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Modification of Randomness by Transesterification of Thermotropic Liquid Crystalline Copolyesters

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ABSTRACT: Several different liquid crystalline copolyesters were thermally posttreated above their melt transition temperatures to increase their degree of randomness. Both poly(ethoxyphenylene terephthalate-*co*-ethylene terephthalate)s (poly(EPT-*co*-ET)) and poly(phenylphenylene terephthalate-*co*-ethylene terephthalate)s (poly(PPT-*co*-ET)) 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. Increased randomness resulted in decreased crystallinities of the copolyesters, as observed by reduced enthalpies of fusion and crystallization, lower melt transitions, and lower crystallization temperatures.

Introduction

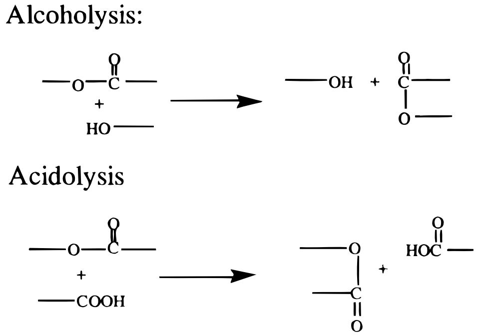
Thermotropic liquid crystalline polyesters, TLCPs, are of interest as reinforcing components for in situ composites.[1−5] One problem in this application of TLCPs is the typically high melt transition temperatures of these highly aromatic polyesters. Commonly used methods for decreasing the melt transition of TLCPs include the inclusion of bulky substituents, copolymerization of different monomers, and the inclusion of flexible spacers.[6−17] Another possible modification of LCPs, and more specifically LC copolyesters, is the variation of the sequence distributions of the monomer units in the copolyester.[15,18−28]

It has been shown by Jin et al.[15,18,19,23] that a more random distribution of comonomer units will lead to lower glass transition temperatures, lower melt transition temperatures, reduced crystallinity, and even different crystal structures. Furthermore, Stupp et al.[20−22] 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.[27] showed that for aromatic copolyimides a change from alternating to random ordering caused a drastic decrease in the solubility of the copolymer. All of 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.

The randomness of a copolyester can be determined by the use of both ^{1}H NMR[29−35] and ^{13}C NMR. The degree of randomness (B), or randomness number, can be calculated by integrating the different proton resonance peaks of the terephthalate groups in copolyesters with different diols.[31] 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 the melt, in which preordered sequences are not used, are expected to yield a random comonomer distribution. However, it has been shown in previous studies[36,37] that, for low-temperature solution copolymerization reactions, the resultant copolyester can have a blocky structure (i.e., $B = 0.3{-}0.5$). Because of the sensitivity of the randomness number calculations toward the copolymer composition, when less than 25−30 mol % of ET units is incorporated into the copolymer, the calculated randomness numbers are inaccurate. Therefore, the first goal of this study was the synthesis of LC copolyesters with at least 25−30 mol % of ET units.

Interchain exchange reactions of polyesters have been reviewed by Kotliar.[38] Two types of reactions can occur between polyester chains, alcoholysis and acidolysis, both of which can result in the transesterification of the chains, as seen below:



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

The use of transesterification reactions of blend components to change the compatibility between the components has been studied extensively.[39−46] Also, while there have been many studies on the effects of thermal treatments on LC copolyesters to cause trans-

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esterification reactions and create a more random distribution of the comonomers, there has been some disagreement about whether the treatments should take place below, within, or above the nematic range.[24,26,47−49] Warner and Lee[50] observed a tripling of the molecular weight of LCPs by postpolymerization heat treatment of fibers. 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.[47,48] reported that transesterification, and, therefore, chemical randomization, was the dominant process only above the crystal−nematic transition, that is, at temperatures from 290 to 450 °C. Samples annealed 40−50 °C below the crystal−nematic transition showed a physical reorganization of the chains into larger crystals, while samples annealed just below the crystal−nematic transition (<10 °C) showed an increase of alternating copolymer sequences via interchain transesterification reactions along with a significant increase in the crystal−nematic transition temperature. Yoon et al.[49] reported that annealing nematic copolyesters 25 °C below the crystal−nematic transition shifted the melt transition by more than 50 °C while also sharpening the transition. It was noted that there was no substantial change to the sequence distribution. Wu and Stupp[26] observed that randomization of nematic copolyesters was prevalent above the nematic−isotropic transition. They also showed that the randomization was both a physical and a chemical process but that intermolecular acidolysis was the primary contributor toward randomization of the LCPs. Jin et al.[24] 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}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 main objective of this study was to prepare several new series of LC copolyesters with varying degrees of randomness. By varying the conditions of the randomization reactions, several new series of LC copolyesters were synthesized, and their randomness numbers, which varied from 0.3 to 1.0, were determined by ^{1}H NMR spectroscopy. The copolymers selected for this study 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)].

The overall goal of this study 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.

Experimental Section

Monomer Synthesis. Ethoxyhydroquinone (EHQ) was synthesized as described previously.[36,51] Phenylhydroquinone (PHQ), ethylene glycol (EG), and terephthaloyl chloride (TC) were purchased from Aldrich Chemical Co. The PHQ and TC were purified by sublimation. EG was used as received in a solution of dry methylene chloride. Triethylamine (TEA) and methylene chloride were distilled over calcium hydride.

Polymer Synthesis. All copolymers were prepared using solution polycondensation reactions as described previously.[11,36] Two methods were used to try to prepare copolymers containing 30 mol % of ET units. The first method utilized a molar excess of EG; that is, instead of using 70 mol % of EHQ and 30 mol % of EG, as was used previously, 60 mol % of EG was used with 70 mol % of EHQ in a solution of methylene chloride. In both cases, the amount of terephthaloyl chloride was kept at 100 mol %. The second method utilized a limitation in the amount of hydroquinone monomer; that is, instead of a 70:30 (nHQ:EG, n is either E or P) 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 which 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 1 h 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 1−2 h 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 24 h at room temperature and then refluxed for 24 h under nitrogen. At the end of the polymerization reaction the copolyesters were precipitated into a 3-fold excess of methanol. The precipitate was filtered, extracted in a Soxhlet extractor with acetone, and dried in a 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 1 g of copolymer, while small batches used approximately 0.1−0.2 g 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 to 330 °C, which was shown to be well below the degradation temperature of the polymers,[37] depending on the thermal transitions of the polymer sample. A temperature controller was used to maintain the instantaneous bath temperature within ± 7 °C, while the average bath temperature was maintained at target. The duration of the reaction was varied from 0.5 to 24 h. Uncatalyzed reactions were studied to avoid enhancement of some of the exchange reactions.

Randomness Determinations. Copolymer randomness values were determined by NMR spectroscopy on the basis of sequence distributions that were determined from the relative areas of the terephthalate proton signals (8.4−8.6 ppm)[29,31,36] (see Figure 1). Differences in the types of units on either side of the terephthalate unit caused changes in the shift of the terephthalate proton peaks because of differences in the amount of shielding that the terephthalate protons experienced. As a result, the protons of the terephthalate units that had EG units on both sides (EG−T−EG) had a different chemical shift than the protons in the terephthalate units with either HQ units on both sides (nHQ−T−nHQ) or with an EG unit on one side and an HQ derivative unit on the other (nHQ−T−EG).

The probability of finding an nPT unit next to an ET unit is given by the following equation:

$$P_{\mathrm{nPT-ET}} = P_{\mathrm{nHQ-T-EG}}/2F_{\mathrm{nPT}}$$

in which $P_{\mathrm{nHQ-T-EG}}$ was the proportion of the integrated

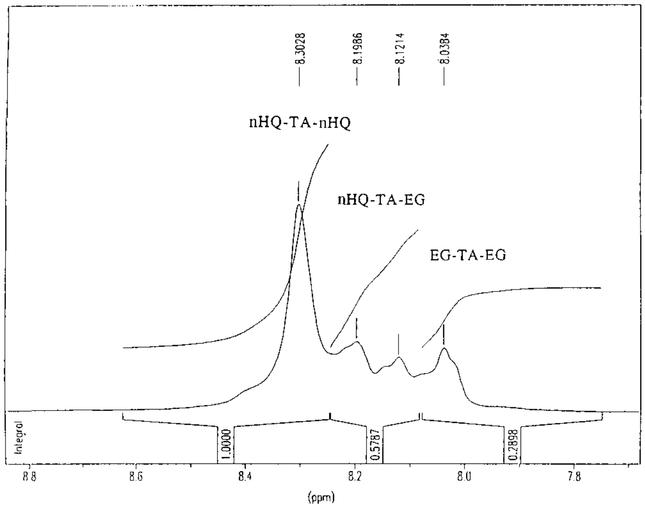


Figure 1. ^{1}H NMR spectra of the terephthalate region of poly(EPT-*co*-ET) copolymer used for randomness determination in trifluoroacetic acid-*d*/chloroform-*d* mixture as solvent.

intensity of the nHQ−T−EG peaks to the total integrated intensity of the terephthalate region, and F_{nPT} was the mole fraction of the nPT units. Similarly, the probability of finding an ET unit next to an nPT unit is given by the equation

$$P_{\mathrm{ET-nPT}} = P_{\mathrm{nHQ-T-EG}}/2F_{\mathrm{ET}}$$

in which F_{ET} was the mole fraction of ethylene terephthalate units. The degree of randomness or randomness number, B, is defined as follows:

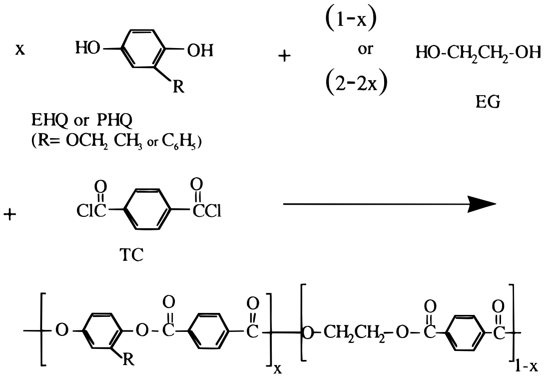
$$B = P_{\mathrm{nPT-ET}} + P_{\mathrm{ET-nPT}} = P_{\mathrm{nHQ-T-EG}}/2F_{\mathrm{nPT}}F_{\mathrm{ET}}$$

with $B = 0$ for a block copolymer, 1 for a complete random copolymer, and 2 for an alternating copolymer.

Polymer Characterization. Copolymers were characterized before and after the thermal posttreatment. 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 Ubbelohde-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 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 7−10 mg were used for the DSC analyses. Copolymer compositions and randomness numbers were calculated from the ^{1}H 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-*d*[24,52] by using the TFAA peak at 11.5 ppm as the internal standard. All samples were completely soluble in the TFAA-*d*/chloroform-*d* solvent unless otherwise noted. 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 an Olympus BH2 series 300 polarizing microscope with a Linkam THMS 600 heating stage.

Results and Discussion

Synthesis of 70:30 Copolyester. The copolyesters studied were prepared in methylene chloride solution by the reaction of either ethoxyhydroquinone (EHQ) or phenylhydroquinone (PHQ) and ethylene glycol (EG), with terephthaloyl chloride (TC) catalyzed by triethylamine as shown below:



Also, as shown in a previous study in our laboratory,[37] ethylene glycol, EG, is much less reactive than any of the hydroquinone monomers. This difference results in only approximately one-half of the added EG (15 mol % instead of the added 30 mol %) being incorporated into the copolymers. This result caused the calculated randomness numbers to be skewed toward higher degrees of randomness, so two methods of increasing the EG contents in the copolymers were used. The results of those polymerizations are summarized in Table 1.

Table 1. Products for the 70:30 PT:ET Copolymerization Reactions

polymer sample	monomer ratios[a] n-HQ:EG	copolymer comp[b] n-PT:ET	inherent viscosity[c] (dL/g)	B[d]
DD58-PPT:ET	(70:60)	(88:12)	2.0	>1
DD59-PPT:ET	(60:40)	(78:22)	1.4	0.7
DD63-PPT:ET	(50:50)	(76:24)	1.3	0.7
DD71-PPT:ET	(50:50)	(67:33)	1.4	0.4
DD67-PPT:ET	(40:60)	(64:36)	0.9	0.4
DD60-EPT:ET	(70:60)	(90:10)	0.7	0.9
DD61-EPT:ET	(60:40)	(80:20)	1.5	0.5
DD62-EPT:ET	(50:50)	(70:30)	0.8	0.4
DD68-EPT:ET	(50:50)	(76:24)	0.8	0.4
DD70-EPT:ET	(50:50)	(63:37)	0.8	0.3
DD65-EPT:ET	(40:60)	(65:35)	0.7	0.4

[a] Molar ratio of n-HQ to EG used in the copolymerization reaction; TC was kept at 100. [b] Molar ratio of n-PT:ET units in copolymer as determined by ^{1}H NMR spectroscopy. [c] Inherent viscosity was measured in a 60:40 mixture of *p*-chlorophenol: tetrachloroethane at 26 °C. [d] Randomness values calculated from ^{1}H NMR spectra.

The copolyesters obtained by using a 2-fold excess of EG (that is, 70 mol % of the hydroquinone-type monomer, 60 mol % of EG, and 100 mol % of TC), as in the polymerizations of DD58 and DD60 in Table 1, did not show any appreciable increase in the amount of ET units incorporated into the copolymers. It was remarkable that, by using a 2-fold excess of EG while keeping the TC constant, high molecular weight polymers were still obtained even though the stoichiometry was far from equal. In contrast, by limiting the amount of the hydroquinone monomers available for the TC to react with (that is, by using only 60, 50, or even 40 mol % of the hydroquinone 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 claims made above that these copolymers had blocky structures, but 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

Table 2. Results of Randomization Reactions for DD62 Poly(EPT-*co*-ET)

polymer sample	reaction conditions	obsd comp[a] (EPT:ET)	B^a	inherent viscosity[b] (dL/g)
DD62.0	original	(71:29)	0.4	0.85
DD62.1	250 °C, 24 h	(74:26)	0.8	[d]
DD62.2	250 °C, 12 h	(74:26)	0.8	[d]
DD62.3	250 °C, 6 h	(72:28)	0.8	[d]
DD62.4	250 °C, 3 h	(70:30)	0.7	1.6
DD62.5	270 °C, 24 h	[c]	[c]	[d]
DD62.6	270 °C, 12 h	(69:31)	0.9	[d]
DD62.7	270 °C, 6 h	(72:28)	0.7	[d]
DD62.8	270 °C, 3 h	(70:30)	0.7	[d]

[a] Compositions and randomness numbers were determined by ^{1}H NMR spectroscopy in a TFAA-*d*/chloroform-*d* solvent mixture. [b] Inherent viscosity measurements were made in a 60:40 mixture of *p*-chlorophenol/tetrachloroethane at 26 °C, 0.5 g/dL. [c] Insoluble in NMR solvents. [d] Insoluble in viscometry solvents.

Table 3. Results of Randomization Reactions for DD65 Poly(EPT-*co*-ET)

polymer sample	reaction conditions	obsd comp[a] (EPT:ET)	B^a	inherent viscosity[b] (dL/g)
DD65.0	original	(62:38)	0.3	0.7
DD65.1	290 °C, 2 h	(64:36)	0.9	1.5
DD65.2	290 °C, 1 h	(65:35)	0.7	1.0
DD65.3	290 °C, 0.5 h	(63:37)	0.5	0.9
DD65.4	290 °C, 3 h	(62:38)	1.0	[c]
DD65.5	270 °C, 2 h	(60:40)	0.6	1.1
DD65.6	270 °C, 1 h	(61:39)	0.5	1.0

[a] Compositions and randomness numbers were determined by ^{1}H NMR spectroscopy in a TFAA-*d*/chloroform-*d* solvent mixture. [b] Inherent viscosity measurements were made in a 60:40 mixture of *p*-chlorophenol/tetrachloroethane at 26 °C, 0.5 g/dL. [c] Insoluble in viscometry solvents.

so much lower than the reactivity of either EHQ or PHQ with TC that even adding excess EG did not measurably increase the amount of ET units in the copolymer. Thus, by limiting the amount of substituted hydroquinone monomer present, the growing polymer chains were forced to react with the EG monomer.

Randomizations. Four different poly(EPT-*co*-ET) copolymer samples were randomized under different conditions of heat treatment. The results of these randomization processes are given in Tables 2−5. Two different poly(PPT-*co*-ET) copolymer samples were also randomized utilizing different reaction conditions, and these results are given in Tables 6 and 7.

Exact measurements of the randomness numbers could not be made because of some uncertainty in the NMR results. The three variables used for the calculation of randomness were (1) the mole fraction of substituted phenylene terephthalate units, (2) the mole fraction of ethylene terephthalate units, and (3) the mole fraction of heterosubstituted terephthalate units. While the nPT and ET mole fractions were very precise measurements, the deconvolution of the terephthalate peaks was not as exact. The computer program that was used to calculate the deconvolution of the peaks (see Figure 2 for an example deconvolution) did not consistently divide the separate peaks. This inconsistency 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. In that manner the randomness numbers were found to vary within ±0.1 of the average value.

Table 4. Results of Randomization Reactions for DD68 Poly(EPT-*co*-ET)

polymer sample	reaction conditions	obsd comp[a] (EPT:ET)	B^a	inherent viscosity[b] (dL/g)
DD68.0	original	(76:24)	0.4	0.8
DD68.1	250 °C, 2 h	(75:25)	0.5	1.2
DD68.2	250 °C, 1 h	(76:24)	0.4	1.0
DD68.3	250 °C, 0.5 h	(76:24)	0.5	0.9
DD68.4	270 °C, 2 h	(77:23)	0.7	1.8
DD68.5	270 °C, 1 h	(75:25)	0.6	1.3
DD68.6	270 °C, 0.5 h	(76:24)	0.4	1.1
DD68.7	290 °C, 2 h	(78:22)	0.9	1.1
DD68.8	290 °C, 1 h	(77:23)	0.7	1.0
DD68.9	290 °C, 0.5 h	(76:24)	0.6	1.1
DD68.10	250 °C, 2 h	(76:24)	0.5	[c]
DD68.11	270 °C, 2 h	(75:25)	0.7	[c]
DD68.12	290 °C, 2 h	(77:23)	0.8	[c]
DD68.13	290 °C, 3 h	(74:26)	0.9	[d]

[a] Compositions and randomness numbers were determined by ^{1}H NMR spectroscopy in a TFAA-*d*/chloroform-*d* solvent mixture. [b] Inherent viscosity measurements were made in a 60:40 mixture of *p*-chlorophenol/tetrachloroethane at 26 °C, 0.5 g/dL. [c] Insufficient sample to run solution viscometry experiments. [d] Insoluble in viscometry solvents.

Table 5. Results of Randomization Reactions for DD70 Poly(EPT-*co*-ET)

polymer sample	reaction conditions	obsd comp[a] (EPT:ET)	B^a	inherent viscosity[b] (dL/g)
DD70.0	original	(63:37)	0.3	0.8
DD70.1	250 °C, 2 h (large)	(63:37)	0.5	1.0
DD70.2	270 °C, 2 h (large)	(63:37)	0.5	1.1
DD70.3	290 °C, 2 h (large)	(63:37)	0.6	1.1
DD70.4	250 °C, 2 h (small)	(64:36)	0.4	[c]
DD70.5	270 °C, 2 h (small)	(64:36)	0.4	[c]
DD70.6	290 °C, 2 h (small)	(64:36)	0.7	[c]
DD70.7	290 °C, 3 h (large)	(66:34)	0.7	1.1
DD70.8	310 °C, 2 h (small)	(65:35)	1.0	[c]
DD70.9	300 °C, 2 h (small)	(63:37)	0.8	[c]
DD70.10	280 °C, 2 h (small)	(63:37)	0.5	[c]
DD70.11	310 °C, 2 h (large)	(66:34)	0.9	[d]
DD70.12	250 °C, 2 h; 280 °C, 2 h (large)	(63:37)	0.4	1.2

[a] Compositions and randomness numbers were determined by ^{1}H NMR spectroscopy in a TFAA-*d*/chloroform-*d* solvent mixture. [b] Inherent viscosity measurements were made in a 60:40 mixture of *p*-chlorophenol/tetrachloroethane at 26 °C, 0.5 g/dL. [c] Insufficient sample to run solution viscometry experiments. [d] Insoluble in solution viscometry solvents.

Table 6. Results of Randomization Reactions for DD67 Poly(PPT-*co*-ET)

polymer sample	reaction conditions	obsd comp[a] (PPT:ET)	B^a	inherent viscosity[b] (dL/g)
DD67.0	original	(65:35)	0.3	0.9
DD67.1	270 °C, 2 h	(63:37)	0.5	1.6
DD67.2	270 °C, 1 h	(63:37)	0.5	1.3
DD67.3	290 °C, 2 h	(64:36)	0.7	1.6
DD67.4	290 °C, 1 h	(63:37)	0.6	1.4
DD67.5	310 °C, 2 h	(63:37)	0.7	1.4
DD67.6	310 °C, 1 h	(62:38)	0.7	1.3
DD67.7	335 °C, 2 h	(68:32)	0.9	1.0

[a] Compositions and randomness numbers were determined by ^{1}H NMR spectroscopy in a TFAA-*d*/chloroform-*d* solvent mixture. [b] Inherent viscosity measurements were made in a 60:40 mixture of *p*-chlorophenol/tetrachloroethane at 26 °C, 0.5 g/dL.

Effects of Temperature and Time. As can be seen in Tables 2−7, the amount of increase of the degree of randomness could be controlled by both the temperature and the duration of the thermal treatment. The amount of control over the reactions is shown in Figures 3 and 4, but because of the random nature of the transesterification reactions, there was no absolute control over the precise increase in degree of randomness. Nevertheless, from the results of the randomization experiments

Table 7. Results of Randomization Reactions for DD71 Poly(PPT-*co*-ET)

polymer sample	reaction conditions	obsd comp[a] (PPT:ET)	*B*[a]	inherent viscosity[b] (dL/g)
DD71.0	original	(67:33)	0.4	1.4
DD71.1	250 °C, 2 h	(67:33)	0.5	1.5
DD71.2	270 °C, 2 h	(66:34)	0.8	1.6
DD71.3	290 °C, 2 h	(66:34)	0.8	1.8
DD71.4	310 °C, 2 h	(67:33)	0.8	2.0
DD71.5	330 °C, 2 h	(69:31)	1.0	[c]
DD71.6	270 °C, 2 h (large)	(66:34)	0.6	1.5
DD71.7	290 °C, 2 h (large)	(66:34)	0.6	1.5
DD71.8	330 °C, 2 h (large)	(68:32)	0.9	0.6
DD71.9	310 °C, 2 h (large)	(63:37)	0.7	1.0

[a] Compositions and randomness numbers were determined by ^{1}H NMR spectroscopy in a TFAA-*d*/chloroform-*d* mixture solvent. [b] Inherent viscosity measurements were made in a 60:40 mixture of *p*-chlorophenol/tetrachloroethane at 26 °C, 0.5 g/dL. [c] Insoluble in solution viscometry solvents.

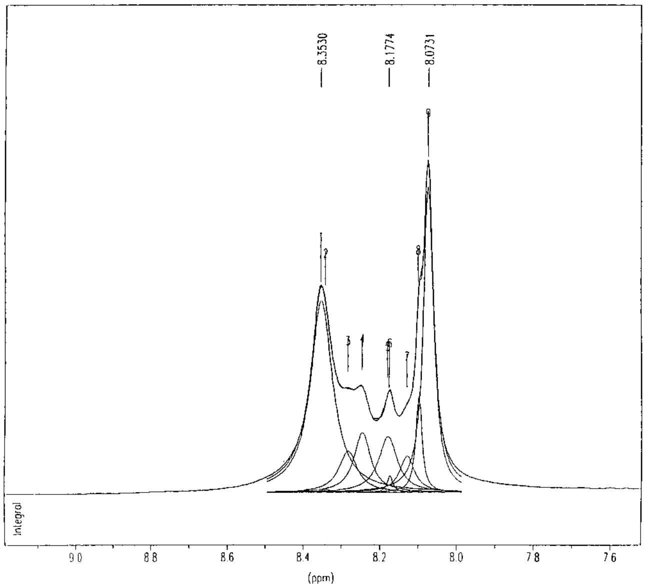


Figure 2. ^{1}H NMR spectra of the terephthalate region of DD70.6 showing the computer deconvolution of the different peaks.

on sample DD62 (see Table 2), it could be concluded that reaction durations of 24 h did not cause significantly greater degrees of randomness than reaction times of 3–6 h.

An interesting observation was in the differences in randomization results for larger samples when compared to smaller samples. From the results of the randomization of sample DD70 (see Table 5) large batch reactions of copolymers caused less randomization than small batch reactions. One possible explanation of this result could be poorer heat distribution in the polymer samples in the center of the larger batches, which would be less of a problem in the smaller test tube.

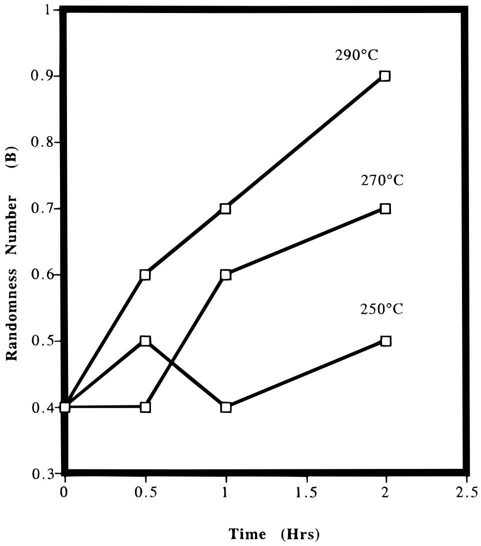


Figure 3. Randomness number (*B*) as a function of reaction duration for DD68–poly(EPT-*co*-ET).

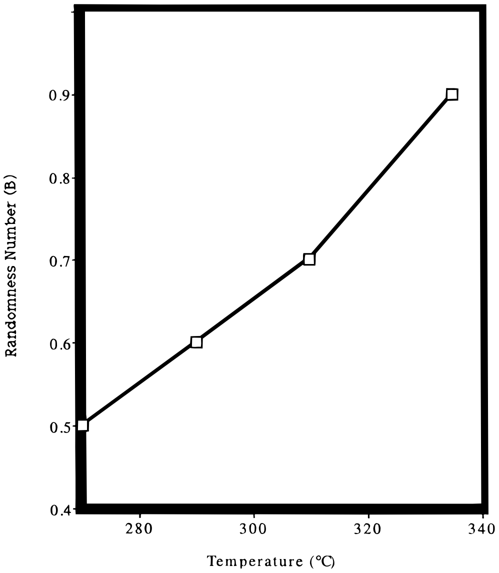


Figure 4. Randomness number (*B*) as a function of reaction temperature (°C) for DD67–poly(PPT-*co*-ET) for a 2 h duration.

The comparison of the randomization reaction temperatures to the melting temperatures of the copolymers (see Tables 8–14) showed that the largest increases in randomization occurred when the copolymers were in the melt state, which agrees with the study by Economy et al.[47] This result explains why it was observed that for poly(PPT-*co*-ET) copolymers, which had much higher melt transitions than poly(EPT-*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.

Copolymer Compositions. The copolymer compositions, which were measured using ^{1}H NMR spectroscopy for samples dissolved in a 1:1 solvent mixture of TFAA-*d*/$CDCl_3$, showed little change as a result of the randomization reaction (see Tables 2–7). Typically, the mole fraction of either component in the copolymer did not vary from the original sample by more than 3%. Therefore, for each separate copolymer that was randomized, the compositional differences were considered negligible so that the effects of their different compositional values on the calculation of the randomness number were ignored.

Molecular Weight. Increases in the inherent viscosities were observed for most of the randomized samples (see Tables 2–7), suggesting substantial increases in the molecular weight of the polymers, although sequence distributions could also affect this property to some extent. For some of the samples, such DD68.4, DD65.1, and DD67.1, the inherent viscosity

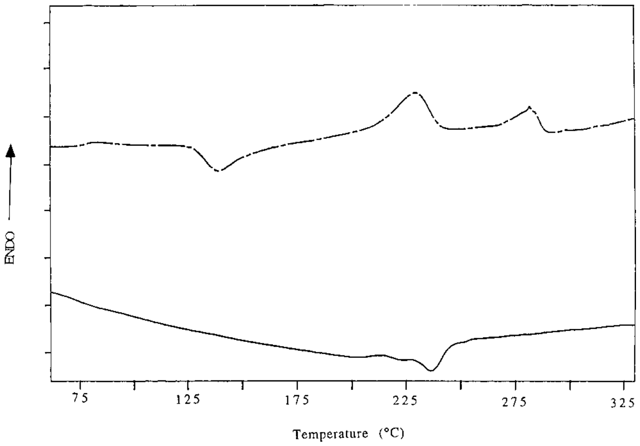


Figure 5. DSC thermogram of a randomized DD70 sample.

values increased as much as 225% of their original value. However, some 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 and could cause a decrease in molecular weight.

Thermal Properties. The effects of the randomization reactions on the thermal properties of the different copolymers are given in Tables 8–13. 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 endotherms or exotherms. Typically, these effects occurred for copolymer samples that had very high degrees of randomness, and the samples were either not crystalline to begin with or, once melted, not able to recrystallize in the time of the DSC heating and cooling cycles.

As can be seen in Tables 9–11, there was a strong dependence of crystallization temperatures on cooling on the degree of randomness of the copolymers, and as the randomness number increased, the crystallization temperature of the copolyester decreased, as expected.

Another interesting observation was the presence of a crystallization exotherm on the second heating cycle for the samples randomized from copolymer DD70 (see Figure 5), although sample DD70 was the only one that displayed a crystallization exotherm on the second heating cycle. As can be seen in Table 11, 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 change 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. The latter suggestion could not be verified due to the difficulty in measuring the T_g of the polymer samples.

Table 8. Thermal Properties of DD62 Poly(EPT-*co*-ET)

polymer sample	B	$T_m{}^a$ (°C)	$\Delta H_m{}^a$ (J/g)	$T_c{}^b$ (°C)	$\Delta H_c{}^b$ (J/g)
DD62.0	0.4	272	2.5	228	5.2
DD62.1	0.8	*d*	d	202	3.5
DD62.2	0.8	*d*	d	213	2.0
DD62.3	0.8	260	1.7	222	3.4
DD62.4	0.7	260	3.1	225	3.8
DD62.5	*c*	*d*	*d*	*d*	*d*
DD62.6	0.9	*d*	*d*	*d*	*d*
DD62.7	0.7	*d*	*d*	200	3.0
DD62.8	0.7	260	2.0	215	2.8

[a] Melt transitions and enthalpy of melting were taken from the second heating cycle at 20 °C/min. [b] Crystallization point and enthalpy of crystallization were taken from the first cooling cycle at 20 °C/min. [c] Sample insoluble in NMR solvents. [d] Thermal transitions not observable with DSC.

Table 9. Thermal Properties of DD65 Poly(EPT-*co*-ET)

polymer sample	B	$T_m{}^a$ (°C)	$\Delta H_m{}^a$ (J/g)	$T_c{}^b$ (°C)	$\Delta H_c{}^b$ (J/g)
DD65.0	0.3	272	8.6	231	3.7
DD65.1	0.9	257	1.9	209	2.8
DD65.2	0.7	273	3.7	221	3.0
DD65.3	0.5	275	5.5	226	4.0
DD65.4	1.0	248	2.1	196	2.0
DD65.5	0.6	277	5.5	225	3.8
DD65.6	0.5	275	5.7	227	3.0

[a] Melt transitions and enthalpy of melting were taken from the second heating cycle at 20 °C/min. [b] Crystallization point and enthalpy of crystallization were taken from the first cooling cycle at 20 °C/min.

Table 10. Thermal Properties of DD68 Poly(EPT-*co*-ET)

polymer sample	B	$T_m{}^a$ (°C)	$\Delta H_m{}^a$ (J/g)	$T_c{}^b$ (°C)	$\Delta H_c{}^b$ (J/g)
DD68.0	0.4	274	4.1	233	5.9
DD68.1	0.5	277	4.4	231	5.5
DD68.2	0.4	277	4.3	235	5.9
DD68.3	0.5	276	3.8	235	5.7
DD68.4	0.7	278	3.1	220	3.9
DD68.5	0.6	278	4.5	230	5.7
DD68.6	0.4	276	4.1	232	5.4
DD68.7	0.9	247	1.1	206	3.3
DD68.8	0.7	253	2.7	216	4.0
DD68.9	0.6	276	3.6	226	5.6
DD68.10	0.5	279	4.0	232	5.4
DD68.11	0.7	279	3.7	223	4.4
DD68.12	0.8	247	2.9	204	3.8
DD68.13	0.9	237	2.6	201	2.5

[a] Melt transitions and enthalpy of melting were taken from the second heating cycle at 20 °C/min. [b] Crystallization point and enthalpy of crystallization were taken from the first cooling cycle at 20 °C/min.

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 Tables 9–11, as the randomness number of a copolymer was increased, the enthalpy of crystallization (that is, the degree of crystallinity) decreased. This trend can be observed in the melt transitions of the copolymers (see Tables 9–11). As expected, an increased degree of randomness of a sample caused the melt transition, T_m, to occur at a decreased temperature, although, unlike the crystallization temperature, T_m did not decrease continuously with increased degrees of randomness. In these tables it can be seen that 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 observa-

Table 11. Thermal Properties of DD70 Poly(EPT-*co*-ET)

polymer sample	B	$T_m{}^a$ (°C)	ΔH_m (J/g)	$T_c{}^b$ (°C)	ΔH_c (J/g)	$T_{xl}{}^c$ (°C)	ΔH_{xl} (J/g)
DD70.0	0.3	228/280	12.5	240	5.2	137	5.3
DD70.2	0.5	223/281	7.1	238	3.6	156	4.5
DD70.3	0.6	258/277	3.4	228	3.2	156	1.0
DD70.4	0.4	229/281	12.3	240	3.6	139	4.4
DD70.5	0.4	228/282	9.3	240	2.9	145	3.6
DD70.6	0.7	259/278	3.1	230	3.5	156	1.0
DD70.7	0.7	260/279	2.7	233	3.4	157	0.5
DD70.8	1.0	*d*	*d*	*d*	*d*	*d*	*d*
DD70.9	0.8	260/276	3.5	222	2.8	*d*	*d*
DD70.10	0.5	226/280	7.0	235	3.7	152	3.3
DD70.11	0.9	257	2.5	218	1.7	*d*	*d*
DD70.12	0.4	223/282	6.5	237	4.2	158	3.4

[a] Melt transitions and enthalpy of melting were taken from the endotherm of the second heating cycle at 20 °C/min. [b] Crystallization point and enthalpy of crystallization were taken from the exotherm of the first cooling cycle at 20 °C/min. [c] Crystallization point and enthalpy of crystallization were taken from the exotherm of the second heating cycle at 20 °C/min. [d] Thermal transitions not observable using DSC.

Table 12. Thermal Properties of DD67 Poly(PPT-*co*-ET)

polymer sample	B	$T_m{}^a$ (°C)	ΔH_m (J/g)	$T_c{}^b$ (°C)	ΔH_c (J/g)
DD67.0	0.3	318	4.1	240	5.9
DD67.1	0.5	312	3.3	221	1.7
DD67.2	0.5	319	2.6	226	0.8
DD67.3	0.7	*c*	*c*	*c*	*c*
DD67.4	0.6	*c*	*c*	*c*	*c*
DD67.5	0.7	*c*	*c*	*c*	*c*
DD67.6	0.7	*c*	*c*	*c*	*c*
DD67.7	0.9	*c*	*c*	*c*	*c*

[a] Melt transitions and enthalpy of melting were taken from the second heating cycle at 20 °C/min. [b] Crystallization point and enthalpy of crystallization were taken from the first cooling cycle at 20 °C/min. [c] Thermal transitions not observable using DSC.

Table 13. Thermal Properties of DD71 Poly(PPT-*co*-ET)

polymer sample	B	$T_m{}^a$ (°C)	ΔH_m (J/g)	$T_c{}^b$ (°C)	ΔH_c (J/g)
DD71.0	0.4	301/324	7.0	240/252	5.9
DD71.1	0.5	300/324	8.3	241/250	6.8
DD71.2	0.8	301/326	7.6	242/250	6.5
DD71.3	0.8	303/326	10.8	243/249	5.6
DD71.4	0.8	325	7.5	241	2.2
DD71.5	1.0	*c*	*c*	*c*	*c*
DD71.6	0.6	301/327	8.5	242/250	7.3
DD71.7	0.6	302/327	7.3	243/249	6.0
DD71.8	0.9	*c*	*c*	*c*	*c*
DD71.9	0.7	324	4.0	235	1.9

[a] Melt transitions and enthalpy of melting were taken from the second heating cycle at 20 °C/min. [b] Crystallization point and enthalpy of crystallization were taken from the first cooling cycle at 20 °C/min. [c] Thermal transitions not observable using DSC.

tions reinforce the conclusion that, as expected, 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 between the two sets of polymers was that, as the PPT-*co*-ET copolymers were randomized, they lost their crystallinity at lower randomness numbers than the EPT-*co*-ET copolymers. For example, DD67 and DD71 copolymers (see Tables 12 and 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. All randomized samples showed liquid crystalline nematic textures very similar to their unrandomized counterparts.

Conclusions

Several different liquid crystalline copolyesters were thermally treated to increase their degree of randomness. Various P(EPT-*co*-ET) and P(PPT-*co*-ET) copolymers were prepared in approximately 70:30 mole ratios and thermally randomized. It was found that the transesterification randomization reactions were most effective when carried out in the melt (nematic) state. The compositions of the copolymers remained constant with increasing randomness, different comonomer sequence distributions, and higher molecular weights.

The thermal properties were also greatly affected by changes in the degree of randomness of the copolymer. Increased randomness caused decreased crystallinity and reduced enthalpies of fusion and crystallization. The more random sequence distributions resulted in lower melt transitions and lower crystallization 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.

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