This is to certify that the

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STUDIES ON SYTHESIS OF
COPOLYESTER-AMIDES

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RHUTESH SHAH

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Ramani Narayan
Major professor

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STUDIES ON SYNTHESIS OF COPOLYESTER-AMIDES

By

Rhutesh Shah

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ABSTRACT

STUDIES ON SYNTHESIS OF COPOLYESTER-AMIDES

By

Rhutesh Shah

Copolyester-amides have been synthesized by two different methods : Copolymerization of ε-caprolactone / ε-caprolactam and ester-amide interchange reaction between Nylon 6 and polycaprolactone (PCL). Different catalysts for the copolymerization of ε-caprolactone and ε-caprolactam have been compared and a new catalyst system has been proposed for the rapid copolymerization of the two monomers. A study on the ester-amide interchange reaction between PCL and Nylon 6 has been done over different time periods. Initially, block copolymer is formed, but it gradually becomes random as the reaction time increases. Formation of copolymers was confirmed by DSC and FT-IR spectroscopy studies, while their composition was obtained by proton NMR spectroscopy. The results show a 23% to 29% incorporation of Nylon 6 in the PCL chains. A brief treatise is also given on the various methods used for the synthesis of caprolactone.

ACKNOWLEDGMENTS

It has been a great pleasure to work on the synthesis of copolyester-amides. However such a work would not have been possible had I not received the guidance and facilities that I did receive. First and foremost, I am thankful to my advisor, Dr. Ramani Narayan, who has been the guiding light all through my work. I am grateful to the staff at Bioplastics Inc. and Michigan Biotech Institute (MBI) for providing me with all the facilities and an excellent working environment. Mike Rich and the staff at CMSC and the Department of Chemical Engineering also extended their fullest help and cooperation.

And finally, a special thanks to all my friends for their assistance and encouragement.

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Chapter 1

Introduction

The biodegradation of synthetic polymers is of considerable interest to environmentalists, industrialists, academicians as well as researchers. The study of biodegradation of polymers was initiated to prevent the polymers from attack by micro-organisms in the environment. However this study gained major impetus because of its ecological value [1].

As an important class of biodegradable polymers, aliphatic polyesters have been widely investigated [2,3]. Unfortunately the softening points (T_m) of synthetic aliphatic polyesters are too low to permit their use as a material in plastic applications. This restricts their applications to the biomedical area [2], adhesives and mold releasing. On the other hand, commercial aliphatic polyamides as a class have a wide range of properties and therefore a wide range of applications. However most of them are non-biodegradable. The large concentration of hydrogen bonds and the high regularity of the polyamide structure are the possible reasons for the inertness of these nylons to biodegradation.

On the basis of the above facts, copolyester-amides composed of esters and amides could potentially be a class of biodegradable polymers which would have better physical properties than polyesters [4,5]. Goodman et al. [5], Ellis [7], and Korshak et al. [8] studied the copolyesteramides synthesized from epsilon caprolactone (monomer for

PCL) and epsilon caprolactam (monomer for nylon-6). Tokiwa et al [4,6] and Chen [9] have shown that these copolyesteramides can be biodegraded by microbial activity or hydrolysis.

1.1 Objective

The goal of this work was to synthesize copolyamide-esters (CPAEs) which have a higher melting point as compared to aliphatic polyesters and at the same time are biodegradable. This would widen the applicability of biodegradable polymers to various fields. To attain this objective, studies were done on the copolymerization of caprolactone and caprolactam with different catalysts. A new catalytic system has been proposed which results in the rapid copolymerization of the monomers. A study was also done on CPAE synthesis by ester-amide interchange reaction between nylon 6 and PCL.

1.2 Structure of the Thesis

The following paragraphs give a brief outline of the contents in each chapter of this thesis :

Chapter 2 gives a basic idea about polymers and the different mechanisms by which polymerization reactions proceed. The chapter also gives a brief idea about copolymerization, the conditions under which copolymers can be synthesized and the problems associated with copolymerization of ring structured monomers of different chemical nature. This is followed by a brief treatise on Exchange reactions.

Chapter 3 provides information on the constituent materials. The monomers, their nature and properties are discussed. It also includes a description of the various catalysts and co-catalyst employed for the copolymerization of ε-caprolactone and ε-caprolactam. Also included is a brief description of the polymers and catalysts involved in the ester-amide interchange reaction.

Chapter 4 is concerned with the synthesis of ε-caprolactone. Various present day methods used for the synthesis of ε-caprolactone are discussed along with their advantages and disadvantages. A novel method for the synthesis of ε-caprolactone from ε-caprolactam has been described along with the results obtained.

Chapter 5 deals with the copolymerization of ε-caprolactone and ε-caprolactam. Different catalysts employed for the copolymerization reactions has been discussed along with their mechanism. A new catalytic system comprising a catalyst and a co-catalyst has been proposed. The mechanism of copolymerization catalyzed by this system has been described in detail. This is followed by the experimental results obtained using different catalysts. An effort has been made to compare the copolymer yields obtained with different catalysts for different times.

Chapter 6 covers the synthesis of CPAEs by esteramide interchange between Nylon 6 and PCL. The identification of the copolymer formed was done by IR and its composition was determined by NMR spectroscopy. The results were compared with those of a Nylon 6 - PCL blend.

Chapter 7 presents the conclusions from the thesis and some recommendations for future work

Chapter 2

Background

High polymers are substances of very high molecular weight, which may be natural or synthetic in origin and which have at least some element of structural regularity.

2.1 Classification

Polymers are classified by several classification schemes [10]. The most common classification is based on the polymer structure. Polymers in which the repeating units are linked together to form a straight chain are termed as *linear polymers.*

X--[- M-M-M.....-M-M -]--Y

X and Y are end groups and they represent only a small fraction of the total weight of the polymer. Hence in most cases they can be ignored. The simplest linear polymers are those in which all structural units are identical. Such materials are called *homopolymers,* whilst polymers incorporating two or more chemically different types of structural unit into the chain are termed as *copolymers.*

Copolymers may generally contain two or three different monomers and accordingly are termed binary or ternary copolymers. If the units are arranged in random sequence along the chain then such copolymers are *random copolymers* :

........AABAAABBAABABABBBAAB.......

If the chain consists of large groups of identical units then such copolymers are termed as *block copolymers* :

..........AAAAAAABBBBBBBBAAAAAAA......

Copolymers in which the units alternate along the chain are *alternating copolymers* :

.........ABABABABABABABABAB.........

If all or some of the monomer molecules are *trifunctional* then the polymer may have a nonlinear structure. If the structural units of the side chain are identical to those of the main chain (or backbone) then the polymer is termed as *branched polymer*. If the side chains of a branched polymer are formed from structural units which are different from those of the backbone, the polymer is termed as *graft copolymer.*

Within a polymer a trifunctional unit may react with another trifunctional unit which may cause the joining of the two chains and eventually the formation of a *cross-linked polymer.*

Polymers are also classified based on it's behavior at high temperatures. The term thermoplastic is applied to materials that soften and flow upon application of pressure and heat. Thus most thermoplastic materials can be remolded several times. The term 'thermoset' is applied to materials that, once heated, react irreversibly so that subsequent applications of heat and pressure do not cause them to soften and flow. In this case, a rejected or scrapped piece cannot be ground up and remolded.

Another classification is based on the *physical state.* Polymer molecules may be partially crystalline or completely disordered. The disordered state may be glassy and brittle, or it may be molten with the viscosity characteristic of a liquid or the elasticity we associate with a rubbery solid.

2.2 Polymer Preparation

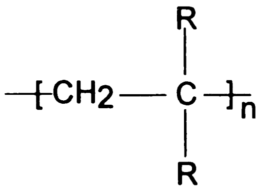
In principle, the main requirement for any molecule to be capable of acting as a structural unit of a polymer is that it should be difunctional. Broadly speaking difunctionality can be achieved in three ways [11, 12] :

1. By opening a double bond (addition polymerization).
2. By using molecules bearing two reactive functional groups (condensation polymerization.).
3. By opening a ring (Ring opening polymerization).

The detailed discussion in this work will be restricted to addition polymerization and ring opening polymerization. However condensation polymerization will be covered briefly.

2.2.1 Addition Polymerization

Substances of the general formula $CH_2{=}CRR'$ are readily polymerized to yield high polymers which can be represented as :



$$-\!\left[\mathrm{CH2} - \underset{\textstyle R}{\overset{\textstyle R}{C}} \right]_n$$

These polymers have a repeat unit which is identical in composition to the monomer, and are formed without loss of any portion of the monomer molecules. Polymers of this type are termed as addition polymers and the reactions producing them are called addition polymerizations.

Addition polymerization of unsaturated monomers invariably proceed by a chain reaction mechanism. Initiation of the chain is usually achieved by addition of an active catalyst, which reacts with the monomer to produce an activated molecule by opening the double bond. Addition of further monomer molecules to those active centers then follows rapidly either until the active center is destroyed by some chemical reaction/ mpurity or until the supply of monomer is exhausted. The polymerization can thus be represented as follows :

I^* + M ===> IM^* ------ Initiation

IM^* + M ===> IMM^*

or in general

$I\text{-}(M)_n{}^*$ + M ===> $I\text{-}(M)_{n+1}{}^*$ ------ Propagation

$I\text{-}(M)_n{}^*$ + ? ===> Inactive polymer ------Termination

The propagating centers in addition polymerization may be any of the following :

1. Free radicals (formed by homolytic opening of the double bond).
2. Anions (formed by heterolytic opening of the double bond).
3. Cations (formed by heterolytic opening of the double bond).
4. Complex coordination compounds.

The mechanism by which growing chains are terminated is dependent upon the nature of the active centers.

Main features of addition polymerization are :

1. Growth occurs by rapid addition of monomer to a small number of active centers.
2. Monomer concentration decreases gradually during the reaction.
3. High molecular weight polymer is present at low conversions.
4. Polymer backbone usually consists exclusively of carbon atoms.

As discussed before, addition polymerization may proceed by free radicals, co-ordinated catalysis, anionic or cationic mechanisms. The focus of this work will be on anionic polymerization systems.

2.2.1.1 Addition Polymerization by anionic mechanism

The term 'anionic polymerization' is used whenever the active bears a negative charge. This does not necessarily imply the presence of a free anion on the growing polymer chain. The negative charge may be a free anion, or a component of an ion pair or a partially ionic bond. Generally all polymerizations initiated by organometallic compounds are referred as 'anionic'.

Initiation of anionic polymerization may take place by :

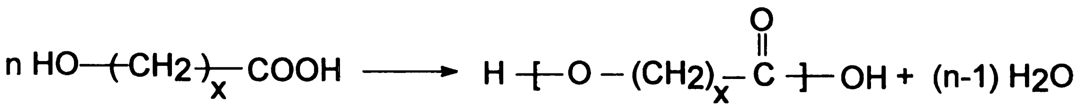
1. addition of an anion to the monomer
2. addition of an electron to produce an anion radical

The most common initiators of the first type are the alkyl and aryl derivatives of the alkali metals, although other substances such as the alkali metal amides, alkoxides, hydroxides and Grignard reagents also fall into this category.

The polymerization then proceeds along by chain reaction mechanism, until the monomer is exhausted or the anion is destroyed by moisture or other impurities. The absence of a termination reaction allows block copolymers of known structure to be prepared by addition of a monomer B to a solution of a living polymer A. However such a reaction is feasible if and only if the living anion of monomer A is capable of initiating polymerization of the second monomer B. It is shown in chapter 5 how this concept has been used efficiently in the synthesis of block copolymers of ε-caprolactone and ε-caprolactam.

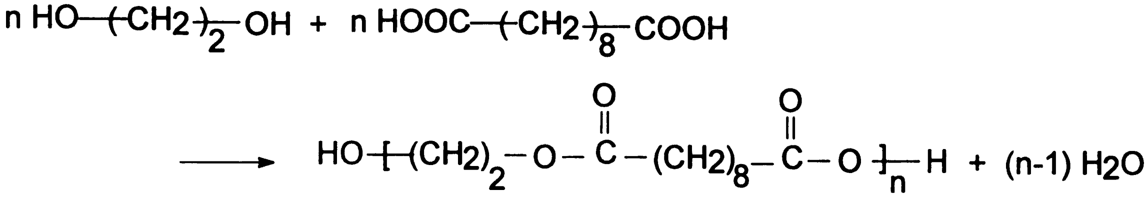
2.2.2 Condensation Polymerization

The term 'condensation polymerization' is used whenever two monomers polymerize with an elimination of water or another simple species. Difunctionality may be achieved by using a single monomer bearing two different functional groups, as for example in the polymerization of a hydroxy acid to yield a polyester :



$$n\,HO-\left(CH_2\right)_x-COOH \longrightarrow H\left[O-(CH_2)_x-\overset{\overset{\displaystyle O}{\|}}{C}\right]OH + (n-1)\,H_2O$$

Alternatively, the two functional groups may be present on different molecules, so that polyesters can also be produced by a diol. An example of this type is the reaction of ethylene glycol with sebacic acid.



$$n\ \mathrm{HO}\!-\!(\mathrm{CH2})_2\!-\!\mathrm{OH} + n\ \mathrm{HOOC}\!-\!(\mathrm{CH2})_8\!-\!\mathrm{COOH} \longrightarrow \mathrm{HO}\!-\![(\mathrm{CH2})_2\!-\!\mathrm{O}\!-\!\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\!-\!(\mathrm{CH2})_8\!-\!\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\!-\!\mathrm{O}]_n\!-\!\mathrm{H} + (n-1)\ \mathrm{H_2O}$$

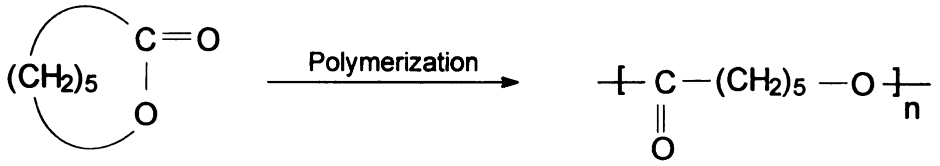
Thus in a condensation polymerization, all of the molecules present are functionally capable of reaction at any time. Polymerization proceeds via stepwise condensation of a molecule with another molecule giving a dimer and then successively giving trimer, tetramer etc. Thus molecular weight increases gradually along with the conversion.

The main features of condensation polymerization are :

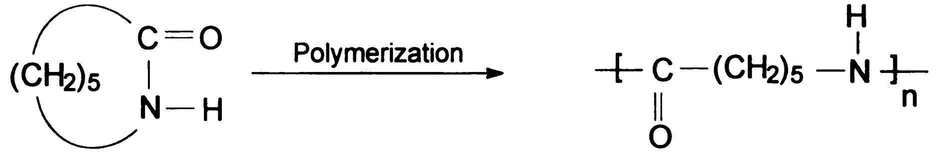
1. Growth occurs by coupling of any two species (monomer or polymer).
2. Monomer disappears well before any high polymer is formed.
3. Polymer molecular weight increases continuously during polymerization. High polymer is present only at very high conversions.
4. Polymer repeat units are normally linked by oxygen and/ or nitrogen atoms.

2.2.3 Ring Opening Polymerization

Polymerization of cyclic monomers to linear polymers by ring-opening mechanisms is a well established method of polymer preparation [12]. It is difficult to classify these reactions into either addition or condensation polymerization since their mechanisms are often typical polyadditions leading to products which are more conveniently considered as condensation polymers. ε-caprolactone can be polymerized by ionic initiation [13].

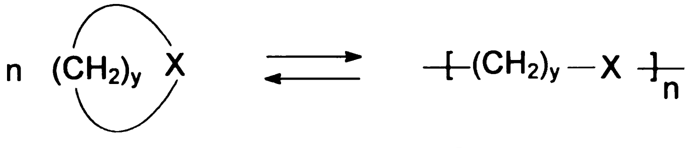


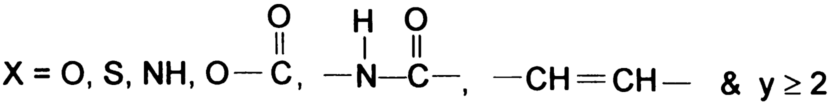
This reaction behaves like a typical addition polymerization reaction; no water is eliminated and the structural unit is directly related to the monomer. However, the product is a linear polyester which would normally be considered as a condensation polymer. Ring opening polymerizations of some compounds may be even more complex, e.g. the polymerization of caprolactam to Nylon 6 [14] :



This reaction involves ring opening polyaddition in the presence of acidic or basic catalysts, but if water is present polymerization may occur in part or my hydrolysis of the monomer to caproic acid followed by polycondensation.

In virtually all such reactions the monomer ring contains atleast one hetero-atom. The classes of structures that may be appropriate for ring opening polymerizations can be simplistically generalized as below [15] :





$$X = O,\ S,\ NH,\ O-\overset{O}{\overset{\|}{C}},\ -\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-,\ -CH{=}CH-\ \ \&\ y \geq 2$$

2.3 Copolymerization

Nowadays copolymerization has grown to be of increasing importance in the industry because of it myriad applications. It is an efficient tool by which the desired properties of two monomers/polymers can be incorporated into one material.

Mayo and Lewis did some pioneering work in the kinetic study of copolymerization reactions and proposed the "Copolymerization Equation"

$$a/b = n = (r_1x + 1) / ((r_2/x) + 1)$$

where,

a/b = the ratio of monomers in the initial polymers.

$x = A/B$ = ratio of monomers in the feed.

$r_1 = K^{aa} / K^{ab}$ = ratio of the propagation constants.

$r_2 = K^{bb} / K^{ba}$ = ratio of the propagation constants.

Copolymerization reactions proceed most commonly by

(a) Free radical mechanism.

(b) Cationic mechanism.

(c) Anionic mechanism.

Block copolymers are readily prepared by the sequential addition of monomers to systems polymerizing under living ionic conditions. However this approach is limited in its applicability by the necessity of meeting two requirements :

1. The monomers involved must all be capable of clean polymerization by the selected propagating mechanism.

   This condition limits the combination of monomers which can be used to make copolymers since, for example, block copolymers of styrene (polymerized anionically) and THF (polymerized cationically) cannot be prepared in this way.

2. The order of monomer addition must be such that the polymer anion generated by the preceding monomer must be capable of initiating rapidly the polymerization of the succeeding monomer.

   This condition restricts the order in which sequences of the polymer segments can be synthesized. For example, living polystyrene can readily initiate the polymerization of ethylene oxide but the alcoholate ion of living polyethylene oxide cannot initiate styrene.

Only a few examples of copolymerization of rings of different chemical nature are known, which is probably associated with the difficulty of running such reactions. The reactivity of ring structured monomers of different chemical nature can differ markedly, as a result of which not copolymers, but a mixture of homopolymers is formed when such monomers are copolymerized [8]. In these cases the task of synthesizing the copolymer reduces to finding such catalysts and such polymerization conditions that the polymerization rate of both monomers will be more or less the same.

2.4 Exchange Reactions

In recent years considerable interest has arisen in the study of reactive blending of polymers and in the exchange reactions which may occur during the melt mixing processes [16, 17]. These reactions provide a facile route for the synthesis / manufacturing of block and random copolymers.

The formation of copolyesters by this route is very popular [45,46]. Studies on the ester interchange reaction in polyethylene terepthalate (PET) has been extensively reported [18, 19].

Simplistically, an ester exchange reaction in polyesters (transesterification) to yield copolyesters is a result of two concurring processes :

1. The formation of copolymer from homopolymers

- A-A-A-A- + -B-B-B-B- ===> -A-A-A-A-B-B-B-B

2. The process in which the copolymer rearranges itself in another copolymer with a different sequence of A and B units along the copolymer chain.

-A-A-A-A-B-B-B-B- =====> -A-B-B-A-A-B-B-A-

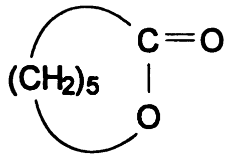
Similar exchange reactions also occur in nylons (transamination reactions)

In this work, copolyamide-esters of Nylon 6 and PCL have been synthesized by an ester- amide interchange reaction (chapter 6).

Chapter 3

Materials

3.1 Epsilon Caprolactone



ε-Caprolactone is an important intermediate in organic synthesis. It is the most commonly manufactured by Baeyer - Villiger reaction between cyclohexanone and peracetic acid. Different variations of this process are used for commercial production. A detailed description of these methods can be found in chapter 4. At present Union Carbide Corp. is the largest producer and supplier of ε-caprolactone in the U.S.

Epsilon caprolactone is an easy to handle, colorless, high boiling liquid that is expected to be a useful chemical intermediate for a wide variety of applications. In chemical synthesis, the molecule is characterized by its reactivity. Cleavage usually takes place at the carbonyl group. The ε-caprolactone used for the co-polymerization reaction with ε-caprolactam was provided by Union Carbide Corporation (Tone® monomer EC). Typical properties of the monomer used are listed in Table 3.1.

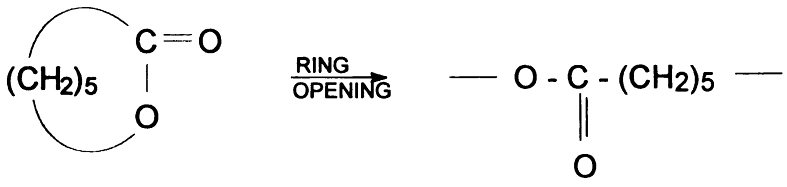
Table 3.1 Physical Properties of Tone® Monomer

Molecular Weight : 114.07
Density (at 20 °C) : 1.0757 g/cc
Boiling Point (at 760 mm Hg) : 235.3 °C
Freezing Point : -1.5 °C
Absolute Viscosity (at 20 °C) : 6.6 cP
Water Solubility (25 °C) : Complete

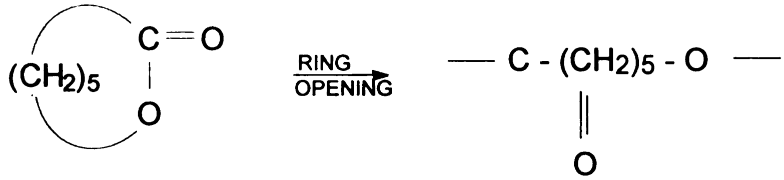
Epsilon caprolactone is also an excellent solvent for many polymers. It can solvate several hard to dissolve resins such as polyurethanes and polyvinylchloride.

It differs in reactivity from its lower homologs, beta-propiolactone and gamma-butyrolactone.

- It is much more prone to polymerize in the presence of active hydrogen compounds and the resulting polymers are not easily depolymerized.
- It is much less prone to react by alkyl oxygen fission than either beta-propiolactone or gamma butyrolactone. Attack by an active hydrogen compound usually takes place at the carbonyl group in ε-caprolactone.



(Very low probability)

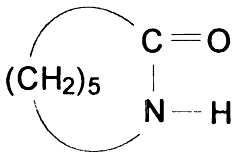


(High Probability)

- Higher reaction temperatures are usually required for reactions with ε-caprolactone than for analogous reactions with beta-propiolactone or gamma-butyrolactone.

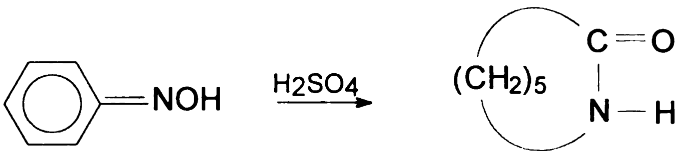
Since ε-caprolactone tends to polymerize easily, it should not be brought into contact with such chemicals which promote its polymerization viz. mineral acids, alkalies, lewis acids, acidic or basic salts and water or water vapor. At elevated temperatures, their effect becomes more pronounced. Ultimately this may lead to gelation or serious reduction in purity. It is advisable to store caprolactone in and inert nitrogen atmosphere.

3.2 Epsilon Caprolactam



ε-Caprolactam is the lactam form of amino caproic acid. It is the commonly used monomer for nylon 6. Caprolactam production in the U.S. rose to 1575 million pounds which was about 4% higher than in 1994 [25].

Caprolactone is manufactured from cyclohexanone oxime (Beckmann rearrangement) which is obtained by treating cyclohexanone with hydroxylamine.



Another process starts with toluene which is oxidized to benzoic acid, hydrogenated to cyclohexane carboxylic acid and then treated with nitrosyl sulfuric acid to produce caprolactam.

ε-Caprolactam is available as highly hygroscopic white crystals which have a melting point of around 70 - 72 °C. Certain basic physical properties are summarized below.

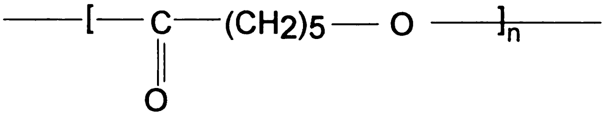
Table 3.2 Physical Properties of ε-Caprolactam

Molecular Weight : 113.16
Boiling Point : 136 °C at 10 mm Hg. 260 °C at 760 mm Hg.
Melting Point : 69 - 72 °C
Refractive Index (liquid) : 1.4797
Density (liquid) : 1.0212
Soluble in : Water, Methanol, Ethanol, Ether, DMF, Chlorinated hydrocarbons

Chemically, caprolactam is capable of forming three series of derivatives, one resulting from substituents on the nitrogen, another from substituents on the carbon chain. It is also used as a solvent for high molecular weight polymers.

ε-Caprolactam used for the synthesis of caprolactone as well as for the copolymerization with ε-caprolactone was supplied by Aldrich. Taking into consideration its hygroscopic nature, it was constantly kept under N_2 atmosphere.

3.3 Polycaprolactone



$$-[-\underset{\underset{O}{\|}}{C}-(CH2)5-O-]_n-$$

Polycaprolactone is a homopolymer of ε-caprolactone.It is a crystalline, low melting (55° C) polymer. It resembles medium density polyethylene in stiffness and has a waxy feel. Commercially available PCL was used for the copolymerization reaction with polycaprolactam (nylon 6). Carothers was the first to carryout the polymerization of ε-caprolactone to PCL by the action of heat and catalysts. The polymerization can proceed by any of the following mechanisms :

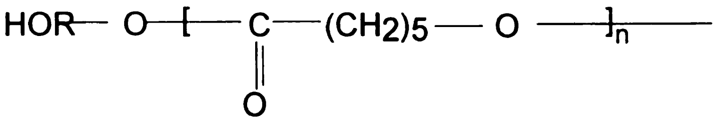
1. Cationic polymerization [20]
2. Anionic polymerization [21]
3. Active hydrogen polymerization [22]
4. Zwitterionic polymerization [23]
5. Coordination polymerization [24]

PCL holds a special advantage over other synthetic polymers : It is biodegradable. It has been shown that PCL resins degrade in environments hospitable to microbial growth. Soil burial tests of molded articles showed degradation, in terms of significant property and weight loss. At the same time it exhibits broad miscibility or mechanical compatibility with many other plastics, including polyethylene, polypropylene, polystyrene, PVC, polycarbonate and PET.

The strength, toughness, low melting point and biodegradability of PCL have been used to advantage in various unique applications :

- Drug delivery system.
- Controlled release of pesticides, herbicides, fertilizers.
- Mulch films, Compost bags.
- Pigment dispersant.
- Improving mold release.
- Adhesive applications.
- Orthopedic applications.

PCL was used supplied by Union Carbide Corporation (TONE® Polymer P-767). This was prepared by initiation with a diol (HO-R-OH) and hence has the following structure :



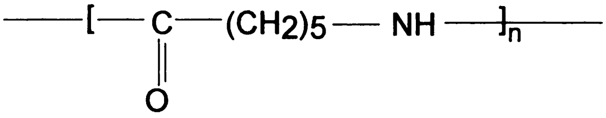
$$HOR-O-[-\underset{\underset{O}{\|}}{C}-(CH_2)_5-O-]_n-$$

Typical physical properties of TONE® Polymer P-767 are listed below :

Table 3.3 Physical Properties of TONE® Polymer P-767

Specific Gravity : 1.1
Melting Point (T_m) : 59 °C
Mn : 30,000 - 40,000
Mw : 45,000 - 60,000

3.4 Polycaprolactam (nylon 6)



$$-[-\underset{\underset{O}{\|}}{C}-(CH_2)_5-NH-]_n-$$

Nylon 6 is a linear homopolymer of ε-caprolactam. It is similar to nylon 66 however there are some basic differences as far as the molecular and crystalline structure is concerned. The fundamental difference lies in the odd number of methylene groups between the amide groups in nylon 6 compared to the even number in nylon 6,6.

Lactam polymerization can proceed by any of the following mechanisms :

1. Cationic polymerization.
2. Anionic polymerization.
3. Hydrolytic polymerization [26].

Pure dry caprolactam does not polymerize when heated for as long as 200 hours. Different catalysts are used for its polymerization and the nature of the catalysts dictates the mechanisms. Recent techniques involve the use of an activating agent (initiator) in addition to a catalyst. Mougin et al [27] talks about such activating agents in his work. Tilman Bartilla [28] was successful in carrying out the polymerization reaction in an extruder. Using hexamethylene diisocyanate as an activator, the reaction reached completion in about 4 - 5 minutes. Other instances of lactam polymerization in an extruder have also been noted [29].

Nylon 6 is white to yellow in color with a melting point of about 223 °C. It is immune to microbiological attack and hence high molecular weight nylon 6 does not biodegrade. It is resistant to most organic chemicals, but dissolved by phenol, cresol, and strong acids. Nylon 6 employed for the copolymerization reaction was supplied by Aldrich. Important physical properties of nylon 6 used are listed below :

Table 3.4 : Physical Properties of Nylon 6

Specific Gravity : 1.084
Melting Point (T_m) : 233 °C
Glass Transition Temperatue (T_m) : 40 °C
Refractive Index : 1.53
Specific Heat : 1.6 J/(g. K)

Nylon 6 has got widespread applications in the manufacturing of tire cords, fishing lines, tow ropes, and woven fabrics.

3.5 Methanol

Anhydrous methanol provided by Aldrich was used for the synthesis of caprolactone. The important physical properties of the methanol used are listed below:

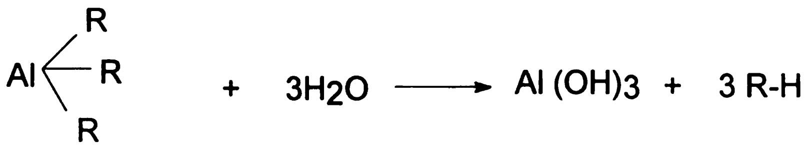
Table 3.5 : Physical Properties of Methanol

Density (25 °C) : 0.78663 g/cc
Boiling Point : 64.7 °C
Freezing Point : -97.68 °C
Viscosity (25 °C) : 0.541 cP
Solubility in water : miscible
Specific heat, liquid (25 °C) : 0.6054 cal/(hr. °C)

3.6 Catalysts

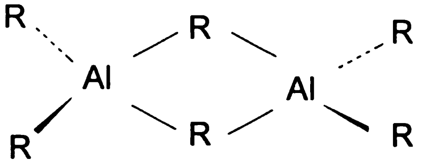
3.6.1 Catalysts for Copolymerization

Different catalysts were employed to catalyze the ε-caprolactam/ε-caprolactone copolymerization reaction. Trialkyl aluminum has been known to be an efficient catalyst for the homopolymerization of lactams and lactones. For this reason, it has been used for the catalysis of the copolymerization reaction of these monomers. However these catalysts are highly moisture sensitive and pyrophoric and hence they require special processing and handling techniques. On exposure to moisture, these react explosively to form aluminum hydroxide.



They are freely soluble in and unreactive with aromatic and saturated aliphatic hydrocarbons. Because such solutions are less likely to ignite simultaneously on contact with air, large quantities are sold in hydrocarbon solution.

Generally R_3Al compounds exist as dimers through electron - deficient bonding. However if the R group is bulky, as in the case of isobutyl, the R_3Al compound is monomeric.



Besides trialkyl aluminum, freshly prepared Na-caprolactam and NaH were also utilized for the anionic copolymerization of epsilon caprolactam and epsilon caprolactone.

3.6.1.1 Triethyl Aluminum (TEA) $Al(C_2H_5)_3$

Triethyl aluminum is the most common of all trialkyl aluminums. Typical properties of TEA used are listed below.

Table 3.6 : Properties of Triethyl Aluminum

State of Association : Dimer
Melting Point : -58 °C
Density (25 °C) : 0.835 g/cc
Viscosity (25 °C) : 2.6 cP

TEA is stable indefinately when stored under an inert atmosphere at ambient temperature. It begins to decompose slowly as shown below at temperatures around 100 °C.

$$(C_2H_5)_3Al \longrightarrow C_2H_4 + (C_2H_5)_2AlH$$

$$(C_2H_5)_2AlH \longrightarrow 2C_2H_4 + Al + 3/2\,H_2$$

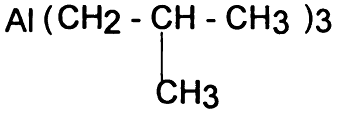
In this work, TEA provided by Aldrich (1.9 M solution in Toluene) was used. Typical present day applications of TEA include :

-- Butadiene Polymerization Catalyst

-- Isoprene Polymerization Catalyst.

-- Propylene Polymerization Cocatalyst.

3.6.1.2 Tri isobutyl Aluminum (TBA)



$$Al(CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3)_3$$

TBA, a higher homolog of the same family differs somewhat from the other trialkyl aluminums because of its branched structure. Typical physical properties of TBA are listed below :

Table 3.7 : Physical Properties of Triisobutyl Aluminum (TBA)

Melting Point : 0 °C
Density (25 °C) : 0.781 g/cc
Viscosity (25 °C) : 1.9 cP

Prolonged exposure to high temperatures may result in the decomposition of TBA. TBA utilized for the copolymerization reactions in this work was provided by Aldrich as a 1.0 M solution in toluene.

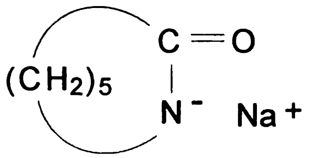
Nowadays TBA is extensively used as a catalyst for several polymerization reactions. These include :

-- Isoprene Polymerization (Ziggler Natta Catalyst)

-- Butadiene Polymerization

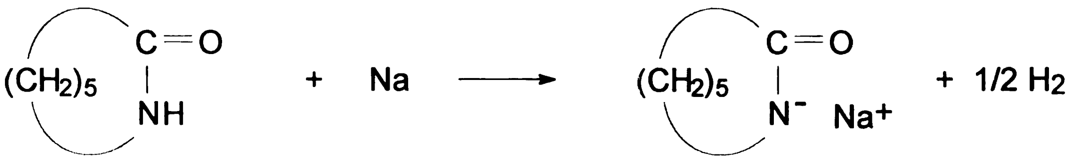
-- Oxetane Polymerization.

3.6.1.3 Na-Caprolactam (NaCL)



Anionic co-polymerization is one of the facile ways for the ring opening copolymerization of caprolactam and caprolactone. The living copolymerization reaction requires initiation by an anionic species. Na-Caprolactam, a sodium salt of caprolactam, has been proved to be nucleophillic enough to initiate the lactam - lactone copolymerization reaction. The mechanism has been discussed in detail in chapter 5.

Freshly prepared Na-caprolactam was used for catalytic purposes. It's synthesis was carried out by two different methods. The basic reaction involved is :



Method I :

Caprolactam was melted at 80 °C in a nitrogen environment. Na metal lumps (under kerosene) were divided into fine particles of about 1 mm size. These were then continuously flushed with N_2 for about 8 hrs to reduce the kerosene content to a minimum. Dried Na was added to molten caprolactam under agitation and was allowed to react/dissolve. The molten reaction mix was then cooled in a teflon tray under N_2.

A thermal analysis of the catalyst formed is shown in fig. 3.1. As seen, it shows a wide melting range from 150 - 240 °C. This can be attributed to the fact that the Na-

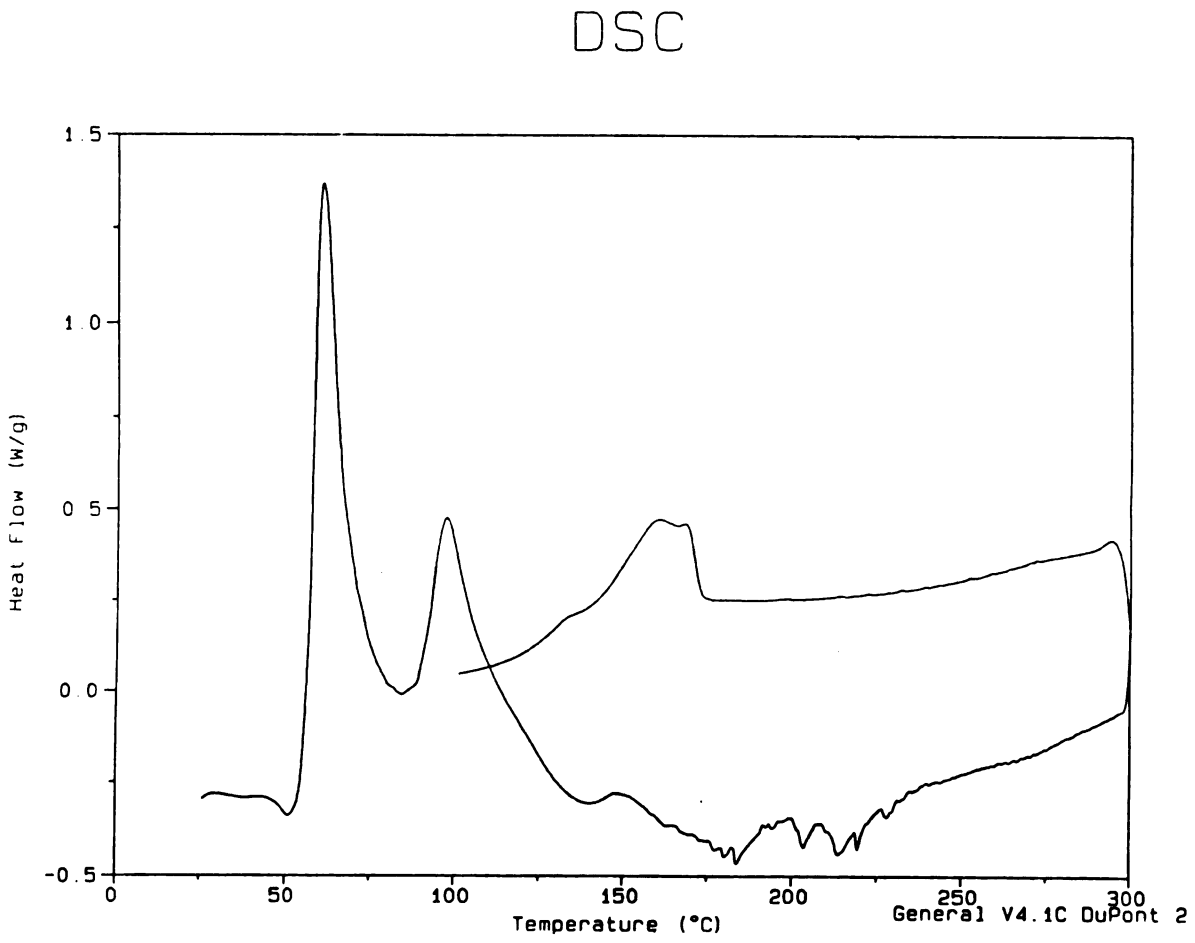


FIGURE 3.1 : DSC PLOT OF SODIUM CAPROLACTAM

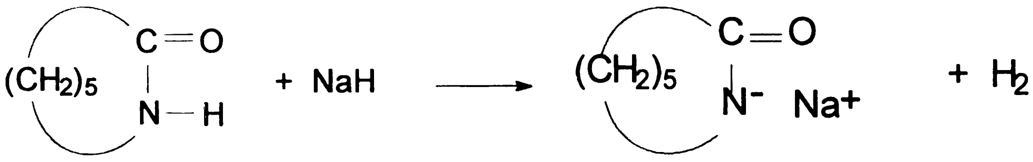
Caprolactam formed, catalyses the polymerization reaction of caprolactam to form high melting polyamides

Method 2 (30) :

Epsilon Caprolactam, Sodium methoxide powder and anhydrous methanol were taken in a flask. ε-Caprolactam was made to react with sodium methoxide under continuous reflux for one hour. Excess methanol was distilled off and the residue was heated under reduced pressure at 120 °C for several hours to remove any residual methanol. The product was stored under nitrogen until required.

3.6.1.4 Sodium Hydride (NaH)

Sodium hydride has alternatively been used to catalyze the ε-caprolactam - ε-caprolactone copolymerization reaction. It reacts with caprolactam for the insitu generation of sodium caprolactam within the reaction mix.



The Na-Caprolactam thus formed catalyzes the copolymerization reaction.

NaH provided as a fine, grey powder by Aldrich Chemicals was used without further purification. Important physical properties of NaH used are listed below :

Table 3.8 : Physical Properties of NaH

Appearance : Grey free flowing powder
Melting Point : 800 °C
Density : 1.396
Reactivity : Reacts explosively with water, violently with lower alcohols, ignites spontaneously on standing in moist air.

3.6.2 Catalysts for Amide - Ester interchange reaction

Zn Acetate has been used as a catalyst for the amide - ester interchange reaction between nylon 6 and PCL. The catalyst was purchased from Aldrich (99.99 %). A few properties of the Zn-Acetate used are listed in table 3.8.

Table 3.9 : Physical Properties of Zinc Acetate

Appearance and Odor : White free flowing powder with an acetous odor
Specific gravity : 1.840
Melting Point : 240 °C

3.7 Activator (Initiator)

Organic polyfunctional isocyanates, usually with two or three isocyanate groups in the molecule, have been particularly useful for the systematic buildup of polymer molecules. As a result they have become the cornerstone of a large new branch of the polymer industry.

Hexamethylene diisocyanate (HDI), a bifunctional isocyanate, was employed as an activator to increase the rate of copolymerization of lactam and lactone. HDI reacts with the Na-Caprolactam catalyst to form an activated catalyst complex which then catalyzes the reaction.

Physically, HDI is a colorless, high boiling liquid. A few important physical properties of the HDI used are listed below in table 3.10.

Table 3.10 : Physical Properties of HDI

Molecular Structure : $O=C=N-(CH_2)_6-N=C=O$
Molecular Weight : 168.2
Boiling Point : 255 °C
Specific Gravity : 1.04
Flash Point : 139 °C

HDI is a highly toxic lachrymator chemical. Exposure to high concentrations can be fatal. Hence great care should be taken during its handling and usage.

Chapter 4

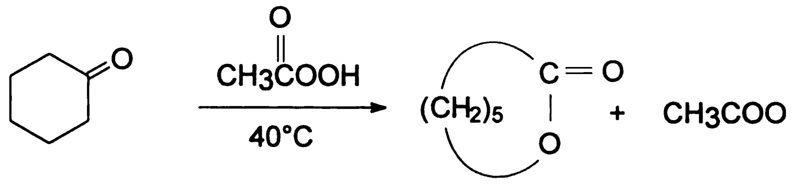
Synthesis of ε-Caprolactone

In the early days ε-caprolactone was prepared by the direct cyclization of ε-hydroxy caproic acid. However, this method is no longer used since intermolecular condensation is a competitive process and both polymer formation and ring closure occur for these 7 membered ring compounds. A variety of synthetic methods are now available for the synthesis of ε-caprolactone. A brief review of these methods is given below. Also a different method was employed for synthesizing caprolactone from caprolactam. A brief description of the method and the results obtained therefrom is also included.

4.1 Different methods for ε-caprolactone synthesis

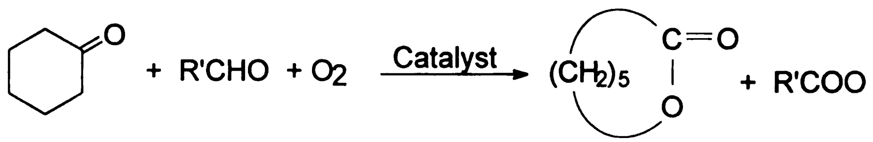
ε-Caprolactone was first synthesized by Baeyer and Villiger in 1899 by oxidation of cyclohexanone. Efforts thereafter were concerned with the use of peroxycompounds such as monopersulfuric acid, mixtures of hydrogen peroxide and acetic acid, anhydrous hydrogen peroxide in hydrogen fluoride and perbenzoic acid as oxidants. However the results obtained by these practices were very poor since, at best, only very small amounts of lactone was obtained.

Phillips et al.[31] disclosed a process using peracetic acid in an inert solvent such as acetone or ethyl acetate. The process gave a yield of 82.5%.



However there were certain disadvantages. The use of peracetic acid is an expensive way of inserting oxygen into a molecule. Additionally, there may be a chance of explosion due to the degradation of peracetic acid.

Union Carbide Corp. discovered a different route [32] for caprolactone synthesis. Cyclohexanone was reacted with an oxygen containing gas and an aldehyde in presence of a metal catalyst to yield ε-caprolactone and a carboxylic acid.



This process had several advantages over the prior methods. The process was relatively less hazardous as compared to the ones involving peroxy compounds. Also, it yields a carboxylic acid as a by product which depends on the aldehyde used. Thus depending on the market position, the aldehyde can be chosen to yield the most advantageous carboxylic acid. However it does have certain disadvantages. The reaction gives a good yield of caprolactone when benzaldehyde is the aldehyde employed (1:1 molar ratio). Benzaldehyde is comparatively expensive and it involves an additional separation cost of separating benzaldehyde from benzoic acid and recycling it.

Recently different processes have come up, which are modified versions of either the basic Baeyer-Villiger process (using peroxy compounds) or the Union Carbide process. Inokuchi et al. [33] synthesized ε-caprolactone by oxidation of cyclohexanone with Ruthenium Dioxide/Manganese Dioxide catalyst in the presence of benzaldehyde (1:3 cyclohexanone to benzaldehyde ratio). They obtained a yield of 79% with the above system in 24 hours. Murahashi et al. [34] synthesized caprolactone by Fe_2O_3 catalyzed Baeyer Villiger oxidation of cyclohexanone with molecular oxygen in the presence of Benzaldehyde (1:3 cyclohexanone to benzaldehyde ratio) and benzene (solvent). They obtained a high isolated yield of 92% of caprolactone in 17 h. Mukaiyama et al. [35] carried out the same oxidation reaction using Nickel (II) complexes as catalysts to obtain a yield of 91% of caprolactone after a 12 h reaction run. Kaneda and Ueno [36] carried out heterogeneous Baeyer-Villiger oxidation of cyclohexanone using an oxidant consisting of molecular oxygen and benzaldehyde in the presence of hydrotalcite catalysts to obtain a 72.6% yield of caprolactone in 5 h.

Frisone and Giovanetti [37] carried out the lactonization of cyclohexanone with hydrogen peroxide using Platinum (II) complexes as catalysts. Jacobson and Mares [38] synthesized caprolactone by the oxidation of cyclohexanone with hydrogen peroxide using arsonated polystyrene resins as catalysts. The results were not encouraging since the caprolactone yield was as low as 40%.

Koch and Chamberlin [38] oxidized cyclohexane to caprolactone using 3-chloro peroxybenzoic acid (m-CPBA) along with Trifluoroacetic acid (TFA). They were able to achieve a high yield of 88% of caprolactone in a short time of 1h. Baeyer Villiger oxidation of cyclohexanone using molecular oxygen and benzaldehyde in the absence of metal catalysts has also been reported [39]. This involved the use of carbon tetrachloride as a solvent. A 90 % yield of ε-caprolactone was obtained after a 5 h reaction.

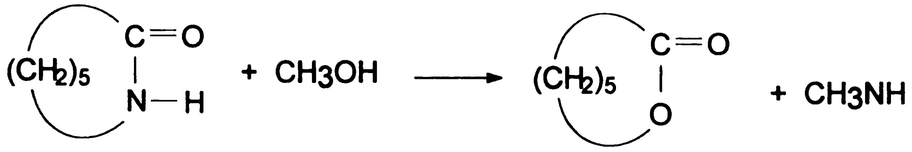
It was shown by Cooper, Henry and Newbold [40] that Urea-hydrogen peroxide (UHP) alone or in combination with carboxylic anhydrides has shown to serve as a valuable alternative to anhydrous hydrogen peroxide in the Baeyer-Villiger reaction. They got a 61% ε-caprolactone yield in a reaction time of 30 minutes.

Besides cyclohexanone, ε-caprolactone can also be synthesized from alcohols or hydroxy esters. Morimoto et al [41] oxidized 1,6 hexanediol with peracetic acid in ethyl acetate in the presence of NaBr catalyst to obtain a 70% yield of ε-caprolactone in 2 hours. Kuno et al [42] carried out the lactonization of ω-hydroxy esters by catalysis with hydrous zirconium (IV) oxide in a glass flow reactor with a fixed bed catalyst. They were successful in achieving a 100% conversion of the ester and a 90.4% yield of caprolactone.

4.2 Synthesis of ε-caprolactone from ε-caprolactam

As seen above, most of the processes for the synthesis of caprolactone involves the use of peracetic acid or other peroxy compounds, or molecular oxygen and benzaldehyde. The use of peroxy compounds is associated with highly hazardous conditions. At the same time the use of benzaldehyde increases the cost of the caprolactone produced. So it was decided to try a different route for the ε-caprolactone synthesis. This involved the usage of cheap and easily accessible products such as ε-caprolactam and methanol. A similar approach was taken by a Polish scientist, Ryszard Heropolitanski [43].

4.2.1 Reaction



4.2.2 Experimental

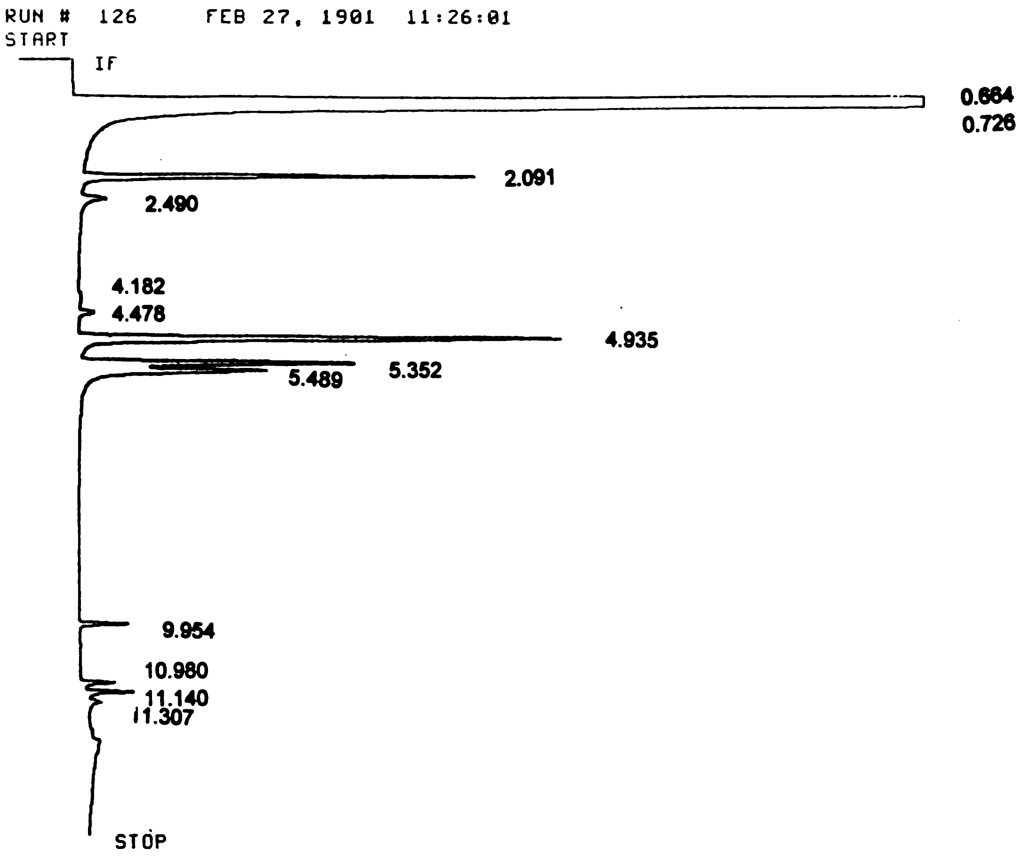
ε-caprolactam was oven dried at 50 °C for 12 hours. 40 g of dried epsilon caprolactam was then dissolved in 103g of anhydrous methanol (molar ratio 1:9). The mixture was then added to a 450 ml bomb reactor (Parr reactor). The reactor was equipped with a pressure gage, a safety rupture disc, gas inlet and outlet tubes, liquid sampling tube, feed back probe and high speed stirrer. The reactor was then sealed. Nitrogen gas was passed through the bomb for 20 minutes to replace the air. The reaction mix was then heated using a heating mantle connected to a Parr 4841 digital controller. The temperature was raised to 290 °C and was held there for 4 hours. The pressure developed during heating was in the range of 1750 - 1820 psi. After 4 hours the heating mantle was replaced by a water bath and the reaction mix was brought down to ambient conditions in about 30 minutes. The reaction run was repeated with a reaction temperature of 310 °C.

4.2.3 Results

At the end of the reaction the volume of the reaction decreased from 164 ml to 146 ml. It was pale yellow in color and had a strong odor of amines which was because of the formation of methyl amine and dimethyl amine. It was then analyzed by gas chromatography.

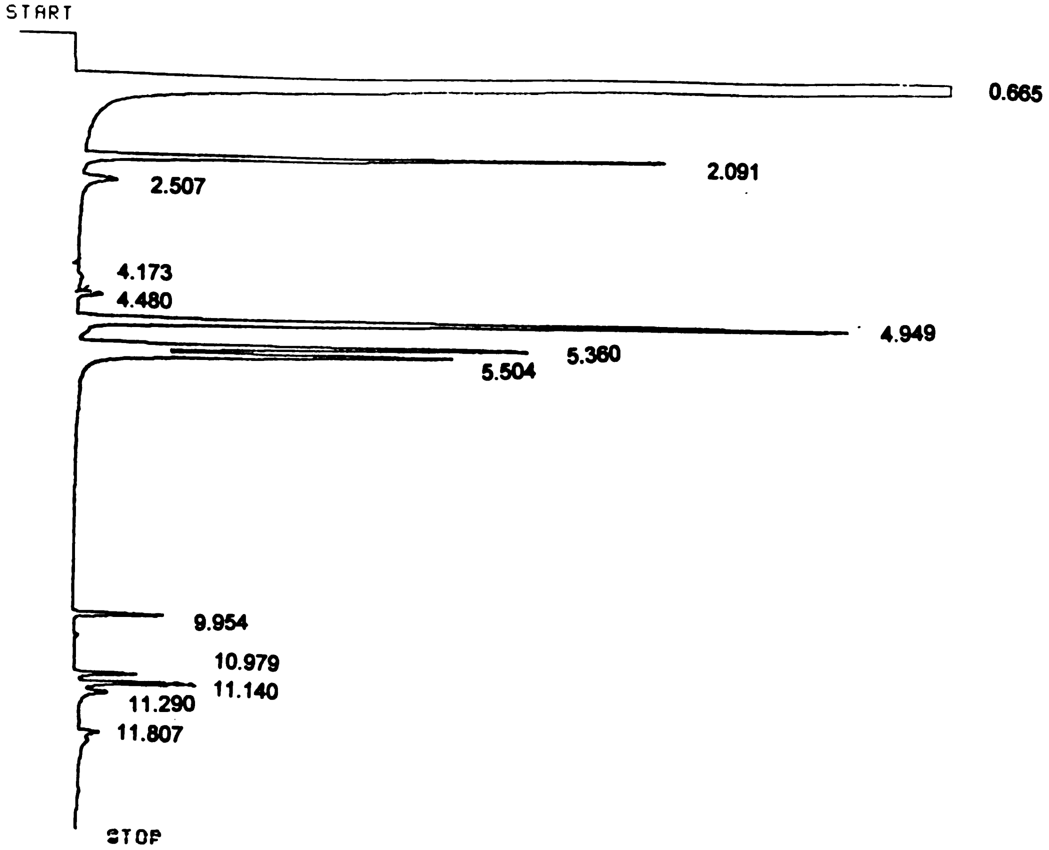
A Hewlett Packard gas chromatograph (model 5890 series II) equipped with an autosampler, was used to analyze the reaction mix. The products were diluted with methanol (1 in 50). The gas chromatogram is shown in figure 4.1. the area under the peaks were compared with the calibration curves for ε-caprolactone and ε-caprolactam. The analysis revealed that the reaction mix contained 1.23 g of ε-caprolactone (RT = 4.478 minutes) and 15.6 g of ε-caprolactam (RT = 5.489). Thus the caprolactam conversion was 61%, however the caprolactone yield based on the caprolactone consumed was 5.04 %. The reaction at 310 °C resulted in similar low yield (figure 4.2). These results do not show any conformity with the results obtained by Heropolitanski [43]. He was successful in obtaining a caprolactone yield of 80% based on the caprolactam consumed.

As seen from the chromatograms, the caprolactam conversion is about 61%. However the selectivity of caprolactone synthesis is very poor and the amount of other products produced are prohibitively high. It is possible that Heropolitanski might have used a catalyst which increases the selectivity of the caprolactone synthesis reaction and at the same time inhibits the formation of other byproducts.



Run time	Area	Width	Area %
0.664	309984000	0.098	86.13254
0.726	41300800	0.044	11.47589
2.091	1654822	0.060	0.45981
2.490	193170	0.102	0.05367
4.182	49704	0.154	0.01381
4.478	100327	0.081	0.02788
4.935	2657554	0.078	0.73843
5.352	1504824	0.078	0.41813
5.489	1382319	0.104	0.38409
9.954	186386	0.050	0.05179
10.980	149799	0.059	0.04162
11.140	230481	0.060	0.06404
11.307	187834	0.149	0.05219

FIGURE 4.1 : GAS CHROMATOGRAM OF CAPROLACTONE SYNTHESIS PRODUCT (@ 290 °C)



Run time	Area	Width	Area %
0.665	341050400	.108	96.19840
2.091	2496842	.061	0.78427
2.507	289072	.117	0.08154
4.173	57579	.143	0.01624
4.480	144286	.080	0.04070
4.949	4301811	.080	1.21339
5.360	2360957	.076	0.66594
5.504	2246600	.087	0.63369
9.954	306322	.048	0.08640
10.979	233156	.053	0.06577
11.140	450499	.055	0.12707
11.290	257321	.113	0.07258
11.807	33562	.065	0.01401

FIGURE 4.2 : GAS CHROMATOGRAM OF CAPROLACTONE SYNTHESIS PRODUCT (@ 310 °C)

Chapter 5

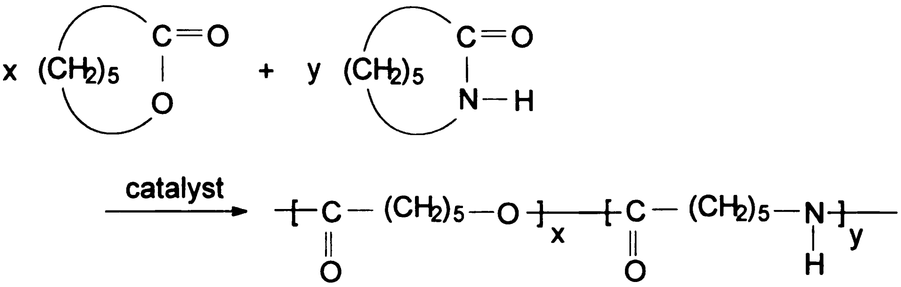
Copolymerization of ε-Caprolactone and ε-Caprolactam

Copolymers of ε-caprolactone and ε-caprolactam were synthesized. Different catalysts and approaches were taken for the synthesis of copolyamide-esters. These were then purified and the reaction time was studied for different degrees of conversion. The principal focus was on achieving the maximum yield in the minimum of time.

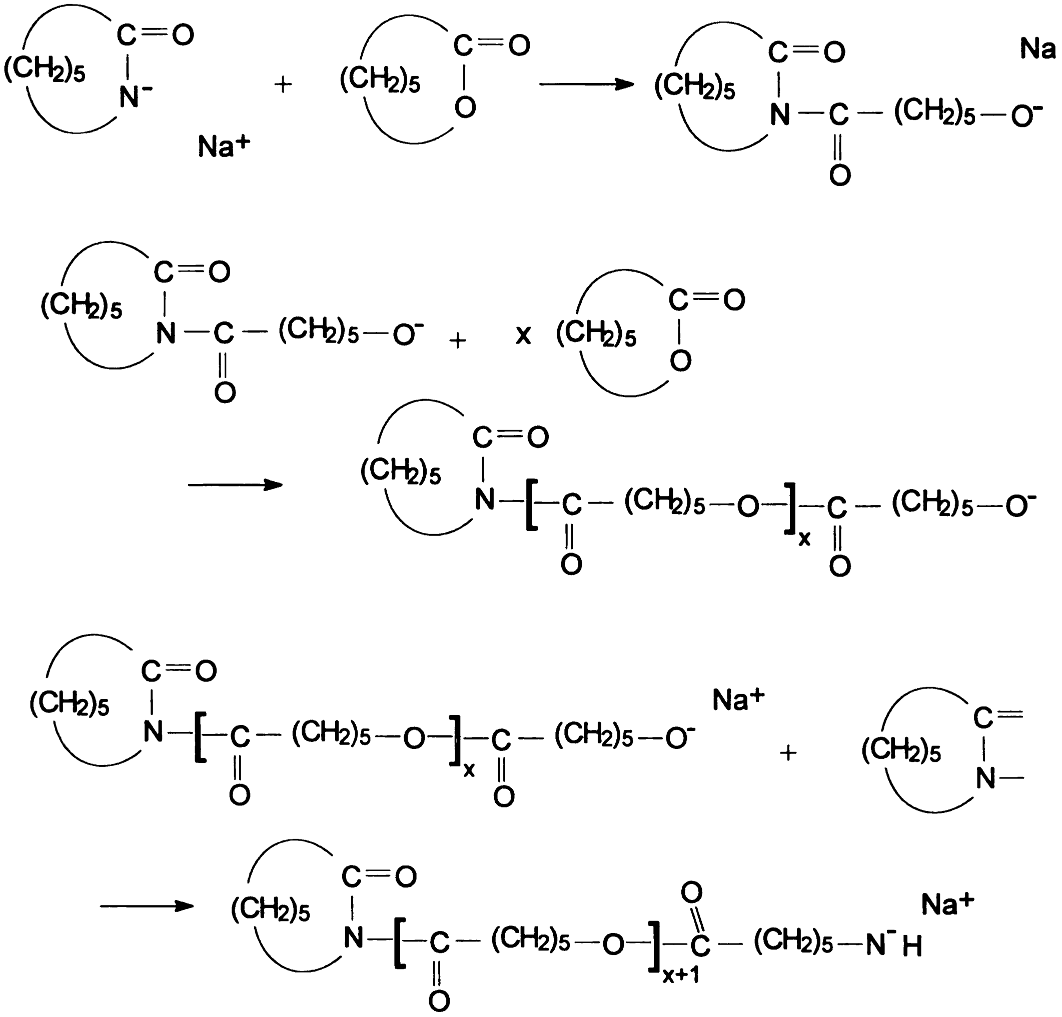
5.1 Pretreatment of Materials :

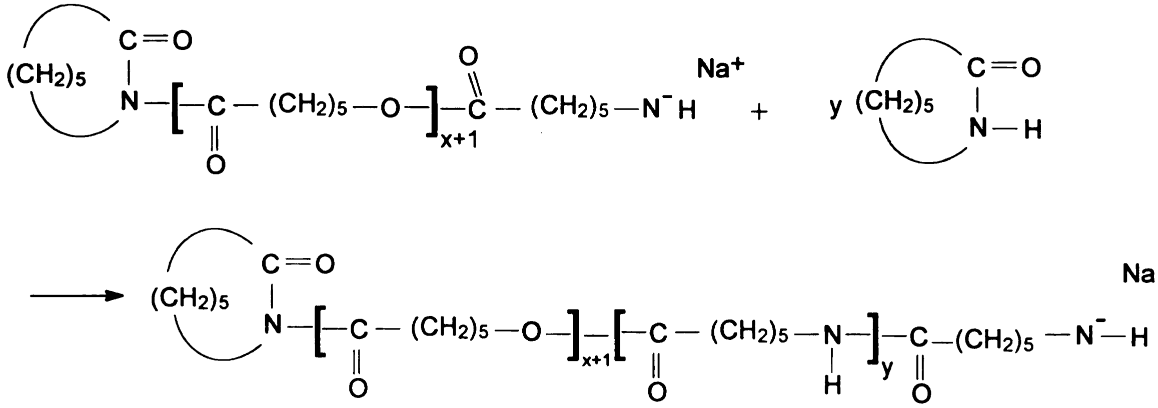
ε-Caprolactone (Tone® monomer) was purchased from Union Carbide Corp. Caprolactam was purchased from Aldrich. Since the copolymerization reaction using sodium caprolactam proceeds by anionic mechanism, it is required that all the reactants and catalysts employed be moisture free. For this purpose, ε-caprolactam was dried in a vacuum oven at 60 °C and 22 in. Hg for 24 hours. Caprolactone which was stored under nitrogen, was heated at 95 °C with calcium hydride for 3 hours to remove all traces of moisture. It was then stored over CaH_2. Na-Caprolactam (synthesized previously) is powdered and dried in a vacuum oven at 60 °C for 24 hours. All materials were stored under nitrogen. Also the transfer of materials was made in the nitrogen glove box.

5.2 Reaction

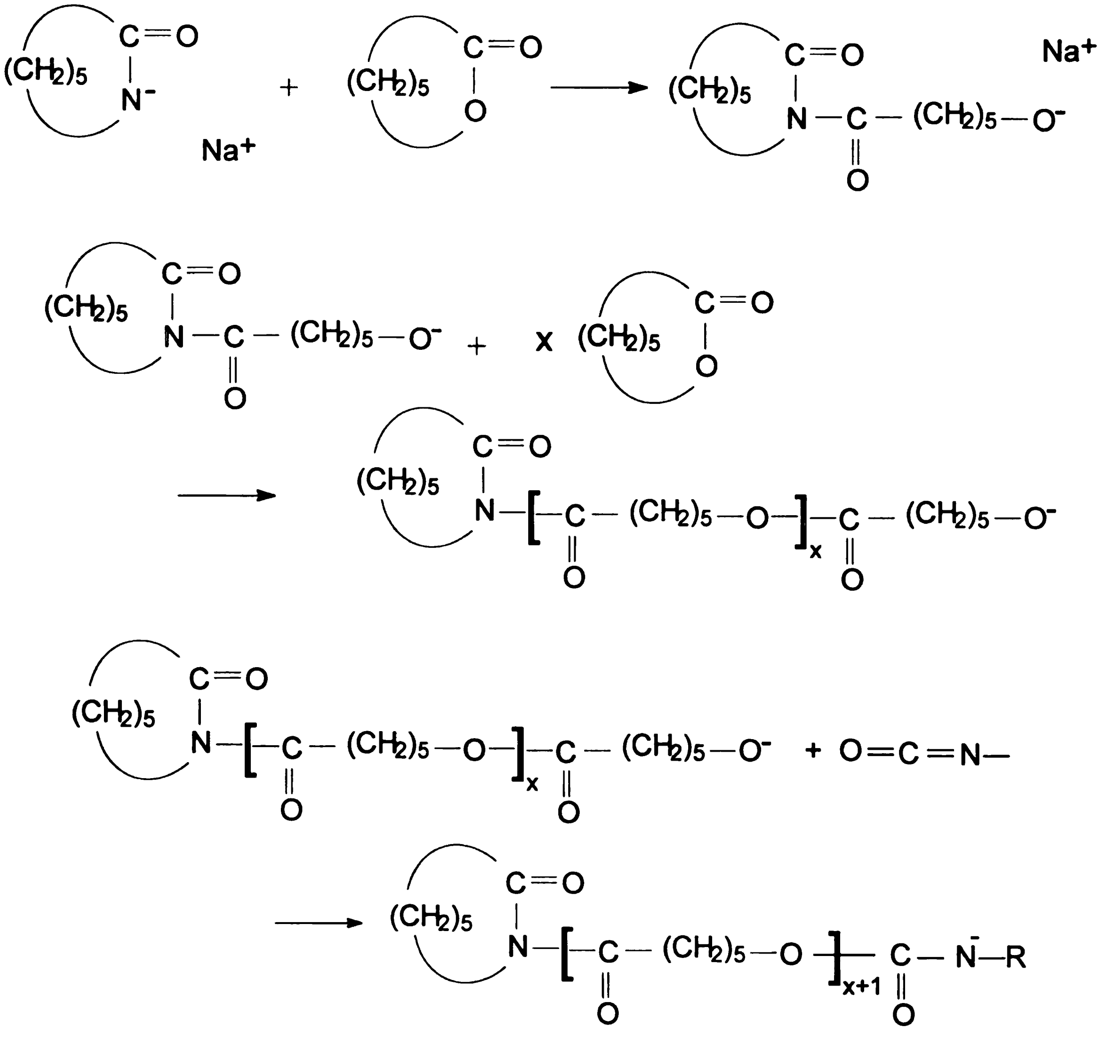


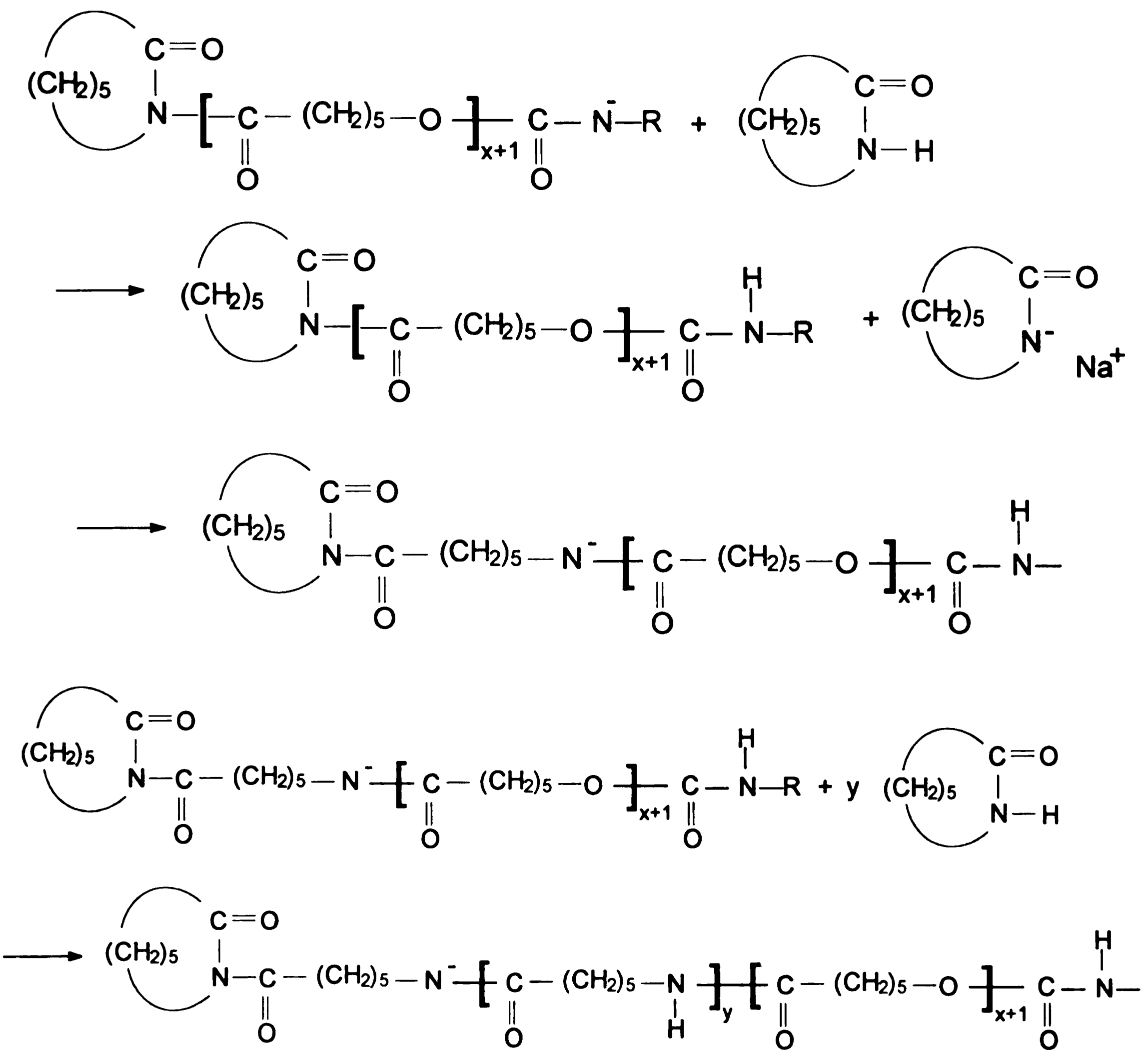
5.2.1 Anionic copolymerization using Na-caprolactam





5.2.2 Anionic copolymerization using Na-caprolactam as catalyst and HMDI as co catalyst.





5.3 Experimental Approach

5.3.1 Copolymerization using Trialkylaluminum as catalyst :

Dried Caprolactam (32.5 g) was taken in a 3 neck flask and melted in an oil bath maintained at 80 °C. TEA was then added (2.3 ml) to it followed by dried caprolactone (17.5 ml). The oil bath was then replaced by another oil bath maintained at 160 °C. The reaction mix was constantly agitated with a stirrer. Typical reaction setup is shown in figure 5.1. Reaction runs were taken for different reaction times. The products were then

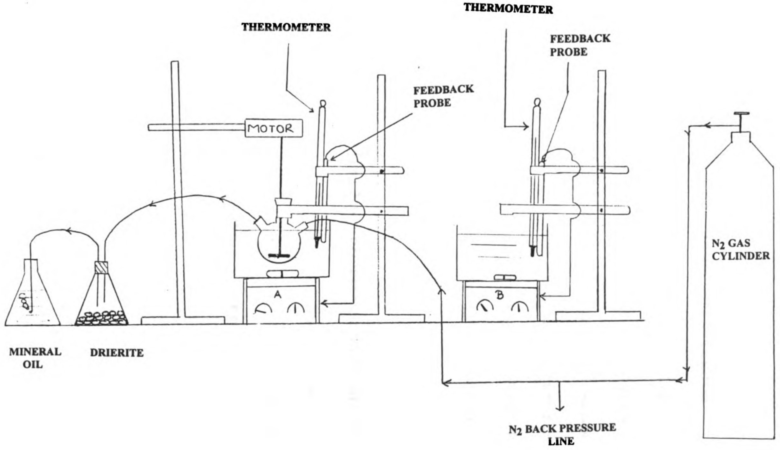


FIGURE 5.1 : EXPERIMENTAL SETUP

quenched at the end of a particular time period. Similar runs were taken using Triisobutyl aluminum (TBA) as catalyst.

5.3.2 Copolymerization using Na-caprolactam as catalyst

Dried Caprolactam (32.5 g) was taken in a 3 neck flask and melted in an oil bath maintained at 80 °C. Dried ε-caprolactone (17.5g) was then added to it and the mixture was allowed to equilibrate for a couple of minutes. 1.0 mole % of Na-caprolactam was added to it [5, 43] and subsequently the oil bath was replaced by another oil bath at 160 °C. The reaction mix was constantly agitated with a mechanical stirrer. Reaction runs were taken for different reaction times. The reaction was terminated by quenching the mix at the end of the stipulated period.

5.3.3 Copolymerization using Na-caprolactam and HMDI (co catalyst)

Dried Caprolactone (17.5 g) was taken in a 3 neck flask and heated at 160 °C. 0.005 g of Na- caprolactam was added to it. The reaction mix was agitated for 5 minutes. Added 0.1 g of HMDI to it followed by molten caprolactam (32.5 g 160 °C). The anionic reaction was stalled by quenching the flask in an ice bath. Runs were taken for different reaction times.

Purification

The reaction products were then purified to obtain polyester-amides. For this a weighed quantity of the solid copolymer was dissolved in a mixture of Chloroform and

Trifluoroethanol (9 : 1). It was then added to diethyl ether, where the copolymer precipitates as a white solid. The copolymer were dried in a vacuum oven at 60 °C for 24 hours.

5.4 Results

Comparison of the copolymer yields obtained using different catalysts for different times is shown in figure 5.2. The structure of the copolymer obtained was confirmed by FT-IR analysis (figure 5.3) which showed a C=O stretching vibration band at 1720 cm^{-1} (ester), C=O stretching vibration band at 1640 cm^{-1} (amide) and N-H bending vibration band at 1550 cm^{-1} (amide).

It can be seen that the caprolactam copolymerization proceeds slowly when complex coordinated catalysts (TEA and TBA) are used. A 1 hour reaction gave a 32% yield of copolymer with TEA and 50% with TBA. On the other hand Anionic copolymerization using Na-caprolactam yielded high yields of 67 % of copolymer in 30 minutes. The addition of an activator HMDI resulted in the rapid incorporation of caprolactam onto the polymer chains. This resulted in a phenomenal 52.5 % yield in 10 minutes and 86 % yield in 30 minutes. The resulting copolymers had very low crystallinity.

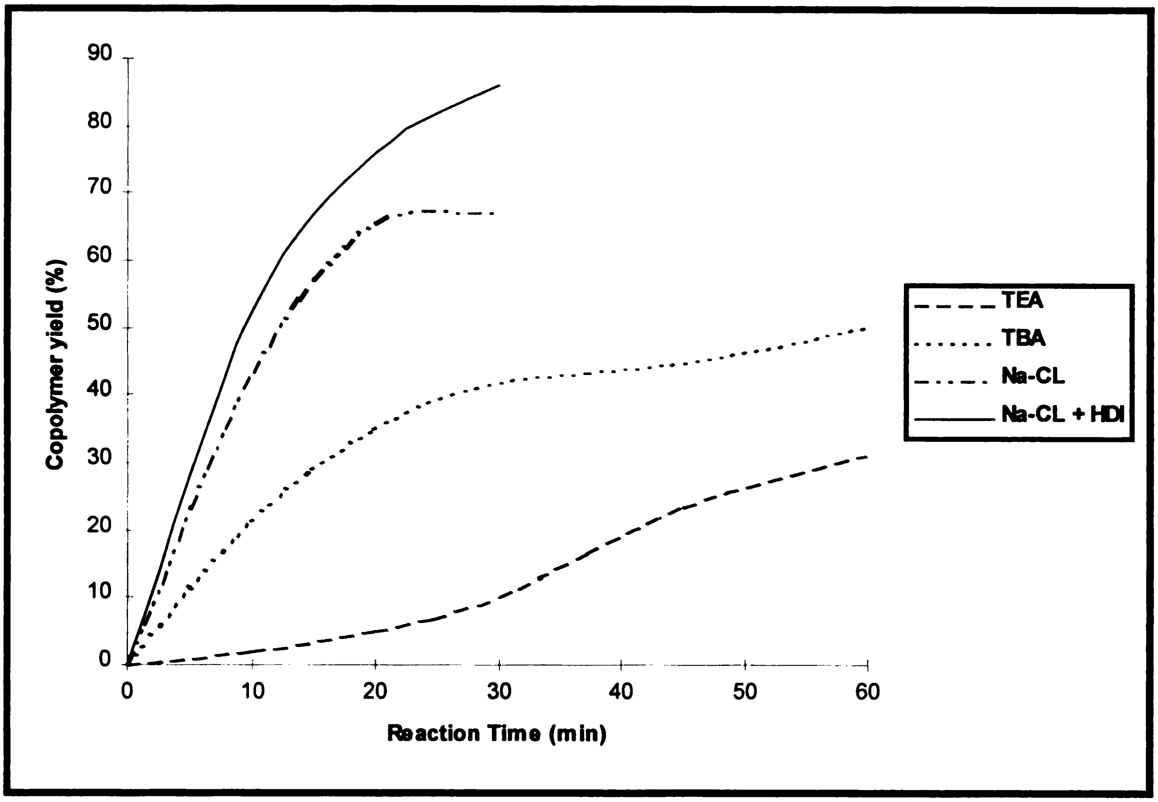


FIGURE 5.2 : COPOLYMER YIELD WITH DIFFERENT CATALSTS FOR DIFFERENT REACTION TIMES

TABLE 5.1 : COPOLYESTER-AMIDE YIELD BY DIFFERENT CATALYSTS OVER DIFFERENT REACTION TIMES

	10 (MIN)	20 (MIN)	30 (MIN)	45 (MIN)	60 (MIN)
TEA	-	-	10.05 %	23.40 %	31.30 %
TBA	21.30 %	-	41.80 %	-	50.30 %
Na-CL	43.50 %	65.34 %	66.99 %	-	--
Na-CL + HDI	52.50 %	76.00 %	86.10 %	-	-

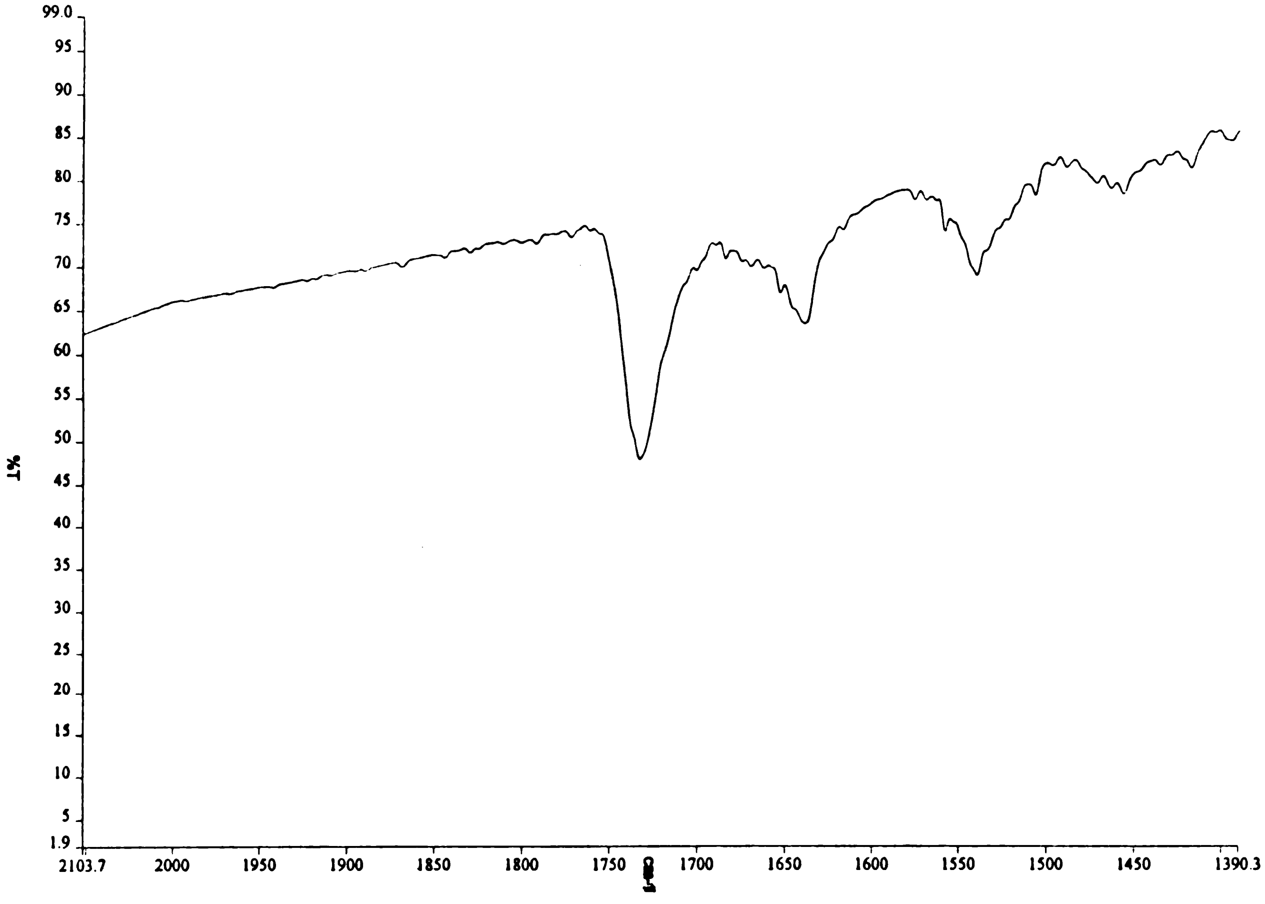


FIGURE 5.3 : IR SPECTRA OF THE COPOLYESTER-AMIDE FORMED

Chapter 6

Ester -Amide Interchange Reaction

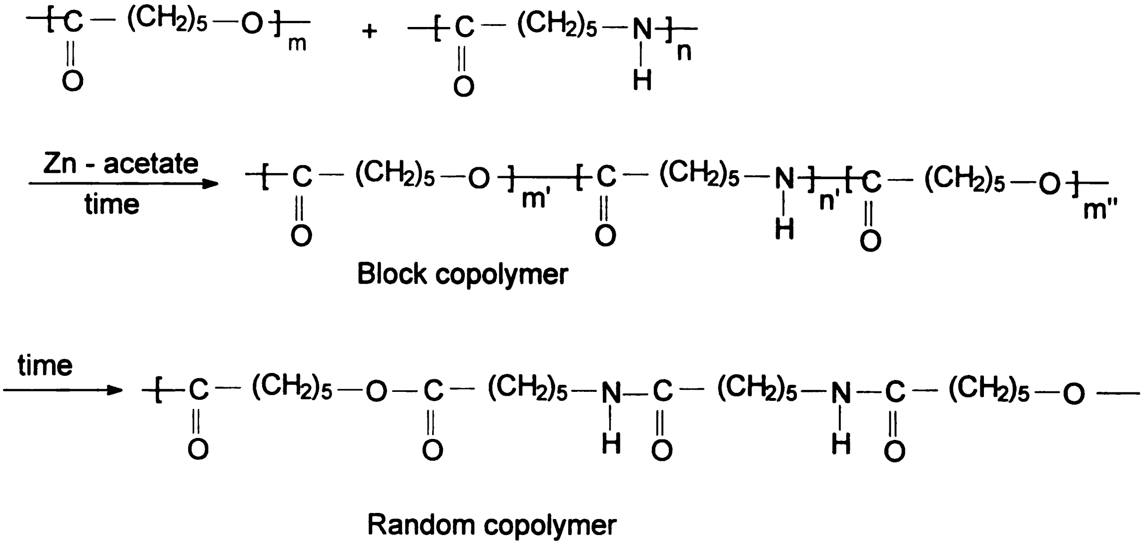
Till now, in this work, the focus for the synthesis of copolyamide - esters (CPAEs) was from the monomers, epsilon caprolactone and epsilon caprolactam. The anionic polymerization of the monomers definitely provides a rapid route to CPAE synthesis. However, there are a sizable number of variables that need to be controlled. An alternate route was also employed for the CPAE synthesis which involved an amide - ester interchange reaction between polyamide and polyester (Nylon 6 and PCL). The structure of the polymer formed was then confirmed by IR and NMR spectroscopy.

6.1 Synthesis of CPAEs

6.1.1 Pretreatment of Materials

Polycaprolactone (TONE ® 767, M_w = 50000) were purchased from Union Carbide Corp. Nylon 6 (M_w = 25000) was purchased from Aldrich Chemical Co. It is required that all materials used, be moisture free. For this purpose, Nylon 6 was dried in a vacuum oven at 70 ° C and 22 in. Hg for 24 hours and PCL was dried at 40° C for 24 hours. The materials were then stored and handled under nitrogen.

6.1.2 Esteramide Interchange Reaction



m', m'' < m and n', n'' < n

An equimolar ratio of PCL and Nylon 6 were taken in a three neck round bottom flask in a nitrogen glove box. 0.5% of anhydrous zinc acetate was added as a catalyst. The mixture was then heated in a heating mantle, under nitrogen and was stirred when it began to melt after a few minutes. The temperature was then raised to 270 ° C and was maintained for a period of 2 hours and 4 hours. Typical experimental setup is shown in figure 6.1. As in the time course of a typical amide - ester interchange reaction, it was found that CPAEs with large blocks were formed in the first stage. The blocks got shortened along with time, and in the final stage random copolymer was formed.

6.1.3 Preparation of Blends

Blends of polyamide and polyester were prepared similarly by stirring PCL and Nylon 6 at 270° C for 2 hours in the absence of a catalyst. Inspite of the absence of a catalyst, a small degree of ester-amide interchange may occur.

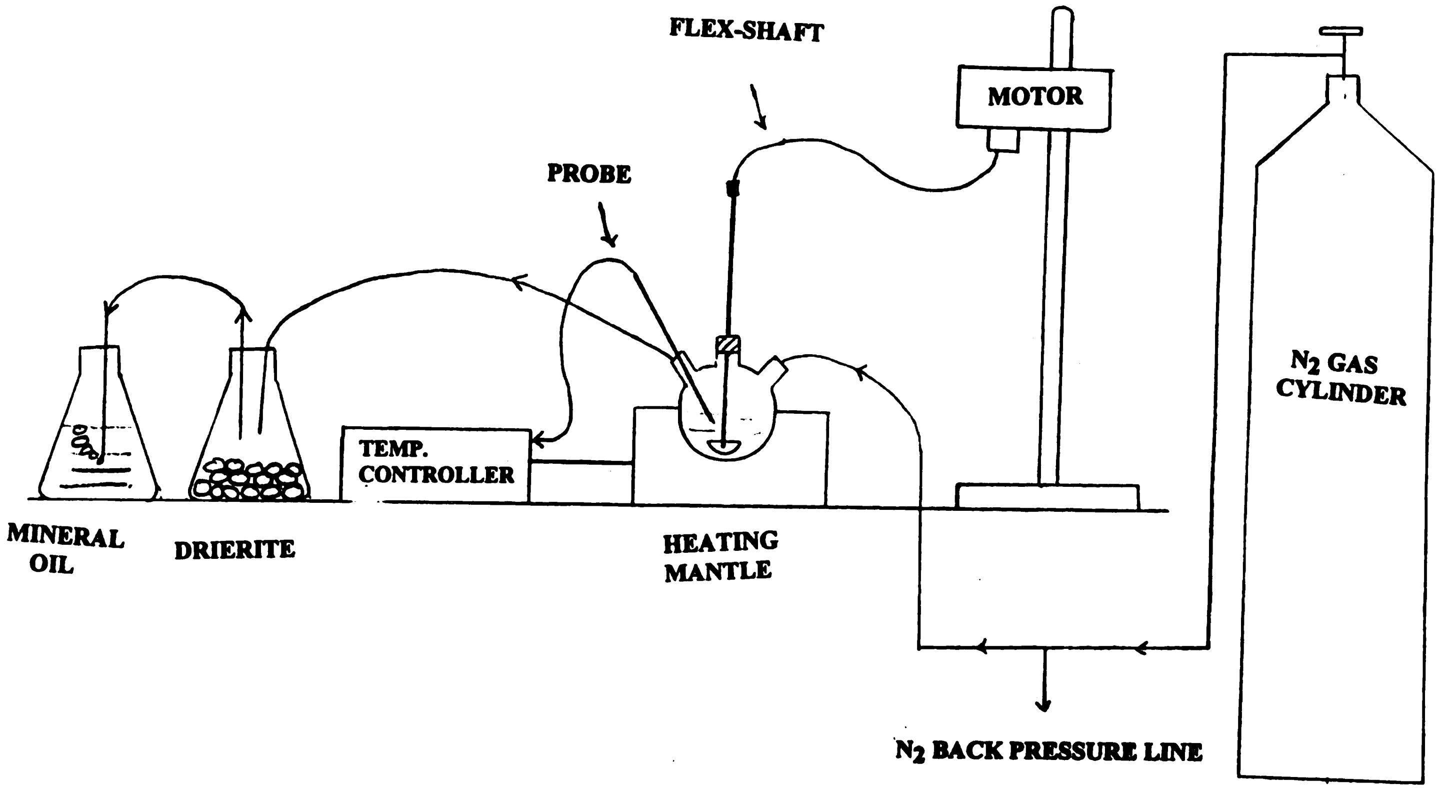


FIGURE 6.1 : EXPERIMENTAL SETUP FOR ESTER-AMIDE INTERCHANGE REACTION

6.2 Analysis

6.2.1 Differential Scanning Calorimetry (DSC)

DSC is an analytical technique in which the difference in heat flow between a sample and an inert reference is measured as a function of time and temperature as both are subjected to a controlled environment of time, temperature, atmosphere and pressure. DSC is used to measure temperatures and heat of transition, specific heat, rate and degree of crystallinity, purity, rate of reaction etc. Since the heating is controlled by a computer it is possible to follow a complex heating algorithm

Thermal Analyst 2200 system (TA Instruments) was used to carryout DSC to observe the depression in the melting point (T_m) of the polymers, especially nylon 6. Conditions of DSC were as follows :

Sample size : 9 - 11 mg

Heating rate : 10° C / min.

Mode : Standard, non-modulated.

6.2.2 Soxhlet extraction

Soxhlet extraction was carried out to separate the nylon incorporated PCL from the PCL incorporated Nylon 6. The extraction apparatus consisted of an Allihn condenser, a soxhlet extractor, a 500 ml flat bottom single necked round flask and cellulose extraction thimbles (figure 6.2) and a hot plate frame.

To extract PCL, chloroform was used since Nylon 6 is insoluble in chloroform. The solid sample was dried and powdered or finely cut. A weighed amount (about 10 g)

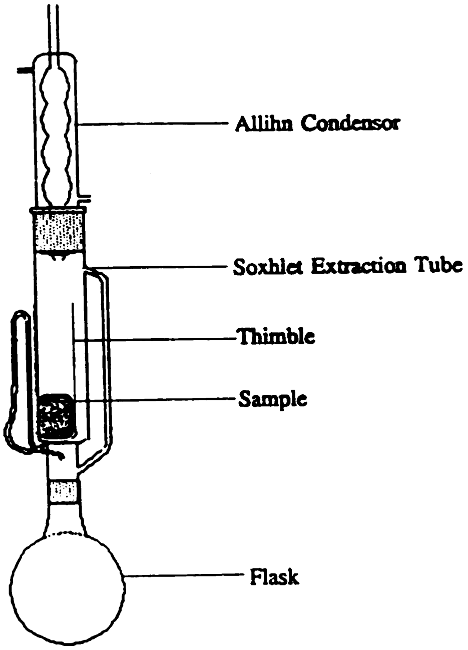


FIGURE 6.2 : SETUP FOR SOXHLET EXTRACTION

of this sample was placed in a cellulose thimble. About 300 ml of chloroform was taken in the dried flask and boiled with the help of a hotplate. The vapors condensed by the water running through the condenser, dripped down into the thimble dissolving PCL. When the solvent level reached a certain height within the extractor, it was automatically flushed back into the flask. Thus the solid copolymer/blend was continuously refluxed with fresh solvent. Extraction was carried out for 48 hours. The thimble were then dried and weighed to give the weight of the residue as the differential weight.

6.2.3 Fourier Transform Infrared Spectroscopy (FT-IR)

The dissolved phase of extraction was then qualitatively analyzed using a FT- IR Spectrometer. A couple of drops of the solution in chloroform were taken on a Type 62 disposable IR cards and were allowed to dry. The cards were then placed in a Perkin Elmer System 2000 FT-IR. The spectrum was recorded in the range of 1400 - 2000 cm^{-1}.

6.2.4 Nuclear Magnetic Resonance Spectroscopy (NMR)

As a confirmatory test for the presence of amide linkages within the PCL chains dissolved in chloroform, a carbon NMR spectrum was collected. The chloroform solution phase from soxhlet extraction was dried in a rotavapor and then in a vacuum oven at 35°C for 24 hours. It was then dissolved in $CDCl_3$ (Duteriated Chloroform) and the solution was then analyzed in a 300 MHz Gemini NMR spectrometer. A proton NMR spectrum was also collected to quantitate the amount of amide within the PCL chains.

6.3 Results and Discussion

The process of the amide ester interchange reaction can be followed by DSC. Fusion peaks for Nylon 6 and PCL are shown in figure 6.3. Fusion peaks in heating, which revealed the reaction between nylon 6 and PCL (molar ratio 1:1) were as shown in figure 6.4. It can be seen that as the reaction proceeds the position of the fusion peaks shifted to lower temperatures, and their shape broadened gradually, possible indicating a decrease in crystallinity. When the reaction time was 240 minutes, the fusion peak due to PCL on the lower temperature side was not detected. Nylon 6 exhibits a clear depression in it's melting point. The fusion peak shifted from 225 °C to 170 °C in 2 hours and to 145 °C in 4 hours. On the other hand, the nylon-PCL blend did not exhibit any major shift in fusion peaks.

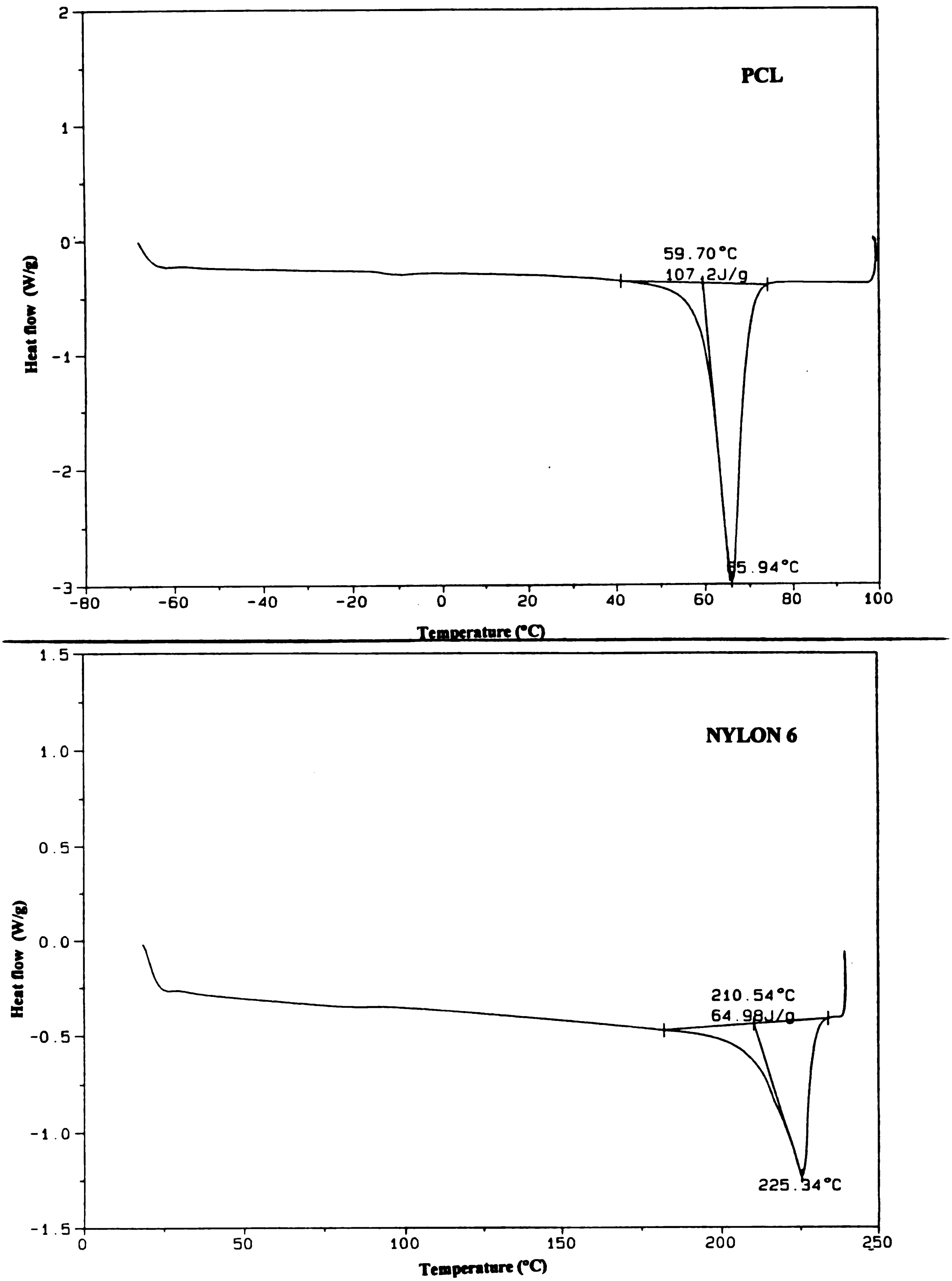


Figure 6.3 : DSC Plots for Nylon 6 and PCL

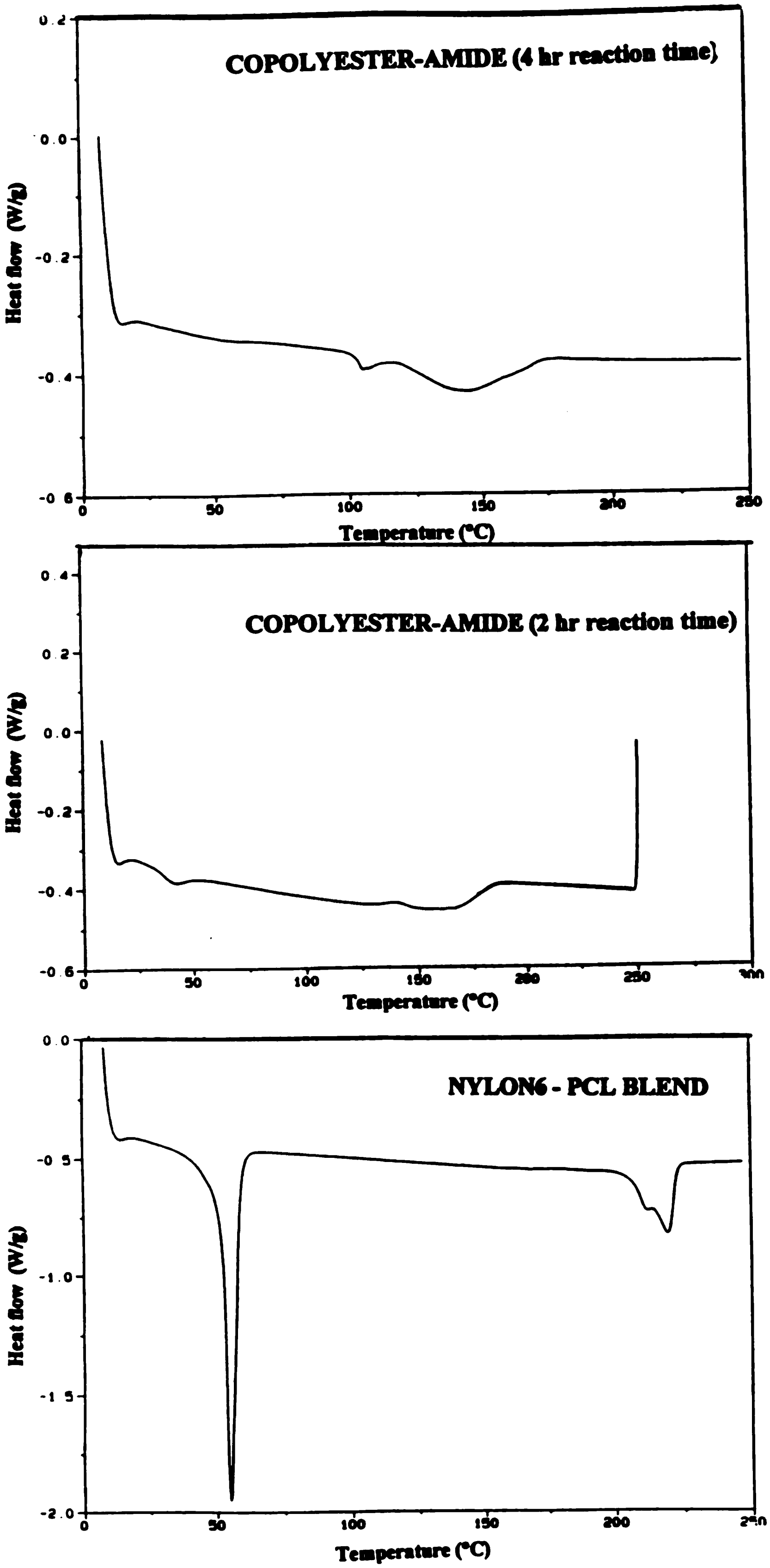


Figure 6.4 : DSC plots of Copolyester - Amides and Nylon-PCL blend

The results of Soxhlet extraction are shown Table 6.1. It is seen that as the reaction time increases the nylon chains get shorter and shorter and more and more of nylon gets incorporated in PCL.

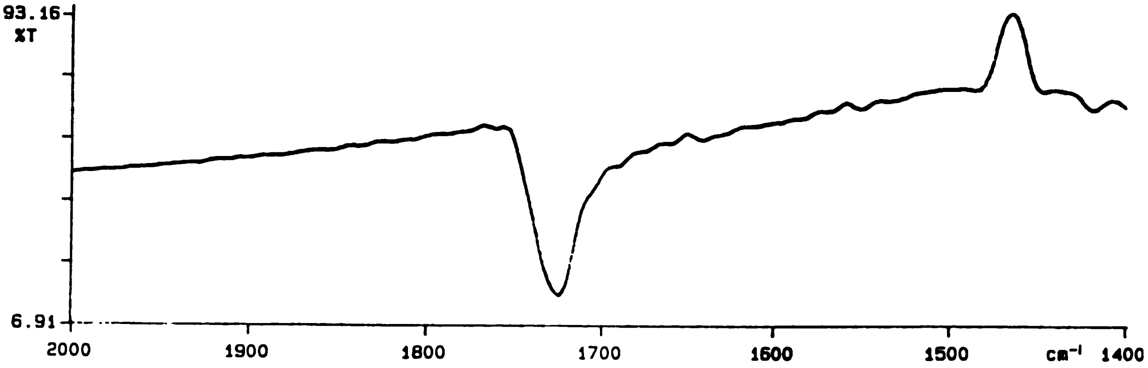
Table 6.1 : Results of Soxhlet Extraction of ester-amide interchange product.

	Sample wt	Sample in solution (g)	Solid Residue (g)	wt% sample in solution	wt % sample in residue
Blend (A)	8.200	5.527	2.673	67.4	32.6
2 h Run (B)	9.880	7.191	2.689	72.8	27.2
4 h Run (C)	10.070	8.455	1.615	83.9	16.1

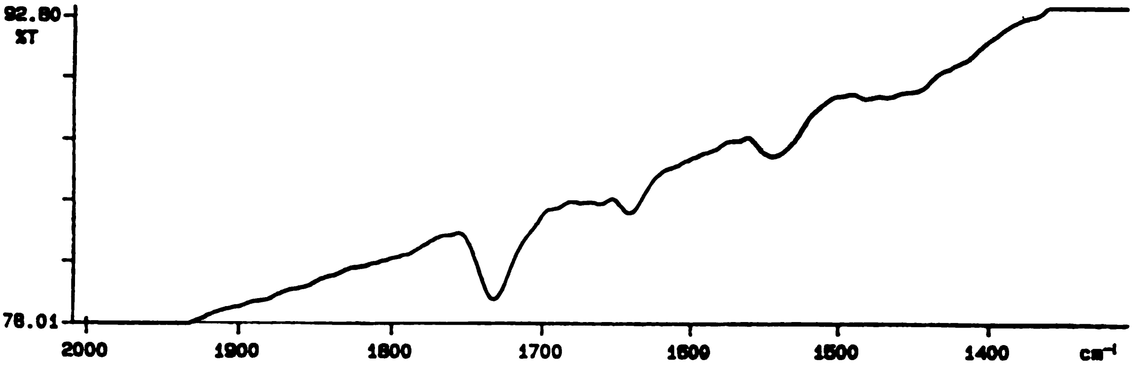
Furthermore, the formation of CPAE was confirmed by infrared analysis of the chloroform soluble fraction (PCL) after soxhlet extraction. Figure 6.5 shows the IR spectra of the product formed after a 4 hour ester-amide interchange reaction. It exhibits an absorption band at 1725 cm^{-1} due to PCL (non-conjugated C=O stretching vibration band). However it also reveals absorption bands due to Nylon 6 at 1640 cm^{-1} (C=O stretching vibration band in amides) and 1550 cm^{-1} (N-H bending vibration band). On the other hand, as shown in figure 6.5, the dissolved phase of the Nylon 6/PCL blend showed the presence of only PCL (1725 cm^{-1}).

To determine quantitatively the amount of amide linkages in PCL, NMR spectroscopy was used. As shown in figure 6.6 and 6.7, the carbon spectra displayed 5 CH_2 peaks of the major component (PCL) and 5 CH_2 peaks of the minor component (Nylon 6). The carbonyl carbon peak of PCL appeared at a shift of 170 ppm. However the carbonyl carbon peak of Nylon 6 was not distinct, but appeared as a shoulder on the carbonyl carbon peak of PCL. The proton NMR on integration demonstrated a PCL to Nylon 6 ratio of 10 : 3 for the two hour ester-amide interchange reaction (figure 6.8) and 10 : 4 for the 4 hour reaction (figure 6.9). The proton NMR of the PCL - Nylon 6 blend displayed only 5 CH_2 peaks corresponding to PCL (figure 6.10).

The above results show that copolyamide-ester was formed by the amide-ester interchange reaction between Nylon 6 and PCL. Another fact that draws attention is that the Nylon incorporation in PCL grew only from 10 : 3 to 10 : 4 when the reaction time was increased from 2 hours to 4 hours. This indicates that in the latter two hour period, the process of the formation of copolymer from homopolymer slows down. However during this period the copolymer rearranges itself into another copolymer with a different and more random sequence of PCL and Nylon 6 along the chain.



PCL-NYLON 6 BLEND



4 HR. ESTER-AMIDE INTERCHANGE REACTION PRODUCT

FIGURE 6.5 : IR SPECTRA OF THE CHLOROFORM SOLUBLE PHASE OF THE REACTION PRODUCT

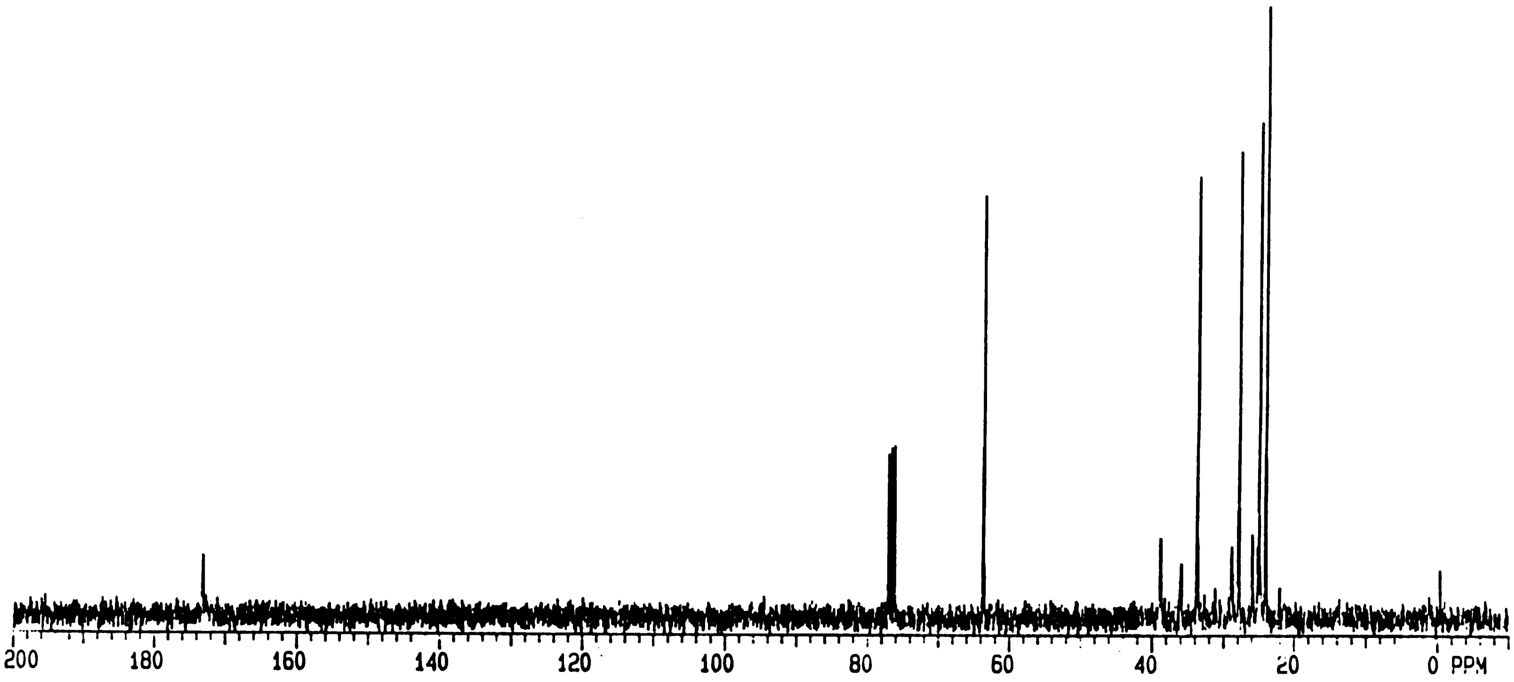


FIGURE 6.6 : CARBON NMR SPECTRA OF THE CHLOROFORM SOLUBLE PHASE OF THE 2 HR. ESTER-AMIDE INTERCHANGE REACTION PRODUCT

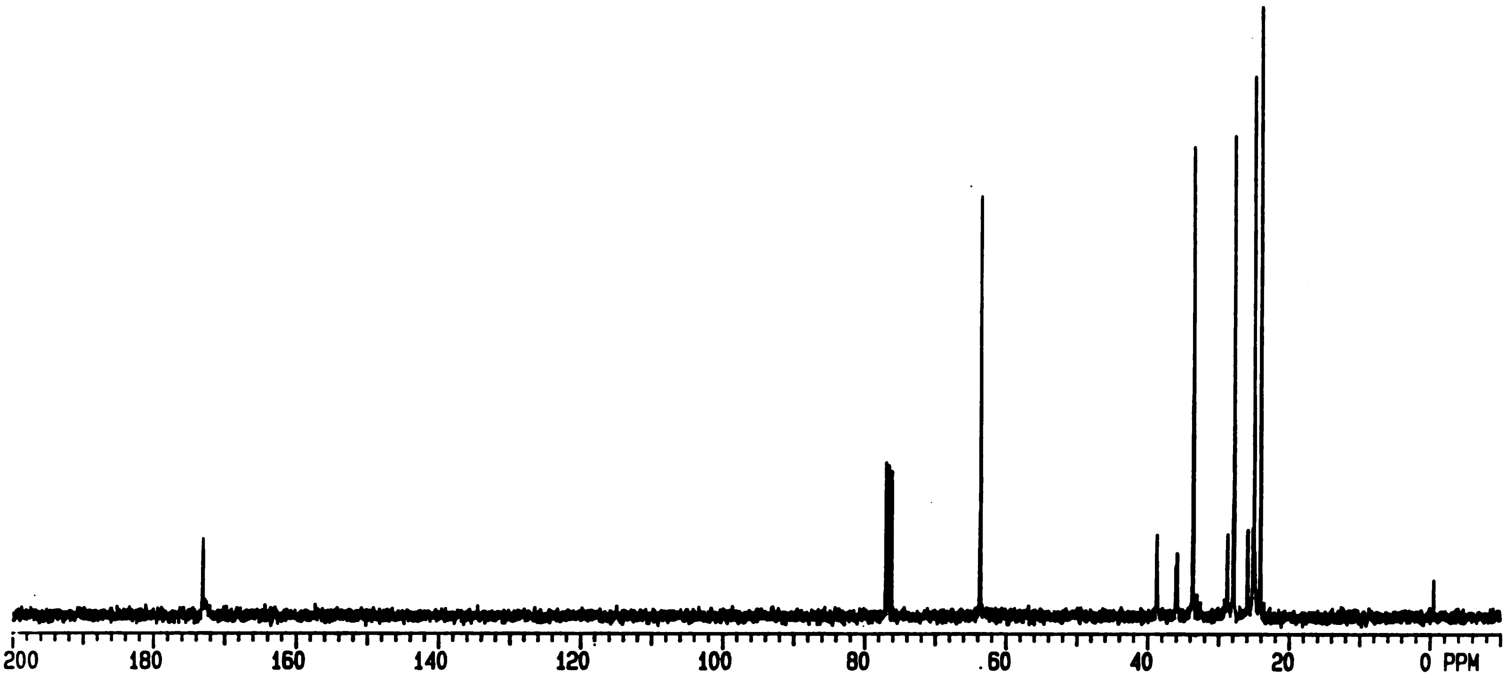


FIGURE 6.7 : CARBON NMR SPECTRA OF THE CHLOROFORM SOLUBLE PHASE OF THE 4 HR. ESTER-AMIDE INTERCHANGE REACTION PRODUCT

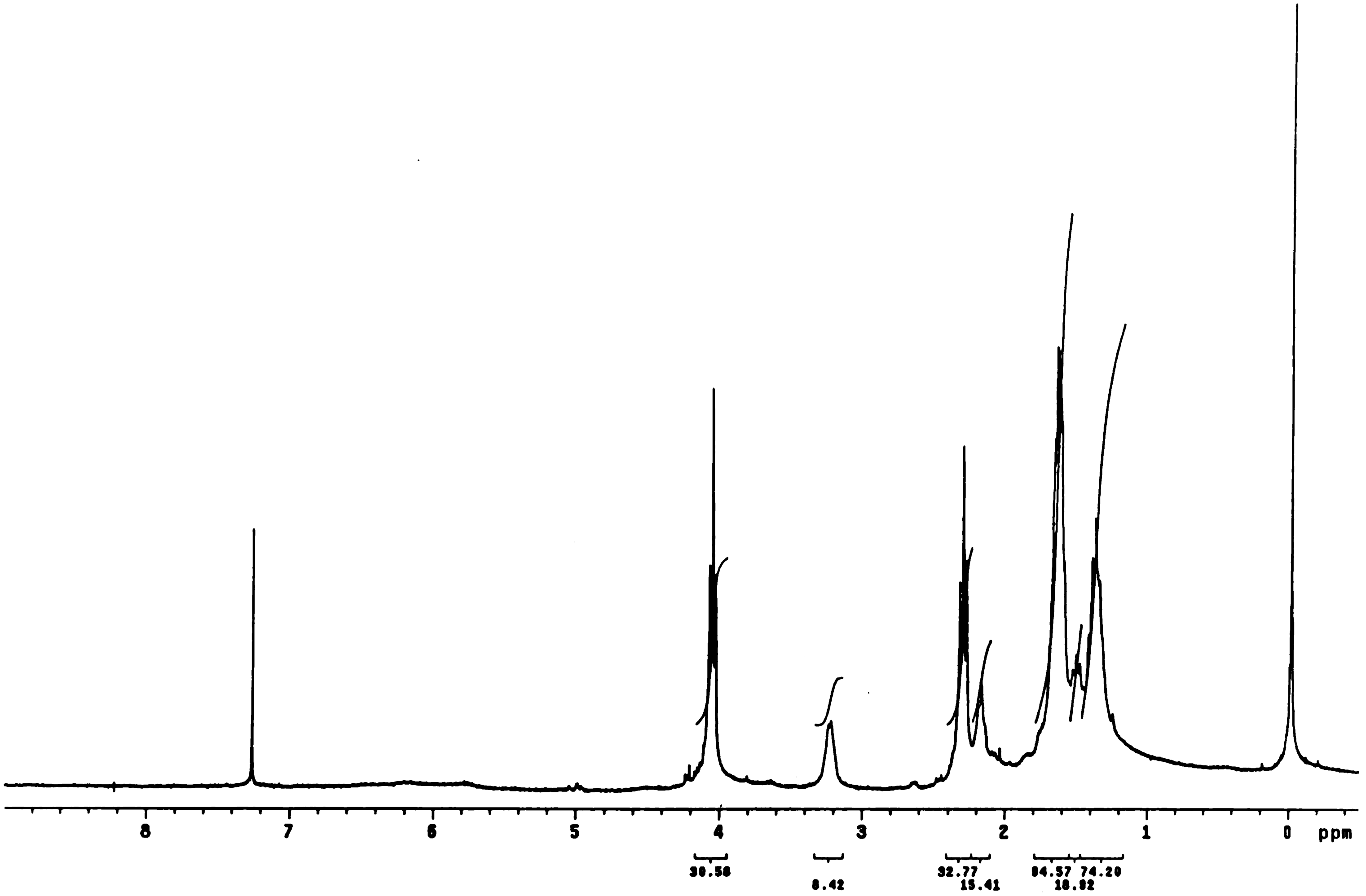


FIGURE 6.8 : PROTON NMR SPECTRA OF THE CHLOROFORM SOLUBLE PHASE OF THE 2 HR. ESTER-AMIDE INTERCHANGE REACTION PRODUCT

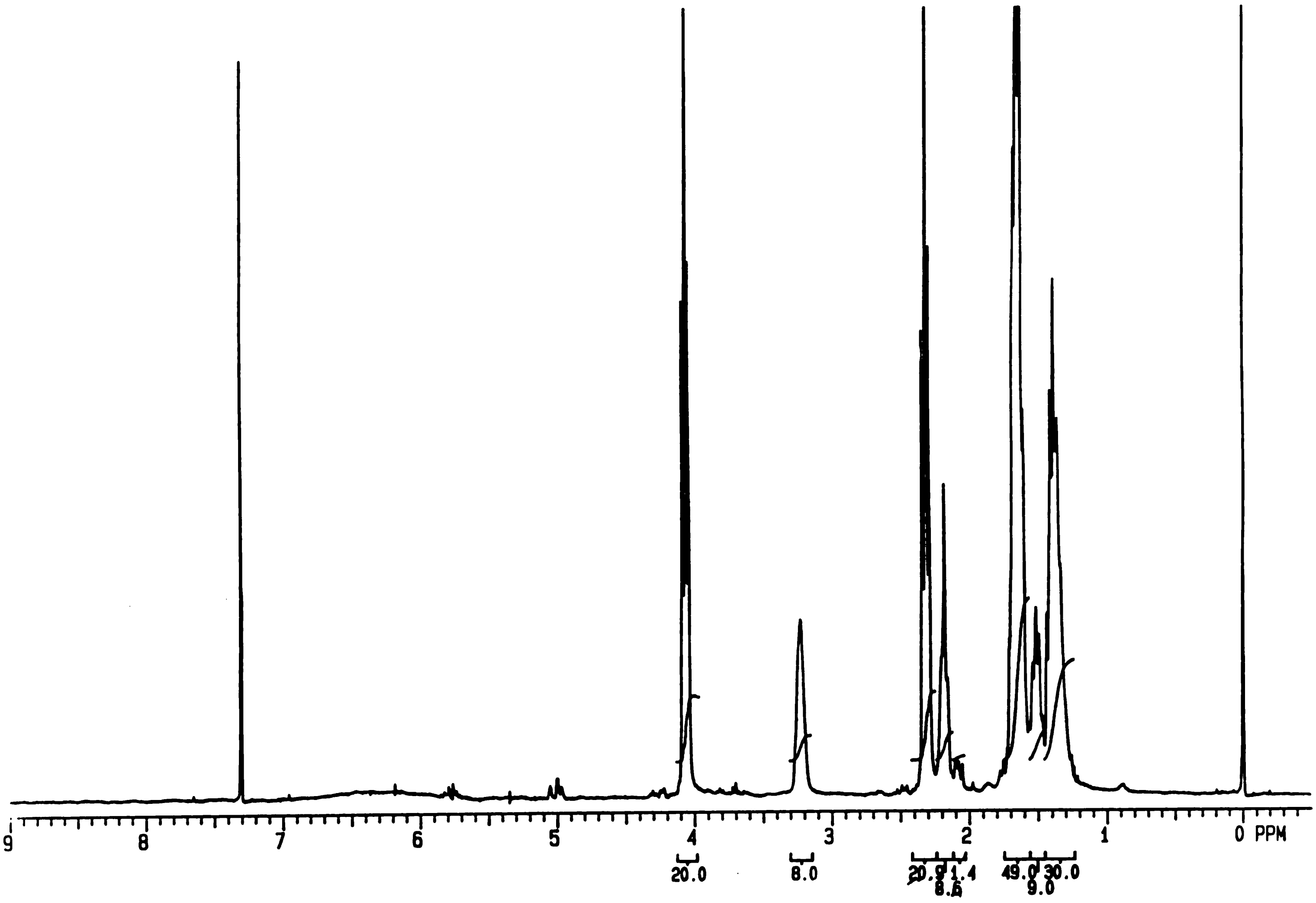


FIGURE 6.9 : PROTON NMR SPECTRA OF THE CHLOROFORM SOLUBLE PHASE OF THE 4 HR. ESTER-AMIDE INTERCHANGE REACTION PRODUCT

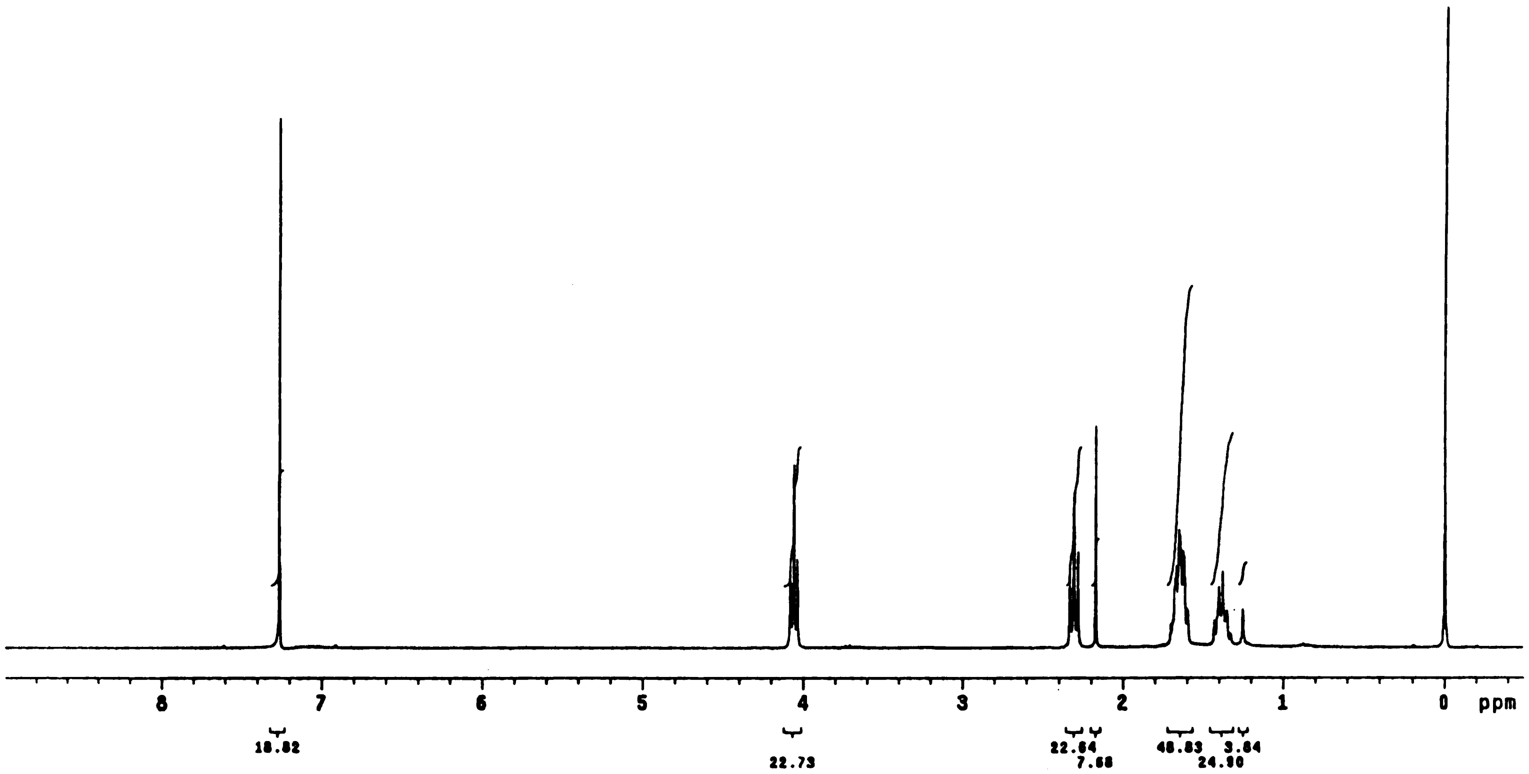


FIGURE 6.10 : PROTON NMR SPECTRA OF THE CHLOROFORM SOLUBLE PHASE OF THE NYLON 6/ PCL BLEND

Chapter 7

Conclusions and Recommendations

7.1 Synthesis of Caprolactone

Studies indicate that the Baeyer Villiger oxidation of cyclohexanone by molecular oxygen and an aldehyde in the presence of a catalyst is the most common method for the manufacturing of ε-caprolactone. However because of the high cost of Benzaldehyde involved, the cost of the caprolactone manufactured remains high. An attempt was made for its synthesis from cheap and easily available material like ε-caprolactam and methanol.

However as shown in chapter 4, the method gives a very low yield of ε-caprolactone. A closer observation of the gas chromatogram indicates that the formation of other complex products from ε-caprolactam is very high. Hence, even though the conversion of caprolactam is about 61%, the yield of ε-caprolactone obtained is unacceptably low. Thus the use of a specific catalyst which may selectively increase the rate of ε-caprolactone formation and simultaneously inhibit other side reactions is required. The discovery of such a catalyst may lead to a commercially viable process for the production of ε-caprolactone ($ 1.9/ lb) from ε-caprolactam ($ 0.90 / lb).

7.2 Synthesis of Copolyamide-esters

Copolyamide-esters were synthesized by two methods :

1. Copolymerization of ε-caprolactam and ε-caprolactone.
2. Ester-amide interchange reaction between Nylon 6 and PCL.

As seen in chapter 4, the copolymerization of ε-caprolactone and ε-caprolactam proceeds much faster with anionic catalysts than by complex coordinated catalysts. However the products formed had very low crystallinity which makes it difficult to measure its melting point. The formation of a copolyamide-ester was confirmed by IR studies. The use of an activator, HMDI along with the catalyst, Na-caprolactam gave a much higher yield of copolymer in a short time. The yield of 52.5 % in 10 minutes and 86% in 30 minutes is much higher than any of the other catalysts. However the molecular weight of the copolymers is very low. If it is possible to further reduce the reaction time, and also increase the molecular weight of the copolymer then it will be possible to carryout an extrusion polymerization in a twin screw extruder, provided proper dry conditions are maintained.

The ester-amide interchange reaction provides a simpler alternative for the CPAE synthesis. The formation of CPAE was confirmed by FT-IR and NMR spectroscopy. The breaking of the polymer chains can be followed by the depression in melting point. Initially block copolymers are formed which gradually rearrange into a more random form as the reaction proceeds. It has been observed that highly random copolymers are more easily biodegraded than the block ones [5]. This is because the polymer chain in a random copolymer, on degradation of PCL linkages will be reduced to monomers and oligomers of caprolactam which degrade easily.

If required a single screw extruder with a pelletizer can be attached at the end of the reactor in which the esteramide reaction has taken place. Thus biodegradable resin pellets can be obtained for further processing like blown film extrusion, injection molding etc.

Since the world is getting more and more environment conscious, such copolymers have a tremendous growth potential in tomorrow's market. A systematic analysis of the mechanical properties of these copolymers may bring out a lot of new applications for it.

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