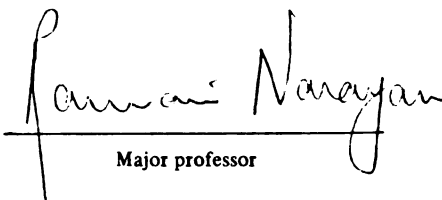


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REACTIVE EXTRUSION WITH STAR-POLYCAPROLACTONE

By

Ryoko Yamasaki

A THESIS

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

MASTER OF SCIENCE

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ABSTRACT
REACTIVE EXTRUSION POLYMERIZATION

By
Ryoko Yamasaki

There are many advantages in carrying out a reaction within the extruder, called a reactive extrusion, such as a lower processing cost, better control over residence time distribution and the temperature profile. In this study, an extruder was utilized to carry out different types of reactions: reactive extrusion polymerization of ϵ -caprolactone to produce a star-polycaprolactone (REX-PCL); reactive extrusion polymerization of REX-PCL and diisocyanate to produce polyurethane; and transesterification of REX-PCL and polyethylene terephthalate. By studying the reactive extrusion processes with different reaction chemistries, limitations with the current reactive extrusion system was also determined. The results of this study showed that the range of the molecular weight of REX-PCL achievable was found to be 20,000 to 210,000 for the particular system used in this study due to the physical limitation with the REX-PCL of different molecular weight. Also, a polyurethane was produced continuously from the production of REX-PCL; however, further analysis are necessary in order to evaluate the usefulness of this product. Finally, the titanium (IV) isopropoxide and dibutyltin dilaurate was found to work effectively in carrying out the transesterification of REX-PCL and polyethylene terephthalate.

**To my family
who has always been there for me...**

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INTRODUCTION

Growing environmental concerns worldwide demand the reduction of environmentally unfavorable waste, as well as the addition of the biodegradability or recyclability of the product as design criteria³⁵. In order to produce environmental friendly materials, various types of biodegradable plastics have been developed, including poly- ϵ -caprolactone, polylactide, and polyethylene succinate. Although the mechanism and rate of degradation of each polymer varies, they were all found to be converted to carbon dioxide with the presence of adequate temperature, humidity and microbial activity³⁰. However, due to their high cost, many plastic products that tend to be disposed in short service life, such as trash bags and disposable utensils, are still being made with traditional (non-biodegradable) plastics.

One of the ways to reduce the production cost of biodegradable plastics is to make the polymer synthesis to be continuous. Traditionally, a synthesis of plastics involves batch polymerization, which is a big stirred pot versions of beakers or flasks⁹. This method is rather costly since it involves series of several steps: first, a container is filled with reactant, followed by the polymerization, then emptying, and sometimes even cleaning, the container. On the other hand, when a polymerization is carried in an extruder, called reactive extrusion polymerization, polymer can be produced continuously, which not only reduces the processing cost, but also provides several advantages over batch polymerization, which will be discussed in the following section.

1.1 Reactive Extrusion Polymerization

In addition to the continuous process that reactive extrusion polymerization can provide, use of extruder is ideal in carrying out a polymerization since it can provide adequate mixing to achieve homogeneous material, as well as good control over residence time distribution and temperature profile. Also the same extruder can be used to combine the polymerization and blending processes which eliminates the extra steps that are typically involved in the production of blended materials^{9,30}.

There are many types of twin screw extruders commercially available. Their difference can be categorized in terms of the degree of intermeshing, the sense of rotation (co- or counter-rotating), and the functions that the screws are designed to perform^{5,8}.

Different types of twin screw extruder will be discussed in Chapter 2.

1.2 Process Conditions

Use of extruder allows one to customize process conditions for each application easily. Parameters that can be adjusted include:

- Reaction temperature
- Screw configuration
- Screw speed
- Number of vent ports
- Die size

Most of the extruders are equipped with a temperature control cooling system so the reaction can be carried isothermally. Also the extruders are usually divided into number of “zones” and their temperatures are controlled individually. Therefore the

temperature of each zone can be varied to design a temperature profile suitable for the process of interest. This feature became convenient in the polyurethane production, which will be discussed in Chapter 4.

By varying screw configuration and screw speed, level of mixing and residence time distribution can be controlled. Detail of screw configuration will be discussed in Chapter 2.

Some of the “zones” are equipped with vent ports, which can be opened or closed for a particular application. For example, when the starch is being processed, one of the vent ports must be open to release the steam generated by heating the starch. On the other hand, vent ports have to be tightly closed for the production of star-polycaprolactone since it must be carried under nitrogen environment. Vent ports can also be used to feed additional material at the middle of the extruder. This feature was also useful in the case of polyurethane production. Although the same die type was used throughout this study, it can be changed depending on the application.

Many features of extruder makes the polymerization in extruder more advantageous, compared to the traditional batch process. However, there are also some unique factors that have to be considered when planning a reactive extrusion polymerization.

One of the examples of the factors to be considered is the viscosity of the materials to be made or processed. In the case of batch polymerization, viscosity of materials can be as low as liquid solvent or as high as viscous polymer (in latter case, the solvent can be used to dilute the polymer for further processing⁹). However, in an extruder, a material of low viscosity may cause “extruder underload” and may result in

inadequate mixing of the materials. On the other hand, if a material has extremely high viscosity, the force required to turn the screws in the extruder (which is usually indicated as “torque %”) exceeds the acceptable level and results in an automatic shut-off of the extruder.

Also the time required to complete a polymerization have to be considered when it is carried out in an extruder. If the reaction takes more than 1000 seconds, the use of extruder is unlikely to be economic, because of high capital cost of an extruder⁹.

1.3 Project Overview

By choosing the appropriate reaction chemistry, the process conditions, and the extruder types, various types of materials can be produced by reactive extrusion process. In this study, three types of fully or partially biodegradable plastics were produced with reactive extrusion polymerization.

The first reaction conducted was reactive extrusion polymerization of ϵ -caprolactone to produce star-polycaprolactone (REX-PCL). Since the procedure to make REX-PCL was already developed by Mohan Krishnan in 1998³⁰, the focus of the study of this topic was to reproduce REX-PCL by following his procedure, and characterize the product. The methods used to characterize REX-PCL were measurement of intrinsic viscosity, thermogravimetric analysis (TGA), and differential scanning calorimeter (DSC). Additionally, linear polycaprolactone was purchased and same characterizations were performed and compared with REX-PCL. Also, Mark-Houwink-Sakurada (MHS) constants were determined from the intrinsic viscosity of REX-PCL and linear PCL. This topic will be discussed in Chapter 3.

The second reaction involves the production of polyurethane by reacting star-polycaprolactone with diisocyanate. This was done by conducting polymerization of REX-PCL, followed by the reaction of REX-PCL and diisocyanate continuously within the same extruder. The diisocyanate used in this experiment was hexamethylene diisocyanate. The characterization of polyurethane produced were done by measurement of intrinsic viscosity, TGA and DSC. This topic will be discussed in Chapter 4.

The last reaction conducted was the transesterification of REX-PCL with polyethylene terephthalate (PET). Catalysts used in this experiment were triphenylphosphine, dibutyltin dilaurate, and titanium (IV) isopropoxide. Products of transesterification were analyzed with TGA and DSC to compare the effect of three different catalysts. This topic will be discussed in Chapter 5.

Since some of the topics, such as the extruder type, screw configurations, and method of polymer characterizations, are applicable to multiple experiments, those topics are discussed in Chapter 2.

BACKGROUND

2.1 Twin Screw Extruders

Twin screw extruders have been used for processing of viscous materials for over a century, and their applications in the plastic industry started in the 1930s and 40s with the efforts of Colombo, Pasquetti, Meskat and Erdmenger, Leistritz, Fuller, and others^{5,21}. Since then, wide varieties of applications have been found for twin screw extruders, and a number of different extruder geometries have been developed to meet each application requirements⁵.

Currently, the geometry of a twin screw extruder mainly depends on the following specifications:

- co-rotating or counter-rotating
- fully, partially, or non-intermeshing
- conjugated or non-conjugated screw profile
- conical or cylindrical geometry
- equal or unequal screw length
- matched or staggered screw configuration

A twin screw extruder is called co-rotating if the screws rotate in the same direction, and it is called counter-rotating if the screws rotate in opposite direction. Both types of extruders can have various degrees of intermeshing, which can be distinguished in three levels: fully intermeshing, partially intermeshing, and non-intermeshing. Non-

intermeshing can be further subdivided into non-intermeshing with distance between two screws, and non-intermeshing without distance between two screws (tangential). Figure 2-1 illustrates the co-rotating and counter-rotating twin screw extruder with various degrees of intermeshings⁵.

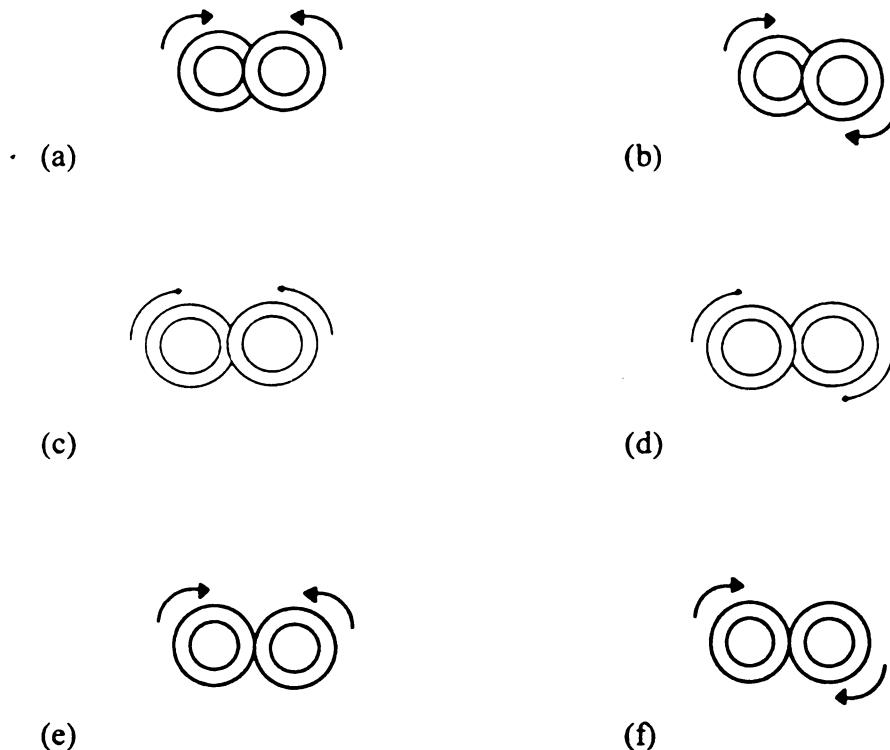


Figure 2-1: A schematic of co-rotating and counter-rotating twin screw extruder with various degree of intermeshing: (a) counter-rotating, fully intermeshing; (b) co-rotating, fully intermeshing; (c) counter-rotating, partially intermeshing; (d) co-rotating, partially intermeshing; (e) counter-rotating, tangential; (f) co-rotating, tangential.

Fully intermeshing extruder can be either closely fitting with wide flights (conjugated screws) or open with narrow flights (non-conjugated screws). Extruders with conjugated screws are generally operated at low screw speeds, around 10 to 20 rpm, to prevent high pressure that can build up in the intermeshing region. On the other hand,

extruders with non-conjugated screws can be operated at high speeds, as high as 600 rpm, because of its rather open structure. One of the disadvantages of the extruders with non-conjugated screws is the possibility of back-flow at a low screw speed due to the poor sealing of the channels by the flights. Figure 2-2 shows geometry of the conjugated and non-conjugated co-rotating twin screws⁵.

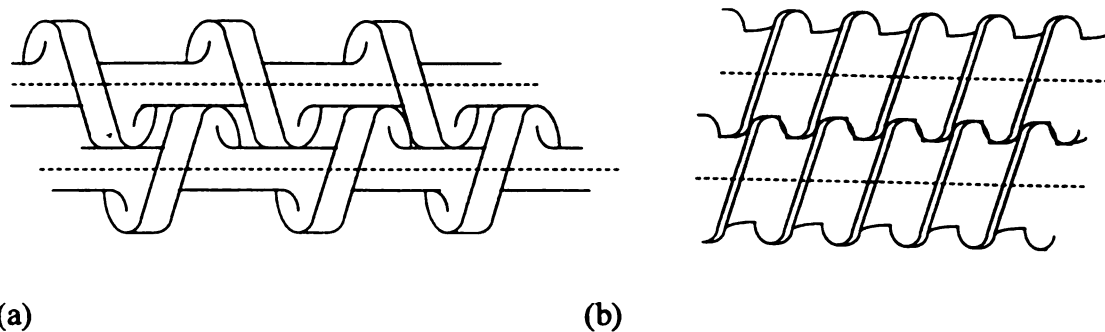


Figure 2-2: A schematic of conjugated and non-conjugated co-rotating twin screws: (a) conjugated; (b) non-conjugated

Although a cylindrical geometry with equal screw length, which has the same diameter throughout the extruder, is the most popular type of twin screw extruder, conical geometry and an extruder with unequal screw length are also available. A conical extruder has a large diameter at the feed end and it is gradually reduced toward the discharge end. This kind of extruder is particularly useful in the case of a low bulk density feed stock or a product with high viscous heat generation. Extruders with unequal screw length has a characteristic of generating high pressure at the single screw area and it is particularly useful in the case of non-intermeshing twin extruder. Figure 2-3 shows the conical twin screw extruders and the cylindrical extruder of unequal screw length⁵.

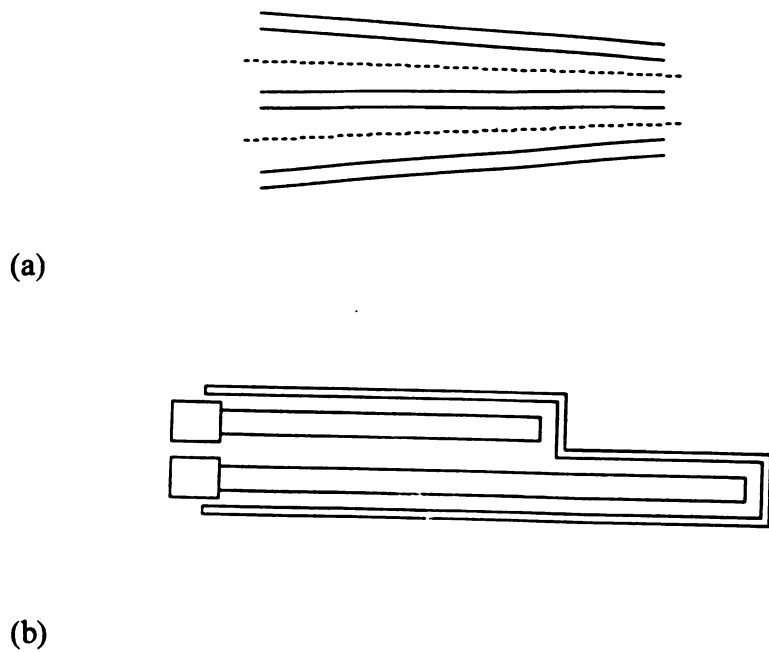


Figure 2-3: A schematic of (a) conical twin screw extruders and (b) cylindrical extruder of unequal screw length.

Non-intermeshing twin screw extruders can also be matched or staggered screw configurations as illustrated in Figure 2-4.

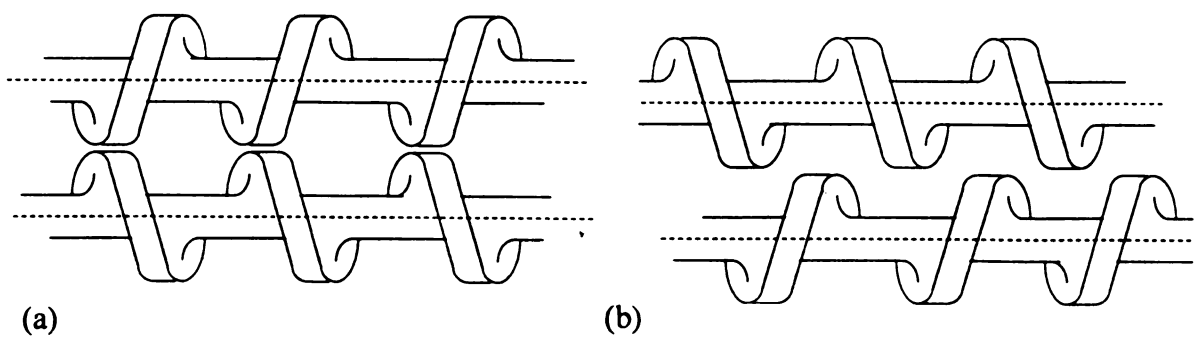


Figure 2-4: A schematic of (a) matched screw configuration and (b) staggered screw configuration.

Twin screw extruders can be designed for any particular applications by combining above specifications, though not all combinations are commercially available. For example, all twin screw extruders are either co-rotating or counter-rotating, and they are fully, partially or non-intermeshing. However, a conical geometry is currently available only for a counter-rotating extruder and an extruder of unequal screw length is only available for a non-intermeshing counter-rotating extruder⁵.

In addition to the extruder specifications, a combination of screw elements, called screw configuration, can be varied to provide various levels of mixing, different conveying rates, and different residence distribution and time.

In this study, Werner Pfleiderer twin screw extruder ZSK-30 was used. The type of this extruder is: 30 mm co-rotating, fully intermeshing screws with barrel length of approximately 960 mm. A photograph of this extruder is shown in Figure 2-5.

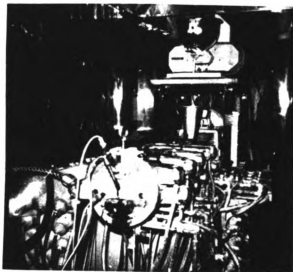


Figure 2-5: Photograph of Werner Pfleiderer twin screw extruder ZSK-30.

2.2 Screw Configuration

Screw configuration in a twin screw extruder primarily consists of two types of elements: screw elements and kneadling blocks.

The screw configuration mainly consists of right-handed screw elements, also called conveying elements, and they are primarily used to convey a material through an extruder with little mixing. They are available in various axial length, pitches, and different flight types such as single, double or triple flight to provide different level of conveying capacity. The screw element is also available in reverse flight (left-handed), which is used for sealing purpose: the flow of a material is stopped at a left-handed screw element until the upstream screw sections over a certain distance are completely filled to build enough pressure to overcome left-handed screw. The type of screw element is usually represented by a set of two numbers, such as X/Y, where X represents the pitch of the screw in millimeter (mm) and Y is the axial length of the element (in mm). In the case of left-handed elements, “LH” follows the two numbers^{5,30}.

Another type of element, a kneadling block, is used to provide various levels of mixing with less conveying capability than screw elements. They are available in various staggered angles and pitches to provide different level of mixing. Kneadling blocks can also be reverse staggered to provide greater level of mixing. In this case, the type of element is usually represented by a set of three numbers, such as X/Y/Z, where X is an angle representing the degree of stagger, Y is the axial length of the element (in mm), and Z is the pitch (in mm). Just as screw elements, reverse staggered element is represented with “LH” following three numbers³⁰.

In this study, two types of screw configurations were used. One of them consists of about 50% kneadling block and the remaining of screw elements, (screw configuration#1), and another one consists only of screw elements, (screw configuration #2). Schematics of those two screw configurations are shown in Figure 2-6.

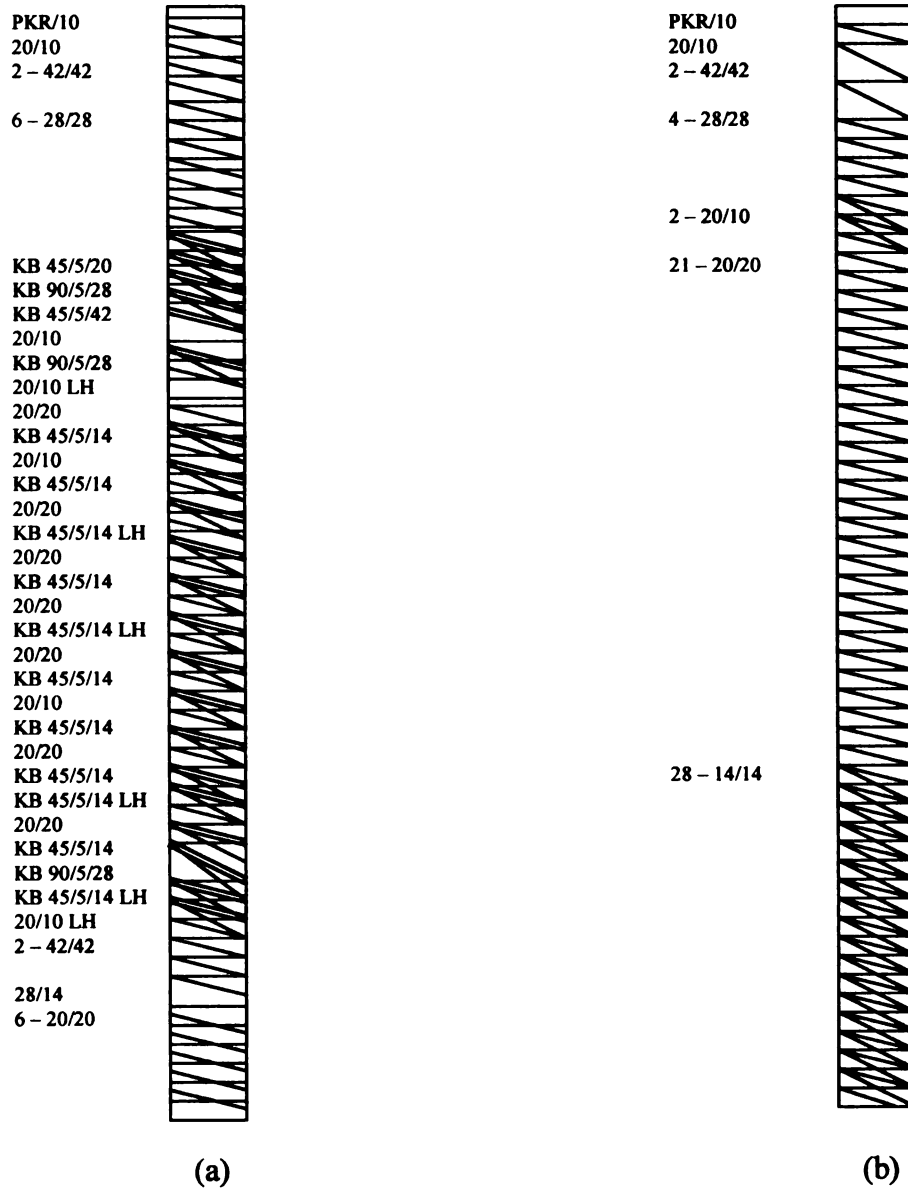


Figure 2-6: Screw configurations used in this study: (a) screw configuration #1; (b) screw configuration #2.

Screw configuration #1 provides good combination of conveying and mixing, and it can be used in wide variety of applications. On the other hand, screw configuration #2 provides large conveying capacity with little mixing. Screw configuration #2 was developed by Krishnan during his study of REX-PCL³⁰ in order to resolve the processing difficulty encountered with the use of screw configuration #1.

The results of Krishnan's study show that, due to the extra hold-up time in the kneadling blocks in screw configuration #1, viscosity of polymer was increased significantly and resulted in complete stoppage of material flow within the extruder. On the other hand, since there is no kneadling block used in screw configuration #2, the high viscosity problem found in screw configuration #1 was not observed in the experiments with screw configuration #2.

2.3 Characterization of Polymers

Once a new material is developed, its properties must be evaluated and usually compared with the properties of already known materials to verify the proposed reaction. Analysis of properties of newly developed material is also important in determining the applications for which the materials can be used.

There are various analytical and evaluative methods currently available. Many of them are equipped with high technology device with computer programs (such as spectroscopic, thermal, and mechanical methods) while some still require more manual processes (such as the determination of intrinsic viscosity using glass viscometer and determination of fractional conversion with the extraction method). Although there is no

single test that can provide all the answers needed, one can obtain a good picture of the type of material the person is dealing with by combining the results of various tests.

The methods used in this study were measurements of intrinsic viscosity using glass viscometer, thermogravimetric analysis (TGA), differential scanning calorimeter (DSC), and the determination of fractional conversion. The following sections discuss each type of analytical method and their standard procedure used in this study.

2.3.1 Measurement of Intrinsic Viscosity

Intrinsic viscosity or limiting viscosity number, $[\eta]$, reflects the contribution of the polymeric solute to the difference between the viscosity of the mixture and that of the solvent¹, and it is defined as:

$$[\eta] \equiv \lim_{c \rightarrow 0} \frac{1}{c} \left(\frac{\eta - \eta_o}{\eta_o} \right)$$

The intrinsic viscosity is constant for a particular polymer/solvent combination at a given temperature¹. Use of glass viscometer, such as Ubbelohde and Cannon-Fenske, is one of the simplest and widely used technique to determine intrinsic viscosity, using dilute polymer solutions²⁸.

Each type of viscometer is available in different sizes, and the type and size to be used depend on the range of viscosity of particular polymer/solvent combination to be measured. Ubbelohde viscometer was used in this study since it is one of the most widely used viscometer, and the size 0C, which is the second smallest size of Ubbelohde

commercially available, was selected because of the low viscosity of polymer/solvent combination that was used in this study.

Following section discusses the procedure used to determine intrinsic viscosity using Ubbelohde viscometer. Although similar procedure can be used with other types of viscometers, it is recommended to read the publication by American Society for Testing and Materials (ASTM) for the specifications applicable to the viscometer of interest.

2.3.1.1 Standard Procedure

First, the dilute polymer solution of known concentration was made by dissolving pre-weighted polymer (between 0.1 to 1.5 g depending on the type of polymer) into known volume of solvent, usually between 50 to 100 ml. There is no particular concentration that can be used for all types of polymers. In other words, any concentration can be used as long as the following specifications are met: efflux time (will be discussed later in this section) is over five minutes and under ten minutes (latter is merely for a convenience, and not a requirement). Toluene was used as a solvent throughout this study: 1 g of polymer per 100 ml of toluene was usually used as an initial concentration.

Both Ubbelohde and solution to be tested must be particle-free, since the diameter of capillary inside the Ubbelohde is very small that even a small particle can be trapped to give inaccurate result.

In order to clean Ubbelohde, the solvent was passed through all three tubes, followed by dry air to remove the final trace of the solvent. Then, enough dilute polymer solution to be tested was introduced through The largest tube (tube A), so level of the

solution is between two lines on the bulb at the bottom of the tube A. The Ubbelohde was placed into a constant-temperature water bath, so the water level is above the bulb on the tube consisting the capillary (tube B). Then the Ubbelohde was left for least 20 minutes to bring water and solution temperature to be at equilibrium. A temperature of 26 °C was used throughout this study. After approximately 20 minutes, the Ubbelohde was vertically aligned inside the water bath, then a finger was placed over the third tube (tube C) and suction was applied to tube B until the solution reaches to the bulb on the tube B. Suction was then removed from tube B, followed by removing the finger from tube C and the solution was allowed to flow freely. The efflux time was determined by measuring the time required for the level of solution in tube B to drop from one line to the other^{1,18}.

Above procedure was repeated at least three times for each solution and the average efflux time was determined.

Determination of intrinsic viscosity can be done by applying either the Huggins equation^{1,29}:

$$c^{-1}(\eta/\eta_0 - 1) = [\eta] + k_H[\eta]^2c$$

or the Kraemer equation^{1,11}:

$$c^{-1}\ln(\eta/\eta_0) = [\eta] - k_I[\eta]^2c$$

where c is the concentration of the polymer solution tested, η is the solution viscosity, η_0 is the solvent viscosity, $[\eta]$ is the intrinsic viscosity and k_H and k_I are the proportional constants associated with each equation. Both constants depend on the type of polymers being tested. For dilute solutions, it can be said that:

$$\eta/\eta_0 = t/t_0$$

where t is the efflux time of dilute polymer solution and t_0 is the efflux time of solvent alone¹. Both t and t_0 were determined as discussed above.

In order to determine the intrinsic viscosity, left-hand-side of Huggins equation and the Kraemer equation were plotted against c and straight lines were drawn through the points for each equation. Lines of both equations yield at the same y-intercept, which represents the intrinsic viscosity of particular polymer¹ as shown in Figure 2-7.

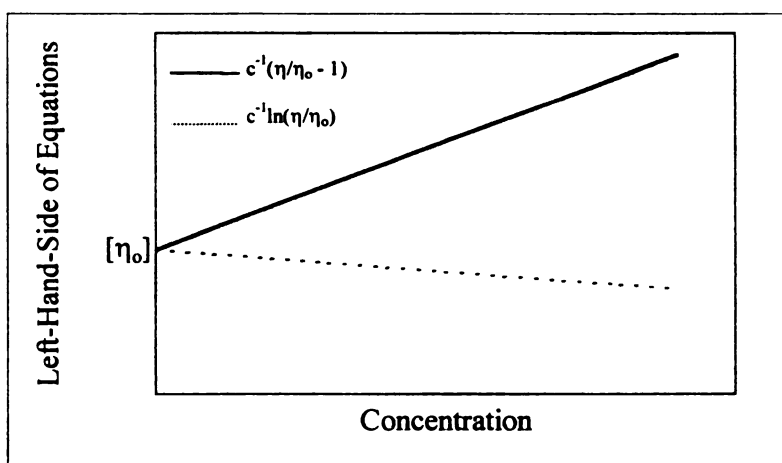


Figure 2-7: An example of graphs used to determine the intrinsic viscosity

Determined intrinsic viscosity were then used for the comparison of different materials and to determine the Mark-Houwink-Sakurada (MHS) constants.

2.3.2 Determination of Mark-Houwink-Sakurada (MHS) Constants

Mark-Houwink-Sakurada (MHS) equation relates intrinsic viscosity ($[\eta]$) of a polymer to a viscosity average molecular weight (M_v) with the equation:

$$[\eta] = K M_v^a$$

in which K and a are called Mark-Houwink-Sakurada constants. MHS constants depend on the polymer, type of solvent used and the solution temperature used for testing^{1,28}. Since MHS constants representing wide range of polymers, with different types of solvents and testing temperature, have been published in various literatures^{1,19,28,30}, M_v can be determined if the intrinsic viscosity of a polymer is determined at the condition in which MHS constants are known.

If MHS constants are unknown for a particular combination of polymer, solvent, and testing temperature, they can be calibrated by determining $[\eta]$ and plotting $\ln[\eta]$ versus $\ln M_w$ or $\ln M_n$, where M_w is the weight average molecular weight and M_n is the number average molecular weight. Since $\ln [\eta]$ is linearly related to $\ln M_w$ or $\ln M_n$ by the equation:

$$\ln[\eta] = \ln K + a \ln M$$

MHS constants can be determined from the slope and intercept of the line passing through the plotted points. M_v then lies between those of the corresponding M_w and M_n , though it is rather closer to M_w than M_n . This method, however, is merely an estimation and determination of exact M_v involves fractionation to divide the whole polymer sample into subspecies of relatively narrow molecular weight distributions, then averaging measured M_n and M_w to calculate M_v ^{1,28}.

In general, MHS equation can be applied to estimate M_w or M_n of unknown samples only if a fraction of a molecular weight distribution is very similar to the sample used for the calibration. However, this restriction does not apply to the polymers with random molecular weight distribution, such as linear polyamides and polyesters

polymerized under equilibrium conditions. For these types of polymers, $M_w = 2M_n$ and the relation

$$[\eta] = KM_n^a$$

can be applied¹.

In this study, MHS constants of linear and REX-PCL were determined by applying the equation above based on two assumptions: (1) a fraction of a molecular weight distribution is very similar between the same type of polymer of different molecular weight; and (2) both linear and REX-PCL have random molecular weight distribution. The latter assumption was based on the report provided by Daisel Chemical Company, which showed that the polydispersity index (M_w/M_n) is close to 2 for both linear and REX-PCL^{1,7}.

MHS constants has been reported in literatures for linear polycaprolactone with various solvents and temperatures, as well as for some types of star-polymers, such as star-polystyrene^{19,28}. However, the values of MHS constants could not be found for the star-polycaprolactone (REX-PCL).

2.3.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is primarily used to determine the thermal stability of polymer by continuously measuring the weight of polymer as the sample temperature is increased (non-isothermal TGA). The increase in the sample temperature results in a weight loss of the sample. At a low temperature, the weight loss may be due to the evaporation of moisture and solvent. However at higher temperatures, it is a result of a polymer decomposition. Therefore, by monitoring sample weight vs. temperature,

degradation temperature and the rate of degradation of the sample^{2,28}. A schematic of TGA output is shown in Figure 2-8.

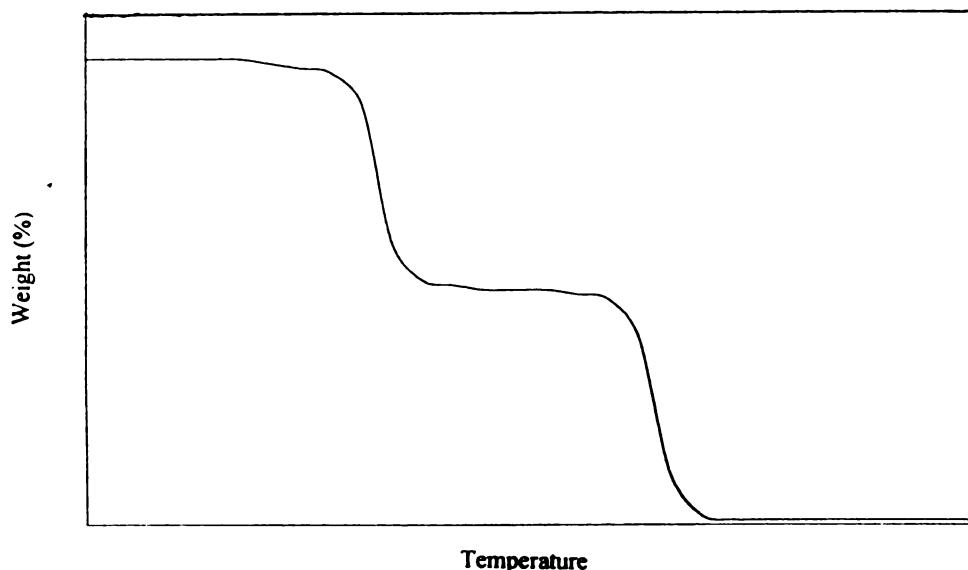


Figure 2-8: A schematic of typical output of Thermogravimetric Analysis

The determination of degradation temperature and the rate of degradation are not only useful to learn about the thermal stability of the material, but also useful in characterizing the unknown materials. This is because the degradation temperature and the rate of degradation are different for many materials, due to the difference in their degradation mechanism. By comparing the results of TGA before and after the reaction can provide some degree of information about the unknown materials.

In this study, TGA was utilized to determine the thermal stability of the materials produced, and to observe the result of reaction attempted, such as in the case of polyurethane production and transesterification. A standard procedure was developed for these purposes and used throughout this study.

2.3.3.1 Standard Procedure

TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyzer was used throughout this study. A photograph of this device is shown in Figure 2-9.

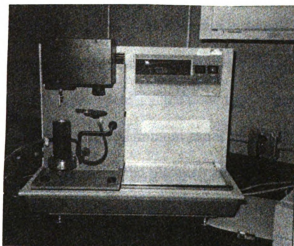


Figure 2-9: A photograph of TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyzer

Heating the sample and measuring the sample weight was entirely controlled by the computer program; however, the initial and final temperature, as well as the rate of heating was specified for the type of materials being used in this study and those conditions are shown in Table 2-1.

Initial temperature	25 °C
Final temperature	500 °C
Rate of heating	25 °C/min

Table 2-1: Heating condition of TGA used in this study.

Results of TGA were plotted in weight % vs. temperature (in °C). Also, the degradation point (in °C) and the rate of weight loss (in weight %/°C) were determined, using the computer program.

2.3.4 Differential Scanning Calorimeter (DSC)

In DSC, a polymer sample and an inert reference, usually an empty pan, are heated and thermal transitions in the sample are measured and recorded. This process is usually carried in a nitrogen atmosphere and the same type of pans must be used for polymer sample and inert reference. Aluminum pan is most commonly used; however, other materials such as gold, graphite, and platinum are also available.

With DSC, the sample and the reference are heated separately, with separate heating source so the temperature increases with the rate specified by an operator. Since energy required to increase the temperature of the sample is different from the energy required to increase the temperature of reference, the difference between two electrical power used for heaters ($d\Delta Q/dt$) is measured and recorded^{12,28}. Figure 2-10 shows a schematic of DSC output.

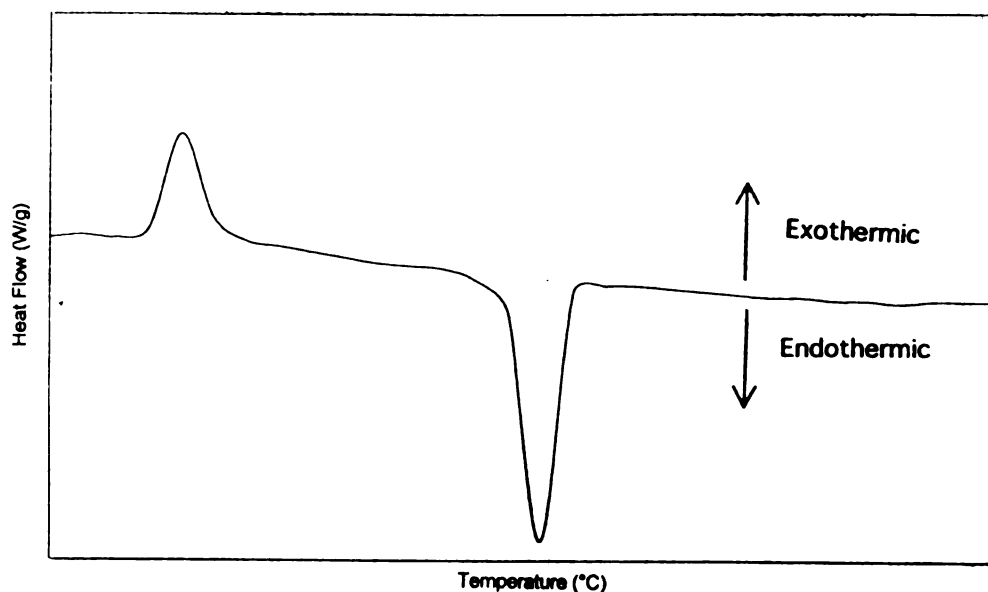
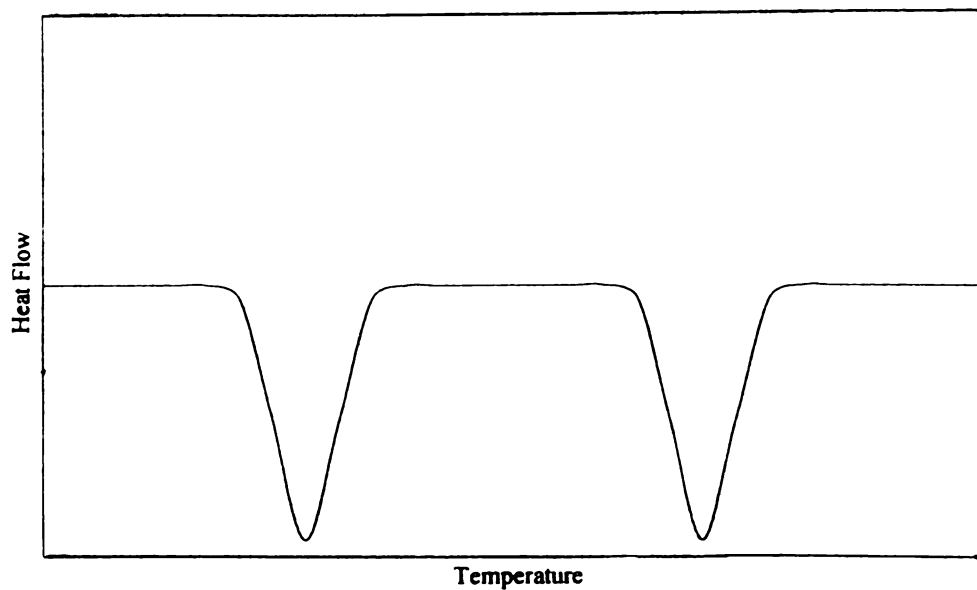


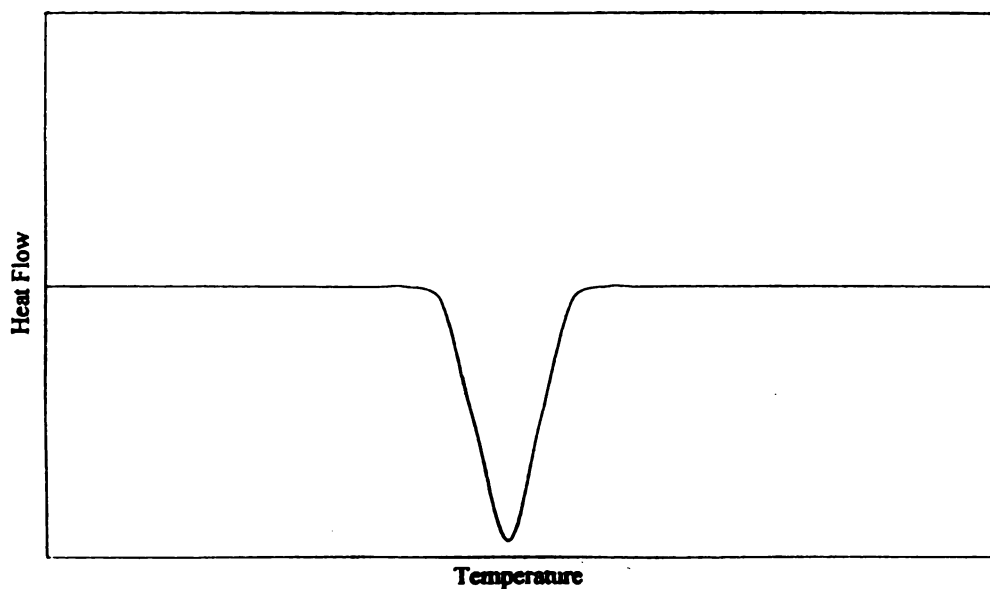
Figure 2-10: A schematic of output from Differential Scanning Calorimeter

Just as the thermal stability of the materials, thermal transition characteristics such as glass-transition temperature and melting temperature, are also different for different materials. Therefore, by comparing the output from DSC, one can determine whether an attempted reaction had taken place. This feature is particularly useful when analyzing the result of transesterification. This is because when two materials are mixed without any reaction in between, there are two melting temperatures associated with each material being mixed. However, once appropriate reaction has taken place between the mixed materials, there will be one melting temperature, which is most likely at the temperature

between the melting temperatures of individual materials. Figure 2-11 shows a schematic of this phenomenon.



(a)



(b)

Figure 2-11: A schematic of how DSC output changes before (a) and after (b) the transesterification

In this study, three types of heating schemes were programmed and utilized for different materials.

2.3.4.1 Standard Procedure

TA Instruments DSC 2920 Modulated DSC was used throughout this study. A photograph of this device is shown in Figure 2-12.

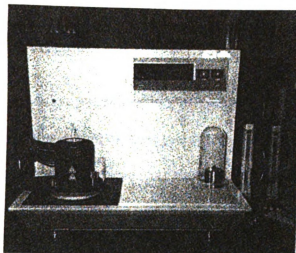


Figure 2-12: A photograph of TA Instruments DSC 2920 Modulated DSC

Heating the sample and measuring the difference in energy were entirely controlled by a computer program; however, initial and final temperatures, as well as the rate of temperature increase were specified for the type of polymers used in this study and they are shown in Table 2-2. Three types of heating conditions were designed and chosen depending on the materials to be analyzed.

(a) Type 1 heating condition

Initial temperature	-60 °C
Final temperature	100 °C
Rate of heating	10 °C/min

(b) Type 2 heating condition

Initial temperature	-60 °C
Final temperature	300 °C
Rate of heating	10 °C/min

(c) Type 3 heating condition

Initial temperature	40 °C
Final temperature	300 °C
Rate of heating	10 °C/min

Table 2-2: Three types of heating conditions of DSC used in this study: (a) Type 1; (b) Type 2; and (c) Type 3.

Type 1 heating condition was primarily used for the analysis of both linear and REX-PCL, since melting temperature of those two materials are approximately 60 °C. On the other hand, higher final temperature was chosen for Type 2 heating condition since melting temperature of polyethylene terephthalate (PET) is approximately 250 °C.

For both Type 1 and 2, low initial temperature (-60 °C) was used in order to observe the thermal transitions that might occur at low temperature.

Type 3 was used for the analysis of products from transesterification. In this case, the initial temperature was chosen to be at 40 °C since the focus of this analysis was to compare different transesterification products, and since there was no significant thermal transition observed below that temperature for either PET or REX-PCL.

Results of DSC were plotted for heat flow (in W/g) vs. temperature (in °C). Also, some characteristic peaks were determined by using the computer program.

2.3.5 Fractional Conversion

When a product seems different from reactants, it does not mean the reaction went to completion. Therefore, it is important to determine the fractional conversion of reactants as a part of the characterization of product.

There are various methods that can be used to determine the fractional conversion such as Gas Chromatography method and dissolution-precipitation gravimetric method³⁰. The latter method was used in this study to determine the fractional conversion of REX-PCL.

2.3.5.1 Standard Procedure

In dissolution-precipitation gravimetric method, unreacted monomer is separated from the polymer by precipitation and the difference in weight before and after the extraction can be used to determine the fractional conversion of monomer.

This experiment was done, first, by dissolving a known amount of REX-PCL (approximately 5 g) in 50 ml of toluene, leaving it for 24 hours at room temperature, then precipitating dissolved REX-PCL with approximately 500 ml of heptane. The precipitate was then filtered and left inside a chemical hood for a few days to allow heptane to evaporate. The remaining polymer was then weighted and compared with the weight before the precipitation. The fractional conversion of ϵ -caprolactone monomer was determined by the equation:

$$\text{Fractional conversion} = \text{Weight after extraction} / \text{Weight before extraction}$$

REACTIVE EXTRUSION POLYMERIZATION OF EPSILON-CAPROLACTONE

3.1 Introduction

Polycaprolactone (PCL) is a semi-crystalline polymer and it belongs to the family of polyesters. Because of its hydrolyzable ester group, polycaprolactone and other aliphatic polyesters are biodegradable, which makes them environmental friendly. Other attractive properties of PCL include its miscibility with number of polymers (such as polycarbonate, polyvinyl chloride, and cellulose propionate) and its compatible mechanical properties to more common polymers (such as polyethylene)³⁰. However, commercially available linear PCL also has some drawbacks, such as its high cost, low melting temperature (about 60 °C), and low melt strength. In order to overcome these disadvantages, a process of synthesizing high molecular weight star-polycaprolactone (REX-PCL) in extruder was developed.

3.2 Background

A process of making REX-PCL was developed by Mohan Krishnan in 1998, and the detail of the process was documented in his doctoral dissertation, titled *Engineering of Compositions Based on Star-Polycaprolactone Derived By Extrusion Polymerization of Epsilon-Caprolactone*³⁰. This process involves a coordination insertion reaction with a

ring-opening polymerization of ϵ -caprolactone monomer, using aluminum tri-sec butoxide as an initiator. The reaction mechanism is shown in Figure 3-1.

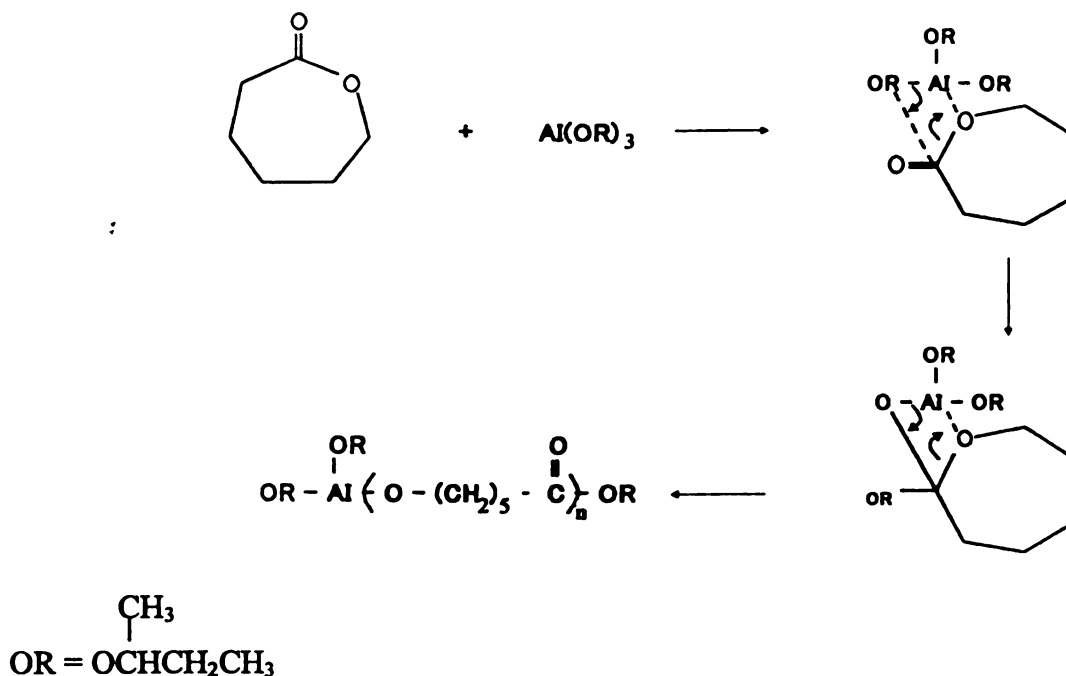


Figure 3-1: Ring-opening polymerization of ϵ -caprolactone to produce REX-PCL

The structure of REX-PCL is so-called “star” shape due to the presence of aluminum atom which connects three PCL molecules. The structures of linear and REX-PCL are shown in Figure 3-2.

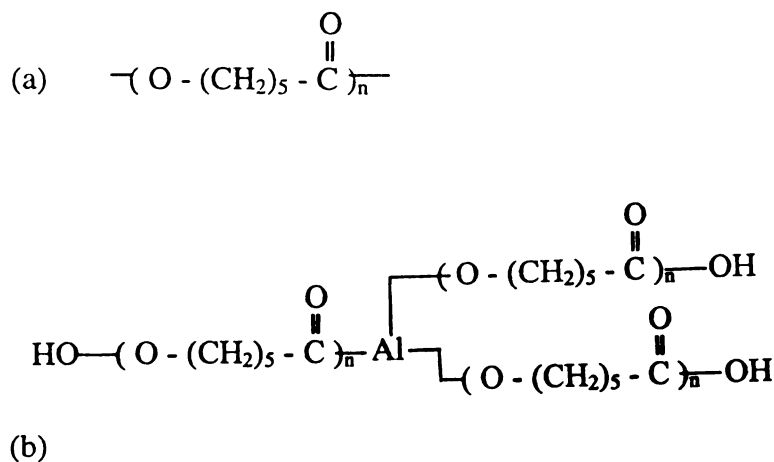


Figure 3-2: The structures of (a) linear PCL and (b) REX-PCL

In his study, wide range of extrusion temperatures were evaluated, ranging from 150 to 220 °C, with two grades of ϵ -caprolactone, TONE EC and TONE ECEQ. The difference between TONE EC and ECEQ are their purity: purity of ECEQ is higher with lower free acid contents³⁰. The results of his study showed that polymerization with ECEQ at the extrusion temperature of 190 °C was found to give best monomer conversion (98 % for the molecular weight of both 80,000 and 120,000). Additionally, screw configuration #2, which consists only of conveying elements, was developed for the production of REX-PCL. The process was developed using Werner Pfleiderer twin screw extruder ZSK-30, and the theoretical molecular weight of REX-PCL produced range from 80,000 to 137,000.

In this study, production of REX-PCL was started by reproducing the procedure developed by Krishnan, then some adjustment in the process conditions were made in order to produce the REX-PCL with wider range of molecular weight.

3.3 Outline of Chapter

This chapter focuses on the production and characterization of REX-PCL of various molecular weight, and it is subdivided into four sections: (1) Reactive Extrusion Polymerization of ϵ -Polycaprolactone to Produce REX-PCL of Various Molecular Weight (section 3.4); (2) Characterization of Star-Polycaprolactone (section 3.5); (3) Reactive Extrusion Polymerization of ϵ -Polycaprolactone from Monomer with Impurities (section 3.6); and (4) Monomer Conversion and Reproducibility (section 3.7).

The first topic discusses the process of making REX-PCL by reproducing the method developed by Krishnan^{30,31}, and the determination of upper and lower limits of molecular weight that can be produced. Various observations made during the process of making REX-PCL will also be discussed in this section.

Next section discusses the characterization of REX-PCL of various molecular weight and compare the result with the one of linear PCL. Method used to characterize the polymers were: determination of fractional conversion, measurement of intrinsic viscosity, Thermogravimetric Analysis (TGA), and Differential Scanning Calorimeter (DSC). Also, Mark-Houwink-Sakurada (MHS) constants for both linear and REX-PCL were determined at temperature of 26 °C with toluene as a solvent.

Additionally, in order to determine the effect of impurities on the formation of star-polycaprolactone, the same procedure was used to produce REX-PCL with the monomer with some water contents. A process of making REX-PCL with the monomer with impurities is discussed in section 3.6.

Finally, the monomer conversion within the extruder, as well as the reproducibility of the process of making REX-PCL were determined from the intrinsic viscosity and they will be discussed in section 3.7.

3.4 Reactive Extrusion Polymerization of ϵ -Caprolactone to Produce REX-PCL of Various Molecular Weight

3.4.1 Objective

Objectives of this experiment were: (1) to make REX-PCL with wide range of molecular weight; (2) to determine the lower and upper limit of molecular weight that can be produced from the same system.

3.4.2 Materials

ϵ -caprolactone monomer (TONE ECEQ) was purchased from Union Carbide and used throughout this study, except the experiments discussed in section 3.6 in which contaminated monomer was used instead. A structure of ϵ -caprolactone is shown in Figure 3-3.

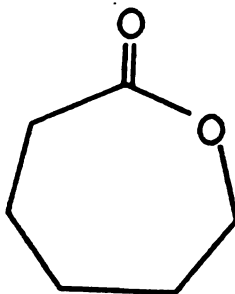


Figure 3-3: A structure of ϵ -caprolactone

Aluminum tri-sec butoxide (ATSB) was used as an initiator and its structure is shown in Figure 3-4.

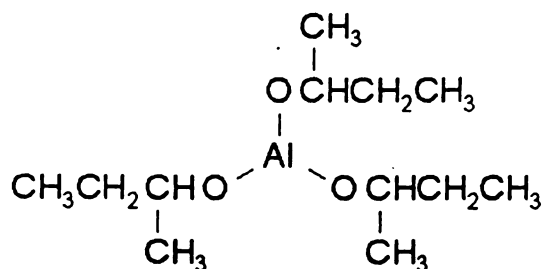


Figure 3-4: A structure of aluminum tri-sec butoxide

Although the polymerization can take place without the presence of any solvent, ATSB was mixed with anhydrous toluene (ATSB solution hereafter). Purpose of mixing ATSB with anhydrous toluene was to increase the flowrate, since required flowrate of ATSB by itself is too small (less than 0.1 g/min in most cases) to be pumped with commercial pump. Also the addition of anhydrous toluene resulted in the better distribution of ATSB throughout the monomer. This was important because the screw configuration used in this experiment lacked mixing characteristics. However, the use of anhydrous toluene also had negative effects. For example, use of toluene increased the production cost, and is also environmentally unfavorable. Furthermore, some amounts of toluene remained in the product had to be evaporated. Therefore, the dilution of ATSB with anhydrous toluene was limited to 5 wt% ATSB.

Note that anhydrous toluene was used instead of a “regular” toluene also to prevent a contact of water with ATSB. Since both monomer and ATSB are sensitive to

moisture, preparation of ATSB solution as well as the production of REX-PCL were carried under dry nitrogen.

3.4.3 Procedure

Procedure discussed in this section was applied to the production of REX-PCL throughout the study.

3.4.3.1 Flowrate Calculation

In most cases, production of REX-PCL starts with the objective of making a REX-PCL of certain molecular weight. For this reason, calculation of monomer and ATSB flowrate also starts with choosing desired theoretical molecular weight. For a fixed theoretical molecular weight, degree of polymerization (DP) was calculated with the equation:

$$DP = (\text{theoretical MW}) \times 3 / (\text{MW of monomer})$$

A term “3” in the above equation came from the fact that ATSB has three arms that can react with a monomer.

Since DP is a molar ratio of monomer to initiator, it can be represented as:

$$DP = (\text{molar flowrate of monomer}) / (\text{molar flowrate of ATSB})$$

in which molar flowrate of monomer can be calculated by choosing volumetric flowrate of a monomer. A choice of volumetric monomer flowrate depends on the size of pump head and tube to be used, as well as the rate of production of REX-PCL to be achieved. Latter is especially important in order to make this process cost effective.

Once volumetric flowrate of monomer is chosen, mass flowrate of monomer can be calculated with the equation:

$$\text{mass flowrate of monomer} = (\text{volumetric flowrate of monomer}) \times \rho_{\text{monomer}}$$

where ρ_{monomer} is the density of monomer. The molar flowrate of monomer was then calculated as:

$$\text{molar flowrate of monomer} = (\text{mass flowrate of monomer}) / (\text{MW of monomer})$$

With a known DP and a molar flowrate of a monomer, a molar flowrate of the ATSB can be calculated as:

$$\text{molar flowrate of ATSB} = (\text{molar flowrate of monomer}) / \text{DP}$$

which can be converted to mass flowrate by:

$$\text{mass flowrate of ATSB} = (\text{molar flowrate of ATSB}) \times (\text{MW of ATSB})$$

Since the mass flowrate of the ATSB itself is very small (less than 1 g/min for most of the experiment done in this study), ATSB was mixed with anhydrous toluene to make the ATSB solution. Then, the flowrate of ATSB solution was calculated as:

$$\text{mass flowrate of solution} = (\text{mass flowrate of ATSB}) / (\text{fraction of ATSB in solution})$$

which can be converted into volumetric flowrate of a solution by the equation:

$$\text{volumetric flowrate of ATSB} = (\text{mass flowrate of solution}) / \rho_{\text{solution}}$$

where ρ_{solution} is the density of ATSB solution, which can be calculated as:

$$\rho_{\text{solution}} = 1 / [(\text{frac of ATSB} / \rho_{\text{ATSB}}) + (\text{frac of Toluene} / \rho_{\text{toluene}})]$$

where ρ_{toluene} is the density of anhydrous toluene.

An example of the calculation sheet used in this study is shown in Table 3-1.

Flowrate Calculation for REX-PCL

pick value

Date:**Run#:**

Theoretical MW =

 $DP = \text{Theoretical MW} \times 3 / 114.14 =$ **ϵ -Caprolactone Monomer**

Volumetric Flowrate of Monomer = ml/min

 $\rho_{\text{monomer}} = 1.030 \text{ g/ml}$ Mass Flowrate of Monomer = Vol Flowrate of Monomer * $\rho_{\text{monomer}} =$ g/min

MW of Monomer = 114.14 g/mol

Molar Flowrate of Monomer = Mass Flowrate / MW of Monomer = mol/min

Aluminum tri-sec Butoxide

Molar Flowrate of ATSB = Molar Flowrate of Monomer / DP = mol/min

MW of ATSB = 246.33 g/mol

Mass Flowrate of ATSB = Molar Flowrate * MW = g/min

Fraction of ATSB in initiator solution =

Mass Flowrate of Solution = Mass Flowrate of ATSB / frac of ATSB = g/min

 ρ of ATSB = 0.967 g/ml ρ of Toluene = 0.865 g/ml ρ of Solution = $1 / [(\text{frac of ATSB} / \rho_{\text{ATSB}}) + (\text{frac of Toluene} / \rho_{\text{Toluene}})] =$ g/mlVolumetric Flowrate of Solution = Mass Flowrate of Sol. / ρ of Sol. = ml/min

Table 3-1: An example of the calculation sheet used to determine the monomer and initiator flowrate

An example of the various monomer and the initiator flowrate to yield different theoretical molecular weight are shown in Table 3-2.

Theoretical Molecular Weight	Monomer Flowrate (ml/min)	ATSB Solution Flowrate (ml/min)	% ATSB in the Solution (wt%)
30,000	40	2.6	5
30,000	80	5.2	5
30,000	20	1.3	5
30,000	80	1.7	15
60,000	50	1.6	5
60,000	150	1.6	15
100,000	80	1.6	5
100,000	80	0.8	10
100,000	40	0.8	5

Table 3-2: An example of the various monomer and the initiator flowrate to yield different theoretical molecular weight of REX-PCL

3.4.3.2 Preparation of ATSB Solution

A preparation of the ATSB solution was carried under nitrogen environment in a glove box/bag. In this section a preparation of ATSB in glove bag will be discussed, however, similar procedure can be followed in the case of using a glove box.

ATSB content of 5 and 15 wt% in anhydrous toluene were mostly used in this experiment; however, these values were chosen merely for the convenience, and any concentration can be used depending on the molecular weight to be made and the type of the pump to be used.

In order to make the ATSB solution, a tube was first connected between the nitrogen cylinder and the glove bag, where all the required materials were placed. Then, the nitrogen flow was started and left for a few minutes to purge inside the bag.

Once purging was done, the glove bag was closed and the bag was filled with nitrogen. Then a scale was used to prepare a catalyst solution of a desired concentration (in weight percent) in a 2 L flask. The ATSB and the anhydrous toluene bottles as well as the flask containing the catalyst solution were tightly closed with parafilm prior to opening the glove bag.

3.4.3.3 Flow Scheme

Flow scheme of ϵ -caprolactone monomer, the ATSB solution, and the nitrogen gas are discussed in this section.

ϵ -Caprolactone Monomer

Schematic of monomer flow is shown in Figure 3-5.

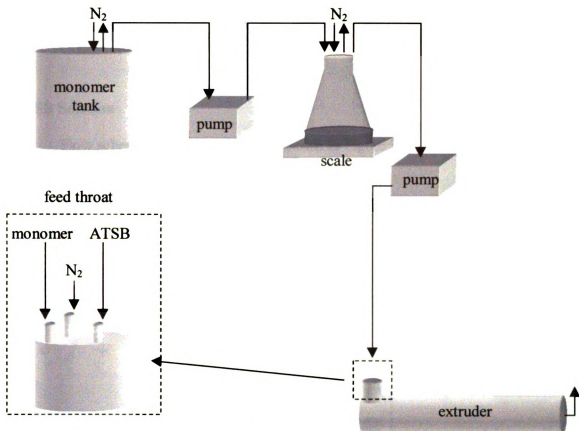


Figure 3-5: Flow scheme of ϵ -caprolactone monomer

The monomer was first pumped out from the monomer tank (55 gal drum was usually used) and entered a transfer vessel (2 L flask) on the scale. The use of a transfer vessel served two purposes: monitoring the flowrate of the monomer, and to prevent from ruining large amount of monomer (in drum) by accident. From the transfer vessel, the monomer was pumped into the extruder through the feed throat. A level of monomer in transfer vessel was kept at about 1.5 L throughout the process. Both the monomer tank and the transfer vessel were tightly closed and only the dry nitrogen was allowed to flow through them to prevent the air from entering the system.

Masterflex® L/S® Easy-Load® pumps and the Masterflex® L/S® precision tubing size 15 were used for the monomer flow. The size of the pump head as well as the tubing

size were determined by considering the typical monomer flowrate (20 ml/min to 220 ml/min) used in this study.

ATSB Solution

Flow scheme of ATSB solution is shown in Figure 3-6.

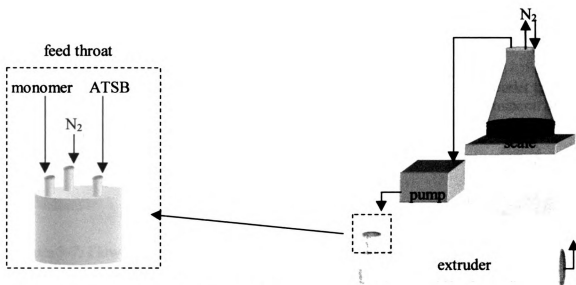


Figure 3-6: Flow scheme of ATSB solution

ATSB solution was made in a 2 L flask and was pumped out and directly fed to the extruder (through feed throat) without using a transfer vessel. The flowrate of ATSB solution was monitored by measuring the weight of 2 L flask. Just as the monomer tank and the transfer vessel, a container of ATSB solution was closed tightly and dry nitrogen was continuously passed through to prevent the air from entering.

Masterflex® L/S® Easy-Load® pumps and the Masterflex® L/S® precision tubing size 14 were used to feed the ATSB solution. The size of the pump head and the tubing size were determined by considering the typical flowrate of ATSB solution (1.4 ml/min to 5 ml/min) used in this study.

Nitrogen

Flow scheme of nitrogen gas is shown in Figure 3-7.

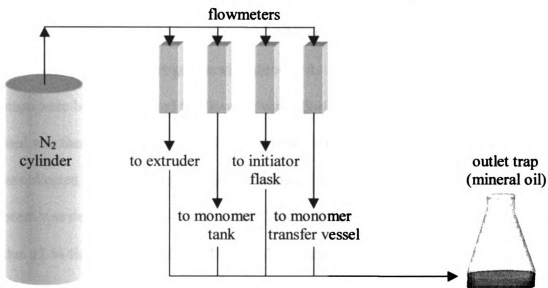


Figure 3-7: Flow scheme of nitrogen gas

Nitrogen was separated into four streams and entered flowmeters. Flowmeters were necessary in order to monitor the nitrogen flowrate. After passing through the flowmeters, each nitrogen stream entered into the four separate containers: the extruder, the initiator flask, the monomer tank, and the monomer transfer vessel. The nitrogen output from the initiator flask, the monomer tank, and the monomer transfer vessel were then led into the separate outlet trap containing mineral oil to prevent a back flow of air.

Tygon® tubes were used for the nitrogen streams, and overall nitrogen flowrate was kept at about 10 psi.

3.4.3.4 Start-Up

An extruder was started first and the temperature of all six zones were set to be at 180 - 190 °C. The water bath was filled while waiting.

The nitrogen flow was started before both the monomer drum and the flask containing ATSB solution were opened. The tubes were carefully connected to each of the containers with the nitrogen flowing through it. Then, the monomer and the initiator pumps were both started and the flowrate was adjusted to the desired value. The screw speed was then gradually increased to 110 rpm. The product coming out from the die was collected in a metal trash can and discarded until the system became stable. The system was determined to be stable when “torque %” of the extruder stayed in the same value ± 2 % for over 20 minutes. The metal trash can was especially important at the beginning of the experiment since the unreacted feed tend to come out from the die for the first 10 to 30 seconds.

3.4.3.5 Collecting Sample and Shut Down

When the system stabilized, the product from the die was passed through a water bath to cool down and pelletized. Air was blown just before the pelletizer to blow the water off the polymer string. The pelletized polymer was then dried in air for a few days before characterization.

When the REX-PCL of different molecular weight were collected continuously without purging (cleaning inside extruder), the flowrate of the monomer and the ATSB solution were gradually changed, with at least 5 minutes at each flowrate. This process

was particularly important in the case of going from a high molecular weight to a lower one (see section 3.4.5 for explanation).

When the desired amount of samples were collected, the monomer and the initiator pumps were stopped. The tubes were disconnected, and the containers were closed. All these steps were done before the nitrogen was turned off, so the air would not enter the monomer or the ATSB containers. Also at the end, a tube used for ATSB solution was cleaned by passing toluene through it. The remaining toluene inside the tube was dried by blowing air through. This last step was necessary in order to prevent the tube from clogging.

3.4.4 Results

The molecular weight of the REX-PCL produced, as well as the feed rate of the monomer and the ATSB solution, a fraction of the ATSB in the solution used, and the resulted torque % were recorded as shown in Table 3-3. The extruder temperature and the screw speed were kept constant at the value indicated in the Procedure section (section 3.4.3.4) for all the molecular weight produced.

Theoretical Molecular Weight (each arm)	Monomer Flowrate (ml/min)	ATSB Solution Flowrate (ml/min)	% ATSB in Solution	Observed Torque %
20,000	20	2	5	15
30,000	40	2.6	5	21
60,000	50	1.6	5	35
80,000	70	1.7	5	37
100,000	80	1.6	5	41
110,000	80	1.4	5	42
120,000	100	1.6	5	45
150,000	130	1.7	5	48
210,000	150	1.4	5	55

Table 3-3: Molecular weight of REX-PCL produced (T = 180 °C, 110 rpm)

3.4.5 Discussion

As shown in Table 3-3, the REX-PCL of molecular weight ranging from 20,000 to 210,000 were produced only by varying the flowrate of reactants. The melt fracture of REX-PCL clearly showed the increase in viscosity as the molecular weight of the polymer was increased. The increase in the torque % also indicated the same phenomenon.

Note that in some extrusion experiments, the temperature of zone 1 (the zone closest to the feed throat) is kept low, such as 60 °C. However, in the production of REX-PCL, it was important to keep the temperature of zone 1 high, such as 180 °C used in this experiment, in order to prevent an overflow of reactants at the feed throat. When the temperature of zone 1 is low, the reaction between the monomer and the ATSB is too slow that the material of low viscosity in the zones closer to the feed throat can not push the viscous material at the later zones out from the die.

Also by varying the flowrate of the monomer and the ATSB solution, the lowest and the highest molecular weight that can be produced with current system was determined. For the lowest limit, a molecular weight of 20,000 was achieved. Although even the lower molecular weight could be obtained, it is not recommended for this particular system since “extruder underload” warning appears every few minutes.

Numerous attempts were made to achieve the high molecular weight. However, the highest molecular weight that could be achieved steadily was found to be 210,000. A molecular weight higher than 210,000 was unable to be achieved because of the poor initiator distribution. To make a polymer with high molecular weight, the monomer to the initiator ratio has to be very high. However, as the ratio increases, the number of

initiator available for the monomer decreases, resulting in some monomer to be left unreacted. This phenomenon was observed in terms of torque % of the extruder. As the monomer to initiator ratio hits a certain level, torque % stops increasing or even start to decrease. In some cases, “oscillation” of torque % was also observed - that is, the torque % fluctuating between 55% and 35% as the polymer coming out of the die showing different melt fracture every few inches. One of the possible solutions to this problem, in order to make even higher molecular weight, is to add a few mixing elements at the feed area to increase the initiator distribution.

Note that the color of commercial linear polycaprolactone is white; however, the color of REX-PCL was found to be light yellow when it is fresh out of the extruder. This yellowish color faded away as the polymer was sitting in the storage. The yellowish color was also found to be darker for the REX-PCL of lower molecular weight, and the color was more like orange than yellow in the case of REX-PCL with molecular weight of 30,000. Additionally, the freshly made REX-PCL smelled like a toluene; however, this too, faded away as the polymer was left in storage for a few days.

These observations suggest that the difference in colors between linear and REX-PCL was most likely due to the toluene used in the ATSB solution. This also explains why the color of REX-PCL of lower molecular weight is darker: for the same concentration of ATSB solution, increasing the flowrate of the solution result in greater toluene content.

3.5 Characterization of Star-Polycaprolactone

Characterization of Star-Polycaprolactone produced were done with four methods: determination of fractional conversion, measurement of intrinsic viscosity, thermogravimetric analysis (TGA), and diffraction scanning calorimeter (DSC). The same characterizations were also done with linear PCL purchased and compared with the results of REX-PCL. Additionally, Mark-Houwink-Sakurada constants were determined for both the linear and the REX-PCL from their intrinsic viscosity and the results were compared.

3.5.1 Determination of Fractional Conversion

3.5.1.1 Objective

Objective of this experiment was to determine the actual molecular weight of the REX-PCL by determining the fractional conversion of ϵ -caprolactone.

3.5.1.2 Materials

The REX-PCL with the molecular weight of 30,000, 60,000, 80,000, 100,000, 120,000, 150,000, and 210,000 were used in this experiment.

Toluene was used to dissolve, and heptane was used to precipitate the polymer from the solution.

3.5.1.3 Procedure

Standard procedure described in Chapter 2 was followed.

3.5.1.4 Results

Fractional conversion of the monomer was determined for the each REX-PCL collected. The results were tabulated as shown in Table 3-3. Also, the actual molecular weight was calculated for each polymer based on the fractional conversion and also shown in Table 3-4.

Theoretical M_n	Fractional Conversion (%)	Actual M_n	standard deviation
30,000	97.4	29,220	1.46
60,000	96.3	57,780	0.78
80,000	98.8	79,040	0.22
100,000	98.3	98,300	0.50
120,000	97.5	117,000	0.29
150,000	95.3	142,950	0.85
210,000	88.5	185,850	2.30

Table 3-4: Fractional conversion and actual molecular weight of REX-PCL produced

3.5.1.5 Discussion

As shown in Table 3-4, high monomer conversion was achieved for the molecular weight up to 120,000. This indicates that, for the theoretical molecular weight up to 120,000, the polymerization had taken place almost to completion and the theoretical molecular weight is very close to the actual molecular weight.

On the other hand, the fractional conversion of 150,000 is slightly lower than the ones of lower molecular weight, resulting in the actual molecular weight to be approximately 5 % lower than the actual molecular weight. The reduction in fractional conversion is even lower for the theoretical molecular weight of 210,000, though this

result was expected since a longer reaction time is required to produce a polymer of higher molecular weight.

One of the possible ways to increase the fractional conversion of REX-PCL with high molecular weight is to increase the residence time by decreasing the screw speed. Increasing the extruder temperature also increases the rate of reaction and can result in higher fractional conversion.

3.5.2 Determination of Intrinsic Viscosity

3.5.2.1 Objective

Objective of this experiment was to determine the intrinsic viscosity of linear and REX-PCL of various molecular weight with Ubbelohde viscometer and compare the results.

3.5.2.2 Materials

Three different molecular weight of linear polycaprolactone ($M_n = 10,000$, 42,500, and 80,000) were purchased to compare with the REX-PCL. The theoretical molecular weight of REX-PCL used in this experiment were 30,000, 60,000, 100,000, 110,000, and 120,000. Toluene was used as a solvent.

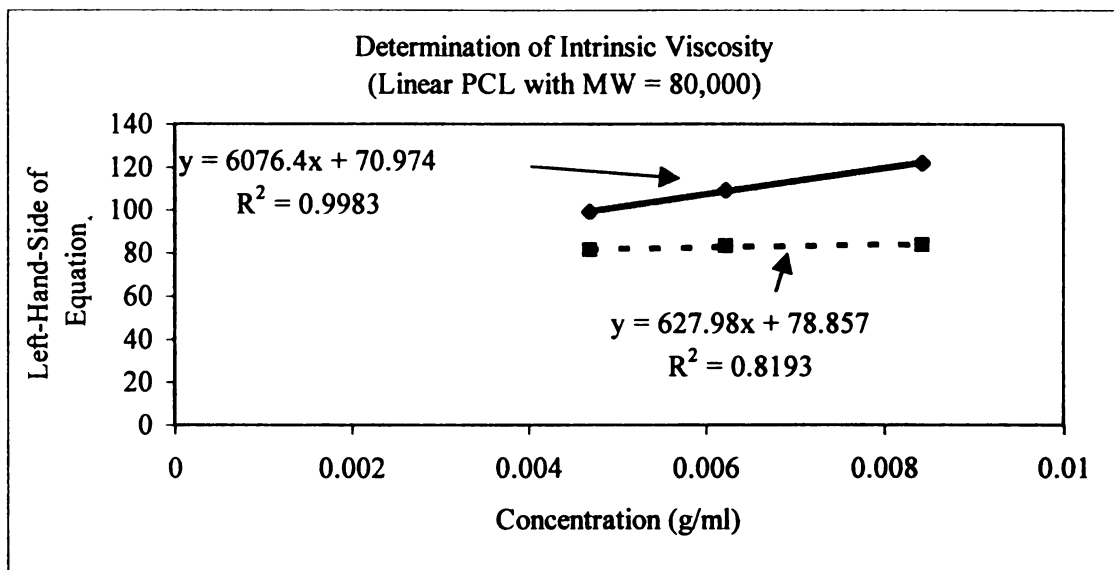
3.5.2.3 Procedure

Intrinsic viscosity of linear and REX-PCL were determined by following the standard procedure discussed in Chapter 2.

3.5.2.4 Results

Examples of a plot used to determine the intrinsic viscosity of REX-PCL and linear PCL are shown in Figure 3-8.

(a)



(b)

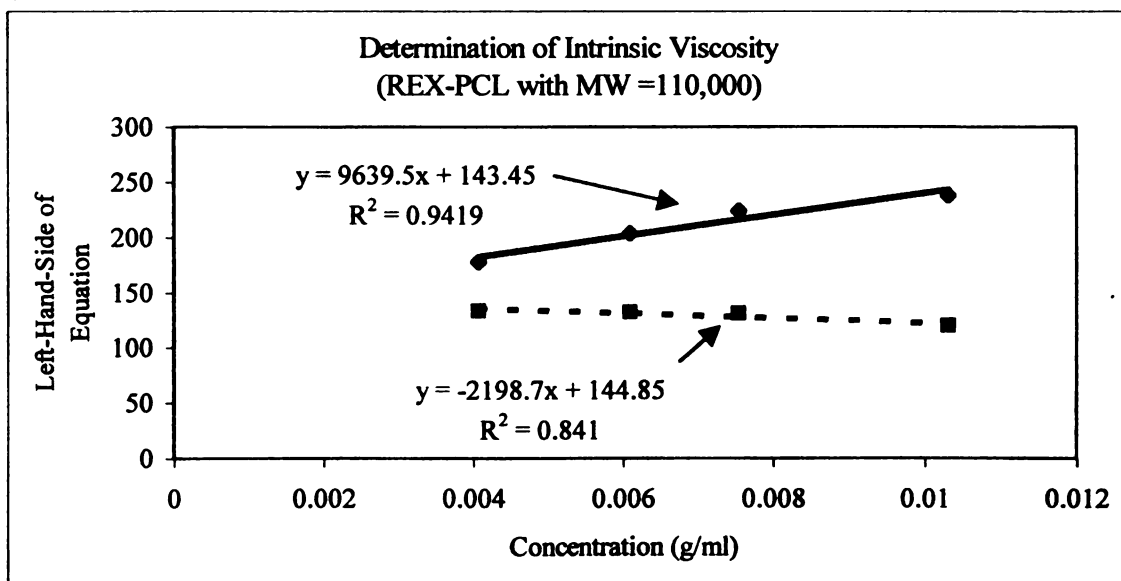


Figure 3-8: An example of plot used to determine the intrinsic viscosity of (a) linear and (b) REX-PCL.

The intrinsic viscosity of the linear and the REX-PCL tested are tabulated in Table 3-5 and 3-6 respectively.

M_n	$[\eta]_{\text{Huggins}}$	$[\eta]_{\text{Kraemer}}$	$[\eta]_{\text{average}}$	standard deviation
80,000	73	79	76	3.0
42,500	60	61	60.5	0.5
10,000	28	27	27.5	0.5

Table 3-5: Intrinsic viscosity of linear PCL

M_n	$[\eta]_{\text{Huggins}}$	$[\eta]_{\text{Kraemer}}$	$[\eta]_{\text{average}}$	standard deviation
120,000	144	148	146	2.0
110,000	143	145	144	1.0
100,000	116	122	119	3.0
60,000	82	77	79.5	2.5
30,000	66	62	64	2.0

Table 3-6: Intrinsic viscosity of REX-PCL

3.5.2.5 Discussion

Figure 3-8 shows that plotting the left-hand-side of Huggins equation ($c^{-1}(\eta/\eta_0 - 1)$) and the left-hand-side of Kraemer equation ($c^{-1} \ln(\eta/\eta_0)$) against concentration yields linear relationship for both the linear and the REX-PCL, as expected.

As also expected, the PCL with higher molecular weight has higher intrinsic viscosity, as shown in Table 3-5 and 3-6. By comparing the intrinsic viscosity shown in Table 3-5 and 3-6, it was found that the intrinsic viscosity of the REX-PCL is higher than the one of linear PCL. This result was also expected since the molecular weight of REX-

PCL used were actually for “each arm”, and the fact that the REX-PCL has a star-shape makes it to have more bulky structure with longer chain than linear PCL.

As shown in Figure 3-8, the intrinsic viscosity determined from Huggins equation and Kraemer equation did not exactly agree. This was due to the fact that the equations used were truncated versions of the power series expression of the form¹:

$$c^{-1}(\eta/\eta_o - 1) = [\eta] + k_H[\eta]^2c + k'_H[\eta]^3c^2 + \dots$$

and

$$c^{-1}\ln(\eta/\eta_o) = [\eta] - k_I[\eta]^2c - k'_I[\eta]^3c^2 - \dots$$

In this study, the average of the intrinsic viscosity calculated from the two equations (Huggins and Kraemer equations) were calculated for a comparison purpose.

3.5.3 Determination of Mark-Houwink-Sakurada Constants

3.5.3.1 Objective

Objective of this experiment was to determine the Mark-Houwink-Sakurada (MHS) constants for both linear and REX-PCL, using toluene as a solvent with the testing temperature of 26 °C.

3.5.3.2 Procedure

Intrinsic viscosity determined in section 3.5.2 were used to plot $\ln[\eta]$ vs $\ln M_n$ for both the linear and the REX-PCL separately. A linear regression was the used to draw a

straight line passing through the data points. The equations of the lines were determined by using a computer program.

3.5.3.3 Results

Plot of $\ln[\eta]$ vs $\ln M_n$ for linear and REX-PCL are shown in Figure 3-9 and 3-10 respectively. Finally, the MHS constants were determined from the plots and the results are tabulated in Table 3-7.

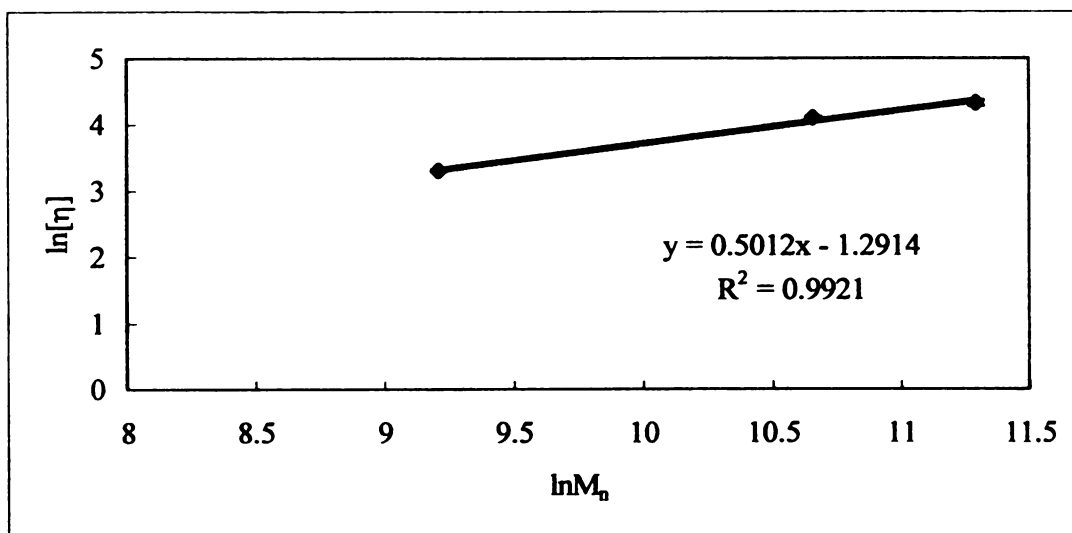


Figure 3-9: Determination of Mark-Houwink-Sakurada constants for linear PCL

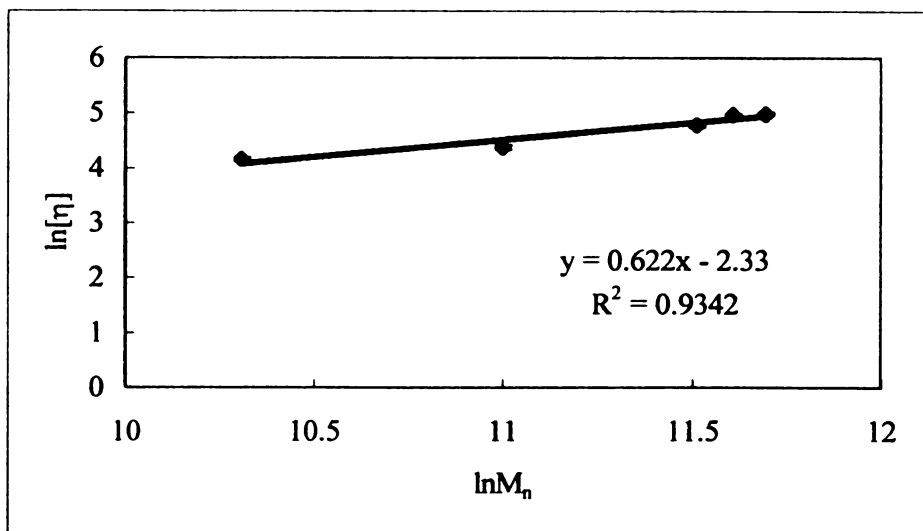


Figure 3-10: Determination of Mark-Houwink-Sakurada constants for REX-PCL

	a	K
Linear PCL	0.5012	0.2749
REX-PCL	0.6220	0.0973

Table 3-7: Mark-Houwink-Sakurada constants

3.5.3.4 Discussion

Both Figure 3-9 and 3-10 show that the measured intrinsic viscosity fits to the linear relationship of MHS equation fairly well. By using the linear regression, one of the MHS constants, a , for the linear and the REX-PCL were found to be 0.5012 and 0.6220 respectively. These values are reasonable since the range of “ a ” is between 0.5 to 1, in which 0.5 represents the randomly coiled polymer in a theta solvent and 1 represents the polymer has rod-like extended chain²⁸.

Another MHS constant, K, for the linear and the REX-PCL were found to be 0.2749 and 0.0973 respectively. These values are also within the range of various reported values of K: the K values generally vary between 10^{-3} to 0.5^{28} .

3.5.4 Thermogravimetric Analysis

3.5.4.1 Objective

Objectives of this experiment was: (1) to determine the thermal stability of REX-PCL and to compare it with the one of linear PCL; and (2) compare the thermal stability of the same type of PCL with different molecular weight.

3.5.4.2 Materials

Linear PCL with the molecular weight of 80,000 and the REX-PCL with the molecular weight of 30,000, 60,000, and 100,000 were tested.

3.5.4.3 Procedure

Standard procedure discussed in Chapter 2 was followed to test both linear and REX-PCL. Also a degradation temperature were determined by using the computer program and recorded.

3.5.4.4 Results

Output of TGA of the REX-PCL with the molecular weight of 30,000, 60,000, and 100,000 are plotted together and shown in Figure 3-11. The output of TGA of linear PCL with the molecular weight of 80,000 was also plotted and shown in Figure 3-11.

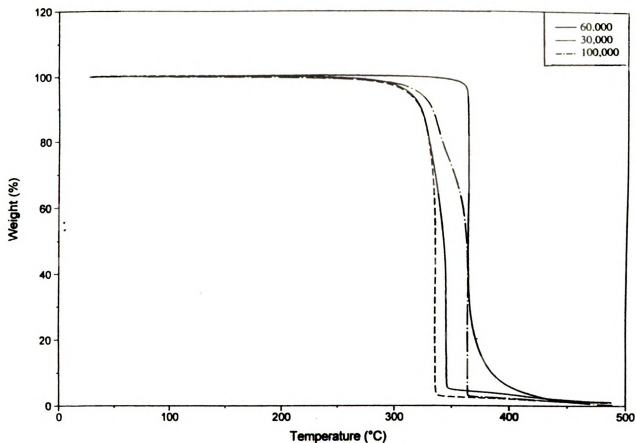


Figure 3-11: The output of TGA for linear and REX-PCL

Also the degradation temperature determined using the computer program were recorded and tabulated in Table 3-8.

Type of Polymer	Degradation Temperature (°C)
Linear PCL ($M_n = 80,000$)	372
REX-PCL ($M_n = 30,000$)	330
REX-PCL ($M_n = 60,000$)	330
REX-PCL ($M_n = 100,000$)	326

Table 3-8: Degradation temperature of linear and REX-PCL

3.5.4.5 Discussion

As shown in Table 3-8, a degradation temperature of linear PCL was found to be 372 °C which is much higher than the degradation temperature of REX-PCL which is at about 330 °C for all three molecular weights. This means the REX-PCL is thermally less stable than the linear PCL.

By comparing the results of REX-PCL of different molecular weight, it was found that the REX-PCL of higher molecular weight is more thermally stable than the REX-PCL of lower molecular weight. Additionally, it was found that the weight loss of linear PCL occurs in small range of temperature with one steep slope; however, the weight loss of REX-PCL was found to occur in wider range of temperature, and the slope became rather bumpy as the molecular weight of REX-PCL increases. These results suggests that the REX-PCL has broader molecular weight distribution than the linear PCL, which also confirms the result obtained from the determination of MHS constants.

3.5.5 Differential Scanning Calorimeter

3.5.5.1 Objective

Objective of this experiment was to determine the thermal transition characteristics of REX-PCL and compare the results between the REX-PCL of different molecular weights.

3.5.5.2 Materials

REX-PCL with the molecular weight of 30,000, 60,000, and 100,000 were tested.

3.5.5.3 Procedure

Standard procedure discussed in Chapter 2, with the type 1 heating condition, was used to test both linear and REX-PCL. Also observed peaks were labeled by using the computer program.

3.5.5.4 Results

DSC output for REX-PCL with the molecular weight of 30,000, 60,000 and 100,000 are shown in Figure 3-12 to 3-14 respectively.

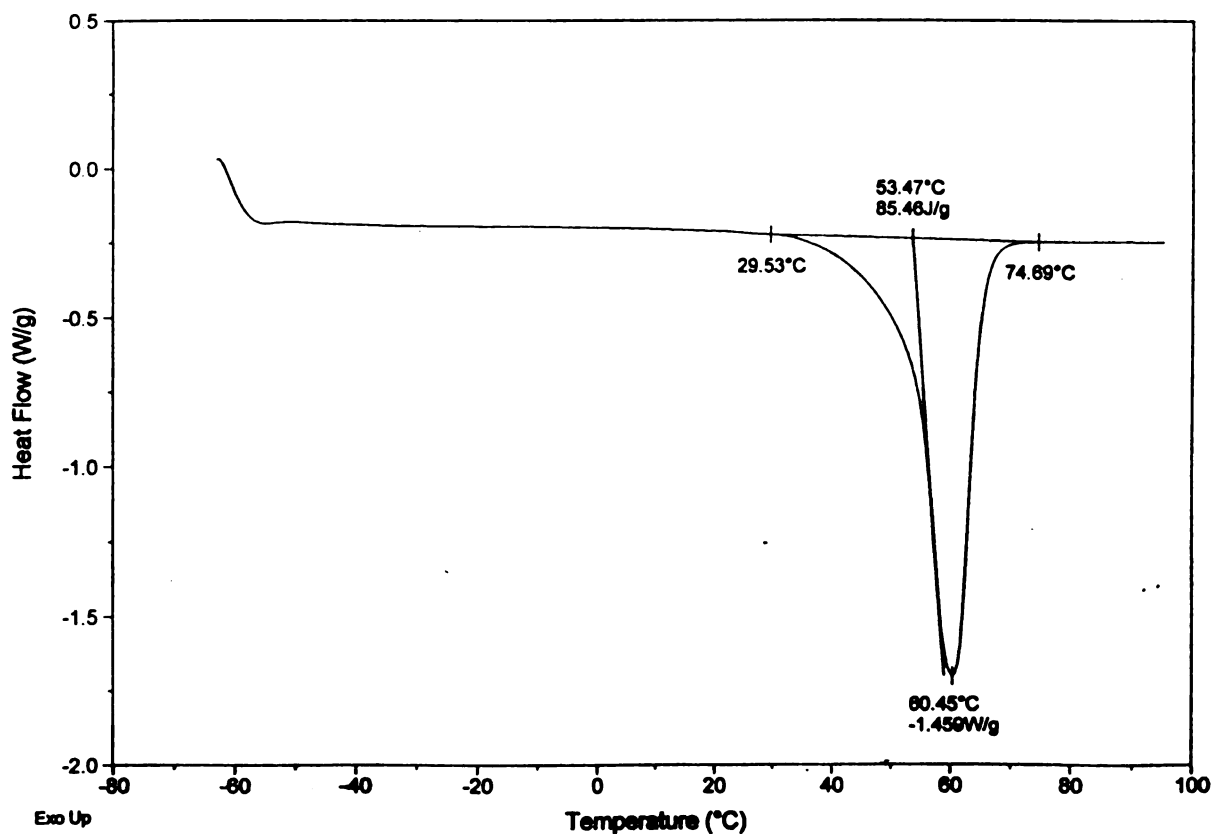


Figure 3-12: The output of DSC for REX-PCL with the molecular weight of 30,000

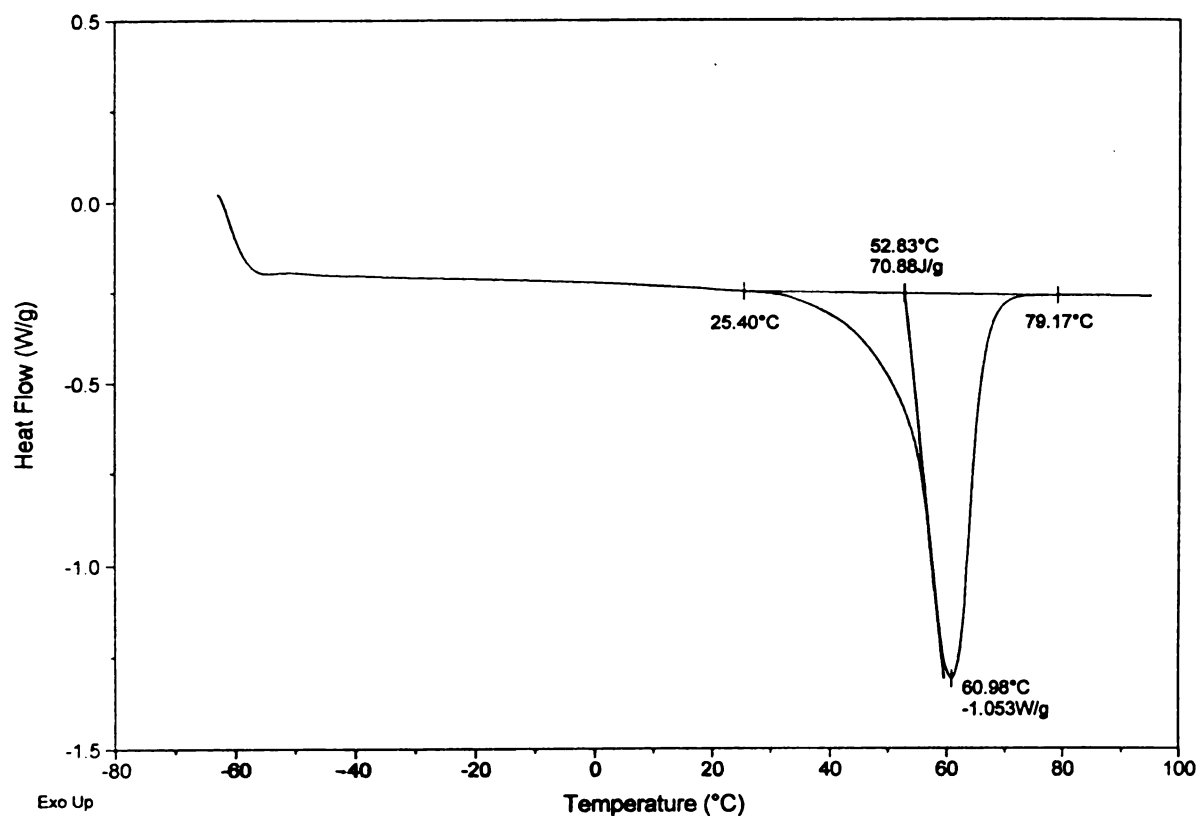


Figure 3-13: The output of DSC for REX-PCL with the molecular weight of 60,000

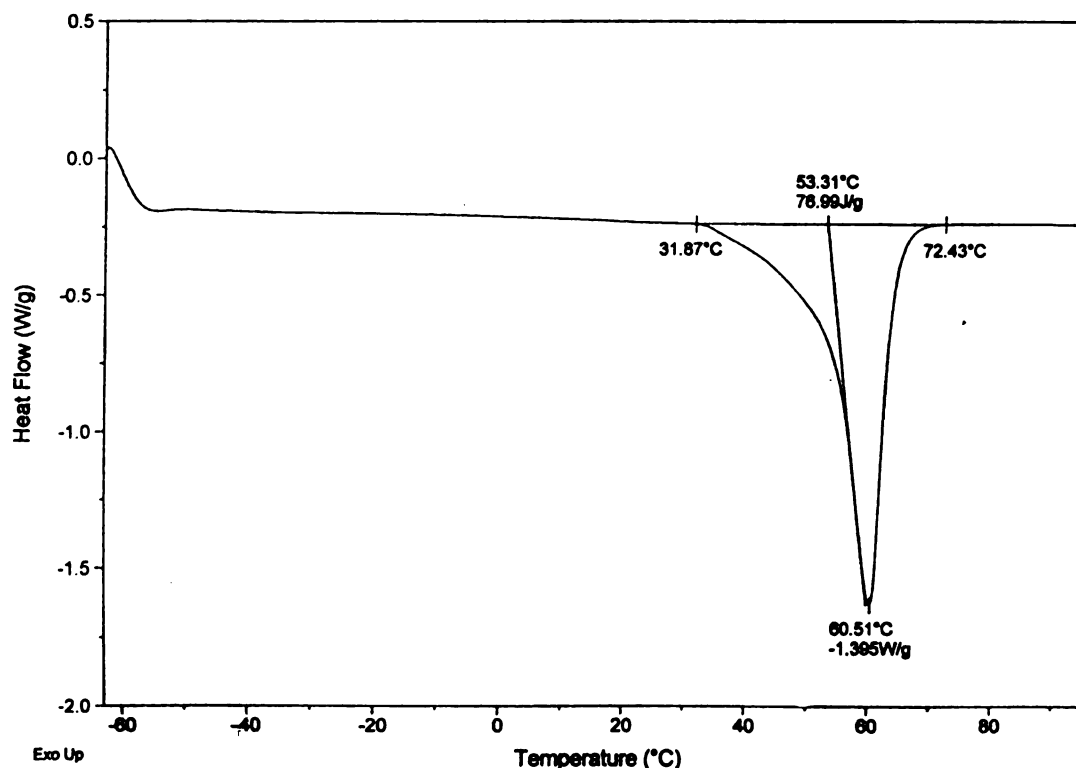


Figure 3-14: The output of DSC for REX-PCL with the molecular weight of 100,000

3.5.5.5 Discussion

As shown in Figure 3-12 to 3-14, the melting temperature of REX-PCL was found to be approximately 53 °C, which is close to the reported melting temperature of linear PCL.

The glass-transition temperature was not observed, although the test was conducted from –60 °C. This was also not surprising since the reported glass-transition temperature of linear PCL is approximately at –60 °C.

These results conclude that linear and REX-PCL go through very similar thermal transitions.

3.6 Reactive Extrusion Polymerization of ϵ -Polycaprolactone from Monomer with Impurities

3.6.1 Objective

Objective of this experiment was to determine the effect of moisture content in the monomer on the production of REX-PCL.

3.6.2 Materials

In order to determine the effect of moisture content, TONE ECEQ was left open to air for approximately 5 minutes.

The same ATSB solution as discussed in section 3.4.2 was used, and the entire process was carried under dry nitrogen to prevent monomer and initiator from further exposure to the moisture.

3.6.3 Procedure

Exactly the same procedure as discussed in section 3.4.3 was followed, except the monomer with moisture content was used instead of the “regular” monomer.

3.6.4 Results

Molecular weight of REX-PCL produced, as well as the feed rate of monomer and ATSB solution, fraction of ATSB in the solution used, and the resulted torque % were recorded and shown in Table 3-9. Same extruder temperature and screw speed as discussed in section 3.4.3.4 were used.

Theoretical Molecular Weight	Monomer Flowrate (ml/min)	ATSB Solution Flowrate (ml/min)	% ATSB in Solution	Observed Torque %
30,000	80	1.7	15	23
60,000	100	1.6	10	32
80,000	70	1.7	5	38

Table 3-9: Molecular weight of REX-PCL produced with the monomer with moisture content

3.6.5 Discussion

With monomer containing moisture, the highest molecular weight of REX-PCL that could be produced was found to be 80,000. Above this value, the product coming out from the extruder became jelly-like with clear yellow color, and changing the process conditions did not change the result. This result suggests that the moisture content of monomer (or anywhere in the system) result in the poor production of REX-PCL possibly due to the reaction of initiator and the moisture which decreases the number of initiator available for the monomer.

3.7 Monomer Conversion and Reproducibility

Fractional conversion of monomer was determined in section 3.5.1 and they were found to be close to 100 % for the most of the molecular weight. However, this does not tell where in the extruder that the reaction reached near completion. Determination of where the reaction reaches completion is important when designing a process in which multiple reactions take place in series, such as in the case of the production of polyurethane, which will be discussed in next chapter.

Therefore, monomer conversion within the extruder was evaluated and it will be discussed in the first part of this section.

Additionally, successful production system requires a production of desired material not once, but over and over again. In other words, a production system must be able to reproduce the product as long as the required conditions are met.

Therefore the reproducibility of REX-PCL was evaluated and it will be discussed in the second part of this section.

3.7.1 Monomer Conversion

3.7.1.1 Objective

Objective of this experiment was to determine the monomer conversion within the extruder during the process of making REX-PCL with the molecular weight of 120,000.

3.7.1.2 Materials

TONE ECEQ monomer, ATSB solution, and nitrogen as discussed in section 3.4.2 were used to make REX-PCL with molecular weight of 120,000.

3.7.1.3 Procedure

Same procedure as making the REX-PCL was followed, except when the system stabilizes, the extruder was stopped and the material at the middle of extruder (zone 3) and at the die were immediately removed from the extruder for evaluation.

The REX-PCL collected from two locations were cooled in air and their intrinsic viscosity were determined by following the standard procedure discussed in Chapter 2.

3.7.1.4 Results

Intrinsic viscosity of two samples collected at different locations, one at die and another one at the middle of the extruder, were measured and tabulated in Table 3-10. Also, by applying these intrinsic viscosity to the MHS equation determined in section 3.5.3, molecular weight of these two materials were estimated as shown in Table 3-10.

Location Collected	Intrinsic Viscosity	Molecular Weight
Middle of Extruder	131.03	107,389
At Die	140.28	119,836

Table 3-10: Intrinsic viscosity of REX-PCL collected at two different locations within the extruder

3.7.1.5 Discussion

As shown in Table 3-10, the intrinsic viscosity of the sample collected at the die was found to be higher than the intrinsic viscosity of the sample collected at the middle of the extruder. Also by applying these result in MHS equation, the molecular weight of the sample collected at the die was found to be approximately equal to the theoretical

molecular weight; however, the molecular weight of the sample collected at the middle of the extruder was found to be about 10 % lower than the expected value.

These results indicate that the REX-PCL with the theoretical molecular weight of 120,000 yields 90 % monomer conversion at the zone 3.

3.7.2 Reproducibility

3.7.2.1 Objective

Objective of this experiment was to determine the reproducibility of the process of making REX-PCL. This was done by comparing the intrinsic viscosity of REX-PCL of same molecular weight produced with same procedure but in different days.

Molecular weight of 100,000 was evaluated in experiment.

Additionally, REX-PCL with the molecular weight of 30,000 were produced with different overall flowrate (same monomer to ATSB ratio) on different days and their intrinsic viscosity were also determined to evaluate the reproducibility of the process.

3.7.2.2 Materials

Just as before, TONE ECEQ monomer, ATSB solution, and nitrogen were used as specified in section 3.4.3.

3.7.2.3 Procedure

REX-PCL with the molecular weight of 100,000 were produced on different days with different ATSB solutions (same ATSB concentration in the solution but prepared on different days). Process condition and the procedure used were the same for both samples.

Also REX-PCL with the molecular weight of 30,000 were produced on two separate days. The difference in the process between those two days was the flowrate of monomer and initiator; a flowrate of the monomer and the ATSB solution were doubled, but the ratio of monomer to ATSB were kept constant for the experiment on second day.

The intrinsic viscosity of all the samples collected were then determined by following the standard procedure discussed in Chapter 2 and their results were compared.

3.7.2.4 Results

A left-hand-side of Huggins equation vs. concentration were plotted for the REX-PCL made on two different days ($M_n = 100,000$) and it is shown in Figure 3-15.

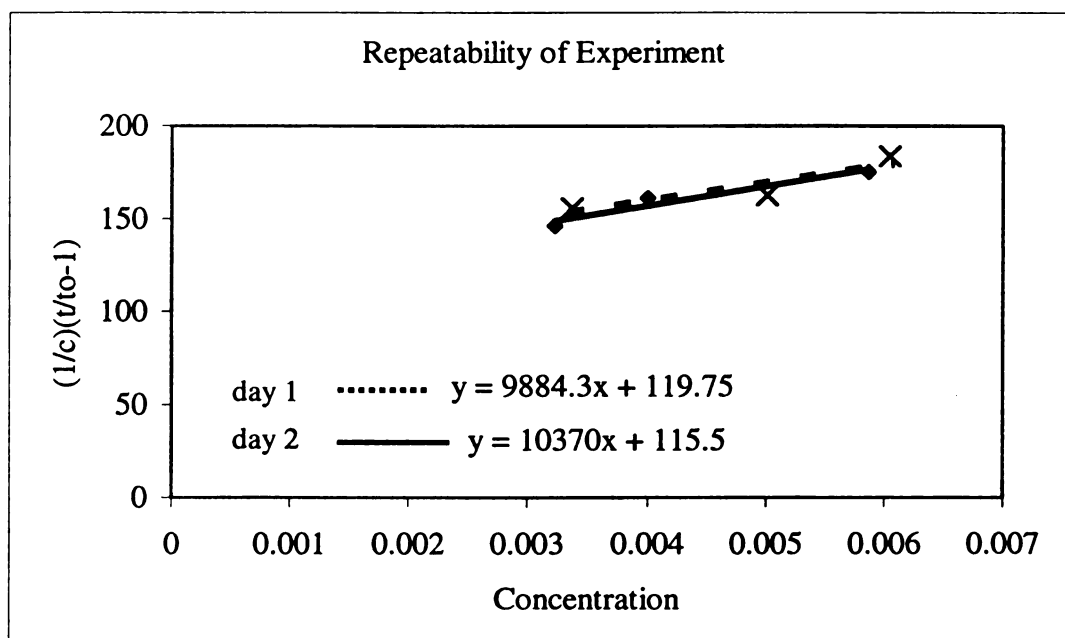


Figure 3-15: A plot used to determine the intrinsic viscosity of REX-PCL made on three different days.

Also, left-hand-side of Huggins equation vs. concentration were plotted for the REX-PCL made with two different flowrates ($M_n = 30,000$) and it is shown in Figure 3-16.

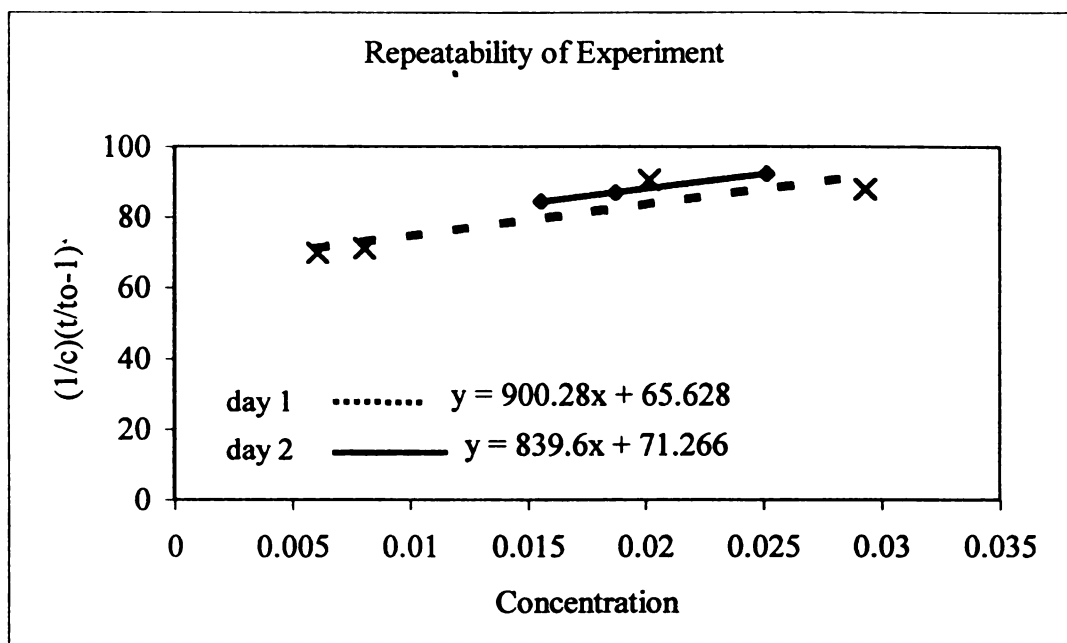


Figure 3-16: A plot used to determine the intrinsic viscosity to REX-PCL made with two different flowrate

3.7.2.5 Discussion

As Figure 3-15 shows, two lines representing the REX-PCL of same molecular weight produced on different days almost coincides. Also the Figure 3-16 shows that the two lines representing the REX-PCL of same molecular weight produced with different reactants flowrate were found to be very close. These results indicate that the process of making REX-PCL has very high reproducibility.

3.8 Conclusions

The REX-PCL of the molecular weight ranging from 20,000 to 210,000 were produced successfully only by varying the monomer to initiator ratio. The REX-PCL with the molecular weight higher than 210,000 was unable to be produced due to the large monomer to initiator ratio which prevent some of the monomer from involving in the polymerization. On the other hand, the lowest limit was determined as 20,000 not because of the poor monomer to initiator reaction but because of the extruder which could not handle such a low viscosity. In either case, the addition of a few mixing elements may help to achieve even broader range of molecular weight.

By determining the intrinsic viscosity of linear and REX-PCL, the MHS constants were determined to be 0.5012 and 0.2749 for the linear PCL and 0.6220 and 0.0973 for the REX-PCL. These values indicates that the linear PCL is more randomly coiled polymer than REX-PCL.

The difference between linear and REX-PCL was also evident from the results of TGA. The output of TGA showed that REX-PCL has lower thermal stability than linear PCL. Also the rate of degradation REX-PCL was found to be slower than the one of linear PCL, and the rate decreased as the molecular weight of REX-PCL increased.

By producing the REX-PCL with the monomer containing some moisture, it was found that the range of the REX-PCL producible was narrowed down to between 30,000 and 80,000. One of the possible explanations to this is the reaction between ATSB and the moisture within the monomer, which reduced the amount of ATSB available for the polymerization.

**REACTIVE EXTRUSION POLYMERIZATION OF STAR-
POLYCAPROLACTONE AND DIISOCYANATE**

4.1 Introduction

Applications of polyurethane widely range from foam materials, fibers and foils to the high elastic coating materials, solvent adhesives and the construction materials of various hardness. This is due to the wide range of properties of polyurethane that can be made by selecting the types and the ratio of reactants³⁹. However, a production of polyurethane of desired properties also requires a greater degree of control over the chemical reaction than many other polymer productions²⁰. This is due to the high reactivity of diisocyanate commonly used to produce the polyurethane.

One of the widely used ways to synthesize polyurethane is by the addition of dihydroxy compounds, such as low-molecular-weight hydroxyl-terminated polyesters, to diisocyanates²⁸ as shown below:

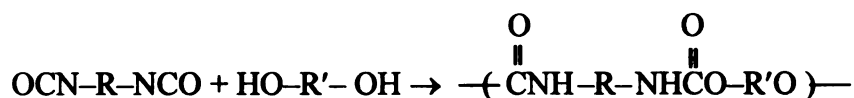


Figure 4-1: Polyurethane synthesis by the reaction of diisocyanate and dihydroxy-group

One of the earliest commercial polyurethane was developed in Germany by reacting 1,6-hexanediisocyanate and 1,4-butanediol. Although this particular process is no longer

used in commercial, use of diisocyanate in the formation of polyurethane is still widely used to manufacture polyurethane fibers, plastics, elastomers, and coatings²⁸.

The production of polyurethane is currently done in various ways. One of the widely used technique is the batch polymerization, such as in the case of making polyurethane foams. The reactive extrusion has also been developed for the production of linear polyurethane^{13,39}.

In this study, a production of polyurethane was also conducted by utilizing extruder. The polyurethane was produced by reacting hydroxyl end-group of REX-PCL with hexamethylene diisocyanate. A reaction mechanism of the formation of polyurethane from hexamethylene diisocyanate and REX-PCL is shown in Figure 4-2.

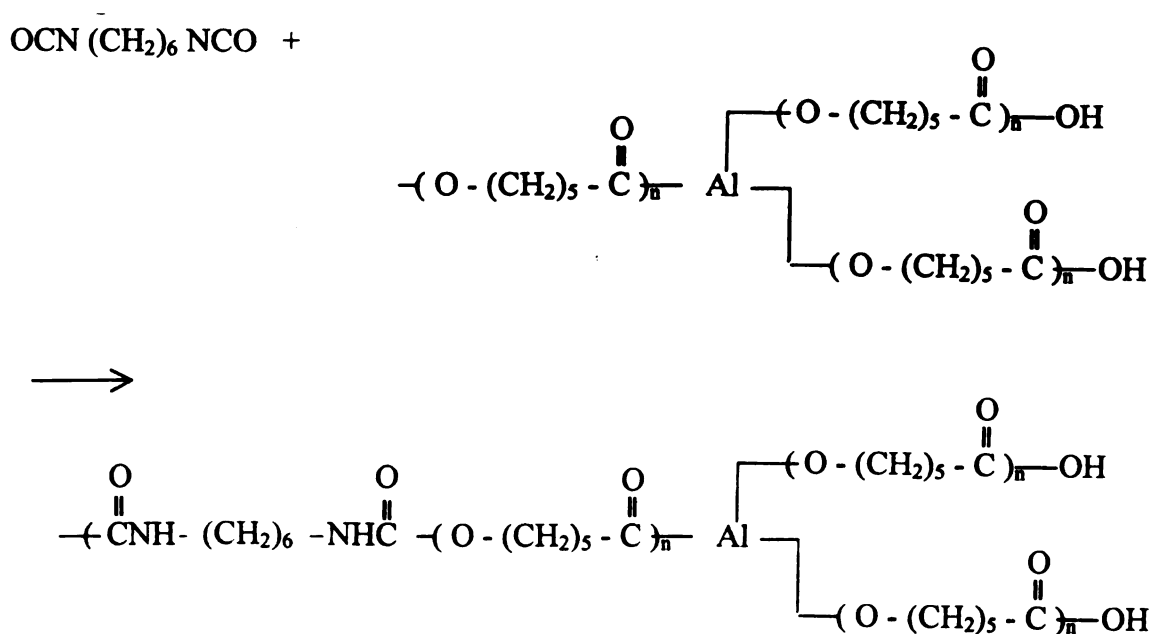


Figure 4-2: A reaction mechanism of the formation of polyurethane with hexamethylene diisocyanate and REX-PCL

4.2 Background

There are many factors influencing the formation of polyurethane, such as the presence of catalysts and water, and the process temperature. This sections addresses how these factors influence the formation polyurethane.

4.2.1 Effect of Catalyst

Synthesis of polyurethane by the addition of hydroxy end-group and isocyanate can take place without the presence of a catalyst; however, tertiary amines and metal compounds are widely used as a catalyst to increase the selectivity of isocyanates reacting with hydroxyl groups rather than water^{20,28}. Some of the examples of a catalyst that can be used include stannous: octanone, N-methylmorpholine, triethylamine and dibutyltin diacetate^{20,39}.

In this study, polyurethane formation was carried without the use of a catalyst mainly due to the fact that the reaction of polyurethane formation is carried immediately after (or at the same time in some cases) the polymerization of REX-PCL. The presence of a strong catalyst may ruin the formation of star-shaped PCL.

4.2.2 Effect of Temperature

Just as any other reactions, temperature has a significant influence on polyurethane synthesis. For example, at a low temperature, say up to 50 °C, a reaction of isocyanates with hydroxyl group, as well as water, proceed relatively easily. However, at a higher temperature, between 50 to 150 °C, formation of allophanates, biurets and isocyanurates occur at a significant rate in the absence of a catalyst. Therefore, the low

temperature (below 50 °C) should be used if a linear polyurethane, without any cross-links or branch, is desired. On the other hand, if cross-linked or branched polyurethane is desired, the temperature between 50 to 150 °C is recommended. It is important, however, to keep the reaction temperature below 150 °C since some of the less stable links start to break down at the temperature over that temperature, and results in partially degraded polymer²⁰. In addition to the above reactions, the residual carboxylic acid ends in polyesters may react with isocyanates to give amides. However, this reaction is of relatively minor importance²⁸

In this study, the extruder temperature of 120 °C was mostly used since it is low enough to prevent the thermal degradation of polyurethane, but high enough to still carry out the polymerization of REX-PCL and keep the product in molten state.

4.2.3 Effect of Water

Water plays a significant role in the reaction of polyurethane. One of the examples of water being used as an advantage is the production of flexible foams. In this case, a reaction involving water results in the formation of carbon dioxide, which is used for blowing the foam²⁰.

On the other hand, a presence of moisture can easily upset the stoichiometric balance of isocyanate to alcohol which determines the structure and molecular weight of the product. For example, 18 parts of water can react with as much isocyanate as 2000 parts of linear polyester. Therefore, water should be eliminated from the system in order to produce linear polyurethane.

In this study, the reactions were carried under nitrogen environment since the formation of polyurethane is carried inside the extruder where the polymerization of REX-PCL also takes place. However, moisture is available in atmosphere as soon as the product exits from the die, thus excess isocyanate or the isocyanate end-group may react with the moisture to form crosslinkage.

4.3 Outline of Chapter

This chapter discusses the reactive extrusion polymerization process to make polyurethane with REX-PCL. Two types of REX-PCL were used for this purpose: REX-PCL of high molecular weight (30,000, 60,000, and 100,000) and the REX-PCL of low molecular weight (3000 and 7500). Each process is discussed in section 4.4 and 4.6 respectively.

In addition, the polyurethane produced were characterized and discussed in section 4.5 for polyurethane made with REX-PCL of high molecular weight and in section 4.7 for polyurethane with REX-PCL of low molecular weight.

4.4 Reactive Extrusion Polymerization of Diisocyanate and REX-PCL with High Molecular Weight Star-Polycaprolactone

4.4.1 Objective

Objective of this experiment was to produce polyurethane by reacting hydroxyl end-group of REX-PCL and diisocyanate. The two reactions in series, starting with polymerization of REX-PCL followed by the reaction of REX-PCL and diisocyanate, were conducted continuously within the same extruder.

4.4.2 Materials

The same TONE ECEQ monomer and ATSB solution as discussed in Chapter 3 were used. Additionally, hexamethylene diisocyanate (HMDI) was used to react with the hydroxyl end-group of REX-PCL to form polyurethane. This particular diisocyanate was chosen because of its wide availability and less toxicity compared to some other types of diisocyanate.

As in the case of ATSB solution, HMDI was mixed with anhydrous toluene to increase the flowrate in order for the commercial pump to be used. The calculation to determine the flowrate of HMDI will be discussed in section 4.4.3.1. Since HMDI is also sensitive to moisture, anhydrous toluene and not “regular” toluene was used as a solvent.

The molecular weight of REX-PCL used in this experiment were 30,000, 60,000, and 100,000. From the results of the determination of the monomer conversion in section 3.7.1, polymerization of the REX-PCL of all three molecular weights were expected to be at near completion at zone 3, where HMDI solution is added.

4.4.3 Procedure

Polyurethane was produced with the similar method as the production of REX-PCL. The only difference between the production of REX-PCL and polyurethane was the additional feed (HMDI) at the middle of the extruder.

4.4.3.1 Flowrate Calculation

Same procedure was followed as discussed in the case of production of REX-PCL to determine the flowrate of the monomer and the ATSB solution. Then, the flowrate of

HMDI feed was calculated so the number of OH end-group is equal to the number of NCO group. The equation used to determine this amount is as follows:

$$\text{Number of OH end-group} = 3 \times \text{Number of ATSB fed}$$

and

$$\text{Number of NCO group} = 2 \times \text{Number of HMDI fed}$$

To have equimolar of OH and NCO groups,

$$\text{Number of OH end-group} = \text{Number of NCO group}$$

then

$$\text{Number of HMDI fed} = 3/2 \times \text{Number of ATSB fed}$$

An example of calculation sheet used in this experiment is shown in Table 4-1.

Reactive Extrusion Polymerization of Polyurethane		pick value
Date:		
Run#:		
	Theoretical MW =	
	DP = Theoretical MW * 3 / 114.14 =	
Monomer		
	Volumetric Flowrate of Monomer =	ml/min
	$\rho_{\text{monomer}} =$	1.030 g/ml
	Mass Flowrate of Monomer = Vol Flowrate of Monomer * ρ_{monomer} =	g/min
	MW of Monomer =	114.14 g/mol
	Molar Flowrate of Monomer = Mass Flowrate / MW of Monomer =	mol/min
Initiator		
	Molar Flowrate of ATSB = Molar Flowrate of Monomer / DP =	mol/min
	MW of ATSB =	246.33 g/mol
	Mass Flowrate of ATSB = Molar Flowrate * MW =	g/min
	Fraction of ATSB in ATSB solution =	0.210
	Mass Flowrate of Solution = Mass Flowrate of ATSB / Fraction of ATSB =	g/min
	ρ of ATSB =	0.967 g/ml
	ρ of Toluene =	0.865 g/ml
	ρ of Solution = $1 / [(\text{frac of ATSB} / \rho_{\text{ATSB}}) + (\text{frac of Toluene} / \rho_{\text{toluene}})] =$	g/ml
	Volumetric Flowrate of Solution = Mass Flowrate of Sol. / ρ of Sol. =	ml/min
HMDI		
	Molar Flowrate of HMDI = Molar Flowrate of ATSB * 3/2 =	mol/min
	MW of HMDI =	168.20 g/mol
	Mass Flowrate of HMDI = Molar Flowrate * MW	g/min
	Fraction of HMDI in HMDI solution =	
	Mass Flowrate of Solution = Mass Flowrate of HMDI / Fraction of HMDI =	g/min
	ρ of HMDI =	1.04 g/ml
	ρ of Toluene =	0.865 g/ml
	ρ of Solution = $1 / [(\text{Frac of HMDI} / \rho_{\text{HMDI}}) + (\text{Frac of Toluene} / \rho_{\text{toluene}})] =$	g/ml
	Volumetric Flowrate of Solution = Mass Flowrate of Sol. / ρ of Sol. =	ml/min

Table 4-1: An example of the calculation sheet used to determine the flowrate of reactants

4.4.3.2 Preparation of ATSB and HMDI Solutions

The HMDI solution refers to the mixture of hexamethylene diisocyanate and anhydrous toluene. Just as the ATSB solution, the weight percentage of HMDI in the HMDI solution was determined merely for the convenience. Typically, 6 and 20 wt% of HMDI in the solution was used.

Preparation of both ATSB and HMDI solution were done in the same glove bag under nitrogen environment, and the same procedure as in the case of preparing ATSB solution (discussed in section 3.4.3) was followed.

4.4.3.3 Flow Scheme

For the production of polyurethane, three streams were added to the system of producing REX-PCL. They were: (1) HMDI solution to extruder (2) nitrogen to container of HMDI solution; and (3) to the extruder where HMDI solution is fed. Streams of HMDI solution and nitrogen were introduced to the extruder from zone 3.

Flow scheme of HMDI solution and two additional nitrogen streams are shown in Figure 4-3:

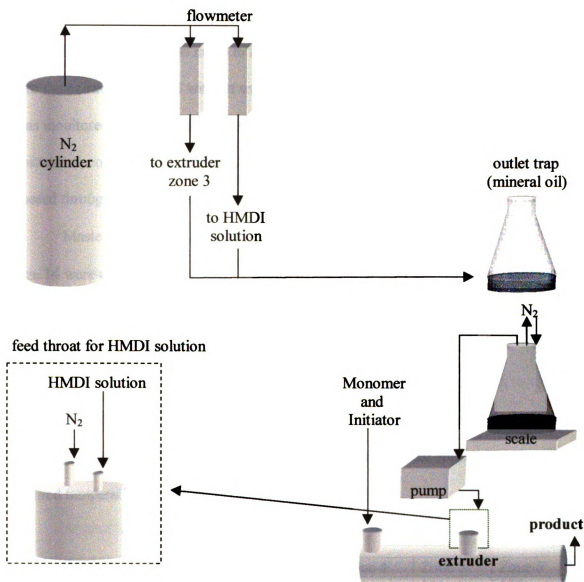


Figure 4-3: Flow scheme of HMDI solution

Just as the nitrogen used in the production of REX-PCL, the nitrogen streams added in this system was divided into two streams, then entered to the flowmeter to monitor the nitrogen flow. The nitrogen was then fed into the extruder (at zone 3) and the container of HMDI solution. The nitrogen flowing out from the container of HMDI

solution was then fed into outlet trap containing mineral oil to prevent back flow of the air.

HMDI solution was made in 2 L flask, and it was pumped out and directly fed into the extruder at zone 3 without using a transfer vessel. Flowrate of HMDI solution was monitored by measuring the weight of 2 L flask. Just as the monomer and the ATSB containers, container of the HMDI was tightly closed and dry nitrogen was continuously passed through to prevent the solution from being exposed to moisture.

Masterflex[®] L/S[®] Easy Load[®] pumps and the Masterflex[®] L/S[®] precision tubing size 14 were used for this system. The size of the pump head and the tubing size were determined by considering the typical flowrate of the HMDI solution used in this study (approximately the same range as the flowrate of the ATSB solution).

4.4.3.4 Start Up

Extruder was started first and the temperature of extruder zones were set to the desired temperature as shown in Table 4-2.

	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6
T (°C)	180	150	120	120	120	120

Table 4-2: An extruder temperature profile used in this experiment

Nitrogen flow was started prior to opening any of the reactant containers. Then all tubes were carefully connected to avoid the solutions from being exposed to moisture while nitrogen flowing through them.

Once the extruder reached the desired temperatures, pumps of the monomer and ATSB solution, but not HMDI solution, were started and adjusted to produce REX-PCL of desired molecular weight. As before, a product coming out from the die was collected in a metal trash can until the system stabilized.

When the system of producing REX-PCL was stabilized, the pump for the HMDI solution was started and adjusted to desired flowrate. The screw speed of 110 rpm was used throughout the process.

4.4.3.5 Collecting Samples and Clean Up

After letting the system run steadily for approximately 20 minutes, the product was collected through the water bath and dried in air for a few days. Approximately 1 lb each of polyurethane, as well as the REX-PCL before the addition of HMDI, were collected for characterization.

4.4.4 Results

Molecular weight of REX-PCL used as well as the feed rate of the monomer, ATSB solution and HMDI solution, fraction of ATSB in the solution used, fraction of HMDI in solution used, and the observed torque % for REX-PCL and polyurethane were recorded and is shown in Table 4-3. The same extruder temperature and screw speed as discussed in Chapter 3 were used.

Theoretical Molecular Weight	30,000	60,000	100,000
Monomer Flowrate (ml/min)	40	50	80
ATSB Solution Flowrate (ml/min)	2.6	1.6	1.6
% ATSB in Solution	5	5	5
HMDI Solution Flowrate (ml/min)	2.2	1.4	1.3
% HMDI in Solution	6	6	6
Observed % Torque (for REX-PCL)	21	35	41
Observed % Torque (for polyurethane)	26	36	38

Table 4-3: Condition used to produce polyurethane

4.4.5 Discussion

Addition of HMDI solution to the process of making REX-PCL was done without any major problems. The only difference observed before and after the addition of HMDI is the melt fracture, which seemed to be thicker when the HMDI was added. However, a significant increase in torque % was observed only with the molecular weight of 30,000.

The next section discusses the characterization of polyurethane produced in this experiment.

4.5 Characterization of Polyurethane made with High Molecular Weight Star-Polycaprolactone

4.5.1 Objective

Objective of this experiment was to determine whether the reaction between REX-PCL and HMDI has taken place. This was done by determining the intrinsic viscosity of polyurethane produced, and comparing with the one of REX-PCL. The

polyurethane was also tested with TGA and DSC, and the results were compared with the results of REX-PCL.

4.5.2 Materials

Polyurethane produced from three different molecular weight of REX-PCL (M_n = 30,000, 60,000, and 100,000) were used.

4.5.3 Procedure

Analysis of polyurethane with TGA and DSC, as well as the determination of intrinsic viscosity were done by following the standard procedures discussed in Chapter 2.

4.5.4 Results

Intrinsic viscosity of polyurethane produced were determined and tabulated in Table 4-4.

Molecular Weight of REX-PCL	Intrinsic Viscosity of Polyurethane	standard deviation
300,000	47	1.32
600,000	73	1.58
100,000	105	0.68

Table 4-4: Intrinsic viscosity of polyurethane

Then, the intrinsic viscosity of polyurethane, as well as the intrinsic viscosity of the linear and REX-PCL previously determined, were plotted for $\ln[\eta]$ vs. $\ln M_n$ and shown in Figure 4-4.

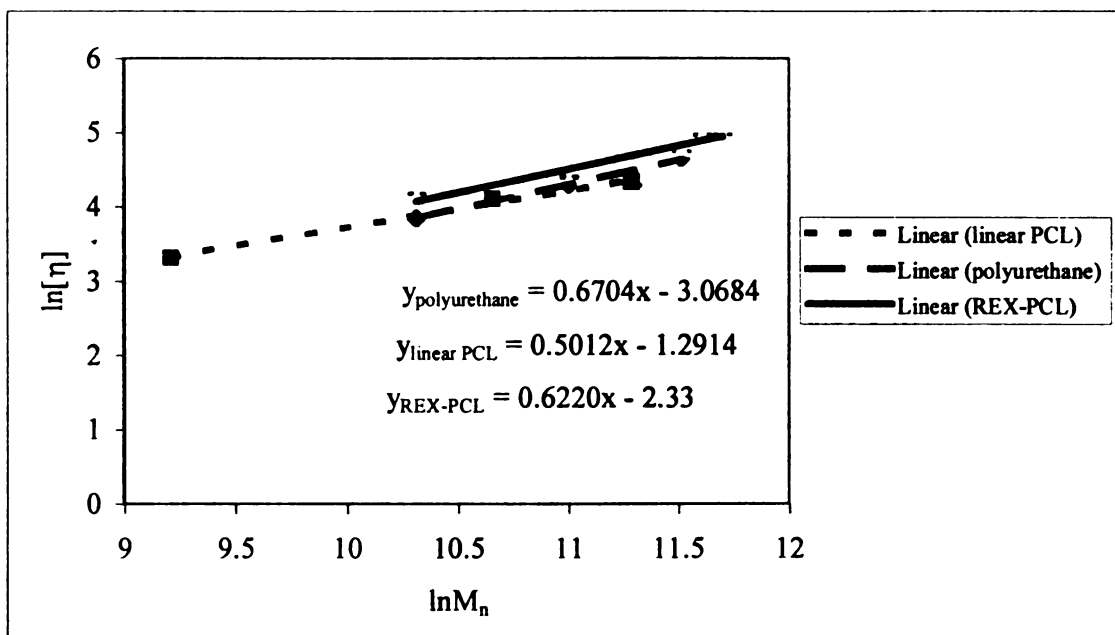


Figure 4-4: Comparison of the intrinsic viscosity of the three types of polymers

The molecular weight of the original REX-PCL were used to plot polyurethane, since the whole purpose of this plot was to do the comparison before and after the reaction. From the Figure 4-4, MHS constants of polyurethane was determined and tabulated with the MHS constants of REX-PCL and linear PCL previously determined in Table 4-5.

	a	K
Linear PCL	0.5012	0.2749
REX-PCL	0.6220	0.0973
Polyurethane	0.6704	0.0465

Table 4-5: MHS constants of three polymers

The results of TGA of polyurethane and the original REX-PCL the polyurethane was made with were plotted together in Figure 4-5 to 4-7 for the molecular weight of 30,000, 60,000, and 100,000 respectively. The results of TGA of three polyurethanes produced were also plotted on the same plot in Figure 4-8 for comparison.

The results of DSC of polyurethane and the original REX-PCL the polyurethane was made with were plotted together in Figure 4-9 to 4-11 for the molecular weight of 30,000, 60,000, and 100,000 respectively.

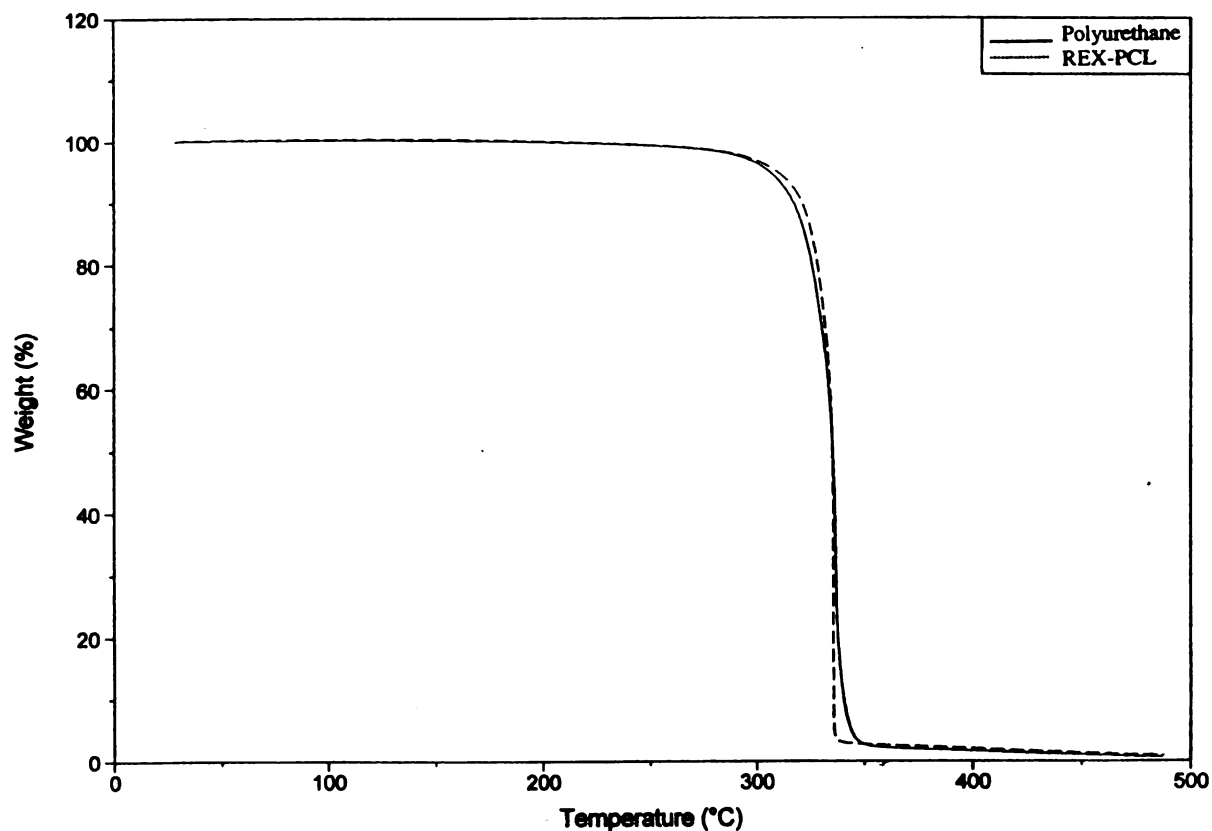


Figure 4-5: Output of TGA for the polyurethane and REX-PCL ($M_n = 30,000$)

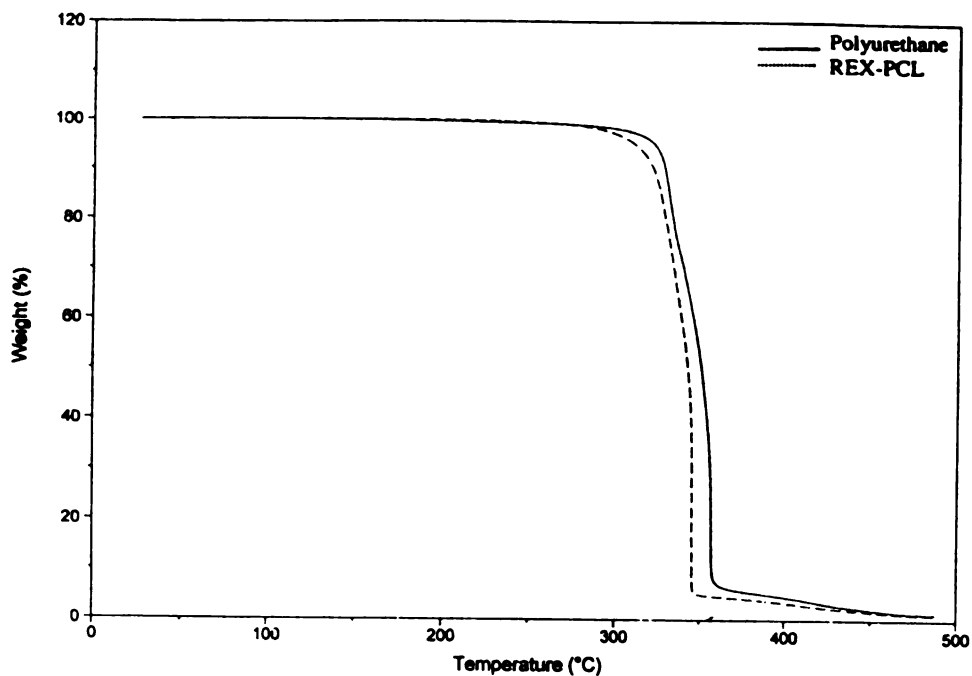


Figure 4-6: Output of TGA for the polyurethane and REX-PCL ($M_n = 60,000$)

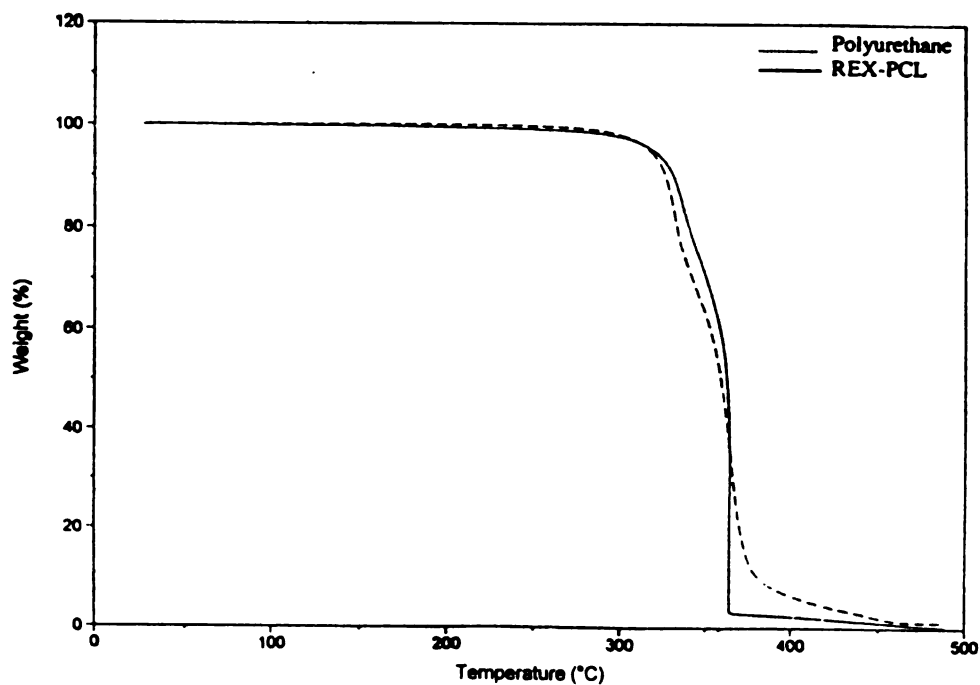


Figure 4-7: Output of TGA for the polyurethane and REX-PCL ($M_n = 100,000$)

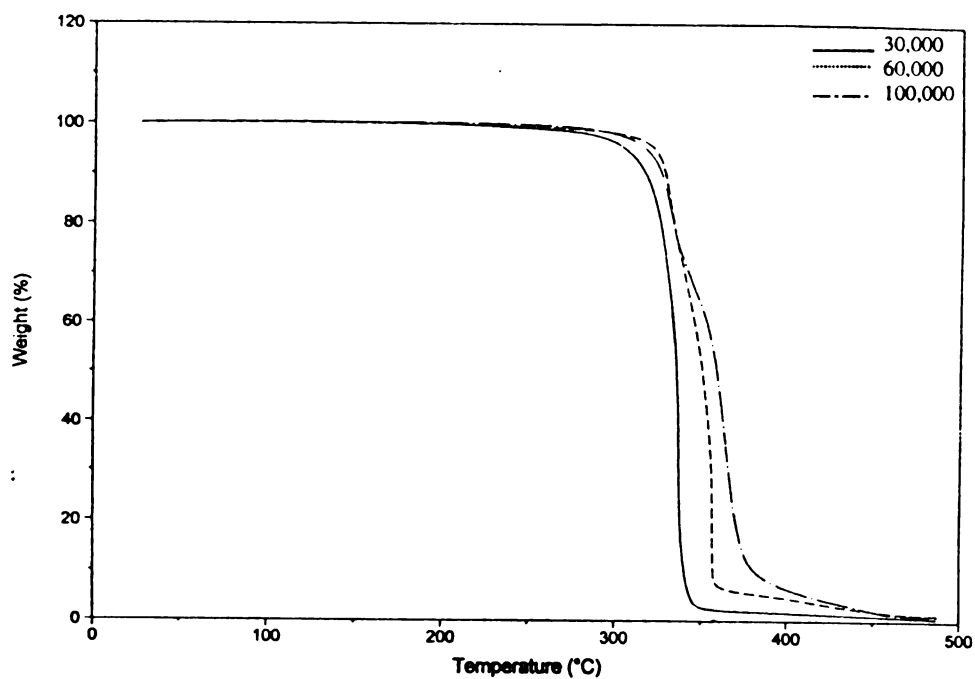


Figure 4-8: Output of TGA for three polyurethanes

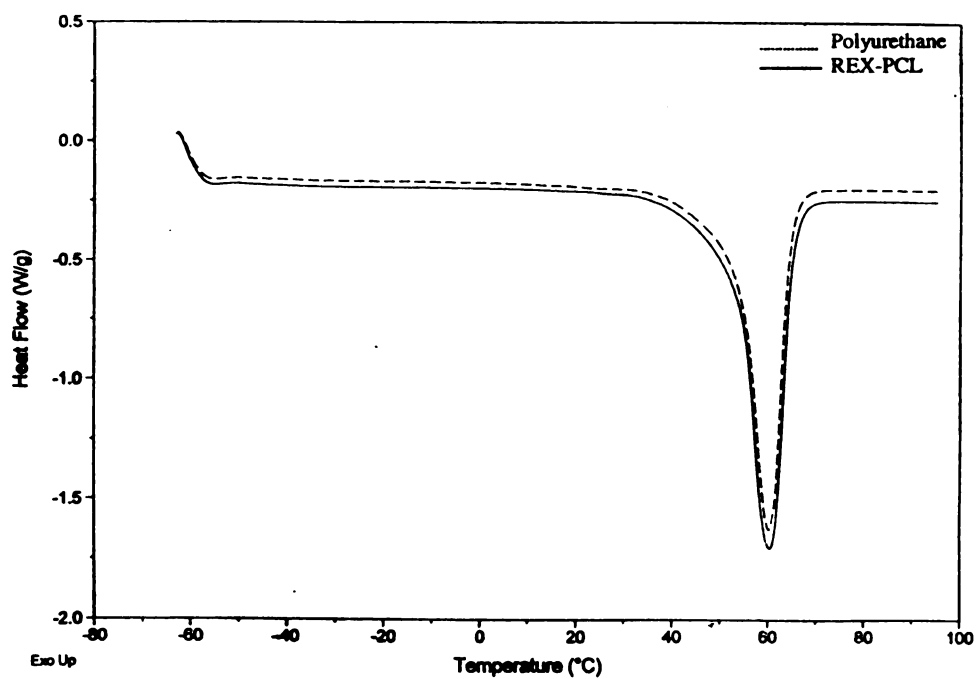


Figure 4-9: Output of DSC for the polyurethane and REX-PCL ($M_n = 30,000$)

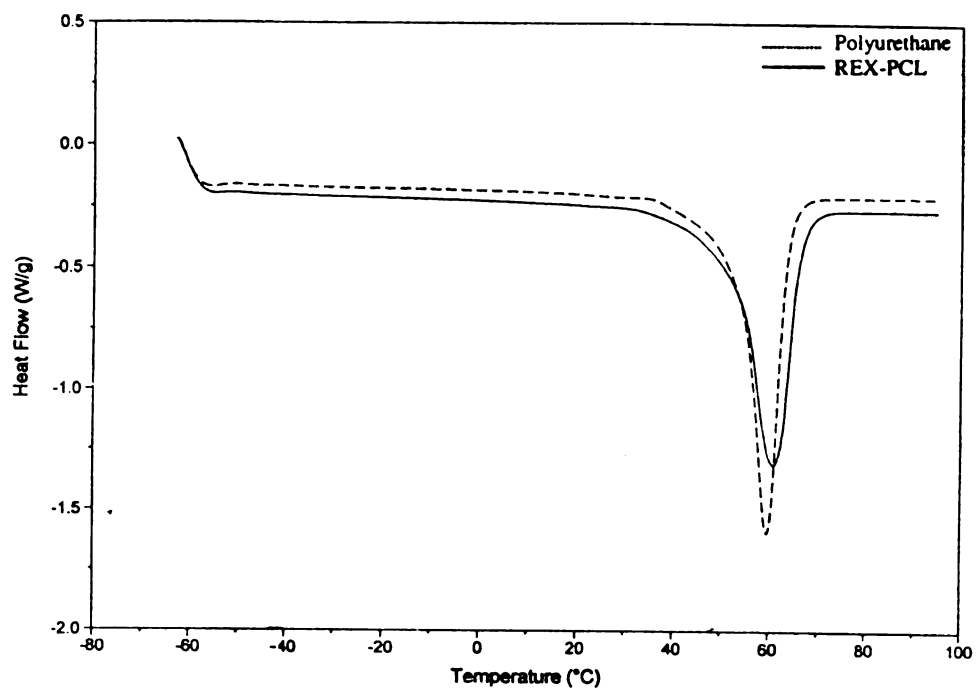


Figure 4-10: Output of DSC for the polyurethane and REX-PCL ($M_n = 60,000$)

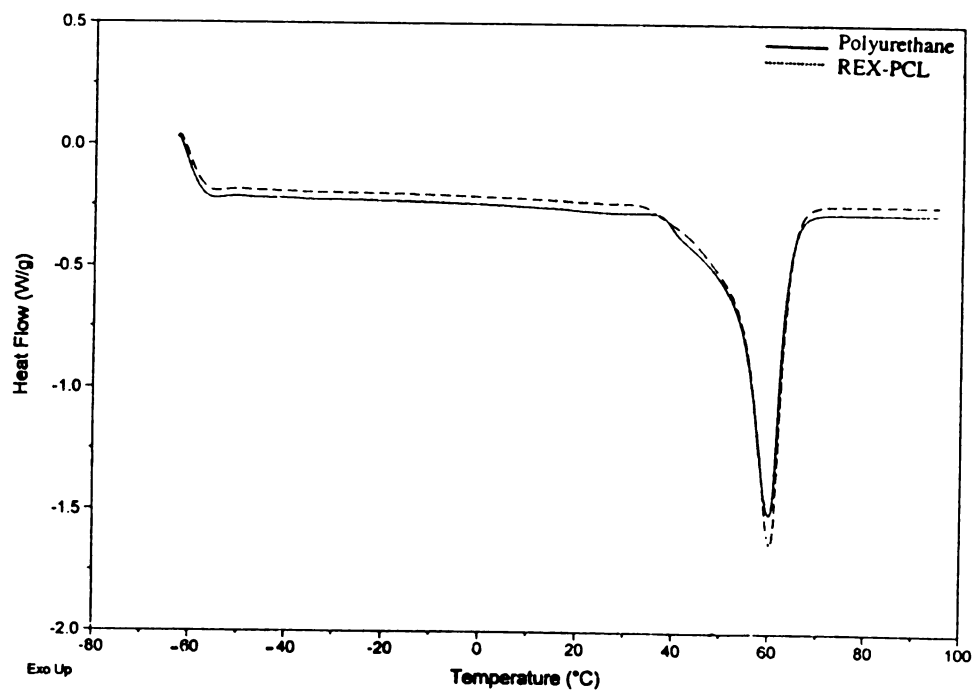


Figure 4-11: Output of DSC for the polyurethane and REX-PCL ($M_n = 100,000$)

4.5.5 Discussion

By comparing the intrinsic viscosity of REX-PCL and polyurethane that was produced from the same REX-PCL, it can be seen that the intrinsic viscosity of polyurethane is consistently lower than the intrinsic viscosity of REX-PCL. Additionally the Figure 4-4 shows that the intrinsic viscosity of polyurethane are very close the one of linear PCL.

One of the possible explanations to this observation is the broken linkage between aluminum at the center and the polycaprolactone arms. If this is the case, the polymer is no longer in the “star” shape, and each of the resulted linear PCL have two OH end-groups. This means that the ratio of OH end-group to NCO group is 2 to 1 instead of 1 to 1, and the product would have OH end-group with the molecular weight of approximately two times that of each “arm”. There will be no crosslinkage in this product.

The results of TGA and DSC show very small difference between the polyurethane and REX-PCL. This was no surprise since the diisocyanate contents in polyurethane were very small. Therefore the reactive extrusion polymerization of polyurethane was done with low molecular weight of REX-PCL in order to observe the reaction between diisocyanate and REX-PCL better.

4.6 Reactive Extrusion Polymerization of Diisocyanate and REX-PCL with Low Molecular Weight Star-Polycaprolactone

4.6.1 Objective

In this experiment, polyurethane was produced from REX-PCL of a low molecular weight, which is more commonly used for the production of polyurethane²⁸

than higher molecular weight used in the previous experiment. The two different amounts of diisocyanate were added to produce different types of polyurethane: excess OH end-group to prevent crosslinkage, and excess NCO groups to have greater amount of crosslinkage.

By using the REX-PCL of low molecular weight, NCO content was increased. This was advantageous in terms of the characterization of polyurethane since the difference between the polymers before and after the reaction will be more significant.

4.6.2 Materials

The TONE ECEQ monomer was used, and ATSB solution and HMDI solution were prepared by following the procedure discussed in section 4.4.3.2

4.6.3 Procedure

The same procedure as discussed in section 4.4 was followed to produce polyurethane, except REX-PCL with the molecular weight of 3000 and 7500 were used instead of 30,000+. Screw Configuration #1 was used opposed to the Screw Configuration #2 used in the past experiments. This was because the molecular weight used in this experiment was so low that the use of Screw Configuration #1 would not result in the flow stoppage. Furthermore the use of Screw Configuration #1 provided an additional mixing which would be desirable to produce homogeneous material.

Two types of feeding locations were evaluated. They are: (1) feeding monomer and initiator at feed throat (before zone 1) and feeding diisocyanate at zone 3; and (2)

feeding monomer and initiator at feed throat and feeding diisocyanate at zone 1.

Temperature profile of two cases are shown in Table 4-6.

	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6
Case 1: T (°C)	180	150	120	120	120	120
Case 2: T (°C)	120	120	120	120	120	120

Table 4-6: The extruder temperature profiles corresponding to the two types of feeding schemes

In case 1, the temperature of zone 1 was kept at 180 °C, just as the temperature of a regular REX-PCL production. Then, from zone 2 to 3, the temperature was gradually decreased to 120 °C to prepare for the reaction with diisocyanate. With this condition, block co-polymer of PCL linked with diisocyanate was expected.

On the other hand, the temperature of case 2 was kept at 120 °C throughout the extruder to prevent degradation of polyurethane at the earlier zones in the extruder. With this condition, the mixture of REX-PCL and diisocyanate links was expected to be more random than the one produced in case 1.

Since the molecular weight of REX-PCL selected were very low, its polymerization was assumed to be completed even at the low temperature profile used in this experiment. For each molecular weight of REX-PCL, the flowrate of HMDI solution were calculated by following the same equation as discussed in section 4.4.3.1. Amount of HMDI solution fed was then varied above and below the stoichiometric amount calculated to produce the different types of polyurethane.

Approximately 1 lb of each polyurethane were collected for characterization. The REX-PCL with the molecular weight of 3000 and 7500 were also collected to be compared with the polyurethane produced.

4.6.4 Results

The molecular weight of REX-PCL used, the amount of monomer, ATSB solution and HMDI solution fed, and torque % were recorded and tabulated in Table 4-7. The last column indicates whether the flowrate of HMDI was above or below the stoichiometric amount.

Theoretical Molecular Weight (each arm)	Monomer Flowrate (ml/min)	ATSB Solution Flowrate (ml/min)	HMDI Solution Flowrate (ml/min)	Torque %	Above or Below Stoich.
3000	20	3.2	1.3	21	below
3000	20	3.2	5.4	26	above
7500	50	3.2	1.3	19	below
7500	50	3.2	5.2	21	above

Table 4-7: Feed conditions used to produce polyurethane (T = 120 °C, 110 rpm)

All the samples collected were produced from the case 2 of the feed schemes. The feed schemes did not work due to the overflow at the zone 3. Detail of this observation will be discussed in the next section.

4.6.5 Discussion

REX-PCL with the molecular weight of 3000 and 7500 were found to have low viscosity, as expected, and it was impossible to be pelletized. Also, the production of

those materials caused a constant “extruder underload” warning due to their low viscosities.

Despite the numerous attempts, case 1 of feed schemes did not work due to the overflow at the zone 3. The overflow was caused by the large viscosity difference between the materials before and after the zone 3. Since diisocyanate was added at zone 3, the polymer after zone 3 suddenly becomes very viscous that the polymer of low viscosity (because of its low molecular weight) coming from earlier zones could not push the material out from the zone 3. On the other hand, case 2 worked without causing any major problems. Therefore the polyurethane listed in Table 4-6 were collected by adding the HMDI solution at zone 1.

As shown in Table 4-7, the torque % indicated the viscosity of the polymer increased as the HMDI was added. The increase in torque % was especially significant before and after the addition of HMDI, since the typical torque % of REX-PCL with the molecular weight of 3000 and 7500 were 9 – 10 %.

4.7 Characterization of Polyurethane made with Low Molecular Weight Star-Polycaprolactone

4.7.1 Objective

In order to characterize the polyurethane produced from the REX-PCL of low molecular weight, REX-PCL before the reaction and polyurethane were tested with TGA and DSC.

4.7.2 Materials

Polyurethane produced in section 4.6 were used in this experiment.

4.7.3 Procedure

Analysis of polyurethane with TGA and DSC were done by following the standard procedures.

4.7.4 Results

The results of TGA and DSC of polyurethane produced from the REX-PCL with the molecular weight of 3000 were plotted in Figure 4-12 and 4-13 respectively. Also the REX-PCL with the molecular weight of 3000 was plotted on the same graphs for the comparison. The results of TGA and DSC of polyurethane produced from the REX-PCL with the molecular weight of 7500 were plotted in Figure 4-14 and 4-15 respectively. The REX-PCL with the molecular weight of 7500 was also plotted on the same graphs for the comparison.

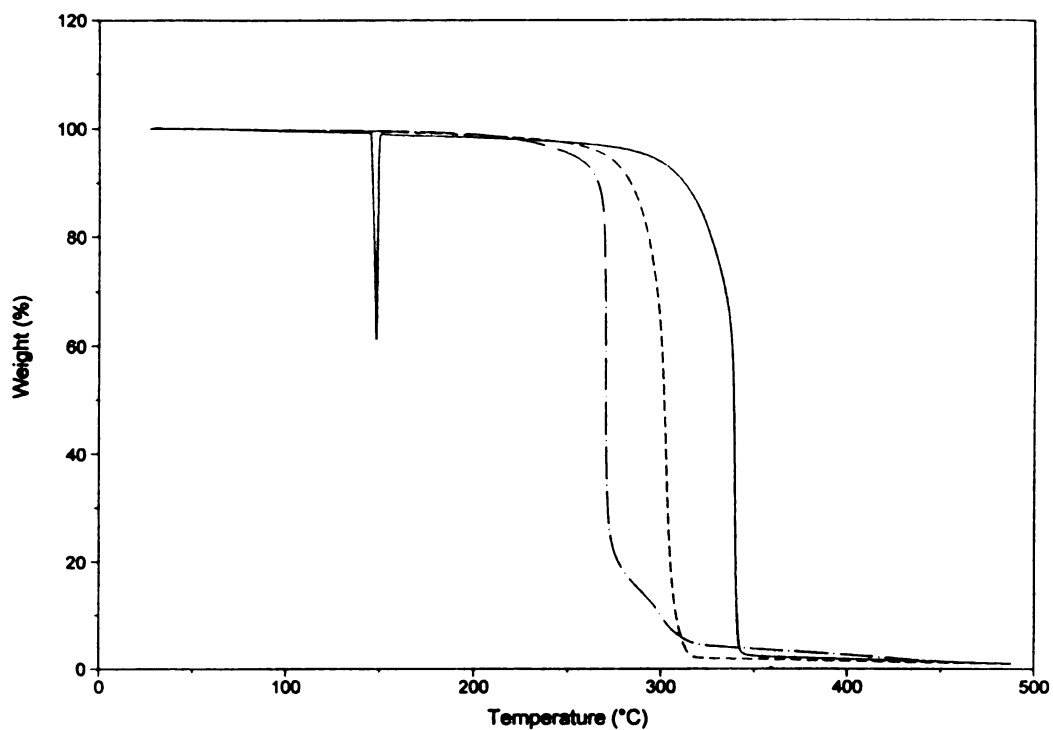


Figure 4-12: Output of TGA for REX-PCL and polyurethane with the molecular weight of 3000

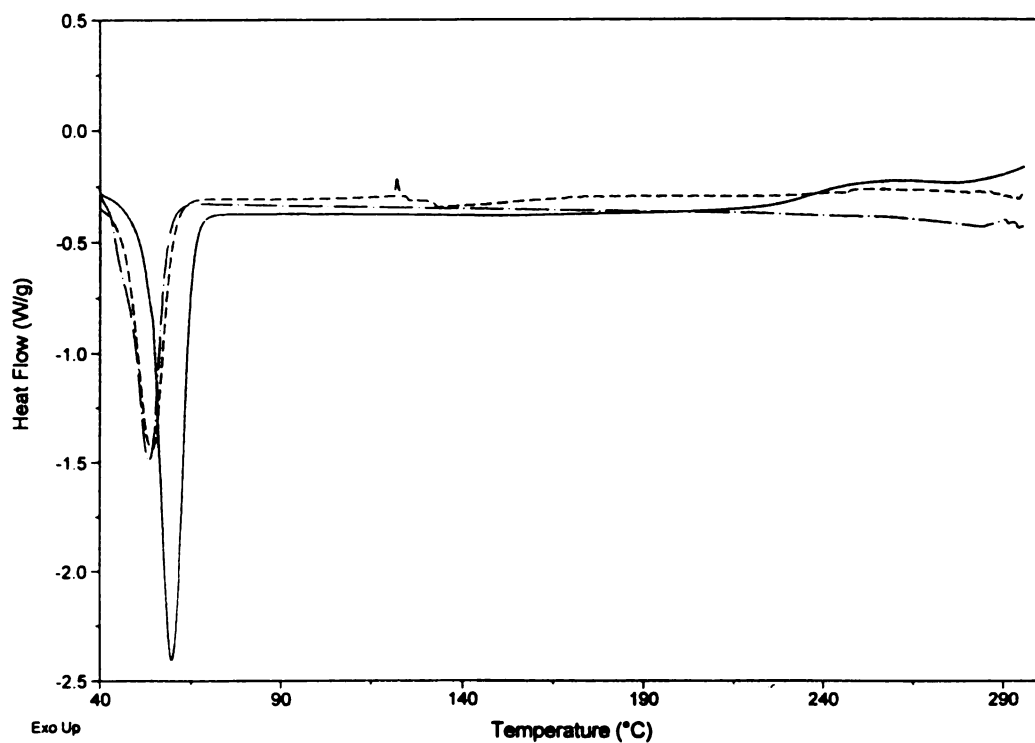


Figure 4-13: Output of DSC for REX-PCL and polyurethane with the molecular weight of 3000

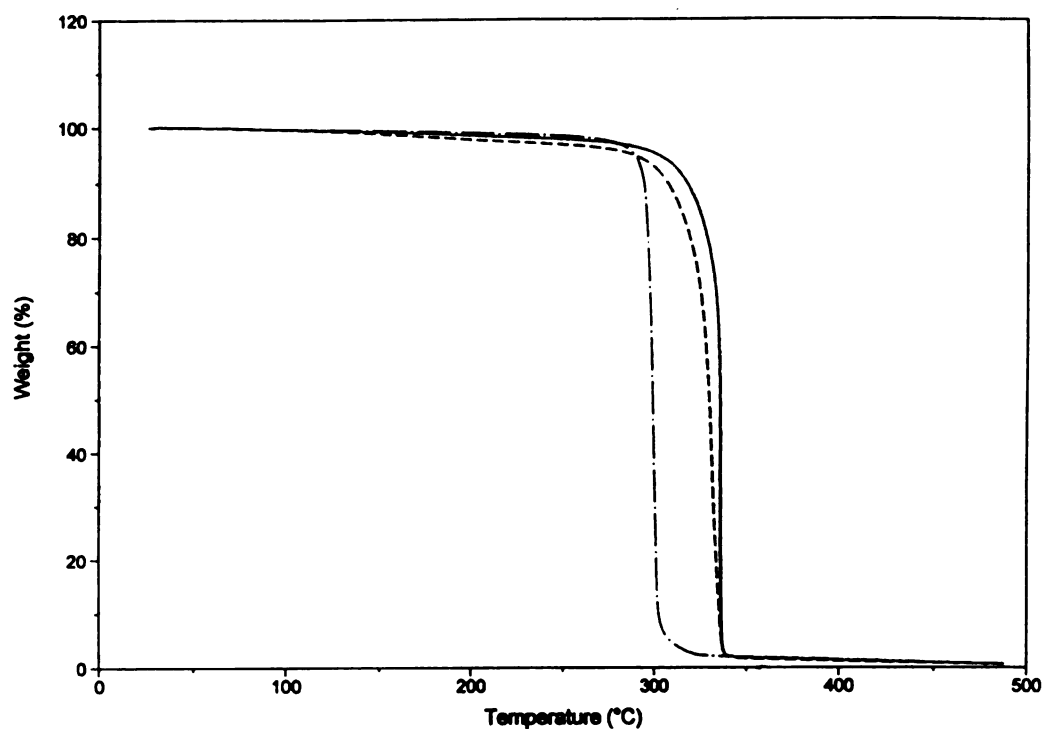


Figure 4-14: Output of TGA for REX-PCL and polyurethane with the molecular weight of 7500

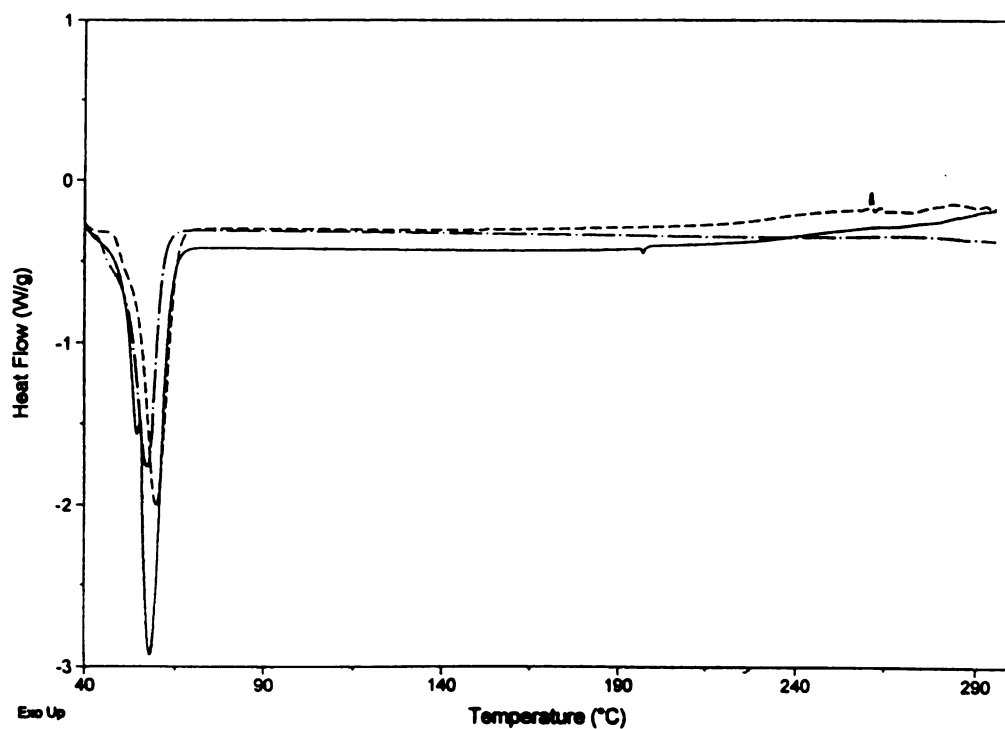


Figure 4-15: Output of DSC for REX-PCL and polyurethane with the molecular weight of 7500

4.7.5 Discussion

Both Figure 4-12 and 4-14 show a significant decrease in thermal stability as the amount of diisocyanate contents increase. This was true for the REX-PCL with the molecular weight of 3000 and 7500; However, the reduction in thermal stability is more significant for the REX-PCL with the lower molecular weight.

A similar trend was observed from the results of DSC. Figure 4-13 and 4-15 show the reduction in melting temperature when the diisocyanate was added. This too was significant for the REX-PCL with lower molecular weight.

4.8 Conclusions

The results of TGA and DSC, as well as the melt fracture observed during the experiments indicates that there had been some reaction taken place between REX-PCL and diisocyanate. However, further analysis of the material properties are necessary in order to determine the type of polymer as well as the application that this type of materials can be used.

TRANSESTERIFICATION OF STAR-POLYCAPROLACTONE AND POLYETHYLENE TEREPHTHALATE

5.1 Introduction

Blending process, such as transesterification, plays an important role in the current polymer industry. By blending two or more materials, one can obtain a material with the properties that was not available from any of the original materials. However, the production of thermodynamically stable polymer blend with high molecular weight polymers is usually difficult, since the chain connectivity makes the entropy of mixing of these systems very small²².

The transesterification is a reaction of esters and alcohols in an acid- or base-catalyzed transformation²⁴. This type of blending process has been studied by a large number of researchers with various types of polymers, catalysts, and process conditions. One of the examples is the transesterification of polyethylene terephthalate (PET) and polycaprolactone (PCL) in a twin screw extruder, using stannous octoate as a catalyst. This process was developed by Weiming Tang et al⁴⁰. In this process, the PET was initially fed to the extruder to melt. When the PET was molten, the catalyst and the caprolactone monomer were added to carry out the transesterification. This scheme would yield low PCL formation. On the other hand, the monomer and the catalyst can be added at the beginning of the extruder to carry out some degree of polymerization. Then, another ingredient such as PET, can be added at the middle of the extruder. This scheme

would result in a more firm control of PCL polymerization. However, whether the PET melts fast enough to react effectively within the extruder remains a question. In addition to the feeding scheme, the choice of a catalyst to be used is an important issue in planning the transesterification process.

In this study, four types of catalyst, triphenylphosphine solution, triphenylphosphine pellets, dibutyltin dilaurate, and titanium (IV) isopropoxide, were evaluated for the transesterification of REX-PCL and PET. The reaction mechanism is shown in Figure 5-1. The various feeding schemes were tested in order to carry out the process successfully.

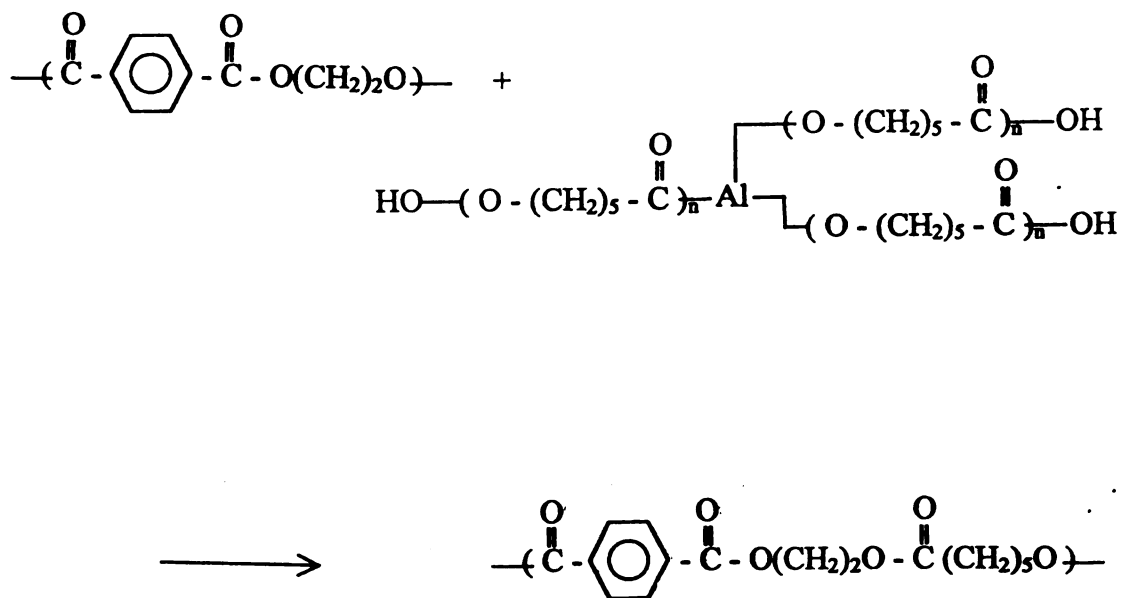


Figure 5-1: A reaction mechanism of the transesterification of REX-PCL and PET

With above mechanism, mixed ester product has no ordered structure, therefore it does not crystallize (amorphous polymer).

The focus of this study was to determine the catalyst and the process conditions that can be used to successfully carry out the transesterification of REX-PCL and PET.

5.2 Background

5.2.1 PET

Polyethylene terephthalate (PET) is one of the most widely used plastics. Its applications range from food storage and container to the electronics packaging and natural gas distribution pipes. PET is a semi-crystalline thermoplastic, and it turns white when heated. Some of the advantage of PET over other thermoplastics, such as nylon and acetal, are its high wear and abrasion resistance, as well as the better resistance to acidic solutions and chlorinated aqueous solutions. Latter property is especially useful for the application of PET in food packaging, because acidic solutions and chlorinated aqueous solutions are commonly used to sanitize food processing equipment²⁵. A structure of PET is shown in Figure 5-2.

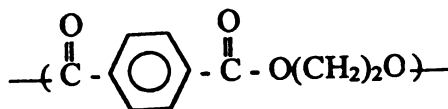


Figure 5-2: A structure of polyethylene terephthalate (PET)

5.2.2 Screw Configuration

In the process of transesterification, different materials are to be mixed randomly, and a catalyst has to be equally distributed throughout the materials. For this reason, screw configuration #1, which consist of approximately equal amount of kneadling and conveying elements, was used for the transesterification process.

5.3 Outline of Chapter

This chapter discusses the steps that took place in order to determine the catalyst and process conditions for the transesterification of REX-PCL and PET.

Section 5.4 discusses the transesterification of REX-PCL and PET, using triphenylphosphine solution (TPP solution) as a catalyst. TPP solution refers to the solution in which triphenylphosphine was dissolved in toluene. Various feeding schemes were tested. This topic will also be discussed in section 5.4.

Due to the problem caused by the solvent used to make the TPP solution, TPP pellets was used as a catalyst, without being dissolved, to carry out the transesterification of REX-PCL and PET. This topic will be discussed in section 5.5.

In sections 5.6 and 5.7, transesterification of REX-PCL and PET with two more catalysts, dibutyltin dilaurate (section 5.6) and titanium (IV) isopropoxide (section 5.7), were done, and the results will be discussed.

Finally in the Conclusion (section 5.8), the recommended process conditions and type of catalyst, as well as the topics to be improved will be discussed.

5.4 Transesterification of REX-PCL and PET with Triphenylphosphine Solution

5.4.1 Objective

Purposes of this experiment were to determine whether triphenylphosphine solution can be used as a catalyst in the transesterification of REX-PCL and PET, and to determine the optimum process conditions for the process. Latter part mainly focused on varying extrusion temperatures and feeding locations.

5.4.2 Materials

REX-PCL with the molecular weight of 100,000 was produced by following the procedure discussed in Chapter 3. The REX-PCL was dried at room temperature for a few days before further processing. The commercial grade PET was obtained from Eastman Chemical Company and used throughout this study. Triphenylphosphine was chosen as a catalyst in this study because it is one of the commonly used catalyst for the transesterifications. It was purchased from Aldrich Chemical Company in the pellet form and used for the first part of this experiment. A structure of triphenylphosphine is shown in Figure 5-3.

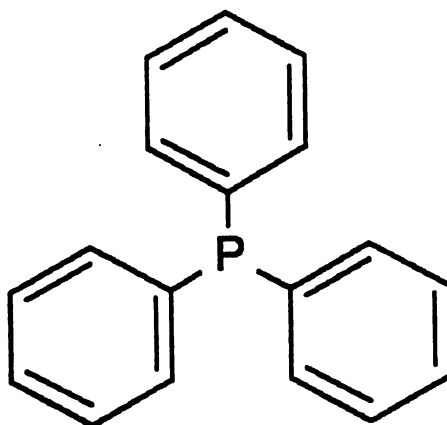


Figure 5-3: A structure of triphenylphosphine

5.4.3 Procedure

5.4.3.1 Preparation of triphenylphosphine Solution

Triphenylphosphine pellets were dissolved in toluene (20 wt% triphenylphosphine) under a chemical hood. The fraction of triphenylphosphine in the solution was chosen as 20 wt%, which was chosen merely for the convenience.

5.4.3.2 Determination of Feeding Location

A schematic of the possible feeding locations are shown in Figure 5-4.

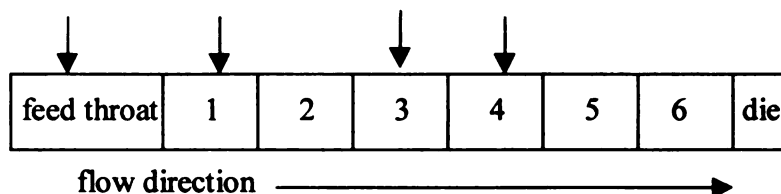


Figure 5-4: A Schematic of possible feeding location

There was no vent port available for additional feed at zones 2 and 5, and zone 6 was not considered as a choice of feeding location since it was too close to the die.

In this experiment, six feeding combinations were tested as shown in Table 5-1:

Combination #	PET	REX-PCL	catalyst
1	feed throat	feed throat	feed throat
2	feed throat	feed throat	zone 1
3	feed throat	feed throat	zone 3
4	feed throat	feed throat	zone 4
5	feed throat	zone 1	zone 4
6	feed throat	zone 3	zone 4

Table 5-1: Six Feeding Combinations Tested

PET was always fed at the feed throat since it has higher melting temperature than REX-PCL.

5.4.3.3 Extrusion Temperature

Since the melting temperature of PET is about 250 °C, the temperature at this range was used in this experiment. This temperature range was still in the “safe” range where REX-PCL does not degrade (based on the results of TGA shown in Chapter 3).

5.4.3.4 Reactive Extrusion Process

Equal ratio of REX-PCL and PET with various amounts of catalyst were fed into the extruder at a various feeding locations discussed in section 5.4.3.2.

The screw speed of the extruder was varied between 30 rpm to 150 rpm to determine the speed that works best for each of the feeding combinations. In addition, the feeding rate of REX-PCL and PET was kept at 20 g/min (total) to minimize the “overflow” at the open zones, which will be discussed later in this chapter. The two different ratios of polymer mixture to catalyst were tested: they were 20 to 1 (5 wt% catalyst) and 40 to 1 (2.5 wt% catalyst).

The mixture of REX-PCL and PET with different amounts of triphenylphosphine solution were collected and tested with TGA and DSC. Also, the mixture of PCL and PET without the catalyst was processed in an extruder at the same processing condition and tested with TGA and DSC for comparison.

5.4.4 Results

The output of TGA of the product with no catalyst and 5 wt% catalyst were plotted in Figure 5-5. The output of DSC of products with no catalyst, 5 wt% catalyst, and 2.5 wt% catalyst were plotted in Figure 5-6.

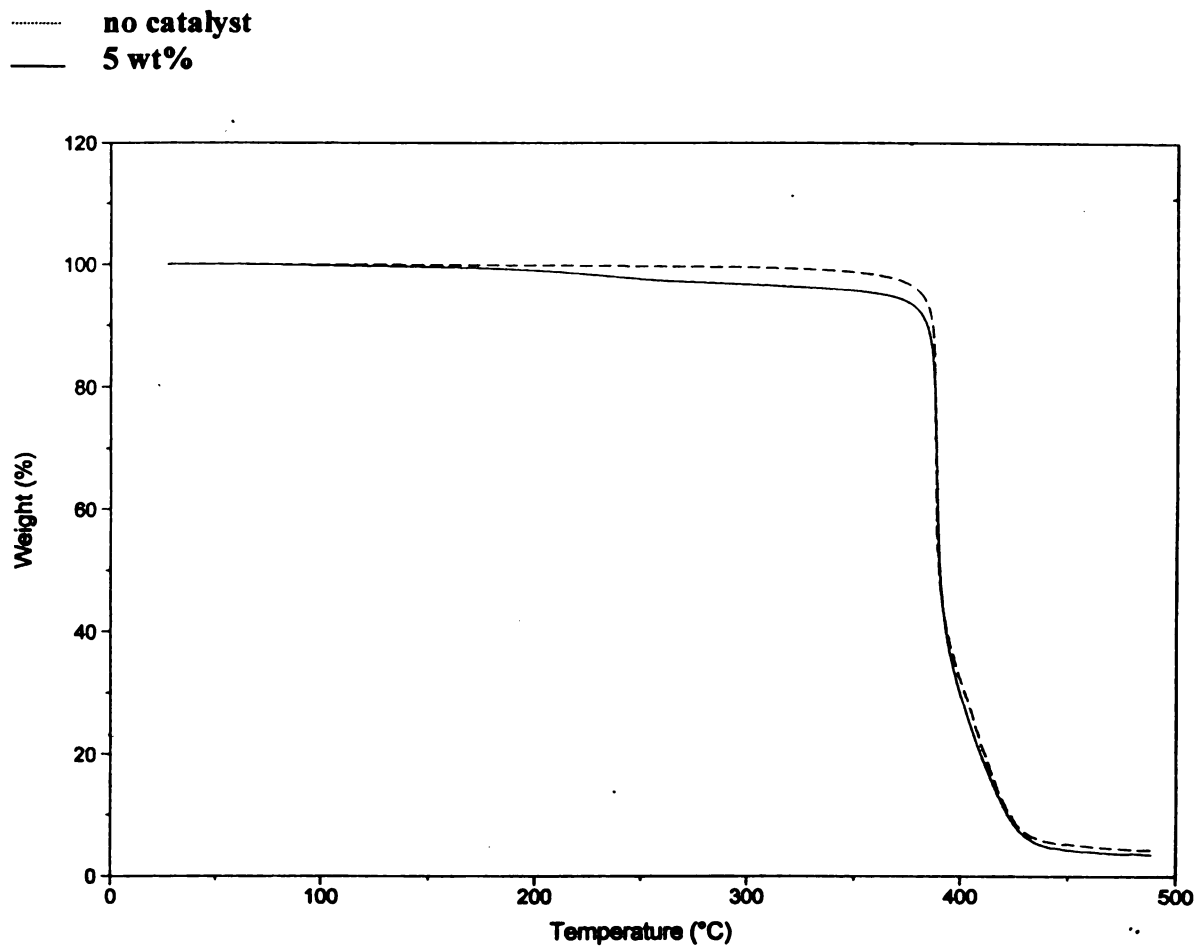


Figure 5-5: Output of TGA for the REX-PCL/PET mixture with triphenylphosphine solution as a catalyst

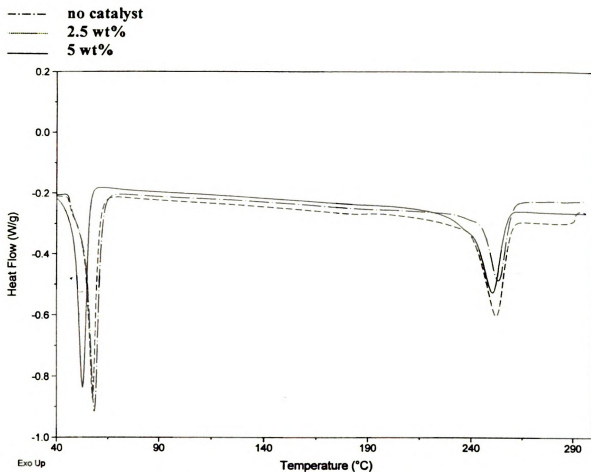


Figure 5-6: Output of DSC for the REX-PCL/PET mixture with triphenylphosphine solution as a catalyst.

5.4.5 Discussion

By evaluating the various feeding combinations, it was found that the feeding combination #4 (PET and REX-PCL were fed at the feed throat and catalyst solution was fed at the zone 4) was the only one that worked in this experiment. This was due to two reasons: when REX-PCL was fed into the extruder from the zones other than feed throat, they tended to stick on the top of molten polymer and accumulates as more REX-PCL was fed; and because the PET did not completely melt until zone 4, feeding the catalyst at the locations other than zone 4 caused the solid polymers to stick to each other and start

to accumulate at the zone. Also, the feed rate of polymer mixture was kept at 20 g/min and the screw speed of 100 rpm was used. This combination was found to work best without having any overflow at the open zones.

The polymers made in this experiment had a rough surface and they looked slightly brown. The brownish color was slightly darker for the one with a higher catalyst content. Additionally, the results of DSC showed that the transesterification did not occur. Furthermore, the result of TGA shows that the polymer with 5 wt% catalyst content started to degrade at low temperature (approximately at 100 °C). These observations may be indicating that the 5 wt% catalyst sample was partially degraded.

One of the possible explanations to this result is the poor choice of the solvent. Toluene was chosen as a solvent because of the fact that both PCL and catalyst can be dissolved in it, and it evaporates quickly at a high temperature. Latter led to the assumption that the immiscibility of toluene and PET has a negligible effect on the transesterification. However, this assumption turned out to be bad since the product polymer did not look well-mixed.

A use of another solvent was considered; however, because the common solvents do not dissolve PET, the triphenylphosphine pellets without being dissolved in a solvent was chosen as a next step. This topic will be discussed in the next section.

5.5 Transesterification of REX-PCL and PET with Triphenylphosphine Pellets

5.5.1 Objective

Since the transesterification of the REX-PCL and PET with triphenylphosphine solution was unsuccessful, possibly due to the use of a toluene as a solvent,

triphenylphosphine pellets (without use of solvent) was used as a catalyst to carry out the transesterification process in this experiment.

Objective of this experiment was to determine the effect of triphenylphosphine as a catalyst in carrying out the transesterification of REX-PCL and PET.

5.5.2 Materials

The same REX-PCL and PET as used in the previous experiment was used. Also, the same triphenylphosphine as used in the previous experiment was used, except in this case, it was fed to the extruder in the form of pellets instead of being dissolved in a toluene.

5.5.3 Procedure

5.5.3.1 Reactive Extrusion Process

Since the solid was only successful to be fed into the extruder from the feed throat, triphenylphosphine pellets were fed into the extruder with REX-PCL and PET at the feed throat. Because all the materials were fed into the extruder from the feed throat, all the other vent port were kept closed. As before, equal weight ratio of REX-PCL to PET was used, and 5 wt% and 2.5wt% catalysts were fed. The same temperature profile and screw speed as used in previous experiment was applied.

5.5.3.2 Characterization

Product obtained from the transesterification of REX-PCL and PET with triphenylphosphine pellets as a catalyst was analyzed with TGA and DSC.

5.5.4 Results

The output of TGA of the product with no catalyst and 5 wt% catalyst are plotted in Figure 5-7. The output of DSC of products with no catalyst, 5 wt% catalyst, and 2.5 wt% catalyst were plotted in Figure 5-8.

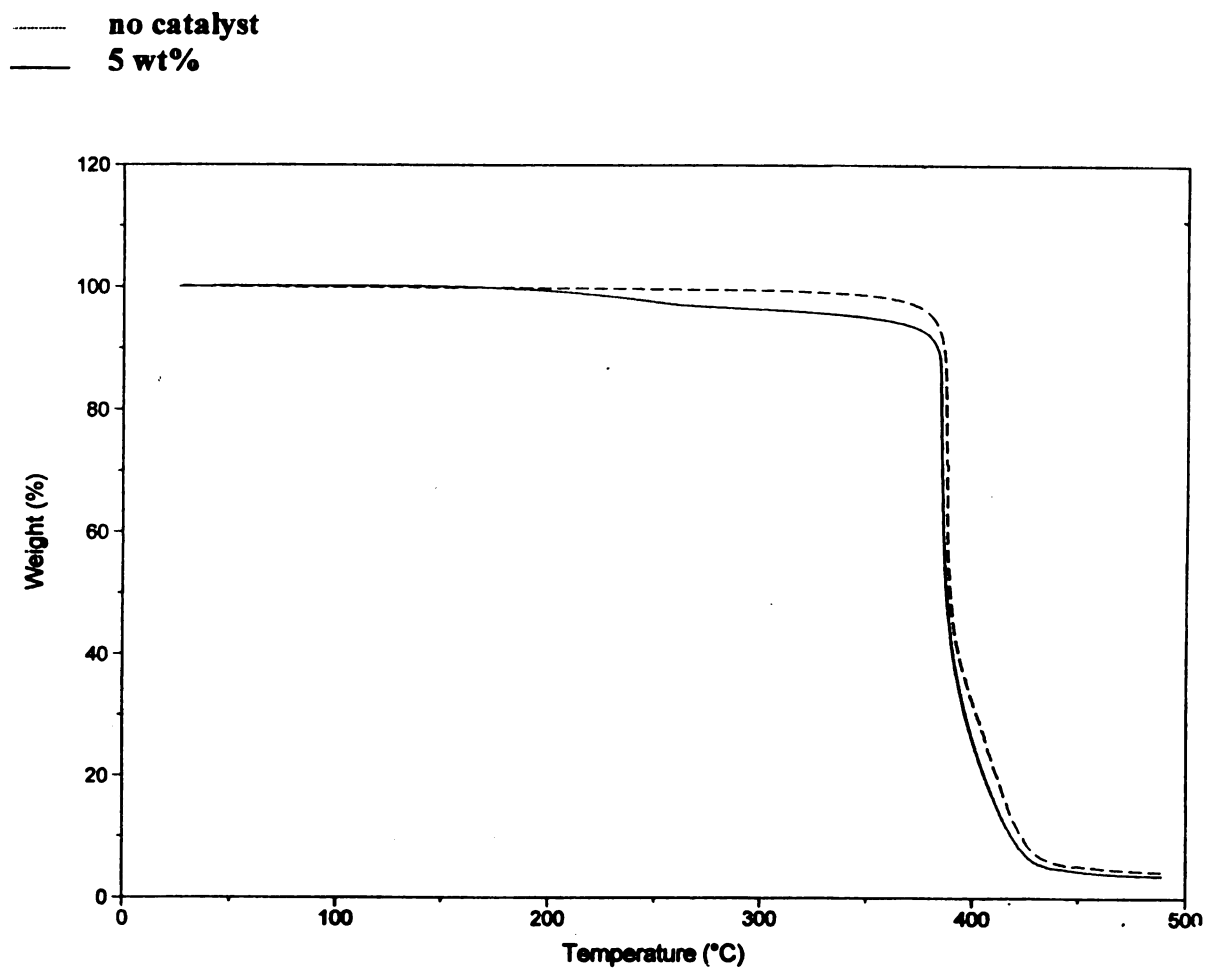


Figure 5-7: Output of TGA of REX-PCL/PET mixture with triphenylphosphine pellets as a catalyst

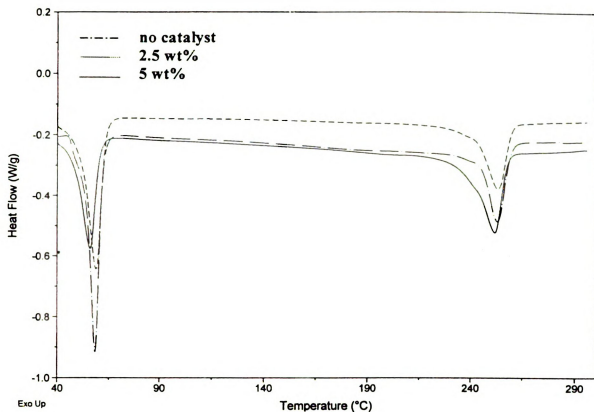


Figure 5-8: Output of DSC for REX-PCL/PET mixture with triphenylphosphine pellets as a catalyst

5.5.5 Discussion

The polymers made in this experiment had smooth appearance, though the ones with catalyst added seemed slightly brown with the one with more catalyst content being darker. The results of DSC showed a reduction in the size of REX-PCL melting point peak; however, no change can be observed with the peak of PET. Also, the result of TGA shows the similar trend as the one observed in the previous experiment (Figure 5-3). These results indicate that the triphenylphosphine is not suitable for the catalyst of transesterification between REX-PCL and PET. Therefore, another type of catalyst was evaluated in the next section.

5.6 Transesterification of REX-PCL and PET with Dibutyltin Dilaurate

5.6.1 Objective

Objective of this experiment was to determine the effect of dibutyltin dilaurate as a catalyst in carrying out the transesterification of REX-PCL and PET.

5.6.2 Materials

Same REX-PCL and PET as previous experiments were used.

Dibutyltin Dilaurate was purchased from Aldrich Chemical Company to be used as a catalyst. A structure of dibutyltin dilaurate is shown in Figure 5-9.

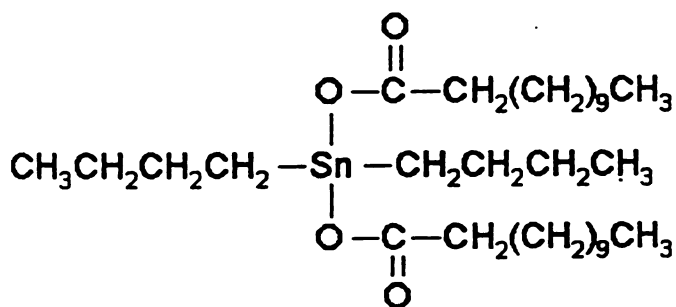


Figure 5-9: A structure of dibutyltin dilaurate

5.6.3 Procedure

5.6.3.1 Reactive Extrusion Process

As before, both REX-PCL and PET (1:1 weight ratio) were fed through the feed throat. However, since dibutyltin dilaurate was purchased in a liquid form, it was fed into

the extruder through zone 4, as it was determined to work best in the previous experiment with TPP solution. Also, the same weight fraction of polymer mixture to catalyst as used in the previous experiments were applied. The same temperature profile and the screw speed used in previous experiments were also applied in this section.

5.6.3.2 Characterization

The product obtained from the transesterification of REX-PCL and PET with dibutyl dilaurate as a catalyst was analyzed with TGA and DSC. Standard procedure as discussed in Chapter 2 was followed.

5.6.4 Results

The output of TGA and DSC of products with no catalyst, 5 wt% catalyst, and 2.5 wt% catalyst were plotted in Figure 5-10 and 5-11 respectively.

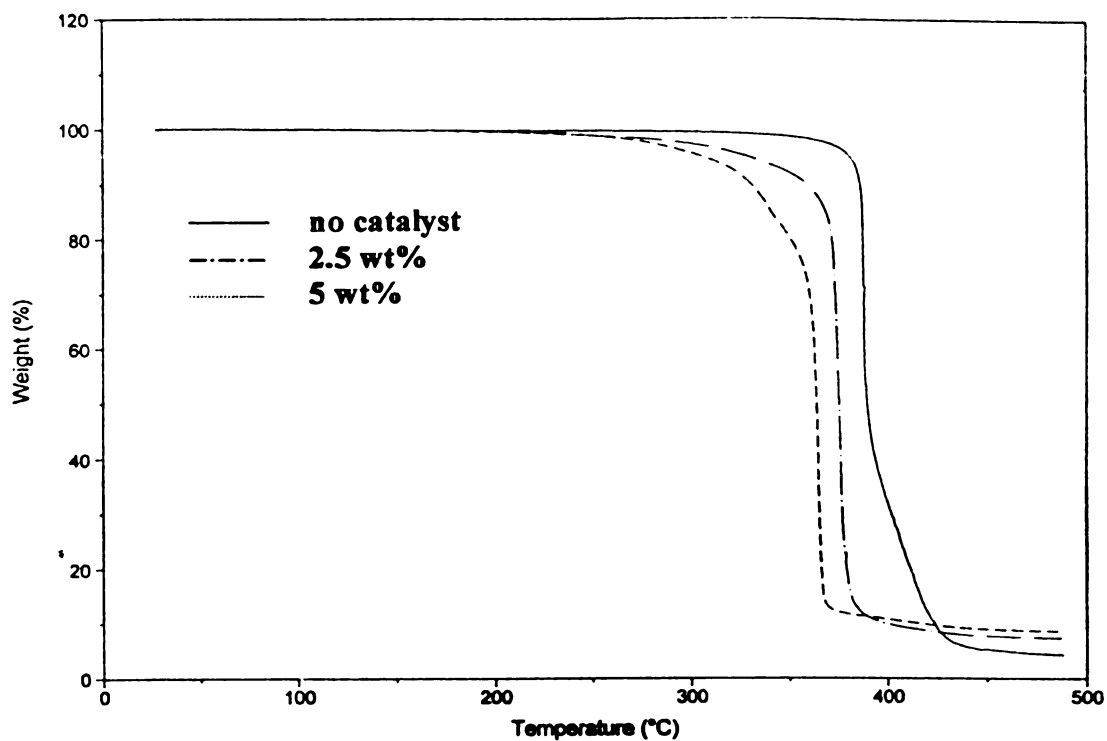


Figure 5-10: Output of TGA for the REX-PCL/PET mixture with dibutyltin dilaurate as a catalyst

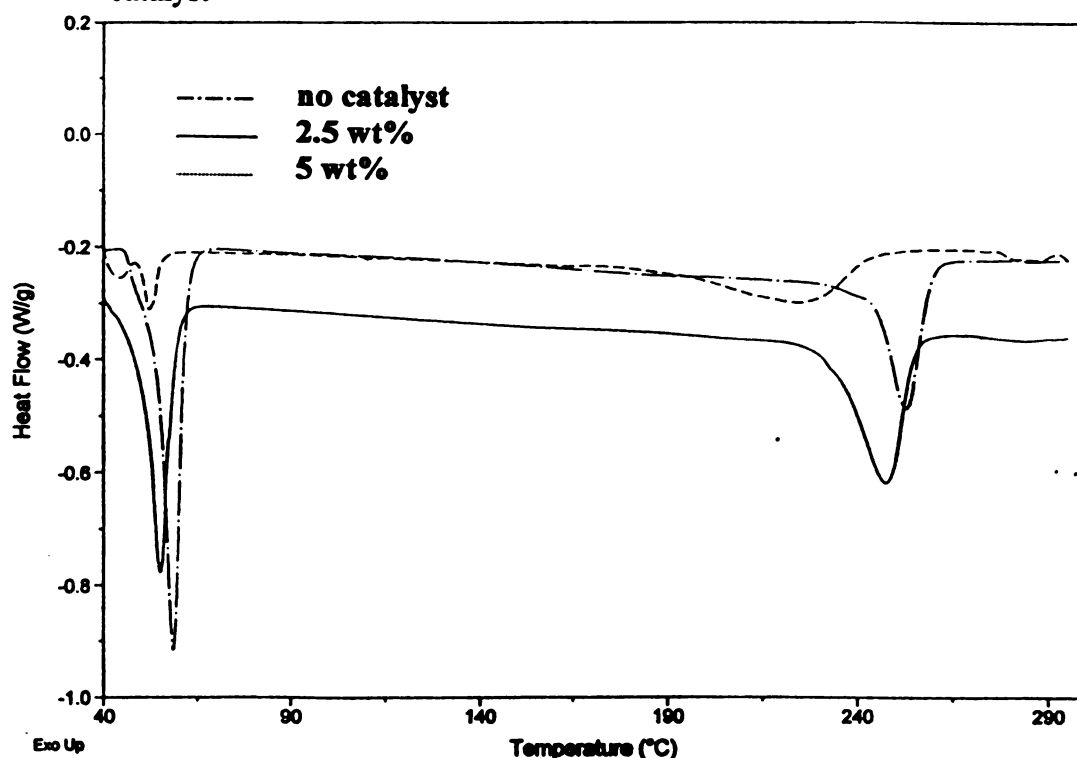


Figure 5-11: Output of DSC for REX-PCL/PET mixture with dibutyltin dilaurate as a catalyst

5.6.5 Discussion

The product seemed less brownish than the ones with triphenylphosphine, and it had a smooth surface. The result of DSC showed the shift in melting temperature and the reduction in the size of the peak occurred for the product with 5 wt% catalyst. Although the change is small, the reduction in the size of the peak and the shift of the melting temperature was also observed for the product with 2.5 wt% catalyst. Additionally, the result of TGA showed a significant reduction in degradation temperature as the amount of catalyst was increased.

These observations indicate that the dibutyltin dilaurate can be used as a catalyst for the transesterification. Also, with the fact that the reduction and a shift in melting point peak was significant when the catalyst content was doubled, indicates that increasing the catalyst content above 5 wt% added may yield even better transesterification between the REX-PCL and the PET.

5.7 Transesterification of REX-PCL and PET with Titanium (IV) Isopropoxide

5.7.1 Objective

Objective of this experiment was to determine the effect of titanium (IV) isopropoxide as a catalyst in carrying out the transesterification of REX-PCL and PET.

5.7.2 Materials

The same REX-PCL and PET discussed in the previous experiments were used.

Titanium (IV) isopropoxide was purchased from Aldrich Chemical Company to be used as a catalyst. A structure of titanium isopropoxide is shown in Figure 5-12.

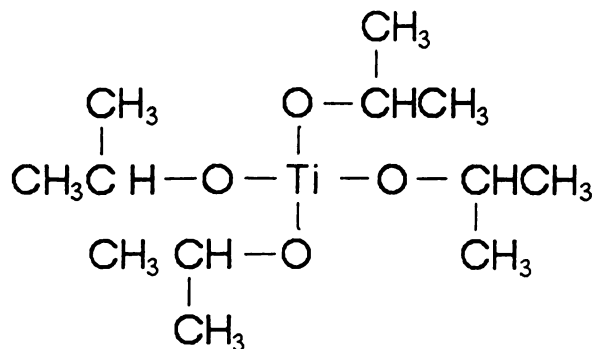


Figure 5-12: A structure of titanium (IV) isopropoxide

5.7.3 Procedure

5.7.3.1 Reactive Extrusion Process

Since titanium (IV) isopropoxide was also purchased in a liquid form, it was fed into the extruder through zone 4. Also, as before, the equal weight ratio of REX-PCL and PET were fed into the extruder through feed throat with the feeding rate of 20 g/min. The same screw speed and temperature profile used in the previous sections were applied. As before, 5 wt% and 2.5 wt% of catalyst was added for evaluation. The entire process was carried under nitrogen environment since the titanium isopropoxide is sensitive to a moisture.

5.7.3.2 Characterization

The product obtained from the transesterification of REX-PCL and PET with titanium isopropoxide as a catalyst was analyzed with TGA and DSC. Standard procedure as discussed in Chapter 2 was followed.

5.7.4 Results

The output of TGA and DSC of products with no catalyst, 5 wt% catalyst, and 2.5 wt% catalyst were plotted in Figure 5-13 and 5-14 respectively.

--- no catalyst
— 2.5 wt%
— 5 wt%

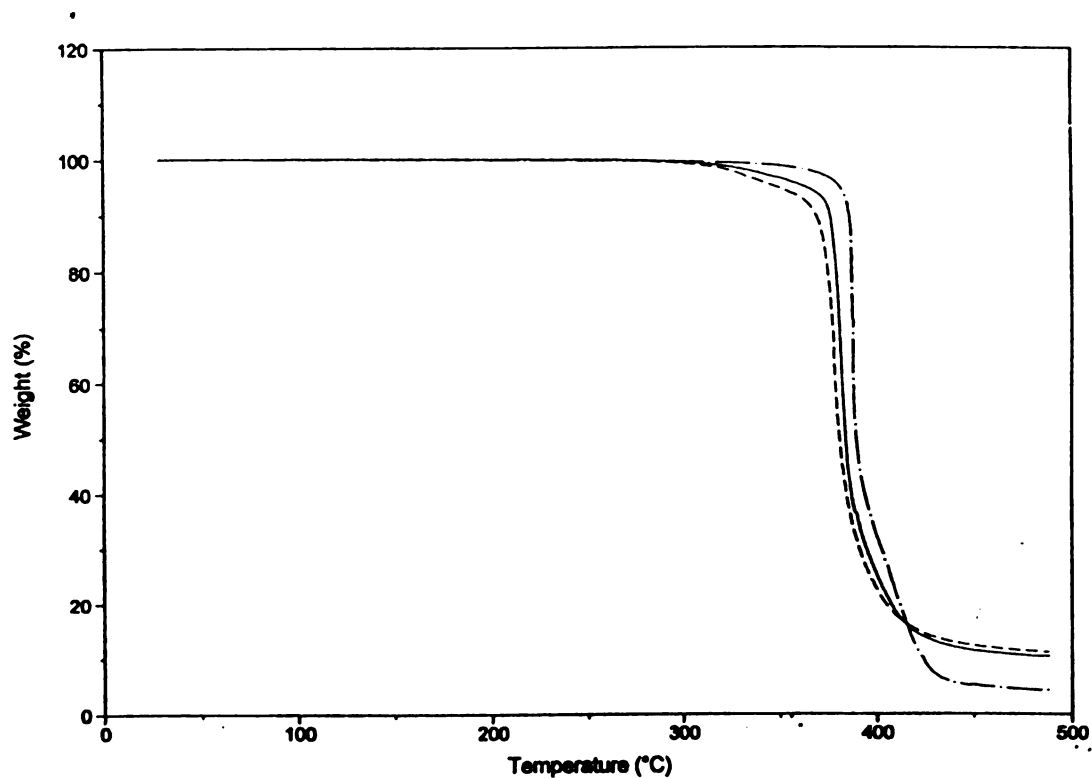


Figure 5-13: Output of TGA for REX-PCL/PET mixture with titanium isopropoxide as a catalyst.

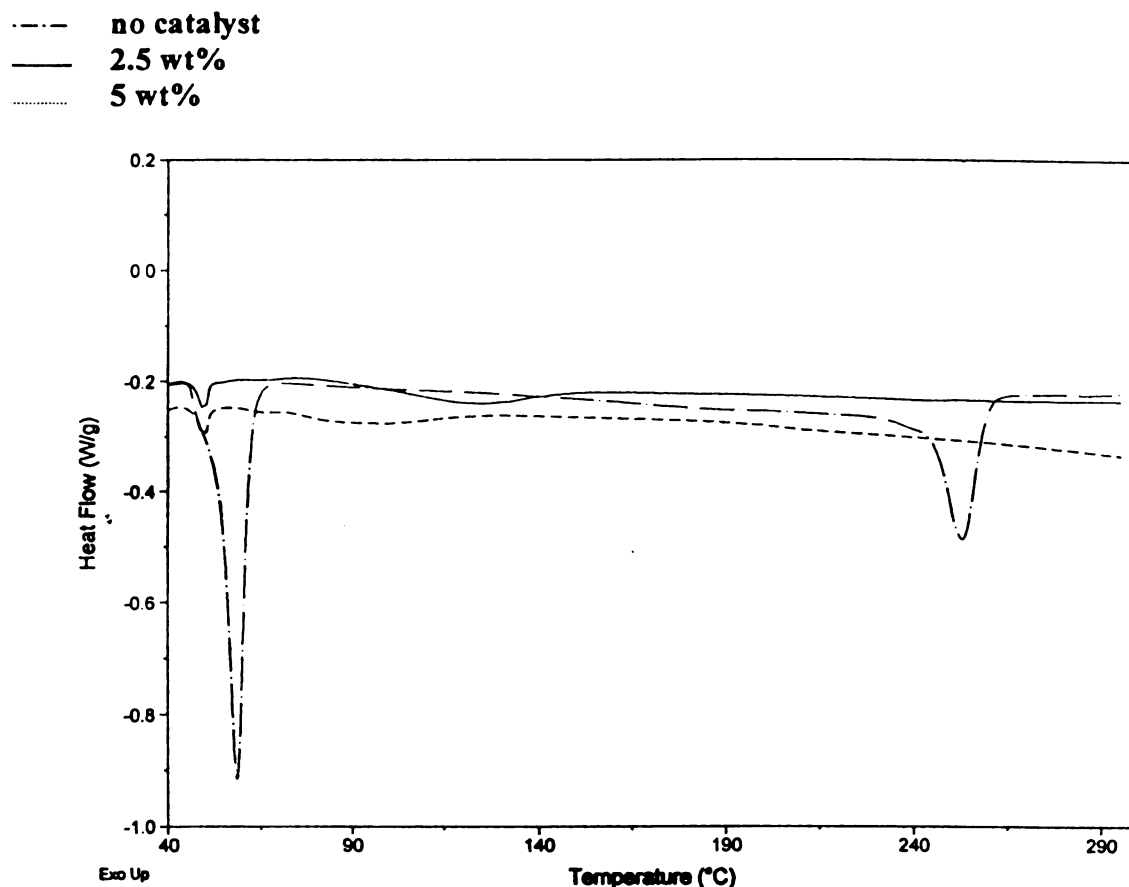


Figure 5-14: Output of DSC for REX-PCL/PET mixture with titanium isopropoxide as a catalyst.

5.7.5 Discussion

The product that came out from the extruder had a dark reddish brown color, somewhat clear, and was very soft. This was true for the products of different catalyst contents, and the color stayed the same even after being left to be dried for a few days, with the same soft, stickiness remaining.

The results of DSC showed the addition of catalyst resulted in the significant reduction of two melting point peaks, and a formation of one broad peak at approximately 120 °C. The result of the polymer with 5 wt% catalyst and 2.5 wt%

catalyst also showed very similar results. These observations indicate that the increase in catalyst content does not carry the transesterification further.

The result of TGA showed slight reduction in degradation temperature; however, the amount of reduction was very small compared to the result of the polymer with dibutyltin dilaurate as a catalyst.

Although the increase in catalyst content did not carry the transesterification further, the increase in temperature residence time may. This can be done by the addition of a few mixing elements in the screw configuration.

5.8 Conclusions

Four types of catalysts were evaluated to conduct the transesterification of REX-PCL and PET. However, only titanium isopropoxide and dibutyltin dilaurate was found to be effective as a catalyst for the transesterification of REX-PCL and PET.

However, because the titanium isopropoxide was found to be most effective does not mean it can be recommended for every application. The mixture of REX-PCL/PET with titanium isopropoxide was found to be very sticky with reddish brown color. Therefore, this type of catalyst cannot be used for the applications where optical properties of the materials is important.

CONCLUSIONS AND RECOMMENDATIONS

6.1 Reactive Extrusion Polymerization of ϵ -Caprolactone

By reproducing the method developed by Krishnan in 1998, with a few adjustments, REX-PCL with the wide range of molecular weight were produced. Due to the large monomer to initiator ratio, the highest molecular weight of REX-PCL produced was limited to 210,000. The lowest molecular weight of REX-PCL was determined as 20,000 due to the low viscosity of the material that resulted in "extruder underload".

The effect of moisture content in the monomer to the formation of REX-PCL was also evaluated. The results showed the range of molecular weight that can be produced was narrowed to 30,000 to 80,000 in the case of the monomer with the moisture contents. As long as the process conditions were met and the moisture was kept away from the system, the production of REX-PCL shows excellent reproducibility.

Also, the results of the characterization of REX-PCL indicated that the monomer conversion is near 100 % with the particular system for the molecular weight up to 120,000. Furthermore, the results of characterizations indicated that the REX-PCL is thermally less stable but more viscous than the linear PCL.

Additional property analysis, such as mechanical tests and determination of the material density, are recommended in order to determine the applications that the REX-PCL can be utilized.

6.2 Reactive Extrusion Polymerization of Star-Polycaprolactone and Diisocyanate

The REX-PCL was reacted with hexamethylene diisocyanate to produce polyurethane. Although the melt fractures of the materials, as well as the results of the characterization, indicated that the reaction between the REX-PCL and the diisocyanate took place, further analysis are required to determine the exact structure of the material as well as the application that this particular material can be used.

6.3 Transesterification of Star-Polycaprolactone and Polyethylene Terephthalate

Transesterification of REX-PCL and PET were performed. Four types of catalysts were evaluated: triphenylphosphine dissolved in toluene; triphenylphosphine pellets; dibutyltin dilaurate; and titanium isopropoxide. Only titanium isopropoxide and dibutyltin dilaurate was found to be effective.

Although above two catalysts were found to be effective to carry out the transesterification of REX-PCL and PET, it is recommended to perform additional experiments with higher catalyst content for dibutyltin dilaurate and longer residence time or higher reaction temperature for titanium isopropoxide.

6.4 Limitation with Reactive Extrusion

Although an extruder can be utilized to perform various types of reactions, there also has been various limitations to the reactive extrusion process that was encountered during this study. For example, solid was unable to be fed at the middle of the extruder since they tend to stick on the top of a polymer melt and accumulates at the feeding zone.

Additionally, the liquid could not be fed into the zones where the solid materials were present.

If these limitations could be overcome, the application of reactive extrusion process will be significantly broaden.

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