STUDIES IN POLYESTER FORMING REACTIONS

Thesis submitted to the

UNIVERSITY OF POONA

for the degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

By

Neeta G. Kulkarni

Division of Polymer Science and Engineering

National Chemical Laboratory

PUNE - 411 008

INDIA

NOVEMBER 2005

DEDICATED TO MY PARENTS

AND

HUSBAND

Declaration

Certified that the work incorporated in the thesis "**Studies in Polyester Forming Reactions**" submitted by **Ms. Neeta G. Kulkarni** was carried out by the candidate under my supervision. Such material as have been obtained from other sources has been duly acknowledged in the thesis.

Place: Pune

Date: 14-11-2005

(**Dr. S. Sivaram**)

Research Guide

Acknowledgements

I convey my deep sense of gratitude to my supervisor Dr. S. Sivaram for his constant guidance and valuable advices that have enabled me to complete my research work successfully. His clever insights and extensive knowledge have always inspired me. I consider myself fortunate to have a chance of working with a person like him, who is a rare blend of many unique qualities. The tremendous faith on his students sets him apart from others.

I take this opportunity to thank Dr. C.V. Avadhani for his help and cooperation throughout my research tenure. I am grateful to him for all his contribution towards my research work.

I am thankful to all my lab-mates and colleagues especially Arun, Gnaneshwar and Yanjarappa for their extensive help and cooperation through the entire period of my research in NCL. I also convey my sincerest thanks to Dr. P.P. Wadgaonkar and Mr. Menon for their helpful attitude at all times of need. I am also thankful to all members of Polymer Chemistry Division, NCL, for maintaining a warm and friendly atmosphere.

My special thanks to NMR facility, Glass blowing and Engineering sections, NCL, for their prompt help, whenever sought for.

The most valuable persons in my life without whom this thesis would have been just a dream are my parents, my dearest husband Gururaja and my sweet son Aaditya. The patience, love and encouragement of my husband have been a major driving force during the years of my research career. I am indebted to my parents, who have been a constant source of inspiration that gave me the moral boost to win against odds. I am thankful to all other members of my family for the affection and faith they have been keeping on me since years.

Finally I thank CSIR for the senior research fellowship and the Director, NCL for allowing me to carry out this work at this prestigious institute.

Neeta Kulkarni

CONTENTS

Chapter 2: Scopes and objectives of the present work

Chapter 3: Synthesis and characterization of poly (butylene adipate)s

Chapter 4: Application of chain extension reactions to aliphatic poly (ester)s

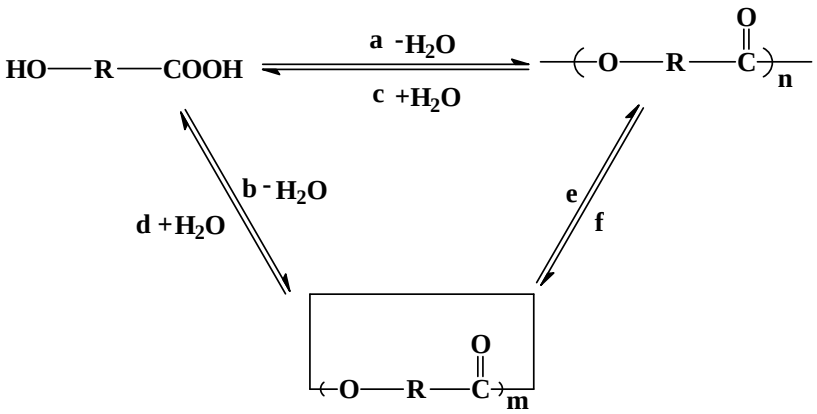
Chapter 1: Structure – property relationships in aliphatic poly (ester)s

1.1 Introduction

Aliphatic polyesters, in recent years, have gained importance as potential environmentally degradable thermoplastics. Interestingly, they received far less attention when Carothers[1-3] first prepared these polyesters in the 1930s from aliphatic acids and diols. Aliphatic polyesters were characterized by low hydrolytic stability and melting points. Currently, there is a renewed interest in the study of aliphatic polyesters or copolyetsers, important among them being poly (butylene succinate-co-adipate), poly (lactic acid) (PLA), poly (caprolactone) (PCL), poly (hydroxy alkanoates), and aliphatic-aromatic copolyesters (AAC). They find a wide variety of applications in injection and blow molded articles, films, bags, thermoformed articles and food contact foam trays to name a few. The AACs have relatively low biodegradability as compared to the other aliphatic polyesters, but can be recycled efficiently like PET. In fact PET production and consumption is strongly driven by the demand for recyclable polymers. The versatility of the ester linkage, to undergo hydrolysis, alcoholysis and acidolysis under certain conditions, makes polyesters the polymers of choice to fulfill the increasing demand for recyclable and/or biodegradable polymers. Hence these polyesters find applications as biocompatible as well as environmentally degradable and recyclable polymers. This chapter broadly discusses the synthetic and mechanistic aspects of aliphatic polyesters, their structure-property relationships and the chemistry of depolymerization of polyesters.

1.2 Synthetic methods for aliphatic poly (ester) s

Synthesis based on ester group formation is of two main types: step-polyesterification reactions of bifunctional reactants and ring opening polymerization of cyclic esters. Another approach is dehydropolycondensation of ω - hydroxy carboxylic acids especially used in the synthesis of poly (lactic acid). The first two types of processes are interrelated by the schematic triangle of equilibria in **Scheme 1.1**, which, for simplicity, illustrates the case of AB-type polyesters, but is expandable to cover all classes of polyesters.



Scheme 1.1: Schematic triangle of equilibria in polyester synthesis

In the self condensation of a hydroxy carboxylic acid, esterification may occur either bimolecularly to form the dimeric hydroxy ester acid or unimolecularly to form the cyclic ester. The dimeric species can react similarly by either of the two routes to form linear trimeric or cyclic dimer, and at each successive step, the same formal possibilities exist leading by path **a** (for wholly intermolecular processes) to linear polyester, or by path **b** (for wholly intramolecular processes) to cyclic oligoesters. The reverse reactions **c** and **d** represent the hydrolysis equilibria of the ester species. Reaction path **e** then represents ring-opening polymerization of the cyclic esters to linear polyesters, and its reverse **f** is the depolymerization of the latter; **e** and **f** together, thus, indicate the possibility of ring – chain equilibration between the species concerned. Which of the processes in the overall scheme actually takes place or dominates in any particular case critically depends on the structures involved, conditions of the reaction, and availability of suitable catalysts. The formation of high molecular weight linear polyesters commonly results in the presence of some proportion of families of cyclic oligomers with various low values of m. Correspondingly, interconversions of the linear and cyclic species to the relevant equilibrium concentrations can be achieved by suitable thermal and/or catalytic treatments.

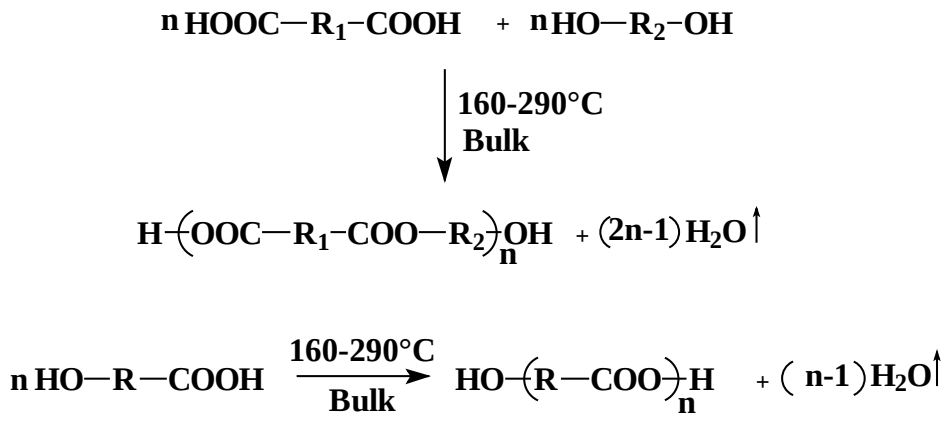
1.2.1 Polycondensation of diols with diacids

Polyesterifications can be divided into three main categories: (i) high-temperature bulk polyesterifications involving mainly hydroxy–carboxy reactions along with hydroxy ester

and carboxy–ester interchange reactions, (ii) non-equilibrium polyesterifications, which are generally low temperature solution reactions involving highly reactive monomers such as acid chlorides or activated carboxylic acids and (iii) enzyme catalyzed polyesterification.

1.2.1.1 High temperature bulk polyesterification

The carboxy–hydroxy reaction (direct esterification) which is the most straightforward method of polyester synthesis was first reported in the 1930s by Carothers[1-3] and is a widely used method for the synthesis of polyesters from diacids and diols or from hydroxy acids (**Scheme 1.2**). The reaction between acid anhydrides/diesters and diols is another convenient method of polyester synthesis as the former are much more reactive than carboxylic acids.



Scheme 1.2: Direct polyesterification

As direct polyesterification of dicarboxylic acids and diols is rather slow at room temperature it is generally carried out at high temperature (150 – 290^{0}C) depending on the monomers and in the presence of catalysts, usually metal salts, metal oxides or metal alkoxides, preferably in bulk. Being an equilibrium process, azeotropic entrainment or vacuum is generally used to distill off reaction byproduct so as to continuously shift the reaction towards the formation of high molecular weight polyester. The progress of reaction and, hence, the molecular weight attained is determined by the efficiency with which the byproduct is removed from the reaction mass.

Generally 10-20 mol% excess of the diol is added to compensate for the physical loss and to form hydroxyl terminated polyesters whose molecular weights can be increased further by interchain alcoholysis. At higher temperatures (>200^{0}C) and in the presence of catalysts, esterification is accompanied by ester-ester exchange reactions resulting in the liberation of diol or dicarboxylic acid and a subsequent increase in molecular weight. Direct polyesterification is particularly well suited to the synthesis of aliphatic polyesters, unsaturated polyesters and aromatic-aliphatic polyesters.

Side reactions, especially those involving aliphatic monomers, with effects on yields, molecular weights, and in some cases leading to undesired changes in the polymer structure may occur at temperatures above 220^{0}C. The intramolecular step competes with linear polycondensation. Cyclic oligomers are formed during step growth polymerizations[4-6], either by reactions between end groups of the same chain or by hydroxy-ester and carboxy-ester "back-biting" reactions. In some cases cyclization is the principal or the only reaction occurring. The presence of cyclics is, therefore, unavoidable in most polyester forming reactions.

Reaction mechanisms and catalysis[7a]

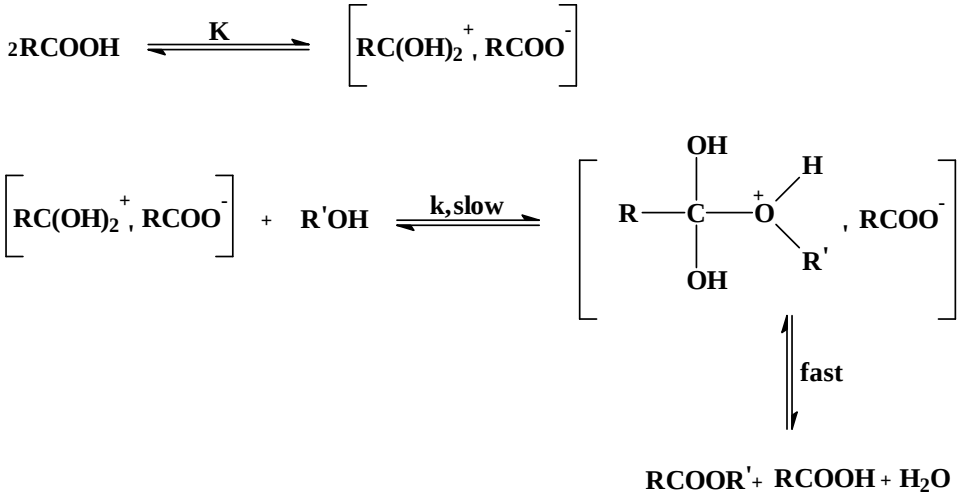
In his early studies on polyesterification kinetics, Flory[7b] demonstrated that reaction stages above ca. 80 % conversion only should be taken into account while discussing the mechanisms of high temperature bulk polyesterifications. Under these conditions polarity no longer changes with conversion and the reaction medium can be considered as an "ideal" dilute solution of reactive groups provided the viscosity is not too high and the reaction is not diffusion controlled. The kinetics and mechanism of diacid–diol polyesterifications have been adequately reviewed[8-9].

Reactions without added catalyst

Flory showed that both mono and polyesterifications are third – order processes and that the reactivity of hydroxyl and carboxyl end groups does not depend on chain length. These early findings have been confirmed by many other studies[10-11]. The proposed mechanism involves an autocatalysis by carboxylic acid, the rate determining step being the nucleophilic addition of the alcohol on protonated carboxylic acid. Assuming that protonation is an equilibrium process and the concentration of protonated carboxylic acid

is very low, the rate equation is as in **Scheme 1.3**. Although the third order mechanism is the most commonly accepted, many others have been proposed[12-18] such as first order, second order etc. Most of these studies, however, were carried out in reaction media which did not fulfill Flory's ideality conditions or in reaction media that are quite different from polyesters (e.g., nonpolar long – chain fatty acid esters)[14].

$$\upsilon = k\,[B][R'OH] = kK[RCOOH]^2[R'OH]$$

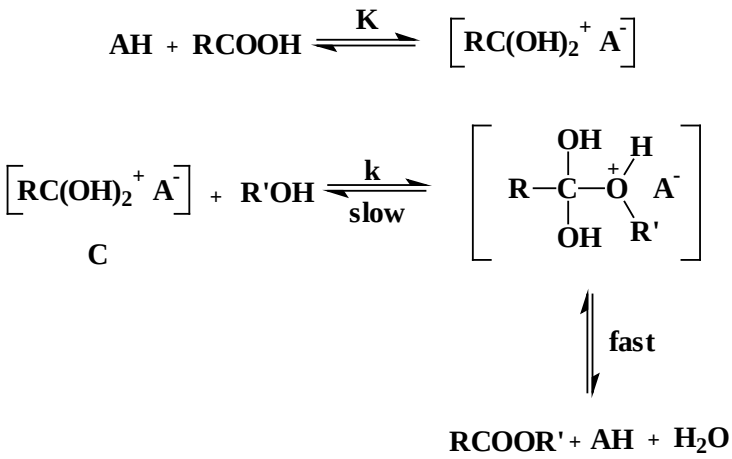


Scheme 1.3: Rate equation for polyesterification reaction without added catalyst

Reactions catalyzed by strong protonic acids

The kinetics of polyesterifications catalyzed by strong protonic acids, mainly sulfuric acid and aryl sulfonic acids, has also been extensively examined. In contrast to the reactions carried out in the absence of catalyst, the mechanism is first order in acid, alcohol and catalyst. At constant catalyst concentration, the reaction can be considered as second order[14]. The generally accepted reaction scheme has a close resemblance to the preceding one with protonation of carboxylic acid by the added protonic acid and formation of ion pairs. From this scheme (**Scheme 1.4**), reaction rate can be expressed by assuming that the concentration of the dissociated form of protonic acid catalyst is negligible with respect to initial catalyst concentration $[AH]_0$.

$$\upsilon = k\,[C][R'OH] = kK[AH]_0[RCOOH][R'OH]$$



Scheme 1.4: Rate equation for polyesterification reaction catalyzed by strong protonic acids

Catalysis by lewis acids and metal alkoxides

Most industrial processes involving direct polyesterification require the use of metal salts or organometallic derivatives as catalysts. Derivatives of practically all elements have been claimed to be esterification or polyesterification catalysts[9]. The catalytic efficiency of various metal derivatives has been estimated by Malek et al[19] from reactions of aromatic acids and aliphatic diols. These studies, as well as others, show that most efficient catalysts are titanium and zirconium alkoxides and tin derivatives such as Bu_2SnO. Other catalysts such as Zn, Pb, Al, Mn, Mg, Cd, Co acetates, Cu and La acetylacetonates, and Sb_2O_3 exhibit much lower reactivity[20]. It is generally accepted that the metal ligands are exchanged with the carboxyl and hydroxyl groups present in the reaction medium. The catalytic effect arises from the complexation of the carbonyl group with the metal atom, which induces a positive charge on the carbonyl carbon atom and favors the nucleophilic attack of hydroxyl groups. The nature of the catalytic species, therefore, changes during the course of the reaction, and the results suggest that catalytic activity depends on the composition of the reaction medium. Moreover, the presence of reaction water, which is unavoidable in direct esterification, may lead to the formation of

metal – oxygen – metal and condensed forms of metal alkoxides. This decreases the number of active exchangeable sites and, therefore, lowers catalytic activity[21]. In view of the complexity of such reactions, it is rather difficult to discuss the kinetics in terms of reaction orders.

Transesterifications, also termed as ester exchange or ester interchange reactions, include hydroxy – ester, carboxy – ester and ester – ester reactions. All these reactions may take place under similar experimental conditions and can be catalyzed by similar class of compounds as direct esterification reactions.

1.2.1.2 Nonequilibrium polyesterification

Nonequilibrium polyesterifications, characterized by their irreversible nature, generally involve highly reactive monomers such as acid chlorides or activated carboxylic acids. They are conducted either in solution or heterogeneous medium and can yield high molecular weight polymers under mild conditions and in short time without ester interchange or degradative side reactions. Poor control of polymer molecular weight and formation of higher amount of cyclic oligomers are some of the drawbacks. In addition environmental concerns connected with the use of acid chlorides and organic solvents, difficulties in getting rid of traces of catalysts or reaction byproducts and the use of relatively expensive starting materials have somewhat limited the interest in these reactions. The most important among these polyesterification reactions for synthesis of aliphatic polyesters is activation polyesterification.

Activation polyesterification proceeds via insitu transformation of one of the reactants, generally the carboxylic acid, into a more reactive intermediate. Activating agents, such as trifluoroacetic anhydride, 1,1'-carbonyldiimidazole carbodiimides, sulfonyl, tosyl, and picryl chlorides and a range of phosphorous derivatives can promote direct solution reactions between dicarboxylic acids and diols or diphenols under mild conditions. The reaction between 1,1'-carbonyldiimidazole[22a] and carboxylic acids proceeds through the formation of N-acylimidazoles, which react with aliphatic diols in the presence of sodium ethoxide catalyst. 2,4,6-Trinitrochlorobenzene (picryl chloride) in pyridine-N-methyl pyrrolidinone (NMP) solutions were later used for the preparation of

polyesters from dicarboxylic acids and diphenols or aliphatic diols. Good results are obtained with sulfonyl chlorides[22b] and phosphorous compounds[8] as activating agents.

N,N'-Dialkylcarbodiimides: N,N'-Dialkylcarbodiimides, particularly N,N'-dicyclohexylcarbodiimide (DCC), are well known condensing agents used in the synthesis of peptides and aliphatic polyesters[23]. Poly (lactic acid) has been synthesized by direct polyesterification in dichloromethane in the presence of DCC and 4-(N,N-dimethylamino) pyridine[24].

1.2.1.3 Enzyme-catalyzed polyesterification

Lipases and esterases belong to a class of enzymes referred to as hydrolases and were found to catalyze a number of in vitro esterification and polyesterification reactions in organic medium. Polyesters have been obtained in organic medium by lipase catalyzed polyesterification reactions[25-30]. Lipases have also been reported to catalyze ester-ester interchanges in solution or in bulk at moderate temperature[31]. Lipase catalyzed polyesterifications can be regarded as equilibrium polycondensation taking place under mild conditions as they catalyze the reverse reaction. Removal of the reaction by product can be accomplished by addition of molecular sieve, Dean-Stark distillation of toluene-water azeotrope, bubbling inert gas in reaction medium or applying vacuum in the case of reactions carried out without solvent. The use of vinyl esters is a convenient way to displace esterification equilibrium as the by-product vinyl alcohol, tautomerizes into acetaldehyde, which cannot participate in the reverse reaction[32]. Activated esters such as 2,2,2-trifluoroethyl-[33], 2-chloroethyl, and 2,2,2-trichloroethyl esters[34] have also been reported to yield high molecular weight polyesters. This method is limited to soluble or low melting polyesters, mainly aliphatic ones and the molecular weights obtained are relatively low.

1.2.2 Ring-opening polymerization (ROP) of cyclic esters

Since the pioneering work of Carothers, lactones, cyclic diesters and their alkyl and aryl substituted derivatives are known to be suitable starting materials for the preparation of linear aliphatic polyesters. This technique allows the synthesis of well defined polymers under mild conditions and in relatively shorter period of time as compared to polycondensation method. However, this technique is restricted to only limited class of

monomers. The ring opening polymerization can be performed in bulk, solution, emulsion or dispersion[35-36] in the presence of initiator and / or catalyst.

1.2.2.1 Polymerizability

Ease of polymerization of the cyclic monomer depends on both thermodynamic and kinetic factors. The single most important factor that determines whether a cyclic monomer can be converted to linear polymer is the thermodynamic factor, that is, the relative stabilities of the cyclic monomer and the linear polymer. The driving force for polymerization stems from the stereochemical factors, release of bond angle strain in small ring monomers and the relief of intramolecular crowding in medium sized rings. Substituents diminish the polymerizability[37] of monomers of all sizes by increasing the ring stability with respect to the open chain, as interactions between substituents are more severe in the linear polymer than in the cyclic monomer. Thermodynamic polymerizability of cyclic monomers can be estimated in principle by the negative change of free energy of polymerization during ROP under given reaction conditions. The main factors affecting the free energy of polymerization are (i) size and nature of the monomer ring affecting the internal strain, (ii) substituents on the monomer (and polymer), (iii) geometric isomerism in the polymer (cis-trans) and (iv) stereochemistry and configurational isomerism of the resulting polymer (tacticity). The nonpolymerizability is due to the positive free energy change, depending on the size, nature and substitution on the ring.

Polymerization requires a kinetic pathway for the ring to open and undergo reaction. The presence of a heteroatom in the ring provides a site for nucleophilic or electrophilic attack by an initiator species, resulting in initiation and subsequent propagation by ring opening. Such monomers polymerize, since, both thermodynamic and kinetic factors are favorable. Overall, polymerizability is higher for rings of 3, 4 and 7 to 11 members, lower for rings of 5 members, and much lower for rings of 6 members.

1.2.2.2 Polymerization mechanism and catalysts

Ring opening polymerization of cyclic monomers can proceed through three different mechanisms depending on the initiator used. These are cationic, anionic and coordination

insertion mechanisms[38-40]. In addition, radical, zwitterionic[41], or active hydrogen initiation is possible, although such techniques are not used to any great extent.

Cationic ring opening polymerization

Among the cyclic esters, 4, 6 and 7 membered rings form polyesters when reacted with cationic catalysts[42-43]. Cationic ring opening polymerization of lactones is achieved with strong protonic acid initiators such as sulfuric acid, trifluoroacetic acid, fluorosulfonic and trifluoromethane sulfonic (triflic) acid. The mechanism involves the attack of positive centre on the exocyclic oxygen (the more basic oxygen) to form a dioxocarbocation followed by nucleophilic attack of monomer. The attack results in ring opening of the positively charged species through an S_N2-type process. The cationic polymerization is difficult to control and often only low molecular weight polymers are formed.

More detailed reviews on cationic ring opening polymerization have been published by Penzeck and coworkers[44-45]. Nomura et al.[46] have reported cationic living ring opening polymerization of lactones using scandium trifluoromethanesulfonate, Sc $(OTf)_3$ as catalyst.

Anionic ring opening polymerization

Anionic ring opening polymerization of cyclic esters proceeds by nucleophilic attack of the negatively charged initiator on the carbonyl carbon or on the carbon adjacent to the carbonyl carbon resulting in linear polyester[47-48]. Anionic polymerization for almost all lactones proceeds by acyl-oxygen bond cleavage rather than alkyl-oxygen bond cleavage and the polymer chain growth proceeds entirely via alkoxide anions. The propagating species is a negatively charged ion balanced by a positive counter ion. Depending on the nature of the ionic propagating chain end and solvent, the reacting complex varies from completely ionic to almost covalent. Use of more active initiators like alkoxides of Mg, Zn, Ti, Zr, $(CH_3)_3SiONa$ lead to significant transesterification reactions which are responsible for molecular weight broadening and cyclization. Jedlinski et al[49] have developed living anionic ROP methods for β-butyrolactone wherein polymerization

proceeds by the attack of anionic initiator on the monomer involving alkyl-oxygen bond scission and the polymer chain growth proceeds entirely via carboxylate anions. A problem associated with anionic ROP is the extensive backbiting reaction, leading to polyesters of low molecular weight[50].

Coordination – Insertion ring opening polymerization

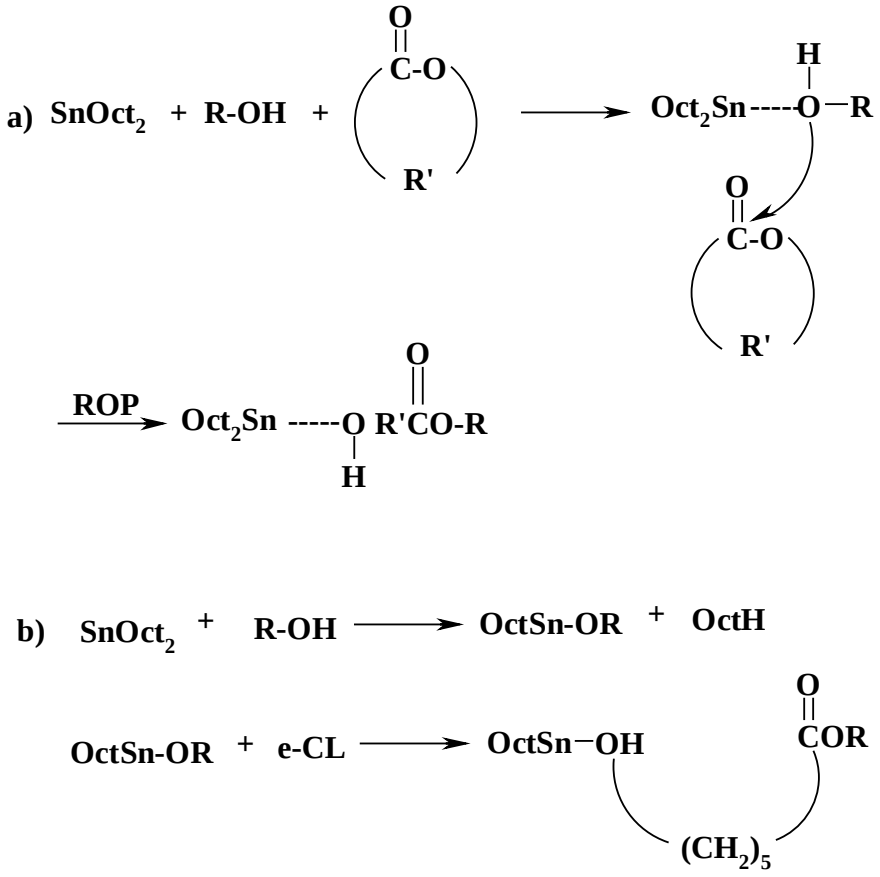
This method of polymerization is also called as pseudo-anionic ring opening polymerization. Propagation is thought to proceed by coordination of the monomer to the metal initiating active species followed by the insertion of the monomer into the metal oxygen bond of the initiator by rearrangement of electrons[38-39]. The growing chain remains attached to the metal through an alkoxide bond during propagation. The reaction is terminated by hydrolysis resulting in hydroxyl end group. The rate of polymerization is first order in both monomer and initiator and number average molecular weight is given by the ratio of monomer to initiator.

A wide range of organometallic compounds like metal bromides[51], metal alkoxides and metal carboxylates initiate polymerization via coordination insertion mechanism. The metal alkoxides with free p or d orbitals act as coordination initiators and not as ionic initiators[52]. Aluminium[53], zinc, tin[54], titanium, magnesium, vanadium and zirconium compounds such as alkyls, oxides, alkoxides[55] and carboxylates are considered as typical complexation initiators[56-57]. Recently salts and organocompounds of lanthanides[39, 58-61] and enzymes[62-63] have been used as initiators for ROP. However oxides, alkoxides or carboxylates of tin, aluminium, titanium and zirconium have been proven to be very efficient organometallic initiators.

Tin compounds are currently the most widely used group of initiators in the ring opening polymerization of lactones[64], lactides[65] and other cyclic diesters[66]. Amongst the variety of tin compounds, the important catalyst/initiator is Sn (II) bis (2-ethyl hexanoate), also referred to as stannous octoate [$Sn(Oct)_2$] used in the ring opening polymerization of lactones and lactides[67]. $Sn(Oct)_2$ is highly efficient, versatile, inexpensive and is approved as a food additive by the American Food and Drug Adminstration (FDA) because of its low toxicity. Although stannous octoate has been

used as initiator for ROP for more than two decades, the complex polymerization mechanism initiated by this tin compound has not been yet fully elucidated[68].

Penczek et al. have published kinetic results which strongly suggest that stannous octoate acts as coinitiator, in the presence of an initiating alcohol or adventitious hydroxy impurities and that polymerization proceeds only through stannous alkoxide active centers derived from the reaction of stannous octoate with the added alcohol initiator. Thus stannous octoate is converted into a tin alkoxide before complexing and ring opening of monomer[69]. Kricheldorf and coworkers have proposed a slightly different reaction pathway[68] where the co-initiating alcohol functionality and the monomer are both coordinated to stannous octoate complex during propagation (**Scheme 1.5**).



Scheme 1.5: Mechanism of ROP with stannous octoate as catalyst (a) complexation of monomer and alcohol prior to ROP and (b) formation of the tin-alkoxide before ROP

Direct observation of tin alkoxide complex has been reported by using MALDI-ToF spectroscopy for both, lactides[70] and ε-caprolactone propagation. Stannous octoate is

a strong transesterification agent and the resulting copolymers normally have a randomized microstructure[71]. The transesterification reactions (intra as well as inter leading to the formation of cyclics) increase with increase in reaction time and temperature[71-73]. Esterification of hydroxyl end groups of polymer chain by the liberated carboxylic acids leads to the formation of carboxylate end groups. The desired molecular weight can be calculated from the ratio of concentration of the monomer to the initiator (alcohol not stannous octoate). This initiator may provide a living system with fully controlled features provided their function is understood and polymerization is carried out under proper reaction conditions. Very little is known about catalytic properties of other tin carboxylates. Dibutyl tin bis (2-ethylhexanoate) ($Bu_2Sn\ (Oct)_2$)[68] showed lower reactivity compared to stannous octoate with ε-caprolactone as monomer. With trimethylene carbonate as the monomer, Bu_2Sn succinate seemed to be more reactive than stannous octoate. The kinetic study and comparison of several dibutyl tin carboxylates allows a better understanding of the structure- property relationships of this class of initiators and sheds more light on the insertion mechanism[74].

Metal alkoxides

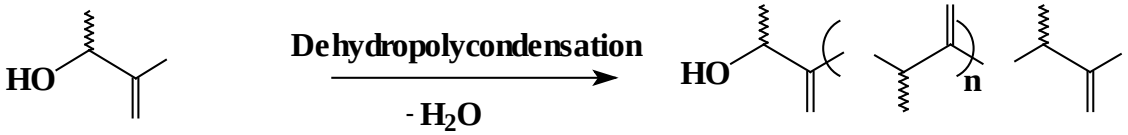
The most often used and thoroughly studied, among the metal alkoxides is aluminium tri (isopropoxide). The initiator yields well defined polymers through living polymerization[75-76] in which the kinetic steps of termination or chain transfer[75] are absent.

Polymerization with aluminium tri-isopropoxide is assumed to proceed through coordination– insertion mechanism, which consists of monomer complexation to the active species and insertion by rearrangement of the covalent bonds. The mechanism leads to cleavage of the acyl-oxygen bond of the monomer and the metal oxygen bond of the propagating species. The propagation is characterized by almost the total absence of side reactions such as transesterification reactions, at least until complete monomer conversion has occurred[77]. The main rearrangement of the polymer occurs when monomers are completely consumed. The initiator is active at low temperatures (reaction temperatures of $0\text{-}25^0C$ are often reported) and is preferentially used in solution polymerization.

Aluminium isopropoxide is known to form strongly bound aggregates. As a result, an induction period during which the initiator is rearranged to form the active species often characterizes the polymerization. These aggregates are known to be a mixture of at least two types of aggregates namely trimeric A_3 and tetrameric A_4. The mixture of A_3 and A_4 can be converted to A_3 or A_4 can be removed by some methods[78] so as to achieve higher rates of polymerization. Although aluminium isopropoxide is aggregated, it does not give aggregated macromolecules. All the alkoxide groups initiate polymerization and M_n is calculated assuming that every alkoxide group gives one chain. The proper substitution of the metal atom provides the required end group. Significant advances in the understanding of the coordination-insertion ROP mechanisms have been made through kinetic studies by Penczek and coworkers[78]. Recently systems have been developed where the aluminium alkoxide is covalently bonded to solid porous silica[79].

1.2.3 Dehydropolycondensation of ω-hydroxy carboxylic acids

Dehydropolycondensation is one of the routes to prepare aliphatic polyesters from ω – hydroxy carboxylic acids. It is basically an acid catalyzed intermolecular esterification of the hydroxyl and carboxylic groups of the hydroxy acid. Numerous lewis acids as well as protonic acids have been studied as catalysts for this process. Dehydropolycondensation, like any other esterification reaction, is an equilibrium controlled process. The rate of polymerization and the final molecular weight depends on the solvent, catalyst, reaction temperature and level of impurities.



Lactic acid **Low molecular weight PLA**

Scheme 1.6: Synthesis of poly (lactic acid) s by dehydropolycondensation of lactic acid

The reaction temperature is restricted by the boiling point of the solvent and therefore it was observed that the rate of polymerization increases as the boiling point of the solvent increases due to the efficient removal of water. It was found that

polymerization rate was accelerated in aprotic hydrocarbon solvents with boiling points above 130^0C, which forms azeotropes with water[80-81].The level of impurities in the polymerization was shown to have a large effect on the final molecular weight by endcapping the polymer and thereby limiting the chain growth.

Most of the studies on dehydropolycondensation were carried out with lactic acid (**Scheme 1.6**). Achieving high molecular weight PLA polymers through the direct dehydropolycondensation of L-lactic acid (LLA) is rather difficult because of various factors, such as kinetic control, limited and inappropriate catalyst activity and lack of suppression of depolymerization.

Tin compounds were found to give the highest molecular weights at the lowest temperatures. A number of lewis acids and different reaction conditions were investigated by Seppala and coworkers[82]. 98% sulfuric acid, stannous octoate, tin (II) lewis acid catalysts such as SnO, $SnCl_2.2H_2O$ etc., activated by various protonic acids[83] also served as effective catalyst for dehydropolycondensation with less racemization. Synthesis of hydroxy telechelic as well as branched lactic acid oligomers by direct dehydropolycondensation of lactic acid with diols or dipentaerythritol as a chain branching agent[84] was achieved using different lewis acid catalysts[85-86]. Direct polycondensation of lactic acid using condensing agents such as 1,1'-carbonyldiimidazole (CDI), N,N,N',N'' – tetramethylchloroformamidium chloride (TMCFAC) and N,N'–dicyclohexylcarbodiimide/4-dimethylaminopyridine (DCC/DMAP) has been carried out and their comparative effectiveness as condensing agents was studied[87-88].

Yamaguchi and workers[89] studied the direct condensation of LLA using various Bronsted and Lewis acid catalysts through continuous azeotropic dehydration. Moon et al.[90-91] examined melt/solid polycondensation of LLA catalyzed by a tin chloride dihydrate/ p-toluenesulfonic acid binary system. Otera J. et al[92] showed that tetrabutyl distannoxane, which are already known to be good esterification and transesterification catalysts and which can retard hydrolysis are also effective catalysts for the dehydropolycondensation of L-lactic acid to poly(lactic acid), where a maximum molecular weight of 75,000 has been attained.

Tetraphenyl tin which has widely been used in the ring opening polymerization of lactides has recently been used as a catalyst for dehydropolycondensation[93]. However dehydropolycondensation of LLA either in bulk or in presence of solvent yields low molecular weight polyesters. Macrocycle formation is a competitive reaction to linear chain growth and is more prominent at higher reaction temperatures, which limits the attainment of high molecular weight polymers. In the absence of solvent, dehydropolycondensation of LLA yields some linear polymer.

1.3 Mechanism of poly(ester) forming reactions

Synthesis of linear polyesters by step polymerization of polyfunctional monomers or by ring opening polymerization of cyclic esters is complicated by degradation reactions like back-biting, which effectively lower the molecular weights and adversely affect the final properties of the polyester. These degradation reactions occur to a small extent in ring opening polymerization of cyclic esters due to the more controlled nature of the polymerization whereas in linear step-growth polymerization they occur to a large extent. In fact in step-growth polymerization the cyclization reactions compete with linear polyester forming reactions.

It is, therefore, of prime interest to examine the various theories on which the mechanism of polyester forming reactions in step-growth polymerization are based and their implications on the polyester properties.

1.3.1 Classical theory of Carothers and Flory

The classical theory of step growth polymerization is mainly based on the experimental work of Carothers[94-95] and the theoretical contributions of Flory[96-97].

The kinetic analysis of reaction in step-growth polymerization with innumerable separate reactions was greatly simplified by assuming that the reactivities of both the functional groups of a bifunctional monomer are the same, reactivity of one functional group of a bifunctional reactant is the same irrespective of whether the other functional group has reacted and the reactivity of a functional group is independent of the size of the molecule to which it is attached. These simplifying assumptions are referred to as concept

of equal reactivity of functional groups which make the kinetics of step–growth polymerization identical to those for the analogous small molecule reaction. This concept was justified by many step polymerization reactions that have rate constants that are independent of the reaction time or polymer molecular weight. Based on this concept of equal reactivity, the kinetics for polyesterification reaction was derived by Flory. The extent of reaction or conversion in polyesterification reaction was given by the expression

$X_n = 1 / (1-p)$ -------- **eqn 1**. This equation relating the degree of polymerization (X_n) to the extent of reaction p was originally set forth by Carothers and is referred to as Carothers equation. The effect of chain terminators which are added to regulate the average DP or an imbalance in stoichiometry (which has the same effect) is given by the expression

$X_n = 1 + r / 1 + r - 2rp$ ---------- **eqn 2** where X_n = DP, $r = N_a / N_b$ = stoichiometric imbalance, p = extent of reaction. The molecular weight distribution in step–growth polymerization was derived by Flory by a statistical approach based on the concept of equal reactivity of functional groups. The derivation applies equally to A-B and stoichiometric A-A plus B-B types of step polymerization and are expressed as the following equations:

$N_x = p^{x-1} (1-p)$ ---------- **eqn 3** where N_x = mole or number fraction of molecules in the polymer mixture that are x-mers (i.e. that contain x structural units).The weight fraction w_x of x-mers (i.e. the weight fraction of the molecules that contains x structural units) $w_x = xN_x / N_0$ is given by $w_x = x (1-p)^2 p^{x-1}$ ---------- **eqn 4**

These two equations give the number and weight distribution functions respectively for linear step growth polymerization at the extent of reaction p. These distributions are usually referred to as the most probable or Flory or Flory – Schulz distributions.

This work of Carothers and Flory is one of the significant milestones in the history of polymer science for three reasons. Firstly they demonstrated that the reactivity of end groups does not depend on the chain length of the oligomers and polymers (dimers or trimers may deviate from this rule in individual cases). This fundamental aspect needs to be emphasized because at the time when Carothers started his experimental studies,

around 1927, Staudinger and other polymer chemists[98] believed that the reactivity of the end groups decreases with higher chain length. Secondly, the polycondensation chemistry opened up a field of polymer synthesis which may be considered as an equivalent to in-vivo synthesis of biopolymers. All synthesis of biopolymers in living organisms involves condensation steps, although the kinetic course is different from that of typical step-growth polymerization. Thirdly, the first man-made fibers based on nylon 6,6 were produced and this event was the starting point for the invention and production of all kinds of textile fibers.

1.3.2 Thermodynamically controlled polymerization and Jacobson–Stockmayer theory

Despite the merits, the classical theory of step growth polymerization has two shortcomings. Firstly it does not consider the contributions of cyclization reactions and secondly it does not differentiate between kinetically controlled and thermodynamically controlled step growth polymerization.

The competition between cyclization and linear polymerization for a particular reactant or a pair of reactants depends on thermodynamic and kinetic considerations of the size of the ring structure which may be formed. Though small rings are kinetically feasible, thermodynamically they are not stable whereas large rings are thermodynamically stable but the kinetic factor becomes progressively less favorable. As step polymerizations are generally carried out using high concentration of reactants, which is highly favorable for linear polymerization, the rate of linear polymerization increases much faster than the rate of cyclization as the concentration of reactants increase. This factor of reactant concentration is superimposed on the previous thermodynamic and kinetic considerations. The concentration factor increases the overall competitive position of linear polymerization relative to cyclization. Moreover as the linear and cyclic structures are interconvertable under appropriate reaction conditions, it is possible to shift the equilibrium in the direction of linear polymer.

For these reasons, the interference of cyclization reactions was not taken into account by Carothers and Flory. However, it was later observed that in many polycondensation reactions, cyclic oligomers were formed via intramolecular

esterification as well as intramolecular transesterification or backbiting reactions from active chain ends. Due to this and other equilibration reactions, the population of reaction products represents the thermodynamically defined energetic minimum of the system at any conversion, and thus, this type of polycondensation may be called "thermodynamically controlled polymerization" (TCP). In contrast to the classical theory, a typical polycondensation reaction contains a mixture of chains of various lengths as well as small, medium and large ring molecules all in equilibrium with each other. To account for the intramolecular reactions leading to reversible formation of polymers and cyclic oligomers, Jacobson and Stockmayer proposed the theory of ring-chain equilibria in TCP which states that ring-chain equilibrium of polymer in TCP will lead to a mixture of cyclic oligomers and polymer in which a critical monomer concentration (CMC) can be defined for each monomer structure such that at concentrations below CMC, only cyclics will be present, while above that concentration, mixture of cyclics and polymer will be present. In principle, it is possible to calculate the concentration of all the individual species produced. The concentrations of the individual chains may be calculated from the number average molar mass of the acyclics, using Flory's relationships. Similarly, the concentrations of individual cyclics may be calculated.

Consider a ring-chain equilibrate, with an equilibrium between x-meric cyclics M_x and linear chains M_y and M_{y-x} thus,

$$\mathbf{M_y} \rightleftharpoons \mathbf{M_x} + \mathbf{M_{y-x}} \text{ ---------- eqn 5}$$

For this system the molar cyclization equilibrium constant K_x for above process is given by $K_x = [M_x] / p^x$ ------- **eqn 6** where p = extent of reaction = 1- M_0 / M_n . For typical ring-chain equilibrates, values of p are close to unity and so K_x values calculated are approximately equal to the concentration of cyclics $[M_x]$.

In 1950, Jacobson and Stockmayer[99-100] described the molecular weight distribution of the cyclics resulting from the ring -chain equilibria in TCPs and provided the first theoretical expression for molar cyclization equilibrium constant K_x which was later extended by Flory. The expression for K_x is as follows:

$K_x = W_x(0) / N_A \sigma_{Rx}$ ---------- **eqn 7** $W_x(0)$ represents the density of end-end vectors in the region corresponding to the close approach of chain ends (i.e. where end-end vector r ≈ 0), N_A is the Avogadro constant and σ_{Rx} is the symmetry number of an x-meric ring. The molar cyclization equilibrium constants are calculated assuming that x-meric chains forming rings obey Gaussian statistics, so that

$W_x(0) = (3 / 2 \Pi \langle r^2_x \rangle)^{3/2}$ ---------- **eqn 8** where $\langle r^2_x \rangle$ represents the mean square end-to end distance of the chains and the units of $W_x(0)$ are molecules dm^{-3}. Substituting for $W_x(0)$ gives $K_x = (3 / 2 \Pi \langle r^2_x \rangle)^{3/2} (1 / N_A \sigma_{Rx})$ ---------- **eqn 9**. Units of K_x are mol / dm^3.

Comparison of the experimental K_x values for cyclics formed in the ring-chain equilibrates with values predicted by **equation 9** provides a powerful method for investigating the statistical conformations of chain molecules in a variety of environments. If the ring-chain equilibration reaction is carried out in melt or in concentrated solution, the mean-square end-to-end distances can be identified with their unperturbed values $\langle r^2_x \rangle$.

Several research groups[101-102], have published experimental studies of such ring-chain equilibria and have confirmed that the J-S theory is in principle correct so far as formation and population of cyclic oligomers are concerned. The J-S theory was and is understood as a modification of the Carothers-Flory (CF) theory. CF theory predicts on the basis of Carothers equation that an ideal polycondensation reaching 100 % conversion will yield one giant chain containing all monomeric units. Modification with J-S theory means that the giant chain obtained at 100% conversion is at one or both the ends in equilibrium with cyclic oligomers.

1.3.3 Concept of chain-chain, ring-chain and ring-ring equilibria

It is very important to know, the role cyclizations play in real polycondensation. In a typical polycondensation, the reaction consists of chains of various lengths as well as rings of different sizes. Thus by definition a TCP involves an equilibration of all components of the reaction mixture. Hence a TCP may be considered as a combination of chain-chain, ring-chain and ring-ring equilibria. To simplify the mathematical treatment

of the ring-size distribution and its correlation with conformational properties, Jacobson and Stockmayer focused their work only on ring-chain equilibria. This simplification is not satisfactory for a proper understanding of the entire course of a TCP upto 100% conversion. In the initial stages of the reaction, the bifunctional monomers react with each other to form dimer, trimer, tetramer, pentamer and so on with the molecular weight building up slowly with time or conversion. At this stage, the reaction mixture consists of mainly linear chains of different lengths with a very small fraction of cyclics. The thermodynamic properties of this reaction mixture are dominated by the chain-chain equilibria since the concentration of linear chains is higher than that of the cyclics.

As the conversion increases, the average length of all the chains increases and the total number of molecules decreases. Due to the intramolecular esterification and transesterification reactions, the molar ratio of cyclics vs. linear chains systematically increases, because long chains can produce large cycles in addition to small ones, whereas the short chains cannot. At this stage of the reaction, the rings and chains are present in sufficient quantities to have a combined effect on the thermodynamical properties of the reaction mixture and a molar frequency distribution curve for cyclics as well as chains at equilibrium can be obtained. Therefore at this point the reaction mixture is described as a ring-chain equilibrium.

As the reaction proceeds towards 100% conversion, at a certain point, the reaction mixture contains more cycles than linear species. From this point onwards, the thermodynamic properties of the reaction mixture are dominated by the ring-ring equilibria. At higher conversions, an ideal TCP may be considered as a ring producing process with linear chains playing the role of a catalyst. Consequently the reaction mixture gradually approaches the final state with 100 % cycles at 100% conversion.

However, all step-growth polymerizations are self diluting systems in terms of molarity of the linear active chains. The molar concentration of the active species (e.g., monomers in the very beginning) decreases according to the **equation 10**

$[La]_p = [La]_0 (1-p)$ ---------- **eqn 10** where $[La]_0$ = initial molar concentration of the active species (monomers at p = 0) $[La]_p$ = molar concentration of the linear active species at a given conversion (including monomers). At 100% conversion the

concentration of active species is zero, and all the reaction products are necessarily cyclics. Thus, thermodynamically controlled polycondensation tend to yield exclusively cycles under ideal reaction conditions.

1.3.4 Implications of multiple equilibria on the nature of polycondensation products

Any TCP involves three kinds of equilibria: the chain-chain, ring-chain, and ring-ring equilibrium because all components of a reaction mixture are engaged in the equilibrium process. The molar ratio of cycles versus linear species increases and the cycles begin to outnumber the linear species as conversion approaches 100%. At 100% conversion all reaction products are necessarily cycles. TCP may be therefore described as a ring-ring equilibrium, because the chain-chain and ring-chain equilibria lose influence on the thermodynamical properties of the system. Thus TCPs tend to end up with ring-ring equilibria and not with the formation of one giant chain in equilibrium with a few cycles. Since the formation of 100% cycles requires 100% conversion and absence of side reactions, it is difficult to achieve an absolute quantitative formation of cycles in real experiments. However, systems containing 95 to 99 wt% of cycles (eg. spirocycles) have been cited. Neither Stockmayer nor Flory have ever presented any experimental evidence for the J-S theory of TCPs. Therefore, the ring-ring equilibrium hypothesis is better substantiated by theoretical considerations and experimental results than the J-S theory.

The chain growth of TCPs is in almost all cases limited by the thermodynamic properties of the ring-ring equilibria and the final state of a TCP at 100% conversion is a neat ring-ring equilibrium given by following equation

$$c(M)_x + c(M)_y \underset{}{\overset{K_C}{\rightleftharpoons}} c(M)_{x+y} \quad \text{---------- eqn 11}$$

$K_c = [\, c(M)_{x+y}] / [\, c(M)_x]\, [\, c(M)_y]$ ---------- **eqn 12**

DP in such a system is given as follows

$DP = 1 / 1\text{-}p\,(1\text{-}1/X^K)$ ---------- **eqn 13** K_c is the ring-ring equilibrium constant and X is a factor > 1. **Equation 13** is a modification of classical Carothers equation, taking into

account the influence of ring-ring equilibria. The assumption of a single equilibrium constant K_c is, of course, a simplification, but it facilitates to illustrate the influence of ring-ring equilibria on the chain growth in a TCP and how real TCPs deviate from the classical C-F and J-S theories.

Equation 13 indicates that the Carothers equation under extreme or limiting case is characterized by the absence of cyclization (K_c = infinity) in case of synthesis of rigid-rod type polyesters from parafunctionalized aromatic monomers. The second extreme and limiting case is $K_c = 0$ which indicates an almost complete formation of thermodynamically stable, strain-free monomeric cycles without propagation as it is known from polycondensation of γ-hydroxy or γ-aminobutyric acid which yield thermodynamically stable γ-butyrolactone or γ-butyrolactam in nearly 100% yields at elevated temperatures[103]. Another example is the acid catalyzed condensations of 1,2 dihydroxyalkanes which yield almost quantitatively 1,4-dioxanes in combination with a few cyclic oligomers[104] but no poly(ethylene glycols). Most TCPs take a course between these two extremes. Thus, ring-ring equilibria determine the maximum DP that can be achieved under ideal reaction conditions and depending on the ring-ring equilibria, either high molar mass rigid polymers or low molar mass cycles may be the main reaction products. In real polycondensation DPs will be lower, due to side reactions, imperfect stoichiometries and incomplete conversions.

However, in technical TCPs conducted in bulk, the fraction of cycles is relatively low (2-5 wt %) like in the synthesis of PET, PBT, nylon-6, nylon-6,6 and polycarbonates. The studies of cycles in technical TCPs are based on extraction of cyclic oligomers. These extractions are far from complete and hence the real content of cyclic oligomers and polymers is underestimated. For all these reasons the rather low content of cyclic oligomers and polymers in technical polycondensates cannot contradict the ring-ring equilibrium theory.

1.4 Structure - property relationships in aliphatic poly (ester)s

Properties of polyesters are determined by molecular weight, chemical composition, proportion of carboxylate ester groups in their structure, geometry, polarity and segmental mobility of their repeating units. Since the intermolecular interactions are not very strong in polyesters, their properties are more sensitive to variations in structure than those of strongly interacting polymers such as polyamides or polyurethanes.

The nature of monomers (diols and diacids) used in the synthesis of aliphatic polyesters exert a profound influence on the properties of polyesters. Hence, the structure of polyesters can be varied to get the desired properties by judicious choice of monomers used in the synthesis of polyesters. This section describes the effect of structure of diols and diacids on polyester properties.

1.4.1 Polyesters containing linear diols and diacids

Polyesters derived from linear diols as well as linear diacids, termed as linear acyclic polyesters, are highly flexible due to linear components in their repeat units, but are less flexible compared to polyethylene, due to the rigidity of the ester linkages. These polyesters have low crystalline melting points (T_m), in the narrow range of 40 to 90^0C. The lower T_m are as a result of lower values of both ΔH and ΔS ($T_m = \Delta H_m / \Delta S_m$). The melting temperature of linear acyclic aliphatic polyesters increases with increased methylene: carboxylate ester group ratio in the repeating units. Thus T_m for poly (ethylene adipate) is 53^0C and that for poly (decamethylene decanedioate) is 92.7^0C.

The linear acyclic aliphatic polyesters with even number of methylene groups melt at higher temperatures compared to odd numbered ones. This is due to alterations in ΔS, ΔS being higher for odd members. However both odd and even series display the same upward trend with increasing proportion of methylene groups eventually tending towards the T_m of polyethylene at low ester group content. As the methylene group content of the repeating unit increases, the influence of the easily rotatable CH_2–O and CH_2-CO groups decreases, and the properties approach those of polyethylene, though the effect is retarded by the rigidifying effect of the ester links. There are a few exceptions such as poly (ethylene succinate) and poly (ethylene oxalate) which melt at 112^0C and 72^0C respectively.

The poly(α-esters) as well as poly(β-esters) have relatively higher melting points, for example poly (glycolic acid) has a remarkably high T_m of around 230^0C. The reason for this behavior may be due to the fact that at smaller alkyl chain lengths, the rigidifying influence of ester groups predominates, resulting in higher T_ms as seen in **Table 1.1**

Table 1.1: Melting point and glass transition temperature of poly (alkylene adipate) s and poly (ω-hydroxyacids)

Repeating–Unit formula	—C(=O)—$(CH_2)_4$—C(=O)—O—$(CH_2)_n$—O—		—O—$(CH_2)_n$—C(=O)—	
n	T_g (°C)	T_m (°C)	T_g (°C)	T_m (°C)
1	-	-	45	228
2	-63	50	-24	93
3	-59	45	-59	64
4	-74	55	-66	58
5	-	-	-64	69
6	-73	61	-	-
9	-	-	-	80
10	-56	80	-46	92
12	-	-	-44	95
14	-	-	-22	97
15	-		-	94

T_g reflects the segmental mobility in the amorphous phases and follows a similar trend as that observed for T_m. Higher the chain flexibility, lower is the T_g. Therefore, linear acyclic aliphatic polyesters have very low T_g in the range of -70 to -30^0C.

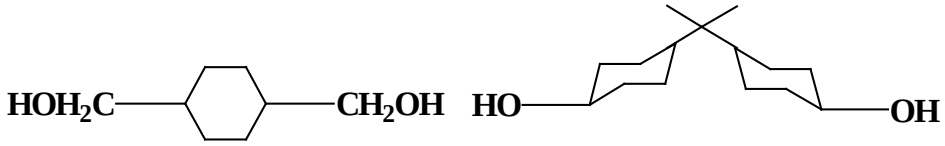
These polyesters are generally crystalline solids due to their linear structure which imparts high structural regularity. However polyesters obtained from unsymmetrical and

racemic components in the diol or diacid or both moieties of polyesters are usually amorphous due to disturbance in structural regularity. Polymorphism is common among these polyesters[105-106].

1.4.2 Polyesters containing cyclic diols and diacids

Aliphatic polyesters derived from monomers in which either diol or diacid (not both) are cyclic, have properties that are highly modified as compared to those of linear acyclic aliphatic polyesters. The cyclic component may be alicyclic, heterocyclic or aromatic. Generally when the cyclic components predominate and polyester is crystalline, it has a T_m higher than acyclic polyesters at equivalent ester group content. The introduction of cyclic components in the polyester induces rigidity or chain stiffness which leads to restriction of chain motion as compared to the acyclic or linear unit of similar length. As a result, lower flexibility leads to lower melting entropy and higher T_m. In these polyesters, the T_m decreases with increasing length of linear or acyclic moieties and increases with increasing proportion of the trans-cycloaliphatic rigid units. The odd-even effect of methylene groups is also seen in these polyesters[107-109]. The glass transition temperature also follows a similar trend. The T_gs are higher irrespective of whether the polyesters are crystalline or amorphous.

A variety of cycloaliphatic diols and diacids have been used in the synthesis of aliphatic polyesters. The effect of the cyclic structures on the properties of aliphatic polyesters will be discussed in the following sections. The use of cycloaliphatic monomers based on cyclohexane, cyclopentane and norbornane ring structures in the synthesis of copolyesters of poly (butylene terphthalate) has been studied[110a]. The alicyclic diol 1,4-cyclohexanedimethanol (CHDM)[110b-112], available commercially as 70-72% trans isomer and 2,2-bis (4-hydroxycyclohexyl) propane (HBPA)[113] are potentially useful diols for synthesis of polyesters.



(1) **(2)**

Table 1.2 shows a series of polyesters of CHDM (**1**)[112] with various linear aliphatic diacids. The rigidity and symmetry of the rings confer high T_m and T_g to the polyesters containing them. Gaughan et al.[114] have reported synthesis of high molecular weight polyesters of HBPA (**2**) with various aliphatic acids using tin catalyst (**Table 1.3**). The thermal and mechanical properties are known to depend on the isomeric composition of starting HBPA.

Poly [2,2-bis(4-oxycyclohexyl)propane adipate] has better physical properties when compared to engineering plastics like PBT,PC and nylon 6,6. The polymer displayed excellent notched impact strength and elongation which is attributed to the structure which can dissipate energy through molecular motion by the chair-boat-chair flipping motion.

Table 1.2: Thermal properties of polyesters derived from 1,4-cyclohexane dimethanol and bicyclo[2.2.2] and [3.2.2] diols with various diacids

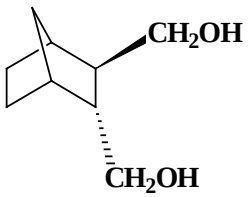
T_m of polyester, (^{0}C)			
Diacid	1,4-cyclohexane dimethanol **(1)**	1,4-bis(hydroxymethyl) bicyclo [2.2.2] octane **(4a)**	1,5-bis(hydroxymethyl)bicyclo [3.2.2] nonane **(4b)**
Adipic	122-124	99-101	80-82
Suberic	94-96	74-77	Amorphous
Azelaic	45-50	34-37	Amorphous
Sebacic	72-78	63-65	Amorphous

The 2,2,4,4-tetramethyl -1,3-cyclobutane diols (TMCBD) are a class of rigid thermally stable, symmetrical alicyclic diols suitable for the preparation of polyesters[110,115-116]. Norbornane (bicyclo [2.2.1] heptane) and norbornane condensed structures are readily available source whose potential for incorporation in polymers has not been fully evaluated.

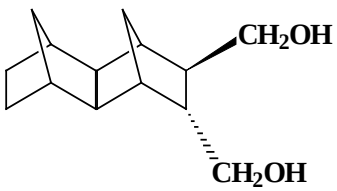
Table 1.3: Thermal properties of polyesters derived from 2,2-bis (4-hydroxycyclohexyl) propane **(2)** with various diacids

Diacid	T_g (^{0}C)	T_m(^{0}C)
Succinic	113	180
Adipic	75	200
Sebacic	25	Non-crystalline

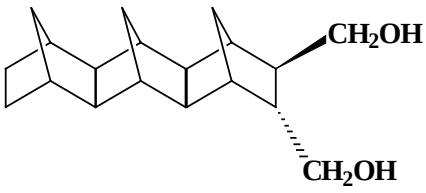
Norbornane and norbornane condensed diesters and dimethanols have been synthesized by Wilson and Hamb[117] for the synthesis of polyesters. Taimr and Smith[118] have studied polyesters containing bicyclo [2.2.2] octane and bicyclo [3.2.2] nonane rings.



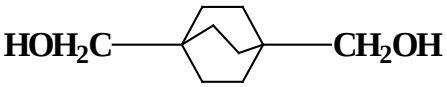
(3a)



(3b)



(3c)

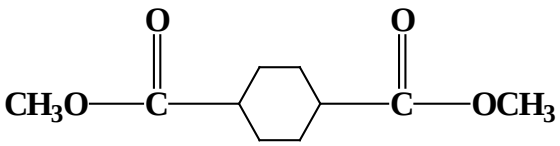


(4a)

(4b)

The diol, 1,4-bis(hydroxymethyl)bicyclo [2.2.2] octane **(4a)**[118-119] has rigid symmetrical structure similar to that of cis-1,4-cyclohexanedimethanol in the boat conformation. (**Table 1.2**)

A number of cyclic diacids/diesters have also been used in the synthesis of aliphatic polyesters. One such monomer is 1,4-cyclohexane dicarboxylic acid (1,4-CHDA) or the methyl ester of 1,4-CHDA (DMCD) **(5)** which is available as a 95% trans isomer



(5)

Polyester synthesized using this ester and linear diol have low T_g. The crystallizable polyesters of cycloaliphatic diacids or derivatives thereof with linear aliphatic diols have relatively high melting points and are UV resistant (**Table 1.4**).The polyesters prepared from the various isomers of diethyl norbornanedicarboxylate and ethylene glycol exhibited low T_g values (approx 40^0C).

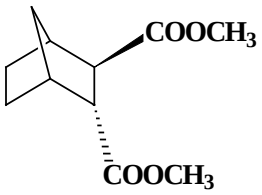
Table 1.4: Polyesters of trans 1,4-cyclohexanedicarboxylic acid with various diols

Diol constituent	$[\eta]^a$	T_g (^{0}C)	Relative cryst., %
Ethylene glycol	0.84	18	0
1,3-propanediol	0.91	-6	0
1,4-butanediol	1.13	-10	19.5
2,2-dimethyl-1,3-propanediol	1.06	30	5

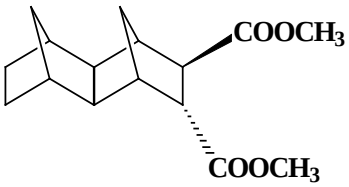
1,4-cyclohexane dimethanol	0.52	52	0
2,2,4,4-tetramethyl-1,3-cyclobutanediol	0.77	169	0

[a]Measured in 60/40 (w/w)phenol-tetrachloroethane at 25^0C

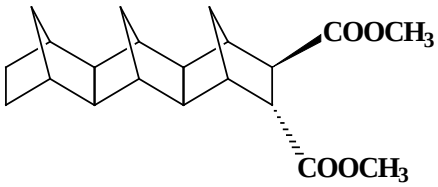
The effect of increasing the concentration of the norbornane moiety on T_g by introducing it as a polymer side chain for the polyesters of dimethyl succinate and norbornane condensed diesters with ethylene glycol and 1,4-cyclohexanedimethanol is shown in **Table 1.5**.



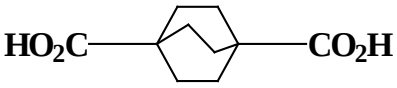
(6a)



(6b)



(6c)



(7a)

(7b)

Polyesters of bicyclo [2.2.2.] and [3.2.2] dicarboxylic acids with various linear aliphatic diols and 1,4 CHDM were synthesized[118] (**Table 1.6**). The polyesters synthesized from bicyclo [3.2.2] nonane dicarboxylate (**7b**) have lower melting points than bicyclo [2.2.2] octane dicarboxylates (**7a**). The polyesters derived from norbornane condensed diacids and diols or 1,4-CHDM have very high T_m s.

Table 1.5: T_g and inherent viscosity values for polyesters prepared from **6a**, **6b**, **6c** with ethylene glycol or 1,4-cyclohexanedimethanol

R_1	**-CH_2CH_2-**	**6a**	**6b**	**6c**

R_2	η_{inh}[b] dl/g	T_g (^{0}C)	η_{inh}[b] dl/g	T_g (^{0}C)	η_{inh}[b] dl/g	T_g (^{0}C)	η_{inh}[b] dl/g	T_g (^{0}C)
—CH_2—CH_2—	0.56	-5[a]	0.98	41	0.56	95	0.27	156
—H_2C—⬡—CH_2—	0.29	-4[a]	0.34	67	0.38	111	0.27	146[a]

[a]2.5^{0}C/min [b]Measured in 1:1 (w/w) phenol-chlorobenzene solution at 25^{0}C

Table 1.6: T_m of polyesters of **7a** and **7b** with various aliphatic diols

T_m of polyester, (^{0}C)		
Diol Unit	**7a**	**7b**
Ethylene glycol	Amorphous	Amorphous
1,3-propanediol	140-143	Noncrystallizable gum
1,4-butanediol	233-238	127-130
1,5-pentanediol	54-56	Noncrystallizable gum
1,6-hexanediol	144-147	50-55
1,4-cyclohexanedimethanol	310-315	188-192

Polyesters derived from cyclic diols as well as cyclic diacids have also been prepared. In these cases, the chain is highly rigid due to the high proportions of cyclic component and, hence, high T_g and T_m are expected (**Table 1.7**).

Table 1.7: T_m of polyesters derived from **7a** and **7b**

Diacid unit

	7a			7b		
Diol unit	T_m (^{0}C)	η_{inh}[a] dl/g	T_{10}[b]	T_m (^{0}C)	η_{inh}[a] dl/g	T_{10}[b]
4a	380-390	0.25	452	225-227	0.24	455
4b	244-246	0.21	455	172-177	0.27	457

[a]Measured in 60/40 (w/w) phenol-tetrachloroethane [b]Decomposition temperature at 10% weight loss

High molecular weight aliphatic polyesters have been synthesized from trans 1,4-cyclohexane dicarboxylic acid and cis/trans 1,4-cyclohexanedimethanol. This polyester poly(1,4-cyclohexanedimethyl-1,4-cyclohexanedicarboxylate) (PCCD) is an aliphatic polyester having desirable properties such as high T_m as well as T_g , crystallinity and resistance to weathering upon exposure to UV radiation. The T_m is in the range of 220-235^{0}C and T_c is in the range of 152-171^{0}C.

T_m of the polymer is dependent on the trans: cis ratio of the cyclic units in the polyester. Higher the trans content results in a higher T_m, higher degree of crystallinity and faster crystallization rates. Thus, all aliphatic polyesters containing a cyclic component have higher T_g and T_m compared to the linear acyclic aliphatic polyesters. The crystallinity of polyesters containing cyclic units is highly dependent on the isomeric state (cis or trans) of the cyclic unit and the amount of cyclic unit incorporated in the polymer chain. Many of these polyesters are amorphous or difficult to crystallize. The crystallinity also depends on the tendency of crosslinking and/or branching reactions, which occur during polymerization. These polyesters are UV resistant, have better thermal stability, hydrolytic stability, physical and mechanical properties as compared to linear acyclic aliphatic polyesters and hence may find applications as structural materials.

1.4.3 Polyesters containing branched diols/diacids

Properties of aliphatic polyesters are markedly affected by changes in chemical structure that influence the geometrical regularity, polar character or segmental mobility of the molecular chains. When one or more hydrogen atoms in the repeating units of the aliphatic polyester chain are replaced by alkyl groups, the intermolecular separation of

adjacent chain backbones is increased and there is often a reduction in the inherent symmetry of the system, leading to lowering of T_m if crystallinity is retained and frequently loss of crystalline character.

Properties of polyesters strongly depend on the number of branches i.e. degree of branching and the length of the branch. Short chain branches reduce T_m and the degree of crystallinity, while long chain branches in addition to reducing T_m and crystallinity also lower the melt viscosity and endow elongational viscosity with tension stiffening behavior. As the polyesters with long chain branches have low melt viscosities, they can be processed at lower temperatures. The radius of gyration and hydrodynamic volume for branched polymers is smaller than that for linear polymers. As the polyester chain becomes more and more branched (that is more number of branches in the chain), the crystallinity, T_g and T_m decrease along with the mechanical properties. The spherulite growth rate also decreases with degree of chain branching and the length of the branch.

Polyesters containing chain branching can be derived from branched diols or diacids or both in which the hydrogen atoms are substituted leading to branching in the main polyester chain[120]. The effect of using diols like 1,2-butanediol or 1,2-decanediol resulting in polyesters with branches has been studied (**Table 1.8**).

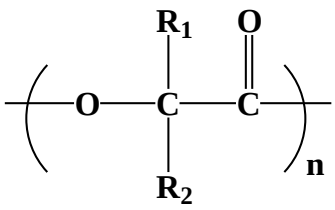
Aliphatic polyesters obtained from unsymmetrical diols like 1,2 propanediol and adipic acid are viscous oils solidifying into amorphous glass (T_g = - 42^0C) at low temperatures. The disturbance to the structural regularity in this polyester is due to two reasons (1) aperiodic spacing of methyl groups along the chain and (2) random atactic distribution of optical configuration. Poly (1,2-propylene sebacate) with sufficiently long methylene sequences is crystallizable and has a very low T_m of 20^0C. Similar behavior was found in copolyesters. Thus, poly (ethylene-co-1,2-propylene adipate)s are crystallizable where 1,2-propylenedioxy group content is below 40 mol %. Polyesters obtained from sterically balanced gem-dialkyl groups are crystalline.

Table 1.8: T_m and T_g of the aliphatic polyesters of succinic acid and 1,2-butane diol (1,2 BD) or 1,2-decane diol (1,2 DD)

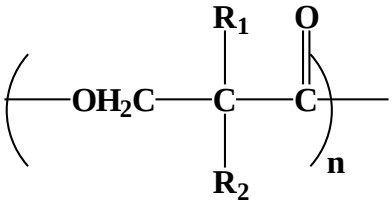
Co-monomer (mol %)	T_m (^{0}C)	T_c (^{0}C)	T_g (^{0}C)

-	116	-6	-37
1,2 BD (04)	112	0.5	-37
1,2 BD (08)	111	2.7	-37
1,2 BD (13)	109	-2 to-5	-38
1,2 DD (03)	110	4.4	-37
1,2 DD (05)	108	6.2	-36
1,2 DD (12)	100	17	-37

Polyesters derived from α, α', δ, δ'– tetramethyl adipic acid with ethylene glycol and neopentyl glycol have T_m values of 67^0C and 65^0C, whereas poly (neopentylene α,α'– dimethyl malonate) has a T_m of 275^0C[121].



(8a)



(8b)

For polyesters derived from hydroxy acids, the presence of single or two non-identical substituents on the chain atom establishes chirality leading to tactic stereoisomerism as displayed in polyesters of lactic acid. The stereospecific isotactic all (S) form is crystalline with T_m varying in the range of 163-215^0C and is optically active. The racemic atactic optically inactive form, on the other hand, is questionably crystalline with different mechanical properties than those of the S isomer. Comparable differences occur between the L and DL forms of **8a**, where R_1 = isopropyl, R_2 = H. High thermal transition temperatures are rather commonly found in gem-disubstituted polyesters of types **8a** and **8b**. Poly (dimethylglycolide), where $R_1 = R_2 = CH_3$ has $T_m = 240^0$C and $T_g = 60^0$C which are values similar to those of unsubstituted polyester. Unlike the

unsubstituted polyesters, the gem disubstituted polyesters is readily soluble in common organic liquids[122]. Polyesters of structure **8b**, with $R_1 = R_2$ = lower alkyl, chloromethyl or aryl, or with $R_1 + R_2 = (CH_2)_5$ have melting temperatures in the range of 230-270^{0}C. Crystalline gem disubstituted polyesters of the type **8a** and **8b** display a considerable resistance to hydrolysis, probably due to steric impedance to the approach of the attacking reagents to the ester groups[123].

Polypivolactone (where $R_1 = R_2 = CH_3$) is an interesting thermoplastic and fiber forming material which has a T_m of 234-245^{0}C (the precise value being affected by polymorphism) good mechanical properties and insensitivity to many organic liquids. Its heat distortion temperature is 180-200^{0}C. It finds applications as component of novel block and graft copolymers. Polyesters of the type **8b** with dissimilar substituents have also been investigated[124-125], their T_m s are generally lower than that of the unsubstituted polymer (122^{0}C).

1.4.4 Hyperbranched polyesters

Step growth polymerization of aliphatic AB_x – type monomers, particularly AB_2 results in a randomly branched macromolecule referred to as hyperbranch polymer[126-129]. Due to their compact, branched structure and to the resulting lack of chain entanglements, dendritic polymers exhibit much lower melt and solution viscosity than their linear counterparts. The extensive branching in hyperbranched polymers prevents crystallization and results in amorphous and brittle materials. The lack of chain entanglements, which are responsible for most of the polymer mechanical properties, explains why hyperbranched polyesters cannot be used as thermoplastics for structural applications. Although some crystalline or liquid crystalline hyperbranched polymers have been reported, most hyperbranched polyesters described so far are amorphous. Glass transition temperature of hyperbranched polyesters is strongly influenced by the nature of end groups. Increasing end-group polarity generally leads to increase in T_g. The T_g values reported for acetate and carboxy terminated hyperbranched polyesters are much higher than those terminated with long alkyl chains. The melt viscosity of hyperbranched polyesters is also strongly influenced by the nature of end groups. Increase in melt viscosity by several orders of magnitude has been reported for aliphatic polyesters when

ester end groups are replaced by more polar hydroxy end groups[128]. High solubility in organic solvents is another remarkable feature of hyperbranched polymers, which strongly depends on the nature of end groups. It is noteworthy to mention that the only aliphatic hyperbranched polyester[130-131] obtained from dimethylol propionic acid has been commercially introduced. Thus the branched architecture and presence of large number of end groups impart to the hyperbranched polymers, properties which are not found in linear polymers.

1.5 Properties of aliphatic poly (ester) s

The properties of aliphatic polyesters depends on several factors such as the composition of repeat units, flexibility of the chain, presence of polar groups, molecular weight, degree of branching, crystallinity and orientation. The properties of these materials can further be tailored by blending and copolymerization or by change in the macromolecular architecture like hyperbranched or star shaped polymers or dendrimers.

1.5.1 Thermal properties

Thermal properties of polyester include glass transition temperature, melting temperature and thermal stability and are very useful in determining the end use as a thermoplastic. Since melting is a thermodynamic equilibrium, melting temperature is given by the classical relationship $T_m = \Delta H_m / \Delta S_m$ *where* ΔH_m *and* ΔS_m *are enthalpy and entropy of melting respectively. Therefore* T_m *can be regarded at first approximation as a measure of both intermolecular interactions, which govern* ΔH_m*, and chain flexibility, which govern* ΔS_m*, parameters that obviously control many of the polymer properties. However melting temperature of semi crystalline polymers might also be influenced by other factors like molecular weight, degree of crystallinity and crystallite size. Linear polyesters do not have strongly interacting groups like hydrogen bonded ones. Consequently* ΔH_m *is not dramatically different for different polyesters and the predominant factor affecting melting temperature is* ΔS_m*, which is the number of conformations available in the molten state or in*

other words chain flexibility. Therefore T_m is very sensitive to the nature or structure of monomers in the polyester chains and as a result varies over a very broad range, from room temperature to temperatures above 500^0C.

Glass transition temperature T_g reflects the segmental mobility in the amorphous phase and follows similar trend as that observed for T_m, increasing chain rigidity leading to increasing T_m and T_g. For semi crystalline polyesters, T_g can be found close to 0.6 T_m to 0.65 T_m (T values in Kelvin)[107]. Amorphous aliphatic polyesters are usually low-T_g viscous oils. The T_g of random binary copolyesters vary monotonically with composition between the T_g of homopolymers and have been reported to satisfy Fox or Gordon – Taylor equations.

Polyesters prepared from linear diols as well as linear diacids have highly flexible chains and hence high entropy of melting and lower melting temperature. These polyesters are semi crystalline and therefore the melting temperature also depends on the molecular weight and crystallinity. Generally higher molecular weights have higher melting temperature. Bionolle[132] is one such linear aliphatic polyester, which has been commercialized. It is a white semi crystalline thermoplastic melting in the range of 90-120^{0}C and has T_g ranging from -45 to -10^{0}C. It is a copolyester prepared by the polycondensation of 1,4-butanediol or 1,2-ethanediol with succinic acid or mixtures of succinic and adipic acids and chain extended with diisocyanates as coupling agents. Depending on the composition, the properties of Bionolle[132] vary between those of LDPE and HDPE.

Aliphatic polyesters having higher T_m and therefore improved properties can be obtained by polymerizing with cyclic diols or diacids or both as discussed in the previous section. Some of these polyesters have been used as engineering plastics (eg. PCCD).

Among the poly (lactones), poly (ε-caprolactone) is the most representative member. It is a semi crystalline polyester, having properties similar to those of LDPE. It has a T_m ranging from 59-64^{0}C and a low T_g of -60^{0}C[133]. Poly (δ-valerolactone) has physical properties similar to those of poly (ε-caprolactone) and has a T_m of 59^{0}C and T_g of -67^{0}C. Poly (1,4- dioxepan-2-one) is another polymer similar to poly (ε-caprolactone), but is a completely amorphous polymer with a T_g of -37^{0}C.

Most poly (α-esters) and poly (β-esters) are high melting semi crystalline polyesters. Poly glycolic acid) PGA has the highest melting point among all aliphatic polyesters and ranges between 220-225^{0}C. Tacticity has a strong influence on the melting point and properties of poly (lactic acid) (PLA). Pure enantiomeric L-lactic acid and L,L lactide produce isotactic poly (L-lactic acid) (PLLA), which is semi crystalline and melts at 170-190^{0}C with a T_g of 61^{0}C. D-lactic acid leads to isotactic poly (D-lactic acid) PDLA, a polymer with similar properties as isotactic PLLA.The poly (β-esters) like poly (β-hydroxy butanoic acid) is highly crystalline, brittle polymer with T_m of 177^{0}C and T_g of 9^{0}C. T_m and T_g can be significantly affected by copolymerization. Copolymerization with branched diols like 1,2-butanediol and 1,2-decanediol reduces T_m as seen in **Table 1.8**.

Copolymers of glycolic acid and lactic acid have a $T_g \geq 35^0$C whereas in case of copolymers of ε-caprolactone and lactide, T_g increases with increase in lactide content in the polymer.

Table 1.9: Properties of poly (CL-co-DXO), poly (VL-co-DXO) and poly (LLA-co-DXO)

Copolyester	%DXO in copolyester	T_g (^{0}C)	T_m(^{0}C)
CD50	50	-56.8	27.8
CD60	41	-57.8	27.2
CD70	29	-55.5	36.0
CD80	18	-61.0	42.8
CD90	8	-65.6	50.5
CD100	0	-65.9	57.6
VD70	33	-56.7	28.0
VD80	25	-56.1	37.7
VD90	7	-59.9	46.0
VD100	0	-63.4	57.5

LD70	28	23.1	154.1
LD85	13	41.1	170.8
LD100	0	58.5	183.8

The copolymers of 3-hydroxy butyrate (3HB) with 4-hydroxy butyrate (4HB) at 91:9 compositions melt 159^0C and the 1:1 copolymer with 3-hydroxy valerate melts at 91^0C. The variation of T_g and T_m with composition in the copolymerization of 1,4-dioxepan-2-one (DXO) with L-lactide (LLA), δ-valerolactone (VL) and ε-caprolactone (CL)[134-135] is shown in **Table 1.9**.

1.5.2 Crystallization and morphology

Many of the aliphatic polyesters are semi crystalline and the extent of crystallinity is critically important in determining the ultimate physical properties. The crystallinity developed is dependent on the average molecular weight and distribution (which influence crystallization kinetics), crystallization/ processing conditions (and its relationship to the T_g of the polymer), chemical structure of the chains (flexible or rigid), and structural regularity. Properties of crystallizable aliphatic polyesters are strongly dependent on the morphological structure (size, shape, perfection, volume fraction and orientation of crystallites), which is formed by crystallization from the molten state.

Some of the semi crystalline aliphatic polyesters which show polymorphism are as follows : poly(ethylene succinate) (α crystal (T_3GT_3G) and β crystal (T_8) [136-137], poly ([R]-3-hydroxy –butyrate) (α crystal with 2_1 helical conformation and β crystal with zigzag conformation)[138], poly(L-lactic acid) (α crystal and β crystal with respective 10/3 and 3/1 helical conformations[139], and poly (β-propiolactone) (α crystal with 2_1 helical conformation, β and γ crystals with the same planar zigzag conformations but different molecular arrangements from the projection to the ab-plane)[140].

Poly (butylene succinate) (PBS) exist in two forms monoclinic α crystal and monoclinic β crystal[141]. Polymorphism of poly (butylene adipate) (PBA) was found in stretched and annealed films. PBA polymorphic crystals can be prepared simply by melt crystallization at different temperatures[142]. Analysis of equilibrium melting temperatures

of PBA crystal forms indicated that PBA α crystal is more stable than the β crystal. The PBA α crystal has higher crystallinity and higher lamellar thickness than the β crystal. The PBA chains in both α and β crystal lattices have similar planar zigzag conformations[143], however the chain packing of α crystal in the monoclinic unit cell and that of β crystal in the orthorhombic unit cell are different, resulting in the corresponding changes of crystal property and morphology. Different spherulite morphologies have been found in the PBA films corresponding to the different crystal structures. The PBA films with mixed α and β crystal structures showed spherulites with banded rings, while the films with either α or β crystal structure did not show banded spherulites.

In case of poly (ε-caprolactone), the crystallinity decreases with increase in molecular weight, because of the lowering segmental mobility associated with longer chains. An unusual morphology with distinct branches in the spherulites was observed for PCL with M_n = 1900. This morphology was due to segregation of the uncrystallizable chains into the interfibrillar regions in the spherulites[144].

PLLA is a semi crystalline polymer and on crystallization yields spherulitic crystalline morphology[145]. The α crystal structure has pseudo orthorhombic unit cell and the β form has an orthorhombic unit cell. It has been reported that α structure has a T_m of 185^0C whereas β structure has T_m of 175^0C, suggesting that α structure is more stable than β structure. The crystallization behavior of PLA is very much dependent on the molecular weight and stereochemical makeup of the backbone.

1.5.3 Crystallization kinetics

Crystallizable polymers form semi crystalline materials containing chains or fractions of chains that are trapped in non-equilibrium, amorphous states. Due to this semi crystalline nature, the crystal morphology, rather than the underlying crystal structure, often controls the final properties of the polymer article. A very important characteristic of semi crystalline polymers that strongly influences the utility of the material for a given application is the crystallization rate. Fast crystallization allows for high production rates of molded articles, since the time needed for the material to solidify in the mold is a function of crystallization rate. Study of bulk crystallization kinetics of polymers is an important step in understanding, predicting and designing structural formation under

various processing conditions. In general, the well-known Avrami equation and secondary nucleation theory, describe well the crystallization kinetics of polymers. The crystallization kinetics of polymers is analyzed using a classical Avrami equation[146-148] given as follows:

$$1-X_t = \exp(-kt^n)$$

where, X_t is the development of crystallinity X_c at time t. k is the overall crystallization rate constant and n is the Avrami exponent. Both k and n depend on the nucleation and growth mechanisms of spherulites. The value of n is usually an integer between 1 and 4 for different crystallization mechanisms. It has also been observed that n is a fraction due to the secondary crystallization or crystal imperfection. For spherulitic growth and athermal nucleation, n is expected to be 3 and that for thermal nucleation, it is expected to be 4. The n value close to 2 may hint an athermal nucleation process followed by a two dimensional crystal growth[149].

Molecular weight is one of the key variables governing the thermodynamic and kinetic parameters of polymer crystallization. The equilibrium melting point (T_m), crystal thickness, crystallization kinetics, degree of crystallinity and crystalline morphology are influenced by molecular weight[150-151]. Crystallization rate generally decreased with increasing molecular weight because of the lower segmental mobility associated with longer chains[152].

Poly (butylene succinate) (PBS) has a high crystallization rate and therefore is particularly well suited for extrusion and injection molding applications. For PBS having an inherent viscosity of 1.32 dl/g (at 30^0C), the non isothermal crystallization from melt resulted in the Avrami exponent n values ranging from 2.1 to 3.4[153]. The overall crystallization kinetics changes from slow crystallization with an Avrami exponent n = 2.1 at 65^0C to n = 2.5-2.9 at 70-75^0C in the faster crystallization and finally approaches n= 3.4 at 80^0C where the crystallization rate is slow again. This indicates that PBS has a spherulitic crystal growth in the early stages of crystallization.

PLA is a slower crystallizing material like PET as compared to PBS, with the fastest rates of crystallization for the pure polymer being in the temperature of 110-130^0C which yield spherulitic crystalline morphology[145]. The slow crystallization may be due to

the pendent methyl groups in the polyester chain which have a retarding effect on the rate of crystallization. Hence it is best used in the applications where crystallinity and strength can be enhanced through mechanical orientation, for example, oriented fibers, biaxially oriented films and soft drink bottles produced by stretch blow molding techniques, which introduce a high degree of orientation in the finished part[154].

For pure PCL homopolymer, the Avrami exponent n was found to be between 3.2 and 2.4 from 38 to 45^0C, in agreement with the previous studies of Goulet et al.[155] that reported values of 3.5, 3.4, 2.5 and 2.7 for 40,45, 47 and 49^0C, respectively. Taking into account that this polymer exhibits spherulites in the optical microscope, the n values indicate a three dimensional growth with a mixed nucleation mechanism[156].

1.5.4 Mechanical properties

The mechanical properties like tensile yield strength, flexural modulus and impact strength play a key role in determining the end use applications as engineering thermoplastics. The impact strength of a polymer depends significantly on the T_g and the kinetics and degree of crystallization[157]. Amorphous polymers exhibit brittle fracture well below their T_g, but they become tougher as T_g is approached. As the temperature increases well above the T_g, a rubbery state is developed and the term impact strength ceases to have significance. In crystalline polymers, the toughness depends on the degree of crystallinity and on the size of the spherulitic structures. Large degrees of crystallinity will lead to inflexible masses, which, in turn will result in moderate impact strength. Similarly large spherulitic structures will also result in low impact strength.

The toughness of a polymer also relates to the ability of parts of the polymer chain to conserve certain mobility even at low temperatures. The low temperature relaxation maximum in the dynamic loss modulus is the hallmark for the temperature region in which these molecular motions begin. Therefore temperature and amplitude of this relaxation is closely related to the toughness of a polymer. Good toughness is usually observed even at low temperature if the γ relaxation occurs at a low temperature and has comparatively high amplitude. Polymers show three transitions, namely α, β and γ transitions corresponding to T_m, T_g and T_γ[158]. The dynamic mechanical analysis of polymers gives insight into the sub-T_g relaxations (low temperature relaxations)

occurring in the polymer chain, γ and δ relaxations. Consideration of dynamic mechanical analysis results of polymers suggest that the γ transition is connected with motions in the aliphatic part of the chain and that T_g (β relaxation) is connected to the phenylene carbonyl bond.

The properties of aliphatic polyesters are shown in **Table 1.10**. Generally the aliphatic polyesters have low impact strength as compared to the aliphatic-aromatic polyesters. Backbone groups that increase the rigidity of polymer chains by increasing steric interactions or by decreasing conformational flexibility often result in polymers with high impact resistance. Monomers which impart high T_g to polyesters generally have good impact strength. Therefore polyesters derived from cycloaliphatic diols and/or diacids have better impact strength compared to the linear aliphatic polyesters. Bionolle has tensile properties between that of polyethylene and polypropylene and stiffness between that of LDPE and HDPE.

The mechanical properties of PLA depend on the molecular weight and stereochemical make up of the backbone. This stereochemical makeup of the backbone is very easily controlled by the polymerization with L-lactide, D-lactide, D,L-lactide or meso-lactide to form random or block stereo copolymers while the molecular weight is directly controlled by the addition of hydroxyl compounds like lactic acid, water, alcohols.

Perego et al. studied the effects of molecular weight and crystallinity on the mechanical properties of poly (L-lactide) or (D, L-lactide) polymers[159]. They found that T_g was not greatly affected by the stereochemical makeup or the range of molecular weights tested. PLA with a molecular weight of 22,000 g/mol still has a T_g of 55^0C which is only about 4-5^0C lower than polymer of infinite molecular weight[160]. The highest modulus and tensile strengths were found at M_n above about 50,000 g/mol. They found that the properties, especially the impact resistance and vicat softening, increased with crystallinity and molecular weight. **Table 1.11** shows the properties of three different systems: amorphous poly (L-lactide), poly (L-lactide) annealed and amorphous poly (D,L-lactide). The impact resistance increased due to cross linking effects of crystalline domains while the tensile strength increased presumably due to the stereo regularity of

the chain[159]. **Table 1.12** shows the various properties of both oriented and unoriented PLA.

Table 1.10: Properties of biodegradable aliphatic polyesters[161]

Polyester	PGA[a]	PLLA[a]	PDLLA[a]	PHB[b]	PHBV[b]	CAPA[c]	Bionolle[d]		Eastar Bio[e]
							PBSU	PESU	
T_m (^{0}C)	225-230	170-190	-	177	135	58	114	104	108
T_g (^{0}C)	40	50-60	50-60	4	-	-60	-32	-10	-30
Density g/cc	1.50-1.69	1.25-1.29	-	1.25	-	1.15	1.26	1.32	1.22
Melt flow index, g/10min (190^{0}C,2.16 kg)	-	10-30	-	-	-	2.9	-	-	28
Tensile strength (MPa)	80-980[f]	120-2300[f]	40-50[g]	40	20	40/43 (MD/TD)[h]	-	-	22/20 (MD/TD)[h]
Tensile Modulus (MPa)	3900-13,800[f]	6900-980[f]	1500-1900[g]	-	-	-	550[i]	580[i]	107/106 (MD/TD)[h]
Elongation at break (%)	30-40[f]	12-26[f]	5-10[g]	3.0	100	-	560	200	700/730 (MD/TD)[h]
Stress at yield (MPa)	-	-	-	-	-	18/16 (MD/TD)[h]	33	20.5	-
Notched Izod impact strength (J/m)	-	16	-	35	300	-	294	98	-

[a]PGA: poly (glycolic acid); PLLA: poly (L-lactic acid); PDLLA: poly (DL-lactic acid); [b]PHB: poly (3-hydroxybutanoic acid); PHBV: poly(3-hydroxybutanoic acid-co-3-hydroxyvaleric acid); [c]CAPA: poly (ε-caprolactone) FB100; [d]Bionolle PBSU: poly (butylenes succinate); Bionolle PESU: poly (ethylene succinate); [e]Eastar Bio: poly (tetramethylene adipate-co-terephthalate); [f]Oriented fiber; [g]Nonoriented fiber; [h]MD: machine direction; TD: transverse direction; [i]Stiffness following JIS-K7203

Table 1.11: Effects of stereochemistry and crystallinity on mechanical properties[162]

Annealed			
	L-PLA	L-PLA	D,L-PLA
Yield strength (MPa)	70	70	53
Tensile strength (MPa)	59	66	44
Flexural strength (MPa)	106	119	88
Notched Izod impact strength (J/m)	26	66	18
Vicat softening (^{0}C)	59	165	52

The wide variance in the oriented properties is due to the degree of orientation and stereochemical composition of the different referenced polymers. The pure stereo complex of 1:1 mixture of pure poly (L-lactide) with pure poly (D-lactide) has a melting point of 230^{0}C and mechanical properties greater than either pure polymer[163-164]. Using lower molecular weight polymers, Loomis and Murdoch report ultimate tensile strengths of 50 MPa for the 1:1 complex versus 31 MPa for pure L-polymer[165].

In its highly crystalline form, poly (glycolic acid) PGA has a very high tensile strength of 69-138 MPa and modulus elasticity of 6900 MPa. Injection molded samples of PCL exhibit a modulus of 400 MPa and yield stress of 15 MPa. The material can be processed without any significant molecular weight reduction by injection molding, film blowing and extrusion.

Table 1.12: Physical properties of high molecular weight PLA[162]

	Unoriented	Oriented[a]
Ultimate tensile strength (MPa)	47 - 53	47 - 165
Tensile yield strength (MPa)	45 - 61	N/A
Tensile modulus (MPa)	3445 - 3996	3886 - 4134
Notched Izod impact (J/m)	16-22	N/A
Elongation at Break (%)	3.1-5.8	15-160
Rockwell hardness	82-88	82-88
Specific gravity	1.25	1.25
Glass transition temperature (T_g ^{0}C)	57-60	57-60

[a]Results depend on degree of orientation and isomer content

1.5.5 Weatherability

The resistance of polymeric materials to weathering is a very important factor in their use in outdoor applications. Most polymeric products require protection against effects of the environment to obtain serviceability. In some applications, weatherability tests are carried out to assure that the materials degrade rapidly after their intended use in order to protect the environment.

Aliphatic polyesters generally have poor hydrolytic stability. Though a desired property, it should be resistant to hydrolysis during use. The hydrolytic stability during use can be accomplished by application of coatings, which offer good hydrolytic stability. Additives like light stabilizers, antioxidants, flame retardants and biocides are generally added to the polymers, which enhance their performance in, prolonged outdoor applications.

Coatings can increase the weatherability of polyesters. These coatings have excellent flexibility and durability with very good weatherability and resistance to UV radiation. Coatings can be classified into thermoplastic and thermosetting coatings. A wide variety of polymers including aliphatic polyesters are used in coatings and these

polymers are generally amorphous materials. Hydroxyl or sometimes carboxyl terminated polyesters are used in coatings. The hydrolytic stability of polyesters for exterior durability is increased by using substituted diols like neopentyl glycol (NPG), 1,4 cyclohexane dimethanol (1,4 CHDM) and trimethylol propane. Low molecular weight, hydroxyl terminated polyester diols and triols derived from the reaction of caprolactone and diol or triol are commercially available.

Powder coatings are also available where the solid powder is converted after application into a liquid, which in turn forms a solid film. T_g and melt viscosity are important considerations for powder coatings. Polymers used in the manufacture of powder coatings are classified broadly as either thermosetting or thermoplastic. Thermosetting coatings, as compared to thermoplastic compositions, are generally tougher, more resistant to solvents and detergents, have better adhesion and do not soften when exposed to elevated temperatures. Polyester resins that exhibit good weatherability and meet the basic T_g requirements for powder coatings are becoming increasingly important, particularly for outdoor applications. Fully aliphatic polyester resins based on cycloaliphatic diols and/or diacids like 1,4 cyclohexanedicarboxylic acids (CHDA), hydrogenated bisphenol A are useful as weatherable powder coating resins[166]. Aliphatic powder coatings for improved UV resistance and flexibility can be prepared using 1,4-CHDA. However, when all TPA is replaced by 1,4-CHDA in the polyester powder coating resin, T_g decreases. This detrimental effect on T_g is overcome by adding one or more additional monomers to compensate for the T_g deficiency. Hydrogenated bisphenol A (HBPA) enhances T_g when used in the coating resins.

1.5.6 Biodegradability

Plastics and polymers have become an essential element of modern life. The inherent advantages of plastics and their use lead to some of the greatest concerns about fossil fuel based materials. The durability of many plastics, under both aerobic and anaerobic conditions, contributes to growing waste and waste disposal problems. Even improving recycling rates for many types of plastics have not kept up with increase in overall plastic consumption. And in some cases recycling yields new problems associated with concentration of the contaminants through the recycling process. The use of

biodegradable or environmentally degradable polymers reduces the impact on the environment to some extent. The biodegradability of a polymer is highly dependent on its backbone structure[167] such as presence of hydrolyzable and or oxidizable linkages in the backbone. The predominant biodegradation reactions of polyesters are chemical and microbial hydrolysis. The degradation rate is influenced by polyester molecular weight, crystallinity, morphology (crystallinity, size of spherulites, orientation), molecular geometry, repeat unit, composition, sequence length hydrophobicity/ hydrophilicity, T_g, surface area, additives, degradation conditions and presence of degradation products. PGA, PLA and their copolymers are hydrophilic polymers and degrade either in vivo or in vitro through an abiotic bulk hydrolysis mechanism, which first affects the amorphous regions. The degree of crystallinity has been reported as the major controlling factor in the enzyme catalyzed hydrolysis of PLA[168]. PHAs, PCL and poly (alkylene adipate) or poly (alkylene succinate) are more hydrophobic than poly (α-esters), and their abiotic hydrolysis occurs more slowly, through surface erosion rather than bulk hydrolysis. Low molar mass polyesters are known to undergo hydrolytic degradation in the presence of lipases and esterase[169]. The degradation products of polyesters are bioassimilated by microorganisms, irrespective of enantiomeric composition. Polymer biodegradation mechanisms and testing methods have been reviewed[170].

The key measurement tool for environmental sustainability is life cycle assessment[171]. The ideal environmentally sustainable product provides equivalent function as products it replaces and is available at competitive costs. It is made from renewable resources, can itself be constantly renewed without degradation in quality or performance, and has a minimum environmental impact. Such a product is made using only substances known to be safe for both humans and the environment. Ideally the life cylce of the sustainable product is in balance with the surrounding ecosystem. Hence sustainable and versatile polymers made from renewable resources are gaining importance.

1.6 Depolymerization of polyesters[172a]

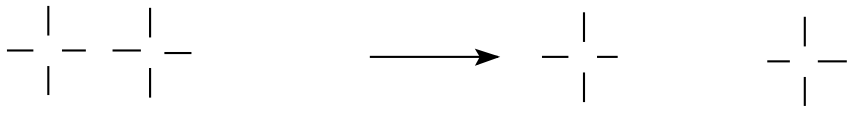
1.6.1 Introduction

Polyesterifications are equilibrium reactions. Depolymerization involves shifting the equilibrium towards the monomers by reacting the polyester with water, methanol, ethylene glycol (EG) or other glycols. Typically, the equilibrium constant K for a polyesterification is no greater than 1-10, while K for transesterification is in the range of 0.1-1. The K values indicate that chemical depolymerization of polyesters does not require very stringent conditions.

Since step-growth polymers are often prepared by reversible reactions, it is feasible to convert them back to their monomers or oligomers/chemicals by solvolytic processes such as hydrolysis, glycolysis, methanolysis, aminolysis, ammonolysis, transesterification, alcoholysis, hydro-glycolysis, acidolysis and transamidation. The principal solvolysis reactions for polyesters are methanolysis, glycolysis and hydrolysis. Among polyesters depolymerization of PET has been extensively studied as compared to other commercially available polyesters. Chemical recycling of PET was initiated nearly parallel to the manufacture of polymers on a commercial scale, as demonstrated by patents, beginning in the 1950s. Initially, recycling was used to recover wastes generated during the production stages. As the environmental movement began to focus seriously on solid waste and recycling issues, PET depolymerization received a boost. More recently depolymerization has been directed towards the chemical recycling of post consumer PET. PET has the second highest scrap value for recycled materials, second only to that of aluminium[172b].

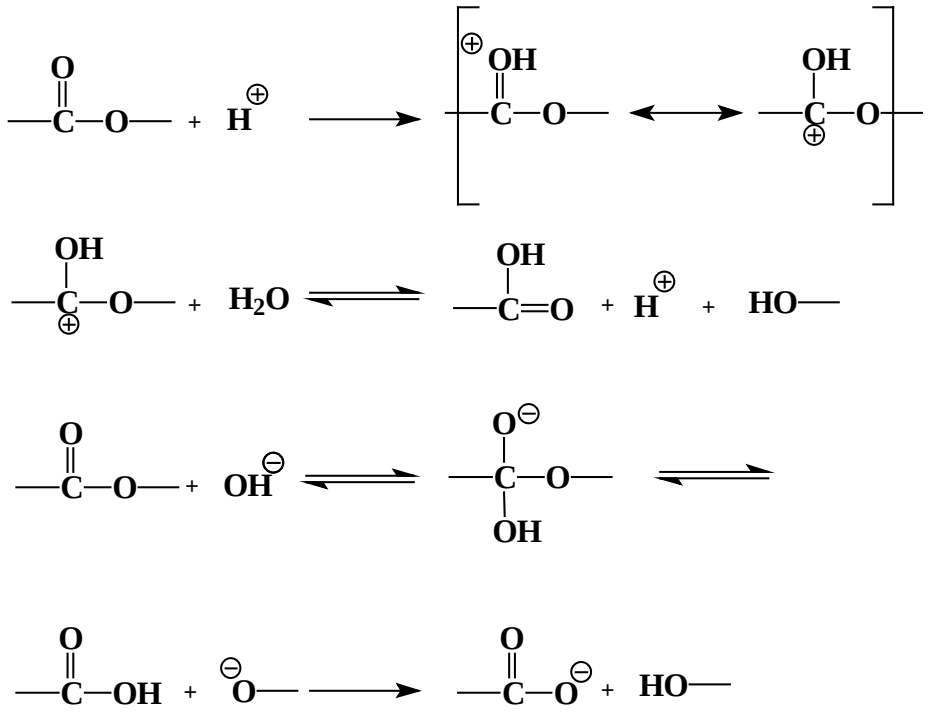
1.6.2 Chemistry of depolymerization reactions

Polyesters are depolymerized by solvolysis reactions such as methanolysis, glycolysis and hydrolysis. In general, the solvolytic reactions of polymers involve the cleavage of the C-X bonds of the polymer chain where X is a hetero atom (O, N). The mechanism of the solvolytic process is shown in ***Scheme 1.7****, where YZ is the solvolytic agent such as water, alcohol, acid, alkali or amine.*



Scheme 1.7: Solvolysis reactions of polymers

The general mechanism for degradation of polyester in an acid and basic solution is shown in ***Scheme 1.8****.*



Scheme 1.8: General mechanisms for degradation of polyester in acid and basic solutions

In an acid environment, the mechanism is the $A_{AC}2$ mechanism where as in an alkaline environment, the mechanism is the $B_{AC}2$ mechanism. Acids such as sulfuric and nitric acids or bases such as sodium hydroxide catalyze the hydrolysis. The rate of alkaline hydrolysis of PET increases in the presence of quaternary ammonium compounds[173-174]. Neutral hydrolysis usually takes place under high temperature and pressure in the presence of alkali metal acetate transesterification catalysts[175]. The catalytic effect of zinc and sodium acetates is thought to be due to the destabilization of the polymer-water interface in the hydrolysis process. Methanolysis involves reaction of polyester with methanol at high temperatures and pressures in the presence of transesterification catalysts such as magnesium acetate, cobalt acetate and lead dioxide. Glycolysis is carried out in the presence of transesterification catalyst, usually zinc, lead, manganese, cobalt, sodium or lithium acetate.

1.6.2.1 Hydrolytic depolymerization

The process of hydrolytic depolymerization was studied in case of PET and the process was patented as early as in 1962 by Eastman Kodak Company. Hydrolysis of PET flakes with water can be either acid-catalyzed (with mineral acids) or base-catalyzed (with NaOH). More recently hydrolysis of PET has been shown to be possible at neutral pH and at temperatures above melting point of PET. Hydrolysis of PET yields hydroxyl and carboxyl end groups which are conveniently measured by end-group analysis.

Acid catalyzed hydrolysis

Polyester waste may be hydrolyzed with strong acids such as sulfuric, phosphoric and nitric acids to produce terephthalic acid (TPA) and ethylene glycol (EG) in high yields without the use of high temperatures and pressures. The process occurs at temperatures of 25-100^{0}C in a few minutes at atmospheric pressure. The hydrolysis product is neutralized with base to produce the TPA salt. After treatment with ion exchange columns, the solution is acidified to produce TPA[176-177]. A major problem with this process is the corrosion caused by the reaction mixture and the production of large amounts of liquid wastes containing inorganic salts and sulfuric acid and the cost due to the need to recycle large amounts of concentrated sulfuric acid and the purification of EG containing sulfuric acid. Yoshioka et al describe a process for acid-catalyzed depolymerization of PET in which PET bottles are digested in 7-13M nitric acid at temperatures ranging from 70-100^{0}C for 72 h to form TPA, EG and oxalic acid. The oxalic acid is produced by the oxidation of EG by nitric acid. The NO is recycled by oxidation and the addition of water to form nitric acid. Since the oxalic acid is more valuable than TPA or EG, the economics of the process are improved compared to the acid catalyzed hydrolysis to produce TPA and EG only.

Base catalyzed hydrolysis

Alkaline hydrolysis of PET involves reacting PET with a 4-20 wt% solution of NaOH under pressure at temperatures in the range of 200-250^{0}C for several hours to form the sodium salt of TPA. Acidification of the sodium salt of TPA yields the TPA on precipitation from solution. Niu has demonstrated the use of quaternary ammonium salts to accelerate the alkaline hydrolysis of PET at 80^{0}C and atmospheric pressure. Collins

and Zeronian[178] have reported that the reaction of PET with methanolic sodium hydroxide accelerates the alkaline degradation of PET compared to the aqueous systems. Oku et al.[179] quantitatively converted PET to disodium terephthalate by reacting the polyester with sodium hydroxide dissolved in anhydrous ethylene glycol at 150^0C. Disodium terephthalate precipitated from the ethylene glycol solution. Yoshioka et al described a process for the conversion of postconsumer PET to TPA and oxalic acid in concentrated sodium hydroxide solution. The production of oxalic acid gives the process an economic boost because oxalic acid has a higher value than ethylene glycol. PET has also been treated with ammonium hydroxide and steam at 200^0C to form diammonium terphthalate and EG. TPA is obtained by acidification with sulfuric acid.

Neutral hydrolysis

Hydrolytic scission of PET has been shown to be possible with water at neutral pH and at temperatures above melting point of PET. Neutral hydrolysis of PET is usually carried out under pressure (1-4 MPa) at temperatures of 200-300^0C[180]. High purity TPA and EG may be obtained by the hydrolytic depolymerization of PET in an autoclave with excess water. A study of the factors involved in neutral hydrolysis of PET showed that depolymerization occurred in 2 h at 265^0C with an initial ratio of 5.1: 1 (w/w) water to PET[181]. Alkali metal acetates typically catalyze the process. The major problem with this process is that the impurities present in the waste PET are carried over with the TPA product, thereby requiring extensive purification of the TPA obtained.

The only advantage of the hydrolysis process is that it can handle PET with up to 40 wt % of contamination. The economics of this process are highly dependent on the scale, purity and markets for end products. It is difficult to purify TPA from the reaction mixture since it has low solubility and low vapor pressure. Purification by multiple crystallization of TPA increases cost. Compared to glycolysis and methanolysis, hydrolytic depolymerization of PET is a slow process.

1.6.2.2 Depolymerization *via* transesterification

Depolymerization can be accomplished by reaction of the polyester with excess of either an alcohol or diol in the presence of catalyst at high temperatures. The transesterification reaction between the polyester and diol or alcohol results in monomers or low molecular

weight oligomers. Depolymerization via transesterification reaction has been extensively studied in case of PET and two methods namely glycolysis and methanolysis have been described.

Glycolysis is one of the oldest methods of PET depolymerization and is used widely on a commercial scale. Generally partial alcoholysis is known as glycolysis. The variables affecting the rate of glycolysis of PET have been studied in detail by Vaidya[182] and Baliga[183]. The kinetics of glycolytic depolymerization of PET have been studied at temperatures in the range of 190-240^{0}C and it was concluded that the glycolysis is second order with respect to ethylene glycol and that the ethylene glycol acts as both a reactant and a catalyst in the glycolysis reaction. A proposed mechanism for PET glycolysis would be (1) glycol diffusion into the polymer (2) swelling of the polymer, which increases the rate of diffusion and (3) transesterification of the glycol hydroxy group with an ester group in the polyester chain. Since it is a transesterification process, metal acetate salts were found to be effective catalysts. Zinc compounds were found to have a catalytic effect on PET glycolysis below 245^{0}C. The reaction is generally performed under a blanket of inert gas to prevent the oxidation of the polyols produced. Glycolysis of PET actually yields the 'true' monomer of the polyester condensation, namely, bis (hydroxyl-ethyl) terephthalate (BHET), along with its respective oligomers. The reaction occurs more rapidly in the presence of an excess of ethylene glycol, however too large excess may lead to formation of diethylene glycol. Sodium acetate trihydrate and water are added to inhibit diethylene glycol formation. Glycols other than ethylene glycol like propylene glycol or 1,4-butanediol, 1,6-hexanediol, polyethylene glycol or even ethylene oxide may be used.

Methanolysis of PET is based on the reaction of PET with methanol at high temperatures (180-280^{0}C) and pressures (20-40 atm) to form DMT and ethylene glycol, which are raw materials for the production of PET. The reaction occurs in the presence of transesterification catalysts such as zinc, magnesium, and cobalt acetates and lead dioxide. The reaction temperature can be achieved by heating and melting PET in the first step, followed by exposure of the hot polymer to methanol or heat necessary to melt the PET polymer by superheated methanol vapors. Naujokas and Ryan[184] invented a process in which the scrap PET is dissolved in oligomers of DMT and ethylene glycol followed by passing of superheated methanol vapors through the solution. The reaction

mixture is held at lower pressures than necessary to keep methanol as a liquid because the resultant DMT is removed as a vapor. Removal of esters and alcohols as vapors allows more contaminated PET to be tolerated than by conventional liquid phase methanolysis. The resultant DMT is purified by distillation which removes all the physical contaminants and yields a high purity material. Besides DMT which is the principal product, methanol, EG, diethylene glycol (DEG), 1,4-cyclohexane dimethanol (CHDM) need to be recovered to make the process economical.

1.6.3 Recycling of waste polyesters *via* depolymerization

Recycling is a process by which materials are separated from waste destined for disposal and remanufactured into usable or marketable materials. The most commonly known polyesters are PET and PBT, although other specialty homo and copolyesters like PTT, PEN, amorphous copolyesters based on IPA and high melting copolyesters of CHDM, EG and pure TPA. In terms of volume and economic importance, thermoplastic polyesters are dominated by PET, which has experienced a tremendous development in fibers and molding resins due to a strong demand for textile applications and in food packaging and bottle markets for glass replacement. PET has a very favorable environmentally friendly image[185], and recycling is a supplementary force driving PET consumption. By comparison with the enormous volume of PET produced, the production of other polyesters appears quite modest.

From both ecological and economic considerations, it is important to evolve strategies for recycling of post consumer plastic waste. The major factors influencing the decision on the selection of an appropriate process/product option for polyester waste recycling are (1) availability of waste in terms of its quantity and quality, (2) polymer characteristics of the waste, (3) cost of recycling in relation to the selling price of the selected final product, (4) potential market size of the final product and (5) legislation on environmental protection

1.6.3.1 Recycling of poly (ethylene terephthalate)s

There are two methods of recycling of PET (a) physical recycling and (b) chemical recycling.

Physical recycling involves remelting of the solid flakes or granules in an extruder for pelletizing into chips or for direct melt processing into value added products, such as coarse denier staple fibers (> 3 dpf), hollow fibers for filling, partially oriented yarns, dope dyed fibers or filament yarns and strappings for packaging. The recycled PET chips can also be used for producing engineering plastic materials through melt compounding in a twin screw extruder into blends/alloys, fiber and mineral reinforced compounds.

In the chemical recycling process, PET waste is depolymerized into either of the starting monomers, namely EG, pure TPA or DMT or oligomers. The oligomers may be used for reconversion into PET by polycondensation or for production of polyurethane or unsaturated polyester resins by subsequent chemical reactions with other monomers. The major advantage of chemical recycling processes is the possibility of using any type of PET waste, irrespective of its polymer molecular weight or additive contamination. The chemical recycling processes are more readily amenable to removal of additive contaminants than the physical recycling route. The different process options for chemical recycling of PET waste may be categorized as follows (i) regeneration of base monomers (methanolysis for producing DMT and hydrolysis for producing pure TPA and EG) (ii) conversion into oligomers (glycolysis and solvolysis) (iii) use of glycolyzed waste for value added products, (iv) conversion into specialty chemicals by aminolysis or ammonolysis (v) conversion into specialty intermediates for use in plastics and coatings.

PET can be depolymerized with water (hydrolysis), methanol (methanolysis), ethylene glycol (glycolysis) and butanediol (diolysis). The main depolymerization processes that have been commercialized are methanolysis and glycolysis. Hybrid solvolytic methods of PET degradation such as glycolysis-hydrolysis, methanolysis-hydrolysis and glycolysis are unique as they can accept contaminated curbside plastic and convert it, by a combination of processes to a high quality PET suitable for food-grade use.

PBT has been produced from PET scrap by transesterification with 1,4-butanediol[172]. In this process, classified and clean polymer flake from post consumer PET bottles is reacted with 1,4BD to give PBT which is an engineering plastic. EG and THF formed during the process are recovered by distillation. Glycolysis may be applied to the

conversion of PET scrap to polyols for the production of important industrial materials such as polyurethanes, saturated resins, alkyd resins and unsaturated polyesters[172,186]. The conversion of scrap PET to polyols may be achieved by reaction with diols such as 1,6-hexanediol, propylene glycol, polyglycols such as polyethylene glycol or ethylene oxide. Unsaturated polyesters are obtained by the reaction of PET based polyols with substances like maleic anhydride. PET based polyols may be reacted with acids like phthalic, isophathalic acid and adipic acid to form saturated resins or fatty acid together with phthalic anhydride to produce alkyd resins which are used in the manufacture of coating materials and paints. The materials obtained from the reaction of PET with a mixture of fatty acids high in linoleic acid content and trimethylol ethane have been used in the preparation of water dispersible coatings. Products of depolymerization of PET with trimethylol propane and pentaerythritol are used in the manufacture of high-solids paints.

The products of degradative transesterification of PET with long chain aliphatic alcohols serve as a plasticizer. Transesterification of PET with 2-ethylhexanol produces dioctyl terephthalate and small amounts of octyl (2-hydroxyethylene) terephthalate and terephthalate oligoesters. This mixture is used as plasticizer for PVC[180]. PET waste has been used in the manufacture of terephthalic electroinsulation lacquers.

Other methods of depolymerization of PET like ammonolysis and aminolysis have also been researched extensively. Ammonolysis involves the reaction of PET with ammonia to form TPA diamide which may be converted into terephthalonitrile which may be further hydrogenated to form p-xylylenediamine and 1,4-bis (aminomethyl) cyclohexane[180]. Aminolysis of PET involves the reaction of PET with primary amines such as methyl amine, ethylamine and ethanol amine[187] to form mono and diamides of TPA.

Collectively all these chemical recycling processes are termed as chemolysis. Selection of the most appropriate recycling technique is dependent on the quality of the available feedstock and the type of end-products required. The different chemical recycling routes for PET essentially differ in the purity and consistency of the intermediates they produce.

1.6.3.2 Recycling of other poly (ester) s

All saturated linear polyesters can theoretically be depolymerized to recover all starting monomers. The basic chemistry and processes are similar for all of the commercial saturated polyesters. Polyesters such as poly (butylenes terephthalate), poly (ethylene naphthalate) and poly (cyclohexylene dimethylene terphthalate) could all be depolymerized to recover 1,4-butanediol, 2,6-naphthalenedicarboxylic acid or 2,6-dimethyl naphthalene dicarboxylate, and 1,4-cyclohexanedimethanol, respectively along with terephthalic acid or dimethyl terephthalate and ethylene glycol. The limitation is not in the chemistry or the process technology. The limitation to practical commercial polyester depolymerization is securing a satisfactory quantity of polymer at a price that permits the economical regeneration of monomers. The choice of technology is dependent, though, on the quality of the available feed and the desired product state.

While depolymerizing poly (ethylene naphthalate) could be attractive on the small scale because of the high commercial price for the naphthalate moiety, even this candidate resin is in too little availability to permit economical depolymerization. Among the polyesters, only PET is available in sufficient quantities to make commercial use of depolymerization potentially attractive.

Among the family of biodegradable aliphatic polyesters, optically active poly (L-lactide) and poly (R-3-hydroybutyrate) have been attracting much attention because they are produced from renewable resources and are biodegradable and compostable without any harmful effects on the environment[162,188]. Moreover, they have high mechanical performance comparable to those of commercial polymers like polystyrene and PET. Recycling of biodegradable polyesters such as PLLA, R-PHB and PCL is crucial to reduce the consumption of renewable resources and the energy for the synthesis of its monomers. The hydrolysis of PLLA, PCL and R-PHB proceeds *via* bulk erosion to yield monomers L-lactic acid, 6-hydroxycaproic acid and 3-hydroxy butanoic acid, and hence these polyesters can be used as recyclable materials.

1.7 References

1 W.H. Carothers, *Chem.Rev*. **8**, 353 (1931)

2 W.H. Carothers, J.W. Hill, *J.Am.Chem.Soc*. **54**, 1577 (1932)

3 W.H. Carothers, *Trans.Faraday Soc*. **32**, 43 (1936)

4 F.R.Jones, L.E.Scales, J.A.Semlyen, *Polymer* **15**, 738 (1974)

5 R.E.Health, B.R.Wood, J.A.Semlyen, *Polymer* **41**, 1487 (1999)

6 J.A.Semlyen, J.J.L.Bryant, S.C.Hamilton, B.R.Wood, *Polym.Prepr. (ACS., Div.Polym.Chem.)*, **38**(2), 189 (1997)

7 (a) T.Rieckmann, S. Volker, *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*, Chapter 2, pg 31, edited by J.Scheirs, T. Long, John Wiley & Sons, Inc. (2003) (b) P.J.Flory, *J.Am.Chem.Soc*. **62**, 2261 (1940)

8 F.Pilati, in *Comprehensive PolymerScience*,Vol 5, p.275, edited by G.Allen, J.C.Bevington, Pergamon, Oxford (1989)

9 A.Fradet, E. Marechal, *Adv.Poly.Sci*. **43**, 51 (1982)

10 W.L.Chang, T.Karalis, *J.Polym.Sci. Part A: Polym.Chem*. **31**,493 (1993)

11 A.Fradet, E.Marechal, *J.Polym.Sci.Polym.Chem.Ed*. **19**, 2905 (1981)

12 D.E.V. Sickle, R.I.Garrity, *Polym.Mater.Sci.Eng*. **70**,163 (1993)

13 I.Vancso–Szmercsanyi, E.Makay–Bodi, *J.Polym.Sci.,Part C*. **16**, 3709 (1968)

14 A. Fradet, E. Marechal, *J.Macromol.Sci.Chem*. **A17**, 859 (1982)

15 C.C Lin, P.C.Yu, *J.Appl.Polym.Sci*. **22**, 1797 (1978)

16 A.J.Amass, *Polymer* **20**, 515 (1979)

17 E.Paatero, K.Naerhi, T.Salmi, M.Still, P.Nyholm, K.Immonen, *Chem.Eng.Sci*. **49**,3601 (1994)

18 K.Uberreiter, W.Hager, *Makromol.Chem*. **189**,1697 (1979)

19 L.Nondek, J.Malek, *Makromol.Chem*. **178**, 2211 (1977)

20 F.Leverd, A.Fradet, E.Marechal, *Eur.Polym.J*. **23**, 695 (1987)

21 F.Leverd. A.Fradet, E.Marechal, *Eur.Polym. J*. **23**,705 (1987)

22 (a) H.A. Staab, *Angew.Chem.Int.Ed.Engl*. **1**, 351 (1962), (b) F. Higashi, N. Akiyama, I. Takahashi, T. Koyama, *J.Polym.Sci.Polym.Chem.Ed*. **22**, 1653, (1984)

23 I.M. Panayotov, N. Belcheva and C. Tsvetanov, *Makromol.Chem*. **188**, 2821 (1987)

24 F.Akutsu, M.Inoki, H.Uei, M.Sueyoshi, Y.Kasashima, K.Naruchi, Y.Yamaguchi, M.Sunahara, *Polym.J.* **30**, 421 (1998)

25 K.F.Brandstadt, J.C.Saam, A.Sharma, *Polym.Prepr.(Am.Chem.Soc. Div.Polym.Chem.)* **41(2)**, 1857 (2000)

26 A.L. Gutman, D. Knaani, T.Bravdo, *Macromol.Symp*. **122**, 39 (1997)

27 F. Binns, P.Harffey, S.M. Roberts, A.Taylor, *J.Polym.Sci.PartA: Polym. Chem.* **36**, 2069 (1998)

28 S.Geresh, Y.Gilboa, *Biotechnol.Bioeng.* **37**, 883 (1991)

29 C. Berkane, G.Mezoul, T.Lalot, M.Brigodiot, E.Marechal, *Macromolecules* **30**, 7729 (1997)

30 S.Kobayashi, H. Uyama, *Makromol.Chem.Rapid Commun*. **14**, 841 (1993)

31 A.Kumar, R.A. Gross, *J.Am.Chem.Soc*. **122**, 11767 (2000)

32 A.K.Chaudhary, B.J.Kline, E.J.Beckman, A.J. Russell, *Polym.Prepr. (Am. Chem.Soc.Div.Polym.Chem.)* **38 (2),** 396 (1997)

33 Y.Y.Linko, Z.L. Wang, J.Seppala, *Enz.Microb.Technol.* **17**, 506 (1995)

34 Z.L.Wang, K.Hiltunen, P.Orava, J.Seppala, Y.Y.Linko, *J.Macromol.Sci. Pure Appl.Chem.* **A33**, 599 (1996)

35 S.Sosnowski, M.Gadzinowski, S. Slomkowski, *Macromolecules* **29**, 4556 (1996)

36 M.Gadzinowski, S.Sosnowski, S. Slomkowski, *Macromolecules* **29**, 6404 (1996)

37 H.K.Hall,Jr., M.K.Brandt, R.M. Mason, *J.Am.Chem.Soc*. **80**, 6420 (1958)

38 A.Lofgren, A-C.Albertsson, P.Dubois, R.Jerome, *J.Macromol.Sci.Rev.Macromol.Chem.Phys.* **C35(3)**, 379 (1995)

39 D.Mecerreyes, R.Jerome, P.Dubois, *Adv.Polym.Sci*. **147**, 1 (1999)

40 H.R. Kricheldorf, I.Kreiser-Saunders, *Macromol.Symp*. **103**, 85 (1996)

41 T.Saegusa, S.Kobayashi, K.Hayashi, *Macromolecules* **11**, 360 (1978)

42 D.B. Johns, R.W. Lenz, A. Luecke, *Lactones, Ring opening polymerization,***1,** 464, edited by Ivin KJ, Saegusa T, Elsevier, London (1984)

43 A-C. Albertsson, R. Palmgren, *J.Macromol.Chem, Pure Appl. Chem.* **A33 (6)**, 747 (1996)

44 S. Penczek, *J.Polym.Sci, Polym.Chem.* **38**, 1919 (2000)

45 P. Kubisa, S. Penczek, *Prog.Polym.Sci*. **24**, 1409 (1999)

46 N.Nomura, A.Taira, K.Tomioka, M. Okada, *Macromolecules* **33**, 1497 (2000)

47 R.Jerome, P.Teyssie in *Comprehensive Polymer Science*, **3(1)**, 501, edited by G.C.Eastmond, A.Ledwith, S.Russo, P.Sigwalt (1989)

48 S.Penczek, S.Slomkowski, *Progress in anionic ring opening polymerization, Recent advances in anionic polymerization*, Chapter 19, 275, edited by T.Hogen-Esch, J.Smid, Elsevier, New York

49 Z.Jedlinski, P.Kurcock, R.W.Lenz, *Macromolecules* **31**, 6718 (1998)

50 K. Ito, Y. Hashizuka, Y.Yamashita, *Macromolecules* **10**, 821 (1977)

51 H.F.Kricheldorf, M.V Sumbel, *Makromol.Chem.* **189**, 317 (1988)

52 H.R Kricheldorf, M Bers, N Scharnagl, *Macromolecules* **21**, 286 (1988)

53 A.Kowalski, A.Duda, S.Penczek, *Macromolecules* **31**, 2114 (1998)

54 A.Kowalski., J.Libiszowski., A.Duda., S.Penczek., *Macromolecules* **33**, 1964 (2000)

55 K. Stridsberg, M.Ryner, A-C Albertsson, *Macromolecules* **33**, 2862 (2000)

56 N.Spassky, M.Wisniewski, C.Pluta, A.Le Borgne, *Macromol.Chem.Phys.* **197**, 2627 (1996)

57 T.M. Ovitt, G.W.Coates, *J.Am.Chem.Soc.* **121**, 4072 (1999)

58 B.M.Chamberlain, Y.Sun, J.R.Hagadorn, E.W. Hemmesch, M.A.Hillmyer, W.B.Tolman, *Macromolecules* **32**, 2400 (1999)

59 V.Simic, N.Spassky, L.G. Hubert-Pfalzgraf, *Macromolecules* **30**, 7338 (1997)

60 S. J. McLain., N. E. Drysdale., *US Patent 5028667* (1991) to E.I. Du Pont de Nemours and Company

61 S. J.McLain, N. E. Drysdale, *Polym. Prep.* **33**, 174 (1992)

62 K.S.Bisht, L.A.Henderson, R.A.Gross, D.L.Kaplan, G.Swift, *Macromolecules* **30**, 2705 (1997)

63 A.Kumar, B.Kalra., A.Dekhterman, R.A.Gross, *Macromolecules* **33**, 6303 (2000)

64 H.R Kricheldorf, A. Stricker, *Macromolecules* **33**, 696 (2000)

65 R.F Storey, A.E Taylor, J Moor, *Pure. Appl.Chem.* **30**, 7075 (1998)

66 J.H Yuk, A Boulares, R.P Kambour, W.J Mac Knight, *Macromolecules* **33**, 3600 (2000)

67 H.R Kricheldorf, J Meier-Haack, *Makromol.Chem.* **194**, 715 (1993)

68 H.R Kricheldorf, I Kreiser-Saunders, A Stricker, *Macromolecules* **33**, 702 (2000)

69 A.Kowalski, A.Duda, S.Penczek, *Macromol.Rapid.Commun.* **19**, 567 (1998)

70 A.Kowalski, A.Duda, S.Penczek, *Macromolecules* **33**, 7359 (2000)

71 M.Bero, B.Czapla, P.Dobrzynski, H.Janeczek, Kasperczyk, *J.Macromol.Chem.Phys.* **200**, 911 (1999)

72 A.Duda, Z.Florjanczyk, A.Hofman, S.Slomkowski, S.Penczek, *Macromolecules* **23**, 1640 (1990)

73 P. Dubois, N. Ropson, R. Jerome, P. Teyssie, *Macromolecules* **29,** 1965 (1996)

74 H.R Kricheldorf, A.Stricker, D.Langanke, *Macromol.Chem.Phys.* **202**, 2963 (2001)

75 R.Quirk, B.Lee, *Polym. Int.* **27**, 359 (1992)

76 L.J.Gold, *Chem. Phys.* **28**, 91 (1958)

77 G.Montaudo, M. S.Montaudo, C.Puglisi, F.Samperi, N.Spassky, A.Le Borgne, M.Wisniewski, *Macromolecules* **29**, 6461 (1996)

78 A.Kowalski, A.Duda, S.Penczek, *Macromolecules* **31**, 2114 (1998)

79 C.Miola, T. Hamaide, R.Spitz, *Polymer* **38**, 5667 (1997)

80 T. M.Abdel-Fattah, T. J. Pinnavaia, *Chem.Commun.* **5**, 665 (1996)

81 L.Trofimoff, T.Aida, S.Inoue, *Chem.Lett.* 991 (1987)

82 K.Hiltunen, J. V Seppala, M. Haerkoenen, *Macromolecules* **30**, 373 (1997)

83 S. I Moon, C. W Lee, T M Miyamoto, Y Kimura, *J. Polym. Sci., Part A: Polym.Chem.* **38**, 1673 (2000)

84 S. H Kim, Y. H Kim, *Macromol. Symp.* **144**, 277 (1999)

85 K.Hiltunen, J. V.Seppala, *J. Appl. Polym. Sci.* **67**, 1011 (1998)

86 K.Hiltunen, J. V. Seppala, *J. Appl. Polym. Sci.* **67**, 1017 (1998)

87 F.Akutsu, M.Inoki, H.Uei, M.Sueyoshi, Y.Kasahima, K.Naruchi, Y.Yamaguchi, M.Sunahara, *Polym. J. (Tokyo).* **30**, 421 (1998)

88 B. Buchholz,. *US 5302694* (1994) to Boehringer Ingelheim GmbH

89 M.Ajioka, K.Enomoto, K.Suzuki, A.Yamaguchi, *Bull.Chem.Soc.Jpn.* **68**, 2125 (1995)

90 S. I Moon, C. W Lee, T M Miyamoto, Y Kimura, *Polymer* **42**, 5059 (2001)

91 S. I Moon, C. W Lee, T M Miyamoto, Y Kimura, *Macromol.Biosci.* **3**, 301 (2003)

92 J.Otera, K.Kawada, T.Yano, *Chem.Lett. Chem.Soc. Jpn.* **3**, 225 (1996)

93 S.Shyamroy, B.Garnaik, S.Sivaram, *J.Polym.Sci.PartA A: Polym.Chem.* **43**, 2164

(2005)

94 W.H.Carothers, *J.Am.Chem.Soc.* **31**, 2548 (1929)

95 *" Collected Papers of W.H Carothers on Polymerization"*, edited by H.Mark and G.S. Whitby, Interscience Publ., New York (1940)

96 P.J. Flory, *Chem.Rev.* **39**, 137 (1946)

97 P.J.Flory, *"Principles of Polymer Chemistry"* Chapters VIII and IX, Cornell University Press, Ithaca, New York (1953)

98 *"High Polymeric Reactions, Their Theory and Practice"*, H.Mark, R.Raff, pp 139-140, 151-155, 176-177, Interscience Publ., New York (1941)

99 H.Jacobson, W.H Stockmayer, *J.Chem.Phys.* **18**, 1600 (1950)

100 H.Jacobson, C.O.Beckmann, W.H.Stockmayer, *J.Chem.Phys.* **18**, 1607 (1950)

101 S.C Hamilton., J.A Semlyen., D.M Haddleton., *Polymer* **39**, 3241 (1998)

102 J.H Youk., R.P Kambour., W.J MacKnight., *Macromolecules* **33**, 3606 (2000)

103 H.R.Kricheldorf., S.Bohme., G.Schwarz., *Macromolecules* **34**, 8879 (2001)

104 S.Inoue., T.Aida., in *Ring-Opening Polymerization*, Chapter 4, p 188, edited by K.J Ivin., T.Saegusa, Elsevier Publ., London, New York (1984)

105 R.Minke, J.Blackwell., *J.Macromol.Sci.Phys.Part B* **16**, 407 (1979)

106 H.D.Keith., *Macromolecules* **15**, 114 (1982)

107 I.Goodman, in *Encyclopedia of Polymer Science and Engineering*, Vol 12, p. 1, 2nd, edited by H.F.Mark., N.M.Bikales., C.G.Overberger, G.Menges, Wiley Interscience, New York (1988)

108 E.J.Tijsma, L. Van der Does., A. Bantjes., *Macromolecules* **27**, 179 (1994)

109 P.J.M Serrano., E.Thuss., R.J.Gaymans., *Polymer* **38**, 3893 (1997)

110 (a) T.E Sandhya, "*Synthesis And Characterization of Aliphatic Aromatic Polyesters*", TH-1380, University of Poona, (2003), (b) C. J. Kibler, A. Bell, J. Smith, G. *J.Polym.Sci Sci*, **2**, 2115 (1964)

111 C. J. Kibler, J. G. Smith, *U S Patent 2,901,466* (1959); *Brit. Pat. 81815* (1959); *Can. Pat. 603,847* (1959) to Eastman Kodak Company

112 P. A. Aspy, E. E. Denison, *Mod.Plast.* 74, (1983)

113 C. A. Boye, *J. Polym. Sci*, **55**, 275 *(*1961)

114 R. G. Gaughan, H. W. Hill, Jr., J. E. Inda, *J. Polym. Sci. Pt A: Polym. Chem.* **24**, 419

(1986)

115 W. J. Jackson, Jr., T. F. Gray, Jr., J. R. Caldwell, *J. Appl. Polym. Sci*. **14**, 685 (1970)

116 J. C. Morris, J. R. Bradley *U.S. Pat. 5,955,565* (1999) to Eastman Chemical Company.

117 J. C. Wilson, F. L. Hamb, *J. Polym. Sci, Polym. Chem.* **10**, 3191 (1972)

118 L. Taimr, J. G. Smith, *J. Polym. Sci, Polym. Chem.*, **9**, 1203 (1971)

119 L. Taimr, J. G. Smith, *J. Polym. Sci, Polym. Chem.*, 239 (1971)

120 H-J Jin, J-K Park, K-H Park, M-N Kim, J-S Yoon, *J.Appl.Polym.Sci*. **77**, 547 (2000)

121 H.J Hagemeyer, *US Patent 3043808* (1962), to Eastman Kodak Company

122 H.Deibig, J.Geiger, M.Sander, *Makromol.Chem*. **145**, 123 (1971)

123 H.A Oosterhof, *Polymer* **15**, 49 (1974)

124 D. Grenier, R.E. Prud'homme, A. Leborgne and N. Spassky, *J.Polym.Sci.Polym.Chem.Ed*. **19**, 1781 (1981)

125 N. Spassky, A.Leborgne, W.E. Hull, *Macromolecules* **16**, 608 (1983)

126 B.Voit, *J.Polym.Sci.PartA: Polym.Chem.Ed*. **38**, 2505 (2000)

127 C.J. Hawker, *Adv.Polym.Sci*. **147**, 113 (1999)

128 A.Hult, M.Johansson, E. Malmstrom, *Adv.Polym.Sci*. **143**, 1 (1999)

129 Y.H.Kim, *J.Polym.Sci.PartA: Polym.Chem*. **36**, 1685 (1998)

130 E. Malmstrom, M.Johansson, A.Hult, *Macromolecules* **28**, 1698 (1995)

131 M.Johansson, E. Malmstrom, A.Hult, *J.Polym.Sci.PartA: Polym.Chem*. **31**, 619 (1993)

132 T.Fujimaki, *Polym.Degrad.Stab*. **59**, 209 (1998)

133 M.Aubin, R.E.Prud'homme, *Polymer* **22**, 1223 (1981)

134 R. Palmgren, S. Karlsson, A-C Albertsson, *J.Polym.Sci.PartA: Polym.Chem*. **35**,1635 (1997)

135 U. Edlund, A-C Albertsson, *J.Polym.Sci.PartA: Polym.Chem*. **38**, 786 (2000)

136 Y. Ichikawa, K. Noguchi, K. Okuyama, J. Washiyama, *Polymer* **42**, 3703 (2001)

137 Y. Ichikawa, J. Washiyama, Y. Moteki, K. Noguchi, K. Okuyama, *Polymer J*. **27**, 1264 (1995)

138 T. Iwata, K. Tsunoda, Y. Aoyagi, Y. Kusaka, N. Yonezawa, Y. Doi,

Polym.Degrad.Stab. **79**, 217 (2003)

139 W.Hoogsteen, AR Postema, AJ Pennings, G. ten Brinke, P. Zugenmaier, *Macromolecules* **23**, 634 (1990)

140 Y. Furuhashi, T. Iwata, Y. Doi, *J.Mater.Sci*. **36**, 4307 (2001)

141 Y. Ichikawa, H. Kondo, Y. Igarashi, K. Noguchi, K. Okuyama, J. Washiyama, *Polymer* **41**, 4719 (2000)

142 Z.Gan, K. Kuwabara, H. Abe, T. Iwata, Y. Doi, *Biomacromolecules* **5**, 371 (2004)

143 T. Iwata, S. Kobayashi, K. Tabata, N. Yonezawa, Y. Doi, *Macromol. Biosci*. **4**, 296 (2004)

144 H-L Chen, L-J Li, W-C Ou-Yang, J C Hwang, W-Y Wong, *Macromolecules* **30**, 1718 (1997)

145 J.J Kolstad, *J.Appl.Polym.Sci*. **62**, 1079 (1996)

146 M. J. Avrami, *J. Chem. Phys.* **7**, 1103 (1939)

147 M. J. Avrami, *J. Chem. Phys.* **8**, 212 (1940)

148 M. J. Avrami, *J. Chem. Phys.* **9**, 177 (1941)

149 B. Wunderlich, *Macromolecular Physics*, Vol 2, Chapter 6, Academic Press, New York (1976)

150 Y. Deslandes, F-N Sabir, J. Roovers, *Polymer* **32**, 167 (1991)

151 B. Wunderlich, *Macromolecular Physics*, Vol 2, Academic Press, New York (1977)

152 J.D Hoffman, *Polymer* **23**, 656 (1982)

153 H-G Chae, S-H Park, B-C Kim, D-K Kim, *J.Polym.Sci.Part B: Polym.Phys.* **42**, 1759 (2004)

154 C. F. Pratt, S. Y. Hobbs, *Polymer* **17**, 12 (1976)

155 L. Goulet, R.E. Prud'homme, *J.Polym.Sci. Polym.Phys.* **28**, 2329 (1990)

156 H.W. Kammer, C. Kummerlowe, *"Advances in Polymer Blends and Alloys Technology"*, vol 5, chap 7,Technomic Publishing Co.Inc., Lancaster (1994)

157 J. Brydson, A. *Plastics Materials* 4th Ed., Butterworth Scientific, London. (1982)

158 G. Farrow, J. McIntosh, I. M. Ward, *Makromol.Chem*. **38**, 147 (1960)

159 G. Perego, G. D Cella, C.Bastioli, *J.Appl.Polym.Sci*. **59**, 37 (1996)

160 K. Jamshidi, S.H Hyon, Y. Ikada, *Polymer* **29**, 2229 (1988)

161 A.Fradet, M Tessier, *Synthetic Methods in Step-Growth Polymers*, *Polyesters*,

Chapter 2, edited by M E. Rogers, T E.Long, John Wiley & Sons, Inc. (2003)

162 M.H. Hartmann, in *Biopolymers from Renewable Resources*, Chap. 15, pp 367, D.L.Kaplan, Ed., Springer, Berlin, Germany (1998)

163 H. Tsuji, Y. Ikada, *Macromolecules* **26**, 6918 (1993)

164 W.M Stevels, M.J.K Ankone, P.J. Dijkstra, J. Feijen, *Macromol.Chem.Phys.* **196**, 3687 (1995)

165 G.L Loomis, J.R Murdoch, *US Patent 4902515* (1990) to E.I. Du Pont de Nemours and Company

166 D. D. Wheeler, *US Patent 3054779* (1962) to Dow Chemical Company

167 A-C Albertsson, *J.Macromol.Sci. Pure.Appl.Chem.A.* **30**, 757 (1993)

168 M.S. Reeve, S.P. McCarthy, M.J.Downey, R.A. Gross, *Macromolecules* **27**, 825 (1994)

169 T.Tokiwa, T.Ando, T.Suzuki, T.Takeda, *Polym.Mat.Sci.Eng*. **62**, 988 (1990)

170 W.Amass, A. Amass, B. Tighe, *Polym.Int*. **47**, 89 (1998)

171 E T.H.Vink, K R. Rabago, D A. Glassner, P R. Gruber, *Polym.Degrad.Stab*. **80**, 403 (2003)

172 (a) D.Cornell, F. Glenn Gallagher, *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*, Chapter 16 and 17, edited by J.Scheirs, T. Long, John Wiley & Sons, Inc. (2003) (b) J.Scheirs, *Polymer Recycling*, Wiley, New York (1998)

173 S.Niu, T.Wakida, S. Ogasawara, H. Fujimatsu, S. Takekoshi, *Textile.Res.Res.J.* **65 (12),** 771 (1995)

174 M.B. Polk, L.L. LeBoeuf, M.Shah, C.Y. Won, X. Hu, Y. Ding, *Polym.Plast.Technol.Eng*. **38 (3),** 459 (1999)

175 J.R. Campanelli, D.G. Cooper, M.R. Kamal, *J.Appl.Polym.Sci*. **53**, 985 (1994)

176 G.E. Brown, R.C. O'Brien, U*S Patent 3952053* (1976) to Safetech Incorporation

177 S.F. Pustaszeri, *US Patent 4355175* (1982)

178 M.J.Collins, S.H. Zeronian, *J.Appl.Polym.Sci*. **45**, 797 (1992)

179 A.Oku, L-C. Hu, E.Yamada, *J.Appl.Polym.Sci*. **52**, 1353 (1994)

180 D. Paszun, T. Spychaj, *Ind.Eng.Chem.Res*. **36**, 1373 (1997)

181 J.R. Campanelli, M.R. Kamal, D.G. Cooper, *J.Appl.Polym.Sci*. **48**, 443 (1993)

182 U.R. Vaidya, V.M. Nadkarni, *J.Appl.Polym.Sci*. **35**, 775 (1988)

183 S.Baliga, W.T. Wong, *J.Polym.Sci.Polym.Chem.Ed*. **27**, 2071 (1989)

184 A. Naujokas, K.M. Ryan, *US Patent 5051*528 (1991) to Eastman Kodak Company

185 D. Kint, S. Munoz-Guerra, *Polym.Int* **48**, 346 (1999)

186 P.Bajaj, N.D. Sharma, "*Reuse of Polymer and Fiber Wa*ste", in *Manufactured Fiber Technology*, p.615, edited by V.B. Gupta, V.K. Kothari, Chapman and Hall, New York (1997)

187 J.Aguado, D.Serrano, *Feedstock Recycling of Plastic Wastes*, p.34, Royal Society of Chemistry, Cambridge (1999)

188 G.B. Kharas, F. Sanchez-Riera, D.K. Severson, in *Plastics from Microbes*, pp 93, edited by D.P Mobley, Hanser Publishers, New York (1994)

Chapter 2: Scope and objectives of the present work

2.1 Introduction

The use of plastics that can be easily recycled or environmentally degraded is an elegant way of dealing with solid waste disposal, which is a critical problem of the society today. Due to increasing environmental awareness of consumers as well as organized society, there is a renewed interest in the area of environmentally degradable, biodegradable or recyclable plastic materials.

Polyesters are a class of polymers that can be either recycled or environmentally degraded. Among polyesters, the aliphatic polyesters on account of their poor hydrolytic stability are environmentally degradable, whereas, the aliphatic-aromatic polyesters present good thermomechanical properties and can be recycled effectively.

Aliphatic polyesters have been traditionally low molecular weight polymers, and, hence, have poor physical properties. Therefore they have found only limited applications as plasticizers[1] and as diols for the synthesis of polyurethanes[2]. However, their poor hydrolytic stability can be viewed as a desirable property for environmental degradability and, hence, these polyesters have attracted greater attention in recent years. However, higher molecular weight polyesters are desired for realizing acceptable physical properties.

Poly (butylene adipate) (PBA) is an aliphatic polyester prepared by melt polycondensation of adipic acid or its diester and 1,4-butanediol. Molecular weight of this polyester prepared by melt polycondensation is limited to only a few thousands due to the degradation reactions occurring during synthesis. Alternatively, molecular weights can be increased by chain extension reactions using chain extenders like diisocyanates, diesters or dicarbonates. Ring opening polymerization (ROP) is another technique for obtaining high molecular weight aliphatic polyesters at lower temperatures and in lesser reaction times. Copolyesters with varying structures can be prepared by ring opening polymerization.

Among the aliphatic-aromatic polyesters, PET is most cost-effective and widely consumed polymer and accounts for about 95 % of total global consumption of polyesters. On account of the aromatic component, it is poorly biodegradable, but it can be recycled effectively. PET has been recycled successfully and has the second highest scrap value after

aluminum[3]. PET can be directly converted into PBT by transesterification with 1,4-butanediol.

The objective of the present work is therefore to study the reactions that lead to polyester formation either by polycondensation, ring opening polymerization or recycling using transesterification reactions, with emphasis on potentials for environmental degradability or reuse.

2.2 Objectives

2.2.1 Synthesis and characterization of fully aliphatic polyester derived from dimethyl adipate and 1,4-butanediol.

Poly (butylene adipate) is a semicrystalline[4] aliphatic polyester obtained by polycondensation of dimethyl adipate and 1,4-butanediol. However synthesis of this polyester by melt polycondensation results in formation of undesirable cyclic oligomers. This degradation reaction limits the attainment of high molecular weights. **The objective of this study is, therefore, to systematically study the synthesis of poly (butylene adipate) (PBA) by melt polycondensation and understand the effect of reaction parameters on the various polyester forming reactions.** *The polyesters will be characterized by techniques, such as, GPC, VPO, NMR, DSC and MALDI-ToF MS with a view to understand the formation of cyclic oligomers that compete with linear step-growth polymerization.*

2.2.2 To explore approaches for the synthesis of high molecular weight fully aliphatic poly (ester) s using chain extension reactions

Synthesis of poly (butylene adipate) by melt polycondensation results in low molecular weight polyester. The molecular weight can be increased by using chain coupling agents. Chain extenders generally react spontaneously with polymer end groups to increase the molecular weight with no formation of byproducts that reverse the reaction. This requires the polyester to have only one type of end group such as hydroxyl, carboxyl or amine etc. which can react with the chain extender. The low molecular weight poly (butylene adipate) therefore, has to be modified so as to produce polyester with one type of end group namely, hydroxyl end group. Various chain extenders have been reported in literature[5]. Most

commonly used are diisocyanates[6] and bis (chloroformates)[7] to prepare poly (ester-urethane)s and poly(ester-carbonate)s.

The objectives of this study are (i) to synthesize low molecular weight poly(butylene adipate) with hydroxyl end groups and (ii) to use chain extenders like, hexamethylene diisocyanate, divinyl adipate, 2,2' bis (2-oxepanone) ethane, bis (4-nitro phenyl carbonate) which react exclusively with the hydroxyl terminated polyester with a view to increase molecular weights. *In reactions with hexamethylene diisocyanate and 2, 2' bis (2-oxepanone), no byproduct results from the reaction of hydroxyl group with the diisocyanate or bis (lactone), whereas, in the case of divinyl adipate and bis (4-nitro phenyl carbonate), a by-product is formed. However, the by product (acetaldehyde or 4-nitrophenol) is not capable of reversing the reaction. The chain extended polyesters will be characterized by IR, NMR, DSC, viscosity and GPC.*

2.2.3 Synthesis of fully aliphatic poly (ester) s by ring opening polymerization of lactones

Coordinative ring opening polymerization with stannous octoate[8] as catalyst for the synthesis of aliphatic homo and copolyesters has been studied extensively. Stannous octoate is less nucleophilic than alkoxide and acts more like a catalyst rather than an initiator and is, therefore, used together with active hydrogen compounds (e.g. alcohols) as co-initiator[9]. Coordinative ring opening polymerization is a suitable method for preparing novel aliphatic polyesters with specific structural features from suitably designed lactones. A number of α and γ substituted ε-caprolactones have been synthesized and polymerized using stannous octoate or aluminium isopropoxide[10-12]. However the ring opening polymerization of δ substituted lactones has not been investigated. Bicyclic compounds[13] are also known to be used as reactive monomers for ROP.

The objective of this study is therefore to synthesize novel lactones, namely, 3-pentadecyl 2-oxepanone and 2-oxabicyclo [3.2.1] octan-3-one and study their homopolymerization. Copolymerization with ε-caprolactone will also be studied to establish relative ease of ring opening polymerization. The lactones will be fully characterized by IR, NMR, elemental analysis, mass and melting points. The copolymer composition will be determined by ^{1}H NMR. The copolyesters will be characterized by NMR, DSC and GPC to understand the effect of their structure on properties.

2.2.4 To establish a method for recycling waste poly (ethylene terephthalate) into higher value poly (ester) s like poly (butylene terephthalate)s, poly (hexamethylene terephthalate)s and poly (1,4-cyclohexyl dimethylene terephthalate)s

It is well known that transesterification reaction of diols with PET scrap is a direct method of producing poly (alkylene terephthalate) s. PBT has been produced from PET scrap by transesterification with 1,4-BD[14]. ***The objective is to explore the synthesis of different poly (alkylene terephthalate)s like poly(butylene terephthalate), poly (1,4-cyclohexyl dimethylene) terephthalate and poly (hexamethylene terephthalate) by transesterification reactions with 1,4-butane diol, 1,4-cyclohexane dimethanol and 1,6-hexanediol respectively. Transesterification reaction with 1,4-BD results in large amounts of THF formation[15]. The objective is therefore to study the effect of various reaction parameters on the THF formation and copolymer composition and to understand the reactions that lead to THF formation during the process.*** The copolyester composition will be determined by ^{1}H NMR and their acid values will be determined by Pohl's method. The polymers will also be characterized by DSC and viscosity measurements.

2.3 References

1. S.F Zawadzki, D. Tabak, L. Akcelrud, *Polym.Plast.Technol. Engin*. **32**, 155 (1993)
2. Z.Wirpsza, *Polyurethanes, Chemistry, Technology and Applications*, Ellis, Horwood, West Sussex, (1993)
3. J.Scheirs, *Polymer Recycling* Wiley, New York, (1998)
4. Z.Gan, K. Kuwabara, H.Abe, T. Iwata, Y.Doi, *Biomacromolecules* **5**, 371 (2004)
5. M.H.Hartmann, *Biopolymers from Renewable Resources*, Chapter 15,367, edited by D.L.Kaplan, (1998)
6. Y.Liu, M.S.Lindblad, E. Ranucci, A-C.Albertsson, *J.Polym.Sci.Polym.Chem*. **39**,630 (2001)
7. E. Ranucci, Y.Liu, M.S.Lindblad, A-C.Albertsson, *Macromol.Rapid. Commun.* **21**,680 (2000)
8. K.M. Stridsberg, Maria Ryner, A-C. Albertsson, *Adv.Polym.Sci.*, **157**, 41 (2002)

9. A. Kafrawy, S.W. Shalaby, *J.Polym.Sci.Polym.Chem Ed.* **25**, 2629 (1987)
10. X. Lou, C. Detrembleur, R. Jerome, *Macromol.Rapid Commun.* **24**,161 (2003)
11. Ph. Lecomte, C. Detrembleur, X. Lou, M. Mazza, O.Halleux, R.Jerome, *Macromol. Symp*. **157**,47 (2000)
12. K.Kullmer, H.Kikuchi, H.Uyama, S.Kobayashi, *Macromol.Rapid Commun.* **19**,127 (1998**)**
13. Encyclopedia of Polymer Science and Engineering, "*Ring Opening Polymerization*" Vol 14, 622-647, edited by H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges, J.I. Kroschwitz, Wiley-Interscience Publication (1988)
14. M.S.Kyber, S.U.Wolfgang, U.Schollar, *US Patent 5266601* (1993) to Zimmer Aktiengesellschaft
15. L.Yurramendi, M.J. Barandiarn, J.M. Asua, *Polymer* **29**, 871 (1988)

Chapter 3: Synthesis and characterization of poly (butylene adipate) s

3.1 Introduction

Aliphatic polyesters were historically the first family of synthetic condensation polymers, which were investigated as a part of Carother's pioneering studies on polymerization in the 1930's[1-2]. Polyesters are typically synthesized by polycondensation of hydroxy acids

or bifunctional monomers like diacids and diols, diacid chlorides and diols or diesters and diols[3-6]. Generally in polycondensation, high molecular weights can only be achieved at very high conversions (>98-99%). Exact stoichiometric balance of monomers is of paramount importance which is readily achieved using purified AB – type monomers and does present a practical problem when AA-BB type monomers are used. Esterification is thermodynamically a reversible reaction. As ester formation is characterized by equilibrium, continuous removal of by-product is necessary to drive the reaction towards higher conversion. To further facilitate high conversion, long reaction times and high temperatures are needed. However, efforts to increase conversion, also lead to undesirable degradation reactions, such as, dehydration of monomers, formation of cyclics, etc. which lead to loss of functional end groups resulting in low conversions and, hence, low molecular weight polyesters.

Cyclization reactions in step-growth polymerizations are inevitable but have been little appreciated. There are two main routes to formation of cyclic structures (i) when the chain ends of the same chain react with each other, intramolecular ring closure reaction and (ii) when the chain end react with the ester linkage within the growing chain, called back-biting reaction. In both cases, the formation of macrocyclic structures strongly depends on the flexibility of the polyester chain. In most polycondensation reactions, ring-ring equilibria exists, leading to the formation of cyclic oligomers, which can affect deleteriously the properties of final polymers[7]. In fact, a general problem connected with esterification- polycondensation process is the difficulty in preparing high molecular weight aliphatic polyesters. The moderate molecular weight leads to materials with low degrees of crystallinity and poor mechanical properties.

Aliphatic polyesters have attracted renewed interest in recent years on account of their ease of environmental degradability. Hence they have found wide applications as fibers, films, bottles and injection-molded products[8]. The inherent degradability of aliphatic polyesters makes them highly interesting for applications where the environmental impact is a concern, e.g. packaging, disposable items and agricultural mulch films.

This chapter examines carefully the influence of reaction conditions on the synthesis and properties of an aliphatic polyester, namely, poly (butylene adipate) (PBA) from dimethyl adipate (DMA) and 1,4-butanediol (BD) by melt polycondensation. Poly (butylene adipate) was chosen for the study for two reasons, firstly because this polymer forms the basis of a commercially relevant biodegradable polyester, Bionolle® introduced by Showa High polymer Co., Ltd., Japan and, secondly, synthesis of this polyester by melt polycondensation has not been described in the literature in adequate details. The objective of this study was, therefore, to gain a better understanding of the effect of reaction conditions on polyesterification and polycondensation with specific reference to the nature of end groups and formation of cyclics.

3.2 Experimental

3.2.1 Materials

Dimethyl adipate (DMA) and 1,4-butanediol (BD) were obtained from Fluka Chemika, Switzerland. Dibutyl tin oxide (DBTO), dibutyl tin dichloride, titanium isopropoxide, 2[(4-hydroxy phenyl) azo] benzoic acid (HABA), and trans-3-indole acrylic acid (IAA) were obtained from Sigma-Aldrich Inc.,USA. Phenol was procured from SD. fine Chemicals, Mumbai, India.

3.2.2 Reagents and purification

Dimethyl adipate (DMA) and 1,4-butanediol (BD) were distilled under vacuum and stored over 4Å molecular sieves. The purity of the both the reactant was determined by GC and was found to be 99.5% for BD and 99.8% for DMA. Titanium (IV) isopropoxide was distilled under vacuum and used as a solution in dry toluene. Phenol was distilled and used. Two tin catalysts were prepared from dibutyl tin oxide and dibutyl tin dichloride according to following procedures: (a) *Synthesis of 1,3-diphenoxy tetrabutyl distannoxane*[9]: 0.0046 mol each of dibutyl tin oxide and phenol were refluxed in 20 mL of benzene for 5 h using a dean and stark apparatus to collect the water of condensation. After refluxing, the solution was cooled and concentrated. The crude product was crystallized from n-hexane.

Elemental analysis: Calculated: C, 50.34; H, 6.89; Sn, 35.57; Found: C, 49.77; H, 6.52; Sn, 34.95. Melting point (^{0}C): Reported: 137-139; Found: 137-139.

(b) *Synthesis of 1,3-dichloro tetrabutyl distannoxane*[10-11]: 0.0046 mol each of dibutyl tin oxide and dibutyl tin dichloride were refluxed in benzene for 5 h. After 5 h of reflux, the solution was cooled and concentrated and crystallized from n-hexane. Elemental analysis: Calculated: C, 34.75; H, 6.52; Sn, 42.98; Found: C, 34.22; H, 6.15; Sn, 42.28. Melting point (^{0}C): Reported: 110-112; Found: 109-110

3.2.3 Synthetic methods

Experiments were carried out to study the effect of reaction temperature on the transesterification reaction of DMA with BD as well as the effect of catalysts, reaction temperature, reaction time and catalyst concentration on the further polycondensation reaction.

Effect of reaction temperature on the transesterification reaction of DMA with BD

Reactions were carried out at four different temperatures 150, 180, 200 and 220^{0}C using stoichiometric amount of DMA (1.74 g, 0.01 mol) and BD (0.9 g, 0.01 mol) and titanium isopropoxide (0.05 mol % of DMA) as catalyst. The reaction mixture was heated under nitrogen flow for 2 h at different temperatures in a two necked round bottom flask fitted with a water condenser and a spiral trap to collect the methanol formed. The poly (butylene adipate) obtained was characterized by GPC without further purification. The distillate collected in the trap was analyzed by GC.

Effect of catalysts on the polycondensation reaction

Effect of catalysts 1,3-diphenoxy tetrabutyl distannoxane, 1,3-dichloro tetrabutyl distannoxane and titanium isopropoxide on the polycondensation reaction of DMA and BD was examined. Stoichiometric amount of DMA and BD was used. Dimethyl adipate (26.16 g, 0.15 mol), BD (13.5 g, 0.15 mol) and catalyst (0.05 wt % of DMA, 0.013065g) were heated under nitrogen flow in a three necked glass reactor equipped with a nitrogen inlet, and an air condenser fitted to a coiled trap to collect the methanol formed. The reactants were first heated under a flow of nitrogen for 30 min at 125^{0}C and 60 min at 150^{0}C. The heating was then continued under reduced pressure, which was slowly

decreased to 1mbar over 90 min. The temperature was then raised to 175^{0}C, and the reaction was continued for 2 h under a vacuum of 1 mbar. The polymer obtained was cooled under vacuum and later on dissolved in 50 mL chloroform and precipitated in 300 mL methanol. The methanol insoluble fraction was washed with methanol and dried, whereas the methanol soluble fraction was concentrated and dried. The distillate collected in the spiral trap was analyzed by GC. It was found to contain a mixture of methanol and THF. The yield of the methanol insoluble fractions varied between 78-84% and that of the methanol soluble fraction between 15-22% by weight.

Effect of reaction temperature on the polycondensation reaction

The effect of temperature was studied by polymerizing DMA (26.16 g, 0.15 mol) with BD (13.64 g, 0.1515 mol) in presence of titanium isopropoxide catalyst (0.05 wt% of DMA, 0.013065g) at 125, 150, 180, 200 and 220^{0}C. Molar ratio of DMA: BD was 1:1.01. The reactants were heated with agitation using magnetic stirrer for 2 h under nitrogen flow in a 250 mL round bottom flask equipped with a nitrogen inlet and an air condenser fitted to a coiled trap. After 2 h, the nitrogen flow was stopped and the pressure inside the flask was reduced to 1 mbar over a period of 1 h. The reactants were further heated for 1 h under vacuum. The product was cooled under vacuum. It was dissolved in 50 mL of chloroform and precipitated in 300 mL methanol. The methanol insoluble fraction was isolated, washed with methanol and dried. The methanol soluble fraction was concentrated and dried. The distillate, which contained THF and methanol, was quantified by GC. Conversions were determined from moles of methanol. In all the experiments carried out at temperatures 150^{0}C and above a portion of the product volatilized during the reaction and condensed as a solid on the air condenser. This compound distilled under high vacuum and the amount distilling out increased with increase in temperature. It was collected and crystallized from n-hexane and further characterized by NMR and FAB-MS. Yield of the polymer (the methanol insoluble fraction) increased with increase in reaction temperature.

Effect of reaction time under vacuum on the polycondensation reaction

DMA (26.13g, 0.15 mol), BD (13.635g, 0.1515 mol) and titanium isopropoxide (0.05 wt% of DMA, 0.013065g) were heated with magnetic stirring under nitrogen flow in a

two necked 250 mL round bottom flask equipped with a nitrogen inlet, and a condenser fitted to a spiral trap. Molar ratio of DMA: BD of 1:1.01 was used. The reactants were heated at 125^0C for 2 h under nitrogen flow. After 2 h the pressure inside the flask was reduced to 1 mbar over a period of 1 h. The reactants were then heated for different lengths of time from 1 to 5 h under vacuum. After heating for required time, the product was cooled. It was dissolved in 50 mL chloroform and precipitated in 300 mL methanol. The methanol insoluble portion was isolated, washed with methanol and dried. The methanol soluble fraction was concentrated and dried. The distillate containing THF and methanol was quantified by GC. Conversions were determined from moles of methanol. Only in the experiment carried out for 5 h under vacuum, a portion of the product distilled out under high vacuum, which was collected and crystallized from n-hexane and further characterized by NMR and FAB-MS. The yield of the polymer (methanol insoluble fraction) increased with increase in reaction time.

Effect of catalyst concentration on the polycondensation reaction

The concentration of titanium isopropoxide was increased from 0.05 wt% of DMA to 0.1 wt% of DMA to examine its effect on the polycondensation reaction. DMA (26.13g, 0.15 mol), BD (13.635g, 0.1515 mol) along with different amounts of titanium isopropoxide were heated with magnetic stirring under nitrogen flow in a two necked 250 mL round bottom flask equipped with a nitrogen inlet, and a condenser fitted to a spiral trap. Molar ratio of 1:1.01 for DMA: BD was used. The reactants were heated at 125^0C for 2 h under nitrogen flow. After 2 h, the pressure inside the flask was varied from 100 to 1 mbar over a period of 1 h. The reaction was further continued for 1 h under vacuum. The product was cooled under vacuum, dissolved in 50 mL chloroform and precipitated in 300 mL methanol. The methanol insoluble portion was isolated, washed with methanol and dried. The methanol soluble fraction was concentrated and dried. The distillate containing THF and methanol was quantified by GC. Conversions were determined from moles of methanol. The yields of the methanol insoluble fraction did not vary much with the catalyst concentration.

3.3 Analysis

3.3.1 Solution NMR measurements

^{1}H NMR spectra were recorded on a Brucker AC 200 spectrometer at 25 ± 1^{0}C, operating at 200 MHz. For measurements, 20 mg of finely powdered polyester samples were dissolved in 0.5 mL of solvent chloroform-d in 5mm diameter NMR tubes. The chemical shifts are reported up field with reference to internal standard chlororform-d at 7.25 δ. ^{13}C NMR analysis was carried out on a MSL 300 spectrometer.

3.3.2 Quantification of methanol and tetrahydrofuran by gas chromatography

Methanol and THF formed during the reactions were estimated using capillary column under the following conditions, by Perkin Elmer Autosystem XL Gas Chromatograph

Column specifications: BP-20 (polar) capillary column made of fused silica material with a bonded poly (ethylene glycol) stationary phase (length = 25 m, I.D. = 0.22mm, O.D. = 0.33 mm, film thickness (stationary phase) = 0.25 micron)

Carrier gas: Nitrogen, Inlet pressure: 7 psi, Flow rate through the column: 0.3 mL/min.

Detector: FID, Flow rate for hydrogen: 45 mL/min, Flow rate for air: 450 mL/min.

Oven programme: 45^{0}C (5 min), 45^{0}C →200^{0}C at a heating rate of 45^{0}C/min, 200^{0}C (7 min), Injector: 220^{0}C, Detector: 250^{0}C.

The retention times for methanol, THF and phenol are 4.7, 4.3 and 14.7 min respectively. In order to estimate accurately the amount of methanol and THF formed during the reaction, calibration curves for methanol and THF using phenol as the internal standard (IS) were obtained as follows: A stock solution of phenol was prepared by dissolving 2.5081 g of phenol in 25 mL acetone. From this stock solution 1 mL was taken for the preparation of solution. Stock solutions of methanol as well as THF were prepared by dissolving 1.0111 g of methanol and 1.0024 g of THF in separate 10 mL volumetric flasks and diluted upto the mark with acetone. From this stock solution 0.2, 0.4, 0.6, 0.8 and 1 mL each of methanol and THF solutions were pipetted out in separate 10 mL volumetric flasks. 1 mL of internal standard (phenol) was added into each of these volumetric flasks and further diluted with acetone up to the mark. 0.5 μL of each of these solutions was injected into the column. A minimum of 3 injections was used to confirm the reproducibility in the analysis. Area ratios of methanol and THF to phenol were

calculated for each injection and all concentrations from the chromatograms. The area ratios were plotted against their corresponding mole ratios. The slopes of the curves 6.57 for methanol and 1.55 for THF were used to calculate the exact quantity of methanol and THF as follows: Mole Ratio (MR) = Area Ratio (AR) x Response Factor (RF). Therefore Moles = Moles of IS x AR x RF.

3.3.3 MALDI-ToF MS analysis

MALDI-ToF MS analysis was performed on a Voyager-DE STR spectrometer equipped with 2 m linear and 3 m reflection flight tubes and 337 nm nitrogen LASER of pulse width 3ns. Analysis was carried out at an accelerating potential of 20 kV and mass spectra from 50-150 laser shots were accumulated to produce the final spectrum. Tetrahydrofuran solutions of samples (4-6 mg / mL) as well as matrix (10-30 mg / mL) were prepared. 2-[(4-hydroxyphenyl) azo] benzoic acid and trans 3-indolacrylic acid were used as matrices for analysis. A droplet of analyte was placed first on the steel sample plate followed by a droplet of matrix solution. The droplets were air dried on the plate. The sample plate was then inserted into the instrument under high vacuum.

3.3.4 FAB analysis

FAB-MS of the THF solution of the oligomer was performed using an AutoSpec FAB mass spectrometer.

3.3.5 Elemental analysis

Elemental analyses (C, H) were obtained on a Carlo-Erba 1100 automatic CHN analyzer. Tin was estimated gravimetrically by digesting the sample in a mixture of sulfuric and nitric acid, followed by a repetition of the cycle of digesting, washing and drying till constant weight.

3.3.6 Molecular weight and molecular weight distribution

Molecular weights (M_n and M_w) and polydispersity (M_w / M_n) were determined with respect to polystyrene standard by size exclusion chromatography on a Thermo Quest GPC instrument with UV100 and RI150 detectors at 25^0C by eluting poly (butylene adipate) solutions of 2-5 mg / ml concentrations in THF, with toluene as internal standard through a series of two μ – Styragel columns one of 100Å pore size and the other of

mixed pore size 50- 10^5Å pore size. THF was used as the mobile phase (flow rate 1mL/min) and both UV and RI detector signals were recorded simultaneously. As the molecular weights were calculated with respect to polystyrene calibration, they were of little significance and hence GPC was mainly used to determine the polydispersity index. The number average molecular weights of the polyesters were determined by KNAUER K-7000 Vapor Pressure Osmometer. The analysis was carried out under the following operating conditions: Cell temperature (T_C) = 35^0C, Head temperature (T_H) = 35 ± 3^0C, Gain = 032, time = 3 min. M_n is given by K_{cal} / $(\Delta T/C)_{C=0}$ where ΔT is the difference in temperature between the sample and solvent probe and C is the concentration of the sample being analyzed in g/lit. ΔT increases with increasing concentration of sample. ΔT was recorded for four different concentrations. A plot of C g/lit versus ΔT/C gives a positive slope. The intercept is given by (ΔT/C) at C = 0. The instrument was first calibrated with an organic compound benzil of known molecular weight and K_{cal} was determined by obtaining the value of intercept from the plot. Using this value of K_{cal} and value of intercept from the plot, M_n of any polyester sample can be determined.

3.3.7 Thermal analysis

Differential scanning calorimetric (DSC) measurements were made on a Waters thermal analyzer model Q-10 under nitrogen atmosphere. Approximately 6-7 mg of polymer samples were weighed in aluminium pans of 50μL capacity and sealed. The sample and blank sealed pans were heated simultaneously from -40^0C to 80^0C at a heating rate of 10^0C / min. After holding for 1 min at 80^0C, the sample was cooled at 100^0C / min to -40^0C. The crystallization and melting temperatures were obtained from the second and first heating curves respectively.

3.4 Results and Discussions

3.4.1 Synthesis of poly (butylene adipate) s by transesterification of dimethyl adipate and 1,4-butanediol

Poly (butylene adipate) s are synthesized by an ester interchange reaction of dimethyl adipate and 1,4-butanediol in the presence of a transesterification catalyst. As this

reaction is characterized by equilibrium, the continuous removal of byproduct methanol is necessary to drive the reaction towards higher conversion.

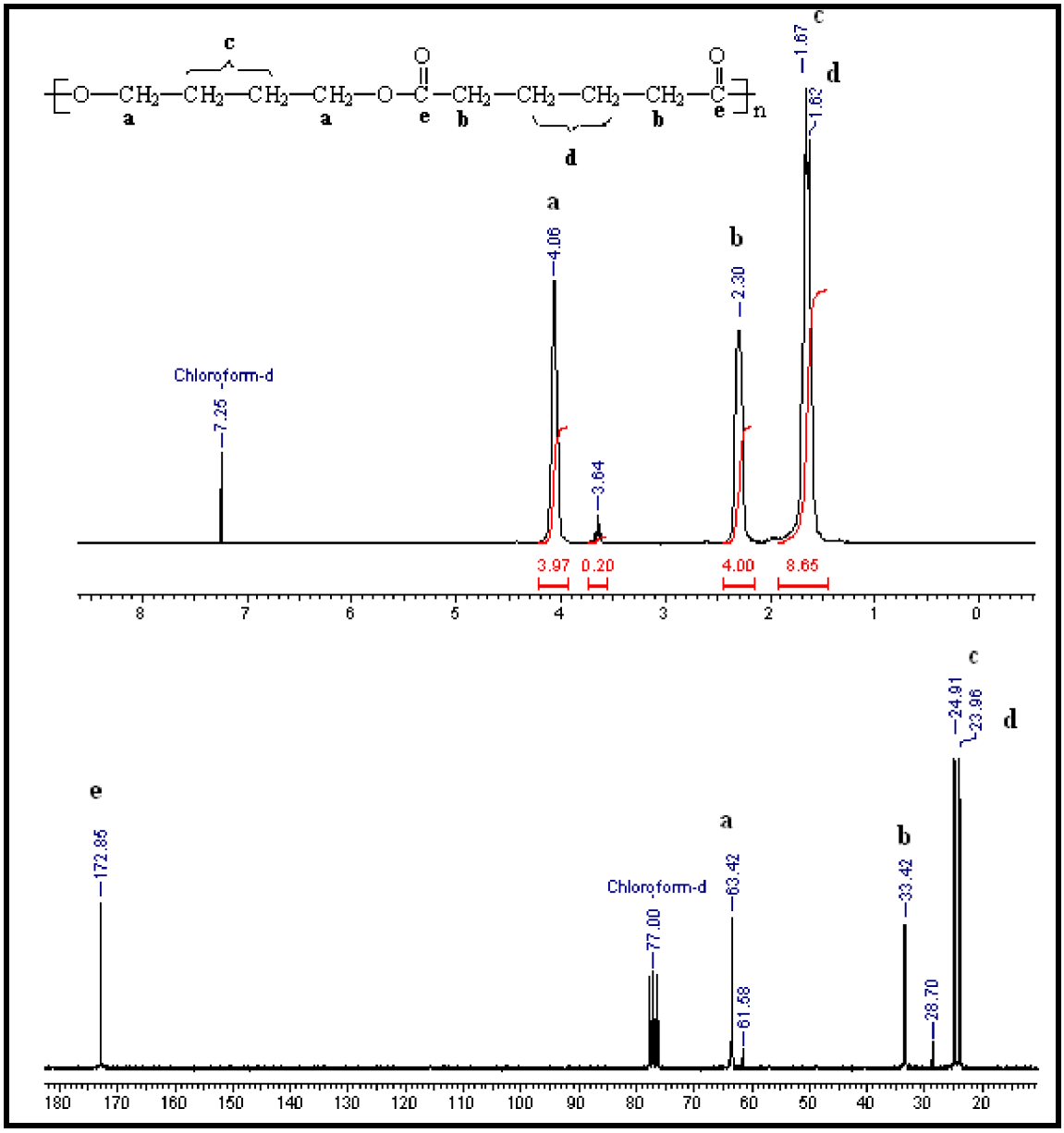


Figure 3.1 ^{1}H and ^{13}C NMR spectra of poly (butylene adipate) (PBA)

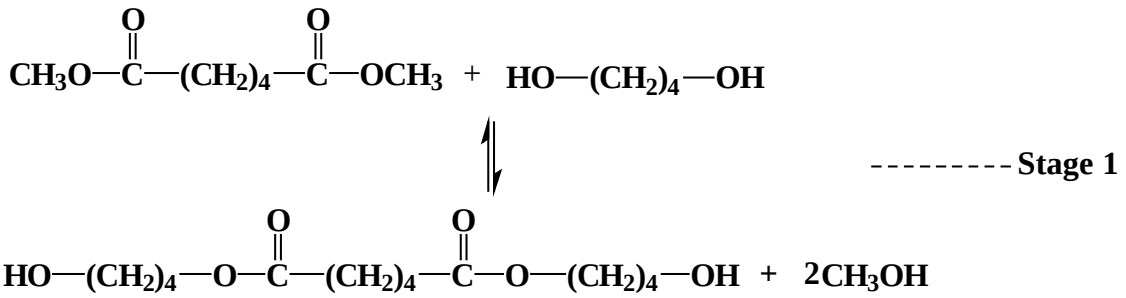
Typical ^{1}H and ^{13}C NMR spectra of poly (butylene adipate) synthesized by melt polycondensation of dimethyl adipate and 1,4 -butanediol are as shown in **Figure 3.1**

^{1}H NMR ($CDCl_3$) of PBAδ: 1.63-1.67 (8H, m, -CH_2); 2.30 (4H, s, -$COCH_2$); 3.64 (-CH_2OH end groups); 4.06 (4H, s, -OCH_2)

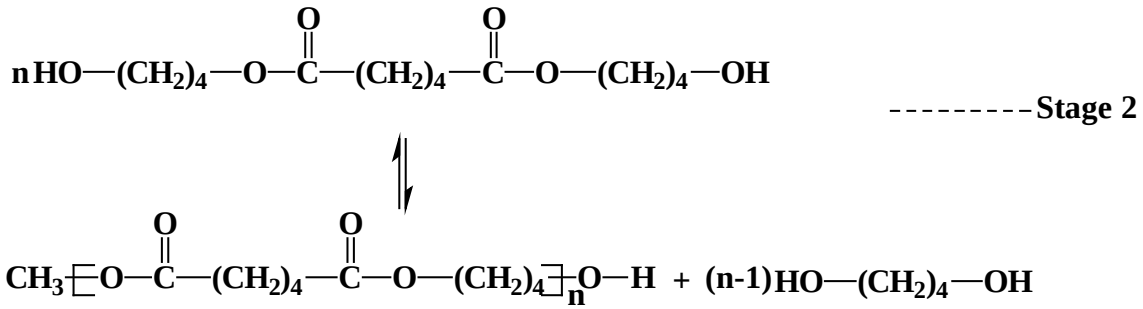
^{13}C NMR ($CDCl_3$) of PBAδ: 23.90 (CH_2); 24.91(CH_2); 33.42 (CH_2CO); 63.42 (CH_2O); 172.85 (carbonyl)

The dialkyl ester first reacts with an excess of diol in a transesterification reaction, in an inert atmosphere at 100-200^{0}C, liberating an alkanol and forming a bis (hydroxyalkyl) ester. In the second stage, the ester is subjected to polycondensation by alcoholysis, at high temperatures and under reduced pressures, resulting in formation of the polyester and liberating a molecule of diol for each step of chain growth.

Transesterification reaction



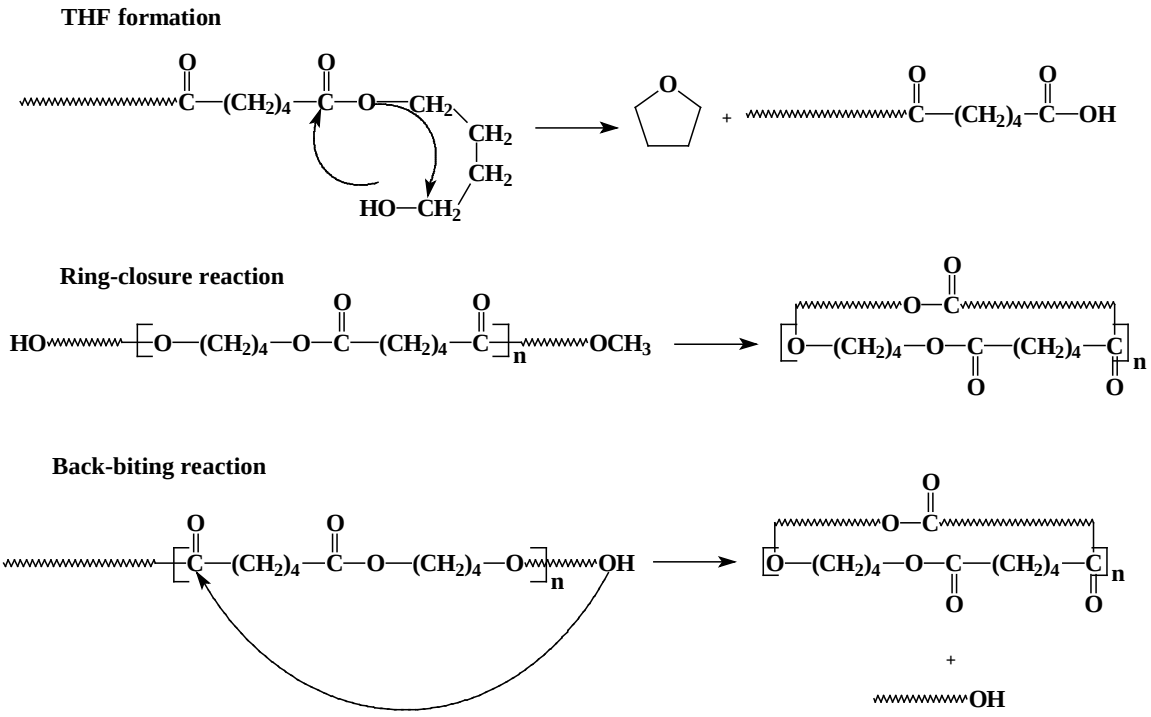
Polycondensation reaction



Scheme 3.1: Synthesis of poly (butylene adipate) by transesterification of DMA with BD

Both the stages are inherently reversible, but the conditions are chosen to drive each reaction in the forward direction by removal of low molecular weight byproduct as it is formed (**Scheme 3.1**) The product at this stage, although nominally the diester, usually contains some proportion of longer chain, hydroxyl-ended oligomers. In polycondensation conversions of 97-98 % are easily obtained irrespective of whether

oligomer or polymer is formed, however high molecular weights are obtained only at conversions greater than 99 %. In general, the chemistry in polycondensation is the same at the oligomer as well as the polymer stage, but the results obtained are very sensitive to how efficiently the byproduct is removed without loss of any functional groups which are very critical for further increase of molecular weight. The higher reaction temperatures, reaction time and vacuum used to push the reaction towards higher conversions, inevitably results in degradation reactions such as formation of cyclics by intramolecular transesterification reactions, and formation of THF, leading to loss of functionality. **Scheme 3.2** shows some of the degradation reactions that can occur during the polycondensation reaction.



Scheme 3.2: Degradation reactions occurring during synthesis of poly (butylene adipate)

Synthesis of poly (butylene adipate) s useful for applications in thermoplastic polyurethanes and elastic fibers has been mainly reported in the patent literature[12]. Melt polycondensation of DMA and BD using potassium titanium oxalate at 230-250^{0}C results in the formation of PBA with relative viscosity of 1.78 along with some sublimation products[13]. However, analysis of these products is not described. Effect of reaction

conditions like temperature, catalyst concentration, monomer ratio on molecular weight of aliphatic polyesters has been reported[14]. However, a detailed understanding of the structure of poly (butylene adipate) obtained by melt polycondensation as a function of the reaction conditions employed is not available in literature.

3.4.1.1 Effect of reaction temperature on transesterification reaction

The effect of temperature on the transesterification was studied by carrying out the reaction using stoichiometric amounts of DMA and BD catalyzed by titanium isopropoxide (0.05 mol% DMA), for 2 h under nitrogen flow, at four different temperatures 150, 180, 200 and 220^{0}C. The molecular weights and distribution were determined by GPC. The results are shown in **Table 3.1**. The distillate was found to contain methanol and about 2 mol% of THF based on BD by GC indicating that THF was formed even at the early stage of transesterification.

Table 3.1 Effect of temperature on transesterification reaction[a] of DMA with BD

No.	Reaction temperature (^{0}C)	%Yield[b]	M^c_n (GPC)	M_w/M_n[c]
1.	150	95	3,420	3.3
2.	180	90	7,480	3.3
3.	200	90	11,120	2.6
4.	220	90	15,340	3.4

a-Reaction conditions: 2 h of heating under nitrogen flow; b-Calculated based on theoretical weight of polymer expected; c-M_n and M_w/M_n of the polymer were determined without precipitation.

THF can be formed by acid catalyzed dehydration of BD or by the intramolecular cyclization of the hydroxy butyl end groups. As there are no acid groups in the reaction medium, THF could probably be formed initially by the intramolecular cyclization of the hydroxy butyl end groups as shown in **Scheme 3.2**. The polymer molecular weight increased with temperature, but the polymers obtained at higher temperatures were colored. The molecular weight distributions were also very broad indicating a non schulz-

flory distribution, generally observed during early stages of poly (esterification) s. The results show that transesterification reactions are favored at higher temperatures resulting in higher molecular weight PBA.

3.4.1.2 Effect of catalyst on polycondensation reaction

Generally, ester interchange reaction proceeds very slowly in the absence of catalysts even at high temperatures[15]. A very large number of substances are reported to catalyze hydroxy-ester interchange reactions. Metal salts, oxides, and alkoxides are the most often cited catalysts for this reaction.

Effect of catalysts 1,3-diphenoxytetrabutyl distannoxane, 1,3-dichloro tetrabutyl distannoxane and titanium isopropoxide were studied. All the three catalysts are effective and well known for the synthesis of polyesters[16-18]. A reasonable mechanism involves the coordination of ester carbonyl to the metal atom, favoring the nucleophilic attack of alkoxy ligands or hydroxyl end groups on the corresponding carbon. It could be written as a succession of (1) ester interchange and (2) ligand exchange, yielding the low molar mass alcohol or diol by-product.

Experiments were carried out using stoichiometric amounts of DMA and BD and a catalyst concentration of 0.05 wt% of DMA by weight. The polymers obtained were precipitated in methanol and dried. The results of the experiments are shown in **Table 3.2**. Titanium isopropoxide was found to be better than tin compounds. The efficacy of a given catalyst depends on the reaction medium. In the present case, the reaction medium consists of a mixture of ester and hydroxyl end groups. Titanium alkoxides are known to be good catalysts for both transesterification and polycondensation reactions. In view of this titanium isopropoxide was used in all subsequent studies. Distillate collected during the reaction was analyzed by GC and was found to contain 2-3 mol% of THF based on BD along with methanol.

Table 3.2 Effect of catalysts on the reaction[a] of DMA with BD

No.	Catalyst (0.05 wt% of DMA)	Yield (%wt.)	M_n[b] (GPC)	M_w/M_n[b]

	wt% of DMA)	Methanol insoluble (%)	Methanol soluble (%)	Total (%)	(GPC)	
1.	1,3-diphenoxy tetrabutyl distannoxane	79	20	99	8,480	2.3
2.	Titanium isopropoxide	84	25	99	14,130	1.8
3.	1,3-dichloro tetrabutyl distannoxane	78	21	99	8,230	2.2

a-Reaction conditions: 125^0C/30 min/N_2, 150^0C/60 min/N_2, 150^0C/90 min/ ambient pressure to 1mbar, 175^0C/120 min/ 1mbar; b-M_n and M_w/M_n of methanol insoluble fraction.

Since no acid is present in the reaction, which can catalyze the dehydration of BD, THF may be formed from the oligomers having hydroxy butyl end groups by the intramolecular cyclization reaction.

3.4.1.3 Effect of reaction temperature on polycondensation reaction

Polycondensation of DMA and BD was studied at five temperatures namely 125, 150, 180, 200 and 220^0C, the results of which are shown in **Table 3.3**. The mass balance, which is a ratio of the total weight of all the products to the total weight of all the reactants, was 100% for all experiments. The obtained polymer was precipitated in methanol. A portion of the product was insoluble in methanol and the remaining fraction was soluble in methanol. Both the fractions were analyzed separately. Melting temperature (T_m) and crystallization temperature (T_c) of only the methanol insoluble fractions were determined by DSC.

Table 3.3 shows that a maximum of 95% conversion based on moles of methanol and 98% conversion based on the M_n determined from VPO could be obtained. Loss of BD as THF accounted for about 3-4 mol % based on BD. A narrow molecular weight distribution of the methanol insoluble fraction can be attributed to the fractionation of the polymer. T_m of the polyesters was approximately around 60^0C.

Table 3.3 Effect of reaction temperature on polycondensation reaction[a] of DMA with BD

No.	Reaction temperature (^{0}C)	Reduced pressure (mbar)	Conv[b]. (%mol)	Conv[c]. (%)	Yield[d] (%wt.)	THF[e] (%mol)	M_n[f] (VPO)	M_w/M_n[f]	T_m[f] (^{0}C)	T_c[f] (^{0}C)
1.	125	0.030-0.027	88	95	27	3.0	3980	1.6	58	22
2.	150	0.045-0.040	92	97	75	3.7	7060	1.5	60	25
3.	180	0.026-0.027	94	98	85	3.7	9010	1.5	61	20
4.	200	0.028-0.025	95	97	86	4.4	7720	1.6	60	21
5.	220	0.025-0.026	93	98	86	3.8	8120	1.6	61	21

a-Reaction conditions: DMA:BD = 1:1.01/ titanium isopropoxide = 0.05 wt% of DMA, reaction temperature (^{0}C)/2 h/ N_2, reaction temperature (^{0}C)/1 h/ 100-1mbar, reaction temperature (^{0}C)/1 h/max vacuum as indicated in table; b-%conversions based on moles of methanol formed as determined from GC; c-% conversion was also calculated using the Carothers equation $X_n = 1/1-p$; d- yield of methanol insoluble fraction calculated based on the total weight of polymer obtained; e-THF calculated based on moles of BD from GC; f- M_n , M_w/M_n , T_m & T_c of methanol insoluble fraction

The molecular weight increases with reaction temperature upto 180^{0}C and attains a limiting value of 9000. In reactions carried out at 150^{0}C and above, a part of the product distilled out under vacuum and deposited on the condenser. The amount of this product distilling out was small (<1 wt%) in the reaction carried out at 150^{0}C. This product was crystallized from n-hexane and its melting point recorded on a Thermonik Campbell melting point apparatus was 97-99^{0}C. The mass of this product was determined to be 400 Da by FAB-MS (**Figure 3.2**) corresponding to an oligomer having a cyclic structure as shown in **Figure 3.3**. The FAB mass spectrum shows peaks corresponding to protonated cyclic oligomers (m/z 201, 401).

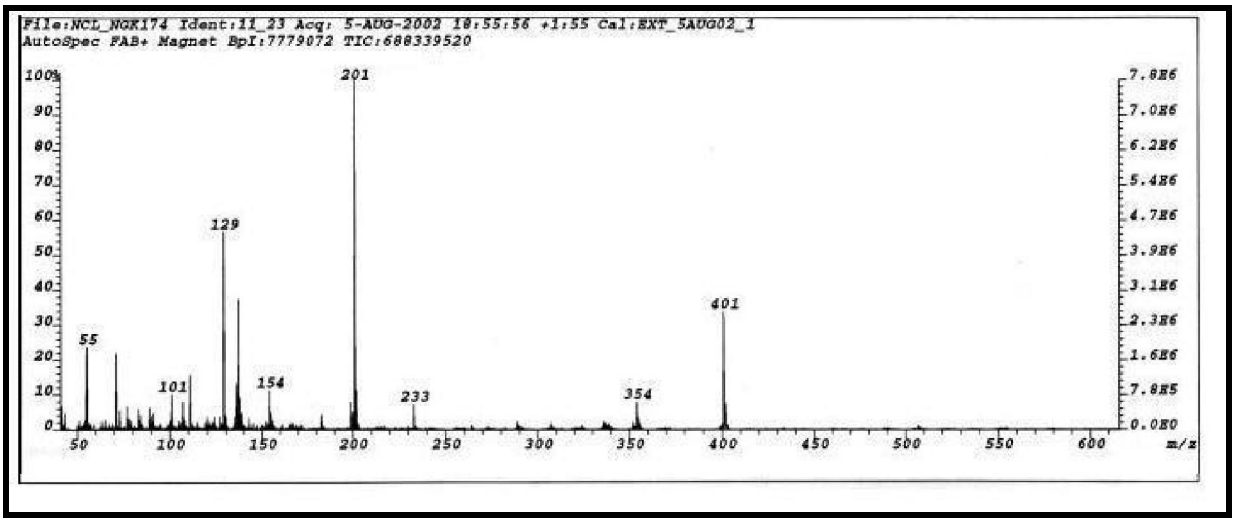
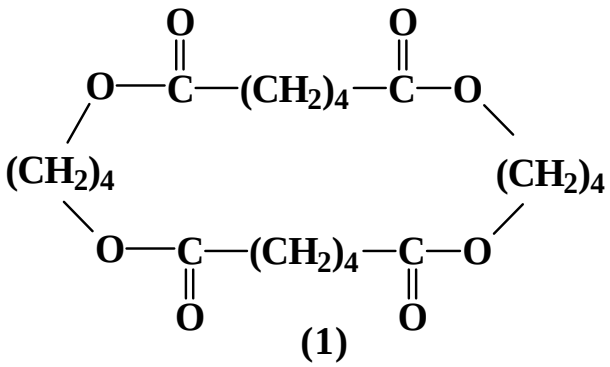


Figure 3.2 FAB mass spectrum of the product that distilled out under vacuum in polycondensation reactions carried out at temperatures ≥ 150^{0}C



(1)

Figure 3.3 Structure of the product that distilled out under vacuum in polycondensation reactions carried out at temperatures ≥ 150^{0}C

^{1}H and ^{13}C NMR of this product are as given in **Figure 3.4**. NMR of this oligomer is similar to that of poly (butylene adipate) repeat unit and shows some amount of hydroxyl group containing impurities.

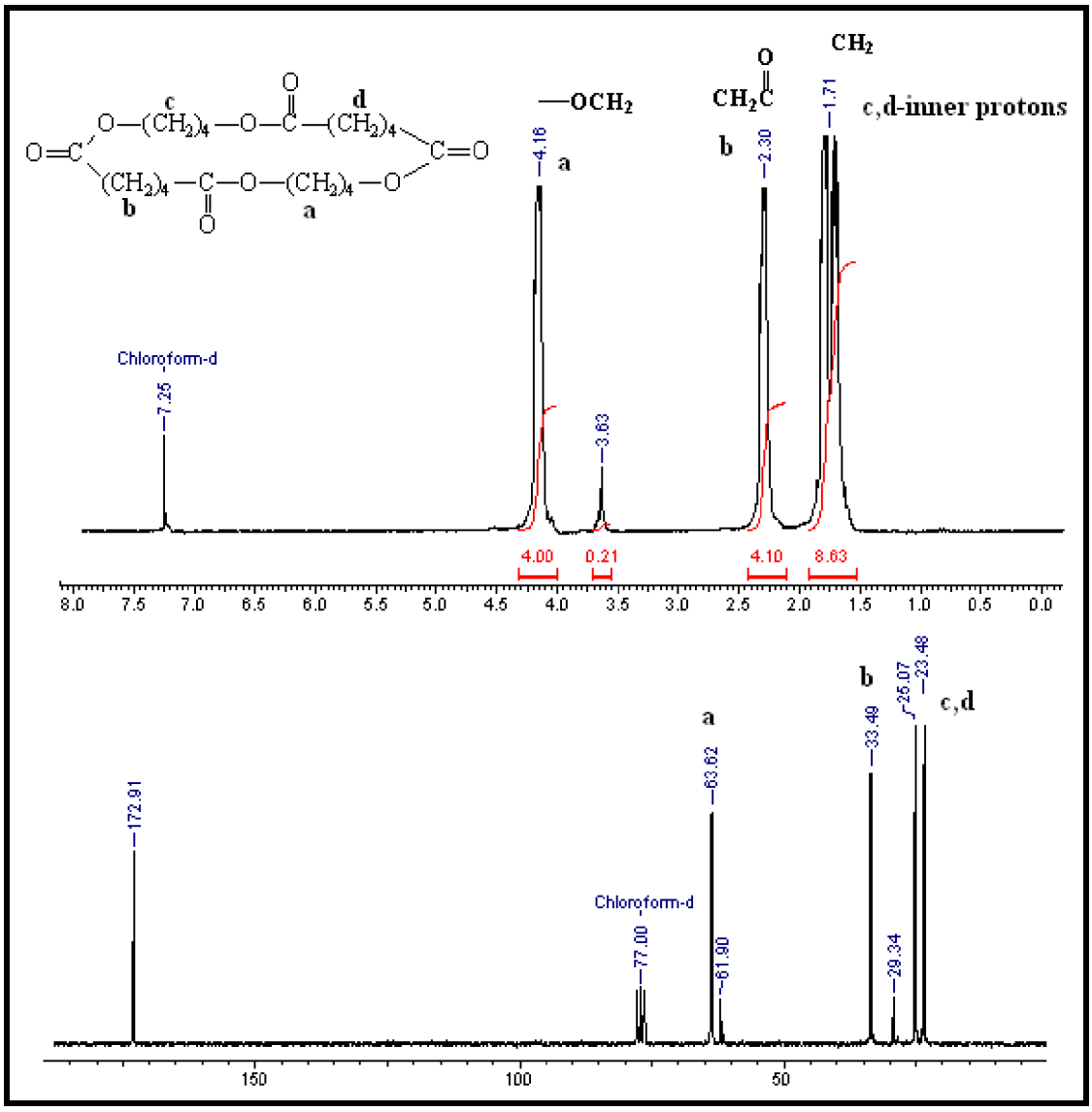


Figure 3.4 ^{1}H and ^{13}C NMR of the product that distilled out under vacuum in polycondensation reactions carried out at temperatures ≥ 150^{0}C

3.4.1.4 Effect of reaction time on polycondensation reaction

Since cyclic product formation appeared to be small at 150^{0}C and was not noticeable at 125^{0}C, the polycondensation of DMA and BD was examined at 125^{0}C with varying reaction time. The results of the experiments are shown in **Table 3.4**. The mass balance was 100% for all experiments. Precipitation of the polymer in methanol led to fractionation of the sample into methanol soluble and insoluble fractions. The yields of both the fractions were calculated based on the total weight of polymer obtained.

The methanol soluble and insoluble fractions were analyzed separately. As the polymer sample was fractionated by precipitation, the molecular weight distribution for the methanol insoluble fraction was narrow. It is observed from the table that a maximum of 93-96% conversion based on moles of methanol and 96-97 % conversion based on M_n determined by VPO were obtained. Loss of BD as THF accounted for about 1-2 mol% based on BD. Conversions and molecular weights obtained were low and did not appreciably increase with increase in reaction time. There was no evidence of cyclic oligomer formation in reactions carried out upto 7 h at 125^0C. A small amount of product could be seen distilling out when the reaction time was extended to 8 h. This was confirmed to be a cyclic oligomer of DP 2 by FAB-MS.

Table 3.4 Effect of reaction time on polycondensation reaction[a] of DMA with BD

No.	Reduced pressure (mbar)/ Time (h)	Total reaction time (h)	Conv[b]. (%mol)	Conv[c]. (%)	Yield[d] (%wt.)	THF[e] (%mol)	M_n[f] (VPO)	M_w/M_n[f]	T_m[f] (^{0}C)	T_c[f] (^{0}C)
1.	0.03-0.027/1	4	92	95	27	1.5	4190	1.6	58	21
2.	0.028-0.029/2	5	92	96	67	1.1	5380	1.5	60	24
3.	0.026-0.027/3	6	96	95	65	1.3	4360	1.5	60	25
4.	0.028-0.025/4	7	93	97	73	1.1	6620	1.5	62	24
5.	0.025-0.026/5	8	92	96	78	1.4	5430	1.5	63	25

a-Reaction conditions: DMA:BD = 1:1.01/ titanium isopropoxide = 0.05 wt% of DMA, 125^0C/2 h/ N_2, 125^0C/1 h/ 100-1mbar, 125^0C/1-5 h/max vacuum as indicated in table; b-%conversions based on moles of methanol formed as determined from GC; c-%conversion was also calculated using the Carothers equation $X_n = 1/1-p$; d- yield of methanol insoluble fraction calculated based on the total weight of polymer obtained; e-THF calculated based on moles of BD from GC; f-M_n , M_w/M_n , T_m & T_c of methanol insoluble fraction.

3.4.1.5 Effect of catalyst concentration on polycondensation reaction

The previous study on the effect of catalyst showed that titanium isopropoxide was the best catalyst among those studied. Effect of its concentration on the polycondensation reaction was studied at 125^0C. The experimental results are presented in **Table 3.5**. The mass balance was 100% for all the experiments. Precipitation of the polymer in methanol led to fractionation of the sample into methanol soluble and insoluble fractions.

Table 3.5 Effect of catalyst concentration on polycondensation reaction[a] of DMA with BD

No	Amount of catalyst (wt% of DMA)	Reduced pressure (mbar)	Conv[b]. (%mol)	Conv[c]. (%)	Yield[d] (%wt.)	THF[e] (%mol)	M_n[f] (VPO)	M_w/M_n [f]	T_m[f] (^{0}C)	T_c[f] (^{0}C)
1.	0.05	0.029-0.028	92	96	67	1.1	5380	1.5	60	24
2.	0.075	0.032-0.029	88	97	66	1.5	6830	1.6	60	26
3.	0.1	0.034-0.030	91	97	63	1.1	5880	1.4	63	22

a- Reaction conditions: DMA:BD = 1:1.01/ titanium isopropoxide as indicated in the table, 125^0C/2 h/ N_2, 125^0C/1 h/ 100-1mbar, 125^0C/1 h/max vacuum as indicated in table; b-%conversions based on moles of methanol formed as determined from GC; c- % conversion was also calculated using the Carothers equation $X_n = 1/1-p$; d- yield of methanol insoluble fraction calculated based on the total weight of polymer obtained; e- %THF calculated based on moles of BD from GC; f- M_n , M_w/M_n , T_m & T_c of methanol insoluble fraction

A maximum conversion of 92% based on moles of methanol and 97% based on M_n determined by VPO were obtained. Loss of BD as THF accounted for 1-2 mol% based on BD. No cyclic oligomer distilled out under vacuum during the reaction. The molecular weight of the polymer varied in the range of 5000-7000. Thus the increase in catalyst concentration did not have any appreciable effect on the molecular weight build up process. Higher concentration of catalyst leads to colored polyesters. Catalyst concentration of 0.05 wt% was thus considered optimum.

3.4.1.6 MALDI-ToF MS analysis of the poly (butylene adipate) oligomers

The preceding study clearly established the limits of transesterification-polycondensation chemistry as applied to a typical aliphatic polyester, namely, poly (butylene adipate). Even at temperatures as low as 125^0C, cyclic oligomers of DP = 2 could be detected. THF formation was also evident under these conditions. Both these reactions lead to loss of end groups in oligomer, thereby, limiting the ability of oligomers to undergo step growth polymerization efficiently leading to high molecular weight polymers.

To obtain a better insight into the nature of end groups, the obtained oligomers were subjected to MALDI-ToF-MS analysis. The samples chosen for MALDI-ToF-MS analysis are shown in **Table 3.6** along with a brief description of conditions used for their preparation. Samples were analyzed using two different matrices 2[(4-hydroxy phenyl) azo] benzoic acid (HABA) and trans-3-indole acrylic acid (IAA). Both IAA and HABA were found to be equally good. The best results using either of the two matrices are reported.

MALDI-ToF MS studies on poly (butylene adipate) oligomers synthesized from diacids and diol[19-20] were shown to possess hydroxy-hydroxy and hydroxy-carboxy end groups along with small amounts of cyclic oligomers. MALDI-ToF and SEC/MALDI have been applied for the structural characterization and molar mass determination of Bionolle® and a series of biodegradable copolyesters synthesized by high temperature melt polycondensation[21]. The MALDI-ToF spectra of these copolymers showed the presence of cyclic oligomers in the lower mass region, in accordance with expectations from polycondensation kinetics, and the presence of all linear species expected from their method of synthesis. The presence of unexpected linear species with olefin and carboxyl as end groups suggested the occurrence of undesirable thermal degradation processes during melt polycondensation reaction. The average molar mass of both the linear and cyclic oligomers was determined. There are yet other reports[22-23] on MALDI-ToF MS analysis of PBA showing the presence of linear oligomers with at least two types of end groups along with cyclic oligomers. Thus MALDI-ToF MS studies on poly (butylene adipate) oligomers show that cyclics are invariably present in the polymer along with linear species having different types of end groups.

Table 3.6 PBA oligomer samples chosen for MALDI-ToF MS analysis

No.	M_n	Synthesis Conditions		
		Catalyst (titanium isopropoxide)	Temperature (^{0}C)	Time (h)
1**A**	3980	0.05 wt% of DMA	125	4
1**B**	1510	0.05 wt% of DMA	125	4
2**A**	7060	0.05 wt% of DMA	150	4
2**B**	2090	0.05 wt% of DMA	150	4
3**A**	9010	0.05 wt% of DMA	180	4
3**B**	2060	0.05 wt% of DMA	180	4
4**B**	2050	0.05 wt% of DMA	220	4
5**A**	5430	0.05 wt% of DMA	125	8
5**B**	1600	0.05 wt% of DMA	125	8
6**A**	5880	0.1 wt% of DMA	125	4
6**B**	1320	0.1 wt% of DMA	125	4

A –Methanol insoluble fraction; **B** – Methanol soluble fraction

However, a study of effect of reaction conditions on the structure of poly (butylene adipate) oligomers has not been studied by MALDI-ToF MS. The MALDI-ToF MS spectra of the oligomers listed in **Table 3.6** are shown in **Figures 3.5** to **3.10**. All the samples were scanned in the mass range of 500 to 5000 Da. However, for purposes of detailed analysis, the data in the mass range of 500-2500 Da was used. Structures of the end-groups deduced from the spectra are tabulated for all the oligomers studied in **Table 3.7**.

Figure 3.5 presents the MALDI-TOF mass spectra of sample 1**A** and 1**B**. The spectrum for 1 **A** shows mainly three types of signals appearing at intervals of 200 Da that corresponds to the molecular weight of repeat unit. All of these peaks appear as sodium adducts. One type of signal corresponding to m/z value of 656 arises due to

chains terminated with H on one side and OCH_3 on the other side. A series of intense peaks of this type appear at intervals of 200 Da at m/z values of 856, 1056, 1255, 1455, 1656, 1856 and correspond to oligomers doped with Na^+ ions of the type $H{-}[O(CH_2)_4O{-}CO{-}(CH_2)_4{-}CO]_n{-}OCH_3{-}Na^+$ (mass = 200n+32+23), n being the value of DP varying from 3 to 9, 23 being the mass number of sodium. A second set of signals at m/z values of 598, 798, 998, 1198, 1399, 1599, 1799 appearing at intervals of 200 Da corresponds to oligomers terminated with ester groups. The series of these peaks correspond to the oligomers doped with Na^+ ions of the type $CH_3OCO{-}(CH_2)_4CO{-}[O(CH_2)_4O{-}CO{-}(CH_2)_4{-}CO]_n{-}OCH_3{-}Na^+$ (mass = 200n+174+23), n ranging from 2-8. A third set of signals though not very prominent appeared at DP 5 at m/z value of 1114 and corresponds to a series of peaks corresponding to oligomers doped with Na^+ ions of the type $H{-}[O(CH_2)_4O{-}CO{-}(CH_2)_4{-}CO]_n{-}O(CH_2)_4OH{-}Na^+$ (mass = 200n+90+23), n ranging from 5 to 8. The potassium adducts of the oligomers were not clearly seen for all the peaks. The peaks due to hydroxy-ester and ester-ester end groups were more intense as compared to peaks due to hydroxy-hydroxy end groups. No peaks with mass = 200n+23 which correspond to oligomers with no end groups (cyclics) were detected.

MALDI-ToF MS spectrum of the methanol soluble fraction 1**B** from the same experiment shows sodium cationized species appearing at intervals of 200 Da at m/z values of 655, 855, 1056, 1256, 1456, 1656, 1856 and correspond to oligomers of the type $H{-}[O(CH_2)_4O{-}CO{-}(CH_2)_4{-}CO]_n{-}OCH_3{-}Na^+$ (mass = 200n+32+23), n being the value of DP varying from 3 to 9, 23 being the mass number of sodium. Another series of intense peaks appearing at intervals of 200 Da arise due to oligomers terminated at both the ends with ester groups. The peaks appearing at m/z values of 597,798, 998, 1198, 1398, 1598, 1798 correspond to oligomers of the type $CH_3OCO{-}(CH_2)_4CO{-}[O(CH_2)_4O{-}CO{-}(CH_2)_4{-}CO]_n{-}OCH_3{-}Na^+$ (mass= 200n+174+23), n ranging from 2-8.

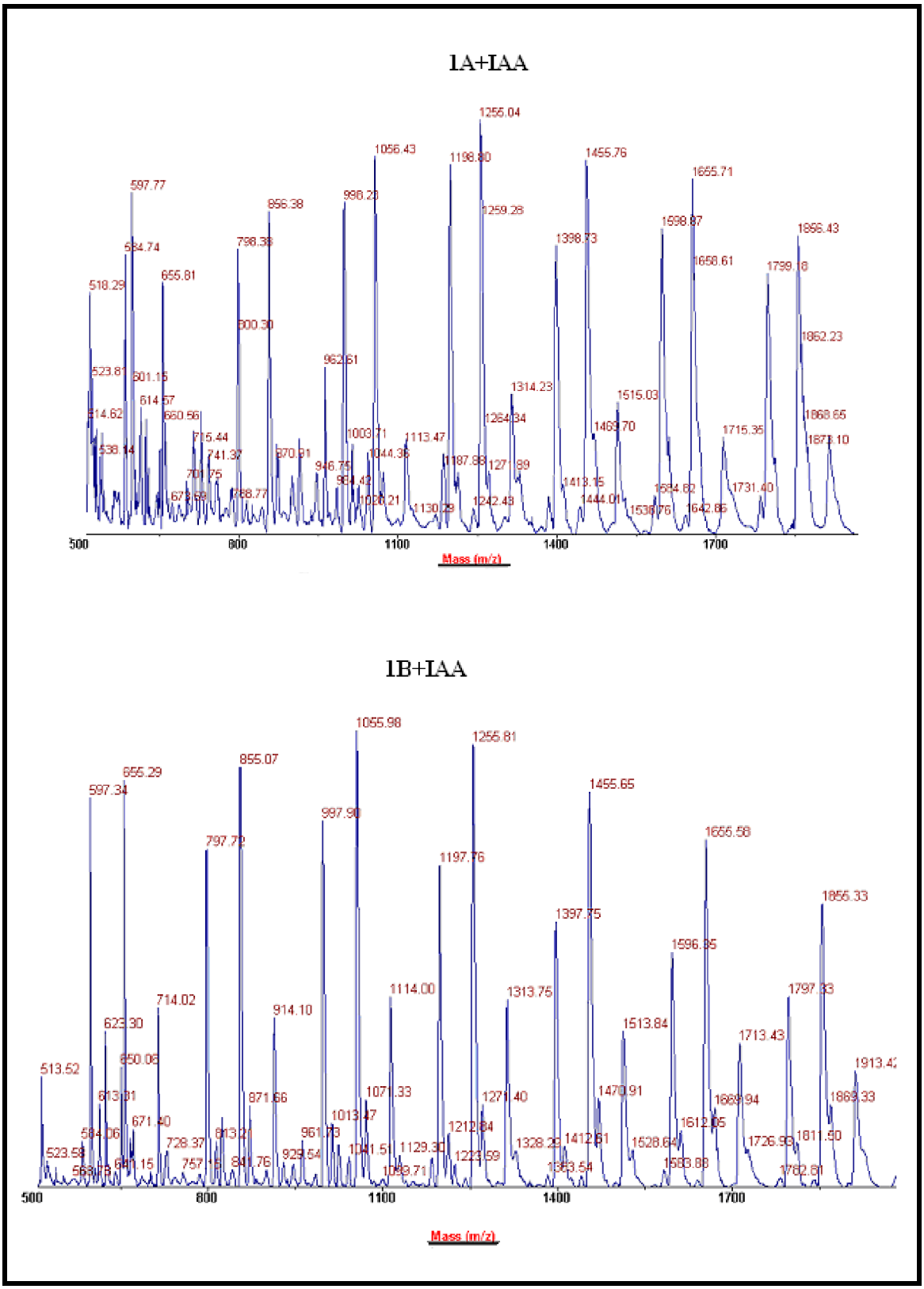
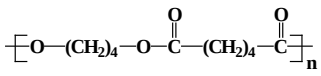
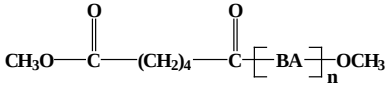
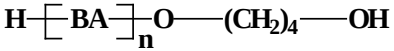
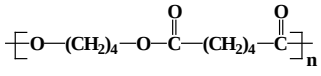
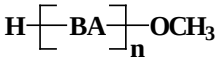
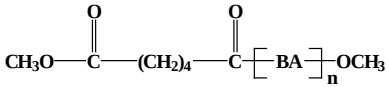
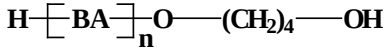
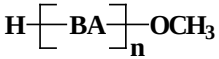
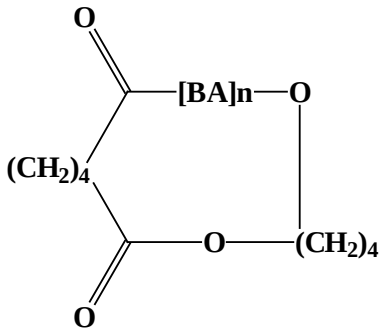
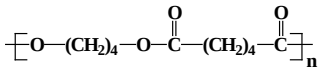
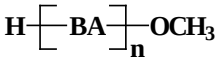
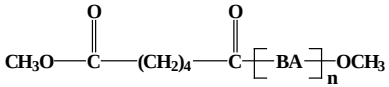
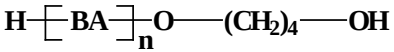
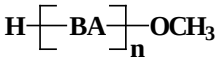
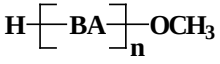
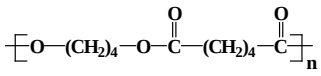
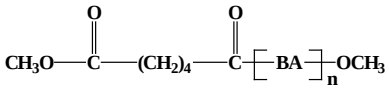
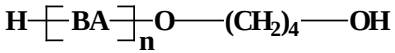
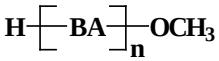
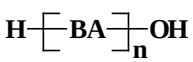
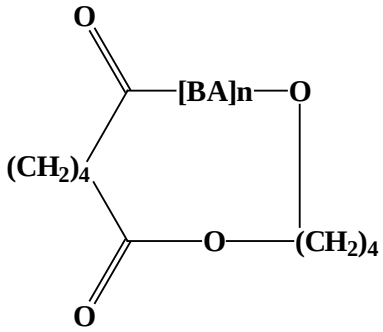
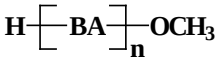


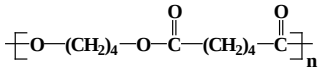
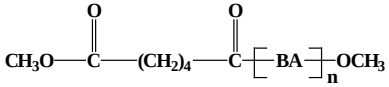
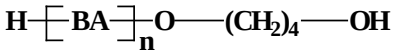
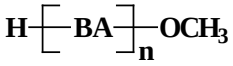
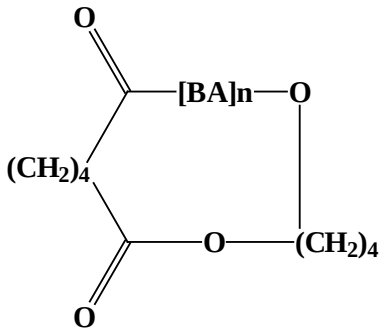
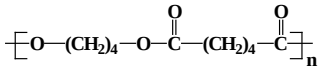
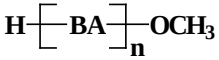
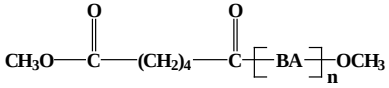
Figure 3.5 MALDI-ToF MS of methanol insoluble fraction 1A and methanol soluble fraction 1B using IAA as matrix

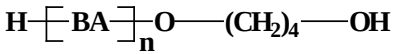
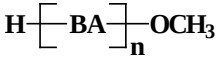
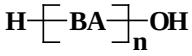
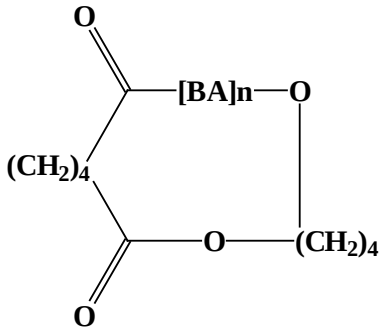
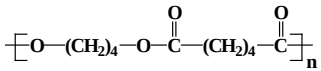
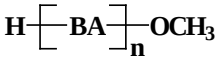
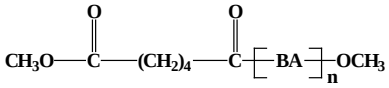
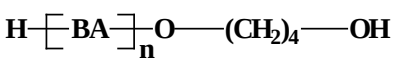
Table 3.7 MALDI-ToF MS analysis of poly (butylene adipate) oligomers

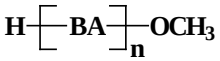
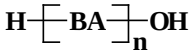
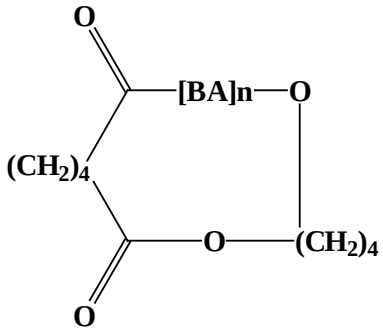
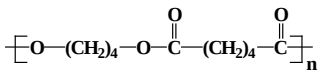
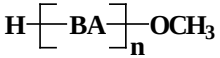
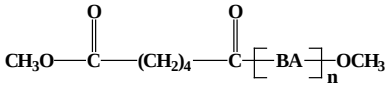
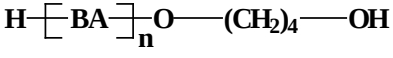
No.	Repeat unit structure	Sum of end groups (observed)	Structure of end groups	Series
1**A**		32-33		656, 856, 1056, 1255, 1455, 1656…… Na^+ adduct
		175-176		598, 798, 998, 1199, 1399, 1599…… Na^+ adduct
		90-92		1113, 1314, 1515, 1715…… Na^+ adduct
1**B**		32-33		655, 855, 1056, 1256, 1456, 1656…… Na^+ adduct
		175		598, 798, 998, 1198, 1398, 1598…… Na^+ adduct
		90-91		714, 914, 1114, 1314, 1514, 1713…… Na^+ adduct
		31-33		671, 872, 1071, 1271, 1471, 1670…… K^+ adduct

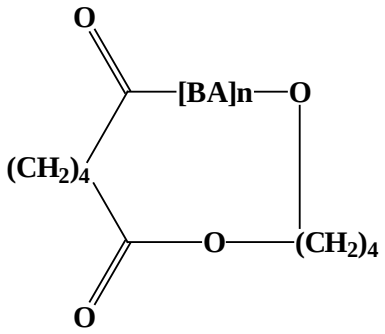
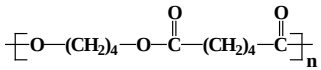
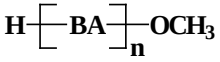
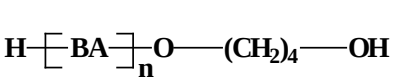
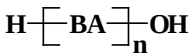
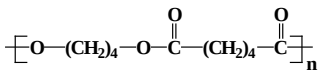
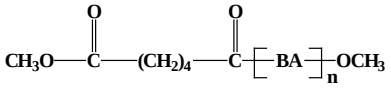
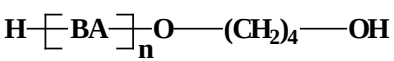
		No end group		623 Na^+ adduct
2**A**		33-34		1056,1257, 1456, 1657, 1856, 2057……Na^+ adduct
		175-176		1198,1399,1598,1799, 1999, 2199…… Na^+ adduct
		92		1115, 1315, 1515, 1715,1915,2115…… Na^+ adduct
		31-33		1071,1271,1472 & 1870 K^+ adduct
2**B**		32-33		655, 855, 1055, 1256, 1456, 1656…… Na^+ adduct

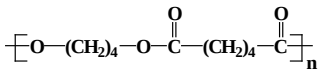
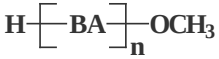
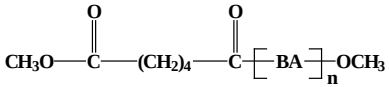
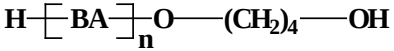
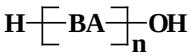
		174-175		797, 998, 1197, 1398, 1598, 1798..... Na^+ adduct
		90-91		713, 914, 1114, 1314, 1514, 1714…… Na^+ adduct
		31-33		1072,1272,1472,1672 & 1870 K^+ adduct
		18-19		1041,1442,1642 & 1842 Na^+ adduct
		No end groups		623, 824, 1024, 1224…… Na^+ adduct
3**A**		33-35		1256, 1458,1657,1857,2058, 2257…… Na^+ adduct

		175-177		1399,1599,1800,2000, 2199, 2399…… Na^+ adduct
		91-93		1316,1516, 1715,1914, 2115, 2315…… Na^+ adduct
		30-33		1672,1872,2069,2469 & 2669 K^+ adduct
		No end groups		1225,1425 & 1624 Na^+ adduct
3**B**		33-34		1056, 1256,1456,1657,1856, 2057…… Na^+ adduct
		175		1198, 1398,1598, 1798,1998, 2198…… Na^+ adduct

		91-93		1114, 1314, 1514, 1715, 1916……. Na^+ adduct
		32-33		1071 & 1272 K^+ adduct
		18-19		1042 & 1241Na^+ adduct
		No end groups		1024, 1224, 1424, 1624, 1824…… Na^+ adduct
4B		33-34		1056, 1257, 1456, 1657, 1856……. Na^+ adduct
		175		1198, 2198, 2398, 2598…… Na^+ adduct
		91-92		1114, 1314, 1514, 1715, 1914…… Na^+ adduct

		29-31		1270 & 1668 K^+ adduct
		17-18		1041,1240,1440 & 1640 Na^+ adduct
		No end groups		1024, 1224, 1424, 1624, 1824…… Na^+ adduct
5**A**		35		1058, 1258, 1458, 1658, 1858…… Na^+ adduct
		176-177		1200, 1399, 1600, 1800, 2000…… Na^+ adduct
		92-94		1117, 1315, 1515, 1716, 1917……. Na^+ adduct

		No end groups		1025 Na^+ adduct
5**B**		33-35		656, 856, 1057, 1257, 1457, 1658……. Na^+ adduct
		91-92		714, 915, 1115, 1315, 1515…… Na^+ adduct
		19		642, 842, 1042 & 1242 Na^+ adduct
6**A**		33-35		1056, 1256, 1457, 1658, 1856…… Na^+ adduct
		174-177		1198, 1397, 1599, 1800, 2000……. Na^+ adduct
		92		1115, 1315, 1515, 1715, 1915……. Na^+ adduct

6**B**		32-33		1256, 1455, 1656, 1856, 2056……. Na^+ adduct
		174-175		1397, 1597, 1798, 1998, 2197……. Na^+ adduct
		91-93		1314, 1514, 1714, 1916, 2114……. Na^+ adduct
		18-19		1242, 1442, 1641, 1841, 2041……. Na^+ adduct

BA- Butylene adipate repeat unit

A third set of peaks appearing at m/z values of 514,714, 914, 1114, 1314, 1514, 1713, 1913 are due to oligomers with hydroxyl end groups. These peaks are less intense as compared to the other two types of peaks. This series of peaks correspond to oligomers doped with Na^+ ions of the type $H{-}[O(CH_2)_4O{-}CO{-}(CH_2)_4{-}CO]_n{-}O(CH_2)_4OH{-}Na^+$ (mass = 200n+90+23), n ranging from 2 to 8. In addition to these peaks a single peak at m/z value of 623 appeared as a sodium adduct. No other peaks of this series appeared at intervals of 200 Da. This peak corresponds to a oligomer with no end groups or a cyclic oligomer of DP 3. Peaks corresponding to higher DP were not detected. The spectrum also shows other peaks of lower intensity appearing at m/z values of 671,872, 1071, 1271, 1471, 1670 and 1870, which desorbed as oligomers doped with K^+ ions and corresponded to oligomers of the type $H{-}[O(CH_2)_4O{-}CO{-}(CH_2)_4{-}CO]_n{-}OCH_3{-}K^+$ (mass = 200n+32+39), n being the value of DP varying from 3 to 9, 39 being the mass number of potassium. Thus polycondensation of DMA and BD carried out at 125^0C for 4 h results in formation of polyester chains with ester-ester, hydroxy-hydroxy and hydroxy-ester end groups and cyclic oligomer of DP 3. It is thus clear that, even at temperatures as low as 125^0C, polycondensation of DMA with BD can yield cyclic oligomers.

Figure 3.6 presents the spectra of sample 2**A** and 2**B**. Spectrum of 2**A** is dominated by a series of intense peaks ranging from a mass of 500 to 5000 Da. The spectrum shows a series of three sets of peaks corresponding to three different types of end groups similar to that for polymer 1**A**. Peaks appearing at m/z values of 1056, 1257, 1456, 1657, 1856, 2057and 2257 correspond to sodium cationized oligomers terminated with H on one side and OCH_3 on the other side, mass = 200n+32+23, n varying from 5-11. A second set of peaks at m/z values of 1198, 1399, 1598, 1799, 1999, 2199 and 2399 correspond to oligomers doped with Na^+ ions and terminated with ester end groups, mass = 200n+174+23, n varying from 5-11. A third set of peaks at m/z values of 1115, 1315, 1515, 1715, 1915, 2115 and 2316 correspond to sodium adducts of oligomers with hydroxyl end groups, mass = 200n+90+23, n varying from 5-11. Peaks due to oligomers with hydroxy-ester and ester-ester end groups were more intense than those due to hydroxy-hydroxy end groups.

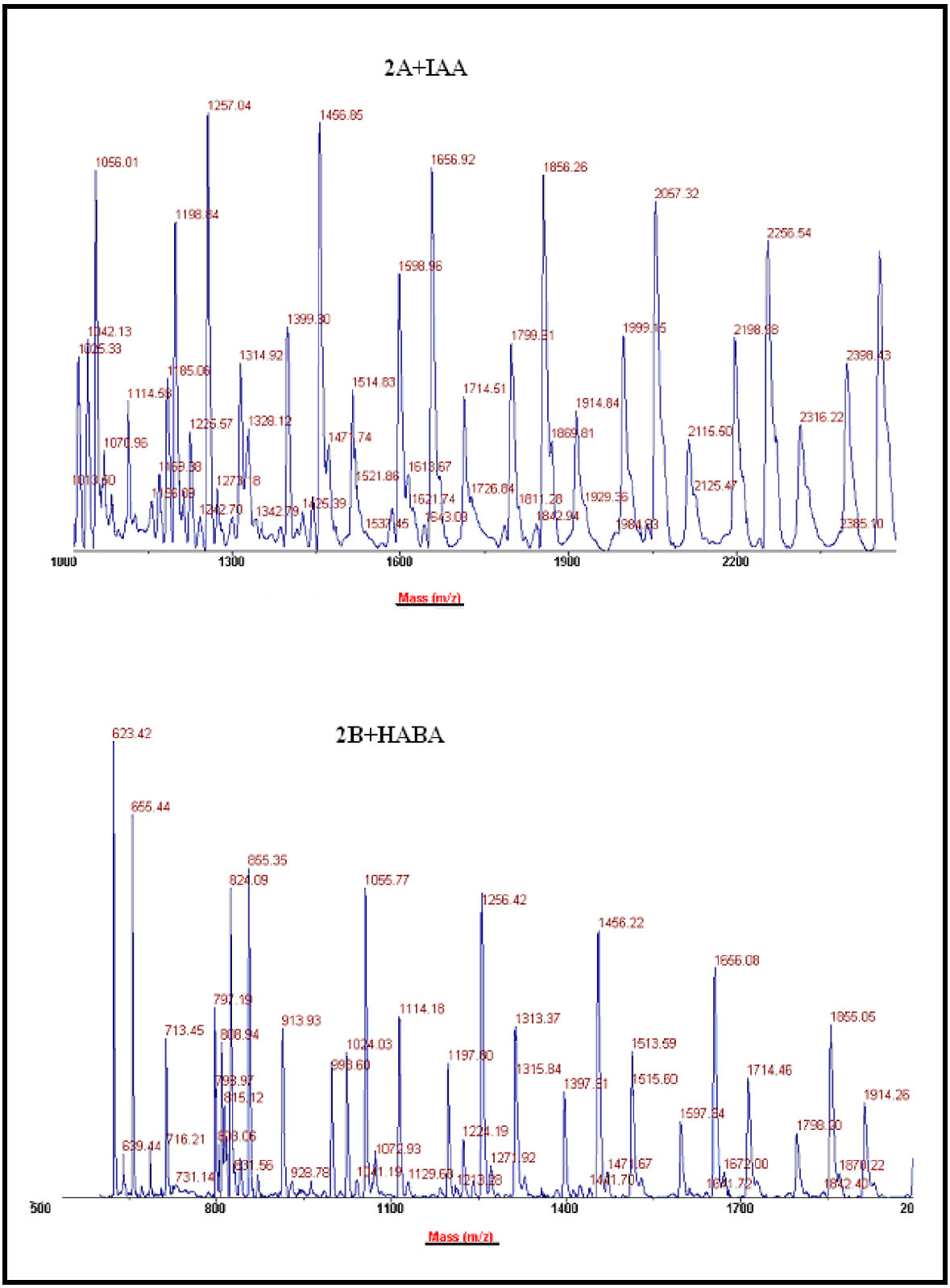


Figure 3.6 MALDI-ToF MS of methanol insoluble fraction 2A and methanol soluble fraction 2B using IAA and HABA matrices respectively

Peaks of very lower intensity appearing at m/z values of 1071, 1271, 1472 and 1870 were detected, which desorbed as oligomers doped with K^+ ions and corresponded to oligomers of the type $H-[O(CH_2)_4O-CO-(CH_2)_4-CO]_n-OCH_3-K^+$ (mass = 200n+32+39), n being the value of DP varying from 5 to 9, 39 being the mass number of potassium. Peaks due to oligomers of mass = 200n+23 were not observed in the spectrum. An isolated peak at m/z value of 1042 was observed. This peak corresponded to an oligomer which desorbed as a Na^+ ion of the type $H-[O(CH_2)_4O-CO-(CH_2)_4-CO]_n-OH-Na^+$. Peaks corresponding to higher DP were not detected.

Spectrum for 2**B** shows a series of peaks due to sodium cationized oligomers with (i) hydroxy-ester end groups appearing at m/z values of 655, 855, 1055, 1256, 1456, 1656 and 1855 (ii) ester-ester end groups appearing at m/z values of 797, 998, 1197, 1398, 1598 and 1798 (iii) hydroxy-hydroxy end groups appearing at m/z values of 713,914, 1114, 1313, 1514, 1714 and 1914. DPs of all these oligomers ranged from 3-8. Peaks with decreasing intensity corresponding to oligomers doped with Na^+ ions (mass = 200n+23), n varying from 3-6, 23 being the mass number of sodium, were observed at m/z values of 623, 824, 1024 and 1224. The cyclic oligomer of DP 3 has the highest intensity. A single peak of very low intensity of m/z value 639 appeared due to the oligomers doped with K^+ ion of mass = 200+39. Peaks of higher DP were not observed. A series of low intensity peaks appearing at m/z values of 1072, 1272, 1472, 1672 and 1870 were detected as oligomers doped with K^+ ions of the type $H-[O(CH_2)_4O-CO-(CH_2)_4-CO]_n-OCH_3-K^+$ (mass = 200n+32+39), n being the value of DP varying from 5 to 9, 39 being the mass number of potassium. Another series of peaks of very low intensity was observed at m/z values of 1041, 1442, 1642 and 1842 and corresponded to the sodium adducts of oligomers of the type $H-[O(CH_2)_4O-CO-(CH_2)_4-CO]_n-OH-Na^+$ (mass = 200n+18+23), n varying from 5 to 9, 23 being the mass number of sodium.

Increasing the temperature of polycondensation from 125 to 150^0C results in increase in the intensity of cyclic oligomer peaks. Cyclic oligomers of DP 3 to 6 were observed, in addition to oligomers with carboxyl end groups. The carboxyl end groups

are presumably being generated via the intramolecular cyclization of the hydroxybutyl groups, leading to acid end groups and THF formation.

Figure 3.7 depicts the spectra of the sample 3**A** and 3**B**. 3**A** shows a series of peaks ranging from 1000 Da to 3000 Da. Peaks corresponding to sodium cationized oligomers with (i) hydroxy-ester end groups appearing at m/z values of 1256, 1458, 1657 and 1857, 2058, 2257, 2458, 2657 and 2857 (ii) ester-ester end groups appearing at m/z values of 1399, 1599, 1800, 2000, 2199, 2399, 2598 and 2799 (iii) hydroxy-hydroxy end groups appearing at m/z values of 1316, 1516, 1715, 1914, 2115, 2315, 2514 and 2717 were detected. DPs of all these oligomers ranged from 6-14. Peaks appearing at m/z values of 1225, 1425 and 1624 as sodium adducts of oligomers were of decreasing intensities and corresponded to oligomers with no end groups and mass = 200n+23, n varying from 2-8. A series of very low intensity peaks of m/z values of 1672, 1872, 2069,2469 and 2669 appeared as potassium adducts of oligomers of the type $H{-}[O(CH_2)_4O{-}CO{-}(CH_2)_4{-}CO]_n{-}OCH_3{-}K^+$ (mass = 200n+32+39), n being the value of DP varying from 8 to 13, 39 being the mass number of potassium. A single peak appeared at m/z value of 1441 as sodium adduct of the oligomer of the type $H{-}[O(CH_2)_4O{-}CO{-}(CH_2)_4{-}CO]_n{-}OH{-}Na^+$ (mass =1400+18+23) corresponding to a DP of 7. Peaks of higher DP were not observed in the spectrum.

The spectrum of 3**B** shows a series of sodium cationized peaks at m/z values of 623, 824, 1024, 1224, 1424, 1624, 1824, 2024, 2223 and 2422 of decreasing intensity corresponding to oligomers with mass = 200n+23, n varying from 2 to 12, 23 being the mass number of sodium. A series of other peaks appearing as sodium adducts of oligomers with (i) hydroxy-ester end groups appearing at m/z values of 1056, 1256, 1456, 1657, 1856, 2057, 2258, 2459, 2660 and 2860 (ii) ester-ester end groups appearing at m/z values of 1198,1398, 1598, 1798, 1998, 2198, 2398, 2598 and 2800 (iii) hydroxy-hydroxy end groups appearing at m/z values of 1114, 1314, 1514, 1715, 1916, 2118, 2315, 2519 and 2715 were detected. DPs of all these oligomers ranged from 5-14. Two peaks of very low intensity appeared at m/z values of 1071 and 1272 as potassium adducts of oligomers of the type $H{-}[O(CH_2)_4O{-}CO{-}(CH_2)_4{-}CO]_n{-}OCH_3{-}K^+$ (mass = 200n+32+39), n being the value of DP varying from 5-6, 39 being the mass number of potassium.

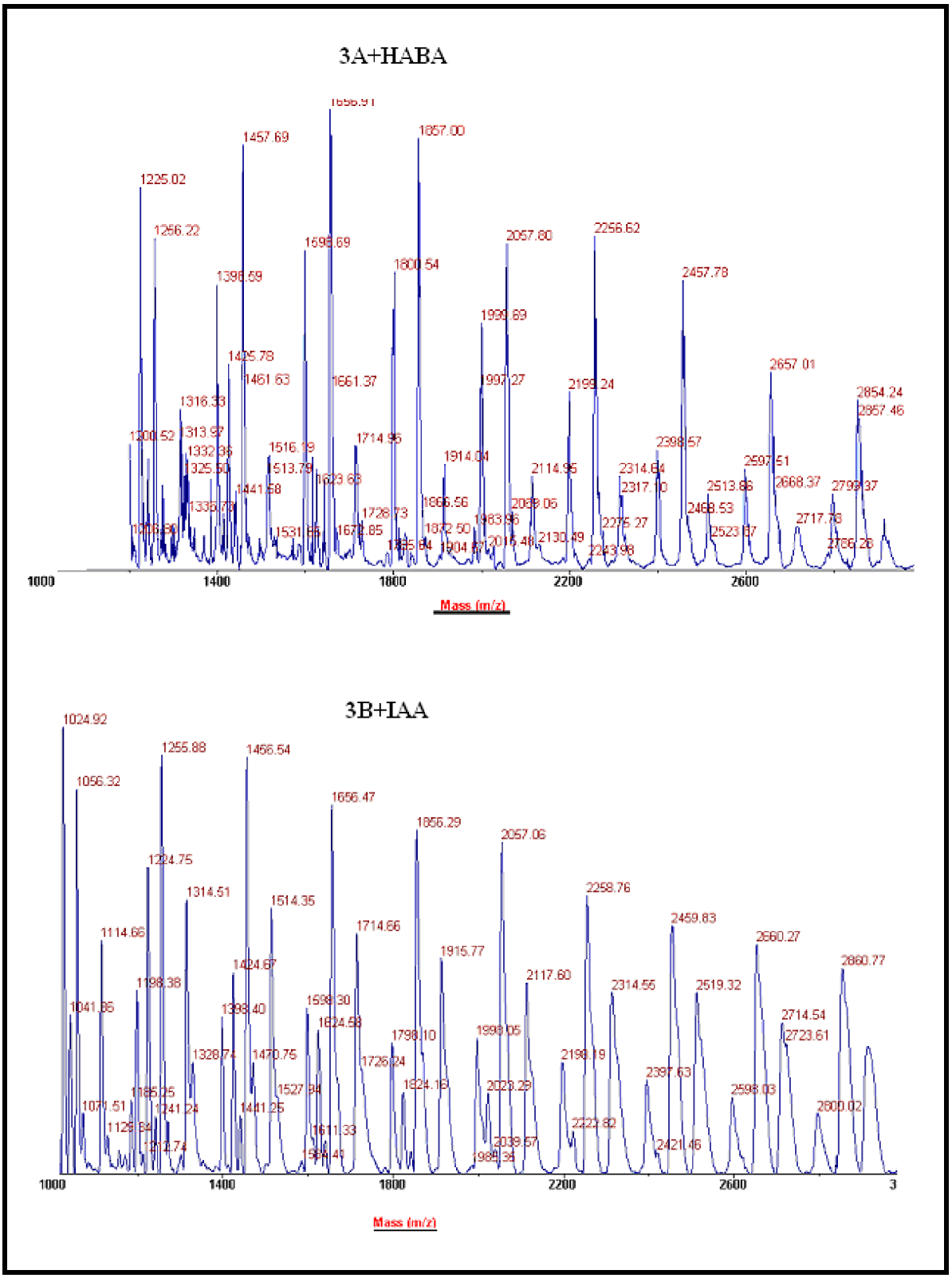


Figure 3.7 MALDI-ToF MS of methanol insoluble fraction 3A and methanol soluble fraction 3B using HABA and IAA matrices respectively

Two peaks of decreasing intensity appeared at m/z values of 1042 and 1241 as sodium cationized oligomeric species of the type $H-[O(CH_2)_4O-CO-(CH_2)_4-CO]_n-OH-Na^+$ (mass =200n+18+23), n = 5-6, 23 being mass number of sodium. Peaks of higher DP were not observed in the spectrum. The methanol insoluble and soluble fractions 3**A** and 3**B** thus contain substantial amounts of cyclics along with the polymeric chains with ester-ester, hydroxyl-ester, hydroxy-hydroxy and carboxy-hydroxy end groups. Thus, increasing the reaction temperature from 150 to 180^0C results in formation of cyclic oligomers of higher DP. Cyclics of DP 10-12, although of low intensity are detected in the methanol soluble fraction. Cyclics of DP less than 9 are of relatively higher intensity.

Methanol soluble fraction 4**B** was analyzed and its spectrum is as depicted in **Figure 3.8**. The spectrum shows a series of peaks of decreasing intensity corresponding to oligomers doped with sodium ions with mass = 200n+23, n varying from 2-10. The intensity of the peaks due to cyclics falls of sharply at higher molecular masses. The peaks arising due to sodium adducts of oligomers with (i) hydroxy-ester end groups appearing at m/z values of 1056, 1257, 1456, 1657, 1856, 2059 and 2260 (ii) ester-ester end groups appearing at m/z values of 1198, 2198, 2398 and 2598 (iii) hydroxy-hydroxy end groups appearing at m/z values of 1114, 1314, 1514, 1715, 1914 and 2115 were detected and were of highly diminishing intensity. DPs of all these oligomers ranged from 5-10. A series of peaks of decreasing intensity appeared at m/z values of 1041, 1240, 1440 and 1640 as sodium adducts of oligomers of the type $H-[O(CH_2)_4O-CO-(CH_2)_4-CO]_n-OH-Na^+$ (mass =200n+18+23), n = 5-8, 23 being mass number of sodium. Another set of peaks of very low intensity appeared at 1071, 1270 and 1668 as potassium adducts of oligomers of the type $H-[O(CH_2)_4O-CO-(CH_2)_4-CO]_n-OCH_3-K^+$ (mass = 200n+32+39), n being the value of DP varying from 5-8, 39 being the mass number of potassium. Peaks of higher DP were not observed. The methanol soluble fraction contains a mixture of cyclic and linear oligomers which appear to be of equal intensity in the spectrum. Thus, further increasing the reaction temperature to 220^0C results in the formation higher amount of cyclics. The amount of cyclic of DP 2 distilling out at 220^0C was maximum.

MALDI-ToF MS spectra of sample 5**A** and 5**B** are as shown in **Figure 3.9**. A single peak of high intensity appeared at m/z value of 1025 and corresponded to sodium adduct of oligomers with no end groups or cyclics.

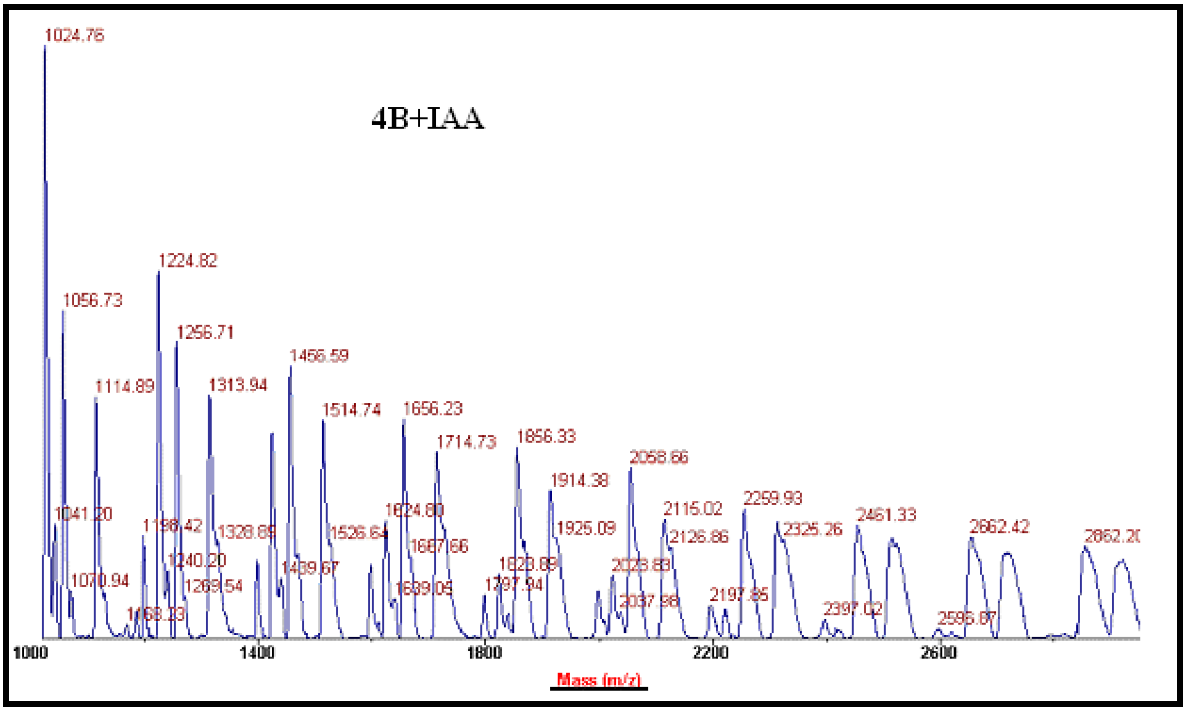


Figure 3.8 MALDI-ToF MS of methanol soluble fraction 4B using IAA matrix

Two other peaks of low intensity were observed at a slightly higher m/z values of 1227 and 1427.Two peaks of diminishing intensities and slightly higher m/z values of 1044 and 1445 appeared as sodium adducts of oligomers of the type $H{-}[O(CH_2)_4O{-}CO{-}(CH_2)_4{-}CO]_n{-}OH{-}Na^+$, mass = 200n+18+23, n = 5 and 7. Peaks corresponding to higher DPs were not observed. A set of peaks appeared as sodium adducts of oligomers with (i) hydroxy-ester end groups at m/z values of 1058, 1258, 1458, 1658, 1858, 2058 and 2259 (ii) ester-ester end groups at higher m/z values of 1200, 1399, 1600, 1800, 2000, 2200 and 2400 (iii) hydroxy-hydroxy end groups at m/z values of 1117, 1315, 1515, 1716, 1917, 2116 and 2316. The potassium adducts of the oligomers with hydroxy-ester and hydroxy-hydroxy end groups did not appear at every DP.

Spectrum of 5**B** did not show presence of any cyclic oligomer. Sodium cationized species appeared at m/z values of 642, 842, 1042 and 1242 and corresponded to

oligomers of the type $H-[O(CH_2)_4O-CO-(CH_2)_4-CO]_n-OH-Na^+$, mass = 200n+18+23, n = 3 – 6.

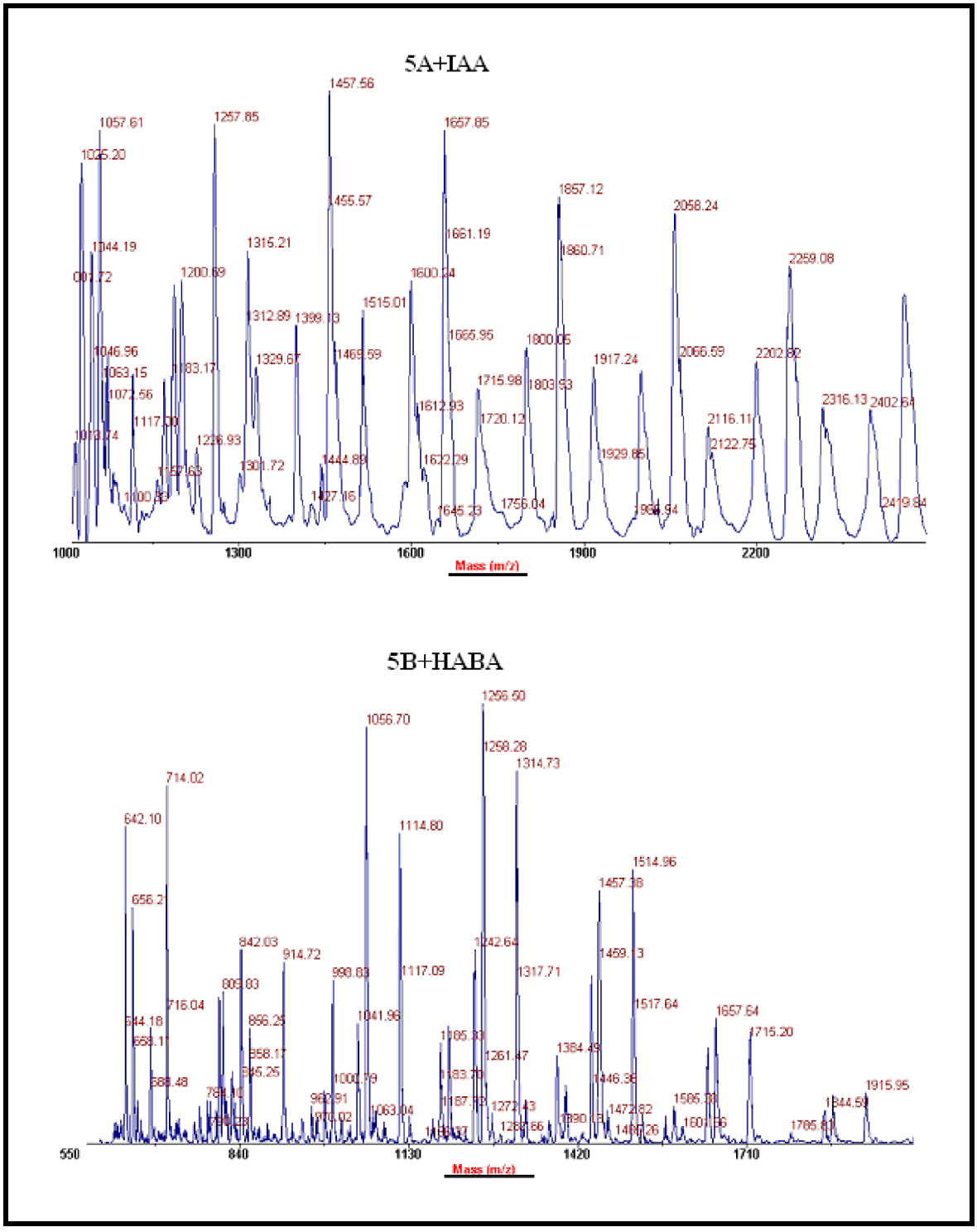


Figure 3.9 MALDI-ToF MS of methanol insoluble fraction 5A and methanol soluble fraction 5B using IAA and HABA

A series of peaks appeared as sodium adducts of oligomers with (i) hydroxy-ester end groups at m/z values of 656, 856, 1057, 1257, 1457 and 1658 (ii) hydroxy-hydroxy end groups at m/z values of 714, 915, 1115, 1315, 1515, 1715 and 916. A single peak due to oligomers with ester end group was observed at m/z value of 998. Potassium adduct of oligomers of the type $H-[O(CH_2)_4O-CO-(CH_2)_4-CO]_n-OCH_3-K^+$ appeared at DP 6 and 7 only and not at all DPs. MALDI–ToF MS analysis of the methanol soluble and insoluble fractions of the experiments carried out at 125^0C for 8 h show that the product obtained contained oligomers with hydroxy-ester, hydroxy-hydroxy, carboxy-hydroxy and ester-ester end groups along with small amount of cyclics of DP$\leq$ 5. Thus, cyclics of maximum DP 5 could be formed during the polymerization. Cyclic of DP 2 distilled out in small quantities during the polycondensation reaction.

Methanol soluble and insoluble fractions (6**A** and 6**B**) were analyzed by MALDI-ToF MS to check for the presence of cyclics. The spectra are shown in **Figure 3.10**. They exhibit a series of peaks appearing as sodium cationized oligomers with (i) hydroxy-ester end groups at m/z values of 1056, 1256, 1457, 1658, 1856, 2057 and 2257 (ii) ester-ester end groups at higher m/z values of 1198, 1397, 1599, 1800, 2000, 2199 and 2399 (iii) hydroxy-hydroxy end groups at m/z values of 1115, 1315, 1515, 1715, 1915, 2116 and 2316. The potassium adducts of the oligomers with hydroxy-ester and hydroxy-hydroxy end groups did not appear at all DPs. Peaks due to oligomers with carboxyl end groups appeared at higher m/z values of 1044 and 1444 as sodium adducts. Spectrum for 6**B** shows a series of peaks appearing as sodium adducts of oligomers with (i) hydroxy-ester end groups at m/z values of 1256, 1455, 1656, 1856, 2056 and 2256 (ii) ester-ester end groups at m/z values of 1397, 1597, 1798, 1998, 2197 and 2397 (iii) hydroxy-hydroxy end groups at m/z values of 1314, 1514, 1714, 1916, 2114 and 2315 (iv) carboxy-hydroxy end groups at m/z values of 1242, 1442, 1641, 1841, 2041 and 2242. No peaks due to cyclics were observed. Thus, experiments carried out using higher catalyst concentration yielded oligomers with hydroxy-ester, ester-ester, hydroxy-hydroxy and carboxy-hydroxy end groups. Both methanol soluble as well as insoluble fractions did not show the presence of cyclics.

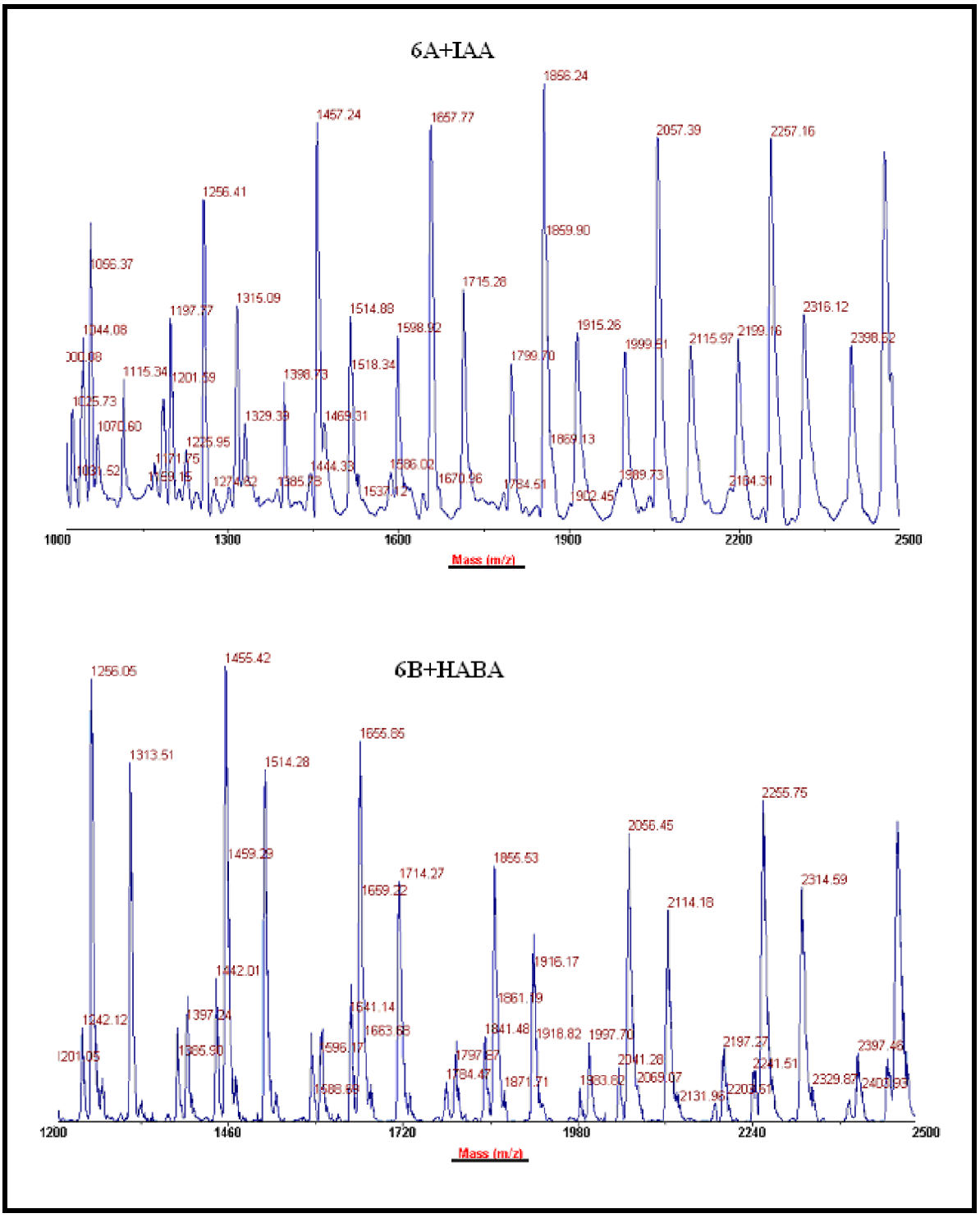


Figure 3.10 MALDI-ToF MS of methanol insoluble fraction 6A and methanol soluble fraction 6B using IAA and HABA matrices respectively

3.4.1.7 Factors limiting chain growth in aliphatic poly (ester) s

Based on the preceding results it appears that reaction temperature is the most critical variable in the polycondensation of DMA and BD. Temperature, in effect, defines the structure of the end groups in the oligomer formed. MALDI-ToF MS analysis shows formation of varying amounts of carboxylic end groups and cyclic oligomers as a function of reaction temperature. The carboxyl end groups are presumably generated as a result of intramolecular cyclization of the hydroxy butyl end groups leading to THF formation. Since no acid groups were present in the reaction medium, the only possible pathway to carboxyl end groups is by intramolecular cyclization. Propensity for the formation of cyclics increases as reaction temperature increases. Cyclic oligoesters are equilibrium components of linear polyesters, and, typically, they compose less than 5 wt% of the total product. Catalyst concentration did not have much effect on the formation of cyclics, whereas some fraction of cyclics was detected by continuing the reaction for 8 h at 125^0C. In all cases cyclics of DP 5 to 9 were of high intensity and intensities of cyclics of higher DP gradually decreased. Cyclics of DP 10-12 were detected but were of low intensity.

Though polycondensation is characterized by an equilibrium process, the reactions are generally forced to be irreversible, by removal of condensation products. As the cyclics are “dead” in the irreversible reaction, their concentration builds up and at complete reaction no linear chains remain. When the reactions were carried out at 125^0C for longer time, the molecular weight did not increase, however cyclics of DP$\leq$ 5 were formed in small amounts. When the reactions were conducted at higher temperatures (> 150^0C), the molecular weight did show an increase. Along with this substantial amount of cyclics were also formed as evidenced by physical separation of cyclic of DP 2 in the distillate. Thus in theory, driving the equilibrium, would ultimately lead to only cyclic oligomers of varying DP.

Synthesis of polyesters and polyamides[24] is accompanied by formation of large amounts of cyclic oligomers, especially, at high conversions and high molecular weights. Cyclization thus competes effectively with propagation at any stage regardless of the concentration of reactants. Cyclic oligomers in condensation polymers such as

polycarbonates and polyesters have been known for quite some time. Early work by Carothers in the 1930s showed that preparation of aliphatic cyclic oligomers was possible via distillative depolymerization[25-26] at elevated temperature and under high vacuum. However there was little interest in 'all-aliphatic' due to low glass transition temperatures of these materials. Cyclic oligomers have been found in commercial grades of polyesters like PET and PBT and are formed in their equilibrium concentration during melt polymerization reactions. The cyclic oligomers have been separated from the polymers and characterized by several groups[27-30]. An extensive study reporting the incidence of cyclic polyesters in 13 types of alkylene iso and terephthalates was detailed by Wick and Zeitler[29]. The mechanism for cyclic formation via depolymerization is the same type of transesterification which occurs during polymerization. Metal alkoxides such as tetra alkyl titanates or dibutyl tin alkoxides have proven to be the most efficient catalysts for such reactions[31]. Cyclics have also been detected in enzyme catalyzed synthesis of poly (butylene adipate) in solution at 60^0C[32]. Cyclic oligomers of poly (decamethylene adipate) and poly (decamethylene terephthalate)[33] were prepared successfully from ring-chain equilibrium reactions in dilute solutions and molar cyclization equilibrium constants K_x were deduced and compared with the corresponding theoretical values predicted by the Jacobson-Stockmayer theory. The formation of macrocycles in the synthesis of polyesters from adipic acid, phthalic anhydride, isophthalic acid, terephthalic acid with 2-butyl-2-ethyl-1,3-propanediol[34] was studied with the aid of molecular modeling and analytical characterization for better understanding of structure-property relationship in saturated polyester resins.

3.5 Conclusions

During the preparation of poly (butylene adipate) s by melt polycondensation of DMA with BD, cyclic oligomers are formed along with linear polycondensates at temperature as low as 125^0C. The concentration as well as DP of these cyclic oligomers increased as the temperature of the reaction was increased. As the polycondensation is carried out in an irreversible manner by removing the condensation byproduct, the cyclics once formed have no further chance to participate in the polymerization and, thus act as sinks for small

molecules in the polymerizing mixtures. The linear chains that remain at any point in the reaction are eventually forced to cyclize when the relative probability for the ends to encounter one another exceeds the probability that the ends will encounter reactive groups on other molecules. Cyclics of lower DP were formed even at 125^0C and at 220^0C cyclics of DP 2 to 12 were formed. Thus, the structure of the oligomers changes from linear hydroxyl terminated oligomers to cyclic oligomers with no end groups. Attempts to increase M_n of the oligomer using a variety of reaction conditions did not succeed in view of the effect of reaction conditions on various equilibria. Formation of THF as well as cyclics, result in loss of end groups, which limits further step growth polymerization of the oligomer. Furthermore, it is generally recognized, that high molecular weight aliphatic polyester can be made only by a suitable end group coupling reactions. Our results show that choice of reaction conditions is critical to obtain an oligomer with the right disposition of end groups suitable for post polymerization coupling reactions.

The results reported in this chapter establish the limits of synthesis conditions for melt polycondensation of DMA with BD resulting in best oligomer DP with minimum accompanying undesirable reactions, such as, formation of cyclic oligomers or polymers with carboxyl end groups.

3.6 References

1. W.H. Carothers, *J.Am.Chem.Soc*. **51**, 2548 (1929)
2. W.H. Carothers, G.A. Arvin, *J.Am.Chem.Soc*. **51**, 2560 (1929)
3. A.C. Albertsson, O. Ljungquist, *J.Macromol.Sci.-Chem*. **A23**, 393 (1986)
4. A.C. Albertsson, O. Ljungquist, *J.Macromol.Sci.-Chem*. **A23**, 411 (1986)
5. A.C. Albertsson, O. Ljungquist, *J.Macromol.Sci.-Chem*. **A24**, 977 (1987)
6. A.C. Albertsson, O. Ljungquist, *J.Macromol.Sci.-Chem*. **A25**, 467 (1988)
7. A.L. Cimecioglu, S.H. Zeronian, K.W. Alger, M.J. Collins, *J.Appl.Polym.Sci*. **32**, 4719 (1986)
8. F.Pilati, "*Comprehensive Polymer Science*", Vol 5, 275, edited by G. Allen, J.C. Bevington, Pergamon Press, Oxford, England (1989)
9. Wm.J. Considine, J.J Ventura, A.J. Gibbons, Jr.A Ross, *Canadian J.Chem.*, **41**,

1239 (1963)

10. R.Okawara, M. Wada, *J.Organomet.Chem*. **1**, 81, (1963)
11. M. Wada, M.Nishino, R.Okawara, *J.Organomet.Chem*. **3**, 70, (1965)
12. (a) M.Takashi, I.Futoshi,.,Japan, *JP 2000110026 A2* (2000) to Toyobo Co.,Ltd, (b) W.Hachiro, Y.Hiroyoshi, H. Kiyoko, *JP 2000038434 A2* (2000) to Nippon Polyurethane Industry Co. Ltd.,Japan
13. Y.Toshiyasu, Y.Masaki, M. Yoshinori, *JP 08301996 A2* (1996) to Kanebo Ltd
14. (a) C.Hoon, J. J.Nam, C. S. Il, K.H.Yeol, H. K.Ho, *PCT Int. Appl. WO 9414870A1* (1994) to Sunkyong Industries (b) H.Shirahama, Y. Kawaguchi, MS. Aludin, H. Yasuda, *J.Appl.Polym.Sci*. **80**, 340 (2001) (c) M. Ishii, M. Okazaki, Y. Shibasaki, M. Ueda, *Biomacromolecules* **2**, 1267 (2001)
15. F.Pilati, A.Munari, P.Manaresi and V.Bonora, *Polymer* **26**, 1745 (1985)
16. A.Fradet, E.Marechal, *Adv.Polym.Sci*. **43**, 51 (1982)
17. M.Ajioka, K.Enomoto, K.Suzuki, A.Yamaguchi, *Bull.Chem.Soc.Jpn*. **68**, 2125 (1995)
18. J.Otera, N. Dan-oh, H. Nozaki, *J.Org.Chem*. **56**, 5307 (1991)
19. J.B. Williams, A.L. Gusev, D.M. Hercules, *Macromolecules* **30**, 3781 (1997)
20. (a) A.K. Chaudhary, G. Critchley, A. Diaf, E. J. Beckman, A.J. Russell, *Macromolecules* **29**, 2213 (1996) (b) S.Salhi, M.Tessier, J-C. Blais, RE. Gharbi, A. Fradet, *e-Polymers*, **043** (2005)
21. C. Sabrina, R. Paola, P. Concetto, *Rapid Commun. Mass Spectrom*. **14 (16)**, 1513 (2000)
22. J.B.Williams, T.M.Chapman, D.M.Hercules, *Anal. Chem*. **75 (13)**, 3092 (2003)
23. J.T.Mehl, R..Murgasova, X.Dong, D.M.Hercules, Anal. Chem. **72(11)**, 2490 (2000)
24. H.R.Kricheldorf, A.Lorenc, J.Spickermann, M.Maskos, *J.Polym.Sci.,Part A: Polym.Chem*. **37**, 3861 (1999)
25. J.W.Hill, W.H.Carothers, *J.Am.Chem.Soc*. **57**, 5031 (1933)
26. E.W.Spanagel, W.H.Carothers, *J.Am.Chem.Soc*. **57**, 929 (1935)
27. L.H.Peebles, M.W.Huffman, C.T.Ablett, *J.Polym.Sci.,Part A-1* **7**, 479 (1969)
28. E.Repin, E.Papanikolau, *J.Polym.Sci.,Part A-1* **7**, 3426 (1969)

29. G.Wick, H.Zeitler, *Angew.Makromol.Chem*. **112**, 59 (1983)

30. G. Montaudo, C.Puglisi, F.Samperi, *Polym.Degrad.Stab*. **42**, 13 (1993)

31. D.J.Brunelle, *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*, Chapter 3, 117, edited by J.Scheirs, T.E.Long, John Wiley and Sons, Ltd. (2003)

32. G.Mezoul, T.Lalot, M.Brigodiot, E.Marechal, *J.Polym.Sci.Part A: Polym.Chem*. **33(16)** , 2691 (1995)

33. (a) B.R.Wood, J.A.Semlyen, *Polymer* **38 (1)**, 191 (1997) (b) S.C.Hamilton, J.A.Semlyen, *Polymer* **38 (7)**, 1685 (1997)

34. L.Ahjopalo, H.Osterholm, H.Jarvinen, L.O.Pietila, *Polymer*, **41**, 8283 (2000)

Chapter 4: Application of chain extension reactions to aliphatic poly (ester) s

4.1 Introduction

Aliphatic polyesters have evoked keen interest in recent years because of their desirable environmental degradability[1]. However they lack the physical and mechanical properties of aromatic polyesters thereby limiting their practical applications. The conventional method of preparing aliphatic polyesters by thermal polycondensation of aliphatic diols with aliphatic diacids or diesters is accompanied by formation of large amounts of cyclics, incomplete conversions and other undesirable products of degradation. High molecular weight aliphatic polyesters possessing suitable thermal and mechanical properties are generally difficult to obtain by this method. The solid-state polymerization technique is also not suitable for aliphatic polyesters on account of their low crystalline melting points.

In view of the above reasons, new approaches are needed to obtain aliphatic polyesters with useful properties. One strategy is to modify the basic structure by copolymerization. This involves introduction of an aromatic or cycloaliphatic group into the polymer structure. While this approach improves polymer properties, it is accompanied by a loss of hydrophilicity and, hence, biodegradability[2]. The use of esterification promoting adjuvents like triphosgene, dicyclohexylcarbodiimide, and carbonyl dimidazole in the polycondensation reaction enhances the molecular weight[3]. However, this process results in higher costs due to increased number of reaction steps, use of dangerous or flammable solvents and additional purification and separation steps of nonrecoverable byproducts. Another strategy involves introducing crosslinks into the polymer chain[4]. Post polymerization chain extension using suitable coupling agents is another strategy frequently employed to improve molecular weights of aliphatic polyesters. Low molecular weight polyesters with appropriate end groups are used as precursors for chain extension reaction. The use of chain extenders overcomes many of the disadvantages of the earlier discussed methods. These reactions are more economically feasible as they can be carried out in melt or using minimum amount of

solvents, at low temperatures, with lower amounts of chain extending agents and with no separate purification steps. These reactions are generally fast and can be carried out during the last stages of the preparation of the polymer or even in an extruder[5]. These benefits render the use of chain extenders very attractive for practical applications[6-7]. The disadvantage of this method is that the final polymer may still contain unreacted chain extending agents, residual metal or polymer impurities. Sometimes the chain extenders used may not be biodegradable or bioabsorbable.

Generally these reactions are of addition or ring opening type with no formation of byproduct. The precursor oligomers are telechelic in nature. A number of chain extenders that react exclusively with either hydroxyl or carboxyl end groups are reported in literature[8]. The precise knowledge of the end group concentration is important for successful chain extension reaction leading to improved molecular weights.

Chain extenders are, typically, bifunctional compounds, thermally stable and nonvolatile at the temperature of processing. Bionolle®, a product of Showa High Polymer Co., Japan is a copolyester of poly (butylene succinate), poly (butylene adipate) and poly (ethylene succinate) chain extended with hexamethylene diisocyanate[9-10]. Several useful chain extenders have been reported eg. bis (epoxides)[11], bis (cyclic carboxylic anhydride), sebacoyl or adipoyl chloride[12-13] and phosgene[14]. Chain extension reactions between the hydroxyl terminated prepolymers and diisocyanate chain extenders to yield poly (ester-urethane) have been extensively studied[15-16]. Chain extension through bis-chloroformate type chain extenders to yield aliphatic poly (ester-carbonate) s has been reported[17]. Some active phenolic esters have been reported to be effective chain extenders[18], however the liberated phenol is an undesirable by-product. Bis (oxazoline) s[19], bis (benzoxazinone) s[20] and bis (N-acyl-lactam) s[21] have also been reported as effective chain extenders. Cross-linked poly (ether-lactone) s have been prepared by simultaneous ring opening polymerization of 1,5-dioxepan-2-one (DXO) in presence of bis(ε-caprolactone) molecules[22]. Use of a 2,2'bis (2-oxepanone) propane and diphenyl carbonate as a chain extender for a diol-ended PLA telechelic prepolymer to obtain a linearly coupled, high molecular weight copolyester of LLA has been explored[23]. Bis (4-nitro phenyl) carbonate has been used as activated chain extender in peptide synthesis

and in the preparation of mixed carbonates[24]. The byproduct, 4-nitro phenol, is a good leaving group and a poor nucleophile.

This chapter describes the results of synthesis of a hydroxyl terminated poly (butylene adipate) telechelic oligomer and exploration of chain extension reactions to realize higher molecular weight polyesters using different coupling agents. The hydroxyl terminated poly (butylene adipate) was prepared by glycolysis of poly (butylene adipate) using 1,4 butanediol. The chain extension reaction of the hydroxyl telechelic oligomer with hexamethylene diisocyanate (HMDI), 2,2'bis (2-oxepanone) propane, bis (4-nitrophenyl carbonate) and divinyl adipate was studied.

4.2 Experimental

4.2.1 Materials

1,4-Butanediol (BD), 2,4,6- trichlorophenol and adipic acid were obtained from Fluka Chemika, Switzerland. Pyridine (AR grade), p-toulene sulphonic acid (PTSA), mercury (II) acetate and hexamethylene diisocyanate (HMDI) were procured from S.D. fine Chemicals, Mumbai, India whereas bis (4-nitro phenyl) carbonate was obtained from Lancaster Chemicals, UK. Titanium isopropoxide, stannous octoate (SO), dibutyl tin dilaurate (DBTL), dimethyl 4-amino pyridine (DMAP), 1,2-phenylene phosphorochloridite (PPC), chromium tris (acetyl acetonate), vinyl acetate and chloroform-d were obtained from Sigma-Aldrich Inc., USA. m-Chloro perbenzoic acid (MCPBA) was obtained from Spectrochem chemicals, Mumbai, India and 2,2'-bis (4-hydroxy cyclohexyl) propane (H-BPA) was procured from New Japan Chemical Co.Ltd.,Tokyo,Japan.

4.2.2 Reagents and purification

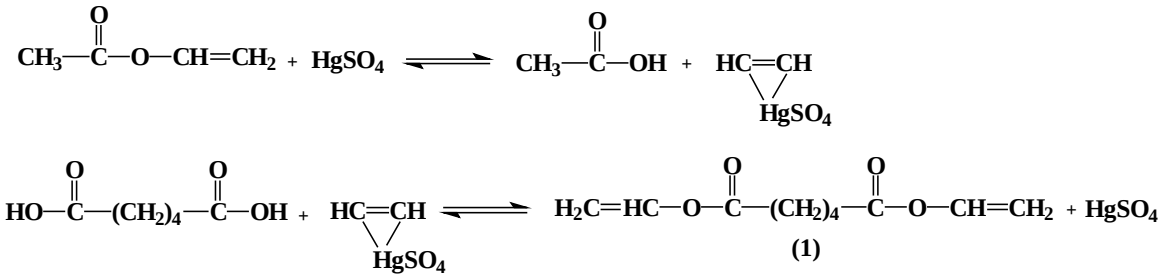
1,4-Butanediol was distilled under vacuum and stored over 4Å molecular sieves. Titanium (IV) isopropoxide and stannous octoate were both distilled under vacuum and used. Titanium (IV) isopropoxide was used as a solution in dry toluene, whereas, stannous octoate was used as a solution in dry THF. Pyridine was distilled and stored over 4Å molecular sieves prior to use. p-Toluene sulphonic acid (PTSA) was freshly

dried azeotropically with benzene and recrystallized from petroleum ether followed by vacuum drying before use. H-BPA was purified by recrystallization with hot toluene. Pyridinium chloro chromate (PCC)[25] used for the oxidation of H-BPA was prepared as follows: 0.185 mL of 6 M HCl (1.1 mol) was added to 100 g (1M) of chromium trioxide (CrO_3) rapidly with stirring. After 5 minutes, the homogeneous solution was cooled to 0^0C and 79.1 g (1M) of pyridine was carefully added over 10 min. Recooling to 0^0C gives a yellow orange solid which was collected in a sintered glass funnel and dried for 1 h in vacuum.

4.2.3 Synthetic Methods

Synthesis of divinyl adipate (DVA)[26]

Divinyl adipate was synthesized by stirring adipic acid (14.614 g, 0.1mol), vinyl acetate (43.045 g, 0.5 mol), mercury (II) acetate (0.23 g), hydroquinone (0.06 g) and sulphuric acid (4 drops) in a 100 mL single necked round bottom flask at room temperature for 96 h under nitrogen atmosphere. The reaction mixture was then poured into sodium carbonate solution (3-5% w/v). The organic layer was extracted with chloroform and washed with brine solution. The aqueous layer was washed with chloroform. The organic layer and the washings were collected and dried over sodium sulfate and later on concentrated and purified by column chromatography. Pet ether was used as a mobile phase. Solvent system used for TLC was a mixture of pet ether + ethyl acetate in 80: 20 proportions.



Scheme 4.1: Synthesis of DVA by interchange reaction of vinyl acetate with adipic acid

Concentrating the pet ether solution followed by drying resulted in DVA in 60% yield. NMR of pure DVA (**Figure 4.1**) was recorded.

^{1}H NMR ($CDCl_3$) of DVAδ: 1.73 (4H, m, -CH_2); 2.43 (4H, m, -CH_2); 4.57-4.59 (2H, d, =CH_2); 4.86-4.91 (2H, d, =CH_2); 7.25-7.32 (2H, m, -OCH=)

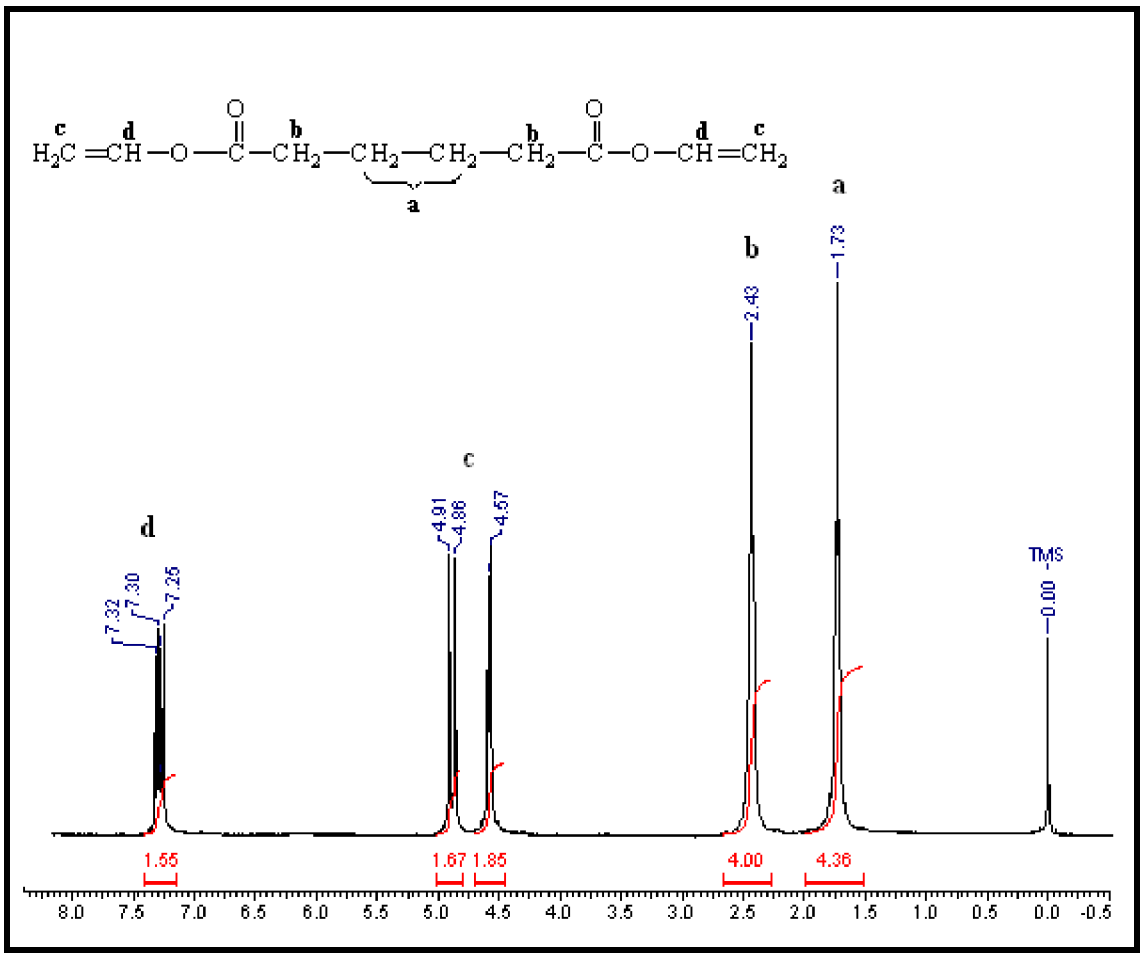
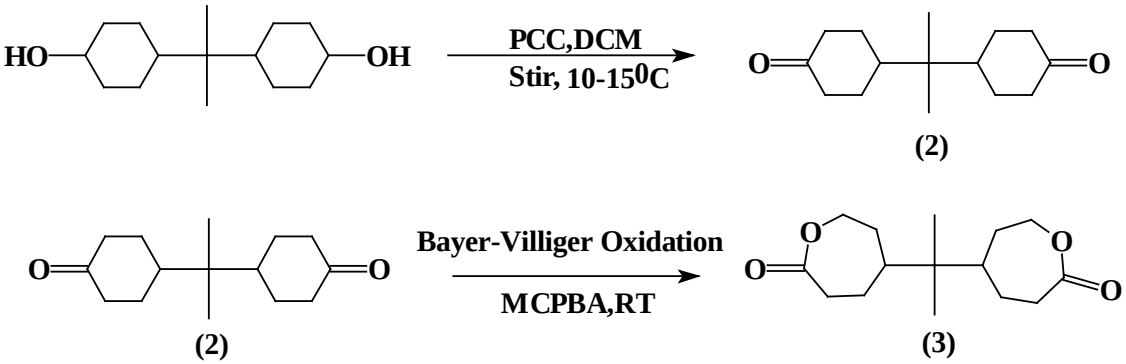


Figure 4.1 ^{1}H NMR spectrum of divinyl adipate (DVA)

Synthesis of 2, 2' bis (2-oxepanone) propane (BOP)

BOP was prepared by oxidation of hydrogenated bisphenol-A (H-BPA) in two steps, namely oxidation of H-BPA to 2,2' bis (4-cyclohexanone) propane and Bayer Villiger oxidation of the ketone to lactone as shown in **Scheme 4.2**.

Step 1: PCC (72 g, 0.335 M) was finely mixed with an equal quantity of silica gel (100-120 mesh size) and dissolved in 300 mL of dichloromethane (DCM) in a 1L three necked round bottom flask fitted with a reflux condenser. H-BPA (20 g, 0.083 mol) dissolved in 200 mL DCM was added in one portion to the magnetically stirred solution. After 4 h of stirring at room temperature, the reaction mixture was filtered through a sintered funnel.



Scheme 4.2: Synthesis of 2, 2' bis (2-oxepanone) propane by oxidation of H-BPA

The round bottom flask was washed 4-5 times with DCM. The filtrate was concentrated and passed through a bed of celite-silica gel. The colorless solution obtained was neutralized using a saturated solution of sodium bicarbonate followed by saturated brine solution. The organic layer was dried over sodium sulfate. The formation of ketone was confirmed by TLC, which showed a single spot due to ketone in a 80: 20 mixture of pet ether and ethyl acetate as eluent system. Concentrating the organic layer resulted in the desired product (**2**) in 80% yield. The structure was confirmed by IR and NMR. **Step 2**: 2,2'bis (4-cyclohexanone) propane (**2**) (1.5 g, 0.00635 mol), MCPBA (4.4 g, 0.0254 mol) and DCM were stirred at room temperature in a 250 mL round bottom flask for 26 h. This reaction mixture was washed with sodium bicarbonate (5 % solution in 300 mL water) followed by water till the washings tested neutral. The organic layer was dried over sodium sulfate. A white powder (1.43 g, 95% yield) was obtained after concentrating the DCM solution. The lactone obtained was soluble in chloroform.

FTIR (chloroform, cm^{-1}): ketone: 2954 (C-H), 1714 (C=O); lactone: 2962 (C-H), 1726 (C=O) (**Figure 4.2**)

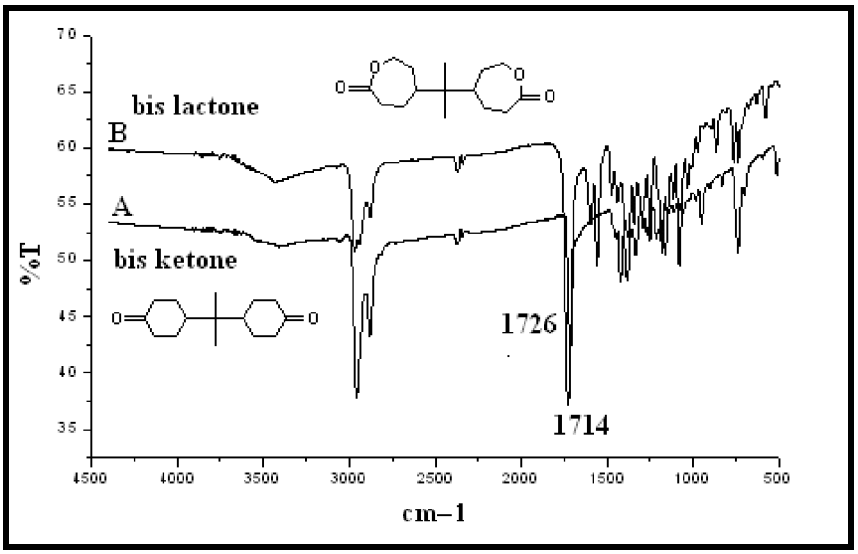


Figure 4.2 FTIR spectra of (A) 2,2' bis (4-cyclohexanone) propane and (B) 2,2' bis (2-oxepanone) propane

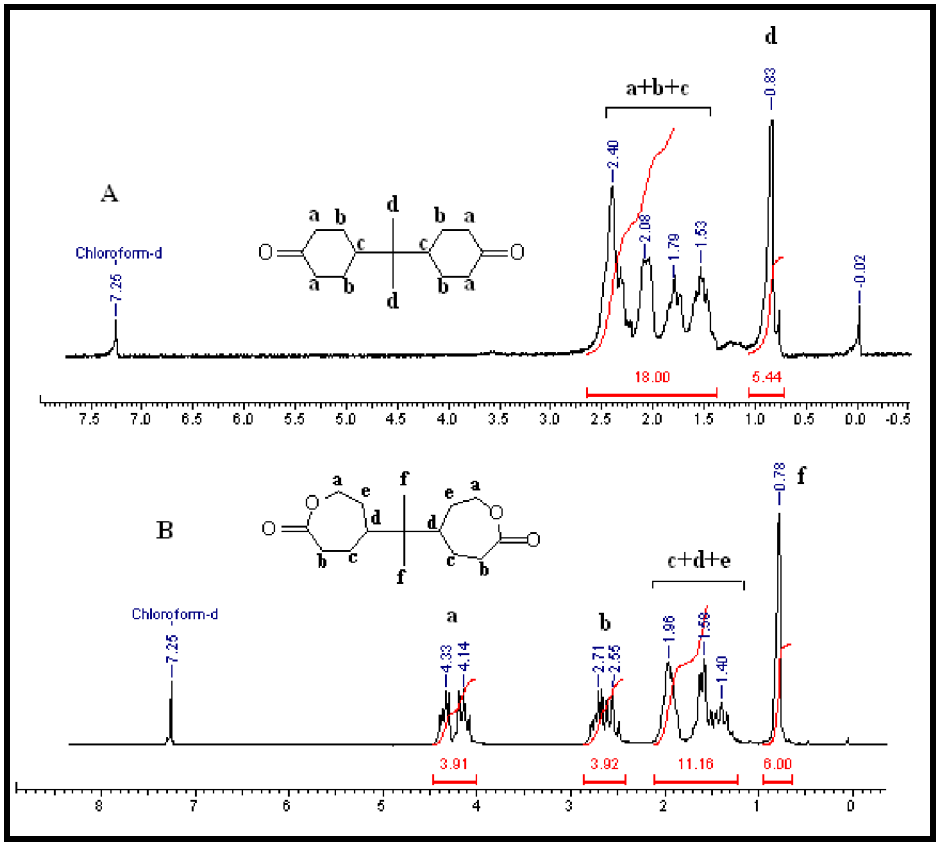


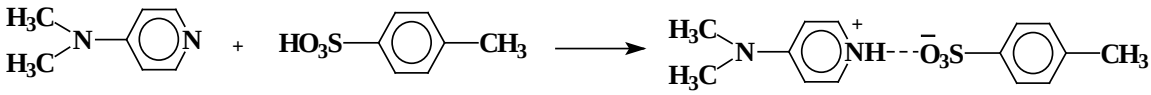
Figure 4.3 ^{1}H NMR spectra of 2,2' bis (4-cyclohexanone) propane and (B) 2,2' bis (2-oxepanone) propane

^{1}H NMR ($CDCl_3$) of 2,2' bis (4-cyclohexanone) propane δ: 0.86 (6H, s, -CH_3); 1.56-2.08 (10H, m, ring protons); 2.42 (8H, m, ring protons adjacent to C=O) (**Figure 4.3A**)

^{1}H NMR ($CDCl_3$) of 2,2' bis (2-oxepanone) propane δ: 0.78 (6H, s, -CH_3); 1.34-1.96 (10H, m, ring protons); 2.49-2.78 (4H, m, -CH_2 on the ring adjacent to C=O); 4.08-4.39 (4H, m, -OCH_2) (**Figure 4.3B**)

Synthesis of 4-(dimethyl amino) pyridinium 4-toluene sulphonate (DPTS)[27]

Dry PTSA (1 g, 0.0058 mol) was dissolved in benzene in a round bottom flask equipped with a dean and stark apparatus and heated to remove traces of moisture. An equi-molar amount of DMAP (0.708g, 0.0058 mol) was added to the stirred solution of PTSA in hot benzene. A white precipitate was formed as a result of this addition. This suspension was stirred for an additional period of 1 h and filtered. The product was recrystallized from saturated chloroform solution and dried. This quaternary ammonium salt DPTS was collected as needle shaped white crystals (yield 95%). Melting point 163-165^{0}C, Reported 165^{0}C[27]



(4)

Scheme 4.3: Synthesis of DPTS

Synthesis of hydroxyl terminated telechelic poly (butylene adipate)s

Poly (butylene adipate) (16 g, 0.08 mol) prepared by melt polycondensation, in chapter 3 (**Table 3.3, entry no. 2**) and 1,4-BD (7.2 g, 0.08 mol) were heated in presence of titanium isopropoxide (0.025 wt% of PBA = 0.004 g) at 150^{0}C for 30 min in a two necked round bottom flask fitted with a reflux condenser and a nitrogen inlet. After heating for 0.5 h, the product was cooled, poured into warm water and washed thoroughly to remove the excess BD. The oligomer was collected, dissolved in chloroform and dried over sodium sulfate. The chloroform was evaporated under vacuum and oligomer was dried (yield = 94%). The oligomer was characterized by NMR (^{1}H and ^{13}C) (**Figure 4.4**), IR (**Figure 4.5**), VPO, GPC (**Figure 4.6**) and MALDI-TOF MS (**Figure 4.7**). The hydroxyl end groups were quantified by ^{31}P NMR (**Figure 4.8**).

FTIR (chloroform, cm^{-1}): 3520, 3440 (O-H), 2950 (C-H), 1728 (C=O)

^{1}H NMR ($CDCl_3$) of PBAδ: 1.63-1.67 (8H, m, $-CH_2$); 2.30 (4H, s, $-COCH_2$); 3.64 ($HO-CH_2$); 4.06 (4H, s, $-OCH_2$)

^{13}C NMR ($CDCl_3$) of PBAδ: 23.90 (CH_2); 24.91(CH_2); 33.42 (CH_2CO); 63.42 (CH_2O); 172.85 (carbonyl)

Chain extension of hydroxy telechelic poly (butylene adipate)s with 1, 6-hexamethylene diisocyanate:

Poly (butylene adipate) oligomer (0.25 g) was placed in a 25 mL round bottom flask fitted with a nitrogen inlet and condenser. The oligomer was heated with stirring under nitrogen atmosphere in an oil bath at 150^0C. HMDI (0.0346 g, 0.033 mL, $2.058x10^{-4}$ mol) was added to the melt and the heating was continued for 3 h under nitrogen atmosphere. Molar ratio of the hydroxyl groups to diisocyanate (NCO) groups was one. Experiments were carried out at two temperatures 70^0C and 150^0C. The polymer was cooled under nitrogen atmosphere and was recovered by dissolving in chloroform and precipitating from methanol followed by drying under vacuum. The obtained polymer was characterized by viscosity measurements, IR, GPC and NMR.

FTIR (chloroform, cm^{-1}): 3300 (N-H), 2950 (C-H), 1728 (C=O), 1530 (O=C-NH-)

^{1}H NMR ($CDCl_3$) δ: 1.63-1.67 (8H, m, $-CH_2$); 2.28 (4H, s, $-COCH_2$); 4.03 (4H, s, $-OCH_2$)

Chain extension of hydroxy telechelic poly (butylene adipate)s with 2,2'bis (2-oxepanone) propane:

Poly (butylene adipate) oligomer (0.25 g) and 2,2'bis (2-oxepanone) propane (0.056 g, $2.058x10^{-4}$ mol) were placed in a two necked round bottom flask fitted with a nitrogen inlet and condenser. Molar ratio of the hydroxyl groups to lactone was one. Stannous octoate ($1.7x10^{-4}$g, $4.116x10^{-7}$ mol) was added as a solution in dry THF. The reactants were heated for 2 h under nitrogen in an oil bath maintained at 180^0C. The final polymer was recovered by dissolving in chloroform and precipitating from methanol followed by drying under vacuum. The polymer was characterized by viscosity measurements, IR, GPC and NMR.

FTIR (chloroform, cm^{-1}): 2950 (C-H), 1728 (C=O)

^1H NMR ($CDCl_3$) δ: 0.78 (s, $-CH_3$ protons from 2,2' bis (2-oxepanone) propane); 1.64-1.67 (8H, m, $-CH_2$); 2.31 (4H, s, $-COCH_2$); 4.07 (4H, s, $-OCH_2$)

Chain extension of hydroxy telechelic poly (butylene adipate) with bis (4-nitro phenyl) carbonate:

Poly (butylene adipate) oligomer (0.25 g), bis (4-nitro phenyl) carbonate (0.0626 g, $2.058x10^{-4}$) and DPTS (0.0605 g, $2.058x10^{-4}$ mol) were heated at 180^0C under nitrogen atmosphere for 4 h in a two necked round bottom flask fitted with a nitrogen inlet and a condenser. Molar ratio of the hydroxyl groups to carbonate was one. The product was dissolved in chloroform and precipitated from methanol and dried. The polymer was characterized by viscosity measurement, IR, GPC and NMR.

FTIR (chloroform, cm^{-1}): 2948 (C-H), 1728 (C=O)

^1H NMR ($CDCl_3$) δ: 1.64-1.67 (8H, m, $-CH_2$); 2.31 (4H, s, $-COCH_2$); 4.07 (4H, s, $-OCH_2$)

Chain extension of hydroxy telechelic poly (butylene adipate) with divinyl adipate:

(a) Poly (butylene adipate) oligomer (0.25 g), divinyl adipate (0.0407, $2.058x10^{-4}$) and titanium isopropoxide (0.5 wt% of oligomer, $1.25x10^{-3}$g) were taken in a two necked round bottom flask. The reactants were dissolved in 2-2.4 mL of dry chloroform. The reaction mixture was refluxed vigorously for 5.5 h. The viscous product was dissolved in small quantity of chloroform and precipitated from methanol. The final polymer was dried under vacuum and was characterized by viscosity measurements, IR, GPC and NMR. (b) The chain extension reaction was also carried out in melt at 150^0C and 70^0C by heating poly (butylene adipate) (0.25 g) and DVA (0.0407 g, $2.058x10^{-3}$ mol) in presence of titanium isopropoxide (0.5 wt% of prepolymer, $1.25x10^{-3}$g) for 3 h and 5 h in an oil bath under nitrogen atmosphere.

4.3 Analysis

4.3.1 Determination of hydroxyl end group concentration of the telechelic oligomer by ^{31}P NMR[28]

Hydroxyl end groups of the poly (butylene adipate) oligomer were estimated by derivatizing the OH end groups of the polyester into O-P linkage using 1,2-phenylenephosphorochloridite (PPC) at room temperature. $CDCl_3$ and 2,4,6-trichlorophenol were used as solvent and internal standard respectively. ^{31}P NMR data were acquired on a 200 MHz NMR spectrometer. Typical acquisition parameters included a 30 degree flip angle and a collection of 32K data points. A pulse delay was chosen so that the total recycle time was 2s. The number of scans was 400.

4.3.2 Solution NMR measurements

^{1}H NMR spectra were recorded on a Brucker AC 200 spectrometer at 25 ± 1^{0}C, operating at 200 MHz. For measurements, 20 mg of polyester samples were dissolved in 0.5 mL of solvent chloroform-d in 5mm diameter NMR tubes. The chemical shifts are reported up field with reference to internal standard chlororform-d at 7.25 δ or down field with reference to TMS. ^{13}C NMR analysis was carried out on a MSL 300 spectrometer.

4.3.3 FTIR spectroscopy

IR spectra were recorded as chloroform solution on sodium chloride cells, on a Perkin-Elmer Infrared Spectrometer Model 16-PC FT-IR. IR bands were expressed in frequency (cm-1).

4.3.4 Molecular weight and molecular weight distribution

Molecular weights (M_n and M_w) and polydispersity (M_w / M_n) were determined with respect to polystyrene standard by size exclusion chromatography on a Thermo Finnigan Spectra Series AS300 machine at 25^{0}C by eluting poly (butylene adipate) solutions of 5-8 mg / ml concentrations in chloroform, with toluene as internal standard through a series of five μ – Styragel columns of pore sizes 10^5, 10^4, 10^3, 500 and 100 Å, respectively and length 30 cm each. Chloroform was used as the mobile phase (flow rate 1mL/min) and both UV and RI detector signals were recorded simultaneously. As the molecular weights were calculated with respect to polystyrene calibration, they were of little significance

and hence GPC was mainly used to determine the polydispersity index. The number average molecular weights of the polyesters were determined by KNAUER K- 7000 Vapor Pressure Osmometer as per the procedure reported in chapter 3.

4.3.5 Viscosity measurements

Inherent viscosities of 0.5% (w/v) solutions of polyesters in chloroform were determined in an automated Schott Gerate AVS 24 viscometer, using an Ubbelohde suspended level viscometer at 25 ± 1^0C. About 50 mg of polyester were weighed in 10 mL volumetric flasks and dissolved in the solvent. Flow times for solvent and samples were recorded Inherent viscosity was calculated and expressed in dL/g.

4.3.6 MALDI-ToF MS analysis

This analysis was performed as described in chapter 3

4.3.7 Thermal analysis

Differential scanning calorimetric (DSC) measurements were made on a Waters thermal analyzer model Q-10 in a nitrogen atmosphere. Approximately 6-7 mg of polymer samples were weighed in aluminium pans of 50 μL capacity and sealed. The measurements were run from –40 to 80 °C at a heating rate of 10 °C/ min and a cooling rate of 100 °C/ min. The crystallinity data and melting temperature were recorded from the second cooling and first heating curves, respectively. The thermal stability of the prepared telechelic oligomer and divinyl adipate was determined by the Perkin Elmer TGA instrument. A known weight of sample was heated from 30 to 800^0C to determine the temperature at which the degradation begins.

4.4 Results and Discussion

4.4.1 Synthesis of hydroxy telechelics and their chain extension reactions

Synthesis of poly (butylene adipate) (PBA) by melt polycondensation as described in chapter 3 results in the formation of linear as well as cyclic oligomers. Driving the reaction towards realizing high molecular weight polymers also results in formation of

macrocylces. The polyesters synthesized at temperatures less than 150^0C contained relatively lesser amount of cyclics.

High molecular weight polyesters can be obtained by chain extension reactions using suitable chain extenders. Chain extension essentially involves a spontaneous reaction between the chain extender and end groups of the polymer chain in a statistical way with no byproduct formation, resulting in the formation of a linear extended chain and consequent increase in molecular weight. This requires the polymer chains to have end groups of the same chemical nature.

Table 4.1 Chain extenders used for different types of end groups

Nature of end groups	Chain extender used	Reference
-COOH	Diisocyanate	[29-32]
	Bis (epoxide)	[33]
	Bis (oxazoline)	[33-34]
-OH	Diisocyanate	[35-36]
	Acid chloride	[3]
	Anhydride	[33]
	Epoxide	[33]
	Orthoester	[33,37]
	phosgene	[38]
$-NH_2$	Diisocyanate	[39]

The polyesters synthesized at temperatures less than 150^0C in chapter 3, contains chains having mixed end groups such as hydroxyl-ester, hydroxyl-hydroxyl and ester-ester end groups which are not suitable for chain extension reactions with any of the known chain extenders. The choice of chain extender depends on the nature of end

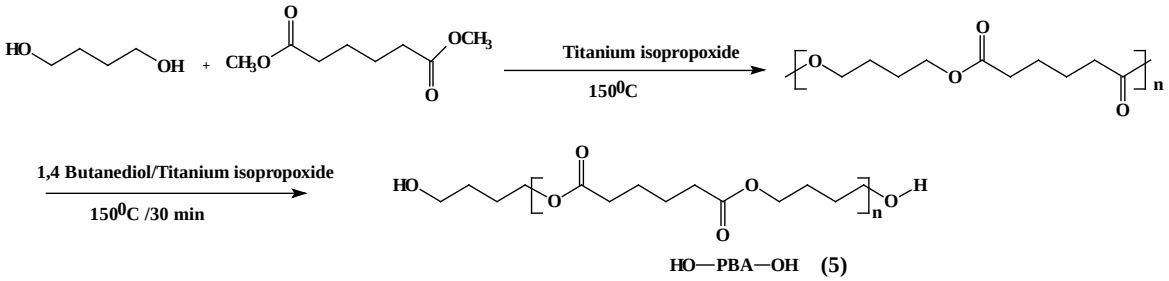
groups of the polymer chain. The most commonly occurring end groups are hydroxyl and carboxyl end groups. A number of bifunctional compounds can be used to link two such end groups. **Table 4.1** shows different chain extenders that can be used for these end groups. Efficiency of the chain extender is measured in terms of the extent of coupling reaction and consequent increase in molecular weight, without any side reactions or degradation reactions leading to insoluble gels and broadening of molecular weight distribution.

Diisocyanates are the most commonly used chain extenders. The high reactivity of isocyanates with functional groups is known from urethane chemistry[40]. A number of aliphatic, cycloaliphatic and aromatic diisocyanates such as hexamethylene diisocyanate (HMDI), 4,4'-dicyclohexylmethane diisocyanate (DES), isophorone diisocyanate, methylenediphenyl diisocyanate (MDI) have been used as chain extenders to enhance the molecular weights of polyesters having hydroxyl as well as carboxyl end groups. The isocyanate groups can also react with moisture, urethane and urea groups to form urea, allophanate and biuret respectively or with each other in isocyanate homopolymerization leading to branching or crosslinking in the polymer and consequently resulting in the formation of insoluble gels. Thus the chain extension reaction between isocyanate and hydroxyl group to give urethane bond has to compete with these side reactions to achieve high molecular weight poly (ester-urethane)s. These side reactions can be minimized by appropriate choice of the OH/NCO ratio so that a large excess of isocyanate groups is not present in the reaction medium. Shorter reaction times and lower temperatures ($\leq 150^0$C) also reduce the occurrence of such reactions. The structure of diisocyanate is also known to affect the chain extension reaction[41]. Thus proper choice of diisocyante, OH/NCO molar ratio, reaction temperature and time can result in effective chain extension with minimum side reactions. A 10-12 fold increase in molecular weight (M_n) with a distribution of 1.8-2.5 by chain extension with HMDI has been reported[42].

2,2'bis (2-oxepanone) propane, bis (4-nitrophenyl carbonate) and divinyl adipate have not been studied as chain extenders for polyester forming reactions.

4.4.1.1 Synthesis and characterization of hydroxy telechelic poly (butylene adipate)s

Poly (butylene adipate)s with two terminal hydroxyl end groups was synthesized by using a stoichiometric excess of 1,4-butanediol in the polycondensation reaction of DMA with BD followed by glycolysis of the polyester with 1,4 butanediol[43] as shown in the **Scheme 4.4**



Scheme 4.4: Synthesis of hydroxyl telechelic poly (butylene adipate)s (5)

The telechelic **(5)** was characterized by FTIR, ^{1}H and ^{13}C NMR. The concentration of the hydroxyl end groups was determined by ^{31}P NMR. The oligomer was also characterized by MALDI-ToF MS, DSC and TGA. The molecular weights were determined by VPO and GPC.

FTIR

The IR spectrum (**Figure 4.4**) exhibited characteristic absorption peaks of ester carbonyl at 1728 cm^{-1} and $-CH_2$ groups at 2950 cm^{-1}. A broad absorption peak at 3440-3520 cm^{-1} appeared due to the hydroxyl groups.

^{1}H and ^{13}C NMR

The NMR spectra are shown in **Figure 4.5**. ($CDCl_3$ at 7.25) δ: 4.06 (m, $-CH_2$-**a** attached to ester linkage in the repeat unit), 3.64 (m, $-CH_2$-**a**$'$ attached to hydroxyl end group), 2.30 (m, $-CH_2$-**b** attached to the carbonyl group in the repeat unit), 1.63-1.67 (m, CH_2-**c**,**d** attached to methylene groups in the repeat unit), 1.98 (s, OH). In the carbon spectrum ($CDCl_3$ at 77) ppm: 172.85 (s, C=O), 63.42 (s, $-CH_2$-**a** carbon attached to ester linkage in the repeat unit), 61.6 (s, $-CH_2$-**a**$'$ carbon attached to hydroxyl end group), 33.42 (s, $-CH_2$-**b** carbon attached to the carbonyl group in the repeat unit), 23.96, 24.91 (s, CH_2-**c**,**d**

carbon attached to methylene groups in the repeat unit), 28.70 (s, CH_2-**e** carbon attached to methylene groups of hydroxyl end group)

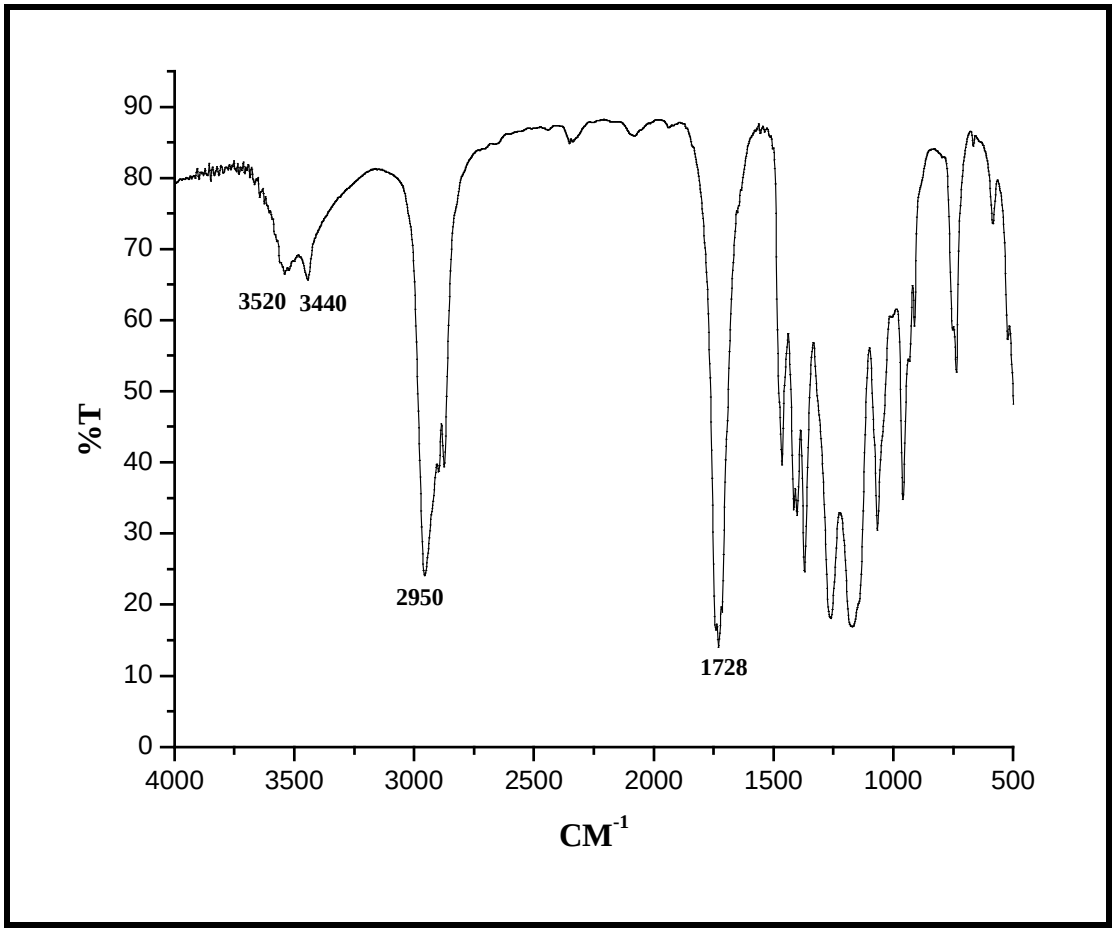


Figure 4.4 IR spectrum of hydroxyl telechelic poly (butylene adipate) (5)

^{31}P NMR

The ^{31}P NMR spectrum (**Figure 4.6**) shows peak due to internal standard at 131.7 ppm. The peak appearing at 127.2 was due to the derivatization of the hydroxyl end groups of the oligomer. The peak at 122.2 ppm was due to moisture present in the system derivatized by PPC. The peak at 129.56 ppm may be due to the carboxyl end groups generated as a result of THF formation during the reaction. The concentration of the hydroxyl groups in unit of meq/ kg was calculated by assigning a value of 10,000 to the peak due to TCP and then dividing the integration of the peak due to hydroxyl end group by the weight of the polymer (in mg) taken for analysis.

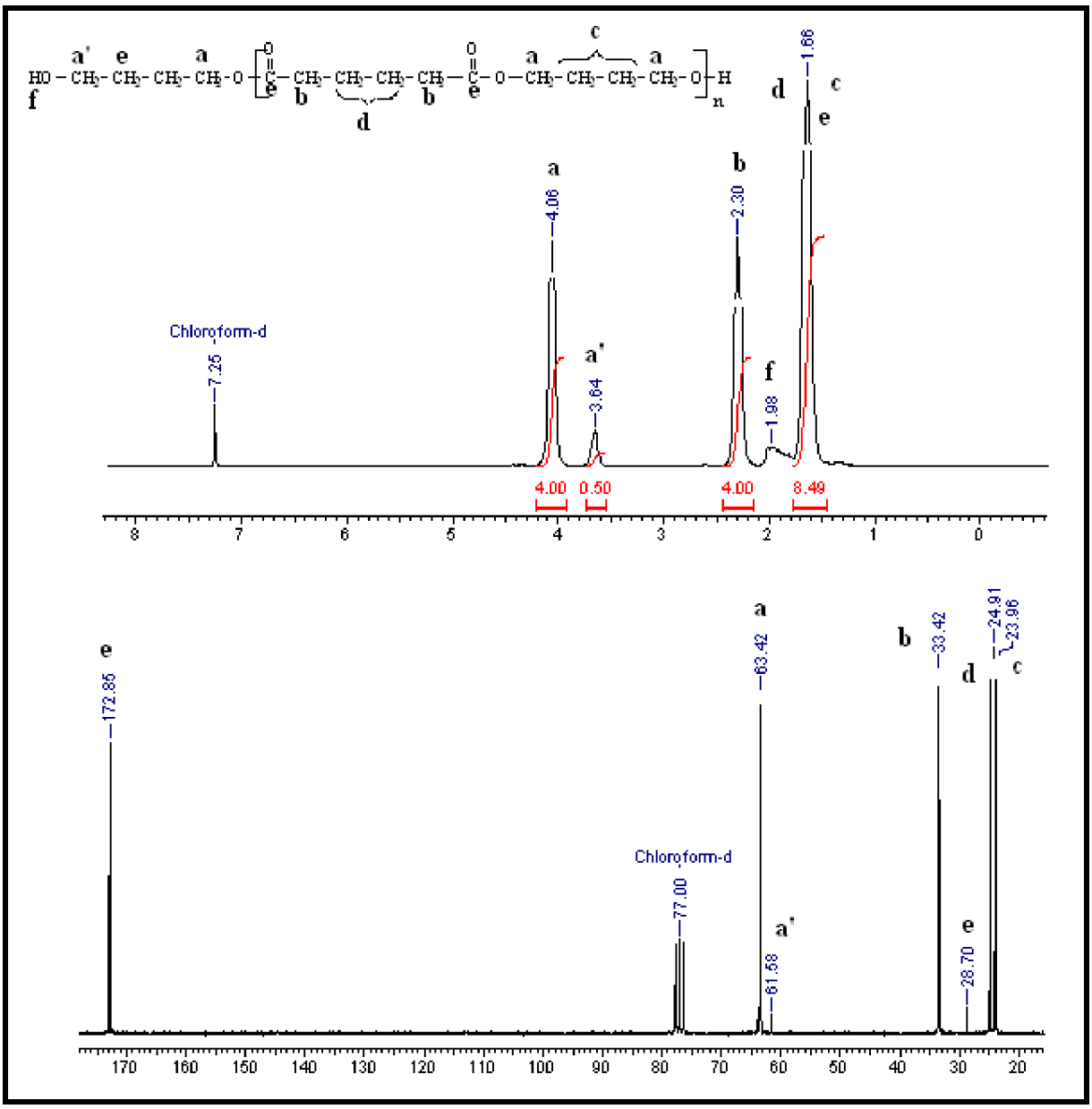


Figure 4.5 ^{1}H and ^{13}C NMR of hydroxyl telechelic poly (butylene adipate) (5)

The concentration of the hydroxyl groups was found to be 8.232×10^{-4} mol/g. The number average molecular weight calculated based on OH end group was calculated to be 2430 g/mol which agreed closely with the value determined by VPO to be 2700 g/mol as shown in **Table 4.3**. Thus the hydroxyl functionality of the telechelic is 0.9.

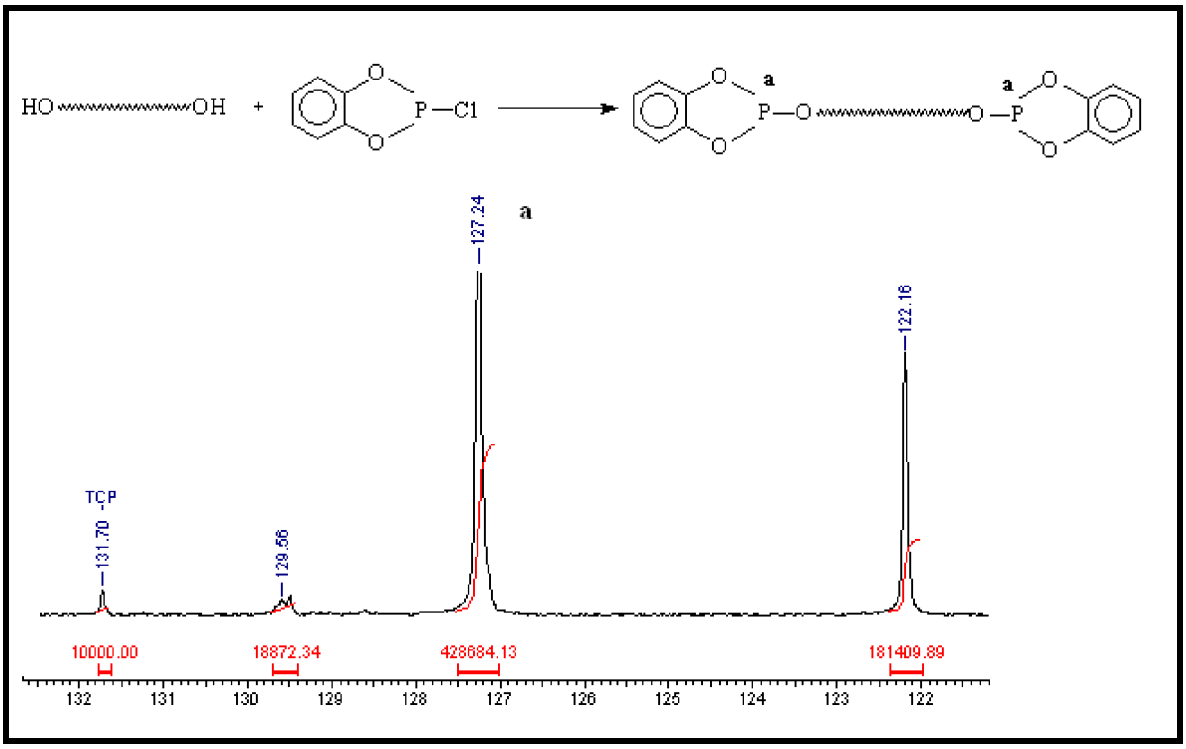


Figure 4.6 ^{31}P NMR spectrum of the hydroxyl telechelic poly (butylene adipate) (5)

MALDI-ToF MS

The MALDI- ToF mass spectrum of the oligomer was obtained using trans 3-indolacrylic acid as the matrix and is as shown in **Figure 4.7**. The sample was scanned in the mass range of 500 to 5000 Da, however for purpose of analysis the data in the mass range of 500-2500 Da was used. The structure of the end groups deduced from the spectrum are tabulated in **Table 4.2**

The spectrum shows a series of very high intensity peaks appearing at m/z values of 1114, 1314, 1513, 1714, 1912, 2114 and 2313 as sodium cationized oligomeric species of the type H-[-O-$(CH_2)_4$-O-CO-$(CH_2)_4$-CO-]$_n$-O-$(CH_2)_4$-OH-Na^+ mass = 200n+90+23, n being the DP of the oligomer and 23 mass number of sodium. Potassium cationized oligomers of the same species appeared as shoulder peaks at m/z values of 1130, 1329, 1530,1730, 1930, 2129 and 2328. A set of low intensity peaks appeared at m/z values of 1056, 1456, 1656, 1856, 2055 and 2255 as sodium adducts of oligomers of the type H-[-O-$(CH_2)_4$-O-CO-$(CH_2)_4$-CO-]$_n$$OCH_3$—$Na^+$ mass = 200n+32+23.

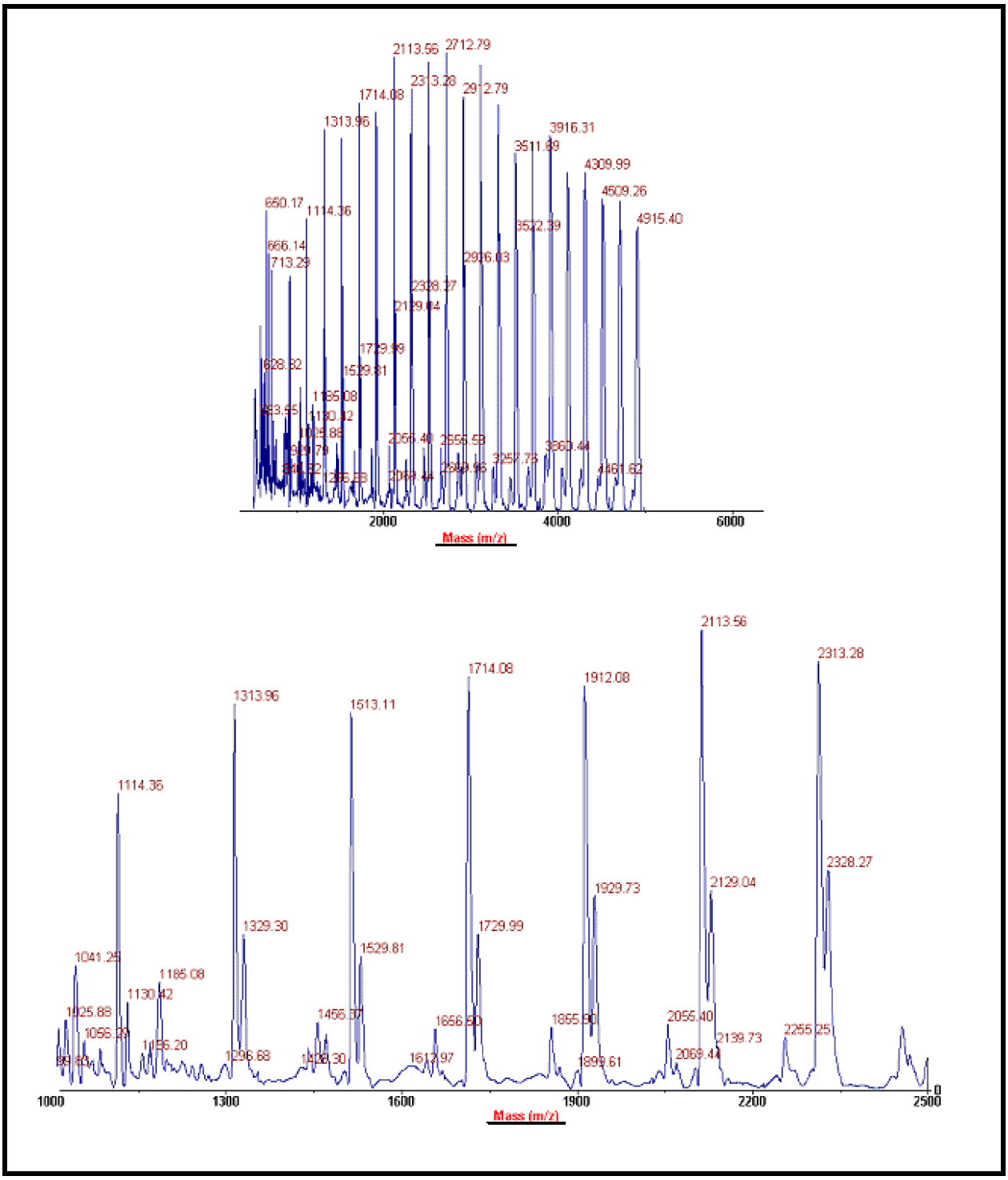
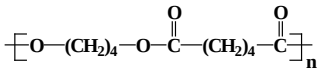
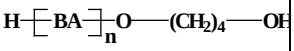
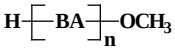


Figure 4.7 MALDI-ToF MS of hydroxyl telechelic poly (butylene adipate) oligomer (5)

An isolated peak appeared at m/z value of 1041 as sodium cationized species of the oligomer of the type H-[-O-$(CH_2)_4$-O-CO-$(CH_2)_4$-CO-]$_n$OH—Na^+. Thus, the analysis shows that the poly (butylene adipate) oligomer (**5**) contains mainly chains with hydroxyl

end groups along with small amounts hydroxy-ester end groups as seen from the relative intensities of the peaks.

Table 4.2 MALDI-ToF MS analysis of hydroxyl telechelic PBA oligomer

Repeat Unit Structure	Sum of end groups (observed)	Structure of end groups	Series
	89-91		1114,1314,1513,1714, 1912,……..Na^+ adduct
	89-91		1130, 1329, 1530,1730, 1930,……..K^+ adduct
	33-34		1056,1456,1656,1856, 2055,…….Na^+ adduct

Molecular weight determination

The molecular weight of the telechelic PBA oligomer was determined by VPO. M_n was found to be 2700 g/mol. GPC of the oligomer is shown in **Figure 4.8**. The salient results of characterization of telechelic PBA oligomer are summarized in **Table 4.3**

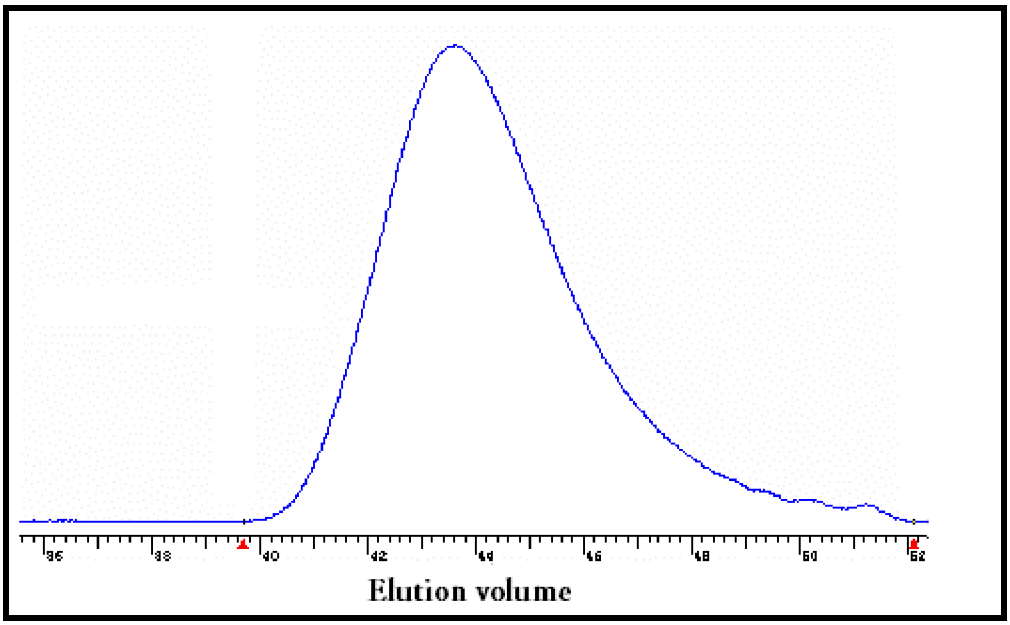


Figure 4.8 GPC of the hydroxyl telechelic poly (butylene adipate) oligomer (5)

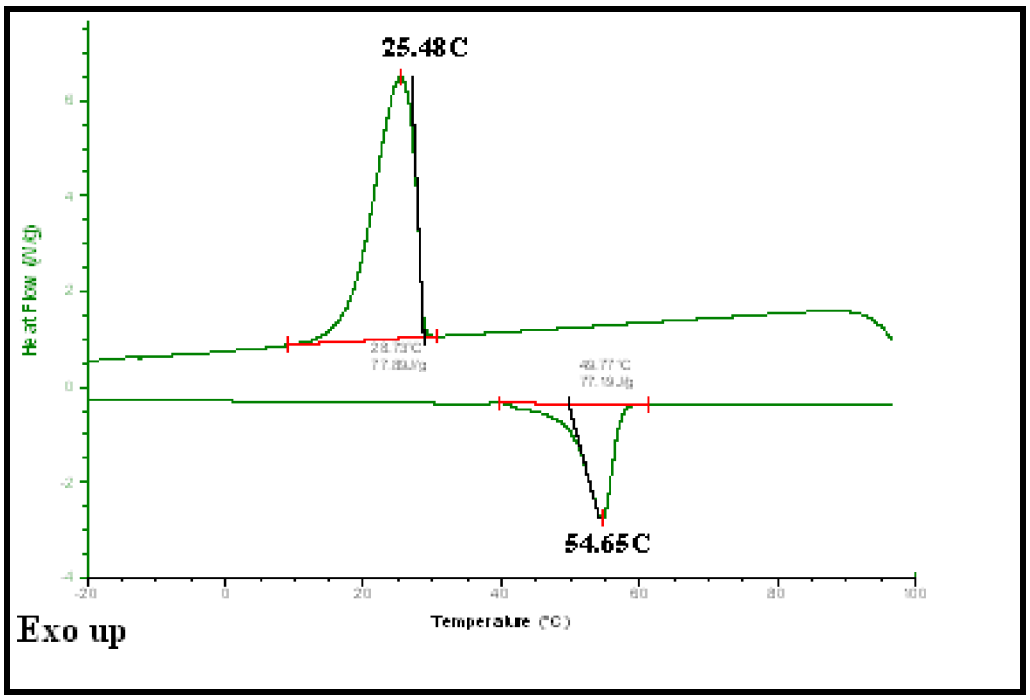


Figure 4.9 DSC curve of hydroxyl telechelic poly (butylene adipate) oligomer (5)

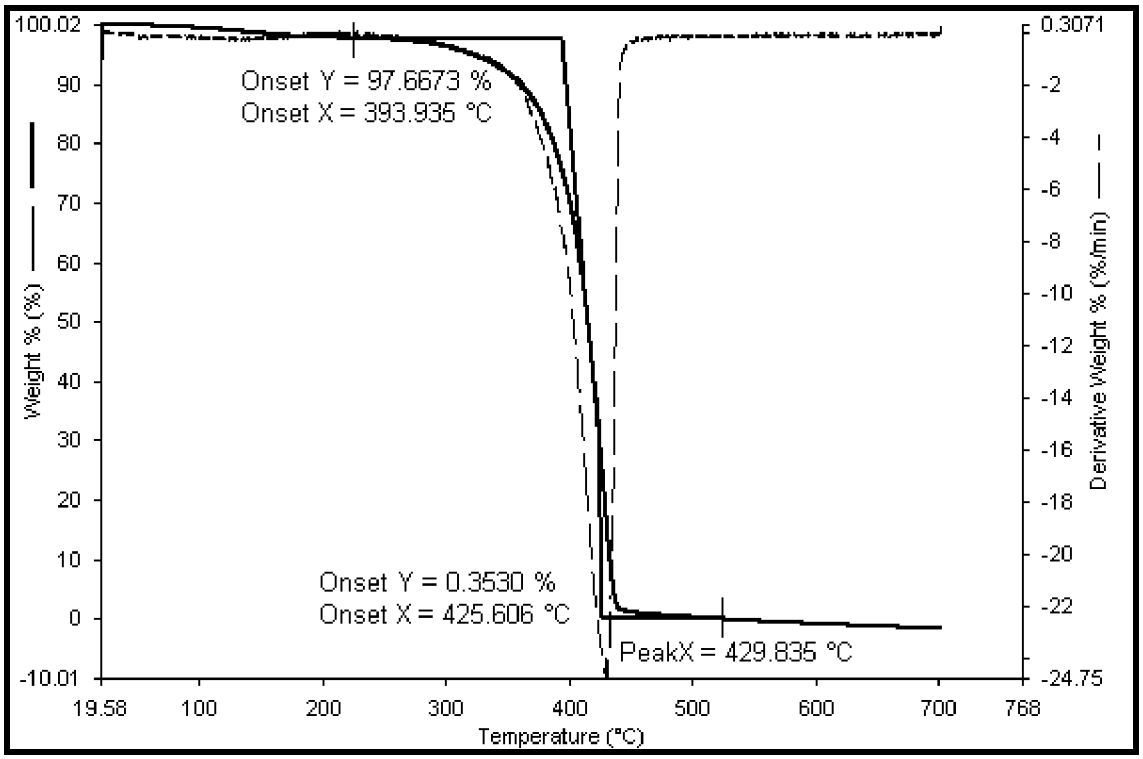


Figure 4.10 Thermogravimetric analysis of hydroxyl telechelic poly (butylene adipate) oligomer (5)

Table 4.3 Analysis of the hydroxyl telechelic (butylene adipate) oligomer (**5**)

η_{inh} in chloroform at 25^0C (dL/g)	M_n (VPO)	M_n (^{31}P NMR)	M_n (GPC)	M_w (GPC)	M_w/M_n	T_m (^{0}C)
0.211	2700	2430	7600	11,930	1.57	55

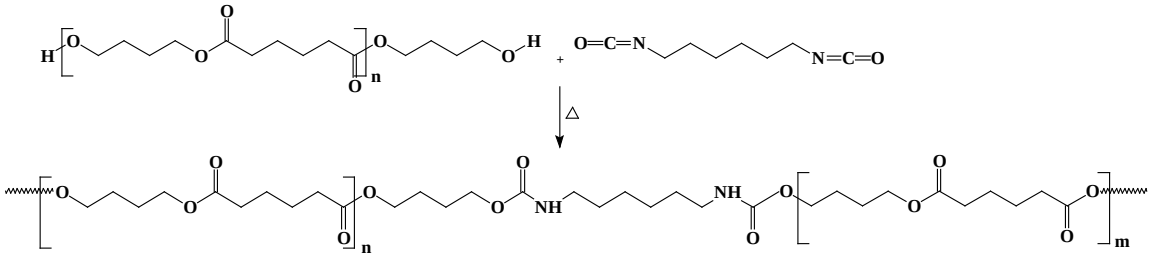
The oligomer shows a crystalline melting point (T_m) at 55^0C and a T_c at 25^0C (**Figure 4.9**). The thermal stability was determined by thermogravimetric analysis (**Figure 4.10**). The TGA curve shows that the polymer begins to degrade well above 200^0C[44]. This information was useful for deciding the range of reaction temperatures that can be used for chain extension reactions.

4.4.1.2 Use of hexamethylene diisocyanate as a chain extender

Polyurethanes are synthesized by the addition reaction of an alcohol with an isocyanate group and contain the urethane group as a characteristic structural element (R−NH−CO−O−R'). In the chain extension reaction using diisocyanate, the hydroxyl telechelic oligomer with low acid number and low water content reacts with a diisocyante. The structure of the diisocyanate, functionality of the prepolymer, nature of the hydroxyl groups, polymerization temperature and OH/NCO ratio influence this polyaddition reaction. The melting temperature depends on the molecular weight whereas the T_g depends on the structure of the diisocyanate and the urethane content in the poly (ester-urethane). Seppala and coworkers used 1,6-hexamethylene diisocyanate to increase the molecular weight of a hydroxyl functional PLA prepolymer from a M_n of 4500 g/mol to 32,000 g/mol. Such a polymer had mechanical properties comparable to high molecular weight PLA made by ring opening polymerization of lactide[45]. A substantial body of literature in the form of patents and publications on the use of diisocyanates as chain extenders is available (**Table 4.1**).

The results of the chain extension reaction (**Scheme 4.5**) of the hydroxyl telechelic poly (butylene adipate) oligomer with 1, 6-hexamethylene diisocyanate are shown in the **Table 4.4**. Reactions at two different temperatures 70^0C and 150^0C were carried out. The IR (**Figure 4.11**) and NMR (**Figure 4.12**) spectra prove that the

polyester has been chain extended with the diisocyanate resulting in a linear poly (ester-urethane). The urethane linkage is characterized by the NH absorption, which occurs at 3300 cm^{-1} and is attributed to hydrogen-bonded NH groups. The amide absorption, which is a characteristic of the urethane functionality, appears at 1530 cm^{-1}.



Scheme 4.5: Chain extension reaction of hydroxyl telechelic oligomer (5) with 1,6-hexamethylene diisocyanate

The ^{1}H NMR spectrum of the chain extended polyester (**Figure 4.12)** is similar to that of the telechelic **(5)**. Small peaks arising due to the hexamethylene moiety in the urethane functionality as a result of chain extension are seen at 3.1δ and 1.27δ.

Table 4.4 Chain extension of poly (butylene adipate) using HMDI[a]

No.	Reaction conditions	Yield[b] (%)	η_{inh}[c] (dL/g)	M^{c}_{n} (GPC)	M_w/M_n[c]	T^{c}_{m} (^{0}C)	T_c[c] (^{0}C)
1.	150^{0}C/3 h	48	0.62	23,510	2.3	55	18
2.	70^{0}C/3 h	60	0.30	11,840	1.7	54	25

a- molar ratio of OH/NCO = 1, b-based on weight of polymer obtained on precipitation from methanol, c- precipitated polymer

The chain extended polyester was characterized by GPC (**Figure 4.13**). The shift in the elution volume of the chain extended polyester towards a lower retention volume as compared to the telechelic demonstrates an increase in the molecular weight by chain extension reaction.

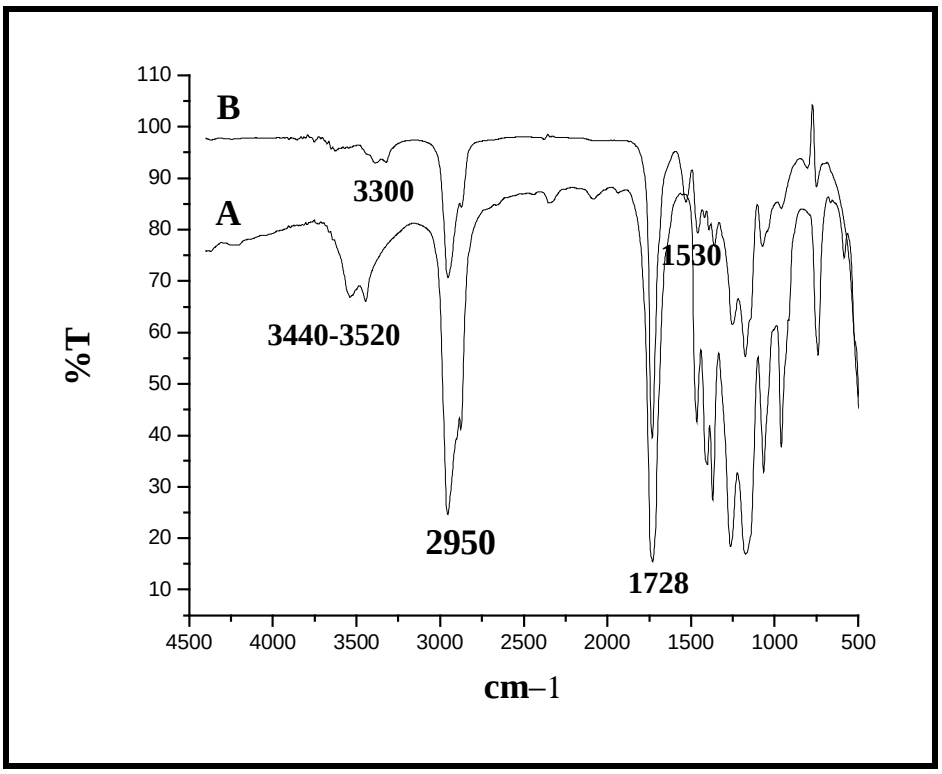


Fig 4.11 FTIR spectra of (A) telechelic oligomer (5) and the corresponding (B) chain extended poly (ester-urethane)

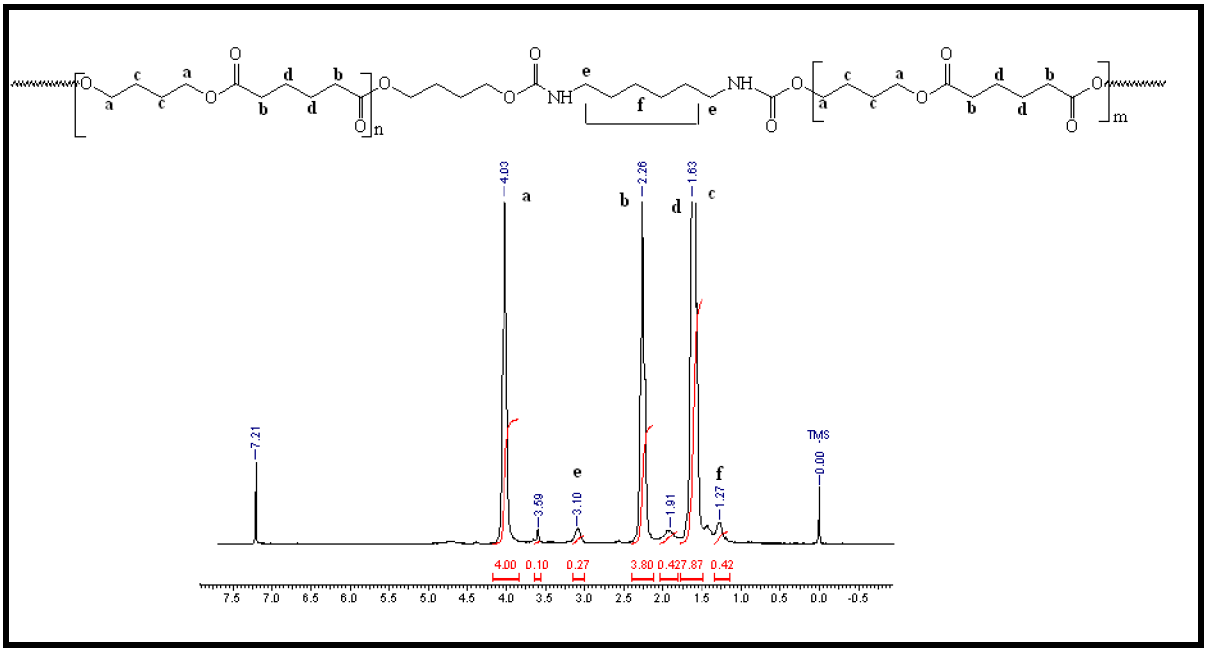


Figure 4.12 ^{1}HNMR spectrum of poly (butylene adipate) chain extended with HMDI

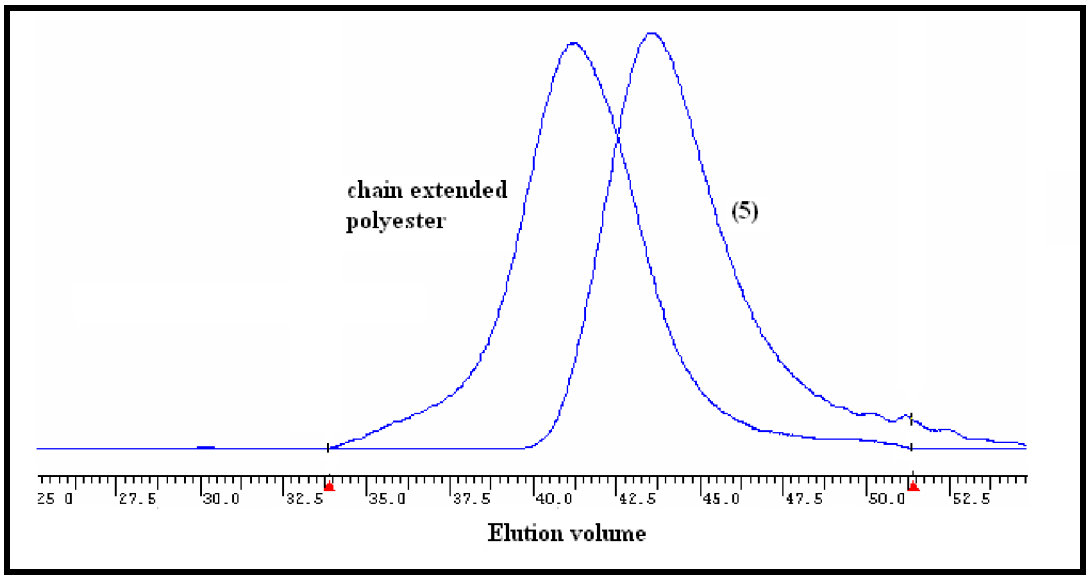
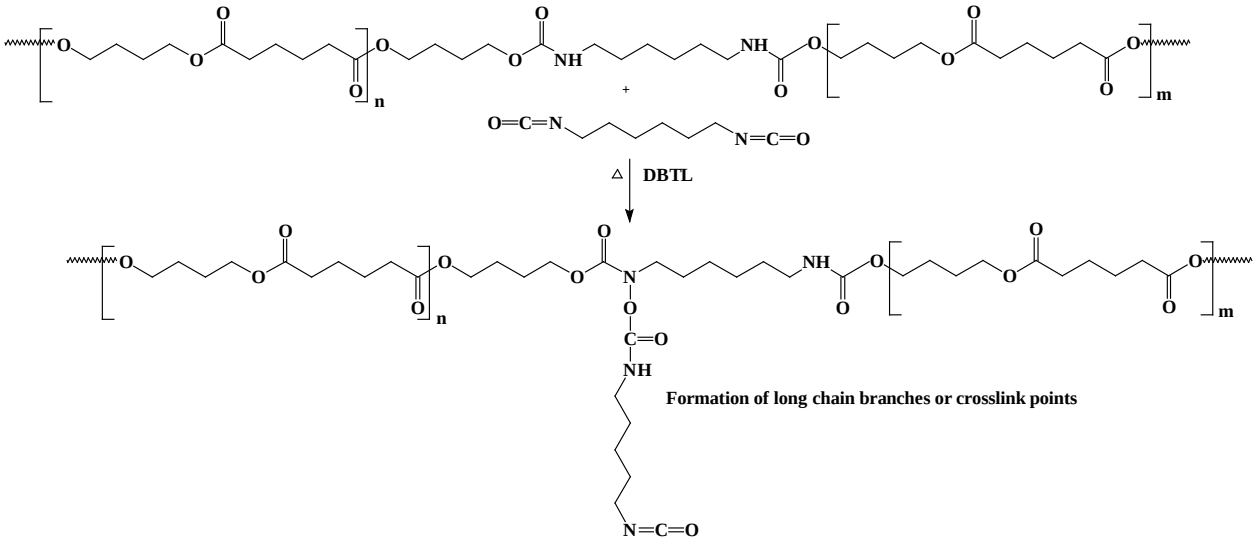


Figure 4.13 GPC of telechelic (5) and the polyester chain extended with HMDI (entry no. 1, Table 4.4)

The molecular weight distribution of the chain extended polyesters does not indicate any chain branching or other side reactions. However the overall yields are low and some portion of the polyester solubilizes in methanol although the hydroxyl telechelic PBA oligomer **(5)** is insoluble in methanol. This may be due to a number of ester exchange or transesterification reactions occurring, resulting in low molecular weight species, which are soluble in methanol. These reactions occur even at 70^0C. Transesterification reaction is favored over the chain extension reaction of the diisocyanate at 150^0C as evidenced by lower yield of chain extended polyester obtained at 150^0C as compared to that obtained at 70^0C. This shows that the ester interchange reactions compete with the chain extension reactions resulting in methanol soluble fraction and small amount of chain extended polyester.

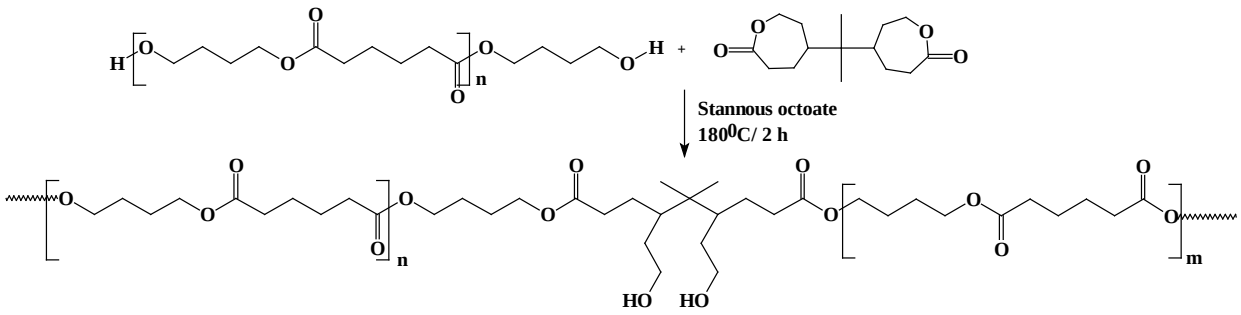
Reactions were also carried out using dibutyl tin dilaurate catalyst. However all these reactions gelled. When the reaction was catalyzed by dibutyl tin dilaurate, the reaction was very rapid and slight excess of the diisocyanate used for the reaction also reacted with the urethane groups (**Scheme 4.6**), resulting in branched polymer chains and ultimately crosslinking of the polymer resulting in a gel. The reactions catalyzed by DBTL gelled even at 70^0C and at a catalyst concentration of 0.02 wt%.



Scheme 4.6: Reaction of the poly (ester-urethane) with isocyanate groups to form branches and crosslink points

4.4.1.3 Use of 2,2' bis (2-oxepanone) propane as a chain extender

2,2' bis (2-oxepanone) is an interesting bis (lactone) which can undergo easy ring opening with hydroxyl end groups in polymer. Consequently, its use was explored as chain extender. Stannous octoate was used as catalyst (**Scheme 4.7**). The reaction was carried out at 180^0C for 2 h. Molar ratio of the lactone to stannous octoate was 500 and that of the hydroxyl groups to lactone was kept 1:1, to avoid any concomitant ROP of the bis (lactone).



Scheme 4.7: Chain extension reaction of hydroxyl telechelic oligomer (5) with 2,2' bis (2-oxepanone) propane

Results are shown in **Table 4.5**. A portion of the product was insoluble in chloroform and the fraction that dissolved in chloroform was precipitated from methanol. The yield was generally low. The pendant hydroxyl groups resulting from the ring opening can lead to branched and ultimately crosslinked structures which are insoluble in chloroform. This is an unavoidable reaction. The ^{1}H NMR (**Figure 4.14**) indicates that oligomer **(5)** was chain extended with 2,2' bis (2-oxepanone) propane. The presence of protons due to the ring opened caprolactone in the spectrum proves the attachment of the lactone to poly (butylene adipate) oligomer through chain extension. The methyl protons of 2,2' bis (2-oxepanone) propane moiety at 0.78 ppm are more prominent among the other protons of the lactone.

Chain extended polyester was characterized by GPC (**Figure 4.15**). A slight shift in the retention volume corresponding to a small increase in molecular weight can be seen. The distribution is very broad indicating some amount of chain branching caused by the reaction of pendant hydroxyl groups.

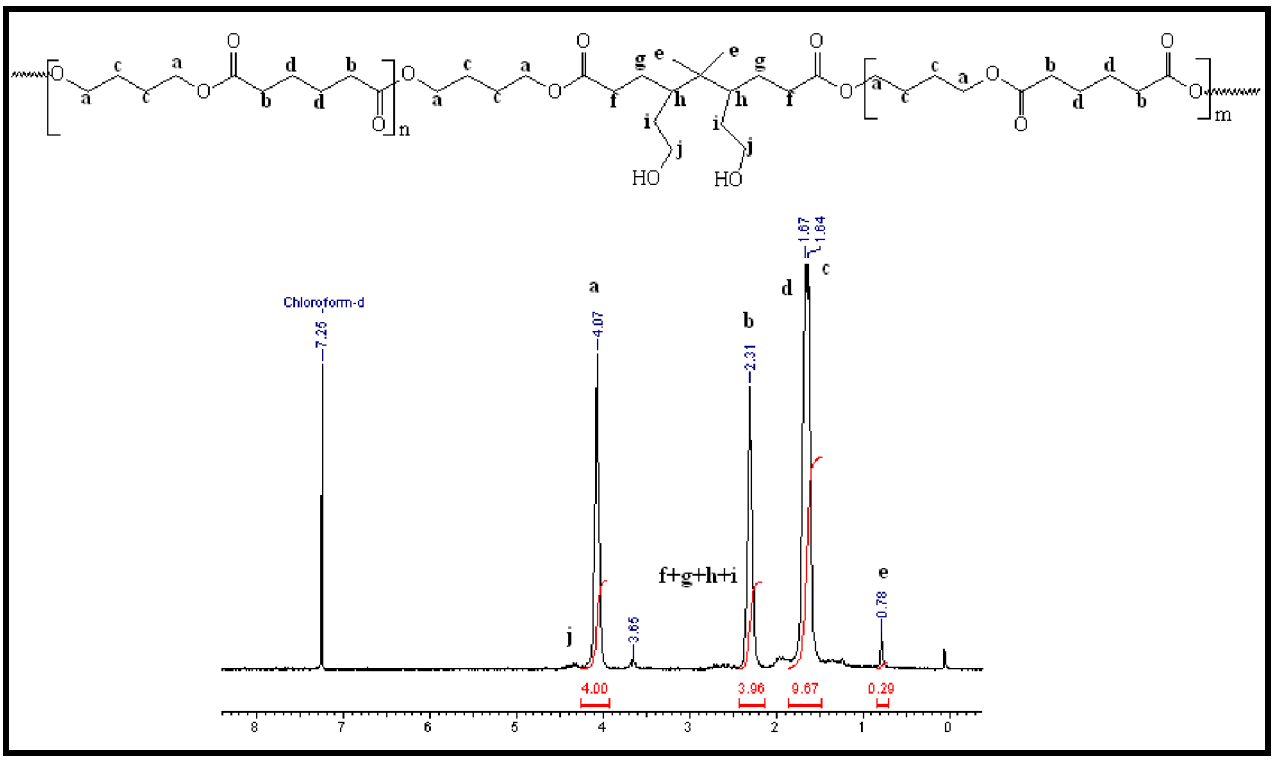


Figure 4.14 ^{1}HNMR spectrum of poly (butylene adipate) chain extended with 2,2' bis (2-oxepanone) propane

Table 4.5 Chain extension of poly (butylene adipate) using 2,2' bis (2-oxepanone) propane[a]

Reaction Conditions	Yield[b] (%)	η_{inh}[c] (dL/g)	M_n[c] (VPO)	M_n[c] (GPC)	M_w/M_n[c]	T^c_m (^{0}C)	T^c_c (^{0}C)
180^{0}C/2h, Stannous octoate	48	0.30	12,100	10,400	4.00	56	22

a- molar ratio of OH/chain extender =1 b- based on weight of polymer obtained on precipitation from methanol, c- precipitated polymer

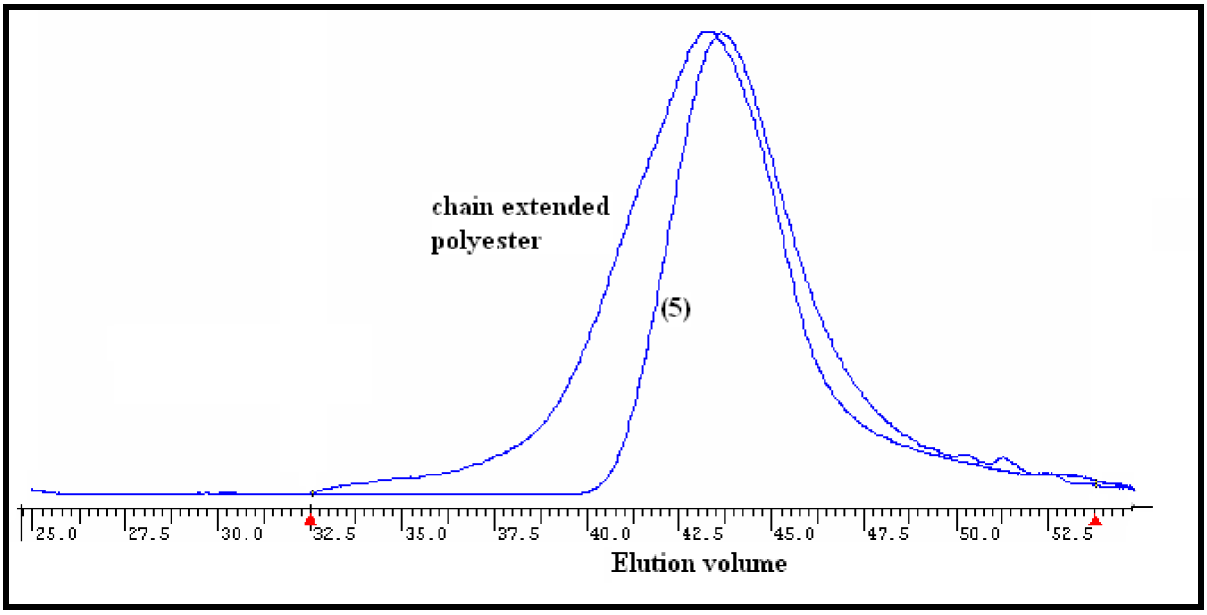
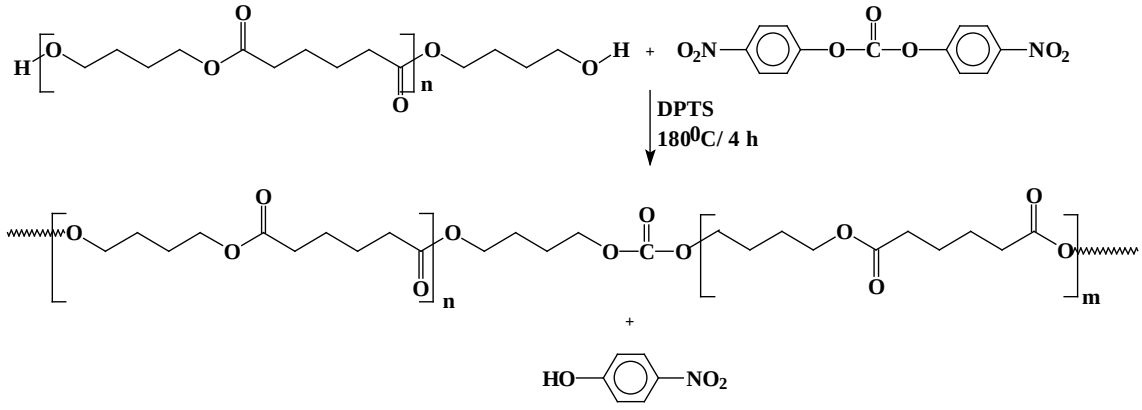


Figure 4.15 GPC of telechelic (5) and the polyester chain extended with 2,2' bis (2-oxepanone) propane (Table 4.5)

4.4.1.4 Use of bis (4-nitro phenyl) carbonate as a chain extender

Synthesis of bisphenol-A polycarbonates via a transesterification reaction of bisphenol-A with slight excess of diphenyl carbonate catalyzed by base is well known. Esters or carbonates of p-nitrophenol serve as activated transesterification agents, due to the fact that p-nitrophenol is a good leaving group and results in irreversible formation of a poor nucleophile, namely, p-nitrophenol[46]. Therefore, chain extension of telechelic poly (butylene adipate) oligomer was explored using bis (4-nitrophenyl carbonate) (**Scheme 4.8)**. The reaction was carried out for 4 h under nitrogen atmosphere at 180^{0}C. Molar

ratio of the hydroxyl groups to bis (4-nitrophenyl carbonate) was 1:1. An equimolar quantity of DPTS was added as catalyst for the reaction. The result of chain extension reaction is shown in **Table 4.6**.



Scheme 4.8: Chain extension reaction of hydroxyl telechelic (5) with bis (4-nitro phenyl) carbonate

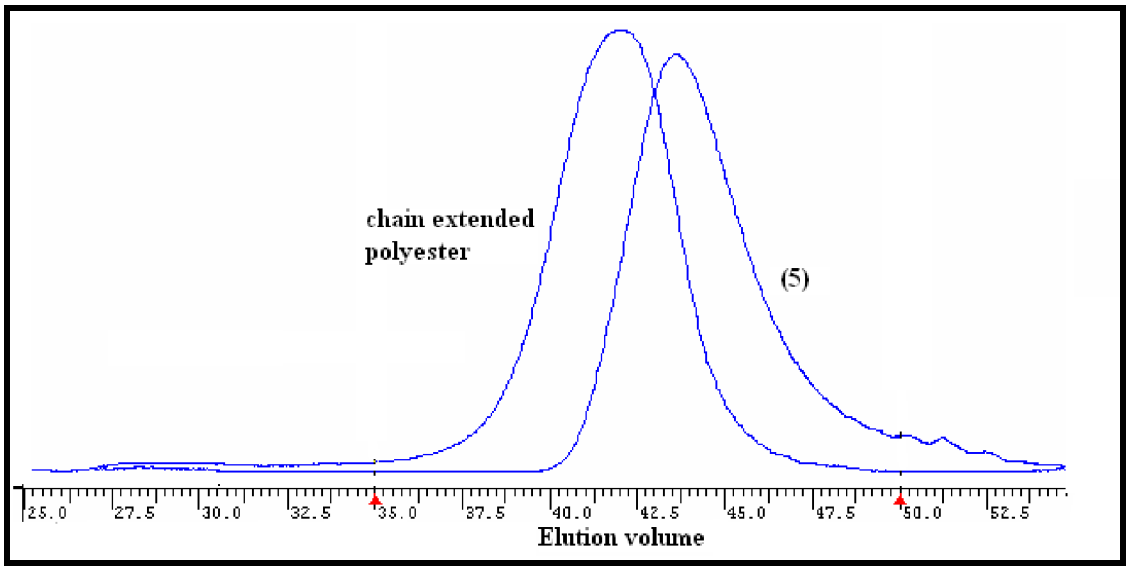


Figure 4.16 GPC of telechelic (5) and the polyester chain extended with bis (4-nitrophenyl) carbonate (Table 4.6)

Approximately 50% of the polymer formed by ester interchange reaction at 180^0C was soluble in methanol. The final polymer obtained was colored. M_n determined by VPO shows increase in molecular weight. A shift in the retention volume of the chain

extended polyester in GPC (**Figure 4.16**) confirms the occurrence of chain extension reaction.

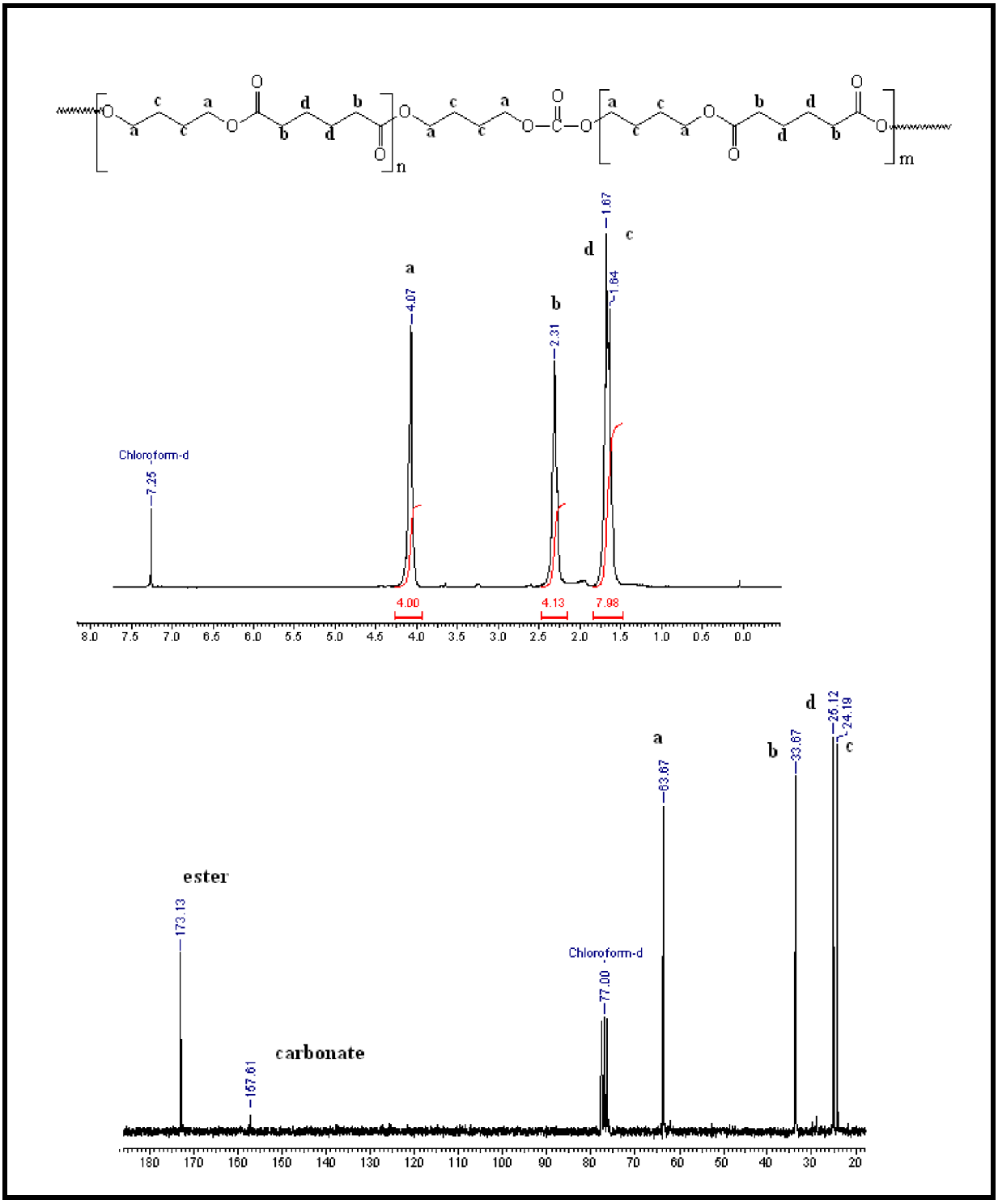


Figure 4.17 ^{1}H and ^{13}C spectra of poly (butylene adipate) chain extended with bis (4-nitrophenyl) carbonate

Table 4.6 Chain extension of poly (butylene adipate) using bis (4-nitro phenyl) carbonate[a]

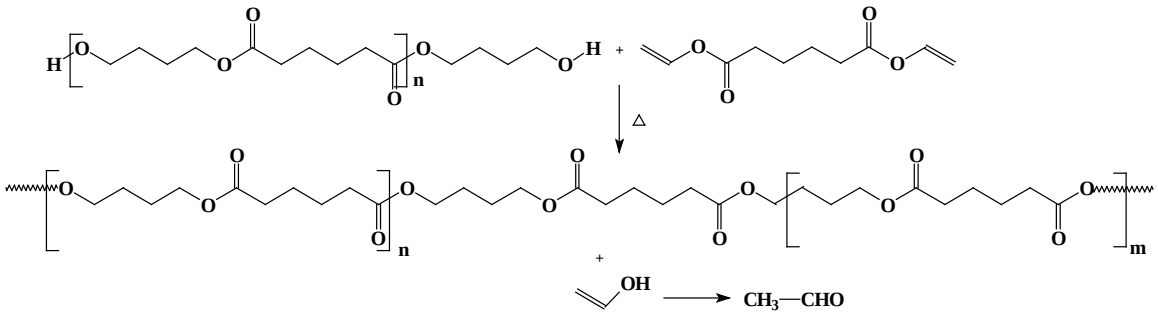
Reaction Conditions	Yield[b] (%)	η_{inh}[c] (dL/g)	M_n[c] (VPO)	M_n[c] (GPC)	M_w/M_n[c]	T^c_m (^{0}C)	T^c_c (^{0}C)
180^{0}C/4 h, DPTS	52	0.31	11,800	20,600	1.74	56	26

a- molar ratio of OH/chain extender =1, b- based on weight of polymer obtained on precipitation from methanol, c- precipitated polymer

^{1}H NMR of the chain extended polyester is shown in **Figure 4.17**. ^{13}C spectrum shows a small peak at 157.81 ppm due to the carbonyl carbon of the carbonate linkage formed as a result of chain extension reaction.

4.4.1.5 Use of divinyl adipate as a coupling agent

The use of divinyl esters as monomers in the enzyme catalyzed synthesis of aliphatic polyesters and as crosslinking agent has been reported[47]. However its use as a chain extender has not been explored. The vinyl functional group in the divinyl esters not only activates the ester end group for faster transesterification but also imparts inherent irreversibility to the process, because, the transesterification byproduct vinyl alcohol rapidly tautomerizes to acetaldehyde, resulting in the continuous shifting of the equilibrium in the forward direction.



Scheme 4.9: Chain extension reaction of hydroxyl telechelic oligomer (5) with DVA

Apart from the irreversibility of the transesterification reaction, it is worth noting that use of divinyl adipate for chain extension results in an ester linkage which is indistinguishable from that of the starting oligomer. Thus, synthesis of high molecular

weight fully aliphatic polyester in the true sense can be achieved. The chain extension using DVA is represented in **Scheme 4.9**. Chain extension reaction of hydroxyl telechelic poly (butylene adipate) oligomer with DVA was attempted in melt phase as well as in solution. The results of the chain extension carried out in refluxing chloroform for different lengths of time are shown in **Table 4.7**.

Table 4.7 Chain extension reaction[a] using DVA carried out at different reaction times

No.	Reaction Conditions	Yield[b] (%)	η_{inh}[c] (dL/g)	M^c_n (GPC)	M_w/M_n[c]	T^c_m (^{0}C)	T_c[c] (^{0}C)
1.	Reflux/2h.45 min	53	0.42	20,180	1.53	57	29
2.	Reflux/5h.30 min	84	0.80	36,570	2.50	59	26

a- molar ratio of OH/DVA =1, b- based on weight of polymer obtained on precipitation from methanol, c- precipitated polymer

An increase in molecular weight is observed as a consequence of chain extension. GPC confirms this observation (**Figure 4.18**). There is a shift in the retention volume of the higher molecular weight chain extended polyester compared to the telechelic **(5)**. The ^{1}H NMR of the chain extended polyester as shown in **Figure 4.19** was identical to that of the precursor telechelic **(5)**.

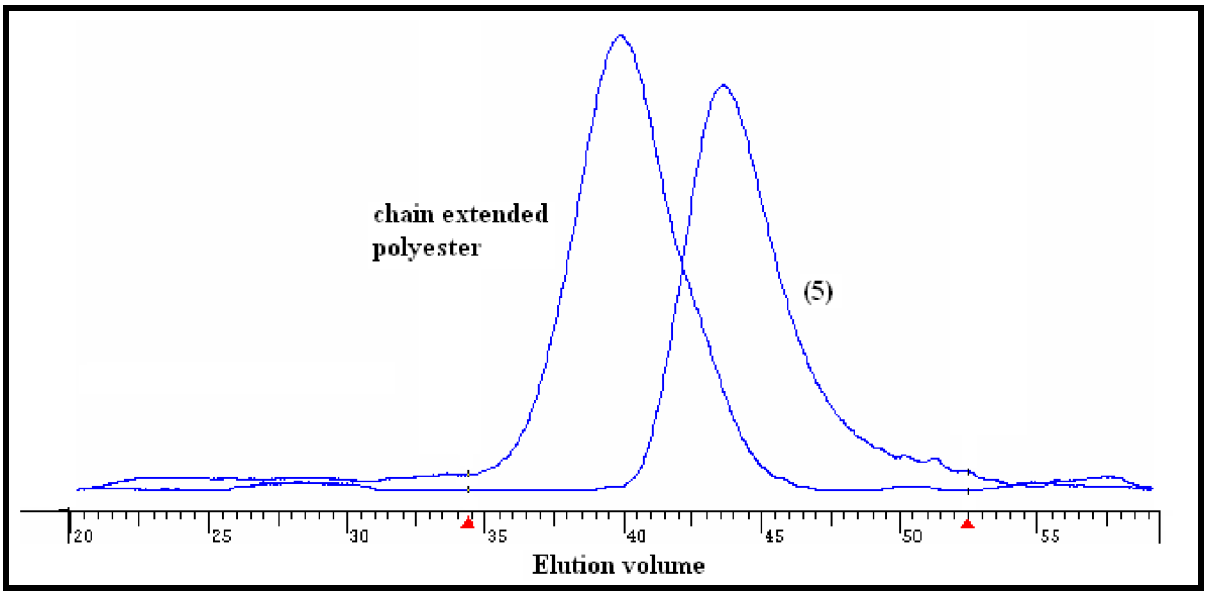


Figure 4.18 GPC of telechelic (5) and the polyester chain extended with DVA (entry no. 2, Table 4.7)

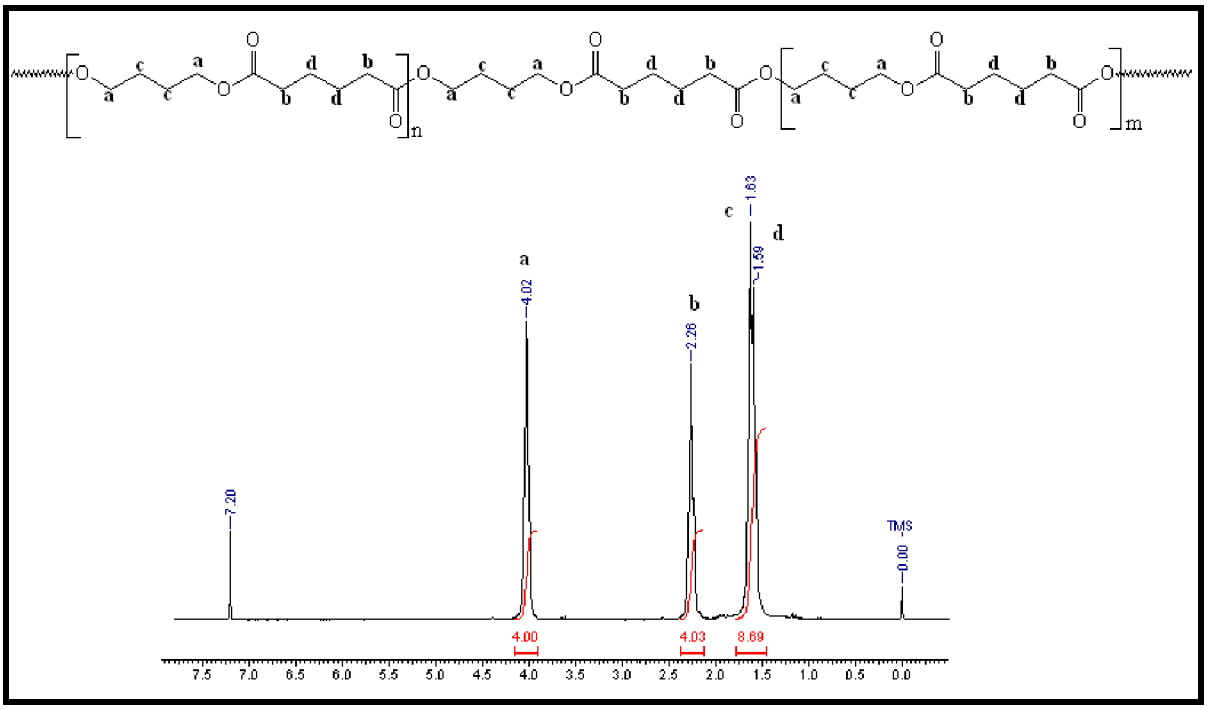


Fig 4.19 ^{1}HNMR spectrum of poly (butylene adipate) chain extended with DVA

An experiment was carried out in a higher boiling solvent, namely, chlorobenzene (130-132^{0}C) to examine the effect of higher temperature. The telechelic oligomer took some time to solubilize in chlorobenzene. The results of the reaction are given in **Table 4.8**. Higher reaction temperature leads to increase in molecular weight as a result of chain extension. GPC (**Figure 4.20**) showed a shift in the retention volume of the product. However, the results obtained at higher temperatures were inferior to those obtained at lower temperature.

Table 4.8 Chain extension reaction[a] with DVA in chlorobenzene as solvent

Reaction Conditions	Yield[b] (%)	η_{inh}[c] (dL/g)	M^{c}_{n} (GPC)	M_w/M_n[c]	T^{c}_{m} (^{0}C)	T^{c}_{c} (^{0}C)
Reflux in chlorobenzene/ 5h	84	0.52	23,470	2.08	60	31

a- molar ratio of OH/DVA =1, b- based on weight of polymer obtained on precipitation from methanol, c- precipitated polymer

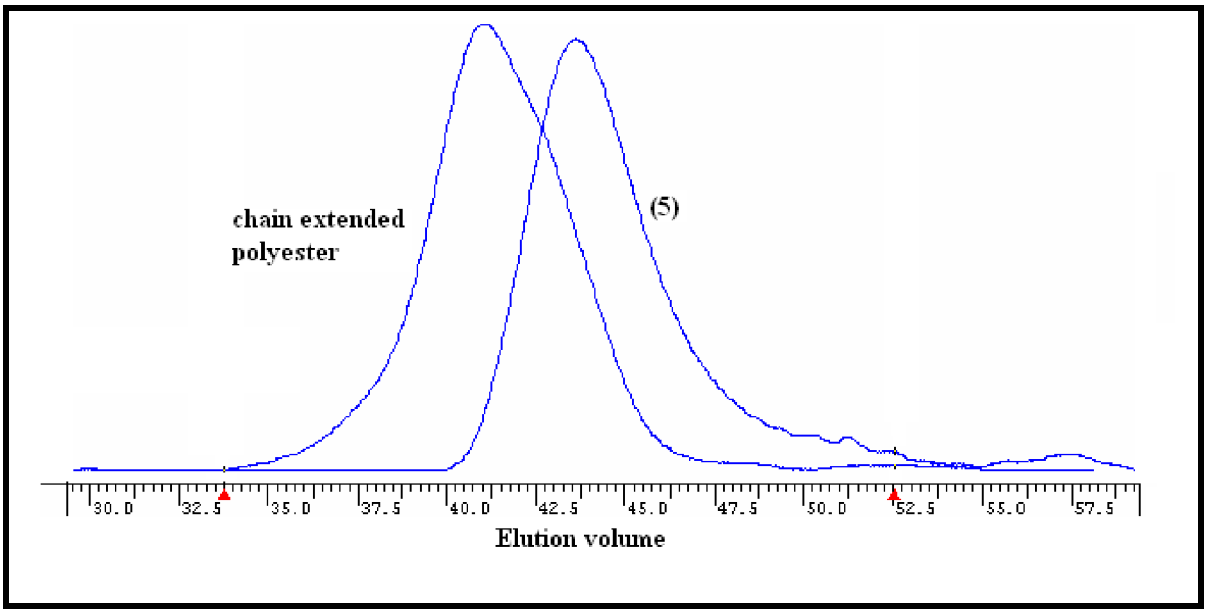


Figure 4.20 GPC of telechelic (5) and the polyester chain extended with DVA (Table 4.8)

Molecular weight distribution of the chain extended polyesters (**Table 4.7** and **4.8**) indicate increase in molecular weight without any significant chain branching or crosslinking.

The effect of OH to DVA molar ratio on the chain extension reaction was studied (**Table 4.9**). Best results were obtained at a molar ratio of 1:0.9.

Table 4.9 Effect of OH to DVA molar ratio on chain extension

No.	Molar ratio of OH to DVA	Reaction Conditions	Yield[a] (%)	η_{inh}[b] (dL/g)	M_n[b] (GPC)	M_w/M_n[b]	T^b_m (^{0}C)	T^b_c (^{0}C)
1.	1:0.9	Reflux/5 h	93	0.87	36,770	2.53	63	25
2.	1:1.1	Reflux/5 h	92	0.76	31,300	2.22	61	26
3.	1:1	Reflux/5 h	84	0.79	35,580	2.50	59	25

a- based on weight of polymer obtained on precipitation from methanol, b- precipitated polymer

The decrease in the retention volume of the chain extended polyester as compared to the telechelic confirms the increase in molecular weight (**Figure 4.21**). No significant chain branching is discernible since the molecular weight distribution is close to 2.0

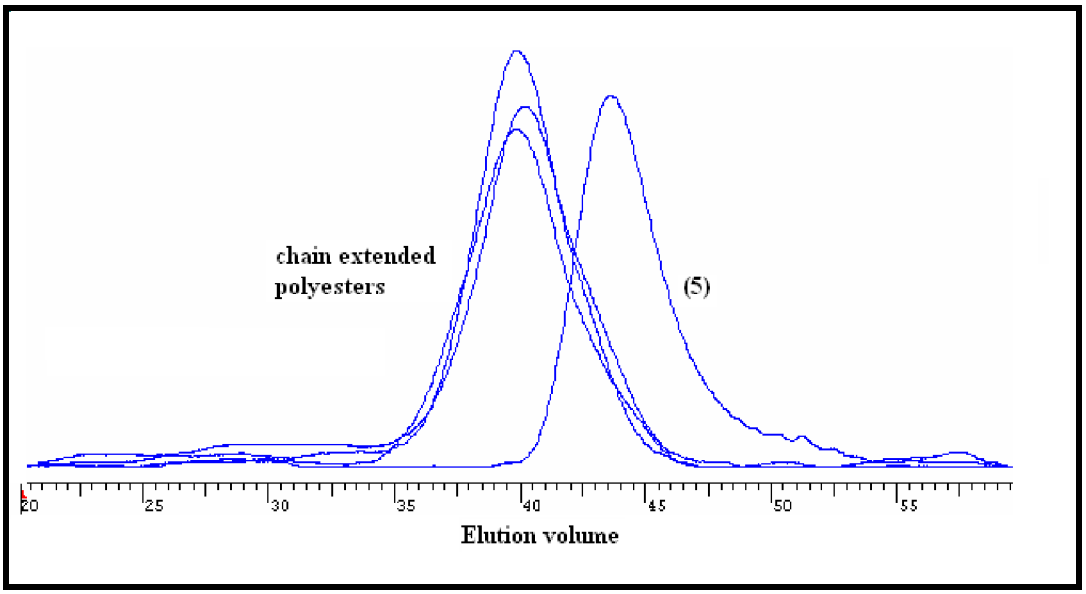


Figure 4.21 GPC of telechelic (5) and the polyesters chain extended with DVA (entries 1, 2, 3 Table 4.9)

The chain extension reactions using DVA were also carried out in melt phase. Reactions were carried out at 150^0C and 70^0C for 5 h. A reaction was also carried out for 3 h to study the effect of reaction time. The results are shown in **Table 4.10**.

Table 4.10 Chain extension reaction[a] using DVA in melt

No.	Reaction Conditions	Yield[b] (%)	η_{inh}[c] (dL/g)	M^c_n (GPC)	M_w/M_n[c]	T^c_m (^{0}C)	T_c[c] (^{0}C)
1.	150^0C/ 3 h	69	0.25	10,960	1.33	59	28
2.	150^0C/ 5 h	57	0.25	12,850	1.36	59	28
3.	70^0C/ 5 h	51	0.24	12,320	1.22	58	30

a- molar ratio of OH/DVA =1, b- based on weight of polymer obtained on precipitation from methanol, c- precipitated polymer

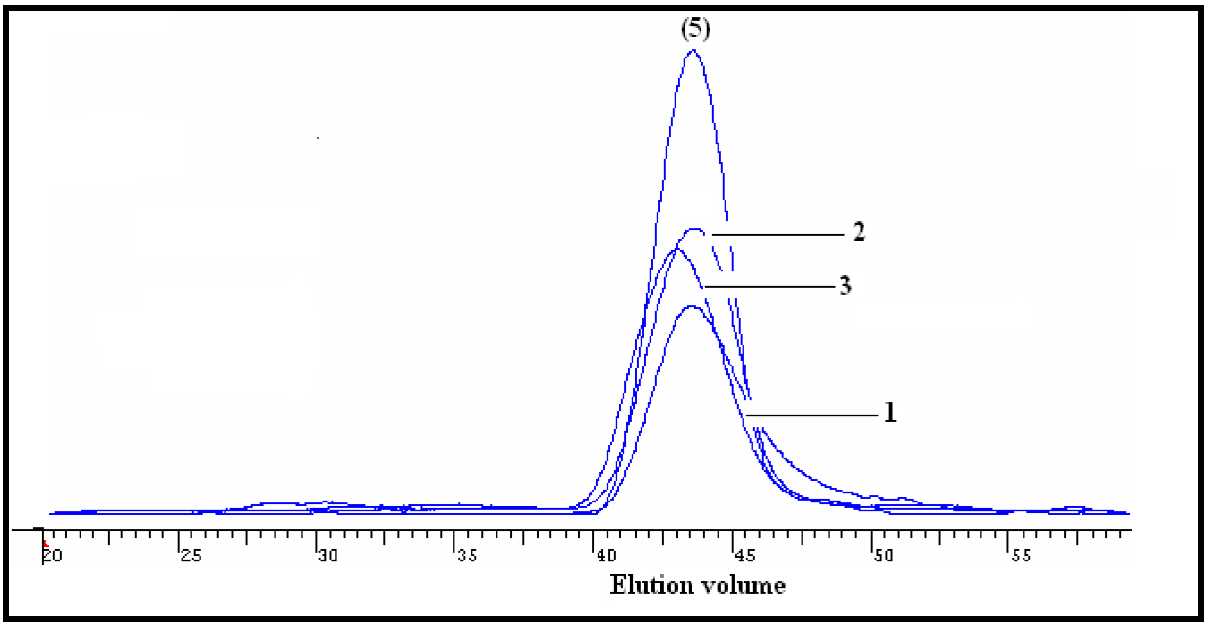


Figure 4.22 GPC of telechelic (5) and the polyesters chain extended with DVA in melt (entries 1, 2, 3 Table 4.10)

The reactions carried out in melt resulted in both lower yields and molecular weights (**Table 4.10**). GPC (**Figure 4.22**) also substantiate this observation. The low polydispersity values can be ascribed to fractionation of the product when precipitated from methanol. The starting telechelic **(5)** is insoluble in methanol but a part of the product obtained after chain extension reaction in melt is soluble in methanol indicating that low molecular weight species are formed during the reaction.

Thermogravimetric curve of DVA is shown in **Figure 4.23**. DVA begins to degrade around 100^0C with complete degradation at 200^0C. Consequently temperatures > 100^0C may not be appropriate for chain extension reaction with DVA. Even at 70^0C the reaction was inefficient with approximately 50% of the product soluble in methanol. Polymers obtained from the melt reactions were also colored. Poor thermal stability of DVA together with the accompanying chain scission reactions could be the cause for poor chain extension in melt.

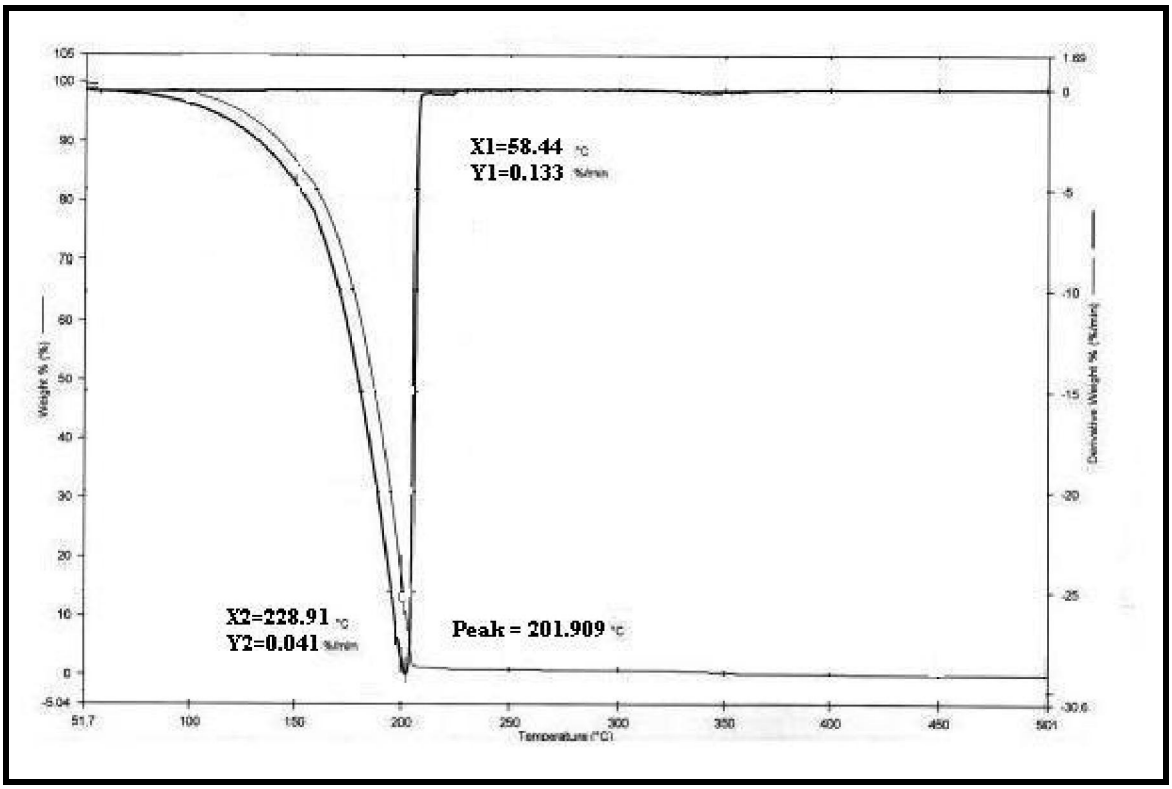


Figure 4.23 Thermogravimetric analysis of DVA

The chain extension reactions using DVA were also carried out in the absence of catalyst, both in melt as well as in solution (**Table 4.11**). The molecular weights and viscosity values indicate very low extent of chain extension in both the cases. The low polydispersity values indicate fractionation of the product upon precipitation from methanol.

Table 4.11 Chain extension reaction[a] using DVA in absence of catalyst

No.	Reaction Conditions	Yield[b] (%)	$\eta_{inh}{}^{c}$ (dL/g)	M^{c}_{n} (GPC)	$M_w/M_n{}^{c}$	T^{c}_{m} (^{0}C)	$T_c{}^{c}$ (^{0}C)
1.	Reflux in chloroform/ 5 h	51	0.26	14,530	1.17	59	29
2.	In melt 70^{0}C/ 5 h	57	0.25	12,360	1.23	58	28

a- molar ratio of OH/DVA =1,b- based on weight of polymer obtained on precipitation from methanol, c- precipitated polymer

The low molecular weight species that are soluble in methanol result from the chain scission reactions which occur both in melt as well as in solution. The GPC curves in **Figure 4.24** show practically no change in retention volumes of the telechelic oligomer **(5)** and the polyesters obtained as a result of reaction with DVA carried out in absence of catalyst, thereby indicating no chain extension in absence of catalyst.

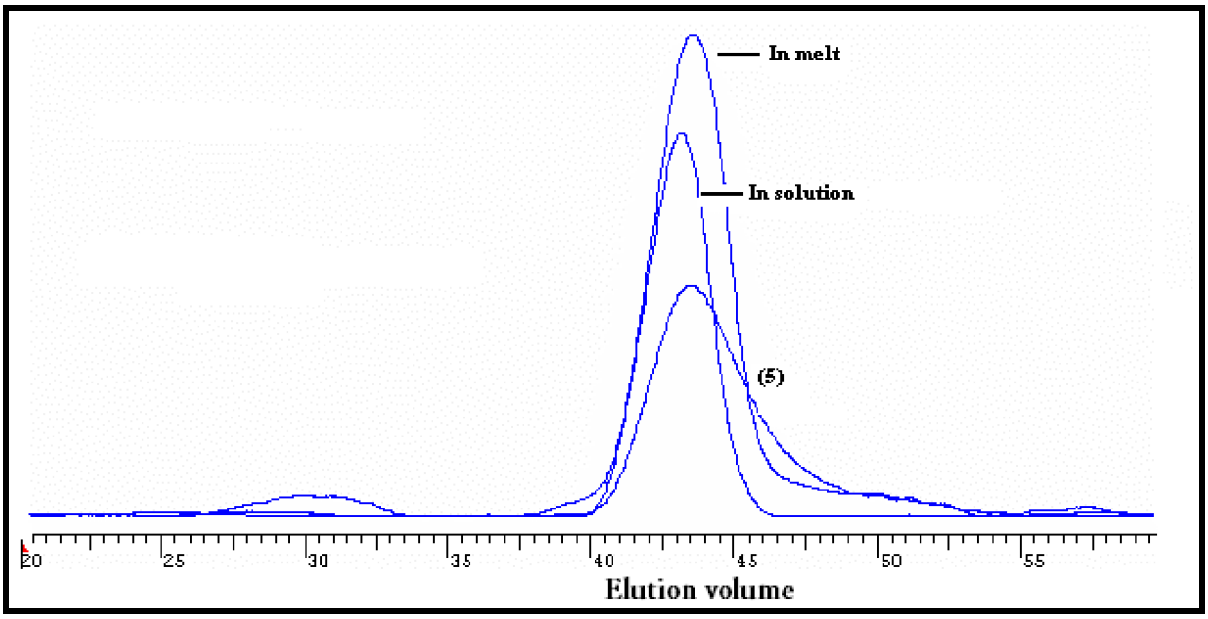


Figure 4.24 GPC of telechelic (5) and the polyesters chain extended with DVA in absence of catalyst (entries 1,2 Table 4.11)

The hydroxyl telechelic oligomer **(5)** has oligomers with hydroxyl-ester end groups along with oligomers having hydroxyl-hydroxyl end groups. Reactions between the hydroxyl end groups of one chain with ester end group of the other, could in principle also lead to chain extension.

To understand the importance of this reaction experiments were carried out in melt and in solution in absence of chain extender. The results are tabulated in **Table 4.12**. Under these conditions only small extent of chain extension is observed. GPC shows practically no shift in the retention volumes (**Figure 4.25**). The low polydispersity values are due to fractionation of product during precipitation from methanol. These observations suggest that chain extenders have a definitive role in causing the chains to grow through a process of chemical reaction with end groups. The extent of chain

extension and consequent increase in molecular weight depend on the efficiency of the chain extender and appropriate reaction conditions.

Table 4.12 Effect of absence of chain extender on molecular weight build up

No.	Reaction Conditions	Yield[a] (%)	η_{inh}[b] (dL/g)	M^b_n (GPC)	M_w/M_n[b]	T^b_m (^{0}C)	T_c[b] (^{0}C)
1.	Reflux in chloroform/ 5 h	41	0.26	14,640	1.41	59	29
2.	In melt 70^{0}C/ 5 h	29	0.25	13,760	1.18	58	30

a- based on weight of polymer obtained on precipitation from methanol, b- precipitated polymer

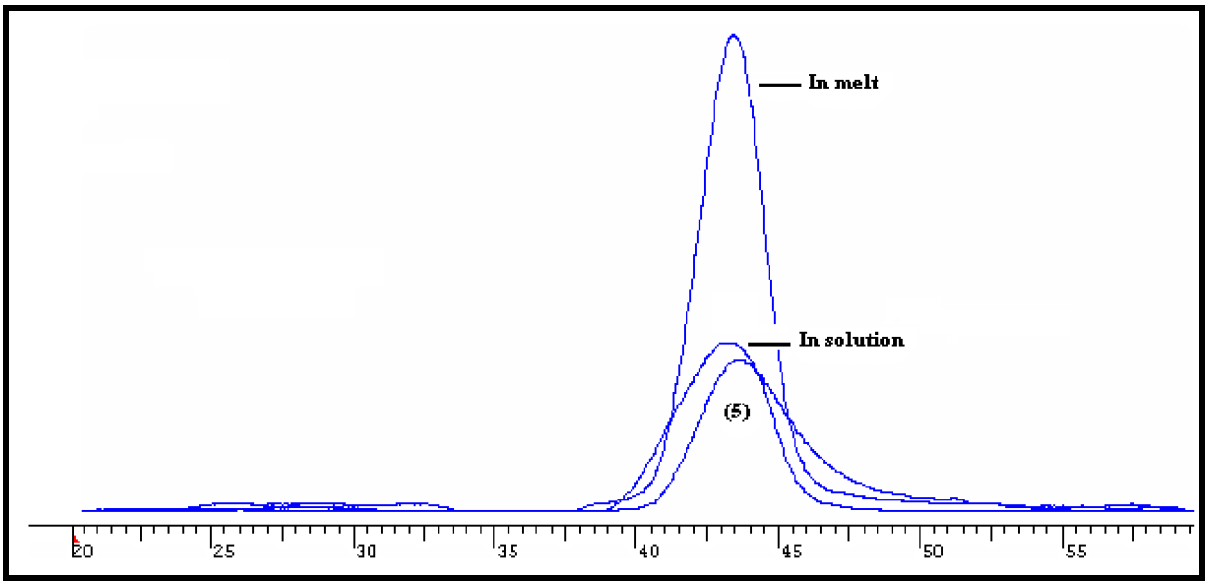


Figure 4.25 GPC of telechelic (5) and the polyesters obtained as a result of reaction in absence of chain extender (entries 1, 2 Table 4.12)

4.5 Conclusions

Chain extension of hydroxyl telechelic poly (butylene adipate) **(5)** can be accomplished using chain extenders like HMDI, 2,2' bis (2-oxepanone) propane, bis (4-nitro phenyl) carbonate and DVA with varying degrees of efficiency. In the absence of chain extenders little or no chain extension occurs. Additionally chain extension is accompanied with transesterification reactions leading to low molecular weight oligomers.

Divinyl adipate was found to be an efficient chain extender for hydroxy telechelic poly (butylene adipate). The reaction was particularly effective in solution and in presence of a catalyst at low temperatures. At higher temperatures several side reactions are apparent which result in the formation of methanol soluble oligomers.

Moderate chain extension was achieved using 1,6-hexamethylene diisocyanate as a chain extender in melt at 150^0C resulting in poly (ester-urethane)s. Yields were low due to formation of low molecular weight oligomers soluble in methanol. The chain extension reactions could be catalyzed by dibutyl tin dilaurate. However, the reaction was very fast and uncontrollable and resulted in the formation of gel.

Chain extension reactions using 2,2' bis (2-oxepanone) propane was not very effective. In case of bis (4-nitrophenyl) carbonate, moderate chain extension was achieved. The polyester obtained as a result of chain extension was colored.

In all the reactions, whether in melt or in solution, a methanol soluble fraction was persistently obtained. This implies competing transesterification reactions leading to lower molecular weight linear or cyclic oligomers.

4.6 References

1. (a) Y.Tokiwa, Sen-i. Gakkaishi, Jpn. **47**, 522 (1991) (b) R.W. Lenz, Adv. Polym.Sci. **107**, 22 (1993) (c) M. Mochizuki, Sen-i. Gakkaishi, Jpn. **52**, 200 (1996)
2. Y.Tokiwa, T.Suzuki, *J.Appl.Polym.Sci*. **26**, 441 (1981)
3. B.Buchholz, *US Patent 5302694* (1994) to Boehringer Ingelheim GmbH
4. M.Nagata, Y. Sato, *Polymer* **45**, 87 (2004)
5. M.K. Akkapeddi, J. Gervasi, *Polym.Prep. Am.Chem.Soc., Div.Polym.Chem*. **29**, 567 (1988)
6. D.Bikiaris, G. Karayannidis, *J.Polym.Sci. Polym.Chem.Ed*. **34**, 1337 (1996)
7. T.Loontjens, K. Pauwels, F.Derks, M.Neilen, C.K.Sham, M. Serne, *J.Appl.Polym.Sci* **65**, 1813 (1997)
8. M.H.Hartmann, *Biopolymers from renewable resources*, Chapter 15, 367, edited

by D.L. Kaplan, Springer, New York (1998)

9. M.Harkonen, K.Hiltunen, M.Malin, J.V.Seppala., *J.Macromol.Sci.-Pure Appl. Chem*. **A (32)4**, 857 (1995)
10. T.Fujimaki, *Polymer Degradation and Stability* **59**, 209 (1998)
11. D.Bikiaris, G. Karayannidis, *Polym.Degrad.Stab*. **63**, 213 (1999)
12. A.C. Albertsson, O. Ljungquist, *J.Macromol.Sci.Chem*. **25**, 467 (1988)
13. H.J. Kang, S.S. Park, *Polymer (Korea)* **20**, 682 (1996)
14. M. Penco, E. Ranucci, P. Ferruti, *Polym.Int*. **46**, 203 (1998)
15. B.Bogdanov, V.Toncheva, E. Schacht, L.Finelli, B. Sarti, M. Scandola, *Polymer* **40**, 3171 (1999)
16. a) S. I. Woo, B. O. Kim, H. S. Jun, H. N. Chang, *Polym. Bull.* **35**, 415 (1995) (b) K. Hiltunen,. *Acta Polytech. Scand. Chem. Technol. Ser.* **251**, 5 (1997)
17. M. Penco, E. .Ranucci, P. Ferruti, *Polym. Int.* **46**, 203 (1998)
18. S.M. Aharoni, C.E. Forbes, W.B. Hammond, D.M. Hindenlang, F. Mares, K. O'Brien, R.O. Sedgwick, *J.Polym. Sci*. **24**, 1281 (1986)
19. N.Cardi, R.Po, G. Giannotta, E. Occhiello, F. Garbassi, G. Messina, *J.Appl. Polym.Sci*. **50**, 1501 (1993)
20. H.Inata, S.Matsumura, *J.Appl.Polym.Sci*. **34**, 2769 (1987)
21. M.K.Akkapeddi, J.Gervasi, *US Patent 4857603* (1989) to Allied-Signal Inc.
22. R.Palmgren, S. Karlsson, A.C. Albertsson, *J. Polym. Sci., Polym. Chem.* **35**, 1635 (1997)
23. S.Shyamroy, *"Synthesis of Biodegradable Poly(Lactic Acid) Polymers"*, TH1365, Thesis submitted to University of Poona (2003)
24. D.J. Brunelle, *Macromolecular Reports* **A28(2)**, 95 (1991)
25. a) G. Piancatelli, A. Scettri, M. D'Auria, *Synthesis* **4**, 245 (*1982)* (b) E. J Corey, *Tet. Lett.* **31**, 2647 (1975)
26. R.L.Adelman, *J.Org.Chem*. **14**, 1057 (1949)
27. J.S. Moore, S.I. Stupp, *Macromolecule* **23**, 65 (1990)
28. K.P.Chan, D.S.Argyropoulos, D.M White, G.W. Yeager, A.S.Hay, *Macromolecules* **27**, 6371 (1994)
29. J.Seppala, J.F.Selin, T.Su, *EP 593271* (1994) to NESTE OY

30. A.J.Pennings, S.Gogolewski, *Makromol.Chem.Rapid Commun* **3**, 839 (1982)

31. R.F.Storey, J.S.Wiggens, A.D.Puckett, *J.Polym.Sci.Part A: Poly.Chem.*, **32**, 2345 (1994)

32. P.Bruin, G.J.Veenstra, A.J.Nijenhuis, A.J.Pennings, *Makromol.Chem.Rapid.Commun*. **9**, 589 (1988)

33. P.V.Bonsignore, *US Patent 5470944* (1995) to ARCH Development Corporation

34. H.Inata, S.Matsumura, *J.Appl.Polym.Sci*.,**30**,3325 (1985)

35. K.Gorna, S.Polowinski, S.Gogolewski, *J.Polym.Sci.Part A: Polym.Chem.* **40**, 156 (2002)

36. K. Hiltunen, J.V.Seppala, M. Harkonen,. *J. Appl. Polym. Sci.* **63**, 1091 (1997)

37. S.M.Aharoni, T.Largman, *US Patent 4417031* (1983) to Allied Corporation

38. (a) E.Ranucci, Y.Liu, M.S.Lindblad, A.C.Albertsson, *Macromol.Rapid.Comm.* **21**, 680 (2000) (b) A.J.Domb, E.Ron, R.Langer, *Macromolecules* **21**, 1925 (1998)

39. C.J.Spaans, J.H. de Groot, F.G.Dekens, A.J.Pennings, *Polymer Bulletin* **41**, 131 (1998)

40. G.Oertel, *Polyurethane Handbook*, Hanser Publishers, Munich (1985)

41. K.Hiltunen, J.V.Seppala, M.Harkonen, *J.Appl.Polym.Sci*. **64(5)**, 865 (1997)

42. J. Kylmae, J.V. Seppala, *Macromolecules* **30**, 2876 (1997)

43. Y-K. Han, S-R. Kim, J.Kim, *Macromolecular Research* **10(2)**, 108 (2002)

44. I.Luderwald, *J.Macromol.Sci.-Chem*. **A13(6)**, 869 (1979)

45. J.Seppala, J.F. Selin, T.Su, *US Patent 5380813* (1995) to NESTE OY

46. (a) M.Chorev, Y.S. Klausner, *J.Chem.Soc. Chem.Commun*. 596, (1976) (b) L.Benoiton, A.Lederc, *Can.J.Chem*. **43**, 991 (1965) and **46**, 1047 (1967) (c) M.Bodanszky and V. duVigneaud, *J.Am.Chem.Soc*. **81**, 5688 (1959)

47. (a) A.K.Chaudhary, E.J.Beckman, A.J.Russell, *Biotechnol. and Bioeng*. **55(1-3)**, 227 (1997) (b) H.Uyama, S.Yaguchi, S.Kobayashi, *J.Polym.Sci.PartA: Polym.Chem.* **37**, 2737 (1999) (c)S.Tsuneyuki, A.Yukiko,S.Makiko, H.Tomohiro, *Macromolecules* **38(5)**, 1627 (2005)

Chapter 5: Synthesis of fully aliphatic poly (ester) s by ring opening polymerization of alkyl substituted and bicyclic lactones

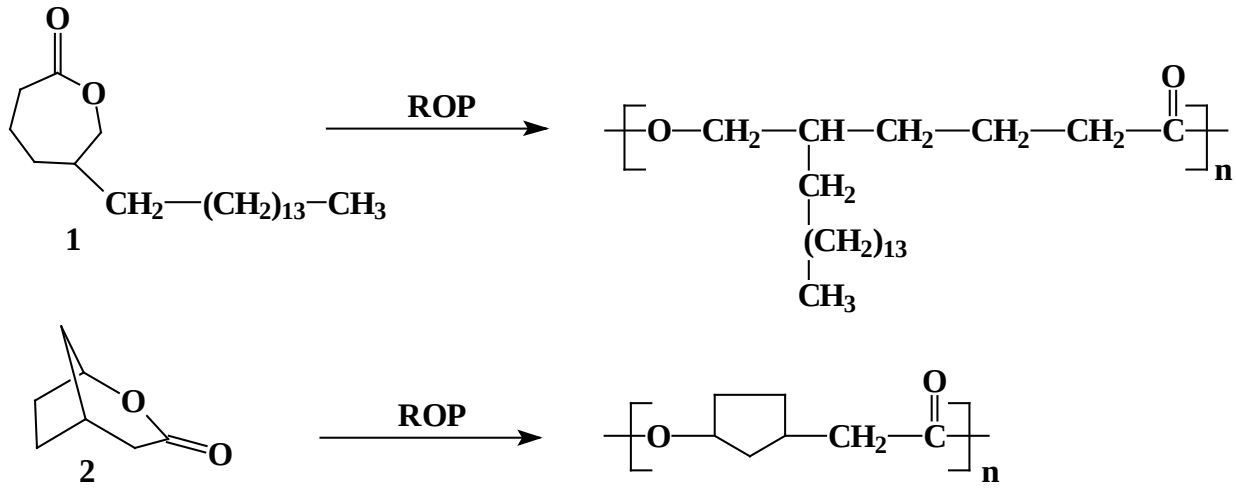
5.1 Introduction

Ring opening polymerization (ROP) of cyclic esters and related compounds is a simple route to the synthesis of aliphatic polyesters. ROP has many advantages compared to traditional condensation polymerization and, is often, the method of choice for the preparation of high molecular weight aliphatic homo and copolyesters. ROP proceeds under milder conditions and shorter reaction times[1-2]. High conversions can easily be achieved without considerations of removal of reaction byproducts and the use of stoichiometric balance of monomers. The ring opening polymerization of lactones and the associated mechanisms as well as initiators are extensively documented in literature[3].

Coordinative ring opening polymerization differs from the ionic (cationic or anionic) polymerization in that the propagating species consists of a covalent bond. This generally reduces the reactivity and the polymerization rate which leads to fewer amounts of side reactions and leads to "living ROP" of lactones under defined conditions. Aluminum alkoxide and stannous octoate are the two extensively studied initiators for coordinative ring opening polymerization of cyclic esters. Carboxylates are less nucleophilic than alkoxides and are considered to behave more like a catalyst than an initiator. Metal carboxylates such as stannous octoate are used together with active hydrogen compounds like alcohol as co-initiators[4]. The mechanism of ROP in the presence of stannous octoate was examined by Kowalski[5] and Kricheldorf[6]. The active species formed during polymerization was identified as an alkoxide which suggested that the polymerization proceeded on a tin (II) alkoxide bond formed from stannous octoate. $Sn(Oct)_2$ catalyst is generally active at elevated temperatures, leading to some intermolecular and intramolecular transesterification reactions[7]. Polyesters with defined molecular weights and functionalized end groups can be prepared by ROP. Recently polyesters with functional groups along the polymer chain have been prepared by ROP. Special attention has been paid to the synthesis of biodegradable polymers bearing

pendant functional groups. The availability of reactive groups along the chains is highly desirable for fine tuning the properties, particularly the chemical reactivity, in order to attach drugs, to improve biocompatibility, control biodegradation rate, promote (bio) adhesion rate and impart hydrophilicity if not water solubility.

The synthesis and ring opening polymerization of cyclic esters bearing functional group is a simple route to functional polyesters[8]. Monomers and polymers based on ε-caprolactone (CL) substituted with hydrophilic groups like hydroxyl, dihydroxyl, carboxylic acid and amine have been reported[9]. ε-CL substituted with bis (hydroxymethyl) or hydroxyethyl groups can undergo self-condensation, which leads to hyperbranched polyesters. ε-CL substituted with halogen like bromine or a pendant activated alkyl bromide serves as both monomer for living ROP as well as initiator for controlled ATRP[9]. Unsaturated aliphatic polyesters are another useful type of functional polyesters. The double bond can be easily transformed by means of cross linking, epoxidation, bromination and hydrosilylation[9]. Homopolymerzation of 2-allyl–ε-caprolactone in bulk using stannous octoate has been reported[10]. Although these functional aliphatic polyesters are potentially degradable and biocompatible, their properties have to be assessed and applications in different fields have to be explored.



Scheme 5.1: Ring opening of lactones (a) 3-pentadecyl 2-oxepanone, 1 (b) 2-oxabicyclo [3.2.1] octan-3-one, 2

In this chapter, the ROP of two novel lactones **1** and **2** (**Scheme 5.1**) are explored. **1** can lead to an aliphatic polyester with fifteen carbon atom branching, whereas **2** can lead to an aliphatic polyester with a confirmationally rigid cyclopentane ring in the backbone.

5.2 Experimental

5.2.1 Materials

Stannous octoate, ε-caprolactone, 3-pentadecyl phenol (Cardanol), norcamphor and Ruthenium on carbon (5%) were obtained from Sigma-Aldrich.Inc.USA. Pyridine, chromium trioxide, hydrochloric acid and THF were procured from Merck, India. m-Chloroperbenzoic (MCPBA) acid was purchased from Spectrochem, Mumbai, India whereas ethylene glycol and n-butanol were obtained from S.D fine chemicals Mumbai, India.

5.2.2 Reagents and purification

Stannous octoate was distilled twice before use. The first distillation was done to remove water and octanoic acid. The second fraction which was collected at 180^0C and 0.085-0.086 mbar pressure, was used. THF was dried according to usual procedures. A stock solution of Sn $(Oct)_2$ was prepared by dissolving an appropriate quantity in dry THF and stored under nitrogen prior to use. ε-CL was dried over calcium hydride overnight and then distilled under reduced pressure and stored under nitrogen. Ethylene glycol (EG) and n-butanol were first ordinarily distilled. They were then refluxed with sodium pieces for few hours and then again distilled under vacuum or nitrogen and stored over 4Å molecular sieves. Stock solution of EG and n-butanol were prepared by dissolving appropriate amounts in dry THF and stored under nitrogen prior to use. Solvents like hexane, chloroform were distilled and used. The other chemicals were used without further purification.

5.2.3 Synthetic methods

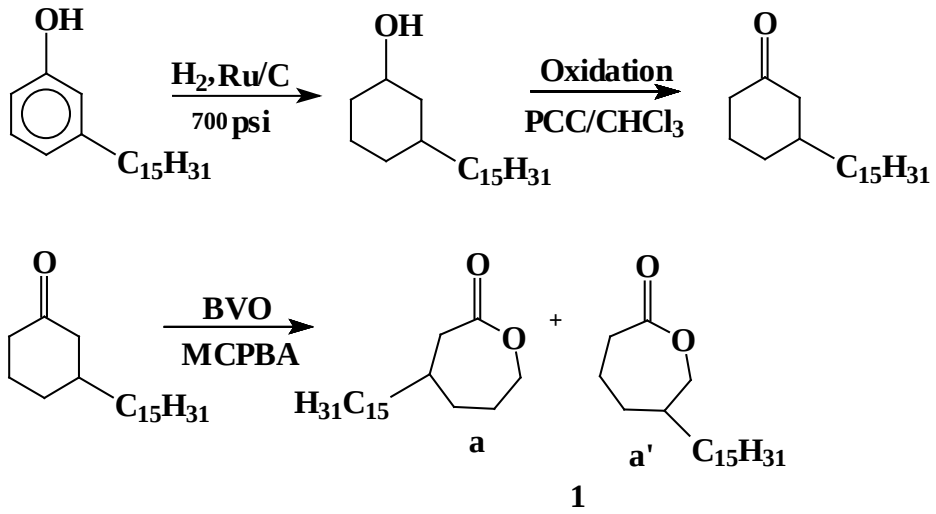
Bayer-Villiger oxidation of 3-substituted cyclohexanone and norbornanone by enzymes[11] has been reported. Bayer-Villiger oxidation of norbornan-2-one using different oxidizing agents has been studied[12] where as that of 3-pentadecyl cyclohexanone has not been

reported. Lactones **1** and **2** were synthesized by Bayer-Villiger oxidation of the corresponding ketones.

5.2.3.1 Synthesis of 3-pentadecyl 2-oxepanone

3-pentadecyl 2-oxepanone (**1**) was obtained from 3-pentadecyl phenol in three steps. In the first stage, cardanol was reduced to 3-pentadecyl cyclohexanol by hydrogenation. In the second step it was oxidized to the corresponding ketone, namely, 3-pentadecyl cyclohexanone and finally in the third step the ketone was further oxidized to the lactone using MCPBA. The synthesis of the lactone is shown in **Scheme 5.2**.

Step1: 3-Pentadecyl phenol (40.35 g, 0.13 mol) was taken in a Parr reactor (300 mL capacity) and dissolved in isopropanol (150 mL). Ru (5 wt% on C) (0.8 g, 2 wt %) was added. Hydrogenation was carried out at 120°C using 700 psi hydrogen pressure. The reaction was continued until there was no further absorption of H_2 (1.5 h).



Scheme 5.2: Synthesis of 3-pentadecyl 2-oxepanone from 3-pentadecyl phenol

Catalyst was separated by filtering the reaction mixture through Whatman filter paper. Isopropyl alcohol was stripped off and the compound was dried under reduced pressure to afford 3-pentadecyl cyclohexanol. Yield: 40.6 g (98%), mp: Found 44-46^{0}C, Reported (45-48^{0}C)[13].

Step 2: Oxidation of reduced cardanol to 3-pentadecyl cyclohexanone[14]- (a) Synthesis of PCC (Pyridinium chloro chromate): 0.185 mL of 6 M HCl (1.1 mol) was added to 100 g (1M) of chromium trioxide (CrO_3) rapidly with stirring. After 5 minutes, the homogeneous solution was cooled to 0^0C and 79.1 g (1M) of pyridine was carefully added over 10 min. Recooling to 0^0C gives a yellow orange solid which was collected in a sintered glass funnel and dried for 1 h in vacuum. PCC (16.16 g, 0.075 mol), finely mixed with equal quantity of silica gel (60-120 mesh size) dissolved in 300 mL dichloromethane (DCM) was taken in a 1L three necked round bottom flask fitted with a reflux condenser. Reduced cardanol (15.5 g, 0.05mol) dissolved in 200 mL DCM was added in one portion to the magnetically stirred solution. After 8-10 h of stirring at room temperature[15], the reaction mixture was filtered through a sintered funnel. The round bottom flask was washed 4-5 times with DCM. The filtrate was concentrated and then passed through a bed of celite-silica gel. The colorless solution obtained was neutralized by a saturated solution of sodium bicarbonate followed by a saturated brine solution. The organic layer was dried over sodium sulfate. The formation of ketone was checked by TLC, which showed a single spot due to ketone in an 80: 20 mixture of pet ether and ethyl acetate as solvent system. Concentrating the organic layer resulted in the desired product with 97-98% yield with mp = Found 41^0C, Reported 41^0C[14]. IR and NMR of the ketone were recorded.

Step 3: 3-pentadecyl cyclohexanone (10 g, 0.0324 mol), MCPBA (14 g, 0.081 mol), sodium bicarbonate (6.8 g, 0.081 mol) and DCM were stirred at room temperature in a 250 mL round bottom flask for 72 h. MCPBA was dried over sodium sulfate before use. A white precipitate was obtained during the reaction which was removed by filtration. This reaction mixture was washed with sodium bicarbonate (5% solution in 300 mL water) followed by brine solution till the washings tested neutral. The organic layer was dried over sodium sulfate. A white solid was obtained after concentrating the DCM solution which was purified by column chromatography. The main impurity was MCPBA. Lactone was eluted from the column using 6% ethyl acetate solution of pet ether. TLC of this product showed a single spot due to lactone. The product obtained from the column was dissolved in minimal amount of n-hexane. By allowing the hexane solution to stand at R.T overnight, a part of the product was obtained as white needles.

The lactone was obtained in 90% yield, mp = 35-60^{0}C. NMR (**Figure 5.1**) and IR (**Figure 5.2**) of the lactone were recorded.

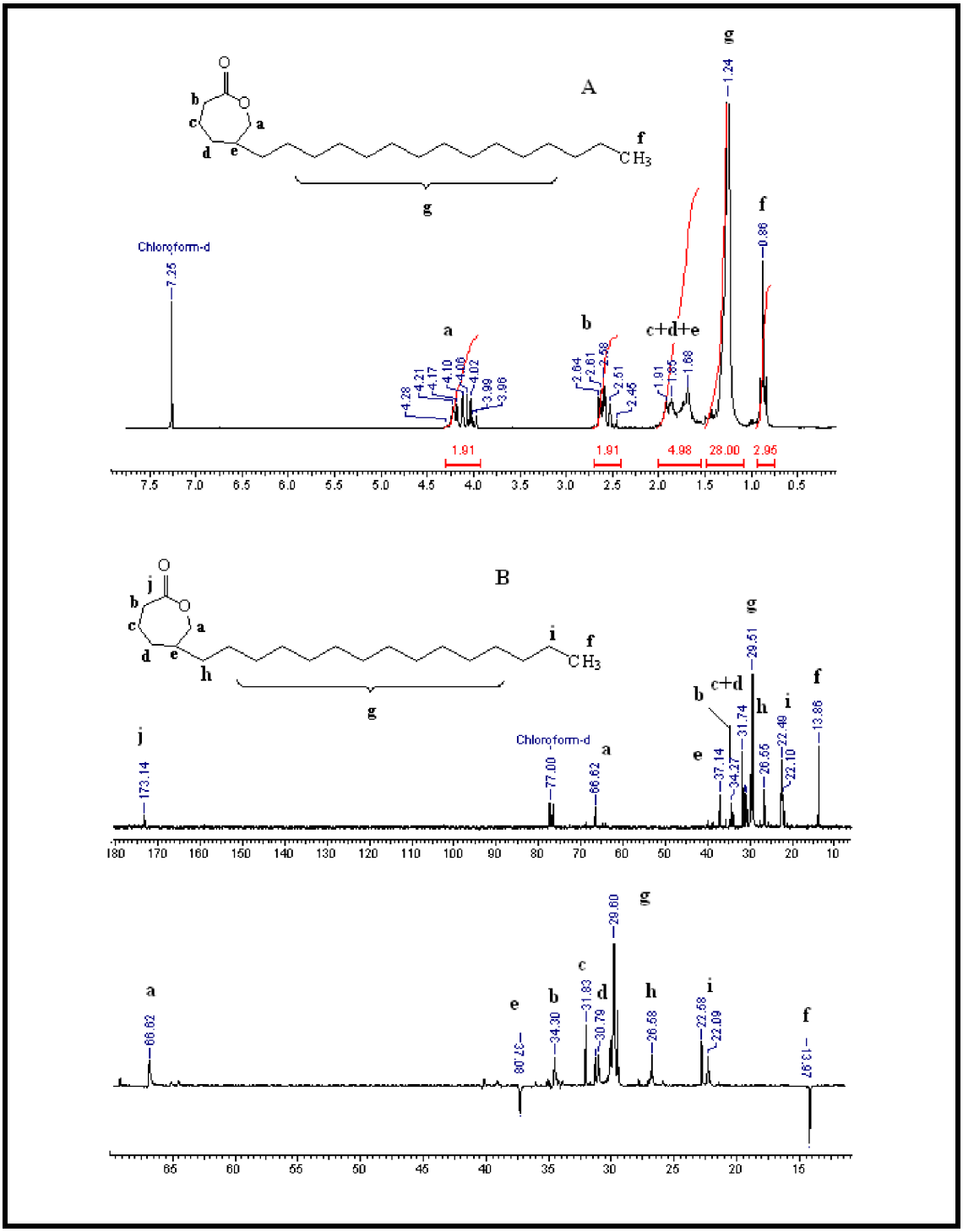


Figure 5.1 (A) ^{1}H NMR, (B) ^{13}C NMR and DEPT spectra of 3-pentadecyl 2-oxepanone

^{1}H NMR δ (ppm, $CDCl_3$) of lactone: 0.86 (t, 3H, $-CH_3$); 1.23 (s, 28H, $-CH_2$); 1.6-1.9 (m, 5H, $-CH_2$, -CH); 2.4-2.6 (m, 2H, $-CH_2$); 3.96-4.21 (m, 2H, $-CH_2$)

^{13}C NMR δ (ppm, $CDCl_3$) of lactone: 13.86 (CH_3); 22.10, 22.5, 26.55, 29.51, 31.74 ($-CH_2$); 34.3 ($-CH_2C=O$); 37.14 (-CH); 66.62 ($-OCH_2$); 173.14 (C=O)

IR (chloroform, cm^{-1}): 2922, 2852 (C-H), 1726 (C=O)

Elemental analysis: Found- C = 76.45%, H = 12.71%; Calculated- C = 77.53%, H = 12.34%

Mass = 324 Da by mass spectrometer

Two isomers **a** and **a'** are expected to be formed. An attempt to separate these isomers and determine their compositions was not made.

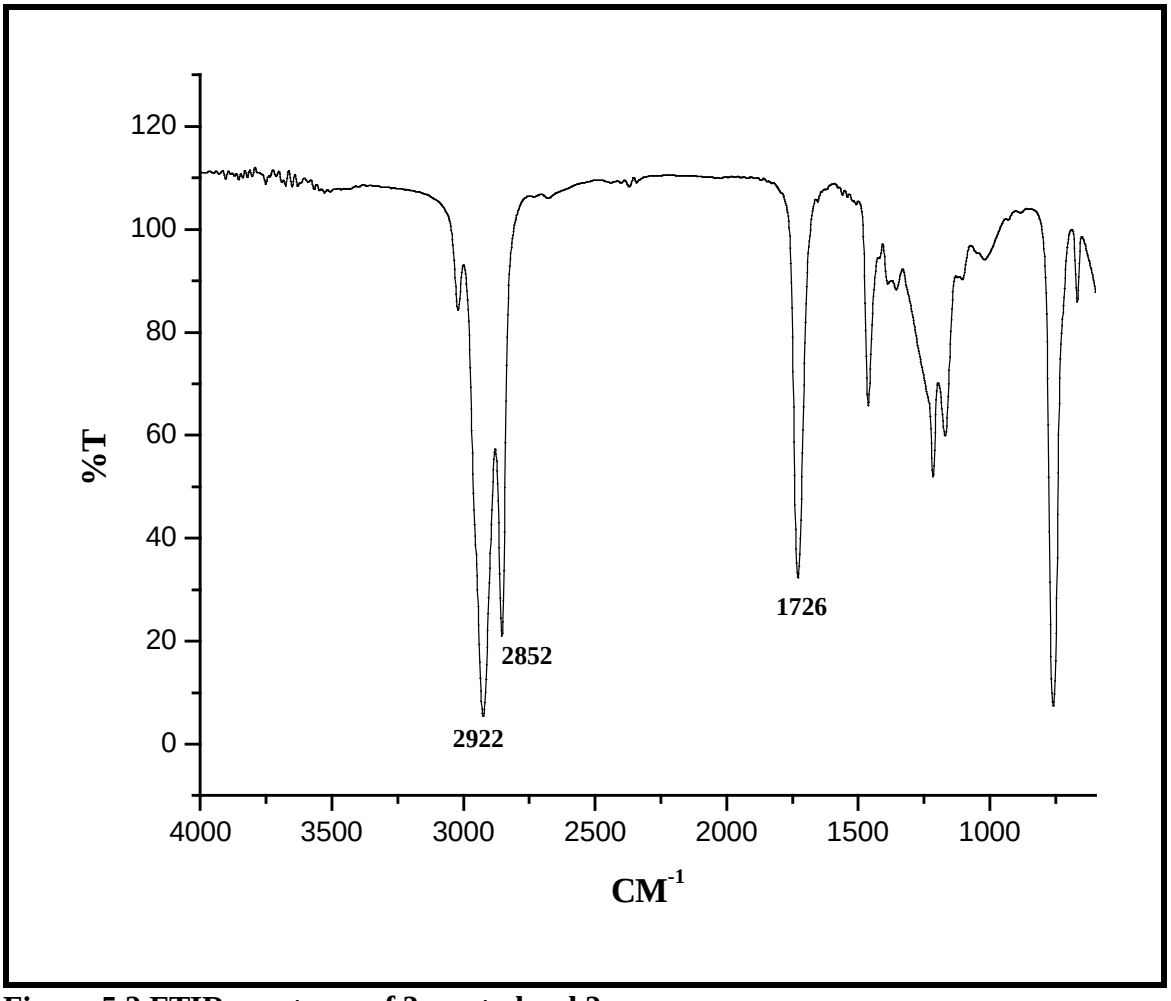
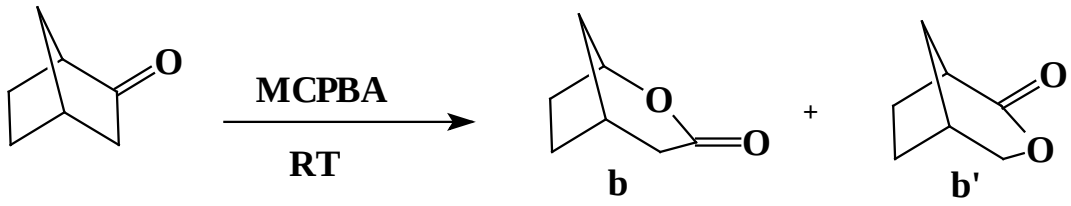


Figure 5.2 FTIR spectrum of 3-pentadecyl 2-oxepanone

5.2.3.2 Synthesis of 2-oxabicyclo [3.2.1] octan-3-one

Lactone (**2**) was obtained by Bayer Villiger oxidation[12] as shown in **Scheme 5.3**. Nor-camphor (5 g, 0.0453 mol), MCPBA (19.5 g, 0.045 x 2.5 = 0.113 mol) and sodium bicarbonate (9.5 g, 0.045 x 2.5 = 0.113 mol) were dissolved in 250 mL chloroform and stirred for 72 h at room temperature. MCPBA was dried over sodium sulfate before use. A white precipitate was obtained during the reaction which was removed by filtration. This reaction mixture was washed with sodium bicarbonate solution (5 % solution in 300 mL water) followed by brine solution till the washings tested neutral. The organic layer was dried over sodium sulfate. The organic layer was concentrated and further purified by column chromatography. The lactone was eluted from the silica gel column with 3% ethyl acetate solution of pet ether.



Scheme 5.3: Synthesis of 2-oxabicyclo [3.2.1] octan-3-one from nor camphor

The semi-solid product obtained was further purified by vacuum distillation. The fraction distilling at 60^0C and 0.03-0.04 mbar pressure was collected which was a clear liquid that solidified on cooling. Two isomers are expected as shown in **Scheme 5.3** but a single spot was shown on TLC due to the lactone. Yield = 80%, mp = 49-52^0C. The lactone was characterized by ^{1}H and ^{13}C NMR (**Figure 5.3**), FTIR (**Fig 5.4**), elemental analysis, melting point and mass.

^{1}H NMR δ (ppm, $CDCl_3$) of lactone: 1.6-2.19 (m, 6H, -CH_2, d + e + f); 2.39-2.76 (m, 3H, -CH_2C=O, -CH, c + b); 4.83 (s, 1H, -CH)

^{13}C NMR ($CDCl_3$) of lactone: 28.17 (s, -CH_2, bridge head carbon, f); 30.82 (s, -CH, c); 31.4 (s, -CH_2, d); 34.64 (s, -CH_2, e); 39.52 (s, -CH_2C=O, b); 79.9 (s, -CH-O-, a); 169.47 (s, -C=O, g, carbonyl carbon)

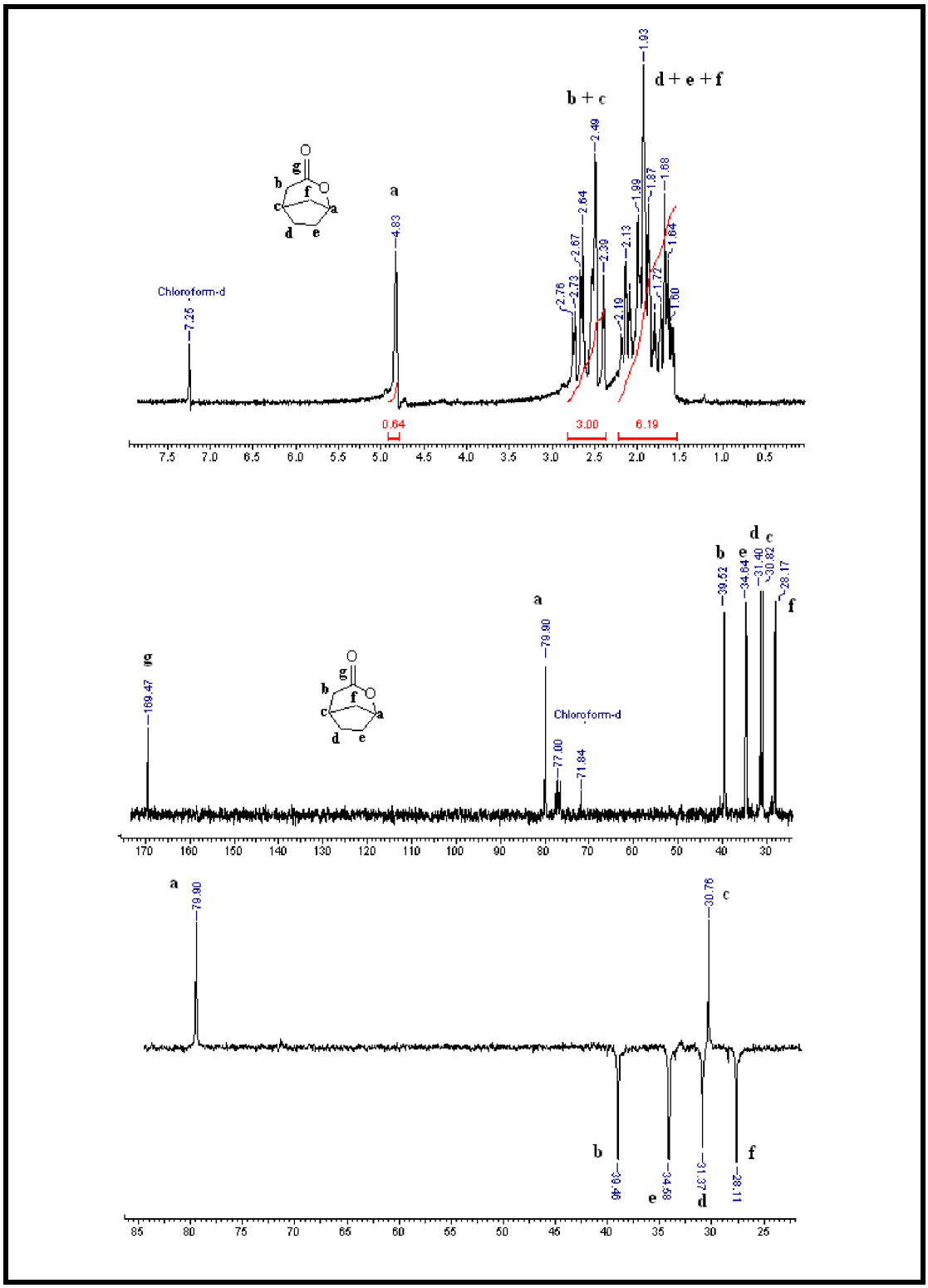


Figure 5.3 (A) ^{1}H NMR, (B) ^{13}C NMR and DEPT spectra of 2-oxabicyclo [3.2.1] octan-3-one

IR (chloroform, cm^{-1}): 2954 (C-H), 1724 (C=O)

Elemental analysis: Found- C = 64.65%, H = 7.67%; Calculated- C = 66.58%, H = 7.92%

Mass = 126 Da by mass spectrometer. In principle, two isomers **b** and **b'** can result from the reaction. No attempt to separate these isomers was not made.

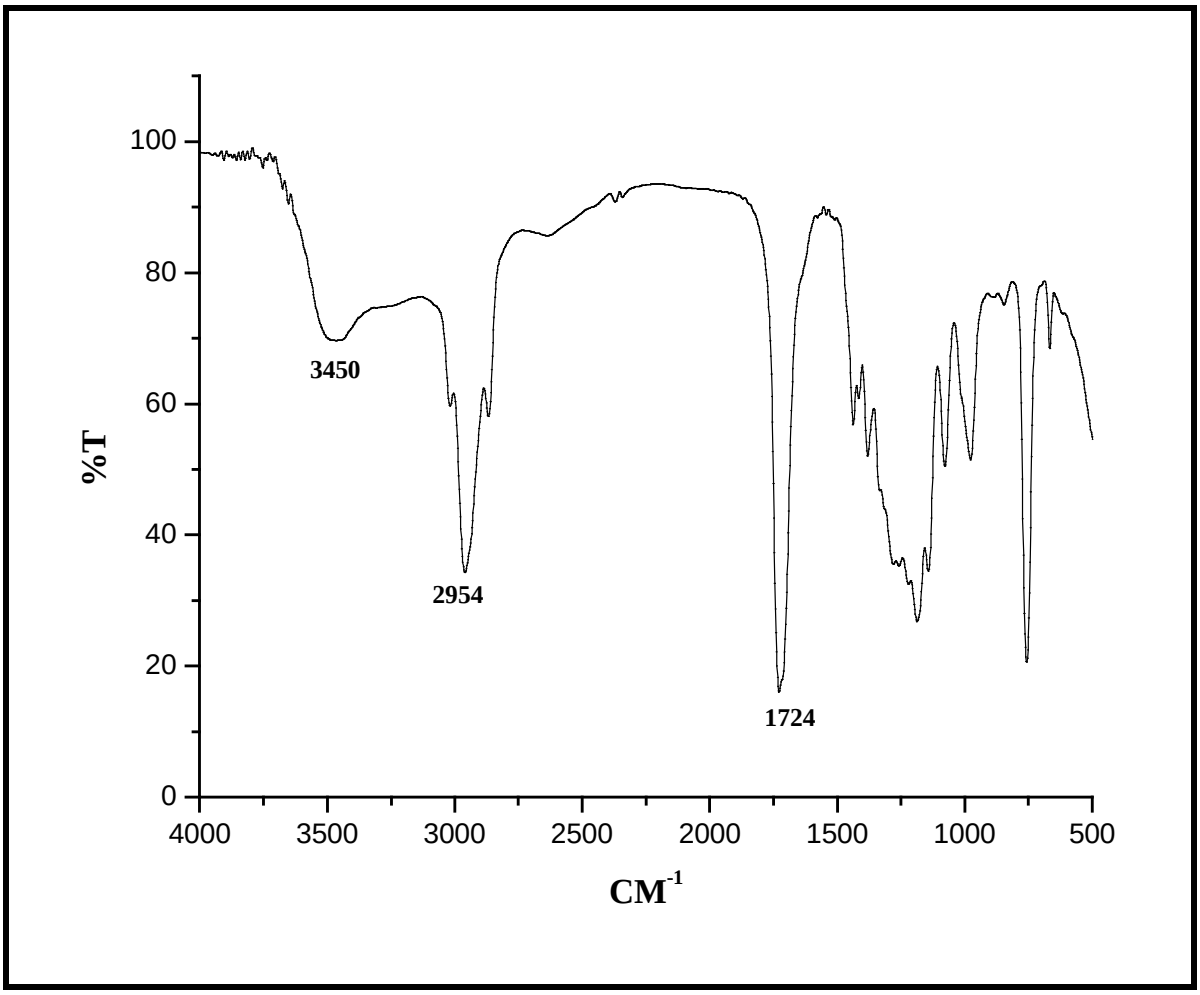


Figure 5.4 FTIR spectrum of 2-oxabicyclo [3.2.1] octan-3-one

5.2.4 Ring opening polymerization (ROP) of lactones

Homopolymerization of 3-pentadecyl 2-oxepanone and 2-oxabicyclo [3.2.1] octan-3-one was attempted using tin carboxylate catalyst. Copolymerization of 3-pentadecyl 2-oxepanone with ε-caprolactone was also studied. Conversions were determined from ^{1}H NMR and molecular weights were obtained using GPC and VPO.

5.2.4.1 ROP of 3-pentadecyl 2-oxepanone

Effect of temperature

The polymerization was performed at three different temperatures 130^0C, 150^0C and 170^0C using ethylene glycol (EG) as initiator. All glasswares were oven dried at 150-200^0C for a minimum of 3 h before use. Lactone **1** (0.5 g, 1.543×10^{-3} mol) was weighed in a two-necked flask and dried under high vacuum for 30 min to 1 h before addition of catalyst and initiator. Sn $(Oct)_2$ (3.12×10^{-3}g, 7.7×10^{-6} mol) and initiator EG (6.207×10^{-3}g, 1×10^{-4}mol) were added into the flask through syringe under nitrogen. THF was removed under vacuum. The flask was immersed in an oil bath heated to the required temperature. Heating was continued for 5 h under nitrogen atmosphere. Thereafter, the flask was cooled under nitrogen. Similar reactions were carried out at 150^0C and 170^0C. The molar ratios of [lactone]/[SO], [lactone]/[EG] and [EG]/[SO] were kept at 200, 15.43 and 12.96 respectively.

Effect of reaction time

Experiments were carried out at 150^0C for 7 h and 24 h under nitrogen atmosphere. Lactone **1** (0.5 g, 1.543×10^{-3} mol) was weighed in a dried two-necked round bottom flask. The lactone was dried under high vacuum for minimum 30 min. EG (6.207×10^{-3}g, 1×10^{-4} mol) and Sn $(Oct)_2$ (1.25×10^{-3}g, 3.086×10^{-6} mol) were added into the flask under nitrogen through syringe. The THF was removed under vacuum and then the flask was kept under nitrogen. It was immersed in an oil bath at 150^0C and heated for the required time under nitrogen atmosphere. The molar ratios of [lactone]/[SO], [lactone]/[EG] and [EG]/[SO] were 500, 15.43 and 32.4 respectively.

Effect of [Lactone]/[SO] ratio

Effect of ratio on the ring opening polymerization and molecular weight was studied by carrying out experiments at two different [lactone]/[SO] ratios. Lactone **1** (0.5 g, 1.543×10^{-3}mol) was dried in a two-necked round bottom flask under high vacuum. EG (2.07×10^{-3}g, 3.33×10^{-5}mol) and SO (3.12×10^{-3}g, 7.7×10^{-6}mol) were transferred into the flask through syringe under nitrogen atmosphere. THF was removed under vacuum. The molar ratio of lactone (**1**) to SO was 200, whereas the molar ratios of lactone to EG and EG to SO were 46.3 and 4.3 respectively. The flask was immersed in an oil bath at 150^0C and

heated for 7 h under nitrogen atmosphere. Another reaction was carried out at [lactone]/[SO] ratio of 500.

ROP with different initiators

Lactone (**1**) was polymerized using two different initiators EG and n-butanol. The molar ratio of lactone to Sn $(Oct)_2$ used was 200. Lactone **1** (0.5 g, 1.543 x 10^{-3}mol) was weighed in a two necked round bottom flask and dried under vacuum. Stannous octoate (3.12 x 10^{-3}g, 7.7 x 10^{-6}mol) and n-butanol (7.4 x 10^{-3}g, 1 x 10^{-4}mol) were added under nitrogen atmosphere through syringe. THF was removed and the contents were kept under nitrogen. The molar ratios of lactone to stannous octoate, lactone to butanol and butanol to stannous octoate were 200, 15.4 and 13 respectively. The flask was immersed in an oil bath at 150^0C. The heating was continued for 24 h. A similar reaction was carried out using EG as initiator.

5.2.4.2 Copolymerization with ε-Caprolactone

Copolymerization at different reaction temperatures

Extent of incorporation of lactone **1** in the copolymer was studied by carrying out the reactions at two different compositions 80/20 and 60/40. The reactions at these two compositions were carried out using EG as initiator under nitrogen atmosphere at 130^0C, 150^0C and 170^0C for 5 h. All glasswares were oven dried for a minimum of 2 h at 150-200^0C. Lactone **1** (0.162 g, 5 x 10^{-4}mol) was weighed in a two necked round bottom flask. ε-Caprolactone (0.23 g = 0.22 mL, 2 x 10^{-3} mol), EG (4.84 x 10^{-3} g, 7.8 x 10^{-5}mol) and Sn $(Oct)_2$ (5.0625 x 10^{-3} g, 1.25 x 10^{-5} mol) were added through syringe under nitrogen atmosphere. THF was removed under vacuum and the flask was then kept under nitrogen atmosphere. The total concentration of the monomers was 0.0025 mol. The composition of ε-caprolactone was 80% and that of lactone (**1**) 20%. The molar ratios of monomer to Sn $(Oct)_2$, monomer to EG and EG to Sn $(Oct)_2$ were 200, 32 and 6.2 respectively. The flask was immersed in an oil bath at required temperature. Similar reaction was carried out using 60% composition of ε-caprolactone monomer and 40% of lactone **1**. The total concentration of the monomers was 0.0025 mol. The molar ratios of monomer to Sn $(Oct)_2$, monomer to EG and EG to Sn $(Oct)_2$ were 200, 25.2 and 7.9.

Conversion and compositions of the copolyesters were determined from ^{1}H NMR of the virgin reaction products.

Copolymerization at different reaction times

Copolymerizations using 80/20 and 60/40 compositions were carried out at varying lengths of reaction time at 130^{0}C to study the extent of incorporation of lactone **1** in the copolymer with time. The reactions were carried out using EG as initiator under nitrogen atmosphere at 130^{0}C for 5, 10 and 20 h. Lactone **1** (0.162 g, 5 x 10^{-4}mol) was weighed in a two-necked round bottom flask. ε-Caprolactone (0.228 g = 0.22 mL, 2 x 10^{-3} mol), EG (4.84 x 10^{-3} g, 7.8 x 10^{-5}mol) and Sn (Oct)$_2$ (5.0625 x 10^{-3} g, 1.25 x 10^{-5} mol) were added through syringe under nitrogen atmosphere. THF was removed under vacuum and the flask was then kept under nitrogen atmosphere. Total concentration of the monomers was 0.0025 mol. The composition of ε-caprolactone monomer was 80% and that of lactone **1** 20%. Molar ratios of monomer to Sn (Oct)$_2$, monomer to EG and EG to Sn (Oct)$_2$ was 200, 32 and 6.2 respectively. The flask was immersed in an oil bath at 130^{0}C and heated for predetermined lengths of time under nitrogen atmosphere. Similar reaction was carried out using 60% composition of ε-caprolactone monomer and 40% of lactone **1**. The total concentration of the monomers was 0.0025 mol and the molar ratios of monomer to Sn (Oct)$_2$, monomer to EG and EG to Sn (Oct)$_2$ were 200, 25.2 and 7.9. Conversion and compositions of the copolyesters were determined from ^{1}H NMR of the virgin reaction products.

Homopolymerization of ε-caprolactone

Polymerization of ε-caprolactone was performed at three different temperatures 130^{0}C, 150^{0}C and 170^{0}C using EG as the initiator to study the influence of temperature on the conversion and molecular weight. All the glasswares were ovendried at 150-200^{0}C for a minimum of 3 h before use. εCL (0.15 g, 1.315x10^{-3} mol), Sn (Oct)$_2$ (2.66 x 10^{-3}g, 6.575 x 10^{-6} mol) and initiator EG (1.862 x 10^{-3}g, 3.0 x 10^{-5}mol) were added into the two-necked flask through syringe under nitrogen. THF was removed under vacuum and then the flask was kept under nitrogen. It was then immersed in an oil bath and heated at the required temperature for 5 h under nitrogen atmosphere. The polymer was recovered by dissolving in chloroform and drying under vacuum. The conversions were determined

from ^{1}H NMR. Similar reactions were carried out at $150^{0}C$ and $170^{0}C$. The molar ratios of [CL]/[SO], [CL]/[EG] and [EG]/[SO] were kept at 200, 43.83 and 4.56 respectively.

5.2.4.3 ROP of 2-oxabicyclo [3.2.1] octan-3-one

Ring opening polymerization of 2-oxabicyclo [3.2.1] octan-3-one (**2)** was attempted at two different temperatures using n-butanol as initiator. The lactone **2** (0.5 g, 3.96×10^{-3}mol) was weighed in an ampoule and dried for at least 30 min. n-butanol (7.412×10^{-3}g, 1×10^{-4}mol) and Sn $(Oct)_2$ (8.019×10^{-3}g, 1.98×10^{-5}mol) were added through syringe into the flask under nitrogen atmosphere. The molar ratio of lactone to Sn $(Oct)_2$ was 200, whereas the molar ratios of the lactone to butanol and butanol to Sn $(Oct)_2$ were 39.06 and 5.05 respectively. THF was removed and the ampoule was sealed under vacuum. The ampoule was then immersed in an oil bath at $150^{0}C$ and the heating was carried out for 24 h. Another reaction was carried out in exactly similar manner with the same quantities at $130^{0}C$ for 24 h under nitrogen. After polymerization the product was dissolved in chloroform and precipitated in methanol. The product of the experiment carried out at $150^{0}C$ was highly colored as compared to that conducted at $130^{0}C$.

5.3 Analysis

5.3.1 Solution NMR measurements

^{1}H and ^{13}C NMR spectra of lactones as well as polyesters were recorded on a Bruker AV 200 MHz NMR spectrometer. About 15-20 mg of the sample was dissolved in chloroform-d. The chemical shifts in parts per million (ppm) are reported up field with reference to internal standard chloroform-d at 7.25 ppm or downfield with reference to TMS. The sample concentration for ^{13}C NMR measurements was 25-30 % by weight. $CDCl_3$ served as solvent as well as internal standard for all ^{13}C-NMR measurements. Relative peak areas were proportional to the number of carbon atoms. Peak areas were calculated by using WIN-NMR software.

5.3.2 Characterization of lactones

FTIR analysis

IR spectra were recorded as chloroform solution on sodium chloride cells using a Perkin-Elmer Infrared Spectrometer Model 16-PC FT-IR. IR bands are expressed in frequency (cm-1).

Melting point determination

Melting points were recorded on the Celsius scale using Thermonik Campbell melting point apparatus

Elemental analysis

Elemental analyses (C, H) were performed on a Carlo-Erba 1100 automatic CHN analyzer.

Mass analysis

The mass spectra of the lactones were recorded using API QSTAR PULSAR mass spectrometer

GC and HPLC analysis

The purity of the lactones was determined by GC as well as HPLC. GC-analysis of lactones was performed using a Perkin Elmer GC Auto System XL-200 by injecting 0.1 µL of chloroform solutions of lactones into BP-20 capillary column. The split ratio was 1:60, the detector was FID, the carrier gas was nitrogen with a pressure of 7 psi and the fuel for FID was hydrogen. The programme for 3-pentadecyl 2-oxepanone was as follows : oven was isothermal at 50 °C for 4 min, followed by heating with a ramp rate of 45^0C/ min from 50^0C to 250^0C. The oven was again isothermal at 250^0C for 12 min. The injector and detector were kept at 300^0C. The heating programme for 2-oxabicyclo [3.2.1] octan-3-one was as follows: Oven was isothermal for 5min at 50^0C, followed by heating at a ramp rate of 45^0C/ min from 50^0C to 200^0C and again isothermal at 200^0C for 6 min.

HPLC analysis was carried out on Waters modular HPLC instrument equipped with an autosampler (Waters 717 plus), RI (Waters 2410) and UV (Waters 996 PDA) detector. 10 µL of the methanol solution of the lactones was injected into zorbax C_8 reverse phase column. The chromatography was done in a isocratic mode using methanol as mobile phase.

5.3.3 Characterization of polyesters

Molecular weight and distribution

Molecular weights (M_n and M_w) and polydispersity (M_w / M_n) were determined with respect to polystyrene standard by size exclusion chromatography on a Thermo Finnigan Spectra Series AS300 machine at 25^0C by eluting polyester solutions of 5-8 mg / ml concentrations in chloroform, with toluene as internal standard through a series of five μ–Styragel columns of pore sizes 10^5, 10^4, 10^3, 500 and 100 Å, respectively and length 30 cm each. Chloroform was used as the mobile phase (flow rate 1mL/min) and both UV and RI detector signals were recorded simultaneously. As the molecular weights were calculated with respect to polystyrene calibration, they were of little significance and hence GPC was mainly used to determine the polydispersity index. The number average molecular weights of the polyesters were determined by KNAUER K- 7000 Vapor Pressure Osmometer as per the procedure reported in chapter 3.

Thermal analysis

Differential scanning calorimetric (DSC) measurements were made on a Waters Thermal Analyzer model Q-10 in a nitrogen atmosphere. Approximately 6-7 mg of polymer samples were weighed in aluminium pans of 50 μL capacity and sealed. The measurements were run from –30 to 70°C at a heating rate of 10 °C/ min and a cooling rate of 5°C/ min. The melting temperature (T_m) and the crystallinity data were recorded from the first heating and second cooling curves, respectively.

5.4 Results and Discussion

5.4.1 ROP of 3-pentadecyl 2-oxepanone (1)

Lactone **1** was characterized by (^{1}H and ^{13}C) NMR and IR (**Figures 5.1** and **5.2**). The structure matched well with the spectra. The peaks due to carbonyl stretching and C-H stretching appeared at 1726 cm^{-1} and 2900 cm^{-1} respectively in the IR spectrum. The protons of the alkane chain appeared at 1.23 δ in the proton spectrum and the carbons at 29.5 δ in carbon spectrum. DEPT spectrum showed two peaks one at 37.08 and the other at 13.97 ppm which were inverted indicating that these were the carbon atoms attached to

odd number of hydrogens in the lactone. The isomers **a** and **a'** could not be distinguished by NMR and, hence, were not separated. The melting point ranged between 35^0C to 60^0C depending on the relative amount of isomer **a** and **a'**. The mass spectrum showed a single peak of high intensity due to the sodium adduct of the lactone at m/z value of 347, which gives the molecular weight of the lactone as 324 Da. The purity of the sample as determined by GC as well as HPLC was 98.8% and 97.7% respectively. The lactone was soluble in chloroform and hexane and insoluble in methanol.

The ROP of lactone **1** was studied under different reaction conditions. The results are summarized in **Tables 5.1** and **5.2**. The products obtained after polymerization were found to be soluble in hexane like the starting monomer. Hence, the products could not be precipitated in hexane. The product could be precipitated in methanol. However, the monomer too was insoluble in methanol. Hence it was difficult to separate the polymer from the unreacted monomer using solvent-non solvent precipitation techniques. The yields of the polymer were therefore not calculated

The polymers were characterized by ^{1}H as well as ^{13}C NMR. The amount of unreacted monomer was determined from the peak at 4.25 due to $-OCH_2$ protons in the unreacted lactone in ^{1}H NMR. The spectra of a representative sample are shown in **Figure 5.5**. In the ^{1}H NMR the protons adjacent to the carbonyl carbon shift from 2.6 ppm in the lactone to 2.3 ppm in the polymer. In the ^{13}C NMR of the polymer, there is a shift in the carbonyl carbon from 173.14 ppm for the lactone to 173.42 ppm for the product and the carbon adjacent to the oxygen (-OCH_2) shifts from 66.6 to 66.7 ppm. Thus, ^{1}H and ^{13}C NMR data are consistent with the structure of the repeat unit resulting from the ring-opening polymerization of lactone **1**. M_n in the range of 4000-4500 by VPO was observed for all the polymers (**Table 5.1** and **5.2**).

In view of the fact that unreacted monomer was not removed form the product before VPO measurements, there could be some ambiguity on the accuracy of the reported values.

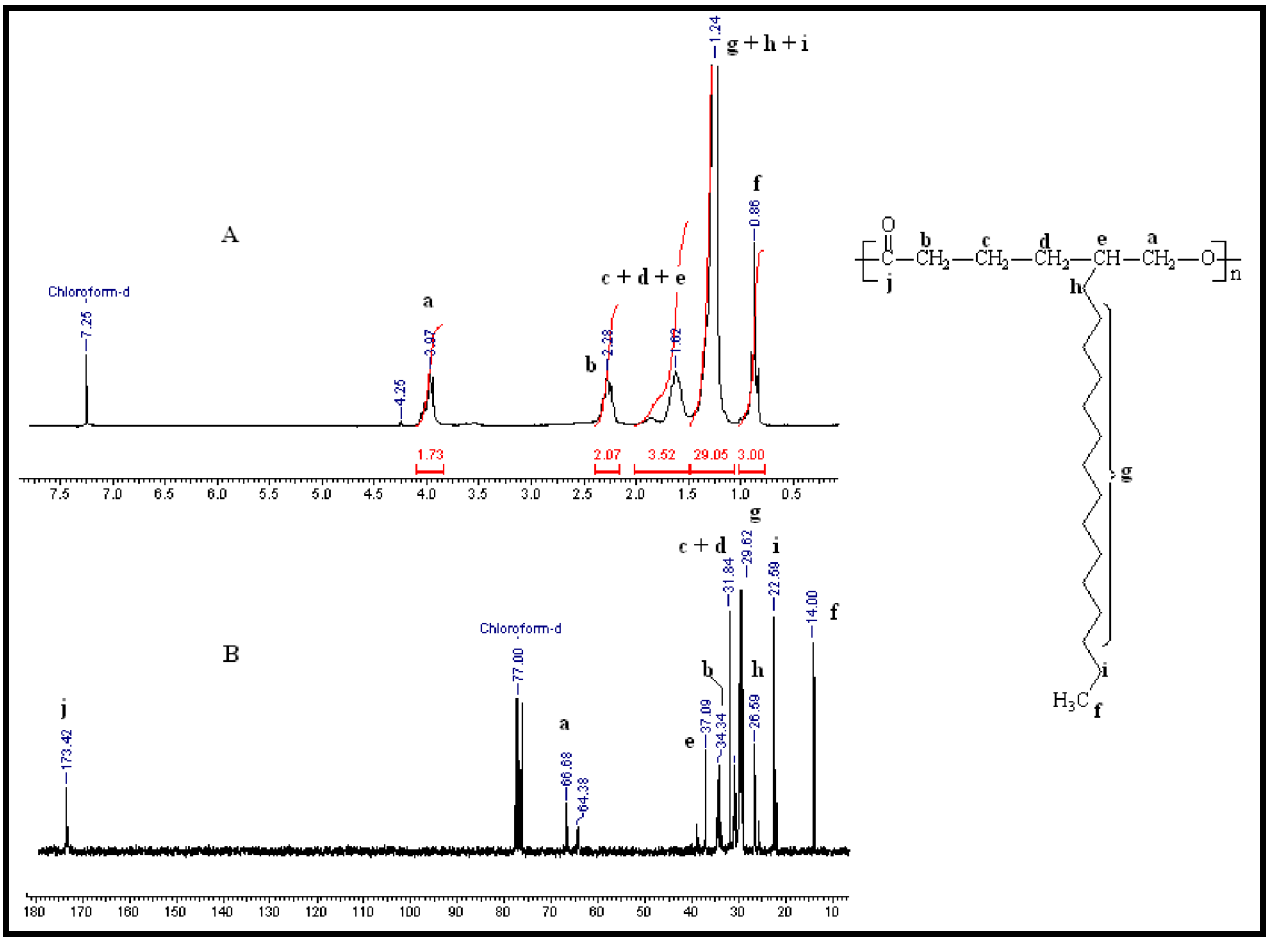


Figure 5.5 (A) ^{1}HNMR and (B) ^{13}C NMR spectra of polymer obtained from 3-pentadecyl 2-oxepanone (entry no. 4 Table 5.1)

Table 5.1 Effect of reaction temperature and time on ring opening polymerization of 3-pentadecyl 2-oxepanone (**1**)

No.	Reaction Conditions	[M]/[SO]	[EG]/[SO]	[M]/[EG]	M^{a}_{n} (calc.)	Conv.[b] (%mol)	M_n (VPO)	M_n (GPC)	M_w/M_n	T_m (^{0}C)	T_c (^{0}C)
Reaction temperature											
1.	130^{0}C/5 h	200	13.0	15.4	3650	73	3860	2570	1.3	30	25
2.	150^{0}C/5 h	200	13.0	15.4	4250	85	4200	4080	1.3	28	22
3.	170^{0}C/5 h	200	13.0	15.4	4250	85	4800	4750	1.3	26	19
Reaction time											
4.	150^{0}C/7 h	500	32.4	15.4	4900	98	4050	7140	1.5	24	17
5.	150^{0}C/24 h	500	32.4	15.4	4900	98	4190	9260	1.4	23	17

[M]-1.543 x 10^{-3}mol/L; [SO] (stannous octoate) – 7.7 x 10^{-6}mol/L (**for [M]/[SO] =200**) and 3.086 x 10^{-6}mol/L (**for [M]/[SO] = 500**);
a- M_n (calc.) based on [M] in g/ [Initiator] in moles x % conversion; b-Conversions determined from NMR

Table 5.2 Effect of [M]/[SO] ratio and initiator on ring opening polymerization of 3-pentadecyl 2-oxepanone (**1**)

No.	Reaction Conditions	[M]/[SO]	[EG]/[SO]	[M]/[EG]	M_n[a] (calc.)	Conv.[b] (%mol)	M_n (VPO)	M_n (GPC)	M_w/M_n	T_m (^{0}C)	T_c (^{0}C)
[M]/[SO] ratio											
6.	150^{0}C/7 h	500	10.8	46.3	14,700	98	3000	6770	1.5	21	13
7.	150^{0}C/7 h	200	4.3	46.3	14,700	98	3860	8630	1.6	20	12
Initiator											
8.	150^{0}C/24 h; EG	200	13.0	15.4	4900	98	4190	9260	1.4	23	17
9.	150^{0}C/24 h; n-butanol	200	13.0	15.4	5000	100	4300	11,490	1.6	21	15

[M]- 1.543 x 10^{-3}mol/L; [SO] (stannous octoate) – 7.7 x 10^{-6}mol/L (**for [M]/[SO] =200**) and 3.086 x 10^{-6}mol/L (**for [M]/[SO] = 500**); a- M_n (calc.) based on [M] in g/ [Initiator] in moles x % conversion; b-Conversions determined from NMR

GPC curves showed tailing due to low molecular weight species in all the samples (**Figures 5.6** and **5.7**). The retention volume of the lactone (**1**) and the product of polymerization were different and unreacted monomer was observed in all cases. The molecular weights (by SEC using polystyrene standards) of the polymerization products increased with increase in reaction temperature. The GPC curves (**Figure 5.6**) also show that the amount of unreacted lactone (**1**) decreases with increase in reaction temperature. Under conditions explored in this study true "living" or "controlled" polymerization of lactone (**1**) was not observed. Although some correspondence between observed and calculated molecular weights were observed at [M]/[SO] = 200, the results were unsatisfactory at [M]/[SO] = 500. The M_w/M_n also observed to be broad, in the range of 1.3-1.6. Collectively these data prove that the polymerization of 3-pentadecyl 2-oxepanone (**1**) to poly-**1** occurs to give a polyester with the expected repeat unit.

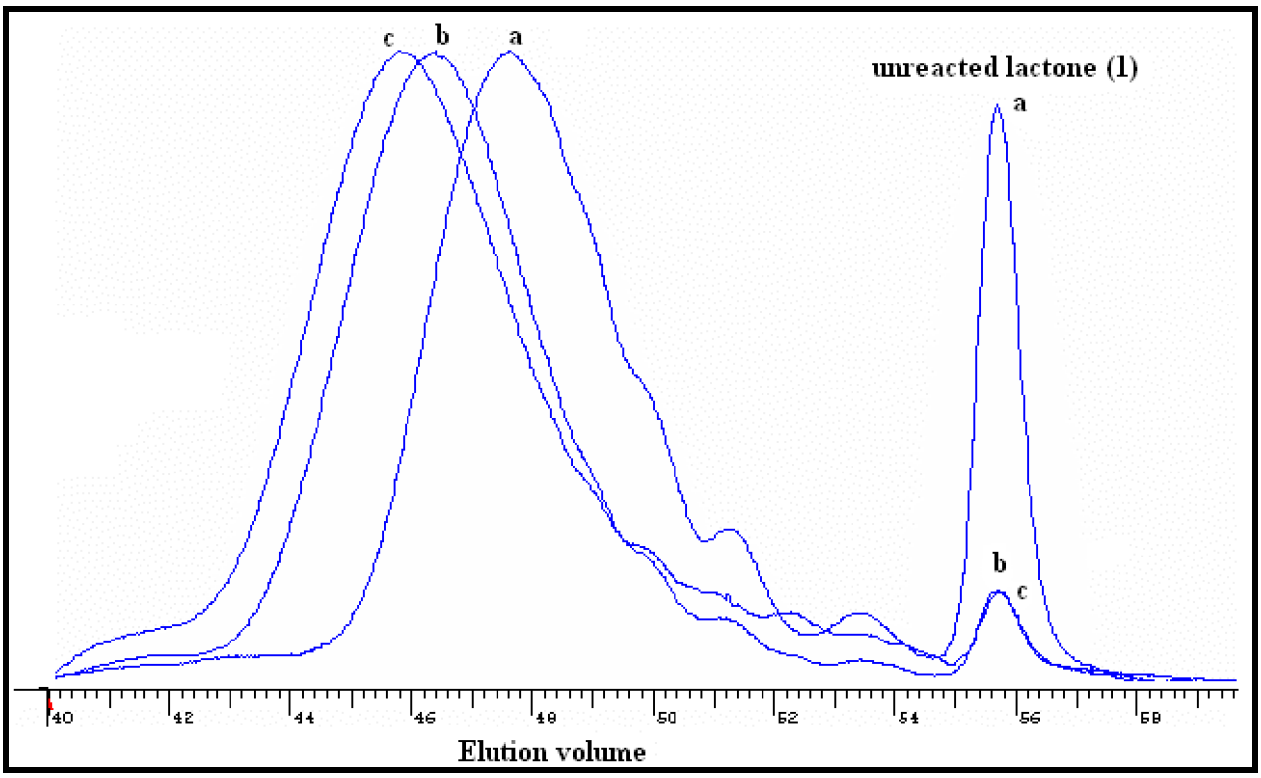


Figure 5.6 GPC of polyester synthesized from 3-pentadecyl 2-oxepanone (1) by ROP (a) 130^{0}C (entry no.1) (b) 150^{0}C (entry no. 2) (c) 170^{0}C (entry no.3) Table 5.1

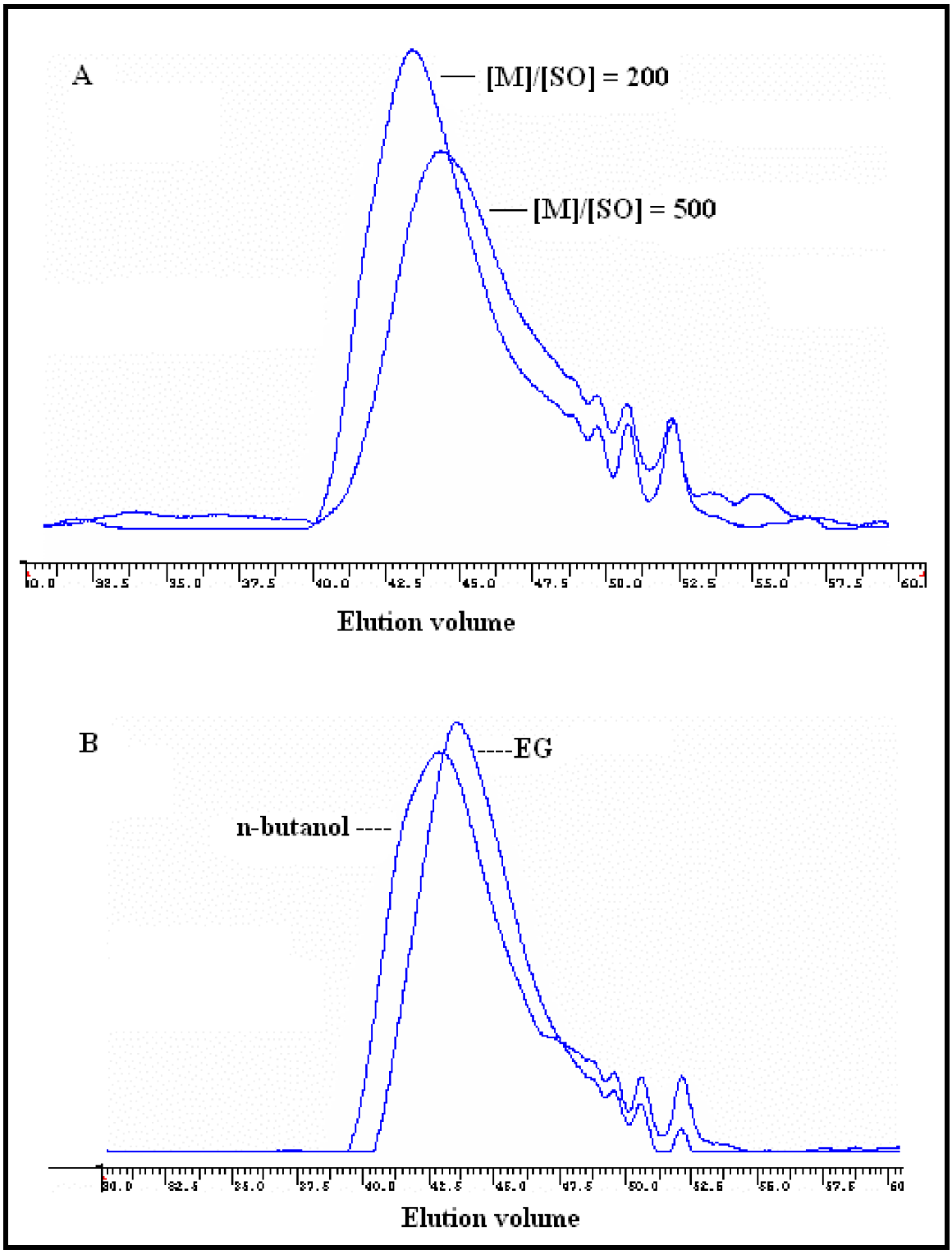


Figure 5.7 GPC of polyester synthesized form 3-pentadecyl 2-oxepanone (1) by ROP using different (A) [M]/[SO] ratios (entries 6 and 7) (B) initiators (entries 8 and 9) Table 5.2

5.4.2 Copolymerization of 3-pentadecyl 2-oxepanone (1) with ε-Caprolactone

Copolymerization of 3-pentadecyl 2-oxepanone with caprolactone was explored to gain better understanding of the relative reactivity of **1** in relation to ε-caprolactone. Copolymerization reactions were performed in bulk using stannous octoate as the initiator and ethylene glycol as co-initiator. As a point of reference, the polymerization of ε-caprolactone was performed under similar conditions. The results are shown in **Table 5.3**

Table 5.3 Homopolymerization of ε-caprolactone

No.	Reaction temperature (^{0}C)	M_n (calc.)	Conversion (%mol)	M^a_n (GPC)	M_w/M_n	T_m (^{0}C)	T_c (^{0}C)
1.	130	4500	90	2300	1.4	50	20
2.	150	4550	91	3220	1.4	52	27
3.	170	4650	93	4130	1.5	55	31

[M]/[SO] = 200, [EG]/[SO] = 4.56, [M]/[EG] = 43.83; [M] = 1.315×10^{-3} mol/L, [SO] = 6.575×10^{-6} mol/L; a-the virgin reaction product was characterized by GPC. M_n (calc.) = [M] (g)/ [I] (mol) x % conversion.

Lactone (**1**) was copolymerized with ε-caprolactone in 80:20 and 60:40 mol% compositions. Effect of reaction temperature and time on the mol% incorporation of lactone (**1**) in copolymer was studied. Poly (ε-caprolactone) could be precipitated from n-hexane; however, the polyester derived from lactone (**1**) could not purified by solvent-nonsolvent precipitation for reasons described in section 5.4.1. Copolyesters obtained were viscous liquids at room temperature. These copolyesters were soluble in hexane and therefore hexane could not be used for precipitation. Due to insolubility of lactone (**1**) in methanol, precipitation in methanol would not cause removal of the unreacted lactone (**1**). Therefore, purification of these copolyesters by precipitation method was not possible. Hence the copolyesters were characterized as obtained, without any further purification.

Copolymerization was performed at 130^{0}C, 150^{0}C and 170^{0}C and time of reaction was 5, 10 and 20 h. The results are shown in **Table 5.4**. Composition of the comonomers in

the polymer was determined using ^{1}H NMR. A typical ^{1}H and ^{13}C NMR spectra of the copolymer is shown in **Figure 5.8**

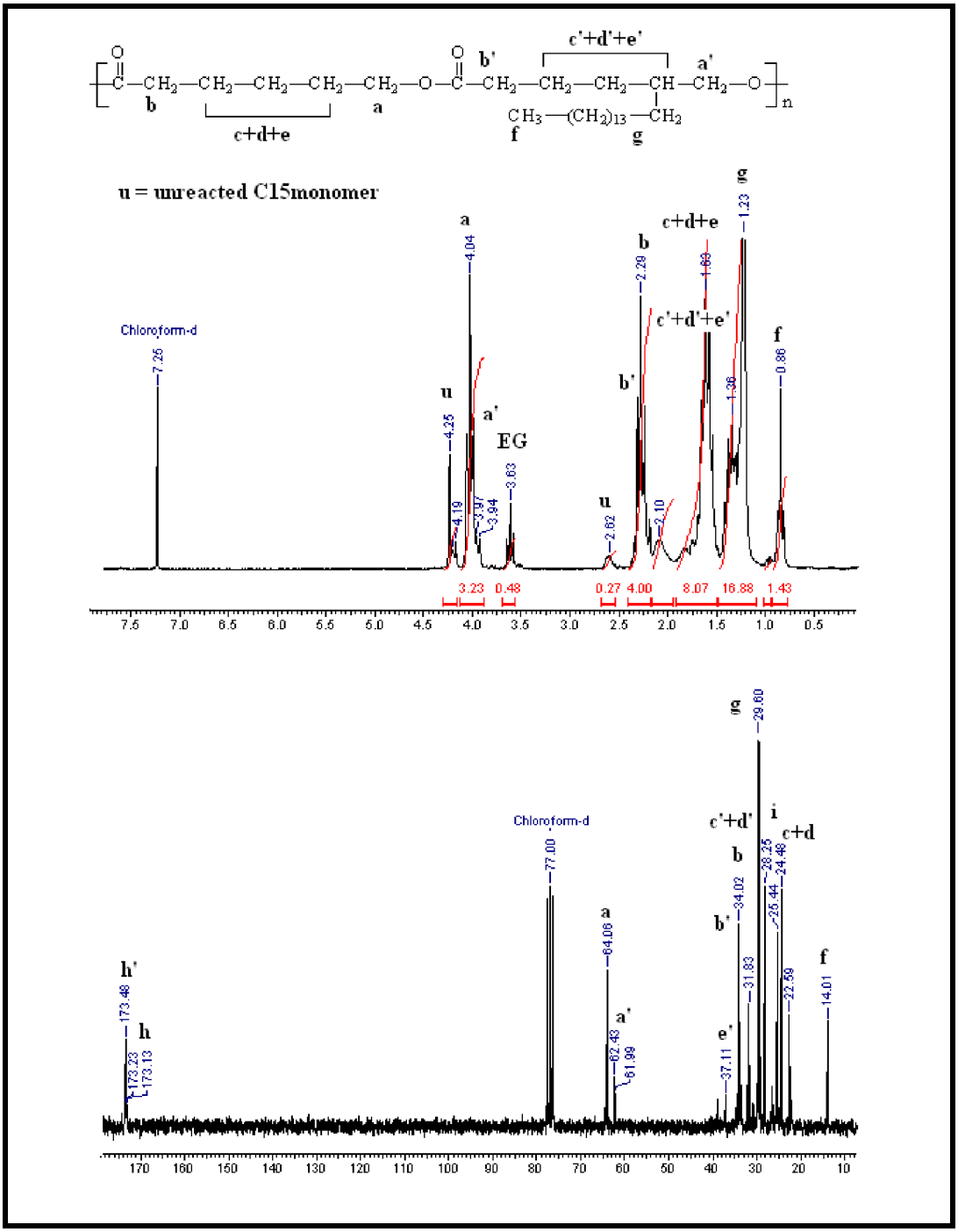


Figure 5.8 ^{1}H and ^{13}C NMR spectrum of copolyester sample (entry no.1) Table 5.4

Copolyester composition of a sample obtained at 130^0C for 5 h using a feed composition of 80:20 mol% (**Figure 5.8**) was calculated as follows:

The total integration of all the protons in the copolyester repeat unit is 36.1.The peak at 0.86 is due to the methyl protons of the alkane side chain. Dividing the intensity due to this peak by total number of methyl protons that is 3 gives the intensity per proton which is 0.48. As the total number of protons in the repeat unit of comonomer (**1**) is 40, the total intensity due to comonomer (**1**) is 19.2 (= 40 x 0.48). The intensity due to caprolactone monomer in the repeat unit is therefore 16.9 (= 36.1-19.2). The peak at 4.25 δ is due to the methylene protons adjacent to the oxygen of the ester group in the unreacted lactone. Homopolymerization studies of ε-caprolactone and lactone (**1**) show that ε-caprolactone has higher reactivity than lactone (**1**). Hence it is expected that ε-caprolactone will react completely and any unreacted monomer would only be lactone (**1**). The peak at 4.25 δ was, therefore, assumed to be due to the methylene protons of the unreacted lactone (**1**). The peak at 4.04 δ is due to the methylene protons in the copolymer. The amount of lactone (**1**) incorporated in the copolymer is calculated from the relative intensities of the peaks at 4.04 δ and 4.25 δ and is 65.3%. Thus, only 65.3% of the lactone (**1**) in the feed is incorporated in the copolymer. The total intensity of protons due to lactone (**1**) incorporated in the copolymer is 12.54 (= 19.2 x 0.653). The total number of protons in caprolactone repeat unit is 10, hence intensity per proton of caprolactone repeat unit M_1 = 16.9/10 = 1.69. Similarly intensity per proton of lactone (**1**) repeat unit M_2 = 12.54/40 = 0.31. Composition of M_1 or M_2 is obtained by dividing M_1 or M_2 by M_1+ M_2.

^{1}H NMR spectra of copolyesters obtained using different reaction conditions are shown in **Figures 5.9** and **5.10**. The copolyesters were also analyzed by GPC (**Figures 5.11** and **5.12**). For comparison, the GPC of poly (ε-caprolactone) is also shown in **Figure 5.13**. Both ^{1}H NMR and GPC show presence of unreacted comonomer (**1**) in the copolymer which could not be removed by precipitation methods. The copolymer compositions indicate that lactone (**1**) has relatively poor reactivity for enchainment during copolymerization.

Table 5.4 Copolymerization of 3-pentadecyl 2-oxepanone with ε-caprolactone at different reaction temperature and time

No.	Reaction temperature (^{0}C)/ time (h)	[CL]:[C15L] (in feed)	[CL]:[C15L] (in copolyester by NMR)	[M]/[SO]	[EG]/[SO]	[M]/[EG]	Conv.[a] (% mol)	M_n (calc.)	M^b_n (GPC)	M_w/M_n
1.	130/5	80:20	84:16	200	6.24	32.05	83	4150	3240	1.3
2.	130/5	60:40	75:25	200	7.92	25.25	83	4150	3500	1.3
3.	150/5	80:20	86:14	200	6.24	32.05	92	4600	5040	1.4
4.	150/5	60:40	76:24	200	7.92	25.25	84	4200	4630	1.4
5.	170/5	80:20	84:16	200	6.24	32.05	84	4200	4880	1.4
6.	170/5	60:40	74:26	200	7.92	25.25	88	4400	5590	1.3
7.	130/10	80:20	90:10	200	6.24	32.05	79	3950	3720	1.4
8.	130/10	60:40	74:26	200	7.92	25.25	85	4250	3500	1.3
9.	130/20	80:20	88:12	200	6.24	32.05	74	3700	3100	1.4
10.	130/20	60:40	72:28	200	7.92	25.25	84	4200	3100	1.4

[M] = 2.5 x 10^{-3} mol/L, [SO] = 1.25 x 10^{-5} mol/L, a – conversions were calculated by taking the mean value of the individual conversions of both the monomers, b-the virgin reaction product was characterized by GPC, M_n (calc.) = [M] (g)/ [I] (mol) x % conversion

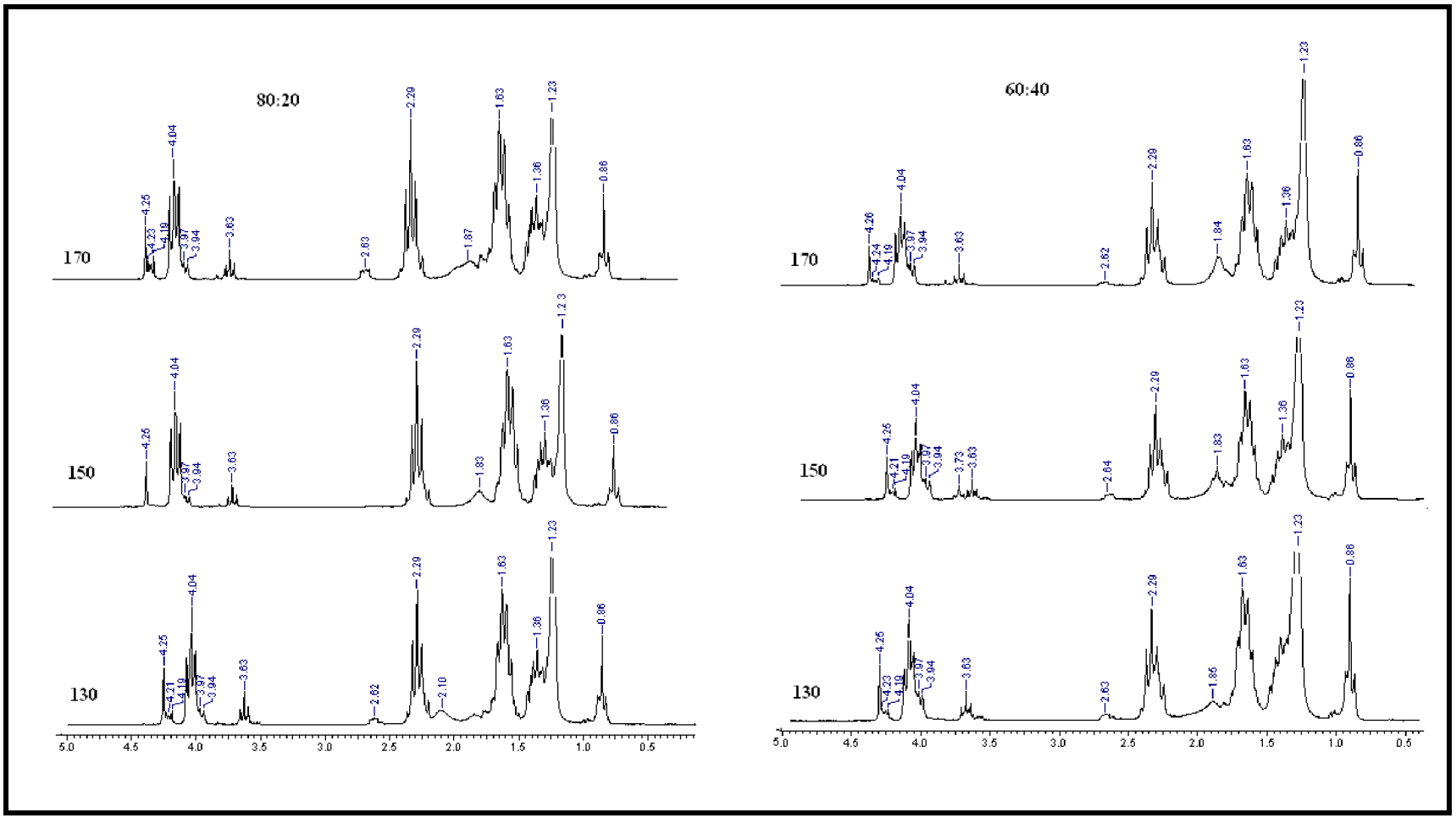


Figure 5.9 ^{1}H NMR spectra of the εCl/Lactone (1) copolyesters initiated with stannous octoate and EG: variation of reaction temperature

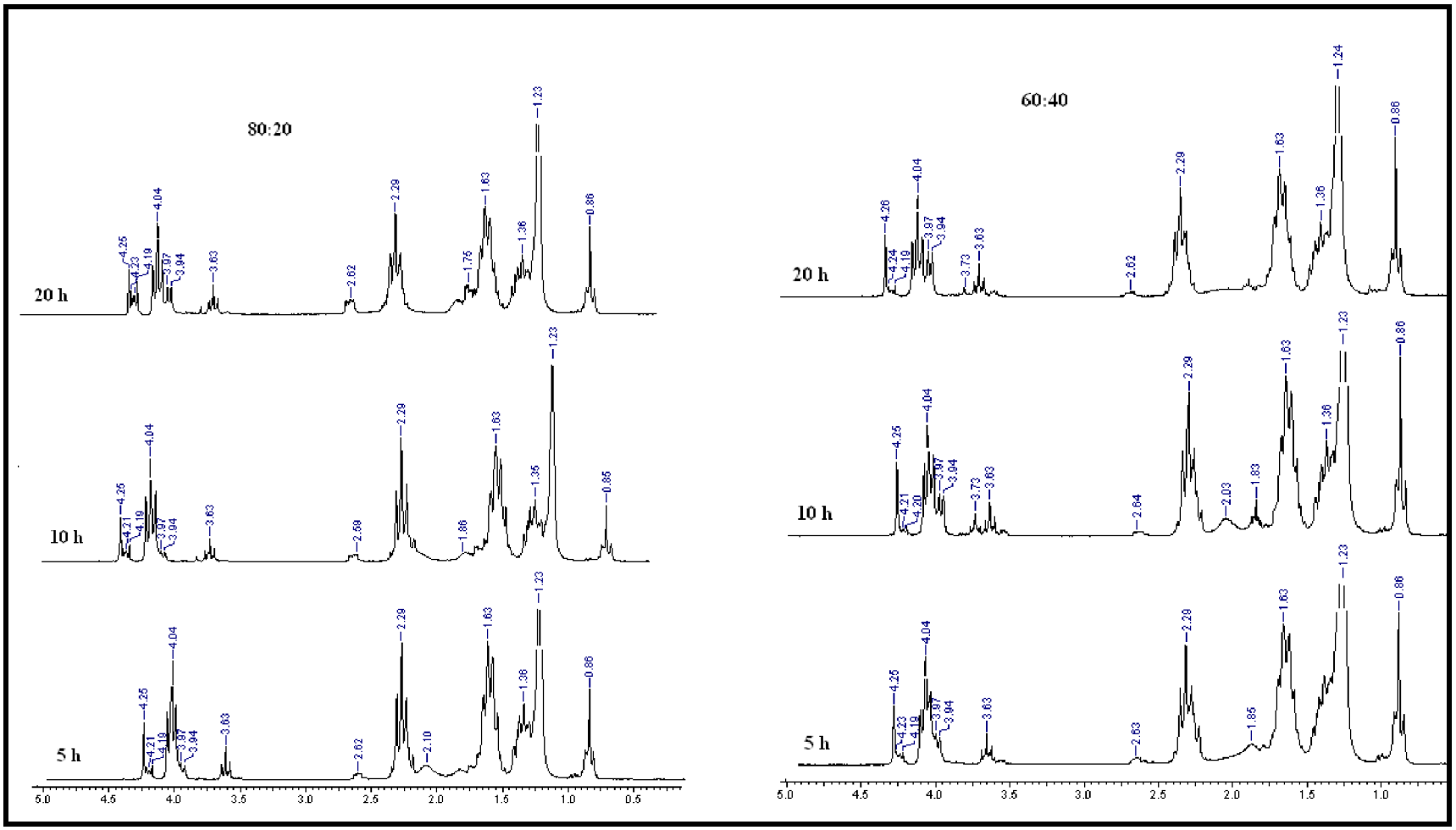


Figure 5.10 ^{1}H NMR spectra of the εCl/Lactone (1) copolyesters initiated with stannous octoate and EG at 130^{0}C: variation of reaction time

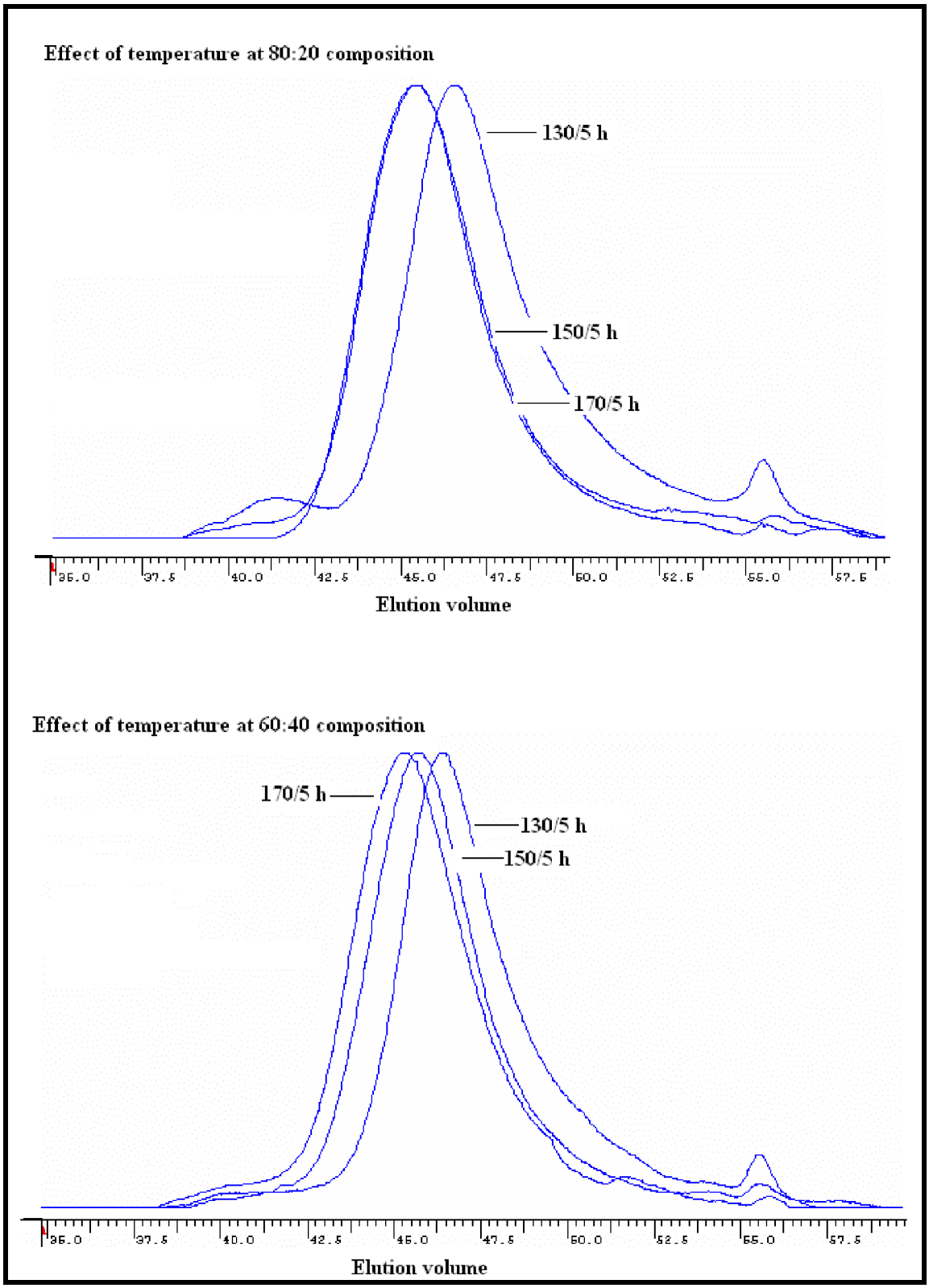


Figure 5.11 GPC of the εCL/Lactone (1) copolyesters synthesized at different reaction temperatures

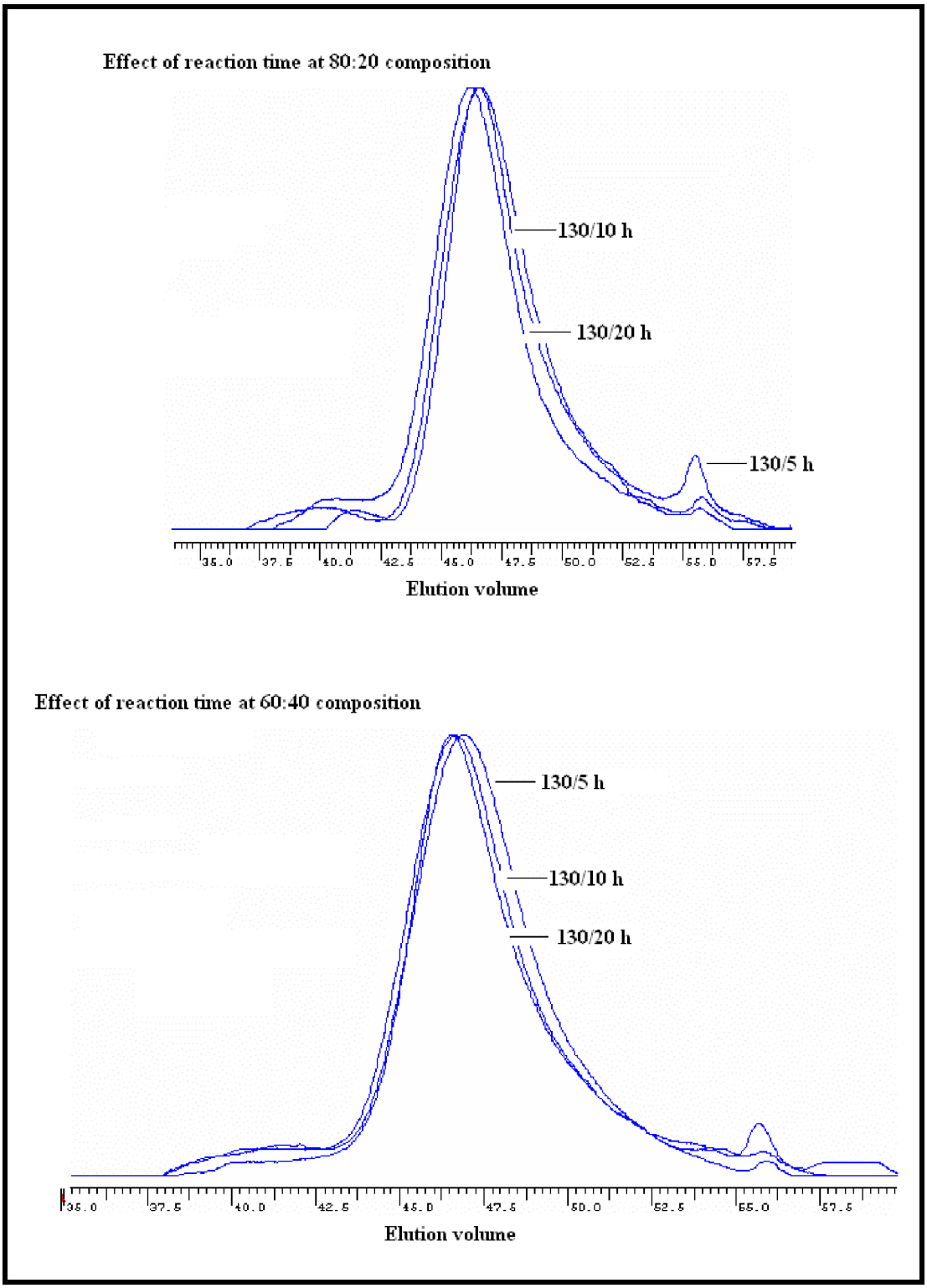


Figure 5.12 GPC of the εCL/Lactone (1) copolyesters synthesized at different reaction time

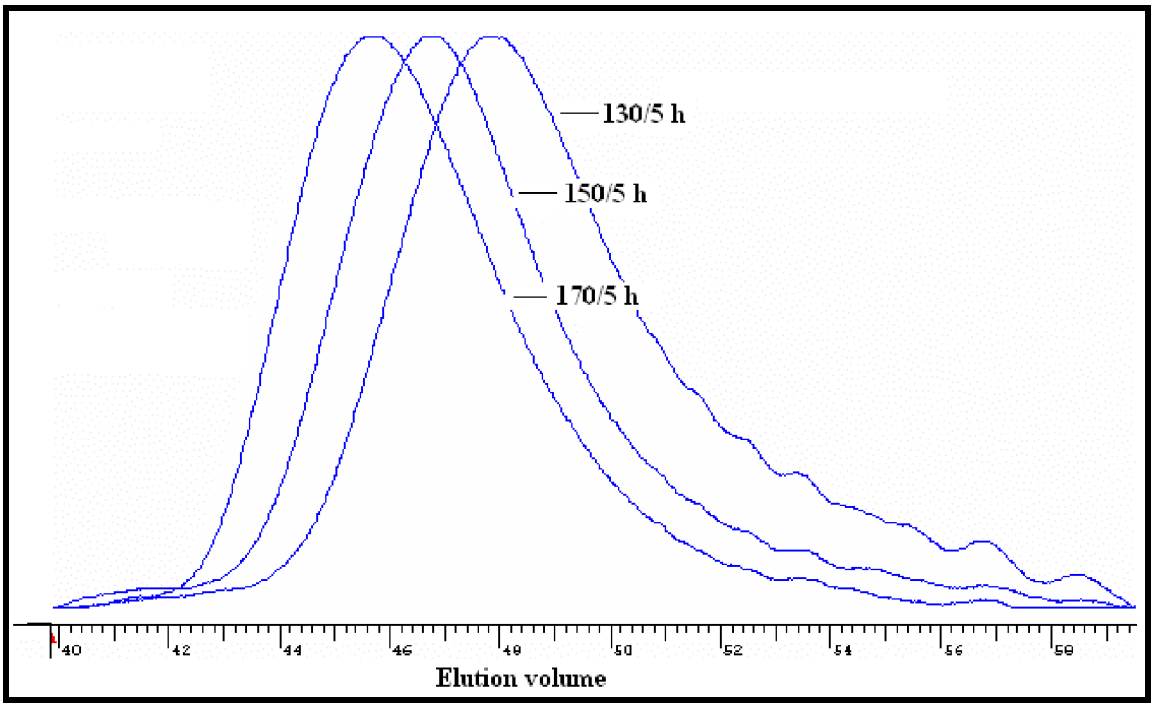


Figure 5.13 GPC of poly (caprolactone) synthesized at different temperatures (entries 1,2,3) Table 5.3

5.4.3 ROP of 2-oxabicyclo [3.2.1] octan-3-one (2)

The monomer was characterized by NMR and IR (**Figures 5.3** and **5.4**). IR spectrum of 2-oxabicyclo [3.2.1] octan-3-one (**2**) shows peaks due to carbonyl stretching and C-H stretching at 1724 cm^{-1} and 2954 cm^{-1} respectively. ^{1}H NMR of (**2**) shows that the **b** isomer is formed exclusively. The ^{1}H and ^{13}C indicate that the carbon adjacent to the oxygen of the ester group is attached to single hydrogen and is adjacent to the bridge head carbon. The peak at 4.83 δ in the proton spectrum is due to a single proton adjacent to the oxygen of the ester group (O-CH). The carbon attached to this proton appearing at 79.9 ppm in DEPT spectrum is different from the other carbons indicating that it is attached to odd number of hydrogen. In the isomer **b'**, the peak at 4.83 δ would correspond to two protons instead of one and would be inverted in the DEPT spectrum. As the NMR spectra match very well with the structure **b** it can be concluded that **b** is formed exclusively. In fact formation of 95:5 mixtures of **b** and **b'** by MCPBA oxidation of the corresponding ketone has been reported[12]. The melting point determined using the melting point apparatus was found to be 49-52^{0}C. The mass spectrum showed a single

peak of high intensity due to sodium adduct of the lactone at m/z value of 149, which gives the molecular weight of lactone as 126 Da. The purity of the lactone was determined to be 99% by GC and 98.8% by HPLC. 2-oxabicyclo [3.2.1] octan-3-one (**2**) was soluble in chloroform, hexane and methanol.

Lactone (**2**) was polymerized using stannous octoate as catalyst and butanol as initiator. The polymerization was conducted at 150^0C and 130^0C for 24 h. The product obtained in the experiment carried out at 150^0C was highly colored as compared to that obtained at 130^0C. The product was recovered by precipitating in hexane. No precipitate was obtained in both the experiments. The removal of hexane yielded an oily liquid which was not analyzed further.

Table 5.5 Ring opening polymerization of 2-oxabicyclo [3.2.1] octan-3-one

No.	Reaction Conditions	[M]/[SO]	[But]/[SO]	[M]/[But]	Yield[a] (%)	M^b_n (calc.)	M_n (GPC)	M_w/M_n
1.	150^0C/ 24 h	200	5.05	39.6	-	5000	-	-
2.	130^0C/24 h	200	5.05	39.6	-	5000	-	-

a- based on polymer recovered by precipitation, b- M_n (calc.) based on [M] g/[I] mol

The absence of polymeric product was confirmed by GPC. Thus, ROP of **2** does not occur under these experimental conditions. According to thermodynamic considerations, ring opening polymerization of seven membered ring is accompanied by an entropy decrease. The only driving force for the conversion of monomer to polymer is the negative enthalpy of polymerization, related to the release of the monomer ring strain[16]. The seven membered cyclic monomers exhibit only moderate ring strain. This results in pronounced reversibility of propagation ($k_p[M] \approx k_d$) leading to high equilibrium monomer concentration ($[M]_{eq}$). Studies on the polymerizability of bridged bicyclic monomers showed that monomers of the bicycle [3.2.1] octane group underwent polymerization with varying facility. It is worth noting that the ring opening polymerization of the corresponding lactam, namely 2-azabicyclo [3.2.1] octan-3-one to give the corresponding polyamide by heating with water has been reported[17].

5.5 Conclusions

The ring opening polymerization of 3-pentadecyl 2-oxepanone (**1**), obtained form cardanol and 2-oxabicyclo [3.2.1] octan-3-one (**2**) was studied and it was demonstrated that **1** can be polymerized by stannous octoate as initiator and EG or butanol as co-initiator. Low molecular weights in the range of 4000-5000 were prepared. However, **2** did not polymerize in the presence of stannous octoate indicating the unfavorable enthalpy of polymerization.

Copolymerization of **1** with ε-caprolactone was studied at 80:20 and 60:40 feed compositions. Quantitative incorporation of lactone (**1**) was not obtained in any of the copolyesters. These results confirm that the substituted lactone **1** polymerizes slowly as compared to unsubstituted monomer ε-caprolactone. The difference in reactivities of the two lactones in the presence of stannous octoate resulted in the non-quantitative incorporation of lactone (**1**) in the copolyester.

Most importantly in this work, we have demonstrated the simple conversion of a naturally occurring cardanol derivative to a monomer **1** that can be polymerized to yield a potentially useful material. On account of the long alkyl chain substitution, this monomer can be copolymerized with other lactones or polymers to prepare polyesters containing long chain branches.

5.6 References

1. R.D.Lundberg, E.F.Cox, "*Lactones, in, Ring opening polymerization*", edited by K.C. Frisch, S.L. Reegen , Marcel Dekker, New York, 247 (1969)
2. A.Lofgren, A.C. Albertsson, Ph.Dubois, R.Jerome, *J.Macromol.Sci. Rev.Macromol. Chem.Phys.* **C35**, 379 (1995)
3. (a) G.L.Borde, J.V. Koleske, *J.Macromol.Sci.Chem.* **A6**, 1109 (1972) (b) D. Mecerreyes, R.Jerome, *Macromol.Chem. Phys.* **200**, 2581 (1999) (c) H.R.Kricheldorf, I.Kreiser-Saunders, *Macromol.Symp.* **103**, 85 (1996) (d) K.Stridsberg, M.Ryner, A.C.Albertsson, *Adv.Polym.Sci.* **157**, 41 (2002) (e) A.Duda, S.Penczek, *Macromolecules* **23**, 1636 (1990) (f) P.Dubois, N.Ropson, R.Jerome, P.Teyssie,

Macromolecules **29**, 1965 (1996)

4. G.Rafler, J.Dahlmann, *Acta Polym*. **43**, 91 (1992)
5. A.Kowalski, A.Duda, S.Penczek, *Macomolecules* **33**, 689 (2000)
6. H.R.Kricheldorf, I.Kreiser-Saunders, A.Stricker, *Macromolecules* **33**, 702 (2000)
7. (a) S.Penczek, A.Duda, *Macromol.Symp*. **107**, 1 (1996) (b) H.R.Kricheldorf, A.Serra, *Polymer Bull*. **14**, 497 (1985)
8. (a) D. Mecerreyes, R.D.Miller, J.L.Hedrick, C. Detrembleur, R. Jerome, *J.Polym.Sci.,Part A: Polym.Chem*. **38**, 870 (2000) (b) C. Detrembleur, M.Mazza, O.Halleux, P.Lecomte, D. Mecerreyes, J.L.Hedrick, R. Jerome, *Macromolecules* **33**, 14 (2000)
9. X.Lou, C.Detrembleur, R.Jerome, *Macromol.Rapid.Commun*. **24**, 161 (2003)
10. D.Tian, O.Halleux, P.Dubois, R.Jerome, R.Sobry, G.van den Bossche, *Macromolecule*, **31**, 924 (1998)
11. G.J. ten Brink, I.W.C.E. Arends, R.A. Sheldon, *Chemical Reviews* **104(9)**, 4105 (2004)
12. G.R.Krow, *Tetrahedron*, **37(16)**, 2697 (1981)
13. S.C.Sethi, B.C.Subbarao, *Ind.J.Chem*. **2**, 178 (1964)
14. C.V.Avadhani, P.P.Wadgaonkar,S. Sivaram, *US Patent 6255439 B1* (2001) to General Electric Company
15. a) G. Piancatelli, A. Scettri, M. D'Auria, *Synthesis* **4**, 245 (1982) (b) E. J Corey, *Tet. Lett*. **31**, 2647 (1975)
16. A.Duda, A Kowalski, J Libiszowski, S Penczek, *Macromol.Symp*. **224**, 71 (2005)
17. H.K.Hall Jr., *J.Am.Chem.Soc*. **80**, 6412 (1958)

Chapter 6: Transesterification of poly (ethylene terephthalate) s to poly (butylene terephthalate) s

6.1 Introduction

Industrialization and urbanization has resulted in large scale generation of plastic waste that is disposed off by landfill, incineration, composting, and recycling. Poly (ethylene terephthalate) (PET) is one of the most widely used consumer packaging material that is currently being recycled. PET waste is available in the form of fibers, films, bottles and off-specification chips. The disposal of large volumes of waste PET by economically viable recycling process has elicited considerable interest in the literature.

Recycling is a process by which materials are separated from waste destined for disposal and remanufactured into usable materials. There are two main approaches to plastics recycling[1] (a) physical recycling which involves recycling by physical and thermal reprocessing of waste plastics singly or in combination with other materials into secondary products and (b) chemical recycling which involves regeneration of monomers/oligomers by depolymerization of off-spec products and in-plant scrap (useful for condensation polymers) and conversion of plastic-rich waste by pyrolysis to oil-type fraction (useful for addition polymers). Two main methods of recycling waste PET[2] are: (1) reaction of polyester wastes with polyols or polycarboxylic acids to give new polyester oligomers[3-4] or (2) depolymerization of PET waste to the starting raw materials and their reuse for the production of polyester[5-16]

In all the methods reported so far, the objective was to convert waste PET to polyester raw materials (PTA, DMT and EG) or to PET for reuse. From the point of view of waste load on the environment, it would be desirable to convert waste PET into another product which has a longer life cycle in the environment. This way a short life cycle product such as PET would get converted to a long life cycle product, thus minimizing the environmental impact of waste generation.

Polyesters derived from 1,4-butanediol (BD) and 1,4-cyclohexane dimethanol (CHDM) are engineering thermoplastics used in such long life cycle applications. Thus, it

would be advantageous to convert waste PET to poly (butylene terephathalate)s (PBT), poly (1,4-cyclohexane dimethylene terephthalate)s (PCHDMT) and poly(1,6-hexamethylene terephthalate)s by direct transesterification of PET with BD, CHDM, and 1,6-hexanediol.

An examination of the prior literature shows that examples of such approaches to waste recycling are rare. Only two patents describing the direct transesterification of PET to PBT using BD[17-18] have been reported. This chapter reports the results of an extensive study to delineate the scope of such transesterification reactions for the valorization of PET waste.

6.2 Experimental

6.2.1 Materials

Shredded flakes of post-consumer PET bottles were supplied by M/s. Futura Polymers, Chennai, India. Antimony trioxide (Sb_2O_3), 1,4-butanediol (BD), 1,4-cyclohexanedimethanol (CHDM), 1,6-hexanediol (HD), and titanium (IV) isopropoxide ($Ti(iPrO)_4$) were obtained from Sigma-Aldrich Inc., USA. Phenol, 1,1,2,2-tetrachloroethane, benzyl alcohol, phenolphthalein, phenol red and potassium hydrogen phthalate (KHP) were obtained from SD fine Chemicals, Mumbai, India.

6.2.2 Reagents and purification

Shredded flakes of post-consumer PET bottles were used as received. Analysis of the PET flakes is shown in **Table 6.1**. BD was distilled and stored over 4Å molecular sieves. CHDM and HD were dried under vacuum prior to use. Antimony trioxide was used as received. Titanium (IV) isopropoxide was distilled under vacuum and used as a solution in dry toluene. Phenol and 1,1,2,2-tetrachloroethane were freshly distilled before use. Reagents like benzyl alcohol, phenolphthalein, and phenol red were used as received. KHP was dried in oven prior to use. 4-hydroxy butyl benzoate (4-HBB) used as model compound for studying THF formation during transesterification reaction was prepared according to reported procedure[19].

^{1}H NMR of 4-HBB (7.27 δ, $CDCl_3$): 1.6-1.9 (4H, m, CH_2), 2.15 (1H, OH), 3.7 (2H, t, CH_2OH), 4.3 (2H, t, -O-CH_2), 7.4-7.6 (3H, m, aromatic protons), 8-8.05 (2H, m, aromatic protons) (**Figure 6.1**)

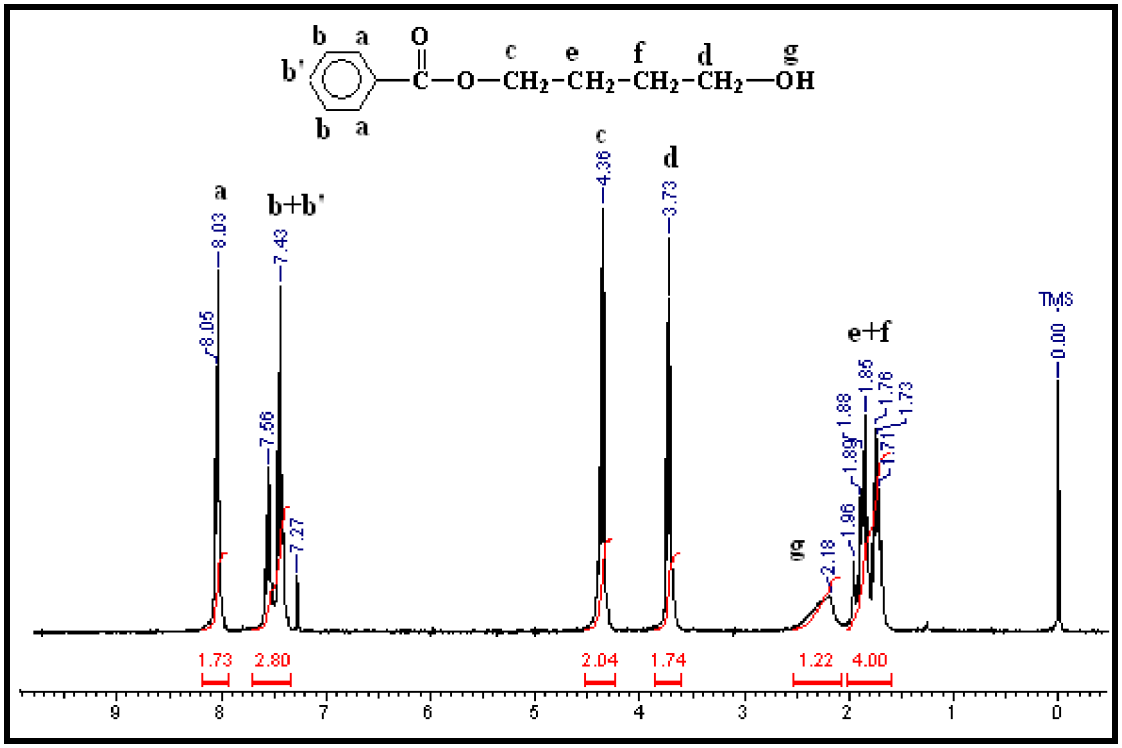


Figure 6.1 ^{1}**H NMR of 4-hydroxy butyl benzoate (4-HBB)**

Table 6.1 Analysis of PET post-consumer bottle waste

Form	Flakes
Color	Blue, Green and Yellow colored flakes
$^a\eta_{inh}$ (dL / g)	0.7
Acid No. (eq/10^6 g)	32
Sb content (ppm)	50

a – Viscosity was measured using 60: 40 mixture of phenol+TCE at 25^0C

6.2.3 Synthetic Methods

The effect of reaction parameters was studied by carrying out experiments under different reaction conditions. The copolyesters obtained were characterized by NMR, viscosity measurements, acid value and DSC.

Effect of reflux time

PET flakes (5 g, 0.026 mol), 1,4-butanediol (5.85 g, 0.065 mol) and antimony trioxide catalyst (0.0025g, 0.05 wt% based on PET) were taken in a two-necked round-bottom flask equipped with a reflux condenser. Molar ratio of PET to BD was 1:2.5. The reaction mixture was heated at 230^0C for varying lengths of time from 1 h to 5 h. Thereafter, the reflux condenser was replaced with an air condenser fitted with a spiral trap, which was cooled in liquid nitrogen to collect the distillate. The pressure inside the flask was decreased to 100 mbar and the temperature was simultaneously raised to 250^oC. The pressure was further gradually reduced from 100 to 1 mbar over a period of 40 to 50 min at 250^oC. The excess butanediol, ethylene glycol and THF distilled out and the polycondensation was further continued at 250^0C and 0.05-0.03 mbar vacuum for 1 h. When no more distillate was collected, the flask was cooled under vacuum and the resulting polyester was isolated. A similar series of experiments were carried out without catalyst.

^{1}H NMR of the transesterified product ($CDCl_3/CF_3COOH$) δ: 2.02 (4H, s, CH_2), 4.4 (4H, s, OCH_2), 8.12 (4H, s, aromatic protons)

Effect of feed (PET: BD) ratio

PET flakes (5 g, 0.026 mol) and varying amounts of 1,4-butanediol (5.85 g, 0.065 mol; 11.7 g, 0.13 mol; 23.4 g, 0.26 mol) corresponding to a PET to BD molar ratio of 1:2.5, 1:5 and 1:10 respectively, were taken in a two-necked round bottom flask equipped with a puckered column fitted to a water condenser and a receiver flask to collect the THF formed during the reaction. The reaction mixture was heated at 230^0C for 4 h. After 4 h of refluxing, the column and water condenser were replaced with an air condenser fitted to a spiral trap, which was cooled in liquid nitrogen to collect the distillate. The pressure inside the flask was reduced to 100 mbar and the temperature was simultaneously raised

to 250^{0}C. The pressure was further gradually decreased from 100 to 1 mbar over a period of 40 to 50 min at 250^{o}C. The excess butanediol, ethylene glycol and THF distilled out and the polycondensation was further continued at 250^{0}C and 0.05-0.03 mbar vacuum for 1 h. The flask was cooled under vacuum and the resulting polyester was isolated. A similar series of experiments were carried out to study the effect of the feed ratios in presence of 0.0025 g (0.05 wt% based on PET) of antimony trioxide and titanium isopropoxide catalysts.

Effect of catalyst

PET flakes (5 g, 0.026 mol), 1,4-butanediol (5.85 g, 0.065 mol) and catalyst (0.0025 g, 0.05 wt% of PET) were heated at 230^{0}C for 4 h in a two-necked round bottom flask equipped with a puckered column fitted to a water condenser and a receiver flask to collect the THF formed during the reaction. Molar ratio of PET to BD was 1:2.5. The catalysts studied were antimony trioxide and titanium (IV) isopropoxide. After 4 h, an air condenser with a spiral trap was fitted to the reaction flask. The trap was cooled in liquid nitrogen to collect the distillate. The pressure inside the flask was reduced to 100 mbar and the temperature was simultaneously raised to 250^{0}C. The pressure was further gradually decreased from 100 to 1 mbar over a period of 40 to 50 min at 250^{o}C. The excess butanediol, ethylene glycol and THF distilled out and the polycondensation was further continued at 250^{0}C and 0.05-0.03 mbar vacuum for 1 h. The flask was cooled under vacuum and the resulting polyester was isolated.

Effect of dilution of carboxyl groups with BD on THF formation

To understand the effect of dilution of the carboxyl groups with 1,4-butanediol, model reactions were carried out in the presence and absence of antimony trioxide catalyst. Benzoic acid (1g, 0.0082 mol) was heated with different amounts of BD (5.9 g, 0.066 mol; 11.75 g, 0.13 mol; 23.4 g, 0.26 mol), and antimony trioxide (0.0025 g) at 230^{0}C for 2 h in a two-necked round bottom flask equipped with a puckered column fitted to a water condenser and a receiver flask to collect the THF formed during the process. Similar experiments were carried out in the absence of antimony trioxide catalyst.

Effect of 4-HBB concentration on THF formation

Transesterification of PET with BD results in formation of polyester chains with hydroxy butyl end groups which can either undergo intermolecular or intramolecular reactions. Intramolecular reactions lead to THF formation, which is unaffected by dilution. To verify this hypothesis, 4-HBB was synthesized[19] and effect of its concentration was studied. Two different concentrations of 4-HBB (1.58 g, 0.0081 mol and 3.14 g, 0.0162 mol) were heated with BD (5.9 g, 0.065 mol) and antimony trioxide catalyst (0.0025 g) at 230^0C for 2 h in a two-necked round bottom flask equipped with a puckered column fitted to a water condenser and a receiver flask to collect the THF formed during the process.

Effect of dilution on THF formation in the presence of 4-HBB

To understand whether dilution has any effect on the THF formation in the presence of 4-HBB, it was refluxed with different amounts of BD in the presence and absence of catalyst. 4-HBB (1.57 g, 0.0081 mol) was heated with two different amounts of BD (5.9 g, 0.066 mol and 11.7 g, 0.13 mol) and antimony trioxide catalyst (0.0025 g) at 230^0C for 2 h in a two-necked round bottom flask equipped with a puckered column fitted to a water condenser and a receiver flask to collect the THF formed during the process. Similar set of experiments were repeated in the absence of antimony trioxide.

Effect of diphenyl ether as a diluent

Two sets of experiments were carried out, in presence as well as absence of titanium isopropoxide catalyst, to understand the effect of diluent diphenyl ether on the transesterification reaction. In the first set, effect of diluent was studied in the absence of titanium isopropoxide catalyst. PET flakes (5 g, 0.026 mol), 1,4-butanediol (5.85 g, 0.065 mol) and diphenyl ether (17.55 g), were heated at 230^0C for 4 h in a two-necked round bottom flask equipped with a puckered column fitted to a water condenser and a receiver flask to collect the THF formed during the reaction. Molar ratio of 1:2.5 of PET to BD was used. Total volume of liquid in the flask (23.4 ml) was equal to the total volume when BD was taken ten times in excess corresponding to a PET to BD molar ratio of 1:10. After refluxing for 4 h, an air condenser fitted to a coiled trap was used to collect the distillate. A vacuum of 100 mbar was applied and simultaneously the flask was heated to 250^0C. The vacuum was gradually increased from 100 to 1 mbar over a period

of 40-50 min at 250^{0}C. The excess butanediol, diphenyl ether, ethylene glycol, and THF distilled out and the polycondensation was further continued at 250^{0}C and 0.05-0.03 mbar vacuum for 1 h. The flask was cooled under vacuum and the resulting polyester was isolated. A similar experiment was carried out without diluent.

In the second set, effect of diluent was studied in the presence of titanium isopropoxide catalyst. PET flakes (5 g, 0.026 mol), 1,4-butanediol (5.85 g, 0.065 mol), diphenyl ether (17.55 g), and titanium (IV) isopropoxide (0.025 g, 0.5 wt% of PET) were heated at 230^{0}C for 4 h in a two-necked round bottom flask equipped with a puckered column fitted to a water condenser and a receiver flask to collect the THF formed during the reaction. Molar ratio of PET to BD was 1:2.5. After refluxing for 4 h, an air condenser fitted to a coiled trap was used to collect the distillate. A vacuum of 100 mbar was applied and simultaneously the flask was heated to 250^{0}C. The vacuum was gradually increased from 100 to 1 mbar over a period of 40-50 min at 250^{0}C. The excess butanediol, diphenyl ether, ethylene glycol, and THF distilled out and the polycondensation was further continued at 250^{0}C and 0.05-0.03 mbar vacuum for 1 h. The flask was cooled under vacuum and the resulting polyester was isolated. A similar experiment was carried out without diluent.

Transesterification with other diols

Transesterification of PET with diols such as 1,4-cyclohexanedimethanol and 1,6-hexanediol was carried out at higher reaction temperatures (280-300^{o}C) and longer reaction times for higher conversions due to the higher melting nature of these diols.

PET flakes (5 g, 0.026 mol), CHDM (15 g, 0.104 mol) and antimony trioxide (0.025 g, 0.5 wt % of PET) were heated at 280^{0}C for 5 h under nitrogen flow in a two-necked round bottom flask equipped with a nitrogen inlet and a reflux condenser. After heating for 5 h, the reflux condenser was replaced with an air condenser and a coiled trap which was cooled to collect the distillate. The pressure inside the flask was reduced to 100 mm of Hg and was further gradually decreased to 1 mm of Hg in 2.5 h at 280^{0}C. The excess CHDM and ethylene glycol distilled out and the polycondensation was further continued at 280^{0}C and 1mm of Hg vacuum for 2 h and at 300^{0}C and 1mm of Hg vacuum for 1 h. The flask was cooled under vacuum and the resulting polyester was isolated.

^{1}H NMR of PET transesterified with CHDM ($CDCl_3/CF_3COOH$)) δ: 1.2-2 (10H, m, cycloaliphatic protons), 4.3-4.4 (4H, m, OCH_2), 8.12 (4H, s, aromatic protons)

In a similar way PET flakes (5 g, 0.026 mol), HD (12.272 g, 0.104 mol) and antimony trioxide (0.025 g, 0.5 wt % of PET) were heated at 280^{0}C for 5 h under nitrogen flow in a two-necked round bottom flask equipped with a nitrogen inlet and a reflux condenser. After heating for 5 h, the reflux condenser was replaced with an air condenser and a coiled trap which was cooled to collect the distillate. The pressure inside the flask was reduced to 100 mm of Hg and was further gradually decreased to 1 mm of Hg in 100 min at 280^{0}C. The excess HD and ethylene glycol distilled out and the polycondensation was further continued at 280^{0}C and 1mm of Hg vacuum for 2 h. The flask was cooled under vacuum and the resulting polyester was isolated.

^{1}H NMR of PET transesterified with HD ($CDCl_3/CF_3COOH$)) δ: 1.6 (4H, m, CH_2), 1.9 (4H, m, CH_2), 4.4 (4H, t, OCH_2), 8.12 (4H, s, aromatic protons)

6.3 Analysis

6.3.1 Determination of acid value of copoly (ester) s

Acid value of the copoly (ester) s was determined by Pohl's method[20]. This procedure involves dissolving the polymer in benzyl alcohol rapidly at temperature above 200^{0}C followed by quickly mixing the solution with chloroform and titrating against NaOH using phenol red as indicator. It was found that hot benzyl alcohol solution of PET could be poured into chloroform to yield either a cold metastable solution or a fine suspension which can be satisfactorily titrated with alkali. Nitrobenzene, 1-methyl naphthalene and tetramethylene sulfone in addition to benzyl alcohol can also act as "high temperature solvents" for this polymer at temperatures 175-210^{0}C. Benzyl alcohol was chosen because of its preferred odor, stability with base and low relative toxicity. The method involves the following steps:

(a) Preparation and standardization of HCl and NaOH solutions

0.1 N Sodium hydroxide solution was prepared by weighing 1.0303 g of NaOH in a 250 mL volumetric flask and diluting it up to the mark with distilled water. Similarly 0.1 N

ethanolic sodium hydroxide solution was prepared by dissolving 1.0544 g of NaOH in ethanol in a 250 mL volumetric flask. 0.1N Hydrochloric acid solution was prepared by dissolving 2.1 mL of 12 N HCl solution in distilled water in a 250 mL volumetric flask. A 10 mL stock solution of phenolphthalein and phenol red indicators in ethanol was prepared by dissolving 12.1 mg of phenolphthalein and 11.5 mg of phenol red in ethanol in a 10 ml volumetric flask.

0.1 N Sodium hydroxide solution was standardized by using potassium hydrogen phthalate (KHP). KHP was dried overnight in the oven prior to use. Solutions of KHP (0.1 g) in distilled water were prepared and titrated against sodium hydroxide solution using phenolphthalein as indicator. The titration readings were used to calculate the exact normality of NaOH solution which was found to be 0.1006 N. This standardized sodium hydroxide solution was used to determine the exact normality of HCl solution. The exact normality of HCl was determined to be 0.0965 N using the relation $N_1V_1 = N_2V_2$.

The exact normality of the ethanolic sodium hydroxide solution was then determined as follows: 1 mL of standardized HCl solution each was taken in three different flasks. 2 mL of distilled water and one drop of phenol red indicator were added in each of these flasks and titrated against ethanolic NaOH solution till solution turned from colorless to pale pink. 0.913 mL was required for neutralization. Exact normality of ethanolic NaOH solution was calculated to be 0.1057 N.

(b) Determination of acid value of PET

The acid value of PET was determined as follows: Benzyl alcohol and chloroform (40 mL each) were taken in a conical flask and 5 drops of phenol red indicator was added. This solution was titrated against 0.1057 N ethanolic NaOH solution. This reading is called the blank reading and is used in the calculations of acid value of polyester. About 1 g of finely ground polyester was weighed in a test tube. 40 mL of benzyl alcohol was added to it. The solution was stirred or shaken mechanically and then immersed in an oil bath heated to 205-210^{0}C. The solution was heated with stirring for 10 min in the oil bath. After 10 min, the test tube was quickly lifted out of the oil bath and immediately lowered into a beaker containing cold water (20-30^{0}C) after wiping off the oil of the test tube, to quench the sample for 6-7 seconds. After quenching, the solution was poured into

a 250 mL conical flask containing 40 mL chloroform. The chloroform acts as a liquefier and dispersant and prevents formation of thick gel. 5 mL of benzyl alcohol was again added to the test tube and heated at 210^0C for 1 min. This was added to the rest of the sample and stirred. 5 drops of phenol red indicator was added and titrated against 0.1057 N ethanolic NaOH solution. The solution was vigorously stirred during titration. The titration was carried out till the first discernible pink color throughout persists for 10 seconds. Amount of ethanolic NaOH required for titration was recorded and acid value was calculated as follows:

Acid Value = (Sample-Blank) mL x 10^{-3} L x Normality of NaOH/ wt of sample (g) x 10^6

The acid value is usually expressed in equivalents per million gram =AV equiv per 10^6 g.

6.3.2 Quantification of tetrahydrofuran by gas chromatography

THF formed during the reactions was estimated by Perkin Elmer Autosystem XL Gas Chromatograph using capillary column under the following conditions:

Column specifications: BP-20 (polar) capillary column made of fused silica material with a bonded poly (ethylene glycol) stationary phase (length = 25 m, I.D. = 0.22mm, O.D. = 0.33 mm, film thickness (stationary phase) = 0.25 micron)

Carrier gas: Nitrogen, Inlet pressure: 7 psi, Flow rate through the column: 0.3 mL/min. Detector: FID, Flow rate for hydrogen: 45 mL/min, Flow rate for air: 450 mL/min. Oven programme: 50^0C (5 min), 50^0C $\rightarrow 220^0$C at a heating rate of 45^0C/min, 220^0C (6 min), Injector: 250^0C, Detector: 280^0C.

Under these conditions, the retention times for THF and phenol were 4.04 and 13.3 min respectively. In order to estimate accurately the amount of THF formed during the reaction, a calibration curve for THF using phenol as the internal standard (IS) was obtained as follows: A stock solution of phenol was prepared by dissolving 2.5030 g of phenol in 25 mL methanol. From this stock solution 1 mL was taken for the preparation of solution. A stock solution of THF was prepared by dissolving 1.0067 g in 10 mL methanol. From this stock solution 0.2, 0.4, 0.6, 0.8 and 1 mL solution were pipetted out in separate 10 mL volumetric flasks. 1 mL of internal standard (phenol) was added into each of these volumetric flasks and further diluted with methanol up to the mark. 0.5 μL

of each of these solutions was injected into the column. A minimum of 3 injections was used to confirm the reproducibility in the analysis. Area ratios of THF to phenol were calculated for each injection and all concentrations from the chromatograms. The area ratios of THF to phenol were plotted against their corresponding mole ratios. The slope of the curve was 2.14 and was used to calculate the exact quantity of THF as follows: Mole Ratio (MR) = Area Ratio (AR) x Response Factor (RF). Moles of THF were given as Moles of IS x AR x RF

6.3.3 Solution NMR measurements

^{1}H NMR spectra were recorded on a Brucker spectrometer at 25 ± 1^{0}C, operating at 200 MHz. About 20 mg of finely powdered polyester was dissolved in 0.5 mL of solvent [$CDCl_3$ + trifluoroacetic acid (4:1 v/v ratio)] for ^{1}H NMR spectra. The spectra were internally referenced to tetramethyl silane.

6.3.4 Viscosity measurements

Inherent viscosities of 0.5% (w/v) solutions of copoly (ester)s in phenol/1,1',2,2'-tetrachloroethane (60:40 w/w) were determined in an automated Schott Gerate AVS 24 viscometer, using an Ubbelohde suspended level viscometer at 25 ± 1^{0}C. Solvent for dissolving the copoly (ester) s was prepared by thoroughly mixing phenol and 1,1',2,2'-tetrachloroethane in the ratio of 3:2 by weight. About 50 mg of finely powdered polyesters were weighed in 10 mL volumetric flasks and dissolved in the solvent. Flow times for solvent and samples were recorded. Inherent viscosity was calculated and expressed in dL/g.

6.3.5 Thermal analysis

The calorimetric measurements were carried out using Perkin Elmer DSC-7. Approximately 8-9 mg of finely powdered polyester samples sealed in aluminium pans of 50 µL capacity were heated from 0^{0}C to 300^{0}C at 10^{0}C/min, held for 1 min at 300^{0}C and then rapidly cooled at 100^{0}C/min in a draught of nitrogen. The melting temperature and heat of fusion were obtained from heating thermogram.

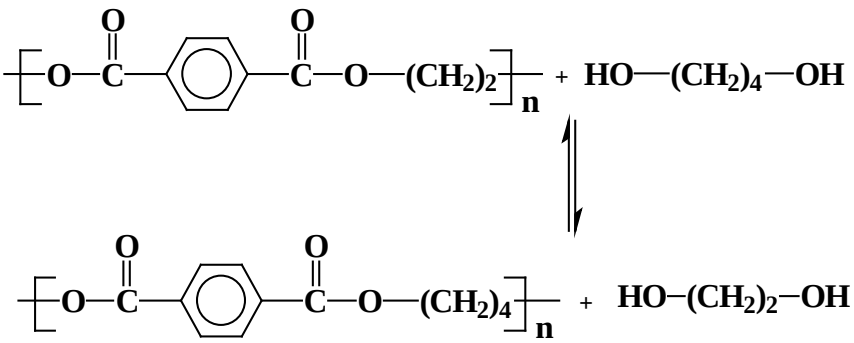
6.3.6 Measurement of mechanical properties

The mechanical properties, namely, the tensile strength and unnotched izod impact strength of PBT obtained upon transesterification of scrap PET, were determined using an Instron (model 1122) and CEAST impact strength tester (model 6545). PBT (commercial sample) was compression molded at 240^0C in Morgan Press (USA). PBT sample prepared by transesterification of scrap PET was mixed with irganox 1010 (0.2 wt%), and then melt mixed in a minimax molder at 245^0C, pelletized in a grinder and compression molded at 250^0C in Morgan Press

6.4 Results and Discussion

6.4.1 Transesterification of poly (ethylene terephthalate) s (PET) using 1,4-butanediol (BD)

Transesterification is a process where one ester is transformed into another through the interchange of an alkoxy moiety. This reaction is an equilibrium reaction catalyzed by acids, bases, amines or alkoxides and occurs, essentially, by mixing the two components[21]



Scheme 6.1: Transesterification of PET using 1, 4-butanediol

The transesterification reaction as an effective method of recycling post consumer PET flakes was studied in detail using 1,4-butanediol (BD). Effects of reaction time, feed ratio, and catalyst type were examined. The composition of the resulting copolyesters was determined from an integration of $(CH_2)_4$- protons at 4.4 δ and -$(CH_2)_2$- protons at 4.8 δ. The conversion of PET to PBT was inferred by the absence of the -$(CH_2)_2$- protons and the

appearance of the -$(CH_2)_4$- protons in the NMR spectra. ***Figure 6.2*** *shows typical spectra of waste PET, virgin PBT and a sample of PBT obtained after transesterification.*

The use of excess diols in these transesterification reaction leads to glycolysis of PET. Further polycondensation leads to polyesters. It is recognized that during transesterification reaction with BD in presence of catalysts, tetrahydrofuran (THF) is formed[22-25]. It has been shown that in the synthesis of PBT from DMT and BD, increase in temperature, BD to DMT feed ratio, or catalyst concentration, leads to higher production of methanol, i.e., higher transesterification. An increase in temperature and BD to DMT ratio also increased THF formation. Higher catalyst concentration caused the amount of THF to decrease[23].

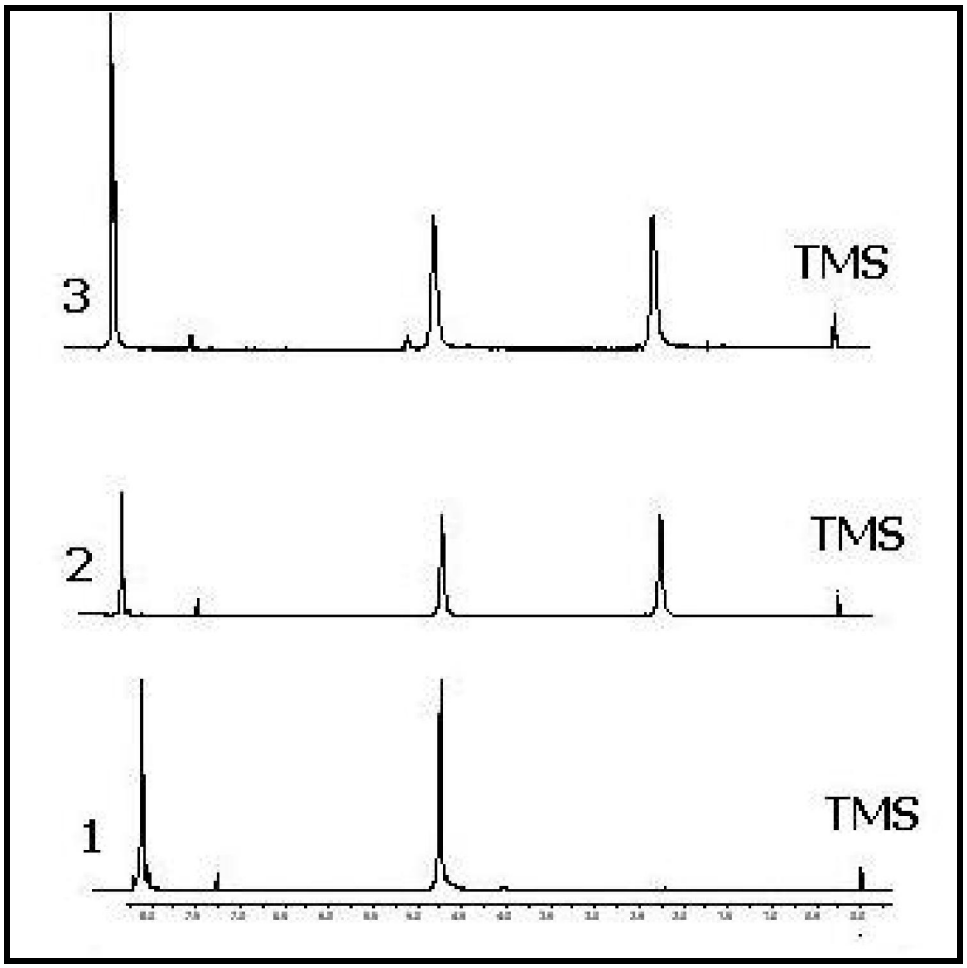


Figure 6.2 ^{1}H-NMR spectra of (1) PET scrap, (2) PBT and (3) transesterified product (97%) (Entry No. 7, Table-6.3)

6.4.1.1 Effect of reflux time

PET flakes (5 g, 0.026 mol) and BD (5.85 g, 0.065 mol) were refluxed for varying lengths of time in the absence as well as presence of antimony trioxide catalyst (0.05 wt% of PET). Molar ratio of PET:BD was 1:2.5. Conversions increased as a function of reflux time as seen in ***Table 6.2*** *and were higher in presence of catalyst. A limiting conversion of 95% was reached in a reflux time of 4 h when the reaction was carried out in the presence of catalyst.*

Table 6.2 Conversion profile in the PET-BD transesterification reaction[a]

No.	Reflux time (h) at 230^{0}C	mol% butylene in PET	Inherent viscosity[b] $[\eta]_{inh}$, dL/g	T_m (^{o}C)
1	1	44	0.31	184
2	2	63	0.33	184
3	3	75	0.32	191
4	4	82	0.35	194
Catalyst (Sb_2O_3) : 0.05 wt% of PET				
5	2	87	0.16	200
6	3	95	0.21	210
7	4	94	0.35	212
8	5	93	0.35	210

a-Reaction conditions: 230^{o}C/no N_2 flow; 250^{o}C/40 min/100-1 mbar, 250^{o}C/1h/0.05-0.03 mbar; PET: BD ratio 1:2.5, no catalyst, mol of BD = 0.065; b–Determined in 60 : 40 mixture of phenol + TCE at 25^{o}C

In case of reactions carried out in the absence of externally added catalyst, moles of THF as well as % mol of THF based on BD increased with reflux time from 0.004 moles to 0.026 moles and 6.5 % to 40 % respectively. The conversion profile of transesterification reactions in presence and absence of catalyst is shown in **Figure 6.3**.

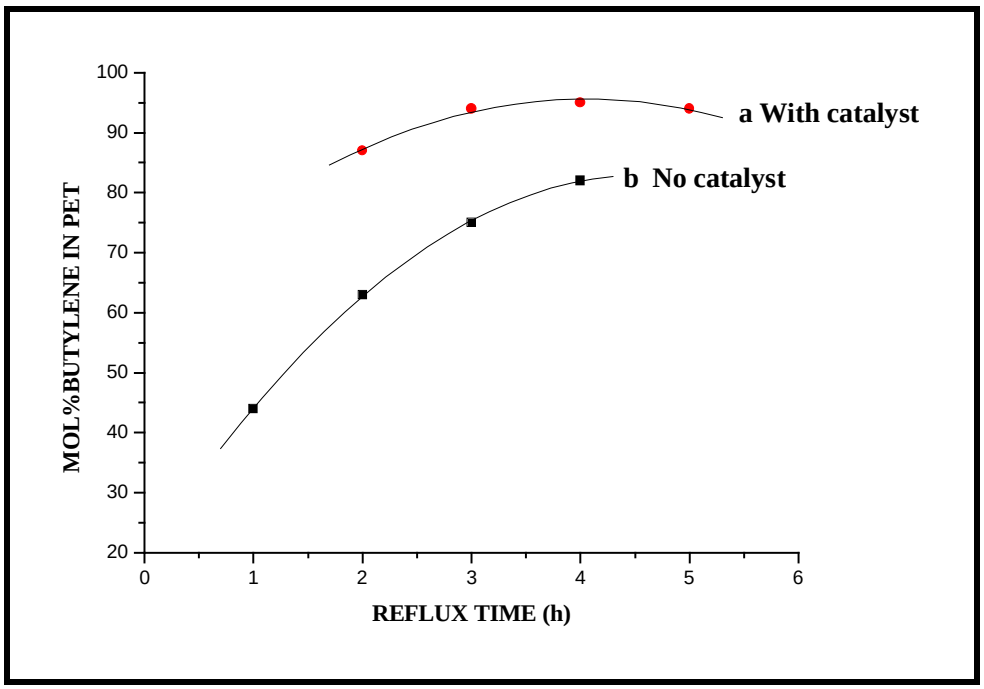


Figure 6.3 Effect of reflux time on transesterification (Entries from Table 6.2)

6.4.1.2 Effect of PET: BD feed ratio

PET and BD in different feed ratios were taken in a round-bottom flask and refluxed (i) without additional catalyst, (ii) with additional Sb_2O_3 catalyst, and (iii) with additional $Ti(iPrO)_4$ catalyst. A catalyst concentration of 0.5 wt% of PET was used for the reaction.

The results of these experiments are shown in **Table 6.3**. It was observed that in absence of any catalyst mol % THF based on BD in the feed decreased inversely as the feed ratio of PET: BD increased. The mol % butylene in PET and viscosity of the obtained copolyester remained constant. The acid value of transesterified polymer was higher than that of the starting material (PET flakes) indicating the occurrence of intramolecular cyclization.

At PET: BD feed ratio of 1:10, a large effect of dilution with BD on THF formation was seen. Therefore, though the amount of THF formed increased with the increase in the amount of BD, the overall mol % THF formed based on moles of BD decreased with increase in BD indicating a dilution effect. In the presence of Sb_2O_3 catalyst too, the mol % of THF formed based on BD decreased as the feed ratio of PET:

BD was increased. Under these conditions only a slight increase in carboxyl group formation was observed in comparison with the PET flakes. Thus, Sb_2O_3 promotes transesterification as seen by the higher mol % butylene incorporation in PET over the dehydration of THF to form acid groups.

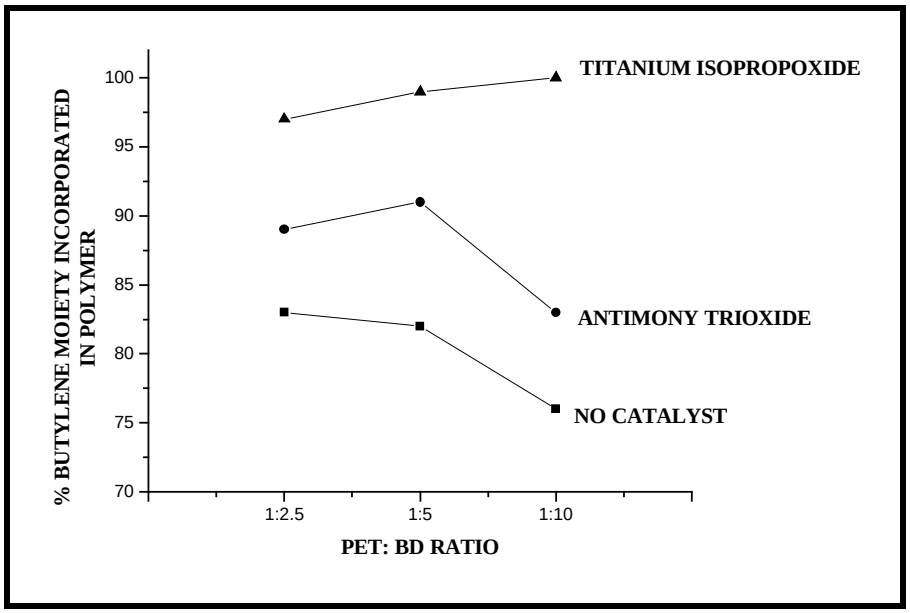


Figure 6.4 Effect of PET: BD feed ratio on conversion (Entries from Table 6.3)

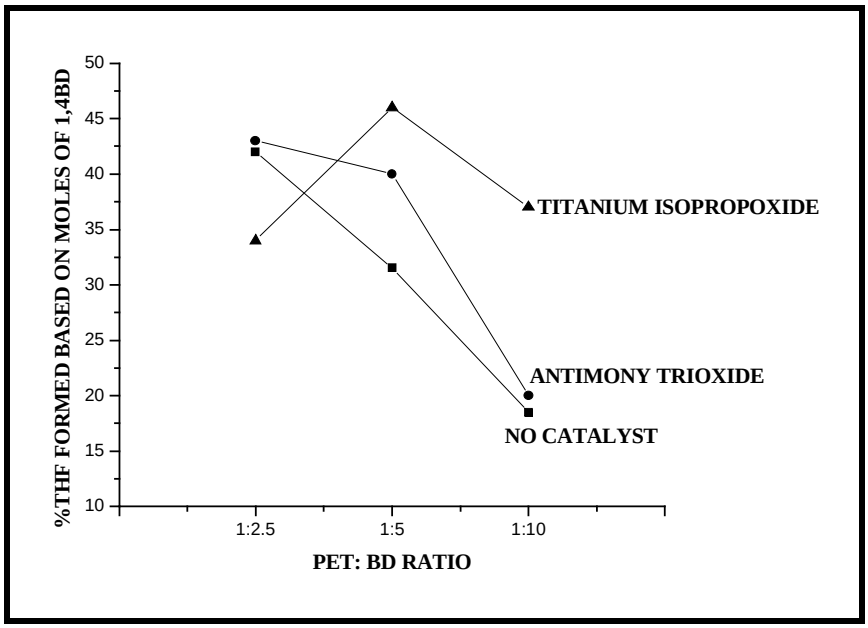


Figure 6.5 Effect of PET: BD feed ratio on THF formation (Entries from Table 6.3)

In case of $Ti(iPrO)_4$, as the PET:BD feed ratio was increased, the mol % THF formed increased from 34 to 46 mol % and at a feed ratio of 1:10, the mol % THF formed decreased to 37 mol %. A substantial increase in the mol % butylene content in PET was observed. The acid value was also lower when $Ti(iPrO)_4$ was used as compared to Sb_2O_3. Thus, $Ti(iPrO)_4$ promotes transesterification as seen by the near complete substitution of butylene moiety in PET over the dehydration of THF to form acid groups (**Figures 6.4** and **6.5**).

6.4.1.3 Effect of catalyst

Effect of catalyst type on the transesterification reaction was studied by refluxing PET (5.0 g, 0.026 mol) and BD (5.85 g, 0.065 mol) with 0.0025 g (0.5 wt% of PET) Sb_2O_3 and $Ti(iPrO)_4$ as shown in **Table 6.4**.

Table 6.4 Effect of catalyst type on transesterification reaction[a]

No.	PET:BD ratio/ catalyst	BD (mol)	THF (mol)	mol %THF based on BD	mol % butylene in PET	T_m (^oC)	Inherent viscosity[b] $[\eta]_{inh}$, dL/g	Acid value[c] eq/10^6 g
1	1:2.5/ Sb_2O_3	0.065	0.028	43	90	210	0.45	46
2	1:2.5/ $Ti(iPrO)_4$	0.065	0.021	32	98	220	0.54	25

a – Reaction conditions: 230^{o}C/4 h/no N_2 flow, 250^{o}C/40 min/100-1 mbar, 250^{o}C/1 h/0.05-0.03 mbar, Catalyst concentration: 0.5 wt% of PET = 0.025 g; b- Determined in 60: 40 mixture of phenol + TCE at 25^{o}C; c –Determined by Pohl's method

Molar ratio of 1:2.5 for PET: BD was used. The results show that $Ti(iPrO)_4$ resulted in a lower mol % of THF formation and a higher mol % butylene incorporation as compared to Sb_2O_3. Sb_2O_3 gave a slightly higher acid value as compared to $Ti(iPrO)_4$. This indicated the higher efficiency of $Ti(iPrO)_4$ as a transesterification catalyst as compared to Sb_2O_3.

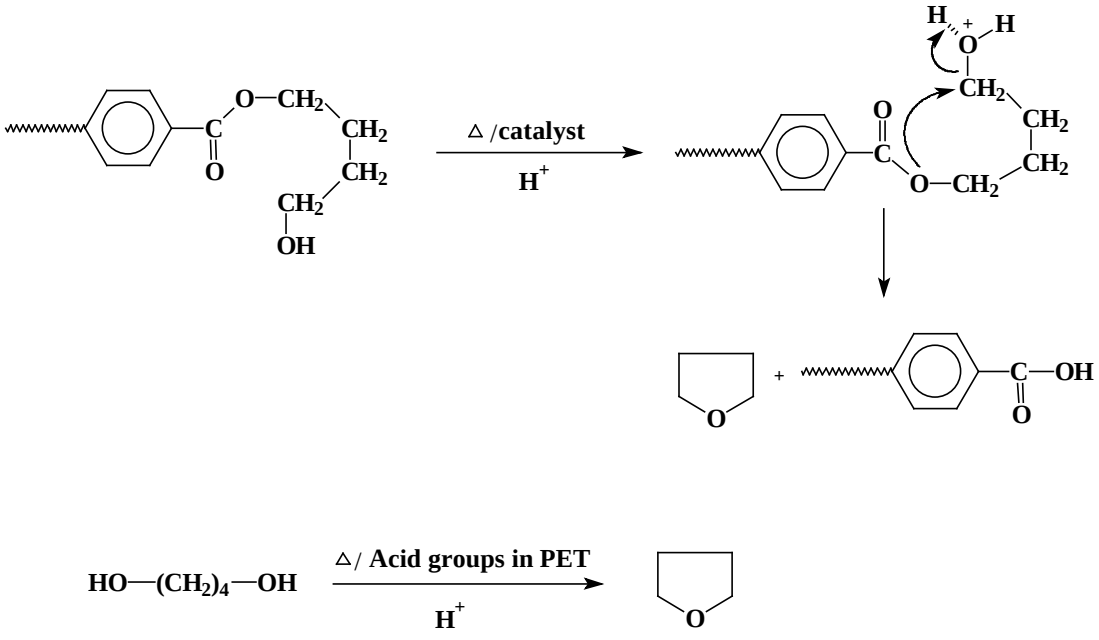
Table 6.3 Effect of PET: BD ratio on conversion and THF formation[a]

No.	PET : BD ratio	BD (mol)	THF (mol)	THF (mol % based on BD)	mol % butylene in PET	Inherent viscosity[b] $[\eta]_{inh}$, dL/g	T_m (^oC)	Acid value[c] eq/10^6 g
1	1:2.5	0.065	0.028	42.0	83	0.35	197	98
2	1:5	0.130	0.041	31.5	82	0.33	197	-
3	1:10	0.260	0.048	18.5	76	0.33	189	102
Externally added catalyst = Sb_2O_3 (0.0025 g)								
4	1:2.5	0.065	0.028	43.0	89	0.43	208	48
5	1:5	0.130	0.052	40.0	91	0.55	212	45
6	1:10	0.260	0.052	20.0	83	0.48	204	49
Externally added catalyst = $(Ti(iPrO)_4)$ (0.0025 g)								
7	1:2.5	0.065	0.022	34.0	97	0.55	220	24
8	1:5	0.130	0.060	46.0	99	0.52	225	24
9	1:10	0.260	0.096	37.0	100	0.48	223	22

a–Reaction conditions: 230^{o}C/4 h/no N_2 flow, 250^{o}C/40 min/100-1 mbar, 250^{o}C/1 h/ 0.05-0.03 mbar; b-Determined in 60 : 40 mixture of phenol + TCE mixture at 25^{o}C; c-Determined by Pohl's method

6.4.1.4 Factors causing THF formation in the transesterification reaction

During the degradation of PET with BD a large number of hydroxybutyl end groups are formed which can either undergo transesterification or cyclization to form THF. Greater the amount of BD, greater will be the degradation of PET and higher will be the concentration of the hydroxybutyl end groups. Intramolecular cyclization of the butyl end groups is unaffected by dilution but this reaction may be reduced indirectly by use of a good transesterification catalyst and / or a higher catalyst concentration. THF can also be formed by dehydration of BD catalyzed by the acid groups generated as a result of intramolecular cyclization of the hydroxybutyl end groups, or from the acid groups already present in PET as shown in **Scheme 6.2**.



Scheme 6.2: Formation of THF and carboxylic acid group during PET-BD transesterification reaction

The total amount of THF formed is thus a net result of these two reactions, i.e., intramolecular cyclization and acid catalyzed dehydration. Catalysis by acid groups is often affected by dilution. The increase in THF from the cyclization reaction is compensated by the decrease in the THF formation by acid catalysis as the dilution increases. To verify this hypothesis the following studies were undertaken.

Effect of dilution of carboxyl groups with BD on THF formation

Effect of dilution of the carboxyl groups with BD on THF formation was studied in presence and absence of Sb_2O_3 catalyst using the following model reactions. Benzoic acid (1 g) was heated with different amounts of BD at 230^oC for 2 h without nitrogen flow. THF was formed indicating that dehydration of BD is catalyzed by benzoic acid. The results (**Table 6.5**) were similar in the presence as well as absence of Sb_2O_3 catalyst, thereby showing that Sb_2O_3 did not have any direct effect on dehydration of BD. It was observed that both in the presence and absence of Sb_2O_3 catalyst, mol % THF formed decreased slightly with increase in the amount of BD, although the amount of THF formed increased with increase in BD content. This showed that there is a slight effect of dilution of the carboxyl end groups with BD on the THF formation catalyzed by carboxyl groups (**Table 6.5** and **Figure 6.6**).

Table 6.5 Effect of dilution of carboxyl groups with BD on THF formation[a]

No.	Amount of BD taken, g (mol)	THF (mol)	THF (mol %based on BD)
Without catalyst			
1	5.92 (0.066)	0.0047	7
2	11.75 (0.13)	0.0064	5
3	23.43 (0.26)	0.0080	3
Catalyst Sb_2O_3: 0.0025 g			
4	5.87 (0.065)	0.0044	7
5	11.77 (0.13)	0.0057	4
6	23.43 (0.26)	0.0074	3

a–Reaction conditions: 230^oC/2 h, no N_2 flow; benzoic acid (1g)

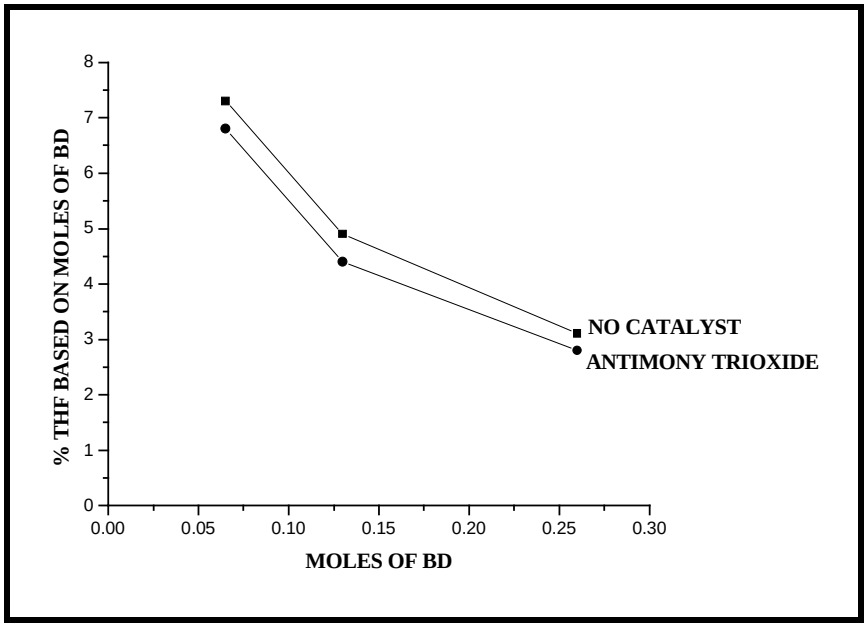


Figure 6.6 Effect of dilution of carboxyl groups with BD on THF formation (Entries from Table 6.5)

Effect of 4-HBB concentration on THF formation

Degradation of PET with BD leads to the formation of hydroxybutyl end groups that can either undergo transesterification or intramolecular cyclization to form THF which is unaffected by dilution. To verify this hypothesis two different concentrations of 4-hydroxybutyl benzoate (4-HBB) were heated with BD at 230^{o}C for 2 h in presence of Sb_2O_3 catalyst. It was observed that increase in 4-HBB concentration lead to higher THF formation (**Table 6.6**). These results show that higher the concentration of the hydroxy butyl end groups in the reaction medium, higher will be the intramolecular cyclization leading to THF formation.

Table 6.6 Effect of 4-HBB concentration on THF formation[a]

No.	Amount of 4-HBB g (mol)	Amount of BD, g (mol)	THF (mol)	mol% THF based on BD
1	1.59 (0.008)	5.93 (0.066)	0.021	33
2	3.14 (0.016)	5.89 (0.065)	0.026	41

a – Reaction conditions: 230°C/2 h, No N_2 flow; Sb_2O_3: 0.0025 g

Effect of dilution on THF formation in the presence of 4-HBB

To explore whether dilution had any effect on the THF formation in presence of 4-HBB, 4-HBB (1.57 g, 0.0081 mol) was refluxed with varying amounts of BD in presence and absence of catalyst

In the absence of transesterification catalyst the mol % THF increased with the amount of BD taken. Increase in THF was due to both intramolecular cyclization as well as dehydration of BD by the formed carboxylic acid groups. No effect of dilution was noticed. In presence of catalyst (Sb_2O_3) also there was no effect of dilution. Thus intramolecular cyclization is not affected by dilution. However, in presence of transesterification catalyst increase in BD increased THF only marginally which could be due to preponderance of the transesterification reaction over the cyclization leading to THF formation (**Table 6.7**).

Table 6.7 Effect of dilution on THF formation in the presence of 4-HBB[a]

No.	Amount of 4-HBB (g)	Amount of BD (g)	THF (mol)	THF (mol% based on BD)
Without catalyst				
1	1.57 (0.0081)	5.92 (0.066)	0.039	61
2	1.59 (0.0081)	11.73 (0.13)	0.110	85
With catalyst Sb_2O_3: 0.0025 g				
3	1.59 (0.0081)	5.93 (0.066)	0.021	33
4	1.58 (0.0081)	11.84 (0.13)	0.050	38

a – Reaction conditions: 230°C/2 h, No N_2 flow

Effect of diphenyl ether (DPE) as a diluent on the transesterification reaction

Effect of diluent on the transesterification reaction was studied by carrying out the reaction using a PET: BD feed ratio of 1:2.5 in the presence of DPE as a diluent (**Table 6.8**). In the absence of $Ti(iPrO)_4$ catalyst and diluent, a higher mol % THF formation was seen indicating higher intramolecular cyclization, while in the presence of a diluent, mol % THF formation and the acid values were lower indicating a favorable effect of dilution. However the conversion (%mol butylene incorporation) was also very low. In the presence of $Ti(iPrO)_4$ catalyst and in absence of diluent a higher mol % THF formation and low acid value was seen in the resulting polyester. In presence of a diluent, low % THF formation was observed, again indicating effect of dilution. In the reactions carried out in presence of catalyst, the conversions (%mol butylene incorporation) were high (98-99%) and were unaffected by the presence of diphenyl ether as diluent.

Table 6.8 Effect of diphenyl ether as a diluent on the transesterification reaction[a]

No.	BD (mol)	Amount of DPE (g)	THF (mol)	THF (mol %based on BD)	mol % butylene in PET	Inherent viscosity[d] $[\eta]_{inh}$, dL/g	Tm (^oC)	Acid value[e] eq/10^6
1	0.065[b]	Absent	0.028	42	83	0.35	197	98
2	0.065[b]	17.55	0.003	5	42	0.27	185	63
3	0.065[c]	Absent	0.016	25	98	0.54	226	39
4	0.065[c]	17.57	0.012	18	99	0.68	222	86

a–Reaction conditions: PET : BD = 1:2.5, 230^{o}C/4 h/no N_2 flow, 250^{o}C/40min/100-1 mbar, 250^{o}C/1 h/0.05-0.03 mbar; b–No catalyst was added; c–0.025 g $Ti(iPrO)_4$ was added as a catalyst; d–Determined in 60 : 40 mixture of phenol + TCE at 25^{o}C; e–Determined by Pohl's method

6.4.1.5 Transesterification of PET with other diols

Transesterification reaction with PET was also carried out using 1,4-cyclohexanedimethanol and 1,6-hexanediol. These reactions resulted in complete transesterification (**Table 6.9**).

The ^{1}H-NMR spectrum of the polymer based on 1,4-cyclohexanedimethanol was characterized by the absence of – $(CH_2)_2$ – protons of PET (4.8 δ, s, 2 H) and the

appearance of –(CH_2)- protons (4.3 – 4.4 δ, m 4 H) and the cycloaliphatic protons (1.0 – 2.0 δ, m 10 H) from 1,4-cyclohexanedimethanol.

Table 6.9 Transesterification of PET with CHDM and HD[a]

No.	Diol	PET: Diol	Reaction conditions	Conv. (mol %)	Inherent viscosity[b] $[\eta]_{inh}$, dL/g	T_m (^oC)
1	CHDM	1:4	283^0C/5h/N_2flow+283^0 C/2.5h/100-1mm of Hg+283^0C/2 h/1 mm of Hg+300^0C/1 h/1mm of Hg	100	0.20	285
2	HD	1:4	280^0C/5h/N_2flow+280^0 C/1h 40 min/100-1mm of Hg+280^0C/2 h/1mm of Hg	100	0.40	137

a – Catalyst: Sb_2O_3 (0.5 wt% of PET, 0.025g); b – Determined in 60: 40 mixture of phenol + TCE at 25^oC

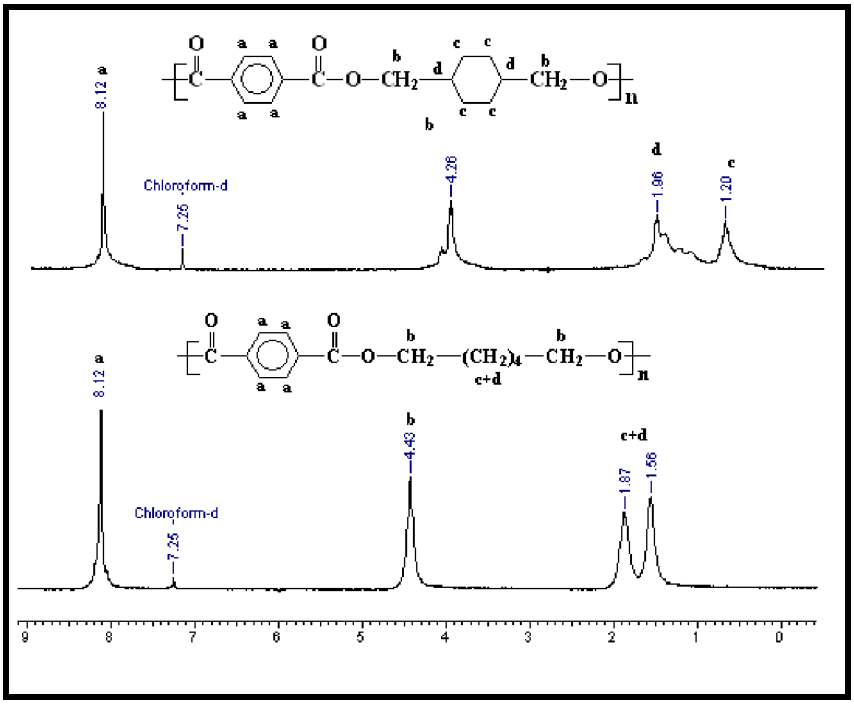


Figure 6.7 NMR of (a) PET transesterified with CHDM and (b) PET transesterified with HD

Similarly, in the ^{1}H-NMR spectrum of the polymer based on 1,6-hexanediol, the $-(CH_2)_2-$ protons of PET (4.8 δ, s, 2 H) were replaced by $-(CH_2)_6-$ protons (4.4 δ, t, 4 H; 1.9 δ, m, 4 H; and 1.6 δ, m, 4 H) from 1,6-hexanediol (**Figure 6.7**)

6.4.1.6 Mechanical properties

The mechanical properties (tensile strength, un-notched izod impact strength and % elongation at yield) of PBT obtained by transesterification of PET with BD were determined according to ASTM methods. The results are shown in **Table 6.10**. These values compared well with a commercial grade of PBT.

Table 6.10 Mechanical properties of PBT generated from post-consumer PET flakes

Properties	PBT Virgin[a]	PBT generated from PET scrap
Tensile strength At yield (MPa) At break (MPa) (ASTM D-638)	 42.5 24.5	 46.6 30.5
Elongation, (%) At yield At break (ASTM D-638)	 20 27	 20 46
Izod impact strength (un-notched) (J/m) (ASTM D-256)	735	620
Color	White	Cement gray
Physical form	Sheet	Powder
η_{inh}[b] (dL/g)	0.90 – 1.00	0.90 – 1.00
Acid No. (eq/10^6)	56-58	72 – 75

T_m (DSC), (^oC)	-	221-225
Ethylene glycol content (mol %)	-	< 3

a–Arnite–T 200 (AKZO); b – Phenol: tetrachloroethane (60: 40 w/w)

6.5 Conclusions

Shredded flakes of post-consumer PET bottles as well as other forms of PET waste could be recycled successfully to PBT by transesterification with BD. In the recycling of PET by transesterification with BD, an optimum reflux time was found to be 4 h for achieving a limiting conversion of 95%. Use of excess BD, does not increase the conversion significantly and a molar ratio of 1:2.5 for PET: BD is sufficient to achieve a conversion of greater than 95%.

The conversions were higher in the presence of externally added catalyst as compared to in its absence. The best results (100% incorporation of butylene moiety) were obtained with a catalyst concentration of 0.5 wt% (0.0025 g). $Ti(iPrO)_4$ appeared to be a better catalyst than Sb_2O_3. However the amount of THF formed increased with increase in BD in the feed, both in presence as well as absence of catalyst. Effect of dilution was observed both in presence as well as absence of catalyst.

The model studies show that formation of THF by acid catalyzed dehydration of BD is affected by dilution and that by intramolecular cyclization of hydroxybutyl end groups is unaffected by dilution. Hence a higher concentration of hydroxy butyl end groups automatically leads to higher THF formation by the intramolecular cyclization. In the absence of diluent, THF formation is high compared to the situation when diluent is present, both in presence as well as in absence of catalyst. Thus a diluent like diphenyl ether can be used, which does not affect conversion and at the same time minimizes the THF formation.

Formation of THF is inevitable during transesterification with BD. As THF is formed by both acid catalyzed dehydration and intramolecular cyclization, its extent of formation depends on both these reactions. However, a definite effect of dilution is observed both in the presence as well as absence of catalyst. A lower feed ratio and

reaction time, use of higher concentration of catalyst like titanium isopropoxide can lead to lower THF formation and higher conversion.

Thus, the composition of the resulting copolyester could be varied by a judicious choice of the diol/PET feed ratio, time, temperature and catalyst used for transesterification. PET could also be converted to other poly (alkylene terephthalate)s, eg., poly(1,4-cyclohexane dimethylene terephthalate) and poly(1,6-hexamethylene terephthalate). The mechanical properties of PBT obtained from scrap PET were comparable with virgin PBT

6.6 References

1. (a) J. Leidner, Plastic Waste; Marcel Dekker: New York, (1981), (b) R.J Ehrig, Ed., Plastics Recycling-Products and Processes; Hanser Publishers: New York, (1992)
2. D.Cornell, F. Glenn Gallagher, *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters, Chapter 16 and 17,* edited by J.Scheirs, T. Long, John Wiley & Sons, Inc. (2003)
3. (a) F.Asaba, K.Doi, T.Nunokawa, A.Morinaga, H.Yamamoto, S.Mukaigawara, K. Fujiwara, H. Shiroshika, Jpn Kokai Tokkyo Koho *JP 2002011719* (2002) to Mitsui Chemicals Engineering Co Ltd. (CA 136: 86812)
   (b) H. Al Ghatta, *Eur Pat Appl EP 1215191A2* (2002) to Sinco Ricerche S.p.A
4. H.Miyake, O.Makimura T.Tsuchida, *US Patent 3951886* (1976) to Toyo Boseki Kabushiki Kaisha
5. A.I. Malik, *US Patent 4078143* (1978) to E.I. Du Pont de Nemours and Company
6. P.C. Kemp, *US Patent 3830739* (1974) to Witco Chem Corp
7. C.F. Burmaster, *US Pat 3728287* (1973) to Eastman Kodak Company
8. B.I.Rosen, *US Patent 5,095,145,* (1992) to Amoco Corporation
9. W.J.G Cudmore, *US Patent 4578502* (1986)
10. H.S. Ostrowski, *US Patent 3884850* (1975) to Fiber Industries, Inc.
11. G.R Svoboda, J.T. Suh, W.L Carlstrom, G.L Maechtle, *US Patent 4048104* (1977) to Freeman Chemical Corporation

12. M.F Meyer, R.L Combs, Jr. W.C. Wooten, *US Patent 3701741* (1972) to Eastman Kodak Company
13. D.E.Morton, *US Patent 3703488* (1972) to Goodyear Tire and Rubber Company
14. F. Ligorati, G. Aglietti, E.V. Nova, *US Patent 3776945* (1973) to Soc Italiana Resine SPA. IT
15. H.B. Whitfield, Jr., F.E. Hoffman, C.E., Holcomb, F.R.Winter, *US Patent 3257335* (1964)
16. S. Baliga, W.T Wong, *J Polym Sci Part A: Polym Chem.* **27**, 2071, (1989)
17. M.S. Kyber, S.U Wolfgang, U.Schollar, *US Patent 5266601* (1993) to Zimmer Aktiengesellschaft
18. V.A Chilukuri, S. Sivaram, *US Patent 5451611* (1995) to Council of Scientific and Industrial Research
19. F.Pilati, P.Manaresi, B.Fortunato, A.Munari, V.Passalacqua, *Polymer* **22** (6) 799, (1981)
20. H. A.Pohl, *Anal Chem.* **26** (10), 1614, (1954)
21. J. Otera, *Chem. Rev* **93**, 14449, (1993)
22. L. Yurramendi, M J. Barandiarn, J M Asua, *Polymer* **29**(5), 871, (1988)
23. L.Yurramendi, M. J. Barandiaran, J. M. Asua, *J Macromol Sci Chem.* **A24**(11), 1357, (1987)
24. S. Sivaram, V. K. Upadhyay, I.S. Bhardwaj, *Polymer Bulletin* **5**, 159, (1981)
25. F.Pilati, P.Manaresi, B.Fortunato, A.Munari, V.Passalacqua, IUPAC 26th Symposium on Macromolecules, Mainz, Prepr Vol 1, p231, (1979)

Chapter 7: Summary and conclusions

7.1 Summary

The key findings and conclusions of the present thesis are summarized below:

Synthesis of poly (butylene adipate)s was examined using the melt polycondensation reaction of dimethyl adipate with 1,4-butanediol using titanium isopropoxide as catalyst. The reaction was characterized by the formation of both linear as well as cyclic oligomers. Formation of cyclic oligomers effectively competed with the linear step growth process, limiting the ability of reaction to produce high molecular weight polymers. Formation of cyclics increased at higher polymerization temperature. Cyclics of DP ranging from 3 to 12 could be detected using MALDI-ToF MS. Consequently, the molecular weight of the polyesters obtained was limited to a few thousands due to incomplete conversions and loss of end groups leading to formation of THF and cyclics.

Direct synthesis of poly (butylene adipate)s by melt polycondensation was, thus, not suitable for the synthesis of high molecular weight polymer. A useful method of increasing molecular weights of polyesters is by chain extension, which involves a fast or irreversible reaction between the reactive chain extender and the end groups of the polymer. Poly (butylene adipate)s with hydroxyl groups at both the ends was obtained by glycolysis of poly (butylene adipate) with 1,4-butanediol in stoichiometric amounts in the presence of titanium isopropoxide. The hydroxyl end group concentration was estimated by ^{31}P NMR. Chain extension reactions with hexamethylene diisocyanate (HMDI), 2,2'-bis(2-oxepanone), bis (4-nitrophenyl carbonate) and divinyl adipate were studied. Chain extension, leading to high molecular weight poly (butylene adipate)s was observed with varying efficiencies with different chain extenders. However, best results were obtained with divinyl adipate as a chain extender.

An alternative route to the synthesis of high molecular weight aliphatic polyesters is via ring opening polymerization (ROP). Ring opening polymerization of substituted lactones leads to polyesters with substitution in their chains. Bond bridged bicyclic compounds are also potential monomers for ring opening polymerization. Hence ROP of 3-pentadecyl 2-oxepanone and 2-oxabicyclo [3.2.1] octan-3-one was attempted using stannous octoate as the initiator and ethylene glycol as co-initiator. Copolymerization of 3-pentadecyl 2-oxepanone with ε-caprolactone was also studied with a view to gain a better understanding of the reactivity of this monomer. 3-pentadecyl 2-oxepanone polymerized in the presence of stannous octoate to yield low molecular weight oligomers. However 2-oxabicyclo [3.2.1] octan-3-one did not polymerize under similar reaction conditions.

Polyesters are a class of polymers that can be either recycled or environmentally degraded. Poly (ethylene terephthalate) PET is the most widely consumed polymer among the aliphatic-aromatic polyesters. Aliphatic-aromatic polyesters are not biodegradable on account of the aromatic component. However PET can be recycled very effectively. The direct conversion of PET to another polyester, namely poly (butylene terephthalate) (PBT) was studied by transesterification of waste PET flakes with 1,4-butanediol using either titanium isopropoxide or antimony trioxide catalysts. The effect of reaction parameters on the incorporation of butylene moiety in the polyester was studied. Copolyesters with 99% incorporation of butylene moiety could be synthesized. A major side reaction is the formation of large amounts of tetrahydrofuran (THF) either by intramolecular cyclization of hydroxy butyl end groups or by dehydration of butane diol catalyzed by the carboxyl end groups of the polyester. Model reactions using benzoic acid and 4-hydroxy butyl benzoate were carried out to understand the path by which THF formation takes place. This reaction was successfully extended to transesterification reactions with diols, such as, 1,4-cyclohexanedimethanol and 1,6-hexanediol. Corresponding copolyesters were obtained.

7.2 Conclusions

- Poly (butylene adipate) was synthesized by melt polymerization of dimethyl adipate and 1,4-butanediol. Specific causes which limit attainment of high molecular weight poly (butylene adipate)s were identified. ***Based on this understanding suitable reaction conditions were identified for the synthesis of poly (butylene adipate) oligomers with minimum accompanying side reactions.***

- Chain extension of hydroxyl terminated poly (butylene adipate) with chain extenders such as hexamethylene diisocyanate (HMDI), 2,2'-bis(2-oxepanone) propane and bis (4-nitrophenyl) carbonate was studied. ***Moderate chain extension of poly (butylene adipate) could be achieved with HMDI and bis (4-nitrophenyl) carbonate, whereas, with 2,2'bis(2-oxepanone) propane the chain extension was poor with substantial broadening of molecular weight distributions.***

- Chain extension of hydroxyl terminated poly (butylene adipate) with divinyl adipate was carried out in melt phase as well as in solution. Coupling with divinyl adipate led to fully aliphatic polyester in which the chain extender could not be distinguished from the rest of the polyester chain. ***Effective chain extension was achieved using divinyl adipate. Thus, divinyl adipate appears to be a very promising chain extender for aliphatic polyesters***

- ***Ring opening polymerization of a novel substituted lactone, namely, 3-pentadecyl 2-oxepanone was achieved using stannous octoate as initiator. 2-oxabicyclo [3.2.1] octan-3-one did not undergo ring opening polymerization using stannous octoate under similar reaction conditions. 3-pentadecyl 2-oxepanone copolymerized with the more reactive ε-caprolactone to yield copolyesters bearing a C15 pendant hydrocarbon branch.***

- Waste PET flakes could be converted directly into PBT by transesterification with 1, 4-butanediol. Other poly (alkylene terephthalate) s were also prepared by transesterification of PET scrap with diols, such as, 1, 4-cyclohexane dimethanol, 1,6-hexanediol. ***Thus PET can be directly converted into other polyesters used in long life cycle applications by direct transesterification of waste PET flakes with the corresponding diols.***

7.3 Future scope of work

Synthesis of high molecular weight aliphatic polyester like poly (butylene adipate) by melt polycondensation leads to a mixture of linear and cyclic oligomers. Higher reaction temperatures that enhance the molecular weight build up process also lead to formation of cyclics due to the competitive nature of the cyclization reaction. Cyclic oligomers of DP 2 could be distilled out under high vacuum. The increase in reaction temperature led to more amount of this cyclic being distilled out.

It would be interesting to study the ring opening polymerization of this cyclic diester using stannous octoate as catalyst as it would lead to a more controlled synthesis of poly (butylene adipate) with fewer side reactions, higher conversions and higher molecular weights.

As higher reaction temperatures lead to colored product with no polymer in the case of ring opening polymerization of 2-oxabicyclo [3.2.1] octan-3-one, polymerization at lower temperatures using aluminium isopropoxide as catalyst can be explored.

Activated esters such as 2,2,2-trifluoroethyl, 2-chloroethyl and 2,2,2-trichloroethyl esters can be studied as chain extenders for the synthesis of high molecular weight poly (butylene adipate).

Poly (butylene adipate) and poly (3-pentadecyl 2-oxepanone) or polycaprolactone are known to be potentially degradable polymers. Poly (butylene adipate) forms a part of the synthesis of commercially available polyester Bionolle®. It would therefore be interesting to modify the properties of poly (butylene adipate) by synthesizing multiblock copolymers consisting of poly (butylene adipate) and polycaprolactone or the poly (3-pentadecyl 2-oxepanone). Modification of properties of poly (butylene adipate) by copolymerization with cycloaliphatic diols or diesters can also be studied.

Ability to introduce long chain branching (via a lactone with C15 alkane chain branch) in aliphatic polyesters, can lead to tuning of hydrophilic-hydrophobic properties. This, in turn, will have an effect on biodegradation using enzymatic hydrolysis.

Consequently, such a monomer can be used to tailor specific biodegradation rates of aliphatic polyesters.

PUBLICATIONS

1. Efficient method for recycling poly (ethylene terephthalate) to poly (butylene terephthalate) using transesterification reaction

Neeta G. Kulkarni, C.V. Avadhani and S. Sivaram

J.Appl.Polym.Sci., 91(6), 3720, 2004

2. Synthesis, characterization and chain extension of poly (butylene adipate)s

Neeta G Kulkarni and S. Sivaram

J.Polym.Sci.PartA : Polym.Chem, (To be communicated)

3. 3-pentadecyl 2-oxepanone : A new monomer for preparing polyesters by ring opening polymerization

Neeta G Kulkarni and S. Sivaram

Designed monomers and polymers, (Under preparation)

4. Fully aliphatic Poly(ester)s: Synthesis, structure and properties

Neeta G. Kulkarni, T. Sandhya and S.Sivaram

J.Macromol.Sci.Chem., Reviews, (Under preparation)