STUDIES IN CRYSTALLIZATION AND SOLID STATE POLYMERIZATION OF AROMATIC AND ALIPHATIC POLYESTERS

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For Appachan and Amma,

Whose love, faith and optimism are my strength

For Simon,

Without whose endurance this thesis would never have been a reality

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DECLARATION

Certified that the work incorporated in this thesis entitled "**Studies in Crystallization and Solid State Polymerization of Aromatic and Aliphatic Polyesters**" submitted by **Nirmala Rachel James** was carried out under my supervision. Such material as obtained from other sources has been duly acknowledged in this thesis.

S. Sivaram

December, 1999
Pune

Dr. S. Sivaram
(Research Guide)

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CONTENTS

CHAPTER 1. GENERAL INTRODUCTION

CHAPTER 2. SCOPE AND OBJECTIVES OF THE PRESENT WORK

CHAPTER 3. CRYSTALLIZATION AND SOLID STATE POLYMERIZATION OF POLY(ARYL ESTER)S

CHAPTER 4. CRYSTALLIZATION AND SOLID STATE POLYMERIZATION OF POLYfETHYLENE TEREPHTHALATE)S

CHAPTER 5. CRYSTALLIZATION AND SOLID STATE POLYMERIZATION OF POLY(ETHYLENE 2,6-DLMETHYL NAPHTHALATE)S

CHAPTER 6. PREPARATION OF POLY(ETHYLENE NAPHTHALATE-CO-TEREPHTHALATE)S *via* SOLID STATE POLYMERIZATION

CHAPTER 7. SUMMARY AND CONCLUSIONS

ABSTRACT

This thesis presents the results of preparation of polyesters, namely, poly(aryl ester)s derived from bisphenol A (BPA), terephthalic acid and isophthalic acids, poly(ethylene terephthalate) (PET), poly(ethylene2,6-naphthlate) (PEN) and poly(ethylenenaphthalate-co-terephthalate) *via* solid state polymerization (SSP) with emphasis on the crystallization of SSP precursors and the structural changes taking place during SSP.

Poly(aryl ester)s are generally prepared by melt polymerization of BPA diacetate and a mixture of terephthalic and isophthalic acids where the by-product is acetic acid. In the present work poly(aryl ester)s were prepared by SSP of oligomers obtained from dimethylesters of terephthalic and isophthalic acids and BPA with evolution of methanol as by product. Poly(aryl ester)s could also be prepared from oligomers with hydroxyl and carboxyl end groups as well as from oligomers with only hydroxyl endgroups with the evolution of water and BPA as by-products respectively. Oligomers were crystallized by diluents prior to SSP. DSC and XRD studies showed that crystallinity decreased during SSP. Titanium tetraisopropoxide ($Ti(O^{i}Pr)_4$) showed higher catalytic activity compared to dibutyltin dilaurate (DBTL) and dimethyl amino pyridine (DMAP).

PET oligomer of very low inherent viscosity (~0.2 dL/g) could be crystallized rapidly and used as precursors for SSP to prepare high molecular weight PET. The nature of catalyst affected crystallization and subsequent SSP of oligomeric PET. Presence of antimony trioxide (Sb_2O_3) enhanced the crystallization rate compared to $Ti(O^{i}Pr)_4$. However the sample with $Ti(O^{i}Pr)_4$ showed better SSP rates. PET oligomers rapidly crystallized into well developed big crystallites which did not undergo major reorganization during SSP. The oligomers prepared by hydrolysis and glycolysis could be subjected to SSP without further crystallization step.

Studies on crystallization of commercial PET pellets showed that crystallinity depends on crystallization temperature and heating rate. Higher crystallization temperature led to higher crystallinity, while, higher heating rate resulted in lower core crystallinity. Difference in surface and core crystallinity decreased at low heating rate and the difference increased at higher crystallization temperature. Average crystal size increased with crystallization temperature. A large crystal size and low core crystallinity favoured SSP rate. Thus, it is possible to get an optimum crystal morphology to achieve highest rate of solid state polymerization

PEN oligomers were crystallized thermally and by contact with suitable diluents for use as SSP precursors. Thermally crystallized oligomers were highly crystalline with large crystals. Diluents with solubility parameter $18.5<\delta<25$ could induce crystallinity in PEN at room temperature. The crystallites grown under diluent induced crystallization methods are smaller (~5 nm) compared to thermally crystallized samples (~15 nm). Oligomers crystallized in both manner underwent SSP. $Ti(O^{i}Pr)_4$ has higher catalytic activity for SSP. SSP at higher temperature yielded material with higher η_{inh}.

Isothermal crystallization studies of PEN oligomers and polymer showed that crystallization half times ($t_{1/2}$) of oligomers varied nominally over a wide range of crystallization temperatures (140-210°C). Oligomers with different catalysts showed slight difference in crystallization behaviour. At all crystallization temperatures, the polymer had larger $t_{1/2}$ than the oligomers, the minimum value being at 200°C. Crystallization isotherms were analyzed with Avrami equation. In the temperature range studied Avrami exponent 'n' changed from 2 to 3 for all the three samples.

PEN is known to crystallize in two different crystal modifications. However there is no agreement in the literature regarding the conditions which determine the crystal modification. From the present work it is found that whenever the crystallization temperature (Tc) was 240°C and above, β modification was formed, while crystallizations at 230°C and below yielded α modification. Neither, the temperature (Tm) from which the material was brought to the crystallization temperature, nor the modification. in which the material was prior to melting, seem to affect the nature of crystal modification. Thus, the crucial factor which determines the modification into which PEN crystallizes is the crystallization temperature.

Poly(ethylenenaphthalate-co-terephthalate) generally prepared by reactive melt blending of PEN and PET, possesses useful properties. But, to obtain desirable properties, transesterification (which determines the compatibility between the two polymers) should be at an optimum level. Controlling transesterification is difficult in the melt processes. Simultaneous solid state polymerization and transesterification could be performed on PET and PEN oligomer mixtures to obtain high molecular weight PET/PEN copolymers with low levels of transesterification. Oligomer mixtures could be crystallized thermally or by diluents to obtain suitable precursors for SSP. Precursors obtained by both methods underwent SSP as well as transesterification. Sequence distribution of samples at different stages of SSP could be analyzed from ^{1}HNMR spectra and X-ray diffraction. DSC studies showed that SSP and transesterification occurs only in the amorphous phase of the semi crystalline precursors. With increase in transesterification and molecular weight crystallization became more and more difficult. A comparison of increase in transesterification and viscosity during the reaction indicates that SSP favours reactions among chain ends.

GLOSSARY

BHEN	Bis(hydroxy ethylene) naphthalate
BHET	Bis(hydroxy ethylene) terephthalate
B	Degree of randomness
BPA	Bisphenol A
DBTL	Dibutyl tindilaurate
DBTO	Dibutyl tinoxide
DEG	Diethylene glycol
D_{hkl}	Miller indices corresponding to h, k and l planes
DMAP	Dimethyl aminopyridine
DMI	Dimethyl isophthalate
DMF	Dimethyl formamide
DMN	2,6-dimethyl naphthalate
DMT	Dimethyl terephthalate
DSC	Differential scanning calorimetry
DP	Degree of polymerization
DPE	Diphenyl ether
DT	Degree of transesterification
EG	Ethylene glycol
FWHM	Full width at half maxima
ΔH	Heat of fusion
IR	Infra red
k	Overall rate constant
L_{nN}	Average sequence length of a naphthalate unit
L_{nT}	Average sequence length of a terephthalate unit
M_n	Number average molecular weight
M_w	Weight average melecular weight
N	Naphthalate unit
n	Avrami exponent
NMR	Nuclear magnetic resonance
PBT	Poly(butylene terephthalate)
PEN	Poly(ethylene 2,6-dimethyl naphthalate)
PET	Poly(ethylene terephthalate)
P_N	Molar fraction of naphthalate unit

P_T	Molar fraction of terephthalate unit
P_{NT}	Probability of finding naphthalate unit next to terephthalate unit
P_{TN}	Probability of finding terephthalate unit next to naphthalate unit
Sb_2O_3	Antimony trioxide
SAXD	Small angle X-ray diffraction
SAXS	Small angle X-ray scattering
T	Terephthalate unit
$t_{1/2}$	Crystallization half time
Tc	Temperature at which material was crystallized
T_c	Crystallization temperature upon heating (cold crystallization)
T_{cc}	Crystallization temperature upon cooling
TCE	1,1',2,2'-tetrachloroethane
T_g	Glass transition temperature
$Ti(O^iPr)_4$	Titanium tetraisopropoxide
Tm	Temperature at which material was melted
T_m	Melting temperature
WAXD	Wide angle X-ray diffraction
WAXS	Wide angle X-ray scattering
XRD	X-ray diffraction
$[\eta]$	Intrinsic viscosity
η_{inh}	Inherent viscosity
δ	Solubility parameter

List of Tables

List of Schemes

List of Figures

CHAPTER 1

GENERAL INTRODUCTION

1.1 Solid State Polymerization

Solid state reactions play an important role in chemistry[1,2]. In polymer chemistry, these reactions are attractive since it can give polymeric materials of scientific and industrial interest with properties which are not obtainable by the usual processes or which cannot be prepared by any other method. The first evidence of polymers obtained by solid state polymerization was reported in 1930s[3-5]. In polymer science, solid state reactions taking place both in chain growth polymerization and in step growth polymerization have to be considered. Much work has been done in the area of solid state chain growth polymerization[6-11].

The present thesis deals with the solid state reactions occurring in step growth polymerizations.

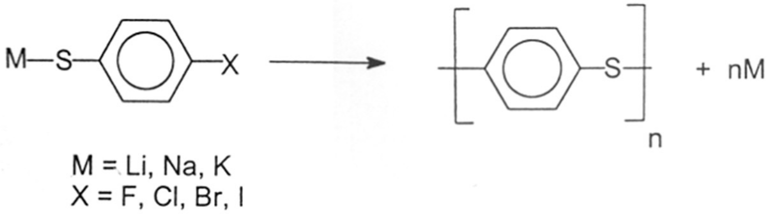
Solid state polymerization (SSP) in polycondensation processes can be divided into two classes depending on whether the starting materials are crystalline monomers or semicrystalline prepolymers[12]. In the first case, monomer is transformed into polymer at a temperature lower than the melting point of both the monomer and the polymer by a reaction consisting of overlapping of chain and step growth polymerization. In the second case, the polymerization is carried out on low or medium molecular weight semicrystalline prepolymers at a temperature below its melting point. It is generally accepted that the polymerization proceeds by step reactions in the amorphous regions of the semicrystalline polymer. Polymer produced by SSP often have improved properties because side reactions leading to defects in the chemical structure and to undesirable by- products are limited or avoided.

SSP is a process that involves chemical reactions whose rate may be affected by the restricted molecular mobility of the reactive end groups and diffusion of volatile by-products. A complete description of SSP should take into consideration, the appropriate kinetics of the chemical reactions as well as the diffusion of by-products out of the particles and their removal from the particle surface.

1.1.1 Solid state polymerization of monomers

This process is of great scientific and commercial interest since it may lead to the direct production of highly oriented polymer fibers from needle like crystals, thus eliminating the expensive spinning process. The technique can also be used to obtain polymers with crystalline structures that would be difficult or impossible to achieve by other means or when the analogous polycondensation in melt or in solution is limited by the high temperature required, by the low solubility of the polymer, by the steric hindrance or the excessive cyclization of the monomer. Lower temperatures employed in SSP minimizes defects such as branching in the chemical structure.

For example, linear poly(1, 4–phenylene sulfide) can be prepared by SSP from the *para*-halogen substituted benzenethiol salts[13] **(Scheme 1.1)** while the polymerization is accompanied by chain branching and crosslinking when the same reaction is carried out in the melt[14].



Scheme 1.1 Preparation of poly(1, 4–phenylene sulifde)s

Polymers prepared by SSP usually contain a lower amount of cyclic oligomers than those prepared in other ways[15].

For a crystalline monomer to be polymerized in the solid state, the reaction has to take place at sufficiently high temperature in order to have appreciable rate. At the same time, the reaction temperature should be sufficiently lower than the melting temperature of both the monomer and polymer to avoid sticking and subsequent change in the nature of the reaction mechanism. In order to improve reaction rates, the reaction temperature can be gradually raised, following the increase in melting point of the polymer with chain growth. Depending on the monomer and the temperature, the reaction time may range from a few hours to several days or weeks. The monomers subjected to SSP can be in the form of single crystals or polycrystalline aggregates[16-18].

During SSP, low molecular weight by-products have to be removed from the system to shift the equilibrium towards the formation of polymer. This can be achieved by performing the reaction under static vacuum or dynamic vacuum or in a stream of an inert gas or by distilling off the by-products along with an inert liquid in which both the crystalline monomer and the polymer are suspended[19-25].

1.1.2 Solid state polymerization of prepolymers

Polycondensation of prepolymers in solid state has been developed mainly for commercial purposes. Industrially it is used to obtain high molecular weight poly(ethylene terephthalate)s (PET), poly(butylene terephthalate)s (PBT), nylon 6 and nylon 66 used as engineering plastic materials[26,27]. Processing techniques like blow-molding and extrusion require high melt viscosities and, hence, high molecular weights in order to avoid the collapse in the soft preformed state[28-30]. During conventional melt condensation processes, polymer melt viscosities rapidly increase with increase in degree of polymerization. Handling of high viscosity melts poses engineering problems. To lower the high viscosities, higher temperatures have to be employed, which can cause side reactions leading to degradation of the materials. These disadvantages can be limited or avoided in solid state processes.

Post polymerization is carried out by heating low or medium molecular weight polycondensates in the form of powder or chips in a stream of gas or under vacuum at a temperature above the polymer glass transition temperature, but below the melting point. Under these conditions, the terminal functional groups would be sufficiently mobile to react. However, the mobility of chain segments and functional groups is considerably restricted in comparison with the situation in the melt. Therefore the completion of the process in the solid state requires more time[31]. The activation energy in the solid state is generally higher than in solution or in the melt[32]. So solid state reactions are very sensitive to temperature, both absolute and relative as well as to the melting point of the reactant[32]. It may be noted that solid state reactions start at much lower temperatures than does homopolycondensations[33].

The main factors that affect SSP include initial particle size, initial molecular weight, number and type of chain end groups, catalyst employed, crystallinity, reaction temperature and time and the technique used to remove by-products. These factors are interrelated and may also depend on the apparatus used.

The types of apparatus that can be used to perform postcondensation are simple and depend on the method employed to remove volatile by-products. Stationary bed reactors or rotary vacuum reactors are commonly used in laboratories, whereas, tumble dryers, fixed or moving bed reactors are usually employed in industry.

Since, no solvent is required, there is no environmental pollution and the process can be a continuous one, thus, SSP has assumed importance in industrial practice. The enormous commercial interest in SSP is evidenced by the intense patenting activity in this area.

1.1.3 Kinetics and mechanism of solid state polymerizaion

The kinetics of solid state polycondensation in polyesters and polyamides have been studied by numerous investigators(35-45).

Zimmerman[35] studied the melt and solid state polymerization of nylon 66. Griskey and Lee studied the mechanism of SSP of nylon 610 in detail[40] and found that the flow rate of nitrogen through the reactor had little effect on polycondensation and the rate of polycondensation was described by the equation, rate = kt^n. This indicates a process in solid material that involves both chemical reaction and diffusion within the material[46]. In another attempt Chen et al studied the effect of combined chemical action and diffusion in more detail[41]. An equilibrium exists in condensation polymers[35,47] $P_1 + P_2 = P_3 + B$, where P_1 and P_2 are polymer chains combining to form P_3 and B is a by-product, a small molecule such as water. Thus there are three possible rate determining stages: i) Chemical reaction ii) diffusion of by product molecules in the solid polymer and iii) transfer of by-product molecules from the solid polymer surface into the inert gas. Chen et al[41] studied the solid state polycondensation of nylon 610 and PET. Based on their studies they reached the following conclusions. Chemical reaction is the rate controlling stage in solid state polycondensation for powders (average diameter 0.21 cm)and for larger particles (average diameter 0.33 cm) at temperatures of 160°C or higher. Diffusion of by-products through the solid is the rate controlling stage for nylon 610 particles of 0.33 cm diameter or more and at temperatures above 140°C .

Henderson and Bouton[42] investigated the solid state polycondensation of nylon 46 in a fluidized bed, with nitrogen as carrier gas over a wide temperature range. It was concluded that reaction kinetics and by-products diffusion both contribute to the overall rate and the data fit into the transition region between the kinetic and diffusion controlled. SSP of the same polymer was also studied by Gaymans and Schkijer[43]. Along with factors like chemical reaction, by-product diffusion into the solid polymer and by-product diffusion from the solid polymer surface into the inert gas, diffusion of the reactive end groups and heat transfer were also considered. It was concluded that the reaction rate depends on the initial molecular weight, reaction temperature and on the reaction time. The rate also depends to a lesser extent on the particle size and water concentration in the reactor gas. The main limiting factor seems to be the diffusion of reactive end groups. Solid state polymerization in the higher temperature range (above 210°C) of PET was studied by Chang who found that the diffusion through a solid polymer was the rate controlling step for particle sizes equal to or larger than 100 mesh[44]. In the case of PET in powder state (20-200 mesh) the crystallinity of the prepolymer and its changes during polycondensation affect the diffusivity and, hence, the polycondensation rate. The diffusivity was linearly proportional to the mass fraction of the PET amorphous phase.

1.1.4 Molecular weight distribution

The theoretically derived molecular size distribution relationships are based on the principle of equal reactivity during polycondensation of all functional groups[47]. In the case of solid state polymerization, the situation is very much complicated. Zimmerman's study on polycondensation of nylon 66 in melt and solid state showed that SSP causes broadening of the molecular weight distribution. Similar results were obtained by Cha[48] Feld[49] and Fakirov[50].

In contrast to the above observations, Gaymans et al[43] showed that SSP of nylon 46 did not lead to a broadening of the molecular weight distribution. Avramova et al[51] and Grehl et al[52,53] reported narrowing of molecular weight distribution after SSP of nylon 6 under vacuum. Polycondensations are reversible reactions and by-product gradients may exist in the solid state particles. Thus, there can be different degrees of polymerization in the same particles[54] leading to broader molecular weight distribution when the entire particle is considered. Meyer[55] suggested that, the broadening may be explained by taking into consideration, the fact that the equilibrium, which is very much related to the kinetics and mechanism of the process, is very rarely achieved.

Flory attributed the narrowing of molecular weight distribution after SSP to the elimination of monomer and oligomers which are usually present in the polycondensates along with the reaction by-products[47].

1.1.5 Factors affecting solid state polymerization

1.1.5.1 Reaction temperature

The reaction temperature is one of the most important factors affecting SSP. Theoretically, the process can take place between the glass transition and melting temperatures[34]. An increase of the SSP temperature usually results in an increase of the overall rate of the process as a consequence of the increment in both reaction and diffusion rates[12]. Reaction temperature is a deciding factor in determining the controlling step of the process[44,56]. Too low temperatures require too long reaction times. The lowest temperature at which SSP takes place in a detectable manner depends on the polymer considered and is usually around 150-170°C for polyamides[12]. In some cases it is desirable to preheat the polymer in order to dry it and avoid sticking. For example, polyamides where moisture contents are high and PET where initial crystallinity may be low.

1.1.5.2 Reaction time

Because of its relatively high diffusion and chain mobility restrictions, solid state polycondensation requires much longer time than conventional melt or solution polycondensation[50]. This is the greatest disadvantage of the solid state process as a commercial technique and any improvement that reduces the processing time enhances the industrial significance of solid state polycondensation.

The two factors, reaction temperature and reaction time, generally tend to operate in opposite directions, so, the effect of one may be compensated by the other.

1.1.5.3 Particle size

Particle size is the third important factor affecting the rate of solid state polymerization[57]. The highest molecular weight obtained after SSP decreases with increase in particle size. But when the particle size is less than 1 mm, the effect is very nominal. The increase in particle size can change the reaction mechanisms under certain conditions[41].

1.1.5.4 Reaction medium

Solid state polymerization can be conducted in vacuum or in an inert gas stream. It is accepted that differences in the molecular weight, achieved by vacuum or inert gas are insignificant[56,58,59]. When an inert gas is used, the nature of the gas and its flow rate has to be considered. Nitrogen is the most frequently used gas, but hydrogen, helium, air and carbon dioxide are also used effectively[56,60]. In the case of polyesters, better quality product was reported, when SSP was carried out in a stream of inert gas containing the corresponding glycol[45].

1.1.5.5 Crystallinity of the starting material

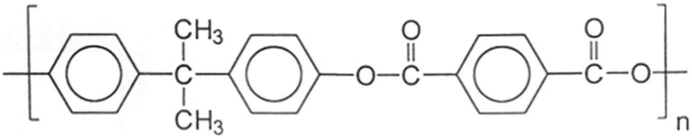
Since, the solid state polycondensation reactions take place in the amorphous regions, the crystallinity of the starting material should have a strong effect on the reaction rate[44]. The effect of crystallinity can be attributed to the influence of crystallintiy on diffusivity. It may be noted that diffusivity is linearly proportional to the mass fraction of the amorphous phase of PET[44]. According to Zimmerman[35], the end groups are in fact excluded from the crystalline regions of the polymer and that the equilibrium in the amorphous region is the same as in a completely amorphous or molten polymer at the same temperature. He suggests that the observed broadening of the molecular weight distribution after SSP resulted from microscopic non-uniformities in the solid particles. Meyer[55] concluded that the equilibrium molecular weight distribution for semicrystalline polycondensates remains unchanged when compared to the amorphous material.

If the starting material is a semicrystalline polycondensate, there are two possible effects on the reaction rate. The crystalline phase restricts chain mobility and diffusivity and can thus reduce the reaction rate. On the other hand, since the end groups are concentrated in the amorphous regions, a higher reaction rate may be expected due to the higher local concentration of reactive moieties. Another advantage is that agglomeration of particles in the reactor can be avoided by the use of semicrystalline polymer as the starting material[61].

1.2 Poly(aryl ester)s

Poly(aryl ester)s are a class of engineering polymers which are wholly aromatic polyesters derived from aromatic dicarboxylic acids and diphenols. Considering the number of available diphenols and aromatic dicarboxylic acids a number of poly(aryl ester) compositions are possible[62].

We will be dealing with amorphous poly(aryl ester)s, derived from bisphenol A and a mixture of isophthalic and terephthalic acids **(I).**



(I)

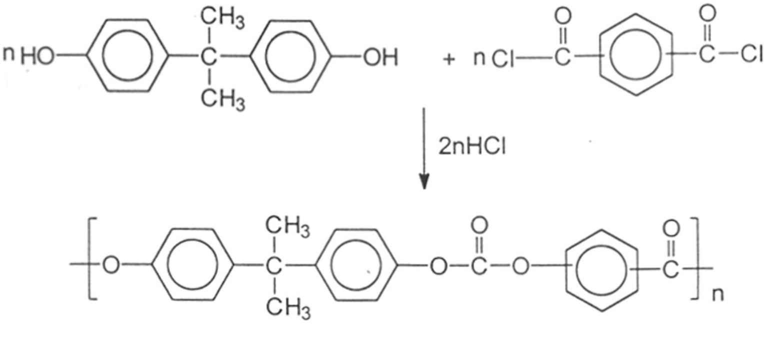
1.2.1 Preparation of poly(aryl ester)s

The direct uncatalyzed reaction of an aromatic diacid with diphenol is inadequate as a general synthetic procedure for the preparation of high molecular weight poly(aryl ester)s[63].

Eliot[64] and East[65] have reported direct preparation of high molecular weight polymer using antimony, tin and titanium from hydroquinones, di-phenols, dicarboxylic acids like terephthalic, isophthalic and naphthalene dicarboxylic acids. This method is not applicable to the preparation of polyesters from diphenols such as bisphenol A. Many other methods have been developed in which at least one of the monomers is derivatized to enhance its reactivity. The poly(aryl ester)s process can be subdivided into three categories, the acid chloride route, the diacetate route and the diphenate route.

1.2.1.1 Acid chloride route

Condensation of an acid chloride with diphenol can be achieved in a variety of ways. The method which has been employed commercially is interfacial.



Scheme 1.2 : Preparation of poly(aryl ester)s by acid chloride route

1.2.1.1.1 Interfacial reaction

The interfacial process for the preparation of poly(aryl ester)s was first reported by Eareckson[66] and Conix[67-69]. The interfacial polycondensation involves the reaction between dialkali metal salt of a diphenol (aqueous solution) and acid chloride dissolved in a water immiscible solvent like dichloromethane or chlorobenzene. The reaction takes place in the interface of the two solvents where a film of the polymer is formed. It will be advantageous if the polymer is soluble in the organic phase. The reactions can be carried out at temperatures of 0-35°C. Phase transfer catalysts such as tertiary amines and quaternary ammonium or phosphonium salts can be used. After the polymerization is completed, the two phases are separated and the polymer is isolated by reprecipitation or by devolatilization. Ueno reported the use of calcium hydroxide in the reactions[70]. Another report describes the use of acid chloride prepared *via* chlorination of corresponding dimethyl esters for the preparation of polyarylates[71].

Interfacial method has been reported to be useful for the preparation of copolyesters[72,73] as well as poly(aryl ester)s of halogenated bisphenols[74]. Hong et al reported the synthesis of block copolymers via two step interfacial polycondensation[75]. The role of different emulsifiers in interfacial polycondensation to prepare poly(aryl ester)as has also been studied[76,77] .

1.2.1.1.2 Solution polycondensation

1.2.1.1.2.1 Low temperature solution polycondensation

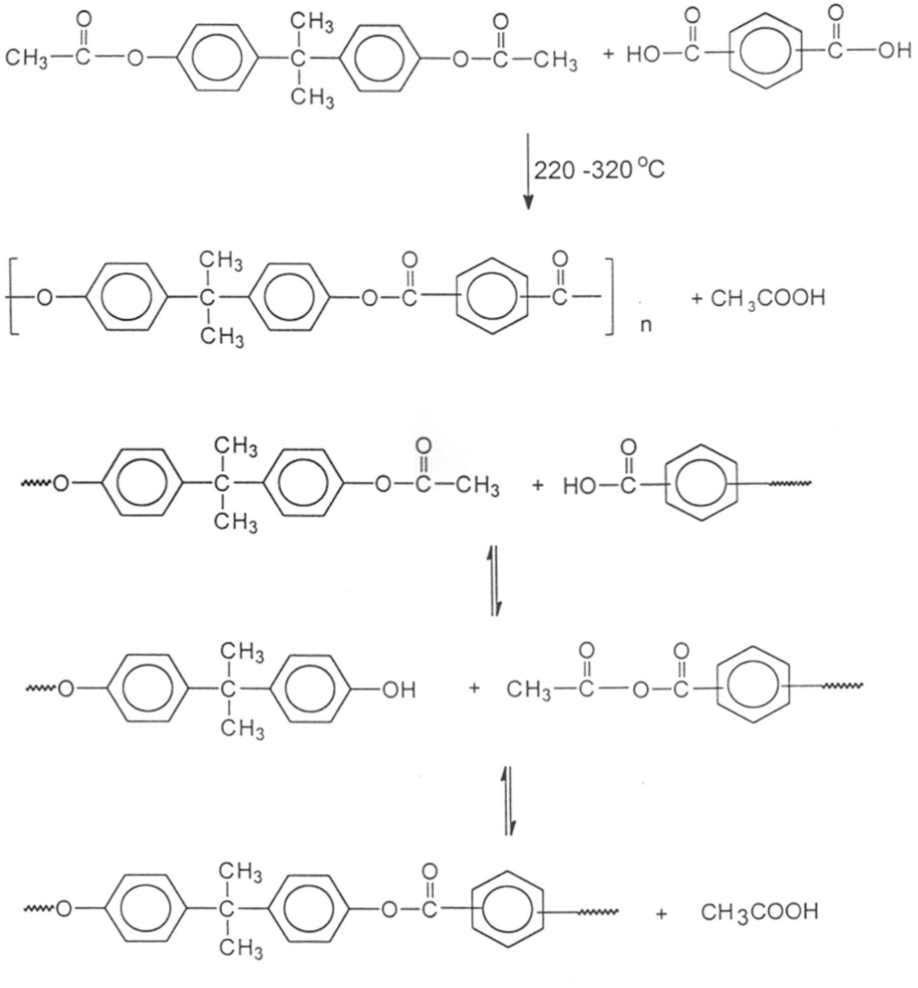
Poly(aryl ester)s can be prepared using the classical Schotten Baumann ester forming reactions[78-81]. Polymer is produced by reacting equivalent amounts of the diacid chloride and dihydroxy compound in an inert solvent like tetrahydrofuran in the presence of an acid acceptor such as pyridine or triethylamine. Reactions are carried out generally at room temperature or below (-10 to 30°C).

1.2.1.1.2.2 High temperature solution polycondensation

The non-catalyzed high temperature reaction of diacid chloride with diphenols in inert solvents yields polyester and hydrogen chloride as by-product. Thus the reaction of isophthaloyl and terephthaloyl chlorides with bisphenol A gave polyester at temperature of 215-220°C in dichloroethyl benzene[84]. The high temperature diacid chloride/ diphenol polymerization can be catalyzed with a large number of Lewis acids and bases [67].

1.2.1.2 Diacetate route

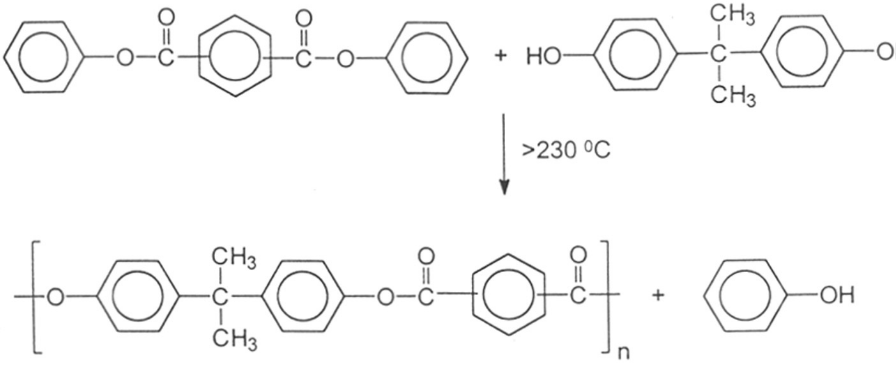
The diacetate process involves the reaction of stochiometric amounts of an aromatic dicarboxylic acid and the diacetate derivative of an aromatic diphenol at high temperature under an inert atmosphere. The reaction is a reversible melt process, which requires continuous removal of acetic acid in order to achieve high molecular weight polymer[66,83] (**Scheme 1.3**). Aromatic ester formation occurs by the reaction of a phenol end group and a mixed anhydride with the elimination of a molecule of acetic acid[84].



Scheme 1.3: Preparation of poly(aryl ester)s by diacetate route

To avoid stochiometric imbalance due to sublimation of diacid and difficulty in handling high melt viscosity, diluents like diphenyl ether, chlorinated biphenyls etc. which are inert under reaction conditions can be used. The reaction rate can be enhanced by esterification catalysts based on antimony, titanium and zinc[85-88]. The diacetate derivative of the aromatic diphenol required for the process can be prepared separately or can be prepared in situ in the polymerization reactor[88-91].

1.2.1.3 Diphenate route



Scheme 1.4 : Preparation of poly(aryl ester)s by diphenate route

The reaction between a diarylester of an aromatic dicarboxylic acid and an aromatic diphenol results in poly(aryl ester)s. The ester interchange reaction can proceed in the absence of a catalyst[92,93]. Rate enhancement can be achieved by using catalysts like lithium phenoxide and sodium borophenoxide to make the process commercially attractive[94-97].

1.2.1.4 Esterolysis route

Direct transesterification of dimethyl esters of terephthalic and isophthalic acids with bisphenol A can give polyarylates with the liberation of methanol as by-product. This route is far less studied than the other methods. Oishi and Hall reported very poor results in terms of polymer yield, molecular weight and colour[98]. Later Idage et al reported that the method can be successfully used if catalysts selected from alkoxides of group IV B metals and derivatives of group IV A metals are employed[99,100]. The process was carried out in two stages. In the first step, low molecular weight prepolymer was prepared from bisphenol A and a mixture of dimethyl esters of terephthalic and isophthalic acid in presence of catalyst in an organic solvent under inert atmosphere. In the second step, the prepolymer was subjected to melt polymerization under reduced pressure at 300-350°C to obtain high viscosities.

1.2.1.5 Solid state polymerization of poly(aryl ester)s

Solid state polymerization of low molecular weight prepolymers can be used to prepare high molecular weight poly(aryl ester)s irrespective of the route which was followed to prepare the prepolymer. Information regarding this kind of processes can mainly be found in patents[101-106]. US patent 5,164,478[101] describes method for preparing bisphenol A poly(aryl ester)s with isophthalic acid/terephthalic acid in the molar ratios of 85:15 to 15:85. The process comprises of a melt polymerization and solid state polymerization. In the first step, bisphenol A, isophthalic acid, terephthalic acid and acetic anhydride were reacted in dowtherm A in presence of lithium hydroxide in acetic acid as catalyst which were co-distilled at 280°C. The reaction was then continued under reduced pressure. The prepolymer thus obtained was crystallized in 2-ethoxyethyl acetate at 150°C. The crystallized preolymer thus obtained was subjected to SSP under dry N_2 gas in the temperature range of 180-225°C to obtain polymer of inherent viscosity (η_{inh}) ~0.6 dL/g. A similar process[102.104] uses bisphenol A diacetate and a mixture of 50-70% isophthalic acid and 30-50 % isophthalic acid as monomers. A number of solvents to be used as crystallizing media are suggested. Crystallization can be performed in hot solvent or at room temperature. When the hot solvent treatment was omitted, less crystallization took place and melting points were lower making subsequent SSP difficult[104].

US Patent 3,684,766[105] describes the preparation of poly(aryl ester)s from bisphenol A diacetate and 50-70 mole% terephthalic acid and 30-50 mol% isophthalic acid. The inventors report that when the acid component is >70%terephthalic acid, the copolymer would have very high melting points, but when it is less than 50%, lower melting points would result making crystallization and subsequent SSP ineffective to build high molecular weights.

US patent 4,314,051[103] reveals a process to prepare semicrystalline prepolymer from bisphenol A diacetate and a mixture of isophthalic/terephthalic acid mixture (composition of isophthalic acid varied from 75-100 mol%). Preparation of prepolymer was done in presence of diphenylether. The inventors claim to have obtained semicrystalline prepolymer and suggest that the presence of diphenyl ether helps the material to achieve higher crystallinity. Melting temperature of the prepolymers are in the range of 335-400°C. Polymer was prepared by subjecting these semicrystalline prepolymers to SSP at temperature range of 265-350°C. No special treatment was necessary to make the prepolymer crystalline.

US Patent 5,714,567[106] reports preparation of poly(aryl ester)s from prepolymer prepared from bisphenol A and a mixture of dialkylesters of isophthalic and terephthalic acid *via* SSP. Prepolymer was prepared by melt polycondensation and crystallization was done in solvents like ethylacetate, acetone, toluene, xylene etc. The advantage of the process is that the by-product is methanol which is less hazardous and low boiling and hence, easily removable.

1.2.1.5.1 Crystallization of poly(aryl ester)s

All the above mentioned patents specify the need to crystallize the prepolymers before subjecting to SSP under vacuum or in an inert gas flow. Since poly(aryl ester)s are difficult to crystallize thermally, the crystallization is done by contacting the material with a crystallizing medium.Diluents which can be used to crystallize the prepolymer are those which swell but do not dissolve the prepolymer particles[102,104,105]. They include many nonhalogenated compounds with solubility parameters (δ) in the range of 16.3 to 22.4 (J cm^{-3})$^{1/2}$. Halogenated compounds tend to be true solvents instead of swelling agents, but mixtures of halogenated hydrocarbons such as dichloroethane, chlorofrom and chlorobenzene with at least 30% by volume of nonsolvents or swelling agents such as saturated hydrocarbons, ketones and alcohols may be used if the solubility parameters of the mixture is 16.3-22.4. Diluents' boiling point should be at least 50°C or can be as high as 300°C. Preferably it can be below 160°C enabling the easy removal. If the boiling point is very high, removal can be facilitated by washing with low boiling solvent such as acetone. Diluents which can be used to swell and crystallize the prepolymer include (solubility parameters are given in brackets) butyl acetate, ethyl butyrate, methyl isopropyl ketone (17.3), diethylcarbonate, xylene, butyl propionate (17.9), toluene, butyl fromate (18.16), ethyl acetate (18.5), benzene (18.7), acetone (20.2), diethyl phthalte (20.4), acetic acid (20.6) and methyl benzoate (21.4). Solvent mixtures which can be used include 60/40 chlorofrom/acetone, 70/30 dichloroethane/heptane, 50/50 chlorobenzene/toluene, 50/50 cyclohexanone/diisopropyl ketone and 50/50 heptane/diethyl malonate (solubility parameters of the solvents: chloroform 18.9, dichloroethane 20, heptane 15.1, chlorobenzene 19.38, cyclohexanone 20.2, diisopropyl ketone 16.3, diethyl malonate 22.4)[104,105].

It can be generalized that the most useful swelling agents include the nonhalogenated aromatic and aliphatic carboxylic acids and nonhalogenated aromatic hydrocarbons having solubility parameter in the range of 16.3-22.4$(Jcm^{-3})^{1/2}$.

Crystallization can be performed by stirring the prepolymer in solvent at room temperature or at high temperature upto 150°C. After crystallization is completed, the hot solvent can be removed by filtration or by distillation under reduced pressure. It has been observed that when the hot treatment is avoided, less crystallization took place causing the particles to stick together during SSP.

1.2.2 Properties and applications of poly(aryl ester)s

Poly(aryl ester)s are tough materials having excellent mechanical and thermal properties. The amorphous bisphenol A based poly(iso/terephthalic) esters are similar to aromatic poly(carbonate)s but, exhibit, significantly higher heat resistance. The most interesting property of poly(aryl ester)s is the behavior upon exposure to ultraviolet light. Although initially the polymers do not have good UV light resistance, they rapidly rearrange on exposure to yield o-hydroxy benzophenone structures which have UV stabilizing effects. This reaction is known as photo-Fries rearrangement and leads to highly stabilized layer of polymer near the surface which protects the bulk of the material beneath the layer. Thus, poly(aryl ester)s can be coated on to polymer substrates like PVC, nylon 66 and PET and the coating allowed the rearrangement to form UV stabilized layer. Due to photo-Fries reaction, poly(aryl ester)s do not exhibit surface haze development on exposure to light and hence, can be used for tinted glazing purposes.

Another interesting property of poly(aryl ester)s is the very high recovery that takes place after release of a deforming stress. This property can be made use of in manufacture of clips, springs and fasteners.

Poly(aryl ester)s are inferior to poly(carbonate)s in impact strength but at elevated temperatures, poly(aryl ester)s show higher impact strength. The heat and impact resistance of these resins suggest applications in solar energy devices, mine safety devices and transportation. The excellent thermal, electrical and flammability properties make polyarylates well suited for electrical hardware. After 8,000 hours of weathering, poly(aryl ester)s show only a slight loss in Notched Izod toughness and first minor changes in tensile modulus and yield strength. Poly(aryl ester)s have outstanding heat resistance, a high heat deflection temperature and modulus retention which make them logical choices for automotive lighting applications.

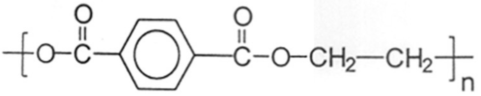
1.3 Poly(ethylene terephthalate)s

Poly(ethylene terephthalate)s (PET) are a major industrial polymer which is extensively used in the form of fibers, films and as moulding material.

PET was discovered and its potential as a fiber forming polymer was recognized by Whinfield and Dickson in 194[107]. In early 1950s, ICI Ltd. (UK) and E.I DuPont Nemours & Co., Inc (USA) started its manufacture. There has been a drastic increase in global PET production from below 500 t in 1970 to over 500,000 t in 1985 and further to 1.2 million t in 1992[108]. This dramatic growth was mainly due to the development of PET beverage bottles. World demand, which was 1.77 million t/year in 1992 is expected to be doubled beyond 2000[109].

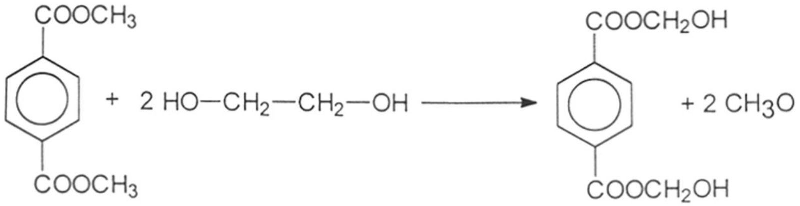
1.3.1 General methods of preparation

Synthesis of PET is only one of the steps in the manufacture of commercial PET fiber [110]. PET is a condensation homopolyester made from dimethyl terephthalate (DMT) and ethylene glycol (EG) and has the repeat unit structure(II).

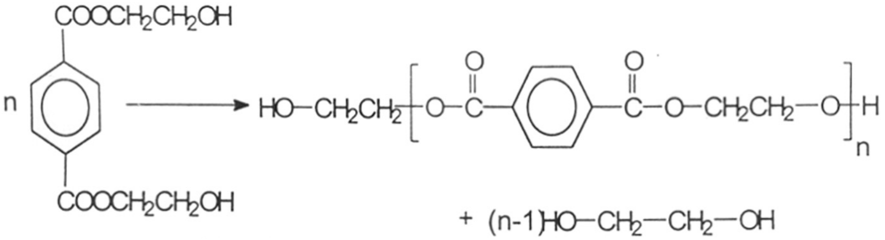


(II)

PET can also be obtained by the direct esterification of EG with terephthalic acid (TPA). The ester is easier to be purified than the acid which sublimes at 300°C and quite insoluble. Thus, many processes were initially developed with DMT. The commercial production of PET involves two steps. Transesterification or direct esterification to form the diol diester, bis(hydroxy ethylene)terephthalate (BHET) **(Scheme 1.5)** and low molecular weight oligomers and a melt polycondensation step which may be carried out in several stages in order to achieve very high molecular weights. DMT to EG molar ratio is usually 1: 2.1-2.2 and the reaction takes place at 180-210°C in the presence of a catalyst. The second step is the polycondensation reaction which takes place at 270-285°C with evacuation to less than 1 mm Hg in presence of a catalyst like antimony trioxide **(Scheme 1.6)**. This also is a transesterification reaction with elimination of EG and building up of the polyester.



Scheme 1.5 : Preparation of BHET



Scheme 1.6: Polycondensation of BHET to PET

Through the elimination of excess of EG, a number average molecular weight (M_n) of ~20,000 is reached. Owing to the very high temperatures during the final stages of the second step, thermal decomposition of end groups to acetaldehyde and or thermal ester scission occurs, competing with the polymer step growth reactions. These side reactions place the upper limit on the M_n that can be realized by the melt condensation reaction[111]. The molten polymer is finally extruded and pelletized. PET pellets can be compounded for moulding, melt-spun into fibers, extruded as films or blown as bottles.

PET with a weight average molecular weight (M_w) of 35,000-40,000 is used for textile fibers, oriented films and reinforcement with glass fibers. To be used in tire cords PET should have M_w of ~50,000 while for injection molded articles it is ~ 80,000. Such high molecular weight PET can be obtained by subjecting the material obtained from melt condensation to SSP.

1.3.2 Catalysts for PET preparation

A good catalyst for PET synthesis is one which accelerates both the transesterification and polycondensation reaction to an equal degree. Furthermore, it should have good solubility in the reaction medium and it should not promote side reactions. Generally two types of catalysts are used, transesterification and polycondensation catalysts. Transesterification catalysts are very active in high and low carboxyl content medium, but they are easily poisoned by small amounts of acid end groups[112,113]. Polycondensation catalysts are insensitive to acid end groups, but their catalytic activity is known to increase as the concentration of hydroxyl end groups decrease.

Transesterification catalysts that have gained commercial importance are acetates of zinc, manganese, calcium and sodium. The relative efficiency of these catalysts is in the following order Zn> Mn> Ca> Na[114].

For the polycondensation stage, antimony trioxide or antimony triacetate catalysts are commonly used. Polycondensation reactions proceed by the nucleophilic attack of hydroxyl end groups upon the ester carbonyl groups. The polycondensation catalysts facilitate the coordination of metal ion to the ester carbonyl bond which increases the polarity of this bond and facilitates the nucleophilic attack[115-118]. In the initial stages of polycondensation, antimony compounds form stable complexes with ligands containing hydroxyl groups and cannot react with carbonyl groups of ester. Thus the catalytic activity of antimony compounds is less at high concentration of hydroxyl groups observed in the initial stages of polycondensation[119]. As the polycondensation reaction progresses the concentration of hydroxyl end groups decreases and the coordination of the carbonyl groups to antimony catalyst becomes possible. Thus the activity of the antimony catalysts increases as the polycondensation reaction proceeds.

1.3.3 Solid state polymerization of PET

In the melt state PET molecules bearing terminal hydroxyl groups are capable of undergoing interchange reactions between the hydroxyl groups and ester linkages. Interchange between the two ester linkages, namely, esterolysis is also possible. Both these reactions can occur intramolecularly or intermolecularly and the products depend on the position of reacting ester linkages along the polymer chain. Free ethylene glycol cannot be formed if the ester linkage is in an inchain position. It is found that the only reaction which give the product an increase in molecular weight is the interchain reaction of a terminal hydroxyl group and terminal ester linkage[60].

In the final stages of melt polymerization, interchain reactions between a hydroxyl group and an inchain ester linkage as well as that between two inchain ester linkages become predominant. In either of these two reactions, there is no increase in the number average molecular weight. Thus it is difficult to prepare PET of molecular weight larger than 30,000 *via* melt polymerization.

To obtain high molecular weight PET, the above mentioned reactions should be minimized or avoided and only the terminal ester linkages should be activated. This condition can be fulfilled if further polymerization is carried out in the solid state. In the solid state polymerization, reaction temperature is kept below the melt temperature of PET, but still high enough to activate the terminal ester linkages, so that interchange reactions between the hydroxyl groups of one PET molecule and the adjacent terminal ester linkage of another molecule can still take place. In this reaction EG is split off and the number average molecular weight is increased[60]. In a practical view point obtaining high molecular weight PET is not possible in melt as the high viscosity of the melt causes stirring difficulties. Solid state polycondensation proceeds at a relatively low temperature, in comparison with that required in the melt and thermal degradation processes are suppressed to a great extent. Only by solid state polycondensation, it is possible to obtain PET free of DEG[120]. It was shown that DEG content strongly affects PET structure and properties[121-123]. The DEG content in PET has a negative effect on many properties such as thermal and light stability[122, 124].

1.3.3.1 Kinetics and mechanism of SSP

In the first part, kinetics and mechanism of SSP was discussed in general. In this section, kinetics, mechanism and the factors affecting these will be looked into, with the emphasis on SSP of PET. As mentioned earlier, the polycondensation rate depends on both chemical and physical processes and the possible rate determining steps are

1. A reversible chemical reaction.
2. Diffusion of the volatile reaction products (predominantly EG) in the solid polymer.
3. Diffusion of the volatile reaction products from the surface of the polymer to the inert gas.

Much work has been done to understand mechanisms operating under various conditions and at different stages of solid state polymerization and diverse models have been used to explain the observations by authors.

Chang[44] interpreted his data using a diffusion controlled model, while Schaaf et al[58] and Chen et al[41] analyzed the data using a purely kinetic model. Diffusion of end groups was taken into consideration in a purely kinetic model by Chen and Chen[125]. Jabarin and Lafgren[59]developed empirical equations relating the final molecular weight and reaction time for specified catalysts and polymer systems. Ravindranath and Mashelkar[126] analysed the previous models and brought out some of the limitations in them. They developed a model considering both diffusion and generation of ethylene glycol during the course of the reaction. They analysed limiting cases of SSP in kinetically or diffusion controlled regimes and were able to predict the influence of particle shape, particle size, temperature etc. They also tried to explain the role of nature of the carrier gas on the basis of gas side resistance, but they could not include crystallization kinetics and its influence on the diffusion rate of EG. But, the model considered diffusivity of EG to be constant which is not true since diffusivity decreases with increase in crystallinity. Additionally, the model could not successfully explain the differences in the degree of polymerization with different carrier gases, namely, helium, carbon dioxide and nitrogen. Later, Devotta and Mashelkar[127] tried to offer an explanation by considering the effect of carrier gas on the fractional free volume in the polymer. They incorporated the possible side reactions also since the quality of PET depends on these. They attempted to account for the change in the mobility of the reactive chain end groups in the model. According to the model, for a specified time, as the particle size decreases, the degree of polymerization increases. The rate of rise of degree of polymerization is very small for larger particle size where the process approaches the diffusion controlled regime. Predicted values agree well with the experimental values for smaller particle sizes, but for the larger particles lower values were predicted than the experimental. The model predicted changes in free volume as a function of time that are brought in due to crystallization and the adsorption of helium, carbon dioxide and helium. Hsu's[60] data regarding the effect of carrier gases ($N_2 < CO_2 <$ He) was explained by the model taking into consideration that helium has relatively higher diffusivity and does not get affected by the changes in crystallinity which resulted in higher free volume growth rate and hence in a higher degree of polymerization. However, the degree of polymerization in the presence of carbon dioxide is found to be higher than that with nitrogen as carrier gas, although the diffusivity of nitrogen is slightly higher than carbon dioxide. This can be because of the higher solubility of carbon dioxide in the polymer[128] compared to nitrogen which can induce plasticization effect enhancing the local mobility[129]. Hsu's[60] study suggest that the concentration of acetaldehyde in the final product depends to an extent on the carrier gas. The model put forward by him predicts that the average concentration of acetaldehyde would be less for carbondioxide compared to nitrogen. This is due to the higher diffusivity of acetaldehyde in presence of carbon dioxide compared to nitrogen. However this has to be proved experimentally[60]. In contrast to these observations a study carried out by Mallon et al proves that there is no effect of the type of purge gas on rate of SSP[130].

According to Hsu[60] there is an optimum value of the flow rate above which only a modest increase in molecular weight is obtained (500 mL/min). The predicted curve from the model agrees reasonably with the experimental data. Predicted results regarding the effect of time on SSP shows increase in molecular weight upto 40 hours and then decreases in molecular weight due to chain degradations. The effect of temperature on SSP rate could be predicted with the model and agreed very well with the experimental data in the literature. As the reaction temperature falls from 250-200°C there is a drastic change in the degree of polymerization achieved[127].

Wu et al[131] developed a model which took into consideration diffusion limitation of end groups and by-products, as well as, the modification of end group concentration in the amorphous phase. In addition to the transesterification and esterification reactions, degradation and other side reactions also were included. Effect of molecular weight of starting material was also investigated. The higher the starting molecular weight, the faster were reaction rates obtained. In the solid state, concentrations of glycol and water in the outer shell of a PET particle are lower than that in its center because of the diffusion limitation of by-products, thus reaction rates of end groups in the outer shell are faster than that in the center, which leads to the difference in end group concentrations and molecular weight between the outer shell and the center. The model predicts higher molecular weights when ratio of COOH/OH end groups are in the range of 0.5-0.8 and this ratio is insensitive to the reaction temperature and the particle size. These results are similar to that of Schaaf's[58]. The variation of the carboxyl end group concentration with reaction time at different concentrations could be predicted which were close to the experimental findings. Carboxyl end group concentrations decreased sharply during the first stage of SSP. Thus it is possible to prepare PET products with low concentration of carboxyl end groups *via* SSP.

Wu et al[131] and Kang[132] tried to incorporate the effect of crystallization on SSP, but could not provide a clear picture. The effect of chain entanglement on chain mobility was also taken into account for the estimation of rate constants by Kang. Assuming that the concentration profiles of volatile by-products in spherical particles are described by a sinusoidal function, the mass transfer rate of the by-products at a given time could be derived as an ordinary differential equation that can be easily treated.

A recent study by Huang and Walsh[133] regarding the effect of particle size and gas velocity on SSP revealed that at a given gas flow velocity, the reaction mechanism for a large sized sample changes from chemical reaction control to interior diffusion control with increasing temperature. At a given reaction temperature, reaction control mechanism for a small sized sample changes from surface diffusion control to chemical reaction control with increasing gas flow velocity, at a given reaction temperature and gas flow velocity, the reaction mechanism changes from interior diffusion control to surface diffusion control with decrease in particle size. In short, the reaction rate is not determined by a single control mechanism but by both diffusion and chemical reactions in the temperature range of 200-220°C.

1.3.3.2 Preparation of PET *via* solid state polymerization

Solid state polymerization has been industrially used to obtain high molecular weight PET required for engineering applications. Because of the commercial interest, improvements and modifications to the process can be found mainly in patents. In this section, information available in this area will be discussed briefly.

SSP of commercial grade PET (M_n 20,000) at 250°C gave ultra high molecular weight[60]. Also samples with initial molecular weights of 15,300, 16,500, 2,400, 8,400 were subjected to SSP to obtain 80,000, 104,00, 18,00, 65,000 respectively. Catalysts used were tetraisopropyl titanate, zinc acetate, antimony trioxide and cobaltous acetate.

Miyagi and Wunderlich[134,135] annealed etched PET oligomer lamellae from the same polymer under vacuum at temperatures between 200 and 260°C for a period between 3-48 h. The sample molecular weight increased, showing that the crystal lamellar surface is chemically reactive.

German Patent 2,415,729[136] describes a method to obtain high molecular weight PET to make moldings of increased crystallinity and thermal dimensional stability by SSP. Precrystallization of PET particles in the form of tubes or pellets were done at 70°C for 2 days followed by SSP at 255-270°C for 4 days.

Droscher and Wegner[120] reported SSP of the precondensate prepared from BHET and terephthaloyl chloride. SSP was carried out under reduced pressure at temperatures between 219 and 254°C. Reaction proceeded with the evolution of HCl. To avoid sticking in the course of heating to the desired annealing temperature, the heating rate was adjusted in such a way that the precondensate undergoes sintering, so that the melting point of the precondensate rises faster than the actual temperature of the sample. During the actual annealing period, the molecular weight increased by condensation of the still unreacted end groups and transesterification.

Takehiko et al[137] obtained high molecular weight PET (limiting viscosity 1.07) by SSP of prepolymer prepared from DMT and EG at 230°C under reduced pressure for 16 hours with residual a content of DMT of 1.2 eq/10^6g, while the final product obtained was of 1.01 limiting viscosity when the residual content was 6.5 eq/10^6g.

US patents 4,755,587[138], 4,876,326[139] and 4,489,497[140] suggest improvements in the process by using prepolymers which was compacted in the form of porous pellets. Prepolymers were crystallized prior to compacting by heating to temperatures between 170 and 180°C for 1-2 h. Inventors claim that the method enhances the SSP rate. Starting from a prepolymer of [η] 0.259 dL/g, PET with an [η] 0.737 dL/g after SSP at 227°C for 16 hours. Similarly material with [η] of 1.04 dL/g was obtained from 0.59 dL/g after SSP at 227°C for 2.5 h. Material with 0.25 dL/g was subjected to SSP at 236°C for 6.5 hours to get material of [η] 0.89 dL/g. Karou et al also describe SSP of PET made into the form of porous pellets[141].

US patent 4,644,049[142] describes crystallization of PET oligomers by solvent vapours and SSP of the crystallized oligomers. Solvents used were chlorinated hydrocarbons, ketones, THF, ethylene oxide or propylene oxide.

SSP of post consumer PET to prepare high performance materials also have been gained importance. Post consumer plastics were chopped into flakes and chunks which were preheated for crystallization[143]. These crystallized materials were further heated under N_2 flow to obtain high molecular weight.

Karayannidis et al[144] subjected PET taken from postconsumer soft drink bottles to SSP after dissolution in various solvents and precipitation in methanol. The solvents used were benzyl alcohol, phenol/tetrachloroethane (60/40) or o-chlorophenol. The highest number average molecular weight $M_n = 60,200$ was obtained from PET with initial $M_n = 20,300$ dissolved in o-chlorophenol after solid state polymerization at 230°C for 8 h. Kumar et al[145] reported a solid state semicontinuous process to make PET foam sheets. In contrast to most of the traditional foam processes in which the polymer has to be melted, PET sheet was kept near the glass transition temperature during the foaming step, thus obtaining a finite length of foam sheet at a time.

The SSP of amorphous and unoriented PET film from Du Pont which was prepared from a specific catalyst and monomer system was studied by Karayannidis et al[146]. The reaction was done in a rotary vacuum evaporator using a 250 mL flask. Reaction temperatures were in the range 210-240°C. Samples were heated to the required temperature, when the pieces stuck together and the transparent films turned opaque. The flask was cooled to the room temperature and the pieces were unstuck with glass rod and the reaction was continued. Starting from an inherent viscosity (η_{inh}) of 0.7 dL/g, they obtained η_{inh} of 1.27 dL/g after 8 h at 240°C.

In most of these reports as well as those discussed in the previous section, it can be seen that the precursor material for SSP is of fairly high viscosity of ~0.6 dL/g. Crystallization of the prepolymers is done by preheating to a lower temperature. One exception is reported, wherein, crystallization was done by diluent vapours[142].

Two patents from Du Pont[147,148] discuss a novel method to crystallize low molecular weight PET oligomers ([η] 0.15-0.2 dL/g) which could then be used as precursor materials for SSP. The inventors claimed unique crystalline structure (crystal size, 13 nm) for such crystallized oligomers. The crystalline form was produced from molten or glassy low molecular weight PET material by means of rapid heat transfer to or from the material.

Mallon et al reported that SSP rates could be enhanced with microwave energy[149]. Theoretical analyses and experimental evidence show that the increase in polymerization rate is not due to an increase in the bulk temperature. Instead, the effect is consistent with directed heating of the condensates leading to enhanced diffusion rates.

A modification of solid state polymerization, which was termed as swollen state polymerization, was introduced by Tate et al[150-152]. Ultra high molecular weight PET was obtained by swollen state polymerization in specific diluents under bubbling nitrogen gas at atmospheric pressure. Suitable diluents were those that could swell PET but did not dissolve it. Diluents having a solubility parameter similar to PET were desirable for attaining higher ultimate intrinsic viscosity at the same polymerization temperature. The material obtained by swollen state polymerization showed a honey comb like structure[151]. Later, reaction kinetics of swollen state polymerization was studied by Tate et al[153] and Parashar et al[154]. According to Tate the rate of swollen state polymerization could be well described by Tomita's kinetics for a melt phase polycondensation reaction and thus there was no essential difference in the kinetics between swollen state and conventional melt phase polycondensation reaction. Compared with the rate constants of conventional solid state polymerization, the propagation rate of swollen state polymerization was about three to five times faster than that of SSP at 220°C, whereas, the rate constant of the degradation reaction in the swollen state was of the same order as that in the solid state.

1.4 Poly(ethylene naphthalate)s

Although the demand of PET is very large, better thermal and mechanical properties are desired for some applications. Polyimides are superior in these properties, but the high price and processing problems remain to be overcome[155]. The new family of polycondensates containing naphthalene groups in the repeat structure shows a great promise to fill this gap[156]. Large scale production of the monomer 2,6-dimethylnaphthalene dicarboxylate by Amoco has already commenced[157].

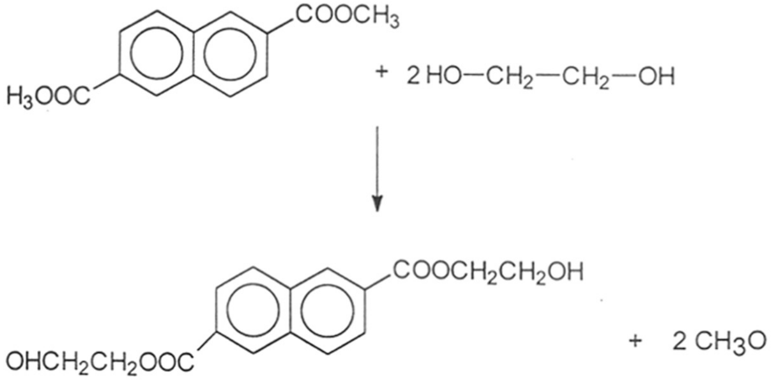
Poly(ethylene 2,6-dimethyl naphthalate)s (PEN) are thermoplastics with outstanding properties. PEN with rigid naphthalene ring and flexible aliphatic diol structure will not be difficult to process and should have superior physical and mechanical properties than widely used PETs. It has a glass transition temperature (T_g) of 118°C (45°C higher than the T_g of PET) as well as excellent mechanical and gas barrier properties[157]. A comparison between PET and PEN in their properties for packaging applications show that PEN has potential for hot-filled products and for applications requiring increased oxygen and carbon dioxide barriers. While PET has about four times the O_2 permeation of PEN, its CO_2 permeation is five times higher. These properties make this polymer very attractive both as packaging and engineering material. PEN is also well known for its photochemical properties[159,160], electrical properties[164] and the ability to from liquid crystalline polymers when polymerized with suitable comonomers[162] such as 4-hydroxy benzoic acid[166,167]. Teijin Ltd.[152] has produced high quality fibers from PEN with flexibility, toughness and resistance to heat and abrasion. An oriented multilayer polyester for magnetic recording tape with good machine direction strength and heat resistance was reported by Tahoda et al[166].

From a structural point of view PEN is interesting, because it can be obtained in two crystal forms[167,168]. The unit cell of α modification was determined by Mencik[169]. It is triclinic with dimensions of a = 0.651 nm, b = 0.575 nm, c = 1.32 nm and angles of α = 81.33, β = 144, γ = 100°[168]. The unit cell of β modification is also triclinic with dimensions of a = 0.926 nm, b = 1.559 nm, c = 1.273 nm and angles of α = 121.6, β = 95.57, γ = 125.52°.

1.4.1 General methods of preparation

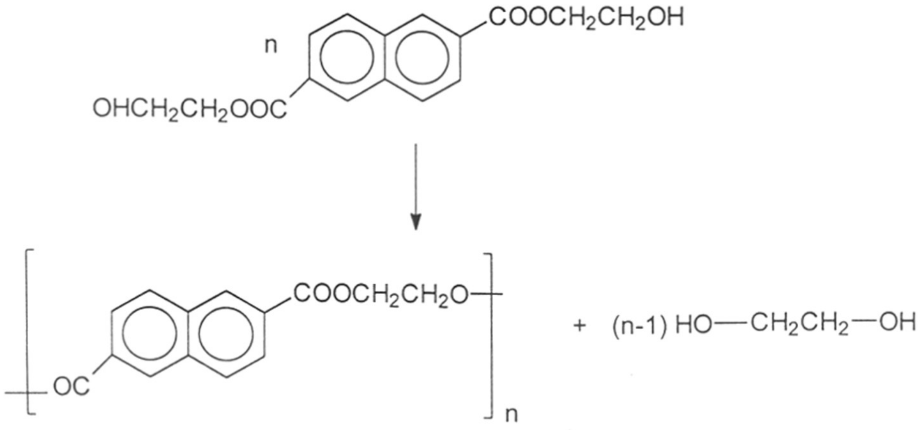
Transesterification process is known to be the preferred process for the manufacture of PEN[170,171]. Similar to the case of PET, there are two steps in the formation of PEN. The first step is the formation of 2,6-bis(hydroxy ethyl) naphthalate (BHEN) from the transesterification of 2,6-dimethyl naphthalate (DMN) with ethylene glycol (EG) and the second step is the PEN formation from the polycondensation of BHEN at elevated temperatures and reduced pressure[155] **(Scheme 1.7 and 1.8).**

i) Esterinterchange or transesterification



Scheme 1.7: Preparation of BHEN

ii) Polycondensation

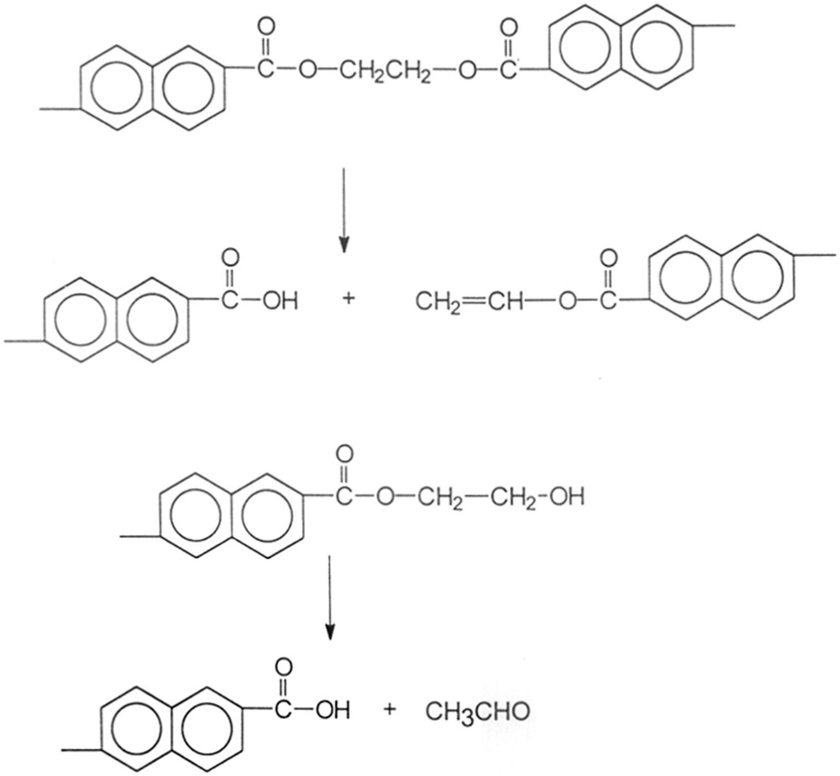


Scheme 1.8: Preparation of PEN by polycondensation

Transesterification takes place in presence of a catalyst like zinc acetate at 185°C with evolution of methanol over a period of 5h. Usually ethylene glycol will be taken in excess for example 1:6. In the polycondensation of BHEN, the reaction would normally be carried out in melt at high temperature, under reduced pressure and in an open sysytem. Due to high temperature at which polymerization is usually performed chain scission and other side reactions can occur leading to carboxyl end group[172,173] . Main side reactions are as shown in **Scheme 1.9.** Controlling the OH/COOH end group ratio is very important for good mechanical and physical characteristics of the final product.

1.4.2 Catalysts for PEN preparation

Zinc acetate, antimony and titanium based catalysts are very active. Titanium based catalysts impart undesirable yellow colour to the final product. Zinc acetate is less active than antimony and titanium based catalysts, but it is the most effective catalyst since it imparts the least colour[155]. Thus to get high molecular weight PEN a little titanium or antimony based catalyst can be added to the zinc acetate system during the polycondensation step. The most effective transesterification catalysts, namely, lead acetate, zinc acetate and cobalt acetate are found to be least effective in the polycondensation of BHEN. Titanium and antimony based catalysts are least active transesterification catalysts[155].



Scheme 1.9: Formation of carboxyl end groups during polycondensation of PEN

1.4.3 Solid state polymerization of PEN

Similar to the case of PET high molecular weight PEN can be produced in a two step process involving i) melt polymerization to a relatively low molecular weight ii) solid state polymerization to a high molecular weight polyester. Thorough studies dealing with mechanism and kinetics of solid state polymerization of PET exist in literature. But in the case of PEN very few reports are found. Information regarding methods employed for SSP of PEN can be obtained only from patents.

Due to the presence of rigid naphthalene group in the polymer backbone, prepolymer obtained *via* melt polymerization is amorphous. Thus it is necessary to convert the amorphous PEN prepolymer to crystalline prepolymer prior to solid state polymerization. The sticking temperature of the crystalline polymer is higher than that of the amorphous polymer and use of the crystalline material will reduce the tendency of the particle to stick together as a solid mass during solid state polymerization[174].

Usually the process of crystallization involves heating the amorphous PEN prepolymer to its crystallization temperature (180-200°C). As the temperature is raised, however the material passes through its sticking temperature (~140°C). In comparison with PET, PEN crystallizes rather slowly and clumping of the particles will occur before the crystallization process is complete[174].

A few methods to obtain crystalline PEN prepolymers to be used as precursors for SSP have been reported.

US Pat. 4,963,644[175] deals with crystallization of PEN pellets. It was found that when PEN pellets were exposed to the required crystallization conditions, the pellets undergo a sudden and rapid expansion as they were heated near to the crystallization temperature, which resulted in a puffed skin of the pellets which subsequently became very sticky and agglomerated into big lumps. To avoid this, the prepolymer was devolatilized at a temperature of 80 to 140°C prior to crystallization, to remove the volatile components of the prepolymer. This treatment prevented the sudden volatilization of the volatile components contained in the pellets during crystallization, thus, avoiding deforming or puffing of the pellets.

US Pat. 5,449,701[176] and 5,478,868[177] describe methods to form foamed PEN which was devolatilized and then crystallized to be used in SSP. In this invention, the last stage of the melt polymerization to prepare prepolymer was performed under vacuum. To produce foamed cubes, the reactor was pressurized with nitrogen while the agitation was continued to whip the nitrogen into the prepolymer melt. Depending on the speed and duration of the agitation after the completion of the melt polymerization and the final reactor pressure used, foamed cubes with various porosities could be obtained. The void fraction of the foamed cubes was about 0.21. Before crystallizing, these cubes were devolatilized at 125°C for 2 hours to remove the trapped by-products which cause severe sticking during crystallization. This was followed by crystallization at 200°C for 1 h and SSP at higher temperature. Solid PEN cubes and porous PEN pellets formed from solid PEN cubes also were subjected to SSP. Foamed PEN underwent SSP about 4 to 4.5 times faster as than the unfoamed PEN, thus, giving productivity advantage of 200% over unfoamed PEN. This unexpected higher rate was explained by taking into consideration the relatively high barrier property of PEN and the dependence of SSP on diffusion rate. Thus any factor which contributes to the reduction in diffusional resistance would result in a greater increase in the SSP rate. Devolatilization step made possible the release of the relatively large amount of by-products as well as nitrogen trapped inside the foamed PEN granules opening up the cells or voids, thus enhancing the diffusion rates of the reaction by products and the overall SSP rate. PEN porous pellets also gave significantly higher SSP rates, but during SSP a considerable amount of fine powder was generated due to disintegration of pellets.

Tung et al[174] coated PEN pellets with ethylene carbonate or propylene carbonate before crystallization. They observed that the coated pellets did not stick during crystallization at 141°C.

Stouffer et al had reported a method to produce crystalline PET oligomers[147,148] to be used as precursors for SSP. Later they employed a similar method to prepare highly crystalline PEN oligomers also[178]. Thus, crystalline PEN oligomers were prepared from molten or glassy low molecular weight material by means of rapid heat transfer to or from the material. The crystalline precursors of $[\eta]$ 0.12 dL/g after SSP at 220°C for 23 h gave material of $[\eta]$ 0.35 dL/g.

Another recent patent by Ben Duh[179] describes the crystallization of PEN at a temperature which is about 10°C below the melting point in presence of diluent or mixtures of diluents that do not degrade the polymer during crystallization. The diluent or diluents employed should have sufficient vapour pressure at the amorphous PEN softening temperature to prevent expansion of pellets. The crystallization was conducted at 170°C in presence of EG or water. In some cases it was necessary to augment the vapour pressure of EG or water with compressed air.

1.4.4 Crystallization of PEN

Published literature on PEN mainly deals with structural variations taking place during processing and the improvements in properties by orientation of PEN films[156, 180-187]. Investigations into the structure of PEN by various analytical techniques also can be found[157,188-193]. In this section information available on crystal structures of PEN and crystallization kinetics will be discussed briefly.

The crystal structure of PEN was determined by Mencik. He reported a triclinic unit cell with cell parameters a = 0.651 nm, b = 0.575 nm, c = 1.32 nm and angles of $\alpha = 81.33$, $\beta = 144$, $\gamma = 100$ °[168] (density 1.407 g/cc). The chains lie parallel to the C-axis. One chain passes through each unit cell. By means of a special spinning process or special annealing process a material with a higher melting point and with better mechanical strength was obtained which crystallized in another crystal modification. Later Zachmann et al showed that PEN could be crystallized in two different crystal modifications[167]. PEN was crystallized isothermally at 167°C and 245°C by heating from the glassy state. Immediately after reaching the crystallization temperature an amorphous halo was observed and later with increasing crystallization time crystal reflections developed. The diffraction which developed at 167°C was different from that obtained at 245°C. Thus PEN crystallized into two different crystal forms: low and high temperature modifications. The low temperature modification can be obtained more easily than the high temperature modification. Low temperature modification once formed often appears again when the sample was melted at 300°C and then recrystallized in the high temperature range. The high temperature modification was obtained when the sample was melted above 330°C, and then cooling it down in 1 or 2 min to 245°C. High temperature modification is thermodynamically more stable but more difficult to nucleate than the low temperature modification. The unit cell of the high temperature modification was determined to be triclinic with cell parameters[168], a = 0.926 nm, b = 1.559 nm, c = 1.273 nm and angles of $\alpha = 121.6$, $\beta = 95.57$, $\gamma = 125.52$ ° (density 1.439 g/cm^3). Four chains pass through each cell. The chains are not completely extended, every naphthalene ring is twisted 180°. The low temperature modification was referred to as α and the high temperature modification as β.

Buchner et al[168] carried out a detailed study to understand kinetics of crystallization and melting behaviour of PEN. The crystallization and melting of PEN was investigated by DSC and by WAXS using synchrotron radiation. By measuring the change of wide angle X-ray scattering during isothermal crystallization using synchrotron radiation it was possible to study the kinetics of crystallization as well as the conditions under which the β modification was formed. At crystallization temperatures up to 200°C only α modification is formed, above this temperature the β modification is formed if the material had been molten at 280°C, while the α modification is formed, if the temperature of the melt was raised to 320°C. This observation is not in agreement with the earlier observation that if the material is molten above 330°C and cool it to crystallization temperature, β modification would be obtained[167].

The half times of crystallization as a function of temperature show a broad minimum ranging from 180 to 240°C. Even though under usual conditions both modifications melt at 270°C, by annealing at 272°C, the melting point was increased to 287°C. This has been attributed to the thickening of the crystals during annealing at high temperatures[168].

1.5 Poly(ethylene naphthalate-co-terephthalate)s

The industrial applications of polymer blends is growing rapidly. This growth is largely caused by the unique combination of properties that can be achieved by blending two or more polymers[194]. In these blends, transesterification (such as alcoholysis, acidolysis or ester exchange) occurs in the molten state, which first produce block copolymers and finally random copolymers[195]. Many studies have been focused on the miscibility and transesterification in polyester blends[196-201]. Suzuki et al reported that polycarbonate and PET could be homogenized by transesterification at 270°C. Later it was reported that the ester carbonate interchange reactions can take place far below the melting point, in solid state. Porter and Kimura studied the phase behaviour and transesterification for a PC and PAr blend[200,201].

PEN in film or molded container form has barrier properties about five times greater than that of PET. Also the relatively high glass transition temperature of PEN makes it useful for hot-fill food and beverage applications where PET is not well suited. Because of the relatively high cost of PEN raw materials and the higher melting point and viscosity of PEN, the polymer is more expensive to use and process than PET. It is therefore desirable to achieve a material that is lower in cost than PEN but has better barrier and hot fill properties than PET[195,202].

One potential approach for combining the attractive economics of PET with the better barrier and thermal properties of PEN is through blends of the polymers. However blending of two polymers often can result in opaque materials with incompatible phases. Stretch-blow moulded bottles prepared from blends of PET and PEN with 50-80 wt% PEN had oxygen permeability approximately half that of PET. But the blends were often hazy, presumably due to immiscibility of PEN and PET and clear bottles were obtained only when sufficient transesterification or interchange occurs during the processing to induce miscibility[203]. The properties of the blend would vary as the interchange reaction proceed[203-206].

1.5.1 Control of transesterification

When the level of transesterification between the two polymers reaches very high levels, the crystallinity and resultant physical properties of the blends can be reduced to the point that they may be undesirable for making containers with many current processes[185]. Thus, it is important to control transesterification in order to obtain products with desirable properties. The optimum degree of transesterification is 25-35%.

The transesterification process for PET is very fast, if samples are heated above T_g. Three different mechanisms are believed to take place in the melt, namely, alcoholysis, acidolysis and ester interchange. The last one seems to be the most important according to the majority of the authors[190]. The process is divided into two steps, the first step is miscibility which is diffusion controlled and the second step is the transesterification which follow Arrhenius law and requires good interfacial contact of the reacting species[190].

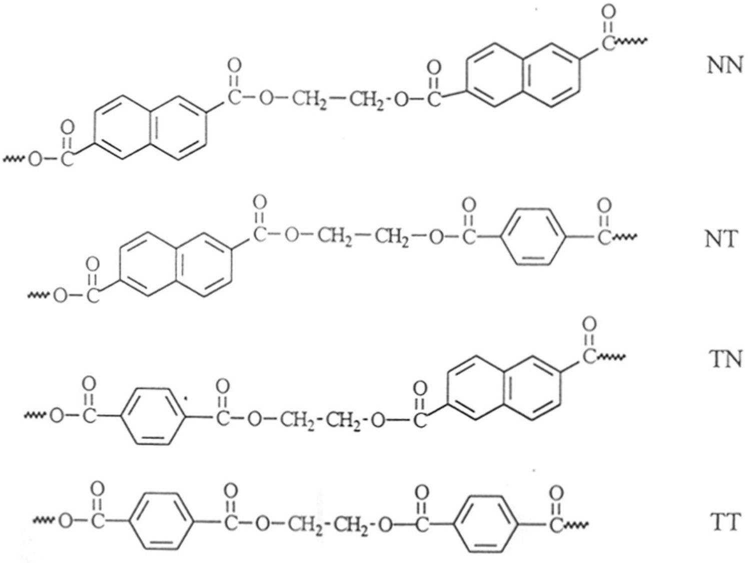
Degree of transesterification is a function of temperature and mixing time, for some authors it is also a function of residual catalyst and inhibitor content as well as naphthalate concentration[208-210]. In contrary, according to some other authors composition of the blend and residual polyester catalysts have little effect on transesterification[206].

Two classes of transesterification inhibitors are reported in the literature: phosphorous and vanadium containing compounds. Similarly, phosphites (dioctadecyl, triphenyl, diphenyl, dibenzyl, decyldiphenyl, bis(dibutyl phenyl), pentaerythritol) are also commonly used[208]. Some authors claim that only the hydrolysed and aged products of these compounds are only active while others suggest that there is no influence at all [209,211]. Inhibitors are applied at concentrations which correspond to two moles per mole of residual catalyst. The chemistry involved is very complex and yet not completely understood.

1.5.2 Phase behaviour and transesterification

In studies regarding the formation of copolymer of PET and PEN the phase behavior is studied by DSC and WAXS while the degree of transesterification is studied by NMR techniques (^{1}H and ^{13}C)[194,195,202,203,212-217]. Blends are obtained by solution precipitation or by melt blending.

Miscibility and effect of transesterification on properties of blends were studied by various investigators. Sequence distribution, block lengths and randomness of the copolymer could be followed by ^{1}HNMR analysis by taking into consideration areas under the peaks for ethylene units. PEN/PET copolyesters could be split into multiplets owing to four possible environments for ethylene units. NN, TT, NT and TN[194,212] **(Scheme 1.10)**.



Scheme 1.10 Possible environments of ethylene units

It was found that at a similar composition ratio and with blending time, the degree of transesterification increases, but the block length decreases showing increase in randomness. The melting peak depressions occur with increasing content of the other component and melting peaks disappear at a similar composition ratio. The crystal peaks of PEN/PET random and block copolyesters disappear at a similar composition ratio indicating that a critical block length is needed for components in order to crystallize. In the case of block copolyesters, inherent viscosity decreased with blending time[194]. The dependence of the phase behaviour on the transesterification could be investigated by DSC. For the PEN/PET (50/50) blend samples, heat treated at 280 °C for 20 min or more, cold crystallization and melting were not observed, which is attributed to the disruption of the chain periodicity as a consequence of transesterification. In the early stages of transesterification, two glass transitions appear, which approach mutually closer with the increase of reaction time. This indicates that the composition difference in two coexisting phases decreases, as the transesterification proceeds[195,212].

A study by Lu and Windle showed that significant crystallinity can be induced in the copolymers of all compositions by hot drawing, even if the compositions in the 50/50 region[218]. The results from wide angle X-ray scattering experiments indicate that in two different composition ranges, these copolymers show distinctly different structures[218,219].

1.5.3 Change of molecular weight with transesterification

Studies carried out by Yoon et al focussed on the change of molecular weight of PEN/PET blend with reaction time[220]. As shown by many studies mentioned above, when only transesterification occur, there is no net change in the number of the molecules, hence the number average molecular weight (M_n) will be unaffected by reorganization process. Thus, molecular weight distribution which was initially bimodal, changes and produces corresponding changes in the weight average molecular weight (M_w) and intrinsic viscosity with reaction. However, there are a few reports in which the increase of the molecular weight due to the end group reaction was quantitatively considered[221].

Yoon et al studied the change[220] in molecular weight of a blend of PEN/PET (50/50w/w) which was prepared by solution precipitation method and kept at 280°C for different periods. Intrinsic viscosity was found to increase with reaction time. This could be due to two reasons i) increase of molecular weight ii) the change of solvent quality. To confirm, weight average molecular weight were measured by means of laser light scattering which showed that apparent molecular weight and hydrodynamic volume also increased with reaction time. They found out the difference between the true molecular weight (M_w) and apparent $M_{wa}{}^{pp}$ and concluded that the molecular weight increases due to end group reactions.

1.5.4 Preparation of poly(ethylene naphthalate-co-terephthalae)s *via* solid state polymerization

Cox et al[202] found that transesterification between PET and PEN can also take place in solid state, where the melt blended, crystallized polymer is held at temperatures below the melting point and subjected to an inert gas flow to raise the molecular weight. If the level of transesterification reaches very high levels, the resultant material could not be used for making articles with good mechanical properties. To limit the transesterification taking place during the reaction to a desirable level (5-20%), 0.25 wt% of a phosphorous stabilizer such as bis(2,4-di-t-butyl phenyl) pentaerythritol diphosphate was added.

Hoffman in US Pat. 5,688,874[219] describes preparation of PET/ PEN blends by solid state polymerization. He also observed increase in transesterification level as well as increase in inherent viscosity during solid state polymerization.

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CHAPTER 2

SCOPE AND OBJECTIVES OF THE PRESENT WORK

2.1 Introduction

Solid state polymerization (SSP) is a commercially important industrial process. It is extensively practiced in the production of polycondensation polymers such as poly(ethylene terephthalate)s (PET), poly(butylene terephthalate)s (PBT) and nylons. Generally, SSP is performed on oligomers with intrinsic viscosity ([η]) ~0.5 dL/g to obtain polymers with [η] ~1 dL/g.

Recently it has been shown that in the case of poly(carbonate)s (PC), SSP can be performed on semicrystalline oligomers having viscosities as low as 0.15 dL/g to obtain high molecular weight PC[1,2]. Patents have been filed for processes in which low molecular weight oligomer is crystallized followed by SSP to raise the molecular weight to the desired level[3-5]. These new processes are awaiting commercial exploitation.

The principal objective of this thesis is to examine in depth, the crystallization and SSP of polyester oligomers having low molecular weights. To this end two types of polyesters have been chosen. The polymers selected are poly(aryl ester)s, PET and poly(ethylene 2,6-dimethyl naphthalate)s (PEN). Poly(aryl ester)s are amorphous polymers and hence, difficult to crystallize. On the other hand, PET and PEN are semicrystalline polymers and are easier to crystallize.

2.2 Objectives of the present work

2.2.1 Crystallization and solid state polymerization of poly(aryl ester)s

Poly(aryl ester)s are generally prepared by the melt polymerization of bisphenol A diacetate (BPA diacetate) and a mixture of terephthalic acid and isophthalic acid (TPA/IPA) where, the by-product would be acetic acid[6-8]. A few reports exist in which modifications of diacetate process have been used to prepare poly(aryl ester)s by a combination of melt and SSP processes[7,8]. Transesterification of dimethyl esters of terephthalic and isophthalic acids with bisphenol A can give poly(aryl ester)s, but this route is far less studied than the other methods. It has been reported that the method can be successfully used if catalysts selected from alkoxides of group IV B metals and derivatives of group IV A metals are employed[9-11]. Application of SSP to amorphous polymers such as poly(aryl ester)s are rare[1], because of the need to crystallize the amorphous oligomers prior to the process. *Thus, the objective of the present work is to explore the feasibility of using solid state polymerization for the preparation of poly(aryl ester)s derived from dimethyl esters of isophthalic and terephthalic acids and* *bisphenol A. Crystallization of amorphous oligomers using suitable diluents prior to SSP will be investigated. To study the effect of end groups on SSP, oligomers with specific end groups will be prepared by degradation of commercial poly(aryl ester)s using different routes. Effects of different classes of catalysts on the rate of SSP will be examined.*

2.2.2 Crystallization and solid state polymerization poly(ethylene terephthalate)s

Most of the applications of PET require polymers of relatively high molecular weights ([η] 0.55-0.85 dL/g)[12]. Commercially, high molecular weight PET has been made by a combination of melt polymerization and solid state polymerization. In solid state polymerization, polycondensation is carried out by heating the semicrystalline oligomer having [η] ~0.5 dL/g in a stream of inert gas or under reduced pressure at a temperature below the polymer melting temperature. Oligomer of [η] ~0.5 dL/g are prepared by melt phase polymerization. PET oligomer in the form of chips or pellets need to undergo a very lengthy crystallization process prior to solid stating. It will be advantageous, therefore, if oligomers with very low molecular weights ([η] ~0.1 dL/g), are used as SSP precursors, since, they can be crystallized more effeciently. *The objective of this investigation is to study, the crystallization and SSP of very low molecular weight PET oligomers (η_{inh} 0.1 -0.2 dl/g) with emphasis on the influence of end groups and different catalysts. Oligomers will be prepared from dimethyl terephthalate (DMT) and ethylene glycol (EG) as well as by controlled degradation of commercial PET to get oligomers with specific end groups. The structural and morphological changes occurring during SSP will be investigated by DSC, WAXS and SAXS. The structure and morphology of the crystallized oligomers will be compared with those of high molecular weight PET pellets used in the conventional SSP process. Low crystallization rate and thermal conductivity of the pellets very often results in morphological differences between skin and core. The effect of crystallization temperature and heating rate on the resultant skin-core morphology will be studied. The influence of crystal morphology on the SSP will also be examined.*

2.2.3 Crystallization and solid state polymerization of poly(ethylene naphthalate)s

PEN contains a rigid naphthalene ring and exhibits superior physical and mechanical properties than widely used PET's. PEN has found application in manufacture of bottles with good gas-barrier properties, transparency and thermal resistance (upto 110°C) and industrial fibers. Due to its extremely high melt viscosity, PEN with an intrinsic viscosity suitable for such applications cannot be produced by melt state polymerization. It is preferable to use a combination of melt and solid state polymerization processes. However solid state polymerization rate of PEN is relatively slow. PEN crystallizes at a lower rate and at a higher temperature than PET. During the crystallization process, low molecular weight PEN particles release volatile products which can produce popcorn like particles. Thus PEN cannot be crystallized like PET or PBT to obtain precursors suitable for SSP[13]. *An objective of this study is to investigate the crystallization and SSP of PEN oligomers of very low molecular weight (η_{inh} ~0.1 dL/g). For this purpose, PEN oligomers will be prepared from 2, 6-dimethyl naphthalate (DMN) and ethylene glycol (EG). The oligomers will be crystallized by using methods (thermal crystallization) similar to those adopted for PET oligomers. Diluent induced crystallization also will be examined. The effect of different catalysts on SSP will be examined.*

The crystallization kinetics of PET has been studied extensively, however, very limited data is available for PEN. Understanding the crystallization kinetics is very critical to enable identification of optimum SSP conditions for PEN. *Thus, another objective of the present work is to study the crystallization kinetics of PEN. Effect of molecular weight and catalysts on the crystallization kinetics will be examined. It has been reported that PEN can crystallize in two modifications, α and β, depending on crystallization conditions[14]. However, there is no agreement on the specific conditions necessary for obtaining these modifications. So it is proposed to investigate the dependence of crystal modification on the crystallization conditions.*

2.2.4 Preparation of poly(ethylene naphthalate-co-terephthalate)s *via* solid state polymerization

Although PEN has superior physical and mechanical properties than PET, its relatively low production volume and high price may limit its application in the near future. As an alternative, poly(ethylene naphthalate-co-terephthalate)s (PNT) in various compositions can be synthesized with the objectives of improving the solubility and processability of PEN and reducing the cost of PEN, while improving physical and mechanical properties of PET[15]. PET/PEN blends are usually prepared by reactive processing[16]. PEN and PET are similar in chemical composition and they will undergo facile transesterification to give random copolymers. However, when the level of transesterification reaches very high levels, the crystallinity and resultant physical properties of the blend can be reduced to the point that they may be undesirable for many applications. Controlling the transesterification levels is difficult in the melt process. Cox et al[16] found that transesterification between PET and PEN can also take place in solid state, where the extent of transesterification will be lower. *The objective of the study is to prepare high molecular weight PET/PEN copolymers from PET and PEN oligomer mixtures by simultaneous solid state polymerization and transesterification. Oligomer mixtures will be melt mixed and crystallized either thermally or by diluent induced crystallization. Sequence distribution at various levels of reaction will be determined by means of ^{1}HNMR. Structure and morphology will be studied by DSC and XRD.*

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CHAPTER 3

CRYSTALLIZATION AND SOLID STATE POLYMERIZATION OF POLY(ARYL ESTER)S

3.1 Introduction

Poly(aryl ester)s are generally prepared by acid chloride route under phase transfer conditions[1-5],or diacetate[6-11] and diphenate process *via* meltcondensation[12-14]. Direct transesterification of dimethyl esters of terephthalic and isophthalic acids with bisphenol A can give poly(aryl ester)s with the liberation of methanol as by-product. This route is far less studied than the other methods. Oishi and Hall[15] reported very poor results in terms of polymer yield, molecular weight and colour. Later Idage et al[16,17] reported that the method can be successfully used, if catalysts selected from alkoxides of group IV B metals and derivatives of group IV A metals are employed.

Even though solid state polymerization can be used to prepare high molecular weight poly(aryl ester)s, the need to crystallize the amorphous oligomer renders an additional degree of complexity to the process. Information regarding this kind of processes can mainly be found in patents [18-23].

In this chapter, the preparation of poly(aryl ester)s by SSP from oligomers prepared by different routes have been investigated. Reactions were carried out under reduced pressure as well as in a flow of nitrogen. Oligomers were prepared from dimethyl esters of isothalic/terephthalic acids using previously reported procedures[16,17]. Poly(aryl ester)s were also prepared from oligomers prepared by the degradation of poly(aryl ester)s to study the effect of end groups. Effects of different catalysts on the rate of SSP were investigated.

3.2 Experimental

3.2.1 Materials

Bisphenol A (BPA) supplied by Aldrich Chemicals, USA was crystallized from dry toluene. Dimethyl isophthalate (DMI) and dimethyl terephthalate (DMT) obtained from Aldrich Chemicals, USA were crystallized from methanol. Diphenyl ether (DPE), dibutyl tinoxide (DBTO), dibutyl tindilaurate (DBTL), and dimethyl aminopyridine (DMAP) (Aldrich Chemicals USA) were used as received. Titanium tetraisopropoxide ($Ti(O^iPr)_4$) (Aldrich Chemicals, USA) was distilled under reduced pressure and was used as solution in dry toluene (1 mL in 25 mL of toluene). Nitrogen gas (INOX Gd. II, Industrial Oxygen Company, Patal ganga, India containing oxygen and moisture of 4 ppm each was used as such without further purification. Methanol and chloroform supplied by Sd. Fine Chemicals were used after distillation.

3.2.2 Measurements

Inherent viscosities (η_{inh}) were measured at 30°C in an automated Schott Gerate AVS 24 viscometer using Ubbelhode suspended level viscometer in chloroform. The X-ray diffraction experiments were performed using Rigaku Dmax 2500 diffractometer. The system consists of a rotating anode generator and wide angle powder goniometer and a slit collimated small angle goniometer. The generator was operated at 40 KV and 150 mA. The samples were ground into a fine powder and were scanned between $2\theta = 10$ to 35° at a speed of 1 deg/min. Crystallinity was calculated as the ratio of the area of the crystalline peaks to the total area. Calorimetric measurements were performed using Perkin Elmer thermal analyzer (DSC 7) at a heating rate of 10°C/min in nitrogen environment. The melting temperature and heat of fusion were obtained from the 1st heating thermogram and T_g from the 2nd heating thermogram. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AC-200 NMR spectrometer.

3.2.3 Preparation of oligomers

3.2.3.1 From BPA, DMI and DMT

Oligomer with $\eta_{inh} \sim 0.1$ dL/g was prepared by melt polycondensation of BPA, DMI and DMT in the presence of DBTO as catalyst and DPE as diluent. Into a 2 L capacity K. K. J SS reactor, equipped with nitrogen inlet, mechanical stirrer and condenser, 45 g BPA (0.2 mol), 19.4 g DMI (0.1 mol), 19.4 g DMT (0.1 mol), 0.25 g DBTO (0.5 mol% of BPA) and 120 mL DPE were charged. The reactor was then heated to 260°C in 30 min. and maintained at that temperature for 12 h under nitrogen atmosphere. During this period, the by-product methanol was continuously distilled out and got collected. The oligomer formed was removed from the reactor by dissolving in chloroform since the material had solidified in the reactor. Chloroform was removed completely under reduced pressure. The material was washed several times with petroleum ether to remove DPE. Pet ether was removed under reduced pressure. The viscous material was dissolved in chloroform, filtered to remove DBTO and then was reprecipitated from methanol. The oligomer was isolated by filtration and was dried under reduced pressure at 70-80°C. Finally the prepolymer obtained was purified by soxhlet extraction in methanol, yield = 54 g, $\eta_{inh} = 0.09$ dL/g, $T_g = 109$°C

Oligomer with $\eta_{inh} \sim 0.3$ dL/g was prepared by post polycondensation of the above oligomer in melt phase in presence of DBTL as catalyst. A mixture of 5g of the oligmer and 0.025 g (0.5 wt%) of DBTL was prepared in chloroform. Chloroform was removed by distillation under reduced pressure. The catalyst oligomer mixture obtained was dried under reduced pressure at 80°C. The catalyst oligomer mixture was taken in a thick walled glass reactor and was flushed with nitrogen for 10 minutes. The oligomer was heated under reduced pressure (0.2 mm Hg) to 300°C and the reaction was continued for 3 h at the same temperature. Then the reactor was cooled to ambient temperature under reduced pressure. The oligomer was isolated by dissolving in chloroform and reprecipitating from methanol, yield = 3.9g, η_{inh} = 0.25 dL/g, T_g = 160°C

3.2.3.2 From commercial poly(aryl ester)s

(i) Degradation of poly(aryl ester)s by methanolic sodium hydroxide

Poly(aryl ester)s (50 g) DKX-140 Lot No; MD 3020111 (Hoechest Celanese Corporation, USA) was taken in a double walled reactor of 2 L capacity with water circulation facility. The poly(aryl ester)s was dissolved in 700 mL of chloroform and stirred (7000 rpm) under reflux. To this was added 25 mL of 0.2 N methanolic NaOH. After 1 min, the reaction mixture was poured into 2500 mL of acidic methanol. The product was isolated by filtration, washed with methanol and was dried under reduced pressure. yield = 47 g, η_{inh} = 0.21 dL/g, T_g = 159°C.

(ii) Degradation of poly(aryl ester)s by BPA in DPE

Poly(aryl ester)s (5 g) was dissolved in 25 mL of DPE at 180°C. 0.0025 g of DBTO was added and was stirred well, added 1.5 g of BPA, stirred well for 2 h. The reaction mixture was washed with pet ether to remove DPE, the oligomer was dissolved in $CHCl_3$ and was reprecipitated from methanol. The product was isolated by filtration, washed with methanol and was dried under reduced pressure, yield = 4g, η_{inh} = 0.18 dL/g, T_g = 158°C

3.2.4 Crystallization of oligomers

Oligomers prepared were completely amorphous. They were crystallized by using appropriate diluents to avoid sticking during SSP. Chloroform, ethyl acetate and toluene were selected for the purpose. Crystallinity was induced by refluxing the material in diluent for 4 h. In a typical experiment 25 mL of the diluent was taken in a 100 mL r. b flask and 5 g of the oligomer was added and stirred well and heated to the refluxing temperature of the diluent. Refluxing was continued for 4 h. Then the diluent was removed by distillation under reduced pressure and the material was dried at 70-80°C under reduced pressure. In the case of the oligomers prepared from DMI, DMT and BPA, catalyst also was added into the solvent so that when the solvent was distilled out, the catalyst got coated on the material. The semicrystalline oligomer obtained was characterized by DSC.

3.2.5 Addition of catalyst

The semicrystalline oligomer (obtained by degradation) was sieved through 25 and 35 mesh sieves (600 microns). Appropriate catalysts were coated on the sieved material. DBTL and $Ti(O^iPr)_4$ were used as solution in toluene while DMAP as solution in methanol. In all the cases catalyst concentration of 0.5 wt% w.r.t the oligomer was used. In a typical experiment, 5 g of the oligmer was mixed with a solution of $Ti(O^iPr)_4$ (0.5 wt%, 0.65 mL) in methanol. Methanol was removed under reduced pressure and the material was dried.

3.2.6 Solid state polymerization

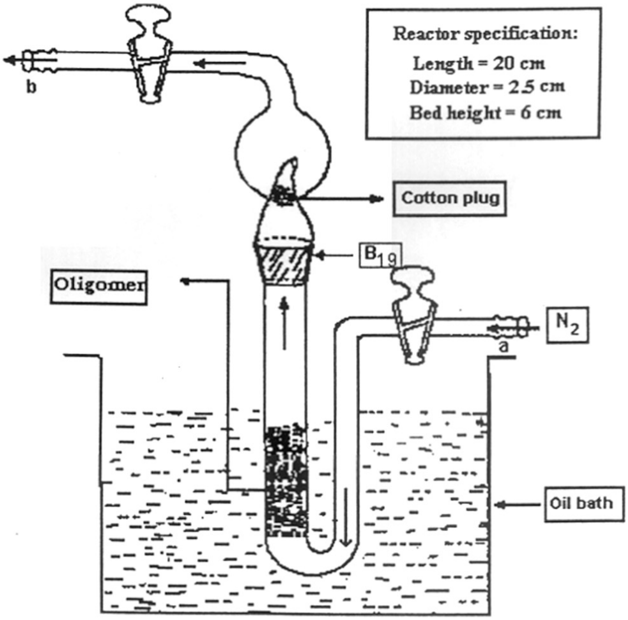


Fig. 3.1 Experimental set up for solid state polymerization

Solid state polymerization reaction was performed in a glass reactor immersed in a thermostated oil bath or salt bath. SSP was carried out either under reduced pressure (0.01 mbar) or in a flow of nitrogen (3 L/min). A schematic diagram of the set up used for the SSP in nitrogen flow is shown in **Fig. 3.1**. Whenever the reaction was carried out under reduced pressure the side valve (inlet for nitrogen, a) was closed and the other valve (b) was connected to the vacuum line. Crystallized oligomers were crushed and sieved to obtain particle size of 600 microns. In the case of samples prepared from the monomers, the oligomer was placed in the reactor and was heated to 180°C and held at that temperature for 1 h followed by 1 h at 210°C and then at 230°C for 6 hours. It was ensured that the material did not stick during any of the stages. Samples were withdrawn at intervals for characterization. In the case of oligomers prepared by the degradation of commercial poly(aryl ester)s, the samples were heated to 210°C directly without prior heating to 180°C.

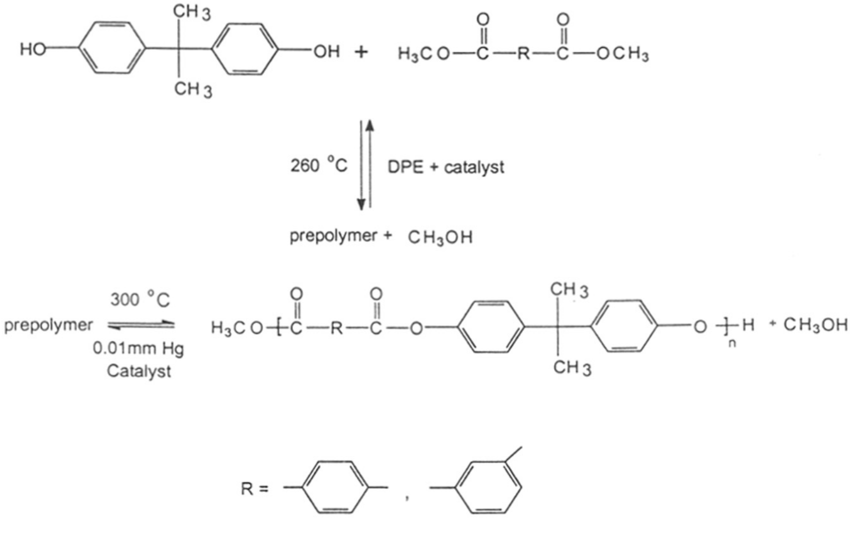
3.3 Results and discussion

In the present work, the oligomers were prepared by two different routes 1) by the reaction of BPA and dimethyl esters of terephthalic acid and isophthalic acids in presence of a catalyst, 2) by the degradation of commercial poly(arylester)s.

3.3.1 Preparation of oligomer from BPA, DMI and DMT

When the oligoarylate (η_{inh} 0.09 dL/g) was prepared from BPA, DMI and DMT it was necessary to use a solvent [24] **(Scheme 3.1)**. In the present case, diphenylether (DPE) was used to avoid any stoichiometric imbalance that might occur as a result of possible sublimation of reactants [16]. DSC thermogram of the sample is given in **Fig. 3.2**. The material is completely amorphous with a T_g of 109°C. The oligomer was subjected to post polycondensation in a glass reactor under reduced pressure at 300°C in presence of DBTO to obtain oligoarylate with η_{inh} ~0.25 dL/g **(Scheme 3.1)**. DSC thermogram is shown in **Fig. 3.2**. The oligomer obtained also is completely amorphous with a T_g of 160°C.

^{1}HNMR and IR spectra are given in **Figs 3.3 and 3.4**. In the region between 8 and 8.4 ppm, typical of terephthalate unit, the NMR spectrum of the oligoarylate shows four additional peaks in addition to the singlet at 8.4 ppm due to the symmetrical aromatic ester substituted terephthalate unit. The additional peaks between 8 and 8.35 ppm show a pattern typical of para-disubstituted benzene having dissimilar end groups. The upfield doublet centered at 8.2 ppm is due to the aromatic protons, ortho to end methyl ester group and the other doublet centered at 8.3 ppm is due to the aromatic protons, ortho to aromatic ester moiety. The symmetrical aromatic ester substituted isophthalic unit shows proton shifts at 9.05, 8.5 and 7.7 ppm. The proton region of the isophthalic unit also shows additional peaks at 8.9, 8.4, and 7.6 ppm. These upfield shifts observed for all the three protons of the isophthalic unit can be attributed to the end methyl ester of the isophthalic unit. Thus the oligomer contains terephthalic/isophthalic units having methyl ester end groups in addition to terephthalic/isophthalic units substituted by aromatic ester groups.



Scheme 3.1: Preparation of oligomer from DMI, DMT and BPA

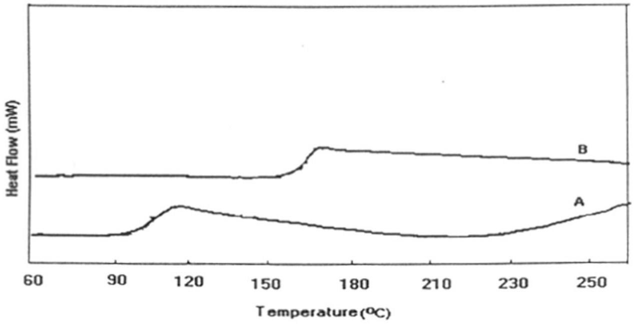


Fig. 3.2: DSC thermograms of oligomers: A) η_{inh} 0.09 dL/g, B) η_{inh} 0.25 dL/g (1st heating runs)

The symmetrical aromatic ester substituted BPA moiety shows aromatic proton shifts in the region 7-7.5 ppm, with the aliphatic proton singlet at 1.68 ppm. In addition to these shifts, additional peaks are observed at higher field in both the regions. The upfield doublet centered at 6.75 ppm is due to aromatic protons, ortho to the end -OH group of BPA moiety. The upfield shift in the aliphatic region is due to the modification in the surroundings of methyl groups in the bisphenol moiety having -OH end group. The intensity measurement of aromatic protons of terephthalic and isophthalic units shows the presence of equal concentrations of terephthalic and isophthalic units in the oligomer. IR spectrum of the oligomer shows absorptions corresponding to -OH at 3500 cm^{-1} and carbonyl stretching at 1740 cm^{-1}.

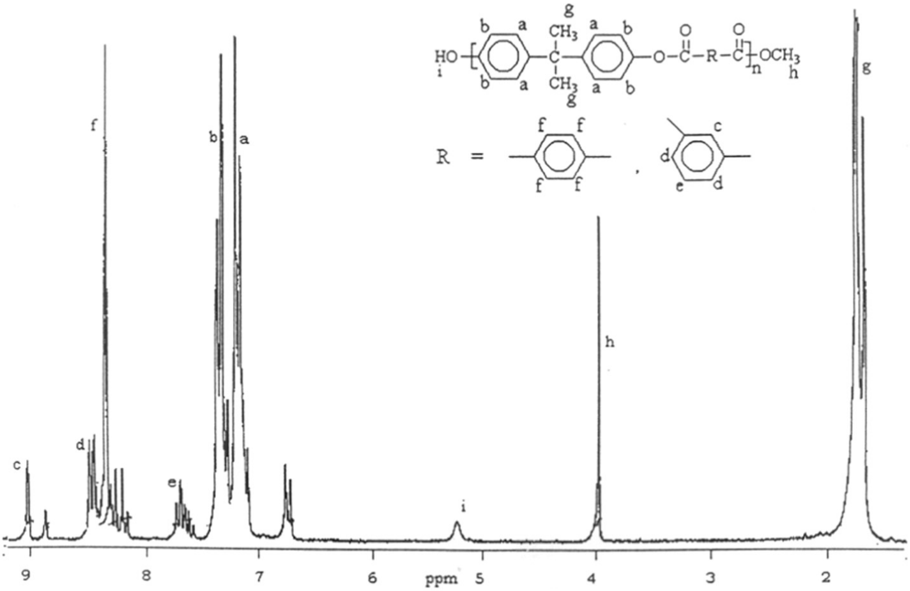


Fig. 3.3: ^{1}HNMR spectrum of oligomer prepared from BPA, DMI and DMT

3.3.2 Crystallization and solid state polymerization of oligomer prepared from DMI, DMT and BPA

Oligomers were subjected to crystallization by contact with a suitable diluent. The diluent interacts with the oligomer and depresses the T_g below the operating temperature. The increased mobility of the amorphous phase leads to crystallization. Crystallization of poly(carbonate)s, an amorphous polymer using various diluents have been well studied[26-30]. Solubility parameter of a particular polymer determines the extent of interaction between the polymer and diluents. To be used as crystallization medium, the diluent should have solubility parameter close to that of the polymer. Even though it is accepted that aromatic poly(aryl ester)s whose sloubility parameter is 22.5 (Jcm^{-3})$^{1/2}$ can be crystallized by diluents with solubility parameters in the range of 16 - 23 (Jcm^{-3})$^{1/2}$ [21,22,25] detailed investigations are not available. In the present work, ethylacetate, toluene and chloroform whose solubility parameters are 18.6, 18.3 and 19 (Jcm^{-3})$^{1/2}$ respectively were used for crystallization.

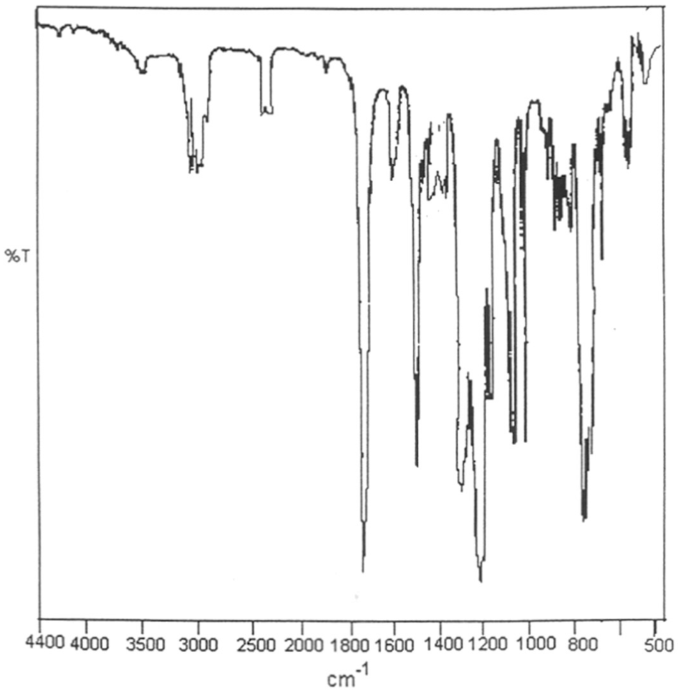


Fig. 3.4: IR spectrum of oligomer prepared from BPA, DMI and DMT.

Table 3.1: Diluent induced crystallization of oligomer

Starting oligomer	Crystallized oligomer		
	Crystallizing medium		
	Toluene (110°C)	Ethylacetate (77°C)	Chlorofrom (70°C)
T_m = nil $\Delta H = 0$ J/g $T_g = 160$°C $\eta_{iinh} = 0.25$ dL/g	T_m = 224°C, 250°C $\Delta H = 2.0$ J/g, 3.2 J/g $T_g = 160$°C, $\eta_{iinh} = 0.25$ dL/g	T_m = 216°C $\Delta H = 21$ J/g $T_g = 160$°C, $\eta_{iinh} = 0.25$ dL/g	T_m = nil $\Delta H = 0$ J/g $T_g = 160$°C $\eta_{iinh} = 0.25$ dL/g

Oligomer was refluxed in diluents for 4 h. Results are given in **Table 3.1**. Ethylacetate and toluene could induce crystallinity in the oligomer while chloroform could not. Diluents which can be used to crystallize the oligomer are those which swell but do not dissolve the oligomer particles[21,22,26]. For further experiments, crystallization in toluene was employed.

Crystallized oligomers were subjected to SSP under reduced pressure. However, for the sample with DBTL, the SSP was performed under N_2 flow as well. The results are given in **Tables 3.2** and **3.3**. In these experiments catalyst was mixed with the oligomer during crystallization step. Catalyst (0.5 wt% w.r.t.oligomer) was added to toluene, into which oligomer was added and stirred under reflux for 4 h followed by removal of toluene under reduced pressure. Starting from oligomer of η_{inh} 0.25 dL/g and T_g of 160°C, after SSP at 230°C for 6 h, poly(ary lester)s with η_{inh} 0.39 dL/g and T_g 176°C was obtained for reaction under reduced pressure, while polyarylate with η_{inh} 0.40 dL/g and T_g of 176°C was obtained under N_2 flow. Thus, SSP proceeds under N_2 flow as well as under reduced pressure. Even though initially two melting points were observed, the lower melting peak disappeared and the melting temperature increased upon progress of reaction.

The oligomer was subjected to SSP in presence of $Ti(O^iPr)_4$ under N_2 flow. Results are given in **Table 3.4**. Starting from oligoarylate of η_{inh} 0.25 dL/g and T_g 160°C, after SSP at 230°C for 6 h, polyarylate with η_{inh} 0.45 dL/g and T_g 186°C was obtained. In this case also initially two melting peaks were observed which coalesced into one during SSP. DSC thermograms are shown in **Fig. 3.5**. Change in η_{inh} during the reaction is shown in **Fig.3.6**.

Table 3.2: SSP of oligomer in presence of DBTL (0.008 mbar)[a]

Sample/Conditions	η_{inh} (dL/g)	T_g (°C)	T_m (°C)	ΔH (J/g)
Starting oligomer	0.25	160	-	-
Crystallized sample	0.25	160	224, 249	2, 3.2
180°C/1h	0.26	161	226, 251	2, 6.0
210°C/1h	0.28	161	230, 254	6.5
230°C/2h	0.34	172	257	6.5
230°C/4h	0.35	172	258	6.5
230°C/6h	0.39	176	260.5	8.4

[a] Prepared from DMI, DMT and BPA

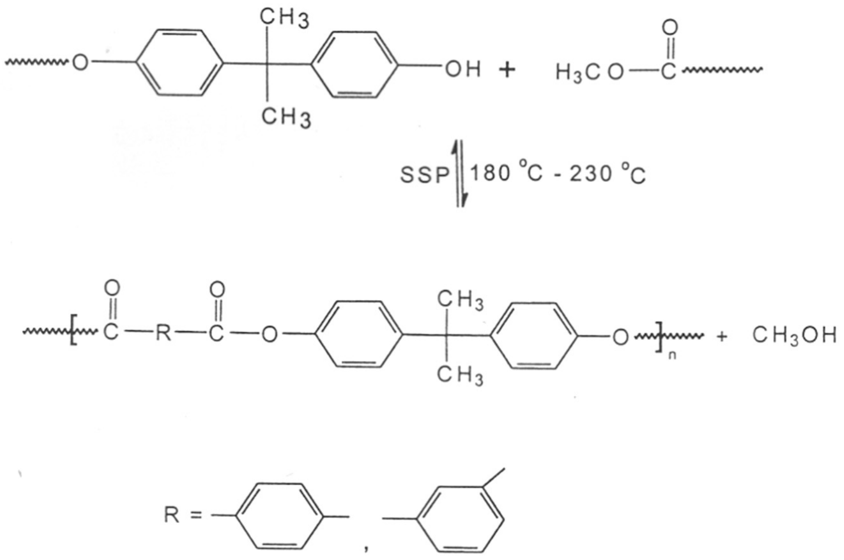
Comapred to DBTL, $Ti(O^iPr)_4$ exhibits higher catalytic activity for SSP. Thus poly(aryl ester)s could be prepared from oligomer with hydroxyl and ester end groups with the evolution of low boiling methanol as by-product (**Scheme 3.2**).

Table 3.3: SSP of oligomer in presence of DBTL (N_2, 3 L/min)[a]

Sample/Conditions	η_{inh} (dL/g)	T_g (°C)	T_m (°C)	ΔH (J/g)
Starting oligomer	0.25	160	-	-
Crystallized sample	0.25	160	190, 220, 24	b
180°C/1h	0.26	161	230, 250	b
210°C/1h	0.28	161	245	17
230°C/2h	0.31	165	253	11
230°C/4h	0.35	171	261	7.0
230°C/6h	0.40	176	262	9.5

[a] Prepared from DMI, DMT and BPA

b Melting peaks were broad and ΔH could not be calculated



Scheme 3.2: Formation of poly(aryl ester)s from oligomer

Table 3.4: SSP of oligomer in presence of Ti(O^{i}Pr)$_4$ (0.008 mbar)^a

Sample/Conditions	η_{inh} (dL/g)	T_g (°C)	T_m (°C)	ΔH (J/g)
Starting oligomer	0.25	160	-	-
Crystallized sample	0.25	160	215, 245	b
180°C/1h	0.26	161	215, 245	b
210°C/1h	0.28	161	221, 247	17
230°C/2h	0.39	174	260	11
230°C/4h	0.43	180	263	7.0
230°C/6h	0.45	186	265	9.5

^{a}Prepared from DMI, DMT and BPA

b Melting peaks were broad and ΔH could not be calculated

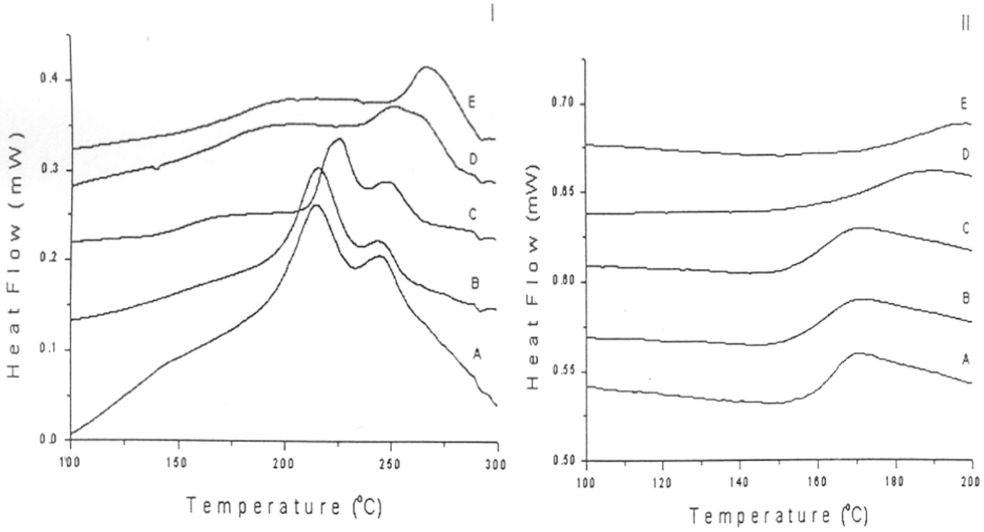


Fig. 3.5: DSC thermograms of oligomer prepared from DMI, DMT, and BPA in presence of Ti (O^{i}Pr)$_4$ during SSP
I) 1st heating thermograms II) 2nd heating thermograms
A) Crystallized sample B) 180°C/1h, C) 210°C/1h, D) 230°C/2h E)230°C/6h

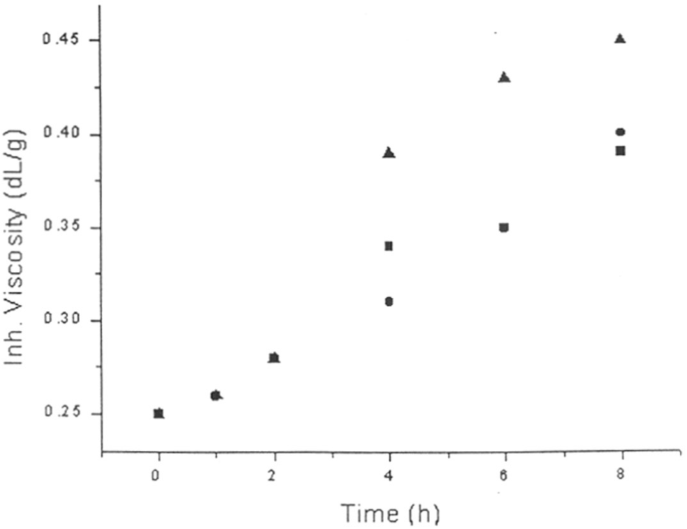


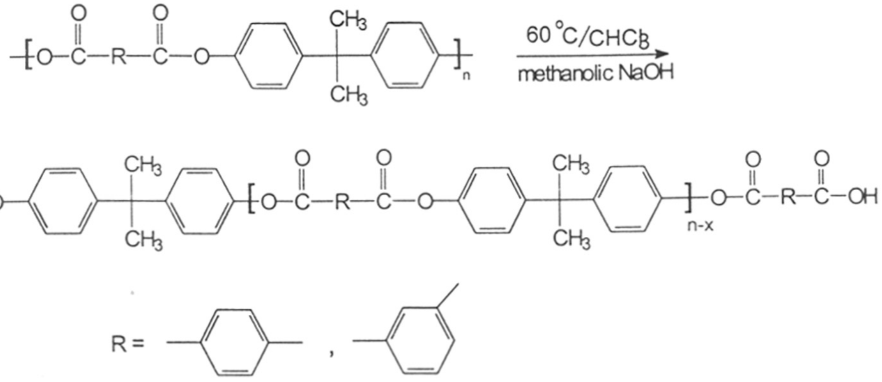
Fig. 3.6: Change in η_{inh} during SSP of oligomer prepared from DMI, DMT and BPA ▲ Ti (O^{i}Pr)$_4$; ● DBTL (under N_2 flow); ■ DBTL (under reduced pressure)

3.3.3 Preparation of oligomer from commercial poly(aryl ester)s

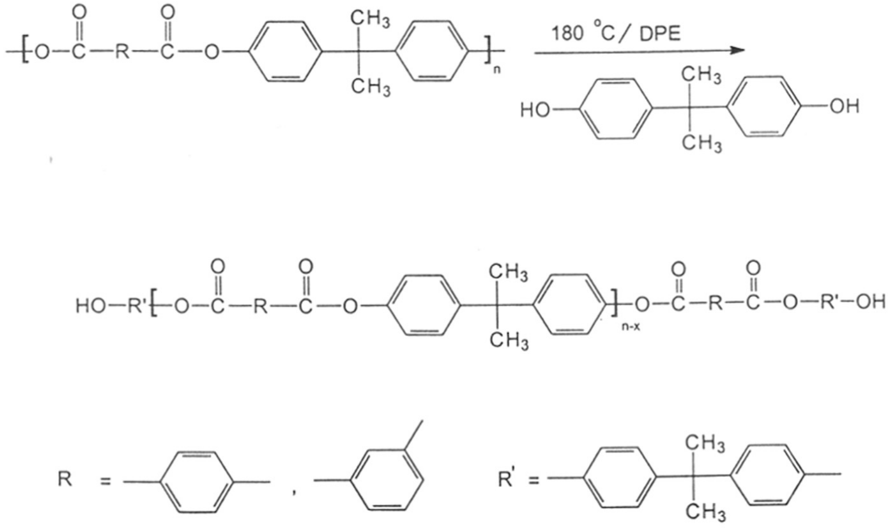
Oligomers were also prepared by degradation of commercial poly(aryl ester)s. Degradation was performed in two methods, by 1) methanolic sodium hydroxide 2) BPA. When methanolic sodium hydroxide was used, degradation occurred very fast and in one minute oligomer of η_{inh} 0.21 dL/g was obtained. When BPA was used for degradation it took 2h to get oligomer with η_{inh} 0.18 dL/g. In the first case end groups should be carboxyl (-COOH) and (-OH) **(Scheme 3.3).** Degradation with BPA would result in hydroxyl (-OH) end groups **(Scheme 3.4**). DSC thermograms are shown in **Fig. 3.7**. ^{1}HNMR spectra of starting poly(aryl ester)s and the oligomers obtained are given in **Figs. 3.8 and 3.9**. The intensity measurement of aromatic protons of terephthalic and isophthalic units shows that terephthalic and isophthalic units are present in a molar ratio of 25:75 in the poly(aryl ester)s as well as in the obtained oligomers. Except for the upfield doublet centered at 6.75 ppm observed in the cases of oligomers, which is due to aromatic protons, ortho to the end -OH group of BPA moiety, all other features are similar in all the three spectra. Unlike the oligomer prepared from BPA, DMI and DMT these oligomers do not show the presence of $-OCH_3$ species. Thus, these oligomers possess hydroxyl and carboxyl end groups only.

3.3.4 Crystallization and solid state polymerization of oligomer prepared by degradation

Oligomers were crystallized and subjected to SSP under reduced pressure in the presence of different catalysts and also without any catalyst. Crystallization was performed by refluxing in toluene for 4 h (110°C). DSC thermograms are given in **Fig. 3.7** Both the samples exhibit single melting peaks



Scheme 3.3: Preparation of oligomer through degradation by methanolic sodium hydroxide



Scheme 3.4: Preparation of oligomer through degradation by BPA

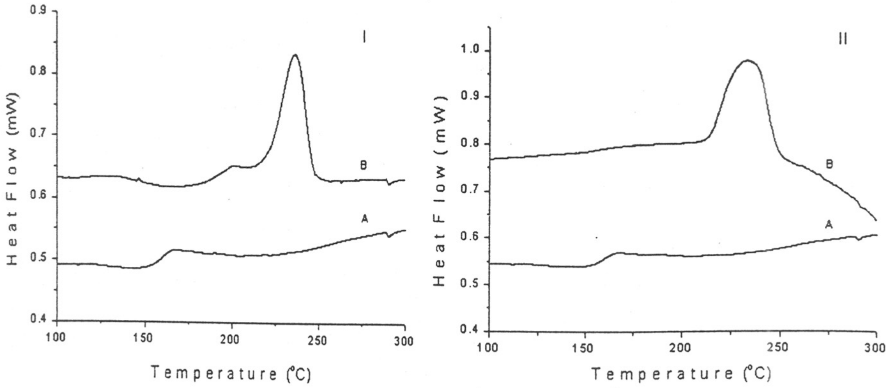


Fig. 3.7: DSC thermograms of oligomer obtained by degradation
I)Degradation by methanolic sodium hydroxide II) degradation by BPA
A) Amorphous oligomer B) crystallized oligomer

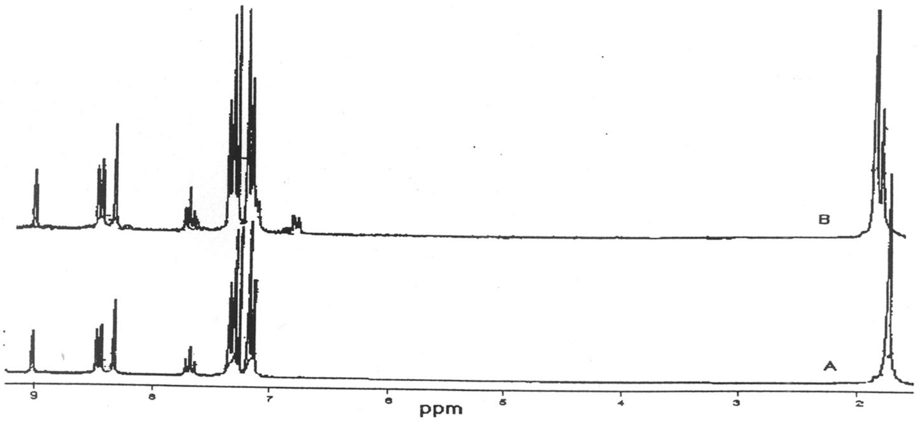


Fig. 3.8: ^{1}HNMR spectra of A) original poly(aryl ester)s B) oligomer obtained through degradation (Degradation by methanolic sodium hydroxide)

Oligomer obtained by degradation of poly(aryl ester)s by methanolic NaOH was subjected to SSP in presence of catalysts, namely DBTL (derivative of group IV A metal), DMAP (mild base) and Ti(O^{i}Pr)$_4$ (alkoxide of group IV B metal). Results are given in **Tables 3.5-3.7.** When SSP was performed in presence of DBTL, starting from oligoarylate of η_{inh} 0.21 dL/g

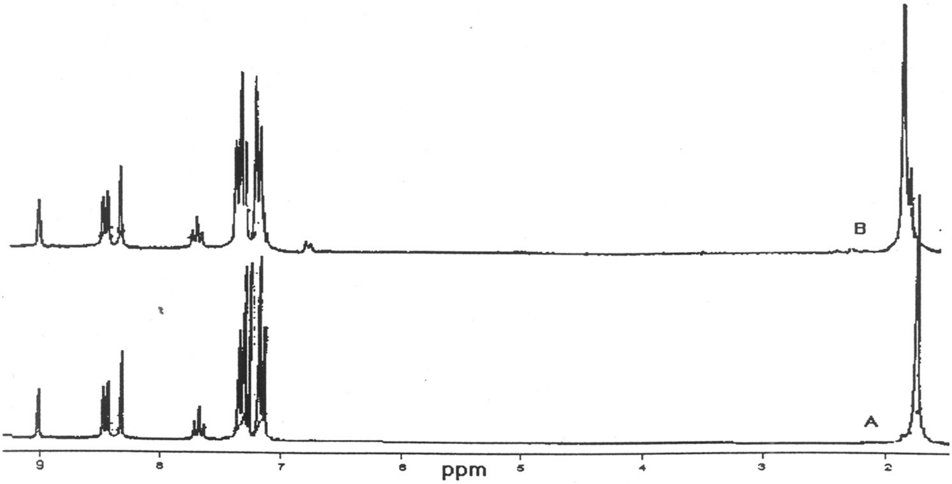


Fig. 3.9: ^{1}HNMR spectra of A)original poly(aryl ester)s B)oligomer obtained through degradation (Degradation by BPA)

and T_g 159°C, poly(arylester)s with η_{inh} 0.32 dL/g and T_g 172°C was obtained (**Table 3.5**). SSP in presence of DMAP gave polymer with η_{inh} 0.37 dL/g and T_g 176° (**Table 3.6**), while $Ti(O^iPr)_4$ gave polymer with η_{inh} 0.47 dL/g and T_g 187°C (**Table 3.7**). SSP was also performed without any catalyst to get polymer with η_{inh} 0.26 dl/g and T_g 166°C (**Table 3.8**). SSP proceeds to a limited extend in the absence of catalyst also, presumably due to the presence of the residual catalyst. $Ti(O^iPr)_4$ exhibits highest catalytic activity. DSC thermograms are given in **Figs. 3.10-3.13**. All the samples show single melting peaks and the melting temperatures increased with time during SSP. Change in η_{inh} during SSP is shown in **Fig. 3.14**.

Table 3.5: SSP of oligomer in presence of DBTL (0.008 mbar)[a]

Sample/Conditions	η_{inh} (dL/g)	T_g (°C)	T_m (°C)	ΔH (J/g)
Crystallized oligomer	0.21	159	235	30
Mixed withDBTL	0.21	159	235	30
210°C/1h	0.22	159	235	28
230°C/2h	0.27	165	248	17
230°C/4h	0.30	167	255	19
230°C/6h	0.32	172	255	19

[a] Prepared by degradation of poly(aryl ester)s by methanolic sodium hydroxide

Table 3.6: SSP of oligomer in presence of DMAP (0.008 mbar)[a]

Sample/Conditions	η_{inh} (dL/g)	T_g (°C)	T_m (°C)	ΔH (J/g)
Crystallized oligomer	0.21	159	235	30
Mixed withDMAP	0.21	159	234	33
210°C/1h	0.21	159	235	27
230°C/2h	0.30	167	244	21
230°C/4h	0.33	172	254	20
230°C/6h	0.37	176	259	22

[a]Prepared by degradation of poly(aryl ester)s by methanolic sodium hydroxide

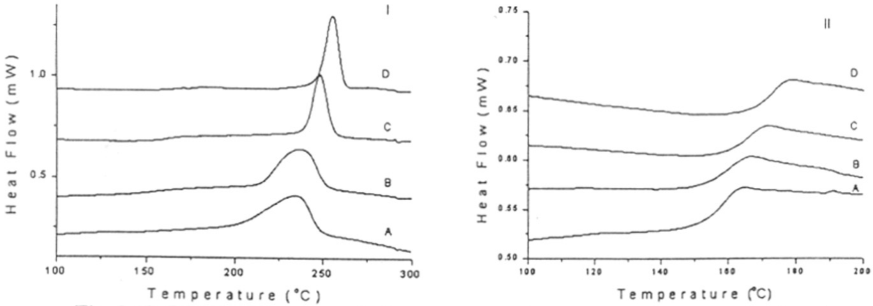


Fig. 3.10: DSC theromograms of oligomer prepared through degradation by methanolic sodium hydroxide during SSP in presence of DBTL.
(i) 1st heating thermograms (ii) 2nd heating thermograms
A) Crystallized sample B) 210°C/1h, C) 230°C/2h, D) 230°C/6h

Table 3.7: SSP of oligomer in presence of Ti(O^{i}Pr)$_4$ (0.008 mbar)[a]

Sample/Conditions	η_{inh} (dL/g)	T_g (°C)	T_m (°C)	ΔH (J/g)
Crystallized oligomer	0.21	159	235	30
Mixed with Ti (O^{i}Pr)$_4$	0.21	163	237	29
210°C/1h	0.26	168	243	27
230°C/2h	0.39	182	262	15
230°C/4h	0.42	186	265	15
230°C/6h	0.47	187	267	16

[a]Prepared by degradation of poly(aryl ester)s by methanolic sodium hydroxide

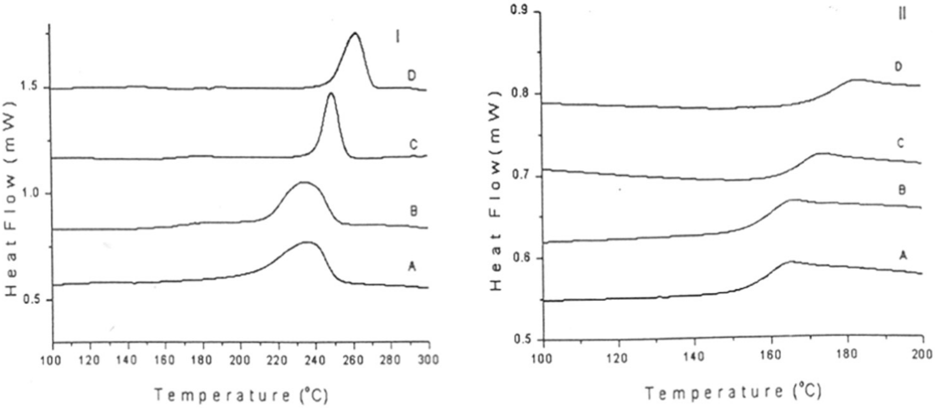


Fig. 3.11: DSC thermograms of oligomer prepared through degradation by methanolic sodium hydroxide during SSP in presence of DMAP
I) 1st heating thermograms II) 2nd heating thermograms
A) Crystallized sample B) 210°C/1h, C) 230°C/2h, D) 230°C/6h

Table 3.8: SSP of oligmer without catalyst (0.008 mbar)[a]

Sample/Conditions	η_{inh} (d	T_g (°C)	T_m (°C)	ΔH (J/g)
Crystallized oligomer	0.21	159	235	30
210°C/1h	0.21	159	243	25
230°C/2h	0.22	162	262	16
230°C/4h	0.24	162	265	18
230°C/6h	0.26	166	267	20

[a] Prepared by degradation of poly(aryl ester)s by methanolic sodium hydroxide

The oligomer prepared by degradation by BPA also was subjected to SSP in presence of $Ti(O^iPr)_4$ and without any catalyst. Results are given in **Table 3.9 and 3.10**. Starting from oligomer with η_{inh} 0.18 dL/g, and T_g 158°C, SSP in presence of $Ti(O^iPr)_4$ gave poly(aryl ester)s with η_{inh} 0.50 dL/g and T_g 190°C, while reaction in the absence of catalyst gave poly(aryl ester)s with η_{inh} 0.27 dL/g and T_g 167°C. DSC thermograms are shown in **Fig. 3.15 and 3.16** Change in η_{inh} during the reaction is shown in **Fig. 3.17**.

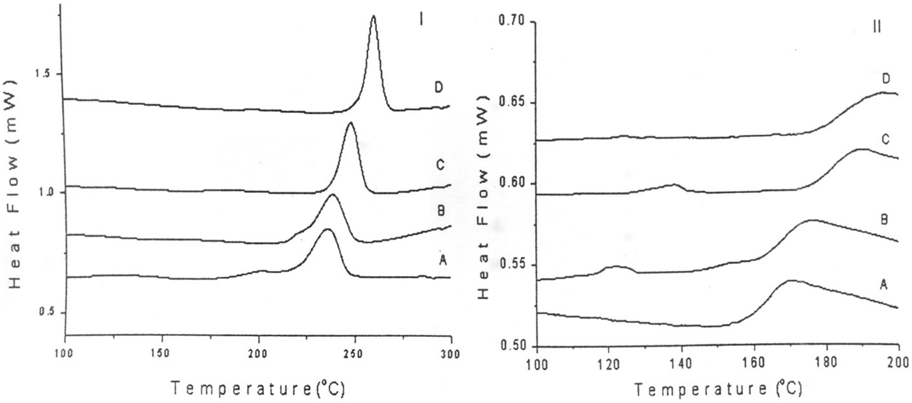


Fig. 3.12: DSC thermograms of oligomer prepared through degradation by methanolic sodium hydroxide during SSP in presence of $Ti(O^iPr)_4$
I) 1st heating thermograms II) 2nd heating thermograms
A) Crystallized sample B) 210°C/1h, C) 230°C/2h, D) 230°C/6h

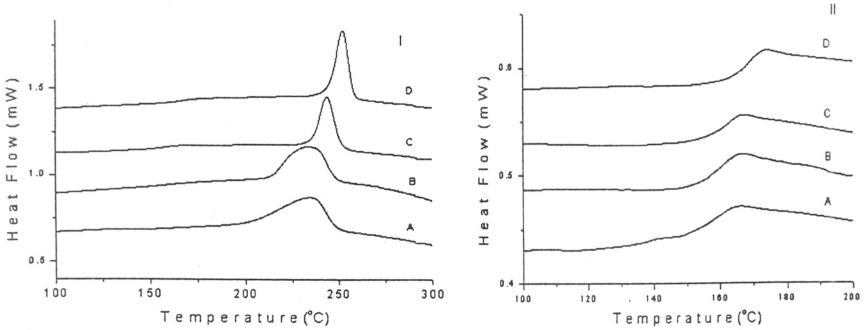


Fig. 3.13: DSC thermograms of oligomer prepared through degradation by methanolic sodium hydroxide during SSP without any catalyst
I) 1st heating thermograms II) 2nd heating thermograms
A) Crystallized sample B) 210°C/1h, C) 230°C/2h, D) 230°C/6h

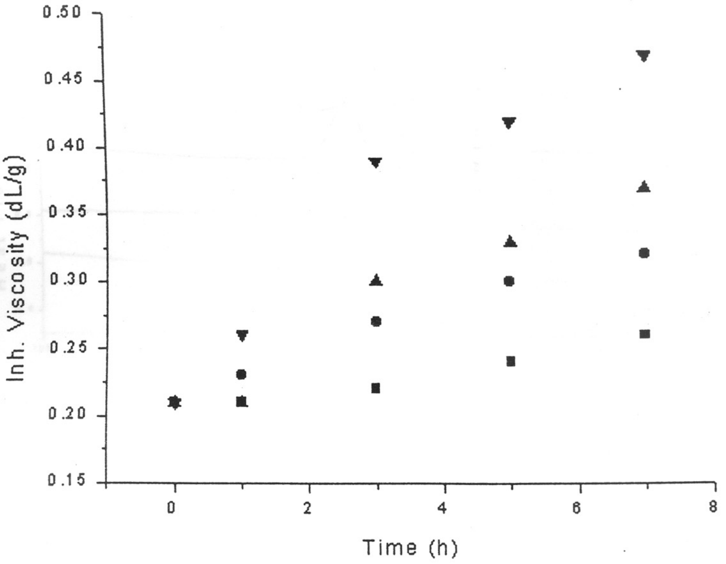


Fig. 3.14: Change in η_{inh} during SSP of oligomer prepared through degradation by methanolic Sodim hydroxide
▼ Ti $(O^iPr)_4$; ▲ DMAP; ● DBTL; ■ without any catalyst

Table 3.9: SSP of oligomer in presence of Ti$(O^iPr)_4$ (0.008 mbar)[a]

Sample/Conditions	η_{inh} (dL/g)	T_g (°C)	T_m (°C)	ΔH (J/g)
Crystallized oligomer	0.18	158	236	19
Mixed with Ti $(O^iPr)_4$	0.18	163	240	19
210°C/1h	0.26	169	240	21
230°C/2h	0.40	184	254	23
230°C/4h	0.48	189	263	21
230°C/6h	0.50	190	266	20

[a] Prepared by degradation of poly(aryl ester)s by BPA

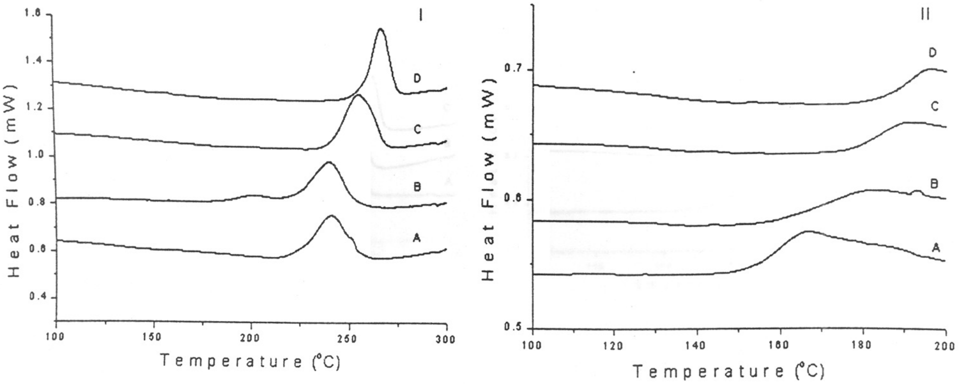


Fig. 3.15: DSC thermograms of oligomer prepared through degradation by BPA during SSP in presence of Ti(O^{i}Pr)
I) 1st heating thermograms II) 2nd heating thermograms
A) Crystallized sample B) 210°C/1h, C) 230°C/2h, D) 230°C/6h

Table 3.10: SSP of oligomer without catalyst (0.008 mbar)[a]

Sample/Conditions	η_{inh} (dL/g)	T_g (°C)	T_m (°C)	ΔH (J/g)
Crystallized oligomer	0.18	158	236	19
210°C/1h	0.18	159	238	20
230°C/2h	0.22	162	248	19
230°C/4h	0.24	162	255	22
230°C/6h	0.27	167	260	20

[a] Prepared by degradation of polyarylate by BPA

Thus in presence of Ti(O^{i}Pr)$_4$ both the oligomers gave considerable increase in η_{inh} as well as in T_g, indicating the formation of high mol.wt. poly(arylester)s. The reactions taking place can be depicted as shown in **Schemes 3.5 and 3.6.** In the first case where, the end groups are carboxyl and hydroxyl, by-product will be water while in the second case, where the end groups are mostly hydroxyl, BPA will be eliminated as the by-product.

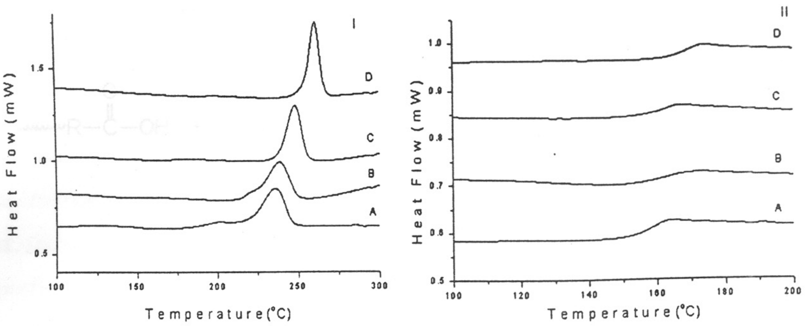


Fig. 3.16: DSC thermograms of oligomer prepared through degradation by BPA during SSP without any catalyst
I) 1st heating thermograms II) 2nd heating thermograms
A) Crystallized sample B) 210°C/1h, C) 230°C/2h, D) 230°C/6h

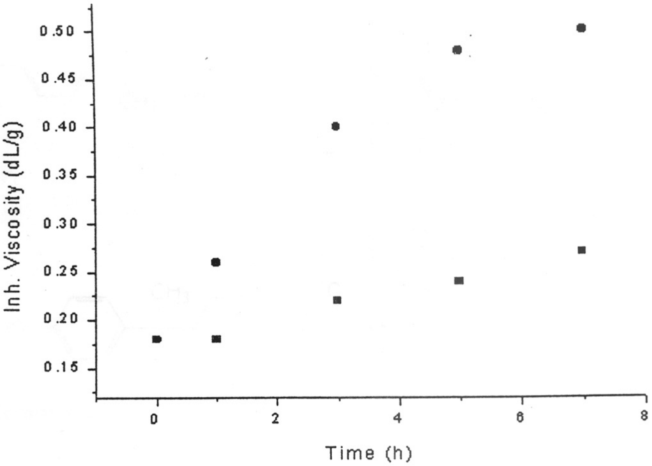
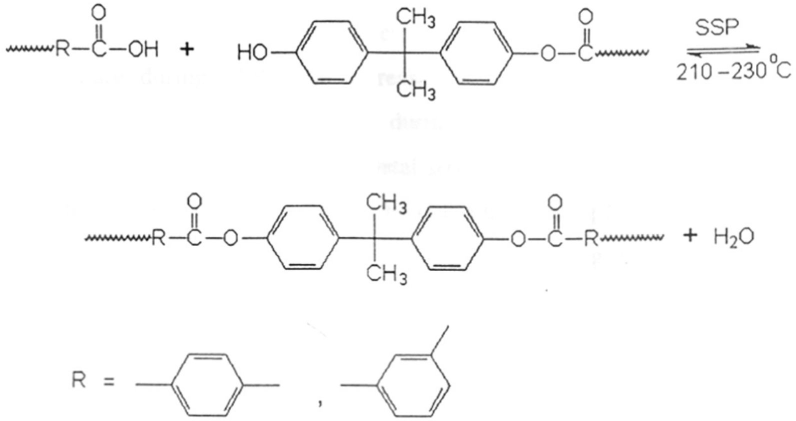
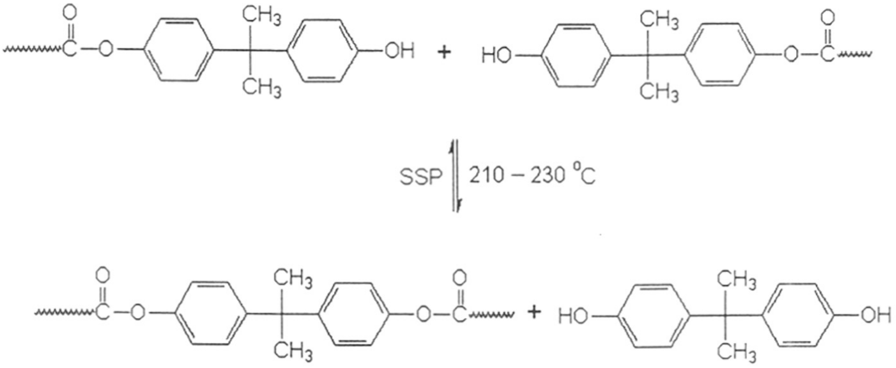


Fig. 3. 17: Change in η_{inh} during SSP of oligomer prepared through degradation by BPA
● in presence of Ti(O^{i}Pr)$_4$; ■ without any catalyst

From **Table 3.7** it can be seen that ΔH values decrease during the first three hours of SSP, then increase nominally, even though the melting temperatures increase during the reaction. It must be kept in mind that the reaction temperature has been raised with the increase in melting temperature. Partial melting would have taken place, when the reaction temperature was raised to 210°C and then 230°C because the melting peaks have tail in the low temperature range. Nevertheless sticking of the particles was not observed. To get a clear picture, % crystallinity and crystal size were determined from XRD analyses. Results are given in **Table 3.11**. XRD patterns are shown in **Fig. 3.18**.



Scheme 3.5: Formation of poly(aryl ester)s from oligomer prepared through degradation by methanolic sodium hydroxide



Scheme 3.6: Formation of poly(aryl ester)s from oligomer prepared through degradation by BPA

It is seen that the oligomer when crystallized in toulene and mixed with the catalyst, acquired a crystallinity of 50%. But crystallinity decreased to 45%, when the temperature was raised to 210°C and then to 30% when the temperature was raised to 230°C. Thereafter, it remained the same for the next 4 hours. ΔH values also showed a similar trend. However the crystal sizes remained almost same throughout the reaction.

Poly(aryl ester)s are very difficult to crystallize as they are amorphous in nature. Hence there is no reports on the semicrystalline structure and morphology of these materials in the literature. The diluent induced crystallization of oligomer and subsequent SSP provides an opportunity to look at the structure and morphology of semicrystalline poly(aryl ester)s. The

DSC and WAXS studies on the oligomer and poly(aryl ester)s provide information on the structure and morphology changes occurring during SSP. The T_m increases from around 230°C for oligomer to 270°C for poly(aryl ester)s. Poly(carbonate)s also shows an increase in melting temperature during SSP[31].The increase in T_m indicates substantial amount of structural reorganization of the crystallites during SSP, leading to lamellar thickening. However, there is no major change in the crystal size, indicating there is no improvement in crystal perfection during SSP. It may further be noted that during SSP crystallinity does not increase (the decrease in crystallinity is due to the partial melting while increasing the SSP temperature).

Table 3.11: Change in crystallinity and crystal size during SSP of oligomer in presence of Ti(O^{i}Pr)$_4$ (0.008 mbar)[a]

Sample/conditions	T_m (°C)	ΔH (J/g)	Crystallinity (%)	Crystal size (nm)
Mixed with Ti(O^{i}Pr)	237	29	50	7.6
210°C/1h	243	27	45	7.5
230°C/2h	262	15	30	7.3
230°C/4h	265	15	30	7.5
230°C/6h	267	16	32	8.3

[a]Prepared by degradation of polyarylate by methanolic sodium hydroxide

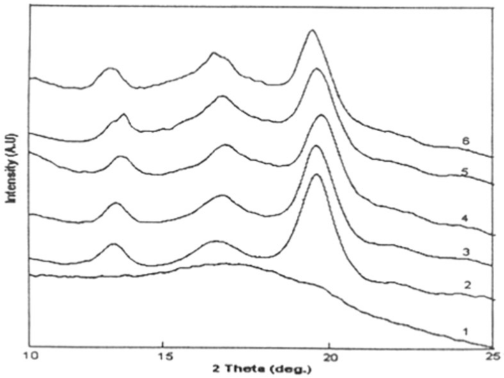


Fig. 3.18: XRD patterns of oligomer prepared through degradation by methanolic sodium hydroxide during SSP in presence of Ti(O^{i}Pr)$_4$; 1) amorphous 2) crystallized 3) 210°C/1h 4) 230°C/2h 5) 230°C/4h 6) 230°C/6h

3.4 Conclusion

The present work demonstrates that high molecular weight poly(arylester)s can be prepared by SSP of oligomers. The SSP could be performed with oligomers having different end groups. The catalyst improves the reaction rate and it has been found that $Ti(O^iPr)_4$ is a better catalyst for SSP.

The solvents having solubility parameter close to that of oligomer act as diluents and crystallize the oligomer. This provided an opportunity to study the structure and morphology of poly(arylester)s. The morphology shows lamellar thickening during SSP without improvement in crystal perfection.

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CHAPTER 4

CRYSTALLIZATION AND SOLID STATE POLYMERIZATION OF POLY(ETHYLENE TEREPHTHALATE)S

I. Crystallization and solid state polymerization of PET oligomers

4.1 Introduction

Poly(ethylene terephthalate)s (PET) are extensively used in the fiber form for textile applications and is increasingly finding application in food grade bottles for storing beverages. Bottle grade and injection molding applications require PET having relatively high molecular weights (intrinsic viscosity, [η] 0.55-0.85 dL/g)[1]. Commercially, high molecular weight PET has been made by a combination of melt polymerization and solid state polymerization. In solid state polymerization polycondensation is carried out by heating the semicrystalline prepolymer having [η] ~0.5 dL/g in a stream of inert gas or under reduced pressure at a temperature just below the polymer melting temperature. Prepolymer of [η] ~0.5 dL/g would be prepared by melt phase polymerization. In solid state polymerization, PET prepolymer in the form of chips or pellets have to undergo a crystallization process prior to solid stating[2].

Many publications deal with various aspects of solid state polymerization of PET such as effects of catalysts[3], gas flow[4,5,] kinetics and mechanism[6-11]. In polycondensation reactions, molecular weight build up is mainly due to esterification and transesterification. Commonly used catalyst for the preparation of PET is Sb_2O_3. It has been reported that even though esterification reaction is independent of the catalyst concentration, transesterification would be enhanced by the presence of the catalyst[3]. There are a number of patents suggesting improvements in the methods of solid state polymerization to obtain high molecular weight PET[12-18]. All these patents concern with solid state polymerization of prepolymers of [η] > 0.5 dL/g.

Recently patents have been filed for the process of preparing high molecular weight PET[2,19] and PEN from crystallized oligomers having [η] ~0.2 dL/g. In these processes oligomers are initially crystallized at temperature where its crystallization rate is maximum and the SSP is performed at temperatures close to melting point. The salient features of the process is that the sample is brought to crystallization temperature very rapidly (called shock crystallization). This has been achieved either by bringing the amorphous pellet in a preheated TMA oven at about 500°C or dropping melt extruded sample on a preheated turn table kept at about 175°C. Also these samples have high carboxyl group content (~200 ppm). The crystallized samples showed large crystal size of about 12 nm.

In this chapter, the SSP of PET oligomers crystallized at 175°C has been studied. Also the effect of catalyst and end groups on crystallization and SSP have been investigated. PET oligomers were prepared from dimethyl terephthalate (DMT) and ethylene glycol (EG) using $Ti(O^iPr)_4$ and Sb_2O_3 as catalysts as well as by hydrolysis and glycolysis of commercial PET to get oligomers with specific end groups ([η] 0.1-0.2 dL/g). Thermal crystallization and SSP of these oligomers were investigated to understand the effect of catalyst, end groups and route of oligomer preparation on crystallization and SSP.

4.2 Experimental

4.2.1 Materials

Dimethyl terephthalate (DMT) obtained from IPCL, Vadodara was recrystallized from methanol before use. Phenol, 1,1',2,2'-tetrachloroethane (TCE), ethylene glycol and benzyl alcohol obtained from Sd. Fine Chemicals, Bombay were distilled before use. Phenol red obtained from Sd. Fine Chemicals was used as 1% solution in ethyl alcohol. Chloro acetic acid obtained from Merck and Sb_2O_3 obtained from Aldrich were used as received. Titanium tetraisopropoxide, $Ti(O^iPr)_4$ was distilled under reduced pressure and was used as a solution in toluene dried over metallic sodium (1 mL in 25 mL of toluene). PET was a commercially available sample with [η] 0.6 dL/g.

4.2.2 Measurements

Inherent viscosity (η_{inh}) of the samples were measured at 25°C in an automated Schott Gerate AVS 24 viscometer using Ubbelhode suspended level viscometer in a 40/60 (wt/wt) phenol/TCE solvent mixture at a concentration of 0.5%. At least four concentrations of samples were used to obtain intrinsic viscosities [η]. Number average molecular weight (M_n) was calculated from the relationship[20] $[\eta] = 1.4 \text{ X } 10^{-3}.\ M_n^{\ 0.64}$

Carboxyl terminal groups were determined by Pohl's method[21]. About 0.2-0.3 g of finely ground oligoester was transferred into a test tube. To the tube was then added 10 mL of benzyl alcohol and transferred to a hot bath maintained at 215 +/-1°C for 1.8 +/-0.5 min. The solution was stirred using a magnetic stirrer while in the hot bath. When the sample had been in bath for the required length of time, the test tube was lifted quickly out of the bath and lowered immediately into a beaker of cold water (20 to 30°C) to quench the sample for 6 to 7 seconds. After quenching, the sample was immediately poured into a beaker containing 15 mL of chloroform. Chloroform acts as a dispersant and prevents gel formation. A rinse of about 5 mL benzyl alcohol was added to the test tube, so that it runs down the walls and washes loose all the gel. The test tube containing the rinse was placed in oil bath maintained at 215°C for 60 +/- 5 seconds and its contents were carefully transferred to the rest of the sample and stirred. Two drops of the indicator (phenol red) solution was then added and the mixture was titrated against 0.01 N NaOH dissolved in ethyl alcohol. The titration was carried out to the first discernable pink colour throughout that persists for 10 seconds. A blank was also performed under the same conditions. A standard correction of 1.6 meq/kg was subtracted from the result to allow for degradation.

$$\text{Carboxyl value} = \left\{\frac{(S-B) \times 10^{-3} \times \text{normality of NaOH}}{\text{Wt. of the sample}}\right\} - 1.6 \text{ meq/kg}$$

NaOH in ethyl alcohol was standardised using potassium hydrogenphthalate (KHP). A known quantity of KHP was dissolved in water and titrated against NaOH in ethanol using phenolphthalein as indicator. The end point is the appearance of permanent light pink colour.

$$\text{Normality of NaOH} = \frac{\text{Wt. of KHP}}{(0.20422 \times \text{Vol. of NaOH})}$$

The X-ray diffraction experiments were performed using Rigaku Dmax 2500 diffractometer. In the case of WAXS studies the samples were scanned between $2\theta = 10$ to 35 deg. at a speed of 1 deg/min and for SAXS, samples were step scanned with a step angle of 0.01 deg and sampling time of 60 seconds. The scanning range was 0.1 to 1.5 deg. The crystal size was calculated from the FWHM of 010 reflection using Scherrer equation: $D_{hkl} = 0.89\lambda/\Delta_{hkl} \cos\theta$. The crystallinity was calculated as the ratio of the area of the crystalline peaks to the total area. The calorimetric measurements were done using Perkin-Elmer DSC-7. The samples were heated/cooled at a rate of 10°C/min. under nitrogen environment. The melting temperature and heat of fusion were obtained from the heating thermogram and crystallization temperature upon cooling (T_{cc}) from the cooling thermogram.

4.2.3 Preparation of PET oligomers

4.2.3.1 From DMT and EG

(i) Preparation of bis(hydroxy ethylene) terephthalate (BHET)

DMT (33.035 g, 0.1701 mol) and 250 mL of EG were taken in a three neck reactor with nitrogen inlet and overhead stirring facility. 0.236 g of chloroacetic acid (1 mmol/ 100mL

EG) and 1.294 g of zinc acetate (0.4 mmol/100 mL EG) were added and stirred well[22]. The temperature was raised to 160°C under nitrogen flow and was further increased to 190°C and kept at that temperature for 2 h under nitrogen. The reaction mixture was left overnight. The mixture was then stirred with distilled water thoroughly. The mixture was filtered to separate the monomer and oligomer from the unreacted EG. The white residue was dried at 70°C. The solid residue was added to distilled water and the mixture was brought to boil. The boiling solution was quickly filtered to separate the BHET which have appreciable solubility in water at 100°C from DMT and oligomers. The mother liquor was allowed to cool to 10°C when crystals of BHET crystallized. The crystals were filtered and dried at 70°C under reduced pressure for 24 h, yield = 25 g, m.p = 109-110°C.

Elemental analysis (%): Found (Calculated)

C : 56.65 (56.70), H : 5.52 (5.51), O : 37.85 (37.79)

IR: 3450 (O-H), 3045 (Ar: C-H), 2900 (Alkyl: C-H), 1700 (C=), 1600 (Ar: C-C), 1150 (C-OH)

(ii) Preparation of PET oligomer from BHET

BHET (30 g) was taken in a glass reactor with nitrogen inlet and facility for overhead stirring. 0.235 mL of catalyst solution (300ppm) was added (0.963g $Ti(O^iPr)_4$ in 25 mL toluene) stirred well, reactor was heated to 278°C in a furnace and maintained at that temperature for 1 h. Reactor was allowed to cool under nitrogen atmosphere, yield = 25 g, η_{inh} = 0.19 dL/g, T_m = 247°C, T_{cc} = 194°C, carboxyl content = 22 ppm.

PET oligomer with Sb_2O_3 as catalyst was prepared using a similar procedure (25 g of BHET, 300 ppm. Sb_2O_3), yield = 23 g, η_{inh} = 0.14 dL/g, m.p (T_m, DSC) = 244°C, T_{cc} = 214°C, carboxyl content = 26 ppm.

4.2.3.2 From commercial PET

(i) Glycolysis

PET (10 g) and 100 mL of ethylene glycol were taken in 250 mL round bottom flask. Temperature was raised to 190°C while pellets were stirred thoroughly. Reaction was continued for 10 h at 190°C. The residue was filtered and washed with hot water and methanol to remove ethylene glycol and was dried at 75°C for 12 h, yield = 7 g,η_{inh} = 0.19 dL/g, $T_{m,}$ = 250°C, T_{cc} = 212°C, carboxyl content = 20 ppm.

(ii) Hydrolysis

Hydrolysis of PET pellets was carried out in a Parr reactor at 180°C. 10 g of PET pellets were stirred with 100 mL of distilled water at 180°C for 1.5 h. During the reaction, pressure rose to 100 psig. The residue obtained was filtered and was dried at 75°C under reduced pressure, yield = 8 g, η_{inh} = 0.15 dL/g, m.p (T_m, DSC) = 250°C, T_{cc} = 212°C, carboxyl content = 380 ppm.

4.2.4 Crystallization of oligomers

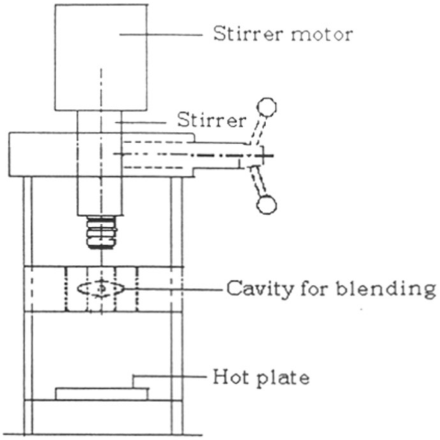


Fig. 4.1: Set up for thermal crystallization

The synthesized samples are crystalline in nature, however, the crystallization conditions are not controlled and hence all the samples were recrystallized under controlled conditions. Samples were melted at 290°C in a CSI Minimax extruder and then allowed to fall onto the hot plate which was maintained at the crystallization temperature 175°C. The clear melt formed hemispherical particles and these were allowed to crystallize on the hot plate. Schematic diagram of the set up is shown in **Fig. 4.1** The samples were removed from the hot plate after the completion of crystallization.

4.2.5 Solid state polymerization

Crystallized oligomers were powdered and sieved through 30 and 25 mesh sieves (600 microns) and were subjected to solid state polymerization for 20 h at 230°C in a glass reactor under nitrogen flow rate of 3 L/min (**Fig. 3.1**). Samples were removed at regular intervals for physical and structural characterizations.

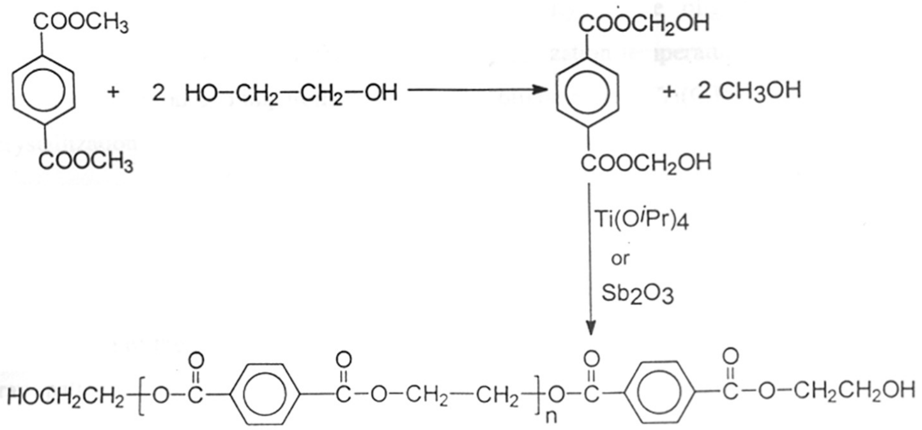
4.3 Results and discussion

4.3.1 Characterization of oligomers

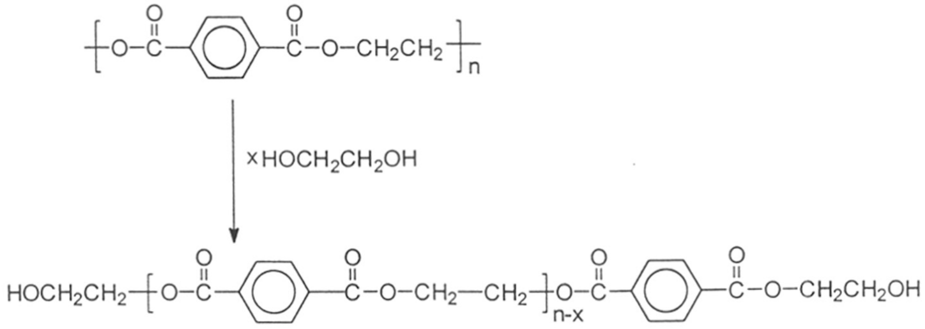
The oligomers with similar inherent viscosities were prepared using several methods Samples 1 and 2 were prepared by refluxing BHET for 1 h in presence of $Ti(O^iPr)_4$ and Sb_2O_3 respectively as catalysts, under nitrogen atmosphere. It was not necessary to continue the reaction under reduced pressure as in the normal melt condensation reactions, since, whenever it was done, η_{inh} increased to ~0.3 dL/g or above in a very short time. Sample 3 was prepared by glycolysis whereas sample 4 was prepared by hydrolysis of commercial PET. Samples 1, 2 and 3 possess hydroxyl end groups predominantly, since they were prepared either from BHET or by glycolysis. **(Scheme 4.1, 4.2)**. Sample 4 was prepared with high carboxyl content **(Scheme 4.3)** to understand its effect on crystallization and subsequent SSP. The inherent viscosity (η_{inh}), carboxyl end group content, crystallization temperature on cooling from the melt at 10°C/min (T_{cc}) for all the samples are listed in **Table 4.1**. Except for the sample containing $Ti(O^iPr)_4$, all other samples have similar crystallization temperature (T_{cc}) upon cooling. The samples 1-3 have comparable carboxyl contents.

Table 4.1 : Characterization of PET oligomers

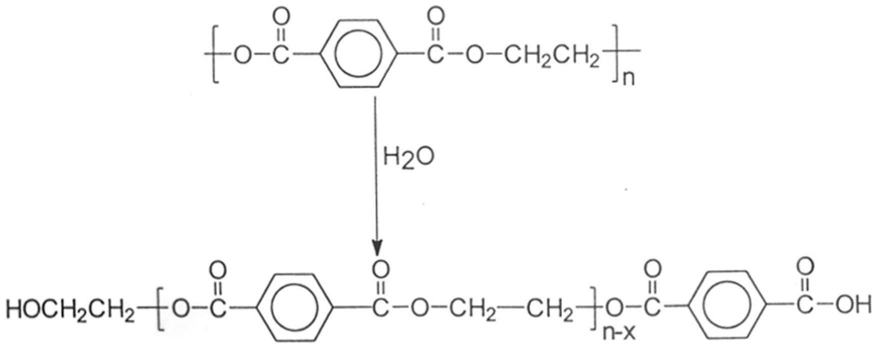
Sample no:	Method of preparation	η_{inh} (dL/g)	Degree of polymerization (DP)	Carboxyl content (ppm)	T_{cc} (°C)
1	Melt condensation in presence of $Ti(O^iPr)_4$	0.19	12	26	194
2	Melt condensation in presence of Sb_2O_3	0.14	7	22	214
3	Glycolysis of commercial PET	0.19	12	20	212
4	Hydrolysis of commercial PET	0.15	8	380	212



Scheme 4.1: Formation of PET from DMT and EG



Scheme 4.2: Degradation of PET by EG



Scheme 4.3: Degradation of PET by water

As prepared, all these oligomers show crystallinity. These oligomers have high crystallization rates as evident from the high crystallization temperatures (T_{cc}) exhibited by the samples on cooling from the melt. The oligomer with $Ti(O^iPr)_4$ has the lowest crystallization temperature and could be quenched into amorphous sample.

4.3.2 Crystallization of oligomers

Crystallization of the oligomers is found to be very rapid and are completed within a minute. The crystallinity, crystal size calculated from 010 reflection and the melting temperature of the crystallized samples are given in **Table 4.2**. **Figs.4.2** and **4.3** show X-ray patterns and DSC thermograms of the samples respectively. The crystallized oligomers show very well defined diffraction patterns with large crystal sizes. The DSC thermograms show no premelting endotherms in these samples and the presence of it would indicate small or imperfect crystallites, which might cause sticking during SSP[2].

Table 4.2: Crystallization of PET oligomers

Sample	Cryst. Temp (°C)	T_m (°C)	% crystallinity	Crystal size (D_{hkl}) (nm)
1	175	247	57	16
2	175	251	54	17
3	-	253	67	10
4	-	249	60	10

The crystallinity and crystal size achieved in these samples during the crystallization process are higher when compared with the crystallinity and the crystal size obtained in a typical high molecular weight PET (40%, 5 nm)[23]. **Fig. 4.4** shows X-ray patterns of the hydrolysed and glycolysed samples. Both the samples show high crystallinity and could be subjected to SSP without further crystallization. It may be noted that the thermal crystallization at 175°C after melting these samples have similar crystallinity as that of the obtained samples.

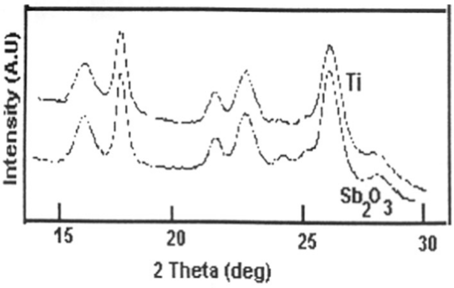


Fig. 4.2: XRD patterns of crystallized PET oligomers

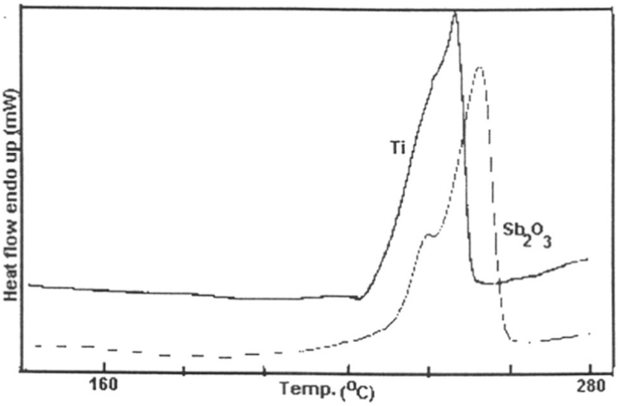


Fig. 4.3: DSC thermograms of crystallized PET oligomers (----) Sb_2O_3, (___) $Ti(O^iPr)_4$

4.3.3 Solid state polymerization

The crystallization data presented in **Table 4.2** shows that the onset of melting is close to 230°C and the samples can be subjected to SSP at 230°C. The change in η_{inh}, with SSP time is shown in **Fig. 4.5**. In **Table 4.3** T_m, T_{cc} and η_{inh}, of the starting and the final materials are given while **Table 4.4** shows the detailed SSP data of samples 1 and 2. **Table 4.5** shows the detailed SSP data of samples 3 and 4. All the samples show increase in viscosity with progress of solid state polymerization. It is apparent from **Fig. 4.5**, and **Table 4.4 and 4.5** that the increase in η_{inh}, is not a linear function of time. The η_{inh}, increases very rapidly during the initial stages of SSP and then slows down. The η_{inh}, increases from 0.19 to 0.68 dL/g just in 4 hours for sample with $Ti(O^iPr)_4$ and then it takes 16 hours to reach a value of 0.76 dL/g. In the case of sample with Sb_2O_3, the viscosity increases from 0.15 to 0.38 dL/g in the first 4hours and then to 0.55 dL/g after 20 h.

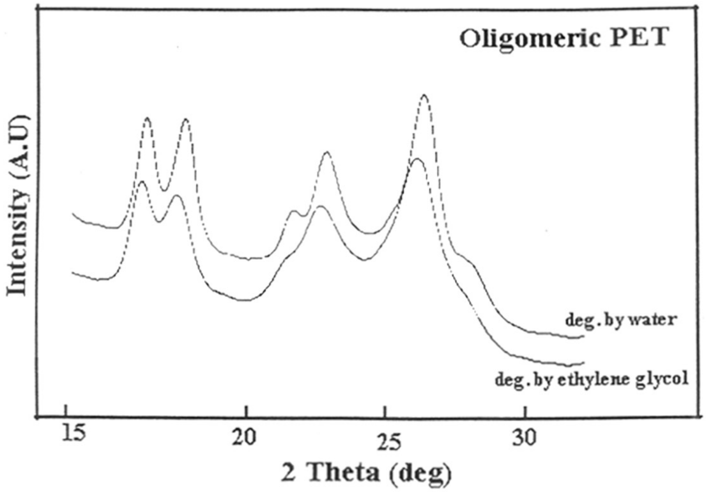
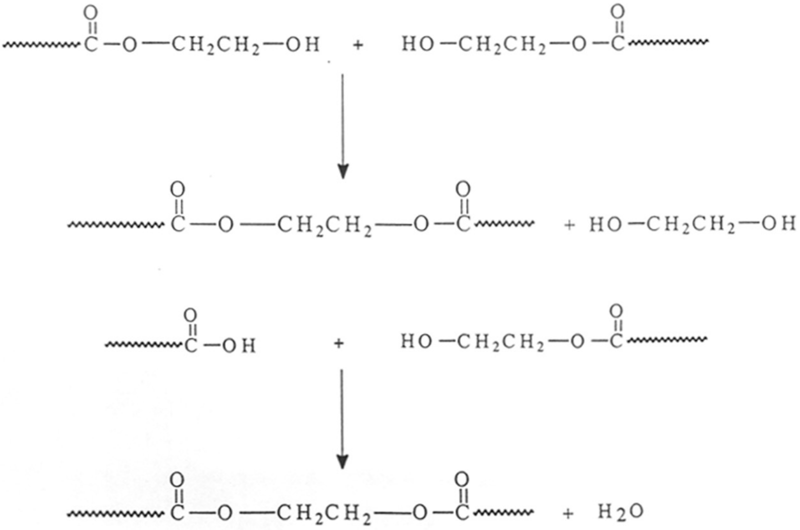


Fig. 4.4: XRD patterns of oligomers prepared by degradation of commercial PET



Scheme 4. 4: Formation of PET from oligomers prepared through degradation

This indicates that the sample prepared with $Ti(O^iPr)_4$ has higher SSP rate. In the case of hydrolysed and glycolysed samples it should be noted that, for SSP no other catalyst was added except the residual catalyst (Sb_2O_3 100 ppm) present in the commercial PET. By comparing the carboxyl values before and after SSP it is clear that in samples 1, 2 and 3 polymerization proceeds mainly by ester interchange reaction[3] while in sample 4 it is by a combination of esterification and ester inter change reactions (**Scheme 4.4**)

Table 4.3: SSP of PET oligomers

Sample	Condition	T_m (°C)	T_c (°C)	η_{inh} (dL/g)	Carboxyl content (ppm)
1	Before SSP	247	194	0.17	22
	230°C/20h	259	160	0.76	20
2	Before SSP	253	216	0.14	26
	230°C/20h	258	198	0.55	23
3	Before SSP	253	212	0.19	22
	230°C/20h	256	186	0.50	20
4	Before SSP	249	212	0.15	380
	230°C/20h	259	196	0.50	60

Table 4.4: SSP of PET oligomers prepared using $Ti(O^iPr)_4$ and Sb_2O_3

Sample/condition	T_m (°C)		T_{cc} (°C)		η_{inh} (dL/g)	
	$Ti(O^iPr)_4$	Sb_2O_3	$Ti(O^iPr)_4$	Sb_2O_3	$Ti(O^iPr)_4$	Sb_2O_3
Crystallized sample	248	253	194	216	0.19	0.14
230°C/4h	254	255	164	212	0.68	0.34
230°C/8h	254	256	161	210	0.71	0.38
230°C/12h	257	256	160	204	0.73	0.43
230°C/16h	257	258	160	202	0.75	0.52
230°C/20h	259	258	160	199	0.76	0.55

However, content of hydroxyl and carboxyl end groups does not seem to have much effect on the increase in viscosity. T_m increases slowly with time. From **Tables 4.4** and **4.5** it is clear that all the samples show the same trend.

The crystallization and polymerization methods described in the present work differs from the conventional SSP of PET. In conventional SSP the prepolymer has a typical inherent viscosity of 0.6 dL/g and the pellets are crystallized at 180°C for more than 1 h. The SSP is performed at 210°C for about 15 h. In the method reported here, the crystallization is completed within a minute and SSP is carried out at 230°C.

Table 4.5: SSP of PET oligomers prepared by glycolysis and hydrolysis

Sample/condition	T_m (°C)		T_{cc} (°C)		η_{inh} (dL/g)	
	Gly.	Hydr.	Gly.	Hydr.	Gly.	Hydr.
Obtained as such	250	250	212	212	0.19	0.15
230°C/4h	248	250	205	204	0.28	0.32
230°C/8h	248	255	193	202	0.33	0.37
230°C/12h	250	255	191	200	0.36	0.42
230°C/16h	253	257	186	198	0.44	0.45
230°C/20h	256	259	185	196	0.50	0.50

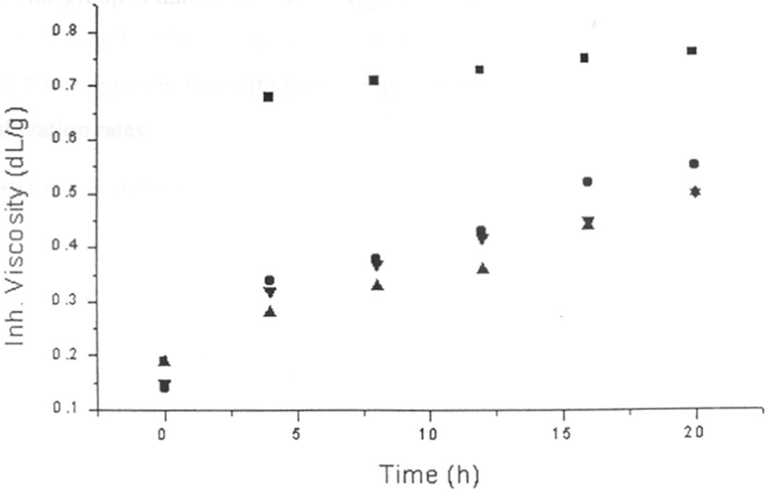


Fig. 4.5: Changes in η_{inh} during SSP
■ $Ti(O^iPr)_4$, • Sb_2O_3, ▼ glycolysed, ▲ hydrolysed

The oligomers prepared in the present investigation show interesting crystallization and SSP behaviour. The crystallization results indicate that the catalyst plays an important role in crystallization of oligomeric PET. The crystallization peak temperature (T_{cc}) on cooling from melt has been taken as a measure of crystallization rate[24]. It has been shown that half time of crystallization in isothermal crystallization correlates with the crystallization peak temperature in non isothermal crystallization[25]. High crystallization temperature during cooling in non isothermal experiments indicates higher crystallization rate. The crystallization temperatures recorded for the various samples are given in **Table 4.1**. It is apparent from the table that the oligomer containing $Ti(O^iPr)_4$ has the lowest crystallization temperature among all the samples examined and hence, has the lowest crystallization rate. The lower crystallization rate in the case of $Ti(O^iPr)_4$ has been attributed to the extensive interactions of PET terminal groups with the catalyst[24] which increases the apparent molecular weight. Because of the low crystallization rate, the sample could be quenched into fully amorphous material, while the samples containing Sb_2O_3 could not be quenched into fully amorphous state. Though the crystallization rate is lower for the sample with $Ti(O^iPr)_4$, the crystallinity and the crystal size achieved are comparable to the other samples. Carboxyl end group concentration does not affect the crystallization rate of these oligomers. This is evident from the observation that oligomer having very high carboxyl end group also have T_{cc} similar to the oligomers with lower carboxyl end group. Pilati et al[24] also suggest that carboxyl content plays a significant role in controlling T_{cc} of high molecular weight PET but not in oligomers. From **Tables 4.4 and 4.5** it is apparent that with increase in viscosity, T_{cc} decreases indicating decrease in crystallization rates.

4.3.4 Structure and morphology

All the oligomeric samples show high crystallinity and large crystal sizes. It is seen from **Fig. 4.2** that the X-ray diffraction pattern is very well developed and peaks are well resolved. The crystal sizes calculated from 010 peak is close to 17 nm. This indicates that the oligomeric PET crystallizes into crystals with less defects than the high molecular weight PET. The nature of the catalyst also seems to affect the SSP rate. Interestingly sample with $Ti(O^iPr)_4$ shows higher SSP rate compared to that with Sb_2O_3. Again the interaction of PET terminal groups with the catalyst[23] could lead to better SSP rates in the case of sample with $Ti(O^iPr)_4$.

The structure and morphology of the PET can be inferred from the WAXS, SAXS and DSC studies on pre SSP and post SSP samples of oligomer prepared with $Ti(O^iPr)_4$. The crystallinity, crystal size and lamellar thickness of the crystallized sample and sample after SSP were determined by WAXS and SAXS and given in **Table 4.6**. The WAXS patterns of the sample with Ti(O^{i}Pr)$_4$ before and after SSP are shown in **Fig.4.6**. These patterns do not show any obvious difference, indicating that there is no significant change in crystallinity or crystal size during SSP. However the long period showed a small increase during SSP. The lamellar thickness also exhibits marginal increase. These results indicate that the crystalline regions do not undergo major structural reorganization during SSP. However, DSC data shows an increase in melting point after SSP and could be attributed to the smoothening of the lamellar surface[26].

Table 4.6: Changes in crystal characteristics during SSP

Sample/condition	Crystallinity (%)	Crystal size (nm)	Long period (nm)	Lamellar thickness (nm)
Crystallized sample	57	16	12.5	7.1
230/20h	63	17	13.0	8.2

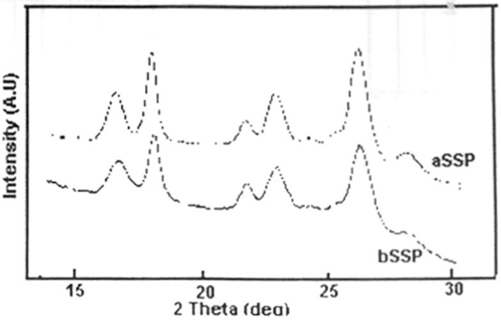


Fig. 4.6: XRD patterns of PET oligomer with Ti(O^{i}Pr)$_4$
bSSP : before SSP, aSSP : after SSP

It is worthwhile to note that the lamellar thickness is about 7.1 nm, while the length of the fully extended oligomer chain is about 12 nm (degree of polymerization is 12 and extended length of the monomer[27] is 1.07 nm). Hence the possibility of chain folding is less and the chain ends are outside the crystals. The large crystal width also indicates that the chain ends are excluded from the lattice and reside in the amorphous phase. Miyagi and Wunderlich[28] produced similar oligomer crystals by etching folded chain PET crystals. During SSP, the chains grow *via* the reaction between the molecules further removed chains in the same or different lamella[28] or with the chains from the adjacent lamella and this leads to more tie molecules. The presence of tie molecules are indicated by the super heating of the crystals at higher heating rate in DSC experiments[28]. A super heating of 5°C is observed for a heating rate of 50°C/minute for sample with $Ti(O^iPr)_4$ and is in agreement with the data reported by Miyagi and Wunderlich[28]. Based on the data, a structural model is proposed and is shown in **Fig. 4.7** for pre and post SSP samples. The rapid increase in η_{inh}, during the initial stages of SSP could be due to the availability of large number of end groups in the amorphous phase. With progress in time, the chains grow and entanglements increase. This increase in entanglement as well as decrease in the end group concentration could retard the rate of SSP during the later stages of SSP.

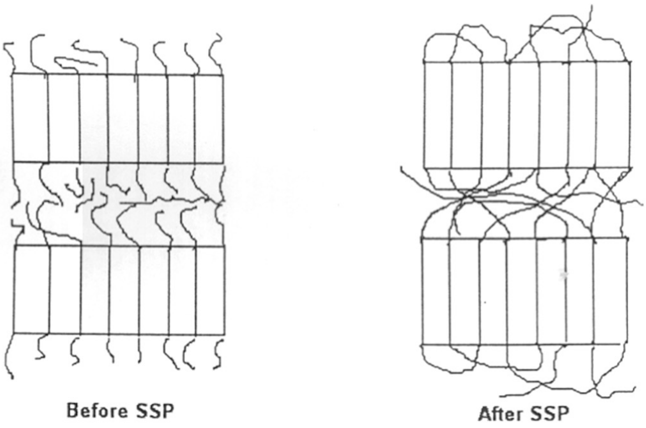


Fig. 4.7: Proposed structural model for PET before and after SSP

4.4 Conclusion

The present study shows that PET oligomer with η_{inh} 0.2 dL/g can be crystallized very rapidly and can be used as precursor for SSP to prepare high molecular weight PET. Nature of the catalyst affects crystallization and subsequent SSP of oligomeric PET. Presence of Sb_2O_3 enhances the crystallization rate compared to $Ti(O^iPr)_4$. However the sample with $Ti(O^iPr)_4$ shows better SSP rates. The better SSP rate with $Ti(O^iPr)_4$ is attributed to the interaction of PET terminal groups with catalyst. In the case of oligomers, the end group concentration does not influence the rate of crystallization. The nature of end groups also has no influence on SSP rate of the samples.

The PET oligomers rapidly crystallize into well developed large crystallites on crystallization at 175°C. This structure does not undergo major reorganization during SSP and SSP is mainly controlled by the chain ends in the amorphous phase. Based on the studies on structure and morphology, structural models have been proposed for crystallized sample and after SSP.

The oligomers can also be prepared by hydrolysis and glycolysis of amorphous high molecular weight PET pellets. These oligomers are highly crystalline and can be subjected to SSP without additional crystallization step. This will have implications in the recycling of PET.

II Crystallization and solid state polymerization of PET pellets

4.5 Introduction

The structure and morphology of PET oligomer and its SSP product have been studied in detail in the previous section. It is of interest to see how the morphology differs from the morphology of PET prepolymer and its SSP product using conventional commercial technique.

In commercial practices, high molecular weight PET required for engineering applications have been obtained by SSP of PET prepolymer in the from of pellets or chips with inherent viscosity ~ 0.5 dL/g or above. Prior to SSP these pellets or chips would be subjected to crystallization to avoid sticking during SSP. Thermal crystallization of amorphous PET at different temperatures and consequent structural morphologies have been examined by various investigators in detail[6,7,29-38]. The structural changes accompanying these crystallization processes often have been investigated using DSC or XRD. However, earlier studies do not address the effect of the crystal morphology on SSP rate.

Low crystallization rate and low thermal conductivity very often results in morphological differences between skin and core. A Sketch of the skin and core of PET pellet arising out of structure and morphology differences between the surface and inside the pellets is shown in **Fig. 4.8**

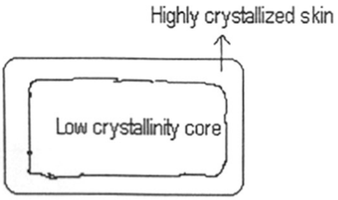


Fig. 4.8: Cross section of crystallized PET pellet

A study was conducted to determine the effect of crystallization temperature on the resulting skin-core crystalline morphology of the amorphous PET pellets. The average degree of crystallinity and the crystal size of the samples were determined by wide angle X-ray diffraction. Effect of crystal morphology on SSP rate was also examined.

4.6 Experimental

4.6.1 Materials

Amorphous PET pellets (l = 20 mm, d = 20 mm) obtained from Futura Chemicals Chennai, India was used.

4.6.2 Measurements

Inherent viscosity (η_{inh}) of the samples were measured at 25°C in 40/60 (wt/wt) phenol/TCE solvent mixture at a concentration of 0.5%. The average degree of crystallinity and crystal size of the samples were determined by WAXD in reflection mode by scanning finely ground samples. The degree of crystallinity and crystal size for the skin of pellets were determined by WAXD in the reflection mode by scanning pellets as such.

4.6.3 Crystallization of PET pellets

Amorphous PET pellets were crystallized at 160°C, 180°C and 220°C at rates of 80°C/min and 5°C/min in a rotary reactor to ensure uniform heating. Samples were kept at crystallization temperature for 5 minutes.

4.6.4 Solid state polymerization

Crystallized pellets (5 g) from each batch were subjected to solid state polymerization at 210°C for 10 h in a stream of nitrogen (3 L/min). Rate of solid state polymerization was determined from the change of η_{inh} with time.

4.7 Results and discussion

4.7.1 Crystal morphology and melting behaviour

In this study, crystallization temperatures of 160°C, 180°C and 220°C and heating rates of 5°C/min and 80°C/min were chosen. This temperature range encompasses the maximum crystallization temperature range. **Table 4.7** gives crystal sizes and % crystallinity of the samples. **Fig. 4.9** shows effects of crystallization conditions on core crystallinity. It can be seen that higher crystallization temperatures lead to higher core crystallinity while higher heating rates tend to decrease core crystallinity. Thus both crystallization temperature as well as heating rate influences crystallinity. Higher crystallization temperatures facilitate higher crystallinity, but under higher heating rates pellet core fails to attain the surface temperature thus lower core crystallinity results. Due to the same reason, difference in surface and core crystallinity decreases at low heating rates and the difference increases at higher crystallization temperatures. **Fig. 4.10** shows effect of crystallization temperature and heating rate on average crystal size.

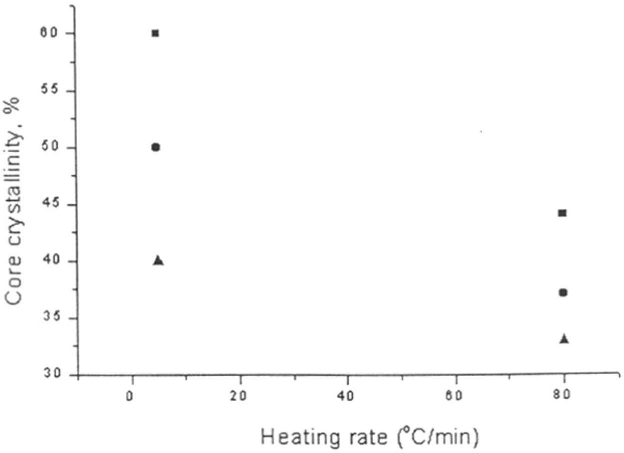


Fig. 4.9: Effect of crystallization temperature and heating rate on core crystallinity
■ 220°C, ●180°C, ▲160°C

Higher crystallization temperature and higher heating rates give larger crystals. Thus, at lower temperatures, crystallization is dominated by nucleation rather than the rate of spherulitic growth and crystal perfection resulting in small crystals. At higher crystallization temperatures, the rate of crystal growth and crystal perfection is higher than the rate of crystal nucleation resulting in large crystals. Higher heating rate also enhances the growth of crystals over nucleation resulting in larger crystals.

Melting behaviour observed for crystallized PET pellets has been found to be directly related to the crystallization temperature. Double melting endotherms were obtained for all the samples. Melting temperatures for the samples are given in **Table 4.7**. Multiple melting endotherms have been observed by many investigators[6,7,34-38] and interpreted on the basis of crystallite size or perfections induced by thermal treatments[6]. The first endotherm can be attributed to the melting of the crystalline material formed during crystallization and the second to the melting of a less stable fraction of the original crystalline material, reorganized into more perfect and larger crystals during DSC scan[7]. The value of the first melting peak reflects the crystallization temperature. The heating rate during crystallization appears to have no effect on either of the two melting peaks. Crystallization at higher temperatures causes a shift of the first melting peak to higher temperature, causing the difference between the first and the second melting peaks to become smaller.

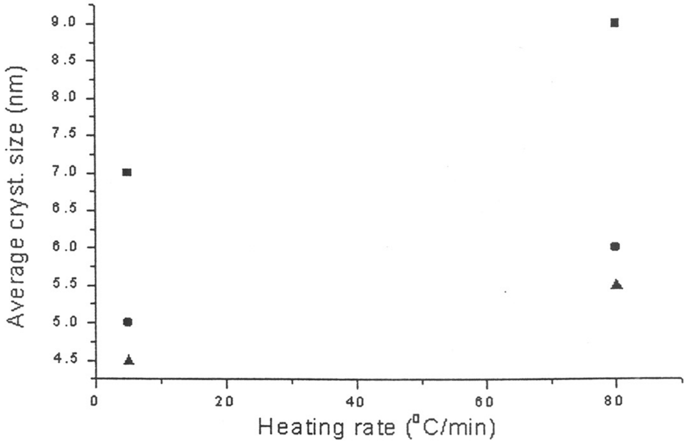


Fig. 4.10: Effect of crystalliztion. temperature and heating rate on average crystal size
■ 220°C, ● 180°C, ▲160°C

4.7.2 Solid state polymerization

About 4 g of each of the crystallized samples were subjected to SSP at 210°C for 10 h. Inherent viscosities were measured at intervals of 2 h. Results are given in **Table 4.8**. Effect of core crystallinity and crystal size on SSP rates are given in **Figs. 4.11 and 4.12**.

As mentioned earlier, lower heating rates always gave higher core crystallinity at the same crystallization temperature, while higher temperature of crystallization resulted in higher crystallinity. Thus crystallization at 220°C under slow heating gave highest core crystallinity, while crystallization at 160°C under fast heating gave the lowest core crystallinity.

Crystallization at 220°C under fast heating gave highest average crystal size, while, crystallization at 160°C under slow heating gave the lowest crystal size. Highest SSP rate was obtained for sample crystallized at 180°C under fast heating which has an intermediate crystal size and core crystallinity. Considering samples crystallized at the same temperature, crystallization under fast heating which led to higher crystal size and lower core crystallinity gave higher SSP rate. Samples crystallized at 160°C have lowest core crystallinity, but crystal sizes are also smaller and gave comparatively lower SSP rates. These effects are clearly seen in **Figs. 4.11 and 4.12**. Thus it can be assumed that a large crystal size and low core crystallinity favour SSP rate.

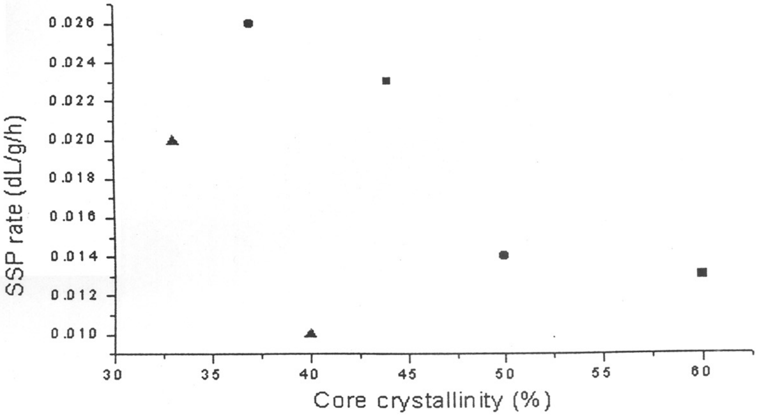


Fig: 4.11: Effect of core crystallintiy on SSP rate

■ 220°C, ●180°C, ▲160°C

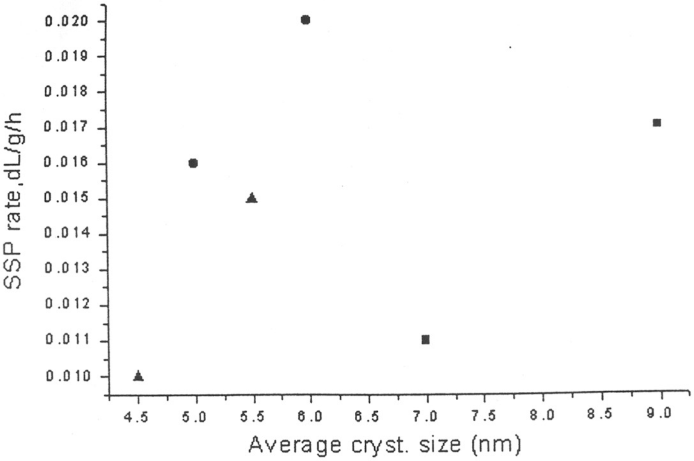


Fig .4.12: Effect of average crystal size on SSP rate

■ 220°C, •180°C, ▲160°C

Table 4.9 shows the change in melting peaks and ΔH during various stages of SSP for a sample crystallized at 180°C under fast heating. It is interesting to note that first melting peak shifted to 225°C from 184°C after 2 h at 210°C, followed by a gradual increase to 236°C at the end of 10 hours. The second melting remained more or less the same. ΔH corresponding to the first peak increases gradually while ΔH corresponding to the second peak decreases. **Fig. 4.13** shows heating thermograms of samples before and after SSP for crystallization at 160°C, 180°C under fast heating. All the samples show similar behaviour. Since ΔH under the first peak increases in comparison with the second peak, it can be assumed that more stable crystalline structures are formed with time which are not transformed during DSC scanning[7].

Table 4.7: Crystallization of PET pellets

Cryst.temp (°C)	Heating rate (°C/min)	Crystal size (nm)		% crystallinity			Melting point (°C)		SSP rate (dL/g/h)	Melting point (°C) (after SSP)	
		Surface	Average	Surface	Core	Average	Tm1	Tm2		Tm1	Tm2
220	80	12	9	54	44	49	223	256	0.023	242	-
	5	9	7	65	60	62.5	224	252	0.011	236	251
180	80	8	6	45	37	41	184	253	0.026	236	250
	5	7.5	5	53	50	51.5	184	253	0.016	225	251
160	80	6	5.5	39	33	36	170	252	0.020	229	249
	5	5	4.5	42	40	41	164	251	0.010	228	249

Table 4.8: SSP of crystallized PET pellets

Cryst. temp. (°C)	Heating rate (°C/min)	η_{inh} (dL/g)						Rise rate (dL/g/h)
		0 h	**2 h**	**4 h**	**6 h**	**8 h**	**10 h**	
220	80	0.54	0.65	0.68	0.71	0.74	0.77	0.023
	5	0.54	0.60	0.63	0.64	0.65	0.65	0.011
180	80	0.54	0.67	0.72	0.75	0.77	0.80	0.026
	5	0.54	0.62	0.65	0.67	0.68	0.70	0.016
160	80	0.54	0.64	0.66	0.70	0.72	0.74	0.020
	5	0.54	0.58	0.59	0.61	0.64	0.64	0.010

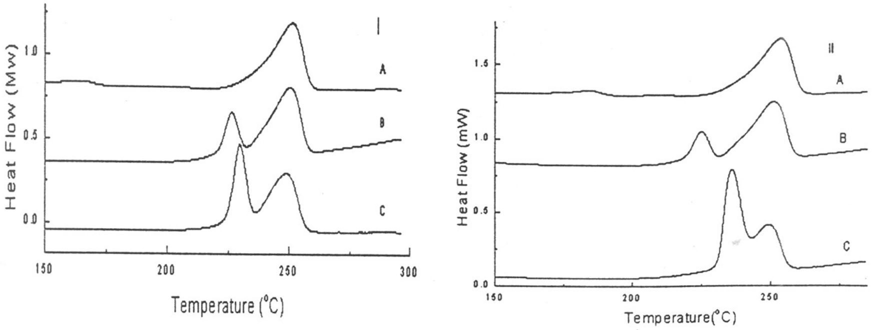


Fig. 4.13: DSC thermograms of PET crystallized at I)180°C II) 160°C A) crystallized B) 210°C/2h C) 210°C/10h

Table 4.9: Melting behaviour of PET during SSP (crystallization at 180°C, 80°C/min)

Sample/Conditions	Tm (°C)		ΔH (J/g)	
	1	2	1	2
Cryst. at 180°C	184	253	2	36
210°C/2h	225	251	7	31
210°C/4h	233	251	14	19
210°C/6h	232	250	15	20
210°C/8h	233	250	18	13
210°C/10h	236	251	21	8

4.6 Conclusion

Crystallinity of PET pellets depends on the crystallization temperature and the heating rate. Higher crystallization temperature leads to higher overall crystallinity, while higher heating rate results in lower core crystallinity. Difference in surface and core crystallinity decreases at low heating rate and the difference increases at higher crystallization temperature. Average crystal size increases with crystallization temperature. A large crystal size and low core crystallinity favours SSP rate. Thus, it is possible to get an optimum crystal morphology to achieve highest rate of solid state polymerization. It is apparent from this study that the structure and morphology differs significantly between the SSP process starting with oligomers ([η] 0.2 dL/g)and prepolymers ([η] 0.5 dL/g). One key structural parameter that controls the SSP is crystal size. Oligomers have very big crystals and have better rates. In the case of prepolymer also the sample with larger crystal size have better SSP rates. However, the crystal size of prepolymers is almost half that of the oligomer. This indicates that crystals are less perfect and defective. The defects arise because of the inclusion of chain ends in the lattice and these chain ends may not be available for SSP. Also these crystals can reorganize during SSP to become more perfect. From the above studies it appears that the crystalline morphology of oligomer seems better suited for SSP. On the other hand, during SSP of higher molecular weight prepolymers, crystal reorganization also takes place resulting in reduction in chain growth rate.

4.9 References

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CHAPTER 5

CRYSTALLIZATION AND SOLID STATE POLYMERIZATION OF POLY(ETHYLENE 2,6-DIMETHYL NAPHTHALATE)S

I Crystallization and solid state polymerization of PEN oligomers

5.1 Introduction

Poly(ethylene 2,6-naphthalate)s (PEN) exhibit superior thermal, mechanical, barrier and chemical resistance properties compared to poly(ethylene terephthalate)s (PET). Consequently there exists significant commercial interest for PEN. Higher tensile strength and dimensional stability render PEN films as excellent materials for the manufacture of magnetic recording tapes and electronic components[1-3,6,7]. Because of its high T_g and superior resistance to gas diffusion, especially, to the diffusion of carbon dioxide, oxygen and water vapour, PEN films are useful for manufacturing food containers, particularly for hot form-fill applications[6].

Most of these applications require polymers of relatively high molecular weights. Melt polymerization of PEN to reach high molecular weight is even more difficult to achieve than PET because of its higher melt viscosity and rapid colour formation in melt phase[8].

These problems can be minimized by the use of SSP methods. However, SSP of PEN is relatively more difficult than that of PET. PEN crystallizes at a lower rate and at a higher temperature than PET and during crystallization process, low molecular weight PEN particles release volatile products which can produce popcorn like particles. Thus PEN cannot be crystallized like PET or PBT to obtain suitable precursors for SSP[8].

A few patents suggest improvements in the methods for crystallization like employing foamed PEN oligomers or pellets coated with an alkylene carbonate[9] or crystallizing the oligomers in presence of water or ethylene glycol under elevated pressure[10]. All these patents concern with materials of η_{inh} 0.5 dL/g or above.

US patent 5,670606[8] reveals a method for preparing crystallized oligomer with melting point of 251°C and crystal size of ~ 14 nm which can be used as SSP precursors. However, the SSP rates obtained were very low and details are not discussed.

There are a few reports in the open literature regarding solvent induced crystallization of PEN[11-13]. DMF, aniline, dioxane and methylene chloride have been suggested as suitable diluents for crystallization. However, crystallization of oligomers by this method and their suitability for SSP are not reported.

This chapter deals with crystallization of PEN oligomers with very low η_{inh} (~0.1 dL/g), and their SSP to obtain high molecular weight PEN. Crystallization and thermal behaviour of these materials have been investigated by DSC and XRD studies.

5.2 Experimental

5.2.1 Materials

2,6-dimethyl naphthalate (DMN) obtained from Aldrich, USA, was used as received. Phenol, 1,1',2,2'-tetrachloroethane (TCE), ethylene glycol and benzyl alcohol were obtained from Sd. Fine Chemicals, Bombay and were distilled before use. Phenol red obtained from Sd. Fine Chemicals was used as 1% solution in ethyl alcohol. Sb_2O_3 and zinc acetate obtained from Aldrich was used as received. Titanium tetraisopropoxide ($Ti(O^iPr)_4$) was distilled under reduced pressure and was used as solution in toluene dried over metallic sodium (1 mL in 25 mL of toluene).

5.2.2 Measurements

Inherent viscosities (η_{inh}) of the samples were measured at 25°C in an automated Schott Gerate AVS 24 viscometer using Ubbelhode suspended level viscometer in a 40/60 (wt/wt) phenol/TCE solvent mixture at a concentration of 0.5%. Carboxyl terminal groups were determined by Pohl's method.

The X-ray diffraction experiments were performed using Rigaku Dmax 2500 diffractometer. The system consists of a rotating anode generator and wide angle powder goniometer and a slit collimated small angle goniometer. The generator was operated at 40 KV and 150 mA. The samples were ground into fine powder and used for the experiments. Samples were scanned between $2\theta = 10$ to 35 deg at a speed of 1 deg/min The crystal size was calculated from the FWHM of 011 reflection using Scherrer equation, $D_{hkl} = 0.89\lambda/\Delta_{hkl} \cos\theta$. The calorimetric measurements were done using Perkin - Elmer DSC-7. The samples were heated/cooled at a rate of 10°C/min. under nitrogen environment. The melting temperature and heat of fusion were obtained from the heating thermogram and crystallization upon cooling (T_{cc}) from the cooling thermogram.

5.2.3 Preparation of oligomers

5.2.3.1 Preparation of bis(hydroxy ethylene) naphthalate (BHEN)

Preparation of BHEN was done according to the procedure by Wang et al[4]. DMN (30 g) and 45.74 g of EG (1:6 mol ratio) were taken in r. b flask. Zinc acetate (0.0045 g) (2×10^{-5} mol/mol of DMN) was added to the mixture and refluxed at 180°C with stirring for 3 h with removal of methanol. Reaction mixture was left standing overnight. The solid residue was isolated by filtration and dried at 90°C for 6 h and was recrystallized from boiling water. Sample was dried at 90°C for 24 h, yield = 30 g, m. p = 129 -131°C, elemental analysis: C = 63.26 (63. 76), H = 5.16 (5.22), O = 31.58 (31.02).

5.2.3.2 Preparation of PEN oligomers from BHEN

BHEN (35 g) was taken in a glass reactor with nitrogen inlet and stirring arrangement. $Ti(O^iPr)_4$ solution (0.175 mL, 300 ppm) was added under nitrogen atmosphere and the mixture was heated to 250°C in a furnace. The temperature was slowly raised to 280°C and the reaction was continued for 1.5 h. The product oligomer had η_{inh} of 0.1 dL/g. Thermal analysis showed no melting peak, indicating that the sample was amorphous.

Similarly, an oligomer was also prepared using Sb_2O_3 as catalyst (0.011 g of Sb_2O_3 for 35 g of BHEN). The oligomer had an η_{inh} of 0.1 dL/g. $T_m = 240°C$, $\Delta H = 15$ J/g, $T_{cc} = 220°C$ Unlike the oligomer with $Ti(O^iPr)_4$, the latter oligomer was crystalline.

5.2.4 Crystallization of oligomers

5.2.4.1 Thermal crystallization

Samples were melted to 290°C in a CSI Minimax extruder and then allowed to fall on a hot plate which was maintained at 175°C, the crystallization temperature **(Fig. 4.1)**. The clear melt formed hemispherical particles upon cooling and these were allowed to crystallize on the hot plate. The samples were removed from the hot plate for a period of ~5 min.

5.2.4.2 Diluent induced crystallization

Crystallization using diluent was performed at room temperature (RT) and in few cases at 110°C. In the first case, the oligomer was taken in a r.b flask containing excess of solvent and stirred for 12 h at RT. The material was removed by filtration and dried under reduced pressure at room temperature. In the latter case, the material was refluxed in solvent for 4 h and the solvent was removed under reduced pressure at 50°C.

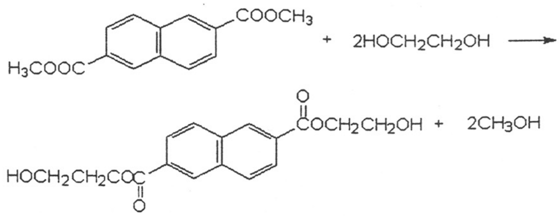
5.2.5 Solid state polymerization

Thermally crystallized oligomers were powdered and sieved through 30 and 25 mesh sieves (600 microns) and were subjected to solid state polymerization for 20 h at 210°C in a glass reactor under nitrogen flow rate of 3 L/minute **(Fig. 3.1)**. Samples crystallized using diluents were in the form of fine powder and were subjected to SSP as obtained. Samples were removed at regular intervals for physical and structural characterizations.

5.3 Results and discussion

5.3.1 Characterization of oligomers

BHEN was prepared from DMN and ethylene glycol (**Scheme 5.1**).



Scheme 5.1: Preparation of BHEN

IR spectrum **(Fig. 5.1)** shows absorptions corresponding to (O-H), (Ar:C-H), (Alkyl:C-H) and (C=O) at 3450, 3050, 2900 and 1720 cm^{-1} respectively.

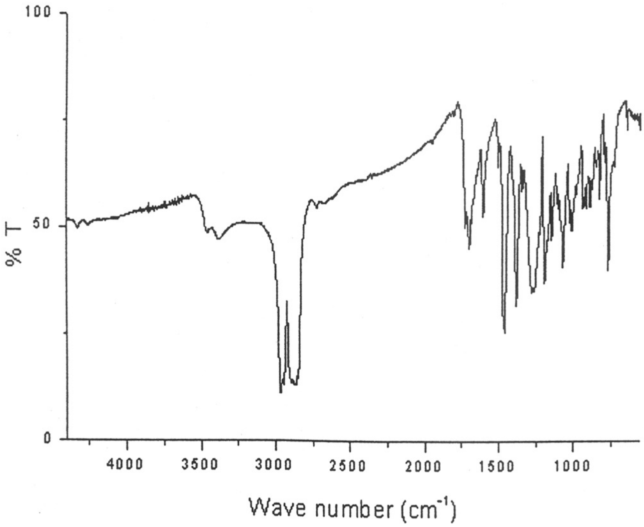
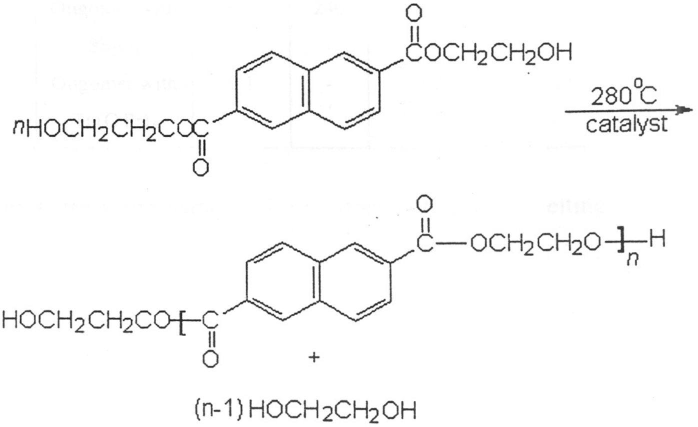


Fig. 5.1: IR spectrum of BHEN

PEN oligomers were prepared by heating BHEN in presence of catalysts (Sb_2O_3 and $Ti(O^iPr)_4$) under nitrogen at 280°C (**Scheme 5.2**). IR and NMR spectra of the obtained oligomers are given in **Figs. 5.2 and 5.3**.



Scheme 5.2: Preparation of PEN from BHEN

IR spectrum of PEN oligomer was very much similar to that of BHEN, except for absorption corresponding to (O-H) was not so intense. NMR spectrum showed the chemical shifts corresponding to aliphatic protons at 4.9 ppm, and aromatic protons at 8.0 and 8.7 ppm.

The η_{inh}, carboxyl end group content, melting temperature and crystallization temperature on cooling from melt are given in **Table 5.1**

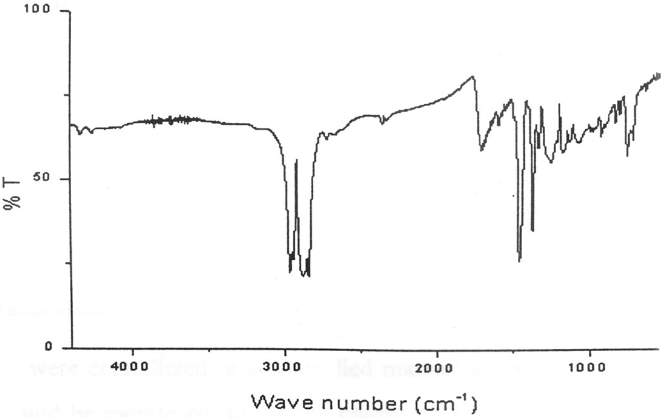


Fig. 5.2: IR spectrum of PEN

Table 5.1 Characteristics of PEN oligomers

Sample	η_{inh} (dL/g)	T_m (°C)	T_{cc} (°C)	Carboxyl content (ppm)
Oligomer with Sb_2O_3	0.1	240	220	27
Oligomer with Ti $(O^iPr)_4$	0.1	-	202	25

The oligomer synthesized using $Ti(O^iPr)_4$ does not show a melting transition, whereas, the oligomer obtained using Sb_2O_3 shows melting transition at 240°C. On cooling from the melt these oligomers crystallize. The crystallization temperatures are 220 and 202°C respectively for oligomers synthesized using Sb_2O_3 and $Ti(O^iPr)_4$ .The lower T_{cc} for PEN (Ti) implies a lower crystallization rate for this oligomer.The delayed crystallization can be due to the extensive interaction of $Ti(O^iPr)_4$ with PEN chain ends causing an apparent increase in molecular weight.

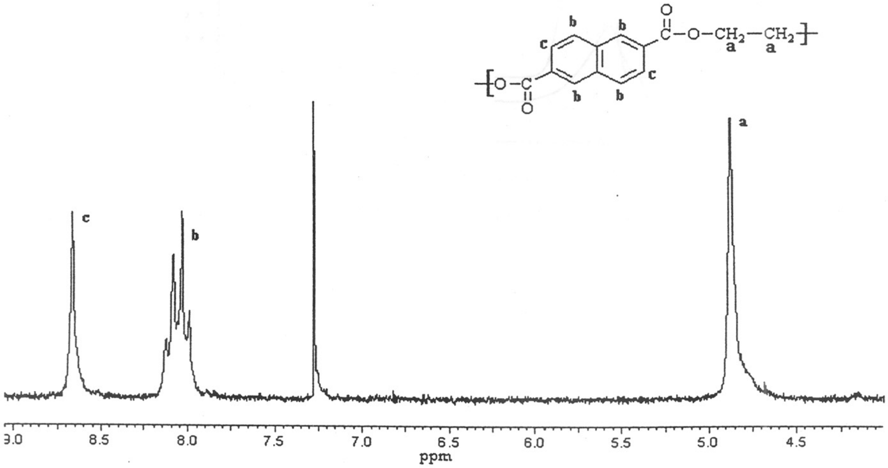


Fig. 5.3: ^{1}HNMR spectrum of PEN oligomer

5.3.2 Crystallization of oligomers

The oligomers were crystallized in a controlled manner so that changes in structure and morphology could be monitored during the course of SSP. Two crystallization methods were followed, namely, 1) thermal crystallization at 175°C, where the crystallization rate is the highest and 2) diluent induced crystallization.

5.3.2.1 Thermal crystallization

The thermal crystallization of oligomers is found to be rapid. However, when compared to PET oligomers, it is slower. This can be due to the presence of rigid naphthalene moieties in PEN backbone. **Figs. 5.4 and 5.5** give DSC thermograms and XRD patterns of the crystallized samples. DSC thermograms of the crystallized samples show melting points at 246°C and 239°C for samples with Sb_2O_3 and $Ti(O^iPr)_4$ respectively. The melting points obtained from the 2nd heating thermograms after cooling at 10°C/min are 263°C and 260°C respectively for oligomers with Sb_2O_3 and with $Ti(O^iPr)_4$. This could be due to the higher crystallization temperature on cooling than the starting material which was crystallized at 175°C. XRD patterns of the crystallized samples showed well defined sharp reflections. The crystal widths calculated from 011 reflection are 18 and 15 nm respectively. The patterns indicate that the samples are crystallized in the α structure

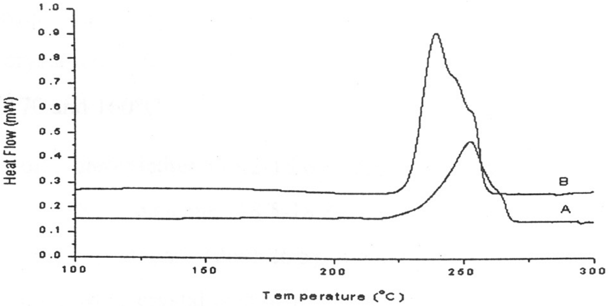


Fig. 5.4: DSC thermograms of crystallized PEN oligomers
A) oligomer with Sb_2O_3, B) oligomer with $Ti(O^iPr)_4$

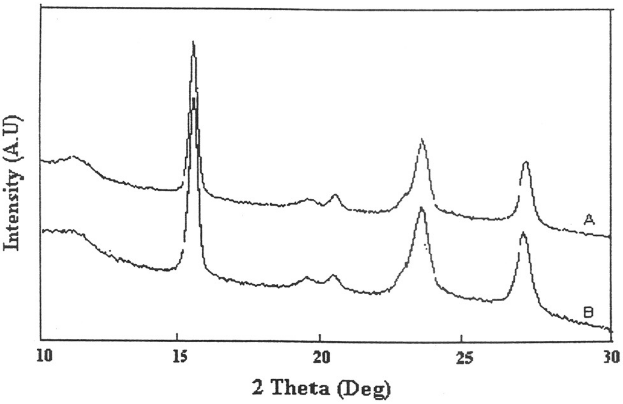


Fig. 5.5: XRD patterns of crystallized PEN oligomers
A) oligomer with Sb_2O_3, B) oligomer with $Ti(O^iPr)_4$

5.3.2.2 Diluent induced crystallization

It is known that in the presence of certain diluents, crystallization of amorphous polymers occurs at temperatures well below the glass transition temperature of the polymer[13]. There are a few reports regarding diluent induced crystallization of PEN. The diluents mainly studied are dioxane, aniline, DMF and methylene chloride whose solubility parameters (δ) are 20.42, 22.6-24.2, 24.9 and 19.9 $(\mathrm{Jcm}^{-3})^{1/2}$ respectively. The solubility parameter of PEN is 20.31$(\mathrm{Jcm}^{-3})^{1/2}$ (calculated by Synthia, method)[27]. Kim et al reported[13] that the samples treated in dioxane above 40°C exhibited α crystal and spherulitic texture, while crystallization at 25°C gave β crystal and amoebae structure. DMF treated samples mainly showed α crystal irrespective of treatment temperature. But a trace of β crystal structure was observed in the sample treated at 10°C. The β crystal occurred at lower treatment temperature in diluent induced crystallization while it occurred at higher crystallization temperatures in thermal crystallization. US patent 5,744,578[10] reveals that PEN could be crystallized in presence of ethylene glycol or water under pressure at temperatures of 170 and 160°C.

In the present work, diethylether (15.2-15.6), carbon tetrachloride (17.7), ethylacetate (18.6), toluene (18.2-18.3), benzene (18.5-18.8), chloroform (18.9-19), dichloromethane (19.9), acetone (20-20.5), ethanol (26.0-26.5), methanol (29.2- 29.7) were examined as diluents. The samples were crystallized at room temperature by stirring the oligomer in the diluents for about 12 h. Samples were isolated by filtration and dried under reduced pressure at 50°C. The XRD patterns of oligomers crystallized as above are shown in **Fig. 5.6.**

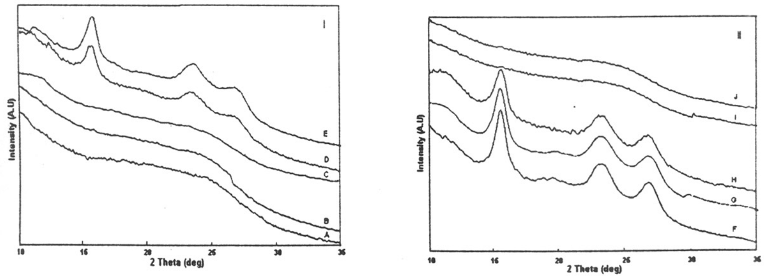


Fig. 5.6: XRD patterns of PEN oliogomer after contact with various solvents A)diethylether, B) carbon tetrachloride, C) ethylacetate, D) toluene E) benzene, F) chloroform, G) dichloromethane, H) acetone, I) ethanol J) methanol

It can be seen that diluents which are having δ < 18.5 and δ >26 are not capable of inducing crystallinity. If the results from earlier studies are also taken into account, diluents with δ> 25 are also not capable of inducing crystallinity. Thus for a diluent to effectively induce crystallinity at room temperature, its δ value should be in between 18.5 and 25 (18.5< δ< 25.0). The XRD patterns showed that all samples have been crystallized in the α form. Crystallization was also performed in toluene at its reflux temperature (110°C). Even though toluene (18.2-18.3) is not capable of inducing crystallinity at room temperature, at elevated temperature it could induce crystallinity giving a fairly well defined XRD pattern which has sharper reflections than the samples crystallized at room temperature. A combined effect of diluent interaction and elevated temperature might have facilitated the effective crystallization. Compared to the samples which have undergone thermal crystallization, samples crystallized using diluents have very broad and less developed peaks in XRD patterns. Similar observations were made by Rebenfield et al[14] in the case of PET crystallized in dioxane and aniline and by Makarewicz et al for PEN[12]. This was attributed to rather small sized yet profuse crystallites induced by the diluents. Crystal sizes obtained and corresponding δ values for various diluents are given in **Table 5.2**.

Table 5.2: Crystallization of PEN by diluents (25°C)

Solvent	δ ($J^{1/2}/cm^{3/2}$)	Crystal size (nm)
Diethylether	15.2 - 15.6	Amorphous
Carbon tetrachloride	17.7	Amorphous
Toluene	18.2 - 18.3	Amorphous
Toluene (110°C)	"	9.0
Benzene	18.5 - 18.8	4.7
Ethylacetate	18.6	4.9
Chloroform	18.9 - 19	5.2
Dichloromethane	19.9 - 19.9	5.4
Acetone	20.0-20.5	5.9
Ethanol	26.0 - 26.5	Amorphous
Methanol	29.2 - 29.7	Amorphous

It can be seen that as the δ values of the diluents approach that of the polymer, crystal sizes tend to increase. More favourable polymer-diluent interaction facilitate more effective crystallization.

5.3.3 Solid state polymerization

Crystallized oligomers were subjected to SSP in a stream of nitrogen flow at 3 L/min. Details of the samples are given in **Table 5.3**. The SSP temperatures are selected on the basis of onset of the melting of the crystallites obtained from thermal studies. Samples 1 and 2 were subjected to SSP at 210°C, while samples 3 and 4 were subjected to SSP at 230°C. All the samples underwent SSP giving increase in η_{inh}.

Table 5.3: Crystallized PEN oligomers for SSP

Sample No:	Sample	Crystallization conditions	Crystal size (nm)	T_m (°C)	T_{cc} (°C)
1	PEN (Sb_2O_3)	Thermal cryst. at 180°C	18	246	220
2	PEN ($Ti(O^iPr)_4$)	Thermal cryst. at 180°C	15	239	201
3	PEN (Sb_2O_3)	Cryst. by toluene at 110°C	9.5	248	221
4	PEN ($Ti(O^iPr)_4$)	Cryst. by toluene at 110°C	9.3	249	198
5	PEN ($Ti(O^iPr)_4$)	Cryst. by EtOAc at room temp.	4.9	247	201

The increase in η_{inh} with time are given in **Tables 5.4-5.8** and **Fig. 5.7**.

Table 5.4: SSP of PEN oligomer prepared using Sb_2O_3

Sample/conditions	η_{inh} (dL/g)	T_m (°C)	T_{cc} (°C)
Cryst. Oligomer[a]	0.10	246	220
210°C/4h	0.21	244, 263	220
210°C/8h	0.26	248, 265	215
210°C/12h	0.30	250, 264	214
210°C/16h	0.33	250, 266	213
210°C/20h	0.35	250, 268	210

[a] Thermal crystallization

Table 5.5: SSP of PEN oligomer prepared using $Ti(O^iPr)_4$

Sample/conditions	η_{inh} (dL/g)	T_m (°C)	T_{cc} (°C)
Cryst. Oligomer[a]	0.1	239	201
210°C/4h	0.22	239, 250	197
210°C/8h	0.26	239, 250	196
210°C/12h	0.30	243	196
210°C/16h	0.35	244	194
210°C/20h	0.40	247	190

[a] Thermal crystallization

Table 5.6: SSP of PEN oligomer prepared usingSb_2O_3[a]

Sample/conditions	η_{inh} (dL/g)	T_m (°C)	T_{cc} (°C)
Cryst.ligomer[a]	0.1	248	221
230°C/4h	0.35	256, 265	212
230°C/8h	0.37	256, 265	206
230°C/12h	0.40	256, 265	202
230°C/16h	0.43	256, 265	202
230°C/20h	0.45	256, 265	202

[a] Crystallized in toluene at 110°C

Table 5.7: SSP of PEN oligomer prepared using $Ti(O^iPr)_4$[a]

Sample/conditions	η_{inh} (dL/g)	T_m (°C)	T_{cc} (°C)
Cryst. oligomer[a]	0.1	249	198
230°C/4h	0.47	247, 259	177
230°C/8h	0.50	250, 261	177
230°C/12h	0.52	250, 260	177
230°C/16h	0.54	251, 260	177
230°C/20h	0.55	251, 260	177

[a] Crystallized in toluene at 110°C

Table 5.8: SSP of PEN oligomer prepared using Ti(O^{i}Pr)$_4$[a]

Sample/conditions	η_{inh} (dL/g)	T_m (°C)	T_{cc} (°C)
Cryst. oligomer[a]	0.10	247	201
210°C/4h	0.26	248, 263	192
210°C/8h	0.30	249, 262	189
210°C/12h	0.35	250, 263	188
210°C/16h	0.40	251, 262	187
210°C/20h	0.42	252, 263	187

[a] Crystallized in ethylacetate at room temp.

It can be seen that increase in η_{inh} is not a linear function of time. Initially the η_{inh} increases rapidly, but progressively slows down. SSP temperature and the nature of catalyst play an important role in determining the rate of SSP. Higher SSP temperature and oligomers prepared using Ti(O^{i}Pr)$_4$ show higher SSP rates. Another noteworthy observation is that, under similar conditions PET shows higher SSP rate than PEN **(Fig. 5.8)**.

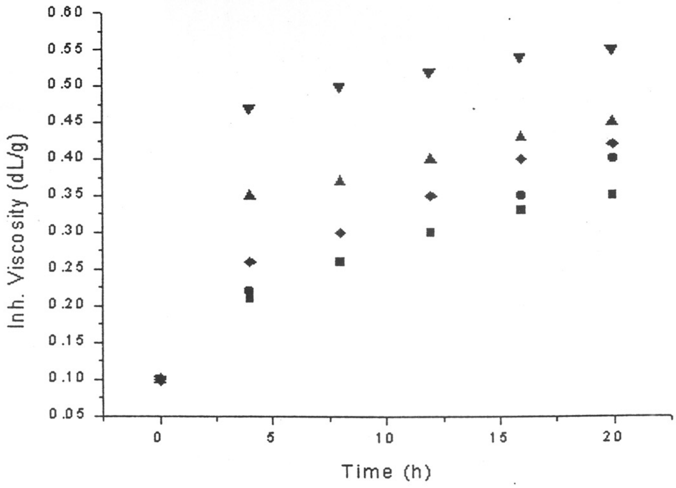


Fig. 5.7: Change in η_{inh} during SSP of PEN oligomers

■ Sb_2O_3 (thermally cryst.), • Ti(O^{i}Pr)$_4$ (thermally cryst),
◆ Ti(O^{i}Pr)$_4$ (cryst. in ethylacetate), ▲ Sb_2O_3 (cryst. in toluene),
▼ Ti(O^{i}Pr)$_4$ (cryst. in toluene)

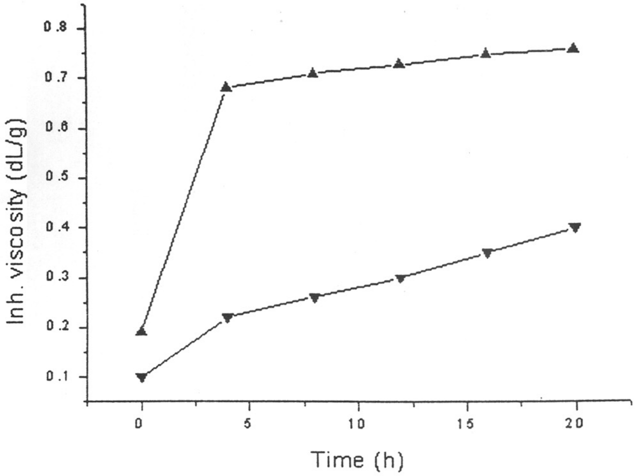


Fig. 5.8: Comparison of rate of SSP of PET and PEN oligomers (thermally crystallized)

▲ PET (Ti(O^{i}Pr)$_4$,), ▼ PEN (Ti(O^{i}Pr)$_4$,)

Larger the difference between the T_g and the operating temperature, higher will be the molecular mobility. Difference between the reaction temperature and T_g is 140°C in the case of PET, whereas it is 100°C for PEN. Thus PET will have higher chain mobility leading to higher SSP rate compared to PEN.

5.3.4 Structure and morphology

The XRD patterns of samples 1, 2, 4 and 5 before and after SSP are given in **Fig. 5.9**. The changes in crystal sizes during SSP for these samples are given in **Table 5.9**. From **Fig. 5.9,** it is evident that the XRD patterns of the thermally crystallized samples do not show any significant change during SSP. The large crystal size of these samples show that these crystals are defect free and the end groups may be outside the crystals. However, in the case of samples crystallized by diluents, changes are observed in the XRD pattern after SSP. The less developed broad peaks becomes sharper and comparable to the thermally crystallized sample. For instance, the crystal size of sample crystallized by toluene increases from 9 nm before SSP to 14 nm after SSP. The poorly developed structure during solvent induced crystallization could have reordered into well developed structure similar to thermally crystallized samples during initial stages of SSP when it is subjected to temperatures above 200°C. The catalyst also does not have major effect on the XRD patterns. In general, the X-ray diffraction studies indicate that during SSP the crystals do not reorganize.

Table 5.9: Change in crystallite. size (calculated from 110 reflection) during SSP

Sample no:	Crystal size (nm)	
	Before SSP	After SSP
1	18	19
2	15	16
4	9	14
5	5	14

The thermal characteristics of these samples, on the other hand, show major changes during SSP. The main feature is the observation of double melting peaks and their change with SSP time. Broadly speaking the crystallized samples show a major peak at about 247°C and a shoulder on the low temperature side at about 220°C.

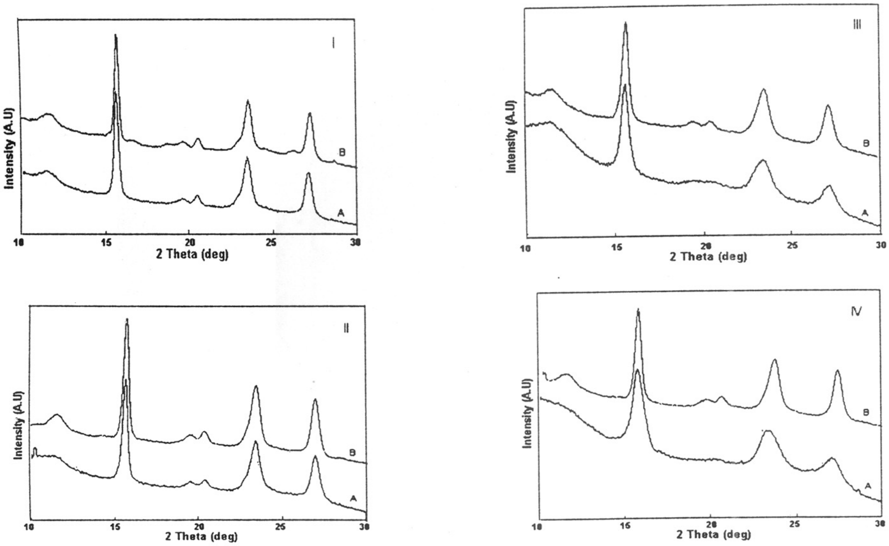


Fig. 5.9: XRD patterns of PEN before (A) and after SSP (B)
(I)PEN (Sb_2O_3), thermally crystallized, (II) PEN (Ti $(O^iPr)_4$), thermally crytsallized
(III) PEN ($Ti(O^iPr)_4$), crystallized in toluene at 110°C, (IV) PEN (Ti $(O^iPr)_4$), crystallized in ethyl acetate

These peaks shift towards higher temperatures and the relative area of the peaks also change. **Figs. 5.10-5.13** give DSC thermograms of various samples at different stages of SSP. The low temperature peak shifts to 255°C and the high temperature peak to 265°C for thermally crystallized samples. In the case of solvent crystallized samples these change from 250 and 260°C respectively. The area under the low temperature peak increases with SSP time while the area under the high temperature peak decreases. The thermally crystallized sample with $Ti(O^iPr)_4$ shows minor variation from the rest of the sample with a major low temperature peak and smaller high temperature peak and during SSP the high temperature component vanishes.

The occurrence of multiple peaks in semicrystalline polymers is well documented in the literature and explained on the basis of partial melting and recrystallization. The low temperature peak is attributed to the melting of crystals that cannot undergo changes during DSC measurement and the high temperature peak is related to the fraction that can reorganize during heating and melts at high temperature. Single melting peak indicates either total reorganization during heating and melting at high temperature or no reorganization during heating and relates to the original crystals that have crystallized under crystallization conditions.

In the present case it appears from the relative areas of the peaks that the SSP causes the non recrystallizable fraction to increase with SSP time. However, the crystallized oligomer samples exhibit a strong tendency to reorganize during heating in DSC and melts at a higher temperature (~250°C) relative to the non recrystallizable fraction (~265°C)

The XRD pattern of these samples, particularly, the thermally crystallized samples, show crystals with high perfection. Thus, further perfection will be limited. So in these cases the reorganization leading to high melting must be occurring at the fold surface, namely, the interface between the crystal and the amorphous phase. However it is difficult to discern the mechanisms operative at the interface.

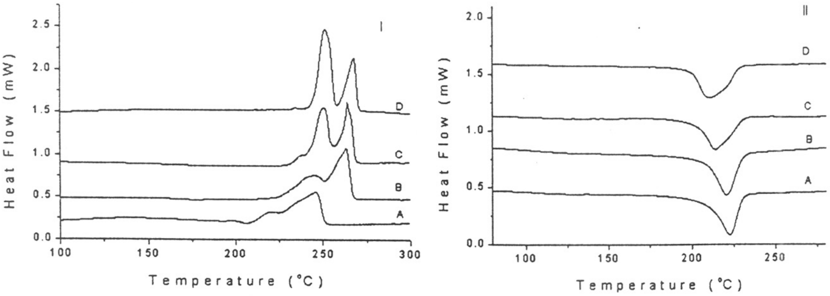


Fig. 5.10: DSC thermograms of PEN (Sb_2O_3) (thermally crystallized) at various stages of SSP (I)1st heating, (II) cooling
A) Crystallized sample, B) 210°C/4h, C) 210°C/12h, D) 210°C/20h

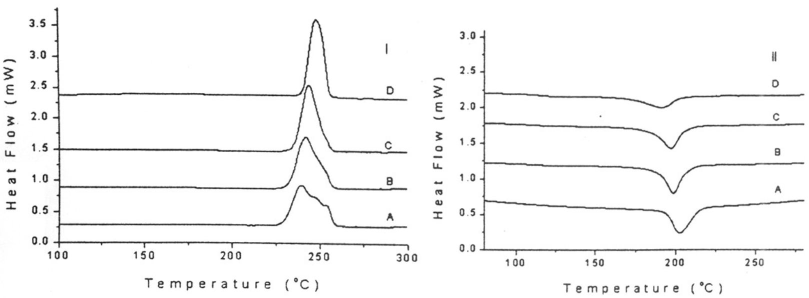


Fig. 5.11: DSC thermograms of PEN ($\mathrm{Ti(O^{i}Pr)_4}$) (thermally crystallized) at various stages of SSP (I) 1st heating, (II) cooling : A) Crystallized sample, B) 210°C/4h, C) 210°C/12h D) 210°C/20h

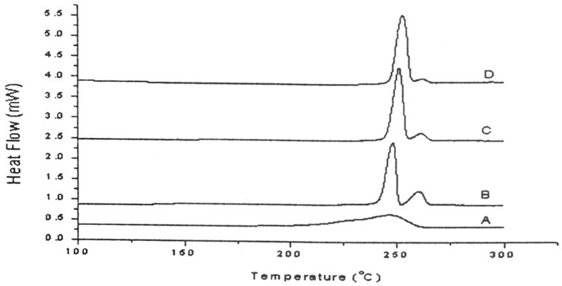


Fig. 5.12: DSC thermograms (1st heating) of PEN ($\mathrm{Ti(O^{i}Pr)_4}$) (crystallized in toluene) at various stages of SSP: A) crystallized sample, B) 230°C/4h, C) 230°C/12h, D) 230°C/20h

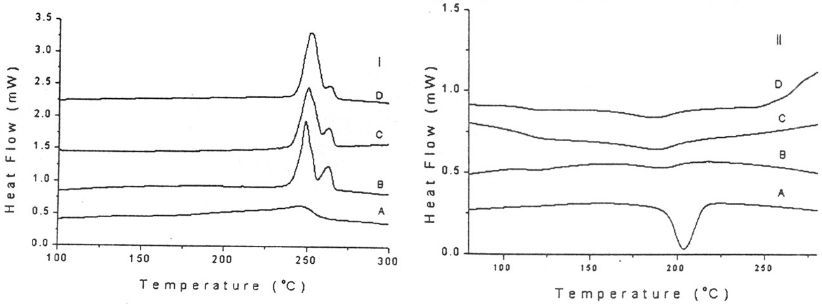


Fig. 5.13: DSC thermograms of PEN ($\mathrm{Ti(O^{i}Pr)_4}$) (crystallized in ethylacetate) at various stages of SSP (I) 1st heating (II) cooling
A) Crystallized sample, B) 210°C/4h, C) 210°C/12h, D) 210°C/20h

5.4 Conclusion

PEN oligomers which can be used as SSP precursors could be prepared by thermal crystallization. Crystallized oligomers produce large crystals and less defects.

Crystallized oligomers underwent SSP to give polymer with higher η_{inh}, T_g and lower T_{cc}. The data indicates that $Ti(O^iPr)_4$ has higher catalytic activity for SSP.

Oligomers could be crystallized by contact with diluents also. Diluents with solubility parameter in the range of 18-25 $(J/cm^3)^{1/2}$ could induce crystallinity in PEN at room temperature. The crystallites grown under diluent induced crystallization methods are smaller (~5 nm) than thermally crystallized (~15 nm). At elevated temperature, toluene also could induce crystallinity resulting in materials with sharper reflections and larger crystals (~9 nm). Oligomers crystallized in this manner also underwent SSP to give material with higher η_{inh}, T_g and lower T_{cc}. During SSP, smaller crystals reorganizes to give larger crystals.

II Crystallization kinetics of PEN

5.5 Introduction

Earlier literature regarding studies on crystallization of PEN mainly deals with structural variations taking place during processing. Investigations into the crystallization kinetics of PEN are very rare. Buchner et al[15] carried out a detailed study to understand the kinetics of crystallization and melting behaviour of PEN. The crystallization and melting of PEN was investigated by DSC and by WAXS using synchrotron radiation. By measuring the changes in wide angle X-ray scattering during isothermal crystallization using synchrotron radiation it was possible to study the kinetics of crystallization as well as the conditions under which the two crystal modifications were formed. The half times of crystallization as a function of temperature shows a broad minimum ranging from 180 to 240°C.

Lee and Cakmak[16] studied the crystallization kinetics of PEN under isothermal and nonisothermal conditions. During isothermal crystallization, relatively high crystallinity develops, with a time dependence described by the Avrami equation with the exponent 'n' equals 2.5. The activation energy for isothermal crystallization was determined to be 60 kcal/mol. The modified Avrami equation proposed by Velisaris was found to describe the primary and secondary crystallization reasonably well. For nonisothermal studies, PEN was crystallized by cooling at rates ranging from 1°C/min to 5°C/min from the melt. The models proposed by Ozawa and Nakamura were used to describe the nonisothermal crystallization kinetics of PEN.

Precursors for SSP have to be crystallized prior to the reaction. Crystallizations should be performed at the temperature at which crystallization is fastest. To find out the ideal conditions for crystallization of PEN oligomers to be used as SSP precursors, a study of isothermal crystallization was performed on PEN oligomers and compared with the kinetics of crystallization of high molecular weight PEN at temperatures ranging from 110°C to 220°C. Crystallization half times were determined from the corresponding DSC thermograms.

5.6 Experimental

5.6.1 Materials

PEN oligomers with η_{inh} of 0.1 dL/g were prepared from 2,6-dimethyl naphthalene dicarboxylate and ethylene glycol in presence of Sb_2O_3 or $Ti(O^iPr)_4$ were used for the study. PEN sample obtained by SSP of the oligomer using $Ti(O^iPr)_4$ as catalyst with an η_{inh} of 0.7 dL/g was also used.

5.6.2 Measurements

Following the standard procedure for studies of crystallization kinetics, PEN oligomers were allowed to crystallize at different temperatures in the range of 110°C to 220°C. In the case of oligomers, crystallizations from 110°C to 180°C and for the polymer from 110°C to 170°C were performed by heating the amorphous sample rapidly to the crystallization temperature and holding at that temperature till the crystallization was completed. Crystallizations from 180°C to 220°C for the oligomers and from 190°C to 220°C were carried out by first heating the samples to 290°C and cooling rapidly to the crystallization temperature and holding at that temperature, till the crystallization was completed. After crystallizations, samples were cooled to 50°C and heated to 300°C at the rate of 10°C/min. Crystallization half times ($t_{1/2}$) were determined from thermograms corresponding to the crystallization.

5.7 Results and discussion

Crystallization temperatures and half times of crystallization for the various samples studied are given in the **Table 5.10** and **Fig. 5.14.** In the lower temperature range, the oligomer with Sb_2O_3 has larger $t_{1/2}$ than oligomer with $Ti(O^iPr)_4$, indicating faster crystallization rates for the latter. But for temperatures above 160°C, crystallization becomes faster for the sample with Sb_2O_3. Since the figure shows very broad minima ranging from 140°C to 190°C for sample with $Ti(O^iPr)_4$ and 150 to 210°C for that with Sb_2O_3, it can be assumed that within this region, crystallization half times do not vary much for both the oligomers. However, the broad minimum has been shifted slightly towards the higher temperature region for the oligomer with Sb_2O_3. For the oligomer with $Ti(O^iPr)_4$, the minimum $t_{1/2}$ occurs in between 170 and 190°C, while it is in between 190 and 210°C for the sample with Sb_2O_3

Table 5.10: Crystallization half times of PEN samples

Cryst. temp (°C)	$t_{1/2}$ (min)		
	1	2	3
110	23.046	4.672	-
120	5.556	1.585	-
130	1.439	1.236	-
140	0.448	0.318	-
150	0.201	0.187	-
160	0.140	0.152	21.205
170	0.085	0.111	9.663
180	0.078	0.107	4.778
190	0.070	0.665	3.163
200	-	1.139	2.103
210	0.353	2.004	4.083
215	0.612	3.950	5.075
220	0.642	7.133	6.672

Sample no: 1 Oligomer prepared using Sb_2O_3
Sample no: 2 Oligomer prepared using $Ti(O^iPr)_4$
Sample no: 3 Polymer prepared by SSP using $Ti(O^iPr)_4$ as catalyst.

Since the change in $t_{1/2}$ is minimal in the range of 140-190°C for sample with $Ti(O^i Pr)_4$ and 150-210°C for sample with Sb_2O_3, crystallization of these oligomers can be carried out at any chosen temperature within the range. To support this further, oligomers were crystallized at 150 and 180°C. XRD patterns are shown in **Fig. 5.15.** The patterns at 150°C and 180°C for both the samples are identical. **Table 5.11** gives crystal sizes (calculated from 110 plane) at each temperature. It can be seen that there is only nominal difference between the crystal sizes obtained at the temperatures.

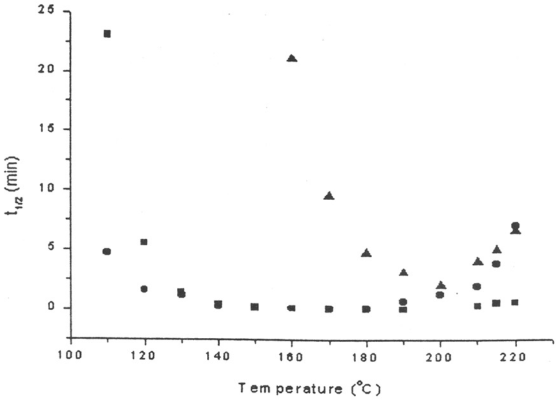


Fig. 5.14: Crystallization half times of PEN samples

■ oligomer with Sb_2O_3,● oligomer with $Ti(O^iPr)_4$, ▲ polymer with $Ti(O^iPr)_4$.

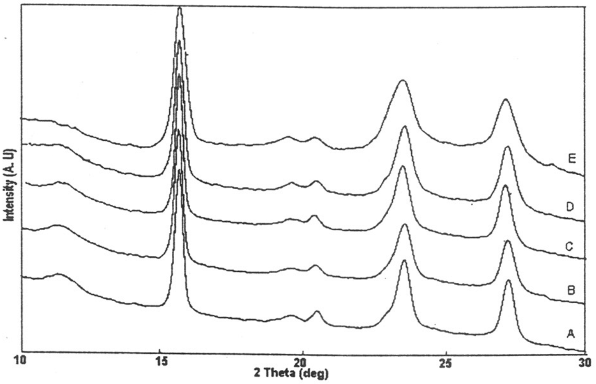


Fig. 5.15: XRD patterns of A) oligomer with Sb_2O_3 crystallized at 150°C, B) 180°C, C) oligomer with $Ti(O^iPr)_4$ crystallized at 150°C, D) 180°C, E) polymer with $Ti(O^iPr)_4$

Table 5.11: Crystal sizes (from 110 plane) at different temperatures

Sample	Cryst.temp (°C)	Crystal size (nm)
Oligomer with Sb_2O_3	150	16
Oligomer with Sb_2O_3	180	18
Oligomer with $Ti(O^iPr)_4$	150	17
Oligomer with $Ti(O^iPr)_4$	180	15
Polymer with $Ti(O^iPr)_4$	200	10

High molecular weight sample exhibits a different crystallization behaviour, with a very narrow minimum region. At almost all the crystallization temperatures, the polymer has larger $t_{1/2}$ than the oligomers as expected and the $t_{1/2}$ minimum occurs at 200°C. Entire curve has been shifted to the higher temperature region. In this case, crystallization should be performed at 200°C to get the fastest crystallization. XRD pattern for the sample crystallized at 200°C is given in **Fig. 5.15** and shows broader reflections compared to the patterns of the oligomers and smaller crystal size than those of oligomers.

The crystallization isotherms were analyzed using the Avrami equation[17-21]

$$\ln[-\ln(1-\theta_t)] = n \ln t + \ln k$$

Where 'k' is the overall kinetic rate constant which depends on the rate of nucleation and growth and 'n' the Avrami exponent which is a parameter that depends on the nature of the primary nucleation and the geometry of growing crystals. The values of 'k' and 'n' can be determined from the intercept and the slope of a straight line in plot of $\ln[-\ln(1-\theta_t)]$ against lnt. Different values which can be obtained for 'n' are given in **Table 5.12**[22]. It is often found that 'n' is not an integer. This behaviour has been discussed by Mandelkern[22]. Values obtained for 'n' and 'k' for all the three samples are given in the **Table. 5.13.** Since the crystallization occurred very rapidly in the range where crystallization half times ($t_{1/2}$) are lower, it was not possible to get the full crystallization isotherms. Hence 'n' and 'k' values were not obtained. Linear correlations were obtained for the plot of $\ln[-\ln(1-\theta_t)]$ against lnt indicating that the crystallization kinetics follows the Avrami equation. In the temperature range studied 'n' changes from 2 to 3 for all the three samples indicating different crystallization mechanisms at different temperatures. The value of 'k' is also very sensitive to temperature and the nature of samples (catalyst system and molecular weight).

Table 5.12: **Avrami exponents for various types of nucleation and growth** [22]

n	Mechanism
4	Spherulitic growth from sporadic nuclei
3	Spherulitic growth from instantaneous nuclei
3	Disc like growth from sporadic nuclei
2	Disc like growth from instantaneous nuclei
2	Rod like growth from sporadic nuclei
1	Rod like growth from instantaneous nuclei

Table 5.13: Analysis of crystallization kinetics data of PEN samples

Cryst temp. (°C)	Oligomer (Sb_2O_3) Sample 1			Oligomer ($Ti(O^iPr)_4$) Sample 2			Polymer ($Ti(O^iPr)_4$) Sample 3		
	$t_{1/2}$ (min)	n	k (min^{-n})	$t_{1/2}$ (min)	n	k (min^{-n})	$t_{1/2}$ (min)	n	k (min^{-n})
110	23.04	3.0	$1.16 X 10^{-5}$	4.67	2.6	$4.83 X 10^{-3}$	-	-	-
120	5.55	2.2	$8.18 X 10^{-3}$	1.58	2.6	$7.61 X 10^{-2}$	-	-	-
130	1.44	2.6	$8.96 X 10^{-1}$	1.23	2.0	$2.13 X 10^{-1}$	-	-	-
140	0.45	2.7	$8.93 X 10^{-1}$	0.32	-	-	-	-	-
150	0.20	-	-	0.19	-	-	-	-	-
160	0.14	-	-	0.15	-	-	21.20	3.0	$3.69 X 10^{-5}$
170	0.085	-	-	0.11	-	-	9.66	2.9	$4.08 X 10^{-4}$
180	0.078	-	-	0.10	-	-	4.78	2.5	$3.87 X 10^{-4}$
190	0.07	-	-	0.66	-	-	3.16	2.2	$1.47 X 10^{-2}$
200	-	-	-	1.14	2.2	$1.02 X 10^{-1}$	2.10	2.2	$3.33 X 10^{-2}$
210	0.35	-	-	2.00	2.3	$4.20 X 10^{-2}$	4.08	2.0	$1.32 X 10^{-2}$
215	0.61	-	-	3.95	2.2	$1.04 X 10^{-2}$	5.05	2.6	$3.00 X 10^{-3}$
220	0.64	2.0	$7.1 X 10^{-2}$	7.13	2.4	$3.12 X 10^{-3}$	6.67	3.0	$8.40 X 10^{-4}$

5.8 Conclusion

Kinetics of crystallization of PEN oligomers and high molecular weight PEN have been studied by isothermal crystallization by DSC measurements. Crystallization half times of oligomers varied nominally over a wide range of crystallization temperatures. So crystallization of these oligomers can be performed at any temperature in this range. Oligomers with different catalyst showed only small difference in crystallization behaviour. At almost all the crystallization temperatures, the polymer has larger $t_{1/2}$ than the oligomer and the $t_{1/2}$ was minimum at 200°C. To get the fastest crystallization rate crystallization should be conducted at this temperature. Crystallization isotherms were analyzed using Avrami equation. In the temperature range studied 'n' varied from 2 to 3 for all the three samples indicating different crystallization mechanisms at different temperatures for different samples. Since the crystallizations were very rapid in the case of oligomers, for a number of crystallization temperatures complete crystallization isotherms could not be obtained.

III Crystal modifications of PEN

5.9 Introduction

The patent[23], which revealed the synthesis of PEN, mentions about its crystallization also. There it is reported that, PEN may crystallize in two forms which differ in melting points and mechanical strengths. Unit cell dimensions of PEN were determined by Mencik[24]. He suggested it to be triclinic (a = 0.651, b = 0.575, c= 1.32 nm, α = 81.33, β = 144 and γ = 100°) with density of 1.407 g/cm^3 . The chains lie parallel to the c-axis. One chain passes through each unit cell. Later, Zachamnn et al noted that the second form could be formed under usual crystallization conditions[25], unit cell dimensions of which was determined to be a = 0.926, b = 1.559, c = 1.273 nm, α = 121.6, β = 95.57 and γ = 122.52 °) with density of 1.439 g/cm^3. Four chains pass through each cell. The chains are not completely extended, every naphthalene ring is twisted by 180°. They called the first to be α and the second to be β[15]. Afterwards attempts have been taken to determine the conditions under which α and β forms are formed, but there is no agreement among different reports.

5.10 Experimental

5.10.1 Materials

PEN ([η] 0.6 dL/g) was obtained from Aldrich Chemicals, USA. The XRD pattern showed that it was crystallized in the α form.

5.10.2 Measurements

The WAXD patterns were obtained by scanning the crystallized samples in Rigaku Dmax 2500 diffractometer between 2θ =10 to 35 deg. at a speed of 1 deg/min.

5.10.3 Crystallization

Amorphous PEN films were prepared by melting the PEN pellets on copper plate and quenching in ice cold water. These films were melted and then brought to the crystallization temperatures (Tc). Films were melted at different temperatures (Tm) to understand the effect of temperature from which the material was brought to the crystallization temperature (Tc). The conditions employed are given in **Table 5.14**.

5.11 Results and discussion

Zachmann et al obtained α form on isothermal crystallization at 167°C and β at 245°C[25]. The low temperature form (α) was obtained more easily than the high temperature form (β). The β form was best obtained when the sample was first melted at 330°C and then cooled down to 245°C and also when the amorphous sample was quickly heated to 245°C. According to them, once the α form had been formed, it often reappeared even when the sample was melted at 300°C and crystallized at 245°C. Thus, both melting temperature (Tm) and crystallization temperature (Tc) influence crystallization .

Later, Buchner et al[15] reported that after melting at 280 and 300°C, the α modification is formed at Tcs below 200°C, while mainly β modification is formed above this temperature, irrespective of which modification was present before melting. If however, the melting occurred at 320°C, the α modification also was obtained above 200°C. It did not make any difference whether the samples were directly brought to the crystallization temperature and heated up quickly afterwards. Furthermore, in a sample crystallized in one of the two forms, no change in the crystal modification could be induced by any annealing below the melting temperature.

In a recent investigation[7] to study the structure of PEN by solid state ^{13}C NMR, Guo and Zachmann obtained α modification by crystallizing the amorphous samples at 210°C which was prepared by melt pressing the sample at 290°C followed by quenching in ice cold water. They obtained β modification by melt pressing the sample at 300°C for 1 min, then crystallization at temperatures from 260-230°C for 20 min.

Vasanthan and Salem[26] who investigated structural and conformational characteristics of PEN by IR spectroscopy, reported that, α modification was obtained when amorphous films were annealed for half an hour at temperatures from 160 to 260°C. and when the sample was melted at 310°C followed by crystallization below 200°C. β modification was formed when crystallization temperature was above 200°C, after melting at 310°C.

In the present work, all the samples were crystallized after melting at different temperatures ranging from 290-340°C. Crystallization was performed at temperature ranging from 220-250°C. Results are summarised in **Table 5.14.** XRD patterns are shown in **Fig. 5.16**

Table 5.14: Crystal modifications of PEN crystallized under different conditions

Tm (°C)	Tc (°C)	Modification
340	220	α
340	230	α
330	230	α
330	240	β
330	250	β
320	240	β
310	230	α
310	240	β
300	230	α
300	240	β
290	230	α
290	240	β

For the sample melted at 340°C, crystallization was performed at 220°C and 230°C. XRD patterns for both showed reflections at 2θ = 15.6, 23.3 and 27.0 corresponding to 010, 100 and 110 diffraction planes which belong to α-modification. The sample melted at 330°C was crystallized at 230, 240 and 250°C. Crystallization at 230°C yielded reflections of α modification, while that at 240 and 250°C gave reflections at 2θ = 16.4, 18.6 and 25.5 corresponding to 111, 020 and 242 which belong to β modification. Sample melted at 320°C was crystallized at 240°C and was in α modification. Crystallization at 230°C after melting at 310°C gave α modification, while that at 240°C gave β modification. Similarly when crystallization was performed at 230°C after melting at 300 and 290°C gave α modification, while crystallization at 240°C yielded β modification. It is clear that irrespective of the melting temperature, whenever the crystallization was

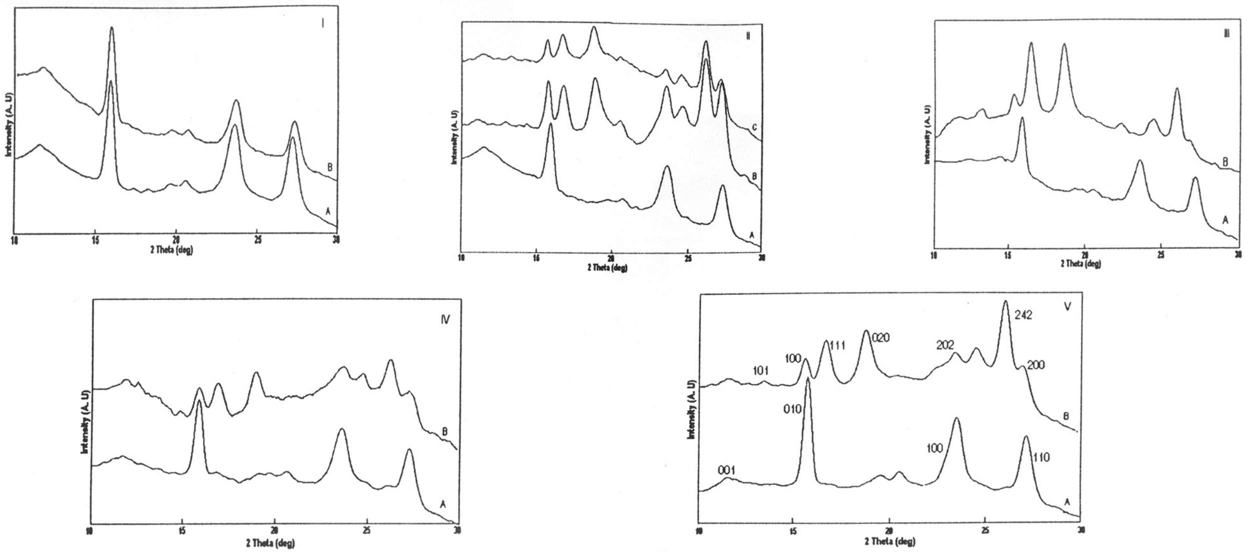


Fig. 5.16:. XRD patterns of crystallized PEN I) Tm: 340°C, Tc: A: 220°C, B: 230°C, II) Tm: 330°C, Tc : A: 230°C, B: 240°C, C: 250°C, III) Tm: 310°C, Tc : A: 230°C, B: 240°C, IV) Tm: 300°C, Tc : A: 230°C, B: 240°C, V) Tm : 290°C, Tc : A: 230°C, B: 240°C

performed at 240°C and above, β modification was obtained, while crystallization below 240°C gave α modification.

Thus it seems crystal modification does not depend on the melting temperature, but only on crystallization temperature.

5.12 Conclusion

PEN was melted at temperatures (Tm) ranging from 340 to 290°C followed by rapid cooling to crystallization temperatures (Tc) ranging from 250 to 220°C. The crystal modification formed in each case was determined from WAXD patterns. It is found that whenever Tc was 240°C and above, β modification was formed, while crystallizations at 230°C and below yielded α modification. The temperature (Tm) from which the material was brought to the crystallization temperature (Tc) does not seem to influence the type of modification. The modification in which the material existed prior to melting also does not affect the crystallization. The crucial factor which determines the modification into which PEN crystallizes appears to be the crystallization temperature. However, the effect of the manner (rapid heating of the amorphous material or rapid cooling from the melt) by which the material is brought to the crystallization temperature remains to be investigated.

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CHAPTER 6

PREPARATION OF POLY(ETHYLENE NAPHTHALATE-CO-TEREPHTHALATE)S via SOLID STATE POLYMERIZATION

6.1 Introduction

PET has been widely used in packaging applications due to its ability to produce higher gas barrier, recyclable clear packages economically. However, in specific applications such as packaging of high-acid content and oxygen sensitive materials and hot fill packaging, higher performance materials are required. Poly(ethylene 2,6-naphthalate)s (PEN) meet these criteria as it possesses an oxygen barrier approximately five times greater than that of PET and a glass transition temperature of 120°C, which is 45°C higher than that of PET. The properties of PEN expand possible polyester markets to include applications which demand a level of performance beyond the capabilities of current PET packagings[1]. But, the relatively high cost of PEN raw materials and the higher melting point and viscosity makes the polymer more expensive to process and use than PET[2,3].

One way to combine the properties of PET with PEN is to use blends of these polymers[2-4]. PEN is known to be immiscible with PET [5] and to achieve compatibility in the PEN and PET blend, it is necessary to induce and control the transesterification between the two polymers [3]. Transesterification reactions in polyester blends and their effects on miscibility have been studied and reviewed thoroughly[6-16]. Even though there is not complete agreement about the possible mechanisms it is generally accepted that the interchange reactions lead to the formation of first block, then random copolymers which enhance the miscibility of the blend[17-27]. Because of the changes in phase behaviour and the production of copolymer, it is possible that the properties of the blend vary as the interchange reactions proceed[2]. Thus it is important to control transesterification in order to produce products with desirable and reproducible properties. Transesterification reactions can be controlled by inhibitors such as, vanadium and phosphorous containing compounds[1,21]. The optimum degree of transesterification is 25-35 % [4].

Studies on PET/PEN blends mainly deals with interchange reactions taking place in the melt state and subsequent changes in phase behaviour and properties[2,3,5,17 -23]. Most of these investigations did not consider the changes in molecular weight or changes in viscosities with progress in transesterification. Cox et al[41] found that transesterification between PET and PEN can also take place in solid state where the melt blended, crystallized polymer is held at temperatures below the melting point and subjected to an inert gas flow to raise the molecular weight. Hoffmann[4] reported the preparation of PET/PEN blend by solid state polymerization.

The present study deals with the preparation of high molecular weight PET/PEN copolymers from PET and PEN oligomer mixtures by simultaneous solid state polymerization and exchange reaction. Oligomer mixtures were melt mixed and crystallized either by thermal method or by diluent induced crystallization. Sequence distribution at various levels of reaction has been determined by means of ^{1}H NMR. Structure and morphology were studied by DSC and XRD.

6.2 Experimental

6.2.1 Materials

PEN obtained from Aldrich Chemicals (USA) was used as such (η_{inh} 0.7 dL/g). PET was a commercial sample obtained from Futura Chemicals, Chennai (India) with η_{inh} 0.75 dL/g and was used as such. Phenol, 1,1',2,2'-tetrachloroethane (TCE) and ethylene glycol were obtained from Sd. Fine Chemicals (India) and were distilled before use. Titanium tetraisopropoxide ($Ti(O^iPr)_4$) was distilled and solution was prepared in toluene [1 mL (0.963g) in 25 mL of toluene]. Toluene was dried over metallic sodium and distilled before use.

6.2.2 Measurements

Inherent viscosities were measured at 25°C in an automated Schott Gerate AVS 24 viscometer using Ubbelhode suspended level viscometer in phenol/ TCE (40/60, w/w) at a polymer concentration of 0.5%. The X-ray diffraction experiments were performed using Rigaku Dmax 2500 diffractometer. Calorimetric measurements were performed using Perkin Elmer thermal analyzer (DSC 7) at a heating/ cooling rate of 10°C/min in nitrogen environment. The melting temperature and heat of fusion were obtained from the 1st heating thermogram. T_g and T_c were obtained by heating quenched amorphous samples. T_g was also determined from the 2nd heating thermogram. ^{1}H NMR spectra were recorded on a Bruker AC-200 NMR spectrometer. Samples were dissolved in $CDCl_3$/TFA (70/30, v/v) mixture. The NMR data were analysed using Specview software.

6.2.3 Preparation of PET oligomer by glycolysis

PET pellets (50 g) and 250 mL ethylene glycol were taken in 1000 mL round bottom flask. Temperature was raised to 190°C while pellets were stirred thoroughly. Reaction was continued for 10 h at 190°C. The residue was filtered and washed with hot water and methanol to remove ethylene glycol and was dried at 80°C for 12 h.

Yield = 44 g, η_{inh} = 0.16 dL/g.

6.2.4 Preparation of PEN oligomer by glycolysis

PEN pellets (60 g) and 250 mL ethylene glycol were taken in 1000 mL round bottom flask. Temperature was raised to 190°C while pellets were stirred thoroughly. Reaction was continued for 10 h at 190°C. The residue was filtered and washed with hot water and methanol to remove ethylene glycol and was dried at 80°C for 12 h.

Yield = 53 g, η_{inh} = 0.18 dL/g

6.2.5 Addition of catalyst

The catalyst was added to the oligomer by a coating technique. $Ti(O^iPr)_4$ was coated on to the oligomers using the following procedure. Methanol (100 mL) was taken in 500mL round bottom flask. To this was added 0.31 mL (300 ppm based on the oligomer) of catalyst solution. To this solution, 40g of PET oligomer was added and methanol was removed in a rotary evaporator under reduced pressure. The sample was dried at 70 °C for 12 h. PEN oligomer was also coated with $Ti(O^iPr)_4$ in methanol using a similar technique.

6.2.6 Preparation of oligomer mixtures

(a) 30/70 PET/PEN

PET oligomer (3 g ,0.156 mols) was thoroughly mixed with 8.8 g (0.0364 mols of PEN

(b) 50/50 PET/PEN

PET oligomer (23.8 g, 0.124 mols) was thoroughly mixed with 30g (0.12 mols of PEN

(c) 70/30 PET/PEN

PET (4.63 g, 0.024 mols) was thoroughly mixed with 2.5 g of PEN (0.010 mols)

6.2.7 Melt mixing and crystallization of oligomer mixtures

6.2.7.1 Thermal crystallization

Thoroughly dried oligomer mixtures were melted in a CSI Minimax extruder at 290°C and then allowed to fall on a hot plate which was maintained at 175°C, the crystallization temperature **(Fig. 4.1)**. Clear melt formed hemispherical particles upon cooling and these were allowed to crystallize on the hot plate for ~5 min. The residence time in the extruder was 1-2 minutes.

6.2.7.2 Diluent induced crystallization

(a) Diluent induced crystallization at ambient temperature

About 5 g of 50/50 mixture was melted on a flat copper plate and quenched in liquid nitrogen. The amorphous material thus obtained was stirred with 25 mL of ethylacetate in a 100 mL round bottom flask at room temperature for 10 h. Ethylacetate was removed under reduced pressure at 50°C. The material was dried at 50°C for 12 h to ensure complete removal of ethylacetate.

(b) Diluent induced crystallization at elevated temperature

About 5 g of the 50/50 mixture was melted on a flat copper plate and quenched in liquid nitrogen. The amorphous material thus obtained was stirred with 25 mL of toluene in a 100 mL round bottom flask at 100°C for 4 h. Toluene was removed under reduced pressure at 80°C. Then the material was further dried at 50°C for 12 h.

6.2.8 Solid state polymerization

Thermally crystallized blends were powdered and sieved through 30 and 25 mesh sieves (600 microns) before subjecting to SSP. Blends crystallized by solvent were in the form of fine powder and subjected to SSP as such. The SSPs were performed in glass reactor **(Fig. 3.1)** for 20 h at 220°C under nitrogen flow of 3 L/min. Samples were removed at regular intervals for characterization.

6.2.9 Melt polymerization

About 7 g of the 50/50 mixture was taken in two neck, 100 mL r. b flask with nitrogen inlet and fitted with a small distillation condenser with facility to apply vacuum. The flask was heated to 280°C in an oil bath while the reaction mixture was being stirred thoroughly. The temperature was maintained at 280°C for 30 minutes and then nitrogen flow was stopped and pressure was reduced to 1 mm of Hg, while the temperature was raised to 300°C. The system was allowed to cool to room temperature under reduced pressure after 60 minutes of reaction. The material obtained was very hard and transparent.

6.3 Results and discussion

6.3.1 Crystallization and solid state polymerization

Fig. 6.1 gives DSC thermograms of starting oligomers (PEN, PET) as obtained. The oligomers are crystalline as evidenced by the melting peaks (PEN 267°C, PET 251°C). For the preparation of copolymers by SSP, these oligomers were mixed in various compositions. Before subjecting the mixtures to SSP, oligomers were melt mixed to provide intimate contact to facilitate transesterification and further solid state polymerization to attain molecular weight build up. In the case of thermal crystallization, oligomer mixtures in the desired compositions were melt mixed in an extruder at 290°C and the clear melt was collected on a hot plate held at 175°C for crystallization. The samples crystallized within 5 minutes. **Fig. 6.2** gives DSC thermograms of the crystallized samples. No crystallization exotherms or premelting endotherms are seen indicating that the samples are well crystallized and can be used as precursors for SSP. Similar methods have been employed by Stouffer et al to produce semicrystalline PET and PEN oligomers to be used as precursors for SSP[28-31]. US Pat. 5,688,874[4] describes the preparation of PET-PEN copolymers by SSP. However they have a lengthy crystallization step by heating the melt extruded samples at temperatures of 150-180°C for 12-16 hours.

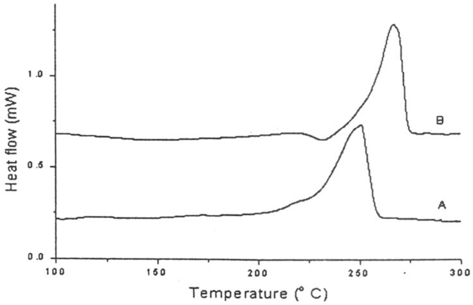


Fig. 6.1 DSC thermograms of oligomers (obtained by degradation)
A) PET, B) PEN

PET and PEN are known to be crystallized by diluents with solubility parameters close to those of the polyesters[32-34]. PEN is reported to be crystallized by dioxane, aniline and DMF[33,34]. Solubility parameters of ethylacetate and toluene are 18.6 and 18.2 $(Jcm^{-3})^{1/2}$ respectively[35]. Solubility parameter of PET is 20.5[35] while that of PEN is 20.31 $(Jcm^{-3})^{1/2}$ (calculated by Synthia method)[39]. The solubility parameter of the PET, PEN mixture also should be within the range (~20)[35] of the constituents .Thus it is expected that diluents whose solubility parameters are close to that of the polymer would swell the polymers, thus inducing crystallinity. Melted and quenched oligomer mixtures were crystallized by ethylacetate and toluene. Crystallization in ethylacetate was done at room temperature while that in toluene was performed at ~100°C. DSC thermograms of crystallized samples are shown in **Fig. 6.2.**

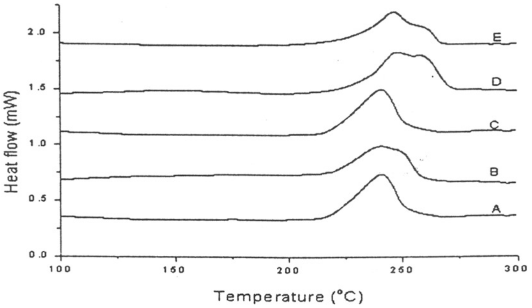


Fig. 6.2: DSC thermograms of crystallized oligomer mixtures
PET/PEN in the molar ratio of A) 70/30, B) 50/50, C) 30/70, D) 50/50, E) 50/50
A, B &C: melt mixed and crystallized at 175°C, D: crystallized in toluene, E : crystallized in ethylacetate

Crystallized oligomer mixtures were subjected to SSP at 220°C for 20 h in nitrogen flow of 3 L/min. **Table 6.1** and **Fig. 6.3** give the change in inherent viscosity (η_{inh}) with time during SSP. All the compositions underwent solid state polymerization to significant extent as indicated by the increase in inherent viscosity with time. The samples showed large increase in η_{inh} during the first two hours, follwed by a slowing down of the rate due to the decreased availability of free chain ends in the amorphous region. Samples 1, 4 and 5 gave relatively higher η_{inh} after 20 h. It should be noted that under identical conditions PET gives higher rate of solid state polymerization compared to PEN due to the higher chain mobilites of PET at the SSP temperature arising out of a larger difference between the T_g and the reaction temperature. Thus it can be expected that the compositions with larger PET content would give higher SSP rates. Samples 4 and 5 which have PET/PEN in 50/50 composition also gave comparable increases in viscosity. This can be attributed to the fact that, these two samples were crystallized by solvents, which resulted in very fine powder and contributed to faster diffusion of by-products in the solid polymer and from the surface of the polymer to the inert gas.

Table 6.1: Changes in η_{inh} during SSP

Sample no[a]:	1	2	3	4	5
	η_{inh} (dL/g)				
Cryst.	0.17	0.17	0.17	0.17	0.17
220°C/2h	0.45	0.42	0.40	0.46	0.47
220°C/4h	0.55	0.53	0.52	0.55	0.56
220°C/8h	0.67	0.60	0.55	0.68	0.68
220°C/12h	0.69	0.64	0.59	0.71	0.70
220°C/20h	0.71	0.67	0.64	0.73	0.72

[a] No:1 PET/PEN 70/30, No:2 PET/PEN 50/50, No:3 PET/PEN 30/70 (samples were crystallized thermally)
No:4 PET/PEN 50/50 (crystallized in toluene), No:5 PET/PEN 50/50 (crystallized in ethylacetate)
η_{inh} of starting materials: PET - 0.16 dL/g, PEN - 0.18 dL/g

It was mentioned earlier that studies concerning PET/PEN copolymers focussed mainly on transesterification taking place at high temperatures in the melt state and subsequent changes in properties. This was because earlier workers dealt with starting materials of fairly high molecular weights (η_{inh} 0.6 dL/g and above) Jun et al[36] reported that in fact there is a reduction in η_{inh} with blending time. However, in a study carried out by Yoon et al[37] on a blend of PEN/PET (50/50 w/w) at 280°C, it was shown that molecular weight increased during reaction along with transesterification. It should be noted that their starting materials also were of η_{inh} 0.6 dL/g. They suggested that the molecular weight increase is due to end group reactions and to correctly understand the physical properties of the system, the end group reactions as well as the transesterification reactions should be considered.

Cox et al[41] reported that there can be limited increase in η_{inh} along with transesterification when melt extruded PET/ PEN blends were subjected to SSP. They started with a material of η_{inh} ~ 0.7 dL/g to get a material with ~ 0.9 dL/g after 8 hours at 230°C. They further found that certain stabilizers mainly phosphites and phosphonites, when added in the blend, could control transesterification while allowing increase in η_{inh}. Later, Hoffman[5] also reported increase in η_{inh} along with transesterification during solid stating of PET/PEN blend.

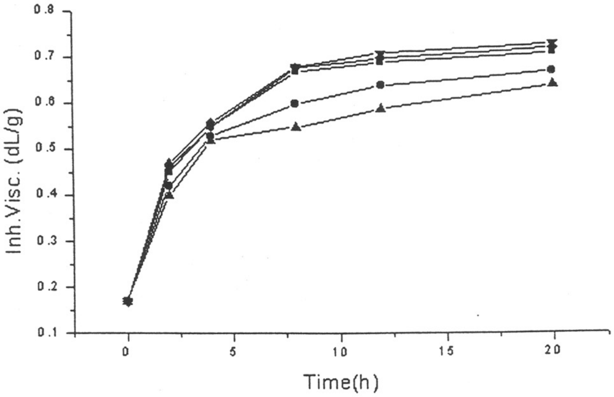


Fig. 6.3: Change in η_{inh} during SSP
■ sample 1, • sample 2, ▲ sample 3 ▼ sample 4, ◆ sample 5

In the present work also considerable increase in η_{inh} (from 0.17 to ~0.7 dL/g) was found to occur. Thus high molecular weight PET/PEN copolymers could be prepared from suitably crystallized PET/PEN oligomer mixtures (blends). An analysis of the extent of transesterification will be of interest and is described in the following section.

6.3.2 Analysis of sequence distribution

The extent of transesterification at various stages of solid state polymerization was determined using the region of ^{1}HNMR spectrum corresponding to ethylene moiety. **Fig. 6.4** gives NMR spectra of (a) PET oligomer (b) PEN oligomer (c) physical mixture of PEN and PET oligomer and (d) PEN/PET copolymer. **Fig. 6.5 (I)** shows region of ethylene peaks of the above spectra. As expected, based on their structures, the homopolymers exhibit one NMR peak associated with the ethylenic protons. The peak for PEN appears at ~4.9 ppm while the peak for PEN appears at ~4.8 ppm. The spectrum of physical mixtures of PET/PEN shows these two peaks corresponding to the homopolymers.

In the spectrum of the copolymer, a third peak appears at 4.85 ppm which is in between the two characteristic peaks of PET and PEN. The new peak is due to ethylene protons which are between naphthalenic and terephthalic moieties in the backbone. Thus ethylene proton resonances of the PEN/PET copolymers are split into multiplets owing to four possible environments for ethylene unit: TT, NN, NT and TN where N and T represent naphthalate and terephthalate unit respectively, as shown in **Scheme 6.1**. The proton resolution peak at 4.85 ppm representing the amount of heterogeneity, shows that NT and TN peaks are overlapping with each other. As mentioned above, the new ethylene proton signals NT or TN are caused by the substitution of a naphthalate unit by a terephthalate unit.

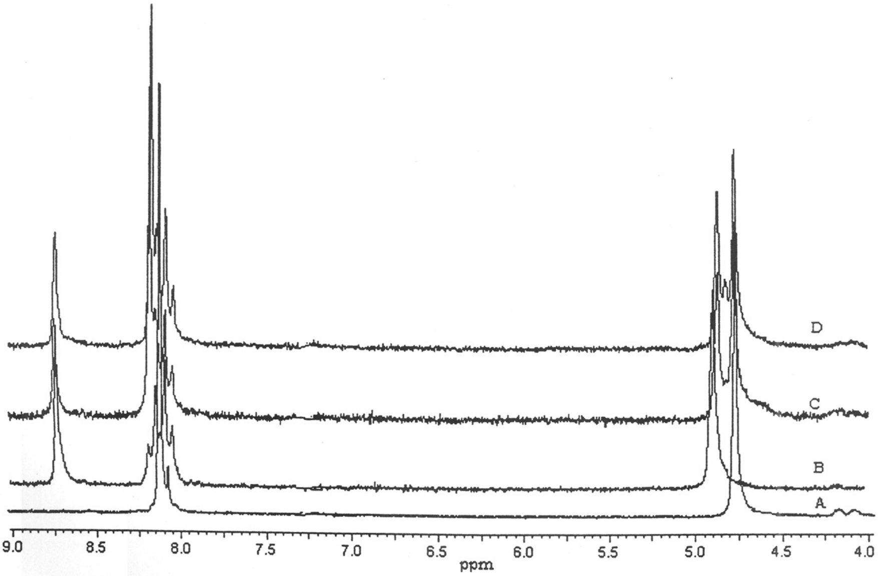
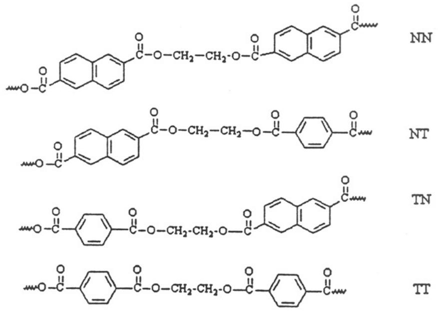


Fig. 6.4: ^{1}HNMR spectra of A) PET, B) PEN, C)PET/PEN physical mixture , D) PET/PEN copolymer

According to Yamadera and Murano[38], if three kinds of signals due to homolinks and heterolinks are observed in the NMR spectrum of the copolymer, one could determine the average sequence length and the degree of randomness of the copolymer. Molar fractions of terephthalate and naphthalate are obtained from the relative intensities of the three kinds of signals in the NMR spectrum



Scheme 6.1: Different environments of ethylenic protons

$$P_T = \frac{(f_{NT} + f_{TN})}{2} + f_{NN}, \qquad P_N = \frac{(f_{NT} + f_{TN})}{2} + f_{TT},$$

P_N = molar fraction of naphthalate unit, P_T = molar fraction of terephthalate unit

f_{NN}, f_{TT}, f_{NT} and f_{TN} correspond to the proportion of the integrated intensities of NN, TT, NT and TN to the total intensity of ethylene moieties respectively.

If one could inspect the units along the copolymer chain from one end to the other, the probability (P_{NT} or P_{TN}) of finding N (or T) unit next to a T (or N) unit would be

$$P_{NT} = \frac{f_{NT} + f_{TN}}{2P_N}, \qquad P_{TN} = \frac{f_{NT} + f_{TN}}{2P_T}$$

with $f_{NN} + f_{NT} + f_{TN} + f_{TT} = 1$

Degree of transesterification (DT) is $\dfrac{f_{NT} + f_{TN}}{f_{NN} + f_{NT} + f_{TN} + f_{TT}} = f_{NT} + f_{TN}$

The degree of randomness (B) is defined by $B = P_{NT} + P_{TN}$.

For random copolyesters B is unity and the probability of finding a copolymer unit belongs to Bernouli statistics. If B is less than unity, the units tend to cluster together in blocks of each unit and the value of B is zero in a mixture of homopolymers. If the value of B is 2 it means alternating distribution.

The number average sequence length of a T unit (L_{nT}) and N unit (L_{nN}) are given by

$$L_{nT} = \frac{2P_T}{f_{NT} + f_{TN}} = \frac{1}{P_{TN}}$$

$$L_{nN} = \frac{2P_N}{f_{NT} + f_{TN}} = \frac{1}{P_{NT}}$$

Fig. 6.5 shows NMR spectra for samples at various stages. **Tables 6.2-6.6** give values of η_{inh}, f_{NN}, f_{TT}, $(f_{NT}+f_{TN})$, P_{NT}, P_{TN}, L_{nN}, L_{nT}, % transesterification and degree of transesterification calculated from relative intensities of peaks as mentioned above. It should be noted that eventhough the feed ratios of PET/PEN are 70/30, 50/50 and 30/70 for samples 1, 2 and 3 respectively, after passing through the extruder for melt mixing and crystallization, the ratios change to 62/38, 47/53 and 31/69. For samples 4 and 5 which were crystallized by solvent, the feed ratio was 50/50 for both. After crystallization it was 53/47 and 51/49. It can be seen form **Fig. 6.5** that the crystallized samples, which are the starting materials for SSP have only peaks for terephthalate and naphthalate units. The level of transesterification in these samples is below the detection limit of the NMR spectrometer and would be assumed that no transesterification took place during melt mixing and subsequent crystallization. The ^{1}HNMR spectra clearly show that the intensity of the middle peak which corresponds to the naphthalate (terephthalate) unit substituted by a terephthalate (naphthalate) unit increases for all the samples with increase in SSP time. **Fig. 6.6** gives graphical representation of changes in f_{NN}, f_{NT+TN} and f_{TT} with reaction time for each sample. **Fig. 6.7** shows changes in P_{NT} and P_{TN} with reaction time. **Fig. 6.8** gives changes in number average sequence lengths with reaction time. **Fig. 6.9** gives change in degree of transesterification and randomness with reaction time. It can be seen form the **Figs 6.6-6.9** that maximum degree of changes in the structure occurs during the first two hours of reaction after which there is only marginal changes. During initial stages of SSP, f_{NT+TN}, which indicates the level of transesterification, increases, while a decrease in f_{NN} and f_{TT} (amount of naphthalate and terephthalate) is observed. This shows transesterification reactions are active during the initial stages of SSP.

The higher levels of transesterification in samples 1, 2 and 3 may be attributed to the higher degree of mixing of PET and PEN. These samples were mixed in a mini extruder resulting in thorough mixing. The samples 4 and 5 were prepared by melting of the physical mixture of PET and PEN on a flat plate without any stirring. In the first case, the mixing was more efficient and facilitated better contact between the two components than the second process. Thus, it is clear that the rate of transesterification is a characteristic of the blend structure generated during melting and crystallization. A similar observation was made by Lee[11] in the case of transesterification during melt blending of PET and PEN.

If we compare the progress of SSP and transesterification, the results indicate that esterification reactions get completed within 3 h. On the other hand, η_{inh} keeps on increasing during entire SSP duration, however, at a reduced rate after 2 to 3 h. The trend is clearer in the case of samples 4 and 5 in which % transesterification increases very slowly. So, along with transesterification the chain ends react leading to molecular weight build up. From ^{1}HNMR analyses it is not possible to find out the reaction among PET chains or PEN chains. But by comparing the η_{inh} values at various stages of all the

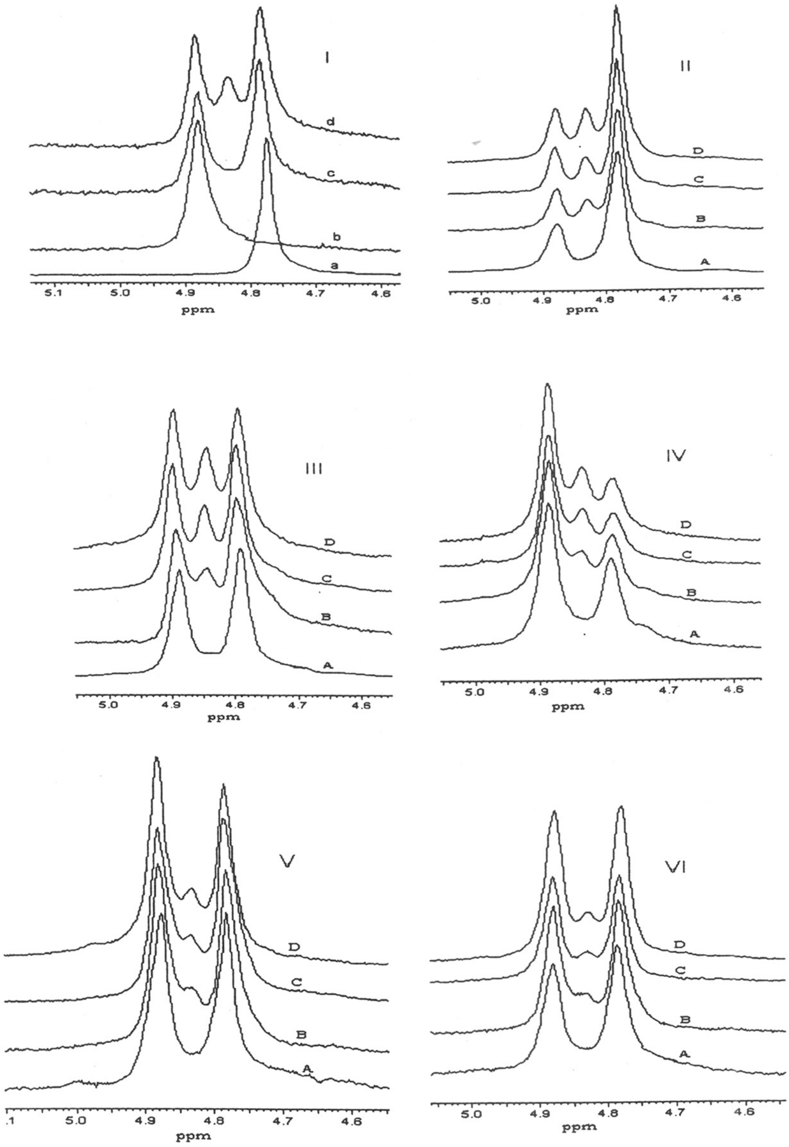


Fig 6.5: Ethylene peak splitting of ^{1}HNMR spectra
I) Expansion of ethylene region of Fig 6.4 ; II) sample 1, III) sample 2, IV) sample 3, V) sample 4, VI) sample 5, :A) Crystallized oligomer mixture B) 220°C/2 h, C) 220°C/8 h, D) 220°C/20 h

samples,it is reasonable to assume that this kind of reaction also takes place. P_{NT} and P_{TN} which indicate the probabilities of a naphthalate (terephthalate) unit next to a terephthalate (naphthalate) unit increase with reaction time and % transesterification. Finally, degree of randomness also increases with increase in reaction time. However the degree of randomness is always below unity, indicating the presence of blocks of homopolymer chains. It is also interesting to note that the sequence length of PET component is larger than PEN for 70/30 composition while PEN has a higher value for 30/70 composition. Both have similar values for 50/50 composition. But as the reaction progresses, block lengths become shorter and shorter, increasing the probability of finding a naphthalate (terephthalate) unit next to a terephthalate (naphthalate) unit.

Copolyester of PET/PEN was also prepared by melt condensation of a 50/50 mixture of PET/PEN at 300°C. Results are given in **Table 6.7** and **Fig. 6.10** shows ^{1}HNMR spectrum of this copolymer. η_{inh} increased to 0.50 dL/g in less than 1.5 h. Transesterification was 47% and the degree of randomness was ~0.94. The number average sequence length and the degree of randomness indicate that still the copolymer is in blocks, but very close to a random distribution. Thus melt reaction leads to very fast transesterification while solid state polymerization enables one to prepare high molecular weight PET/PEN copolymer with lesser degree of transesterification.

Table 6.2 : Sequence analysis, PET/PEN 70/30 (molar ratio), crystallized at 175°C

Sample/ conditions	η_{inh} (dL/g)	f_N	f_T	f_{NT+TN}	P_{NT}	P_{TN}	L_{nN}	L_{nT}	% transest	B
Crystallized	0.17	0.31	0.69	-	-	-	-	-	-	-
220°C/2h	0.45	0.24	0.60	0.16	0.250	0.117	4.00	8.50	16	0.37
220°C/4h	0.55	0.24	0.59	0.17	0.261	0.126	3.82	7.94	17	0.39
220°C/8h	0.67	0.22	0.60	0.18	0.290	0.130	3.44	7.66	18	0.42
220°C/12h	0.69	0.21	0.60	0.19	0.311	0.137	3.21	7.31	19	0.45
220°C/20h	0.71	0.21	0.59	0.20	0.322	0.145	3.10	6.90	20	0.47

Table 6.3 : Sequence analysis, PET/PEN 50/50 (molar ratio), crystallized at 175°C

Sample/ conditions	η_{inh} (dL/g)	f_N	f_T	f_{NT+TN}	P_{NT}	P_{TN}	L_{nN}	L_{nT}	% transest.	B
Crystallized	0.17	0.45	0.55	-	-	-	-	-	-	-
220°C/2h	0.42	0.35	0.47	0.18	0.204	0.161	4.89	6.22	18	0.36
220°C/4h	0.53	0.34	0.46	0.20	0.222	0.178	4.54	5.60	20	0.40
220°C/8h	0.60	0.33	0.46	0.21	0.241	0.186	4.14	5.38	21	0.43
220°C/12h	0.64	0.35	0.41	0.24	0.255	0.226	3.91	4.42	24	0.48
220°C/20h	0.67	0.35	0.40	0.25	0.263	0.238	3.80	4.20	25	0.50

Table 6.4 : Sequence analysis, PET/PEN 30/70 (molar ratio), crystallized at 175°C

Sample/ conditions	η_{inh} (dL/g)	f_N	f_T	f_{NT+TN}	P_{NT}	P_{TN}	L_{nN}	L_{nT}	% transest.	B
Crystallized	0.17	0.62	0.38	-	-	-	-	-	-	-
220°C/2h	0.40	0.55	0.27	0.18	0.141	0.250	7.11	4.00	18	0.39
220°C/4h	0.52	0.54	0.24	0.22	0.169	0.314	5.91	3.18	22	0.48
220°C/8h	0.55	0.54	0.23	0.23	0.175	0.333	5.70	3.00	23	0.51
220°C/12h	0.59	0.54	0.23	0.23	0.175	0.333	5.70	3.00	23	0.51
220°C/20h	0.64	0.53	0.24	0.23	0.185	0.343	5.42	2.92	24	0.53

Table 6.5 : Sequence analysis, PET/PEN 50/50 (molar ratio), crystallized in toluene (110°C)

Sample/ conditions	η_{inh} (dL/g)	f_N	f_T	f_{NT+TN}	P_{NT}	P_{TN}	L_{nN}	L_{nT}	% transest.	B
Crystallized	0.17	0.49	0.51	-	-	-	-	-	-	-
220°C/2h	0.46	0.44	0.46	0.10	0.102	0.098	9.80	10.2	10	0.20
220°C/4h	0.55	0.42	0.48	0.10	0.106	0.943	9.40	10.6	10	0.20
220°C/8h	0.68	0.42	0.47	0.11	0.116	0.105	8.64	9.54	11	0.22
220°C/12h	0.71	0.41	0.47	0.12	0.127	0.113	7.83	8.83	12	0.24
220°C/20h	0.73	0.40	0.47	0.13	0.140	0.121	7.15	8.23	13	0.26

Table 6.6 : Sequence analysis, PET/PEN 50/50 (molar ratio), crystallized in ethylacetate (25°C)

Sample/ conditions	η_{inh} (dL/g)	f_N	f_T	f_{NT+TN}	P_{NT}	P_{TN}	L_{nN}	L_{nT}	% transest.	B
Crystallized	0.17	0.47	0.53	-	-	-	-	-	-	-
220°C/2h	0.47	0.46	0.46	0.08	0.080	0.080	12.5	12.5	8	0.16
220°C/4h	0.56	0.46	0.45	0.09	0.089	0.091	11.2	11.0	9	0.18
220°C/8h	0.68	0.46	0.44	0.10	0.098	0.102	10.2	9.80	10	0.20
220°C/12h	0.70	0.45	0.44	0.11	0.109	0.111	9.18	9.00	11	0.22
220°C/20h	0.72	0.45	0.44	0.11	0.109	0.111	9.18	9.00	11	0.22

Table 6.7 : Sequence analysis, PET/PEN 50/50 (molar ratio), melt polymerized

Sample/ conditions	η_{inh} (dL/g)	f_N	f_T	f_{NT+TN}	P_{NT}	P_{TN}	L_{nN}	L_{nT}	% transest.	B
Melt polym.	0.56	0.26	0.26	0.48	0.469	0.469	2.13	2.13	48	0.94

f_{NN}, f_{TT}, f_{NT}, f_{TN} : dyads fractions of NN, TT, NT and NT units where N represents naphthalate unit and T represents terephthalate unit
P_{NT}, P_{TN} : probability of finding N (or T) unit next to a T (or N) unit
B: degree of randomness

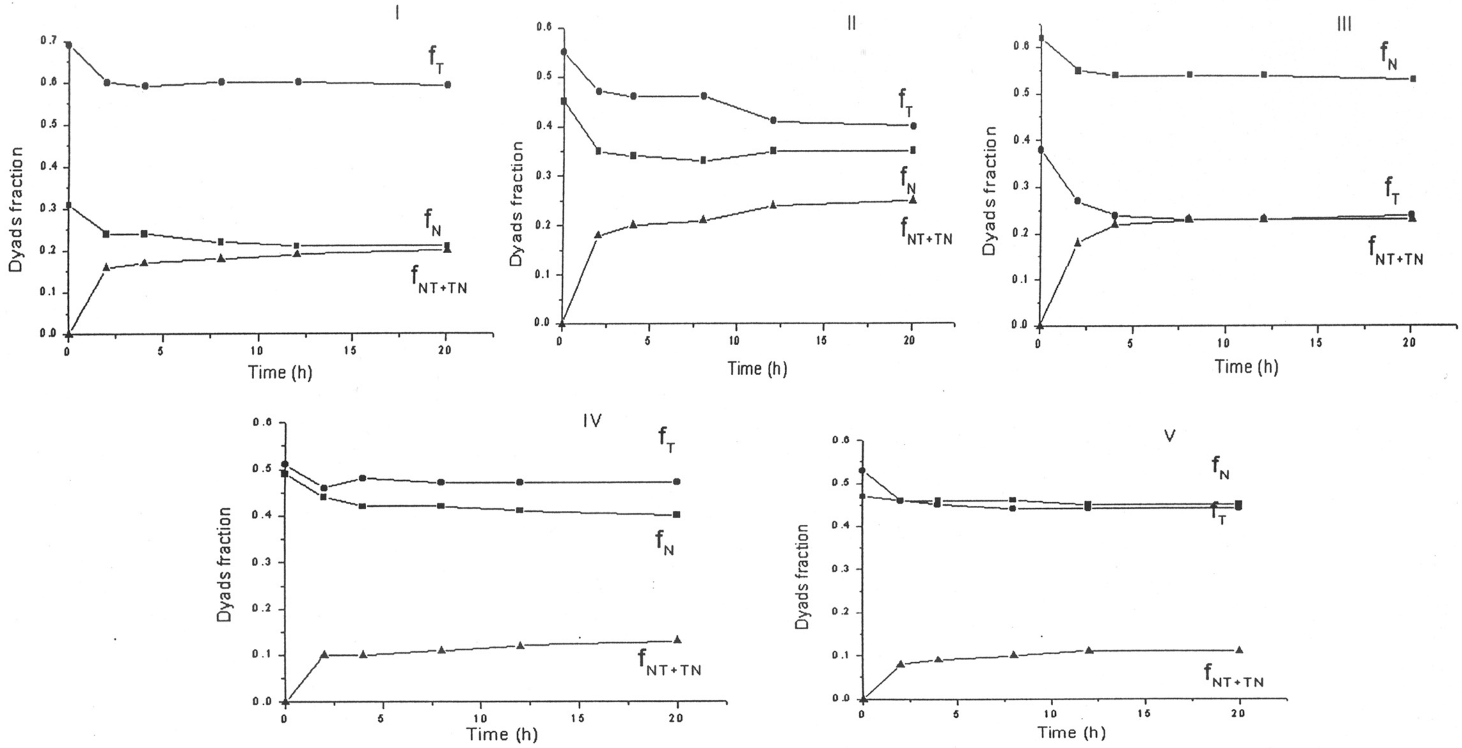


Fig 6.6 : Change in dyads fraction with reaction time I) sample 1 II) sample 2 III) sample 3 IV) sample 4 V) sample 5

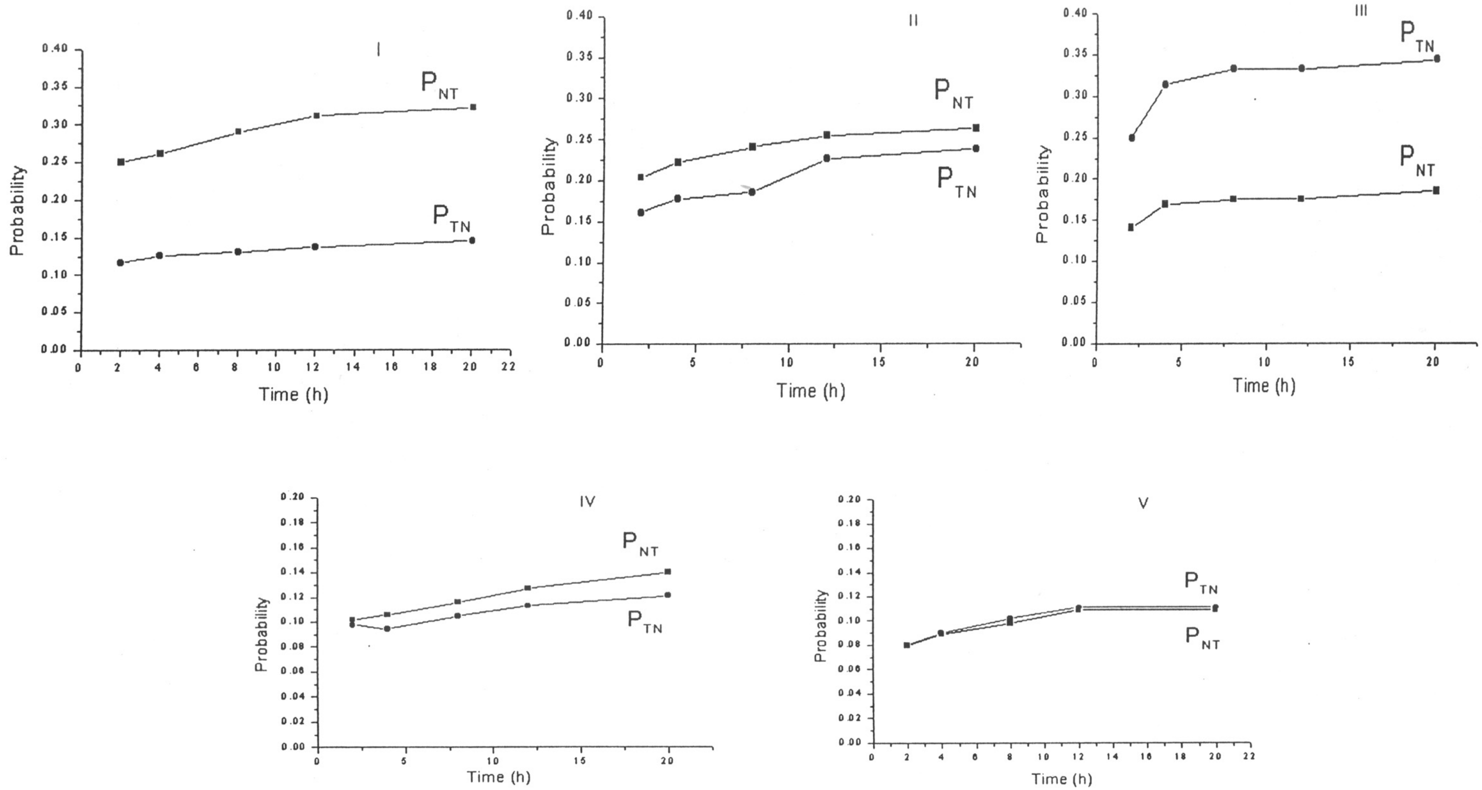


Fig. 6.7: Change in P_{NT}, P_{TN} : (probability of finding N (or T) unit next to a T (or N) unit) with reaction time I) sample 1, II) sample 2, III) sample 3, IV) sample 4, V) sample 5

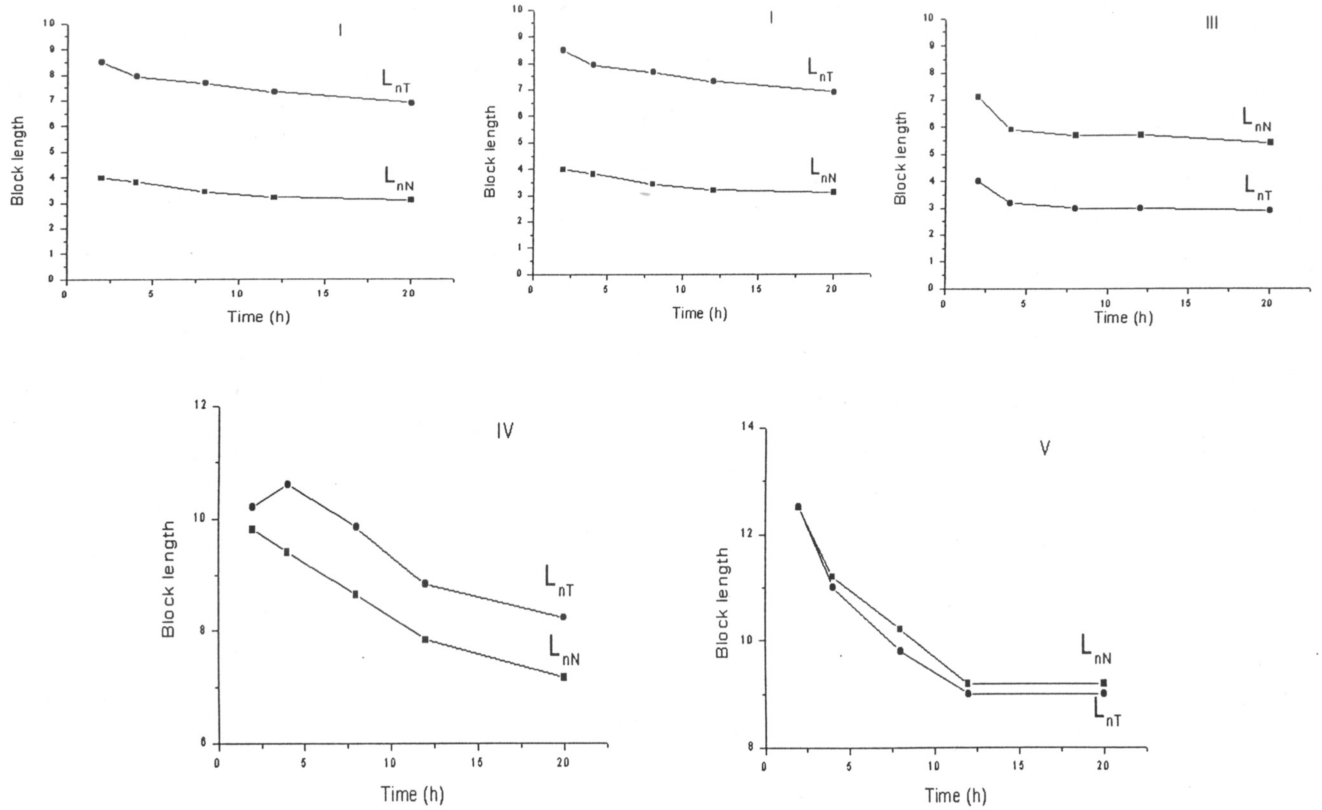


Fig. 6.8 : Change in block lengths with reaction time I) sample 1 II) sample 2 III) sample 3 IV) sample 4 V) sample 5

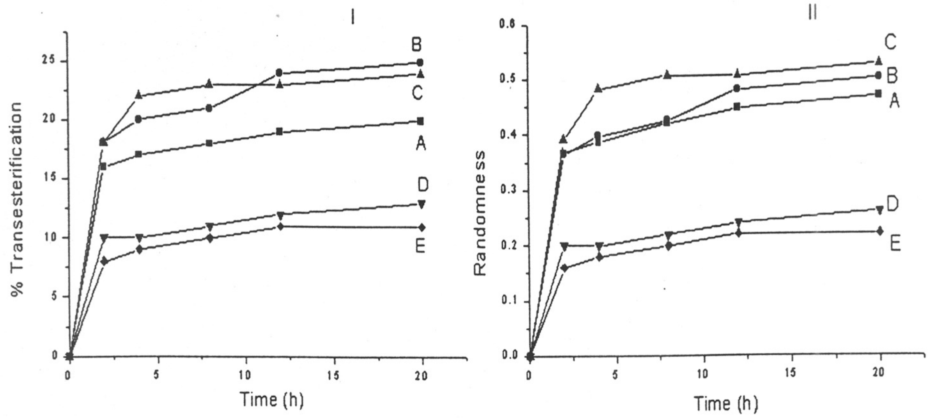


Fig. 6.9: Change in I) % transesterification, II) randomness with reaction time: A)sample 1 B) sample 2 C) sample 3 D) sample 4 E) sample 5

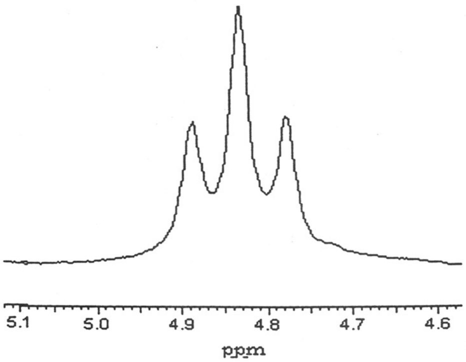
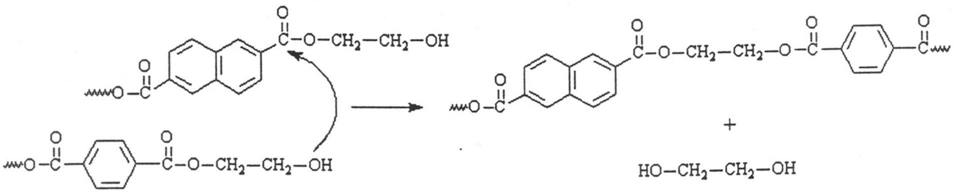


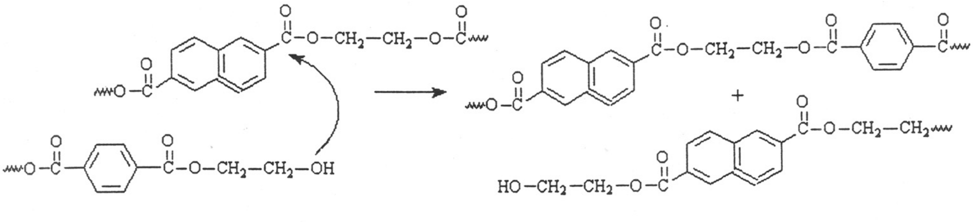
Fig. 6.10: Ethylene peak splitting of ^{1}HNMR spectrum of PET/PEN copolymer prepared by melt condensation

Possible reactions which can take place between PET and PEN are given in **Scheme 6.2.** Of these, reactions 1 and 3 lead to increase in molecular weight along with transesterification. Reactions 2, 4 and 5 result in transesterification, but due to chain scissions, reaction 5 can also cause decrease in molecular weight. In addition to these, reactions can take place among PET and PEN chains themselves giving hikes in molecular weight (reactions 6, 7, 8 and 9). In the present case, viscosities increase considerably during SSP, indicating increase in molecular weight. It seems that mainly, reactions 1, 3, 6, 7, 8 and 9 are dominating during SSP. The mild conditions under which SSP is performed may not be sufficient to activate the chains to such an extent to cause inchain reactions as in 2, 4 and 5. On the other hand melt condensation at much higher temperatures facilitate these reactions giving nearly random copolymers.

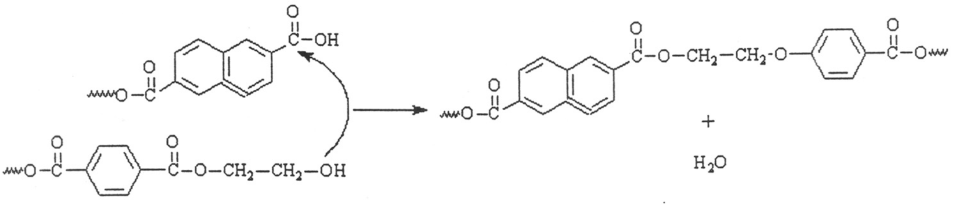
1. Alcoholysis (outer-outer)



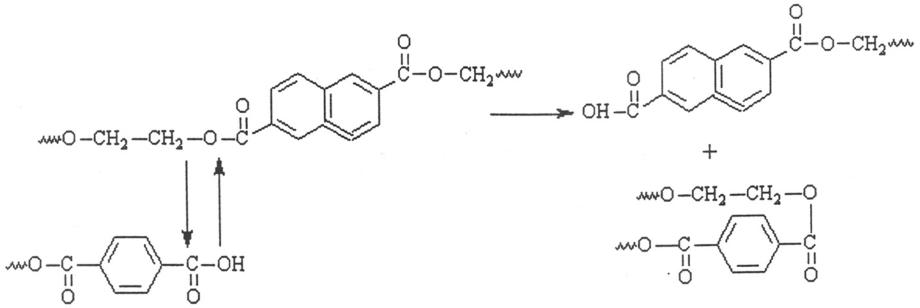
2. Alcoholysis (inner-outer)



3. Acidolysis (outer-outer)

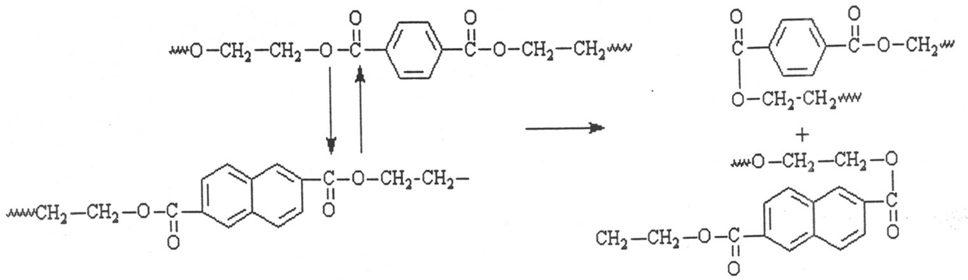


4. Acidolysis (inner-outer)

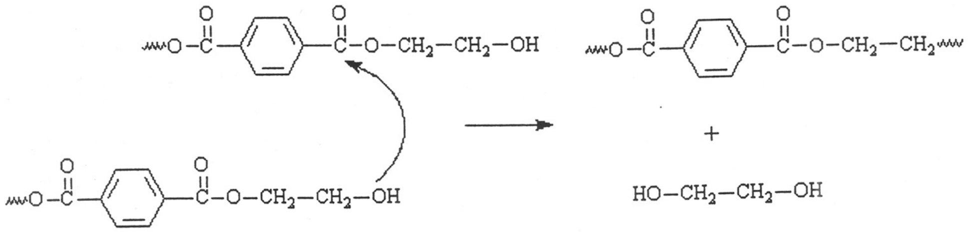


(Continued ...)

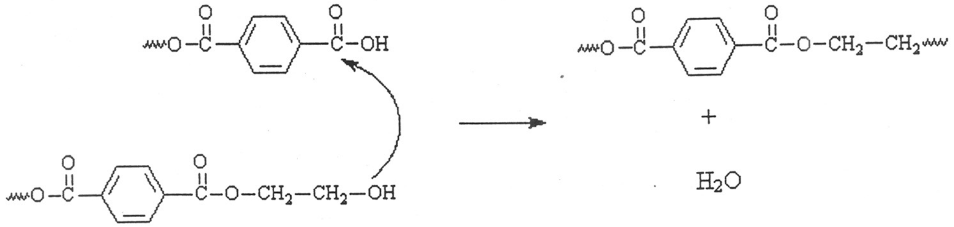
5. Ester exchange



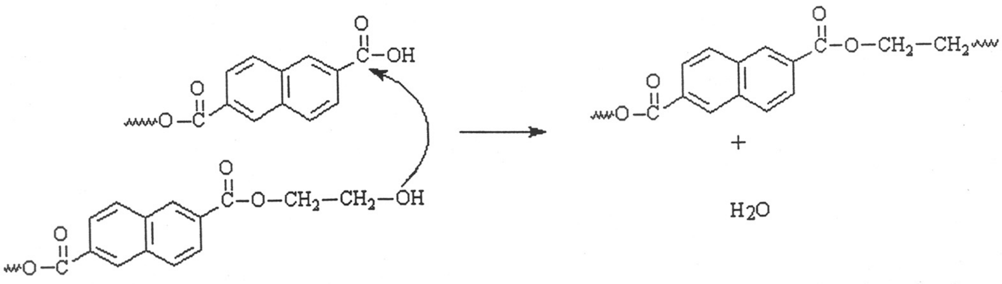
6. Alcoholysis (outer-outer)



7. Acidolysis (outer-outer)



8. Acidolysis (outer-outer)



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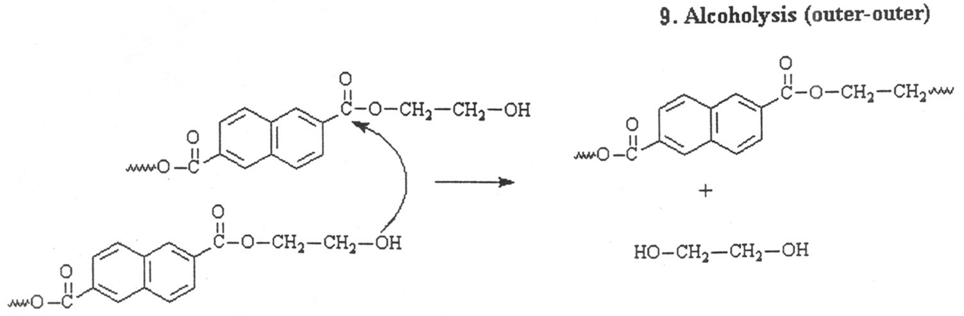


Scheme 6.2: Possible reactions during SSP

6.3.3 Thermal properties

DSC thermograms of the crystallized samples are shown in **Fig. 6.2.** In general, thermally crystallized samples exhibit broad peak at about 240°C, while the samples crystallized by diluents show two distinct peaks at 246°C and 262°C. The melting peaks after SSP are shown in **Fig. 6.11-6.14.** The broad peaks become sharp during SSP and peak position shift from 240 to 246°C. The samples crystallized by dilution show variation from thermally crystallized samples **(Fig. 6.12-6.14).** During SSP, the low temperature peak predominates, while the high temperature peaks slowly disappear. This shows that the structure of the samples crystallized by solvents are similar to thermally crystallized samples after SSP. No attempt has been made to identify and assign the peaks to PET or PEN. The melting point data indicates that both PET and PEN melting points are depressed by each other.

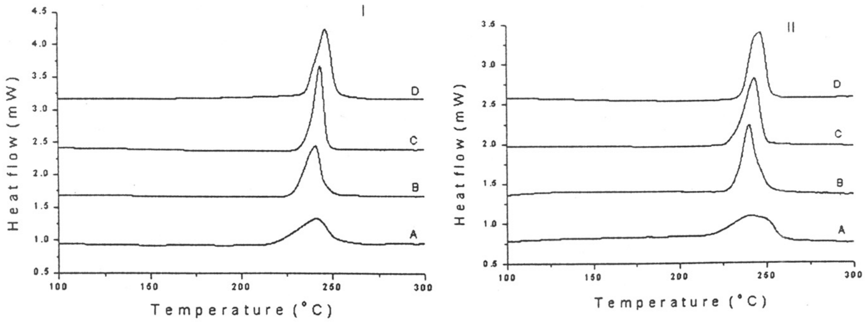


Fig. 6.11: 1st heating thermograms of I) sample 1 II) sample 2: A) Crystallized oligomer mixture B) 220°C/2 h, C) 220°C/8 h, D) 220°C/20 h

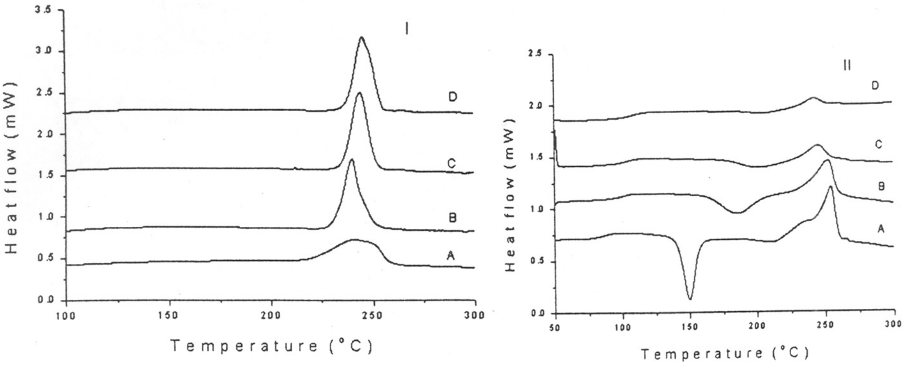


Fig. 6.12: DSC thermograms of sample 3: I) 1st heating, II) 1st heating after quenching A) crystallized oligomer mixture, B) 220°C/2 h, C) 220°C/8 h , D) 220°C/20 h

The heat of fusion registers an increase **(Table 6.8-6.12)** along with T_m. It may be noted that the crystallinity was developed in these samples before performing SSP and during SSP the samples retained the crystallinity. Hence, the T_m and heat of fusion were not representative of the copolymer sample after SSP.

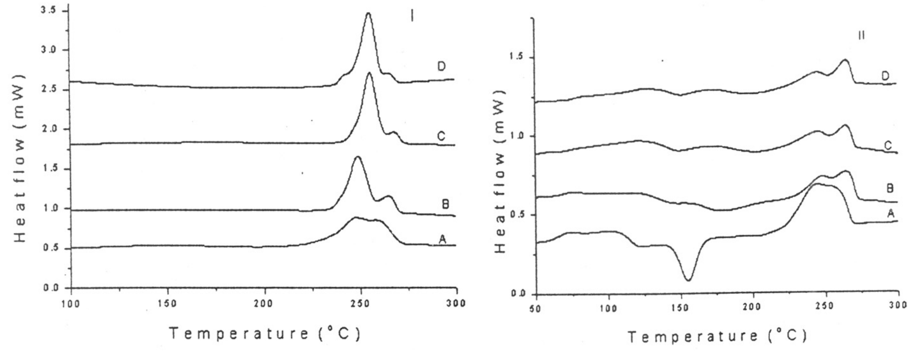


Fig. 6.13: DSC thermograms of sample 4 I) 1st heating II) 1st heating after quenching A) crystallized oligomer mixture B) 220°C/2 h, C) 220°C/8 h , D) 220°C/20 h

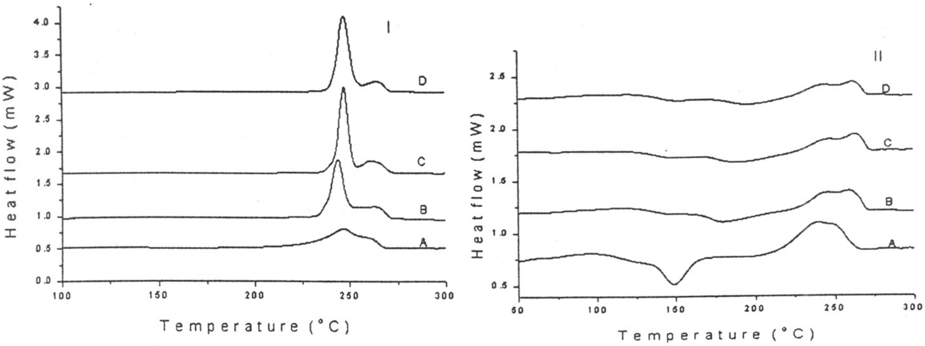


Fig. 6.14: DSC thermograms of sample 5 I) 1st heating II) 1st heating after quenching
A) crystallized oligomer mixture B) 220°C/2 h, C) 220°C/8 h , D) 220°C/20 h

The glass transition temperature is one of the key physical parameter of blends. Glass transition temperatures (T_g) were not observed in the first heating runs. Second heating runs of all the samples showed single T_g **(Table 6.8-6.12),** but no crystallization exotherms or melting endotherms were observed. T_gs obtained cannot be treated as the actual values, since the samples were at high temperatures for considerable time (held at 300°C for 1 min followed by cooling to 50°C at 10°C/min) and further transesterification can take place in DSC itself [2]. Hence separate set of DSC scans were performed for each sample after melting and rapidly quenching in liquid nitrogen to avoid any further transesterification. Also this operation destroyed all the crystallinity in the samples as well. ^{1}HNMR analysis confirmed that there was no change in transesterification during this treatment, and T_gs obtained may be representative of the actual T_gs of samples obtained from SSP. On heating in DSC these samples showed T_g, T_c and T_m. All these events are representative of the copolymers. The thermograms are shown in **Fig. 6.12-6.14**. T_g, T_c, ΔH and T_m are given in **Tables 6.13-6.17.** All the samples showed the effect of transesterification on glass transition, crystallization and melting. Single broad T_gs were observed for all thermally crystallized samples. T_g region is rather broad and it is likely that they do not posses a single phase but there is significant solubility of both components in each phase. This partial miscibility can account for the broad T_gs [2]. Exposing this sample to high temperature will increase transesterification and improve the miscibility and would narrow the T_g region. In order to confirm this, the 4th sample from sample 3 (PET/PEN 30/70, 220/8 h) was analyzed by NMR after DSC scanning (50°C-300°C at 10°C/min, 1min at 300°C, 300-50°C at 10°C/min). The sample had a degree of transesterification of 40% while the original sample had transesterification of 23%.

Table 6.8: DSC data for sample 1 (PET/PEN 70/30, crystallized at 175°C)

Sample/conditions	1st heating		T_g (°C)[a]
	T_m (°C)	ΔH (J/g)	
Crystallized	241	48	76
220°C/2h	241	51	88
220°C/4h	243	55	89
220°C/8h	243	55	90
220°C/12h	245	55	89
220°C/20h	246	61	90

Table 6.9 : DSC data for sample 2 (PET/PEN 50/50, crystallized at 175°C)

Sample/conditions	1st heating		T_g (°C)[a]
	T_m (°C)	ΔH (J/g)	
Crystallized	240	42	84
220°C/2h	240	52	96
220°C/4h	242	51	97
220°C/8h	243	55	97
220°C/12h	243	54	98
220°C/20h	246	54	99

Table 6.10: DSC data for sample 3 (PET/PEN 30/70, crystallized at 175°C)

Sample/conditions	1st heating		Tg (°C)[a]
	T_m (°C)	ΔH (J/g)	
Crystallized	240	42	96
220°C/2h	240	54	105
220°C/4h	242	54	105
220°C/8h	244	54	107
220°C/12h	245	55	107
220°C/20h	245	55	107

Table 6.11: DSC data for sample 4 [PET/PEN 50/50 (crystallized in toluene)]

Sample/conditions	1st heating		T_g (°C)[a]
	T_m (°C)	ΔH (J/g)	
Crystallized	247, 262	60	95
220°C/2h	249, 257	59	96
220°C/4h	251, 260	56	97
220°C/8h	255, 260	57	97
220°C/12h	255, 260	58	98
220°C/20h	255, 260	58	98

Table 6.12: : DSC data for sample 5 [PET/PEN 50/50 (crystallized in ethylacetate)]

Sample/conditions	1st heating		Tg (°C)[a]
	Tm (°C)	ΔH (J/g)	
Crystallized	246, 262	43	95
220°C/2h	244, 262	63	96
220°C/4h	245, 262	63	97
220°C/8h	247, 262	63	97
220°C/12h	247, 262	65	98
220°C/20h	247, 262	65	98

[a] T_g obtained from 2nd heating of samples

Table 6.13: DSC data for sample 1 (quenched, PET/PEN 70/30, crystallized at 175°C)

Sample/ conditions	T_g (°C)	T_c (°C)	ΔH (J/g)	T_m (°C)	ΔH (J/g)
Precursor	62, 92	126, 146	33	242	63
220°C/2h	85	-	-	237	22
220°C/2h	87	-	-	237	26
220°C/2h	87	-	-	240	20
220°C/2h	87	-	-	235	17
220°C/2h	89	-	-	231	7

Table 6.14: DSC data for sample 2 (quenched, PET/PEN 50/50, crystallized at 175°C)

Sample/ conditions	T_g (°C)	T_c (°C)	ΔH (J/g)	T_m (°C)	ΔH (J/g)
Precursor	-	104, 158	9, 21	244	59
220°C/2h	91	182	14	241	29
220°C/2h	94	191	10	243	19
220°C/2h	94	-	-	240	8
220°C/2h	94	-	-	237	7
220°C/2h	94	-	-	235	4

Table 6.15: DSC data for sample 3 (quenched, PET/PEN 30/70 crystallized at 175°C)

Sample/ conditions	T_g (°C)	T_c (°C)	ΔH (J/g)	T_m (°C)	ΔH (J/g)
Precursor	85	149	39	254	54
220°C/2h	97	184	31	252	36
220°C/2h	102	196	14	247	24
220°C/2h	104	202	12	247	13
220°C/2h	-	205	7	247	8
220°C/2h	104	205	4	241	7

Table 6.16: DSC data for sample 4 [quenched, PET/PEN 50/50 (crystallized in toluene)]

Sample/ conditions	T_g (°C)	T_c (°C)	ΔH (J/g)	T_m (°C)	ΔH (J/g)
Precursor	65, 92	120, 155	39	244	55
220°C/2h	68, 113	147, 178	23	240, 264	32
220°C/2h	66, 113	147, 187	21	240,263	29
220°C/2h	73	148, 200	18	240, 264	20
220°C/2h	76, 115	150, 205	10	240, 265	20
220°C/2h	77, 118	150, 202	10	240, 264	17

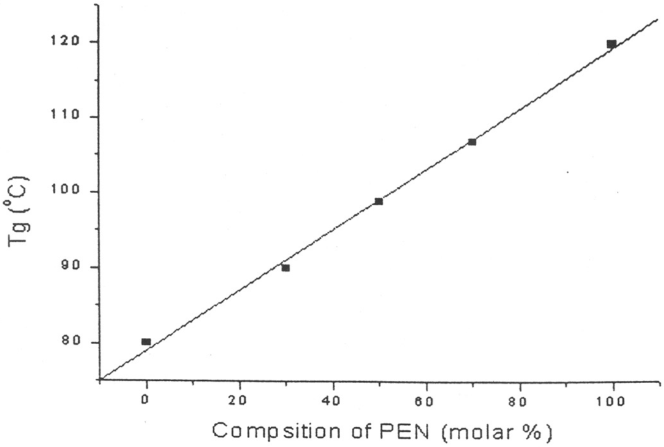
Table 6.17: DSC data for sample 5 [quenched, PET/PEN 50/50 (crystallized in ethylacetate)]

Sample/ conditions	T_g (°C)	T_c (°C)	ΔH (J/g)	T_m (°C)	ΔH (J/g)
Precursor	72, 95	125, 148	39	238	55
220°C/2h	78, 108	147, 178	25	240, 258	34
220°C/2h	79, 110	147, 180	23	240, 260	29
220°C/2h	79, 114	147, 187	18	240, 263	29
220°C/2h	100	179	17	240, 258	24
220°C/2h	74, 113	147, 195	11	240, 262	24

The cold crystallization peaks (T_c) are evident for the precursor samples. These peaks progressively shift towards higher temperature and become smaller and broader after SSP and transesterification. The heat of fusion and melting temperature also decrease. These thermal behaviours suggest that crystallization is hindered due to the disruption of chain periodicity as a consequence of transesterification[3] as well as due to the increase in molecular weight.

Samples crystallized by diluents, show two T_gs corresponding to constituent PET and PEN when scanned after quenching. These samples distinctly exhibited two crystallization peaks corresponding to PET and PEN (**Figs. 6.13 and 6.14**.) The melting endotherm also shows double peaks. These samples have higher heat of crystallization and fusion values compared to thermally crystallized samples. This may be due to the low levels of transesterification and miscibility in these samples.

It has been pointed out earlier that, the T_g obtained during the second heating after exposing the sample to 300°C is not representative of the copolymer sample prepared, because of the additional transesterification occurring at high temperatures. However, this T_g provides some valuable information on the effect of composition. The T_g of the final samples shows a linear relationship with composition and is shown in **Fig 6.15**. These values agree well with the computed values on the basis of linear relationship between T_g and blend composition[40].



.**Fig. 6.15:** Variation of T_g with composition of PEN

In the case of sample prepared by melt condensation where the transesterification was 46%, the sample was completely amorphous with T_g of 99°C. However this sample could not be crystallized while heating. This inability to crystallize shows that the periodicity was disrupted to such an extent that crystallization was completely inhibited. According to Jun et al[12], an average sequence length higher than 3 is required to form crystallites, while it is 2 in this case .

6.3.4 X-ray diffraction studies

The room temperature structure of these samples were analysed by WAXS. **Fig 6.16 (I)** gives XRD patterns of the crystallized samples. The diffraction patterns, in general, show peaks corresponding to PET and PEN. However for compositions 50/50 and 30/70 the peaks of PEN appear to be dominating. This would imply that the crystallization of PET in the presence of PEN is retarded, even though PET has a higher crystallization rate. To understand the crystallization of PET and PEN when in melt blends, PET and PEN where crystallized individually at 175°C and physical mixtures were prepared in 30/70, 50/50 and 70/30 molar compositions. XRD patterns of these physical mixtures are given in **Fig. 6.16 (II)** along with patterns of PET and PEN. The patterns of the mixtures are very similar to those of respective melt blended samples. This indicates that both PET and PEN are crystallized fully in the melt blend samples as in the case with homopolymers.

The XRD patterns are well developed and the reflections are very sharp for the crystallized samples. The crystal width calculated from 010 reflection of PEN and 110 and 010 reflection of PET are 20, 13 and 16 nm respectively. The large crystal size shows that the crystals are big and defect free. **Fig. 6.17** gives XRD patterns of samples before and after SSP. **Table 6.18** gives change in crystal sizes during SSP. The patterns after SSP do not vary significantly from the crystallized samples. This indicates that the crystallites do not undergo changes or reorganization during SSP.

Table 6.18: Changes in crystal sizes during SSP

Sample	Crystal size (nm), reflection at (2 θ)					
	15.6° (010, PEN)		16.2°(011, PET)		17.5°(010 PET)	
	Before SSP	After SSP	Before SSP	After SSP	Before SSP	After SSP
1	20	19	13	14	16	17
2	24	22	10	12	22	20
3	22	21	10	13	18	19
4	13	18	8	15	11	14
5	12	17	7	16	10	15

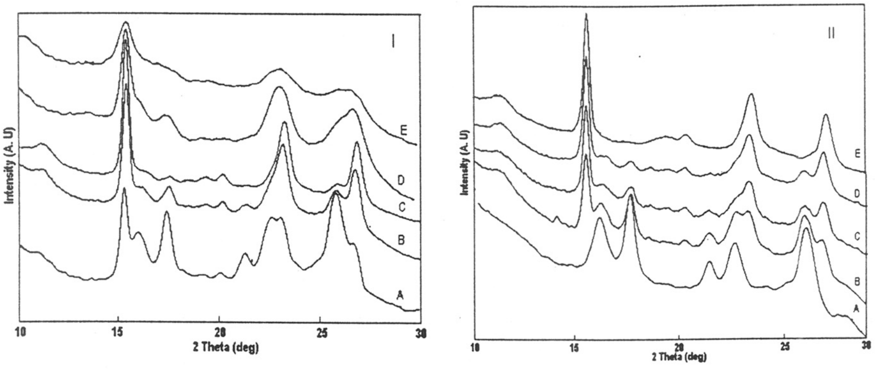


Fig. 6.16 XRD patterns of I) melt mixed and crystallized oligomer mixtures: A) sample 1, B) sample 2, C) sample 3, D) sample 4, E) sample 5, II) physical mixtures of crystallized oligomers A) PET oligomer crystallized at 175°C, B, C,& D) PET and PEN oligomers individually crystallized at 175°C and physically mixed in the molar ratios of 70/30, 50/50 and 30/70 respectively, E) PEN oligomer crystallized at 175°C.

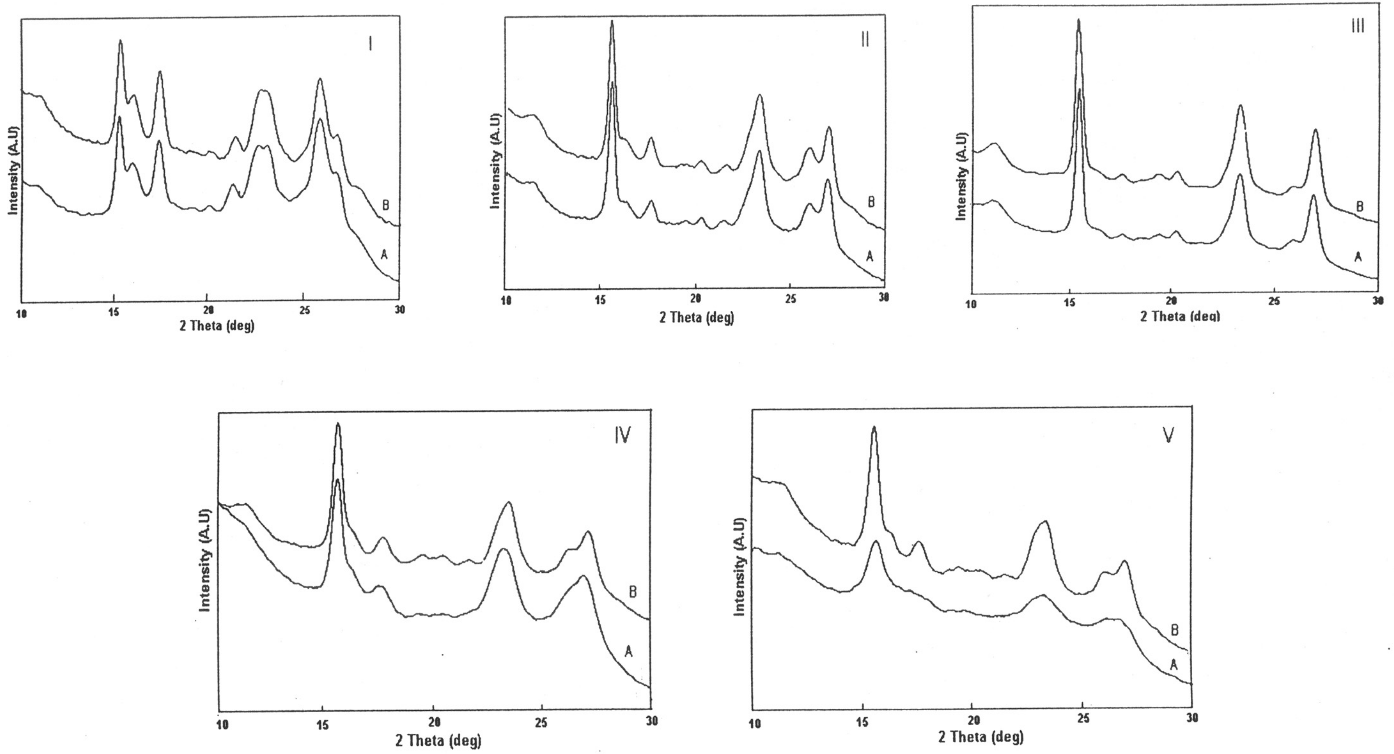


Fig. 6.17: XRD patterns of samples before and after SSP I) sample 1, II) sample 2, III) sample 3, IV) sample 4, V) sample 5, A) before SSP, B) after SSP

However, XRD patterns varied significantly between crystallized samples and samples after 2 h of SSP, in the case of diluent crystallized samples. As crystallized, these samples show broad peaks indicating small crystals. These crystals reorganize into bigger crystals during the initial stages of SSP and later remains unchanged on further SSP.

The invariance in WAXD pattern and DSC data indicate that the SSP and transesterification take place in the amorphous phase while crystalline phase remains unaltered. This suggests that the transestefication occurs only in the amorphous phase and at the crystal amorphous interface. It is reasonable to assume that the crystallinity of the starting sample is about 60%. Then only 40% of the material in the amorphous phase is available for transesterification. The calculated 20% transestrefication relates to the 40% of the material and simple calculation shows that 50% of the amorphous phase has undergone transestefication. This value is comparable to the melt condensed sample which has 50% transesterification. However, it occurs in 60 minutes at 300°C while in SSP it takes about 180 min at 220°C.

6.4 Conclusion

Simultaneous solid state polymerization and transesterification can be performed on PET and PEN oligomer mixtures to obtain high molecular weight PET/PEN copolymers. Oligomer mixtures could be crystallized thermally or by diluents to obtain suitable precursors for SSP. Precursors obtained by both methods underwent SSP as well as transesterification. Sequence distribution of samples at different stages of SSP could be analyzed from ^{1}HNMR spectra. X-ray diffraction and DSC studies showed that SSP and transesterification occurs only in the amorphous phase of the semicrystalline precursors. DSC studies on the SSP samples showed that with increase in transesterification and viscosity, crystallization became more and more difficult. A comparison of increase in transesterification and viscosity during reaction indicates that SSP favours reactions predominantly among chain ends.

6.5 References

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CHAPTER 7

SUMMARY AND CONCLUSIONS

7.1 Summary

A summary of the main findings of the present investigations reported in the previous chapters of this thesis and conclusions are given below.

Poly(aryl ester)s were prepared from oligomers synthesized from dimethylesters of terephthalic and isophthalic acids and BPA with evolution of methanol as by product *via* SSP. Poly(arylester)s were also prepared from oligomers with hydroxyl and carboxyl end groups as well as from oligomers with only hydroxyl end groups with the evolution of water and BPA as by products respectively. These oligomers were crystallized prior to SSP by treatment with diluents. DSC and XRD studies showed that the induced crystallinity decreased during SSP. $Ti(O^iPr)_4$ showed higher catalytic activity compared to DBTL and DMAP.

The results show that PET oligomer with very low inherent viscosity (~0.2dL/g) crystallizes very rapidly and can be used as precursors for SSP to prepare high molecular weight PET. The nature of catalyst affected crystallization and subsequent SSP of oligomeric PET. Presence of Sb_2O_3 enhanced the crystallization rate compared to $Ti(O^iPr)_4$. However, the sample with $Ti(O^iPr)_4$ showed better SSP rates.

Studies on structure and morphology showed that PET oligomers crystallize rapidly into well developed large defect free crystals with chain ends outside the crystal. These crystals did not undergo major reorganization during SSP. SSP is mainly controlled by the chain ends in the amorphous phase. The oligomers prepared by hydrolysis and glycolysis could be subjected to SSP without further crystallization step. This would have implications in the recycling of PET.

Studies on crystallization of commercial PET pellets showed morphological differences between the skin (surface) and the core of the pellets. The skin core effect depends on crystallization temperature and pellet heating rate. Higher crystallization temperature led to higher crystallinity, while higher heating rate resulted in lower core crystallinity. Difference in surface and core crystallinity decreased at low heating rate and the difference increased at higher crystallization temperature. Average crystal size increased with crystallization temperature. The samples with large crystal size and low core crystallinity showed higher SSP rate.

The crystallization and SSP behaviour of PEN oligomers was very similar to the PET oligomers. Thermally crystallized oligomers were highly crystalline with defect free large crystals(~15 nm). Crystallized oligomers underwent SSP to give polymer with higher η_{inh} and T_g. Solvents with solubility parameter $18.5<\delta<25$ $(Jcm^{-3})^{1/2}$ could induce crystallinity in PEN at room temperature. Diluent induced crystallization produced smaller crystals (~5 nm) and underwent SSP to give material with higher η_{inh} and T_g. However, during SSP, the smaller crystals reorganizes to give larger crystals. The data on PEN also indicated that $Ti(O^iPr)_4$ has higher catalytic activity for SSP, while its crystallization rate was lower.

Isothermal crystallization studies of PEN oligomers showed that crystallization half time was minimum over a wide range of crystallization temperatures (140 -210°C). So crystallization of these oligomers can be performed at any temperature in this range. Oligomers with different catalysts showed slight difference in crystallization behaviour. On the other hand, for high molecular weight PEN sample the minimum occurred at 200°C. At almost all the crystallization temperatures, the polymer had larger $t_{1/2}$ than the oligomers. Crystallization isotherms were analyzed using Avrami equation. In the temperature range studied, the Avrami exponent 'n' changed from 2 to 3.

In the present work it was found that whenever the crystallization temperature (Tc) was 240°C and above, β modification was formed, while crystallizations at 230°C and below yielded α modification. Neither the melt temperature from which the material was brought to the crystallization temperature nor the modification in which the material existed prior to melting did not seem to affect the crystallization. Thus, the crucial factor which determined the modification into which PEN crystallizes was the crystallization temperature.

Simultaneous transesterification and SSP of PET and PEN oligomer mixtures produced a copolymer, namely, poly(ethylenenaphthalate-co-terephthalate)s. Oligomer mixtures could be crystallized thermally or by diluents to obtain suitable precursors for SSP. Precursors obtained by both methods underwent SSP as well as transesterification. Sequence distribution of samples at different stages of SSP could be analyzed from ^{1}HNMR spectra. X-ray diffraction and DSC studies showed that SSP and transestrification occured only in the amorphous phase of the semi crystalline precursors. DSC studies on the SSP samples showed that with increase in transesterification and viscosity crystallization became progressively more difficult. A comparison of increase in transesterification and viscosity during reaction indicated that SSP favoured reactions among chain ends.

7.2 Conclusions

The key conclusion of this work is that low molecular weight polyester oligomers can be crystallized and then subjected to SSP to obtain high molecular weight polymers. This process provides an alternate route for preparing high molecular weight polymers. Copolymers can be prepared by simultaneous transesterification and SSP of oligomers.

In PET and PEN, the crystallites do not undergo reorganization during SSP, while chain extension takes place by the reaction of chain ends in the amorphous phase. On the other hand for poly(aryl ester)s, crystalline regions also undergoes structural reorganization during SSP. This appears to reduce the SSP rate of poly(aryl ester)s.

The crystal size seems to be an important parameter that controls the SSP rate. Large crystals, are essentially defect free and give higher SSP rates. In these crystals there is no chain folding and the chain ends are out side the crystals. The effect of crystal size also is evident in the studies with PET pellets. However, the crystal sizes are smaller and the rates are lower. It is worth pointing out that in the case of PET pellets it is extremely difficult to achieve the crystal perfection of the oligomers even if it is crystallized very close to melting temperatures for long times. Because of chain folding there will be always some chain ends trapped into the lattice and limiting the crystal size and these chain ends may not be available for SSP.

The catalyst also has a role in crystallization and SSP. In this work, it has been found that the catalyst $Ti(O^iPr)_4$ has a positive effect on SSP rates while it retards the crystallization rate. Pilati and co-workers[1] have shown that $Ti(O^iPr)_4$ interacts with the terminal groups of PET and lead to an apparent increase in viscosity, which in turn decreases the crystallization rate. However, this association of end groups has a positive effect on SSP as the reactive end groups are organized around the catalytic sites. SSP data on all polyesters presented in this work uniformly supports this contention.

Another important conclusion is that the SSP rate depends on the flexibility of the molecule. In this study poly(aryl ester)s has the lowest mobility and the PET has the highest. PEN is more rigid than PET. The PET exhibits the highest rate while poly(aryl ester)s the lowest.

The crystallization studies on PEN shows that it exists in β modification when crystallized above 240°C. This finding assumes importance in the high speed spinning of PEN fibres where the material crystallizes in the spin line under stress. Because of stress, the supercooling needed for crystallization is low and crystallizes at high temperature. It is speculated that in the above conditions PEN may be crystallizing in the β modification.

7.3 Perspectives

The present work opens up a new field on the SSP of oligomers to obtain high molecular weight polymer. Some suggestions are made for the future work

It is found that the molecular mobility of the amorphous phase is important for better rates. The chain mobility may be increased by the addition of suitable plasticizers and its effect on crystallization and SSP could be investigated.

In the present work the copolymer has been prepared by simultaneous SSP and crystallization from two crystalline polyesters. The same process could be used to prepare copolymers from a crystalline and amorphous oligomers, for instance nylon 66 which is crystalline and aromatic polyamide, which is amorphous. In the PET/PEN system the crystalline morphology did not reorganize during SSP and transestification. It is of interest to study the morphology changes when one of the components reorganizes during the process. The present process of simultaneous SSP and transesterification leads to low levels of exchange reactions. However, during the melt processing in the extruder, further exchange reactions will take place. Studies can be made to control these reactions by encapping or by the addition of suitable inhibitors.

The PEN oligomer may be crystallized in the β- modification and study the effect of crystalline modification on SSP.

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SYNOPSIS

The thesis entitled 'Studies in crystallization and solid state polymerization of aromatic and aliphatic polyesters' consists of six chapters and chapter 7 summarizes the work reported in the thesis

Introduction

Solid state polymerization (SSP) is a commonly practiced technique to obtain high molecular weight crystalline polymers such as poly(ethylene terephthalate)s[1]. In this technique, polycondensation is generally carried out by heating the semicrystalline polymer in a stream of an inert gas or under reduced pressure at a temperature just below the polymer melting temperature. In SSP, the prepolymer is handled in the form of a powder or chip. This simplifies the design of the reactor. The reaction temperatures employed in SSP are substantially lower than that used in the melt process. This minimizes side reactions as well as thermal degradation. SSP enables very high molecular weight polymers to be prepared without the difficulty of handling high melt viscosities. It is generally accepted that the polymerization proceeds by step reactions in the amorphous regions of the semicrystalline polymer[1].

Application of SSP to amorphous polymers are rare[2]. This is because, amorphous polymers soften above T_g and hence difficult to polymerize in the solid state. However this limitation can be overcome by introducing a small amount of crystallinity in such polymers. Different methods for the introduction of crystallinity in amorphous polymers have been reported [3-9].

Poly(aryl ester)s are an important class of engineering thermoplastics[10,11]. Various synthetic routes have been reported for the synthesis of poly(aryl ester)s. Poly(aryl ester)s are generally prepared by melt polymerization of bisphenol A diacetate (BPA diacetate) and a mixture of terephthalic acid (TPA)/ isophthalic acid (IPA)[12-14]. A few reports exist in which modifications of the diacetate process have been used to prepare aromatic polyesters by a combination of melt and SSP process[13,14].

Poly (ethyleneterephthalate) (PET) is a commercially important thermoplastic which is extensively used in the fiber form for textile applications. It is increasingly finding application in food grade bottles for storing beverages as well as in injection molded goods. Most of the applications of PET require polymer of relatively high molecular weight. Commercially, high molecular weight polymers have been made by melt polymerization or solid state polymerization of oligomers. In solid state polymerization, PET oligomers in the form of pellets or chips have to undergo a relatively lengthy crystallization process prior to solid stating. Therefore better polymerization processes for PET are required[15].

Although the demand for PET is very large, better thermal properties are desired for some applications[16]. Structurally related poly (ethylene naphthalate) (PEN) which is obtained from 2,6- dimethyl naphthalate and ethylene glycol is a high performance polymer. PEN contains a rigid naphthalene ring and exhibits superior physical and mechanical properties than widely used PET's. Much attention has been focused recently on the preparation and applications of PEN[17]. Due to its enhanced physical and mechanical properties, PEN has found application in manufacture of bottles with good gas-barrier properties, transparency and thermal resistance (upto 110°C) and industrial fibers. Due to its extremely high melt viscosity, PEN with an intrinsic viscosity suitable for such applications cannot be produced by melt state polymerization. It is preferable to use a combination of melt and solid state polymerization processes. However solid state polymerization rate of PEN is relatively slow[18].

Although PEN has superior physical and mechanical properties than PET, its relative low production volume and high price may limit its application in the near future. As an alternative, poly(ethylene naphthalate-co-terephthalate)s (PNT) in various compositions can be synthesized with the objectives of improving the solubility and processability of PEN, reducing the cost of PEN, while improving physical and mechanical properties of PET[17]. PET/PEN blends are usually prepared by reactive processing[19]. Blending of two polymers often can result in opaque materials with incompatible phases. PEN and PET are similar in chemical composition and they will transesterify to the extent that clear materials would be obtained .But when the level of transesterification reaches very high levels, the crystallinity and resultant physical properties of the blend can be reduced to the point that they may be undesirable for many applications[20]. Controlling the transesterification levels is difficult in the melt process [21].

SYNOPSIS

Objectives of the present work

1. One of the objectives of the present work is to explore the feasibility of solid state polymerization for the preparation of high molecular weight aromatic polyesters derived from dimethyl esters of phthalic acid and bisphenol A. This route leads to low boiling by product methanol, which is less toxic and less hazardous than those derived from conventional acidolysis route. Inducement of crystallinity in the amorphous oligomers by diluent will be examined.

   Oligomers will also be prepared by degradation of commercial poly(aryl ester)s to get oligomers with specific end groups. Solid sate polymerization of these oligomers will be carried out in presence of different catalysts, namely dibutyltin dilaurate (DBTL), Titanium tetraisopropoxide ($Ti(O^iPr)_4$) and dimethyl amino pyridine (DMAP)

2. One of the objectives of the study is to investigate in depth, crystallization and solid state polymerization of very low molecular.weight PET (η_{inh} 0.1-0.2 dL/g). A method recently disclosed by Du Pont (US)[17] will be adopted for crystallization in which the sample is brought to the crystallization temperature in a rapid manner under a time scale shorter than the nucleation rate and growth. The sudden change in the temperature affects the mobility of the amorphous phase such that it crystallizes in well defined defect free crystals. Oligomers will be prepared from dimethyl terephthalate (DMT) and ethylene glycol (EG) as well as by controlled degradation of commercial PET to get oligomers with specific end groups. Solid state polymerization of crystallized oligomers will be studied .

   Effect of end groups and catalysts on the crystallization kinetics of oligomers will be studied by isothermal crystallization method.

   Another objective is to determine the effect of crystallization temperature on the resultant skin-core crystalline morphology of amorphous PET pellets. The difference in degree of crystallinity between surface (skin) and core decrease at high temperature. Effect of crystal morphology on the solid state polymerization also will be examined.

3. Another objective of the work is to study the crystallization and SSP of PEN oligomers. PEN oligomers (η_{inh} 0.1-0.2 dL/g) will be prepared from dimethyl naphthalate (DMN) and EG. The oligomers will be subjected to crystallization thermally[20], as well as by contact with a diluent and will be used as precursors for SSP in presence of two different catalysts namely $Ti(O^{i}Pr)_4$ and Sb_2O_3.

   Crystallization kinetics of the oligomers and the high molecular weight polymer obtained by SSP will be studied by isothermal crystallization method.

   A detailed investigation of change in crystal forms (α, β) during crystallization at different temperatures will be performed by wide angle X-ray diffraction (WAXD) measurements.

4. An objective of the present work is to explore the possibility to prepare PET/PEN blends from oligomers by SSP. Oligomers will be crystallized by thermal methods or by contact with diluent. Amount of transesterification at various stages of SSP will be measured by NMR analyses.

Chapter 1. General introduction

A general literature survey, inclusive of patents on preparation of high molecular weight polyesters with emphasis on solid state polymerization has been presented in this chapter.

Chapter 2. Objectives in undertaking the present work.

This chapter discusses the scope and objectives of the present work.

Chapter 3. Crystallization and solid state polymerization of poly(aryl ester)s

This chapter describes results of the following studies:

1. Preparation of oligomers from DMI, DMT and BPA and by degradation of commercial poly(aryl ester)s by methanolic sodium hydroxide as well as by BPA in diphenyl ether.

2. Crystallization of oligomers in presence of diluents

3. Solid state polymerization of oligomers in presence of DMAP, DBTL and $Ti(O^iPr)_4$

Chapter 4. Crystallization and solid state polymerization of poly(ethylene terephthalate)s

This chapter describes the results of the following studies:

1. Preparation of oligomeric PET from DMT and EG in presence of $Ti(O^iPr)_4$ and Sb_2O_3, from commercial PET by hydrolysis and glycolysis
2. Thermal crystallization and solid state polymerization of these oligomers
3. Crystallization kinetics of oligomers by isothermal crystallization method
4. Effect of crystallization temperature on skin-core crystalline morphology of PET pellets and effect of crystal morphology on the rate of solid state polymerization
5. Change in crystal structure during SSP by small angle X-ray diffraction (SAXD) measurements

Chapter 5. Crystallization and solid state polymerization of poly(ethylene 2,6-naphthalate)s

This chapter describes the results of the following studies:

1. Preparation of PEN oligomers from DMN and EG in presence of $Ti(O^iPr)_4$ and Sb_2O_3
2. Thermal and diluent induced crystallization and solid state polymerization of these oligomers
3. Crystallization kinetics of oligomers and high molecular weight PEN obtained by SSP by isothermal crystallization method
4. Crystal structure modification of oligomers occuring at different crystallization temperatures by WAXD measurements

Chapter 6 Preparation of poly(ethylene naphthalate-co-terephthalate) *via* solid state polymerization

This chapter describes the results of the following studies:

1. Thermal and diluent induced crystallization of PET and PEN oligomeric mixtures in various compositions

2. Solid state polymerization of the crystallized oligomeric mixtures.

3. Determination of sequence distributions and quantification of transesterification by NMR analyses

Chapter 7 Summary and conclusions

This chapter summarizes the results and conclusions of the work.

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