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Alternating, Block, and Random Copolymers of a Triad Mesogen with Alkylene Terephthalate Flexible Segments

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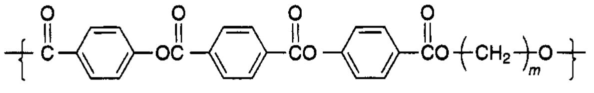
ABSTRACT: Alternating, block, and random copolymers of the rigid moiety terephthaloyl bis(4-oxybenzoyl) (Triad) with either ethylene terephthalate (ET) or butylene terephthalate (BT) flexible units were prepared by polycondensation in solution. The Triad mesogen was incorporated using either terephthaloyl bis(4-oxybenzoyl chloride) (TOBC) or α,ω-bis[(4-hydroxybenzoyl)oxy]butane (T4). Use of the latter monomer resulted in the formation of terephthaloyl (4-oxybenzoyl) (Diad) moieties in the copolymer. The block copolymers exhibited nematic liquid crystalline texture, whereas the behavior of the random and alternating copolymers depended on the flexible alkylene terephthalate content and method of synthesis.

Introduction

Polymer blends containing thermotropic liquid crystalline polymers (TLCPs) have attracted a great deal of interest during the past several years.[1,2] TLCPs have been used to reinforce other polymer matrices to form high-performance molecular composites. Such a molecular composite does not have a fiber-matrix interface usually present in fiber-reinforced composites. A small quantity of the TLCP can also reduce the melt viscosity of the polymer blend, while maintaining a preferred orientation during processing. TLCPs have other interesting properties such as low thermal shrinkage and excellent thermal stability. However, improvement of some of properties of the blends is achieved through good compatibility between the TLCP and the polymer matrix. To enhance the compatibility of TLCPs with poly(ethylene terephthalate) (PET) or poly(butylene terephthalate) (PBT), copolymers of the TLCP with ethylene terephthalate (ET) or butylene terephthalate (BT) moieties were studied. The TLCP moiety was comprised of a Triad mesogen having two or four flexible methylene spacers:



Triad-*m*, *m* = 2 or 4

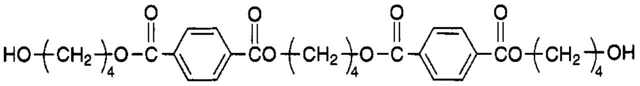
Although there are several papers in the literature pertaining to both random and block liquid crystalline copolyesters,[3−10] this is the first time a systematic study of the alternating, block, and random copolymers containing the same mesogenic and isotropic segments is reported.

Results and Discussion

Syntheses. Since the main objective of this study was to compare the properties of the copolymers containing liquid crystalline and isotropic moieties arranged in alternating, block, and random manner, polycondensation in solution at approximately 200 °C was preferred over polymerization in the melt to maintain the regularity of polymer structure.[11] Melt polycondensation, which is the most frequently used method, relies on transesterification reactions and often utilizes a transesterification catalyst for polymerization. The structural integrity of moieties can be affected by the harsh conditions of polymerization. High molecular weight products are usually obtained by a subsequent solid state polymerization under vacuum, during which further structural reorganization can occur. Furthermore, the residual catalyst present in the polymer can adversely affect the polymer properties. Solution polymerization at lower temperatures minimizes these problems.

Incorporation of the terephthaloyl bis(4-oxybenzoate) (Triad) moiety in the copolymer was accomplished by using either terephthaloyl bis(4-oxybenzoyl chloride) (TOBC) or α,ω-bis[(4-hydroxybenzoyl)oxy]butane (T4) monomer. The flexible BT or ET moiety was introduced using bis(hydroxybutyl) terephthalate (BHBT) or bis(hydroxyethyl) terephthalate (BHET). The general scheme for the synthesis of alternating copolymers is shown in Scheme 1.

The synthesis of Triad-*alt*-2BT copolymer **2** involved a similar scheme using TOBC and 1,4-bis[[(ω-hydroxybutoxy)terephthaloyl]oxy]butane whose structure is



The random copolymers **3** and **7** were obtained by polymerizing either BHBT or BHET with adequate amounts of TOBC and terephthaloyl chloride as illustrated in Scheme 2. Another method of obtaining the random copolymers **4** and **8** was also evaluated, using the "premesogenic" monomer T4 instead of TOBC, as depicted in Scheme 3.

The block copolymers **5** and **9** were synthesized by a one-reactor method, shown in Scheme 4, involving two steps wherein the monomers were added sequentially as described elsewhere.[12]

All copolymers studied in this paper are summarized in Table 1. The inherent viscosities of the BT copolymers were relatively high and reached values as high as 1.52 dL/g by carefully controlling the purity of the monomers and by optimizing the reaction conditions.

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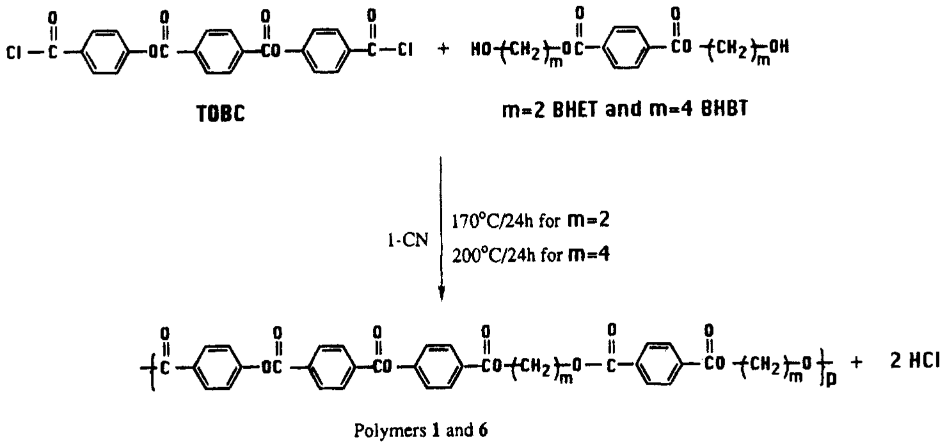
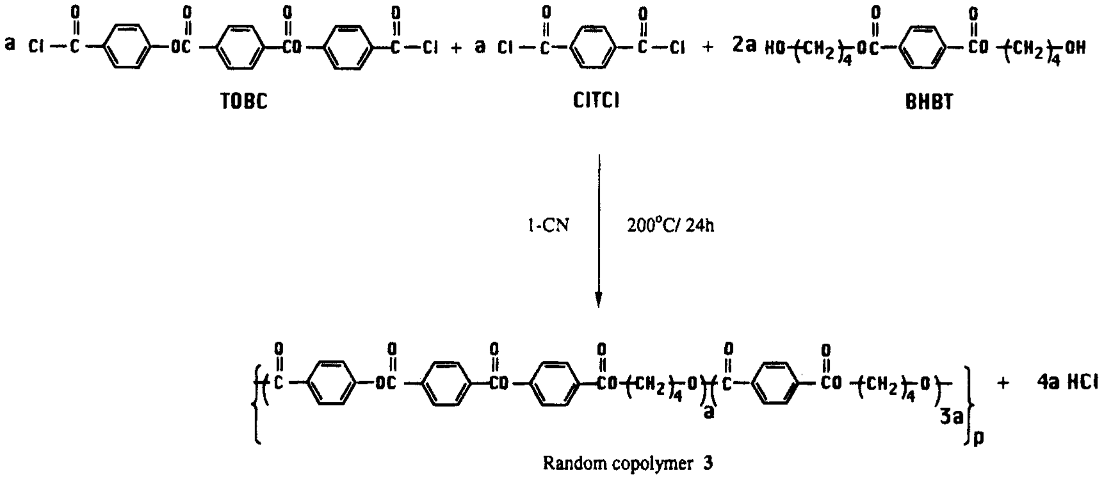
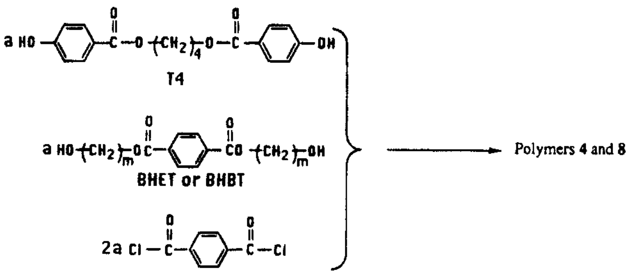
Scheme 1. Synthesis of Alternating Copolymers



Scheme 2. Synthesis of Random Copolymers



Scheme 3. Synthesis of Random Copolymers

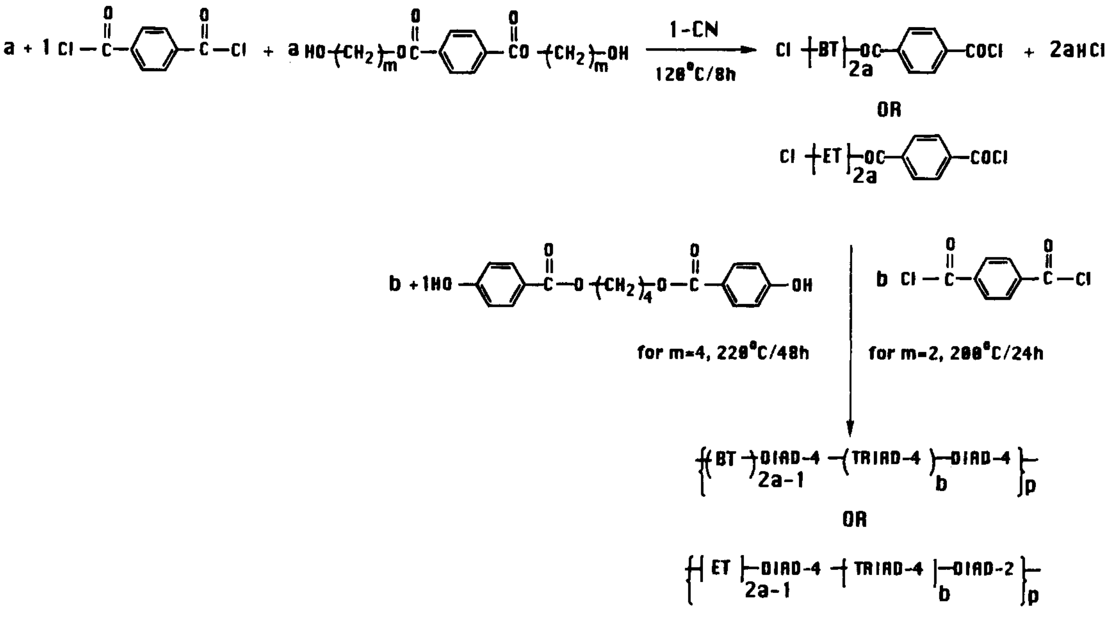


The ET copolymers had low inherent viscosities irrespective of the reaction conditions used. In the latter case, the best value of inherent viscosity was obtained when the polymerization was carried out in methylene chloride (MC) at 40 °C; at this temperature the formation of higher molecular weight was prevented by precipitation of the copolymer from MC. Another synthesis of ET copolymers containing 3-ethoxyphenylene terephthalate segments, using a similar procedure,[13] produced polymers with inherent viscosities of the order of 1.5 dL/g. In this case, although the copolymer precipitated from the reaction medium, the mixture of MC and triethylamine used as the reaction medium may have had the appropriate solubility parameters for swelling the precipitated copolymer, thereby facilitating further polymerization in the swollen state. During the polycondensation to incorporate the Triad mesogen, the solvent system of MC and triethylamine probably did not adequately swell the precipitated copolymer. To enhance the molecular weight, it is important to select an appropriate solvent system which is capable of swelling the copolymer, as was demonstrated in the synthesis of ultrahigh molecular weight PET.[14]

When the synthesis of ET copolymers was carried out in 1-CN, even at 170 °C, side reactions prevented the formation of a high molecular weight copolymer.[15] ^{1}H NMR spectra of copolymers **6**, **7**, and **9** contained unexpected resonances at 3.8 and 4.69 ppm associated with diethylene glycol terephthalate, which accounted for approximately 9 mol % of the copolymer composition. Formation of side products was also substantiated by the differences between the calculated and found molar compositions of the BT and ET copolymers. As seen in Table 1, the amount of ET found in ET copolymers **6** and **7** was much lower than the expected molar compositions. These molar compositions were calculated from the ^{1}H NMR spectra of the copolymers using a method reported previously.[12,15]

A comparison of the ^{1}H NMR spectra of the BT copolymers in the region 8.5–8 ppm, shown in Figure 1, revealed the subtle differences in the structures of the copolymers when synthesized with either TOBC or the premesogenic monomer, T4. The ^{1}H NMR spectrum of copolymer **1** contained peaks at 8.4 (a) and 8.21 ppm (c) due to the four terephthalate and four 3,5-*p*-oxybenzoyl protons, respectively, of the Triad moiety. The peak at 8.21 ppm was expected to be a doublet, as seen in the monomer TOBC, but the second peak was masked by the resonances of the four terephthalate protons of the BT moiety at 8.1 ppm (d). However, copolymer **4** and **5** synthesized from the T4 monomer had additional peaks at 8.34 and 8.29 ppm (b) and a multiplet between 8.23 and 8.15 ppm (c) associated with the terephthalate

Scheme 4. Synthesis of Triad-4-*co*-PBT Block Copolymers: One-Reactor Procedure



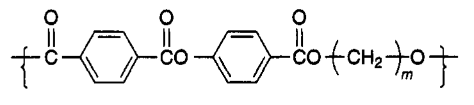
Polymers **5** (m=4) and **9** (m=2)

Table 1. Comparison of BT and ET Copolymers

BT copolymers[a]						ET copolymers[a]					
		mol % composition by ^{1}H NMR						mol % comparison by ^{1}H NMR			
polymer	η_{inh}		BT	Triad	Diad	polymer	η_{inh}		BT	Triad	Diad
1 Tr-*alt*-BT	1.52	found	52	48	0	**6** Tr-*alt*-ET	0.20	found	33	67	0
		calcd	50	50	0			calcd	50	50	0
2 Tr-*alt*-2BT	1.25	found	65	35	0						
		calcd	66	33	0						
3 Tr-*co*-BT	1.0	found	75	25	0	**7** Tr-*co*-ET	0.14	found	55	45	0
		calcd	75	25	0			calcd	66	33	0
4 Tr-*co*-BT	0.84	found	53	19	27	**8** Tr-*co*-ET	0.32	found	49	21	30[c]
		calcd[b]	50	50				calcd[b]	50	50	
5 Tr-*co*-BT	0.86	found	50	32	18	**9** Tr-*co*-ET	0.27	found	49	22	29[c]
		calcd	54	30	16			calcd	54	30	16

[a] Polymers **1**, **2**, and **6** are alternating copolymers prepared according to Scheme 1; **3** and **7** are random copolymers prepared according to Scheme 2; **4** and **8** are random copolymers prepared according to Scheme 3, which generates Diad moieties; **5** and **9** are block copolymers prepared according to Scheme 4. [b] The molar compositions of the individual Triad and Diad moieties cannot be calculated from the stoichiometry of the reactants, although the calculated sum of Triads and Diads equals 50 mol %. [c] Sum of the Diad-4 and Diad-2 moieties present in the copolymer.

protons of a Diad moiety,[12] whose structure is



Diad-2 (*m* = 2)
Diad-4 (*m* = 4)

A comparison of the ^{13}C NMR spectra of Tr-*alt*-BT polymer **1** and the random copolymer **4**, in the region 124–138 ppm, is shown in Figure 2. There were two additional peaks for polymer **4** at 137.2 (a) and 135.4 ppm (d) which can be attributed to the quaternary carbons of the terephthalate group in the Diad moiety. Similarly, the peaks at 133.4 (f), 132.7 (g), and 130.6 ppm (h) had adjacent, closely spaced peaks, which may be due to the Diad moiety.

The Diad moieties that were formed during the polycondensation involving the T4 monomer were avoided by using the TOBC monomer, provided the reaction conditions did not promote transesterification reactions. The acid-catalyzed attack of the oxybutylene unit of either BHBT or the Triad-4 moiety itself can lead to the formation of Diad segments. Therefore, the absence of any Diad moiety in both BT and ET copolymers synthesized from TOBC suggests that the reaction conditions used in Schemes 1 and 2 were not sufficiently severe to bring about structural reorganization induced by transesterification.

Thermal Behavior. a. BT Copolymers. The first DSC heating scans of the BT copolymers are shown in Figure 3, and their transition temperatures and enthalpies are summarized in Table 2. The Tr-*co*-BT block copolymer **5** exhibited two distinct melting peaks at 201 and 282 °C, respectively, associated with the separate melting of the BT and Triad-4 domains present in the block copolymer.[12] POM studies revealed that isotropization of liquid crystalline domains occurred only above 340 °C. The transition temperatures of the BT random copolymer depended on the mode of synthesis, copolymer composition, and microstructure. The random copolymer **4**, obtained from the T4 monomer, exhibited two distinct but not so well separated peaks at 211 and 249 °C, which may be attributed, respectively, to the melting of BT and Triad-4 domains. POM of the copolymer showed that isotropization occurred at 280 °C. The random copolymer **3** had only one melting endotherm at 237 °C, as shown in curve b of Figure 3, and the polymer is not liquid crystalline.

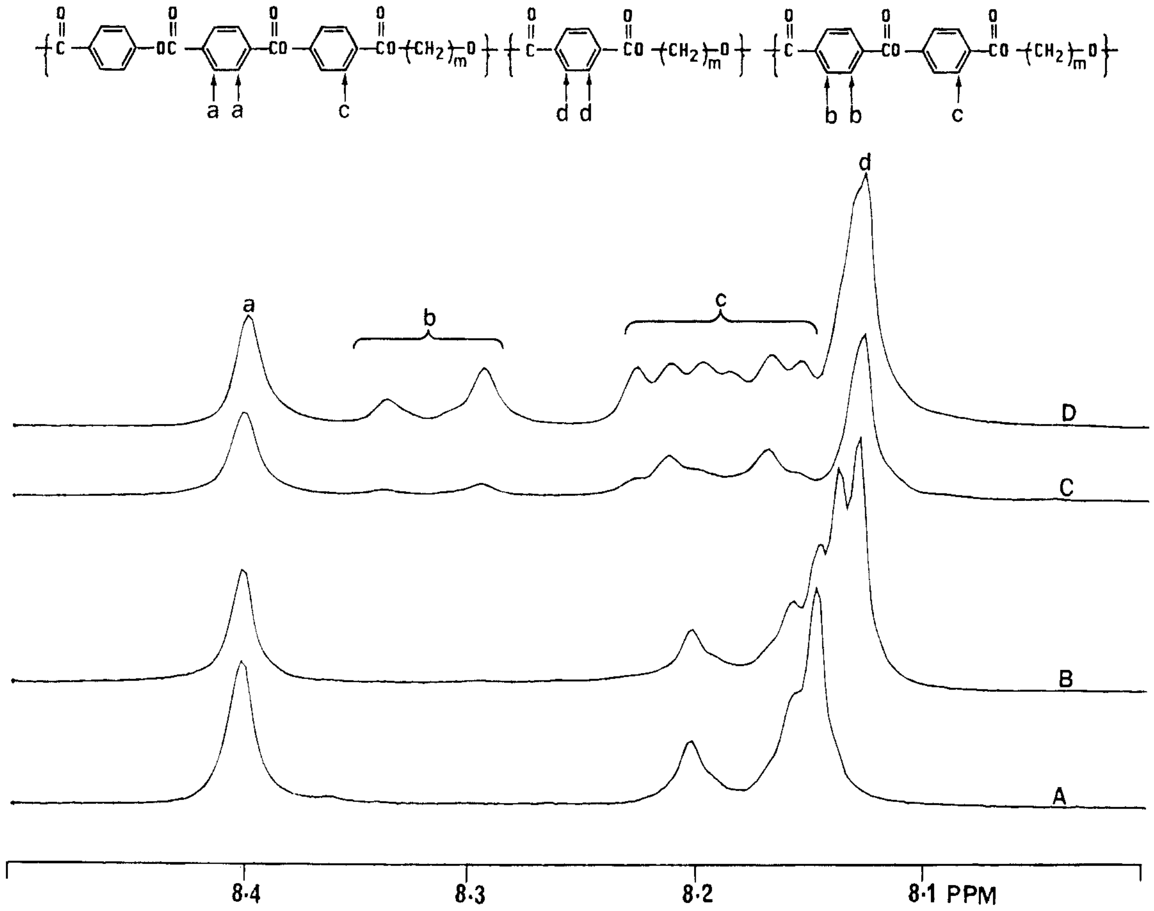


Figure 1. ^{1}H NMR spectra of BT copolymers in the region 8–8.5 ppm: (A) alternating copolymer **1**, (B) random copolymer **3**, (C) block copolymer **5**, and (D) random copolymer **4**.

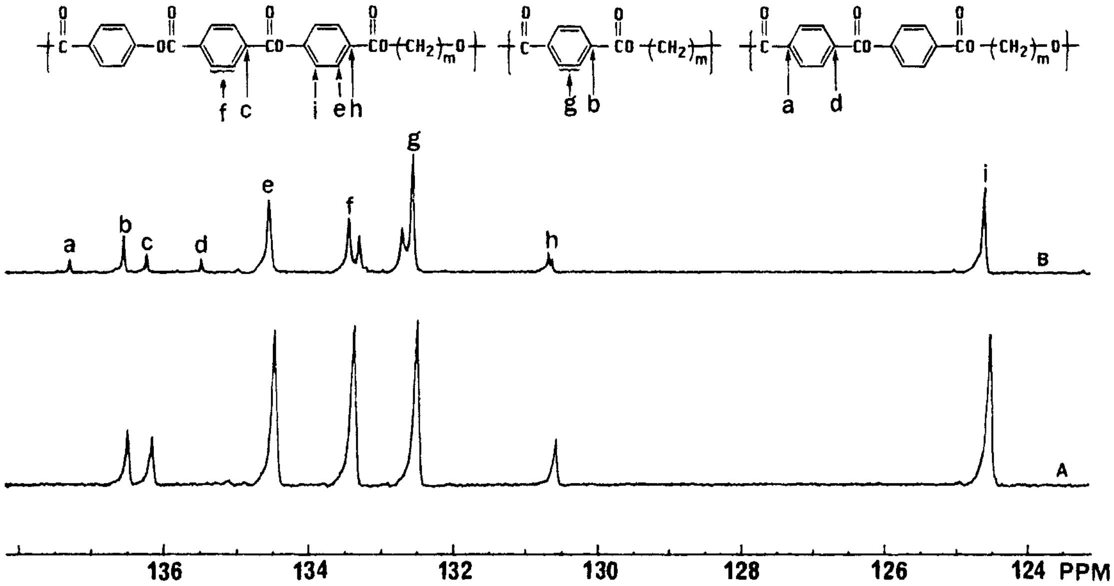


Figure 2. ^{13}C NMR spectra of BT copolymers in the 124–138 ppm region: (A) alternating copolymer **1** and (B) random copolymer **4**.

The thermal behavior of the alternating copolymers **1** and **2** depended on the overall BT content. The alternating copolymer **1** with 52 mol % BT moieties exhibited two major transitions at 278 and 296 °C. Observation of the sample by POM revealed that the polymer had a nematic liquid crystalline texture, and the DSC peaks at 278 and 296 °C were due to crystal-to-nematic and nematic-to-isotropic transitions, respectively. As the amount of BT moiety in the alternating copolymer was increased to 65%, as in polymer **2**, liquid crystallinity disappeared and the polymer exhibited only a single melting endotherm at 247 °C.

Figure 4 shows the first DSC cooling curves of the BT copolymers. The transition temperatures and the corresponding enthalpies are summarized in Table 2. The Tr-*co*-BT block copolymer **5** had two crystallization exotherms at 253 and 161 °C, arising from the crystallization of the Triad and BT domains, respectively.[12] Similarly, the random copolymer **4** also exhibited two crystallization exotherms, but at lower temperatures of 191 and 166 °C, which was consistent with the somewhat blocky nature of the copolymer **4**. The random copolymer **3** had only one crystallization peak at 201 °C.

Table 2. Thermal Transitions of BT and ET Copolymers[a]

BT copolymers						ET copolymers					
	heating transitions			cooling transitions			heating transitions			cooling transitions	
polymer	T_m (°C)	T_{k-n} (°C)	T_{n-i} (°C)	T_c (°C)	T_{n-k} (°C)	polymer	T_m (°C)	T_{k-n} (°C)	T_{n-i} (°C)	T_c (°C)	T_{n-k} (°C)
1 Tr-*alt*-BT[b]		278 (25)	296 (9)		242 (20)	**6** Tr-*alt*-ET	multiple transitions from ~200 to ~325			no distinct transition	
2 Tr-*alt*-2BT[c]		237 (39)			214 (16)						
3 Tr-*co*-BT[c]		237 (33)			201 (15)	**7** Tr-*co*-ET	229 (17),	260 (10),	282 (8)	210 (17),	250 (12)
4 Tr-*co*-BT	211 (8)	249 (6)	290[d]	166 (8)	191 (8)	**8** Tr-*co*-ET	221 (41)	286 (5)	>340[d]	176 (22)	235 (4)
5 Tr-*co*-BT	201 (11)	282 (18)	340[d]	161 (9)	253 (11)	**9** Tr-*co*-ET	242 (42)		>340[d]	188 (20)	236 (3)

[a] Transition enthalpies in J/g are given in parentheses. [b] On cooling, this polymer shows a T_{i-n} transition at 282 °C with an enthalpy of 11 J/g. [c] One endotherm was observed which includes all three transitions, T_m, T_{k-n} and T_{n-i}. [d] Transition observed by POM.

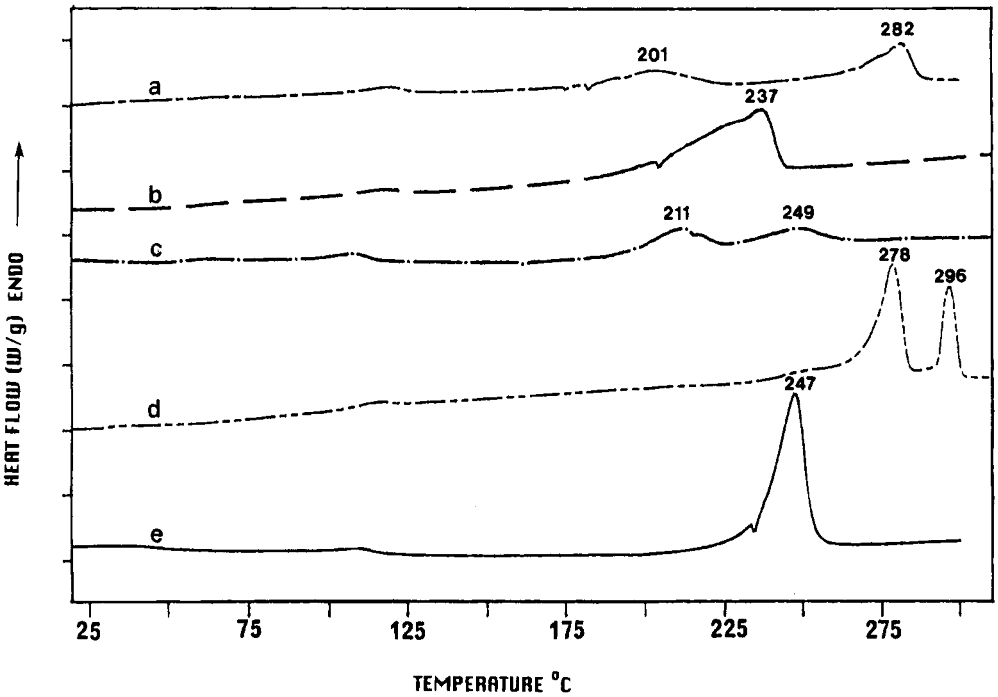


Figure 3. DSC thermograms of BT copolymers obtained during the first heating cycle: (a) block copolymer **5**, (b) random copolymer **3**, (c) random copolymer **4**, (d) alternating copolymer **1**, and (e) alternating copolymer **2**.

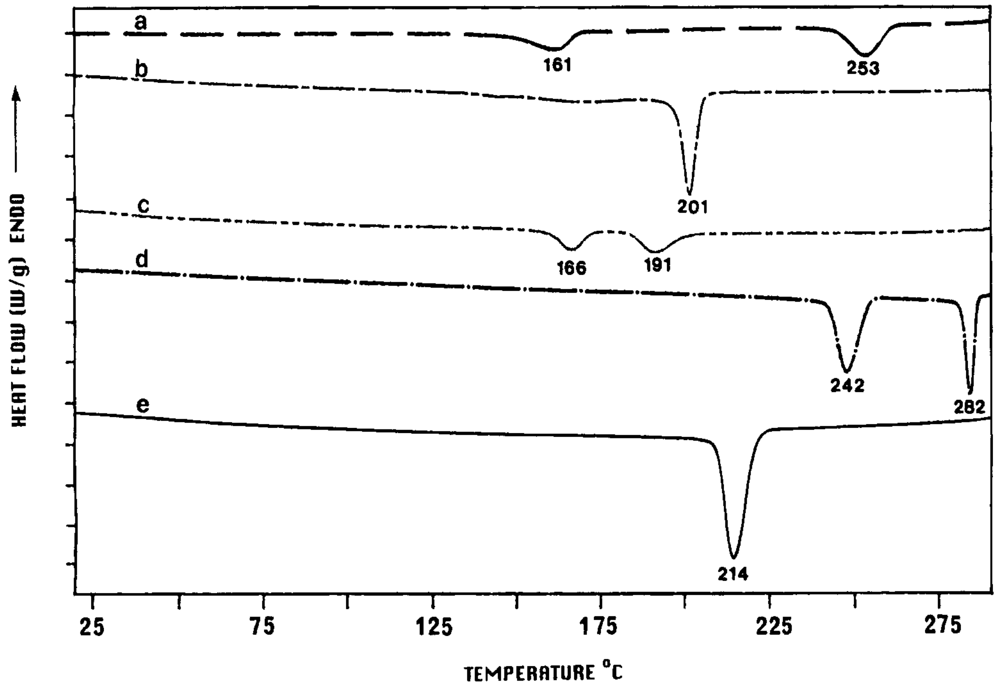


Figure 4. DSC thermograms of BT copolymers obtained during the first cooling cycle: (a) block copolymer **5**, (b) random copolymer **3**, (c) random copolymer **4**, (d) alternating copolymer **1**, and (e) alternating copolymer **2**.

The alternating copolymer **1** showed two cooling exotherms at 282 and 242 °C. POM of the polymer showed that the 282 °C peak corresponded to the isotropic-to-nematic transition and the peak at 247 °C to the nematic-to-crystal transition. However, when the BT content increased to 65%, copolymer **2** exhibited only

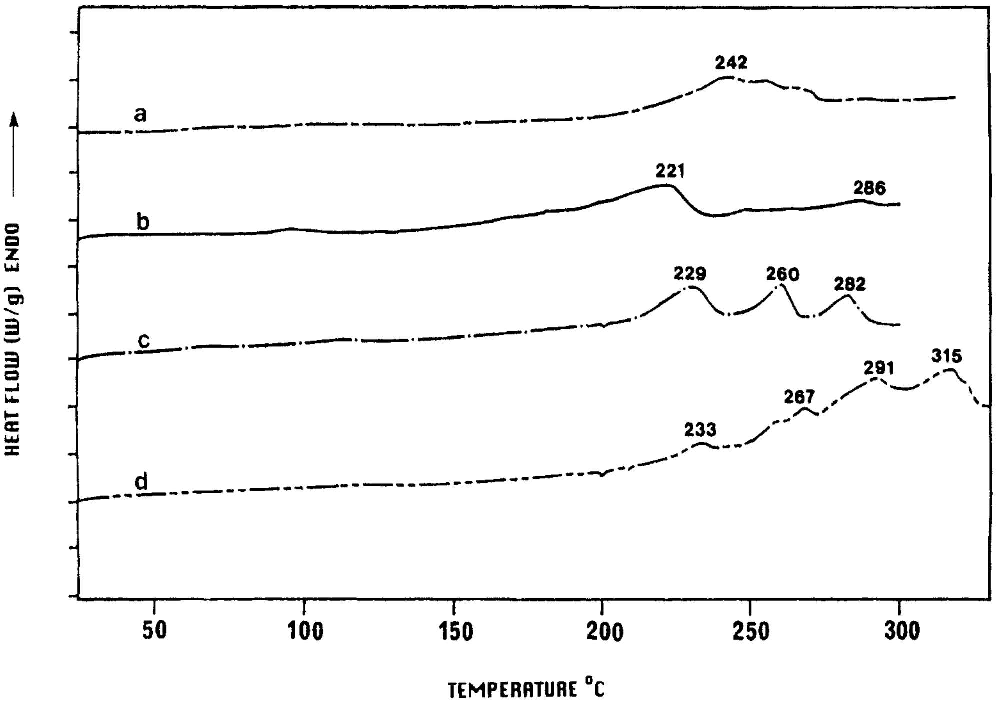


Figure 5. DSC thermograms of ET copolymers obtained during the first heating cycle: (a) block copolymer **9**, (b) random copolymer **8**, (c) random copolymer **7**, and (d) alternating copolymer **6**.

one crystallization peak at 214 °C.

The second thermal cycle of all copolymers was very similar to the first cycle, except for the block copolymer **5**. For this copolymer, the melting temperature of the Triad domains remained unchanged, but the enthalpy associated with the transition was lower in the second and subsequent heating cycles. This difference could be due to the imperfect crystallization of the Triad domains on cooling from the nematic state at a rate of 20 °C/min.

The BT copolymers **1**, **4**, and **5** were liquid crystalline and had a nematic texture, while copolymers **2** and **3** were not liquid crystalline. The block copolymer **5** exhibited a phase-separated domain structure. When copolymer **5** was heated to above the melting point of the BT domains and the polymer was observed under polarized light, the BT domains became dark and the birefringent liquid crystalline domains appeared to be dispersed among the dark background. This biphasic behavior continued above the melting point of the Triad domains, where the large domains broke up into smaller ones, until the clearing temperature. Clearing occurred above 340 °C, which was similar to the thermal behavior of the Triad-4 homopolymer.[16]

Formation of the mesophase and its stability in both alternating and random BT copolymers depended on the BT content. Both the alternating copolymer **1** and the random copolymer **4**, which have approximately 50 mol % BT units, were liquid crystalline, but their clearing temperatures were reduced to 290 °C from higher than 340 °C for the block copolymer **5**. When the BT content was increased to 65% or above, as in copolymers **2** and **3**, liquid crystalline behavior was not evident.

b. ET Copolymers. Some differences existed between BT and ET copolymer that can significantly influence their thermal properties. ET copolymers had very low inherent viscosities, and the transition temperatures have been shown to depend on molecular weight.[17] The formation of low molecular weight products was attributed to competing secondary reactions occurring during polymer synthesis, thereby affecting the structure of the final product. For example, it was described earlier that there was about 9 mol % of diethylene glycol units formed. The presence and distribution of these diethylene glycol units in either the rigid or flexible segments affected the polymer properties. A second difference was that ET copolymers **8** and **9** had both Diad-2 and Diad-4 moieties present in their structures. A third difference was due to differences in the number of flexible methylene spacers separating the Triad and flexible segments. All of these differences may have an effect in controlling the properties of the ET copolymers.

The first DSC heating scans of the ET copolymers are presented in Figure 5. The ET block copolymer **9** had a broad endotherm from about 200 to about 275 °C. POM studies showed that this broad endotherm contained both the melting of the ET phases at ~240 °C and the melting of the liquid crystalline domains at ~270 °C, where the polymer showed a highly birefringent threaded nematic texture. As the liquid crystalline domains melted and broke up, a biphasic morphology became visible and, on further heating, clearing occurred above 340 °C. The random copolymer **8** exhibited similar behavior. This random copolymer was prepared from T4 and BHET monomers at 40 °C in the presence of triethylamine as a catalyst. Due to the difference in reactivity of the phenolic and alcoholic hydroxyl groups toward terephthaloyl chloride, this polymer was expected to be more blocky than random.

The random copolymer **7**, prepared from TOBC at high temperature, exhibited three endotherms at 229, 260, and 282 °C. However, the peak at 260 °C disappeared in a subsequent heating scan. This random copolymer had a nematic texture that cleared at 300 °C. The alternating copolymer **6** exhibited a broad, ill-defined endotherm ranging from ~210 to ~320 °C, with several maxima. POM showed that the polymer melted to a highly birefringent nematic texture at 290 °C, where these domains started to break up, resulting in a biphasic structure up to 335 °C, where clearing occurred.

The first DSC cooling scans of the ET copolymers are shown in Figure 6. The block copolymer **9** exhibited two

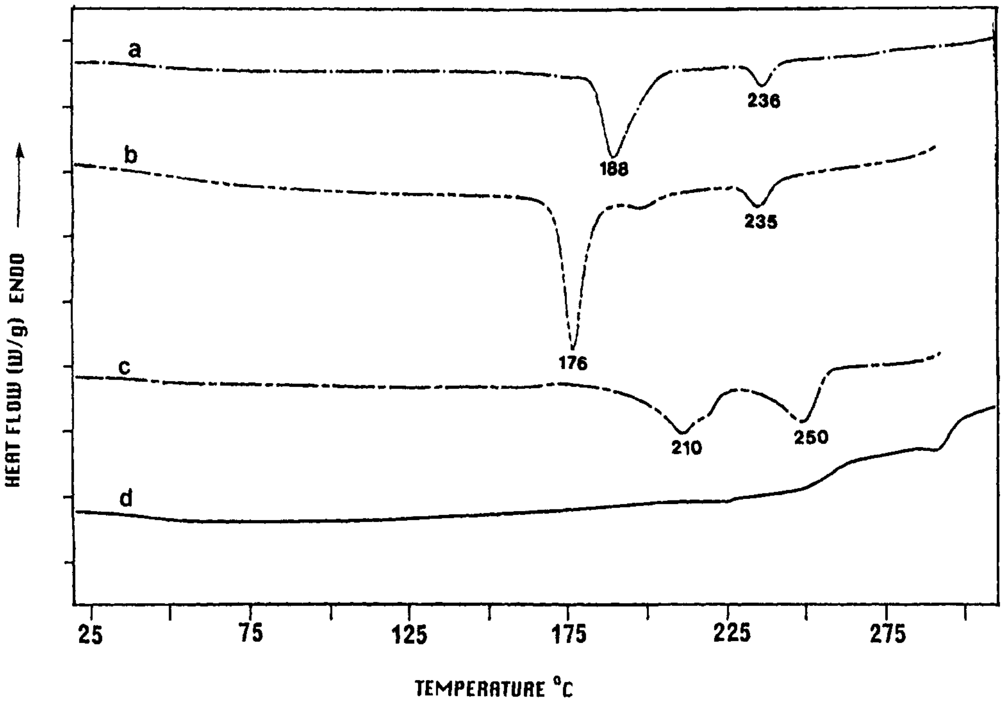


Figure 6. DSC thermograms of ET copolymers obtained during the first cooling cycle: (a) block copolymer **9**, (b) random copolymer **8**, (c) random copolymer **7**, and (d) alternating copolymer **6**.

crystallization exotherms at 236 and 188 °C, associated with the crystallization of Triad-4 and ET domains, respectively. The cooling curve of the random copolymer **8** also showed the two crystallization exotherms, suggesting the blocky nature of this random copolymer. The random copolymer **7** had two closely spaced exotherms at 210 and 250 °C, associated with the crystallization of ET-rich and Triad-rich domains. Although no distinct peaks were visible in the cooling curve of the alternating copolymer **6**, POM studies showed that on cooling from the isotropic state, liquid crystalline droplets formed at 320 °C, which grew in size until the crystallization temperature of 155 °C.

Conclusions. Copolyesters that incorporate both rigid Triad moieties and flexible alkylene terephthalate segments in the main chain have been synthesized. Using polycondensation schemes in solution with appropriate starting materials and reaction conditions, alternating, block, and random copolyesters have been prepared and characterized. While high molecular weight copolymers can be readily prepared using butylene terephthalate segments (BT), analogous copolymers with ethylene terephthalate segments (ET) produce lower molecular weight samples. The principal reasons for this difference are competing side reactions and higher product insolubility in the case of ET copolymers. ^{1}H and ^{13}C NMR studies of the copolymers show that their syntheses from the premesogenic monomer T4 invariably leads to the formation of Diad moieties in the copolymer, whereas TOBC, the triad acid chloride monomer, under favorable reaction conditions does not form Diad moieties, thus preserving the regularity of the polymer structures.

In the case of alternating and random copolymers, the formation and stability of the mesophase depend on the content of flexible units. For example, above 65% BT, the polymer is not liquid crystalline. This behavior is in contrast to that of the block copolymer, which is liquid crystalline and exhibits microphase-separated liquid crystalline domain morphology, even at low mesogen content.

The ET copolymers have a more complex thermal transition behavior than the BT analogues. These results have not been studied further since the ET copolymers involve side reactions that modify the chemical structure.

Experimental Section

Materials. Terephthaloyl chloride, 1,4-butanediol, 4-hydroxybenzoic acid, benzyl chloride, benzyl alcohol, ethyl chloroformate, thionyl chloride, 1-chloronaphthalene (1-CN), deuterated trifluoroacetic acid, pyridine, triethylamine, methylene chloride, and THF were purchased from Aldrich Chemical Co. Terephthaloyl chloride was sublimed under vacuum just before use. The solvents 1-CN and methylene chloride were refluxed with CaH_2 overnight and then distilled. 1,4-Butanediol was stirred with a small quantity of CaH_2 before distillation under vacuum. Triethylamine and pyridine were distilled over KOH. All reagents were carefully stored under argon after distillation.

Polymer Characterization. The inherent viscosities of all polymers were measured at a concentration of 0.5 g/dL in a 60/40 (v/v) *p*-chlorophenol/tetrachloroethane mixture, using an Ubbelohde viscometer at 26 °C. The ^{1}H NMR spectra were recorded on a Bruker AC-200 MHz spectrometer. The polymer samples were prepared in deuterated trifluoroacetic acid, and the NMR spectra were calibrated using TMS as an internal standard. ^{13}C NMR data were acquired on a Bruker MSL-300, operating at 75 MHz.

A Perkin-Elmer DSC-7, operating under N_2 atmosphere, was used to study the thermal behavior. A scanning rate of 20 °C/min was adopted. The texture of the polymers was studied using a Carl-Zeiss polarizing optical microscope, at a magnification of 400×, equipped with a Mettler FP2 hot stage. For optical observations, thin film samples were prepared by heating a polymer sample between two microscope slides at temperatures up to 300 °C on a Fisher-Johns melting point apparatus.

Monomers. a. Terephthaloyl Bis(4-oxybenzoyl chloride) (TOBC) was synthesized in two stages using the method described by Bilibin and co-workers.[17] In the first step, terephthaloylbis(4-oxybenzoic) acid was prepared by the interfacial condensation of terephthaloyl chloride with 4-hydroxybenzoic acid. In the second step, terephthaloylbis(4-oxybenzoic) acid was refluxed with excess thionyl chloride to form TOBC. The product was recrystallized from dry chloroform. Anal. Calcd for TOBC: C, 59.59; H, 2.70; Cl, 16.03. Found: C, 59.30; H, 2.82; Cl, 16.33. ^{1}H NMR (CF_3COOH-*d*) 8.4 (4H, s, terephthalate), 8.2–8.17 (4H, d, 3,5 protons of

4-oxybenzoyl unit), 7.41–7.38 (4H, d, 2,6 protons of 4-oxybenzoyl unit) ppm.

b. Bis(hydroxybutyl) terephthalate (BHBT) was prepared from terephthaloyl chloride and 1,4-butanediol according to the procedure reported in the literature.[18] The product was purified by extracting it with hot water in a Soxhlet apparatus for 2 days. The hot water solution was cooled to precipitate BHBT. It was filtered, collected, and recrystallized from ethyl acetate. The purity was checked by HPLC.

c. 1,4-Bis[[(ω-hydroxybutoxy)terephthaloyl]oxy]butane was obtained as a byproduct during the synthesis of BHBT.[18] This product was extracted with water to remove BHBT, and then the residue was recrystallized from ethanol. The purity of the monomer was confirmed by HPLC.

d. **α,ω-Bis[(4-hydroxybenzoyl)oxy]butane** (T4 monomer) was synthesized form 4-hydroxybenzoic acid according to a previously reported reaction scheme.[16]

Polymers. a. Alternating Copolymers. 1. Triad-4-*alt*-BT, Polymer 1 (Scheme 1). A mixture of 5.000 g (0.01128 mol) of TOBC and 3.5000 g (0.01128 mol) of BHBT was polymerized in 100 mL of 1-CN for 24 h at 200 °C under an argon atmosphere. The reaction mixture was cooled, precipitated in methanol, filtered, extracted in a Soxhlet with acetone/ethanol (1:1), and dried under vacuum at 80 °C for at least 24 h: yield 7.4 g (96%) of polymer **1**; ^{1}H NMR (CF_3COOH-*d*) 8.4 (4H, s, terephthalate of Triad), 8.2–8.1 (8H, d, terephthalate of BT and 3,5-*p*-oxybenzoyl of Triad), 7.41–7.38 (4H, d, 2,6-*p*-oxybenzoyl of Triad), 4.5 (4H, s, methylenes adjacent to ester oxygen), and 2.1 (4H, s, methylenes adjacent to ether oxygen) ppm.

2. Triad-4-*alt*-2BT, Polymer 2 (Scheme 1). A procedure similar to that for polymer **1** was used. TOBC [1.000 g (2.2561 mmol)] and 1.1950 g (2.2561 mmol) of BHBT dimer were condensed at 200 °C in 30 mL of 1-CN: yield 1.9 g (93%) of polymer **2**; ^{1}H NMR (CF_3COOH-*d*) 8.4 (4H, s, terephthalate of Triad), 8.2–8.1 (8H, d, terephthalate of BT and 3,5-oxybenzoyl of Triad), 7.41–7.38 (4H, d, 2,6-*p*-oxybenzoyl of Triad), 4.5 (4H, s, methylenes adjacent to ester oxygen), and 2.1 (4H, s, methylenes adjacent to ether oxygen) ppm.

3. Triad-2-*alt*-ET, Polymer 6 (Scheme 1). A procedure similar to that for polymer **1** was used. TOBC [1.000 g (2.2561 mmol)] and 0.5735 g (2.2561 mmol) of BHET were condensed in 30 mL of 1-CN at 170 °C for 24 h: yield 1.3 g (92%) of polymer **6**; ^{1}H NMR (CF_3COOH-*d*) 8.4 (4H, s, terephthalate of Triad), 8.2–8.1 (8H, d, terephthalate of BT and 3,5-*p*-oxybenzoyl of Triad), 7.41–7.38 (4H, d, 2,6-*p*-oxybenzoyl of Triad), 4.8 (4H, s, methylenes) ppm.

b. Random Copolymers. Two methods of synthesis were studied based on the monomer used for incorporating the Triad mesogen: Scheme 2 uses the TOBC monomer, whereas Scheme 3 uses the "premesogenic" monomer, T4.

1. Triad-4-*co*-BT, Polymer 3 (Scheme 2). A mixture of TOBC [1.4282 g (3.2221 mmol)], terephthaloyl chloride [0.6541 g (3.2221 mmol)], and BHBT [2.000 g (6.4442 mmol)] was weighed into a vessel and then 20 mL of 1-CN was added. The reaction was carried out for 24 h at 200 °C under a current of argon. The solution was cooled and precipitated in methanol. The solid polymer was filtered, extracted with a mixture of acetone and ethanol (1:1), and dried under vacuum at 80 °C for 24 h. The yield of polymer **3** was 3.2 g (89%): ^{1}H NMR (CF_3COOH-*d*) 8.4 (4H, s, terephthalate of Triad), 8.2–8.1 (8H, d, terephthalate of BT and 3,5-*p*-oxybenzoyl of Triad), 7.41–7.38 (4H, d, 2,6-*p*-oxybenzoyl of Triad), 4.5 (4H, s, methylenes adjacent to ester oxygen), and 2.1 (4H, s, methylenes adjacent to ether oxygen) ppm.

2. Triad-*co*-ET, Polymer 7 (Scheme 2). A procedure similar to the one above for polymer **3** was used. TOBC [1 g (2.2561 mmol)] 0.2290 g (1.1281 mmol) of terephthaloyl chloride, and 0.8603 g (3.3843 mmol) of BHET were used. The molar ratios of reactants corresponded to TOBC:ClTCl:BHET 2:1:3. The reaction was carried out in 30 mL of 1-CN at 178 °C for 24 h under argon. The yield of polymer **7** was 1.5 g (81%): ^{1}H NMR (CF_3COOH-*d*) 8.4 (4H, s, terephthalate of Triad), 8.2–8.1 (8H, d, terephthalate of BT and 3,5-*p*-oxybenzoyl of Triad), 7.41–7.38 (4H, d, 2,6-*p*-oxybenzoyl of Triad), and 4.8 (4H, s, methylenes) ppm.

3. Triad-4-*co*-BT, Polymer 4 (Scheme 3). A mixture of 1.000 g (3.272 mmol) of T4 monomer, 0.9394 g (3.0272 mmol) of BHBT, and 1.2291 g (6.0544 mmol) of terephthaloyl chloride was weighed into a reaction flask flushed with argon gas. 1-CN (20 mL) was added, and the reaction was performed at 200 °C for 24 h. The yield of polymer **4** was 2.4 g (88%): ^{1}H NMR (CF_3COOH-*d*) 8.4 (4H, s, terephthalate of Triad), 8.2–8.1 (8H, d, terephthalate of BT and 3,5-*p*-oxybenzoyl of Triad), 7.41–7.38 (4H, d, 2,6-*p*-oxybenzoyl of Triad), 4.5 (4H, s, methylenes adjacent to ester oxygen), and 2.1 (4H, s, methylenes adjacent to ether oxygen) ppm.

4. Triad-4-*co*-ET, Polymer 8 (Scheme 3). A solution of T4 monomer [2.000 g (6.0544 mmol)], BHET [1.5392 g (6.0544 mmol)], and terephthaloyl chloride [2.4582 g (12.108 mmol)] in 100 mL of MC and 5 mL of triethylamine was allowed to react for 12 h at room temperature under an atmosphere of argon. The temperature was raised to 40 °C, and the reaction was continued for another 24 h. The polymer was precipitated in methanol and purified in the same manner as polymer **1** to yield 4.6 g (89%) of polymer **8**: ^{1}H NMR (CF_3COOH-*d*) 8.4 (4H, s, terephthalate of Triad), 8.2–8.1 (8H, d, terephthalate of BT and 3,5-*p*-oxybenzoyl of Triad), 7.41–7.38 (4H, d, 2,6-*p*-oxybenzoyl of Triad), 4.8 (4H, s, methylenes of ET unit), 4.5 (4H, s, methylenes adjacent to ester oxygen), and 2.1 (4H, s, methylenes adjacent to ether oxygen) ppm.

c. Block Copolymers. 1. Triad-4-*co*-PBT, Polymer 5 (Scheme 4). BHBT [1.8789 g (6.054 mmol)] was accurately weighed into the reaction vessel, and 20 mL of 1-CN was added. The vessel was immersed in an oil bath at 120 °C to give a clear solution. A clear yellow solution of 1.5364 g (7.5677 mmol) of terephthaloyl chloride in 20 mL of 1-CN was added through a dropping funnel. The dropping funnel was washed several times using additional small quantities of 1-CN. The funnel was removed and replaced by a reflux condenser. The reaction was allowed to proceed under argon gas for 8 h at 120 °C. After about 8 h, when the solution became cloudy and viscous, the vessel was transferred to a salt bath at 200 °C to give a clear solution. Terephthaloyl chloride [1.2291 g (6.054 mmol)] and 2.5000 g (7.568 mmol) of T4 monomer were added, and the reaction was stirred at 220 °C for 48 h. The flask was cooled, and the contents were poured into 1.5 L of methanol. The precipitate was filtered, extracted with acetone, and dried under vacuum at 80 °C. Polymer **5** was obtained as a white, fibrous sample, 5.5 g, yield 89%. The ^{1}H NMR (200 MHz) spectrum of the polymer in trifluoroacetic acid-*d* has the following peaks, and the peak assignments are similar to those of polymer **1**: 8.4, 8.1, 7.35, 4.5, and 2.0 ppm. The ^{13}C NMR (75 MHz) spectrum of the polymer in trifluoroacetic acid-*d* has the following peaks: 171.9, 136.5, 132.5, 69.1, 27.5, 137.3, 135.5, 169.7, 136.2, 133.6, 157.5, 124.6, 134.5, and 130.6 ppm.

2. Triad-4-*co*-PET, Polymer 9 (Scheme 4). The polycondensation reaction was performed under an atmosphere of argon. Terephthaloyl chloride [2.8747 g (14.159 mmol)] in 30 mL of 1-CN was added to 3.000 g (11.799 mmol) of BHET dissolved in 300 mL of 1-CN. The solution became pale yellow, and the reaction was carried out at 120 °C for 8 h. The temperature of the reaction mixture was raised to 200 °C, and 1.9165 g (9.43998 mmol) of terephthaloyl chloride and 3.8979 g (11.7998 mmol) of T4 monomer were added. The polycondensation was continued for another 24 h. The polymer solution was cooled, and the polymer was precipitated in methanol, washed with methanol, and acetone, and dried in vacuum at 80 °C for 24 h to yield 9.6 g of polymer **9** (yield 96%). The ^{1}H NMR spectrum in trifluoroacetic acid-*d* contains the following peaks: 8.4, 8.1, 7.4–7.2, 4.8, 4.5, and 2.1 ppm.

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