Spring 1989

Thermotropic liquid crystalline polyesters based on the monomer of poly(ethylene terephthalate)

Satish Baliga
New Jersey Institute of Technology

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Thermotropic liquid crystalline polyesters based on the monomer of poly(ethylene terephthalate)


New Jersey Institute of Technology, 1989
THERMOTROPIC LIQUID CRYSTALLINE POLYESTERS
BASED ON THE MONOMER OF POLY(ETHYLENE TEREPTHALATE)

by

BANTWAL SATISH BALIGA

Dissertation submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology in partial
fulfillment of the requirements for the degree of
Doctor of Engineering Science
1989
Title of Dissertation:
Thermotropic Liquid Crystalline Polyesters based on the monomer of Poly(ethylene Terephthalate)

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ABSTRACT

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Satish Baliga, Doctor of Engineering Science, 1989

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A series of thermotropic liquid crystalline polyesters were synthesized, based on Bis-hydroxyethyl terephthalate (BHET), para-acetoxybenzoic acid (PAB) and terephthalic acid (TA). Structural studies of these aromatic polyesters using Nuclear Magnetic Resonance (NMR), Infrared Spectroscopy (IR) and X-ray diffraction techniques indicated the existence of substantial amounts of rigid -PAB-PAB- linkages within the mesogenic backbone. Optical study of their melts using Polarizing Microscopy indicated a "threaded" microstructure typical of a nematic mesophase. Morphological rearrangements were found to occur at higher temperatures as was evident from a two-phase structure, one phase speculated to be rich in flexible Poly(ethylene Terephthalate) (PET) segments and the other rich in -PAB-PAB- segments. At elevated temperatures, thermal degradation occurred before these polyesters could become completely isotropic. Thermal
analysis using Differential Scanning Calorimetry (DSC) showed that the melting and crystallization transitions of these polyesters were dependent on composition and thermal history. Most of these polyesters showed multiple endotherms on melting to the nematic phase.

A detailed study was also conducted on the depolymerization of PET into its monomer, BHET, by glycolysis in the presence of metal acetate catalysts. A model describing an equilibrium reaction between BHET, dimer and ethylene glycol (EG) has been proposed. The relative effectiveness of the four catalysts used, in terms of the initial rate of depolymerization, was as follows:

\[ \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Mn}^{2+} > \text{Co}^{2+} \]

The PET used in this study was reclaimed from post-consumer soft drink bottles, in an effort to find an economically viable end-use for this material. The BHET monomer thus obtained was used as a building block in the synthesis of the liquid crystalline polyesters.
"Researching the unknown is like trying to climb to the top of an unfamiliar mountain without a map. In research work you never know exactly where you are. But you know each time you take a step upward, a bit further into the unknown. Just a tiny step up each day eventually will lead to the top, where you will see the future spread out before you. It is then that tomorrow opens up to you."

Robert W. Lucky

An excerpt from an article which appeared in the Star-Ledger on April 5, 1987
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This dissertation is dedicated to
my beloved parents
Radha and Purushotham Baliga
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Above all, I would like to thank my parents who have encouraged and supported my education and I dedicate this work to them.
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CHAPTER I

INTRODUCTION

In recent years, there has been a considerable interest in the development of low weight polymers with ultrahigh tensile modulus and strength. The reason for this interest can be attributed to the commercial success of synthetic organic fibers that have tensile strengths approximately five times as high as that of steel wire, when compared on a weight basis. Today, Kevlar fibers developed by Du Pont, have replaced steel, asbestos, and graphite in a variety of applications, including radial tires, armorplate, brake linings, and composites. Table 1 shows the tensile properties of high strength-high modulus aromatic yarns compared with those of glass and steel fibers [1]. Over the past decade, several methods have been reported for the development of high strength-high modulus polymers [1 - 5].

It has been found that from a molecular standpoint, ultrahigh strength in polymers can be achieved by preparing anisotropic morphologies of oriented and extended molecular chains. Depending on whether the polymer molecules have a flexible chain conformation or a stiff, rod-like conformation, the approach to maximizing chain extension and orientation is different. In the case of flexible chain systems, the aim is to minimize the formation of chain
folding while simultaneously maximizing molecular orientation. Theoretically, the maximum strength realizable with flexible chain polymers is achieved when all the molecules are fully extended. For example, for polyethylene it has been calculated that the ultimate tensile strength, when all its molecules are fully extended, is 3.6 GPa and the corresponding modulus is 184 GPa. However, in practice, the observed tensile strength, even after elaborate schemes to stretch out the molecules [3], is much less (upto 0.5 GPa). This limitation on the full potential of mechanical strength is attributed to chain folding, trapped entanglement, kinks and other steric hinderances. In stiff chain polymers, chain folding does not occur as it does in flexible chain polymers. In such cases molecular orientation, which to a great extent is dictated by steric hinderance, determines the modulus of the material. Generally, these polymers exhibit high strength and modulus in the direction of molecular orientation, but comparatively poor mechanical strength in the transverse direction.

Many of the stiff chain aromatic polymers that are used as high strength-high modulus materials exhibit liquid crystalline behaviour. The state of matter termed liquid-crystalline has structural properties intermediate between those of an isotropic fluid and a three dimensionally ordered crystalline solid. The first to encounter the liquid crystalline state was the Austrian botanist Reinitzer [6]
in 1888, who found very interesting properties in cholesteryl benzoate, which he had synthesized. Crystals of this substance formed a turbid melt at 145 °C and on further heating to 175 °C the turbid liquid transformed into an ordinary transparent melt. By studying this substance with a polarizing microscope, Lehmann [7] determined that the turbid phase was optically anisotropic. He called this state "liquid-crystalline" and proved that it was an independent thermodynamic state of matter which showed anisotropy not only in its optical properties, but also in its electrical, magnetic and mechanical properties.

A conventional view of liquid crystalline order is that it is a substance that possesses many of the characteristic mechanical properties of fluids yet has a sufficient degree of molecular order so as to diffract x-rays according to Bragg's law. Hence, this texture is more rightly denoted as a mesophase originating from the Greek term "mesos" meaning "intermediate" and "morphe" meaning "form". Orientation of chains in the fluid state can be achieved in solution (lyotropic) or in the melt (thermotropic). According to the Flory theory of concentrated polymeric solutions [8], lyotropic liquid crystals typically consist of comparatively elongated, rigid-rod molecules, and a mesophase is formed when their concentration reaches a certain critical value in a specific solvent. In contrast to lyotropic systems,
thermotropic polymers show liquid crystal-like properties over a particular temperature range without the addition of any solvent. It is widely recognized that liquid crystal-like properties can be induced in a polymer by the incorporation of suitable rigid mesogenic groups into the molecule. These groups can either be included in the main chain, although usually separated by less rigid groups, or they may occur as side groups attached to the main chain directly or via a less rigid sequence.

Following the early work of Robinson and others [9-11] on lyotropic synthetic polypeptides, researchers at Du Pont discovered that certain aromatic polyamides gave anisotropic solutions in alkylamide and alkylurea solutions. As a result, the ultra-high modulus Kevlar aramid fiber, made by the reaction of p-phenylene diamine and terephthloyd chloride at low temperature in an appropriate solvent, was developed and commercialized [12]. In 1976, Jackson and Kuhfuss [2] from Tennessee Eastman demonstrated that thermotropic liquid crystalline behaviour existed in copolymers based on poly(ethylene terephthalate) (PET) and para-acetoxy benzoic acid (PAB). In these copolymers, while PET has a flexible chain conformation, PAB has a stiff rodlike conformation which is necessary for the development of a mesophase. The processing of this copolymer system has been shown by these authors to lead to highly anisotropic fluids, whose melt viscosity behaves in a rather anomalous
way when contrasted with conventional thermally processable, flexible chain polymers. Specifically, when compared to the PET homopolymer, the PET-PAB copolymer containing 60 mole percent PAB was found to be extremely shear sensitive and exhibited non-Newtonian shear thinning behaviour at low shear rates. At a shear rate of 1000 sec\(^{-1}\) the melt viscosity of this copolymer was less than 5 % that of PET.

Although virtually every polymer manufacturer has active research programs on thermotropic liquid crystal polymers (TLCP's), only a few have been commercialized in the United States. Table 2 lists some of the typical properties of commercially available TLCP's. In general, they have very high tensile strength, stiffness and Izod impact, measured in the flow, or machine direction of the polymer melt. The coefficient of thermal expansion of these polymers is significantly lower than that of conventional isotropic polymers. Therefore, the shrinkage of molded parts after molding is negligible. In addition, due to its low viscosity and high heat distortion points, the molding cycle is much faster than that of conventional polymers. These impressive properties are due to the near rigid and linear segments in the polymer chain backbone. These mesogenic units show spontaneous anisotropy and the high modulus is associated with the high degree of orientation generated during the flow of their shear sensitive thermotropic melts.
Generally, liquid crystalline order is classified into three types of mesomorphic arrangements: nematic, smectic and cholesteric. As shown in figure 1(a), in a nematic phase, the centers of gravity of the molecules are arranged at random, but in localized regions these molecules have the same orientation. Hence, a rod-like system of preferential unidirectional order is established due to the nematic ordering. For those systems displaying high strength or high modulus, it is the nematic morphology that is preferentially induced.

The term "smectic" (derived from the greek word for soap) describes long molecules arranged side by side in a series of stratified layers. As shown in figure 1(b), the center of gravity of these molecules are arranged in equidistant planes which make up the corresponding layers. Depending on the relative degree of molecular orientation in each layer, there are at least nine or ten known smectic structures for liquid crystal polymers. As discussed by Shibaev [13], polymeric liquid crystals that arise due to mesogenic side groups, have a tendency to preferentially arrange in the smectic morphology. Due to the lack of molecular backbone overlap in the orientation direction, the smectic texture does not exhibit high modulus performance.

The cholesteric mesophase shown in figure 1(c), is a special form of the nematic texture. Molecules are brought
together in each layer according to the nematic form, but each layer rotates or twists a certain degree from its neighbouring layer; consequently, the overall structure is helical. Due to the lack of molecular overlap between the long axis of the molecules arranged between two adjacent layers, it is not likely that these structures would promote high strength or high modulus in contrast to that of the purely nematic mesophase. They do, however suggest a means of producing a biaxial orientation.

As suggested by Viney and Windle [20], the term liquid crystal when applied to polymers can be said to define a state which has one or more of the following characteristics in common with low molecular weight liquid crystals:

(a) Anisotropy of properties, for example optical anisotropy in the absence of three-dimensional crystalline order [14,15];
(b) Anomalously low solution or melt viscosity [2,15];
(c) Possibility of inducing molecular orientation by magnetic or electric fields [15,16];
(d) Production of characteristic NMR line shapes [17];
(e) Miscibility with a known small-molecule liquid crystal [18];
(f) An endotherm detectable by differential scanning calorimetry (DSC) at the temperature where a thermotropic mesophase first flows freely, and again where this
phase is replaced by an isotropic one [18].

In this study an attempt is made to develop and characterize a low melting liquid crystal polymer whose basic chemical structure would be similar to the PET PAB copolymer developed by Jackson and Kuhfuss at Tennessee Eastman company. However, instead of PET, its monomer Bis-hydroxyethyl terephthalate (BHET) is used as the basic building block in the synthesis of the liquid crystal polymer. BHET is first reacted with terephthalic acid (TA) to form a pre-polymer mixture containing both hydroxyl and carboxyl terminated chain segments. The pre-polymer is then reacted with PAB to form a polyester with a high level of rigidity in the mesogenic backbone. The rationale for using a three component system involving BHET, TA and PAB instead of just PET and PAB is as follows:

(1) Researchers at Du Pont [19] have shown that BHET is much more effective than PET in lowering the copolymer melting point;

(2) By changing the relative amounts of BHET and TA in the pre-polymer, one could change the amount of flexible \(-\text{CH}_2\text{CH}_2-\) segments in the polymer chain and thereby control the rigidity of the final polyester;

(3) If BHET could be successfully used as a building block
for synthesizing a liquid crystal polymer it would make the depolymerization of reclaimed PET into BHET an economically viable process.

Considering the urgency with which several states are imposing mandatory recycling laws for post-consumer PET soft drink bottles, this investigation could perhaps provide the groundwork for studying the feasibility of using reclaimed PET in secondary non-food applications. Results of the glycolysis of PET reclaimed from post-consumer soft drink bottles are presented in this work. Also, the relative effectiveness of four metal acetates (zinc, lead, cobalt and manganese acetate) in the depolymerization reaction is studied.
CHAPTER II

LITERATURE REVIEW

In recent years several reviews and books have been published on the properties of ultra high strength and high modulus materials that are formed from rod-like polymers [1,21-26]. Most of these rod-like polymers exhibit liquid crystalline behaviour in the melt or in the solution, and the high modulus characteristics have been attributed to the significant amount of order that is present in the liquid crystalline state. The purpose of this chapter is to review literature related to thermotropic liquid crystal polymers with major emphasis on the Eastman PET/PAB copolymer. Also reviewed are recent publications concerning the depolymerization of PET and the effectiveness of transesterification catalysts used in this process.

A. Classification of Thermotropic Liquid Crystalline Polymers

As mentioned before, the liquid crystalline state is a liquid phase in which some of the molecular order characteristic of the solid phase is retained because of the molecular structure and short range molecular interaction. In thermotropic systems, this order can be disrupted by the action of heat which causes a transition from the solid state to the isotropic state as follows:
SOLID ➟ LIQUID CRYSTAL ➟ ISOTROPIC LIQUID
STATE ➟ STATE ➟ STATE

It has been shown by Flory and Ronca [27], that rod-like molecules having an aspect ratio (i.e. length to diameter ratio of the molecule) lower than 6.4 are capable of undergoing a transition in the melt, from the liquid crystalline state to the isotropic state. Rod-like molecules with an aspect ratio greater than 6.4 have very high melting temperatures and generally decompose before melting without forming a mesophase. However, at critical concentrations in suitable solvents, such molecules could possibly display liquid crystalline order.

From a molecular structural viewpoint, thermotropic liquid crystalline (TLCP's) polymers can be classified into two groups: main chain liquid crystalline polymers and side chain liquid crystalline polymers. In a recent paper, Chung [28] has presented a historical development of both main chain and side chain TLCP's. He has reviewed in some detail synthesis routes, characterization techniques, criteria to form liquid crystalline phases and various approaches used to reduce the melting point of main chain TLCP's. As explained by Chung, in main chain TLCP's the mesogenic groups form the backbone of the molecular chain, with the groups either linked directly or through flexible spacers.
If the mesogenic groups are directly linked a rigid rod polymer backbone is produced. On the other hand, if the mesogenic groups are connected via flexible spacers (e.g. alkyl chains), a semi-flexible polymer consisting of rigid and flexible segments will result. In side chain TLCP's, the mesogenic units link to the polymer backbone as pendants in the side chain, either directly or through flexible spacers. As stated by Chung [28], the general structures of these two groups can be illustrated as shown in Figure 2. The spacer between the mesogenic groups in main chain TLCP's or between the backbone and mesogenic units in side chain TLCP's is sometimes necessary to form the liquid crystal phase.

The chemical constitutions of mesogenic units in TLCP's usually have at least two linear substituted cyclic units that may or may not be linked by a short rigid central bridging group. In most cases, the mesogenic units have the appearance of ellipsoids, but flat and disk shapes have also been observed [29]. The spacer may be a combination of a functional unit (an ester or an ether) with a polyethylene, or a polyethylene glycol. The multiple bond character in both the central linkage group and the spacer is of great importance in maintaining polymer rigidity and linearity. Though there is no double bond in the ester group, the ester linkage unit develops some double bond characteristics. This is due to the fact that the electron-rich aryl or phenyl group slightly shifts its bonding electrons to the carboxyl
group and forms a double bond link with it. In the remainder of this section main chain and side chain TLCP's will be discussed in some detail. Based on published findings of various investigators, an attempt will be made to elucidate the characteristic features of both these polymer systems.

1. Main Chain Liquid Crystalline Polymers

The formation of TLCP's with rigid and flexible segments can be explained by using theories by Flory [8] and Di Marzio [30]. In 1956, using the lattice model, Flory calculated the statistics of packing of monodisperse macromolecules and solvent molecules without considering any dispersion interactions. He observed that the critical concentration of the liquid crystalline phase was a function of molecular weight and flexibility of the polymer. Based on this theory, Di Marzio showed that in the case of a stable lyotropic phase of rigid molecules, the solvent molecules could be withdrawn and replaced by flexible polymers and that Flory's theory would still be valid. This results in thermotropic liquid crystalline polymers with rigid and flexible segments.

The first report in a scientific journal of the preparation and properties of a thermotropic main chain polymer appears to be that by Roviello and Sirigu [31] in 1975. They prepared three alkanoates of 4,4'-dihydroxy-κ,κ,'
-dimethylbenzalazine with 6, 8, and 10 methylene groups in the aliphatic chain. Their general structure is shown in Figure 3(a). Earlier, in 1972, Cottis and coworkers [32] had described a family of aromatic copolyesters, which were recognized sometime later to form liquid crystalline melts. In 1976, Jackson and Kuhfuss [2] reported an independent study on the preparation and characterization of a series of thermotropic, main chain copolymers based on PET and PAB. The structure of this copolymer is shown in Figure 3(b). Their work and subsequent research on this copolymer system by other investigators will be discussed in detail in the next section.

Calundann and Jaffe [33] at Celanese have compared and summarized most industrial developments and patents on thermotropic main chain polyesters. As reported by Chung [28], most industrial aromatic TLCP's are synthesized through a condensation (mostly transesterification) reaction. Though the exact role of catalysts is still unknown, it has been found that, in general, anhydrous sodium or potassium acetates are very effective in increasing the polycondensation rate.

Jin, Antoun and coworkers [34] have presented chemical structures of various aromatic liquid crystal polyesters obtained through patented literature. These structures are shown in Table 3. Lenz and coworkers [34-36] have developed
a series of rigid and flexible polyesters based on substituted hydroquinones and terephthalic acid. The copolymers they studied contained a series of bisphenols which were selected to determine the effect of copolymer structure and composition on the thermotropic behaviour. From their investigations they found that nonlinear bisphenol spacers containing large or bulky central substituents between the two phenolic rings were more effective in destroying the liquid crystal properties than those with smaller substituents. They concluded that the geometric and steric effects imparted to the polymer chain backbones by the co-monomers were the most important controlling factors affecting the liquid crystallinity of the aromatic copolyesters. The electronic or polar effects of the substituents on the liquid crystalline properties were not as clear as the steric effects and seemed to be relatively minor in comparison. Thermal studies [35] using a Differential Scanning Calorimeter (DSC) showed that these polyesters had broad and small melting endotherms especially for the compositions containing from 40 to 60 mole percent of the bisphenol co-monomers. According to these authors, this result was understandable because these copolyesters would be expected to have low degrees of crystallinity or to be completely amorphous. These polyesters were examined visually for the occurrence of stir opalescence [37] in the melts. Almost all of these polyesters showed a gradual
reduction in the intensity of stir opalescence as the bisphenol content was increased. This indicated that the presence of bisphenol decreased the ability of the polymer to form the liquid crystal mesophase. The mesophase to isotropic phase transition of these polyesters could not be determined from DSC measurements because the polymers underwent thermal decomposition before the transition to the isotropic melt. Another important observation made was that even polymers which showed essentially no crystalline melting transitions on the DSC and presumably were amorphous in nature, exhibited stir opalescence. This observation indicated that even apparently amorphous linear polyesters could form liquid crystal states above their glass transition if the structure of the polymer favored parallel alignment of its chains in the melt.

Main chain TLCP's mostly appear to have nematic order. This texture can be identified using a hot-stage and polarizing microscope and examining a thin film of the polymer at various temperatures above the crystal-nematic transition. Hartshorne [38] and Demus and Richter [39] have described the test methods and summarized the means of identification. For various main chain TLCP systems, a threaded schlieren texture has been reported [20, 40-42] which is characteristic of the nematic mesophase. Mesophase identification will be dealt with in greater detail in the next section while discussing the optical characterization.
of the Eastman PET-PAB copolymer.

Although a highly rigid, rod-like main chain TLCP offers attractive mechanical and thermal properties, its high melting point results in processing difficulties. For example, the liquid crystal polymer XYDAR, manufactured at Dartco, has a melting point of 793°F. This necessitates the installation of high temperature ceramic heaters to their extruder barrels. Also, in order to run the resin, the molds have to be maintained between 400 and 535 °F (at least 450°F to obtain good surface finish) [43]. This disadvantage may offset the unique properties which this TLCP has to offer. Several techniques have been developed by investigators for lowering the melting point and controlling the properties of rigid main chain TLCP's. These techniques have been reviewed by Chung [28] and can be summarized as follows:

1. The use of nonrigid groups, termed as flexible spacers, in combination with the rigid mesogenic groups in the main chain to reduce the aspect ratio of the latter.

2. The unsymmetrical placement of substituents on the mesogenic groups to disrupt the regularity of the repeating units within the polymer.

3. The use of non-linear comonomers to introduce "kinks" in the polymer chain. The use of Crankshaft monomers to offset the linearity of the rigid cores.
4. Inserting anisodiamicetric bridging groups.

a. Effect of Spacers

Polymers with mesogenic units and flexible spacers in the main chain were first reported by Roviello and Sirigu [31]. In the same year, de Gennes [44] predicted that, theoretically, linear polymers with rigid blocks interconnected by flexible spacers in the main chain would be nematic. Since then several investigators [34-36, 41, 42, 45,47,48,51,52] have reported the effect of spacers on the molecular structure and properties of various main chain liquid crystalline polymer systems. From these investigations it is apparent that flexible spacers cause at least one of the following three accompanying effects:

1. A decrease in the polymer transition temperatures.
2. An odd-even zig-zag variation in the transition temperatures as well as in the enthalpy and entropy of isotropization.
3. A change in the micromolecular packing structure.

Finkelmann and coworkers [55-60], Shibaev and Plate [61, 62] and Lipatov [63] have proposed and summarized most models to explain the effects of flexible spacers. In summary, the reduction of steric hinderance of the main
backbone on mesogenic cores is the major role of the flexible spacer. Depending on the length and flexibility of the spacers and the thermodynamic driving force, a nematic or smectic structure is formed. Figure 4 shows the dependence of melting point ($T_m$) and the isotropization temperature ($T_i$) of a main chain TLCP on the number of methylene units [64]. An increase in the length of spacers results in a decrease in the $T_i$ in a zig-zag fashion. In most cases, as illustrated by Lenz [36], polymers containing an even number of methylene units have a higher $T_i$ and isotropization entropy change than those having odd units. Also, the former melt to give a nematic phase, while the latter form a smectic phase. However, Krigbaum et al. [65] have reported main chain TLCP's where the exact opposite is true. According to their investigation, polymers having an even number of methylene groups have higher degrees of crystallinity and melt to form a highly ordered smectic structure that is stable over a broad range of temperatures. On the other hand, the odd-methylene polymers have less crystallinity and only form a nematic phase in a certain temperature range.

Vasilenko and others [53] have developed a theoretical model to explain the ordering in melts of polymers with stiff and flexible fragments in the main chain. Other models by Gray and others [66-68], based on the behaviour of low molecular weight compounds, assume that the entire molecule
behaves as a rigid cylinder. Any change in geometry caused by the rotation of bonds in the flexible unit, that leads to a violation of the cylindrical shape results in the formation of an isotropic phase. An increase in spacer length causes an increase in the number of possible conformations of the long spacers. This leads to distortions of the cylindrical shape of the molecule and results in the reduction of clearing temperatures. In general, the odd-even effect is strongly related to the trans and gauche conformation of the flexible spacer. According to the rigid rod theory, trans conformations favor the liquid crystalline state, whereas the addition of gauche bonds reduces the mesophase order. For 'even' chains in trans conformation, the polarizability along the molecular axis is greater than the polarizability perpendicular to the axis. For 'odd' chains, it is almost equal in both directions. Stronger attractions exist between mesogens with even end groups, and consequently these compounds have higher isotropization temperatures. Regarding the consequence of rigidity and packing structure changes, Jackson and Kuhfuss [69] reported that the mechanical properties (tensile and flexural strength), heat deflection temperature and melting point of injection molded 4,4'-(alkylenedioxy) dibenzoic acid polyesters decreased with an increase in methylene groups.
b. Effect of Ring Substituents

Morgan et al. [70] at Du Pont were pioneers in the study of the effects of ring substituents on the properties of main chain TLCP's. They successfully demonstrated that, by using a ring substitution method, the unmeltable polymer derived from 1,4-phenylene-diamine and terephthalaldehyde, could be modified to give a variety of thermotropic polyazomethines. Their data clearly indicates that the substituents strongly affect the mechanical properties of heat-treated fibers. In other words, the growth of liquid crystalline order and packing of molecular chain during annealing is associated with the type of substituent. Jackson [71] reported that the presence of a phenyl substituent group on the aromatic ring significantly reduced the time for fiber heat treatment. Moreover, para-chloro-ring-substituted polymers showed better thermal stability than para-methyl substituted ones. This result is consistent with the findings of Kalyvas and McIntyre [72] who claimed that for low molecular weight liquid crystals, the order of thermal stability due to ring substituents is as follows:

\[ \text{CH}_3\text{CONH, NH}_2 > \text{CH}_3\text{O} > \text{NO}_2 > \text{Cl} > \text{CH}_3 \]

Lenz and coworkers [34, 41, 45, 73-76] have worked extensively in this area. According to their investigations, an introduction of halogen and alkyl groups into an aromatic ring of a mesogenic unit depresses the polymer's glass
temperature, melting point, and isotropization temperature. This implies that both the melting point and thermal stability of mesophases decrease with an increase in the size of the cycloalkyl substituent. Polymers lose liquid crystal order if they contain long alkyl ring substituents. Interestingly, an even-odd effect discussed in the previous section was also observed in the melting points of alkyl-substituted TLCP's. Polymers with an even number of carbon atoms seem to have more stable mesophases than the odd series. Detailed discussions regarding this behaviour can be obtained from the references mentioned above.

c. Effect of Kinks and Crankshaft monomers

Incorporation of kinks or nonlinear comonomers has been found by many investigators to be very effective in reducing the melting point of rigid main chain TLCP's. Also, in all-aromatic rod-like polyesters, addition of crankshaft monomers like 2,6 functionally di-substituted napthalene, offsets the linearity of the rigid core and makes the polymer more processable. Both these methods have been investigated extensively by researchers at Celanese [33,77,78] and Eastman-Kodak [71,79,80] and also by Griffin and Cox [81].

At Eastman, all-aromatic copolyesters prepared with 2,6-oriented napthalene derivatives were shown to have lower
melting points than those prepared with 1,4 and 1,5-oriented monomers. This phenomenon arises from the fact that the 2,6-derivative is longer than the other isomers and has the most difficulty in fitting into a liquid crystal. High melting (> 400 °C) copolyesters of 2,6-napthalenedicarboxylic acid, terephthalic acid and hydroquinone have been modified by the addition of varying amounts of meta-hydroxybenzoic acid or resorcinol. This has been found to reduce the melting points so that melt processibility could be attained without thermal decomposition. The softening point of such polyesters was also observed to be depressed to a large extent. The advantage of the relatively low softening points of these polyesters is that extruded sheets can be thermally formed into various shapes at temperatures close to the softening points. If little or no crystallinity is present, they can be formed at temperatures near the heat-deflection temperatures, which are lower than the softening points. As explained by Jackson [79], introduction of rigid kinks in the polymer reduces the degree of extended-chain orientation that can be obtained. Consequently, substantial modification with kinking components can greatly reduce the liquid crystallinity and the level of tensile and stiffness properties that can be achieved in injection-molded parts and melt-spun fibers. Moreover, it is also very likely that the resultant polymer could lose its oxidative [82] and hydrolytic stability [33].
d. Effect of Anisodiamicetric Bridging Groups

A variety of main chain and side chain TLCP's have been developed using the method of anisodiamicetric bridging groups [51,61,73,83-85]. Because of the thermal and chemical stability of the central bridging units, TLCP's prepared from this approach seem to be better than those from the spacer and kink method. Chiellini and Galli [130] studied the structure of chiral liquid crystal polyesters, and found the effectiveness of the central bridging group in extending the mesogenic behaviour to follow the given order:

\[-\text{CH} = \text{C(CH}_3\text{-} > -\text{N} = \text{N(O)-} > -\text{N} = \text{N-} > -\text{CH} = \text{CH-CO0-}\]

Their stability [84,85] however will be in the following order:

\[-\text{N} = \text{N(O)-} > -\text{CH} = \text{C(CH}_3\text{-} > -\text{N} = \text{N-} > -\text{CH} = \text{CH-CO0-}\]

2. Side Chain Liquid Crystalline Polymers

Finkleman, Ringsdorf, and others [54,58,60] have performed significant amount of work on side chain polymers that exhibit liquid crystalline behaviour. Mesogenic side chain polymers consist of two components, the mesogenic moieties and the polymer main chain to which they are attached. The linkage of the mesogenic group to the polymer chain can be direct or via flexible spacers. In the case of
direct linkage, anisotropic orientation of the mesogenic side groups is hindered due to the tendency towards a statistical chain conformation. Formation of liquid crystalline order can also be suppressed by steric hinderance. The use of flexible spacers enables the decoupling of the rigid rod-like mesogenic groups from the polymer chain. In such a case liquid crystalline behaviour will be exhibited because the motion of the polymer main chain would not affect the anisotropic orientation of the mesogenic groups. The final properties of the polymer can be varied by using different chemical structures and/or lengths of the flexible spacers. It has been observed that as the length of the substituent on the mesogenic group increases, or the length of the flexible spacer increases, the nematic phase changes to a smectic phase [58,60]. Since, in general, side chain polymers do not exhibit high strength-high modulus behaviour, hence they will not be reviewed in detail in this study.

B. Eastman Kodak PET/PAB Copolyester

As mentioned earlier, the liquid crystal polymer series developed in this study are structurally similar to the PET/PAB copolyesters developed at Eastman Kodak. Hence in order to gain a better understanding of the various techniques involved in characterizing these polymers, an in-depth review of the Eastman copolyester is reported in this
section based on published and patented literature. It should be pointed out that while refering to the PET/PAB copolymer structure and composition, most investigators use the term PHB synonymously and interchangeably with PAB. This is because the unit \(-O-\text{CH}_{2}\text{COO}-\) could be derived either from PAB or from hydroxy benzoic acid (PHB).

1. Preparation of PET/PAB copolyesters

As reported by Jackson and Kuhfuss [2,86,87], the Eastman copolyesters are prepared by a melt-phase ester interchange reaction between Poly(ethylene terephthalate (PET) and para-acetoxy benzoic acid (PAB). The actual reaction involves a two-step process:

1. cleavage of PET by PAB at 275 °C in an inert atmosphere,
2. condensation under vacuum of the carboxyl-terminated and acetate-terminated segments (including the self-condensation of PAB) to form high molecular weight copolyesters.

Transesterification catalysts like zinc acetate and antimony triacetate have been shown to be effective in catalyzing these reactions. The reaction mechanism as given by these authors is as follows:

\[
\begin{align*}
\text{I} & \quad \text{CH}_3\text{C}-\text{O}\text{-CH}_2\text{C}-\text{OH} \\
\text{II} & \quad \text{CH}_3\text{C}-\left[\text{O-CH}_2\text{C}-\text{O}\text{-CH}_2\text{C}\right]^{-\text{OH}} + \text{CH}_3\text{C}-\text{OH}
\end{align*}
\]
The final product may thus contain segments of PET (III), PAB homopolymer (II) and the copolymer (IV) in varying proportions. As mentioned earlier, the ester linkage sandwiched between the two electron rich aryl groups develops some double bond characteristics and imparts rigidity to the backbone. The ethylene group, \(-\text{CH}_2\text{CH}_2\)-, serves as a flexible spacer and reduces the effect of steric hinderance and lowers the transition temperatures. The PAB homopolymer segments are in themselves rigid and have been shown to exhibit mesomorphic character [88,89]. A series of copolyesters containing 0 to 90 mole percent of PAB units has been prepared at Eastman and studied for liquid crystalline behaviour. By heating these polymers under reduced pressure (0.05-0.1 mm) at 210-280 C for 4-16 hours, the molecular weights have been increased by solid-phase polymerization. Inherent viscosities (IV) between 0.4 and 0.8 have been reported for these copolymers. These
copolymers have limited solubility in most organic solvents. Depending on the mole percent of the rigid PAB units, chloroform, phenol-tetrachloroethane (60:40) or tri-fluoroacetic acid is used as a solvent for purification purposes and for IV measurements. Details of the preparation of these polymers can be obtained from the references mentioned above. Based on their investigations, Jackson and Kuhfuss have reported that the copolymer must contain at least 30 mole percent of PAB for it to show mesomorphic behaviour. Also, the copolymer containing 60-70 mole percent PAB exhibited the most favorable properties with respect to tensile strength, flexural moduli, notched Izod impact strength and melt viscosity (minimum when PAB content is between 60 and 70 mole percent).

2. Chemical Structure and Sequence Distribution

Structural analysis has been performed by several investigators at Eastman [80,87,90] using proton and carbon NMR spectra of these copolymers in solution (in trifluoroacetic acid) or in melts. The presence of segments II, III and IV has been confirmed for the copolymer containing 60 percent PAB by Jackson and Kuhfuss [86,87]. Their NMR studies suggested that the PAB unit has a random distribution in the copolymer. Absence of a peak at 4.1 ppm (due to ether methylene protons) or at 6.6 ppm (due to the
aromatic hydrogen atoms ortho to the ether linkage) indicated the absence of any p-ethyleneoxybenzoate groups. The random distribution of PAB units was confirmed by McFarlane and coworkers [80] who performed carbon-13 NMR studies on these copolymers. Garozzo et al [91] performed direct pyrolysis mass spectrometry on copolyesters containing 20 to 80 mole percent PAB. Their results indicated that these copolymers behaved as statistical copolymers and had a random distribution of the two units in the chain.

Recent experimental investigations by Nicely and others [90] showed that the sequence distribution for the PET/PAB copolyesters containing 20 to 70 mole percent PAB, could be described in terms of a probability model in which PAB had a slightly greater than random chance of being bonded to another PAB. While the deviations from randomness of the sequence distributions were slight at lower PAB fractions, they became more significant at higher PAB levels in the copolymer. These deviations from randomness lead to perturbations in the distributions of sequence lengths at higher PAB levels. Proton wide-line NMR spectra on melts showed that for copolymers containing more than 35 mole percent PAB, phase separation into liquid crystalline and isotropic phases occurred at high temperatures. At 280°C, the isotropic and anisotropic phases were found to contain 35 and 80 mole percent PAB units respectively. Nicely and his
coworkers offered a qualitative explanation for the above mentioned phenomenon. According to them, the formation of a liquid crystalline phase requires significant amounts of sequences of four or more PAB's. At compositions with enough PAB to separate a liquid crystalline phase, shorter sequences of PAB were found to partition between the phases to further enrich the PAB rich phase.

There is general agreement based upon a variety of measurements [92,103] that the PET/PAB polymers are two-phase systems for PAB content greater than 30 mole percent. However, there is disagreement about how the chain sequence statistics relate to the phase separation. Zachariades and others [92] concluded from etching and diffraction measurements that the PET/PAB copolymer containing 80 mole percent PAB was a blocky copolymer with long sequences of ordered PAB units. However, Blackwell and coworkers [102,103] have argued that the presence of ordered regions did not necessarily imply blockiness. Instead, the ordered regions might actually consist of a segregated copolymer rich in PAB rather than homopolymer blocks. For the 80 mole percent copolymer, even a fully random structure would contain extensive sequences rich in PAB and it would not be surprising that this copolymer would be more ordered than the copolymer containing 60 mole percent PAB. By utilizing the technique of chemical etching on the PET-PAB
copolymers, Joseph et al [93-95] have reported that at low PAB levels (i.e. 50 mole % PAB), a PET rich phase was the continuous phase while at PAB levels equal to or greater than 60 mole %, it was the PAB rich phase that appeared to form more of a continuous matrix. Their study indicates that the morphology of this copolyester system is non-homogeneous in nature. This, however does not necessarily imply a non-random sequence distribution.

Based on the observations of the investigators mentioned above, it would thus appear that the PET-PAB copolymer system containing less than 80 mole percent PAB, would in most part behave as a random copolymer. In fact, the probability model developed by Nicely et al [90] which predicts the NMR data, shows that for PAB contents below 60 mole percent the deviations of the sequences from those of a random sequence are so small that they can be considered to be negligible. Even for the copolymer containing 60 mole percent PAB, the deviation from the random model is small and extended blocks of PAB are unlikely to be the reason for any unusual properties such as domains found by etching.

3. Thermal Analysis

In order to get a better perspective of the thermal transitions that occur in the PET/PAB copolymers, it would be appropriate to distinguish between the morphologies of
conventional linear polymers like PET and that of rigid main chain nematic polymers. As illustrated by Blundell [113], this can be schematically represented as shown in Figure 5. Conventional semicrystalline polymers like PET are a complex mixture of amorphous and crystalline phases. It is generally assumed that their morphology consists of thin crystalline lamellae separated from each other by amorphous layers and connected by tie molecules through the amorphous phase. The thickness of these lamellae is typically of the order of 100 Å and the polymer crystals are oriented perpendicular to the plane of the lamellae. This is possible only if the polymer molecules are folded back and forth several times at sharp angles. Figure 5 (a), shows the structure of a typical chain folded lamellar crystal at a temperature below the melting point. Above the melting temperature, unfolding of the chains within the lamellae leads to a system of randomly entangled chains giving rise to an amorphous or isotropic liquid (Figure 5 (b)). The melting transition then, as recorded on a DSC, would represent the enthalpy change associated with structural changes occurring from the crystal state to the isotropic state. In rigid chain nematic polymers, as illustrated in Figures 5 (c) and 5 (d), there is no significant change in the overall chain configuration as the temperature is raised above the melting temperature ($T_m$). The main motion that becomes available to the chains on melting would be
longitudinal translation, chain rotation and minor internal chain motions that are not capable of altering the overall configuration. The attainment of a rigid state in the interval between $T_g$ and $T_m$, can be attributed to the presence of crystallites linking together the rigid chains. Thermal scan of such a polymer on the DSC should then give an endothermic transition related to the melting of these crystallites. As discussed by Blundell [113], rigid chain nematic polymers usually exhibit very low enthalpies of fusion. The main cause for these low enthalpy values is the imperfections within the crystal lattice causing poor cohesion of chains.

For the case of the Eastman PET/PAB copolymer, one would expect the flexible PET segments in the copolymer to crystallize in the form of chain folded lamellar crystals. The melting of these crystals should then give a DSC endotherm at a temperature below the melting point of PET homopolymer (260 °C). As stated by Economy et al [152], the PAB homopolymer is a crystalline solid consisting of a double helical structure made up of two polyester chains with reversed head-to-tail order. The homopolymer shows a reversible high temperature crystalline transition at 325-360 °C. This is not a transition to an isotropic state but instead represents some loss of crystal order. The overall hexagonal symmetry of the structure is still retained. Therefore in a copolymer of PET/PAB, where one would expect
a certain distribution of PET and -PAB-PAB- segments, at temperatures below 260°C, the melting endotherm as recorded on a DSC would correspond only to the PET crystallinity. Unless higher temperatures are reached, the crystallinity due to the -PAB-PAB- segments would not be detected on the DSC.

Thermal analysis of the PET/PAB copolyester was first performed by Jackson and Kuhfuss [2] at Eastman Kodak. Their DSC results indicated that the glass transition (Tg) increased as the PAB content increased up to 30 mole percent. For compositions containing 30-50 mole percent PAB, two Tg's were observed, the upper Tg according to the authors being presumably due to short PAB segments. A Tg was not observed when the PAB content of the copolyester was increased above 50 mole percent. A gradual decrease in the crystalline melting point was observed as the PAB content was increased up to 50 mole percent. Above this composition, the melting points could not be detected except for very weak endotherms for copolymers containing 70 and 80 mole percent PAB.

Krigbaum and Salaris [98] studied the thermal properties of the PET/PAB copolymer containing 30 mole percent of PAB. On the basis of polarizing microscope and DSC experiments, they concluded that this copolymer exhibited a crystal to nematic transition at 207°C and a
nematic to isotropic transition at 244 °C. However, subsequent work by Lader and Krigbaum [99] indicated that the endotherm at 244 °C was actually a crystal to isotropic transition associated with the melting of crystallites formed during a high-temperature annealing step.

Multiple endotherms have been observed by Viney and Windle [20] for the PET/PAB copolyesters containing 60 mole percent of PAB. According to these authors, a transition at 70 °C suggested a glass transition corresponding to a discontinuous increase in specific heat. A marked endothermic peak at 190 °C corresponded to the onset of mobility representing a possible "melting out " of regions of local order which, at low temperatures , determines the microstructure. Another endotherm was detected at 340 °C followed by isotropization with significant sample degradation at 420 °C. As explained later, optical study of this sample indicated that the endotherms at 190 and 340 °C were transitions to the "smectic C" and nematic mesophases respectively. A small endotherm at 250 °C was attributed to the loss of correlation between segregated PAB segments.

Joseph et al [93,94] performed DSC studies on compression moulded films of the PET/PAB copolyesters containing 30-80 mole percent of PAB. Their results indicated that while the glass transition Tg remained unchanged with the addition of PAB, the crystallization
temperature $T_{ch}$ (on heating) and the melting endotherm peak ($T_m$) was lowered with respect to PET. The near constant $T_g$ with the addition of stiff PAB units along the backbone suggested a non-random chain structure. This conclusion was further supported by the fact that the experimental melting points were higher than the corresponding values predicted by Flory's theory for random copolymers [8]. The lowering of $T_{ch}$ was speculated to be due to a nucleating effect caused by the PAB moities, while the decrease in $T_m$ was caused by a partial diluent effect. Also, it was apparent that as the PAB content increased, the enthalpy of crystallization and hence, the degree of crystallinity decreased systematically. This result, according to the authors, is not surprising since the observed crystallization is due to PET and, as the PET content is lowered, the overall degree of crystallization is also lowered. A small endotherm was observed for samples molded at 235°C containing 30, 40 and 60 mole percent PAB, slightly beyond the major melting endotherm. This was associated to the melting of a crystalline phase rich in PAB, that also contained low levels of PET. On rescanning these samples, they observed that the small endotherm was no longer present. Moreover, the PAB crystallinity was absent in the films molded at 260 and 280°C, indicating that a morphological rearrangement occurred at higher temperatures. This result was consistent with their findings from optical microscopy studies.
Wunderlich and coworkers [96,97] have made a detailed study of phase transitions occurring in PET/PAB copolyesters. By thermal pretreatment they produced a series of samples of different crystallinities which were then scanned to systematically determine the effect of copolymer composition on glass transition $T_g$ and melting. Their results indicated that the $T_g$ remained nearly constant with increasing PAB concentration. Moreover, as expected for the shorter and more rigid PAB repeating unit, the heat capacity increase at $T_g$ was much lower. In contrast to the $T_g$, the melting point $T_m$ and the overall crystallinity decreased with an increase in PAB content. However, the $T_m$ decrease was less than that for eutectic PET copolymers, suggesting a partial isodimorphism or a partial eutectic phase separation in the PET/PAB copolymers. Copolymer samples containing more than 65 mole percent PAB clearly showed a tendency to phase-separate into melts of two phases with glass transitions differing by 100 °K, of which the higher $T_g$ phase shows polyoxybenzoate behaviour. The transition to the isotropic phase could not be analyzed because of prior decomposition.
4. Identification of mesomorphic phase transitions

Due to its extremely promising mechanical properties, the morphology of PET/PAB copolymer containing 60 mole percent PAB has been studied by several investigators [20,93,104] in order to correlate its physical and structural characteristics. Mackley et al [104] have studied the optical texture of these copolyesters heated up to 350°C between glass slides. At 220°C, the sample was observed to become mobile and further heating to 350°C resulted in the emergence of dark threads and ringed domains. According to the authors, the threads were probably associated with line singularities known as disclinations, caused by rapid changes in refractive index. The ringed domains occurring at elevated temperatures were thought to be associated with some form of a chemical or physical segregation process due to differences in chemical composition or molecular weight.

Following the work of Mackley et al., Viney and Windle [20] made a comparison of the optical textures exhibited by the PET/PAB copolyester (60 mole % PAB), at different temperatures with textures previously reported for low molecular weight liquid crystals. By heating the copolyester sample at 20°C per minute and examining it in transmitted polarized light, they were able to observe the microstructure changes as a function of temperature. Between 190 and 340°C the equilibrium microstructure as seen between
crossed polars consisted of discrete groups (or knots) of dark extinction bands, separated by regions of generally low contrast. Based on comparisons with low molecular weight liquid crystals, this texture was identified to be "interrupted schlieren", a texture normally characteristic of the smectic C modification. When held at 340 °C the birefringent phase showed a transient texture known as the "myelin" texture normally seen only in small molecules. Between 340 and 350 °C, the extinction bands became continuous, giving rise to a "continuous schlieren " texture. Beyond 350 °C, the isotropic phase was nucleated. However, at the same time the optical texture showed disclinations of strengths ± 1/2, typical of liquid crystals in the nematic modification. The nematic phase coexisted with the isotropic phase until 420 °C at which the entire specimen became isotropic, accompanied by significant degradation. A DSC trace of this copolyester showed endotherms at 190, 340 and 420 °C, each corresponding to the respective phase transition observed in the optical study. The authors, however, have pointed out that the mesophase existing above 190 °C, which they identified as being smectic C, could have actually been a biaxial nematic. Such a proposal is more compatible with NMR [17] and electric field induced flow instabilty observations [105], both of which have been interpreted as implying a nematic phase at all temperatures where the material is liquid crystal-like.
Joseph et. al. [93,94] reported that optical study of the copolyester containing 60 mole percent PAB indicated structural rearrangements to occur at about 220-225°C. At 250°C, a distinct two phase structure was formed. The region which showed liquid crystalline texture and greater depolarization was speculated to be richer in ordered PAB units. On cooling the sample back to room temperature, the mesophase texture was preserved and was found to be similar to the nematic-like texture observed by Mackley et. al. [104].

Based on DSC and optical studies performed by several investigators, the thermal properties of PET-PAB copolymers can be summarized as follows:

1. The glass transition temperature ($T_g$) remains nearly constant for the copolymesters containing 30-80 mole % PAB. Some of these copolymesters exhibit two $T_g$'s, the upper $T_g$ is presumably due to short, rigid PAB segments.

2. The DSC endothermic peak associated with the melting of PET segments which crystallize in the form of chain folds, represents the temperature $T_m$ at which the melt becomes mobile and begins to exhibit mesophase textures. Hot stage microscopy study of these melts indicate that these textures are characteristic of liquid crystals in the smectic C or nematic modifications.

3. An increase in PAB content in the copolymer causes a
lowering of the crystallization temperature $T_{ch}$ (on heating) and the melting temperature $T_m$. The lowering of $T_{ch}$ is speculated to be due to a nucleating effect caused by the PAB moieties, while the decrease in $T_m$ is caused by a partial diluent effect. Also, the enthalpy of crystallization decreases systematically as the PAB content is increased. This is due to the fact that the observed crystallization is due to PET and, as the PET content is lowered, the overall degree of crystallization is also lowered.

(4) Copolymers containing more than 60 mole percent PAB show a tendency to phase-separate into melts of two phases, one phase speculated to be rich in PET segments and the other rich in ordered PAB units.
5. X-Ray Analysis

In order to obtain a better understanding of the crystal structure and molecular orientation of the PET/PAB copolyester systems, x-ray scattering and diffraction studies have been carried out by several investigators [93,94,106-110]. Similar studies have been made by researchers for other mesomorphic polymer systems [35,108 111-115].

Joseph et. al. [93,94] carried out wide-angle x-ray scattering (WAXS) studies of PET/PAB copolyester films that were compression molded at three different temperatures and quenched. Films molded at 235 °C and quenched, showed scattering patterns that appeared mostly diffuse except for a few weak, sharp rings obtained in the lower PAB content materials. As the amount of PAB was increased, the overall diffuseness of the scattering pattern decreased indicating an increase in order caused by the rigid PAB units. The pattern of the film containing 60 mole percent PAB showed a distinct ring corresponding to the d-spacing of pure PAB (4.54 Å). Very little PET crystallinity was observed. In samples annealed at 150 °C , strong reflections corresponding to PET crystallinity were observed in the low PAB content materials. In films molded at 260 °C and 280 °C, no PAB crystallinity was observed even for the samples containing
60 mole percent PAB. This indicated a complete melting out of the PAB crystals at higher temperatures. Similar WAXS measurements have been performed by Acierno et. al on this copolyester in the fiber form [107].

Viola et. al. [106] have used WAXS studies to determine the effect of shear and extensional flow on molecular orientation for the PET-PAB copolymers containing 60 and 80 mole percent PAB. Their studies have indicated that extensional flow had a greater capacity for orienting such materials than shear flow. Samples annealed at their softening points showed no significant loss of orientation indicating that once orientation was produced it remained in the melt for a long period of time. Wang and Yeh [109], have studied the effect of composition on molecular alignment in PET/PAB copolymers by means of differential radial distribution function (DRDF) analysis of WAXS data. Their study indicated the presence of locally aligned chain segments in these copolymers. As the PAB content was increased from 30 to 60 mole %, a substantial improvement in the lateral chain alignment was observed. Martin and Stupp [110], used X-ray diffraction methods to study the effect of electric fields and mesophase ageing on films made from the PET-PAB copolymer containing 80 mole % PAB. They observed that electric fields enhanced molecular orientation when the exposure to the field began below the solid-to-mesophase
6. Rheology

Rheological studies performed by Jackson and Kuhfuss [2] indicated that the PET/PAB copolymers show unusual behaviour with respect to their melt viscosities. Specifically, Figure 6 shows that the melt viscosity increases initially with PAB and then starts to decrease at a PAB composition of 30 mole percent. This corresponds to the onset of liquid crystalline behaviour, as has been confirmed by the presence of optical anisotropy at this composition. The viscosity reaches a minimum at a PAB content of about 60 mole percent and it is interesting to note that it represents a value approximately two orders of magnitude lower than that for the PET homopolymer. Above 60 mole percent PAB, the viscosity is observed to increase as a result of the stronger associated structure of the PAB component leading to possible crystallinity of these units. Another interesting observation, as shown in Figure 7, is that with increasing PAB content, the polymer becomes shear sensitive at lower shear rates. This behaviour in the melt is due to the increasing presence of oriented, rigid macromolecular chains in the liquid crystalline phase of the copolymer. In general, macromolecules in the nematic state
are readily oriented under shear stress.

Jerman and Baird [116] studied the rheological properties of the 60 and 80 mole percent PAB copolyesters and also observed very low viscosity values compared to pure PET. Also, die swell was observed to increase with processing temperatures and a value of approximately 1 was observed at low processing temperatures. Moreover, it appeared that die swell was less shear sensitive at lower temperatures.

Baird and Wilkes [117] have compared the die swell behaviour and primary normal stress values of the 80 mole percent PAB material and found them to be in agreement. Both, the die swell and the primary normal stress difference, were observed to reach a minimum at 305 C. An increase in both these values at higher temperatures was speculated to be due to an increase in mobility of the molecules.

Rheological studies performed by Wissbrun [118], on the 60 mole percent PAB material, indicated that this material has long relaxation times estimated from the shear rate dependence of viscosity. The melt rheology was found to be sensitive to temperature and also on thermal history. Similar studies have been made by Done and Baird [119] for the 60 and 80 mole percent PAB materials. The dependence on
thermal history has been attributed to the destruction and/or growth of crystallites from blocks of one comonomer.

7. Mechanical Properties

As reported by Jackson and Kuhfuss [2], the mechanical properties of injection molded specimens of PET/PAB copolyesters were found to be exceptionally high. As shown in Figure 8, mechanical properties such as tensile strength, flexural modulus and impact strength go through a maximum in the 60 mole percent PAB region. The unusually high mechanical property values have been explained in terms of the high degree of orientation in the direction of the melt flow. Also, the temperature at which the copolyesters were injection molded was found to affect the orientation of the polymer chains and hence the mechanical properties. As the temperature was increased, the melt viscosity decreased, the speed of the polymer melt injected into the mold increased, and the orientation of the polymer chains therefore increased. As expected, higher molecular weights gave higher values of tensile strength, stiffness, and impact strength for the 60 mole percent PAB copolymer. For example, as the inherent viscosity (IV) increased from 0.42 to 0.72, the tensile strength increased from 14,700 psi to 37,900 psi. However, the mechanical properties of these
polymers was found to be highly anisotropic with for example, the flexural modulus along the flow approximately 12 times that of the modulus across the flow.

C. Depolymerization of Poly(ethylene terephthalate)

Depolymerization of Poly(ethylene terephthalate) (PET) by glycolysis in an excess diol, such as ethylene glycol, propylene glycol, and di-ethylene glycol, has been studied for many years. Most of these studies are proprietary, related to industrial production of polyols and unsaturated polyesters, and are only revealed in a few patents [120-123]. Reacting as much to profit potential as to threats of sterner anti-litter legislation, several companies are fine tuning their recycling technology for recovering bottle-grade PET for re-use. Last year, beverage bottle manufacturers used close to a billion pounds of virgin PET of which almost 20% was recovered and reused. Recently, Vaidya and Nadkarni [124,125] reported the preparation of unsaturated polyester using the products of PET waste glycolyzed by propylene glycol in the presence of zinc acetate as catalyst. They showed that the glycolyzed products consisted mostly of hydroxyl-terminated monomer, bis-hydroxyethyl terephthalate (BHET), and small quantities of dimer and trimer. The extent of depolymerization was observed to increase with the amount of propylene glycol.
They repeated the glycolysis study using ethylene glycol [126] and observed that in excess ethylene glycol (EG), the glycolyzed products contained predominantly BHET.

PET glycolysis which involves a transesterification reaction between PET and ethylene glycol can be described as follows:

$$\text{PET + EG (excess) } \rightarrow \text{HOCH}_2\text{CH}_2\text{OC}(-\text{O})\text{-COCH}_2\text{CH}_2\text{OH (BHET)}$$

+ Higher oligomers (small quantities)

+ unreacted EG

The extent of depolymerization depends on the amount of excess EG used, the reaction temperature and the catalyst. Though high temperatures favor the reaction rate, glycolysis is normally carried out close to the boiling point of EG (197 °C) so as to minimize losses due to volatalization. If higher temperatures are to be used then a glycol recovery system has to be provided to make the depolymerization process economically viable. Metal acetates have been found to be effective in catalyzing transesterification reactions and are therefore generally used in the depolymerization process.
A. Depolymerization of Poly(ethylene terephthalate)

Two grades of reclaimed poly(ethylene terephthalate) (PET) flakes (clear and green) were obtained from the pilot plant of the Center for Plastics Recycling Research at Rutgers University and from independent private companies. Their typical intrinsic viscosity was stated to be around 0.65 dl/g corresponding to a number average molecular weight of about 28,000 [127].

In all experimental runs, 96 g. of PET flakes (clear), equivalent to 0.5 moles of repeating unit (molecular weight 192) in the PET chain, was added to 124 g. of ethylene glycol (EG), such that the molar ratio of PET repeating unit to EG was 1:4. The mixture, together with 0.48 g. of catalyst (0.5 % by weight of PET), was charged to a four-necked reaction kettle fitted with a stirrer, reflux condenser, nitrogen inlet, and thermometer. A microprocessor-based temperature controller connected to a K-type thermocouple, was used to regulate power to the heating mantle so as to maintain reaction temperature at the desired level. The experimental set-up is illustrated in Figure 9. Initially, the temperature was raised to 190°C in 30 minutes and then depolymerization via glycolysis was
out under a nitrogen atmosphere for a period of 8 hours. Small samples were removed periodically from the reactor to monitor the progress of the reaction. Four different metal acetates were used as catalysts namely, Pb(CH₃COO)₂·3H₂O, Co(CH₃COO)₂·4H₂O, Mn(CH₃COO)₂·4H₂O, and Zn(CH₃COO)₂·2H₂O. A single run was also performed without a catalyst. In order to find out whether clear and green reclaimed PET might yield different glycolyzed products, one run was also performed with green reclaimed PET using lead acetate as catalyst.

At the end of eight hours, the contents of the reactor were allowed to cool to room temperature under nitrogen. About one liter of chilled distilled water was added and the solution was vigorously agitated. The solution was filtered and the filtrate containing free glycol, the water soluble catalyst and small quantities of oligomer (mainly monomer) was discarded. The residue was transferred to a beaker containing 500 ml. of distilled water and the suspension was boiled with stirring to extract the monomer bis-hydroxyethyl terephthalate (BHET). While still hot, the suspension was quickly filtered and the filtrate was cooled in an ice bath to precipitate out fine, white crystals of BHET. The BHET crystals were filtered out and dried overnight in a vacuum oven at 50°C. Melting point measurements by DSC confirmed that these crystals were indeed that of BHET as expected.
B. Hydroxyl value determination

Samples that were periodically removed from the reactor were analyzed for their hydroxyl value as follows: Each sample was separated into two parts, the first (fraction #1) representing the reaction product before free glycol removal and the second (fraction #2) from which free glycol was to be removed before hydroxyl value determination. Fraction #2 was added to 150 ml. distilled water and the solution was vigorously agitated. The water would dissolve the free unreacted glycol, the water soluble catalyst and small amounts of PET oligomers (mainly BHET). After filtration, the small amount of dissolved PET oligomers were recovered from the filtrate by concentration via boiling and then precipitation by chilling. The residue obtained upon filtration was combined with the residue from the first filtration and will henceforth be labelled as the glycolyzed product (GP). The GP was dried overnight under vacuum at 60°C and then analyzed for its hydroxyl value.

In one of the runs, a part of fraction #2 was further separated into three fractions as follows: First, fraction #2 was added to about 100 ml of distilled water and vigorously agitated. As before, after filtration, the small amount of dissolved PET oligomers was recovered from the filtrate by concentration via boiling and then precipitation
by chilling. This residue obtained upon filtration will be henceforth named as the M fraction. The residue from the first filtration was added to boiling water to extract the BHET monomer. The hot solution was filtered and the filtrate was immersed in an ice bath to precipitate out the monomer. The white crystals which precipitated out were dried overnight under vacuum at 60 °C and will henceforth be labelled as the MC fraction. The residue from the boiling suspension was washed with boiling water and filtered several times. The resulting residue was oven dried as before and will henceforth be labelled as the O fraction. The M, MC, and O fractions were analyzed using end-group analysis, DSC and liquid chromatography (HPLC).

The hydroxyl values of fraction #1, the glycolyzed product (GP), and the M, MC, and O fractions were determined by end-group analysis according to ASTM D2849 Method A. This method is briefly described as follows. About 0.5 g. of sample was accurately weighed and added to 10 ml. of acetylating solution, containing 88:12 (v/v) pyridine and acetic anhydride, in a 50 ml round-bottom flask. The flask was fitted with a vertical reflux condenser and heated with stirring in a boiling water bath for about two hours. The mixture was then cooled to room temperature and hydrolyzed by 100 ml. of chilled distilled water in another flask. Under vigorous stirring, 20 ml. of benzene was added. The resulting solution was titrated against 0.1 N KOH standard
using phenolphthalein as indicator. A blank run, i.e. without the sample, was also performed and the hydroxyl number in mg. of KOH/g. sample was calculated as follows:

\[
\text{Hydroxyl \#} = (56.1)(A-B)(\text{Normality of KOH})/\text{mass of sample}
\]

where 

\[A = \text{ml. of KOH required to titrate sample},\]

\[B = \text{ml. of KOH required to titrate blank}\]

C. Preparation of Liquid Crystal Polyesters

A mixture of BHET (10-35 mole%), terephthalic acid (TA) (15-60 mole%) and 500 ppm Sb\textsubscript{2}O\textsubscript{3} (w.r.t BHET) was placed in a 150 ml. flask equipped with a stainless steel stirrer and a nitrogen inlet. The nitrogen outlet was connected to a small condenser, which led to a receiver for collecting acetic acid and other distillates from the reaction. The receiver was connected through a three-way valve to a vacuum pump. The complete experimental set-up is as shown in Figure 10. The reaction flask was evacuated and purged with nitrogen to remove any traces of air. It was then immersed in a molten NaNO\textsubscript{2}-KNO\textsubscript{3} salt bath maintained at 280 C and the reaction was allowed to proceed under nitrogen with stirring for 90 minutes. A microprocessor-based temperature controller connected to a K-type thermocouple, was used to regulate power to the heating mantle so as to maintain reaction temperature at the desired level.
At the end of 90 minutes, the nitrogen flow was halted and the stirred reaction system was placed under vacuum for about 2 minutes. The vacuum was then released, stirring stopped and the system was allowed to cool under nitrogen. The white, brittle reaction product was easily loosened with a spatula and transferred to a large agate mortar. Para-acetoxybenzoic acid (PAB) (30-70 mole%) was added and the mixture was thoroughly ground until uniform. The mixture was now transferred back to the flask, the flask was evacuated and purged with nitrogen as before and then immersed in the salt bath maintained at 280° C. Acetic acid was allowed to distill out slowly for two hours as the reactants were stirred under nitrogen. The nitrogen flow was then halted, a vacuum of about 0.5 mm was applied and the reaction allowed to proceed for one more hour at 280° C. Temperature was now raised to 300° C in a few minutes and the reaction continued for two more hours. The reaction melt was clearly turbid and on cooling under nitrogen, a tan colored solid was formed. The material was observed to have strong adherence to glass, and hence the flask had to be carefully broken so that the polymer could be recovered.

The polyesters were identified according to the mole percent of each component in the reaction mixture as shown below. Series I polyesters contain a 10 mole% of BHET whereas in series II polyesters mole percent of BHET is varied between 15 and 35.
The actual composition of the polyesters was determined by NMR analysis as will be discussed later.

D. Sample Purification

The samples were ground in an agate mortar and added to an excess of 60 : 40 (w/w) phenol/1,1,2,2-tetra-chloroethane solvent. The solutions were heated to 60°C with stirring for 3-6 hours. For series I polyesters, in all cases, two fractions of the polymeric products were
obtained, one soluble and the other insoluble in the solvent. Each was isolated and purified by either reprecipitation or by suspension respectively, in a large excess of methanol. Series II polyesters were almost completely soluble in the TCE/Phenol solvent mixture and the polymers were recovered in a similar manner. The polymer fractions were dried overnight in a vacuum oven at 80°C.

E. Chemical structure by NMR spectra analysis

Proton NMR spectra of the purified polymers were determined in (70:30 v/v) deuterated chloroform / trifluoroacetic acid solvent mixtures. The proton spectra, at 300 MHz, were obtained on a GE model QE-300 NMR spectrometer at Hunter College of the City University of New York. The spectrometer was equipped with an integrator for quantification of the NMR spectra.

In each case, 20-25 mg. of purified (and dried) samples were dissolved in 1 ml. of the deuterated solvent mixture. In most cases, the solutions were clear and the polymer remained in solution. The solutions were filtered, placed into 5mm NMR tubes and the spectra obtained at room temperature.

F. Intrinsic Viscosity Measurements

Dilute solution viscosity of the polymers was
measured with a Cannon-Ubbelohde Four-Bulb Shear Dilution Viscometer. The polymer samples (purified and dried) were accurately weighed and dissolved in known amounts of 60 : 40 (w/w) phenol/1,1,2,2 tetrachloroethane solvent mixture to obtain solutions of concentration between 0.5 to 0.8 g./dl. The solutions were allowed to cool to room temperature and then filtered before viscosity measurements.

For each run, the viscometer was cleaned with acetone and dried by passing clean, dry filtered air through the instrument. The viscometer was charged with 10 ml. of the pure solvent and then placed in a constant temperature water bath at 25°C (± 0.1°C) for approximately 20 minutes (to attain thermal equilibrium). The efflux time of the solvent was measured for each bulb to the nearest 0.01 second. The solvent was then replaced by the polymer solution and its efflux times were measured in a similar manner for each bulb. The solution was then successively diluted with 10 ml. of pure solvent and the efflux times at each dilution were determined. The efflux times were converted to kinematic viscosities by multiplying them by their respective bulb constants. Intrinsic viscosities of the polymer samples were calculated using the Huggins equation [128] and standard methods described in literature [129].
G. Chemical Structure by Infrared (IR) Spectroscopy

Infrared spectra of the polymer samples (BTP series) as well as that of PET, BHET and the PET dimer were obtained on a Perkin Elmer Model 1310 Infrared Spectrometer. The samples were thoroughly dried at 70°C in a vacuum oven for 24 hours before analysis. About 1 mg. of each sample was ground in an agate mortar with about 100 mg. of pure KBr crystals. The samples were pelletized using a Model 6102 Beta-Press. The barrel containing the pellet was mounted on the cell slide of the spectrometer and IR spectra were obtained at scan times of 3 or 12 minutes.

H. Differential Scanning Calorimetry (DSC)

Thermal studies using a Perkin-Elmer DSC-2 calorimeter were done on the polymer samples (BTP series) and on PET and its oligomers. Transitions that could be measured were - the glass transition temperature (Tg), crystallization temperature (Tc) and the melting temperature (Tm). Areas under the exothermic and endothermic peaks, representing enthalpies of crystallization and melting respectively, were measured using a Lasico Model L20M compensating polar planimeter. Indium (ΔHf = 6.8 cal/g) was used as the calibration standard.

Samples (5-15 mg.) which had been dried thoroughly in a vacuum oven at 70°C for 24 hours, were encapsulated in
aluminum pans and analyzed in a nitrogen atmosphere. Except for the case of the PET oligomers, all thermal or mechanical history in the sample was considered to be erased by the first step in the experimental sequence, in which the sample was held at 280 °C for 6-8 minutes. The samples were then cooled to 50 °C at 320 °C/minute or quenched in liquid nitrogen. The PET oligomers were analyzed without prior thermal treatment. A scan rate of 20 °C/minute was used in all cases. Depending on the sample, a sensitivity of 1, 2 or 5 mcal./second was used.

I. Optical studies

Optical studies were performed using a Bristoline optical microscope equipped with a rotating polarizer, a fixed analyzer, a high-intensity illuminator, and a metal platform to carry the hot stage. A Nikon SMZ-10 camera with a Model AFX microprocessor based exposure controller was connected to the eyepiece of the microscope to record the transitions occurring as a function of temperature. The BTP polymer series were examined for their mesomorphic textures whereas PET and its oligomers were scanned for their typical crystallization mechanisms.

In all cases, the samples were sandwiched between glass covers which were thoroughly pre-cleaned. Heating rates were variable, with high rates (10-15 °C /minute) used at
temperatures far away from transitions and low rates (2-5°C/minute) when approaching transitions. The power to the hot-stage could also be regulated to maintain the temperature of the sample approximately constant. The samples were examined, both during heating and cooling. For the BTP series, it was necessary to gently press the glass covers at temperatures close to the melting point, in order to obtain a film thin enough to exhibit optical birefringence.

J. X-Ray Diffraction

X-ray powder determinations were carried out on a Philips X-ray diffractometer. The source of radiation was copper with a nickel filter. Typically, the operating conditions for the diffraction generator were a 35 kV voltage and a beam current of 15 mA. The samples were thoroughly ground in an agate mortar, dried at 90°C under vacuum and the required thermal history was introduced into the sample before the x-ray analysis. The sample to film distance was 5.75 cm and the exposure time to the x-ray beam was 16 hours.

H. Chromatographic methods

To determine whether the glycolyzd product from the depolymerization of PET contained oligomers other than BHET
and dimer, it was analyzed by HPLC using a Scientific Systems Model 510 isocratic liquid chromatograph. The chromatograph was equipped with a Micrometric Model 787 variable UV/Vis detector set at 254 nm. The analysis procedure was essentially similar to that by Cimecioglu, et al [130], who studied the properties of PET oligomers.

Sample solution was prepared by dissolving about 5 mg. of the glycolyzed product in 10 ml. of chlorofrom with 10 % isopropanol (containing 10 % concentrated NH$_4$ OH), which is used as the mobile phase. It was injected into a 10 μl sample loop and then swept into a Spectra Physics Spheri-5 Silica (5 μm size) normal phase column at a mobile phase flow rate of 1 ml/minute. HPLC scans of purified BHET and dimer were also performed in a similar manner. All scans were carried out upto 10 minutes.

Gas Chromatographic techniques were used to measure the amount of unreacted ethylene glycol (EG) at the end of the depolymerization reaction. The gas chromatograph used was a Hewlett-Packard Model 5730A GC equipped with a flame ionization detector and a 0.31 mm I.D x 25 m capillary glass column. The column was packed with fused silica coated with a liquid film of CP wax 57. A Hewlett-Packard Model integrator was used to quantify the results. The column was maintained at a constant temperature of 210°C and nitrogen at a pressure of 30 psig was used as a carrier gas.
Calibration was performed using a series of ethylene glycol-distilled water standard mixtures of known compositions.

A known amount (about 1 gram) of the depolymerization reactor product was dissolved in 25 ml. of chilled distilled water in a 50 ml beaker. After prolonged stirring, with the beaker immersed in an ice bath, the solution was filtered to remove all unreacted glycol, catalyst and possibly minute quantities of BHET. Two μl of the filtrate was injected with a syringe into the column and the amount of free glycol was determined by integrating the peak areas. The measurements were repeated a few times to obtain reproducible results.
RESULTS AND DISCUSSION

I. Depolymerization of PET

1. Effect of catalysts on depolymerization

In Figure 11, the hydroxyl number of glycolyzed product obtained from clear recycled PET is plotted against glycolysis time for the four catalysts tested. It is clear that in all cases, the hydroxyl number increases with reaction time, approaching a steady value eventually, and that different catalysts definitely have significant effects on the rate to attain this equilibrium value. The theoretical hydroxyl numbers of pure BHET and dimer can be calculated to be 441.5 and 251.3 mg KOH/g, respectively. The ranges of hydroxyl numbers depicted in Figure 9 all fall between these two values, implying that the glycolyzed product consists of a mixture of BHET and oligomers. While the composition of the glycolyzed products, as measured by the hydroxyl number at equilibrium, was about the same (within experimental errors) for the four catalysts, the relative effectiveness of the four catalysts used, in terms of the initial rate of depolymerization, was as follows: Zn$^{2+}$ > Pb$^{2+}$ > Mn$^{2+}$ > Co$^{2+}$. This order of catalytic activity is comparable to the results of Tomita [131] who studied the effects of several metal acetates on the polycondensation of
In Figure 12, the glycolysis reactions of clear and green recycled PET are compared. It shows that within experimental errors, these two types of recycled PET yielded practically similar glycolyzed products and showed analogous glycolysis kinetics. Therefore the pigment present in the green recycled PET apparently does not affect the extent of depolymerization, although it tends to discolour the glycolyzed products, unless an extra extraction step is taken to separate it.

2. Hydroxyl number of PET oligomers

The hydroxyl numbers of the M, MC, and O fractions were determined to be 436, 420.84, and 254 mg KOH/g, which are very close to the respective hydroxyl numbers of BHET (441.5) and dimer (251.3). The fact that the hydroxyl number of the MC fraction was lower than that of the M fraction implies that the oligomers, especially the dimer, are soluble in boiling water to some extent, but not at all in room temperature water.

3. Differential Calorimetric Studies

Figure 13 displays the DSC scans of the M and O fractions as well as of the glycolyzed products, at a heating rate of 10°C/min. The melting onset temperatures of the M
and O fractions are, respectively, 107 and 155°C, and peak temperatures are 110.5 and 162°C. Complete melting of these fractions occurs at 112 °C and 168 °C respectively. These results agree favorably with the known melting point data (BHET 109-110°C ; dimer 170-174°C) reported in the literature [122,131-133]. On the other hand, the DSC scan of the glycolyzed product consists of two endothermic peaks: the first peak, centered at around 106°C, can be reasonably associated with the melting of BHET, whereas the second peak, centered at around 148°C, is quite broad and hence is not readily identifiable with the melting of dimer. Thus, if the glycolyzed product can be assumed to consist predominantly of BHET and dimer, as indicated by the melting points and hydroxyl numbers of the M and O fractions, then its DSC scan seems to suggest that there exist some interactions between the monomer and dimer at elevated temperatures. One possible explanation would be that the BHET could act as a diluent in depressing the melting point of the dimer substantially.

4. Chromatographic studies

Figures 14(a) and (b) show the HPLC results for the M and O fractions, respectively. In either case, only one dominant peak was detected, although the M fraction revealed
a small but conspicuous peak at a retention time corresponding to that of the O fraction (2.50 min). This implies that the dimer has a slight solubility in boiling water and can not be completely removed by repeated separation. Figure 14(c) shows the HPLC of the glycolyzed product with two peaks at retention times of 2.5 and 2.75 min., corresponding to those of the O and M fractions, respectively. All HPLC scans were carried out up to ten minutes and no other peaks were detected. If there were higher (linear) oligomers, they would have retention times shorter than that of dimer [134]. Therefore, if they did exist in the glycolyzed products, their concentrations were too minute to be detected.

Using the calibration curve obtained from the standard ethylene glycol-distilled water solutions, the amount of free (unreacted) glycol at the end of the depolymerization reaction (for each of the four catalysts used) was estimated by peak area integration. Free glycol values were converted to glycol reacted values and are compared in Table 4 with the values obtained from end-group analysis and from a model proposed in this study (discussed later). In short, however, about 25% of the original ethylene glycol was consumed which agrees well with the stoichiometric amount as stated by Ostrowski [122].
5. Infrared analysis

In order to confirm that the products of depolymerization of PET were indeed BHET and dimer, IR analysis of these materials was carried out and their spectrum was compared to that of PET. The infrared absorption spectrum of BHET, dimer and PET is interpreted by assignment of the absorption bands to atomic groups in the molecule. The spectra are shown in Figures 15 to 17 and based on IR data in published literature [135-137], assignments of absorption peaks to the corresponding vibration modes are made, as shown in Table 4. Depending on their relative intensities, absorption peaks are named very weak, weak, medium or strong.

Except for a slight shifting of the peaks (± 10 cm⁻¹) in some cases, the spectra in Figures 10-15 are almost identical, indicating that the products of depolymerization are definitely the linear oligomers of PET viz. BHET and dimer. Lin and Koenig [136] have reviewed work by other investigators that indicate that absorption bands near 1473, 1343, 973 and 848 cm⁻¹ could be assigned to the trans isomer of the ethylene glycol segment of PET, whereas, bands near 1453, 1372, 1042 and 898 cm⁻¹ represent the vibration mode of the gauche isomer of the ethylene glycol segment. On examining bands close to the ones mentioned above, it appears that for BHET, the ethylene glycol segments have
mainly a gauche conformation, whereas, in the dimer and PET, both the gauche and trans isomers seem to be present. Another interesting observation is that unlike as in PET and the dimer, in BHET the strong absorption band near 1700 cm\(^{-1}\) which represents the carbonyl group stretching vibration, shows a clear case of peak splitting. It is a known fact that the vibrations of specific molecules is often influenced by the proximity and spatial geometry of various groups surrounding them. It is possible therefore, that the gauche conformation of the ethylene glycol segment in BHET might somehow cause resonance or some other coupling interaction to occur, thereby causing the peak to split. This reasoning is merely speculative and further work would have to be carried out in order to confirm it.
6. Equilibrium Model proposed for PET Depolymerization

From experimental data presented in the last section, it is clear that the extent of depolymerization of recycled PET in the presence of any of the four catalysts tested is substantial and that the glycolyzed products consist of the monomer BHET and dimer. Furthermore, it is apparent that after a reaction time of 8 to 9 hours, the hydroxyl number of the glycolyzed product approaches a steady value intermediate between that of BHET and dimer. Since no other oligomers were detected, this would indicate that the two species viz. BHET and dimer reach a chemical equilibrium in the glycol solution.

Based on these inferences, the following model, consisting of an equilibrium reaction between BHET, dimer, and EG, is proposed for glycolysis of recycled PET:

\[ n_{\text{PET}} \text{PET} + n_{\text{EG}} \text{EG} \rightleftharpoons n_B \text{BHET} + n_D \text{DIMER} \quad (1) \]

\[ \frac{K}{2} \text{BHET} \rightleftharpoons \text{DIMER} + \text{EG} \quad (2) \]

where n's are the number of moles, subscripts B, D, and EG stand for BHET, dimer, and ethylene glycol, respectively. The equilibrium constant K is defined as,
\[ K = \frac{[D][EG]}{[B]^2} \]  

where \([.]\) is the equilibrium molar concentration. Then, from simple mole balances, it can be easily shown that

\[ a = \frac{[D]}{[B]} = \frac{M_B}{M_D} \frac{H_B - H_1}{H_1 - H_D} \]  

(4)

\[ n_B = \frac{1}{1 + 2a} \frac{n_{PET}}{n_{PET}} \]  

(5)

\[ n_D = \frac{a}{1 + 2a} \frac{n_{PET}}{n_{PET}} \]  

(6)

\[ m_{EG} = \frac{H_0m_0 - H_BM_Bn_B - H_DM_Dn_D}{H_{EG}} \]  

(7)

\[ K = a(1 + 2a) \frac{m_{EG}}{M_{EG} \frac{n_{PET}}{n_{PET}}} \]  

(8)

where \(n_{PET}\) = number of moles of PET repeating units = 0.5 moles

\(m_0\) = total mass of reacting system

\(m_{EG}\) = mass of free EG when glycolysis reaches equilibrium

\(H_0\) = measured hydroxyl number before glycol removal when reaction reaches equilibrium
$H_i$ = measured hydroxyl number of glycolyzed products when reaction reaches equilibrium

and M's are molecular weights (BHET, 254; DIMER, 446; EG, 62) and $H_B$, $H_D$, $H_{EG}$ are theoretical hydroxyl numbers of BHET(441.5), DIMER(251.3), and EG(1809.7), respectively. Then, the percentage of EG consumed, when glycolysis reaches equilibrium, is given by

$$\% \text{ EG consumed} = (1 - \frac{m_{EG}}{m_{EG}^0}) \times 100 \quad (9)$$

where $m_{EG}^0$ is the initial mass of EG used (= 124 g.). However, it was found that about 7.5 g. of EG were lost during the course of the reaction, due to incomplete reflux of EG by the condenser. Therefore, $m_{EG}$ was nominally taken to be equal to 116.5 g. Finally, given the experimentally measured value of $a$, the theoretically expected percentage of EG consumed is given by

$$\text{theoretical } \% \text{ EG consumed} = \frac{1+a}{1+2a} \left( 1 - \frac{1}{n_{PET}} \frac{M_{EG}}{m_{EG}} \right) \times 100 \quad (10)$$

where $n$ is the average number of repeating units in a PET molecule chain. For bottle grade PET (IV = 0.68 to 0.72), $n$ is greater than 100.
In Table 5, the values of a, n_B, n_D, m_{EG}, K, and the actual % EG consumed and theoretically expected % EG consumed are listed for the four metal acetate catalysts used. It shows that in all cases, while there are some variations in the compositions of BHET and DIMER in the glycolyzed products, only about 25% of the initial EG was consumed, which agrees satisfactorily with the theoretically expected values calculated from Eq.(10) (with n = 100). However, it should be noted that this value of EG consumption (corresponding to an initial weight ratio of PET to EG 43.8:56.2) contradicts the results reported by Vaidya and Nadkarni [126]. They studied the glycolysis of PET by EG in the presence of zinc acetate as catalyst, at various weight ratios of PET to EG (62.5:37.5 to 37.5:62.5). They found that in this weight ratio range, only about 4.5 to 5.5% (with respect to the total mass of the reaction) of glycol were consumed. This amount of glycol consumption can be easily shown, by simple mole balance calculation, to be unrealistically low, since they stated that their glycolyzed products consisted predominantly of BHET, especially when a high excess of EG was used.

The compositions of the glycolyzed product (BHET/DIMER in mole percent) shown in Table 4 were 79.2/20.8, 77.3/22.7, 77.3/22.7, and 75.0/25.0, respectively for zinc, lead, manganese, and cobalt acetates. Although these figures calculated from the measured hydroxyl numbers of the
glycolyzed products and based on a model of an equilibrium between BHET and dimer, have not been cross checked by other independent analyses, they do imply that the extent of depolymerization was substantial, with the products consisting mostly of monomer.

Several studies on the equilibrium of melt-polycondensation in the PET system have been reported in the literature [139-142]. Challa [139-141] performed a systematic study on the equilibrium reaction between BHET, dimer, and higher oligomers and EG, over a range of temperature and without the presence of a catalyst. He found that the equilibrium constant varied only slightly in the temperature range from 195 to 282 °C, but increased monotonically with the extent of polycondensation. Furthermore, he observed that the monomer concentration was abnormally higher than that predicted from Flory's Principle of equal reactivity. He therefore concluded that Flory's Principle did not apply to the PET system, at least was not applicable to the monomer or lower oligomers. Based on these assumptions, Challa proposed a model which showed good agreement with experimental results. Specifically, he showed that if the equilibrium constant for ester interchange reaction between polymer molecules is $1.2$, then the equilibrium constant between two monomers and a dimer and EG would have a value of $0.37$. On the other hand, Challa had
also discussed in his paper the study on the equilibrium between PET and small amounts of initially added EG and found that the overall equilibrium constant was between 0.86 to 1.1. Subsequently, Stevenson and Nettleton [142] followed Challa's techniques and studied the equilibrium reaction of trimer in the presence of antimony oxide as catalyst. They found that over the range of temperature from 231 to 251 °C, the average value of the equilibrium constant was about 0.36. While this value is somewhat lower than that obtained by Challa, which they claimed can be attributed to experimental errors, they observed that the reaction rates were faster than those in the uncatalyzed reaction and that the polycondensation rate and the redistribution rate increased with increasing catalyst concentration.

In Table 5, the equilibrium constant (K) between two BHET molecules and a dimer and EG molecules, deduced in the present study, is shown to be lying between 1.13 to 1.53 at 190 °C, versus a value of 0.37 at 262 °C obtained by Challa. This discrepancy (a factor of 3 to 4) could be explained by the fact that the amount of initially added free glycol in the present study was much higher than in any of the experiments done by Challa. While the magnitudes of the equilibrium constant K given in Table 4 for the four catalysts used are quite close, the spread in values (1.13 to 1.53) is most probably due to experimental errors, because K is expected to be very sensitive to measurement.
accuracy of the BHET, dimer, and EG concentrations.

Recently, Choi [143] carried out a detailed mathematical modeling of the melt transesterification of DMT with EG in the presence of metal acetate catalyst. He found that the degree of oligomerization depends strongly on the EG/DMT mole ratio. When this ratio is between 2.0 to 2.5, i.e. in the presence of excess glycol, the oligomers produced at high conversion of methyl ester end group are mostly dimers and the BHET concentration reaches a steady state. Thus, the model proposed in the present study, namely an equilibrium between BHET, dimer and EG, is consistent with the theoretical findings by Choi.
B. Liquid crystal Polymer studies

1. Reaction scheme for polymer formation

As mentioned in the experimental section, the polymerization reaction was carried out in two stages. In the first stage, BHET and terephthalic acid (TA) were reacted together in the presence of $\text{Sb}_2\text{O}_3$ to form low molecular weight prepolymers or oligomers. The reactants being bi-functional, chain propagation could occur at either or both ends of the chain. Depending on the molar ratio of BHET and TA in the reactant mixture, the chains could be -CH$_2$CH$_2$OH or -COOH terminated or could have an equal distribution of these endgroups. The reaction scheme for the prepolymerization is therefore as follows:

1. $n \text{ HOCH}_2\text{CH}_2\text{OC} \rightarrow \text{COCH}_2\text{CH}_2\text{OH}$ $\text{Sb}_2\text{O}_3$ 280°C

$$\begin{align*}
\text{COCH}_2\text{CH}_2\text{OH} + (n-1) \text{ HOCH}_2\text{CH}_2\text{OH} + (n-1) \text{ HOCH}_2\text{CH}_2\text{OH}
\end{align*}$$

2. $$\begin{align*}
\text{COCH}_2\text{CH}_2\text{OH} + \text{HOOC} \rightarrow
\text{COCH}_2\text{CH}_2\text{OC} \rightarrow \text{COOH} + \text{H}_2\text{O}
\end{align*}$$
At the end of the prepolymerization step, the distillate collected appeared to be a mixture of water and glycol as was evident from its slightly viscous nature. Also, IR spectra of this solution gave absorption bands characteristic of ethylene glycol. However, further work involving kinetic and thermodynamic considerations will have to be carried out in order to confirm the occurrence of the above reactions.

In the second stage of the reaction, acetic acid was allowed to distill out, with the reaction initially carried out in a nitrogen atmosphere and subsequently under reduced pressure. A reaction scheme similar to the one proposed by Jackson and Kuhfuss [2] is given below.

\[
\begin{align*}
1. \quad & 2\text{CH}_3\text{CO-} & \quad \rightarrow & \quad \text{CH}_3\text{C-O-} \\
& \quad \text{COH} & \quad \text{COH} & \quad \text{COH} + \text{CH}_3\text{COH} \\
\text{I} \\
2. \quad & \text{CH}_3\text{CO-} & \quad \rightarrow & \quad \text{HOCH}_2\text{CH}_2\text{OC-} \\
& \quad \text{COH} & \quad \text{OC} & \quad \text{OC} + \text{H}_2\text{O} \\
\text{II}
\end{align*}
\]
Chains containing -CH2CH2OH endgroups could also react with each other to form PET like segments, with the evolution of ethylene glycol. The reaction of PAB with itself, results in the formation of rigid homopolymer segments \[88,89\]. The final polyester would therefore contain segments I, II, III and IV as well as PET segments.

2. Polyester structure and composition from NMR studies

Figures 18.1 through 18.11 show the proton NMR spectra of PET and of I and series II polyesters in TFA/chloroform
solution. The spectra of the series I and II polyesters shows three distinct NMR signals and is similar to the Eastman PET/PAB copolymer spectra given by Nicely et al [90]. The signal at 4.8 ppm corresponds to the 4 methylene protons of the ethylene glycol residue -CH₂CH₂O- in the polymer chain. The 2 aromatic protons in the 3,5 positions of the 4-oxybenzoyl moiety give peaks at 7.4 ppm and 7.5 ppm. The peak at 7.5 ppm corresponds to the protons on the PAB unit which is connected to another PAB unit, whereas the peak at 7.4 ppm corresponds to the protons on the PAB unit connected to the PET residue. The peaks at 8.2 ppm and 8.4 ppm can be assigned to the 4 aromatic protons of the PET residue and the 2 protons in 2,6 positions of the PAB unit, respectively. The chemical shifts of the various protons relative to tetramethyl silane (TMS) and assignments to the corresponding molecules are given in Table 6.

Based on the assignments of the NMR signals to characteristic proton chemical shifts, the structure of the polyester series was deduced to be:

\[
\begin{array}{c}
\text{O} \quad \text{H} \quad \text{H} \quad \text{O} \\
\text{C} \quad \text{O} \quad \text{C} \\
\text{H} \quad \text{H} \\
\end{array}
\]

\[
\begin{array}{c}
\text{O} \quad \text{H} \quad \text{H} \quad \text{O} \\
\text{C} \quad \text{O} \quad \text{C} \\
\text{H} \quad \text{H} \\
\end{array}
\]

\[
\begin{array}{c}
\text{O} \quad \text{H} \quad \text{H} \quad \text{O} \\
\text{C} \quad \text{O} \quad \text{C} \\
\text{H} \quad \text{H} \\
\end{array}
\]

\[
\begin{array}{c}
\text{O} \quad \text{CH}_2\text{CH}_2\text{O} \\
\end{array}
\]

where \(x, y, z\) are the mole fractions of the PET, PAB and ethylene glycol residues in the polymer chain respectively.
If,

\[ A = \text{total intensity for the 4x phenyl protons of PET and the 2y protons in the 2,6 positions of PAB}, \]
\[ B = \text{intensity for the 2y protons in the 3,5 positions of PAB}, \]
\[ C = \text{intensity for the 4z methylene protons of the ethylene glycol residue}, \]

then, following the method given by Lenz et. al. [148], the copolymer composition was calculated by the following equations:

\[ X_{PAB} = \frac{2B}{2A - C} \]

where \( X_{PAB} \) is the mole fraction of the PAB units in the copolymer.

Also, the ratio of flexible methylene groups to the rigid PAB units was calculated as follows:

\[ \frac{4z}{2y} = \frac{C}{B} \]

Therefore, \(-OCH_2CH_2O-\) \( = \frac{z}{y} = \frac{C}{2B} \)

The fraction, \( xC (X_{PAB}) \), of PAB units which are directly connected to another PAB unit in the copolymer can be calculated as follows:
Intensity of the 3,5 protons of PAB connected to another PAB unit

\[ \propto (X_{PAB}) = \frac{\text{Total intensity of the 3,5 protons of PAB}}{\text{Area under peak at 7.5 ppm}} \]

Sum of areas under peaks at 7.4 and 7.5 ppm

The feed compositions and the compositions from NMR integration for the polymer samples are given in Table 7. For series I polymers, it is observed that the mole% of (BHET + TA) units calculated from NMR integration is much lower than that which was present in the feed. The discrepancy is high especially for the samples with high TA content in the feed. This can be explained as follows.

During the prepolymerization step for series I polymers, it was observed that at the reaction temperature (280 °C), a large amount of TA (melting point > 310 °C), being in excess, did not dissolve in the molten BHET and hence may not have completely reacted. Subsequently, in the second stage of the reaction, there were substantial amounts of unreacted TA in the system. During this stage the TA can react only with the acetoxy group of PAB and therefore its consumption would be less than that of oligomers with \(-\text{CH}_2\text{CH}_2\text{OH}\) endgroups. Hence, due to the excess amount of TA initially taken in the feed, at the end of the second stage there would still be

81
significant amounts of unreacted TA. As explained later, IR analysis of the insoluble fraction of series I polymers showed absorption bands characteristic of TA. This implies, that during the purification step of these polymers, substantial amounts of TA (insoluble in TCE/phenol) would be lost, thereby explaining the low values of (BHET + TA) calculated from NMR integration.

For series II polymers, since equal amounts of BHET and TA were taken in the feed, hence during the prepolymerization step, complete dissolution of TA in BHET occurred at the reaction temperature. Moreover, it was observed that series II polymers were soluble in the TCE/Phenol solvent mixture indicating complete incorporation of the TA units in the polymer chain and insignificant losses during the purification process. Thus, as shown in Table 7, for series II polymers, there is good agreement between the feed composition for (BHET + TA) and the composition calculated from NMR integration.

For both series I and series II polymers, the ratio of flexible methylene groups to the rigid PAB units in the feed are observed to be consistently higher than those calculated from NMR analysis. This indicates that there was some loss of ethylene glycol (boiling point 196 °C) from the reactor. Ethylene glycol is formed primarily in the prepolymerization stage of the reaction during which BHET molecules could
react with each other via transesterification. As mentioned before, the distillate collected after the prepolymerization stage indicated the presence of ethylene glycol. Similar losses of ethylene glycol from the reactor have been reported by Balchandar et al [138] who have synthesized copolyesters of PET and substituted PAB.

In Figure 19, \( \alpha (X_{\text{PAB}}) \), the mole % of PAB present as \(-\text{PAB-PAB-}\) in the copolymer is plotted as a function of mole percent PAB, for the series I and series II BTP polymers. Also shown in this figure are the corresponding data reported by Nicely et al [90] for the Eastman PET/PAB copolymer and a theoretical curve which predicts the mole percent of PAB present as \(-\text{PAB-PAB-}\) for a completely random copolymer containing PET and PAB. The theoretical curve was obtained by using the equation given by Lenz et al [148] as follows:

\[
\alpha' (X_{\text{PAB}}) = \frac{X_{\text{PAB}}}{X_{\text{PAB}} + 2 (1 - X_{\text{PAB}})}
\]

where \( \alpha' (X_{\text{PAB}}) \) is the fraction of PAB units which would be adjacent to another PAB unit in a totally random copolymer. The data for the BTP polymers indicates that as expected the mole percent of PAB present as \(-\text{PAB-PAB-}\) increases continuously with PAB content. However, it is interesting to note that their values are consistently higher than the
corresponding value for the Eastman PET/PAB copolymer. This would imply that the reaction conditions used in the preparation of the BTP polymers favors the formation of the -PAB-PAB- linkage as compared to the Eastman copolymers. Almost all compositions of the BTP polymers give an \( \zeta(X_{PAB}) \) value of more than 50 mole percent. This observation is of significant importance because -PAB-PAB- linkages impart rigidity to the polymer chain and their presence favor the formation of a nematic mesophase.

As observed in Figure 19, the Eastman data show noticeable deviations from the theoretical curve especially at high PAB mole fractions. Nicely et al interpreted this as evidence of blocked sequence distributions in these copolymers at high PAB contents. In order to make similar interpretations regarding sequence distributions for the BTP polymers under study, the probability model developed by Nicely et al for a two component system would have to be modified to account for the presence of a third component - terephthalic acid (TA). This would clearly not be straightforward due to the fact that the (BHET + TA) prepolymer prepared in this study would most likely contain a mixture of -BHET-TA- segments, -BHET-BHET- segments, and unreacted TA. The relative amounts of these segments would depend on the prepolymer feed composition and their determination would be necessary to fully define the probability model.
To summarize, NMR data for the BTP polymers indicates that a substantial amount of -PAB-PAB- linkages are formed. As will be discussed in subsequent sections, the presence of these linkages has been confirmed by IR spectra and optical microscopy studies. In order to obtain information regarding sequence distribution, a probability model would have to be developed that would account for the non-homogeneity of the prepolymer mixture.

3. Polyester structure from IR analysis

IR analysis of the BTP polymer series (purified fraction) was carried out to confirm the presence of -PAB-PAB- and PET segments in the polymer chain. PAB homopolymer was synthesized by heating the PAB monomer at 200 °C in a nitrogen atmosphere for 1 hour and then under a vacuum (0.5 mm) at 280 °C for 2 hours. The IR spectra of all BTP polymers was similar to the IR spectrum of the Eastman PET/PAB copolymer, indicating that the basic structure of these polymers was identical. Figures 17, 20-23 show the IR spectra of PET, BTP117 polymer, Eastman PET/PAB (40 : 60) copolymer, PAB homopolymer and PAB monomer. The characteristic absorbance peaks and the corresponding assignment to the vibration modes for BTP117, PAB homopolymer and PET are listed in Table 8.

For the BTP polymer, peaks at 1190 and 1150 (cm⁻¹)
indicate the presence of -PAB-PAB- segments. There is no absorbance at these wavenumber for PET. At the same time, like PET, the BTP polymers show noticeable absorbance at 1100 and 1335 (cm\(^{-1}\)), whereas the PAB homopolymer shows no absorbance at these wavenumbers. This would then imply that the BTP polymer chains contain both PET and -PAB-PAB- segments.

Absence of strong bands at 1680, 1430, 1370, 1318 and 1220 (cm\(^{-1}\)) for the BTP polymers, indicates the absence of appreciable amounts of free PAB monomer in these polymers. This would imply that either the PAB monomer has completely reacted or that all unreacted PAB is removed during the purification step. In order to determine whether the latter case is true, IR analysis of the insoluble fraction of BTP 145 was carried out and is shown in Figure 25. Comparison of this spectrum with that of pure PAB monomer indicates absence of absorbance peaks at 1370 (methyl group), 1318, 1220 and 790 (cm\(^{-1}\)) which implies that there is an absence of significant amounts of free PAB monomer in the insoluble fraction. However, IR of this fraction gives strong absorbance bands at 1680, 1410, 1285 and 1150 (cm\(^{-1}\)) very characteristic of TA [153]. This would imply that the insoluble fraction of series I polymers contains substantial amounts of unreacted TA. This result is consistent with NMR data, which indicated that significant amounts of TA were
lost during the purification process. Absorption peaks at 1190 and 1135 cm\(^{-1}\) do indicate that some small amounts of \(-\text{PAB-PAB}-\) homopolymer were lost due to their insolubility in the solvent [88].

For the BTP series II polymers, the monomer feed mixture contained equal number of moles of BHET and TA. Therefore, it is expected that in the prepolymerization stage, most of the TA reacts with the BHET to form short chain PET like oligomers. As shown in Figure 34, the IR spectrum of the (BHET + TA) prepolymerized product is very similar to the PET spectrum (Figure 17). Absence of strong absorption bands at 1680, 1285 and 1150 (cm\(^{-1}\)), characteristic of TA as shown in literature [153], indicates that most of the TA is incorporated into the polymer chain and unreacted TA (if any) is present in only negligible amounts. Thus during the purification of the series II polymers, there is insignificant loss of TA from the polymer system. This conclusion is consistent with the NMR results for series II polymers discussed in the previous section.

4. Intrinsic Viscosity Measurements

Intrinsic viscosities of the BTP polymers were determined by extrapolating reduced viscosity and inherent viscosity data to infinite dilution by means of the Huggins [128] and Kraemer [144] equations. The equations are as follows:
Huggins equation: \[ \frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \]

where \( k' \) is a constant for a series of polymers of different molecular weights in a given solvent and \( C \) is the concentration of the polymer in the solvent.

Kraemer equation: \[ \frac{\ln \eta_v}{C} = [\eta] + k'' [\eta]^2 c \]

where \( k'' \) is a constant such that \( k' - k'' = 0.5 \). The common intercept of these two equations at \( C = 0 \), gives the intrinsic viscosity of the polymer.

Viscosity data for the BTP 333 polymer is presented in Table 9 and Figure 26. Intrinsic viscosities of the other polymers are obtained in a similar manner and are summarized in Table 10. The constants \( k' \) and \( k'' \) for each of the polymers are also presented in this table. The low intrinsic viscosity value for these polymers indicates that sufficient molecular weight build up has not occurred in these polymers. This can be explained by the fact that as in most polycondensation systems, during the latter stages of the reaction, removal of the condensation molecule out of the system (in this case acetic acid), is restricted by the viscosity of the melt. Therefore, as explained by Jackson and Kuhfuss [2], in such systems, molecular weight build-up is normally achieved by solid phase polymerization. This involves grinding the polymers to a size finer than 20 mesh.
and then heating them at predetermined temperatures (around 20 °C below melting) under reduced pressure (0.05 - 0.01 mm) for about 16 hours. However, in this study it was not possible to obtain such low pressures and hence attempts to build up molecular weight were not successful. Low viscosity liquid crystalline polymers have also been reported by other investigators [145,146]. The Huggins constant \( k' \) of these polymers, is observed to vary between 0.24 and 0.54 and the difference \( k' - k'' \) is very close to 0.5, which is consistent with the corresponding values found for most polymeric systems in general.
5. DSC Studies

DSC studies of the BTP polyesters (purified) were carried out in order to obtain information on the thermal transitions of these systems. The samples (5-15 mg), encapsulated in aluminum pans, were first held at 280 °C for 6-8 minutes and then immediately quenched in liquid nitrogen. They were then scanned at 20 °C/min to 280 °C and then cooled at the same rate back to 50 °C. Figures 27 to 30 show the heating and cooling traces for series I and II polyesters.

It was observed that almost all samples gave weak but broad multiple endotherms in the temperature range 135 - 230 °C. The melting temperature $T_m$ was taken to be the peak maximum of the high temperature endotherm. For all samples, areas under the endotherms was summed up to determine the total enthalpy change ($\Delta H_f$) associated with the melting process. During the heating scan, some of the samples, especially the series II polyesters, gave crystallization exotherms between 90 and 106 °C. Once again, the transition peak was used to represent the crystallization temperature during heating, $T_{ch}$, and the area under each transition was determined to calculate the enthalpy change ($\Delta H_{ch}$) due to this transition. In almost all cases, a glass transition, $T_g$, associated with an increase in degrees of freedom from a glassy state to a rubbery state, could not be detected. However, some of the series I polymers, showed weak
endothersms between 69 and 74 °C, corresponding to glass transitions. Tables 11 and 12 list the important transitions and enthalpy changes that occurred during the first heating and cooling cycle for series I and II polymers.

In order to examine if any morphological re-arrangement occurred in the polymer during the DSC scan, the samples were rescanned at 20 °C/min to 280 °C and then back to 50 °C at the same rate. Figures 31 and 32 show the DSC traces for the rescan experiment for these polymers and the corresponding transitions are listed in Table 13. It is observed, that in most cases, the melting endotherms are better defined in the rescan experiment as compared to the initial scan, indicating possible morphological reorganization.

For copolymer systems such as these, interpretation of thermal studies is not straightforward. This is due to the fact that the problems involved in the crystallization and melting of copolymers cannot be uniquely formulated. When a copolymer crystallizes, participation in the transformation by all the differing chain elements is not an apriori requirement. A wide variety of possibilities exist. These depend on the crystallization conditions, the concentration of the different chain units, their sequence distribution, and the stereochemical relations that exist between them.

Multiple endotherms like the ones observed in these
copolymers have been reported by several investigators [42,45,52,98,99,147,150]. Based on annealing studies done on PET, Bell and Murayama [151] thought that multiple endotherms were caused by two different non-interconvertible crystal morphologies that existed in such polymer systems. The lower-temperature endotherm was a result of the melting of a folded-chain crystal morphology, and the higher temperature endotherm was thought to result from the melting of a more linear chain arrangement, i.e., a partially extended chain crystal.

More recent studies of PET crystallization by Sweet et al [100] and Holdsworth et al [101] have shown that multiple melting phenomenon is a result of a recrystallization process of the polymer chains. The lower-temperature endotherm was associated with the melting of imperfect crystals which were formed during an annealing process or during the cooling of the polymer from the melt state. The higher-temperature endotherm apparently resulted from the melting of the polymer crystals which were formed by simultaneous melting and recrystallization at lower temperatures during the DSC scan. Moreover, as shown by these authors, the relative areas of these endotherms were dependent on the cooling rates and annealing temperatures. The implication of such an explanation would be that there exists two interconvertible forms of PET, which differ from each other only in degree of crystal size and perfection,
and not from fundamental differences in crystal morphology. Griffin and Havens [52] have extended this explanation to mesogenic polymer systems which showed multiple melting transitions. According to them, the lower-temperature endotherm represents the transition to the nematic phase of the polymer which was recrystallized during the annealing process and which crystallizes to the higher temperature form as soon as it melts during the DSC scan. The higher-temperature endotherm corresponds to the transition to the nematic phase of polymer which was recrystallized during the DSC scan.

In this study, the explanation for the presence of multiple endotherms will be based on the interpretations made by Griffin and Havens as discussed above. In all cases, the higher-temperature endotherm was taken to be associated to the solid-nematic transition. As will be explained later, the formation of the nematic mesophase above these temperatures was confirmed by visual observation of the textures in the melt, using a microscope equipped with cross polarizers. None of the polyester samples showed an endotherm corresponding to a nematic to isotropic transition. Instead, after the crystal-nematic endotherm, the slope of the DSC baseline was observed to change drastically indicating thermal degradation. This was once again confirmed by optical studies to be discussed later.
As mentioned earlier, all polymer samples were first held at 280°C for 6 to 8 minutes and then quenched in liquid nitrogen. However, as shown by optical studies, these polymers with the exception of BTP 333 are not completely isotropic at this temperature. The rigid unmelted PAB segments, could then possibly act as nuclei for crystallization of the melted chain segments. As a result, even at high quenching rates there is a possibility for the formation of crystallites which are most likely to vary in size and perfection. This would then explain the presence of multiple endotherms corresponding to the melting of these imperfect crystals. The higher-temperature endotherm would then correspond to the transition to the nematic phase of the polymer which was crystallized during the DSC scan. In general, during the rescan, the endotherms appeared to be better defined indicating less degree of imperfections in the crystals. This is not altogether surprising because the samples heated during the first scan were cooled at 20 C/min allowing more time for the crystals to increase in size and perfection. Sweet and Bell [100] have made similar interpretations to explain the effect of cooling rate on the shape and size of multiple endotherms occurring in PET.

Table 11 shows that for copolymer series II, the total enthalpy of fusion $\Delta H_f$ and the enthalpy of crystallization $\Delta H_{ch}$ decreases systematically with an increase in PAB
content. These values and their trends are consistent with that reported by other investigators [92,93,97] for the Eastman PET/PAB copolymers. These observations are not surprising, because both these enthalpy changes are associated with the melting and crystallization respectively of the PET segments in the copolymer. Hence, as the PET content is lowered, the enthalpy changes are lowered proportionally. Meesiri et. al. [97] have stated that this phenomenon is a sign of partial isodimorphism or eutectic phase separation in these polymers. Also, the onset of crystallization and the crystallization temperature (peak) were observed to decrease with increasing PAB content indicating that the PAB segments may act as nucleating agents for the crystallization of the PET chains.

Surprisingly, the melting temperatures \( T_m \) (peaks) did not show a systematic trend for the series I copolymers. Instead they showed an almost zig-zag behaviour reminiscent of the "odd-even" alternation found in main chain mesogenic polymers with different lengths of flexible spacers [45]. However, for the system under study, such an explanation can be ruled out due to the fact that the length of the flexible methylene spacers remained constant at two for all polymer samples. One possible explanation for this unsymmetric behaviour could be that as shown in Table 10, these samples had different molecular weights (intrinsic viscosities). Hence a direct comparison of \( T_m \)'s may not be altogether
appropriate. Moreover, it should be pointed out that due to the broad nature of these endotherms, there may be some degree of uncertainty in measuring the peak temperatures. According to Antoun et. al. [45], the polydisperse nature of the molecular weights of such polymers and kinetic effects that affect the transitions may be the major contributing factors that lead to the occurrence of the broad endotherms. For the BTP 226 copolymer, a small endotherm was detected at 260°C similar to the ones observed by Joseph et. al. [92,93] and Viney and Windle [20] for some of the Eastman PET/PAB copolyesters. As explained by these authors, this endotherm could be due to a loss of correlation between the segregated PAB segments or due to the melting of a crystalline phase rich in PAB, that also contains low levels of PET.

As mentioned earlier, the BTP 333 copolymer showed a single, prominent and well defined endotherm. Microscopic study of this sample has indicated that at 280°C it is completely isotropic and does not exhibit mesophase textures. Hence, on quenching this sample in liquid nitrogen, an almost completely amorphous polymer is obtained. Thus, on the subsequent scan at 20°C/minute, due to the absence of imperfect crystals, no multiple melting transitions occurred. Instead, this sample showed a distinct exotherm at 106°C. According to Griffin et. al. [52], these exotherms are presumably due to a premelt crystallization to
a more thermally stable crystal form. The presence of both, the crystallization exotherms and the multiple endotherms in the other series II copolymers, indicates the presence of both, the amorphous PET regions and imperfect crystallites in these polymers.

As shown in Figure 30 and Table 12, the series II copolymers exhibit prominent exotherms when cooled at 20 °C/min from the melt state. As stated by Griffin et. al., these exotherms are associated with the nematic to crystal transition. The reversible nature of these transitions implies that these copolymers are enantiotropically thermotropic [42]. However, the high values of (T_m - T_cc) imply a high degree of supercooling indicating that a substantial amount of entropy is lost in reordering the nematic state to the crystalline state. Similar large supercooling values have been reported for the Eastman PET/PAB copolyesters [99] and other thermotropic systems [31,52]. For the BTP 225 sample, a small low temperature exotherm was also observed at around 120 °C. This may be associated with the formation of some small, imperfect crystals which would then melt at lower temperatures during the heating scan.

As shown in Table 13, except for the BTP 117 sample, rescan of the series II copolymers did not greatly affect T_m or ΔH_m. However, for the BTP 117 polymer, a new endotherm
was observed at 212 C indicating that either a reaction or some morphological rearrangement occurred during the first thermal scan. Kotek and Krigbaum [147] have mentioned that for such polymer systems, the internal linkage in the hard segment is very susceptible to chemical reaction. Interchange or transesterification reactions might occur between a carboxy end group and an ester, thereby changing the mesomorphic characteristics of the polymer. Lenz et. al. [148], have discussed the possibility of crystallization-induced reactions (CIR) for the Eastman PET/PAB copolymer system. In the CIR process, the non-crystallizable comonomer units adjacent to the crystalline regions are replaced by the crystallizable units through an interchange or isomerization reaction. The latter then irreversibly crystallize into the crystalline domain, thus increasing the crystalline domain size and thereby the overall degree of crystallinity as well as the sequence length of the crystalline unit. The latter effect, in turn, results in an increase in the melting point. It is possible then, that these explanations may be relevant to the behaviour of the BTP 117 polymer. For the BTP 226 polymer, the small endothermic peak that appeared in the initial scan was no longer present, once again indicating some type of morphological rearrangement in the melt during the initial DSC scan.

It is surprising and unusual that the series II polymers
did not exhibit glass transitions (Tg's) either during the first scan or the rescan. One possible explanation could be that these transitions (if present) might have been distorted by the significant curvature of the baseline found in such polymer systems [149]. Also, the proximity of these transitions (10-15 °C) to the onset of the crystallization process which occurs during the DSC scan, might make them difficult to detect. Jackson and Kuhfuss [2], have reported two glass transitions for the Eastman copolymers, for PAB content between 30 and 50 mole %. Above 50 mole % PAB, no Tg's were detected. It may be appropriate to point out that some of the high temperature glass transitions (159-166°C), reported by them, are in the same temperature range as the low temperature endotherms observed for the polymers investigated in this study. It is possible therefore, that some of these low temperature endotherms may in fact be Tg's, corresponding to a phase rich in PAB segment [97].

The thermal behaviour of the series I polyesters is somewhat different as compared to that discussed above for the series II polymers. Specifically, the temperatures Tm and Tcc showed a systematic increase with increasing PAB content. However, the enthalpy changes ∆Hm and ∆Hcc showed a zig-zag behaviour, normally exhibited by thermotropic polyesters with even and odd number of methylene spacers between the mesogenic units [147]. Since, series I
polyesters contain a constant number (equal to 2) of methylene units, the explanation given by Kotek and Krigbaum [147], is not exactly relevant to this unusual behaviour. Unlike as in series II samples, these polyesters contain a variable BHET to TA ratio. This introduces another degree of difficulty in correlating thermal transitions with the polymer composition. Flatter baselines for the BTP 154, 145 and 136 samples enabled the detection of small glass transitions. However, in the rescan, these transitions were not present, once again indicating some morphological rearrangement occurring in the melt during the first DSC scan.

To summarize, it may be stated that both series I and series II polyester systems exhibit complex thermal behaviour. This may be attributed to factors such as solid-solid phase transitions, various crystal imperfections or even different polymorphic crystal forms. It is evident that the results from thermal studies are not independently conclusive with regards to the mesophase character of these polymers. The interpretations made here have to be corroborated by optical microscopic studies in order to achieve a better understanding of these polymers.
6. Optical Microscopy Studies

By using optical microscopy, the results obtained from DSC measurements were correlated with visual observations of the texture of the melt as a function of temperature. In all cases, a small amount of the polyester sample was sandwiched between thin glass cover slips which had previously been thoroughly cleaned. The samples were then heated on the hot stage from room temperature to between 280 to 320 °C and transitions as a function of temperature were recorded. Initially, the heating rate was maintained at around 10 to 15 °C/min but at temperatures close to that at which transitions were recorded on the DSC, the scan rate was reduced to 2 to 5 °C/min. Samples were examined under both, normal illumination and cross polarized light at magnifications of 200 or 860.

In order to distinguish the characteristic melting and crystallization behaviour of PET from that of the BTP polyesters, a sample of PET (clear reclaimed PET flake) was analyzed under the microscope. The sample, sandwiched between glass cover slips was heated at 15 °C/min and observed under cross polars at a magnification of 860. At a temperature of about 260 °C, the sample became completely isotropic (dark under cross polars) with no visible textures at intermediate temperatures. As discussed earlier, the melting of PET is associated with the unfolding of molecular
chains in the lamellar crystals and results in a completely disordered orientation of the chains (amorphous or liquid state). The sample was maintained at 260°C for about 5 minutes and then slowly cooled to 170°C (temperature at which PET has its maximum crystallization rate). It was held at this temperature for about 15 minutes and then slowly cooled down to room temperature. As indicated in Figure 33, the polymer chains crystallize to form spherulites as is evident from the strong Maltese cross pattern characteristic of this morphological texture. Similar unbanded spherulites have been reported in literature [154] for polyethylene adipate crystallized from the melt. On the basis of a variety of experimental observations, a number of aspects of the structure of spherulites have been elucidated [154-156]. The spherulites are considered to be aggregates of lamellar radiating from a nucleation site. The latter can be either a spontaneously formed single crystal or a foreign body. Though spherulites are observed under the microscope as being two-dimensional, actually the lamellae spread out radially from the nucleus in three dimensions and the crystallites branch out to generate a spherical morphology. The thickness of individual lamellae is typically of the order of 100 Å. As will be discussed later, the morphology of BTP polymers in the melt state is completely different from that of the PET homopolymer and its textures when cooled from the melt will
be shown to be typical of nematic polymers.

At room temperature, the BTP polymers were typically an opaque tan color. As the temperature was raised, a gradual decrease in the intensity of this tan color was observed. In general, transitions as observed from microscopic studies were about 5 to 8 degrees higher than that recorded by DSC analysis. Several factors could contribute to this discrepancy, viz. point of temperature measurement, response of the thermocouple, thickness of the sample and thermal conductivity of the glass cover slips. When the polymer samples were sufficiently softened (usually around 20 °C lower than the melting point peak), the top glass cover slip was gently pressed to spread the sample into a thin film. However, in most cases it was difficult to prepare samples that had uniform thickness over extended regions and usually small air or gas bubbles would form in some areas.

At temperatures around 5 to 8 °C higher than \( T_m \) (as recorded on the DSC), the samples were observed to exhibit mobility. As explained by Viney and Windle [20], the onset of mobility which corresponds to an endotherm in the DSC, possibly represents a "melting out" of regions of local order which, at low temperatures, pin the microstructure. At this point, the top cover slip was given a back and forth movement to enable the polymer melt to exhibit textures. According to several investigators [20,52,104] this shearing
motion is required, because unlike as in small molecule liquid crystals, the high viscosity of the polymeric nematic phase prevents a spontaneous parallel alignment of chains. Hence some external force would be necessary to coax the bundles of polymer chains into aligning parallel to the surface of the glass cover. Moreover, due to surface forces, there is a tendency for the polymer chains to form a homeotropic alignment, where the polymer chains will align perpendicular to the glass cover. In such a case no textures can be observed.

In all cases, at temperatures just above $T_m$, on shearing the sample, the polymers exhibited brilliant colors of varying intensities. This optical anisotropy, known as "birefringence", is characteristic of mesomorphic phases and is due to the heterogeneity in the refractive index which varies from point to point in the material. Non-liquid crystalline polymers, like PET, are isotropic in the molten state and when examined under cross-polars, are completely dark, indicating a total elimination of the light intensity. Hence, this proves without any doubt that the endotherm at $T_m$, for the copolyesters in this study, represents a transition from the crystal state to a mesophase, i.e., these polymers are definitely thermotropic.

On further heating, the birefringent melts began to exhibit definite textures. Highly mobile dark threads were
observed to move rapidly in the melt when sheared. These threads have been associated with line singularities known as disclinations [152] and are typical of nematic mesophases examined by several investigators [20,40,46,81,104,147]. In addition to threads, ringed domains were observed in some regions for some of the polymer samples. These domains were almost immobile and gradually grew in size depending on both temperature and time. Figure 34 shows an optical micrograph of BTP 145 sample at 245°C viewed between crossed polaroids. This figure clearly shows the presence of nematic threads and the ringed domains. On cooling this sample back to room temperature, most of the nematic-like texture was "frozen in", and the region within the rings became heavily threaded. The presence of threaded material within these rings strongly suggests that the rings are not bubbles. Similar textures were observed by Mackley et. al. [104] for the Eastman PET/PAB copolyester containing 60 mole % PAB. These authors have stated that the emergence of ringed domains is associated with some form of chemical or physical segregation process due to difference in chemical composition or molecular weight. The heavily threaded texture shown in Figure 35, is of a low melting polyester obtained from the Celanese corporation. Though the exact composition of this polyester was not provided, it was made known to this author, that these polyesters exhibited nematic textures in the melt. This figure also shows the
presence of a large bubble containing a very thin section of the sample presumably attached to the lower glass cover. This thin section is observed to be strongly colored indicating the presence of local birefringence. Its appearance is visibly different from the structure observed within the ringed domain of Figure 34. Unlike the ringed domains, bubble formation is not a characteristic feature of a nematic mesophase. Bubbles are normally formed due to the evolution of volatiles from the polymer melt which either causes a partial wetting of the melt on the glass cover results in a complete absence of the polymer melt within the bubble.

Another highly visible nematic texture observed in some of these polyester samples, at elevated temperatures, was that of regions of varying contrast and intensity. As explained by Viney and Windle [20] and Mackley et. al. [104], this microstructure consisting of discrete groups of dark extinction bands, separated by regions of low contrast, represents a nematic schlieren texture. Figures 36 and 37 show optical micrographs of the polyester sample BTP 225 at 250 °C, at two different locations observed under crossed polarizers. These micrographs clearly show a highly birefringent anisotropic phase and a completely dark isotropic phase in which light intensity is completely eliminated. The co-existence of the anisotropic and
isotropic phases has very important morphological implications and will be discussed in detail later. The anisotropic regions show extinction bands organized as fourfold "brushes" radiating from a point. On rotating the polarizer, these brushes were observed to rotate in the same direction at approximately the same angular velocity. As discussed by Mackley et. al [104], these "centered textures" are associated with the existence of disclinations of strength ±1 running vertically between the glass slides. Similar observations have been made by other investigators [20,40]. These authors have also identified textures in which only two extinction bands radiate from a point and these have been associated with disclinations of strength ±1/2. By tracing the movement of the extinction bands as a function of the polarizer rotation, Viney et. al. and Mackley et. al. have mapped out the "trajectories" of the apparent optical axis, thereby determining the possible spatial orientation of the local optical director in the specimen plane. Figure 38 shows a different location of the same sample (BTP 225) at 250°C, which shows a faint outline of an air (or gas) bubble within the large isotropic region. On gently pressing the glass cover, neither the bubble nor the isotropic fluid exhibited any local birefringence. This rules out the presence of any polymer chains that could have aligned perpendicular to the glass surface (homeotropic alignment) in either of these regions. If such an alignment
did exist, the application of shear would have forced the polymer chains into aligning parallel to the glass surface and resulted in either local birefringence or motion of the nematic threads. Under plane polarized light, the interface between the bubble and the isotropic fluid could be easily observed, thereby confirming the presence of the air bubble.

As mentioned earlier, observation of the co-existence of two phases is a very important factor in the interpretation of the morphological rearrangements that occur at elevated temperatures. For most of the polyesters in this study, there existed a sufficiently large temperature range (30 to 40 °C) within which the nematic phase coexisted with the isotropic phase. Figures 39 and 40 indicate very distinctly the phase separation which occurred in polymer samples BTP 225 and BTP 226 respectively. Sample BTP 225 was rapidly cooled from 300 °C to room temperature on a cold metal block whereas sample BTP 226 was gradually cooled on the hot stage down to ambient temperature. In both cases, the mesomorphotic textures were "frozen in", as is evident from the significant amount of birefringent regions in the two phase microstructure. The distinctly darker regions, which represent areas of relatively lower amount of depolarization, are speculated to be rich in PET segments, whereas the more birefringent regions are thought of as containing higher amounts of PAB. This interpretation is consistent with that made by Joseph et. al. [93] for the
Eastman PET/PAB copolyesters. The phenomenon of phase separation indicates the heterogeneity of such polymer systems and validates the earlier assumptions made, based on DSC and NMR studies respectively, that morphological reorganization occurs at elevated temperatures and that there are substantial amounts of -PAB-PAB- segments in the polymer chain. It should also be noted that the fact that the "PET rich" segments in the BTP 226 polymer crystallized from the melt, inspite of the rapid quenching, substantiates the earlier claim (based on DSC studies) that the rigid PAB units would act as nuclei for the melted PET chain segments. However, the close similarity in the PET-rich phase of the BTP 225 and BTP 226 samples, inspite of the different cooling rates, makes it difficult to compare possible differences in crystal size and imperfections in these two samples. Within the PET-rich phase, crystallization of PET segments is presumably in the form of lamellar crystals built up from successive layers of folded chains. Spherulite formation of the type shown in Figure 31 is not obvious probably due to the fact that spherulites could mutually impinge on each other and form an irregular layered structure. However, for such inferences to be accurate, the samples would definitely have to be prepared under more controlled conditions and examined at much higher magnifications.
It should also be pointed out that mesomorphic textures are related in some complex manner to the thickness of the sample, interactions with the glass cover and on mechanical and thermal history. In very thin sections, especially at the edges of the sample, the textures appeared to be more birefringent and to some extent striated, indicating possibly the effects of shear stress (Figure 41). Ringed domains and nematic threads were generally restricted to thicker regions in the bulk of the sample. Similar observations have been made by Mackley et. al. [104], for the PET/PAB copolyesters. Figure 42 shows the texture of the BTP 145 sample which was quenched from 300°C, rescanned to 260 °C and then cooled back to room temperature. Dark extinction bands are clearly visible, interspersed among regions of higher contrast, once again indicating that the nematic state is preserved on cooling.

In Table 23, the temperatures at which the BTP polymers flow and exhibit mobile nematic textures under the microscope, is compared to the peak temperatures and the temperatures at which complete melting occurs as recorded on the DSC. It is observed that the temperatures recorded for the onset of mesophase flow as measured by optical microscopy are in reasonably good agreement with the temperatures corresponding to complete melting of the polymer as measured by DSC. The melting temperatures which mark the onset of mobility are considerably lower (about 20
to 30 °C lower). However, it should be noted that the transition temperatures obtained from visual observations of the melt are highly sensitive to sample thickness and the exact location of the thermocouple recording these temperatures. This would then explain the 5 to 10 °C difference between the transition temperatures as recorded by the DSC and by hot stage microscopy.

To confirm that polymer degradation occurred before complete isotropization, the isotropic regions in samples held at 300 °C were examined under plane polarized light. Discoloration (brownish) in some regions indicated that these areas were gradually undergoing thermal degradation. Also, it appears that the copolymer should contain more than 30 mole % of PAB, for it to exhibit anisotropy in the melt. Sample BTP 333 which contained 31.9 mole % PAB, turned almost completely isotropic at 230 °C. Small droplets containing some local birefringence were observed but their size and number reduced drastically at elevated temperatures. On cooling, this sample exhibited PET-like crystallinity indicating that this polymer was definitely not mesomorphic. As shown in Figure 43, BTP 334, which contained 40.6 mole % PAB, gave a biphasic melt at 240 °C. The photomicrograph, taken on cooling the melt to room temperature, clearly shows the two-phase region characteristic of mesomorphic behaviour. This would indicate
that around 40 mole % PAB is sufficient to make these copolymers exhibit a mesophase. As suggested by Chen and Lenz [46], the relative amounts of the two phases can be considered to be an indication of the "degree of liquid crystallinity" in the polymer.

Some of the polymer samples were examined carefully at temperatures in between the low and high temperature endotherms as recorded by the DSC. It was observed that the polymers did not show any fluidity due to a transition of the "less perfect" crystal form to the nematic phase. However, it is speculated that the partial melting of sample still leaves the crystal structure of the more stable form intact, and it would not be expected that the sample as a whole would become fluid until both crystal forms had melted.

It thus appears, that in general, the optical microscopy technique was extremely useful for identifying mesophase transitions and for making qualitative explanations for the multiple endothermic transitions occurring during the DSC scan. Moreover, the presence of phase separation confirms the NMR results which had shown that large number of -PAB-PAB- segments were formed.
7. X-ray Diffraction Studies

Due to limited access to the x-ray facilites, the diffraction studies were restricted to a single representative sample from the BTP polymer series. A small amount (about 30 mg) of BTP 145 (containing 68.2 mole % PAB, as determined from NMR) was thoroughly ground in an agate mortar in a small, shallow aluminum pan. The pan was heated on a hot plate under a inert blanket obtained by flowing nitrogen through an inverted glass funnel placed on the pan. The sample was maintained at 260 °C for about 5 minutes and then cooled slowly to room temperature on the hot plate. The scattering pattern of the sample exposed for 16 hours to the x-ray beam was obtained. The d-spacings calculated from the scattering pattern are given in Table 24 along with the d-spacings of pure PET and PAB homopolymer obtained from literature [94]. It is observed that, the BTP 145 sample has d-spacing values corresponding to both PET and PAB homopolymers. Specifically the reflections at 4.5 Å, 3.7 Å and 3.18 Å correspond to that seen in pure PAB and the reflections at 5.10, 4.13 and 3.8 Å correspond to that seen in pure PET.

From these results, it becomes apparent that the BTP polymers contain both PET and PAB type of crystallinity. This could not be confirmed by DSC data because in most cases the sample degraded at the high temperatures required
for the PAB crystalline transitions to appear. However for one of the samples (BTP 226) a small endotherm was detected at 260 °C, which as explained before, could very well correspond to the melting of a crystalline phase rich in PAB segments. Nevertheless, the fact that d-spacings similar to that found in the diffraction pattern of the PAB homopolymer, were present in the polyester sample, gives additional evidence of the formation of -PAB-PAB- linkages.
CHAPTER V

CONCLUSIONS

A. DEPOLYMERIZATION OF PET

1. Depolymerization of reclaimed PET flakes by a glycolysis reaction catalyzed by metal acetates is initially very rapid. Almost complete breakdown of PET into short chain oligomers occurs within one hour.

2. An equilibrium is reached between BHET and dimer which limits the yield of the monomer to be between 75 to 80 % (mole basis).

The equilibrium model can be described as:

\[ K = \frac{[\text{DIMER}][\text{EG}]}{[\text{BHET}]^2} \]

3. Of the four metal acetates tried, zinc acetate appeared to be the most effective with regards to the initial rate of depolymerization. The relative effectiveness of the catalysts was as follows:

\[ \text{Zn}^{2+} > \text{Pb}^{2+} > \text{Mn}^{2+} > \text{Co}^{2} \]
B. LIQUID CRYSTALLINE POLYESTERS FROM BHET

1. Based on assignments of NMR signals to characteristic proton chemical shifts, the structure of the polyester series was deduced to be:

\[
\begin{array}{c}
\text{O} \\
|| \\
\text{C} - \text{O} - \text{O} - \text{C} \\
\text{H} \text{H} \\
\end{array}
\]

\[
\begin{array}{c}
\text{O} \\
|| \\
\text{C} - \text{O} - \text{O} - \text{C} \\
\text{H} \text{H} \\
\end{array}
\]

\[
\begin{array}{c}
\text{OCH}_2\text{CH}_2\text{O} \\
\end{array}
\]

\[
x \quad y \quad z
\]

where \(x, y, z\) are the mole fractions of the PET, PAB and ethylene glycol residues in the polymer chain respectively. Though the actual sequence distribution of the polymer could not be obtained, the NMR analysis did confirm the formation of substantial amounts of -PAB-PAB- linkages which is known to impart rigidity to the chain backbone.

2. Rigidity of the -PAB-PAB- linkage is due to the presence of an ester group sandwiched between two benzene molecules as follows:

\[
- \text{O} - \text{C} - \text{O} - \text{O} - \text{O} -
\]

The presence of this ester group was confirmed through IR absorption spectroscopy which gave an absorption band.
3. Low intrinsic viscosity values for these polyesters in a phenol/TCE solvent mixture at 25 °C indicated that sufficient molecular weight build-up had not occurred. Molecular weight can be raised by conventional solid phase polymerization techniques.

4. DSC study indicated that all these polyesters gave weak but broad multiple endotherms in the temperature range 135 - 230 °C. The higher-temperature endotherm was taken to be associated to the solid to nematic transition whereas the lower temperature endotherms were attributed to the melting of imperfect crystals formed during the cooling of the polymer from the melt state. The enthalpies of fusion and crystallization corresponding to the PET segments in the chain were found to depend significantly on the composition and thermal history of the polymer. The rigid -PAB-PAB segments were thought to act as nuclei for the crystallization of the more flexible PET segments. In general, the polyester samples exhibited a somewhat complex thermal behaviour which may be attributed to factors such as solid-solid phase transitions, various crystal imperfections or even different polymorphic forms.
5. Optical study of the polyester melts using polarizing microscopy indicated that on application of shear a "threaded" microstructure typical of a nematic mesophase was formed. In most cases, the melts were observed to be highly birefringent and the nematic phase was found to be preserved on cooling the polymers from the mesophase state. In general, the textures of these polymers in the melt state was heterogenous and morphological rearrangements occurring at high temperatures led to the formation of a two-phase structure. One phase was speculated to be rich in PET segments and the other rich in \(\text{-PAB-PAB-}\) segments. At elevated temperatures, thermal degradation occurred before these polymers could become completely isotropic. Absence of optical anisotropy in the melt for the polyester sample containing 31.9 mole percent PAB indicated that a higher PAB content was required for liquid crystalline behaviour. The sample containing 40.6 mole percent PAB was showed a distinct nematic texture indicating that an intermediate concentration of PAB (say, atleast 35 mole percent PAB) was required for the formation of a mesophase.

6. X-ray diffraction studies of a representative sample of these polyesters, though not independently conclusive, showed the presence of both PET and PAB type of
crystallinity in these polyesters. The formation of PAB crystals once again corroborated the evidence from NMR, IR and optical microscopy that substantial amounts of rigid -PAB-PAB- linkages existed in the polymer chain.
CHAPTER VI

RECOMMENDATIONS FOR FUTURE WORK

1. Determine the sequence distribution of these polyesters by $^{13}$C NMR and develop a probability model for this system.

2. Build up the molecular weight of these polyesters by solid state polymerization techniques.

3. Test the polymers for mechanical strength and determine their rheological properties.

4. Determine the effect of thermal history of these polymers on their x-ray diffraction patterns.

5. Utilize chemical etching techniques to determine the morphology of the two phase system and estimate the size of each domain.

6. Study the effect of incorporating limited amounts of non-linear structural units in the backbone of the polymer. For example, part of the terephthalic acid monomer could be replaced by isothalic acid which would introduce "kinks" in the polymer main chain. Similarly, a part of
the para-acetoxybenzoic acid (PAB) monomer could be replaced by its non-linear isomer, namely, meta-acetoxybenzoic acid. The incorporation of "kinks" or non-linear co-monomers has been found by many investigators to be very effective in reducing the melting point of rigid main chain liquid crystalline polymers.
REFERENCES


130


131. Tomita, K., Polymer, 17, 221 (1976).


<table>
<thead>
<tr>
<th>Tensile Properties of High Strength/High Modulus Aromatic Yarns in comparison with those of Glass Fibers and Steel Wire [1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength</td>
</tr>
<tr>
<td>------------------</td>
</tr>
<tr>
<td>Aromatic Polyamide Yarn</td>
</tr>
<tr>
<td>S-Glass</td>
</tr>
<tr>
<td>Steel Wire</td>
</tr>
</tbody>
</table>
TABLE 2: Typical Properties of Commercial Thermotropic Liquid Crystal Polymers

<table>
<thead>
<tr>
<th></th>
<th>XYPAR</th>
<th>VECTRA</th>
<th>PET</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Manufacturer</strong></td>
<td>DARTCO</td>
<td>CELANESE</td>
<td>EASTMAN</td>
</tr>
<tr>
<td><strong>Grade</strong></td>
<td>SRT500</td>
<td>A900</td>
<td>several</td>
</tr>
<tr>
<td><strong>Specific gravity</strong></td>
<td>1.35</td>
<td>1.38</td>
<td>1.34-1.39</td>
</tr>
<tr>
<td><strong>Melting Point, F</strong></td>
<td>&gt; 750</td>
<td>535</td>
<td>490</td>
</tr>
<tr>
<td><strong>Tensile Strength (10^3 psi)</strong></td>
<td>18.2</td>
<td>89.0</td>
<td>8.0</td>
</tr>
<tr>
<td><strong>Tensile Modulus (10^6 psi)</strong></td>
<td>1.9</td>
<td>6.3</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Elongation (%)</strong></td>
<td>4.8</td>
<td>1.8</td>
<td>240</td>
</tr>
<tr>
<td><strong>Limiting Oxygen Index (%)</strong></td>
<td>42</td>
<td>35</td>
<td>21</td>
</tr>
<tr>
<td><strong>Izod Impact Strength (notched) (ft-lb/in.)</strong></td>
<td>3.9</td>
<td>6.0</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Chemical Structure:

**PET:**

\[
\begin{array}{c}
\text{PET :} \\
\left[ \begin{array}{c}
\text{C-} \\
\text{O-C-O-CH}_2\text{CH}_2\text{O} \\
\end{array} \right]_n
\end{array}
\]

**XYDAR:**

\[
\begin{array}{c}
\text{XYDAR :} \\
\left[ \begin{array}{c}
\text{O-O} \\
\text{O-C} \\
\end{array} \right] \\
\left[ \begin{array}{c}
\text{O-C} \\
\text{C-O} \\
\end{array} \right] \\
\left[ \begin{array}{c}
\text{O-C} \\
\text{C-O} \\
\end{array} \right]
\end{array}
\]

**VECTRA:**

\[
\begin{array}{c}
\text{VECTRA :} \\
\left[ \begin{array}{c}
\text{O-C} \\
\text{C-O} \\
\end{array} \right] \\
\left[ \begin{array}{c}
\text{O-C} \\
\text{C-O} \\
\end{array} \right] \\
\left[ \begin{array}{c}
\text{O-C} \\
\text{C-O} \\
\end{array} \right]
\end{array}
\]
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<th>COMPANY</th>
<th>STRUCTURAL UNITS</th>
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<td>DU PONT</td>
<td><img src="image1" alt="Diagram" /></td>
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<tr>
<td>DU PONT</td>
<td><img src="image2" alt="Diagram" /></td>
</tr>
<tr>
<td>EASTMAN KODAK</td>
<td><img src="image3" alt="Diagram" /></td>
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<tr>
<td>EASTMAN KODAK</td>
<td><img src="image4" alt="Diagram" /></td>
</tr>
<tr>
<td>CELANEA</td>
<td><img src="image5" alt="Diagram" /></td>
</tr>
<tr>
<td>CARBORUNDUM</td>
<td><img src="image6" alt="Diagram" /></td>
</tr>
<tr>
<td>WAVE # (CM(^{-1}))</td>
<td>RELATIVE INTENSITY</td>
</tr>
<tr>
<td>----------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>BHET</td>
<td>DIMER</td>
</tr>
<tr>
<td>720</td>
<td>strong</td>
</tr>
<tr>
<td>790</td>
<td>--</td>
</tr>
<tr>
<td>810</td>
<td>weak</td>
</tr>
<tr>
<td>830</td>
<td>weak</td>
</tr>
<tr>
<td>870</td>
<td>medium</td>
</tr>
<tr>
<td>890</td>
<td>medium</td>
</tr>
<tr>
<td>970</td>
<td>--</td>
</tr>
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</table>
TABLE 4 (Continued)

<table>
<thead>
<tr>
<th>WAVE #</th>
<th>RELATIVE INTENSITY</th>
<th>ASSIGNMENT TO VIBRATION MODE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM⁻¹</td>
<td>BHET</td>
<td>DIMER</td>
</tr>
<tr>
<td>1010</td>
<td>medium</td>
<td>medium</td>
</tr>
<tr>
<td>1038</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1110</td>
<td>strong</td>
<td>strong</td>
</tr>
<tr>
<td>1170</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1260</td>
<td>v.strong</td>
<td>v.strong</td>
</tr>
<tr>
<td>1340</td>
<td>v.weak</td>
<td>medium</td>
</tr>
<tr>
<td>1370</td>
<td>weak</td>
<td>weak</td>
</tr>
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</table>
TABLE 4 (Continued)

<table>
<thead>
<tr>
<th>WAVE #</th>
<th>RELATIVE INTENSITY</th>
<th>ASSIGNMENT TO VIBRATION MODE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM$^{-1}$</td>
<td>BHET</td>
<td>DIMER</td>
</tr>
<tr>
<td>1400</td>
<td>medium</td>
<td>medium</td>
</tr>
<tr>
<td>1445</td>
<td>weak</td>
<td>weak</td>
</tr>
<tr>
<td>1470</td>
<td>--</td>
<td>v.weak</td>
</tr>
<tr>
<td>1500</td>
<td>weak</td>
<td>weak</td>
</tr>
<tr>
<td>1570</td>
<td>--</td>
<td>v.weak</td>
</tr>
<tr>
<td>1605</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1680</td>
<td>v.strong</td>
<td>--</td>
</tr>
<tr>
<td>1710</td>
<td>--</td>
<td>v.strong</td>
</tr>
<tr>
<td>2880</td>
<td>weak</td>
<td>v.weak</td>
</tr>
<tr>
<td>2950</td>
<td>weak</td>
<td>weak</td>
</tr>
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### TABLE 5: Summary of the Glycolysis Data for Recycled PET

<table>
<thead>
<tr>
<th></th>
<th>Zn&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>Pb&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>Mn&lt;sup&gt;2+&lt;/sup&gt;</th>
<th>Co&lt;sup&gt;2+&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_0 ), mg KOH/g</td>
<td>959.22</td>
<td>953.46</td>
<td>967.57</td>
<td>935.46</td>
</tr>
<tr>
<td>( H_1 ), mg KOH/g</td>
<td>381.49</td>
<td>381.09</td>
<td>376.90</td>
<td>371.34</td>
</tr>
<tr>
<td>a</td>
<td>0.263</td>
<td>0.293</td>
<td>0.293</td>
<td>0.333</td>
</tr>
<tr>
<td>( n_B ), moles</td>
<td>0.328</td>
<td>0.315</td>
<td>0.315</td>
<td>0.300</td>
</tr>
<tr>
<td>( n_D ), moles</td>
<td>0.086</td>
<td>0.092</td>
<td>0.092</td>
<td>0.100</td>
</tr>
<tr>
<td>%EG consumed</td>
<td>24.8</td>
<td>25.0</td>
<td>23.6</td>
<td>26.8</td>
</tr>
<tr>
<td>(end-group analysis)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%EG consumed</td>
<td>26.7</td>
<td>22.3</td>
<td>25.0</td>
<td>23.9</td>
</tr>
<tr>
<td>(GC analysis)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%EG consumed</td>
<td>21.9</td>
<td>21.5</td>
<td>21.5</td>
<td>21.1</td>
</tr>
<tr>
<td>(from model)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>1.13</td>
<td>1.30</td>
<td>1.33</td>
<td>1.53</td>
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TABLE 6: Assignment of Characteristic Proton Chemical Shifts for Series I and Series II Polyesters

<table>
<thead>
<tr>
<th>NMR CHEMICAL SHIFT</th>
<th>PROTON ASSIGNMENT</th>
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<tbody>
<tr>
<td>4.8 PPM</td>
<td>( H H ) ( -O-C-C-O- ) ( H H )</td>
</tr>
<tr>
<td>7.4 ppm</td>
<td>( O ) ( H ) ( O ) ( O ) ( C-) ( O-C-) ( O-C-) ( H )</td>
</tr>
<tr>
<td>7.5 ppm</td>
<td>( O ) ( H ) ( O ) ( C-) ( O-C-) ( O-C-) ( H )</td>
</tr>
<tr>
<td>8.2 ppm</td>
<td>( O ) ( H ) ( H ) ( O ) ( C-) ( O-C-) ( H H )</td>
</tr>
<tr>
<td>8.4 ppm</td>
<td>( O ) ( H ) ( O ) ( C-) ( O-C-) ( H H )</td>
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</tbody>
</table>
TABLE 7: Feed Compositions and Compositions from NMR Integration for Series I and Series II Polymers

<table>
<thead>
<tr>
<th>SAMPLE ID</th>
<th>FEED COMPOSITION</th>
<th>COMPOSITION FROM NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BHET</td>
<td>PAB</td>
</tr>
<tr>
<td></td>
<td>+ TA</td>
<td>----</td>
</tr>
</tbody>
</table>

SERIES I

<table>
<thead>
<tr>
<th>SAMPLE ID</th>
<th>FEED COMPOSITION</th>
<th>COMPOSITION FROM NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTP 163</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>BTP 154</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>BTP 145</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>BTP 136</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>BTP 127</td>
<td>30</td>
<td>70</td>
</tr>
</tbody>
</table>

SERIES II

<table>
<thead>
<tr>
<th>SAMPLE ID</th>
<th>FEED COMPOSITION</th>
<th>COMPOSITION FROM NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTP 333</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>BTP 334</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>BTP 225</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>BTP 226</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>BTP 117</td>
<td>30</td>
<td>70</td>
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</table>
### TABLE 8: Assignment of Vibration Mode to Characteristic Absorption Bands for the BTP Series Polymers, PAB Homopolymer and PET

<table>
<thead>
<tr>
<th>WAVE # CM⁻¹</th>
<th>RELATIVE INTENSITY</th>
<th>BTP</th>
<th>PAB</th>
<th>PET</th>
<th>ASSIGNMENT TO VIBRATION MODE</th>
</tr>
</thead>
<tbody>
<tr>
<td>970</td>
<td>weak</td>
<td>-</td>
<td>-</td>
<td>weak</td>
<td>trans EG segment</td>
</tr>
<tr>
<td>1100</td>
<td>medium</td>
<td>-</td>
<td>strong</td>
<td>C-O stretch from O \parallel C-OCH₂H₂OH</td>
<td></td>
</tr>
<tr>
<td>1150</td>
<td>medium</td>
<td>medium</td>
<td>-</td>
<td>C-O stretch from O \parallel C-OCH₂CH₂OH</td>
<td></td>
</tr>
<tr>
<td>1190</td>
<td>medium</td>
<td>medium</td>
<td>-</td>
<td>C-O stretch from O \parallel -C-O</td>
<td></td>
</tr>
<tr>
<td>1335</td>
<td>weak</td>
<td>-</td>
<td>medium</td>
<td>CH₂ in trans EG segment</td>
<td></td>
</tr>
<tr>
<td>1445</td>
<td>v.weak</td>
<td>-</td>
<td>weak</td>
<td>CH₂ scissor</td>
<td></td>
</tr>
<tr>
<td>1680</td>
<td>v.weak</td>
<td>v.weak</td>
<td>-</td>
<td>C=O from acid</td>
<td></td>
</tr>
<tr>
<td>1710</td>
<td>-</td>
<td>-</td>
<td>strong</td>
<td>C=O from ester</td>
<td></td>
</tr>
<tr>
<td>1730</td>
<td>strong</td>
<td>strong</td>
<td>-</td>
<td>C=O from ester</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 9: Dilute Solution Viscosity Data for BTP 333
Dissolved in 60:40 (w/w) Phenol/1,1,2,2
Tetrachloroethane at 25°C.

\( \eta_0 = \text{Dynamic viscosity of solvent} = 4.2225 \text{ cs} \)

<table>
<thead>
<tr>
<th>CONCENTRATION (g/dl)</th>
<th>BULB</th>
<th>EFFLUX TIME (SEC)</th>
<th>( \eta_s ) (cs)</th>
<th>AVERAGE ( \eta_s ) (cs)</th>
<th>( \eta_{sp} ) (dl/g)</th>
<th>( \ln \eta_r ) (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8027</td>
<td>1</td>
<td>141.01</td>
<td>4.6928</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>135.84</td>
<td>4.6906</td>
<td>4.6923</td>
<td>0.1386</td>
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<tr>
<td></td>
<td>3</td>
<td>144.28</td>
<td>4.6934</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4013</td>
<td>1</td>
<td>133.85</td>
<td>4.4543</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>128.96</td>
<td>4.4530</td>
<td>4.4528</td>
<td>0.1359</td>
<td>0.1323</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>136.82</td>
<td>4.4508</td>
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\[ [\eta] = 0.1336 \text{ dl/g} \]

146
TABLE 10: Intrinsic Viscosity Data for Series I and Series II polymers

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<th>[\eta]</th>
<th>k'</th>
<th>k''</th>
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<tr>
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<td>Sample ID</td>
<td>PA (mol %)</td>
<td>T(_g)</td>
<td>T(_c)</td>
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<tr>
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### SERIES II

<p>| BTP 333   | 31.1       | --     | 106    | 2.92          | 202    | 9.78           |
| BTP 334   | 39.2       | --     | 102    | 1.32          | 214    | 6.89           |
| BTP 225   | 51.0       | --     | 102    | 0.60          | 202    | 3.66           |
| BTP 226   | 63.2       | --     | 98     | 0.19          | 190    | 0.84           |
| BTP 117   | 69.5       | --     | --     | --            | 200    | 0.55           |</p>
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<th>PAB</th>
<th>T&lt;sub&gt;cc&lt;/sub&gt;</th>
<th>ΔH&lt;sub&gt;cc&lt;/sub&gt;</th>
<th>(T&lt;sub&gt;m&lt;/sub&gt;−T&lt;sub&gt;cc&lt;/sub&gt;)</th>
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<td>50</td>
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<tr>
<td>BTP 117</td>
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<td>0.99</td>
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TABLE 13: DSC Results of Polyesters Rescanned to 280 C
at 20 C/min. (Second heating experiment)

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<tr>
<th>Sample ID</th>
<th>PAB (mol %)</th>
<th>Tg C</th>
<th>Tch C</th>
<th>ΔHch cal/g</th>
<th>Tm C</th>
<th>ΔHm cal/g</th>
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<tbody>
<tr>
<td>SERIES I</td>
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<td>BTP 163</td>
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<td>--</td>
<td>--</td>
<td>179</td>
<td>1.67</td>
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TABLE 14: Comparison of Transitions Occurring in DSC and Polarizing Microscope

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<td>T_m (°C)</td>
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<tr>
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<td>195</td>
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<tr>
<td>BTP 145</td>
<td>218</td>
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<td>BTP 127</td>
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<td>218</td>
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<td>SERIES II</td>
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<td>BTP 334</td>
<td>228</td>
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<tr>
<td>BTP 225</td>
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<td>BTP 145 °A</td>
<td>PET °A</td>
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<tr>
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FIGURE 1. Three general forms of liquid crystalline order
**FIGURE 2.** Schematic representation of main chain and side chain liquid crystal polymers [28].
FIGURE 3. Examples of main chain liquid crystal polymers
(a) Alkanoates of 4,4'-dihydroxy - \( \sim C, \sim C' \),
-dimethylbenzalazine [31].
(b) Copolyesters of PET/PAB [2].
FIGURE 4. Dependence of melting point ($T_m$) and the isotropization temperature ($T_i$) on the number of methylene units [64].
FIGURE 5. Schematic diagram of the morphologies above and below the melting point for:
(a) Conventional polymer with chain folded lamellar crystals
(c) Rigid chain nematic polymer

The thicker parts of the lines represent regions where the chain forms three-dimensional crystal lattices [113]
FIGURE 6. Melt viscosity at 275 C of PET modified with p-hydroxybenzoic acid (PHB) [2].
FIGURE 7. The effect of shear rate on melt viscosities for PET/PHB copolyesters [2].
FIGURE 8. Mechanical properties of PET modified with PHB.
(a) Flexural modulus
(b) Tensile strength
(c) Impact strength
FIGURE 9. Experimental set-up for PET depolymerization
FIGURE 10. Experimental set-up for liquid crystal polymer synthesis
FIGURE 11. Hydroxyl number of glycolyzed products as a function of glycolysis time for four metal acetates.
FIGURE 12. Hydroxyl number of glycolyzed products of clear and green reclaimed PET as a function of glycolysis time with lead acetate as catalyst.
FIGURE 13. DSC scans of glycolyzed products
(a) M fraction
(b) O fraction
(c) glycolyzed product
FIGURE 14. HPLC of glycolyzed products
(a) M fraction
(b) O fraction
(c) glycolyzed product

RETENTION TIME (minutes)
166
FIGURE 15. Infrared absorption spectrum of the M fraction (BHET) obtained from the glycolyzed product.
FIGURE 16. Infrared absorption spectrum of the O fraction (Dimer) obtained from the glycolyzed product.
FIGURE 17. Infrared absorption spectrum of PET
FIGURE 18. Proton NMR spectrum at 300 MHz of polyester samples dissolved in chloroform/trifluoroacetic acid mixture (70 : 30 v/v)

18.1  NMR Spectrum of PET
18.2  NMR Spectrum of BTP 163
18.3  NMR Spectrum of BTP 154
18.4  NMR Spectrum of BTP 145
18.5  NMR Spectrum of BTP 136
18.6  NMR Spectrum of BTP 127
18.7  NMR Spectrum of BTP 333
18.8  NMR Spectrum of BTP 334
18.9  NMR Spectrum of BTP 225
18.10 NMR Spectrum of BTP 226
18.11 NMR Spectrum of BTP 117
FIGURE 18.2 NMR Spectrum of BTP 163
FIGURE 18.3 NMR Spectrum of BTP 154

CHEMICAL SHIFT (ppm)
FIGURE 18.4 NMR Spectrum of BTP 145
FIGURE 18.6 NMR Spectrum of BTP 127
FIGURE 18.7 NMR Spectrum of BTP 333
FIGURE 18.8 NMR Spectrum of BTP 334
FIGURE 18.9 NMR Spectrum of BTP 225
FIGURE 18.10  NMR Spectrum of BTP 226
FIGURE 18.11 NMR Spectrum of FTP 117
FIGURE 19. Mole percent of PAB connected directly to another PAB as a function of PAB content

(●) Series I polymers

(■) Series II polymers

(○) Eastman PET/PAB copolymers [90]

(—) Random copolymers of PET/PAB [90]
FIGURE 20. Infrared absorption spectrum of BTP 117 polymer
FIGURE 22. Infrared absorption spectrum of PAB homopolymer
FIGURE 23. Infrared absorption spectrum of PAB monomer
FIGURE 24. Infrared absorption spectrum BTP 145 insoluble fraction
FIGURE 25. Infrared absorption spectrum of (BHET + TA) pre-polymer
FIGURE 26. Intrinsic viscosity of BTP 333 in phenol/1,1,2,2 tetrachloroethane solvent mixture (60:40 w/w) at 25°C.
FIGURE 27. Differential Scanning calorimetric scans of Series I polyesters that had been heated to 280°C, quenched in liquid nitrogen and then scanned in the DSC at 20°C/minute. (Initial heating experiment)
FIGURE 28. Differential Scanning Calorimetric scans of Series I polyesters cooled at 20 C/minute from the melt (280 C).
FIGURE 29. Differential Scanning calorimetric scans of Series II polyesters that had been heated to 280 C, quenched in liquid nitrogen and then scanned in the DSC at 20 C/minute. (Initial heating experiment)
FIGURE 30. Differential Scanning Calorimetric scans of Series II polyesters cooled at 20 C/minute from the melt (280 C).
FIGURE 31. Differential Scanning Calorimetric scans of Series I polyesters rescanned at 20 C/minute (Second heating experiment).
FIGURE 32. Differential Scanning Calorimetric scans of Series II polyesters rescanned at 20 C/minute (Second heating experiment).
FIGURE 33. Spherulites of PET showing Maltese cross pattern when observed between cross polaroids (x 860)
Figure 34. Micrograph of BTP 145 at 245 °C, showing threads and ringed domain (x 200)
Figure 35. Celanese liquid crystal polyester at 250°C, showing a heavily threaded texture and a bubble containing a birefringent film (x 200)

198
Figure 36. Highly birefringent film of BTP 225 at 250°C, showing extinction bands organized as a four-fold "brush" (x 200)
Figure 37. Nematic Schlieren texture of BTP 225 showing extinction bands which rotate at the same rate and in the same direction as the crossed polar
Figure 38. Micrograph of BTP 225 at 250°C, showing birefringent phase, isotropic fluid and an air bubble (x 200)
Figure 39. Two phase microstructure of BTP 225 cooled rapidly from 300 °C to room temperature (x 200)
Figure 40. BTP 226 sample cooled slowly from 300°C to room temperature, showing two phase region which is "frozen in" inspite of slow cooling (x 200)
FIGURE 41. Thin, stressed section of BTP 226 showing local birefringence (x 200).
FIGURE 42. Extinction bands seen in BTP 145 which was quenched from 300°C, heated to 260°C and then cooled back to room temperature (x 200)
FIGURE 43. Phase separation in BTP 334, indicating that 40 mole % PAB units is sufficient for mesophase formation (x 200)