apparent PDI trend with catalyst concentration. These results indicate that transesterification as measured by PDI development has a similar

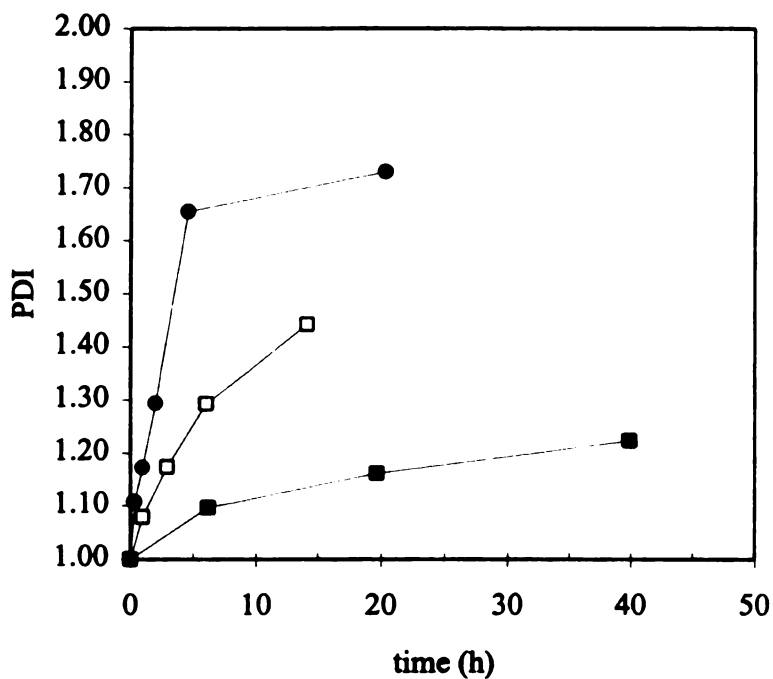


Figure 3-26. $PDI(t)$ curves for lactide polymerization at 130°C with various catalyst concentrations: $M/I = 1,000$ mol lactide/mol Sn(II) (●); $M/I = 3,000$ (□); $M/I = 20,000$ (■).

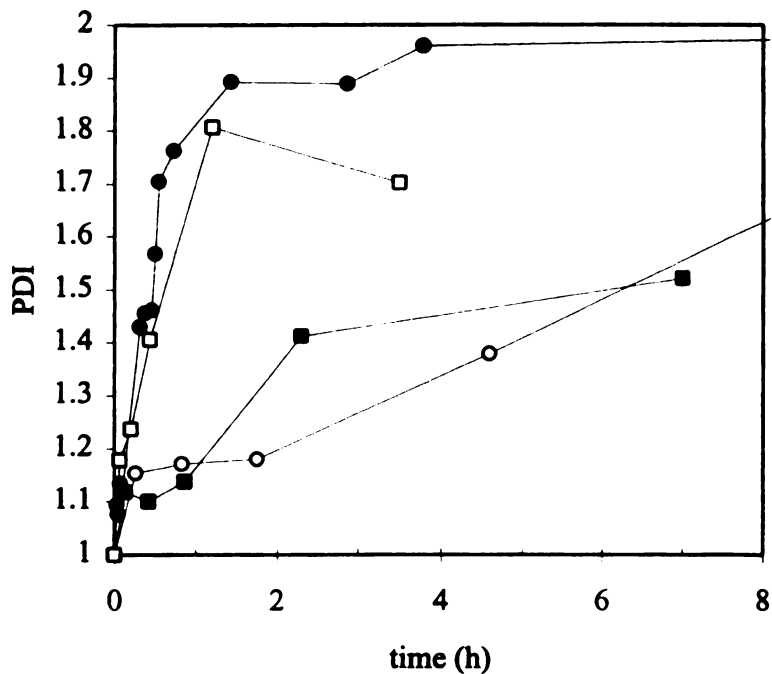


Figure 3-27. $PDI(t)$ curves for lactide polymerization at 220°C with various catalyst concentrations: $M/I = 10,000$ mol lactide/mol Sn(II) (●); $M/I = 20,000$ (□); $M/I = 40,000$ (■); $M/I = 80,000$ (○).

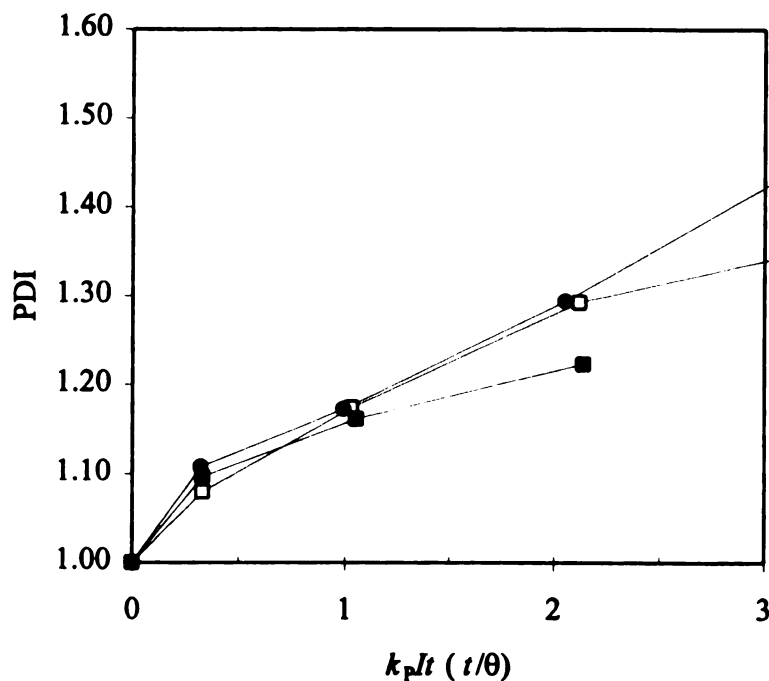


Figure 3-28. *PDI* versus $k_p I t (t/\theta)$ for lactide polymerization at 130°C with various catalyst concentrations: $M/I = 1,000$ mol lactide/mol Sn(II) (●); $M/I = 3,000$ (□); $M/I = 20,000$ (■).

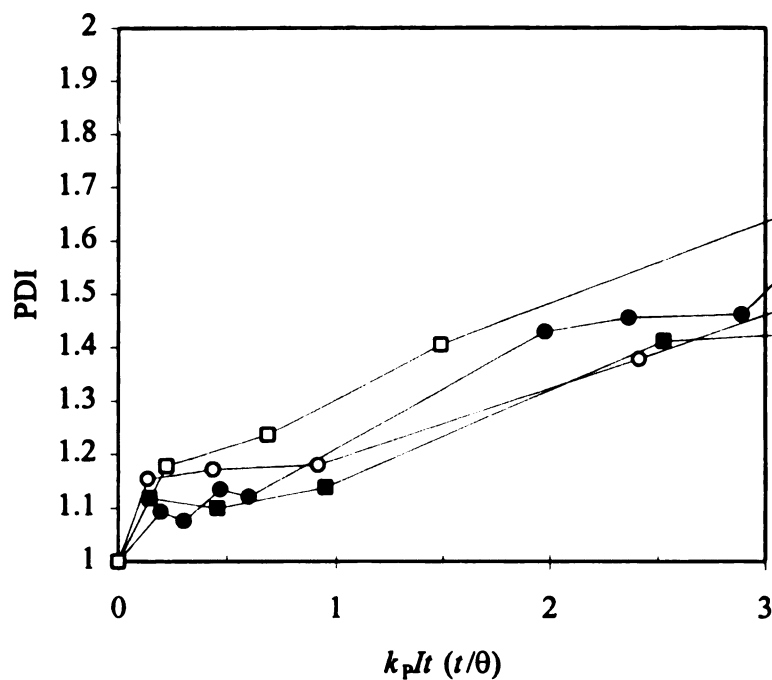


Figure 3-29. *PDI* versus $k_p I t (t/\theta)$ for lactide polymerization at 220°C with various catalyst concentrations: $M/I = 10,000$ mol lactide/mol Sn(II) (●); $M/I = 20,000$ (□); $M/I = 40,000$ (■); $M/I = 80,000$ (○).

catalyst dependence as polymerization. Both types of reactions involve catalyzed hydroxyl attack on an ester group — lactide ester group with polymerization, PLA ester group with polymer interchange.

Importance of Initiation and Degradation on μ_0 During Polymerization

Transesterification reactions redistribute the repeat units among the polymer chains but do not affect the number of polymer chains, μ_0 . Information on how μ_0 changes with time because of slow initiation or degradation reactions is required to determine the transesterification rate constant. Slow initiation exhibits an increase in μ_0 at early time whereas non-hydrolytic degradation increases μ_0 throughout polymerization.

Figures 3-30 and 3-31 presents plots of μ_0 versus $k_p I t$ for various lactide polymerizations at 130°C and 220°C. The μ_0 values are determined from conversion and molecular weight data analyzed by GPC, $\mu_0 = X_{\text{mon}} * 1\text{E}6 / M_n$. Differences in μ_0 between curves are a result of lactide purity differences prior to polymerization (M/OH values). There is no evidence of increased μ_0 during polymerization at 130°C (the high μ_0 value near 80 mmol/kg is an outlier). This indicates that initiation is fast and degradation unimportant at 130°C. The 220°C data, however, has an upward μ_0 trend during polymerization because of non-hydrolytic chain cleavage. A non-hydrolytic degradation rate model is presented in Section 3.5. Initiation at 220°C is fast compared to polymerization.

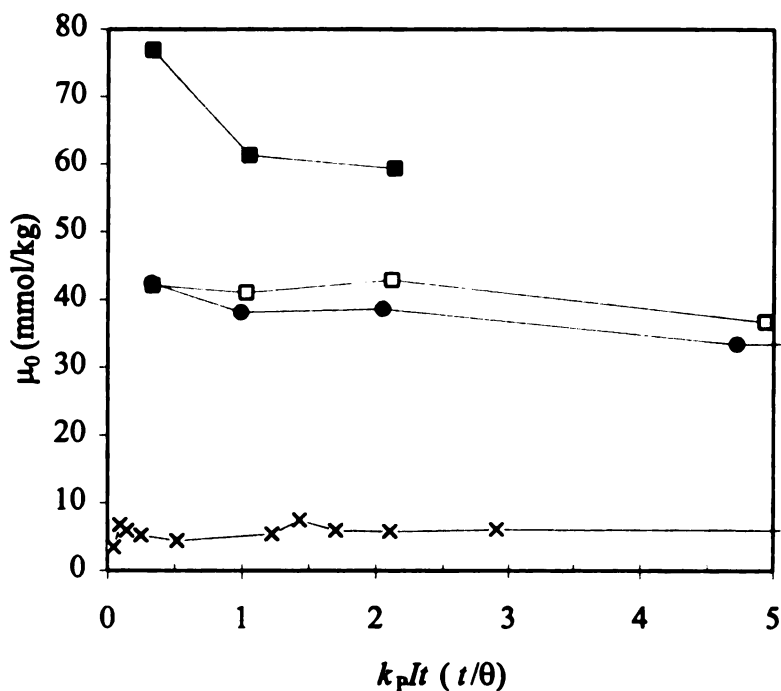


Figure 3-30. μ_0 versus $k_p I t \ (t/\theta)$ for lactide polymerization at 130°C with various catalyst concentrations: $M/I = 1,000$ mol lactide/mol Sn(II) ($\bullet$); $M/I = 3,000$ ($\square$); $M/I = 10,000$ ($\times$); $M/I = 20,000$ ($\blacksquare$). The results indicate that initiation is fast and degradation reactions are unimportant at 130°C.

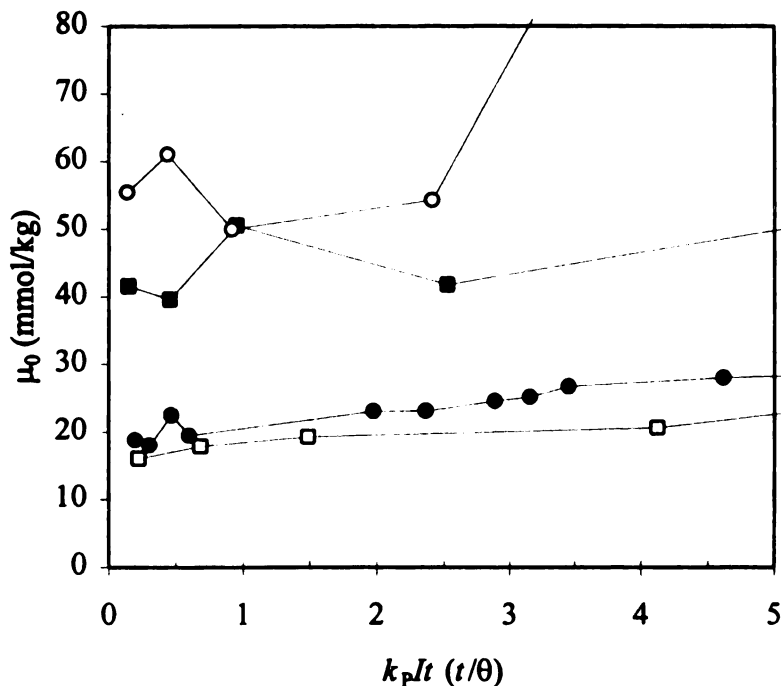


Figure 3-31. μ_0 versus $k_p I t \ (t/\theta)$ for lactide polymerization at 220°C with: $M/I = 10,000$ mol lactide/mol Sn(II) ($\bullet$); $M/I = 20,000$ ($\square$); $M/I = 40,000$ ($\blacksquare$); $M/I = 80,000$ ($\circ$). The positive slope of μ_0 is a result of non-hydrolytic chain degradation at 220°C.

Conclusions

Polymer interchange reactions represent the approach to an equilibrium distribution of molecular sizes (most probable distribution). They are responsible for the development of very high molecular weight PLA chains late in the polymerization. The results of a chain population simulation of reversible lactide polymerization with known kinetics confirm that the effect of reversibility on the MWD is unimportant for practical polymerization times. During lactide polymerization the *PDI* rise versus conversion decreases with increased temperature; therefore, polymerization has a greater activation energy than transesterification as measured by *PDI*. Analyses of polymerization data over a wide range of temperatures and catalyst concentrations indicate that transesterification reactions among polymer chains are catalyzed by the polymerization catalyst. Initiation is found to be fast compared to polymerization at 130 and 220°C. Non-hydrolytic degradation reactions during polymerization are unimportant at 130°C. However, nonhydrolytic degradation is important at 220°C and needs to be taken into account in the determination of the transesterification rate constant.

3.4.2 Transesterification Kinetic Schemes

In this section we investigate the role of the Sn(II)ethylhexanoate catalyst during lactide polymerization by evaluating two alternative transesterification kinetic models with vial polymerization data. The free-catalyst kinetic scheme assumes equal catalysis of all chains; the catalyst is effectively free to coordinate transesterification between any OH end group and ester. The catalyst is presumed to be either physically free in the reaction

mixture or that it can swap in and out of chains at a rate that is fast compared to propagation and polymer interchange. In the Sn(II) alkoxide insertion kinetic scheme only chains bonded to the catalyst can initiate an ester group. A polymer ligand (or OH ligand) is assumed to have an alkoxide bond with the catalyst. In this kinetic scheme we track the location of the catalyst molecules in the polymer chains. The transesterification reactions must swap the reaction centers among polymer chains at a sufficient rate such that a unimodal distribution is preserved among the living (catalyst containing) and dormant chain populations.

Free-Catalyst Kinetic Scheme

In the free-catalyst kinetic scheme the Sn(II) catalyst is free to facilitate transesterification between *any* nearby terminal hydroxyl group and either a lactide ester group (propagation) or a polymer ester group (polymer interchange by alcoholysis). Reaction between a carboxylic acid end group and an ester may also occur but the rate is known to be considerably slower than that of alcoholysis and is not considered here. With the free-catalyst kinetic scheme we first derive the polymer chain population balances for catalyzed intermolecular transesterification. Then we transform these balances to ordinary differential equations describing the moments of the molecular weight distribution. The moment equations are solved by numerical integration and the rate parameters are estimated from $X_{\text{mon}}(t)$, $M_n(t)$, and $M_w(t)$ L-lactide batch polymerization data at temperatures and catalyst concentrations of industrial interest. The PLA transesterification rate constant is determined between 160-220°C.

In deriving the chain population balances for polymer interchange we assume equal reactivities of functional groups. We must include the factor I/μ_0 (ratio of Sn(II) catalyst to total number of chains) with the rate constants to properly account for the probability that a certain terminal OH group will initiate transesterification in this kinetic scheme. We will first consider only polymer interchange and later add the effect of polymerization on the chain distribution. The following nomenclature is used: P_n , k_x , μ_0 , and μ_1 are the number of polymer chains of length n , the transesterification rate constant, the total number of polymer chains (zeroth moment of the molecular weight distribution), and the total number of repeat units (first moment of the molecular weight distribution), respectively. The polymer interchange reaction may be written as,



The change of P_n with time during polymer interchange can be described by three loss terms and five generation terms:

Loss terms

$$-\frac{\mu_0}{k_x I} \frac{dP_n}{dt} = (n-1)P_n(\mu_0 - P_n) \quad \text{Attack on } P_n \text{ by all chains except those of length } n.$$

$$-\frac{\mu_0}{k_x I} \frac{dP_n}{dt} = 2(n-1)P_n(P_n - 1) \quad \text{Attack on } P_n \text{ by all other chains of length } n.$$

$$-\frac{\mu_0}{k_x I} \frac{dP_n}{dt} = P_n [(\mu_1 - \mu_0) - (n-1)P_n]$$

Attack by P_n on all chains except P_n .

Generation terms

$$\frac{\mu_0}{k_x I} \frac{dP_n}{dt} = P_n \sum_{i=1}^{n-1} P_i$$

Attack by all chains smaller than n on P_n .

$$\frac{\mu_0}{k_x I} \frac{dP_n}{dt} = P_n \sum_{j=n+1}^{\infty} P_j$$

Attack by P_n on all chains bigger than n .

$$\frac{\mu_0}{k_x I} \frac{dP_n}{dt} = \sum_{j=n+1}^{\infty} P_j \left[\left(\sum_{i=n+1}^{\infty} P_i \right) - 1 \right]$$

Attack by a chain $> n$ on chain $> n$.

$$\frac{\mu_0}{k_x I} \frac{dP_n}{dt} = \sum_{i=1}^{n-1} P_i \sum_{j=n+1}^{\infty} P_j + \sum_{i=n+1}^{\infty} P_i \left[\left(\sum_{j=1}^{n-1} P_j \right) - P_1 \right]$$

Attack by a chain $< n$ on chain $> n$.

$$\frac{\mu_0}{k_x I} \frac{dP_n}{dt} = \sum_{i=2}^{n-1} P_i \left(\sum_{j=n+1-i}^{n-1} P_j - \sum_{i \geq (n+1)/2}^{n-1} P_i \right)$$

Attack by a chain $< n$ on chain $< n$.

Combining loss and generation terms, simplifying, and dividing through by $1/N_A^2$ to

convert from a molecular basis to a molar basis we obtain

$$-\frac{\mu_0}{k_x I} \frac{dP_n}{dt} = [(n-3)\mu_0 + \mu_1 + P_n]P_n - \sum_{j=n+1}^{\infty} P_j \left(\sum_{i=1}^{n-1} P_i + \mu_0 - P_n - P_1 \right) - \sum_{i=2}^{n-1} P_i \sum_{j=n+1-i}^{n-1} P_j \quad (3-19)$$

This relationship is further simplified by substituting

$$\sum_{i=1}^{n-1} P_i \sum_{j=n+1-i}^{\infty} P_j = \sum_{i=1}^{n-1} P_i \sum_{j=n+1-i}^{n-1} P_j + \sum_{i=1}^{n-1} P_i \sum_{j=n+1}^{\infty} P_j + P_n \sum_{i=1}^{n-1} P_i$$

to obtain

$$-\frac{\mu_0}{k_x I} \frac{dP_n}{dt} = [(n-2)\mu_0 + \mu_1]P_n - \mu_0 \sum_{j=n+1}^{\infty} P_j - \sum_{i=1}^{n-1} P_i \sum_{j=n+1-i}^{\infty} P_j \quad (3-20)$$

When $I = \mu_0$ (or for uncatalyzed transesterification) equation (3-20) is identical to that found by Hermans⁴⁴ for polymer interchange. Polymer interchange reactions do not affect the number of polymer chains and Equation (3-20) has the property

$$\begin{aligned} \frac{-\mu_0}{k_x I} \frac{d \sum_{n=1}^{\infty} P_n}{dt} &= (\mu_0 - P_1)(\mu_1 - \mu_0) + (\mu_1 - \mu_0)\mu_0 + (-\mu_1 + 2\mu_0 - P_1)\mu_0 \\ &\quad + (-\mu_1 + \mu_0)\mu_0 - (\mu_0 - P_1)^2 + P_1(\mu_1 - 2\mu_0 + P_1) \end{aligned}$$

or

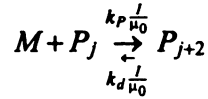
$$\frac{d \sum_{n=1}^{\infty} P_n}{dt} = \frac{d\mu_0}{dt} = 0 \quad (3-21)$$

Table 3-6 summarizes the species balances for reversible ring-opening polymerization with polymer interchange.

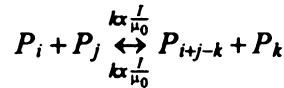
The tracking of each chain species is computationally intensive, and it is worthwhile to reduce the population balances to ordinary differential equations for the moments of the molecular weight distribution. This makes practical sense because we correlate polymer physical properties to the moment averages (e.g., M_n , M_w , M_z). A discussion on the use of mathematical methods to calculate molecular weight distributions from kinetic schemes is provided by Bamford and Tompa.⁴⁵

Table 3-6 Summary of Free-Catalyst Kinetic Scheme and Resulting Species Population Balances

Reversible Polymerization



Transesterification



Monomer Balance

$$\frac{-dM}{dt} = k_p I (M - M_{eq})$$

Lactic Acid Balance ($n = 1$)

$$\frac{-dP_1}{dt} = \frac{k_p I}{\mu_0} (MP_1 - M_{eq}P_3) + \frac{k_x I}{\mu_0} (\mu_1 P_1 - \mu_0^2)$$

Lactoyllactic Acid Balance ($n = 2$)

$$\frac{-dP_2}{dt} = \frac{k_p I}{\mu_0} (MP_2 - M_{eq}P_4) + \frac{k_x I}{\mu_0} (\mu_1 P_2 - \mu_0^2 + \mu_0(P_2 + P_1))$$

PLA Chain Balances ($n = j > 2$)

$$\begin{aligned} \frac{-dP_j}{dt} = & \frac{k_p I}{\mu_0} \{M(P_j - P_{j-2}) - M_{eq}(P_{j+2} - P_j)\} \\ & + \frac{k_x I}{\mu_0} \left\{ (\mu_1 + (j-2)\mu_0)P_j - \mu_0 \sum_{j=i+1}^{\infty} P_j - \sum_{i=2}^{j-1} P_i \sum_{k=j+1-i}^{\infty} P_k \right\} \end{aligned}$$

Overall Chain Balance

$$\frac{d \sum_{j=1}^{\infty} P_j}{dt} = \frac{d\mu_0}{dt} = 0$$

The k^{th} moment of the molecular weight distribution is related to the chain species populations as follows: $\mu_k = \sum_n n^k P_n$. Differentiating this equation with respect to time

yields $\frac{d\mu_k}{dt} = \sum_n n^k \frac{dP_n}{dt}$. By substituting this equation into the population balances in Table 3-6 we obtain ordinary differential equations of the form

$$\frac{d\mu_k}{dt} = f_k(\mu_0, \mu_1, \mu_2, \mu_3) \quad k = 0, 1, 2 \quad (3-22)$$

After substitution and algebraic manipulation the resulting ODEs are presented in Table 3-7.

The ODEs describing the moments are open-ended because each moment ($k > 1$) is a function of the next higher moment. Therefore, a closure method is required to solve the ODEs. The procedure is to truncate the moment equations at some $k > 2$ and close the ODEs by transforming $\mu_k = f(\mu_0, \mu_1, \dots, \mu_{k+1})$ into $\mu_k = f(\mu_0, \mu_1, \dots, \mu_{k-1})$. A common moment closure procedure is based on the Γ -distribution (Schultz-Zimm distribution) and is outlined by Saidel and Katz.⁴⁶ For $k = 3$ this procedure yields the result provided by Tai et al.⁴⁷ and Gupta et al.⁴⁸:

$$\mu_3 \cong \frac{\mu_2(2\mu_2\mu_0 - \mu_1^2)}{\mu_1\mu_0} \quad (3-23)$$

We check the accuracy of this approximation by calculating μ_3 from GPC data ($M(t)$, M_n , M_w , M_z) for the vial polymerizations described in Section 3.2 where: μ_0 (mol/L) = $72\mu_1/M_n$; μ_1 (mol/L) = $2(M_0 - M(t))$, μ_2 (mol/L) = $M_w\mu_1/72$, and μ_3 (mol/L) = $M_z\mu_2/72$. Figure 3-32 presents measured and calculated $\mu_3(t)$ for a lactide polymerization at 190°C and $M/I = 10,000$. Good agreement between measured and calculated $\mu_3(t)$ is

observed. We generally find that the error in using equation (3-23) to estimate $\mu_3(t)$ is insignificant during most of the polymerization and less than 5% at the conclusion of lactide polymerization, $t = 3\theta$.

**Table 3-7 Moment Balances for Reversible Lactide Polymerization
with Polymer Interchange for Free-Catalyst Kinetic Scheme**

Zeroth Moment

$$\frac{d\mu_0}{dt} = 0$$

First Moment

$$\frac{d\mu_1}{dt} = -2k_p I (M_{eq} - M)$$

Second Moment

$$\frac{d\mu_2}{dt} = -\frac{k_p I}{\mu_0} \{4\mu_1(M_{eq} - M) - 4\mu_0(M_{eq} + M)\} - \frac{k_x I}{\mu_0} \left\{ \frac{1}{3}\mu_0(\mu_3 - \mu_1) - \mu_1\mu_2 + \mu_1^2 \right\}$$

where

$$M(t) = M_{eq} + (M_o - M_{eq})\exp(-k_p I t)$$

$$k_p \left(\text{mol}\% \text{cat}^{-1} \text{hr}^{-1} \right) = 86.0 \exp \left(-8528 \left(\frac{1}{T(K)} - \frac{1}{448} \right) \right)$$

$$\mu_0 = [OH]$$

$$\mu_1 = 2(M_o - M(t))$$

$$\mu_3 = f(\mu_0, \mu_1, \mu_2, \mu_3, \mu_4)$$

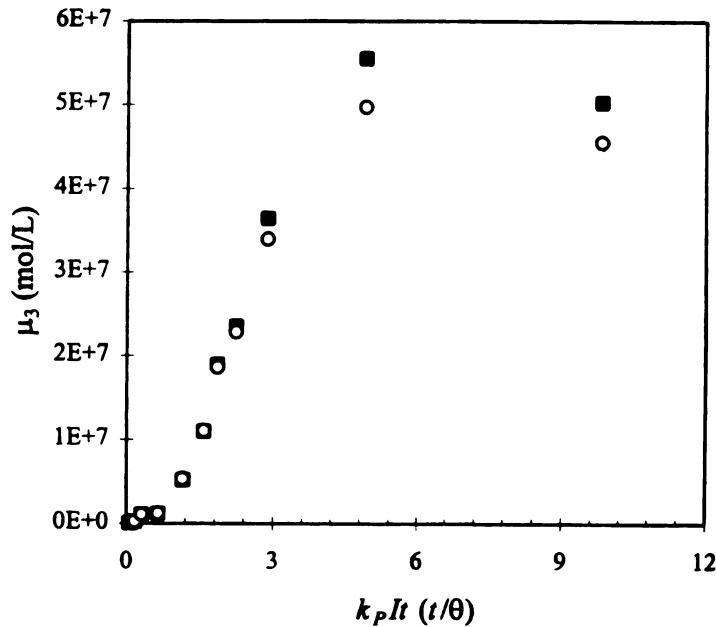


Figure 3-32. Measured (■) and calculated (○) μ_3 versus dimensionless polymerization time for batch lactide polymerization at 190°C and M/I (mol/mol) = 10,000.

With μ_0 known prior to polymerization from [OH] GC analytical data, $\mu_1(t)$ calculated from known polymerization kinetics, and the moment equations truncated at $\mu_3 = f(\mu_2)$, we obtain a single differential equation for $\mu_2(t)$. Substituting $\mu_1 = 2(M_0 - M(t))$ and $\mu_3 = f(\mu_2)$ into $d\mu_2/dt$ in Table 3-7 and simplifying ($\mu_1 M \gg \mu_0 M$, $\mu_0 \mu_3 \gg \mu_0 \mu_1$, and $\mu_0 \mu_3 \gg \mu_1^2$) we obtain

$$\frac{d\mu_2}{dt} = -8 \frac{k_p I}{\mu_0} (M_0 - M(t))(M_{eq} - M(t)) - \frac{1}{3} \frac{k_x I}{\mu_0} \left[\frac{\mu_0}{(M_0 - M(t))} \mu_2^2 - 8(M_0 - M(t)) \mu_2 \right] \quad (3-24)$$

This first-order nonlinear differential equation is in the form of Ricatti's equation:

$$\frac{dy}{dx} = P(x) + Q(x)y + R(x)y^2. \text{ At steady state } d\mu_2/dt = 0, M(t) = M_{eq}, \text{ and } \mu_1, \mu_2, \text{ and } \mu_3$$

reduce to:

$$\mu_1 = 2(M_0 - M_{eq}) \quad (3-25)$$

$$\mu_2 = \frac{8(M_0 - M_{eq})^2}{\mu_0} \quad (3-26)$$

$$\mu_3 = \frac{48(M_0 - M_{eq})^3}{\mu_0^2} \quad (3-27)$$

Therefore, at steady state M_w/M_n and M_z/M_w reduce to their expected values:

$$PDI = \frac{M_w}{M_n} = \frac{\mu_2 \mu_0}{\mu_1^2} = 2 \quad (3-28)$$

$$\frac{M_z}{M_w} = \frac{\mu_3 \mu_1}{\mu_2^2} = 1.5 \quad (3-29)$$

The procedure for determining k_x for a L-lactide vial polymerization is as follows:

- (1) determine the propagation rate constant, k_p , by regression of $X_{\text{mon}}(t)$ data (Section 3.2);
- (2) determine $\mu_0(t)$ from $X_{\text{mon}}(t)$ and $M_n(t)$ data; (3) determine k_x by numerically integrating equation (3-24) for $\mu_2(t)$ and fitting $X_{\text{mon}}(t)$, $M_n(t)$, and $M_w(t)$ data. That is, we find k_x that best fits the $PDI(t)$ data with known $M(t)$, $\mu_0(t)$, and k_p .

The numerical integration for $\mu_2(t)$ was performed in Microsoft Excel using a simple Euler method. Step (2) is required because μ_0 increases somewhat during the vial polymerizations. This may be a result of non-instantaneous initiation, moisture leakage during the experiment, or slow thermal degradation. For each polymerization, $\mu_0(t)$ data

were fit to either a polynomial model or a three parameter exponential model of the form $\mu_0(t) = p_1 + (p_2 - p_1)\exp(p_3 \cdot t)$. By accounting for the measured change of μ_0 with time the $PDI(t)$ fits were improved. However, the k_x values did not change much when μ_0 was taken to be constant.

The transesterification rate constant, k_x , was determined for L-lactide vial polymerizations at 160-220°C and 10,000-80,000 M/I (mol/mol). Figures 3-33 to 3-38 present the $PDI(t)$ fits for k_x . The first three figures are for $M/I = 10,000$ polymerizations at 160, 190, and 220°C, respectively. The agreement between data and model for this kinetic scheme is generally good. Figures 3-36 to 3-38 present $PDI(t)$ fits for 220°C polymerizations at $M/I = 20000$, 40000, and 80000, respectively. These plots have limited data but give an order-of-magnitude value for k_x . The curve fits at 220°C differ from those at lower temperatures in that the model underestimates the early time PDI data. In all figures the kinetic PDI model has an initial increase and decrease after zero time. This is a result of the initialization condition (all chains are chosen to start at size P_2) and does not affect the regressed k_x value.

A summary of k_x and k_p kinetic rate constants at the various I and T polymerization conditions is presented in Table 3-8. Without the incorporation of the I/μ_0 factor that appears with the rate constants in the kinetic scheme we cannot draw inferences on the temperature dependency of the transesterification rate constant. This confirms the first-order catalyst dependency and supports the mechanistic hypothesis that the rate of a certain OH group initiating esterification is proportional to the concentration ratio of catalyst molecules to OH end groups (ratio of living to dormant chains at a given

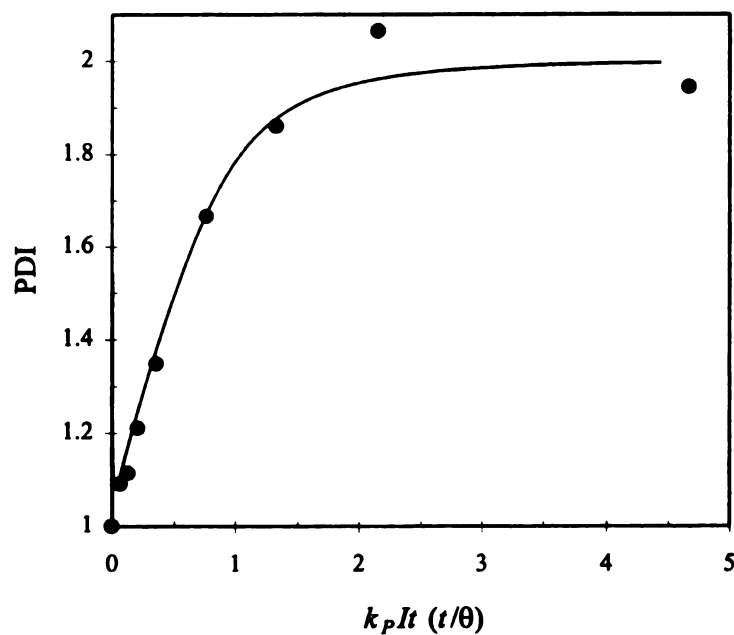


Figure 3-33. Kinetic model (solid line: $k_x = 0.13 \text{ mol\%cat}^{-1}\text{hr}^{-1}$; $k_p = 40.1 \text{ mol\%cat}^{-1}\text{hr}^{-1}$) and data (●) for L-lactide vial polymerization at 160°C and $M/I \text{ (mol/mol)} = 9885$.

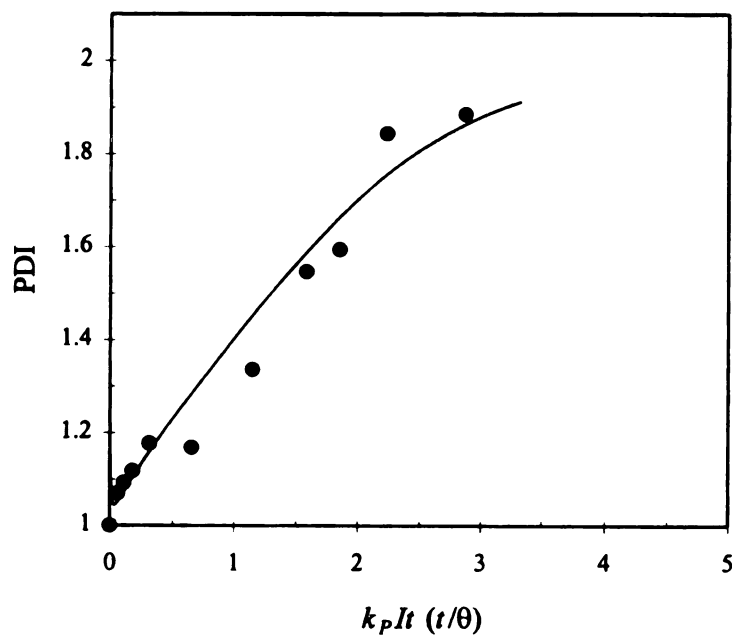


Figure 3-34. Kinetic model (solid line: $k_x = 0.27 \text{ mol\%cat}^{-1}\text{hr}^{-1}$; $k_p = 136 \text{ mol\%cat}^{-1}\text{hr}^{-1}$) and data (●) for L-lactide vial polymerization at 190°C and $M/I \text{ (mol/mol)} = 10,015$.

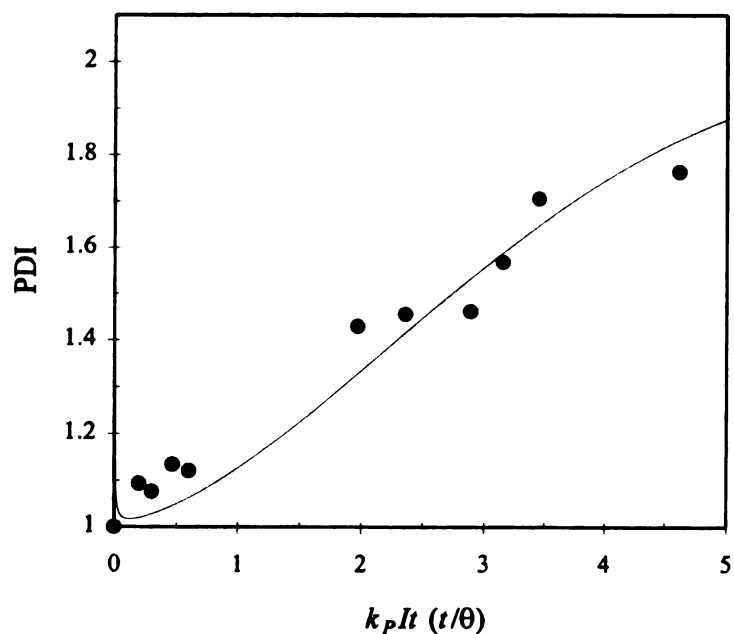


Figure 3-35. Kinetic model (solid line: $k_x = 0.48 \text{ mol\%cat}^{-1}\text{hr}^{-1}$; $k_p = 639 \text{ mol\%cat}^{-1}\text{hr}^{-1}$) and data (●) for L-lactide vial polymerization at 220°C and $M/I \text{ (mol/mol)} = 10,070$.

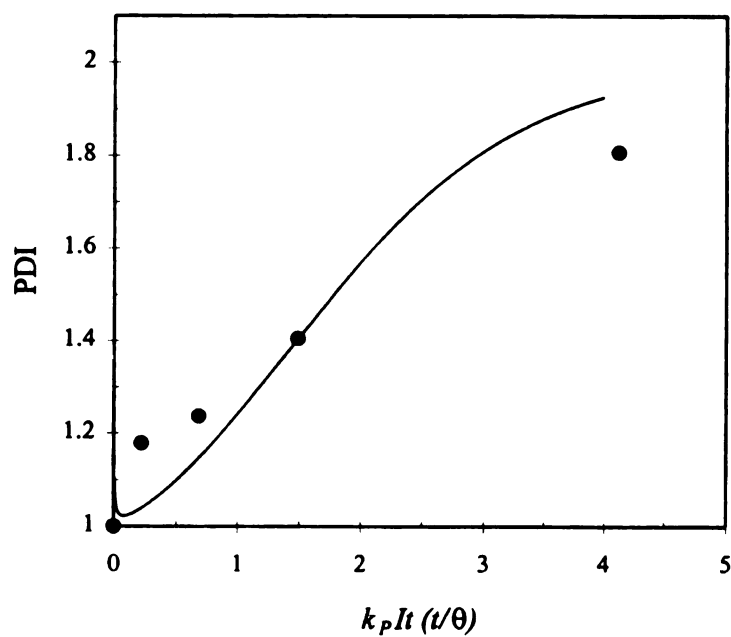


Figure 3-36. Kinetic model (solid line: $k_x = 1 \text{ mol\%cat}^{-1}\text{hr}^{-1}$; $k_p = 687 \text{ mol\%cat}^{-1}\text{hr}^{-1}$) and data (●) for L-lactide vial polymerization at 220°C and $M/I \text{ (mol/mol)} = 19,980$.

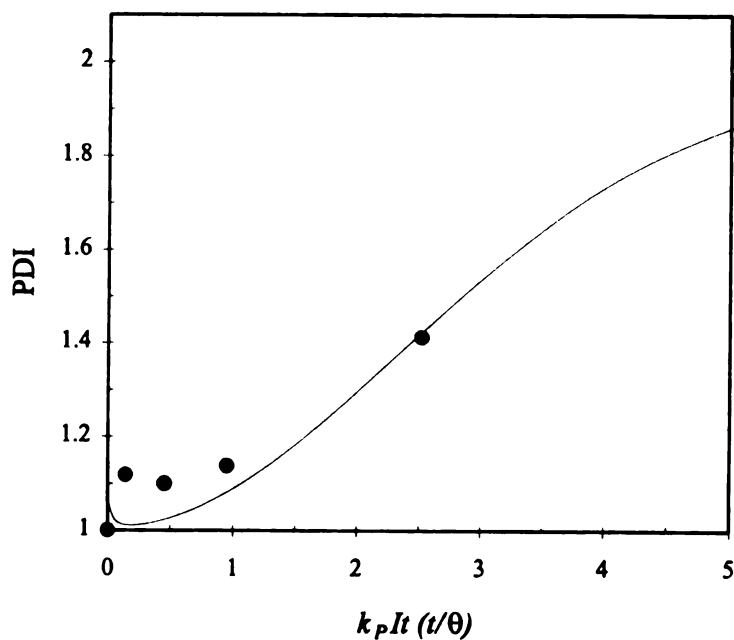


Figure 3-37. Kinetic model (solid line: $k_x = 1 \text{ mol\%cat}^{-1}\text{hr}^{-1}$; $k_p = 435 \text{ mol\%cat}^{-1}\text{hr}^{-1}$) and data (●) for L-lactide vial polymerization at 220°C and $M/I \text{ (mol/mol)} = 39,585$.

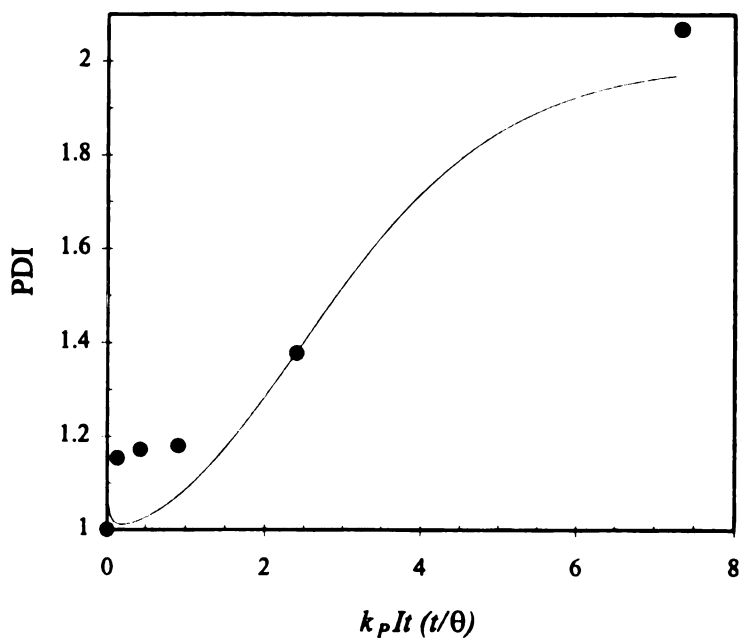


Figure 3-38. Kinetic model (solid line: $k_x = 1 \text{ mol\%cat}^{-1}\text{hr}^{-1}$; $k_p = 416 \text{ mol\%cat}^{-1}\text{hr}^{-1}$) and data (●) for L-lactide vial polymerization at 220°C and $M/I \text{ (mol/mol)} = 79,320$.

instant). In other words, only OH groups currently associated with catalyst molecules can initiate transesterification (propagation or polymer interchange) and all other OH groups (dormant chains; $\text{OH} > \text{I}$) must "wait their turn."

Table 3-8 Summary of Kinetic Rate Constants for Sn(II) Ethylhexanoate Catalyzed Lactide Polymerization

T (°C)	$\mu_0(\text{ave})$ (mol/L)	M/I (mol/mol)	I (mol%cat)	$k_x I / \mu_0$ (mol/L-hr) ⁻¹	k_x (mol%cat-hr) ⁻¹	k_p/k_x
160	0.0076	9,885	0.0101	0.18	0.13	300
190	0.0192	10,015	0.0100	0.14	0.27	500
220	0.0207	10,070	0.0099	0.23	0.48	1,300
220	0.0196	19,980	0.0050	<i>0.3</i>	<i>1</i>	
220	0.0454	39,585	0.0025	<i>0.05</i>	<i>1</i>	
220	0.0600	79,320	0.0013	<i>0.02</i>	<i>1</i>	

data in italics represent approximate values owing to incomplete PDI(t) data

The transesterification rate constant has an Arrhenius temperature dependence:

$$k_x \left(\text{mol\%cat}^{-1} \text{hr}^{-1} \right) = 0.19 \exp \left(-4600 \left(\frac{1}{T(K)} - \frac{1}{448K} \right) \right) \quad (3-30)$$

The activation energy of transesterification is 38 kJ/mol and is considerably lower than that of lactide propagation, $E_a = 70.9$ kJ/mol. This is consistent with the inferences made in Section 3.4.1 and indicates that for batch lactide polymerization to a given extent of equilibrium (e.g., $t = 3\theta$) a higher polymerization temperature will yield a lower *PDI*. At bulk lactide polymerization temperatures the lactide propagation rate doubles for a temperature increase of 16°C, whereas the transesterification rate doubles for a 32°C

increase. Figure 3-39 presents an Arrhenius plot comparing $k_p(T)$ to $k_x(T)$. The ratio k_p/k_x has an average increase of 330 to 1000 between 160 and 220°C. Because there are two ester units in lactide, $(k_p/2)/k_x$ represents the ratio of OH preference for a lactide ester to its preference for a polymer ester. When there is an equal amount of repeat units in unreacted monomer and polymer, an OH end group is 165 times more likely to initiate a lactide ester than a polymer ester at 160°C (99.4% of events).

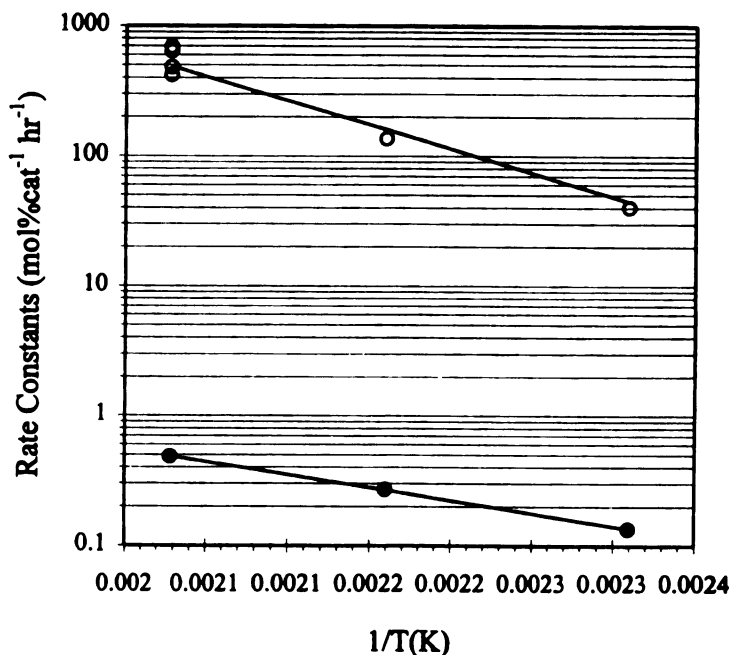


Figure 3-39. Kinetic rate constant data between 160-220°C: (○) k_p data; (●) k_x data. The solid lines represent Arrhenius fits referenced to 448K for k_p ($E_a = 70.9$ kJ/mol) and k_x ($E_a = 38$ kJ/mol).

Table 3-9 summarizes the methodology to estimate lactide conversion and MWD batch kinetics for input values of temperature, catalyst concentration, and initial OH concentration. The complete simulation is provided in Section 3.4.3 (FORTRAN code 2). This program assumes fast initiation and no degradation but can be amended for $\mu_0 = f(t)$.

Table 3-9 Summary of Methodology to Estimate $M(t)$ and MWD(t) For Batch L-Lactide Polymerization with the Free-Catalyst Kinetic Scheme

I. Input Polymerization Conditions: T , M/I , M/OH (by GC analysis)

II. Calculate Temperature Dependent Properties

$$\rho(\text{g/L}) = \frac{1145}{1 + 0.0007391(T(C) - 150)} \quad M_0(\text{mol/L}) = \frac{\rho}{144}$$

$$M_{eq}(\text{mol/L}) = \frac{\rho}{144} \exp\left(\frac{-23300}{8.314(T(C) + 273)} + \frac{22}{8.314}\right)$$

$$k_P I(\text{hr}^{-1}) = \left(\frac{100}{M/I}\right) 86 \exp\left(\frac{-70900}{8.314}\left(\frac{1}{(T(C) + 273)} - \frac{1}{448}\right)\right)$$

$$k_X I(\text{hr}^{-1}) = \left(\frac{100}{M/I}\right) 0.19 \exp\left(\frac{-38000}{8.314}\left(\frac{1}{(T(C) + 273)} - \frac{1}{448}\right)\right)$$

III. Calculate $M(t)$ and Moments

$$\mu_0(\text{mol/L}) = [OH] = \frac{M_0}{M/OH} = \text{constant}$$

$$\mu_1(t) = 2(M_0 - M_{eq})(1 + \exp(-k_P I t)) \quad M(t) = M_0 - \frac{\mu_1(t)}{2}$$

$\mu_2(t) \Rightarrow$ numerically integrate equation(3-24)

$$\mu_3(t) = \frac{\mu_2(2\mu_2(t)\mu_0 - \mu_1(t)^2)}{\mu_1(t)\mu_0}$$

IV. Calculate Lactide Conversion and MW Averages

$$X_{\text{mon}}(t) = 1 - \frac{M(t)}{M_0} \quad M_n(t) = 72 \frac{\mu_1(t)}{\mu_0} \quad M_w(t) = 72 \frac{\mu_2(t)}{\mu_1(t)} \quad M_z(t) = 72 \frac{\mu_3(t)}{\mu_2(t)}$$

The importance of condensation (polymer interchange at the COOH end group) on the $PDI(t)$ during polymerization was investigated with the free-catalyst kinetic scheme using a FORTRAN Monte Carlo type simulation (code 3 in Section 3.4.3.). The objective was to determine if condensation can account for increased PDI early in the polymerization where the prior model underpredicted PDI at 220°C. In this simulation initial amounts of OH impurities (P_2), lactide molecules, and catalyst molecules are input and the OH end groups are randomly chosen to initiate three different types of repeat units: lactide, polymer COOR, and polymer COOH groups. The susceptibility of attack on these three types of repeat units is input as probability factors (rate constant information). The basic strategy is: (1) randomly pick a polymer chain (OH) to attack, (2) randomly pick which type of repeat unit is attacked based on input probability factors, (3) once a repeat unit type is chosen pick which repeat unit is hit, (4) update size of attacking chain and receiving molecule, (5) repeat until desired lactide conversion is achieved. Liberated water on condensation is treated as a chain of length zero and is available for further initiation. The number of lactide molecules and size of each polymer chain are tracked throughout the simulation, and the PDI is determined as a function of the number of achieved characteristic times (calculated from conversion).

The simulation was performed with the condensation probability factor equal to: zero, that of polymer interchange, and that of lactide propagation. The results indicate that the $PDI(t)$ is unaffected when the condensation probability factor is changed from zero to that of polymer interchange. The Monte Carlo $PDI(t)$ simulation results are in agreement with the results of the moment-based program described in Table 3-9. When

the condensation probability factor was set equal to the propagation probability factor $PDI(t)$ increased, but the increase occurred over all time, not just at early time. Furthermore, the increased $PDI(t)$ can be matched by simply increasing the transesterification probability factor, or k_x in the moment-based model. Therefore, we make no change to the moment-based kinetic model to account for the case where the condensation rate constant is different from the transesterification rate constant.

The Monte Carlo simulation was also used to determine the average number of polymer interchange events per chain during polymerization. Figure 3-40 presents the results for 160, 190, and 220°C lactide polymerization with $M/OH = 700$ ($M_n = 100,000$ at complete conversion). At time equal to 3θ (95% of polymerization equilibrium) there are less than 9 interchange events/chain at 160°C, less than 5 interchange events/chain at 190°C, and less than 3 interchange events/chain at 220°C. At 3θ there are on average 645 dyads in each chain, indicating that only about 1% of the dyads are disrupted by intermolecular transesterification during polymerization at 160°C. This low quantity of dyad disruption is in accord with numerous NMR literature studies⁴⁹⁻⁵¹ that find minimal evidence of transesterification during lactide copolymer polymerization. However, this low frequency of polymer interchange events during polymerization is sufficient to broaden the MWD towards the Most Probable Distribution.

Sn(II) Alkoxide Insertion Kinetic Scheme

Zhang et al.⁴⁰ suggest that the true catalyst in the Sn(II)ethylhexanoate-lactide system may be stannous alkoxide formed by the reaction of Sn(II)ethylhexanoate with

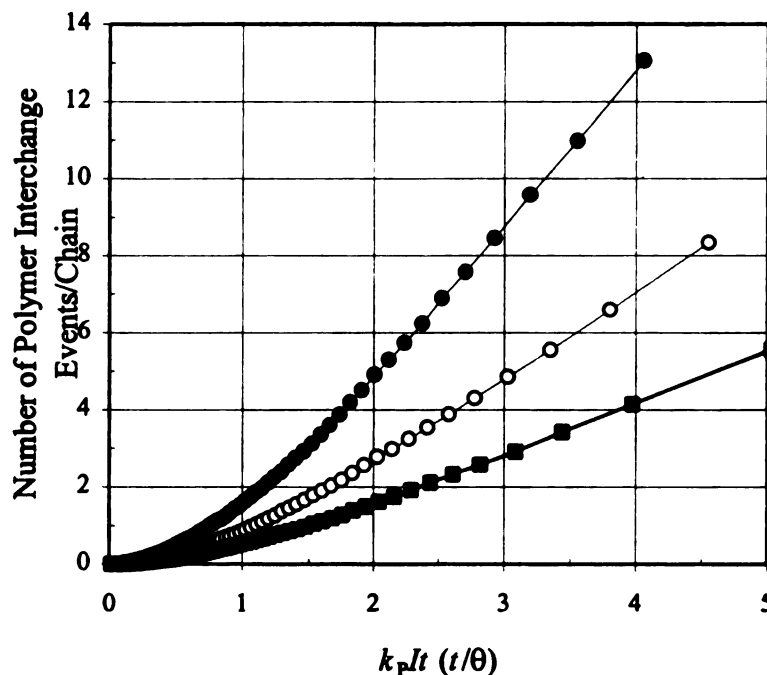


Figure 3-40. Monte Carlo simulation results for the average number of polymer interchange events per chain versus the characteristic polymerization time for $M/OH = 700$ ($M_n = 100,000$ at complete conversion): 160°C (●, $k_p/k_x = 330$); 190°C (○, $k_p/k_x = 500$); 220°C (■, $k_p/k_x = 1000$).

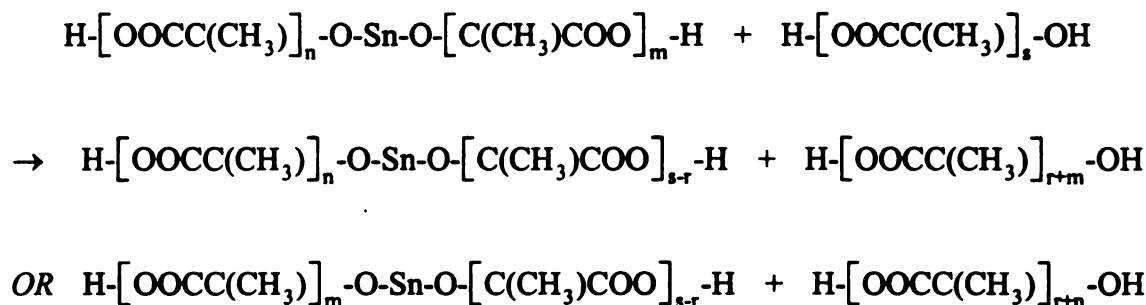
hydroxy substances to liberate free 2-ethylhexanoic acid. Van De Weij⁴² demonstrated that Sn(II)ethylhexanoate undergoes hydrolysis to yield the catalytically more active Sn(II) hydroxy derivative. Hydroxy impurities may react with either Sn(II)ethylhexanoate or another Sn(II) hydroxy derivative to form a stannous alkoxide derivative:



Aluminum and Sn(II) alkoxide catalysts are believed to catalyze lactide polymerization through a coordination-insertion mechanism.^{9,11,12,14,19,36,37} With the alkoxide insertion mechanism the Sn(II) is attached to the chain ("bound" rather than "free"). If instead the

Sn(II) prefers to form a salt with the polymer acid end group (carboxylate form) then insertion would lead to an unstable anhydride linkage and therefore a different mechanism would be required to explain polymerization.

In the alkoxide insertion kinetic scheme the Sn(II) catalyst facilitates transesterification between one of its alkoxide ligands (polymer chain or OH) and either a nearby lactide ester group (propagation) or a polymer ester group (polymer interchange). Because the catalyst participates in a polymer chain we must track the location of the catalyst molecules in the polymer chains in addition to monitoring the size of the polymer chains. The following is an example of polymer interchange by alkoxide insertion:



We abbreviate this reaction as $P_n\text{-I-}P_m + P_s = P_n\text{-I-}P_{s-r} + P_{r+m}$ OR $P_m\text{-I-}P_{s-r} + P_{r+m}$. Either n or m indices can have a value of zero to represent a hydroxy ligand (e.g., $P_n\text{-I-}P_m$ where $n = 0$ is $\text{OH-Sn-O-}[\text{C}(\text{CH}_3)\text{COO}]_m\text{-H}$). Propagation by alkoxide insertion is abbreviated as $M + P_n\text{-I-}P_m = P_{n+2}\text{-I-}P_m$ OR $P_n\text{-I-}P_{m+2}$.

Because of the need to track both living and dormant chain populations the moment equations are very complex. Instead we use a FORTRAN Monte Carlo type simulation (code 4 in Section 3.4.3). In this simulation initial amounts of lactide, living

chains of size 2 (catalyst chains), and dormant chains of size 2 are input and the living chains are randomly chosen to initiate one of three types of esters: lactide ester, living polymer ester, and dormant polymer ester. The k_p/k_x ratio is also input to adjust the probabilities of which ester type is attacked. For simplicity only one polymer ligand per catalyst molecule is assumed (i.e., $P_n-I + M = P_{n+2}-I$; $P_n-I + P_s = P_{n+r}-I + P_{r+n}$). This affects the definition of the rate constants but not the results. The basic simulation strategy is: (1) randomly pick a living chain to attack, (2) randomly determine if a monomer or polymer molecule is hit based on the input rate constant ratio, (3) if a polymer chain is hit determine whether it is a dormant or living chain, based on the number of repeat units, and randomly choose which repeat unit is hit, (4) update size of attacking living chain and receiving molecule, (5) repeat until desired lactide conversion is achieved. In each simulation the $M_n(t)$ and $PDI(t)$ for the dormant chains, living chains, and total chains are determined as a function of the characteristic polymerization time.

The simulation was performed for k_p/k_x values between 1-1000. When k_p/k_x is high $PDI(t)$ is reasonable but most of the dormant chains have not entered the high polymer distribution and remain at size 2 at time = 30. This results in $M_n(t)$ increasing to unreasonably high values. At low k_p/k_x values $M_n(t)$ is reasonable (all dormant chains participate in high polymer distribution) but $PDI(t)$ reaches its equilibrium value of 2 immediately (e.g., $t < 0.10$) and therefore is unreasonable. The model was amended to differentiate between condensation (attack at COOH repeat unit) and polymer interchange (attack at COOR) and also to differentiate between attacking molecules having either a polymer or OH ligand. In total six different rate constants are input:

Attacking Molecule	Receiving Molecule		
	Lactide	COOH	COOR
-Sn-OH	$k_{1,M}$	$k_{1,H}$	$k_{1,R}$
-Sn-OR	$k_{2,M}$	$k_{2,H}$	$k_{2,R}$

However, no combination of rate constants was found that gave both $PDI(t)$ and $M_n(t)$ that match real lactide vial polymerization kinetics.

The Monte Carlo simulation results indicate that the mechanism whereby the reaction centers are swapped among chains *solely* through transesterification reactions is not consistent with the $PDI(t)$ and $M_n(t)$ behavior of lactide polymerization. However, this is not to say that the insertion mechanism is invalid — the kinetic scheme as posed is invalid. If the rate of the reverse reaction for Sn(II) alkoxide formation (i.e., carboxylate formation: $-\text{COOH} + -\text{Sn-OR} = \text{ROH} + -\text{Sn-OOC-}$) is fast compared to propagation by alkoxide insertion then the catalyst would be effectively "free" in the reaction mixture, and the free-catalyst kinetic scheme presented in Table 3-9 would be valid. In other words, if the alkoxide insertion mechanism for Sn(II)ethylhexanoate lactide polymerization is indeed correct then it seems reasonable that there is a dynamic equilibrium between carboxylate and alkoxide forms where the catalyst swaps in and out of polymer chains at a rate that is fast compared to propagation and transesterification.

Conclusions

A moment-based Sn(II)ethylhexanoate catalyzed L-lactide batch polymerization and transesterification kinetic model was developed from $X_{\text{mon}}(t)$, $M_n(t)$, and $M_w(t)$ data taken at temperatures and catalyst concentrations of industrial interest. The model

predicts lactide conversion and MWD dynamics for given temperature, catalyst concentration, and initial OH impurity concentration. The model is in reasonable agreement with experimental data. Like polymerization, transesterification is first-order in the Sn(II) catalyst concentration but has a considerably smaller rate constant ($k_p/k_x = 330\text{-}1000$ for $160\text{-}220^\circ\text{C}$), and a lower activation energy (38 kJ/mol).

Although the exact mechanism of lactide polymerization and transesterification with Sn(II)ethylhexanoate remains unknown, the batch kinetics of lactide conversion and MWD(t) are now established. The polymerization kinetics are consistent with a process where the catalyst is free to coordinate initiation with any terminal OH group. Monte Carlo simulation results suggest that if the mechanism is by alkoxide coordination-insertion then the catalyst must swap in and out of polymer chains at a rate that is fast compared to propagation. This may occur through the approach toward a dynamic equilibrium between Sn(II) carboxylate and alkoxide forms.

Polymer interchange reactions are responsible for the broadening of the MWD towards the Most Probable Distribution. However, less than 1% of the dyad repeat units are disrupted during polymerization to 95% of equilibrium conversion at 190°C and $M_n = 100,000$. This amounts to a frequency of less than 5 interchange events per chain during the course of polymerization (time = 30).

3.4.3 FORTRAN Programs

1. MWD(t) for Reversible Polymerization/No Transesterification (Section 3.4.1)

```
PROGRAM polym
INTEGER J,I,K
DOUBLE PRECISION T,WMO,MOH,MI,EA,A,DH,DS,TF,KP,WMEQ,DT,PI,PT,WM,NT
```

```

DOUBLE PRECISION MN,MW,PD,TIME,CONV,DENS,M,MEQ,WKP,WPJ,MO,SUM,
DOUBLE PRECISION MDUM,ACTCON,MNSUM,MWSUM,P,O,THETA
DIMENSION P(1:10000),O(1:10000)
OPEN(3,FILE='DUMMY.XLS')

```

```

C
C THIS PROGRAM SIMULATES REVERSIBLE LACTIDE POLYMERIZATION
C   GIVEN INITIAL MONOMER CONCENTRATION, TEMPERATURE, Sn(II)
C   CATALYST CONCENTRATION, HOH INITIATOR CONCENTRATION, AND FINAL
C   TIME. THIS PROGRAM ASSUMES MOL Sn(II)=MOL HOH INITIATOR AND NO
C   TRANSESTERIFICATION.
C

```

C VARIABLE DICTIONARY

```

C   WM = WEIGHT FRACTION MONOMER
C   TIME = TIME(HR)
C   T = TEMP(C)
C   WMO = INITIAL MONOMER WT FRACTION
C   MOH = MOLAR RATIO OF MONOMER TO HYDROXYL IMPURITIES
C   MI = MOLAR RATIO OF MONOMER TO Sn(II) CATALYST
C   PI = MOL/L CAT = MOL/L LIVE POLYMER
C   FT = MAXIMUM NUMBER OF TIME STEPS
C   EA = ACTIVATION ENERGY OF PROPAGATION (J/MOL)
C   DH = ENTHALPY OF POLYMERIZATION (J/MOL)
C   DS = ENTROPY OF POLYMERIZATION (J/MOL-K)
C   A = PRE-EXPONENTIAL ARRHENIUS CONSTANT AT 448K (HR-1*MOL%CAT-1)
C   WKP = PROPAGATION RATE CONSTANT IN (HR-1*MOL%CAT-1)
C   KP = PROPAGATION RATE CONSTANT IN (HR-1*(MOLCAT/L)-1)
C   WMEQ = EQUILIBRIUM WT FRACTION OF MONOMER IN POLYMER
C   CONV = FRACTIONAL MONOMER CONVERSION
C   ACTCON = ACTUAL MONOMER CONVERSION FROM INTEGRATED MODEL
C   DT = TIME STEP
C   NT = NUMBER OF TIME STEPS
C   MN = NUMBER AVERAGE MOLECULAR WEIGHT
C   MW = WEIGHT AVERAGE MOLECULAR WEIGHT
C   PD = MW/MN
C   PT = MAXIMUM DEGREE OF POLYMERIZATION
C   DENS = DENSITY (G/ML)
C   P(J) = MOL/L POLYMER OF SIZE J
C   WPJ = WEIGHT FRACTION OF P(J)
C   M = MOL/L MONOMER
C   MEQ = MOL/L MONOMER IN EQUILIBRIUM WITH POLYMER
C   THETA=CHARACTERISTIC TIME OF POLYMERIZATION
C

```

C POLYMERIZATION PARAMETERS

```

C
C   T=220.
C   DENS=1.145/(1+.0007391*(T-150.))
C   WMO=1.
C   MO=WMO*DENS*1000./144.
C   MOH=1000.
C   MI=1000.
C   PI=1./MI/(1.+1./MI)*DENS/144.*1000.
C   EA=70900.
C   A=86.
C   DH=-23300.

```

```

      DS=-22.
C
C  CALCULATING KP AND MEQ
C
      WKP=A*EXP(-EA/8.314*(1/(273.+T)-1/448.))
      KP=WKP*14.4/DENS
      WMEQ=EXP(DH/8.314/(273+T)-DS/8.314)
      MEQ=WMEQ*DENS*1000./144.
C
C  IRREVERSIBLE OPTION
C
      MEQ=0.
C
      WMEQ=0.
C
      THETA=1./WKP/(100./MI/(1.+1./MI))
      TF=5.*THETA
      NT=10000
      DT=TF/NT
      PT=10000.
      WRITE(3,110)
      WRITE(3,150)T,MOH,THETA
      WRITE(3,100)WKP,WMEQ
110   FORMAT(1X,T MOH THETA KP MEQ')
100   FORMAT(5X,F10.5,5X,F10.5)
150   FORMAT(5X,F10.5,5X,F10.5,5X,F8.5,\)
C
C  INITIAL CONDITIONS
C
      TIME=0.
      M=MO-PI
      CONV=(MO-M)/MO
      MN=18.+72.*2.
      MW=MN
      PD=MW/MN
      SUM=PI
      ACTCON=0.
      WRITE(3,120)
120   FORMAT(1X,'t(h) conv sum actcon Mn Mw PDI')
      WRITE(3,200)TIME,CONV,SUM,ACTCON
      WRITE(3,300)MN,MW,PD
200   FORMAT(5X,F15.9,5X,F15.7,5X,F8.5,5X,F15.7,\)
300   FORMAT(5X,F10.2,5X,F10.2,5X,F8.4)
      WM=M/(DENS*1000./144.)
      P(1)=0.
      O(1)=P(1)
      J=1
      WPJ=P(J)/(1000.*DENS)*(18.+72.*J)
      P(2)=PI
      O(2)=P(2)
      J=2
      WPJ=P(J)/(1000.*DENS)*(18.+72.*J)
      DO 1 J=3,PT
          P(J)=0.
          O(J)=P(J)
          WPJ=P(J)/(1000.*DENS)*(18.+72.*J)

```



```

1      CONTINUE
C
C      SIMULATE POLYMERIZATION VERSUS TIME
C
      K=0
      DO 10 I=1,NT
          K=K+1
          TIME=I*DT
          MDUM=M
          M=M-DT*KP*(M*PI-MEQ*(PI-P(2)))
          SUM=0.
          MNSUM=0.
          MWSUM=0.
          J=2
          P(2)=P(2)-DT*KP*(MDUM*P(2)-MEQ*P(4))
          SUM=SUM+P(2)
          MNSUM=MNSUM+P(J)*(18.+72.*J)
          MWSUM=MWSUM+P(J)*(72.*J+18)**2
          DO 12 J=4,PT-2,2
              P(J)=P(J)-DT*KP*(MDUM*(P(J)-O(J-2))-MEQ*(P(J+2)-P(J)))
              SUM=SUM+P(J)
              MNSUM=MNSUM+P(J)*(18.+72.*J)
              MWSUM=MWSUM+P(J)*(72.*J+18)**2
12         CONTINUE
              P(PT)=P(PT)-DT*KP*(-MDUM*O(PT-2)+MEQ*P(PT))
              SUM=SUM+P(PT)
              MNSUM=MNSUM+P(PT)*(18.+72.*PT)
              MWSUM=MWSUM+P(PT)*(72.*J+18.)**2
              MN=MNSUM/SUM
              MW=MWSUM/MNSUM
              PD=MW/MN
              ACTCON=(1.-WMEQ/WMO)*(1.-EXP(-WKP*100./MI/(1.+1./MI)*TIME))
              DO 13 J=2,PT
                  O(J)=P(J)
13         CONTINUE
C
C      OUTPUT
C
          IF(K.EQ. 100) THEN
              WM=M/(DENS*1000./144.)
              CONV=(1-WM)/1
              WRITE(3,200)TIME,CONV,SUM,ACTCON
              WRITE(3,300)MN,MW,PD
              K=0
          ENDIF
10     CONTINUE
      STOP
      END

```

2. Lactide Polymerization Kinetics for Free-Catalyst Kinetic Scheme (Section 3.4.2)

```

PROGRAM MOMENT
INTEGER J,I

```

[illegible]C
C
CC
C
C

100
200
300
~
~
~

```

REAL T,MI,TF,DT,NT,MN,MW,PD,TIME,CONV,DENS,M,MEQ,MO
REAL KXI,KPI,KXT,KPT,THETA,CT,MOH,UO,U1,U2,U3,MOTO,MZ
OPEN(3,FILE='pdi.XLS')
C
C THIS PROGRAM SIMULATES LACTIDE POLYMERIZATION KINETICS WITH
C   SN(II)ETHYLHEXANOATE USING THE FREE-CATALYST KINETIC SCHEME
C
C VARIABLE DICTIONARY
C   T=TEMPERATURE(C)
C   MI=MOLAR RATIO OF MONOMER TO CATALYST
C   MOH=MOLAR RATIO OF MONOMER TO OH IMPURITIES
C   DENS=DENSITY(G/L)
C   MO=INITIAL LACTIDE CONCENTRATION(MOL/L)
C   MEQ=LACTIDE EQUILIBRIUM CONCENTRATION(MOL/L)
C   MOTO=INITIAL LACTIDE CONCENTRATION AFTER INITIATION OF OH IMPURITIES
C   KPI=PRODUCT OF PROPAGATION RATE CONSTANT AND CATALYST (HR-1)
C   KXI=PROD. OF TRANSESTERIFICATION RATE CONSTANT AND CATALYST (HR-1)
C   M=LACTIDE CONCENTRATION(MOL/L)
C   CONV=FRACTIONAL MONOMER CONVERSION
C   UO=ZEROth MOMENT OF MWD (MOL/L)
C   U1=FIRST MOMENT OF MWD (MOL/L)
C   U2=SECOND MOMENT OF MWD (MOL/L)
C   U3=THIRD MOMENT OF MWD (MOL/L)
C   MN=POLYMER NUMBER AVERAGE MOLECULAR WEIGHT
C   MW=POLYMER WEIGHT AVERAGE MOLECULAR WEIGHT
C   MZ=POLYMER Z AVERAGE MOLECULAR WEIGHT
C   PD=POLYDISPERSITY INDEX
C
C INPUT POLYMERIZATION CONDITIONS
C
C   T=190
C   MI=10000
C   MOH=700
C
C CALCULATE TEMPERATURE DEPENDENT PROPERTIES
C
C   DENS=1145/(1+.0007391*(T-150))
C   MO=DENS/144
C   UO=MO/MOH
C   MEQ=DENS/144*EXP(-23300/8.314/(273+T)+22/8.314)
C   MOTO=MO-UO
C   KPI=100/MI*86*EXP(-70900/8.314*(1./(273+T)-1./448))
C   KXI=100/MI*0.19*EXP(-38000/8.314*(1./(273+T)-1./448))
C
C OUTPUT PROPERTIES
C
C   WRITE(3,100)T,MI,MOH
C   WRITE(3,200)MO,MEQ,UO,KPI,KXI
C   WRITE(3,300)
100  FORMAT(1X,'T,MI,MOH= ',3X,F5.0,3X,F8.0,3X,F8.0)
200  FORMAT(1X,'MO,MEQ,UO,KPI,KXI= ',3X,2F7.4,3X,F7.4,3X,2F10.5)
300  FORMAT(1X,'CT,CONV,MN,MW,MZ,PD ')
C
C INITIAL CONDITIONS AND INTEGRATION STEP SIZE

```

C

C

C

C

C

C

C

400

10

3.

C

C

```

C
  TIME=0
  THETA=1/KPI
  TF=5*THETA
  NT=100000.
  DT=TF/NT
  M=MOTO
  CONV=(MO-M)/MO
  U1=2*(MO-M)
  U2=2*U1
  U3=2*U2
C
C  EVALUATE M AND MOMENTS WITH TIME
C
  I=0
  DO 10 J=1,NT
    I=I+1
    TIME=J*DT
    M=MEQ+(MOTO-MEQ)*EXP(-KPI*TIME)
    U1=2*(MO-M)
    KPT=-KPI/UO*8*(MO-M)*(MEQ-M)
    KXT=-KXI/UO/3*(UO*U2**2/(MO-M)-8*(MO-M)*U2)
    U2=U2+DT*(KPT+KXT)
    U3=U2*(2*U2*UO-U1**2)/U1/UO
    CONV=(MO-M)/MO
    MN=72.*U1/UO
    MW=72.*U2/U1
    MZ=72*U3/U2
    PD=MW/MN
C
C  OUTPUT LACTIDE CONVERSION AND MW AVERAGES
C
    IF(I.EQ.NT/20)THEN
      CT=TIME/THETA
      WRITE(3,400)CT,CONV,MN,MW,MZ,PD
      I=0
    ENDIF
400  FORMAT(1X,F7.4,3X,F6.5,3X,3F8.0,3X,F6.4)
10  CONTINUE
    STOP
  END

```

3. Monte Carlo Type Simulation for Free-Catalyst Kinetic Scheme (Section 3.4.2)

```

PROGRAM VARFRE
DIMENSION D(1000)
INTEGER J,D2,M,UO,P,U1T,S,U1D,U1Q,K,DUM,MO,B,H,I
INTEGER DNSUM,DWSUM,COOH,COOR,COUNT
REAL MI,MOH,CONV,DPDI,DMN,THETA,DMW,RH,RR,RM,X,Y,KPKX
CALL SEED(-1)
C
C  THIS PROGRAM SIMULATES THE FREE-CATALYST KINETIC SCHEME WITH A

```

```

C      MONTE CARLO TYPE SIMULATION
C
C      VARIABLE DICTIONARY
C      UO=NUMBER OF POLYMER CHAINS
C      MI=MOLAR RATIO OF MONOMER TO SN(II)ETHYLHEXANOATE CATALYST
C      MOH=MOLAR RATIO OF MONOMER TO HYDROXYL IMPURITIES
C      M=NUMBER OF LACTIDE MOLECULES
C      MO=INITIAL NUMBER OF LACTIDE MOLECULES
C      SN=NUMBER OF CATALYST MOLECULES
C      D2=INITIAL NUMBER OF POLYMER CHAINS OF SIZE 2
C      U1T=TOTAL NUMBER OF REPEAT UNITS (72 G/MOL)
C      D(J)=SIZE OF POLYMER MOLECULE J
C      KPKX= $K_p/K_x$  RATIO OF PROPAGATION/TRANSESTERIFICATION RATE CONSTANTS
C      Y=TRANSESTERIFICATION RATE CONSTANT VARIABLE THAT ADJUSTS THE
C          PROBABILITY OF A POLYMER ESTER UNIT BEING SELECTED BY
C          ARTIFICIALLY CHANGING THE NUMBER OF POLYMER ESTER UNITS
C          NOTE THAT Y IS RELATED TO  $2 \cdot K_x/K_p$ 
C      X=CONDENSATION RATE CONSTANT VARIABLE THAT ADJUSTS THE PROBABILITY
C          OF A COOH END GROUP BEING SELECTED BY ARTIFICIALLY CHANGING
C          THE NUMBER OF COOH GROUPS
C      TEMP=TEMPORARY ASSIGNMENT OF GENERATED RANDOM NUMBER
C      COOH=NUMBER OF COOH END GROUPS
C      COOR=NUMBER OF POLYMER ESTER UNITS
C      RH=PROBABILITY OF SELECTING A COOH GROUP
C      RR=PROBABILITY OF SELECTING A COOR GROUP
C      RM=PROBABILITY OF SELECTING A MONOMER
C      CONV=FRACTIONAL MONOMER CONVERSION
C      THETA=NUMBER OF CHARACTERISTIC TIMES ACHIEVED =  $K_p I t$ 
C      DMN=NUMBER AVERAGE MOLECULAR WEIGHT FOR POLYMER MOLECULES
C      DMW=WEIGHT AVERAGE MOLECULAR WEIGHT FOR POLYMER MOLECULES
C      DPDI=POLYDISPERSITY INDEX
C
C      INITIAL CONDITIONS; START WITH M, Sn(II), and D2
C
C          UO=1000
C          MI=10000
C          MOH=347
C          MO=MOH*UO
C          M=MO-UO
C          SN=M/MI
C          D2=UO
C          U1T=2*(M+D2)
C          DO 1 J=1,D2
C              D(J)=2
1      CONTINUE
C
C      ASSIGN WEIGHTINGS FOR RATE CONSTANTS
C
C          KPKX=1300.
C          Y=2./KPKX
C          X=0.
C
C      RANDOMLY PICK A MOLECULE TO ATTACK A RANDOM INTERMOLECULAR REPEAT
C      UNIT

```

```

C      B=0
      COUNT=0
      DO 10 K=1,1000000
        B=B+1
        CALL RANDOM(TEMP)
        P=1+TEMP*D2
C
C      PICK WHICH REPEAT UNIT IS ATTACKED: M,COOH,COOR
C
      H=0
      DO 21 J=1,D2
        IF(D(J).EQ.0)THEN
          H=H+1
        ENDIF
21      CONTINUE
      COOH=UO-H
      COOR=UIT-COOH-2*M
      RH=X*REAL(COOH)/(X*REAL(COOH)+2*REAL(M)+Y*REAL(COOR))
      RR=Y*REAL(COOR)/(X*REAL(COOH)+2*REAL(M)+Y*REAL(COOR))
      RM=1-RH-RR
      CALL RANDOM(TEMP)
C
C      CHECK IF HIT MONOMER
C
      IF(TEMP.LE.RM)THEN
C-----HIT MONOMER
        D(P)=D(P)+2
        M=M-1
        GOTO 3
      ENDIF
C
C      CHECK IF HIT POLYMER COOH GROUP
C
      IF(TEMP.LE.RM+RH)THEN
C-----HIT COOH END GROUP
        CALL RANDOM(TEMP)
        S=1+TEMP*COOH
        I=0
        DO 22 J=1,D2
          IF(D(J).NE.0)THEN
            I=I+1
          ENDIF
          IF(I.EQ.S)THEN
            GOTO 23
          ENDIF
22      CONTINUE
23      CONTINUE
        IF(J.EQ.P)THEN
          GOTO 3
        ENDIF
        D(J)=D(J)+D(P)
        D(P)=0
      ELSE

```

```

C-----HIT COOR REPEAT UNIT
      COUNT=COUNT+1
      CALL RANDOM(TEMP)
      S=1+TEMP*COOR
      I=0
      U1Q=0
      DO 5 J=1,D2
            I=I+D(J)-1
            IF(I.GE.S)THEN
                  IF(J.EQ.P)THEN
                        GOTO 3
                  ENDIF
                  D(J)=D(P)+I-S+1
                  D(P)=S-U1Q
                  GOTO 3
            ENDIF
            U1Q=I
5      CONTINUE
      ENDIF
3      CONTINUE
C
C      PRINT MN AND PDI RESULTS
C
      IF(B.EQ.10000)THEN
            B=0
            CONV=(1-REAL(M)/REAL(MO))
            THETA=-LOG(1-CONV)
            DNSUM=0
            DWSUM=0
            U1D=0
            DUM=0
            DO 18 J=1,D2
                  IF(D(J).GT.2)THEN
                        DUM=DUM+1
                        DNSUM=DNSUM+D(J)
                        DWSUM=DWSUM+D(J)*D(J)
                  ENDIF
                  U1D=U1D+D(J)
18      CONTINUE
            DMN=72*REAL(DNSUM)/REAL(DUM)
            DMW=72*REAL(DWSUM)/REAL(DNSUM)
            DPDI=DMW/DMN
            U1T=2*M+U1D
            PRINT*,'CONV,THETA,DPDI',CONV,THETA,DPDI
            PRINT*,'DMN,U1T,COUNT',DMN,U1T,COUNT
      ENDIF
10     CONTINUE
      STOP
      END

```


4. Monte Carlo Type Simulation for Alkoxide Insertion Kinetic Scheme (Sect. 3.4.2)

```

PROGRAM SEMLIV
DIMENSION L(100),D(1000)
INTEGER J,D2,M,UO,P,U1T,S,U1D,U1Q,K,LOHO,DUM,MO,B,L,D,UDT,ULT
INTEGER LNSUM,LWSUM,DNSUM,DWSUM,I,COOR
DOUBLE PRECISION MI,MOH,CONV,LPDI,DPDI,PDI,LMN,DMN,THETA,ALLMN
DOUBLE PRECISION LMW,DMW,Y,KPKX,RM
OPEN(3,FILE='LIVING.XLS')
CALL SEED(-1)

C
C THIS PROGRAM SIMULATES THE ALKOXIDE INSERTION KINETIC SCHEME USING A
C MONTE CARLO APPROACH
C
C VARIABLE DICTIONARY
C UO=NUMBER OF POLYMER CHAINS
C MI=NUMBER RATIO OF INITIAL MONOMER TO CATALYST
C MOH=NUMBER RATIO OF INITIAL MONOMER TO OH IMPURITIES
C M=NUMBER OF LACTIDE MOLECULES
C MO=INITIAL M
C LOHO=NUMBER OF LIVING CHAINS
C D2=NUMBER OF DORMANT CHAINS
C U1T=TOTAL NUMBER OF REPEAT UNITS
C D(J)=SIZE OF DORMANT CHAIN J
C L(J)=SIZE OF LIVING CHAIN J
C KPKX=KP/KX RATIO OF PROPAGATION/TRANSESTERIFICATION RATE CONSTANTS
C COOR=NUMBER OF POLYMER REPEAT UNITS
C RM=PROBABILITY THAT A LACTIDE IS ATTACKED FOR A CERTAIN INITIATION
C CONV=FRACTIONAL LACTIDE CONVERSION
C THETA=NUMBER OF CHARACTERISTIC TIMES ACHIEVED =  $K_{pl}t$ 
C LMN=NUMBER AVERAGE MW FOR LIVING CHAINS
C DMN=NUMBER AVERAGE MW FOR DORMANT CHAINS
C LMW=WEIGHT AVERAGE MW FOR LIVING CHAINS
C DMW=WEIGHT AVERAGE MW FOR LIVING CHAINS
C LPDI=PDI FOR LIVING CHAINS
C DPDI=PDI FOR DORMANT CHAINS
C PDI=PDI FOR ALL CHAINS
C ALLMN=NUMBER AVERAGE MW FOR ALL CHAINS
C
C INPUT INITIAL CONDITIONS; START WITH M,  $\text{Sn}(\text{OH})_2$ , and D2
C
UO=1000
MI=10000
MOH=350
M=MOH*UO
MO=M
LOHO=2*M/MI
D2=UO-LOHO
U1T=2*(M+D2+LOHO)
DO 1 J=1,LOHO
    D(J)=2
    L(J)=2
1 CONTINUE

```

```

      DO 2 J=LOHO+1,D2
        D(J)=2
2      CONTINUE
C
C      OUTPUT INITIAL CONDITIONS
C
      WRITE(3,100)UO,D2,LOHO,M,U1T
100    FORMAT(1X,'UO,D2,LOHO,M,U1T',5I8)
      WRITE(3,201)
201    FORMAT(1X,'K,CONV,THETA,LPDI,DPDI,PDI,LMN,DMN,ALLMN')
C
C      INPUT KP/KX
C
      KPKX=100.
      Y=2/KPKX
C
C      RANDOMLY PICK A LIVING MOLECULE TO ATTACK A RANDOM INTERMOLECULAR
C      REPEAT UNIT
C
      B=0
      DO 10 K=1,400000
        B=B+1
        CALL RANDOM(TEMP)
        P=1+TEMP*LOHO
C
C      PICK WHICH REPEAT UNIT IS ATTACKED: M,D,OR L
C
      COOR=U1T-2*M
      RM=1.-Y*REAL(COOR)/(Y*REAL(COOR)+2*M)
      CALL RANDOM(TEMP)
      IF(TEMP.LE.RM)THEN
C-----HIT MONOMER
        L(P)=L(P)+2
        M=M-1
        GOTO 13
      ELSE
C-----HIT POLYMER; CHECK IF HIT DORMANT OR LIVING CHAIN
        ULT=0
        DO 4 J=1,LOHO
          ULT=ULT+L(J)
4        CONTINUE
        UDT=U1T-ULT-2*M
        CALL RANDOM(TEMP)
        S=1+TEMP*(ULT+UDT)
        IF(S.LE.UDT)THEN
C-----HIT DORMANT CHAIN
          I=0
          U1Q=0
          DO 5 J=1,D2
            I=I+D(J)
            IF(I.GE.S)THEN
              D(J)=L(P)+I-S+1
              L(P)=S-1-U1Q
              GOTO 13
            
```

```

                                ENDIF
                                U1Q=I
5                                CONTINUE
                                ELSE
C-----HIT LIVING CHAIN
                                I=0
                                U1Q=0
                                DO 6 J=1,LOHO
                                    I=I+L(J)
                                    IF(I.GE.S-UDT)THEN
                                        IF(J.EQ.P)THEN
                                            GOTO 13
                                        ENDIF
                                        L(J)=L(P)+I-(S-UDT)+1
                                        L(P)=S-UDT-1-U1Q
                                        GOTO 13
                                    ENDIF
                                    U1Q=I
6                                CONTINUE
                                ENDIF
                                ENDIF
13                                CONTINUE
C
C    PRINT MN AND PDI RESULTS
C
                                IF(B.EQ.5000)THEN
                                    B=0
                                    CONV=(1-REAL(M)/REAL(MO))
                                    THETA=-LOG(1-CONV)
                                    LNSUM=0
                                    LWSUM=0
                                    DNSUM=0
                                    DWSUM=0
                                    U1D=0
                                    DUM=0
                                    DO 17 J=1,LOHO
                                        LNSUM=LNSUM+L(J)
                                        LWSUM=LWSUM+L(J)*L(J)
17                                CONTINUE
                                    DO 18 J=1,D2
                                        IF(D(J).GT.2)THEN
                                            DUM=DUM+1
                                            DNSUM=DNSUM+D(J)
                                            DWSUM=DWSUM+D(J)*D(J)
                                        ENDIF
                                        U1D=U1D+D(J)
18                                CONTINUE
                                    UT=LNSUM+DNSUM
                                    U1Q=LWSUM+DWSUM
                                    LMN=72*REAL(LNSUM)/REAL(LOHO)
                                    DMN=72*REAL(DNSUM)/REAL(DUM)
                                    LMW=72*REAL(LWSUM)/REAL(LNSUM)
                                    DMW=72*REAL(DWSUM)/REAL(DNSUM)
                                    LPDI=LMW/LMN

```

```

DPDI=DMW/DMN
ALLMN=72*REAL(UT)/REAL(DUM+LOHO)
PDI=REAL(U1Q)/REAL(UT)/REAL(UT)*(REAL(LOHO)+REAL(DUM))
U1T=2*M+LNSUM+U1D
WRITE(3,200)K,CONV,THETA,LPDI,DPDI,PDI,LMN,DMN,ALLMN
200      FORMAT(1X,I7,8F15.5)
PRINT*,U1T
ENDIF
10      CONTINUE
C
C      PRINT DISTRIBUTIONS
C
      DO 11 J=1,LOHO
          WRITE(3,300)J,L(J)
300      FORMAT(1X,2I6)
11      CONTINUE
      DO 12 J=1,D2
          WRITE(3,300)J,D(J)
12      CONTINUE
      STOP
      END

```

3.5 Process Degradation Kinetics

A comparison of PLA's relative thermal stability to commodity plastics and an introduction to the important PLA degradation reactions was presented in Section 2.2.4. In this section we develop simple, practical rate equations that describe the kinetics of the M_n degradation of PLA at processing conditions.

3.5.1 Non-hydrolytic Degradation

It is not possible to practically remove all adsorbed water from PLA pellets that have been exposed to the atmosphere (or water trough). For this reason it is difficult to elucidate the contribution of non-hydrolytic mechanisms to M_n degradation. However, during polymerization water and hydroxyl initiators are quickly consumed, and once equilibrium lactide conversion is reached the M_n will remain constant in the absence of degradation reactions; polymer interchange reactions do not effect M_n and lactide

propagation and depropagation proceed but are balanced at equilibrium. Therefore, by continuing to monitor M_n after equilibrium polymerization is approached we are able to determine the importance of non-hydrolytic degradation at various processing conditions.

Figure 3-41 presents a M_n versus time curve during the long time vial polymerization of lactide at 180°C and $M/I = 20,000$ lactide/Sn(II) (mol/mol). The characteristic time of polymerization at these conditions is: $\theta = 1/(k_p I) = 1/(106 \cdot 0.005) = 1.88$ h, using equation (3-4) to determine k_p at 180°C. Samples were taken for lactide and molecular weight analysis up to 8θ (15 h); 3θ represents the upper practical time for lactide polymerization (95% of equilibrium). The M_n reaches a maximum at about 6 h and then decreases from 123,000 to 93,400 g/mol in the remaining 9 h. The average rate of chain scission events between 6 and 15 h is determined by taking the quotient of the net

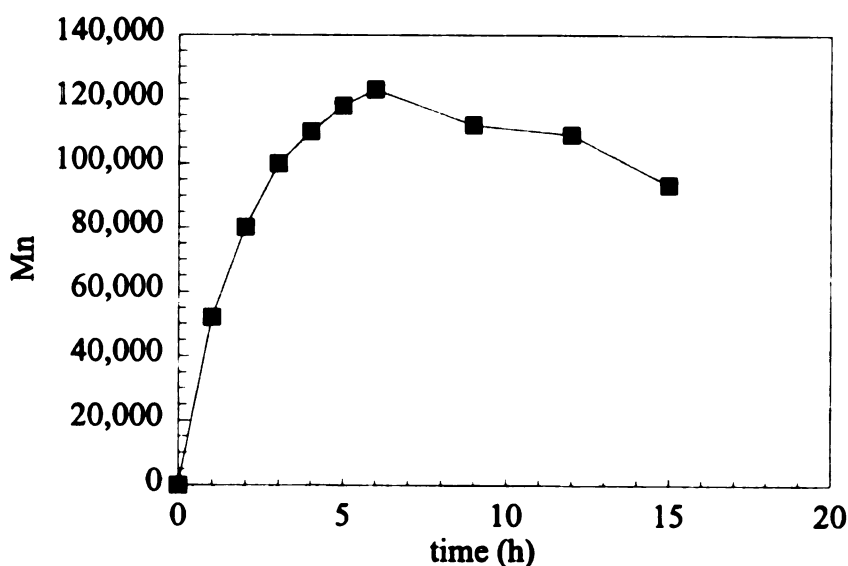


Figure 3-41. Long time thermal degradation of PLA during a vial polymerization at 180°C and $M/I = 20,000$ lactide/Sn(II) (mol/mol). A rate constant of 0.3 mmol/kg-h is regressed from the 6-15 h data using equation (3-31).

increase in the number of polymer chains per mass and time:

$$\frac{\Delta\mu_0}{\Delta t} = \frac{\left(\frac{10^6}{M_n(t_f)} - \frac{10^6}{M_n(t_0)}\right)}{(t_f - t_0)} = \frac{(10.7 - 8.1)}{(15 - 6)} = 0.3 \text{ mmol/kg/h} \quad (3-31)$$

Table 3-10 presents a summary of non-hydrolytic chain scission rates determined during long time lactide polymerizations at 160, 180, 190, and 210°C. A zeroth-order rate equation is a reasonable description of PLA non-hydrolytic degradation:

$$\mu_0(t) = \mu_0(t_0) + k_{\text{deg}}t \quad (3-32)$$

The rate constant k_{deg} is in units of mmol/kg-h and has an Arrhenius temperature dependence:

$$k_{\text{deg}} = A_{\text{deg},448} \exp\left(\frac{-E_{a,\text{deg}}}{R} \left(\frac{1}{T(K)} - \frac{1}{448}\right)\right) \quad (3-33)$$

Equation 3-32 is commonly used to define the rate constant of chain breakage.⁵²

Preliminary results suggest that Sn(II) catalyst concentration is unimportant in non-hydrolytic PLA degradation. More work is required to confirm this. The Arrhenius fit to the rate data is presented in Figure 3-42. An excellent fit is observed with $A_{\text{deg},448}$ and $E_{a,\text{deg}}$ values of 0.20 mmol/kg-h and 126 kJ/mol. This activation energy corresponds to a doubling of rate every 10°C in this temperature range. The final model to predict PLA non-hydrolytic M_n degradation as a function of temperature and time is:

$$\mu_0(t) = \frac{10^6}{M_n(t)} = \frac{10^6}{M_n(t_0)} + 0.20 \exp\left(\frac{-126,000}{8.314} \left(\frac{1}{T(K)} - \frac{1}{448}\right)\right) t(h) \quad (3-34)$$

**Table 3-10 Summary of
Rate Constants for PLA
Non-Hydrolytic Degradation**

T (°C)	k_{deg} (mmol/kg-h)
160	0.07
180	0.3
190	0.6
210	2.3

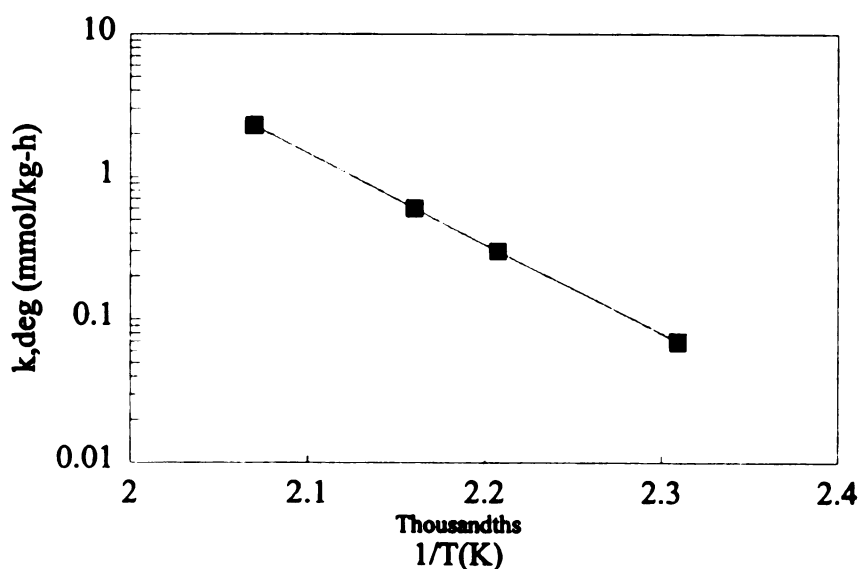


Figure 3-42. The temperature dependence of the non-hydrolytic degradation rate constant for PLA. The solid line is the Arrhenius model defined in equation (3-33): $E_{a,deg} = 126$ kJ/mol, $A_{deg,448} = 0.20$ mmol/kg-h.

If we consider an M_n decrease of 100,000 to 95,000 in 10 min processing time the cutoff for "important" degradation (i.e., 3 mmol/kg-h), then thermal degradation becomes an important contribution to M_n degradation at temperatures above 215°C. This result is

based on equation (3-34) which was determined from lactide polymerization in the absence of stabilizers. It may be possible to reduce non-hydrolytic PLA degradation rates with the aid of various polymer stabilizers.

Conclusions

A rate equation for non-hydrolytic M_n degradation was determined from long time lactide vial polymerization data at 160-210°C. There does not appear to be a dependence of non-hydrolytic degradation on the Sn(II) polymerization catalyst but more work is required to confirm this. The activation energy of non-hydrolytic chain scission is 126 kJ/mol. Thermal degradation becomes important in PLA melt processing above 215°C.

3.5.2 Melt Hydrolysis

The melt hydrolysis kinetics of PLA (~17% *meso*) were determined at temperatures (150-210°C) and times (0-32 min) common to resin processing equipment. Initial moisture levels between 100-13,000 ppm were studied. This represents the range from thoroughly dried to 100% relative humidity. The importance of polymerization catalyst on melt hydrolysis kinetics is determined.

Role of catalyst

The effect of polymerization catalyst on the rate of PLA melt hydrolysis was determined over a wide range of Sn(II) ethylhexanoate concentrations, 0.0025-0.02 mol% ($M/I = 40,000$ -5,000 lactide/Sn(II) (mol/mol)). Four PLA samples were powderized and

exposed to air. Testing was performed in DSC cells at 200°C for 20 min. The molecular weight of the four samples was determined before and after thermal exposure. The results are summarized in Table 3-11. The extent of hydrolysis is found to be first order in catalyst concentration, Figure 3-43.

Table 3-11 Effect of Stannous Ethylhexanoate Concentration on PLA Hydrolytic Degradation

M/I (mol/mol)	I (mol%)	M_n (g/mol)	time (min)	μ_0 (mmol/kg)	$\Delta\mu_0/\Delta t$ (mmol/kg/h)
5,000	0.02	63,810	0	15.67	
5,000	0.02	23,707	20	42.18	79.5
10,000	0.01	38,697	0	25.84	
10,000	0.01	26,280	20	38.05	36.6
20,000	0.005	74,630	0	13.40	
20,000	0.005	45,450	20	22.00	25.8
40,000	0.0025	47,680	0	20.97	
40,000	0.0025	42,775	20	23.38	7.2

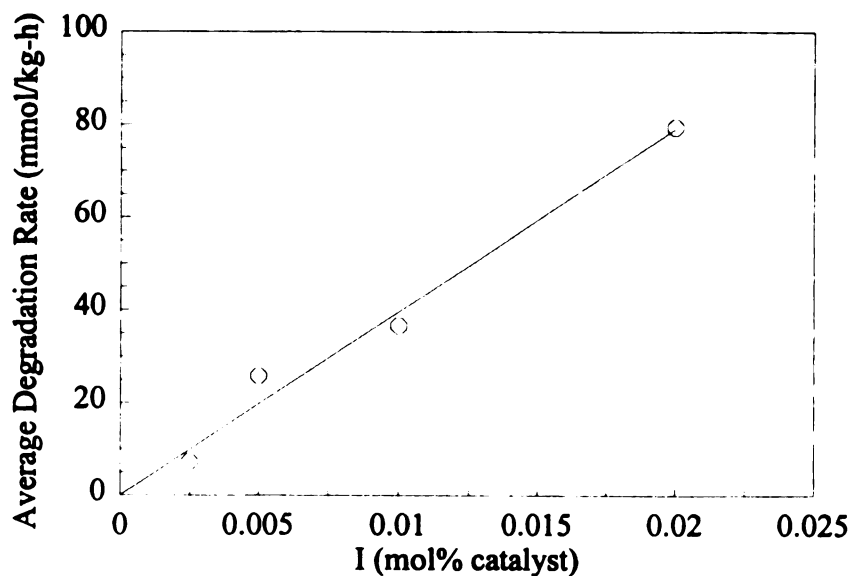
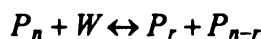


Figure 3-43. First order catalyst dependence of PLA melt hydrolysis at 200°C, 20min.

Although the moisture content was not measured prior to the DSC degradation studies, it is clear that the rate of degradation is orders of magnitude greater than that of thermal degradation at 200°C. In PET systems the rate of hydrolytic degradation has been found to be several orders of magnitude greater than the rate of thermal M_n degradation.⁵³⁻⁵⁴ Similar to our findings, PET melt hydrolysis is also known to be catalyzed by metal salts.⁵⁵

Hydrolysis Rate Model

The hydrolysis of a PLA chain yields two PLA chains of lower molecular weight. Both hydrolysis and transesterification lead to the Most Probable Distribution. However, polymer interchange reactions do not lower M_n .



The rate of water consumption is equivalent to the rate of increase in polymer chain concentration and is expected to be first order in catalyst, water, and ester units,

$$\frac{-dW}{dt} = \frac{d\mu_0}{dt} = k_w IW \sum_{n=1}^{\infty} (n-1)P_n = k_w IW(\mu_1 - \mu_0(t)) \quad (3-35)$$

where μ_1 is the total concentration of repeat units. In this model we assume that the variance in concentration of acid end groups (COOH) is unimportant in high molecular weight PLA melt hydrolysis in the presence of the Sn(II) catalyst. The change in water

concentration with time is obtained by integrating water concentration between W_0 and $W(t)$, and time between 0 and t ,

$$W(t) = W_0 \exp(-k_w I t) \quad (3-36)$$

Substituting this result into equation (3-35) and integrating between $\mu_0(t_0)$ and $\mu_0(t)$ gives the increase in polymer chains with time,

$$\frac{\mu_0(t) - \mu_0(t_0)}{W_0/18} = (1 - \exp(-k_w I t)) \quad (3-37)$$

where W_0 , k_w , and I are in units of ppm, $\text{mol}\%^{-1} \text{h}^{-1}$, and mol%. The degradation rate in units of mmol/kg-h is obtained by taking the derivative of $\mu_0(t)$ with respect to time,

$$\frac{d\mu_0(t)}{dt} = \frac{W_0 k_w I}{18} \exp(-k_w I t) \quad (3-38)$$

Therefore, the initial hydrolytic degradation rate is proportional to the product of the catalyst concentration and initial water concentration:

$$\left. \frac{d\mu_0(t)}{dt} \right|_{t=0} = \frac{W_0 k_w I}{18} \quad (3-39)$$

The hydrolysis rate constant is expected to have an Arrhenius temperature dependence,

$$k_w = A_{w,448} \exp\left(\frac{-E_a}{R} \left(\frac{1}{T(K)} - \frac{1}{448}\right)\right) \quad (3-40)$$

Experimental

PLA melt hydrolysis experiments were performed between 150-210°C and 100-13,000 ppm initial pellet moisture content. Ten different amorphous PLA (17% initial *meso*) pellet samples were conditioned in a humidity chamber employing various salt solutions and water (100% RH) to control the percentage relative humidity. Initial moisture content was determined with a 684 KF coulometer by Brinkmann. A Haake Rosand RH7-2 capillary viscometer was used as a hydrolysis reactor. The sample pellets were added to the viscometer barrel, air was removed with a plunger after melting, and upon thermal equilibration, melt samples were discharged at predetermined intervals between time-zero and 32 min. Molecular weights were determined by GPC for all discharged samples.

Results

The raw data for the PLA melt hydrolysis experiments are presented in Table 3-12. Figure 3-44 presents a plot of the dimensionless extent of melt hydrolysis, LHS of equation (3-37), versus time at 150, 180, and 210°C at an initial pellet water content of $W_i = 2970$ ppm. The solid lines represent the model fits. After 0.5 h and 210°C complete consumption of water is observed and the extent of hydrolysis is unity. Melt hydrolysis after 0.5 h is incomplete at 180 and 150°C. The data is well represented by the model at all temperatures with k_w values of 240, 501, and 682 mol%⁻¹h⁻¹ for the data at 150, 180, and 210°C, respectively. However, the regressed W_0 values were considerably lower than W_i (about 10% W_i). Because hydrolysis is effectively irreversible at these molecular

Table 3-12 Raw Data for PLA Melt Hydrolysis Experiments
 (all data at $I = 0.02$ mol%, except last data at $Wi = 113$ which is at $I = 0.01\%$)

T (°C)	Wi (ppm)	time (h)	Mn	T (°C)	Wi (ppm)	time (h)	Mn
150	7,700	0	30,800	210	2,970	0	38,800
		2	26,700			2	23,400
		3	26,600			3	21,000
		7	21,300			7	16,600
		15	18,900			15	14,900
		31	16,500			31	13,500
180	7,700	0	35,600	180	13,000	0	27,900
		1	34,700			1	21,100
		3	20,400			3	17,300
		4	19,200			4	16,000
		8	15,900			8	12,800
		16	13,200			16	10,700
210	7,700	32	13,500	180	710	0	54,100
		0	35,600			2	45,500
		1	21,600			3	41,400
		3	17,400			7	37,300
		8	13,300			15	31,900
		16	11,200			31	31,800
150	2,970	0	43,600	180	430	0	48,300
		2	39,500			1	45,000
		3	36,700			3	41,600
		7	31,200			5	41,100
		15	25,100			10	39,300
		31	21,500			15	35,000
180	2,970	0	42,500	180	113	30	35,300
		2	31,700			45	33,700
		3	27,400			0	87,600
		7	21,500			2	77,100
		15	17,000			3	82,700
		31	15,000			7	84,900
						15	75,300
						31	69,600

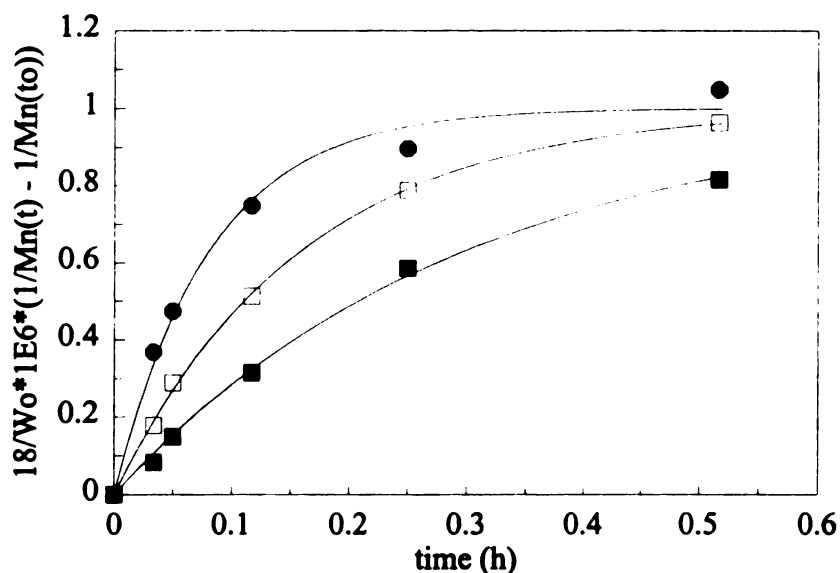


Figure 3-44. Extent of melt hydrolysis versus time with $W_i = 2970$ ppm at 210°C (●, $k_w = 682$ mol%⁻¹h⁻¹, $W_0 = 1090$ ppm); 180°C (□, $k_w = 501$ mol%⁻¹h⁻¹, $W_0 = 868$ ppm); 150°C (■, $k_w = 240$ mol%⁻¹h⁻¹, $W_0 = 548$ ppm).

weights (Section 1.2.3), this finding suggests that a considerable amount of water has been vaporized during the melting and air removal of the pellets in the capillary viscometer.

A summary of the melt hydrolysis results are presented in Table 3-13. The k_w and W_0 parameters were determined by nonlinear regression of the $M_n(t)$ data using equation (3-37). The initial moisture content, W_i , as determined by Karl Fisher titration was found to be in large excess of the fit W_0 values. The fraction of initial pellet water that initiated hydrolysis, W_0/W_i , was higher at lower W_i and increased with viscometer temperature, Figure 3-45. These trends are consistent with the explanation of pellet water evaporation during melting and air removal. At low initial pellet moisture content most of the water is consumed. In practical PLA processing the initial moisture content is low (thorough drying) and melting often occurs in a closed chamber. For this reason it is reasonable to

assume that $W_i = W_0$ during PLA processing, and resulting melt hydrolysis predictions using equation (3-37) represent a conservative upper bound on hydrolytic degradation.

Table 3-13 Summary of PLA Melt Hydrolysis Kinetics Experiments

T (°C)	I (mol%)	Initial W_i (ppm)	W_0 (ppm)	W_0/W_i	k_w (mol% ⁻¹ h ⁻¹)	$k_w I$ (h ⁻¹)	$\Delta\mu_0/\Delta t$ (mmol/kg-h)
150	0.02	7,700	548	0.07	240	4.8	146
180	0.02	7,700	868	0.11	501	10.02	483
210	0.02	7,700	1,090	0.14	682	13.65	827
150	0.02	2,970	520	0.18	167	3.34	97
180	0.02	2,970	806	0.27	314	6.28	281
210	0.02	2,970	830	0.28	617	12.34	569
180	0.02	13,000	1,150	0.09	418	8.36	536
180	0.02	710	241	0.34	483	9.66	129
180	0.02	430	154	0.36	350	7	60
180	0.01	113	74	0.66	355	2.37	10

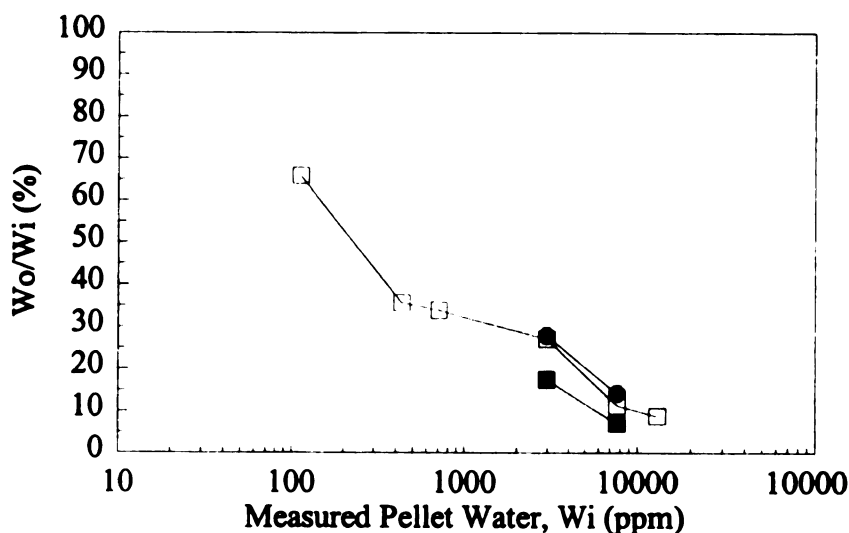


Figure 3-45. Percent of initial measured pellet water that was available for hydrolysis at time-zero versus initial measured pellet water at 210°C (●), 180°C (□), and 150°C (■).

The average degradation rate, $\Delta\mu_0/\Delta t$, increases with both water content and temperature. At 180°C, $I = 0.02$ mol%, $W_0 = 150$ ppm (thoroughly dried pellets), and $t = 0.5$ hr the average PLA hydrolysis rate is 200 times greater than that of nonhydrolytic degradation at 180°C (0.3 mmol/kg-h). The hydrolysis rate constant, k_w , is independent of catalyst and water concentration and is a function of temperature only. The activation energy, E_a , and preexponential constant, $A_{w,448}$, were determined to be 33.4 kJ/mol and $351 \text{ mol}\%^{-1}\text{h}^{-1}$ by linear regression using equation (3-40). The Arrhenius fit is presented in Figure 3-46. As would be expected, the Sn(II) catalyzed melt hydrolysis activation energy is considerably lower than that of non-hydrolytic degradation (126 kJ/mol).

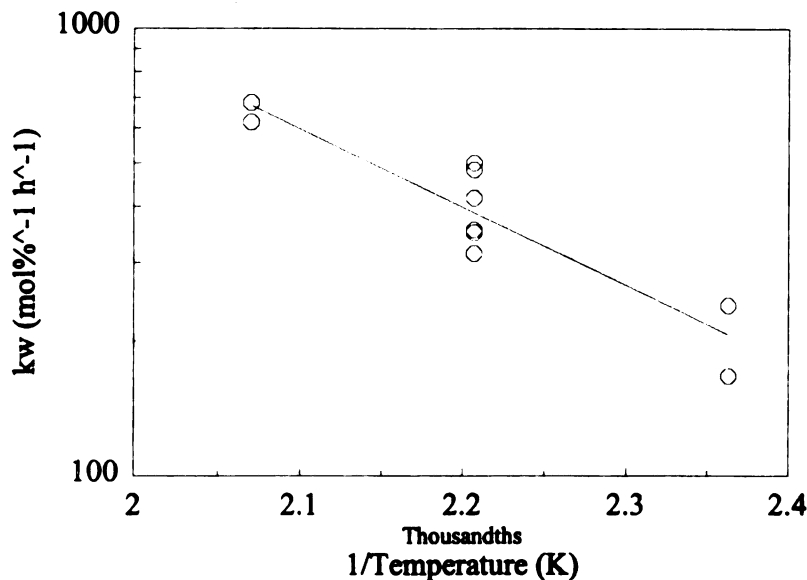


Figure 3-46. The Arrhenius temperature dependence of the PLA melt hydrolysis rate constant. The activation energy of Sn(II) catalyzed PLA melt hydrolysis is 33.4 kJ/mol.

The final model to estimate the change in $M_n(t)$ during PLA melt hydrolysis with known I , T , t , and W_0 is

$$\frac{1E6}{M_n(t)} = \frac{1E6}{M_n(t=0)} + \frac{W_0(\text{ppm})}{18} \exp(1 - \exp(-k_w I t)) \quad (3-41)$$

$$k_w = 351 \exp\left(\frac{-33,400}{8.314} \left(\frac{1}{T(K)} - \frac{1}{448}\right)\right) \quad (3-42)$$

Conclusions

A PLA melt hydrolysis kinetic model was developed from experimental data to predict molecular weight degradation at typical processing conditions. Hydrolytic degradation is first order in Sn(II) polymerization catalyst concentration and has an activation energy of 33.4 kJ/mol.

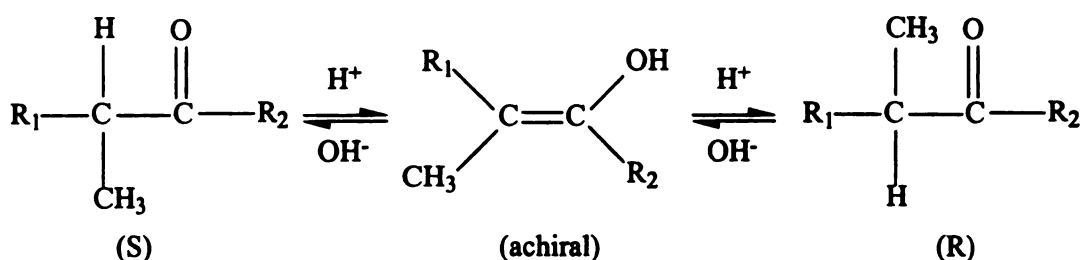
3.6 Racemization

In this section we develop a kinetic rate model for the racemization of L-mer to D-mer during polymerization. There has been relatively little published concerning the rate of PLA racemization at bulk polymerization conditions. The quantification of racemization is essential for engineering design and manufacturing practices aimed at producing semicrystalline and amorphous PLA grades of high quality.

Kricheldorf and Serra³ screened 72 L-lactide polymerization catalyst systems (metal oxides, carbonates, and carboxylates) for racemization (optical rotation), yield, and product coloration. The polymerizations were conducted at a very high catalyst concentration, $M/I = 100$ mol/mol. Alkalimetal carbonates were found to have considerable racemization which increased with the basicity of the catalyst. All sodium salts resulted in a high degree of racemization. The most effective catalysts in terms of

yield, decreased racemization, and color were SnO, Zn-sterate, Bi-ethylhexanoate, and Sn-ethylhexanoate. SnO demonstrated the lowest extent of racemization during polymerization. Owing to their finding that racemization is related to basicity, the authors suggest monomer deprotonation as the likely mechanism.

In ketone systems where the stereocenter is α to the carbonyl group, racemization occurs through formation of an intermediate enol form having an achiral planar configuration,⁵⁶



where $\text{R}_1 \neq \text{CH}_3$ or H , (chiral). The rate of racemization is equal to the rate of enolization which is acid or base catalyzed:⁵⁶ $\text{rate} = k_{\text{acid}}[\text{ketone}][\text{H}^+]$ or $\text{rate} = k_{\text{base}}[\text{ketone}][\text{OH}^-]$.

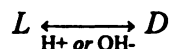
In both lactic acid and PLA we have found that racemization is first order in acid end group concentration. Hence, M_n PLA at equilibrium polymerization has a lower tendency to polymerize than lower M_n PLA. We also observe, as did Kricheldorf and Serra,³ that Na^+ catalyzes racemization during polymerization. These observations are consistent with the acid/base catalyzed enolization route and we believe that this is the dominant racemization mechanism.

Experimental

The stereochemistry (D-mer/L-mer) of the lactide polymerization products in Section 3.2 were determined by hydrolysis and subsequent chiral chromatography.

Racemization Rate Model

At stereochemical equilibrium PLA contains 50% L- and D-mer. Therefore, the rate constants of the forward and reverse racemization of L-mer are equivalent, k .



Assuming only acid end group catalyzed racemization for now, the rate of L-mer racemization is

$$\frac{-dL}{dt} = k[\text{COOH}]L - k[\text{COOH}]D = k\mu_0(2L - 1) \quad (3-43)$$

where $L + D = 1$ (mer mole fractions) and $[\text{COOH}]$ is independent of time (fast initiation) and equivalent to the number of polymer chains μ_0 (mmol/kg) = $X_{\text{mon}} * 1\text{E6}/M_n$, where X_{mon} is fractional lactide conversion. In this model we do not attempt to differentiate between repeat units in lactide and polymer. Integration by substitution between initial L-mer fraction, L_0 , and $L(t)$ yields

$$L(t) = \frac{1}{2}[1 + (2L_0 - 1)\exp(-2k_{\text{eff}}\mu_0 t)] \quad (3-44)$$

$$D(t) = 1 - L(t) = \frac{1}{2}[1 - (2L_0 - 1)\exp(-2k_{\text{eff}}\mu_0 t)] \quad (3-45)$$

where The effective rate constant, k_{eff} , incorporates possible contributions of base catalysts or polymerization catalyst effects. We use equation (3-45) to calculate k_{eff} from the Section 3.2 vial polymerizations with known final M_n , D-mer, X_{mon} , T , and time.

Results and Discussion

The chiral chromatography results for the polymerization samples are summarized in Table 3-14. Separate analyses of the $M/I = 1,000$ and $M/I = 10,000$ data yield a common activation energy, 115-125 kJ/mol, but different effective rate constants (preexponential factor). The dependence of k_{eff} on the catalyst concentration is presented as a log-log plot in Figure 3-47. Between $I = 0.01$ and 0.1 mol% there is an increase in k_{eff} at all temperatures. However, k_{eff} becomes less sensitive to I with decreasing I ; it is apparent that racemization occurs in the absence of polymerization catalyst ($I = 0$). The hypothesis that the two ethylhexanoic acid ligands are responsible, by acid catalysis, for the increased racemization with catalyst concentration was tested by replacing μ_0 with $\text{COOH} = \mu_0 + 2I$ (mmol/kg) in equation (3-44). However, only a slight lowering of the rate constant at higher I was found with this change, and we reject the hypothesis that the acid ligands in the catalyst are responsible for the increased racemization rate.

The nonlinearity of $\ln k_{\text{eff}}$ versus $\ln I$ indicates that a power law incorporation of I into k_{eff} is inappropriate. Instead, the data suggests an exponential relationship, Figure 3-48: $\ln k_{\text{eff}} = \ln k_{\text{rac}} + aI$, or $k_{\text{eff}} = k_{\text{rac}} * \exp(aI)$, where a is a rate parameter and $k_{\text{eff}} = k_{\text{rac}}$ at

Table 3-14 Racemization During L-Lactide Polymerization

<i>T</i> (°C)	time (h)	100* <i>X</i> _{mon} (%)	<i>M/I</i> (mol/mol)	<i>I</i> (mol%)	μ ₀ (mmol/kg)	L-mer (%)	D-mer (%)	<i>k</i> _{eff} (kg/mmol-h)
130	4.6	95.83	1,000	0.1	20.5	99.92	0.08	8.49E-06
130	24	99.57	1,000	0.1	11.1	99.93	0.07	2.63E-06
130	6.07	92.15	2,940	0.034	42.1	99.96	0.04	1.57E-06
130	14.13	99.68	2,940	0.034	42.1	99.96	0.04	6.73E-07
130	49.09	94.81	10,300	0.0097	6.03	99.98	0.02	6.76E-07
160	5	97.65	1,000	0.1	12.5	99.61	0.39	6.24E-05
160	5	97.94	1,000	0.1	13.6	99.66	0.34	5.04E-05
160	11.52	95.75	9,890	0.0101	12	99.82	0.18	1.30E-05
160	45	99.57	9,890	0.0101	12	99.78	0.22	4.08E-06
190	1.4	95.42	1,000	0.1	15.4	99.23	0.77	3.61E-04
190	1.4	97.00	1,000	0.1	13.3	99.25	0.75	4.06E-04
190	14.47	96.77	10,000	0.01	19.7	98.28	1.72	6.14E-05
190	22.62	96.98	10,000	0.01	19.7	97.76	2.24	5.14E-05
220	0.5	95.72	1,000	0.1	14	96.50	3.50	5.18E-03
220	0.5	95.33	1,000	0.1	14	96.95	3.05	4.50E-03
220	2.87	94.63	10,100	0.0099	23.2	97.84	2.16	3.32E-04
220	3.79	95.62	10,100	0.0099	23.2	97.14	2.86	3.35E-04
220	3.5	94.83	20,000	0.005	19.3	97.65	2.35	3.56E-04
220	2.3	88.14	39,600	0.0025	54	95.93	4.07	3.42E-04
220	14	96.04	79,300	0.0013	50	81.81	18.19	3.23E-04

$I = 0$. Because a is approximately constant with temperature (similar slopes in Figure 3-48), we can simply incorporate the Arrhenius temperature dependency terms into k_{rac} .

The resulting three-parameter (a , $A_{rac,448}$, $E_{a,rac}$) racemization model is:

$$D(t) = \frac{1}{2}[1 - (2L_0 - 1)\exp(-2\mu_0 k_{rac} \exp(aI)t)] \quad (3-46)$$

$$k_{\text{rac}} = A_{\text{rac},448} \exp \left(\frac{-E_{\text{a},\text{rac}}}{R} \left(\frac{1}{T(K)} - \frac{1}{448} \right) \right) \quad (3-47)$$

The three parameters were determined by linear regression of

$$\ln k_{\text{eff}} = aI + \ln A_{\text{rac},448} - E_{\text{a},\text{rac}}/R(1/T - 1/448): a = 23.9 \pm 1.9 \text{ mol\%cat}^{-1}, A_{\text{rac},448} = 1.63\text{E-}05 \pm$$

0.20E-05 kg/mmol-h, $E_{\text{a},\text{rac}} = 120 \pm 4 \text{ kJ/mol}$. An Arrhenius plot of $\ln k_{\text{rac}} (= \ln k_{\text{eff}} - aI)$

versus $1/T(K)$ is presented in Figure 3-49. The data are well represented by the model

having an activation energy of 120 kJ/mol. It is noteworthy that the activation energy of

self-catalyzed lactic acid racemization is 114 kJ/mol (Witzke unpublished data) indicating

the same temperature dependence and mechanism. The total model accounts for over

99% of the variance in D-mer data having an RMSE of 0.004 D-mer (0.4% D-mer).

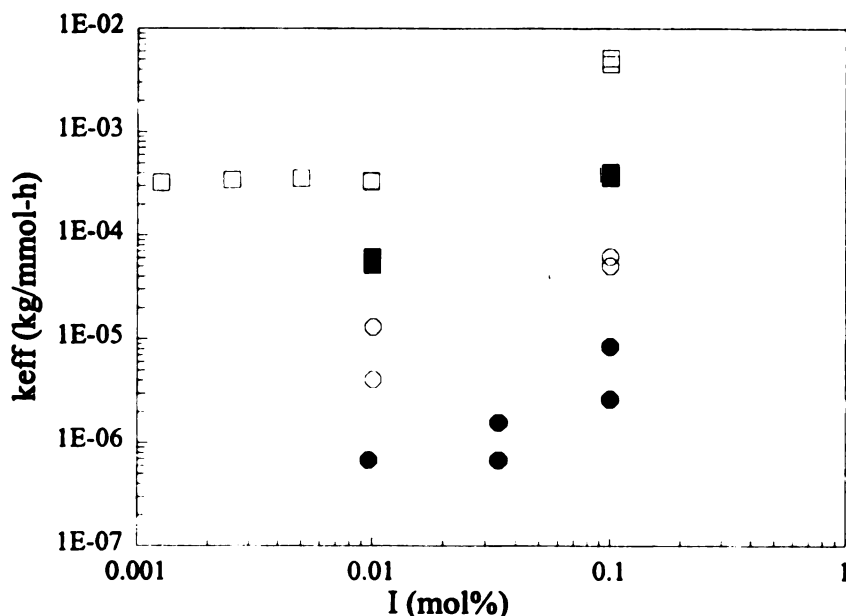


Figure 3-47. Importance of catalyst concentration on the effective racemization rate constant defined in equation (3-44): 220°C (□), 190°C (■), 160°C (○), and 130°C (●).

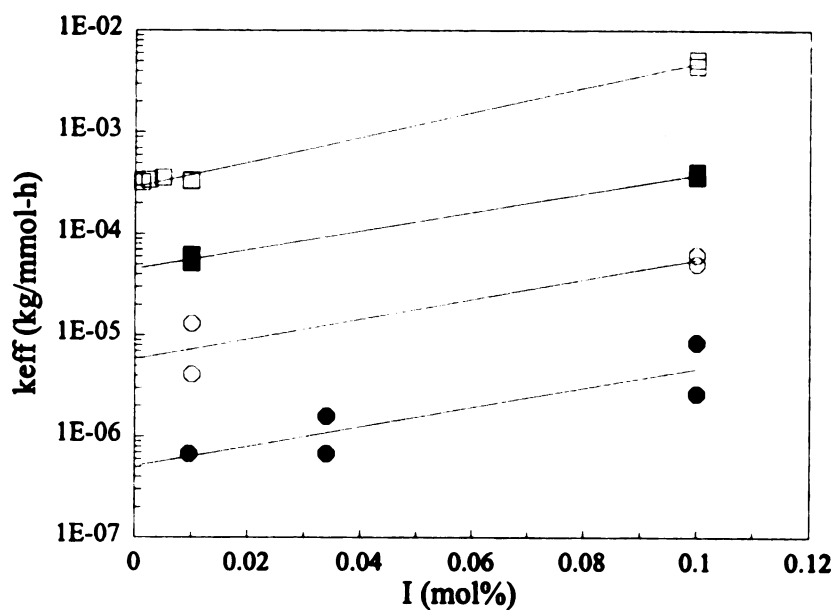


Figure 3-48. Linear relationship between $\ln k_{\text{eff}}$ and I at 220°C (□), 190°C (■), 160°C (○), and 130°C (●). The racemization rate is non-zero at $I = 0$.

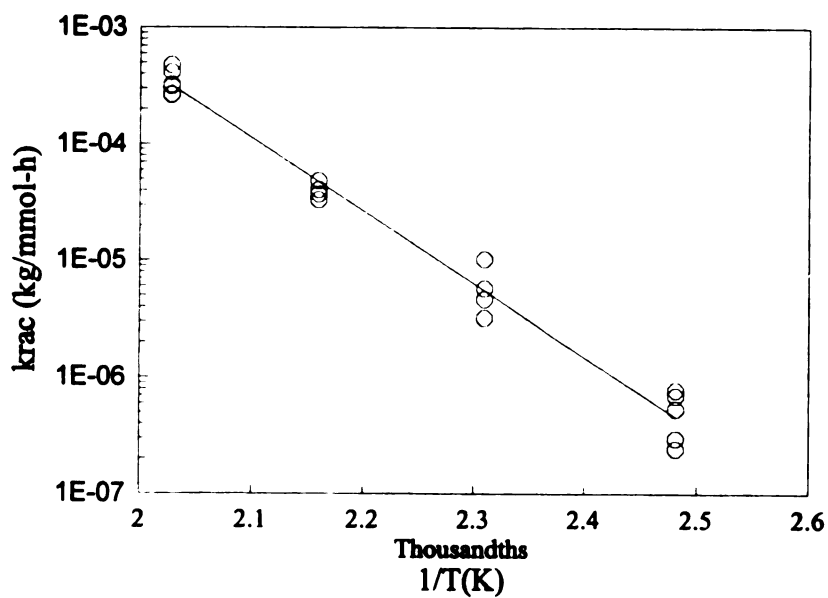


Figure 3-49. Arrhenius temperature dependence of the racemization rate constant, k_{rac} . The activation energy of PLA racemization is 120 kJ/mol.

The lactide obtained from Boehringer Ingelheim for the polymerization work is presumably very pure. However, in this work we did not measure cation impurities such as Na, Mg, and Ca which are also known racemization catalysts. To account for racemization by base catalysis (cations, possibly including the catalyst) a separate rate constant(s) having its own activation energy could be added explicitly to the rate form and regressed to racemization experimental data having various cation distributions.

Although racemization is catalyzed by the Sn(II)ethylhexanoate polymerization catalyst, racemization is reduced using *high* catalyst concentrations for practical polymerization to 95% of equilibrium, $3\theta = 3/(k_p I)$. This is because lactide polymerization is first order in catalyst, and a higher catalyst concentration substantially reduces the polymerization time and lowers the extent of racemization at a given temperature. In other words, the importance of I on racemization is lower than its effect on the rate of lactide polymerization. Table 3-15 presents racemization simulation results for L-lactide plug flow or batch polymerization up to 3θ assuming a lactide feed containing 1% D-mer and 10 mmol/kg hydroxy acid impurities ($M_n = 100,000$ at full conversion). The simulations were conducted with catalyst levels and temperatures between $M/I = 5,000$ -80,000 mol/mol and 180-220°C (180°C represents an approximate lower polymerization temperature limit for adequate melt pumping and mixing of high molecular weight PLA). Figure 3-50 presents the racemization simulation results graphically. It is apparent that racemization is reduced at high catalyst concentrations and low polymerization temperatures. If we consider a net increase of 0.5% D-mer an acceptable level of racemization (i.e., 99% to 99.5% L-mer), we find that the minimum

Table 3-15 Simulated Racemization During L-Lactide Polymerization at Various Catalyst Levels and Temperatures
($D_0 = 1.0\%$, $\mu_0 = 10$ mmol/kg)

M/I (mol/mol)	I (mol%)	T (°C)	k_p (mol%cat ⁻¹ h ⁻¹)	time = 3θ (h)	D-mer (%)
5,000	0.02	180	106	1.4	1.05
		190	159	0.94	1.07
		200	235	0.64	1.09
		210	342	0.44	1.12
		220	489	0.31	1.15
10,000	0.01	180	106	2.8	1.08
		190	159	1.9	1.11
		200	235	1.3	1.15
		210	342	0.88	1.19
		220	489	0.61	1.24
20,000	0.005	180	106	5.7	1.15
		190	159	3.8	1.20
		200	235	2.6	1.26
		210	342	1.8	1.34
		220	489	1.2	1.43
40,000	0.0025	180	106	11.3	1.28
		190	159	7.5	1.37
		200	235	5.1	1.49
		210	342	3.5	1.63
		220	489	2.5	1.81
80,000	0.00125	180	106	22.6	1.54
		190	159	15.1	1.72
		200	235	10.2	1.94
		210	342	7.0	2.22
		220	489	4.9	2.55

catalyst levels for acceptable racemization are: $M/I = 40,000$ at 180°C - 200°C ; and $M/I = 20,000$ at 210 - 220°C . An increase of 0.5% D-mer corresponds to an estimated 20% increase in the crystallization half-time of the PLA resin at 110°C (extrapolation of Kolstad results cited in Section 2.2.1). From these results we can also conclude that racemization should be unimportant at resin processing (part fabrication) conditions (< 20 min, $< 250^{\circ}\text{C}$).

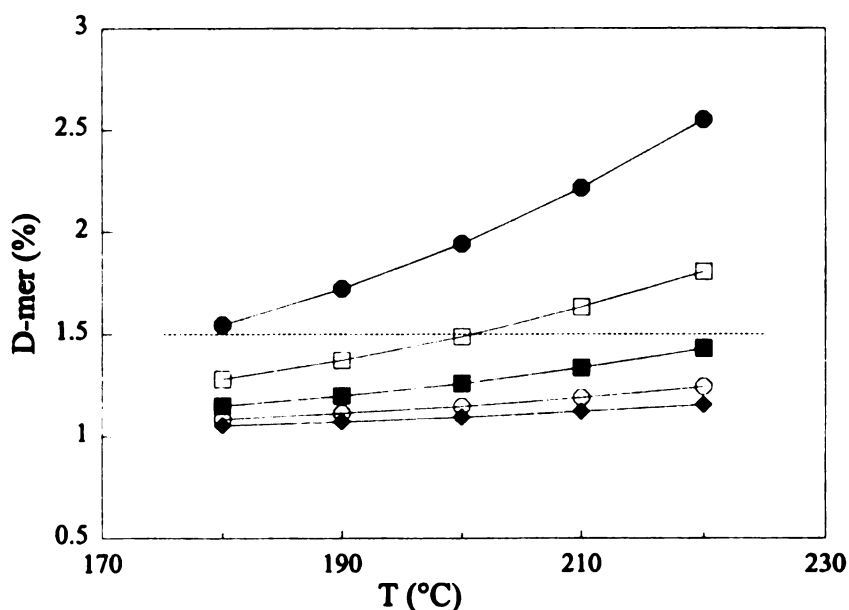


Figure 3-50. Simulation of racemization during L-lactide plug flow or batch polymerization ($\mu_0 = 10$ mmol/kg) starting with 1% initial D-mer at various I and T : $M/I = 80,000$ (●); $M/I = 40,000$ (□); $M/I = 20,000$ (■); $M/I = 10,000$ (○); $M/I = 5,000$ (◆).

Conclusions

A PLA racemization rate model was developed from chiral chromatography results of vial polymerizations conducted over a wide range of temperatures and Sn(II)ethylhexanoate catalyst concentrations. The racemization rate has a first order dependence on acid end groups and like-mer repeat units. The activation energy of PLA

racemization is 120 kJ/mol. Racemization occurs in the absence of polymerization catalyst but its rate increases at high catalyst concentration. However, the effect of catalyst on racemization is less important than its role in reducing polymerization time, and the net result is that racemization is reduced during polymerization at high catalyst concentrations. Calculations indicate that racemization is unimportant at resin processing (part fabrication) conditions.

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Chapter 4 Process Design and Engineering of PLA

4.1 Introduction

In this chapter we apply the physical and chemical properties results of Chapters 2 and 3 to introduce the basic design equations and engineering concepts for bulk PLA production using stannous ethylhexanoate. In Sections 4.2 and 4.3 we design and analyze continuous pilot plant experiments to confirm the developed polymerization and devolatilization design equations using steady state data. An overview of PLA resin drying is presented in Section 4.4 and is based on PLA-water phase equilibrium data. We conclude Chapter 4 by characterizing PLA melt stability and degradation during resin processing. The consequences of imperfect drying are shown experimentally with amorphous PLA injection molding tests and subsequent molecular weight analysis. Calculations are performed to predict molecular weight degradation and lactide depolymerization at various process conditions using the reaction rate equations developed in Chapter 3.

A general process block flow diagram for PLA article manufacture from lactide monomer is presented in Figure 4-1. Because lactide polymerization is first-order-reversible having a significant lactide equilibrium concentration at polymerization conditions, lactide may be removed from the reaction mixture prior to

diminishing returns of lactide conversion (80-90% conversion per pass). This is obvious in a conversion versus time batch polymerization plot (e.g., Figure 3-4). The lactide recovered from melt devolatilization has high purity and must be recycled back to the polymerization step or further back in the process. Following monomer removal the polymer is extruded through a strand die into water where it is cooled to solid form and pelletized. The surface of the strands are exposed to water for a matter of seconds (minimum time can be calculated from thermal conductivity: Section 2.6) and surface hydrolysis is negligible. Pellet drying is essential prior to packaging and subsequent PLA article manufacture. PLA resin is processed at temperatures and times at which melt hydrolysis and lactide depolymerization affect both part cost and performance.

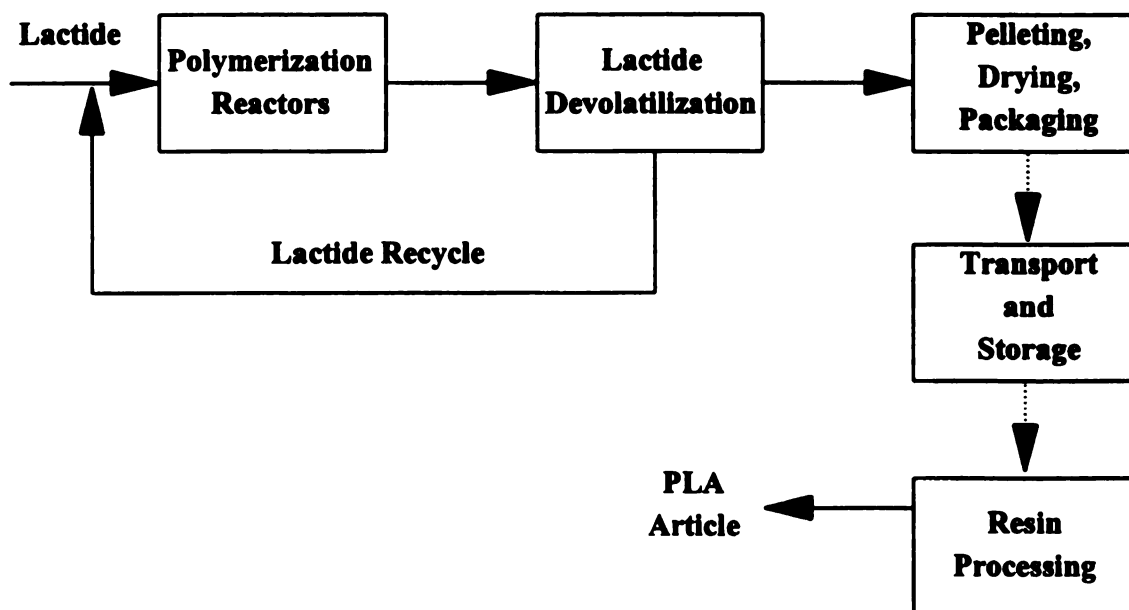


Figure 4-1. Basic block flow diagram for bulk PLA article manufacture from lactide.

4.2 Reaction Engineering

4.2.1 Conceptual Design Considerations

The following issues are critical to lactide polymerization engineering:

polymerization catalyst, energy balance, molecular weight distribution, undesirable side reactions, and conceptual polymerization reactor design and configurations.

Polymerization Catalyst

The choice of polymerization catalyst affects both the polymerization rate and the index of stereospecificity for L-lactide ring-opening polymerization. There are numerous lactide polymerization catalysts.¹⁻³⁰ Most are based on metal catalysts such as tin (II and IV), zinc, aluminum, magnesium, and titanium. In addition, PLA may be prepared from lactide using trivalent catalysts based on the lanthanide series rare earth metals (e.g., yttrium and lanthanum catalysts).¹ Some of these catalysts are considerably more active than the tin-based catalysts. Such systems allow for direct polymerization in an extruder (reactive extrusion) where residence times are typically less than 17 min. However, high melt hydrolysis and high depolymerization rates accompany high polymerization rates (Principle of Microscopic Reversibility). The catalyst must be removed or deactivated with fast polymerization systems to allow for the production of melt stable PLA.

Stannous ethylhexanoate has a reasonable balance of polymerization, depolymerization, and melt hydrolysis rates. For this reason along with other attributes mentioned in Section 3.2 (low racemization rate, FDA approval as food additive) we limit our engineering calculations in this chapter to the stannous ethylhexanoate-PLA system.

However, the rate form and polymerization thermodynamics (e.g., monomer equilibrium) are generally independent of the metal catalyst choice. Hence, the developed rate and engineering equations are still valid with other catalyst systems by using a different rate constant and activation energy.

The optimum polymerization catalyst concentration may depend on such issues as polymerization time (total reactor volume), PLA melt stability, and environmental concern over ultimate tin catalyst disposal. If a catalyst removal or deactivation process step is provided after polymerization, higher catalyst concentrations may be used to minimize polymerization residence time and reactor size. However, if the catalyst is not deactivated then lower catalyst amounts (e.g., 80,000 lactide/Sn (mol/mol)) may be needed to prevent PLA melt instability (i.e., hydrolysis and depolymerization reactions).

As referenced in Chapter 3, acids are known to deactivate the stannous ethylhexanoate catalyst. For biomedical applications, the catalyst is deactivated by dissolving the polymer in solvent, stirring with acidified water, separating the organic and aqueous phases, and removing the polymer from the organic phase (Bendix et al., US 4960866). For commodity PLA applications the catalyst must be deactivated in the bulk where the required good mixing between acid additive and viscous polymer is non-trivial.

Energy Balance Considerations

The relatively low heat of lactide polymerization (-23.3 kJ/mol) compared to most industrial polymers (-73 to -93 kJ/mol)³¹ reduces the heat transfer problems normally

expected in bulk polymerization. The steady-state energy balance for lactide polymerization under conditions of adiabatic operation and negligible stirring work is

$$\int_{T_0}^T C_p(T) dT = -\Delta H_{lc} X_{mon}(T) \quad (4-1)$$

where C_p and $X_{mon,eq}$ are functions of temperature and were determined in Sections 2.2.3 and 3.2.1,

$$C_p^l(T) = 1.71 + 0.00147 T(C) \quad (4-2)$$

$$X_{mon,eq} = 1 - M_{eq} = 1 - \exp\left(\frac{-23,300 \text{ J/mol}}{R(273 + T(C))} + \frac{22 \text{ J/mol/K}}{R}\right) \quad (4-3)$$

The adiabatic temperature for equilibrium lactide polymerization, T , is determined by substituting $C_p(T)$ and $X_{mon,eq}(T)$ into equation (4-1) and integrating between the initial monomer charge temperature, T_0 , and T . Equation (4-4) presents this relationship where the heat of polymerization, ΔH_{lc} , is -161.7 kJ/g.

$$0 = 1.71(T - T_0) + \frac{0.00147}{2}(T^2 - T_0^2) - 161.7\left(1 - \exp\left(\frac{-23300}{8.314(273 + T)} + \frac{22}{8.314}\right)\right) \quad (4-4)$$

For a lactide charge temperature of 160°C the adiabatic temperature is calculated to be 236°C at an equilibrium conversion of $X_{mon}(236^\circ\text{C}) = 0.943$. The adiabatic temperature rise, $\Delta T_{ad} = T - T_0$, decreases by 1°C per 10°C T_0 increase (e.g., $\Delta T_{ad} = 79^\circ\text{C}$ at $T_0 = 130^\circ\text{C}$,

$\Delta T_{ad} = 76^{\circ}\text{C}$ at $T_0 = 160^{\circ}\text{C}$, and $\Delta T_{ad} = 73^{\circ}\text{C}$ at $T_0 = 190^{\circ}\text{C}$). Therefore, at bulk temperatures the adiabatic temperature rise for lactide equilibrium polymerization is approximately 76°C .

The heat removal requirement for continuous isothermal operation of a lactide polymerization reactor depends on the rate of polymerization and hence the catalyst choice, catalyst concentration, and polymerization temperature. Using the reversible polymerization model, equation (3-6), and an energy balance on the specific polymerization reactor (i.e., overall heat transfer coefficient and surface area), the heat removal requirement is calculated for stannous ethylhexanoate catalyzed lactide polymerization.

Molecular Weight Distribution

The number average molecular weight, M_n , is determined by the number of hydroxyl impurities in the lactide feed and is generally independent of polymerization temperature. The metered addition of lactic acid or water to a very pure lactide is a convenient way to control M_n . Although the number of chains and M_n are controlled by the hydroxyl impurities, the manner in which the repeat units are distributed among the polymer chains (polydispersity) depends on two factors: (1) the goodness of mixing in the reactors and (2) the extent of transesterification among PLA chains. Polymer interchange reactions (transesterification) decrease the effect of incomplete mixing by randomly rearranging the repeat units and slowly bringing the molecular weight distribution towards the Most Probable Distribution (e.g., $PDI = M_w/M_n = 2.0$). The direction of

approach toward the Most Probable Distribution depends on the reactor type and its mixing characteristics.

In a continuous stirred tank reactor (CSTR) the exiting polymer chains have a distribution of ages. Some polymer chains quickly exit the reactor following initiation and have a low degree of polymerization; others are back-mixed and experience much longer times in the high monomer concentration pool and achieve a higher degree of polymerization. Back-mixing results in a lower lactide consumption rate (first-order in lactide) and a longer mean polymerization time. In addition, incomplete mixing is likely in a CSTR and acts to broaden the molecular weight distribution. For this reason transesterification reactions tend to *decrease* the *PDI* towards 2.0 in a CSTR.

In a plug flow type reactor (PFR; i.e., batch kinetics) all of the polymer chains should experience close to the same polymerization time and the molecular weight distribution is initially narrow. PFR transesterification *increases* the *PDI* towards 2.0.

The importance of transesterification with respect to polymerization was found to decrease with temperature in Chapter 3. Because bulk polymerization temperatures must be above 160°C for viscosity reasons, a PFR may result in a PLA having a $PDI < 2$. In a series of CSTRs the molecular weight distribution depends on the goodness of mixing, polymerization residence time distribution, polymerization reactor temperatures, and catalyst concentration. The transesterification rate model (Section 3.4) may be used with the residence time distribution to predict the MWD for various polymerization conditions and reactor designs. In CSTRs the rate of PLA transesterification is generally not

sufficient to cancel the effect of incomplete mixing on the polydispersity. PDI of 2.0-3.5 are typical for two CSTRs in series.

In concept, by properly choosing the number of ideal reactor stages and polymerization conditions, PLA with specific molecular weight properties can be targeted for specific products. Because many polymer properties are dominated by the population of large size polymer chains and better correlate with higher moment molecular weight averages than M_n (e.g., viscosity correlates with M_w), a polydisperse polymer has industrial significance. However, because of bulk viscosity, mixing, undesirable degradation, and melt stability requirements, the choice of polymerization temperature and catalyst concentration is limited. In addition, multiple ideal reactor stages are required to minimize the extent of racemization and color formation which are both zeroth order in monomer concentration: these reactions are insensitive to monomer conversion and depend only on temperature, time, and any rate enhancing impurities. Chemical modification (e.g., limited cross-linking) offers an alternative approach to achieving high polydispersity PLA in a narrow residence time distribution bulk process.

To repeat, M_n is controlled by the monomer feed purity, and the molecular weight distribution is determined by polymerization process conditions and reactor cascade design.

Undesirable Side Reactions

Undesirable side reactions in bulk lactide polymerization include racemization, color formation, and non-hydrolytic chain cleavage. In the polymerization experiments

conducted in Chapter 3 the extent of these side reactions were found to increase with temperature for a given monomer conversion. The ratio of activation energies for racemization and stannous ethylhexanoate polymerization are $E_{a,rc}/E_{a,p} = (120 \text{ kJ/mol}) / (70.9 \text{ kJ/mol}) = 1.7$. The ratio of activation energies for non-hydrolytic degradation and polymerization are $E_{a,deg}/E_{a,p} = (126 \text{ kJ/mol}) / (70.9 \text{ kJ/mol}) = 1.8$. In addition, we observe that the extent of color formation during lactide bulk polymerization increases with temperature for a given conversion and therefore has an effectively greater activation energy than lactide propagation.

Approaches to minimizing these undesirable side reactions during bulk lactide polymerization include lowering reactor temperatures (toward the bulk viscosity constraint), using a high catalyst concentration to decrease polymerization time, and decreasing the residence time distribution by using a reactor cascade having a large number of ideal stages (or PFR). The latter approach is a result of these side reactions having zeroth order kinetics with respect to lactide concentration, compared to the first-order kinetics of the forward polymerization reaction.

Polymerization Mode

Bulk lactide ring-opening polymerization mixtures are miscible at all conversions (homogeneous above T_m). Continuous polymerization is attractive for the large scale production of PLA when there are not frequent product changes. However, when frequent product changes are required from the same polymerization line, a batch polymerization mode may be employed to minimize the production of off-grade polymer.

Polymerization Reactors and Process Configurations

There are basically four common types of continuous polymerization reactors: continuous stirred tank reactor (CSTR), continuous agitated vertical column, continuous externally pressurized reactor (CEPR), and drag flow reactor (DFR).

The CSTR is the most prevalent polymer reactor. As previously mentioned, a CSTR has a broad residence time distribution and tends to give a polydisperse polymer. Helical agitators are used to handle high viscosity reaction mixtures. The continuous agitated vertical column is basically a high L/D CSTR. In this reactor, monomer enters the top of the column and polymer exits the bottom. The column is agitated to provide radial mixing and has limited longitudinal mixing owing to the high L/D. This reactor can be modeled as a series of vertical CSTRs in series (about 5 ideal stages depending on the L/D ratio and agitator design).

The CEPR is a tubular reactor that can be operated in the turbulent (low conversion and viscosity) or laminar (high viscosity) regimes. Although used for polyethylene manufacture, this type of reactor has found limited use for other bulk polymerization reactions. This is because of the high viscosities that are encountered at relatively low conversions which result in difficulties in controlling reaction temperature (radial temperature gradient) and polydispersity. In addition, flow occlusion often occurs because of the accumulation of slow moving viscous material along the reactor walls. A DFR is normally an extruder or a kneading disc type reactor that provides flow by internal pressurization (conveying). For this reason DFRs are generally preferred over CEPRs for high viscosity reactions. The kneading disc type DFRs provide longer reaction

times than extruders which are normally limited to about 17 min. These reactors generally have very little longitudinal mixing and have narrow residence time distributions. CEPRs and DFRs may be modeled as plug flow reactors.

Rational reactor cascade design for PLA manufacture is dominated by the need to maximize the specific rate of polymerization to minimize the undesirable side reactions (racemization, color formation, and non-hydrolytic chain cleavage). For this purpose, the reactor cascade must have a narrow residence time distribution and be operated at the lowest temperature that still allows for adequate melt mixing and pumping. A narrow residence time distribution maximizes the effective lactide concentration and gives the lowest mean residence time of polymerization. The incorporation of degradation stabilizers and identifying and removing degradation accelerating impurities may permit greater flexibility in reactor cascade design and lactide polymerization conditions.

The following general reactor cascades are reasonable for continuous bulk lactide polymerization:

- (1) Cascade of CSTRs, $n \geq 3$
- (2) CSTR followed by DFR
- (3) CEPR followed by DFR (plug flow cascade)
- (4) Agitated vertical column, possibly with DFR finishing.

Process configuration (1) entails equal volume reactors having intermediate fractional lactide conversions (for $n = 3$) of approximately 0.50 and 0.80 for a final

pre-devolatilization conversion of 0.90 (see simulation results in Section 4.2.2). Process configurations (2) and (3) employ DFRs as secondary or finishing reactors. In case (2) the DFR provides for a much narrower residence time distribution and decreased mean polymerization time. In case (3) the DFR takes effluent from the primary reactor after a reaction viscosity is reached where it is no longer economically feasible to operate the CEPR. The agitated vertical column, case (4), may be easier to operate than a cascade of CSTRs. Depending on final viscosity and mixing behavior a DFR may be needed as a high viscosity finishing reactor.

4.2.2 Reactor Design Equations and Simulations

PLA reactor design equations are derived from the reversible kinetics model, equation (3-6). In this subsection we present the basic PLA reactor design equations along with their simulation results at practical polymerization conditions. From these results we draw inferences about rational lactide polymerization design.

Basic Design Equations

The following nomenclature is used: V = reactor volume, m = reaction mass or mass rate (dotted m), ρ = density, I = mol% catalyst, R = ideal gas constant (8.314 J/mol-K), M_0 = initial lactide weight fraction, X_{mon} = fractional lactide conversion, k_p = lactide propagation rate constant, and M_{eq} = lactide equilibrium mass fraction. Equations for ρ , k_p (stannous ethylhexanoate), and M_{eq} were determined in Sections 2.3 and 3.2,

$$\rho(\text{g/cm}^3) = \frac{1.145}{1 + 0.0007391(T(\text{C}) - 150)} \quad (4-5)$$

$$k_p = 86 \text{ hr}^{-1} \text{ catmol}\%^{-1} \exp\left(\frac{-70,900 \text{ J/mol}}{R} \left(\frac{1}{T(\text{K})} - \frac{1}{448\text{K}}\right)\right) \quad (4-6)$$

$$M_{eq} = \exp\left(\frac{-23,300 \text{ J/mol}}{RT} + \frac{22 \text{ J/mol/K}}{R}\right) \quad (4-7)$$

The following design equations were obtained by integrating the lactide mole balance with the reversible polymerization model. Equation (4-8) is the batch reactor volume required for a given lactide mass charge. In a CSTR the volume required for a given mass rate is calculated using equation (4-9). For 2 CSTRs in series the volume requirement for the first reactor depends on the intermediate conversion, $X_{mon,1}$, and is described by equation (4-9). The second CSTR volume requirement is calculated using equation (4-10). The kinetics in a plug flow reactor are equivalent to that of batch kinetics and the PFR volume requirement for a given production rate is calculated using equation (4-11). For a CSTR and PFR in series the V_1 and V_2 volume requirements are calculated using equations (4-9) and (4-12), respectively.

$$V^{\text{batch}} = \frac{-\dot{m}}{\rho k_p I} \ln \left[\frac{M_0(1 - X_{mon}) - M_{eq}}{M_0 - M_{eq}} \right] \quad (4-8)$$

$$V^{\text{CSTR}} = \frac{\dot{m}}{\rho k_p I} \frac{X_{mon}}{[M_0(1 - X_{mon}) - M_{eq}]} \quad (4-9)$$

$$V_2^{\text{CSTR}} = \frac{\dot{m}}{\rho k_p I} \frac{(X_{mon,2} - X_{mon,1})}{[M_0(1 - X_{mon,2}) - M_{eq}]} \quad (4-10)$$

$$V^{\text{PFR}} = \frac{-\dot{m}}{\rho k_p I} \ln \left[\frac{M_0(1 - X_{\text{mon}}) - M_{\text{eq}}}{M_0 - M_{\text{eq}}} \right] \quad (4-11)$$

$$V_2^{\text{PFR}} = \frac{-\dot{m}}{\rho k_p I} \ln \left[\frac{M_0(1 - X_{\text{mon},2}) - M_{\text{eq}}}{M_0(1 - X_{\text{mon},1}) - M_{\text{eq}}} \right] \quad (4-12)$$

Simulation Results

The importance of a multiple staged polymerization system on reducing the longitudinal back-mixing and the mean polymerization time, τ , is demonstrated by calculating τ and the cumulative residence time distribution as a function of the number of ideal stages. These calculations of τ for a series of reactors are facilitated by the first-order-reversible kinetics property that the total volume of n CSTRs is minimized when the individual reactors are of equal volume,

$$V_1 = V_2 = \dots = V_n \quad (4-13)$$

Equation (4-13) is easily derived algebraically from first-order-reversible kinetics and CSTR design equations. To calculate τ for n stages the intermediate conversions must be determined such that the reactors are of equal volume and the total residence time is minimized. This can be solved graphically by constructing a plot of $-1/\text{rate}$ versus conversion whereby the intermediate conversions are manipulated until all CSTR volumes (area under curve) are equal. However, this is quite labor intensive for more than

a few CSTRs and a mathematical solution is desirable. For this purpose, we set up and solve the following optimization problem to calculate τ for n ideal stages:

Objective Function

$$\text{MIN } \tau(h) = \frac{1}{k_P I} \left[\frac{X_1}{(1 - X_1 - M_{eq})} + \frac{X_2}{(1 - X_2 - M_{eq})} + \dots + \frac{X_n}{(1 - X_n - M_{eq})} \right] \quad (4-14)$$

The objective is to minimize the total average polymerization time for a cascade of n reactors.

Fixed Variables

$$T, I, X_n$$

Manipulated Variables

$$X_1, X_2, \dots, X_{n-1}$$

Constraint Equations

$$X_1 = (X_2 - X_1) \frac{(1 - X_1 - M_{eq})}{(1 - X_2 - M_{eq})}$$

$$X_2 = X_3 - X_1 \frac{(1 - X_3 - M_{eq})}{(1 - X_1 - M_{eq})}$$

•
•
•

$$X_{n-1} = X_n - X_1 \frac{(1 - X_n - M_{eq})}{(1 - X_1 - M_{eq})}$$

$$0 \leq X_1 \leq X_2; \quad X_2 \leq X_3; \quad \dots; \quad X_{n-1} \leq X_n$$

The above optimization problem was solved for $n = 1-6$ and compared to the PFR result in Table 4-1 for polymerization conditions of 180°C ($M_{\text{eq}} = 0.029$, $k_p = 106.1 \text{ h}^{-1}\text{mol\%cat}^{-1}$), $X_n = 0.90$, and various catalyst concentrations: $M/I = 5,000 - 80,000$ lactide/Sn (mol/mol). The solutions were solved in Microsoft Excel using the provided nonlinear programming solver (Newton search algorithm with forward derivatives and tangent estimates).

Table 4-1 Simulation Results for the Effect of The Number of Ideal CSTR Stages on the Polymerization Time for Various Catalyst Concentrations at 180°C and $X_n = 0.90$

number stages	Total Mean Polymerization Time (hr)				
	$M/I = 5,000$ (0.02 mol%cat)	$M/I = 10,000$ (0.01 mol%cat)	$M/I = 20,000$ (0.005 mol%cat)	$M/I = 40,000$ (0.0025 mol%cat)	$M/I = 80,000$ (0.00125 mol%cat)
1	5.97	11.95	23.89	47.79	95.57
2	2.54	5.09	10.17	20.34	40.69
3	1.97	3.93	7.87	15.74	31.47
4	1.74	3.48	6.96	13.92	27.84
5	1.62	3.24	6.48	12.95	25.91
6	1.54	3.09	6.18	12.36	24.72
PFR	1.23	2.47	4.93	9.86	19.72

At 90% final conversion the average polymerization time is decreased by 57% when 2 stages are employed instead of 1 CSTR. The single stage CSTR has nearly 5 times the residence time (or reactor volume) as a PFR. Since the polymerization is first-order in catalyst concentration, τ is proportional to I . At $M/I = 5,000$ the polymerization is quite fast but catalyst deactivation is required for resin processing melt

stability. At $M/I = 80,000$ the polymerization times are still very reasonable and the resulting PLA has decent melt stability. However, the longer mean residence time at this low catalyst concentration results in more pronounced side reactions such as racemization, non-hydrolytic degradation, and yellow color formation.

The effect of temperature on the mean polymerization time of stannous ethylhexanoate catalyzed lactide polymerization is determined directly from the activation energy of propagation, 70.9 kJ/mol. For a 10°C temperature increase the propagation rate constant increases by 50% and the mean polymerization time decreases by 33%. However, racemization, color formation, and non-hydrolytic degradation have higher activation energies and these reactions become more important with increasing temperature.

In an equal volume 2 CSTR system the intermediate conversion is $X_1 = 0.71$ with $X_2 = 0.9$. The viscosity in the first reactor is quite high and mixing problems (e.g., lactide channeling) may occur because of the addition of lactide (about 1 cP, Section 2.8) to this reaction mixture (about 10,000 cP, Section 2.5.3). The mixture viscosity in the first reactor can be decreased by decreasing the volume of the first reactor and increasing the volume of the second. For example, at $X_1 = 0.5$ the mixture viscosity is significantly lowered and the ratio of reactor volumes is $V_2/V_1 = 5.3$. This unequal reactor volume design comes at a cost of increasing the mean polymerization time by 24%.

The ideal generalized cumulative residence time distribution for a series of n CSTRs of equal volume is given by

$$F(t) = 1 - \exp\left(\frac{-nt}{\tau}\right) \left[1 + \frac{nt}{\tau} + \frac{1}{2!} \left(\frac{nt}{\tau}\right)^2 + \dots + \frac{1}{(n-1)!} \left(\frac{nt}{\tau}\right)^{n-1} \right] \quad (4-15)$$

where t , τ , and $F(t)$ are time, mean polymerization time (from Table 4-1), and the fraction of repeat units that have exited the reactor cascade. This is shown graphically in Figure 4-2 for $n = 1-6$ and the PFR result at 180°C , $X_n = 0.90$, and $M/I = 20,000$. Although the mean residence time for the 2 CSTR case is 10.2 h, 5% of the repeat units remain in the reactor after 24 h. For all cases the times at $F(t) = 0.95$ are: 72 h, 24 h, 16 h, 13 h, 12 h, 11 h, and 4.93 h for $n = 1-6$ and PFR, respectively. The residence time distribution (extent of longitudinal mixing) is particularly sensitive to values of $n = 1-4$.

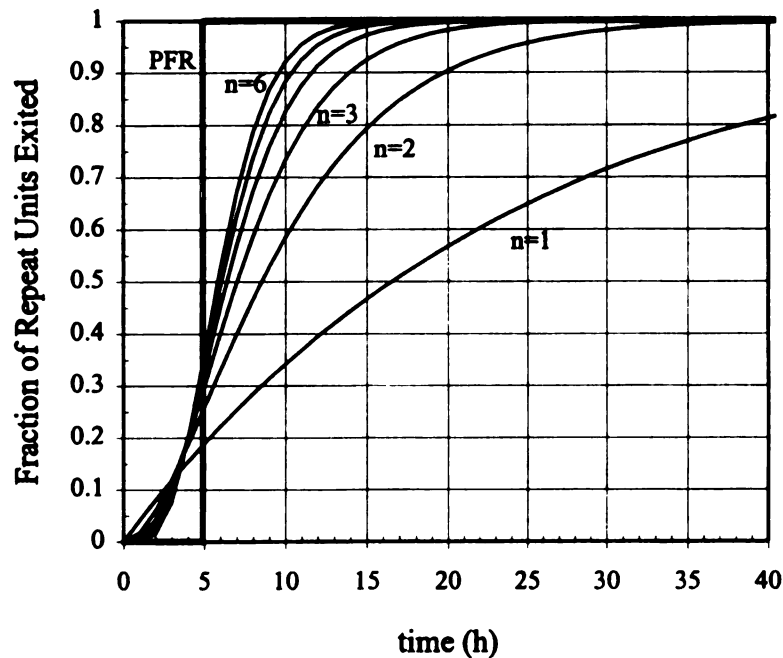


Figure 4-2. Cumulative residence time distribution for lactide polymerization at 180°C , $M/I = 20,000$ mol lactide/mol Sn , and $X_n = 0.90$.

4.2.3 Pilot Plant Experimental Data

Using the reversible lactide polymerization model, equation (3-6), and the reactor design equations presented in Section 4.2.2 we designed a 2 CSTR pilot plant that was operated continuously for two years by Cargill Inc. with a fully staffed operations team. In this subsection we present continuous pilot plant data from a kinetics study we designed and analyzed with the aid of the Cargill operations team. The continuous pilot plant experiments were conducted over a wide range of temperatures, 170-200°C; catalyst concentrations, $M/I = 10,000\text{--}60,000$ mol lactide/mol Sn; and final monomer conversions, $X_{\text{mon}} = 0.76\text{--}0.96$.

Pilot Plant Design

The bulk lactide polymerization pilot plant was designed by a team of Michigan Biotechnology Institute engineers including myself. The pilot plant consists of 2 CSTRs in series having helical agitators and flood volumes of 1.2 and 6.1 gallons. A reactor volume ratio of $V_2/V_1 = 5$ was selected to ensure good mixing in the first CSTR. The pilot plant was designed for 5 lb/h continuous PLA production. The pilot plant is owned and operated by Cargill Inc.

Experimental Plan

Ten continuous pilot plant runs were performed at various temperatures and catalyst levels with a lactide mass rate of 2 kg/h. Lactic acid was added continuously (0.02 g/min) to the lactide feed to lower and maintain a M_n such that the lower

temperature conditions could be achieved. The catalyst was tin(II) ethylhexanoate (Aldrich). CSTR1 and CSTR2 were operated 80% full at 15 rpm and 65% full at 5 rpm, respectively. The time between experimental runs was 2.8 average residence times (about 24 h); based on the ideal two CSTR residence time distribution this suggests that 97% of the material was at the desired catalyst level prior to data collection. Gel Permeation Chromatography (Section 3.2 for setup) was used to determine monomer concentration and polymer molecular weights.

The ten experimental runs were based on targeted final conversions from the reactor cascade kinetics model. At this scale the volume of the pipe (0.44 gallons) between the 2 CSTRs is significant and is modeled as a PFR between the 2 CSTRs:

$$X_{1,\text{CSTR}}, X_{2,\text{PFR}}, X_{3,\text{CSTR}}.$$

Results

The results of the pilot plant lactide polymerization experimental design are presented in Table 4-2. The actual and model prediction X_{mon} are in good agreement for 9 of the 10 experimental runs. The reason for the low conversion in Run 5 is unknown. In general, the pilot plant data falls within a few percent of either side of the model predictions. The reversible polymerization kinetics model is confirmed over the industrial range of temperatures and catalyst concentrations using normal reactor design equations. Furthermore, the success in achieving targeted conversions between 80-95% where depolymerization (reversibility) is important confirms an accurate quantitative description of monomer-polymer chemical equilibrium (thermodynamics).

Table 4-2 Pilot Plant Continuous Bulk Lactide Polymerization Kinetics Results

Run	T_{ave} (°C)	M/I target (mol/mol)	M/I measured (mol/mol)	M_n (g/mol)	PDI (M_w/M_n)	Model X_{mon}	Actual X_{mon}
1	195.1	10,000	9,730	62,900	1.93	96.1	95.4
2	184.6	10,000	10,570	72,600	2.13	95.9	95.3
3	175.1	10,000	10,070	74,700	2.14	95.6	95.1
10	200.4	67,000	61,340	82,100	1.94	84.5	87.4
7	184.3	28,000	29,950	80,400	2.21	89.2	87.3
4	173.5	20,000	20,080	46,300	1.69	89.0	92.1
8	197.2	42,000	40,610	75,800	2.06	89.2	85.2
6	174.1	20,000	20,450	89,100	1.94	89.5	84.4
9	182.8	45,000	53,050	74,500	1.86	76.7	78.7
5	171.4	30,000	29,160	62,400	1.92	82.5	69.8

In general, we have observed equivalent kinetics in lactide polymerizations over a wide scale: DSC cells (10 mg), vial polymerizations (5 g), Parr Reactors (1 liter), 1 and 5 gallon pilot CSTRs. In addition, this same reversible kinetics model was used by a team of Cargill engineers to design the polymerization cascade for Cargill's 10 million lb/y PLA plant in Savage, MN. We conclude that the presented reversible polymerization model and appropriate reactor design equations are valid for engineering calculations for bulk lactide polymerization using stannous ethylhexanoate.

4.3 Devolatilization

After polymerization polylactide contains about 5-15% unreacted lactide. This is a result of practical polymerization time constraints owing to diminishing returns of lactide conversion with time (increasing importance of polymerization reversibility). Minimizing polymerization time is also important to limit the extent of undesirable side reactions, which are independent of lactide concentration.

Although generally non-toxic, lactide must be removed from PLA to facilitate resin processing where lactide will diffuse from the hot polymer melt, in high surface area-to-volume processes, and sublime as low bulk density crystals on the processing equipment. This would result in frequent and expensive shutdowns for equipment cleaning. Furthermore, lactide is more readily hydrolyzed than PLA and facilitates resin process degradation by hydrolyzing to lactoyllactic acid (DP2) which further transesterifies with PLA to decrease molecular weight.

In this section we investigate the effects of melt devolatilization process conditions on the removal of lactide using a Leistritz 34 mm co-rotating twin screw extruder equipped with two separate vacuum zones with nitrogen sweeping.

Lactide Removal Processes

Processes to remove lactide from polylactide include: (1) solvent extraction, (2) reactive batch devolatilization, (3) crystallization with continued amorphous phase polymerization at low temperature, and (4) melt devolatilization.

In the biomedical literature lactide is removed from polylactide by dissolving the polymer in a solvent (e.g., chloroform) and then precipitating PLA in another solvent (e.g., methanol) where the lactide remains in solution. In the methanol system, lactide quickly transesterifies with the solvent (ring-opening) and can not easily be recovered and recycled. Although solvent systems will remove unreacted lactide, yellow color, and catalyst, the solvent must itself then be removed from PLA. This is not especially easy because of the low required final solvent concentration and the low desired PLA processing temperature.

Reactive devolatilization employs a separate batch step where amorphous PLA pellets are heated to about 100-130°C and then subjected to high vacuum where lactide will diffuse (no boiling) from the polymer melt (fused pellets). In addition, the amorphous phase polymerizes (at least initially) toward the low monomer equilibrium concentration at this temperature. After about one day a low monomer concentration is obtained and the polymer is mechanically removed and re-pelletized. Although a convenient method for small lab samples, large-scale reactive devolatilization would most likely be impractical.

Potentially crystalline PLA pellets can be pre-crystallized and then polymerized in large hoppers at about 100-130°C to low lactide concentrations. In this system vacuum is not required and the driving force toward low monomer concentration is the removal of PLA from the reactive amorphous system by crystallization (Section 3.2),

$$M_{eq,apparent} = (1 - \omega)M_{eq,amorphous} \quad (4-16)$$

where ω is the crystalline mass fraction. Pre-crystallization prevents fusing of the pellets at these temperatures and bin pressures, and the resulting pellets can be directly packaged for shipping. However, polymerization is slow at these low temperatures and about one week is required to obtain less than 0.5% lactide with high catalyst concentrations (calculated from Section 3.2 equations). Because of this long time and the fact that low catalyst concentrations may be desired for resin melt stability (hence, much longer post-polymerization times would be needed) this lactide removal approach is probably not practical at large scale.

Continuous melt devolatilization is fast and economical and is the predominant monomer removal process for commodity plastics. Melt devolatilization consists of briefly exposing a high surface area-to-volume polymer melt to vacuum where the monomer boils and is removed with the vapor phase (e.g., starve-fed extruder with vacuum venting zones and subsequent pelleting). In the remainder of this section we consider only melt devolatilization.

4.3.1 Melt Devolatilization Requirements

There are two major difficulties of lactide devolatilization which are uncommon to commodity polymers: (1) lactide is a very high boiling temperature monomer and has a low vapor pressure at devolatilization temperatures (e.g., T_b (lactide) = 255°C; T_b (styrene) = 145°C); (2) lactide is devolatilized to below its liquid monomer equilibrium concentration and the devolatilization temperature must be lower than otherwise desired (for phase equilibrium) to minimize depolymerization.

Thermodynamic Pressure Requirement

An approximate lactide-poly(lactide) phase equilibrium model was developed in Section 2.7.1. This relationship is used to calculate the lactide boiling pressure requirement, P_1 , for devolatilization to a certain monomer fraction, ϕ_1 , at a given temperature,

$$P_1 = a_1 P_1^{\text{sat}} = \exp \left(\ln \phi_1 + (1 - \phi_1) + 0.3(1 - \phi_1)^2 \right) \exp \left(21.0 - \frac{7600}{T(K)} \right) \quad (4-17)$$

The vacuum requirement increases with decreasing lactide fraction. This is shown graphically in Figure 4-3 for $\phi_1 = 0.01, 0.0075, 0.005, 0.0025, 0.001, 0.0005$ at temperatures between 180-250°C. At 220°C and 1 mmHg pressure the calculated theoretical limit for lactide devolatilization is 0.1% lactide; this value is more than an order of magnitude greater than the monomer concentration achieved in polystyrene devolatilization.

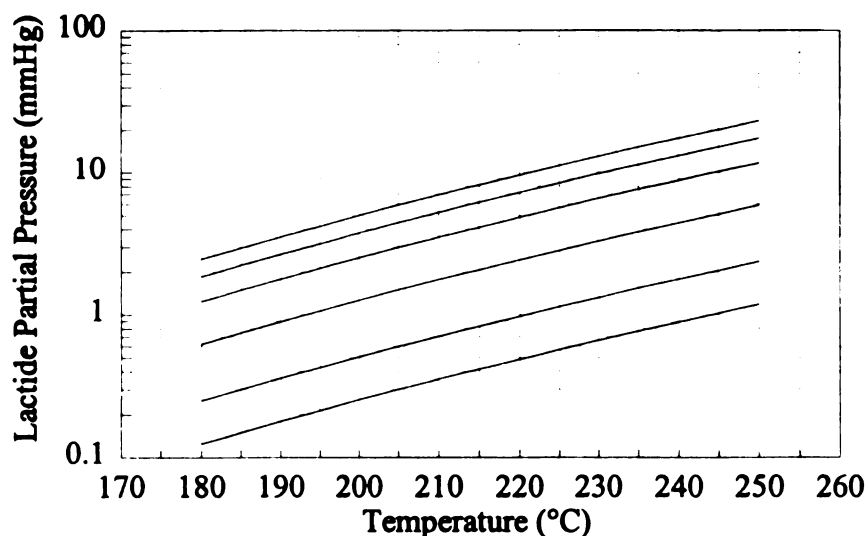


Figure 4-3. Boiling pressure requirement for PLA devolatilization to various lactide concentrations; (in order of increasing pressure) 0.05%, 0.1%, 0.25%, 0.5%, 0.75%, 1%.

The vacuum requirement for lactide devolatilization is reduced (higher pressure) by the addition of an inert gas such as nitrogen to the vapor phase,

$$P = \frac{a_1 P_1^{\text{sat}}}{y_1} \quad (4-18)$$

where y_1 is the mole fraction of lactide in the vapor phase. Because of the low vapor pressure of lactide the addition of an inert gas to dilute the lactide vapor concentration and increase the activity driving force is very important for lactide devolatilization. In addition, the inert may be injected into the melt to increase vapor surface area (foaming) and improve the lactide mass transfer rate.

In lactide devolatilization liquid-vapor phase equilibrium competes with lactide-poly lactide chemical equilibrium. At 220°C and 1 mmHg the liquid-vapor equilibrium is 0.1% lactide but the liquid lactide equilibrium concentration is 4.8%. Lactide polymerization equilibrium and liquid-vapor equilibrium between 180-250°C are presented in Figure 4-4. The actual achieved monomer concentration during devolatilization falls between these two equilibrium curves and depends on the relative rates of mass transfer (surface area-to-volume, surface renewal) and depolymerization (catalyst concentration) at given process conditions, T and P .

Experimentally we have observed that an optimum temperature exists for the melt devolatilization of a specific polylactide. With increasing devolatilization temperature from 180°C, the polymer's lactide concentration decreases (improved separation) because of increased lactide vapor pressure and diffusion coefficient. However, when the

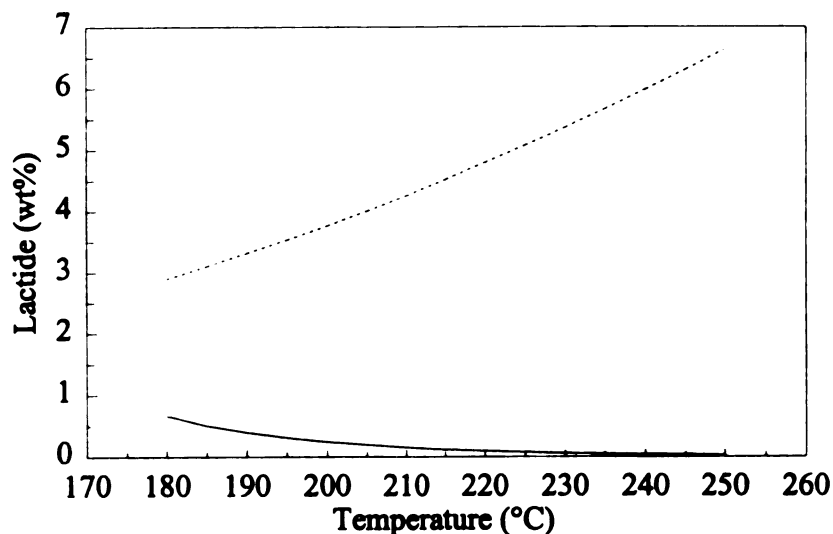


Figure 4-4. Lactide chemical (reversible polymerization; dashed line) and phase (vapor-liquid; solid line) equilibrium at 1 mmHg.

temperature increases beyond a certain value, the polymer's lactide concentration begins to increase with temperature because of increased depolymerization. The effect of depolymerization on increasing the percent lactide following devolatilization to 0.1% at 220°C is predicted in Figure 4-5 for 5,000 mol lactide/mol Sn(II) and 80,000 mol lactide/mol Sn(II), using the reversible model (equation 3-6; $M_0 = 0.001$). In less than 0.5 min the high-catalyst PLA develops a lactide concentration in excess of 0.5%. It takes the low-catalyst sample 8 min to develop the same extent of depolymerization. Clearly, lower catalyst levels improve melt devolatilization by decreasing lactide reformation in the pressurized zone after devolatilization and prior to melt quenching. The optimum devolatilization temperature depends on the polymer molecular weight, catalyst concentration, system pressure, and process configuration and conditions.

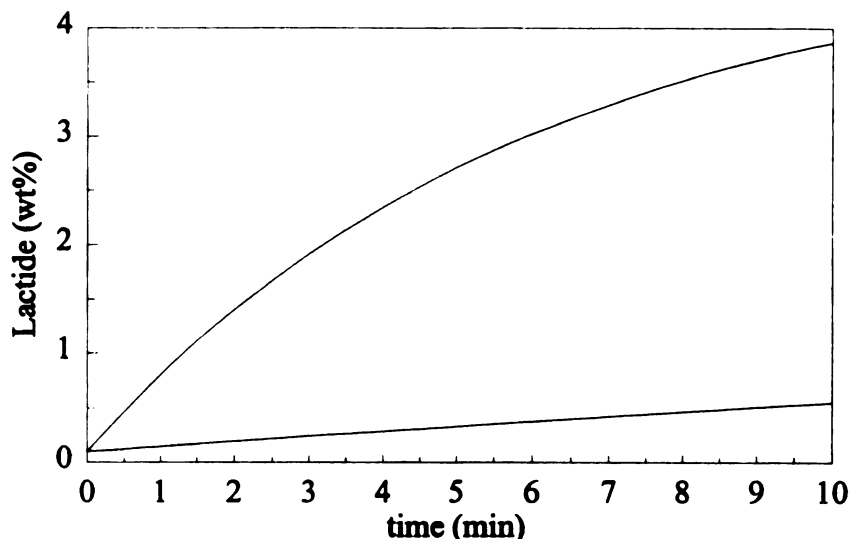


Figure 4-5. Depolymerization at 220°C following devolatilization to 0.1% lactide; 5,000 mol lactide/mol Sn (top curve), 80,000 mol lactide/mol Sn (bottom curve). Predictions are based on the reversible model (equation (3-6), $M_0 = 0.001$, $M_{\infty}(220^{\circ}\text{C}) = 0.0479$, $k_p(220^{\circ}\text{C}) = 488.7 \text{ h}^{-1}\text{mol}\%\text{cat}^{-1}$).

Rate Effects

The flux of lactide vapor from the melt depends on the lactide activity driving force; the interfacial surface generation, renewal, and contact time provided by the devolatilization equipment; and the interfacial mass transport (diffusion = $f(T, M_w)$).

Equipment

Vented single screw extruders, twin screw extruders, wiped film evaporators, and high viscosity disk processors are used for the devolatilization of polymers when shearing is required to reduce the monomer concentration to low levels. Biesenberger³² recommends the use of high viscosity wiped film evaporators for devolatilization when side reactions are important.

4.3.2 Pilot Plant Experimental Data

The effects of screw speed, mass rate, and a nitrogen vapor sweep on the efficiency of lactide devolatilization in a twin screw extruder equipped with two separate vacuum zones were studied at 220°C and 5 mmHg. We used a 10 zone Leistritz 34-mm, L/D = 40, co-rotating twin screw extruder with the following screw configuration: feed zone (60° flight helix angle (pitch)), zone 1 (45°), zone 2 (30°), zone 3 (6K kneading disks followed by 60°), zone 4 (45° followed by 6K kneading disks), zone 5 (shearing disk followed by 30°), zone 6 (vacuum vent 1, 30° followed by 60°), zone 7 (nitrogen injection and melt seal, 60° followed by 3K kneading disks, followed by 30°), zone 8 (vacuum vent 2, 30° followed by 45°), zone 9 (45° followed by 30°), screen changer, strand die, water trough, and pelletizer. Electrical draw was generally about 8 amps.

Amorphous Cargill PLA pellets, $M_n = 45,000$ and $M_w = 110,000$, $M/I = 10,000$ mol lactide/mol Sn, containing 5% residual lactide were used. The PLA was well dried and directly conveyed to the extruder in a nitrogen purge. Lactide concentrations and molecular weights of extrudate samples were determined by GPC. M_n degradation during processing was small (generally about 5,000 g/mol). The execution of our devolatilization experimental plan was made possible by Randy Mazzocchi, Cargill engineer. The Leistritz 34-mm co-rotating twin screw extruder is owned and operated by Cargill.

Results

Three separate devolatilization experiments were performed on the 34-mm twin screw extruder to investigate the effects of screw speed, mass rate, and nitrogen vapor

sweep at 5 mmHg and approximately 220°C (melt temperature in venting zones was difficult to determine precisely). All three effects were found to be statistically significant. The results are summarized in Table 4-3.

As expected, increasing screw speed was found to have an important effect on the lactide separation, Figure 4-6. The influence of mass rate on lactide devolatilization is presented in Figure 4-7. The data indicates that the devolatilization efficiency decreases significantly after about 20 lb/h on this equipment. Mass rates less than 8 lb/h resulted in loss of melt seal (vacuum). The separation efficiency enhancement with increasing screw speed and decreasing mass rate (starve fed) is common in polymer devolatilization and indicates that the separation process is mass transfer limited. The nitrogen sweep rate (Run 3) was tested at 3 levels (0, 0.6, and 1.2 L/min (STP)) and was found to improve the lactide separation, Figure 4-8. The nitrogen was not foamed through the melt but simply injected into the vapor space of the venting zones. For this reason, the increase in lactide separation with nitrogen sweep is explained by enhanced thermodynamics (bigger activity driving force). Therefore, we find that the lactide devolatilization experiments were conducted in a regime where both kinetics and thermodynamics are important.

With the 34-mm twin screw extruder we can achieve a reduction of lactide from 5% to about 0.9% without nitrogen addition at 20 lb/h (Run 3 data). Data from Runs 1-2 were somewhat more favorable. The estimated thermodynamic limit based on equation (4-17) is 0.5% at 220°C and 5 mmHg. This represents a separation efficiency of $E_{DV} = (\text{amount realized})/(\text{amount possible}) = (0.05-0.009)/(0.05-0.005) = 0.91$. This result is fairly good and is not atypical for devolatilization in twin screw extruders. In all

**Table 4-3 Lactide Devolatilization Data with
34-mm Leistritz Twin Screw Extruder at 220°C, 5
mm Hg, and with 5% initial lactide**

Lactide (%)	Extrudate Mass Rate (lb/h)	Screw Speed (rpm)	Nitrogen/Lactide (mol/mol)
RUN 1			
0.71	12	195	0
1.13	12	150	0
1.05	12	195	0
0.25	12	250	0
0.25	12	300	0
0.95	12	250	0
0.55	12	300	0
1.78	12	150	0
RUN 2			
0.45	8.7	300	0
0.59	19.1	300	0
0.76	9.6	300	0
1.18	29.7	300	0
0.76	17.4	300	0
1.36	29.1	300	0
RUN 3			
0.59	20	300	0.8794
0.76	20	300	0.8794
1.00	20	300	0.4397
0.88	20	300	0
0.79	20	300	0.4397
1.11	20	300	0
0.95	20	300	0
0.49	20	300	0.8794

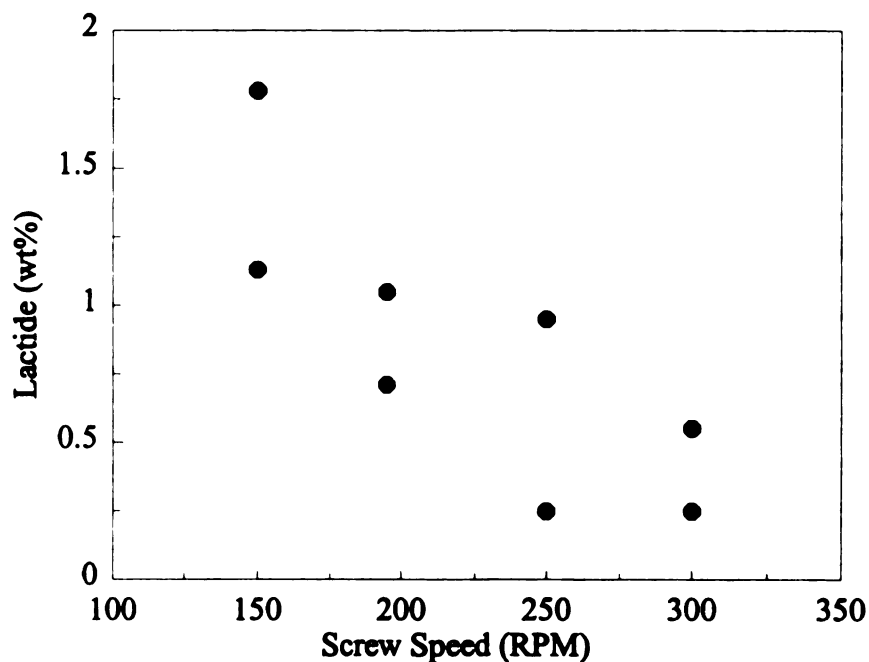


Figure 4-6. Effect of screw speed on the devolatilization of lactide at 220°C, 5 mmHg, 12 lb/h, and with an initial lactide amount of 5 wt%.

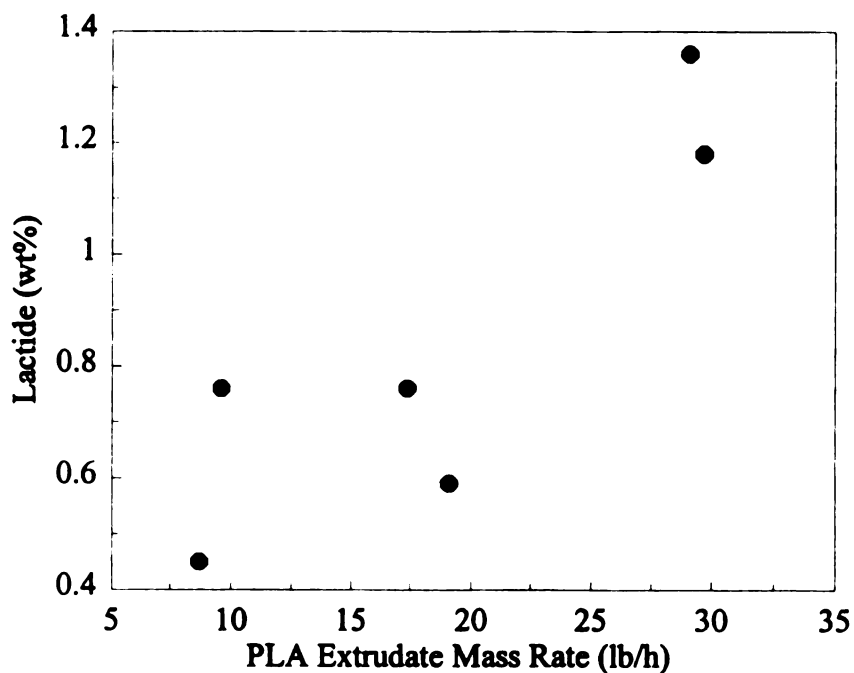


Figure 4-7. Effect of mass rate on the devolatilization of lactide at 220°C, 5 mmHg, 300 rpm, and with an initial lactide amount of 5 wt%.

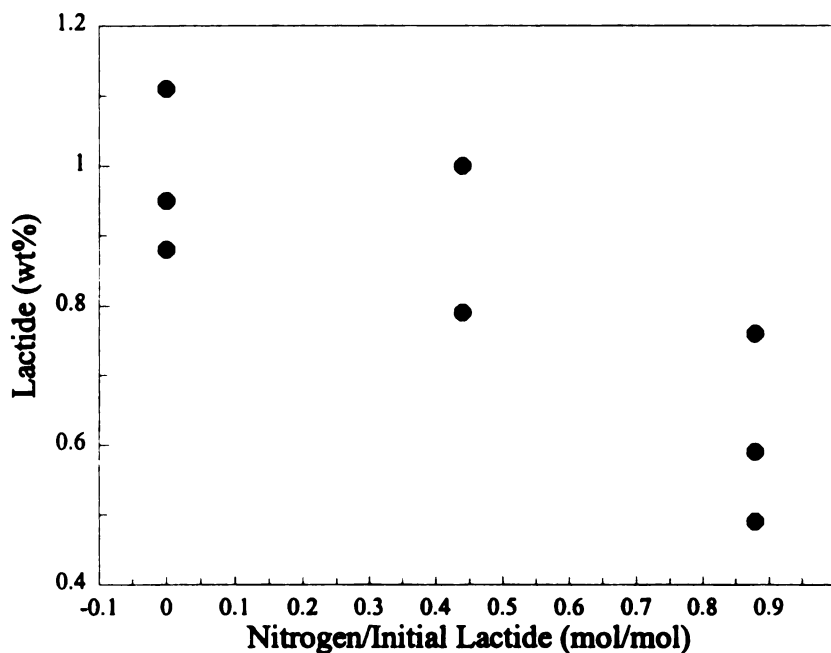


Figure 4-8. Effect of nitrogen vapor sweep on the devolatilization of lactide at 220°C, 5 mmHg, 20 lb/h, 300 rpm, and with an initial lactide amount of 5 wt%.

devolatilization experiments (5 mmHg and about 220°C) lactide boiling was observed in the sight glasses at each vapor vent. This observation along with the estimated separation efficiency suggest that the lactide vapor-liquid activity model described in equation (4-17) is reasonable for engineering calculations.

Twin screw extruders for devolatilization scale with the 2.5-to-3.0 power of the diameter. The Leistritz 34-mm co-rotating twin screw extruder was effective for lactide devolatilization up to 20 lb/h. Therefore, for 1000 lb/h a hypothetical extruder would have a diameter of $34 \cdot (1000/20)^{(1/2.5)} = 163$ mm to achieve similar performance. However, we would expect significantly higher final lactide amounts in PLA at commercial scale for the following three reasons:

- (1) For large-scale practical polymerization there would be at least 10% lactide entering devolatilization instead of the 5% used in this experiment.
- (2) The PLA molecular weights would be higher than the rather low MW PLA used in this experiment ($M_w = 110,000$). Higher MW gives somewhat lower mass transfer rates owing to increased viscosity(T).
- (3) Because of a decreasing surface area-to-volume ratio with increasing extruder diameter, depolymerization can better compete with phase equilibrium and becomes increasingly important at large scale.

Conclusions

1. PLA devolatilization is a critical issue because of application and processing requirements. PLA devolatilization is complicated by a low lactide vapor pressure (high boiling point) and the need to remove lactide below the equilibrium lactide concentration in the polymer melt. Therefore, catalyzed depolymerization is a significant competing reaction during devolatilization and the lowering or deactivation of the polymerization catalyst will considerably enhance the lactide removal.
2. The lactide devolatilization data indicates that we operated the 34-mm twin screw extruder in a regime where both kinetics and thermodynamics are important. Lactide-PLA separation improved at higher screw speeds, lower mass rates, and with the addition of a nitrogen vapor sweep to reduce the activity of lactide in the vapor phase.

3. The lactide-poly lactide vapor-liquid equilibrium model developed in Section 2.7.1 gives lactide boiling pressure and temperature requirements that are reasonable compared to experimental observations.

4.4 Drying

PLA drying below T_g is required after water pelletizing and resin storage to minimize melt hydrolysis during processing. Complete PLA pellet drying is not feasible and about 100 ppm water remain after drying. PLA hydrolysis is essentially irreversible and each adsorbed water molecule on a PLA pellet has the potential to initiate a new polymer chain and lower the molecular weight. The potential final molecular weight after hydrolysis is determined from the initial moisture content (ppm: g water/g total *1E6) and initial molecular weight,

$$M_{n,final} = \frac{1E6}{\frac{1E6}{M_{n,initial}} + \frac{H_2O(ppm)}{18}} \quad (4-19)$$

For example, with 100 ppm water the final M_n value at complete hydrolysis for a 50,000 initial M_n PLA is 39,100, or a 21.7% decrease. With a 300,000 M_n PLA the final M_n after 100 ppm water hydrolysis is 112,500, or a 62.5% decrease.

The below T_g hydrolysis of PLA during storage or use is slow and defines the article shelf life. Melt hydrolysis, however, is fast and has kinetics that can be predicted from the polymerization catalyst concentration, temperature, and initial moisture content (Section 3.5).

Rate of Water Adsorption

The rate of water adsorption on amorphous PLA pellets in a humidity chamber at 23°C and 50% relative humidity is presented in Figure 4-9.³³ The water adsorption was determined by weighing. The pellets initially contained 200 ppm water (determined by Karl-Fisher Coulometry) and reached their final value of 2200 ppm after 20 h. In the first 15 min of exposure the moisture content of the pellets increased by 140 ppm. This represents a very significant increase in potential processing degradation and exemplifies the importance of thorough drying and proper storage.

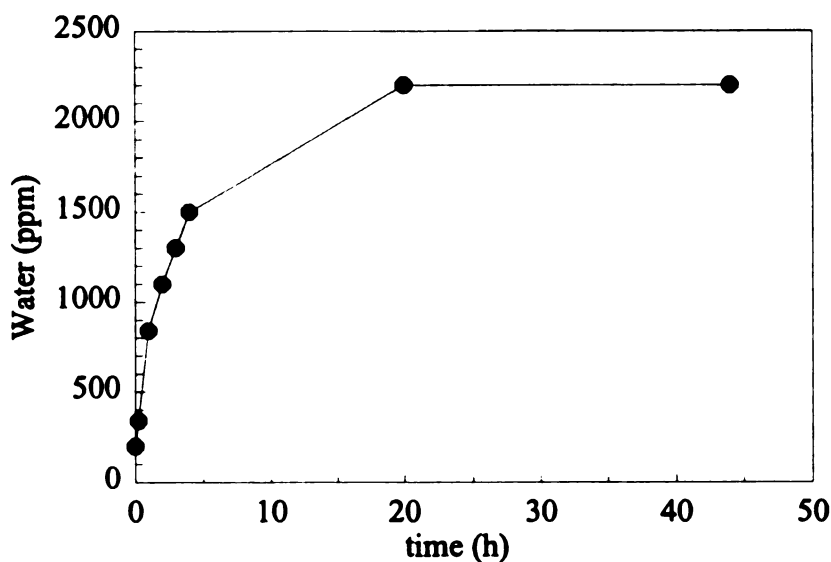


Figure 4-9. Rate of water adsorption on amorphous polylactide pellets at 23°C and 50% relative humidity.

Water Sorption Equilibrium

A water sorption equilibrium curve was determined from room temperature moisture adsorption experiments³⁴ with high molecular weight amorphous PLA pellets ($M_n = 50,000$ -100,000; devolatilized). The PLA pellets were determined to have a

porosity of 8.24%, with a total pore area of 36.8 m²/g, and an average pore diameter of 0.0072 μm by mercury porosimetry (Section 2.3.2 for experimental details). Experiments were conducted in a relative humidity chamber using various solutions to control relative humidity: KAcetate, CaCl, KBr, and H₂O. Water equilibrium values were determined at 29%, 52%, 78%, and 92% relative humidity (measured values). Samples were taken at 24, 48, and 72 h to ensure that equilibrium was obtained. Water adsorption was determined by Karl-Fisher coulometry. Hysteresis was tested by placing the 52% and 78% relative humidity equilibrium samples into the 29% relative humidity chamber for 72 and 92 h. Although important in many water adsorption systems, hysteresis was not found to be significant with the water-PLA system.

The water-PLA sorption equilibrium results are summarized in Figure 4-10. The solid line represents the following empirical model fit,

$$\text{Water(ppm)} = 40.8RH(\%) + 6.6 \times 10^{-7} RH(\%)^5; \quad RH \leq 92\% \quad (4-20)$$

Because the abscissa (%RH) is 100 times the ratio of water partial pressure and water pure component vapor pressure, the equilibrium moisture curve should be fairly insensitive to moderate temperature changes. The equilibrium water adsorption for PLA at 50% relative humidity is compared to values for other polymers³⁵ in Figure 4-11. Although PLA has somewhat higher water adsorption than PE or PS, PLA is considerably less hygroscopic than polyamides, polyacrylic acids, and cellulose-based polymers. In general, water sorption increases with polarity (PLA is moderately polar)

and is highly correlated with the solubility parameter. The solubility parameter for water is $48 \text{ MPa}^{0.5}$, and water sorption decreases with the difference of the polymer solubility parameter from this value: cellulose triacetate ($\delta \sim 30 \text{ MPa}^{0.5}$), nylon 6,6 ($\delta = 28$), PMMA ($\delta \sim 21$), PLA ($\delta = 21$), PVC ($\delta = 20$), PS ($\delta = 19$), PE ($\delta = 16$).

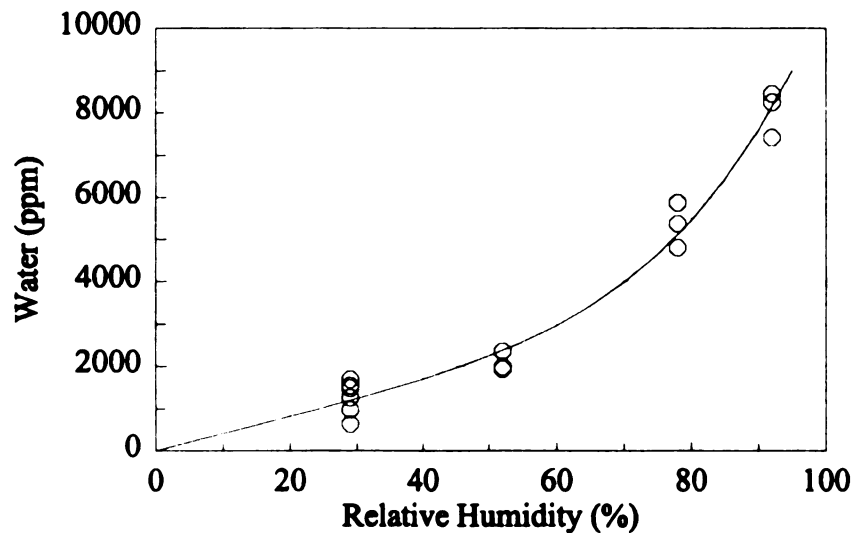


Figure 4-10. Equilibrium moisture curve for amorphous polylactide pellets at 25°C.

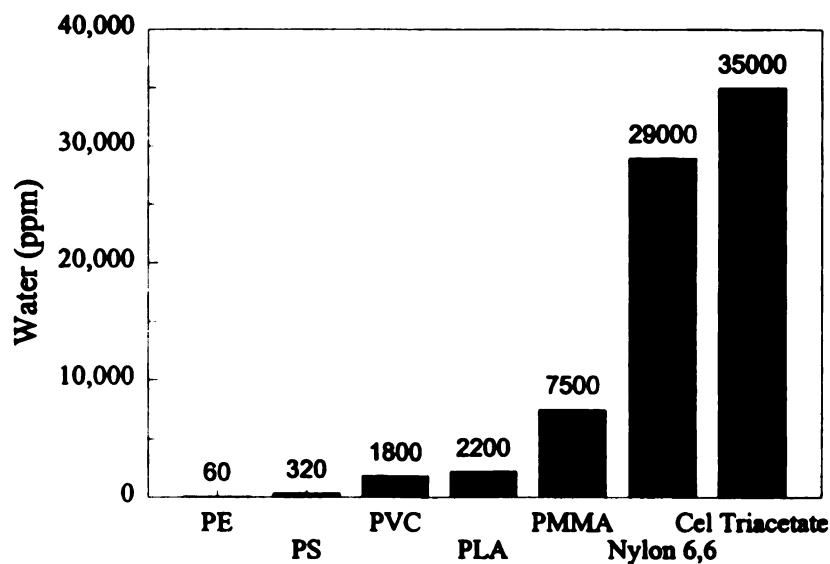


Figure 4-11. Water sorption equilibrium for various polymers at 50% relative humidity. Data for other polymers published in Crank and Park³⁵ by J.A. Barrie.

PLA Drying Below T_g

The upper-drying temperature for amorphous PLA pellets is about 50°C (set by T_g). Semi-crystalline PLA can be dried at significantly higher temperatures (e.g., 80-120°C depending on the extent of crystallization). PLA is dried in conventional polyester resin drying equipment; pellets are conveyed through a hopper exposed to forced air with a low dew point (-40°C). Two molecular sieve beds are cycled between air drying and bed regeneration steps. PLA drying is a continuous process with a minimum residence or drying time of 4 h. Figure 4-12 depicts a representative drying curve for amorphous PLA pellets. In 4 h the moisture in the pellets is reduced from 1000 to 100 ppm using 0.5 cfm/lb dry air (-40°C dew point) at 40°C.

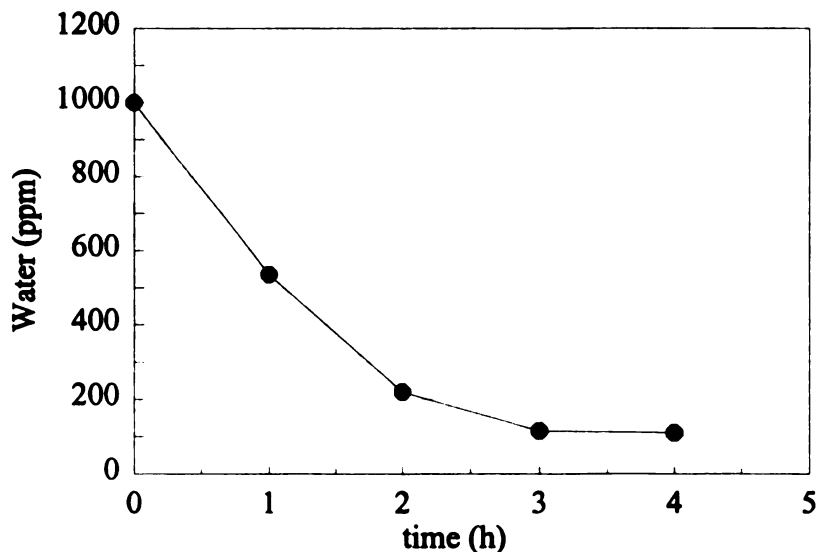


Figure 4-12. Drying curve for amorphous PLA pellets at 40°C. Air with a -40°C dew point is forced through a bed of PLA pellets at 0.5 cfm/lb.

Water in PLA should be reduced to 100 ppm prior to processing. The relationship between PLA moisture content and dew point temperature is easily derived from the

equilibrium sorption curve and the pure component vapor pressure of water. At relative humidity less than 30%, the equilibrium moisture content of PLA is approximately linear with relative humidity (i.e., Henry's Law) and can be expressed as

$$Water(ppm) = 44.64RH(\%); \quad RH \leq 30\% \quad (4-21)$$

The relative humidity can be related to the air temperature and dew point temperature using the Antoine coefficients for the vapor pressure of water,

$$\log_{10}RH(\%) = 2 + 1750.286 \left(\frac{1}{T_{air}(C) + 235} - \frac{1}{T_{dp}(C) + 235} \right) \quad (4-22)$$

Using equations (4-21) and (4-22) the equilibrium PLA moisture content is calculated for dew point temperatures between 0 and -30°C.

Table 4-4 Calculated Equilibrium PLA Water Content at Dew Point Temperatures Between 0 and -30°C

T_{dp} (°C)	Relative Humidity at 20°C (%)	PLA water content (ppm)
0	26	1,160
-5	18	800
-10	12	540
-15	8	360
-20	5	240
-25	3	150
-30	2	95

The calculations indicate that the equilibrium moisture content of PLA is acceptable at a dew point temperature of -30°C with a 20°C air temperature. With a 50°C air temperature, a T_{dp} of -10°C is the calculated requirement to achieve 100 ppm PLA moisture at equilibrium. This moisture requirement can generally be achieved in 4 h. using conventional drying equipment with $40\text{--}50^{\circ}\text{C}$ air controlled at a -40°C T_{dp} set point.

4.5 Resin Processing

Poly lactide resins are converted into service articles by typical polymer processes such as injection molding, blow molding, sheet extrusion, paper coating, and fiber spinning. At Michigan State we have processed polylactides by injection molding, compression molding, and extrusion using pilot scale equipment. As previously mentioned, the catalyst concentration and moisture content of the PLA resin contribute to undesirable depolymerization and hydrolytic degradation reactions. Unlike current commodity polyesters, the equilibrium monomer concentration in PLA is significant at processing conditions (e.g., 4.7 wt% at 220°C) and the tendency to reform lactide (after devolatilization) is an issue in resin processing. Depolymerization leads to equipment shutdown from lactide crystal accumulation, and storage/process M_n instability through lactide hydrolysis to lactoyllactic acid, and subsequent transesterification with polymer. Hydrolysis represents a loss of polymer physical properties and quality control. In addition, non-hydrolytic chain cleavage is important at temperatures above 215°C . The extent of these reactions define the melt stability of the PLA resin.

Typical processing temperatures and times for PLA resins are 180-250°C and 2-10 min. The higher temperature is typical for PLA fiber spinning and the lower temperature is common for injection molding applications. In addition, an overall long-tailed residence time distribution is realized in processes such as injection molding where flashings, mold runners, and defective parts can make up to 30% of output, and regrinding and recycling of this material is required to achieve good yield. This regrind addition can significantly contribute to melt instability if a thorough drying of recycled material is not performed.

In Section 2.2.4 we presented the important degradation reactions and compared the relative thermal stability of PLA to that of commodity plastics. In Sections 3.2 and 3.5, rate equations were developed for lactide depolymerization, PLA melt hydrolysis, and PLA non-hydrolytic chain cleavage. In this section we characterize the practical limits of PLA melt stability by calculating the extent of depolymerization, hydrolysis, and non-hydrolytic degradation at typical processing conditions for PLA. We conclude by measuring process M_n degradation during injection molding trials of PLA resins varying in initial *meso*-lactide.

4.5.1 Predicting Melt Degradation at Processing Conditions

Lactide Reformation During Processing

The reversible polymerization model developed in Section 3.2 is used to predict depolymerization as a function of catalyst concentration, temperature, and time, for a PLA of starting lactide weight fraction M_0 .

$$M(t) = M_{eq} + (M_0 - M_{eq})\exp(-k_p I t) \quad (4-23)$$

where M_{eq} and k_p are functions of temperature only:

$$M_{eq} = \exp\left(\frac{-23300}{8.314T(K)} + \frac{22.0}{8.314}\right) \quad (4-24)$$

$$k_p = 86 \exp\left(\frac{-70900}{8.314}\left(\frac{1}{T(K)} - \frac{1}{448}\right)\right) \quad (4-25)$$

At 180, 215, and 250°C M_{eq} and k_p have values of 0.029, 0.045, 0.066; and 106, 409, 1320 catmol%⁻¹h⁻¹, respectively.

Depolymerization simulation results at 180, 215, and 250°C, and $M/I = 5,000$ and 80,000 lactide/Sn (mol/mol) are presented in Table 4-5 for $M_0 = 0.005$. The high catalyst concentration has considerably greater depolymerization at all temperatures. At 180°C and $M/I = 80,000$ depolymerization is insignificant for normal processing times. At 215°C and $M/I = 80,000$ depolymerization becomes important for processing times longer than about 3 min. At 250°C depolymerization is important at very low catalyst concentrations; at such extreme temperature complete catalyst deactivation is necessary for successful resin processing.

Table 4-5 Calculated % Lactide Reformation at Typical PLA Processing Conditions

time (min)	T = 180°C		T = 215°C		T = 250°C	
	0.02 catmol%	0.00125 catmol%	0.02 catmol%	0.00125 catmol%	0.02 catmol%	0.00125 catmol%
	M/I=5,000 (mol/mol)	M/I=80,000 (mol/mol)	M/I=5,000 (mol/mol)	M/I=80,000 (mol/mol)	M/I=5,000 (mol/mol)	M/I=80,000 (mol/mol)
0	0.50	0.50	0.50	0.50	0.50	0.50
1	0.58	0.51	1.01	0.53	2.68	0.67
2	0.66	0.51	1.46	0.57	4.09	0.83
3	0.74	0.52	1.85	0.60	5.00	0.99
4	0.82	0.52	2.19	0.63	5.58	1.14
5	0.89	0.53	2.49	0.67	5.96	1.29
6	0.96	0.53	2.75	0.70	6.20	1.43
7	1.03	0.54	2.97	0.73	6.35	1.57
8	1.09	0.54	3.17	0.77	6.46	1.71
9	1.15	0.55	3.34	0.80	6.52	1.84
10	1.22	0.55	3.49	0.83	6.56	1.97

Hydrolytic M_n Degradation During Processing

A kinetic model predicting hydrolytic M_n degradation as a function of polymerization catalyst concentration, I , initial water content, W_0 , and temperature was developed in Section 3.5,

$$\frac{1E6}{M_n(t)} = \frac{1E6}{M_n(t=0)} + \frac{W_0(\text{ppm})}{18}(1 - \exp(-k_w I t)) \quad (4-26)$$

where k_w is a function of temperature only,

$$k_w = 351 \exp \left(\frac{-33400}{8.314} \left(\frac{1}{T(K)} - \frac{1}{448} \right) \right) \quad (4-27)$$

At long time (total water consumption) equation (4-26) reduces to equation (4-19) and final M_n is directly calculated from known initial moisture content and initial M_n . At 180 and 215°C k_w has values of 388 and 733 catmol%⁻¹h⁻¹, respectively. At these temperatures hydrolysis is the most important M_n degradation mechanism during PLA processing.

Hydrolytic M_n process degradation was simulated at 100 and 800 ppm moisture, at 180 and 215°C, for 100,000 M_n PLA having M/I = 5,000 and 80,000 lactide/Sn (mol/mol). The two different moisture contents represent thoroughly dried PLA and PLA that has been exposed to 50% relative humidity air for 1 h. Higher M_n PLA would experience a greater M_n decrease for an equivalent extent of hydrolysis.

The simulation results are presented in Table 4-6. The high catalyst concentration has considerably greater degradation at all conditions of moisture and temperature. At 180°C, M/I = 80,000, and 100 ppm moisture, 100,000 M_n PLA is melt stable with only 2% M_n degradation after 5 min. However, at 800 ppm water, 180°C, and M/I = 80,000 the 100,000 M_n PLA undergoes a 15% reduction in M_n after 5 min. The 100% water consumption final M_n values are calculated using equation (4-19). With 100 and 800 ppm water, full hydrolysis gives 64,300 and 18,400 M_n PLA. These full hydrolysis values are approached in 10 min for the simulations at 215°C and M/I = 5,000 PLA. In contrast, at 215°C, M/I = 80,000, and 100 ppm moisture, PLA is relatively stable having only a 8% M_n drop after 10 min. Certainly the key to hydrolytically melt stable PLA is low initial

moisture content (good drying and storage) and low polymerization catalyst concentration.

Table 4-6 Calculated Hydrolytic M_n Degradation at Typical PLA Processing Conditions

time (min)	100 ppm Water				800 ppm Water			
	T = 180°C		T = 215°C		T = 180°C		T = 215°C	
	0.02 catmol%	0.00125 catmol%	0.02 catmol%	0.00125 catmol%	0.02 catmol%	0.00125 catmol%	0.02 catmol%	0.00125 catmol%
	M/I=5000	M/I=80000	M/I=5000	M/I=80000	M/I=5000	M/I=80000	M/I=5000	M/I=80000
	(mol/mol)	(mol/mol)	(mol/mol)	(mol/mol)	(mol/mol)	(mol/mol)	(mol/mol)	(mol/mol)
0	100,000	100,000	100,000	100,000	100,000	100,000	100,000	100,000
1	93,700	99,600	89,300	99,200	65,000	96,500	50,900	93,700
2	88,800	99,100	82,300	98,400	49,700	93,300	36,800	88,200
3	84,800	98,700	77,600	97,600	41,200	90,400	30,200	83,400
4	81,700	98,300	74,300	96,800	35,800	87,600	26,500	79,200
5	79,100	97,800	71,900	96,100	32,100	85,000	24,200	75,400
6	76,900	97,400	70,100	95,400	29,400	82,600	22,600	72,000
7	75,100	97,000	68,700	94,700	27,400	80,400	21,500	68,900
8	73,600	96,600	67,700	94,000	25,900	78,200	20,800	66,200
9	72,400	96,200	66,900	93,300	24,700	76,200	20,200	63,700
10	71,300	95,900	66,300	92,700	23,700	74,300	19,800	61,400

Non-Hydrolytic M_n Degradation During Processing

At temperatures above 215°C, non-hydrolytic degradation becomes an important contributor to M_n degradation. A rate equation for non-hydrolytic chain cleavage was developed in Section 3.5,

$$\frac{1E6}{M_n(t)} = \frac{1E6}{M_n(t=0)} + k_{deg}t \quad (4-28)$$

$$k_{\text{deg}} = 0.20 \exp \left(\frac{-126000}{8.314} \left(\frac{1}{T(\text{K})} - \frac{1}{448} \right) \right) \quad (4-29)$$

At 180, 215, and 250°C the non-hydrolytic chain cleavage rate constants are 0.30, 3.3, and 26 mmol/kg-h. In the absence of water we can use this rate equation to estimate M_n degradation, Table 4-7. The results indicate that non-hydrolytic degradation is insignificant at 180°C but is important at 215°C.

Table 4-7 Calculated Non-Hydrolytic M_n Degradation (Absence of Water)

time (min)	T = 180°C	T = 215°C	T = 250°C
0	100,000	100,000	100,000
1	99,950	99,460	95,840
2	99,900	98,930	92,020
3	99,850	98,400	88,490
4	99,800	97,880	85,220
5	99,750	97,360	82,180
6	99,710	96,850	79,350
7	99,660	96,340	76,710
8	99,610	95,840	74,240
9	99,560	95,340	71,930
10	99,510	94,850	69,750

Contributions of the Important Degradation Reactions to Melt Instability

In Table 4-8 we estimate the importance of hydrolysis, thermal degradation, and depolymerization on the melt instability of PLA. The mathematical simulations were performed at 180, 215, and 250°C with a 100,000 M_n PLA at two catalyst levels, $M/I =$

5,000 and 80,000 lactide/Sn (mol/mol), and an initial moisture content of 100 ppm (thoroughly dried). The final M_n are reported at 10 min. The extent of degradation is determined by calculating the change in the number of polymer molecules per mass, $\mu_o = 1E6/M_n$. The extents of degradation were used to determine the relative contribution of hydrolytic and non-hydrolytic chain cleavage to the M_n degradation. At high catalyst concentration ($M/I = 5000$) hydrolysis accounts for 99% of M_n degradation at 180°C and 56% of degradation at 250°C. At $M/I = 80,000$, hydrolysis accounts for 90% of M_n degradation at 180°C and only 23% of degradation at 250°C. For higher initial water concentration the amount of degradation attributed to hydrolysis increases significantly.

Table 4-8 Calculated Contributions of Depolymerization, Hydrolysis, and Non-Hydrolytic Chain Cleavage to PLA Melt Instability (100 ppm Water, $M_n = 100,000$, 0.5% Initial Lactide, 10 min Processing Time)

T(°C)	M/I (mol/mol)	Final % Lactide	Final M_n	Hydrolysis		Non-Hydrolytic Cleavage	
				Extent of Degradation (mmol/kg)	Percent contribution to degradation	Extent of Degradation (mmol/kg)	Percent contribution to degradation
180	80,000	0.55	95,400	0.43	90	0.05	10
	5,000	1.22	71,200	4.0	99	0.05	1
215	80,000	0.83	88,300	0.79	59	0.54	41
	5,000	3.49	63,900	5.1	90	0.54	10
250	80,000	1.97	64,100	1.3	23	4.3	77
	5,000	6.56	50,500	5.5	56	4.3	44

4.5.2 Injection Molding Degradation Experimental Data

Six polylactides with between 10–40% initial *meso*-lactide were injection molded into tensile coupons using a New Britian 75 machine (Michigan State University). The

average temperature and time of injection molding was 177°C and 8 min. The PLA samples contained $M/I = 10,000$ lactide/Sn (mol/mol). The samples were dried for a minimum of 2 h at 50°C under vacuum. The samples were then stored in large desiccators prior to molding. The polydispersity index before and after processing averaged 2.0 and varied between 1.75-2.24. The tensile coupons were used for mechanical testing in Chapter 2.4 and other experimental details concerning analysis and equipment are found there.

Measured PLA degradation during injection molding is summarized in Table 4-9. The extent of degradation is determined by calculating the change in the number of polymer molecules per mass, $\mu_o = 1E6/M_n$. The extents of degradation varied between 0.9-8.2 mmol/kg. This amounts to the consumption of between 15-150 ppm water, with an average of 82 ppm. Although the water content was not measured before molding, between 40-385 ppm initial water, average of 210 ppm, was back-calculated for these data using equation (4-26). These initial water estimations, based on the processing conditions of 177°C and 8 min, are reasonable. The extent of degradation is independent of initial *meso*-lactide concentration and the observed degradation is explained by the relatively high catalyst concentration (hydrolysis).

Table 4-9 Molecular Weights Before and After Injection Molding for the Amorphous Poly(L-co-meso-lactide)s

Polymer	Pellets Before Molding				After Molding			Extent of Degradation (mmol/kg)
	T_g (°C)	M_n (g/mol)	PDI	μ_0 (mmol/kg)	M_n (g/mol)	PDI	μ_0 (mmol/kg)	
90L/10meso	57.4	132,500	1.75	7.5	63,700	1.91	15.7	8.2
88L/12meso	56.1	66,500	2.15	15.0	54,000	1.89	18.5	3.5
80L/20meso	55.2	87,400	2.18	11.4	71,300	2.11	14.0	2.6
78L/22meso	55.2	62,500	1.95	16.0	59,300	1.85	16.9	0.9
66L/34meso	52.5	61,400	1.95	16.3	41,000	2.24	24.4	8.1
60L/40meso	51.5	95,300	1.98	10.5	68,400	2.05	14.6	4.1

Conclusion

Regardless of polymerization process (condensation or ring-opening) all commercially useful PLA must be melt stabilized by: (1) thoroughly drying the resin below 100-200 ppm; (2) removing oligomers and lactide from PLA to improve storage stability and facilitate processing; (3) removing or deactivating the metal polymerization catalyst to minimize melt hydrolysis and depolymerization. The addition of free radical scavengers and hydroxyl end-capping may further enhance the melt stability of PLA. Examples of techniques to improve the melt stability of PLA are found in the patent literature (e.g., Gruber et al. (Cargill): US 5338822, US 5539081, US 5446123; Suizu et al. (Mitsui Toatsu): US 5496923).

4.6 References

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Chapter 5 Dissertation Conclusions and Prospects of Polylactides

5.1 Dissertation Conclusions

We investigated the physical, reaction, and engineering properties of polylactides from a bulk production perspective. *Meso*-lactide, major L-lactide racemization comonomer, was found to influence the thermal, mechanical, and rheological properties of predominately L-lactide PLA to different degrees. The concentration of the stannous ethylhexanoate polymerization catalyst was found to have a first order influence on esterification type reactions including lactide propagation/depropagation, transesterification among polymer chains, and melt hydrolysis. The choice of catalyst concentration is an important consideration for the reaction engineering, devolatilization, and resin processing of PLA.

In general, the measured PLA physical properties agree with what is expected from polymer structure-property relationships. The thermal, mechanical, and rheological behavior of polylactides are consistent with a high molecular mass polymer having a glass transition temperature of $T_g = 46\text{--}61^\circ\text{C}$. Polylactide's T_g is particularly high for an aliphatic polyester and is a result of the 33% ester bonds in the backbone (stiff bonds, moderate H-bonding) and the methyl groups that provide for an additional $10\text{--}15^\circ\text{C}$ T_g increase. The PLA T_g decreases with the amount of initial *meso*-lactide. The infinite

molecular weight T_g for poly(L-lactide), poly(*meso*-lactide), and poly(D,L-lactide) were determined to be 61, 46, and 53°C, respectively. The production of *meso*-lactide through controlled racemization provides a means to produce amorphous as well as semi-crystalline PLA from the same feedstock, catalyst, and process. However, *meso*-lactide must be minimized for the preparation of semi-crystalline PLA having acceptable crystallization rates. The average crystalline melting temperature of poly(L-lactide) decreases by 3°C/%-*meso*, and lactide random copolymers containing more than 18% *meso*-lactide are strictly amorphous. Based on thermogravimetric analysis, PLA has similar thermal stability to PVC but is considerably less stable than PS, PP, PE, and PET. The onset of significant PLA thermal decomposition is about 215°C.

Physical aging occurs in amorphous PLA between -45 and 58°C (T_g to T_g). Molded amorphous PLA articles are initially tough yielding plastics at room temperature but apparently age rapidly (< 1 day) at room temperature and become brittle upon failure. For this reason, unmodified amorphous polylactides are brittle plastics like polystyrene. We hypothesize that this ductile-brittle transition could be delayed by increasing the T_g of PLA through random copolymerization with other degradable monomers (e.g., morpholinedione based on alanine-lactic). Unmodified amorphous poly(L-co-*meso*-lactide) is a stiff, brittle, and strong plastic that has mechanical properties and clarity that very closely resemble polystyrene. Amorphous PLA is well-suited for the replacement of PS in moderate temperature applications. The tensile modulus for amorphous poly(L-co-*meso*-lactide) (549-587 kpsi) is significantly higher than that of other unmodified commercial plastics (PS, LLDPE, LDPE, HDPE, PP, PVC, PET, PC,

Nylon 66). The tensile yield strength for amorphous poly(L-co-*meso*-lactide) decreases with initial *meso*-lactide fraction (7800 psi for 10% *meso*-, and 6800 psi for 34-40% *meso*).

The zero-shear viscosity of amorphous PLA depends on its isomeric makeup, and was found to increase to a power of 3.38 with M_w and vary with temperature between T_g and $T_g + 100^\circ\text{C}$ according to the WLF equation referenced to 100°C ($T_g + 45^\circ\text{C}$) with constants $c_1 = 15.6$, and $c_2 = 110^\circ\text{C}$. The viscosity of all amorphous polylactides (T , M_w , w_{meso} , $w_{\text{L-mer}}$) with PDI ~ 2 follows a master curve of η/η_0 vs. $\omega\tau_0$ fit to a modified Eyring model. This curve is in good agreement with a master curve for all amorphous polymers of PDI ~ 2 . All tested amorphous polylactides were found to obey the principle of time-temperature superposition. Based on the estimation of the plateau modulus from dynamic oscillatory shear experiments, PLA's characteristic entanglement molecular weight is calculated to be 7,300 g/mol. An empirical constitutive viscosity equation was determined for amorphous polylactides at typical processing conditions. This equation may be used to predict the viscosity of amorphous PLA for a wide range of M_w (75,000-400,000), temperatures (150 - 220°C), and shear rates (100 - $20,000\text{ s}^{-1}$).

The major bulk PLA reactions are esterification type reactions that have a first-order catalyst dependence. These reactions include reversible polymerization, transesterification among polymer chains (interchange reactions), and melt hydrolysis of PLA. Racemization is influenced to a lesser extent by the Sn(II) ethylhexanoate catalyst. Non-hydrolytic chain cleavage is believed to be independent of catalyst concentration. The polymerization kinetics of reversible lactide polymerization, transesterification, melt

hydrolysis, non-hydrolytic degradation, and racemization have been determined and characterized mathematically for the stannous ethylhexanoate system.

Both polymerization and depolymerization are accurately described by a reversible model with a propagation term that is first order in monomer and catalyst. The activation energy of propagation is $70.9 \pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$. The equilibrium lactide concentrations at 130, 160, 190, and 220°C are 1.3, 2.2, 3.3, and 4.7 wt%, respectively. This corresponds to an enthalpy, entropy, and ceiling temperature of $-23.3 \pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$, $-22.0 \pm 3.2 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and $786 \pm 87^\circ\text{C}$, respectively. However, the ceiling temperature is based solely on depolymerization degradation and is of no practical significance because thermal degradation mechanisms become important at temperatures above 215°C. Crystallization increases the propagation rate and decreases the apparent monomer equilibrium in proportion to the degree of crystallinity. The observed linear relationship between M_n and lactide conversion is consistent with a mechanism where chain initiation is fast, monomer does not react with monomer, and there is no termination of reaction centers.

The kinetics of lactide polymerization is consistent with a living polymerization but the MWD is not narrow. This is a result of PLA being both a ring-opening polymer and a condensation polymer susceptible to transesterification reactions. We describe the stannous ethylhexanoate-PLA system as *semiliving*, where at a given instant a fraction of chains, defined by the catalyst concentration, is living and the remainder of chains ($[\text{OH}] - [\text{Sn}]$) are dormant. The stannous ethylhexanoate-PLA system differs from a truly living system in that (1) polymer interchange reactions are significant and (2) the initiator and

catalyst are different species with different concentrations; hence, M_n is independent of catalyst.

Natural hydroxyl impurities (water, lactic acid, lactic oligomers) stoichiometrically control the polymer molecular weight but do not significantly affect the propagation rate. Transesterification reactions determine the PLA MWD in a batch system and represent the approach to an equilibrium distribution of molecular sizes (most probable distribution). They are responsible for the development of very high molecular weight PLA chains late in the polymerization. A moment-based transesterification rate model was developed that predicts lactide conversion and $MWD(t)$ for given temperature, catalyst concentration, and hydroxyl impurity concentration. The transesterification rate constant is 2-3 orders of magnitude smaller than that of propagation and has a lesser temperature dependence ($E_{a,x} = 38$ kJ/mol). For lactide polymerization at 190°C (95% of equilibrium conversion and $M_n = 100,000$) less than 5 interchange events per chain are responsible for broadening the MWD towards a PDI of 2. This results in a disruption of less than 1% of the dyads in the polymer chains.

A melt hydrolysis kinetic model was developed that is a good representation of M_n degradation during PLA resin processing. Hydrolytic degradation is found to be first order in polymerization catalyst and has an activation energy of 33.4 kJ/mol. A non-hydrolytic M_n degradation rate equation was developed based on long time vial polymerization M_n degradation data (absence of any water). Non-hydrolytic degradation has an activation energy of 126 kJ/mol and is important for temperatures greater than about 215°C. A racemization rate model was developed using data obtained from

polymerization samples that were hydrolyzed and analyzed by chiral chromatography. PLA racemization is first order in acid end group concentration and like-mer repeat units, and has an activation energy of 120 kJ/mol. Racemization occurs in the absence of polymerization catalyst but is enhanced at high polymerization catalyst concentration. However, the effect of catalyst on racemization is less important than its role in reducing polymerization time, and the net result is that racemization is reduced during polymerization at high catalyst concentrations.

The engineering of polylactides (polymerization, devolatilization, and resin processing) is largely determined by the polymerization catalyst concentration. High catalyst concentrations lead to lower polymerization times and minimize undesirable side reactions such as racemization, color formation, and non-hydrolytic chain cleavage. Low catalyst concentrations improve lactide removal during devolatilization by reducing depolymerization. A low catalyst concentration is required to minimize depolymerization and melt hydrolysis during resin processing and provide for a melt stable PLA.

In the polymerization cascade, the final M_n depends on the concentration of initial hydroxyl impurities and the final lactide conversion. The MWD is affected by the extent of transesterification (temperature, catalyst concentration, mean residence time) and the goodness of mixing in the reactors. The basic reactor design equations were developed using the reversible polymerization model. Simulations demonstrate that at least 3 ideal stages (CSTRs) are desired because of the significant reduction in the mean polymerization time. A greater number of stages reduces the mean polymerization time but lowers PLA polydispersity. A pilot plant was designed for continuous lactide

polymerization based on the ideal reactor design equations for two CSTRs in series. The reversible polymerization kinetics developed for stannous ethylhexanoate were verified in continuous operation at both pilot and commercial scale.

Continuous devolatilization experiments were conducted with a twin screw extruder at pilot scale. Important devolatilization issues include low monomer vapor pressure at process conditions and the competition of melt depolymerization to reform lactide. A developed lactide-poly lactide vapor-liquid equilibrium model is adequate for calculating devolatilization pressure and temperature requirements for the removal of lactide to a given concentration.

Using rate equations developed for melt hydrolysis, non-hydrolytic chain cleavage, and depolymerization, the extent of melt degradation was predicted for various resin processing conditions. At processing temperatures below about 215°C, a low catalyst concentration (e.g., $M/I = 80,000$ lactide/Sn (mol/mol)) is required to reduce depolymerization and melt hydrolysis to acceptable levels. At higher temperatures the catalyst should be deactivated or removed to prevent excessive depolymerization.

Non-hydrolytic chain cleavage is an important degradation mechanism above 215°C and is responsible for about 77% of degradation in 10 min at 250°C with 100 ppm initial water. For thoroughly dried PLA resin (i.e., 100 ppm water) melt hydrolysis remains the only important M_n degradation mechanism below 215°C. PLA resin processing degradation was investigated with injection molding tests at about 180°C. The observed melt degradation was consistent with expectations for stannous ethylhexanoate catalyzed melt hydrolysis. Regardless of polymerization process (condensation or ring-opening) all

commercially useful PLA must be melt stabilized by: thoroughly drying the resin below 100-200 ppm, removing oligomers and lactide from PLA to improve storage stability and facilitate processing, and removing or deactivating the metal polymerization catalyst to minimize melt hydrolysis and depolymerization.

Based on these conclusions, we identify three critical technical requirements to facilitate PLA application: (1) melt deactivation of catalyst following polymerization; (2) development of manufacturing processes to achieve complete stereochemical control of polylactides for the production of useful semicrystalline and amorphous PLA; (3) modification of the base thermal, mechanical, and rheological properties of PLA to produce biodegradable PLA resins that have wider potential application.

5.2 Recommendations for Further Work

Although polylactides inherently have numerous redeeming qualities, including the potential for low cost (0.50 - 1.00 \$/lb), we find several technical obstacles to their widespread application – it is not simply a matter of market development.

Recommendations for further work are: develop effective additives for the melt deactivation of the polymerization catalyst; develop a complete polymerization simulation model that incorporates reversible polymerization, transesterification, non-hydrolytic degradation, and racemization to be used in designing PLA processes that have complete control of stereochemistry and molecular architecture; develop biodegradable chemically modified PLA resins to target applications where PLA is not inherently suited (e.g., flexible films and high temperature food contact plastics).

Although there has been recent patent activity concerning the deactivation of lactide polymerization catalysts in the melt, most literature involves the removal of catalyst in dilute solution. High viscosities and difficult mixing on the molecular level make melt deactivation of the lactide polymerization catalyst non-trivial. There remain opportunities for the development of effective catalyst deactivation additives or catalyst removal processes. Another possibility involves the development of a catalyst-free product through the use of a supported catalyst polymerization reactor. However, the heterogeneous reactor design must overcome the high melt viscosity (mass transfer limitation) and provide for a high overall polymerization rate to avoid undesirable side reactions that are independent of catalyst and lactide concentration.

A manufacturing process for the production of PLA with complete control of stereochemical makeup and molecular architecture requires the following knowledge: (1) complete characterization of racemization in lactic acid, prepolymer, lactide, and PLA manufacturing steps; (2) complete characterization of transesterification reactions; (3) thorough understanding of how reactor configurations affect the residence time distribution. With this information a mathematical model can be developed and used to design a process having the flexibility to produce semicrystalline or amorphous PLA resins of certain MWD, molecular architecture, and stereochemical makeup. Further work is required to more fully develop the rate equations necessary for a complete process simulation.

Unmodified PLA is suitable for single-use cold polystyrene applications but otherwise has limited commodity potential. This is a result of its intermediate glass

transition temperature and unacceptable crystallization kinetics. However, the intermediate T_g allows for greater potential application through the development of both low and high T_g modified PLAs. Lowering or increasing the T_g by about 40°C provides for a tough semicrystalline PLA-based material or a high modulus amorphous PLA-based material having an upper-use temperature equivalent to polystyrene. PLA's backbone functionality and reactive end groups make it amenable to chemical modification.

The following four technical development areas provide opportunities to increase the utility of PLA-based resins through chemical modification:

- (1) The development of effective nucleating agents to enhance crystallization rates and allow for commercially useful semi-crystalline PLA.
- (2) The development of a PLA having long chain branching (greater than the entanglement molecular weight: > 7300 g/mol) to significantly alter the time-dependent elongational viscosity and provide for the appropriate "melt strength" required for such processes as film extrusion paper coating, blow molding, fiber melt spinning, and sheet formation.
- (3) The development of a tough or flexible PLA-based material (e.g., high impact material or flexible semicrystalline film) by decreasing the T_g or adding another low T_g component.
- (4) The development of an amorphous PLA-based resin having an upper use temperature equivalent to PS (e.g., biodegradable foam containers for hot food applications). This may be accomplished by increasing the T_g through copolymerization.

We assume the market requirements for such modifications would include maintaining complete biodegradability. Additives derived from annually renewable resources would be desirable.

We have found no reports of highly effective nucleating agents for PLA crystallization. The identification of good nucleating agents was critical in the development of many industrial plastics including PET.

There are a number of publications regarding the branching or cross-linking of PLA.¹⁻¹¹ Like other linear polymers, PLA has poor "melt strength". Through long chain branching the time-dependent elongational viscosity is modified resulting in improved melt strength. Methods to branch or partially cross-link PLA include: limited peroxide cross-linking (H-abstraction),¹⁻⁴ end group coupling with multifunctional coupling agents, copolymerization with multifunctional ring-opening monomers such as bislactones (Figure 5-1),⁴⁻⁶ multifunctional epoxide ring-opening agents,¹ and multifunctional hydroxyl initiators.⁷⁻¹¹ Although several branching techniques have been established, very little work has been aimed at tailoring the molecular architecture of PLAs to obtain the desirable flow characteristics required for applications such as film extrusion paper coating, blow molding, fiber melt spinning, and sheet formation.

The T_g of PLA can be decreased through the addition of plasticizers. However, a -10°C T_g represents the approximate practical limit with this approach. Crystallization of a plasticized PLA is required to allow for an upper-use temperature above room temperature (e.g., 90°C). Such PLA would be tough and ductile but would not be highly flexible (requires a considerably lower T_g).

Block copolymers and polymer blends offer a more attractive long-term approach to developing flexible or tough PLA-based materials. Several lactone monomers can be copolymerized (ring-opening) with lactide to produce flexible or tough biodegradable

polymers. Soft segment (several $\text{-CH}_2\text{-}$ and/or -O- flexible bonds) ring-opening monomers include caprolactone (homopolymer $T_g = -65^\circ\text{C}$, $T_m = 60^\circ\text{C}$),¹²⁻²⁵ valerolactone (homopolymer $T_g = -66^\circ\text{C}$, $T_m = 52^\circ\text{C}$),²⁶⁻²⁹ trimethylene carbonate (homopolymer $T_g = -21^\circ\text{C}$, amorphous),^{10,22,30-35} and *p*-dioxanone (homopolymer $T_g = -17^\circ\text{C}$, $T_m = 110^\circ\text{C}$), Figure 5-1. The PLA component of these block copolymers must be semicrystalline for most applications to provide for an adequate upper-use temperature.

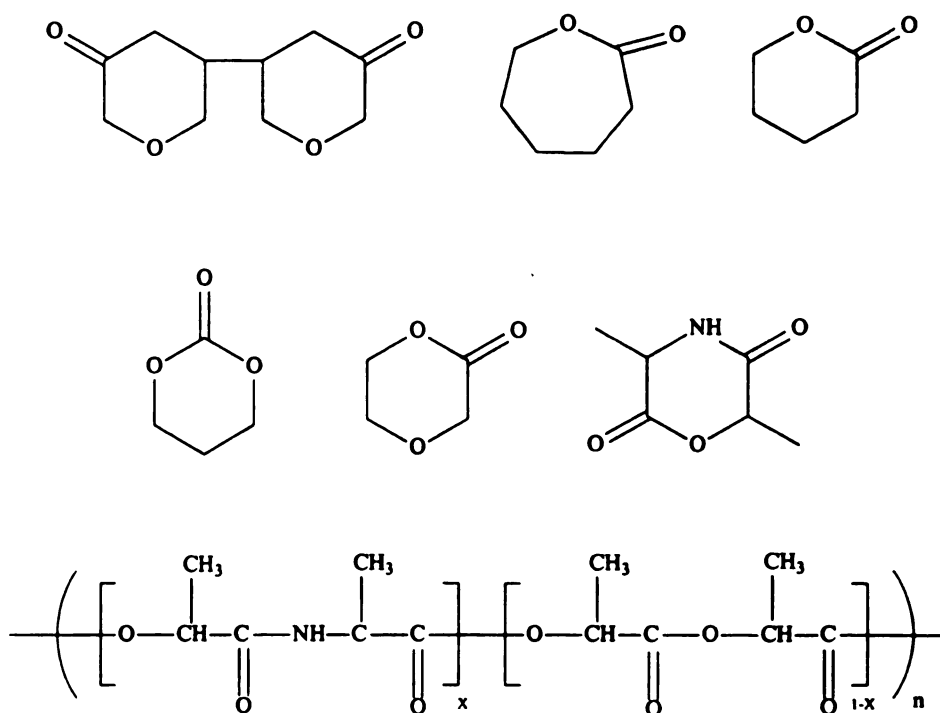


Figure 5-1. Examples of PLA modifiers through ring-opening polymerization: bislactone (provides branching), ϵ -caprolactone, δ -valerolactone, trimethylene carbonate, *p*-dioxanone, dimethylmorpholinedione based on lactic acid and alanine, polyester-amide from random copolymerization of lactide with morpholinedione based on lactic acid and alanine.

For example, a PCL-PLA block copolymer flexible film may be synergistic: has a low T_g PCL component (lacking in PLA) with a high T_m PLA component (PCL T_m is too low for most applications). To prevent the PCL blocks from crystallizing, methyl-substituted caprolactone monomers may be used. The ring-opening soft segment lactone monomers can also be homopolymerized and cross-linked to produce low T_g amorphous biodegradable rubbers. These rubbers can then be compounded with PLA to produce an impact modified biodegradable resin (similar to impact modified PS). A small amount of transesterification during blending would provide for good compatibilization and stabilization of the rubber-PLA morphology. Grijpma et al.³⁴ and Joziassse et al.³⁵ report on the rubber toughening of PLA.

PLA has a particularly high T_g for an aliphatic polyester and there are a very limited number of options to increase its T_g to that of PS (100°C). Although fillers increase the modulus of PLA above T_g they do not significantly affect the upper-use temperature. High T_g amorphous polymers (e.g., aromatics) are generally non-biodegradable and good blend candidates to increase T_g are scarce. Copolymerizing lactide with morpholinediones³⁶⁻⁴⁴ (Figure 5-1) probably represents the most attractive approach to increasing T_g . Morpholinediones are 6-membered rings that are half α -hydroxy acid (e.g., lactic or glycolic acid) and half α -amino acid (e.g., alanine or glycine) on hydrolysis. Morpholinedione homopolymers are polydepsipeptides with 95-117°C T_g . Reported molecular weights have been low (10,000 - 25,000 M_w), and we expect the T_g to be higher with increased molecular weight. These polymers are biodegradable and have been investigated for biomedical applications. Schakenraad and

Dijkstra⁴³ report that poly(DL-lactic acid-co-glycine) is biocompatible and degrades to natural residues in the body.

Lactide and alanine- or glycine-based morpholinediones form random copolymers with $T_g \approx 70\text{-}100^\circ\text{C}$ for 30-80% morpholinedione (i.e., 15 - 40% amino acid). Although considerable development would be required to determine feasibility, copolymers of lactide and morpholinediones are attractive for the following reasons: (1) they may be produced using stannous ethylhexanoate and form random copolymers having a single T_g ; (2) they are biodegradable; (3) they can be made from 100% annually renewable resources (e.g., alanine, commercially available from Ajinomoto U.S., can be fermented from corn sugar or possibly derived synthetically from lactic acid); (4) they can make transparent amorphous plastics with a T_g above 100°C (avoids the need to crystallize for higher upper-use temperature); (5) the morpholinedione comonomer can be half lactic acid; (6) they should have significantly improved barrier properties because of the enhanced H-bonding and higher T_g ; (7) they may provide for improved impact resistance because of the decreased physical aging rate with the high T_g . Although not recognized as such in the literature, we believe that copolymers based on lactic acid and alanine (or glycine) have considerable potential as single-use disposable PS replacements.

In summary, we identify the following opportunities for further work: (1) develop effective additives or processes for the melt deactivation of the polymerization catalyst; (2) further develop the appropriate rate equations to enable a complete polymerization simulation that can be used to develop a PLA process with complete control of

stereochemistry and molecular architecture; (3) develop chemically modified PLA resins that retain biodegradability but have a wider range of application owing to one or more of the following improvements: increased upper-use temperature, improved melt strength, and improved flexibility and toughness.

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