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Synthesis, randomization, and characterization of liquid crystalline copolyesters containing substituted phenylene terephthalate and ethylene terephthalate units for blending studies with poly(ethylene terephthalate) (PET).

Darius K. Deak
University of Massachusetts Amherst

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SYNTHESIS, RANDOMIZATION, AND CHARACTERIZATION
OF LIQUID CRYSTALLINE COPOLYESTERS CONTAINING
SUBSTITUTED PHENYLENE TEREPTHALATE AND
ETHYLENE TEREPTHALATE UNITS FOR BLENDING
STUDIES WITH POLY(ETHYLENE TEREPTHALATE) (PET)

A Dissertation Presented
by
DARIUS K. DEAK

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
of the requirements for the degree of
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Polymer Science and Engineering
SYNTHESIS, RANDOMIZATION, AND CHARACTERIZATION OF LIQUID CRYSTALLINE COPOLYESTERS CONTAINING SUBSTITUTED PHENYLENE TEREPHTHALATE AND ETHYLENE TEREPHTHALATE UNITS FOR BLENDING STUDIES WITH POLY(ETHYLENE TEREPHTHALATE) (PET)

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ABSTRACT
SYNTHESIS, RANDOMIZATION, AND CHARACTERIZATION OF LIQUID CRYSTALLINE COPOLYESTERS CONTAINING SUBSTITUTED PHENYLENE TEREPTHALATE AND ETHYLENE TEREPTHALATE UNITS FOR BLENDING STUDIES WITH POLY(ETHYLENE TEREPTHALATE) (PET)
FEBRUARY 1997
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Directed by: Professors Robert W. Lenz and Simon W. Kantor

The main objective of this dissertation was the synthesis and modification of thermotropic liquid crystalline copolyesters to be blended with isotropic engineering thermoplastics such as PET. There has been a lot of interest in the last several years in the blending of thermotropic LCPs with engineering thermoplastics to form in situ composites. Yet, due to the typically high melt transitions of highly aromatic thermotropic LCPs, several methods have been studied in this dissertation to reduce the melt transitions of LCPs to within the processing window of engineering thermoplastics.

Three series of thermotropic, aromatic copolyesters derived from EHQ, PHQ, HQ, EG, and TA were synthesized, and characterized by PLM, DSC, NMR, TGA, and solution viscometry. It was shown that the melt transition was effectively reduced
through the copolymerization of the monomers. For melt blending with engineering thermoplastics, such as PET, the transition temperatures for the Series III samples were too high, while some of the Series I and II copolymers with low amounts of PT units had thermal transitions in the range which would make them more favorable for blending.

Several different liquid crystalline copolyesters were thermally post-treated successfully to increase their degree of randomness. Both poly(ethoxyphenylene terephthalate-co-ethylene terephthalate)s and poly(phenylphenylene terephthalate-co-ethylene terephthalate)s were thermally randomized. It was found that increased randomness numbers caused decreased melt transition temperatures and crystallization temperatures. The more random sequence distributions also resulted in a decreased crystallinity of the copolyesters as observed by reduced enthalpies of fusion and crystallization.

Two different LC copolyesters, poly(EPT-co-ET) and poly(PPT-co-ET), were solution blended with PET using a mixture solvent of TFAA/Chloroform. Four different samples of each LC copolyester, with varying degrees of randomness, were used in the blends. The blends were characterized by DSC, polarized light microscopy, and rheological testing. It was observed that the melt viscosity of the blend had a strong dependence on the degree of randomness of the LC copolymer used. The copolyesters with high degrees of randomness caused a reduction of the melt viscosity.
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CHAPTER 1

LIQUID CRystalline POLYMERS

Introduction

Liquid crystals (LC) are a rod-like molecules which form a mesophase (short for mesomorphic phase) with properties of both a crystalline solid and an isotropic liquid. LCs exhibit the long range order representative of crystalline solids, while possessing flow properties similar to isotropic liquids. While a crystalline solid may have positional and orientational order, an LC will lose the positional order but retain some of the orientational order. This is unlike an isotropic liquid which would lose both positional and orientational order\(^1\) (See Figure 1.1). The positional disordering of liquid crystals represent one of three different possible mesophases. The other two are plastic crystals, which show orientational disordering, and condis crystals, which show conformational disordering\(^2\-4\).

A liquid crystalline polymer (LCP) is any macromolecule which exhibits an LC phase. A polymer is a macromolecule made up of sequences of repeat units called monomers. For the polymer to form an LC phase, either the monomer units must induce the
Figure 1.1: Illustration of the differences in ordering between a crystalline solid, a liquid crystal, and an isotropic liquid.

Mesophase, or the polymer chain as a whole must cause the added orientation of the LC phase.

The ability of an LCP to obtain orientational order is a result of intermolecular repulsions of rigid units, or *mesogens*, in the molecules, which occur because at a critical concentration of these rigid units a random mutual arrangement of the chains is no longer possible. At this point, to minimize both the volume and the free energy, the rigid polymers order themselves into an anisotropic state. The critical concentration necessary to produce the liquid crystalline state is a function of molecular weight, molecular weight distribution, temperature, solvent, and the
degree of asymmetry of the macromolecule (determined as the ratio of the equilibrium length to the diameter of the chain). There can be several causes for the asymmetry (or rigidity) of the polymer chains, such as:

1) restrictions on the free rotation of the chain due to inclusions in the backbone of cyclic units
2) cyclization (i.e., helical conformation formation) through intramolecular hydrogen bonds
3) quasi-conjugation and coplanarity of amide groups
4) 'ladder' polymer formation.

Typically these rigid units are in the shape of rigid rods, but there are several shapes which still maintain the anisotropy of shape which is a fundamental requirement for the formation of a liquid crystalline phase. Disk-like, pyramid-like, and phasm-like (from the name of the six-legged stick-like insects) mesogens have all been shown to form LC phases.

LCPs are often categorized by the placement of the mesogen on the polymer chain, whether they are main-chain LCPs or side-chain LCPs (also called comb LCPs). However, Brostow has created a more comprehensive classification scheme for a precise description and definition of LCPs by the placement and shape of the mesogen (See Table 1.1). The only major omission in Brostow's list of LCP structures is that of a dendritic or hyperbranched LCP. There are several examples in the literature
Table 1.1: Classification of liquid crystalline polymers by molecular structure.

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of LC hyperbranched polymers. Percec and coworkers and Ringsdorf et al. have studied LC hyperbranched and dendridic polyethers\textsuperscript{8-11}. Also Kim has shown the existence of LC hyperbranched polyamides\textsuperscript{12}.

Though knowledge of LCPs has existed since the 1950s\textsuperscript{13,14}, it was not until the 1970's that the potential for the use of these materials in high strength and stiff fibers was realized\textsuperscript{15,16}. The high performance of these fibers is a result of the orientation imparted on the LCP during processing which is maintained in the solid state. There are two important relaxation rates for an LCP; one is the relaxation rate for the orientation and the other is the relaxation rate of the stress. The time for the stress to relax is many times shorter than the time for the orientation to relax\textsuperscript{17}. This longer orientational relaxation rate allows an LCP sample which has been oriented, for example by fiber hot drawing, to maintain a large amount of the orientation after the stress on the fiber is removed. In essence, elastic energy is stored to produce the desired orientation and this results in a high modulus fiber.

Another reason that LCPs are of interest, is that in some LC phases the melt viscosity is much lower than the melt viscosity of typical engineering thermoplastics in the isotropic state\textsuperscript{18,19}. Besides the improved mechanical properties and lower melt viscosities, when compared to typical engineering thermoplastics such as poly(ethylene terephthalate) (PET) or polycarbonate, LCPs have several other properties which make them attractive for use
in fibers or films. They have superior chemical stability, lower flammability, very low isobaric expansivity (or thermal expansion coefficient), low water absorption, and excellent barrier properties.

**Liquid Crystalline Phases**

LCPs can also be classified by the liquid crystalline phase which they display. There are two major classes of LC phases, the nematic phase and the smectic phase. The nematic phase can be divided into ordinary nematics and twisted nematics (also called cholesterics). The smectic phase can be sub-divided into several distinct phases which are marked conventionally as smectics A through K. For several of the more common LC phases, such as the nematic, smectic A, and smectic C phases, characterization is possible through the use of polarized light microscopy (PLM) (or polarizing optical microscopy). By viewing a LC phase between crossed polarizers, the birefringent nature of the LC phase allows the observation of a liquid crystalline *texture*. The texture of an LC is analogous to the morphology of a solid crystal. The features of a texture are caused by various defects in the liquid crystal such as point defects or disclinations. For those LC phases which are more difficult to classify through PLM, the characterization is typically performed using X-ray analysis.
The Nematic Phase

The nematic LC phase is characterized by a high degree of long range orientational order. The average direction of the long axis of the chains defines the director $\mathbf{n}$, which is a unit vector (see Figure 1.2a). The degree of alignment of the liquid crystal is defined by the order parameter or anisotropy factor $s$:

$$s = 0.5\langle 3\cos^2\theta - 1 \rangle$$

where $\theta$ is defined as the angle between the long axis of a given molecule and the director $\mathbf{n}$. An applied external magnetic or electric field or the application of viscous flow can result in a uniform alignment of the nematic phase.

The twisted nematic phase (or cholesteric phase) is similar to the ordinary nematic phase in that each layer has the same long range orientational order without positional order. The difference is that the individual director is turned through a fixed angle from layer to layer in the cholesteric phase. The pitch, $p$, is defined as the distance between layers with equivalent director vectors (see Figure 1.2b).

The third types of nematic LC phases are the cybotactic nematic phases, which show a short-range smectic-like ordering of the molecular centers in plane. There are two types of cybotactic nematic phases, the skewed cybotactic phase (where
Figure 1.2: Schematic molecular arrangement in a) nematic and b) cholesteric phases.
the molecules are skewed at and angle \( \alpha \) and the normal cybotactic phase\(^6,21\).

There are several characteristic textures of the nematic phase which distinguish them from other liquid crystalline phases. The first such texture are nematic droplets. As a nematic liquid crystal is cooled down from the isotropic state, small round 'droplets' will form. With further cooling, the droplets will coalesce into larger structures. Another texture characteristic of nematic phases is the Schlieren texture, which appears between crossed polarizers as an irregular network of black brushes branching out from several scattered points and passing continuously from one point to another. While the Smectic C phase also displays a Schlieren texture, the two can be differentiated by the strength of the disclinations, \( S \), which is determined from the number of dark brushes meeting at one point:

\[
|S| = \text{number of brushes}/4
\]

The nematic Schlieren texture can have values of \( S = \pm 1/2 \) or \( \pm 1 \), while the smectic C phase can only have \( S = \pm 1 \). Another possible texture of the nematic phase is the threaded texture which is due to disclinations lying more or less perpendicular to the glass slide used for the microscopy experiments. So while the end may be attached to the glass surface, the rest of the chain floats freely in the sample, giving the appearance of 'threads' flowing through the
sample. Lastly, the nematic marbled texture consists of several areas with different molecular orientation. The interference color is nearly constant within each individual area which indicates nearly homogeneous regions.

The Smectic Phase

Although the number of different smectic phases seems to be constantly growing, the existence of the smectic A (S\text{A}) through K (S\text{K}) phase are well documented\textsuperscript{21,22}. Smectic phases display a higher degree of order than nematic phases. The different smectic phases can be placed into three general categories with the one exception being the smectic D phase. The S\text{D} phase, while characterized as a smectic as a consequence of history, has an overall cubic symmetry and is more likely a plastic crystal than a liquid crystal\textsuperscript{6}.

The first category of smectics are smectic phases with unstructured layers. This includes the S\text{A} and S\text{C} phases. The smectic A phase consists of a parallel arrangement of molecules that form into layers (see Figure 1.3a). The long axis of the molecules tend to be orthogonal to the layer planes, forming a two-dimensionally oriented liquid. The S\text{A} phase is the least ordered of the smectic phases. The S\text{C} phase is a tilted analog of the S\text{A} phase (see Figure 1.3b). Chiral molecules can show a twisted smectic C (S\text{C}*) phase.
The 'hexatic' smectics include the smectic B, F, and I phases. The 'hexatic' smectic B phase ($S_{BHex}$) consists of molecules which tend to be perpendicular to the layers, and are arranged on a triangular lattice. The layers are again oriented as a two-dimensional liquid. The $S_F$ and $S_I$ phases are tilted analogs of the $S_{BHex}$. In the $S_F$ phase, the molecules are tilted towards the sides of the hexagon, and in the $S_I$ phase the molecules are tilted towards the apices of the hexagonal net. Chiral $S_F$ ($S_F^*$) and $S_I$($S_I^*$) phases are also possible.

The 'crystalline' smectics include the smectic B, E, G, H, J, and K phases. These phases are classified as smectic phases on the basis of polarizing light microscopy experimentation, but X-ray studies have shown that these phases possess three-dimensional
positional order. Because of the highly ordered nature of these phases, they are more accurately termed crystals (though soft crystals due to weak interlayer forces) not liquid crystals.\footnote{\textit{^*}}

Though differentiation of all the smectic phases through observation of their LC textures is difficult, there are some various textures which are characteristic of smectic phases. Smectic 'batonnets', elongated sharp-pointed smectic particles, are formed when the $S_A$ phase is cooled directly from the isotropic liquid phase. The focal-conic fan-shaped texture results when the batonnets grow and merge as the $S_A$ phase is further cooled. Also, oily streaks, which are long transversely striated bands consisting of chains of focal conic groups, are possible in the $S_A$ phase. The smectic C phase can also form batonnets and the fan-shaped texture. The only difference between the $S_C$ and the $S_A$ focal-conic textures is that the $S_C$ phase is divided into domains of different tilt orientations by inversion walls. Also, as stated above, the smectic C phase can display a Schlieren texture. Chiral smectic C phases may lead to the formation of a twisted smectic texture.\footnote{\textit{\textsuperscript{6,21,22}}}.

\textbf{Liquid Crystalline Phase Formation}

As mentioned above, when a critical concentration of the rigid mesogens is reached, an LC phase can form. For lyotropic LCs the critical concentration can be achieved by a solution of the rigid molecules in an appropriate solvent. An LC phase can be obtained by raising the temperature for thermotropic liquid
crystals, but the critical concentration is high and requires the bulk molecule in the melt to form the LC phase\textsuperscript{23}. Two other classes of LCPs are \textit{amphotropic}, which can reach the liquid crystalline phase either in solution or in the melt, and \textit{barotropic}, which can reach the liquid crystalline phase through pressure elevation\textsuperscript{7,24}.

**Lyotropic Liquid Crystalline Polymers**

A lyotropic liquid crystalline phase is formed when the concentration of rigid-chain polymers in an appropriate solvent reaches the critical value necessary to cause LC phase formation. A liquid crystalline phase is not typically observed in the melt for lyotropic LCPs because of the extremely high melt transitions of these polymers.

Above the critical concentration, the rheological behavior of lyotropic solutions can be typically divided into three regions: (1) a shear thinning region at low shear rates; (2) a Newtonian plateau region at intermediate shear rates; and (3) another shear thinning region at high shear rates\textsuperscript{25,26}.

Most of the interest in lyotropic polymers is due to the attractive tensile and thermal properties of the fibers spun from the lyotropic solutions. Aromatic polyamide fibers have shown high tensile strength ($\sigma_b > 2$ GPa), low elongation at break ($\varepsilon_b <$
6%, and high modulus (50 < E < 400 GPa). The physical properties of the fibers are due to several factors including the presence of impurities and voids, the chain length distribution, the strong anisotropy of the forces between atoms, the disorientation of the chains with respect to the fiber axis, and the non-uniformity of the structure and morphology in the cross-section and along the fiber\textsuperscript{27}. Thermally, aromatic polyamide fibers have been shown to be stable up to extremely high temperatures. Poly(p-phenylene terephthalamide) (PpPTA) (Figure 1.4a) has a decomposition temperature above 600°C. A heterocyclic polymer, such as poly (6,9-dihydro-6,9-dioxobenzimidazo benzo phenanthroline-3,12-diyl) (BBB)\textsuperscript{28} (Figure 1.4e), has shown thermal stability up to 700°C. Benzobisazo polymers have shown thermal stability above 600°C\textsuperscript{29}. Some examples of lyotropic LCPs are shown in Figure 1.4. Other examples of lyotropic LCPs not included in Figure 1.4 are polyethers\textsuperscript{30}, poly(diacetylenes)\textsuperscript{31}, and many cellulose derivatives\textsuperscript{1}.

**Thermotropic Liquid Crystalline Polymers**

A thermotropic liquid crystalline phase is formed in the bulk when the LCP is heated through the melt transition. Unlike lyotropic liquid crystalline polymers, thermotropic LCPs typically have significantly lower thermal transitions so that a transition from the crystalline state to the liquid crystalline state exists below the thermal degradation of the polymer. The crystalline
Figure 1.4: Lyotropic liquid crystalline polymers:  a) PpPTA, b) PBO, c) PBT\textsuperscript{27}, d) PBG\textsuperscript{32}, and e) BBB\textsuperscript{28}
to-liquid crystalline transition, along with the liquid crystalline-to-isotropic liquid transition, are governed by changes in temperature, pressure, and deformation.

As a result of the potentially useful properties of LCP, such as higher chemical resistance, lower flammability, higher modulus, lower isobaric expansivity (sometimes as low as zero), and lower melt viscosities, interest in LCPs has increased, especially in the area of thermotropic liquid crystalline polyesters. An expansive amount of papers have been written documenting the synthesis and characterization of various LC polyesters\textsuperscript{33-70}(See Figures 1.6 and 1.7). Other types of thermotropic LCPs in the literature include, but are not limited to, polyamides\textsuperscript{71-75}, poly(ester amides)\textsuperscript{76,77}, polyurethanes\textsuperscript{72,78-80}, poly(ester imide)s\textsuperscript{81}, poly(amide-imide)s\textsuperscript{82}, poly(ester sulfides)\textsuperscript{83}, poly(ester carbonates)\textsuperscript{84,85}, poly(azoxy-esters)\textsuperscript{86}, poly(carbonate-co-styrene)\textsuperscript{87} (See Figures 1.6 and 1.7).

Because of the typically high cost of LCPs when compared to typical engineering thermoplastics, there has been a lot of interest in the blends of thermotropic LCPs with engineering thermoplastics\textsuperscript{7,61,88-97}. These blends are typically referred to as \textit{in situ} composites because of the reinforcing fibrils formed by the LCP during processing. Through this technique, the improved properties of the LCP can be imparted to the blend while only using a small weight percent of the expensive LCP.
The addition of LCP to engineering thermoplastics such as PET has been shown to: 1) impart increased strength and modulus through the improved overall orientation of the blend; 2) increased dimensional stability due to the very low isobaric expansivity of LCPs; and 3) increased processing output, and reduced wear and tear on the processing machines due to the decreased overall melt viscosity of the blends. Baird and Sun showed that films reinforced by LCPs had a tensile modulus 3 to 4 times higher than that of neat films. Joseph, et al. showed that blends of LCPs with PET had increased rates of crystallization, and a three-fold increase in the bending modulus. Brown and Alder have written a good comprehensive overview of the reinforcing abilities of LCPs utilized by in situ composites. In our laboratory Narayan showed that just 2.5 weight percent of an LCP in PET can reduce the melt viscosity by an order of magnitude. Though Heino, et al. observed that it took 30 weight percent of an LCP to appreciably decrease the melt viscosity of the LCP/polypropylene blend. The amount of LCP needed to reduce the melt viscosity appreciably will be dependent on both the exact LCP/engineering thermoplastic system used, and the compatibility of the blend.

The most significant problem with the blending of LCPs with engineering thermoplastics is that typically the highly aromatic thermotropic LCPs have much higher thermal transitions than the engineering thermoplastics. Baird and Sukhadia suggested a possible solution by using a dual extruder mixing technique. This method allows two polymers with widely different thermal
transitions to be processed together by extruding the two components separately. The two extruders are then connected to a static mixer where the two streams are blended together. Another advantage of this technique is the production of continuous TLCP fibrils with none of the skin-core morphology which tends to lower the mechanical properties of the blend\textsuperscript{100}. The only drawback of the technique is that it does not take advantage of the low melt viscosity of the TLCP. By extruding the two components separately, the TLCP can not improve the processability of the engineering thermoplastic through a reduction of the blend melt viscosity.

In many industrial applications the improved processability is just as important as the improved mechanical properties. In these cases modifications of the TLCPs are necessary to lower the thermal transitions to a level where processing with engineering thermoplastics is possible\textsuperscript{20,101,102}. Lenz and coworkers, and others have done expansive research on different techniques to modify the liquid crystalline properties of the polymers. Flexible spacers in combination with the rigid mesogens were found to lower the transition temperatures by reducing the aspect ratio\textsuperscript{33,35,36,43,64,103} (see Figure 1.5a). Typical flexible spacers used include methylene units (CH\textsubscript{2}) and ethylene oxide units(CH\textsubscript{2}CH\textsubscript{2}O). Lenz, et al. have shown that there is an odd-even effect for the thermal transitions due to the length of the spacer. Flexible spacers with an even number of atoms generally have higher thermal transitions than odd-lengthed spacers. Also after
a critical length, the flexible spacer was found to cause a change of the LC phase from nematic to smectic. 

Nonlinear or kinked monomers can decrease the thermal transitions by lowering the persistence length of the chain and by disrupting intermolecular interactions (see Figure 1.5b). Possible "kinked" monomers include meta- or ortho-linked phenyls, 1,6- or 2,5-linked naphthalenes. Kinked bonds within the monomers are also effective, and include -C(CH$_3$)$_2$-, -CH$_2$-, -O-, -S-, -SO$_2$-, or -CO-. Kinks can also be incorporated by adding kinked functionalities such as anhydride or carbonate bonds. Yet, because the mechanical properties of TLCP ultimately depend on the rod-like quality of the polymer, the introduction of kinks can have an adverse effect on the mechanical properties.

Asymmetrically placed and/or bulky substituents on the mesogenic groups generally cause a reduction of the transition temperatures because of steric effects which decrease the overall length-to-width ratio, and frustrates the lateral packing (see Figure 1.5c). It was found that the size of the substituent was a more important factor than the polarity of the substituent for lowering the thermal transitions.

Copolymerization of monomers with different mesogenic units can either reduce the thermal transitions by lowering the symmetry of the polyester and disrupting the lateral packing or
Figure 1.5: Possible architectural modifications of TLCPs to lower thermal transitions including: a) inclusion of flexible spacers; b) inclusion of asymmetrically placed and/or bulky substituents; c) copolymerization of monomers; and d) use of kinked or nonlinear monomers.
Poly(amide-imides)

Polyamides

Aromatic Polyesters

Copoly(ether-ester) Elastomers

Polyesters

Figure 1.6: Thermotropic LCPs\textsuperscript{33,57,71,82,112}. 

23
Poly(azoxy-esters)

\[
\begin{array}{c}
\text{O} \quad \text{N=NN} \quad \text{O} \\
\text{O} \quad \text{OC(CH}_2\text{nC)} \\
\end{array}
\]

\[n \leq 14\]

Poly(cabonate-co-styrene)

\[
\begin{array}{c}
\text{O} \quad \text{OC(CH}_2\text{6O)} \\
\text{O} \quad \text{OCH}_2\text{CHOCO(CH}_2\text{6O)} \\
\end{array}
\]

Chlorinated Polyesters

\[
\begin{array}{c}
\text{O} \quad \text{OC} \\
\text{O} \quad \text{Cl} \\
\end{array}
\]

Side-Chain Polymers

\[
\begin{array}{c}
\text{O} \quad \text{Si} \\
\text{O} \quad \text{OCH}_3 \\
\text{(CH}_2\text{)}_2\text{O} \\
\text{(CH}_2\text{)}_2\text{O} \\
\end{array}
\]

Aliphatic Substituted Polyesters

\[
\begin{array}{c}
\text{O} \quad \text{S(CH}_2\text{nCH}_3) \\
\text{O} \quad \text{S(CH}_2\text{nCH}_3) \\
\text{O} \quad \text{OCH}_3 \\
\text{O} \quad \text{O} \\
\end{array}
\]

\[n = 7, 11, 15\]

Figure 1.7: More thermotropic LCPs\(^{86,87,113-116}\).
increase thermal transitions by either imparting stronger intermolecular attractions through hydrogen bonding or dipole interactions (see Figure 1.5d). Also copolymerization of monomers tends to increase the temperature ranges of mesophase stability. Industrially, comonomer combinations with different substituents, which cause frustrated packing are preferred because they tend to have higher degrees of liquid crystallinity due to a more rod-like nature. This can lead to better high temperature performance, and improved chemical and hydrolysis resistance when compared to TLCPs which have kinks or flexible groups\textsuperscript{20,34,48,51,61,62,67,103,107-111}.

Another possible modification of LC polyesters, and more specifically LC copolyesters, that has been studied is the modification of the sequence distribution of the different monomers in the copolyester\textsuperscript{42,48,110,117-124}. It has been shown by Jin, et al.\textsuperscript{48,110,117,120} that a more random distribution of monomers will lead to lower glass transition temperatures, lower melting points, reduced crystallinity, and even different crystal structures. Stupp, et al.\textsuperscript{42,118,119} showed that the nematic-isotropic transition for ordered LC polyesters was over a very narrow 5°C range, while the disordered polyester had a very broad nematic-isotropic transition over a 120°C biphasic range. Park, et al.\textsuperscript{124} showed that for aromatic copolyimides, a change from alternating to random ordering can have drastic changes in the solubility of the copolymer.
Amphotropic Liquid Crystalline Polymers

Some LCPs can obtain their LC phase through both critical concentrations in solution and transitions into the melt state. (Acetoxypropyl)cellulose displays LC phases thermotropically between 85°C and 174°C (depending on molecular weight), and lyotropically in acetone above 50 weight percent\(^{125,126}\). Also Aharoni showed that poly(isocyanates)\(^{127}\) will form liquid crystalline phases in the melt above 120°C to 170°C, and in solutions of tetrachloroethane.

Dissertation Outline

The main objectives of this project have been described in three different sections in this thesis. The first section deals with the synthesis of novel thermotropic liquid crystalline copolyesters. As stated above, it was shown in our laboratory\(^ {61}\) that only 2.5 weight percent of a liquid crystalline copolyester composed of ethoxyphenylene terephthalate units and ethylene terephthalate units effectively reduced the melt viscosity of poly(ethylene terephthalate) (PET). The only drawback was that the ethoxyhydroquinone monomer used in the LC copolyester is expensive to make, so the objective was to look at other possible monomers that could replace the ethoxyhydroquinone monomer in the copolyester. Once the new copolymers were synthesized they were thoroughly characterized by DSC, NMR, TGA, solution
viscometry, and polarizing light microscopy. This work is presented in Chapter 2.

The next section of this study pertains to the thermal randomization of liquid crystalline copolyesters. Two specific copolyesters, poly(ethoxyphenylene terephthalate-co-ethylene terephthalate) and poly(phenylphenylene terephthalate-co-ethylene terephthalate), were thermally post-treated in the bulk to increase the randomness of their sequence distributions through transesterification reactions. The objective was to study the changes in the LC properties of the copolymers with changes in randomness. The randomized copolymers were characterized primarily by NMR, DSC, and solution viscometry. This work is presented in Chapter 3.

Chapter 4 of this dissertation covers the effects of the different randomized LC copolymers on blends with PET. The LCPs were solution blended with PET at a five weight percent level. The objective of this work was to study the effect of the randomization of the copolymers on their effectiveness as processing aids. The blends were characterized by DSC, polarizing light microscopy and rheological experimentation.

The last section of this dissertation includes a summary of all the work discussed in the previous chapters. Also suggestions for future work on the project are discussed there. This will be covered in Chapter 5.
References


CHAPTER 2

THERMOTROPIC LIQUID CRYSTALLINE COPOLYESTERS
CONTAINING SUBSTITUTED PHENYLENE TEREPTHALATE AND
ETHYLENE TEREPTHALATE UNITS

Introduction

Aromatic polyesters, which exhibit thermotropic liquid crystalline (LC) behavior, are of great interest because of their many unique properties. It is well known that in the nematic phase their reduced melt viscosity allows for much easier processing to form, for example, highly oriented fibers. There is also a great deal of interest in the formation of in situ composites of thermotropic LC polyesters with common thermoplastics such as poly(ethylene terephthalate) (PET), poly(ethylene naphthylate) (PEN), and polycarbonate. The main problem in the processing of LC polyesters is that, because of their high aromatic content, they typically have very high melting transitions and low solubilities in all but very aggressive solvents. These factors often make them difficult to process.

Several different types of structural modifications used to reduce the melting transition and increase solubility have been
investigated, including the following: (1) insertion of flexible spacers between the rigid rod mesogens to reduce the transition temperatures by reducing the aspect ratio of the polymer chain \(^2-^4\); (2) asymmetrically placed and/or bulky substituents on the mesogenic groups to reduce the transition temperatures because of steric effects which decrease the overall length-to-width ratio, and disrupt the lateral packing\(^2,5-12\); (3) copolymerization of monomers with different mesogenic units to reduce the thermal transitions by lowering the symmetry of the polyester and by disrupting the lateral packing\(^3,10,11,13-18\); (4) use of nonlinear or kinked monomers to decrease the thermal transitions by lowering the persistence length of the chain, and by disrupting intermolecular interactions\(^7,10,19,20\); and (5) modification of the sequence distribution of the different monomers in a LC copolyester to generate a more random distribution of monomers, thus lowering thermal transitions by breaking up the rod-like blocky regions\(^16,17,21-29\). This chapter will focus on the use of bulky substituents and the copolymerization of different monomers to reduce the melting temperatures of the TLCPs.

LC polyesters and copolyesters based on ethoxyhydroquinone (EHQ) and terephthalic acid (TA) were reported by Lenz and coworkers in this laboratory\(^8,9,18\). It was observed that small amounts of poly(2-ethoxy-1,4-phenylene terephthalate-co-ethylene terephthalate), \{poly(EPT-co-ET)\}, blended with poly(ethylene terephthalate), (PET), caused a decrease in the melt viscosity. However, because the EHQ
monomer was not readily available, there was interest in finding a more accessible LC copolyester with similar properties. Skovby, et al.\textsuperscript{7} reported the synthesis of LC copolyesters derived from phenylhydroquinone (PHQ) and TA. Because of the commercial availability of PHQ monomer, it was decided to study copolyesters based on TA, EG, EHQ, PHQ, and unsubstituted hydroquinone (HQ) which is also readily available.

This chapter will describe the synthesis and characterization of three series of copolyesters with varying compositions. Series I copolymers included ratios of HQ to EHQ varying from 70:0 to 0:70, but the amount of EG in the reaction mixture was held constant at 30%. The HQ, EHQ, and EG monomers were reacted with an equimolar amount of TA. Copolymers of Series II and III were prepared with variable molar ratios of HQ:PHQ and EHQ:PHQ, respectively, in the same fashion as Series I (see Scheme 1).

**Experimental**

**Monomer Synthesis**

EHQ was synthesized from 3-ethoxy-4-hydroxybenzaldehyde, hydrogen peroxide and sodium hydroxide, as described previously\textsuperscript{9,18}, according to Scheme 2. In a 1000 mL Nalgene flask with a three-holed rubber stopper fitted with a thermometer and an argon gas inlet were placed a magnetic stirrer, 40g (0.24 moles) of 3-ethoxy-4-hydroxybenzaldehyde,
Scheme 1. Copolymerization of EH, PH, H, and EG with TC

and 690 mL of a sodium hydroxide solution (19.3g [0.48 moles] of NaOH in 690mL of water). The benzaldehyde was allowed to dissolve completely before 29.5mL of 30% by weight of hydrogen peroxide aqueous solution was added to the reaction vessel, under positive argon flow, through the third hole in the rubber stopper using a syringe. Care was taken with the addition of the hydrogen peroxide because of the extreme exothermic nature of the reaction, which caused the temperature of the reaction solution to rise from room temperature to about 50-60°C and turned the solution to either a dark brown or black color. The reaction was
carried out until the solution temperature decreased to room
temperature in a few hours. The solution was then acidified with
80mL of 1:1 solution of HCl and water, placed in a 1000mL
separatory funnel, and the ethoxyhydroquinone was extracted
four times using ethyl ether (100-150mL each extraction). The
ether solution was washed 3 times with a saturated aqueous
sodium metabisulfite solution (50-75mL each) and 3 times with
water (50-75ml each). The decanted ether solution, which was
still black, was dried over magnesium sulfate overnight, filtered
the next morning, and the ether was distilled off. The remaining
product was placed under vacuum to remove all traces of ether
until the monomer was completely solidified. 250mL of
chloroform was added to dissolve the monomer, and the solution
was placed in a refrigerator overnight to allow the monomer to
precipitate. Ethoxyhydroquinone was filtered, dried, and purified
by sublimation at 120-130°C under vacuum to yield white
crystals. The $^1$H NMR spectrum of the monomer dissolved in
trifluoroacetic acid (TFAA) contained peaks at 1.5(-CH$_3$), 4.2(-
OCH$_2$-), and 6.9(phenyl group) ppm. The solid state $^{13}$C NMR
spectrum contained phenyl peaks at 150 (-COH, ortho to ethoxy
carbon), 147 (-COEt), 136 (-COH, meta to ethoxy carbon), 114 (-
CH, ortho to ethoxy carbon), 104 (-CH, meta to ethoxy carbon), and
100 (-CH, para to ethoxy carbon), 63 (-OCH$_2$-) and 13 (-CH$_3$) ppm.
The purity of the monomer was characterized by differential
scanning calorimetry (DSC), which showed a sharp peak at the
melt transition at 117°C.
Phenylhydroquinone (PHQ), hydroquinone (HQ), ethylene glycol (EG), and terephthaloyl chloride (TC) were purchased from Aldrich Chemical Company. The PHQ, HQ, and TC were all purified by sublimation. EG was used as received in a solution of dry methylene chloride. Triethylamine and methylene chloride were distilled over calcium hydride.

**Polymer Synthesis**

All copolymers were prepared by solution polycondensation reactions according to Scheme 1. A 500 mL three-necked round bottom flask was equipped with a magnetic stirring bar, a reflux condenser, a dropping funnel, and a nitrogen inlet tube. All substituted hydroquinone monomers (70 mole percent) and EG (30 mole percent) were charged into the flask and then dissolved in methylene chloride. A two-fold molar excess of triethylamine (TEA) was added as an acid acceptor, and as a cosolvent for all the hydroquinone monomers. A TEA-HQ, -PHQ, or -EHQ complexes were formed improving their solubility and changing the reaction solution to a yellow color. Terephthaloyl chloride was dissolved in methylene chloride and added dropwise.
into the reaction solution. A polymer precipitate was observed within one hour of the addition of TC, as the reaction solution turned turbid. When EHQ was one of the monomers, the reaction solution color changed with the addition of TC in the first 1 to 2 hours from a transparent yellow, to a transparent green, to an opaque blue, to a final color of opaque white. When EHQ was not used as a monomer, the color would change directly from a transparent yellow to an opaque white. Copolymers were reacted for 24h at room temperature and then refluxed for 24h under nitrogen. At the end of the polymerization reaction the copolyesters were precipitated into a three-fold excess of methanol. The precipitate was filtered, purified in a Soxhlet extractor with acetone, and dried in vacuum for 24-48 h at 70°C. All copolymers used were prepared with a 70:30 mole ratio of the hydroquinone monomers to EG, and an equimolar amount of TC.

**Polymer Characterization**

Inherent viscosities (IV) of the copolyesters were measured in a p-chlorophenol: tetrachloroethane solution (60 : 40 by weight) at 26°C at a copolymer concentration of 0.5 g/dL with a Cannon Ubelohde-type viscometer. Phase transitions were measured using a Perkin-Elmer 7 DSC under a nitrogen flow with a heating and cooling rate of 20°C/min from 50°C to 350°C. The melting transitions were taken from the peak of the melting endotherm on the second heating cycle of the sample. The crystallization transitions were taken from the peak of the cooling exotherm on
the first cooling cycle of the sample. Polymer samples weighing 7 to 10 mg were used for the DSC analyses. The thermal stability of the copolymers was measured by thermogravimetric analyses (TGA) on a DuPont TGA-2950 at a heating rate of 20°C/min from ambient temperature to 500°C in a nitrogen atmosphere. The values for the degradation temperature (T<sub>d</sub>) in the tables are given when a 5% weight loss occurred. Polymer samples weighing 8-15 mg were used for the TGA analysis. The <sup>1</sup>H NMR spectra were recorded using a Bruker AC200 Spectrometer operating at 200 MHz in both trifluoroacetic acid-d, and a 1 : 1 mixture by volume of trifluoroacetic acid-d (TFAA-d) : chloroform-d<sup>26,30</sup> using the TFAA peak at 11.5 ppm as the internal standard. The mesophases of the copolyesters were identified by polarizing light microscopy (PLM) on a Olympus BH2 series 300 polarizing microscope with a Linkam THMS 600 heating stage.

Results and Discussion

Polymer Compositions and Structure

<sup>H</sup><sup>1</sup> NMR spectra were used to calculate the compositions of the copolymers. Compositional calculations were based on the integral ratios of the ethoxy peaks (1.4 and 4.1 ppm), oxyethylene peaks (4.8 ppm), oxyphenylene peaks (7.0-7.4 ppm) and terephthalate peaks (8.4-8.6 ppm) (see Figures 2.1-2.3). For the compositional determination of Series I, x = the mole fraction of EPT units, y = the mole fraction of PT units, z = the mole fraction
of ET units, a, b, c, and d = integrals of the peaks as labeled in Figure 2.1, and Q and R = arbitrarily assigned variables in the following equations:

\[
\frac{5x}{4z} = \frac{a+b}{c} = Q
\]

\[
x = \frac{(4/5)Qz}{1}
\]

\[
\frac{3x+4y}{4z} = \frac{d}{c} = R
\]

\[
y = Rz - \frac{3}{5}Qz
\]

\[
x + y + z = 1
\]

\[
z = \left(\frac{1}{5}Q + R + 1\right)^{-1}
\]

Similar computations can be made for Series II where \(x'\) = the mole fraction of PPT units, \(y\) = the mole fraction of PT units, \(z\) = the mole fraction of ET units, and a, b, and c = integrals of the labeled peaks in Figure 2.2. From the spectra in Figure 2.2, the composition can be determined using the following equations:

\[
\frac{(8x' + 4y)}{4z} = \frac{b}{a} = Q
\]

\[
z = \frac{(2x' + y)}{Q}
\]

\[
\frac{(4x' + 4y + 4z)(8x' + 4y)}{\frac{(8x' + 4y)}{Q}} = \frac{c}{b} = R
\]

\[
z = x'(2R - 1) + y(R - 1)
\]

\[
x' + y + z = 1
\]
Similar calculations can be made for Series III copolymers to determine their composition where $x' = \text{the mole fraction of PPT units}$, $x = \text{the mole fraction of EPT units}$, $z = \text{the mole fraction of ET units}$, and $a, b, c, \text{and} d = \text{integral values of the labeled peaks in Figure 2.3}$. The composition can be determined using the following equations (see Figure 2.3):

\[
\frac{(8x' + 3x)}{4z} = \frac{d}{c} = Q
\]

\[
z = \frac{(2x' + 3/4x)}{Q}
\]

\[
\frac{5x}{4z} = \frac{(a + b)}{c} = R
\]

\[
x = 4/5Rz
\]

\[
x' + x + z = 1
\]

Both TFAA and a TFAA : chloroform mixture were used as NMR solvents. Although the copolymers were only partially soluble in TFAA, it was possible that they were sufficiently soluble to obtain accurate compositional values from the NMR spectra. This assumption was erroneous. With TFAA as the NMR solvent, copolymer compositions were found to contain from 20 to 40% ethylene terephthalate (ET) units (see Tables 2.4 and 2.5 and Figures 2.4 and 2.5). With the TFAA : chloroform mixture, which was found to be a good solvent for the copolymers, the spectra showed that only 10 to 20% of the units in the copolymers were ET units (see Tables 2.4 and 2.5 and Figures 2.4 and 2.5). From these results, it can be concluded that TFAA preferentially
solubilizes copolymer molecules with a high ET content. Even with the TFAA: chloroform solvent mixture copolyesters with high PT content were only partially soluble, and the corresponding NMR spectra showed increased amounts of ET units. Thus, whenever the copolyesters were not completely soluble, the copolymer molecules with a high ET content were preferentially solubilized.

This observation would lead to the conclusion that, as expected, the copolymers consisted of a mixture of different compositions, some with higher amounts of ET units than others. This supposition was proven by fractionating one of the copolymers and determining the composition of the different fractions. DD43 was fractionated by dissolving the copolymer in TFAA and separating the soluble and insoluble fractions by filtration, after which the soluble fraction was precipitated and both were extracted with excess acetone. Evaluation of the compositions of the two fractions showed that the TFAA soluble fraction had approximately a five times greater amount of ET units than the insoluble fraction. The observation that only about 30 to 60% of the added EG was incorporated into the copolymer is reasonable because EG is much less reactive than the HQ monomers. Therefore, many of the polymer chains with high ET content would be of sufficiently low molecular weight and crystallinity to be soluble and removed from the final product during the filtration and extraction processes. These oligomers were collected as described by Majnusz and Lenz and compositional analyses by NMR showed that these oligomers had
Figure 2.1: $^1$H-NMR spectra of Series I copolymers, polymer DD13, in trifluoroacetic acid-d/ chloroform-d mixture as solvent.
Figure 2.2: $^1$H-NMR spectra of Series II copolymers, polymer DD35, in trifluoroacetic acid-d/ chloroform-d mixture as solvent.
Figure 2.3: 1H-NMR spectra of Series III copolymers, polymer DD52, in trifluoroacetic acid-d/ chloroform-d mixture as solvent.
Figure 2.4: ET unit content as a function of EPT content for Series I copolymers: -○- theoretical ET content, -□- observed ET content in TFAA-d, and -Δ- observed ET content in TFAA-d/CDCl₃.
Figure 2.5: ET unit content as a function of PPT content for Series II copolymers: -O- theoretical ET content, -□- observed ET content in TFAA-d, and -Δ- observed ET content in TFAA-d/CDCl₃.
very high contents of ET units. Further evidence that EG is less reactive than any of the hydroquinone monomers used is the low degree of homopolymerization of EG with TC to form poly(ethylene terephthalate) using the same reaction conditions as for the copolyesters in this study. The resultant polymer had an inherent viscosity of 0.02 dL/g at 26°C at a polymer concentration of 0.5 g/dL in a solution of p-chlorophenol:tetrachloroethane.

While it was expected that both the EHQ and PHQ monomers should be more reactive than the HQ monomer, because of the greater solubility of the EHQ and PHQ monomers, it was not known which of the two substituted hydroquinones would be more reactive. From the compositions calculated for the Series III copolymers (see Table 2.6), it can be concluded that about 5% more EHQ monomer was incorporated into the copolymers than expected. This result would indicate a greater reactivity of the EHQ monomer even though the PHQ monomer was slightly more soluble than the EHQ monomer.

Randomness Determinations

Copolymer randomness values were determined by NMR spectoscopy based on sequence distributions which were calculated from the terephthalate proton peaks (8.4-8.6 ppm)\textsuperscript{18,32,33} (see Figure 2.6). Differences in the types of units on either side of the terephthalate unit caused changes in the shift of the terephthalate protons because of differences in the amount of
Figure 2.6: $^1$H-NMR spectrum of the terephthalate region of DD22 from Series II copolymers used for randomness determination in trifluoroacetic acid-d/ chloroform-d mixture as solvent.
shielding that the terephthalate protons experienced. As a result, the protons of the terephthalate units which had EG units on both sides (EG-TA-EG) had a different chemical shift than the protons in the terephthalate units with either HQ units on both sides (xHQ-TA-xHQ) or with an EG unit on one side and a HQ derivative unit on the other (xHQ-TA-EG). Although the TA protons had different shifts with EG and HQ units, the TA protons were not sensitive enough to distinguish the different HQ monomers. Therefore all calculations for randomness or average sequence length were based only on the differences between the ET and xPT units, not on the different xPT units.

The probability of finding an xPT unit next to an ET unit was given by the following equation:

$$P_{xPT-ET} = P_{xHQ-TA-EG}/2F_{xPT}$$

in which $P_{xHQ-TA-EG}$ was the proportion of the integrated intensity of the xHQ-TA-EG peaks to the total integrated intensity of the terephthalate region, and $F_{xPT}$ was the mole fraction of the xPT units. Similarly, the probability of finding an ET unit next to an xPT unit is given by the equation:

$$P_{ET-xPT} = P_{xHQ-TA-EG}/2F_{ET}$$

in which $F_{ET}$ was the mole fraction of ethylene terephthalate units. The degree of randomness or randomness number, $B$, is defined as follows:
\[ B = P_{\text{XPT-ET}} + P_{\text{ET-XPT}} = P_{\text{xHQ-TA-EG}/2F_{\text{PTFET}}} \]

and \( B = 0 \) for a block copolymer; 1 for a complete random copolymer; and 2 for an alternating copolymer.

Randomness values were calculated from spectra obtained in both TFAA and TFAA : chloroform solvents, but the values from spectra using TFAA : chloroform gave much higher randomness values. With TFAA as the solvent, randomness values were between 0.3-0.5, while with TFAA : chloroform as the solvent the values were between 0.9 and 1.5 (see Tables 2.4 and 2.5). Even though all of the copolymers were synthesized by a solution copolymerization reaction, which should yield random copolymers, these results indicate that copolymer molecules were formed with a high enough ET content to be of a blocky structure. The increased randomness values in the mixed solvent, which would indicate a random copolymer, results from the low levels of ET units in the copolymers which invariably skewed the calculations towards higher randomness values. These copolymers most likely had blocky tendencies as well, but there was an insufficient amount of ET incorporated to give accurate randomness number calculations.

By using the same set of calculations as that for the randomness values\(^{32,33}\), the average length of the ET segments (\( L_{\text{ET}} \)) and the average length of the PT (substituted and
unsubstituted) segments ($L_{PT}$) were calculated for all three series of copolyesters (see Tables 2.4-2.6).

$$L_{ET} = 2P_{ET}/P_{XHQ-TA-EG}$$
$$L_{PT} = 2P_{XPT}/P_{XHQ-TA-EG}$$

Because of the small amount of ET units incorporated into the copolymers, the average segment length for the ET units was typically close to unity, indicating that there were, on average, no significant blocks of ET units (hence the high randomness values). Because of their large compositional percentage, the average PT segment length was much greater than the average ET segment length, varying from four to nine units. This result would indicate that while the randomness values of these copolymers were large, there were still some blocky tendencies, as can be seen from the high average PT segment lengths.

**Molecular Weight**

The copolymers were insoluble, or only partially soluble, in common organic solvents such as chloroform, THF, DMF, or TFAA. The polymers were soluble in several solvent mixtures, including p-chlorophenol-tetrachloroethane and TFAA-chloroform. Also, fluorinated solvents, such as pentafluorophenol were found to be good solvents. In the Series I copolymers, as the phenylene terephthalate (PT) unit content in the copolymer reached 35%, the solubility greatly decreased (see Table 2.1). This insolubility was
expected because of the rigidity of sequences of the PT units. Series II copolymers showed a similar trend to those in Series I, except that even at 35% PT content, the copolymer was insoluble (see Table 2.2). This result is unexpected, because with the bulkier phenyl side group it was expected that those copolymers should have poorer lateral packing than those in Series I and, therefore, greater solubility. All Series III samples were soluble in the mixed solvents as expected because that series contained none of the rigid, tightly packed PT units (see Table 2.3).

The inherent viscosities (IV) of the Series I copolymers in a p-chlorophenol-tetrachloroethane mixture varied from 0.6 to 1.2 dL/g (see Figure 2.7). The IV values for Series II copolymers were in the range of 0.8 to 1.5 dL/g. Since the IV values of Series II copolymers were only slightly greater than those of the Series I copolymers, without actual molecular weight data it is difficult to determine whether the increases in IV were due to increases in molecular weight or due to differences in the stiffness of the chains in the viscometry solvent. The IV values for Series III copolymers, in the range of 0.9 to 1.9 dL/g, were generally much greater than for either Series I or II samples (see Figure 2.7). This result was expected because of the greater solubility of copolymers with ethoxyphenylene terephthalate (EPT) and phenylphenylene terephthalate (PPT) units. This higher solubility allowed the growing polymer molecules to stay in solution longer which resulted in an increase in the molecular weight of the copolymers.
Figure 2.7: Inherent viscosity as a function of substituted hydroquinone monomer content for Series I to III copolymers: -□- Series I, -Δ- Series II, -○- Series III (IV was measured in a 40/60 mixture of p-chlorophenol/tetrachloroethane at 25°C, and 0.5 g/dL).
For the IV values in this study ranging from 0.6 to 1.9 dL/g, according to Han and Bhowmik, one can assume that the molecular weights were sufficiently high so that the effects of molecular weight on the thermal properties and optical textures of the copolyesters was negligible. However, because of the low solubilities of these copolymers, it was not possible to estimate molecular weights by gel-permeation chromatography (GPC).

In a study reported by Majnusz and Lenz of aromatic liquid crystalline polyesters derived from alkyl substituted hydroquinones and TA, some of the polymer molecular weights were determined by vapor pressure osmometry. They derived the following empirical formula for relating IV to number average molecular weight: \( M_n = 6100(IV) \). Han and Bhowmik were also able to evaluate some LC polyester molecular weights by GPC and found similar values for number average molecular weight, but the values for weight average molecular weight were in the range if 36,000 to 128,000, with a large polydispersity index in the range of 7.2 to 12.8. Although the copolymers in the present study had more flexible units than in either of the two studies stated above, which would cause a lower IV for comparable molecular weights, it can be assumed that the polymers in this study had number average molecular weights in the range of 3,000 to 15,000, and weight average molecular weights in the range of 30,000 to 170,000.
Thermal Transitions

For the copolymer of Series I and II, typical DSC thermograms for a fusible sample showed only a single broad peak, which was attributed to the T_m of the copolymer (see Figure 2.9). The T_m values of the copolymers of Series I varied from 255 to 288°C (see Figure 2.8). It was expected that an increase in PT content would raise the T_m of the copolymer because of improved packing, but other than a very slight decrease in T_m with increased PT content, below a critical amount the PT content had little effect on the T_m of the Series I copolyesters (see Table 2.1). Above a critical content of HQ the copolymers from Series I and II were no longer fusible, probably due to the occurrence of long PT segments which would increase the T_m above the degradation temperature.

It was expected that the melting transition of copolyesters from Series II would be lower that those of Series I due to the larger phenyl substituent of the PPT units. However the opposite proved true. The T_m values of samples from Series II varied from 286 to 315°C (see Table 2.2 and Figure 2.8). While it is unknown why the larger phenyl side group caused an increase in the melt transitions, one possible explanation is that the phenyl side group causes an increase in the stiffness of the chain. The biphenyl unit in the chain could be inhibiting the rotations about the chain, thereby making the chain stiffer. In this series increasing the PT content in the copolymer caused slight increases
Figure 2.8: Melt transitions for Series I to III copolymers as a function of observed content of substituted hydroquinone monomer content: -□- Series I, -Δ- Series II, -○- Series III.
Figure 2.9: DSC thermogram of polymer DD16 from Series I copolymers; second heating and cooling cycles (heating and cooling rates of 20°C/min).
the $T_m$. For example, comparing samples DD35 and DD36, the $T_m$ increased almost 10°C with an increase of PT content of 15%. Though the changes in $T_m$ with PT content were not large, it is unknown at this time why the addition of PT units caused different trends in Series I and II. In Series II, as well as in Series I, above a critical content of PT the copolymers were no longer fusible.

DSC thermograms showed that, as expected, all copolymers from Series III were fusible. They also had much higher transition temperatures than the samples from Series I or II in general, ranging from 290 to 332°C (see Table 2.3 and Figure 2.8). This result seems counter-intuitive when considering the poorer packing of the Series III copolymer which contains two different substituents. This increase in $T_m$ could be due to a lower amount of ET units included in the Series III copolymers when compared to Series I and II copolyesters (see Tables 2.4-2.6). Inclusion of the larger, bulkier monomer (PHQ) caused an increase in $T_m$. Above 65% EPT content there was a steady decline in $T_m$ with increased EPT content. As mentioned above, the bulkier phenyl groups may have caused an increase in the stiffness of the chains which would cause the increased melt transitions that were observed.

Another interesting phenomenon observed in all of the samples in Series III was a sharp double melting endotherm in the second heating cycle (see Figure 2.10). This type of double
endotherm has been attributed by others to a reorganization of defect crystals into larger crystals during the first heating and cooling of the sample\textsuperscript{34-36}. Also of note here is the much larger enthalpy of melting ($\Delta H_m$) during heating and cooling in the Series III samples when compared to those of Series I and II (see Figure 2.11). While it may be thought that the increased PT content would increase the crystallinity of the copolymers because of better packing, the opposite was apparently true. Even though Series III copolymers contained units with two different, bulky pendant groups, these copolymers had a much higher $\Delta H_m$ than the samples in Series I and II, indicating a more crystalline material.

No peak for the nematic-to-isotropic phase transition was observed for any sample while heating at $20^\circ C$/min because of degradation of the sample. For example, when polymer DD52 was heated at $80^\circ C$/min\textsuperscript{31} a broad endothermic peak occurred between 400 and 450$^\circ C$ (see Figure 2.12), which could be attributed to the $T_i$ of the sample, but this phase transition occurred in the region in which thermal degradation also occurred ($T_d = 428^\circ C$ from Table 3).

All of the copolymers which melted exhibited the property of stir opalescence, which indicated the formation of a liquid crystalline phase. The textures observed by PLM for the copolymers from all of the series were essentially identical. All meltable copolyesters showed the characteristic threads of a
Figure 2.10: DSC thermogram of polymer DD50 from Series III copolymers; second heating and cooling cycles (heating and cooling rates of 20°C/min).
Figure 2.11: Enthalpy of fusion as a function of observed content of substituted hydroquinone monomers for Series I to III copolymers: -□- Series I, -Δ- Series II, -○- Series III.
nematic texture with a high degree of birefringence above their respective melting transitions (T_m) (see Figures 2.13 and 2.14). The only differences between the textures of the samples was the relative density of the threads. The isotropization temperature (T_i) was not observable by heating at a rate of 20°C/min using optical microscopy because of degradation of the samples. Even at higher heating rates it was difficult to distinguish between the sample isotropization and degradation; especially since the process was not a reversible one.

**Thermal Stability**

Thermal stabilities of the copolymers were determined in a nitrogen atmosphere by thermal gravimetric analysis (TGA) measurements. A typical TGA plot of a Series III copolyester is shown in Figure 2.15. The degradation temperature was taken as the temperature at which a 5% weight loss occurred. Series I copolymers showed T_d values ranging from 412°C to 327°C (see Table 2.1 and Figure 2.16), and there was a noticeable downward trend in the in T_d with increasing PT content. Series II copolymers showed T_d values in the range of 430°C to 327°C (see Table 2.2), and these copolyesters also showed a similar decrease in T_d with increasing PT content. Series III copolymers showed a 5% weight loss in the range of 438°C to 408°C (see Table 2.3). The high thermal stability for all of the copolyesters, except those with high PT content, indicated that these copolymers could be processed in the melt at temperatures below 390°C.
Figure 2.12: DSC thermogram of polymer DD52 from Series III copolymers; first heating at 60°C/min showing the possible existence of $T_i$ at temperatures between 425°C and 460°C.
Figure 2.13: Polarized light micrographs of copolyesters: (a) DD22 from Series I (at 296°C, 250x mag.); and (b) DD35 from Series II (quenched from 316°C, 250x mag.)
Figure 2.14: Polarized light micrograph of copolyester DD54 from Series III (quenched from 330°C, 250x mag.).
Figure 2.15: TGA thermogram of polymer DD16 with Series I copolymers; the 5% weight loss temperature, $T_d$, is indicated (heating rate of 20°C/min under flowing N$_2$).
Figure 2.16: Degradation temperature, $T_d$, at a 5% weight loss by TGA for Series I to III copolymers: □- Series I, △- Series II, ○- Series III.
Conclusions

Three series of thermotropic, aromatic copolyesters derived from EHQ, PHQ, HQ, EG, and TA were synthesized, and characterized by PLM, DSC, NMR, TGA, and solution viscometry. All of the copolyesters displayed the characteristic threads of a nematic texture. The nematic-to-isotropic transition temperatures (T$_{n-i}$) were not observable by PLM because of degradation of the samples. DSC analysis showed that the T$_{n-i}$ peak overlapped the degradation peak of the copolyesters in the 400°C to 450°C range. Increasing the PT content decreased the solubility and fusibility of the copolymers. Melt transitions were found to vary from 255°C to 325°C, and the degradation temperature was found to vary from 330°C to 440°C. Increases in PT content were found to cause decreases in the thermal stability of the copolyesters. The inherent viscosity was found to vary from 0.6 to 1.9 dL/g, which indicated a number average molecular weight in the range of 4000 to 13000. NMR analysis was used to determine both the composition and the randomness of the copolyesters. It was found that only approximately half of the added EG was incorporated into the copolymers. Because of the low amount of EG in the copolymers, the randomness values were skewed towards higher values.

One goal of the work presented in this chapter was the reduction of the melt transitions of several highly aromatic liquid crystalline copolyesters. This objective was to be accomplished by the copolymerization of different monomers and the use of bulky
substituents. It was shown that the melt transition was effectively reduced through the copolymerization of the monomers, although the effects were not always as expected. The monomer with a bulky phenyl side group, which was used in Series II and III copolymers, was chosen because it was believed that the size of the substituent would frustrate the packing of the chains enough to cause a reduction in the thermal transitions. The opposite was observed, and this result may be caused by an increase in the stiffness of the chains which the phenyl substituents caused by an inhibition of chain rotation. So while Series III copolyesters containing EPT, PPT, and ET units had the largest amount of substituents along the chain, they also had the highest thermal transitions and the highest thermal stabilities. They were the most crystalline and had the highest molecular weights. Nevertheless, for melt blending with engineering thermoplastics, such as PET, the transition temperatures for the Series III samples were too high, while some of the Series I and II copolymers with low amounts of PT units had thermal transitions in the range which would make them more favorable for blending.
Table 2.1: Properties of copolyesters of Series I:

poly(ethoxyphenylene terephthalate-co-phenylene terephthalate-co-ethylene terephthalate), poly(EPT-co-PT-co-ET)

<table>
<thead>
<tr>
<th>Sample</th>
<th>EPT/PT/ET</th>
<th>IV (dL/g)†</th>
<th>Yield %</th>
<th>Tm (°C)</th>
<th>Tc (°C)</th>
<th>ΔHm (J/g)a</th>
<th>Td (°C)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD10</td>
<td>70/0/30</td>
<td>1.2</td>
<td>90.9</td>
<td>288</td>
<td>242</td>
<td>4.4</td>
<td>412</td>
</tr>
<tr>
<td>DD13</td>
<td>63/7/30</td>
<td>0.9</td>
<td>84.9</td>
<td>275</td>
<td>235</td>
<td>3.2</td>
<td>407</td>
</tr>
<tr>
<td>DD16</td>
<td>56/14/30</td>
<td>0.8</td>
<td>89.2</td>
<td>277</td>
<td>225</td>
<td>2.5</td>
<td>399</td>
</tr>
<tr>
<td>DD18</td>
<td>49/21/30</td>
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<td>85.0</td>
<td>269</td>
<td>222</td>
<td>4.2</td>
<td>394</td>
</tr>
<tr>
<td>DD20</td>
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<td>87.1</td>
<td>265</td>
<td>216</td>
<td>2.9</td>
<td>398</td>
</tr>
<tr>
<td>DD22</td>
<td>35/35/30</td>
<td>0.6</td>
<td>88.1</td>
<td>255</td>
<td>222</td>
<td>1.7</td>
<td>384</td>
</tr>
<tr>
<td>DD23</td>
<td>28/42/30</td>
<td>**</td>
<td>85.1</td>
<td>260</td>
<td>***</td>
<td>***</td>
<td>391</td>
</tr>
<tr>
<td>DD25</td>
<td>21/49/30</td>
<td>**</td>
<td>83.7</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>363</td>
</tr>
<tr>
<td>DD26</td>
<td>14/56/30</td>
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<td>*</td>
<td>*</td>
<td>353</td>
</tr>
<tr>
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<td>**</td>
<td>87.0</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>370</td>
</tr>
<tr>
<td>DD28</td>
<td>0/70/30</td>
<td>**</td>
<td>86.6</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>327</td>
</tr>
</tbody>
</table>

†--Inherent viscosity was measured in a 60/40 mixture of p-chlorophenol/tetrachloroethane at 26°C at a concentration of 0.5 g/dL

a--Enthalpy of melting taken from the area of the melting endotherm of the second heating cycle

b--T_d corresponding to the temperature (°C) at which a 5% weight loss occurred

*--Degradation occurred before melting

**--Samples were insoluble in solution viscometry solvents

***--Unable to discern a crystallization peak or to calculate ΔH_m
Table 2.2: Properties of copolyesters of Series II:

poly(phenylphenylene terephthalate-co-phenylene terephthalate-co-ethylene terephthalate), poly(PPT-co-PT-co-ET)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymer</th>
<th>PPT/PT/ET</th>
<th>Calc'd Molar Ratio</th>
<th>IV (dL/g)†</th>
<th>Yield %</th>
<th>Tm (°C)</th>
<th>Tc (°C)</th>
<th>ΔHm (J/g)a</th>
<th>Td (°C)b</th>
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</thead>
<tbody>
<tr>
<td>DD43</td>
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<td></td>
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<tr>
<td>DD66</td>
<td>63/7/30</td>
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<td>81.9</td>
<td>291</td>
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<td>5.4</td>
<td>431</td>
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<td></td>
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<td>56/14/30</td>
<td>1.0</td>
<td>82.6</td>
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<td>421</td>
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<td>82.1</td>
<td>294</td>
<td>251</td>
<td>4.6</td>
<td>418</td>
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<td>296</td>
<td>256</td>
<td>2.6</td>
<td>405</td>
<td></td>
<td></td>
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<tr>
<td>DD64</td>
<td>35/35/30</td>
<td>**</td>
<td>81.4</td>
<td>300</td>
<td>247</td>
<td>1.3</td>
<td>396</td>
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<tr>
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<td>28/42/30</td>
<td>**</td>
<td>83.2</td>
<td>315</td>
<td>***</td>
<td>***</td>
<td>386</td>
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<tr>
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<td>**</td>
<td>78.5</td>
<td>*</td>
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<td>**</td>
<td>71.4</td>
<td>*</td>
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<td>*</td>
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<tr>
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<td>74.1</td>
<td>*</td>
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<tr>
<td>DD28</td>
<td>0/70/30</td>
<td>**</td>
<td>86.6</td>
<td>*</td>
<td>*</td>
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<td>327</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

†--Inherent viscosity was measured in a 60/40 mixture of p-chlorophenol/tetrachloroethane at 26°C at a concentration of 0.5 g/dL

a--Enthalpy of melting taken from the area of the melting endotherm of the second heating cycle

b--Td corresponding to the temperature (°C) at which a 5% weight loss occurred

*--Degradation occurred before melting

**--Samples were insoluble in IV solvent

***--Unable to discern a crystallization peak or to calculate ΔHm
Table 2.3: Properties of copolyesters of Series III:

poly(phenylphenylene terephthalate-co-ethoxyphenylene terephthalate-co-ethylene terephthalate), poly(PPT-co-EPT-co-ET)

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>PPT/EPT/ET Calc'd Molar Ratio</th>
<th>IV (dL/g)†</th>
<th>Yield %</th>
<th>T_m (°C)</th>
<th>T_c (°C)</th>
<th>ΔH_m (J/g)a</th>
<th>T_d (°C)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD43</td>
<td>70/0/30</td>
<td>1.4</td>
<td>83.1</td>
<td>332</td>
<td>257</td>
<td>13.2</td>
<td>421</td>
</tr>
<tr>
<td>DD46</td>
<td>63/7/30</td>
<td>1.2</td>
<td>85.3</td>
<td>326</td>
<td>249</td>
<td>11.5</td>
<td>438</td>
</tr>
<tr>
<td>DD45</td>
<td>56/14/30</td>
<td>0.9</td>
<td>78.4</td>
<td>300</td>
<td>252</td>
<td>7.4</td>
<td>432</td>
</tr>
<tr>
<td>DD47</td>
<td>49/21/30</td>
<td>1.9</td>
<td>92.1</td>
<td>308</td>
<td>251</td>
<td>6.2</td>
<td>424</td>
</tr>
<tr>
<td>DD48</td>
<td>42/28/30</td>
<td>1.8</td>
<td>84.0</td>
<td>318</td>
<td>272</td>
<td>7.0</td>
<td>432</td>
</tr>
<tr>
<td>DD49</td>
<td>35/35/30</td>
<td>1.3</td>
<td>83.9</td>
<td>315</td>
<td>276</td>
<td>8.6</td>
<td>424</td>
</tr>
<tr>
<td>DD50</td>
<td>28/42/30</td>
<td>1.5</td>
<td>77.9</td>
<td>324</td>
<td>277</td>
<td>9.7</td>
<td>427</td>
</tr>
<tr>
<td>DD52</td>
<td>21/49/30</td>
<td>1.7</td>
<td>84.9</td>
<td>322</td>
<td>281</td>
<td>8.0</td>
<td>428</td>
</tr>
<tr>
<td>DD53</td>
<td>14/56/30</td>
<td>1.4</td>
<td>81.4</td>
<td>310</td>
<td>272</td>
<td>8.5</td>
<td>408</td>
</tr>
<tr>
<td>DD54</td>
<td>7/63/30</td>
<td>1.9</td>
<td>84.4</td>
<td>303</td>
<td>258</td>
<td>6.3</td>
<td>414</td>
</tr>
<tr>
<td>DD10</td>
<td>0/70/30</td>
<td>1.2</td>
<td>90.9</td>
<td>288</td>
<td>242</td>
<td>4.4</td>
<td>412</td>
</tr>
</tbody>
</table>

†—Inherent viscometry was measured in a 60/40 mixture of p-chlorophenol/tetrachloroethane at 26°C at a concentration of 0.5 g/dL.

a—Enthalpy of melting taken from the area of the melting endotherm of the second heating cycle.

b—T_d corresponding to the temperature (°C) at which a 5% weight loss occurred.
Table 2.4: Compositional data from NMR spectra for copolyesters of Series I

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Molar Ratios: EPT/PT/ET</th>
<th>B†</th>
<th>L&lt;sub&gt;ET&lt;/sub&gt;</th>
<th>L&lt;sub&gt;PT&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD19</td>
<td>70/0/30</td>
<td>60/0/40</td>
<td>85/0/15</td>
<td>0.9</td>
</tr>
<tr>
<td>DD13</td>
<td>63/7/30</td>
<td>62/12/26</td>
<td>83/3/14</td>
<td>0.9</td>
</tr>
<tr>
<td>DD16</td>
<td>56/14/30</td>
<td>61/7/32</td>
<td>69/13/18</td>
<td>0.9</td>
</tr>
<tr>
<td>DD18</td>
<td>49/21/30</td>
<td>52/12/36</td>
<td>65/22/13</td>
<td>1.2</td>
</tr>
<tr>
<td>DD20</td>
<td>42/28/30</td>
<td>44/19/37</td>
<td>52/30/18</td>
<td>1.0</td>
</tr>
<tr>
<td>DD22</td>
<td>35/35/30</td>
<td>44/20/36</td>
<td>46/33/21*</td>
<td>0.9</td>
</tr>
<tr>
<td>DD23</td>
<td>28/42/30</td>
<td>26/37/37</td>
<td>38/43/19*</td>
<td>1.0</td>
</tr>
<tr>
<td>DD25</td>
<td>21/49/30</td>
<td>37/19/44</td>
<td>37/39/24*</td>
<td>0.8</td>
</tr>
<tr>
<td>DD26</td>
<td>14/56/30</td>
<td>31/23/46</td>
<td>29/38/33*</td>
<td>0.6</td>
</tr>
</tbody>
</table>

*--Only Partially Soluble in TFAA/CDCl<sub>3</sub> mixture solvent
†--Randomness numbers and average lengths of ET and PT units were determined by 1H-NMR spectroscopy in TFAA-d/Chloroform-d mixture solvent as determined in TFAA/CDCl<sub>3</sub> mixture solvent
Table 2.5: Compositional data from NMR spectra for copolyesters of Series II

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Molar Ratios: PPT/PT/ET</th>
<th>B†</th>
<th>PET</th>
<th>PPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calc'd</td>
<td>Obsv'd in TFAA</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DD43</td>
<td>70/0/30</td>
<td>72/0/28</td>
<td>87/0/13</td>
<td>&gt;1</td>
</tr>
<tr>
<td>DD66</td>
<td>63/7/30</td>
<td>69/12/19</td>
<td>&gt;1</td>
<td></td>
</tr>
<tr>
<td>DD35</td>
<td>56/14/30</td>
<td>56/19/25</td>
<td>73/14/13</td>
<td>&gt;1</td>
</tr>
<tr>
<td>DD36</td>
<td>49/21/30</td>
<td>48/29/23</td>
<td>58/29/13</td>
<td>&gt;1</td>
</tr>
<tr>
<td>DD37</td>
<td>42/28/30</td>
<td>35/37/28</td>
<td>61/24/15</td>
<td>&gt;1</td>
</tr>
<tr>
<td>DD64</td>
<td>35/35/30</td>
<td>24/27/49</td>
<td>51/31/18*</td>
<td>&gt;1</td>
</tr>
<tr>
<td>DD39</td>
<td>28/42/30</td>
<td>16/59/25</td>
<td>25/58/17*</td>
<td>&gt;1</td>
</tr>
<tr>
<td>DD40</td>
<td>21/49/30</td>
<td>10/60/30</td>
<td>28/59/13*</td>
<td>&gt;1</td>
</tr>
<tr>
<td>DD41</td>
<td>14/56/30</td>
<td>**</td>
<td>9/72/19*</td>
<td>&gt;1</td>
</tr>
</tbody>
</table>

*--Only Partially Soluble in TFAA-d/CDC13 mixture solvent
**--No NMR Data in TFAA
†--Randomness numbers and average lengths of ET and PT units were determined by 1H-NMR spectroscopy in TFAA-d/
Chloroform-d mixture solvent as determined in TFAA/CDC13 mixture solvent
Table 2.6: Compositional values from NMR spectra for copolyesters of Series III

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Molar Ratio: PPT/EPT/ET Calc'd</th>
<th>Molar Ratio: PPT/EPT Calc'd</th>
<th>Observed*</th>
<th>PET</th>
<th>PPT</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD46</td>
<td>63:7:30 76:14:10</td>
<td>90:10 85:15</td>
<td>0.5 4.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DD45</td>
<td>56:14:30 68:23:9</td>
<td>80:20 75:25</td>
<td>0.5 4.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DD47</td>
<td>49:21:30 56:28:16</td>
<td>70:30 66:34</td>
<td>1.0 5.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DD48</td>
<td>42:28:30 52:40:8</td>
<td>60:40 56:44</td>
<td>0.5 5.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DD49</td>
<td>35:35:30 39:50:11</td>
<td>50:50 44:56</td>
<td>0.9 7.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DD51</td>
<td>28:42:30 31:64:5</td>
<td>40:60 33:67</td>
<td>0.4 7.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DD52</td>
<td>21:49:30 26:64:10</td>
<td>30:70 29:71</td>
<td>0.9 8.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DD53</td>
<td>14:56:30 17:74:9</td>
<td>20:80 18:82</td>
<td>0.9 9.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DD54</td>
<td>7:63:30 8:82:10</td>
<td>10:90 8:92</td>
<td>1.1 9.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*--Compositional values and average lengths of ET and PT units were determined by 1H-NMR spectroscopy in TFAA-d/Chloroform-d mixture solvent.
References


CHAPTER 3

MODIFICATION OF SEQUENCE DISTRIBUTION BY TRANSESTERIFICATION OF THERMOTROPIC LIQUID CRYSTALLINE COPOLYESTERS

Introduction

Thermotropic liquid crystalline polyesters, TLCPs, have generated a lot of interest for their use as the reinforcing component for in situ composites. One problem in this application of TLCPs is the typically high thermal transitions of these highly aromatic polyesters. Chapter Two was focused on two ways of reducing the thermal transitions of the TLCPs: (1) by the inclusion of bulky substituents; and (2) by the copolymerization of different monomers. Another possible modification of LCPs, and more specifically LC copolyesters, that was briefly mentioned in the earlier chapters, is the variation of the sequence distributions of the monomer units in the copolyester.

It has been shown by Jin, et al. that a more random distribution of comonomer units will lead to lower glass transition temperatures, lower melting points, reduced crystallinity, and
even different crystal structures. Stupp, et al.\textsuperscript{8-10} showed that the nematic-isotropic transition for ordered LC polyesters occurred over a very narrow temperature range of 5°C, while the disordered polyester had a very broad nematic-isotropic transition over a 120°C biphasic range. Park, et al.\textsuperscript{16} showed that for aromatic copolyimides, a change from alternating to random ordering caused a drastic change in the solubility of the copolymer. All the above studies compared the properties of a "random" copolymer to those of an "ordered" copolymer, but there have been no systematic studies on the properties of an entire series of copolymers with varying degrees of randomness.

It was shown in Chapter 2 that the randomness of a copolyester can be determined by the use of both \textsuperscript{1}H-NMR\textsuperscript{18-24}, and \textsuperscript{13}C-NMR. The degree of randomness (B) can be calculated by integrating the proton resonance peaks of the terephthalate groups in copolyesters with different diols\textsuperscript{20}. The values for B range from 0 for a completely blocky copolymer, to 1 for a completely random copolymer, to 2 for a completely alternating copolymer.

Polycondensation reactions of copolyesters, in which preorder sequences are not used, are expected to yield a random comonomer distribution. Nevertheless, it has been shown in Chapter 2 and previous studies\textsuperscript{25} that, for low temperature solution copolymerization reactions, the resultant copolyester can have a blocky structure (i.e. B=0.3-0.5). Also, as shown in Chapter
2, EG is much less reactive than any of the hydroquinone monomers. This difference results in only approximately one-half of the added EG (30 mole percent) being incorporated into the copolymers. Yet, because of the sensitivity of the randomness number calculations towards the copolymer composition, when less than 25-30 mole percent of ET units are in the copolymer the randomness numbers calculated are inaccurate. Therefore, the first goal of the work presented in this chapter was the synthesis of LC copolyesters with at least 25-30 mole percent of ET units.

Interchain exchange reactions of polyesters have been reviewed by Kotliar. There are two types of reactions that can occur between polyester chains, alcoholysis and acidolysis, both of which can result in the transesterification of the chains, as seen below:

**Alcoholysis:**

\[
\begin{align*}
\text{O} \quad \text{O} \\
\text{+} \quad \text{HO} \\
\text{OH} + \text{O} \\
\end{align*}
\]

**Acidolysis**

\[
\begin{align*}
\text{O} \quad \text{O} \\
\text{+} \quad \text{COOH} \\
\text{O} + \text{HOOC} \\
\end{align*}
\]

The interchain alcoholysis and acidolysis reactions take place when chains are terminated either by hydroxyl or carboxyl
groups, respectively. In this chapter, transesterification is used as a general term to describe these interchange reactions.

The use of transesterification reactions on blend components to change the compatibility between the components has been studied extensively. Also, there have been many studies on the effect of thermal annealing on LC copolyesters to cause transesterification reactions and create a more random distribution of the comonomers depending upon whether annealing takes place either within or above the nematic region. Warner and Lee observed a tripling of the molecular weight of LCPs fibers by post-polymerization heat treatment, but they did not measure changes in sequence distributions because they had assumed a random copolymer to begin with, although the transesterification reactions were run at only 255°C, which was more than 20°C below the crystal-to-nematic transition of the LCP studied. In contrast, Economy, et al. reported that transesterification, and therefore chemical randomization, was the dominant process only above the crystal-nematic transition, that is, at temperatures from 290°C to 450°C. Below the crystal-nematic transition, physical reorganization of the chains into larger crystals dominated. Wu and Stupp observed that randomization of nematic copolyesters was prevalent above the nematic-isotropic transition. They also showed that the randomization was both a physical and chemical process, but that intermolecular acidolysis was the primary contributor towards randomization of the LCPs. Jin, et al. were
the only ones to study the correlation between heat treatment (varying the time of the heat treatment while keeping the temperature constant) and the amount of randomization that occurred as measured by the appearance of certain triads by $^{13}\text{C}$ NMR spectroscopy. Their randomization experiments were carried out above the crystal-nematic transition. Nevertheless, there have not been any studies on changing the parameters of the heat treatment (i.e. both temperature and time) to allow the preparation of an entire series of copolymers with varying degrees of randomness, as measured by the randomness value by proton NMR spectroscopy.

The goal of the work presented in this chapter was to prepare several new series of LC copolyesters with varying degrees of randomness. By varying the conditions of the randomization reactions and measuring the changes in sequence distribution through $^1\text{H}$-NMR, several new series of LC copolyesters with randomness numbers varying from 0.3 to 1.0 were synthesized and characterized. The copolymers chosen to be randomized were the 70:30 copolyesters of both poly(ethoxyphenylene terephthalate-co-ethylene terephthalate) [poly(EPT-co-ET)] and poly(phenylphenylene terephthalate-co-ethylene terephthalate) [poly(PPT-co-ET)]
Experimental

Monomer Synthesis

Ethoxyhydroquinone (EHQ) was synthesized as described in Chapter 2. Phenylhydroquinone (PHQ), ethylene glycol (EG), terephthaloyl chloride (TC), triethylamine (TEA), and methylene chloride were all purified as described in Chapter 2.

Polymer Synthesis

All copolymers were prepared using solution polycondensation reactions\textsuperscript{25,37} as described in Chapter 2. Two methods were used to try to prepare copolymers containing 30 mole percent of ET units. The first method utilized a double molar excess of EG; that is, instead of using 70 mole percent of EHQ, and 30 mole percent of EG, as was used in Chapter 2, 60 mole percent of EG was used with 70 mole percent of EHQ in a solution of methylene chloride. The second method utilized a limitation in the amount of hydroquinone monomer; that is, instead of a 70:30 (xHQ:EG) ratio for the polymerization, either a 60:40, or a 50:50 mole ratio was used. A double molar excess of triethylamine (TEA) was added as an acid acceptor, but it also served as a cosolvent for all the hydroquinone monomers. TEA-PHQ and TEA-EHQ complexes were formed and improved the solubility of these monomers, and the reaction solution changed to a yellow color. Terephthaloyl chloride, TC, was dissolved in methylene chloride.
and added dropwise into the reaction solution. A polymer precipitate was observed to form within one hour of the addition of TC, as the reaction solution turned turbid. When EHQ was one of the monomers, the color of the reaction solution changed with the addition of TC in the first 1 to 2 hours from transparent yellow, to transparent green, to opaque blue, to a final color of opaque white. When EHQ was not used as a monomer, the color changed directly from transparent yellow to opaque white. The reaction was run for 24h at room temperature and then refluxed for 24h under nitrogen. At the end of the polymerization reaction the copolyesters were precipitated into a three-fold excess methanol. The precipitate was filtered, extracted in a Soxhlet extractor with acetone, and dried in vacuum for 24-48 h at 70°C.

Randomization Reactions

Thermal randomization of the copolymers was performed using the bulk copolymer. The copolymer samples were placed in a specially designed thick-walled test tube with a tapered neck which was kept under vacuum and placed into a high temperature salt solution bath. Two different sample sizes were used. Large batches were run with at least one gram of copolymer, while small batches used approximately 0.1 to 0.2 grams of copolymer. The larger batch randomization reactions were run in similarly designed test tubes, which were slightly larger in size. The reaction temperature was varied from 250°C to 330°C depending on the thermal transitions of the polymer sample. A temperature
controller was used to maintain the bath temperature within ± 7°C. The duration of the reaction was varied from 0.5 hours to 24 hours. Uncatalyzed reactions were studied to avoid enhancement of some of the exchange reactions.

**Polymer Characterization**

Copolymers were characterized before and after the thermal post-treatment. Inherent viscosities (IV) of the copolyesters were measured in a p-chlorophenol: tetrachloroethane solution (60 : 40 by weight) at 26°C and a sample concentration of 0.5 g/dL with a Cannon Ubelohde-type viscometer. Phase transitions were measured with a Perkin-Elmer 7 DSC under a nitrogen flow with heating and cooling rates of 20°C/min from 50°C to 350°C. The reported melting transitions were taken from the peak of the melting endotherm on the second heating cycle. The reported crystallization transitions were taken as the peak of the cooling exotherm on the first cooling cycle of the sample. Polymer samples weighing 7 to 10 mg were used for the DSC analyses. Copolymers compositions, and randomness numbers were calculated from the H¹ NMR spectra, which were recorded using a Bruker AC200 Spectrometer operating at 200 MHz in a 1 : 1 mixture by volume of trifluoroacetic acid-d (TFAA-d) and chloroform-d¹³,³⁸ by using the TFAA peak at 11.5 ppm as the internal standard. Deconvolution of the peaks in the terephthalate region was performed using a WIN-NMR program. The mesophases of the copolyesters were identified by polarized light
microscopy (PLM), performed on a Olympus BH2 series 300 polarizing microscope with a Linkam THMS 600 heating stage.

Results and Discussion

Synthesis of 70:30 Copolyester

\[
\text{X} \quad \text{HO} \quad \text{OH} \quad \text{R} + \quad \frac{1-X}{2(1-X)} \quad \text{HO-CH}_2\text{CH}_2\text{-OH} \quad \text{Ethylene Glycol}
\]
\[
+ \quad \text{1} \quad \text{Cl-} \quad \text{O} \quad \text{CCl} \quad \text{Terephthaloyl Chloride}
\]

\[
\begin{array}{c}
\quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{R} \quad \text{Poly(EPT-co-ET)} \\
\text{R} \quad \text{Poly(PPT-co-ET)}
\end{array}
\]

As discussed in Chapter 2, only approximately one-half of the added ethylene glycol monomer was incorporated into the polymers because of its lower reactivity compared to those of the hydroquinone monomers. This result caused the calculated
randomness numbers to be skewed towards higher degrees of randomness, so two methods of increasing the EG contents in the copolymers were used. The results of those polymerizations is summarized in Table 3.1.

The copolyesters obtained by using a two-fold excess of EG (that is 70 mole percent nHQ monomer, and 60 mole percent EG), as in the polymerizations of DD58 and DD60, did not show any appreciable increase in the amount of ET units incorporated into the copolymers. In contrast, by limiting the amount of hydroquinone monomers available for the TC to react with (that is, by using only 60, 50, or even 40 mole percent of nHQ monomers) the copolyesters obtained had increased amounts of ET units, and these copolymers had a decrease in the degree of randomness.

This result further supports the conclusions in Chapter 2 that these copolymers had blocky structures; when not enough ET units were present in the copolymers the blockiness was not detectable. Also, this result showed that the reactivity of the EG with the TC was so much lower than the reactivity of the nHQ with the TC that even adding excess EG could increase the amount of ET units in the copolymer. That is, the reactivity of the EG was low enough that the only way to get more ET units into the copolymer was to limit the amount of substituted hydroquinone monomer present. In that manner the growing polymer chains were forced to react with the EG monomer.
Table 3.1: Results for 70:30 (nPT:ET) copolymerization reactions

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Monomer Molar Frctions Used (nHQ:EG)</th>
<th>Observed* Copolymer Molar Fraction (nPT:ET)</th>
<th>Inherent Viscosity (dL/g)</th>
<th>Random Number †</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD58-PPT:ET</td>
<td>(70:30) 2xEG</td>
<td>(88:12)</td>
<td>2.0</td>
<td>&gt;1</td>
</tr>
<tr>
<td>DD59-PPT:ET</td>
<td>(60:40)</td>
<td>(78:22)</td>
<td>1.4</td>
<td>0.7</td>
</tr>
<tr>
<td>DD63-PPT:ET</td>
<td>(50:50)</td>
<td>(76:24)</td>
<td>1.3</td>
<td>0.7</td>
</tr>
<tr>
<td>DD71-PPT:ET</td>
<td>(50:50)</td>
<td>(67:33)</td>
<td>1.4</td>
<td>0.4</td>
</tr>
<tr>
<td>DD67-PPT:ET</td>
<td>(40:60)</td>
<td>(64:36)</td>
<td>0.9</td>
<td>0.4</td>
</tr>
<tr>
<td>DD60-EPT:ET</td>
<td>(70:30) 2xEG</td>
<td>(90:10)</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>DD61-EPT:ET</td>
<td>(60:40)</td>
<td>(80:20)</td>
<td>1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>DD62-EPT:ET</td>
<td>(50:50)</td>
<td>(70:30)</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>DD68-EPT:ET</td>
<td>(50:50)</td>
<td>(76:24)</td>
<td>0.8</td>
<td>0.4</td>
</tr>
<tr>
<td>DD70-EPT:ET</td>
<td>(50:50)</td>
<td>(63:37)</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>DD65-EPT:ET</td>
<td>(40:60)</td>
<td>(65:35)</td>
<td>0.7</td>
<td>0.4</td>
</tr>
</tbody>
</table>

a—Compositions were determined by $^1$H-NMR spectroscopy using a 1:1 mixture of TFAA-d : chloroform-d as the solvent

b—Inherent viscosity was measured in a 60:40 mixture of p-chlorophenol : tetrachloroethane at 26°C

†—Randomness values as calculated from $^1$H-NMR spectra
Randomizations

Four different poly(EPT-co-ET) copolymer samples were randomized under different randomization conditions. The results of these randomizations are given in Tables 3.2 through 3.5. Two different poly(PPT-co-ET) copolymer samples were also randomized utilizing different reaction conditions. These results are given in Tables 3.6 and 3.7.

The requirement in all of these experiments was the accurate measurement of the randomness number for all of the different copolymers, and these measurements were far from exact. The equations for the randomness number calculations are given in Chapter 2. The three variables used in the calculations were: (1) the mole fraction of substituted phenylene terephthalate units, (2) the mole fraction ethylene terephthalate units, and (3) the mole fraction of hetero-linked terephthalate units. While the xPT and ET mole fractions were very precise measurements, the deconvolution of the terephthalate peaks was not as exact. The computer program which was used to calculate the deconvolution of the peaks (see Figure 3.1 for an example deconvolution) did not consistently divide the separate peaks. This caused the fractional area of the different peaks to vary. To compensate for this problem, the peak deconvolutions were performed three times, and the average was taken for use in the randomness number calculations. Randomness numbers were found to vary within $\pm 0.1$ of the average value.
Figure 3.1: 1H-NMR spectra of the terephthalate region of DD70.6 showing the computer deconvolution of the different peaks.
Effects of Temperature and Time

As can be seen in Tables 3.2 through 3.7, the amount of increase of the degree of randomness could be controlled by both the temperature and the duration of the thermal post-treatment. The amount of control over the reactions is shown in Figures 3.2 and 3.3, but because of the random nature of the transesterification reactions, there was no absolute control over the exact increase in degree of randomness.

From the results of the randomization experiments on DD62 (see Table 3.2) it could be concluded that reaction durations of several hours did not cause significantly greater degrees of randomness than reaction times of fewer hours. However, the samples which were randomized for six or more hours were less soluble than the samples which were reacted for shorter durations, and solubility was very important because solution blending was used for some of the copolyesters randomized (see Chapter 4). Therefore, for the other copolymers which were randomized, reaction times were kept at three hours or less.

Another interesting observation is the differences in randomization results for larger batches when compared to smaller batches. From the results of DD70 randomizations (see Table 3.5) large batch randomization reactions form copolymers which were randomized less than small batch reactions. One possible explanation of this result could be poorer heat
Table 3.2: Results of randomization reactions for DD62--poly(EPT-co-ET).

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Reaction Conditions</th>
<th>†Observed Composition (EPT:ET)</th>
<th>Randomness Number</th>
<th>°Inherent Viscosity (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD62.0</td>
<td>Original</td>
<td>(71:29)</td>
<td>0.4</td>
<td>0.85</td>
</tr>
<tr>
<td>DD62.1</td>
<td>250°C, 24h</td>
<td>(74:26)</td>
<td>0.8</td>
<td>**</td>
</tr>
<tr>
<td>DD62.2</td>
<td>250°C, 12h</td>
<td>(74:26)</td>
<td>0.8</td>
<td>**</td>
</tr>
<tr>
<td>DD62.3</td>
<td>250°C, 6h</td>
<td>(72:28)</td>
<td>0.8</td>
<td>**</td>
</tr>
<tr>
<td>DD62.4</td>
<td>250°C, 3h</td>
<td>(70:30)</td>
<td>0.7</td>
<td>1.6</td>
</tr>
<tr>
<td>DD62.5</td>
<td>270°C, 24h</td>
<td>*</td>
<td>*</td>
<td>**</td>
</tr>
<tr>
<td>DD62.6</td>
<td>270°C, 12h</td>
<td>(69:31)</td>
<td>0.9</td>
<td>**</td>
</tr>
<tr>
<td>DD62.7</td>
<td>270°C, 6h</td>
<td>(72:28)</td>
<td>0.9</td>
<td>**</td>
</tr>
<tr>
<td>DD62.8</td>
<td>270°C, 3h</td>
<td>(70:30)</td>
<td>0.7</td>
<td>**</td>
</tr>
</tbody>
</table>

†---Compositions and randomness numbers were determined by 1H-NMR spectroscopy in TFAA-d/Chloroform-d mixture solvent
a---Inherent viscosity measurements were made in 60:40 mixture of p-chlorophenol/tetrachloroethane at 26°C, and 0.5 g/dL
*---Insoluble in NMR solvents
**---Insoluble in viscometry solvents
Table 3.3:  Results of randomization reactions for DD65--poly(EPT-co-ET).

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Reaction Conditions</th>
<th>†Observed Composition (EPT:ET)</th>
<th>Randomness Number</th>
<th>aInherent Viscosity (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD65.0</td>
<td>Original</td>
<td>(62:38)</td>
<td>0.3</td>
<td>0.7</td>
</tr>
<tr>
<td>DD65.1</td>
<td>290°C, 2h</td>
<td>(64:36)</td>
<td>0.9</td>
<td>1.5</td>
</tr>
<tr>
<td>DD65.2</td>
<td>290°C, 1h</td>
<td>(65:35)</td>
<td>0.7</td>
<td>1.0</td>
</tr>
<tr>
<td>DD65.3</td>
<td>290°C, 0.5h</td>
<td>(63:37)</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>DD65.4</td>
<td>290°C, 3h</td>
<td>(62:38)</td>
<td>1.0</td>
<td>*</td>
</tr>
<tr>
<td>DD65.5</td>
<td>270°C, 2h</td>
<td>(60:40)</td>
<td>0.6</td>
<td>1.1</td>
</tr>
<tr>
<td>DD65.6</td>
<td>270°C, 1h</td>
<td>(61:39)</td>
<td>0.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

†--Compositions and randomness numbers were determined by 1H-NMR spectroscopy in TFAA-d/Chloroform-d mixture solvent
a--Inherent viscosity measurements were made in 60:40 mixture of p-chlorophenol/tetrachloroethane at 26°C, and 0.5 g/dL
*--Insoluble in viscometry solvents
<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Reaction Conditions</th>
<th>†Observed Composition (EPT:ET)</th>
<th>Randomness Number</th>
<th>aInherent Viscosity (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD68.0</td>
<td>Original</td>
<td>(76:24)</td>
<td>0.4</td>
<td>0.8</td>
</tr>
<tr>
<td>DD68.1</td>
<td>250°C, 2h</td>
<td>(75:25)</td>
<td>0.5</td>
<td>1.2</td>
</tr>
<tr>
<td>DD68.2</td>
<td>250°C, 1h</td>
<td>(76:24)</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>DD68.3</td>
<td>250°C, 0.5h</td>
<td>(76:24)</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>DD68.4</td>
<td>270°C, 2h</td>
<td>(77:23)</td>
<td>0.7</td>
<td>1.8</td>
</tr>
<tr>
<td>DD68.5</td>
<td>270°C, 1h</td>
<td>(75:25)</td>
<td>0.6</td>
<td>1.3</td>
</tr>
<tr>
<td>DD68.6</td>
<td>270°C, 0.5h</td>
<td>(76:24)</td>
<td>0.4</td>
<td>1.1</td>
</tr>
<tr>
<td>DD68.7</td>
<td>290°C, 2h</td>
<td>(78:22)</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>DD68.8</td>
<td>290°C, 1h</td>
<td>(77:23)</td>
<td>0.7</td>
<td>1.0</td>
</tr>
<tr>
<td>DD68.9</td>
<td>290°C, 0.5h</td>
<td>(76:24)</td>
<td>0.6</td>
<td>1.1</td>
</tr>
<tr>
<td>DD68.10</td>
<td>250°C, 2h</td>
<td>(76:24)</td>
<td>0.5</td>
<td>*</td>
</tr>
<tr>
<td>DD68.11</td>
<td>270°C, 2h</td>
<td>(75:25)</td>
<td>0.7</td>
<td>*</td>
</tr>
<tr>
<td>DD68.12</td>
<td>290°C, 2h</td>
<td>(77:23)</td>
<td>0.8</td>
<td>*</td>
</tr>
<tr>
<td>DD68.13</td>
<td>290°C, 3h</td>
<td>(74:26)</td>
<td>0.9</td>
<td>**</td>
</tr>
</tbody>
</table>

†—Compositions and randomness numbers were determined by \textsuperscript{1}H-NMR spectroscopy in TFAA-d/Chloroform-d mixture solvent
a—Inherent viscosity measurements were made in 60:40 mixture of p-chlorophenol/tetrachloroethane at 26°C, and 0.5 g/dL
*—Insufficient sample to run solution viscometry experiments
**—Insoluble in viscometry solvents
Table 3.5: Results of randomization reactions for DD70--poly(EPT-co-ET).

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Reaction Conditions</th>
<th>(^{\dagger})Observed Composition (EPT:ET)</th>
<th>Randomness Number</th>
<th>(^{a})Inherent Viscosity (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD70.0</td>
<td>Original</td>
<td>(63:37)</td>
<td>0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>DD70.1</td>
<td>250°C, 2h, (large)</td>
<td>(63:37)</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>DD70.2</td>
<td>270°C, 2h, (large)</td>
<td>(63:37)</td>
<td>0.5</td>
<td>1.1</td>
</tr>
<tr>
<td>DD70.3</td>
<td>290°C, 2h, (large)</td>
<td>(63:37)</td>
<td>0.6</td>
<td>1.1</td>
</tr>
<tr>
<td>DD70.4</td>
<td>250°C, 2h, (small)</td>
<td>(64:36)</td>
<td>0.4</td>
<td>*</td>
</tr>
<tr>
<td>DD70.5</td>
<td>270°C, 2h, (small)</td>
<td>(64:36)</td>
<td>0.4</td>
<td>*</td>
</tr>
<tr>
<td>DD70.6</td>
<td>290°C, 2h, (small)</td>
<td>(64:36)</td>
<td>0.7</td>
<td>*</td>
</tr>
<tr>
<td>DD70.7</td>
<td>290°C, 3h, (large)</td>
<td>(66:34)</td>
<td>0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>DD70.8</td>
<td>310°C, 2h, (small)</td>
<td>(65:35)</td>
<td>1.0</td>
<td>*</td>
</tr>
<tr>
<td>DD70.9</td>
<td>300°C, 2h, (small)</td>
<td>(63:37)</td>
<td>0.8</td>
<td>*</td>
</tr>
<tr>
<td>DD70.10</td>
<td>280°C, 2h, (small)</td>
<td>(63:37)</td>
<td>0.5</td>
<td>*</td>
</tr>
<tr>
<td>DD70.11</td>
<td>310°C, 2h, (large)</td>
<td>(66:34)</td>
<td>0.9</td>
<td>**</td>
</tr>
<tr>
<td>DD70.12</td>
<td>250°C, 2h; 280°C, 2h, (large)</td>
<td>(63:37)</td>
<td>0.4</td>
<td>1.2</td>
</tr>
</tbody>
</table>

\(^{\dagger}\)--Compositions and randomness numbers were determined by \(^1\)H-NMR spectroscopy in TFAA-d/Chloroform-d mixture solvent

\(^{a}\)--Inherent viscosity measurements were made in 60:40 mixture of p-chlorophenol/tetrachloroethane at 26°C, and 0.5 g/dL

*--Insufficient sample to run solution viscometry experiments

**--Insoluble in solution viscometry solvents
Table 3.6: Results of randomization reactions for DD67--poly(PPT-co-ET)

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Reaction Conditions</th>
<th>†Observed Composition (PPT:ET)</th>
<th>Randomness Number</th>
<th>aInherent Viscosity (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD67.0</td>
<td>Original</td>
<td>(65:35)</td>
<td>0.3</td>
<td>0.9</td>
</tr>
<tr>
<td>DD67.1</td>
<td>270°C, 2h</td>
<td>(63:37)</td>
<td>0.5</td>
<td>1.6</td>
</tr>
<tr>
<td>DD67.2</td>
<td>270°C, 1h</td>
<td>(63:37)</td>
<td>0.5</td>
<td>1.3</td>
</tr>
<tr>
<td>DD67.3</td>
<td>290°C, 2h</td>
<td>(64:36)</td>
<td>0.7</td>
<td>1.6</td>
</tr>
<tr>
<td>DD67.4</td>
<td>290°C, 1h</td>
<td>(63:37)</td>
<td>0.6</td>
<td>1.4</td>
</tr>
<tr>
<td>DD67.5</td>
<td>310°C, 2h</td>
<td>(63:37)</td>
<td>0.7</td>
<td>1.4</td>
</tr>
<tr>
<td>DD67.6</td>
<td>310°C, 1h</td>
<td>(62:38)</td>
<td>0.7</td>
<td>1.3</td>
</tr>
<tr>
<td>DD67.7</td>
<td>335°C, 2h</td>
<td>(68:32)</td>
<td>0.9</td>
<td>1.0</td>
</tr>
</tbody>
</table>

†—Compositions and randomness numbers were determined by \(^1\)H-NMR spectroscopy in TFAA-d/Chloroform-d mixture solvent

a—Inherent viscosity measurements were made in 60:40 mixture of p-chlorophenol/tetrachloroethane at 26°C, and 0.5 g/dL
Table 3.7: Results of randomization reactions for DD71--poly(PPT-co-ET)

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Reaction Conditions</th>
<th>†Observed Composition (PPT:ET)</th>
<th>Randomness Number</th>
<th>aInherent Viscosity (dL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD71.0</td>
<td>Original</td>
<td>67:33</td>
<td>0.4</td>
<td>1.4</td>
</tr>
<tr>
<td>DD71.1</td>
<td>250°C, 2h</td>
<td>67:33</td>
<td>0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>DD71.2</td>
<td>270°C, 2h</td>
<td>66:34</td>
<td>0.8</td>
<td>1.6</td>
</tr>
<tr>
<td>DD71.3</td>
<td>290°C, 2h</td>
<td>66:34</td>
<td>0.8</td>
<td>1.8</td>
</tr>
<tr>
<td>DD71.4</td>
<td>310°C, 2h</td>
<td>67:33</td>
<td>0.8</td>
<td>2.0</td>
</tr>
<tr>
<td>DD71.5</td>
<td>330°C, 2h</td>
<td>69:31</td>
<td>1.0</td>
<td>*</td>
</tr>
<tr>
<td>DD71.6</td>
<td>270°C, 2h, (large)</td>
<td>66:34</td>
<td>0.6</td>
<td>1.5</td>
</tr>
<tr>
<td>DD71.7</td>
<td>290°C, 2h, (large)</td>
<td>66:34</td>
<td>0.6</td>
<td>1.5</td>
</tr>
<tr>
<td>DD71.8</td>
<td>330°C, 2h, (large)</td>
<td>68:32</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>DD71.9</td>
<td>310°C, 2h, (large)</td>
<td>63:37</td>
<td>0.7</td>
<td>1.0</td>
</tr>
</tbody>
</table>

†--Compositions and randomness numbers were determined by $^1$H-NMR spectroscopy in TFAA-d/Chloroform-d mixture solvent

a--Inherent viscosity measurements were made in 60:40 mixture of p-chlorophenol/tetrachloroethane at 26°C, and 0.5 g/dL

*--Insoluble in solution viscometry solvents
Figure 3.2: Randomness number (B) as a function of reaction duration for DD68--Poly(EPT-co-ET).
Figure 3.3: Randomness Number (B) as a function of reaction temperature (°C) for DD67--Poly(PPT-co-ET) for a 2 hour duration.
distribution in the polymer samples in the center of the larger test tubes, and this would be less of a problem in the smaller test tube.

The comparison of the randomization reaction temperatures to the melting temperatures of the copolymers (see Tables 3.8 through 3.14), showed that the largest increases in randomization occurred when the copolymers were in the melt state. This result explains why it was observed, that for poly(PPT-co-ET) copolymers, the reaction temperatures necessary to cause significant increases in the degree of randomness were greater than the reaction temperatures necessary to significantly increase the degree of randomness of the poly(EPT-co-ET) samples. The poly(PPT-co-ET) samples had much higher melt transitions than the poly(EPT-co-ET) samples.

Copolymer Compositions

The copolymer compositions, which were measured using $^1$H-NMR spectroscopy in a 1:1 solvent mixture of TFAA-d/CDCl$_3$, showed little change as a result of the randomization reaction (see Tables 3.2 to 3.7). Typically, the mole fraction of either component in the copolymer did not vary from the original sample by more than three percent. Therefore, for each separate copolymer which was randomized, the compositional differences were considered negligible so that the effects of their different compositional values on the calculation of the randomness number was ignored.
Molecular Weight

Increases in the inherent viscosities were observed for most of the randomized samples (see Tables 3.2 through 3.7). This would indicate an increase in the molecular weight of the polymers. For some of the samples, such as DD68.4, DD65.1, and DD67.1, the inherent viscosity values increased as much as 225% of their original value.

A few samples, such as DD71.8, DD71.9, and DD67.7 showed a much smaller increase, or even a decrease, in the inherent viscosity when compared to the other samples from the same copolymer batch. This decrease may have been caused by the high temperatures used for the randomization reaction of these samples because, at these elevated temperatures, the thermal degradation reactions could compete with the transesterification reactions. This competition could limit the increases in the molecular weight and could even cause a decrease.

Thermal Properties

The effects of the randomization reactions on the thermal properties of the different copolymers are outlined in Tables 3.8 through 3.13 and Figures 3.4 through 3.9. Those samples, for which no thermal data are reported, were either amorphous (showing only a T_g in both heating cycles) or they had a melt transition in the first heating cycle but had no subsequent
Table 3.8: Thermal properties of DD62.

<table>
<thead>
<tr>
<th>Polymer Sample Number</th>
<th>Randomness Number</th>
<th>Tm$^\dagger$ (°C)</th>
<th>$\Delta$H$_m$ (J/g)</th>
<th>Tc$^a$ (°C)</th>
<th>$\Delta$H$_c$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD62.0</td>
<td>0.4</td>
<td>272</td>
<td>2.5</td>
<td>228</td>
<td>5.2</td>
</tr>
<tr>
<td>DD62.1</td>
<td>0.8</td>
<td>**</td>
<td>**</td>
<td>202</td>
<td>3.5</td>
</tr>
<tr>
<td>DD62.2</td>
<td>0.8</td>
<td>**</td>
<td>**</td>
<td>213</td>
<td>2.0</td>
</tr>
<tr>
<td>DD62.3</td>
<td>0.8</td>
<td>260</td>
<td>1.7</td>
<td>222</td>
<td>3.4</td>
</tr>
<tr>
<td>DD62.4</td>
<td>0.7</td>
<td>260</td>
<td>3.1</td>
<td>225</td>
<td>3.8</td>
</tr>
<tr>
<td>DD62.5</td>
<td>*</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>DD62.6</td>
<td>0.9</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>DD62.7</td>
<td>0.7</td>
<td>**</td>
<td>**</td>
<td>200</td>
<td>3.0</td>
</tr>
<tr>
<td>DD62.8</td>
<td>0.7</td>
<td>260</td>
<td>2.0</td>
<td>215</td>
<td>2.8</td>
</tr>
</tbody>
</table>

$^\dagger$—Melt transitions and enthalpy of melting were taken from the second heating cycle at 20°C/min

$^a$—Crystallization point and enthalpy of crystallization were taken from the first cooling cycle at 20°C/min

*—Sample insoluble in NMR solvents

**—Thermal transitions not observable using DSC
Table 3.9: Thermal properties of DD65.

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Randomness Number</th>
<th>$T_m$ $\dagger$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_c^a$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD65.0</td>
<td>0.3</td>
<td>272</td>
<td>8.6</td>
<td>231</td>
<td>3.7</td>
</tr>
<tr>
<td>DD65.1</td>
<td>0.9</td>
<td>257</td>
<td>1.9</td>
<td>209</td>
<td>2.8</td>
</tr>
<tr>
<td>DD65.2</td>
<td>0.7</td>
<td>273</td>
<td>3.7</td>
<td>221</td>
<td>3.0</td>
</tr>
<tr>
<td>DD65.3</td>
<td>0.5</td>
<td>275</td>
<td>5.5</td>
<td>226</td>
<td>4.0</td>
</tr>
<tr>
<td>DD65.4</td>
<td>1.0</td>
<td>248</td>
<td>2.1</td>
<td>196</td>
<td>2.0</td>
</tr>
<tr>
<td>DD65.5</td>
<td>0.6</td>
<td>277</td>
<td>5.5</td>
<td>225</td>
<td>3.8</td>
</tr>
<tr>
<td>DD65.6</td>
<td>0.5</td>
<td>275</td>
<td>5.7</td>
<td>227</td>
<td>3.0</td>
</tr>
</tbody>
</table>

$\dagger$—Melt transitions and enthalpy of melting were taken from the second heating cycle at 20°C/min.

a—Crystallization point and enthalpy of crystallization were taken from the first cooling cycle at 20°C/min.
Table 3.10: Thermal properties of DD68.

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Randomness Number</th>
<th>$T_m^\dagger$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_c^a$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD68.0</td>
<td>0.4</td>
<td>274</td>
<td>4.1</td>
<td>233</td>
<td>5.9</td>
</tr>
<tr>
<td>DD68.1</td>
<td>0.5</td>
<td>277</td>
<td>4.4</td>
<td>231</td>
<td>5.5</td>
</tr>
<tr>
<td>DD68.2</td>
<td>0.4</td>
<td>277</td>
<td>4.3</td>
<td>235</td>
<td>5.9</td>
</tr>
<tr>
<td>DD68.3</td>
<td>0.5</td>
<td>276</td>
<td>3.8</td>
<td>235</td>
<td>5.7</td>
</tr>
<tr>
<td>DD68.4</td>
<td>0.7</td>
<td>278</td>
<td>3.1</td>
<td>220</td>
<td>3.9</td>
</tr>
<tr>
<td>DD68.5</td>
<td>0.6</td>
<td>278</td>
<td>4.5</td>
<td>230</td>
<td>5.7</td>
</tr>
<tr>
<td>DD68.6</td>
<td>0.4</td>
<td>276</td>
<td>4.1</td>
<td>232</td>
<td>5.4</td>
</tr>
<tr>
<td>DD68.7</td>
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<td>1.1</td>
<td>206</td>
<td>3.3</td>
</tr>
<tr>
<td>DD68.8</td>
<td>0.7</td>
<td>253</td>
<td>2.7</td>
<td>216</td>
<td>4.0</td>
</tr>
<tr>
<td>DD68.9</td>
<td>0.6</td>
<td>276</td>
<td>3.6</td>
<td>226</td>
<td>5.6</td>
</tr>
<tr>
<td>DD68.10</td>
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<td>279</td>
<td>4.0</td>
<td>232</td>
<td>5.4</td>
</tr>
<tr>
<td>DD68.11</td>
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<td>279</td>
<td>3.7</td>
<td>223</td>
<td>4.4</td>
</tr>
<tr>
<td>DD68.12</td>
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<td>3.8</td>
</tr>
<tr>
<td>DD68.13</td>
<td>0.9</td>
<td>237</td>
<td>2.6</td>
<td>201</td>
<td>2.5</td>
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</table>

$^\dagger$--Melt transitions and enthalpy of melting were taken from the second heating cycle at 20°C/min

$a$--Crystallization point and enthalpy of crystallization were taken from the first cooling cycle at 20°C/min
Table 3.11: Thermal properties of DD70.

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Randomness Number</th>
<th>$T_m$ $^\dagger$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_c$ $^a$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
<th>$T_{xl}$ $^b$ (°C)</th>
<th>$\Delta H_{xl}$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD70.0</td>
<td>0.3</td>
<td>228/280</td>
<td>12.5</td>
<td>240</td>
<td>5.2</td>
<td>137</td>
<td>5.3</td>
</tr>
<tr>
<td>DD70.2</td>
<td>0.5</td>
<td>223/281</td>
<td>7.1</td>
<td>238</td>
<td>3.6</td>
<td>156</td>
<td>4.5</td>
</tr>
<tr>
<td>DD70.3</td>
<td>0.6</td>
<td>258/277</td>
<td>3.4</td>
<td>228</td>
<td>3.2</td>
<td>156</td>
<td>1.0</td>
</tr>
<tr>
<td>DD70.4</td>
<td>0.4</td>
<td>229/281</td>
<td>12.3</td>
<td>240</td>
<td>3.6</td>
<td>139</td>
<td>4.4</td>
</tr>
<tr>
<td>DD70.5</td>
<td>0.4</td>
<td>228/282</td>
<td>9.3</td>
<td>240</td>
<td>2.9</td>
<td>145</td>
<td>3.6</td>
</tr>
<tr>
<td>DD70.6</td>
<td>0.7</td>
<td>259/278</td>
<td>3.1</td>
<td>230</td>
<td>3.5</td>
<td>156</td>
<td>1.0</td>
</tr>
<tr>
<td>DD70.7</td>
<td>0.7</td>
<td>260/279</td>
<td>2.7</td>
<td>233</td>
<td>3.4</td>
<td>157</td>
<td>0.5</td>
</tr>
<tr>
<td>DD70.8</td>
<td>1.0</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>DD70.9</td>
<td>0.8</td>
<td>260/276</td>
<td>3.5</td>
<td>222</td>
<td>2.8</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>DD70.10</td>
<td>0.5</td>
<td>226/280</td>
<td>7.0</td>
<td>235</td>
<td>3.7</td>
<td>152</td>
<td>3.3</td>
</tr>
<tr>
<td>DD70.11</td>
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<td>257</td>
<td>2.5</td>
<td>218</td>
<td>1.7</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>DD70.12</td>
<td>0.4</td>
<td>223/282</td>
<td>6.5</td>
<td>237</td>
<td>4.2</td>
<td>158</td>
<td>3.4</td>
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</tbody>
</table>

$^\dagger$--Melt transitions and enthalpy of melting were taken from the endotherm on second heating cycle at 20°C/min

$^a$--Crystallization point and enthalpy of crystallization were taken from the exotherm on the first cooling cycle at 20°C/min

$^b$--Crystallization point and enthalpy of crystallization were taken from the exotherm on the second heating cycle at 20°C/min

*--Thermal transitions not observable using DSC
Table 3.12: Thermal properties of DD67.

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Randomness Number</th>
<th>Tm (°C)</th>
<th>ΔHm (J/g)</th>
<th>Te (°C)</th>
<th>ΔHc (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD67.0</td>
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<td>318</td>
<td>4.1</td>
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<td>5.9</td>
</tr>
<tr>
<td>DD67.1</td>
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<td>3.3</td>
<td>221</td>
<td>1.7</td>
</tr>
<tr>
<td>DD67.2</td>
<td>0.5</td>
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<td>2.6</td>
<td>226</td>
<td>0.8</td>
</tr>
<tr>
<td>DD67.3</td>
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<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>DD67.4</td>
<td>0.6</td>
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<td>*</td>
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<td>*</td>
</tr>
<tr>
<td>DD67.5</td>
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<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>DD67.6</td>
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<td>*</td>
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<td>*</td>
</tr>
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<td>DD67.7</td>
<td>0.9</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

†--Melt transitions and enthalpy of melting were taken from the second heating cycle at 20°C/min

a--Crystallization point and enthalpy of crystallization were taken from the first cooling cycle at 20°C/min

*--Thermal transitions not observable using DSC
Table 3.13: Thermal properties of DD71.

<table>
<thead>
<tr>
<th>Polymer Sample</th>
<th>Randomness Number</th>
<th>$T_m^+$ ($^\circ$C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_c^a$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DD71.0</td>
<td>0.4</td>
<td>301/324</td>
<td>7.0</td>
<td>240/252</td>
<td>5.9</td>
</tr>
<tr>
<td>DD71.1</td>
<td>0.5</td>
<td>300/324</td>
<td>8.3</td>
<td>241/250</td>
<td>6.8</td>
</tr>
<tr>
<td>DD71.2</td>
<td>0.8</td>
<td>301/326</td>
<td>7.6</td>
<td>242/250</td>
<td>6.5</td>
</tr>
<tr>
<td>DD71.3</td>
<td>0.8</td>
<td>303/326</td>
<td>10.8</td>
<td>243/249</td>
<td>5.6</td>
</tr>
<tr>
<td>DD71.4</td>
<td>0.8</td>
<td>325</td>
<td>7.5</td>
<td>241</td>
<td>2.2</td>
</tr>
<tr>
<td>DD71.5</td>
<td>1.0</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>DD71.6</td>
<td>0.6</td>
<td>301/327</td>
<td>8.5</td>
<td>242/250</td>
<td>7.3</td>
</tr>
<tr>
<td>DD71.7</td>
<td>0.6</td>
<td>302/327</td>
<td>7.3</td>
<td>243/249</td>
<td>6.0</td>
</tr>
<tr>
<td>DD71.8</td>
<td>0.9</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>DD71.9</td>
<td>0.7</td>
<td>324</td>
<td>4.0</td>
<td>235</td>
<td>1.9</td>
</tr>
</tbody>
</table>

$^+$--Melt transitions and enthalpy of melting were taken from the second heating cycle at 20°C/min

$^a$--Crystallization point and enthalpy of crystallization were taken from the first cooling cycle at 20°C/min

*--Thermal transitions not observable using DSC
Figure 3.4: Crystallization temperature \( T_c \) as a function of randomness number (B): -○- polymer DD65, -△- polymer DD68, and -□- polymer DD70.
Figure 3.5: Enthalpy of crystallization ($\Delta H_c$) as a function of randomness number (B): -\(\bigcirc\)- polymer DD65, -\(\triangle\)- polymer DD68, and -\(\square\)- polymer DD70.
Figure 3.6: Melt transitions ($T_m$) as a function of randomness number (B): -○- polymer DD65, -Δ- polymer DD68, and -□- polymer DD70.
Figure 3.7: Enthalpy of fusion ($\Delta H_m$) as a function of Randomness Number (B): -□- polymer DD68, -○- polymer DD70.
Figure 3.8: DSC thermogram of a randomized DD70 sample.
Figure 3.9: Crystallization temperature, $T_{cr}$ (\sqcap -), and crystallization enthalpy, $\Delta H_{cr}$ (\circ -), as a function of randomness number (B) for DD70.
endotherms or exotherms. Typically, this occurred for copolymer samples which had very high degrees of randomness, and the samples were either not crystalline to begin with or, once melted, they were not able to recrystallize in the time of the DSC heating and cooling cycles.

As can be seen in Figure 3.4, there was a strong dependence of the degree of randomness of the copolymers on their crystallization temperatures on cooling, and as the randomness number increased the crystallization temperature of the copolyester decreased, as expected.

Another interesting observation was a crystallization exotherm on the second heating cycle for the samples randomized from copolymer DD70 (see Figure 3.8). Polymer DD70 was the only sample which displayed a crystallization exotherm on the second heating cycle. As can be seen in Figure 3.9 increases in the degree of randomness of the sample had a clear effect on the temperature at which this crystallization takes place. As the degree of randomness of a sample increased, the peak of the exotherm was shifted to higher temperatures. This is an opposite trend when compared to the shift of the crystallization peak on cooling for all the other polymer samples. Two possible explanations are that either the increased molecular weight or an increased glass transition temperature ($T_g$) caused the peak of the exotherm to shift to higher temperatures. This could not be
verified due to the difficulty in measuring the T_g of the polymer samples.

Further evidence that as the degree of randomness of a copolymer sample increased the sample became less crystalline, can be seen in the enthalpy of crystallization of the copolymer samples. As shown in Figures 3.5 and 3.9, as the randomness number of a copolymer was increased, the enthalpy of crystallization and, therefore, the degree of crystallinity, decreased. This trend can be observed in the melt transitions of the copolymers (see Figures 3.6 and 3.7). As expected, an increased degree of randomness of a sample caused the melt transition to occur at a decreased temperature. Although unlike the crystallization temperature, T_m did not decrease continuously with increased degrees of randomness. As can be seen in Figure 3.6, at a critical randomness number there was a sharp decrease in the melt transition. The reason for the step dependence of the melt transition on the degree of randomness is unknown, but the enthalpy of fusion also decreased as the randomness number of a sample increased. Both of these observations reinforce the expectation that as the degree of randomness of a copolymer is increased the sample becomes less crystalline.

A comparison of the results of poly(EPT-co-ET) and poly(PPT-co-ET) indicates that the biggest difference was that as the PPT-co-ET copolymers were randomized they lost their crystallinity sooner than the EPT-co-ET copolymers. For example,
DD67 and DD71 copolymers (see Tables 3.12 and 3.13, respectively) no longer showed melt or crystallization exotherms for samples with randomness numbers above 0.5 and 0.8, respectively. In comparison, the EPT-co-ET copolymers, such as DD65, DD68, and DD70, showed both crystallization and melting endotherms for samples with randomness numbers less than or equal to 1.0.

**Liquid Crystalline Textures**

It was expected that the changes in the crystallinity of the copolymers caused by changes in degrees of randomness, should result in changes in the liquid crystalline properties, but this was not the case. All randomized samples showed liquid crystalline nematic textures very similar to their unrandomized counterparts (see Figures 3.10 through 3.13). For DD70 (poly(EPT-co-ET)) copolymers there was a increase in the density of threads with increased degrees of randomness, but DD71 (poly(PPT-co-ET)) showed almost no textural differences between the samples with different degrees of randomness. So, while the changes in randomness had profound effects on the thermal properties of the copolyesters, there was little to no change in the liquid crystalline texture of the copolymers.
**Figure 3.10:** Polarized light micrographs for DD70 poly(EPT-co-ET) copolymers (250x mag.) quenched from 300°C: a) DD70.0, $B = 0.3$; and b) DD70.2, $B = 0.5$. 
Figure 3.11: Polarized light micrographs for DD70 poly(EPT-co-ET) copolymers (250x mag.) quenched from 300°C: a) DD70.7, $B = 0.7$; and b) DD70.11, $B = 0.9$. 
Figure 3.12: Polarized light micrographs of DD71 poly(PPT-co-ET) copolymers (250x mag.) quenched from 340°C: a) DD71.0, B = 0.4; and b) DD71.6, B = 0.6.
Figure 3.13: Polarized light micrographs of DD71 poly(PPT-co-ET) copolymers (250x mag.) quenched from 340°C: a) DD71.9, B = 0.7; and b) DD71.8, B = 0.9.
Conclusions

Several different liquid crystalline copolyesters were thermally post-treated successfully to increase their degree of randomness. Both poly(ethoxyphenylene terephthalate-co-ethylene terephthalate)s and poly(phenylphenylene terephthalate-co-ethylene terephthalate)s were prepared in 70:30 mole ratios of EPT:ET and PPT:ET and thermally randomized. The randomization reactions were controlled by variations in the duration and temperature of the reaction. The compositions of the copolymers remained constant in these reactions while the comonomer sequence distribution was changed. The inherent viscosities of the copolymers increased as a result of the reaction presumably because of increases in molecular weight.

The thermal properties were also greatly affected by changes in the degree of randomness of the copolymer. Increased randomness numbers caused decreased crystallinity of the copolyesters as observed by reduced enthalpies of fusion and crystallization. The more random sequence distributions resulted in melt transitions and crystallization temperatures to occur at reduced temperatures. While the degree of randomness had a large effect on the thermal properties of the copolymers, the liquid crystalline textures were relatively unaffected by the changes in randomness number. All copolyesters displayed the threaded texture characteristic of the nematic phase, although the densities of threads changed.
The overall goal of the work described in this chapter was to investigate a different approach to modifying highly aromatic liquid crystalline copolyesters to reduce their melt transition temperatures so that they would be easier to process in blends with common engineering thermoplastics. While Chapter 2 focused on some more traditional ways of reducing the thermal transition, especially through the use of bulky substituents and the copolymerization of monomers, the work in this chapter was concerned with the use of varying comonomer sequence distribution to achieve the lower melting temperatures, $T_m$. It was found that high degrees of randomness could significantly reduce $T_m$. 
References


CHAPTER 4

RHEOLOGICAL AND THERMAL STUDIES OF BLENDS OF POLY(ETHOXYPHENYLENE TEREPHTHALATE-CO-ETHYLENE TEREPHTHALATE) AND POLY(PHENYLPHENYLENE TEREPHTHALATE-CO-ETHYLENE TEREPHTHALATE) WITH POLY(ETHYLENE TEREPHTHALATE)

Introduction

As compared to common engineering thermoplastics, LCPs are far superior in terms of higher chemical resistance, lower flammability, higher modulus, lower isobaric expansivity (sometimes as low as zero), and lower melt viscosities. Yet because of the expense of LCPs, an economical solution for preserving their superior properties, which has been of interest for the last 10 years, has been to blend them with common engineering plastics to form an *in situ* composite. The use of LCPs as a reinforcing agent for engineering thermoplastics has many advantages over the use of other reinforcing fibers, such as glass fibers, including: wider processing options, improved surface appearance, more uniform product properties, recyclability, and decreased power consumption. Also, reinforcing fibers tend to increase the melt viscosity significantly which can
lead to problems of quick freeze-off, poor mold filling, and longer cycle times\textsuperscript{37,41}.

LCPs form the reinforcing phase during processing when drops of the LCP form oriented fibrils which have larger lengths and smaller diameters than glass fibres. The formation of the elongated fibrils depends on the presence of strong extensional flows. Three major method have been used to form the fibrillar morphology: fibre spinning, injection molding, and extrusion. It has been found that fibre spinning is the most effective for producing the fibrillar morphology. The reinforcement effect from the LCP is due to the larger aspect ratio of the fibrillar LCP phase and the better orientation of the LCP chains\textsuperscript{7,42}. The effectiveness of the LCP fibrils are dependent of the compatibility between the LCP and the matrix polymer. If the two phases are too incompatible then poor surface adhesion and non-uniform LCP dispersion can result. At the other extreme, if the two phases are too compatible, then the LCP phase can become too finely dispersed to effectively form a fibrillar morphology\textsuperscript{39}. Therefore, careful control of the compatibility of the two phases is essential for proper fibrillar formation, and hence, polymer reinforcement.

The addition of LCPs to engineering thermoplastics such as PET to form \textit{in situ} composites has been shown to: 1) increase strength and modulus by improving the overall orientation of the blend; 2) increase dimensional stability due to the very low isobaric expansivity of LCPs; and 3) reduce wear of the processing
machines while increasing the processing speeds by decreasing the overall melt viscosity of the blends. Also, the addition of common engineering thermoplastics to LCPs can improve the weak lateral strength of the LCPs and improve the compressive resistance of the oriented polymer.

Studies of blends of LCPs and engineering thermoplastics, such as, polycarbonate\textsuperscript{2,6-8,10,11,13-15,38,40,42}, polystyrene\textsuperscript{9,13}, polyamides\textsuperscript{2,10,16}, poly(ethylene terephthalate)\textsuperscript{13,17,18,21,26,31}, poly(butylene terephthalate)\textsuperscript{1-3,10,36}, polypropylene\textsuperscript{4,28,34,39}, poly(ether imide)\textsuperscript{2,8,33,37}, poly(ether ether ketone)\textsuperscript{2,19,33}, poly(ether sulfone)\textsuperscript{2}, poly(phenylene sulfide)\textsuperscript{23,33}, poly(arylate)\textsuperscript{2,22}, and poly(vinyl chloride)\textsuperscript{12}, to form \textit{in situ} composites have been well documented. For example, Baird and Sun\textsuperscript{33} showed that films of poly(ether imide) (PEI) reinforced by LCPs had a tensile modulus 3 to 4 times higher than that of neat films. Joseph \textit{et al.}\textsuperscript{31} showed that blends of LCPs with PET had increased rates of crystallization, and a three-fold increase in the bending modulus. In our laboratory Narayan\textsuperscript{24} showed that just 2.5 weight percent of an LCP in PET can reduce the melt viscosity by an order of magnitude. Heino \textit{et al.}\textsuperscript{34} observed that it took 30 weight percent of an LCP to decrease appreciably the melt viscosity of the LCP/polypropylene blend. Lee \textit{et al.}\textsuperscript{37} observed that the melt viscosity of PEI decreased continuously with increasing LCP content.
Most of the previous studies of *in situ* composites have focused on the effects of LCP concentration, processing conditions, and compatibilization on the blend properties. There has been less of an emphasis on the effects of LCP modification on the blend properties. Also, while there have been studies on the effects of different comonomer sequence distributions on the LC copolyester properties, there have been no studies looking at the effect of changes in the sequence distribution of an LC copolyesters on the blend properties of the LC copolyester with isotropic thermoplastics such as PET. In this study, several LC copolyesters with different degrees of randomness were blended with PET to study the effect of the different sequence distributions on the blend properties.

**Experimental**

**Materials**

The TLCPs used in this research were polymer DD70, poly(ethoxyphenylene terephthalate-co-ethylene terephthalate) [poly(EPT-co-ET)], and polymer DD71, poly(phenylphenylene terephthalate) [poly(PPT-co-ET)], that were synthesized and randomized in Chapter 3. Four samples from each copolymer with different randomness numbers were used. Polymer DD70.0 (B = 0.3), polymer DD70.2 (B = 0.5), polymer DD70.7 (B = 0.7), and polymer DD70.11 (B = 0.9) were used from the poly(EPT-co-ET) sample. From poly(PPT-co-ET) polymer DD71.0 (B = 0.4), polymer
DD71.6 ($B = 0.6$), polymer DD71.9 ($B = 0.7$), and polymer DD71.8 ($B = 0.9$) were used. The engineering thermoplastic used was a PET supplied by the Akzo Corp. The PET was blended as received without further purification.

**Blending**

TLCP content was kept at 5 weight percent due to the small amount of LCP available. LCPs and PET were blended in solution. The solvent used was a 1:1 mixture of trifluoroacetic acid and chloroform. The polymers were blended in solution, rather than in the melt, to avoid transesterification reactions between the two polymers during the blending process. After being placed into solution, the blends were dropwise co-precipitated into a 10 fold excess acetone. The blends were washed with acetone several times and dried in a vacuum oven at 90°C for at least 48 hours. The properties of the LCPs which were blended with PET is shown in Table 4.1.

**Blend Characterization**

Thermal properties of the blends were investigated using the modulated DSC program of a Du Pont 2910 DSC under nitrogen flow. The samples were heated to 350°C, rapidly quenched to room temperature, and finally heated at a rate of 5°C/min to 350°C. The modulated heating rate, on the second heating cycle, was +/- 1.0°C every 60 seconds. The melting transitions and
<table>
<thead>
<tr>
<th>Blend</th>
<th>LCP&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Random&lt;sup&gt;b&lt;/sup&gt; Number</th>
<th>Inherent&lt;sup&gt;c&lt;/sup&gt; Viscosity (dL/g)</th>
<th>T&lt;sub&gt;m&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt; (°C)</th>
<th>T&lt;sub&gt;c&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blend 1</td>
<td>DD70.0</td>
<td>0.3</td>
<td>0.8</td>
<td>228/280</td>
<td>240</td>
</tr>
<tr>
<td>Blend 2</td>
<td>DD70.2</td>
<td>0.5</td>
<td>1.1</td>
<td>223/281</td>
<td>238</td>
</tr>
<tr>
<td>Blend 3</td>
<td>DD70.7</td>
<td>0.7</td>
<td>1.1</td>
<td>260/279</td>
<td>233</td>
</tr>
<tr>
<td>Blend 4</td>
<td>DD70.11</td>
<td>0.9</td>
<td>*</td>
<td>257</td>
<td>218</td>
</tr>
<tr>
<td>Blend 5</td>
<td>DD71.0</td>
<td>0.4</td>
<td>1.4</td>
<td>301/324</td>
<td>240/252</td>
</tr>
<tr>
<td>Blend 6</td>
<td>DD71.6</td>
<td>0.6</td>
<td>1.55</td>
<td>301/327</td>
<td>242/250</td>
</tr>
<tr>
<td>Blend 7</td>
<td>DD71.9</td>
<td>0.7</td>
<td>0.95</td>
<td>324</td>
<td>235</td>
</tr>
<tr>
<td>Blend 8</td>
<td>DD71.8</td>
<td>0.9</td>
<td>0.6</td>
<td>**</td>
<td>**</td>
</tr>
</tbody>
</table>

a--The synthesis and randomization of polymers DD70.0, 70.2, 70.7, and 70.11 [poly(EPT-co-ET)] and polymers DD71.0, 71.6, 71.9, and 71.8 [poly(PPT-co-ET)] was described in Chapter 3

b--Randomness numbers were determined by <sup>1</sup>H-NMR spectroscopy in TFAA-d/Chloroform-d mixture solvent

c--Inherent viscosity measurements were made in 60:40 mixture of p-chlorophenol/tetrachloroethane at 26°C, and 0.5 g/dL

d--Thermal transitions were measured by DSC at a heating and cooling rate of 20°C/min

*--Insoluble in viscometry solvents

**--Thermal transitions not observable because of a lack of crystallinity
Recrystallization points were taken from the peak of the melting endotherm and recrystallization exotherm, respectively, on the second heating cycle. The glass transition temperature, $T_g$, of the blend was also measured on the second heating cycle. The modulated DSC program was used because it gave added sensitivity and resolution over normal DSC. An Olympus BH2 series 300 polarizing microscope with Linkam THMS 600 heating stage was used to conduct polarized light microscopy (PLM) to study the dispersion of the liquid crystalline phase in the matrix polymer.

**Rheological Measurements**

The dried blends were compression-molded at 280°C to 290°C under vacuum into discs of 25 mm diameter to ensure a 100% contact with the fixtures of the rheometers, especially the edges. Dynamic mechanical measurements were carried out on a Rheometrics dynamic spectrometer (RDS-7700). The sample geometry featured a gap width of 1 mm in a parallel plate arrangement, with a plate radius of 12.5 mm. During frequency sweep experiments, the frequency was varied from 1 to 159 rad/sec. Measurements were taken at 290°C, 280°C, 275°C, 270°C, 265°C, 260°C, 250°C, and 240°C in that order. Blends 5 through 8 were held at 320°C for a few minutes, before equilibrating at 290°C for testing, to try and completely melt the LCP. In order to avoid destruction by oxidation, the samples were held under a dry nitrogen atmosphere during all tests.
Results and Discussion

Thermal Properties

Modulated DSC (MDSC) utilizes a rapid heating rate oscillation along with the conventional linear temperature ramp. The oscillatory heating rate increases the instantaneous heating rate above the underlying heating rate. Since DSC sensitivity is proportional to the instantaneous heating rate, increased heat flow sensitivity can be produced without sacrificing temperature resolution. The MDSC also provides added information on both the reversible and nonreversible characteristics of thermal events. The total heat flow signal is divided into the reversing, nonreversing, and heat capacity components through a Fourier transform deconvolution process. As can be seen in Figure 4.1, the reversible heat flow contains information on the glass transition and the melt transition while the nonreversible heat flow contains information about the recrystallization peak. MDSC was used for these blends because of its added sensitivity for trying to discern any transitions or transition changes due to the LCP phase.

The results of the thermal analysis of the blends are given in Table 4.2. A typical thermogram showing only the total heat flow of a blend is displayed in Figure 4.2. Neither the glass transition temperatures ($T_g$), melting temperatures ($T_m$), nor recrystallization temperatures ($T_c$) showed any significant changes
between PET and any of the blends: the Tg was in the range of 75 ± 3°C; the Tm was in the range of 252 ± 2°C; and the Tc was in the range of 130 ± 5°C. The lack of a change in thermal transition was probably because of the small amount of LCP used in the blends. With only 5 weight % of LCP in the blends, any effects they would have on the thermal transitions of the PET would be negligible, since thermal transitions of blends often follow the rule of mixtures. On the other hand, the enthalpies of fusion and recrystallization showed significant differences between PET and the blends. The enthalpies of PET sample were much lower than the enthalpies of the blends. This result would indicate that the LCPs induced a greater degree of crystallinity on the PET matrix. Another observation worth noting was that changes in the degree of randomness of the copolymers did not significantly affect the $\Delta H_c$ values or the thermal transition temperatures of the blends. Yet while the values of $\Delta H_m$ did show a significant amount of change from one blend to another, the differences in the values of $\Delta H_m$ did not show any direct dependence on the degree of randomness of the LCP used in the blends.

Rheological Experiments

The rheology of LCPs has been studied extensively\textsuperscript{43-46} as well the rheology of blends of LCPs with isotropic thermoplastics\textsuperscript{5,6,8,12,35,47}. Baird and Wissbrun have each written excellent review articles about the rheology of LCPs\textsuperscript{48,49}. According to Wissbrun and others\textsuperscript{50,51}, LCPs have been found to
Figure 4.1: Modulated DSC thermogram of Blend 1 showing the reversible, nonreversible, and total heat flow.
<table>
<thead>
<tr>
<th>Sample</th>
<th>LCP&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$T_g$ (°C)&lt;sup&gt;b&lt;/sup&gt;</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_c$ (°C)</th>
<th>$\Delta H_c$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>--</td>
<td>78</td>
<td>251</td>
<td>37.6</td>
<td>129</td>
<td>15.2</td>
</tr>
<tr>
<td>Blend 1</td>
<td>DD70.0</td>
<td>75</td>
<td>253</td>
<td>52.4</td>
<td>127</td>
<td>32.3</td>
</tr>
<tr>
<td>Blend 2</td>
<td>DD70.2</td>
<td>73</td>
<td>253</td>
<td>50.4</td>
<td>127</td>
<td>32.3</td>
</tr>
<tr>
<td>Blend 3</td>
<td>DD70.7</td>
<td>73</td>
<td>252</td>
<td>58.2</td>
<td>126</td>
<td>37.0</td>
</tr>
<tr>
<td>Blend 4</td>
<td>DD70.11</td>
<td>74</td>
<td>254</td>
<td>51.2</td>
<td>127</td>
<td>33.4</td>
</tr>
<tr>
<td>Blend 5</td>
<td>DD71.0</td>
<td>75</td>
<td>254</td>
<td>50.5</td>
<td>128</td>
<td>32.8</td>
</tr>
<tr>
<td>Blend 6</td>
<td>DD71.6</td>
<td>78</td>
<td>253</td>
<td>43.9</td>
<td>132</td>
<td>30.3</td>
</tr>
<tr>
<td>Blend 7</td>
<td>DD71.9</td>
<td>78</td>
<td>252</td>
<td>44.3</td>
<td>135</td>
<td>30.7</td>
</tr>
<tr>
<td>Blend 8</td>
<td>DD71.8</td>
<td>76</td>
<td>251</td>
<td>48.6</td>
<td>130</td>
<td>31.6</td>
</tr>
</tbody>
</table>

<sup>a</sup>Properties of polymers DD70.0, 70.2, 70.7, and 70.11 [poly(EPT-co-ET)] and polymers DD71.0, 71.6, 71.9, and 71.8 [poly(PPT-co-ET)] are given in Table 4.1

<sup>b</sup>Thermal transitions and enthalpies measured by MDSC at a heating rate of 5°C/min and a heating modulation of +/-1.0°C every 60 seconds.
Figure 4.2: Modulated DSC thermogram of Blend 3 showing the total heat flow.
have quantitative and qualitative differences from isotropic thermoplastics. The lower viscosities and longer relaxation times of the LCPs summarize the quantitative differences between LCPs and isotropic thermoplastics. The qualitative differences include: shear thinning at low shear rates; little or no extrudate swelling; occasional shear thickening behavior; transient negative normal stress difference; and flow behavior dependent on thermal and mechanical history.

Typically, simple, well defined flows, such as simple shear and simple elongational, are used to characterize polymeric fluids. In simple shear flow, material planes are moved relative to one another without stretching, while in elongational flow the material units are stretched (see Figure 4.3). These flows are termed steady simple shear or steady simple elongational flow when the reological properties no longer change with time. Elongational flows can be generated using devices which deform cylindrically shaped specimens so that the length is increased exponentially. In this study, the simple shear flows were generated using a plate-plate (or parallel plate) conformation, but cone-and-plate, and couette devices can also be used.  

The blends in this study were measured using dynamic oscillatory shear flow. The measurements were carried out at a strain level where the stresses were directly proportional to the strains. In dynamic oscillatory shear flow studies, \( G' \), the storage modulus, and \( G'' \), the loss modulus, are measured as a function of
Figure 4.3: Schematic drawing of two flows commonly used in rheological studies\(^48\).

The angular frequency, \(w\). \(G'\) represents the amount of energy stored per cycle of deformation, while \(G''\) represents the amount of energy lost per cycle of deformation. The complex modulus, \(G^*\), can be defined as:

\[
G^* = G' + iG''
\]

or

\[
G^* = (G'^2 + G''^2)^{1/2}
\]
The complex viscosity, $\eta^*$, can be defined as:

$$\eta^* = \eta'' + i\eta'$$

or

$$\eta^* = G^*/\omega$$

The loss tangent, $\tan\delta$, can be defined as:

$$\tan\delta = G''/G'$$

In this study, the complex viscosity of the blends was of particular interest to investigate the LCPs effectiveness as a processing aid for the PET.

The results of the frequency sweeps on the blends at 240°C, 265°C, and 290°C are shown in Figures 4.4 through 4.9. The first observation was that with only 5 weight percent of an LCP added to the PET, there was a significant difference between the melt viscosity of the PET and the blends. That is, a very low weight percentage of LCP had a large effect on the PET matrix viscosity. The blockier LC copolymers (Blends 1, 2, 5, 6, and 7) caused an increased melt viscosity of the blend above that of the neat PET sample, which was very unexpected because LCPs in the nematic state typically have lower melt viscosities than isotropic thermoplastics. Conversely, the more random LC copolyesters (Blends 3, 4, and 8) caused a decrease in the melt viscosity of the blend. In some instances, the difference between the melt
viscosities of the blends with the blockier LC copolymers and the more random LC copolymers was as large as an order of magnitude.

There are several possible explanations for the large differences in the melt viscosities of the blends. The first is that the blockier LC copolymers may have had larger demixing interfaces, and these interfaces could act as physical crosslinks, which would cause an increase in the melt viscosity of the blend. Another possible explanation is that the blockier copolymers had longer segments of ethylene terephthalate (ET) units, and these longer segments of the flexible units could have created more entanglements, which would have also acted as physical crosslinks. In contrast, the more random LCPs would have had much shorter segments of the flexible ET units which would not participated in as many entanglements. Also, in the case of Blend 8, the reduced inherent viscosity, and hence reduced molecular weight, of the LCP used (polymer DD71.8) could have also contributed to the decrease in the melt viscosity of the blend.

Another possible explanation for the increased melt viscosity for Blends 5, 6, and 7 was the possible existence of crystalline regions of the LCP in the molten blend. That is, although the blends were held at 320°C for a few minutes to melt the LCP, it was possible that LCPs were not completely melted. Any remaining crystals would act as physical crosslinks, which would increase the melt viscosity of the blends. The effect of
crystals acting as physical crosslinks can be observed in Figure 4.10, which shows the melt viscosity of two different samples of Blend 5. One sample was heated to 320°C for a few minutes before testing, while the other sample was heated to 290°C before testing. As can be seen in the graph the sample that was not heated to 320°C before testing had a higher melt viscosity than the sample that was pre-melted because of the presence of crystals which acted as physical crosslinks. A similar trend for Blend 8 was not observed because the LCP used (polyDD71.8) was an amorphous polymer.

Polarized Light Microscopy

Figures 4.21 through 4.24 shows the polarized light micrographs of the blends. The blends of PET with poly(EPT-co-ET) (Blends 1 through 4) appear quite different from the blends of PET with poly(PPT-co-ET) (Blends 5 through 8). Blends 1 through 4 displayed dispersed particles of the LCP, many of which appeared to be in the form of elongated fibrils. The LCP dispersed phase could have been elongated into fibrils through the shearing of the coverslip of the sample. While Blends 5 through 8 displayed dispersed LCP particles, these LCP particles were not elongated into fibrils. This could be due to a finer dispersion of the LCP particles. If the LCP phase is too finely dispersed, the LCP can not effectively form fibrils. Also, while a large number of LCP particles were observed for Blends 5 and 6, much smaller numbers of particles were observed for Blends 7 and 8. Another
Figure 4.4: Complex viscosity as a function of frequency at 240°C for: -□- PET, +- Blend 1, -▽-Blend 2, -Δ-Blend 3, and -○- Blend 4.
Figure 4.5: Complex viscosity as a function of frequency at 265°C for: -☐- PET, ++ Blend 1, -▼-Blend 2, -△-Blend 3, and -○- Blend 4.
Figure 4.6: Complex viscosity as a function of frequency at 290°C for: -□- PET, +- Blend 1, -▼-Blend 2, -△-Blend 3, and -○- Blend 4.
Figure 4.7: Complex viscosity as a function of frequency at 240°C for: -□- PET, -+ Blend 5, -▼ Blend 6, -Δ Blend 7, and -○- Blend 8.
Figure 4.8: Complex viscosity as a function of frequency at 265°C for: [○] PET, [++] Blend 5, [▼] Blend 6, [▲] Blend 7, and [●] Blend 8.
Figure 4.9: Complex viscosity as a function of frequency at 290°C for: -□- PET, -+- Blend 5, -V-Blend 6, -Δ-Blend 7, and -O-Blend 8.
Figure 4.10: Complex viscosity as a function of frequency for Blend 5 at 290°C, 265°C, and 240°C: □ - sample heated to 290°C before testing; △- sample heated to 320°C before testing.
Figure 4.11: Polarized light micrographs of: a) Blend 1 (quenched from 292°C, 50x mag.); and b) Blend 2 (quenched from 292°C, 50x mag.).
Figure 4.12: Polarized light micrographs of: a) Blend 3 (quenched from 292°C, 100x mag.); and b) Blend 4 (quenched from 292°C, 100x mag.).
Figure 4.13: Polarized light micrographs of: a) Blend 5 (quenched from 327°C, 50x mag.); and b) Blend 6 (quenched from 327°C, 50x mag.).
Figure 4.14: Polarized light micrographs of: a) Blend 7 (quenched from 327°C, 100x mag.); and b) Blend 8 (quenched from 327°C, 50x mag.).
observation was that the optical textures were not affected by changes in the degree of randomness of the LCP in Blends 1 through 4.

Conclusions

Two different LC copolyesters, poly(ethoxyphenylene terephthalate-co-ethylene terephthalate) [poly(EPT-co-ET)] and poly(phenylphenylene terephthalate-co-ethylene terephthalate) [poly(PPT-co-ET)], were solution blended with PET using a mixture solvent of TFAA/Chloroform. Four different samples of each LC copolyester, with varying degrees of randomness, were used in the blends. The blends were characterized by DSC, polarized light microscopy, and rheological testing.

Results of the thermal analysis showed that there was no change in the temperature of the thermal transitions with the addition of the LCP. This was most likely because only a small amount of the LCP was added. That is, only 5 weight percent of the LCP was used, and this amount may not have been sufficient to cause changes in the thermal transitions of the PET. Also, it was observed that the addition of the LCP to PET caused a significant increase in the enthalpy of the of the thermal transitions. This result would indicate that the LCP induced greater crystallinity in the PET matrix, either by acting as a nucleating agent or by accelerating the rate of crystal growth. These changes in the degree of crystallinity were not consisantly
affected by the degree of randomness of the LC copolymer incorporated into the blends.

Polarized light microscopy showed a dispersed LC phase in the PET matrix. It was observed that the dispersed LCP phase in blends with poly(EPT-co-ET) (Blends 1 through 4) was partially in a fibrillar-type morphology. On the other hand, for blends of PET with poly(PPT-co-ET) (Blends 5 through 8) a similar fibrillar-type morphology was not observed. This was most likely because of a too finely dispersed LCP phase which would inhibit the formation of fibrils. Also, while changes in the degree of randomness of the LCP in Blends 1 through 4 did not affect the observed textures, there was an observed reduction of the number of dispersed LCP particles for Blends 7 and 8 when compared to Blends 5 and 6.

Rheological testing of the blends showed that blends with more random LC copolymers had much lower melt viscosities than blends with the more blocky LC copolymers. The difference between the melt viscosities of blends containing blocky LC copolyesters and blends containing random LC copolyesters was more than an order of magnitude. The reduction of the melt viscosity could have resulted from an enhanced miscibility in the blends containing the more random LC copolymers. Enhanced compatibility would cause a reduction in the area of the demixing interfaces which could act as physical crosslinks. Another possible explanation was that blockier copolymers, which had longer segments of the flexible ET units, could take part in entanglements
which could also act as physical crosslinks. For Blend 5 through 7, their increased melt viscosities could be due to the presence of crystals of the LCP that remained unmelted. These crystals would act as physical crosslinks, which would increase the melt viscosity. Blend 8, which had a much lower melt viscosity than any other blend, incorporated polyDD71.8 which was an amorphous sample so there would be no crystals to act as physical crosslinks. Also polyDD71.8 had the lowest inherent viscosity of all the LCPs which could have contributed to the decreased melt viscosity of the blend.

The goal of the research presented in this chapter was to investigate the effects of the sequence distribution of a LC copolymer on the blend properties. It was observed that the melt viscosity of the blend had a strong dependence on the degree of randomness of the LC copolymer used. The copolyesters with high degrees of randomness caused a reduction of the melt viscosity. This result would indicate that, for blending purposes, more random LC copolyesters have several advantages over the more blocky LC copolyesters. Besides improving the processing speeds through a reduction of the melt viscosity, highly random LC copolyesters also tend to have lower melt transitions than their blocky counterparts. This affect would allow processing of the blends at lower temperatures.
References


CHAPTER 5

CONCLUSIONS AND SUGGESTED FUTURE WORK

Conclusions

The main objective of this dissertation research was the synthesis and modification of thermotropic liquid crystalline copolyesters to be blended with isotropic engineering thermoplastics such as PET. There has been a lot of interest in the last several years in the blending of thermotropic LCPs with engineering thermoplastics to form in situ composites. By blending small amounts of the more expensive LCPs with the less expensive isotropic thermoplastics it is possible to impart the improved properties of the LCP on the blend in a cost effective manner. However, because of the typically high melting transition temperatures of highly aromatic thermotropic LCPs, methods must be used to reduce the transition temperatures to within the processing window of the engineering thermoplastic with which they are blended. Different chapters in this dissertation have focused on different methods for the reduction of the thermal transitions of the LCPs. The copolymerization of different comonomers with different types of bulky substituents were utilized in Chapter 2 to reduce the melt transitions of the LCPs. In
Chapter 3, thermal transesterification reactions were utilized to increase the randomness of the LC copolyesters and reduce the thermal transition temperatures of the LCPs. These randomized copolyesters were solution blended with PET and then tested rheologically to study their effectiveness as processing agents in Chapter 4.

Three series of thermotropic, aromatic copolyesters derived from EHQ, PHQ, HQ, EG, and TA were synthesized, and characterized by PLM, DSC, NMR, TGA, and solution viscometry in Chapter 2. One goal of the work presented in this chapter was the reduction of the melt transitions of several highly aromatic liquid crystalline copolyesters. This objective was to be accomplished by the copolymerization of different monomers having bulky substituents. It was shown that the melt transition was effectively reduced through the copolymerization of the monomers, although the effects were not always as expected.

The monomer with a bulky phenyl side group, which was used in Series II and III copolymers, was chosen because it was believed that the size of the substituent would frustrate the packing of the chains enough to cause a reduction in the thermal transitions. The opposite was observed, and this result may have been caused by an increase in the stiffness of the chains caused by the phenyl substituents inhibiting chain rotation. That is, while Series III copolyesters containing EPT, PPT, and ET units had the largest amount of substituents along the chain, they also...
had the highest thermal transitions and the highest thermal stabilities. They were the most crystalline and had the highest molecular weights. Nevertheless, for melt blending with engineering thermoplastics, such as PET, the transition temperatures for the Series III samples were too high, while some of the Series I and II copolymers with low amounts of PT units had thermal transitions in the range which would make them more favorable for blending.

In Chapter 3, several different liquid crystalline copolyesters were thermally post-treated successfully to increase their degree of randomness. Both poly(ethoxyphenylene terephthalate-co-ethylene terephthalate)s and poly(phenylphenylene terephthalate-co-ethylene terephthalate)s were prepared in 70:30 mole ratios of EPT:ET and PPT:ET and thermally randomized. The overall goal of the work described in this chapter was to investigate a different approach to modifying highly aromatic liquid crystalline copolyesters to reduce their melt transition temperatures so that they would be easier to process in blends with common engineering thermoplastics. While Chapter 2 focused on some more traditional ways of reducing the thermal transition, specifically the use of bulky substituents and the copolymerization of monomers, the work in this chapter was concerned with the use of varying comonomer sequence distribution to achieve the lower melting temperatures, $T_m$. It was found that increased randomness numbers caused decreased melt transition temperatures and crystallization temperatures.
The more random sequence distributions also resulted in a decreased crystallinity of the copolyesters as observed by reduced enthalpies of fusion and crystallization.

In Chapter 4, two different LC copolyesters, 
poly(ethoxyphenylene terephthalate-co-ethylene terephthalate) [poly(EPT-co-ET)] and poly(phenylphenylene terephthalate-co-ethylene terephthalate) [poly(PPT-co-ET)], were solution blended with PET using a mixture solvent of TFAA/Chloroform. Four different samples of each LC copolyester, with varying degrees of randomness, were used in the blends. The blends were characterized by DSC, polarized light microscopy, and rheological testing. Results of the thermal analysis showed that there was no change in the temperature of the thermal transitions with the addition of the LCP. The goal of the research presented in this chapter was to investigate the effects of the sequence distribution of a LC copolymer on the blend properties. It was observed that the melt viscosity of the blend had a strong dependence on the degree of randomness of the LC copolymer used. The copolyesters with high degrees of randomness caused a reduction of the melt viscosity. This would indicate that, for blending purposes, more random LC copolyesters have many advantages over the more blocky LC copolyesters. Besides improving the processing speeds through a reduction of the melt viscosity, highly random LC copolyesters also tend to have lower melt transitions than their blocky counterparts, which would allow processing of the blends at lower temperatures.
Suggested Future Work

Several of the results from this dissertation research raised several interesting questions, which because of time constraints, could not be investigated. Suggested future work on the studies of each of the previous chapters is discussed below.

Chapter 2

One of the more unexpected results from the work in this chapter was the effect that the phenyl substitution had on the thermal transitions and crystallinity of the LC copolyesters. While it was expected that the bulky phenyl side group of the phenylhydroquinone monomer would decrease the melt transitions, and lower the crystallinity of the copolymers, the reverse was observed. The study of the crystal structure of copolymers from Series II and III [poly(PPT-co-PT-co-ET) and poly(PPT-co-EPT-co-ET)] would provide further insight into the effects that different substituents have on the properties of the copolymer.

Because of the insolvability of the copolymers in GPC solvents, the only molecular weight measurements run were inherent viscosity measurements, which only give relative molecular weights. Light scattering experimentation on several different samples would provide more thorough characterization of the three copolymer series.
Another possible study would be to increase the amount of ET units in the LCPs. In this chapter all LCPs were synthesized using a 30% mole fraction of EG. Studying the effects of the increases of ET units on the LCP properties, particularly their rheological properties, would allow us to find the best possible candidate to use as a processing aid for engineering thermoplastics.

Chapter 3

One of the more interesting observations from this chapter was the step function decrease in the melt transition with increased degrees of randomness. A more thorough study of the changes in the degree of crystallinity and crystal structure of samples on either side of the step function to determine what changes these properties had on the step-drop in the melt transition.

Chapter 4

It was observed in this chapter that the addition of the LCP did not affect the thermal transition temperatures of the blend. This result was probably due to the small amount of LCP (5 weight percent) used in the blends. Therefore, blends with larger weight percents of LCP should be prepared to observe any changes in the thermal transitions of the blends. Changes in the thermal transitions of the blends can show differences in the
compatibilization of PET and LCPs with differing degrees of randomness. Another possibility would be to vary the amount of the ET units in the LCP to study the effect of flexible segments on the blend properties (specifically the rheological properties). Also rheological studies of blends with larger amounts of LCP, and even the pure LCP, would be of interest to try and find the optimum amount of LCP in the blends for use as a processing aid.

Two other techniques which would allow better understanding of the dispersion of the LCP particles in the PET matrix are solid state NMR and SEM. NMR spectroscopy can detect the presence of the polymer units in environments on the order of magnitude of Å in radius. That is, depending on the relaxation times of the blends, solid state NMR can be used to determine if phase separation has occurred between the two blend components. With SEM, direct observation of the morphology and domain size of the dispersed LCP phase is possible.

While the blending studies in this Chapter focused on PET as the matrix polymer, it would be interesting to study the effect of the LCPs on different isotropic thermoplastics. Some possible candidates for blending might be poly(ethylene naphthalate) (PEN), poly(butylene terephthalate) (PBT), or polycarbonate. Also along with studying the rheological properties of the blends, it would be interesting to study the mechanical properties of the blends as well.


Irwin, R. S., Macromol., 27, 3739-3745, 1994.


