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Synthesis and Characterization of Block Copolymers Containing Rigid Liquid Crystalline and Flexible Butylene Terephthalate Segments

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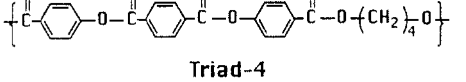
ABSTRACT: A series of novel thermotropic block copolyesters based on poly(tetramethylene 4,4′-(terephthaloyldioxy)dibenzoates) (Triad-4) and poly(butylene terephthalate) (PBT) were synthesized by high-temperature polycondensation in solution to minimize sequence randomization by transesterification. Three different schemes were examined in order to facilitate the systematic variation of block length and block content. All reaction schemes predict the formation of tetramethylene 4-(terephthaloyloxy)benzoate (Diad-4) moieties in the block copolymers. Diad-4 homopolymer and its block copolymer with PBT were synthesized and characterized and were compared to Triad-4-*co*-PBT block copolymers. The compositions of all block copolymers were determined from ^{1}H NMR spectroscopy. The DSC thermogram of a typical block copolymer revealed the presence of two major melting transitions, corresponding to the separate melting of PBT and Triad-4 domains. During the cooling cycle separate and distinct crystallization exotherms were also observed. Polarizing optical microscopy showed that all block copolymers were liquid crystalline and exhibited a nematic texture.

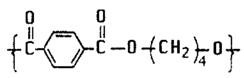
Introduction

Blends of thermotropic liquid crystalline polyesters (TLCPs) with thermoplastics have attracted considerable attention during the past several years.[1,2] TLCPs are expected to impart improved mechanical and thermal properties to the blend. Moreover, a small quantity of the TLCP can drastically reduce the melt viscosity of the sample, while maintaining a preferred orientation during processing. However, the improvement of the properties of the blends is influenced by the compatibility between the TLCP and the isotropic polymer. Most of the TLCPs are incompatible with conventional thermoplastics due to self-aggregation and phase separation. Several approaches have been examined in the literature to exhance compatibility between the rigid-rod and flexible-coil polymers. The following three have received the most attention: synthesis of segmented block copolymers consisting of rigid-rod and flexible-coil segments,[3] synthesis of graft copolymers with rigid-rod backbones and flexible-coil oligomers as side chains,[4] and blends of TLCPs and polymer matrix pairs with active sites capable of promoting specific interactions such as acid/base or hydrogen bonding.[5]

In this investigation, we were interested in achieving molecular level reinforcement of poly(butylene terephthalate) (PBT) or poly(ethylene terephthalate) (PET), by using a segmented block copolymer containing TLCP segments. The TLCP block copolyester contained Triad-4 and PBT moieties represented as follows:



Triad-4



PBT

Some of the preliminary results regarding the synthesis and characterization of these novel block copolyesters have been presented earlier.[6] The literature includes several examples of block copolyesters based on TLCPs and an isotropic noncrystalline polymer.[7-10] Except for a very recent paper,[11] there are no reported cases of any extensive investigations of liquid crystalline block copolyesters containing an isotropic, crystallizable polymer such as PBT.

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.

Monomers. Bis(hydroxybutylene terephthalate) (BHBT; **I**) was synthesized from terephthaloyl chloride and excess 1,4-butanediol according to the reported procedure.[12] The final product was carefully purified by Soxhlet extraction with water to remove higher oligomers. The purity was ascertained by HPLC (C_{18} column, methanol eluant) indicating a product that was >99% pure.

α,ω-Bis[(4-hydroxybenzoyl)oxy]butane (**II**) was synthesized from 4-hydroxybenzoic acid according to a reaction scheme reported by Lenz et al.[13]

The synthesis of terephthaloyl(4-oxybenzoyl) dichloride (**III**) involved several steps,[14] illustrated by Scheme 1. This monomer was isolated from the reaction medium by removing the excess thionyl chloride under vacuum, and subsequently purified by crystallization from Hexane/$CHCl_3$.

Polymers. All polycondensation reactions, except the synthesis of Diad-4 homopolymer, were carried out in the absence of a base, at high temperature, under a current of argon, using 1-CN as the reaction medium. All block copolymers were obtained by either a one-reaction vessel or a two-reaction vessel procedure. Two different reaction schemes were adopted in the one-reactor procedure. Typical polycondensation experiments are described below.

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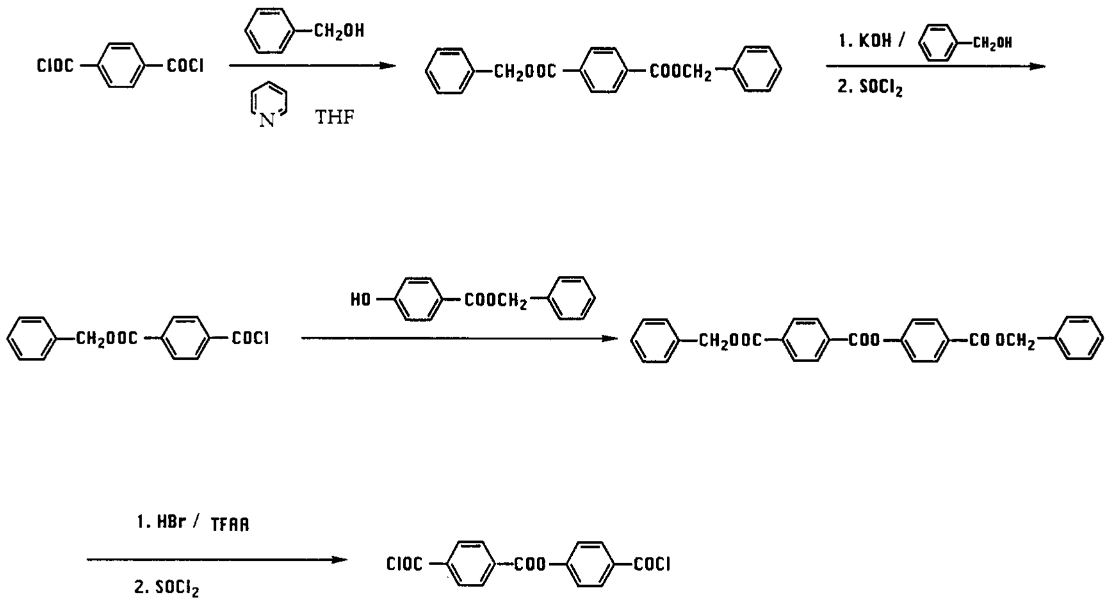
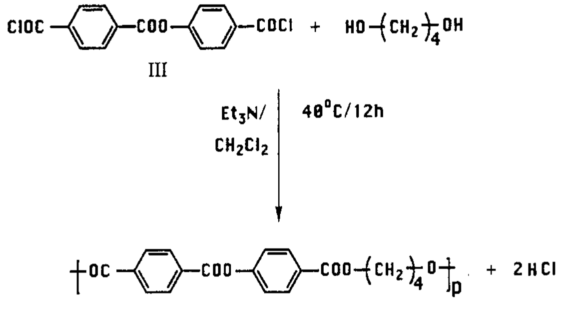
Scheme 1. Synthesis of Diad Diacid Chloride (III)



(III)

Scheme 2. Synthesis of the Diad-4 Homopolymer



Diad-4 Homopolymer (Scheme 2). Monomer III (1.000 g, 3.0959 mmol) was carefully weighed into a reaction vessel purged with argon gas. Ten milliliters of distilled methylene chloride was added to obtain a clear yellow solution. Butanediol (0.2790 g, 3.0959 mmol) in 2 mL of triethylamine and 5 mL of methylene chloride were added to above solution, and the reaction mixture was heated under reflux for 24 h. The polymer was precipitated into a large volume of methanol, filtered, extracted with acetone, and was finally dried under vacuum at 80 °C to give 0.95 g, 90% yield of the polymer. ^{1}H NMR (200 MHz, trifluoroacetic acid-*d*): δ 2.05 (s, 4H); 4.52 (s, 4H); 7.24 (d, 2H); 8.29–8.1 (m, 6H). A ^{13}C NMR (75 MHz) spectrum of the polymer in trifluoroacetic acid-*d* is shown in Figure 1. The peak assignments (ppm) are as follows: a, 172.3; b, 137.3; c, 132.3; d, 133.3; e, 135.5; f, 157.6; g, 124.6; h, 134.5; i, 130.6; j, 170.2; k, 69.5, l, 27.5; s, denotes solvent peaks.

Synthesis of Diad-4-*co*-PBT Block Copolymer (Scheme 3). Diad diacid chloride (**III**; 1.1201 g, 3.4678 mmol) was dissolved in 10 mL of 1-CN to give a clear yellow solution. To this solution was added 0.2340 g (2.6 mmol) of butanediol, and the temperature was raised to 150 °C. The reaction was carried out under an argon atmosphere for 12 h. Then 0.8070 g (2.6 mmol) of BHBT and 0.3520 g (1.7338 mmol) of terephthaloyl chloride were added to the same reaction vessel, and the temperature was increased to 200 °C. After 24 h, the solution was cooled and precipitated in a large volume of methanol. The precipitate was filtered, extracted with acetone, and dried at 80 °C under vacuum to yield 2.0 g (93%) of the polymer. ^{1}H NMR (200 MHz, trifluoroacetic acid-*d*): δ 2.05 (s, methylene protons adjacent to ether oxygen of Diad-4 and PBT moieties); 4.52 (s, methylene protons adjacent to ester oxygen of Diad-4 and PBT moieties); 7.24 (d, protons ortho to the oxygen in the oxybenzoyl group of the Diad-4 moiety); 8.29–8.1 (m, protons adjacent to the carbonyl in the oxybenzoyl group of the Diad-4 moiety and terephthaloyl protons of the PBT moiety).

Triad-4-*co*-PBT Block Copolymers. (a) One-Reactor Method (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 small quantities of 1-CN. The funnel was removed and replaced by a reflux condenser. The reaction was allowed to proceed under a sweep of argon gas for 4–5 h at 120 °C. After about 5 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 monomer **II** 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 I was obtained as a white fibrous sample (5.5 g), yield 89%. A ^{1}H NMR (200 MHz) spectrum of the polymer in trifluoroacetic acid-*d* is shown in Figure 2. The peak assignments (ppm) are as follows: a, 8.4; b, 8.1; c, 7.35; d, 4.5; e, 2.0. A ^{13}C NMR (75 MHz) spectrum of the polymer in trifluoroacetic acid-*d* is shown in Figure 3. The peak assignments (ppm) are as follows: a, 171.9; b, 136.5; c, 132.5; d, 69.1; e, 27.5; f, 137.3; g, 135.5; h, 169.7; i, 136.2; j, 133.6; k, 157.5; l, 124.6; m, 134.5; n, 130.6; s, denotes solvent peaks.

(b) One-Reactor Method (Scheme 5). Monomer **II** (2.5000 g, 7.568 mmol) and 1.2291 g (6.054 mmol) of terephthaloyl chloride were weighed into a reaction vessel, and 20 mL of 1-CN was added. The reaction vessel was placed in a salt bath at 200 °C, under a slow current of argon. The terephthaloyl chloride dissolved quickly, whereas monomer **II** dissolved slowly to give a clear solution. The solution turned cloudy when left overnight at 200 °C. The temperature was increased to 220 °C, and 1.8789 g (6.054 mmol) of BHBT and 1.5364 g (7.568 mmol) of terephthaloyl chloride was added followed by 20 mL of 1-CN. The reaction was allowed to continue for another 48 h, and then it was cooled and precipitated into a large volume of methanol. The precipitate was filtered, extracted with acetone, and dried under vacuum at 80 °C to give a 5.6-g (90%) yield of polymer **VIII**.

(c) Two-Reactor Method (Scheme 6). BHBT (0.9394 g, 3.0269 mmol) in 10 mL of 1-CN and 0.6828 g (3.3632 mmol) of terephthaloyl chloride were mixed in a reaction vessel fitted with a reflux condenser and were allowed to react overnight at 160 °C under a current of argon. In another similar vessel 1.0000 g (3.0272 mmol) of monomer **II** and 0.5462 g (2.6903 mmol) of terephthaloyl chloride were reacted in 20 mL of 1-CN at 180 °C under argon

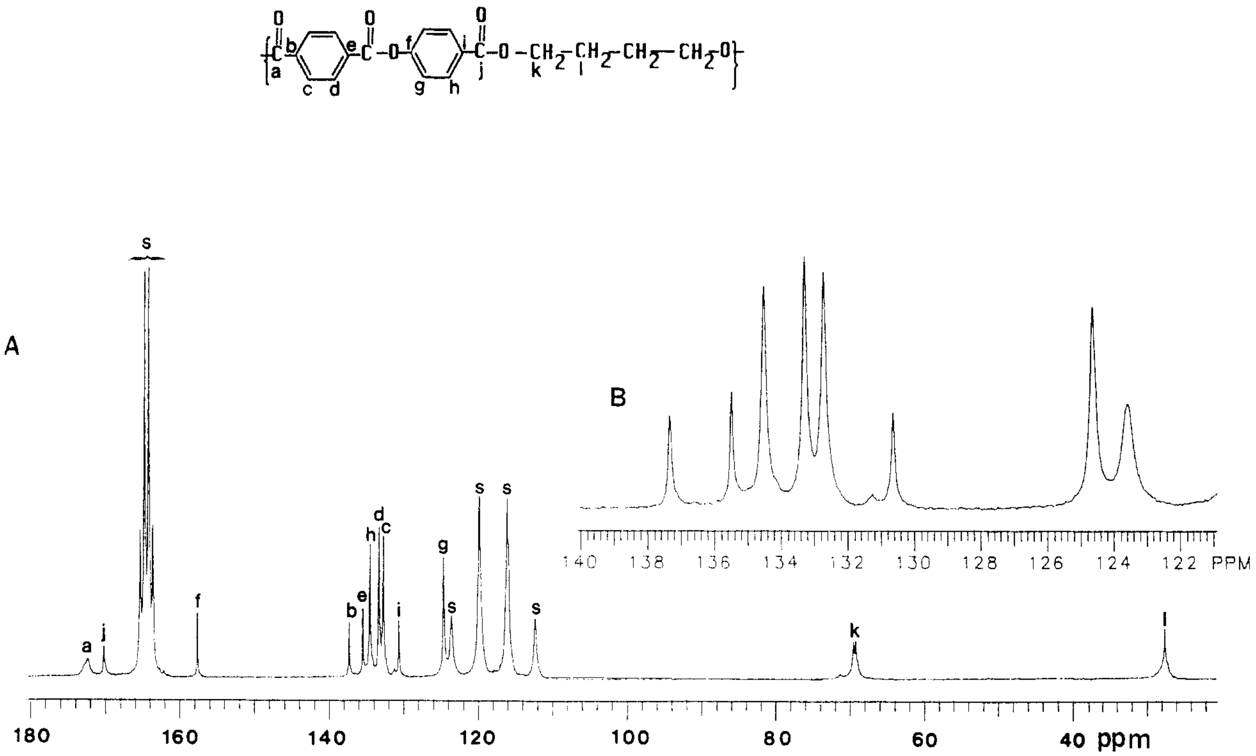
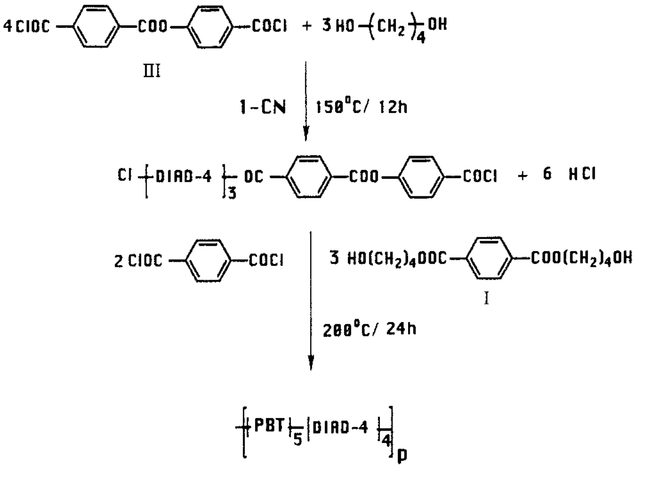


Figure 1. (A) ^{13}C NMR spectrum of Diad-4 homopolymer. (B) Expanded 122–140 ppm region.

Scheme 3. Synthesis of Diad-4-*co*-PBT Block Copolymer



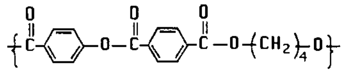
for 12 h. The contents of the first flask were carefully transferred, under argon, to the second flask and were washed several times with small quantities of the solvent. The temperature of the bath was raised to 220 °C, and the reaction was continued for 48 h. The solution was cooled, precipitated in methanol, and filtered. The polymer precipitate was extracted with acetone and dried under vacuum at 80 °C to give 2.5 g, 92% yield, of polymer **XV**.

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 ^1H NMR spectra were recorded on a Bruker 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 Varian XL-300, operating at 75 MHz.

Thermal stability measurements were carried out under a N_2 atmosphere, on a Perkin-Elmer TGA-2. A Perkin-Elmer DSC-7, operating under a N_2 atmosphere, was used to study the thermal behavior. For both instruments, 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 to 300 °C, on a Fisher-Johns melting point apparatus.

Results and Discussion

The principal objective of this study was to synthesize segmented block copolyesters containing PBT and Triad-4 segments. In order to retain the oligomeric segments as designed, polycondensation in solution at elevated temperatures was chosen instead of melt polycondensation. The latter would have to be performed at high temperatures, at which transesterification reactions leading to less well-defined structures could occur. Three different reaction schemes were devised in order to obtain these block copolyesters. The three polymer schemes use a "premesogenic" monomer (**II**), which reacts with terephthaloyl chloride to form the Triad-4 segment. However, when this premesogenic monomer is used in the block copolymer synthesis, two Diad-4 moieties shown below, per repeating unit, are formed connecting the PBT and Triad-4 segments.



Diad-4

The formation of the Diad-4 units is clearly illustrated by the reaction Schemes 4–6. The presence of the Diad-4 moieties strongly influence the properties of these segmented block copolyesters. In order to characterize the block copolyesters containing the Diad-4 moieties, a Diad-4 homopolymer and a Diad-4-*co*-PBT (4:5) block copolymer were synthesized. Although Lenz et al.[13,14] studied both random and alternating diad sequence distributions in polymers containing polymethylene and poly(oxymethylene) spacers, polymers containing tetramethylene spac-

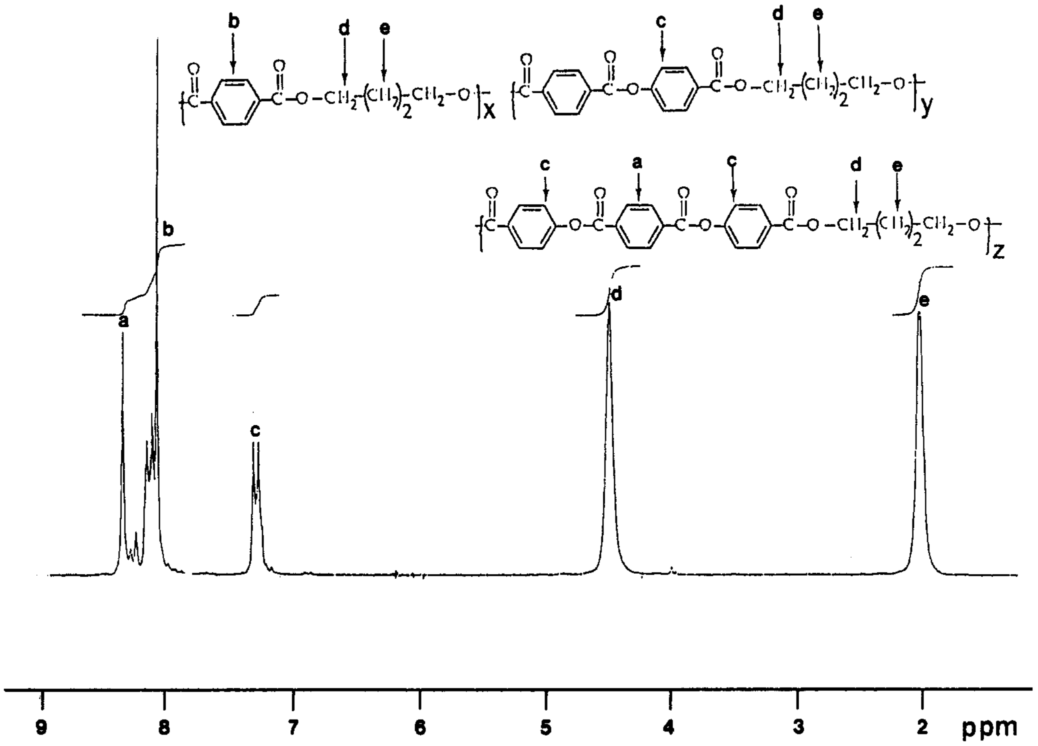
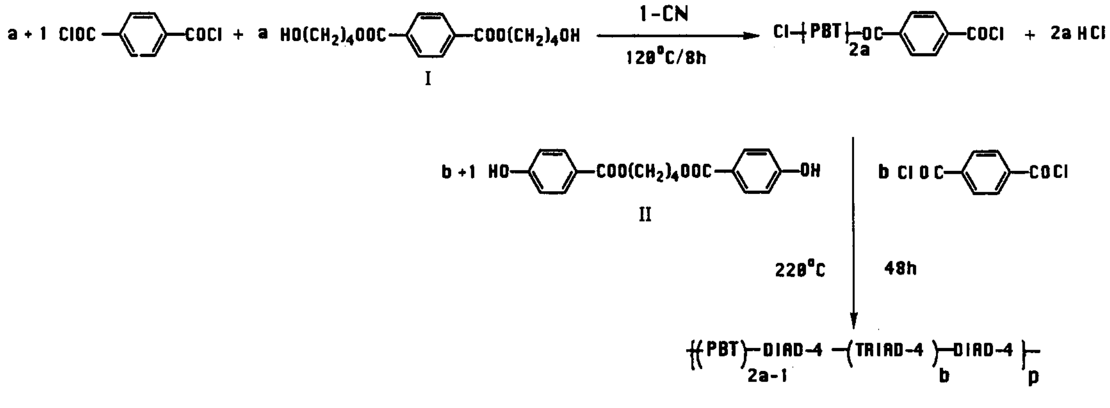


Figure 2. ^{1}H NMR (200 MHz) spectrum of block copolymer III.

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



Polymers I, II, III, IV, V, VI and VII

ers were not reported. Therefore, the first part of this report is devoted to the synthesis and characterization of a Diad-4 homopolymer and a Diad-4-*co*-PBT block copolymer.

Diad-4 Homopolymer and Diad-4-*co*-PBT Block Copolymer. Synthesis of the Diad-4 homopolymer involved the polycondensation of the Diad diacid chloride (III) with butanediol at 40 °C in the presence of triethylamine as the acid acceptor, as illustrated by the reaction Scheme 2. The Diad-4-*co*-PBT block copolymer was synthesized by a two step procedure, in which the first step consisted of the preparation of acid chloride end-capped Diad-4 oligomer, and the second step involved in situ formation of PBT oligomer and block copolycondensation initiated by adding appropriate amounts of BHBT (I) and terephthaloyl chloride as shown in Scheme 3. The properties of the Diad-4 polymers are summarized in Table 1. We were able to obtain higher molecular weights than reported for other Diad polymers,[14] by isolating and crystallizing the intermediate Diad-4 diacid chloride, although no effort was made to optimize the molecular weights of the polymers. The structures of the polymers were verified by ^{1}H and ^{13}C NMR spectroscopy. Figure 1 shows the ^{13}C NMR spectrum of the Diad-4 homopolymer. Peak assignments were made from calculated chemical shift values.

Figure 4 shows the DSC thermogram of the Diad-4 homopolymer obtained during the first heating and cooling scan. The thermogram exhibits a broad but distinct endothermic peak, having maximum at 219 °C, followed by another broad less pronounced peak centered around 258 °C. Polarizing optical microscopic observation of the polymer on a hot stage revealed that the first peak corresponds to a crystalline-to-nematic phase transition and the second to the isotropization of the mesophase. Similarly, on cooling the DSC trace showed two exotherms at 226 and 160 °C, which are due to the isotropic-to-nematic and the nematic-to-crystal transitions, respectively. The sample exhibits a similar thermogram during the second heating and cooling cycle. However, the transition temperatures and the corresponding enthalpies are lower than those for the first thermal cycle (see Table 1). The Diad-4 homopolymer is a low molecular weight sample (η_{inh} = 0.3 dL/g), containing a sufficient amount of acid

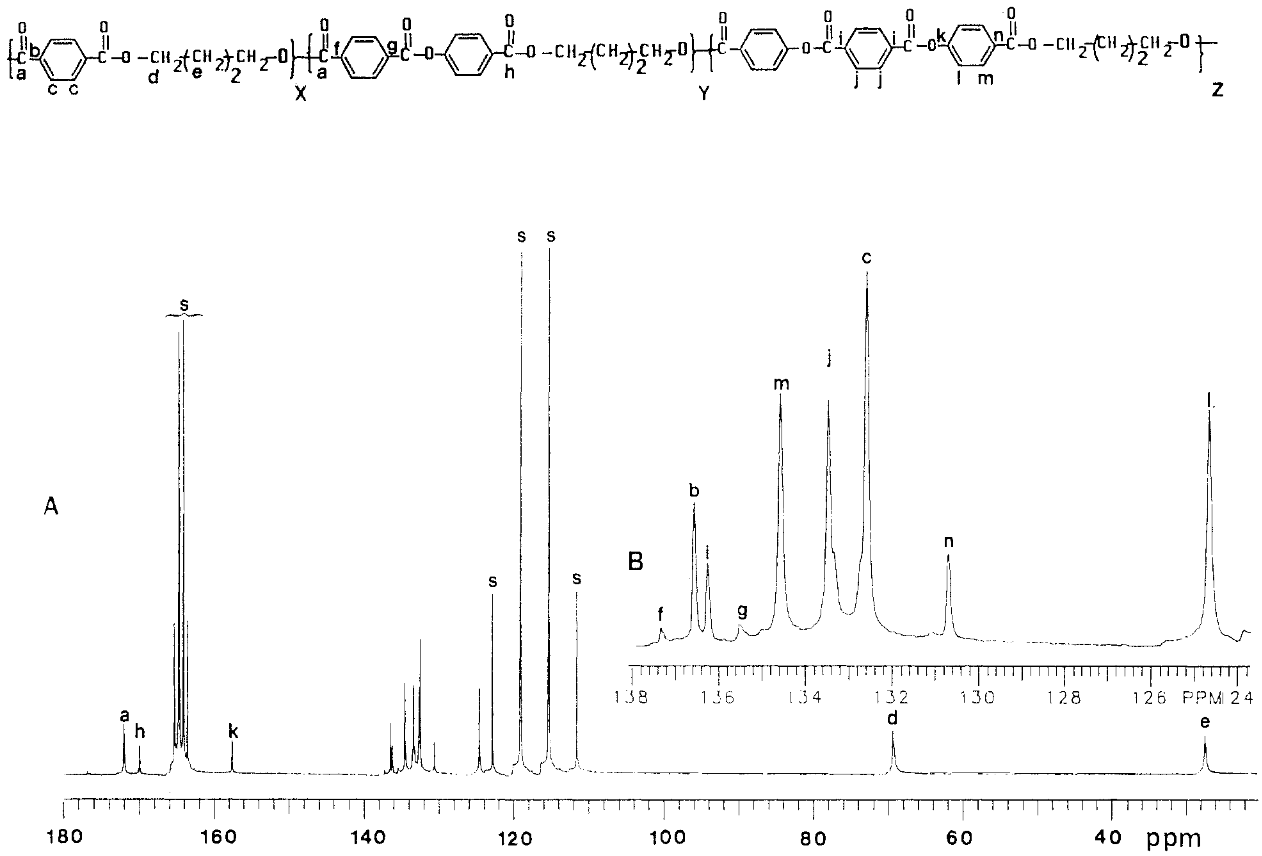
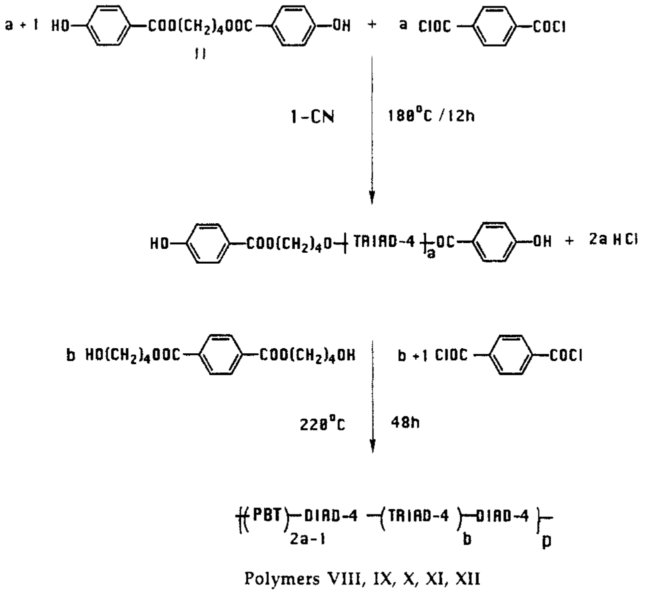


Figure 3. (A) ^{13}C NMR spectrum of polymer III. (B) Expanded 124–138 ppm region.

Scheme 5. Synthesis of Triad-4-*co*-PBT Block Copolymers: One-Reactor Procedure



end groups that can catalyze transesterification reactions when heated to 300 °C, which is well above the isotropization temperature. Such transesterification reactions can affect the structural integrity of the Diad-4 polymer during the first heating scan, thus affecting the transition temperatures in the subsequent heating and cooling scans.

The first heating DSC thermogram for the Diad-4-*co*-PBT block copolymer shows three separate transitions (see Figure 5). The transition at 50 °C corresponds to the glass transition of the PBT segments present in the block copolymer. The origin of the second transition, observed at 100 °C and present only in the first heating scan of all block copolymers studied, will be discussed with the Triad-4-*co*-PBT block copolymers in the next section. The broad endothermic peak at 160–210 °C has a maximum at 196 °C. This is several degrees lower than the melting points of high molecular weight PBT or of the Diad-4 homopolymer, which melt respectively at 212 and 219 °C, under the same experimental conditions. Considering the short segment lengths of both PBT and Diad-4 sequences, it is reasonable to assume that the broad peak at 196 °C encompasses the melting of the two segments present in the block copolymer. Moreover, polarizing optical microscopy of the polymer showed that the polymer is completely isotropic above 210 °C. Upon cooling, isotropic-to-nematic transition occurs at 185 °C and crystallizations of the PBT and Diad-4 segments take place at 158 °C. During the second scan, except for the disappearance of the minor peak observed at 100 °C, the transition temperatures remain the same (see Table 1). When the higher molecular weight Diad-4-*co*-PBT block copolymer (η_{inh} = 0.72 dL/g) is heated to 300 °C, which is well above its isotropization temperature, there are insufficient end groups to catalyze transesterification reactions which cause sequence randomization. The transition temperatures appear unaffected by the different heating cycles.

Triad-4-*co*-PBT Block Copolymers. The synthesis of the Triad-4-*co*-PBT block copolymers was carried out according to one scheme for the two-reactor method or two schemes for the one-reactor method. In the two-reactor method, phenol-end-capped Triad-4 oligomer, Oligomer B, and the acid chloride-end-capped PBT oligomer, Oligomer A, were first synthesized separately; these oligomers were mixed subsequently to undergo polycondensation to yield the segmented block copolymer as shown in Scheme 6. In the one-reactor method, either the PBT segments or the Triad-4 segments, having appropriate reactive end groups, were synthesized first, and then appropriate monomers for the formation of the

Scheme 6. Synthesis of Triad-4-*co*-PBT Block Copolymer: Two-Reactor Method

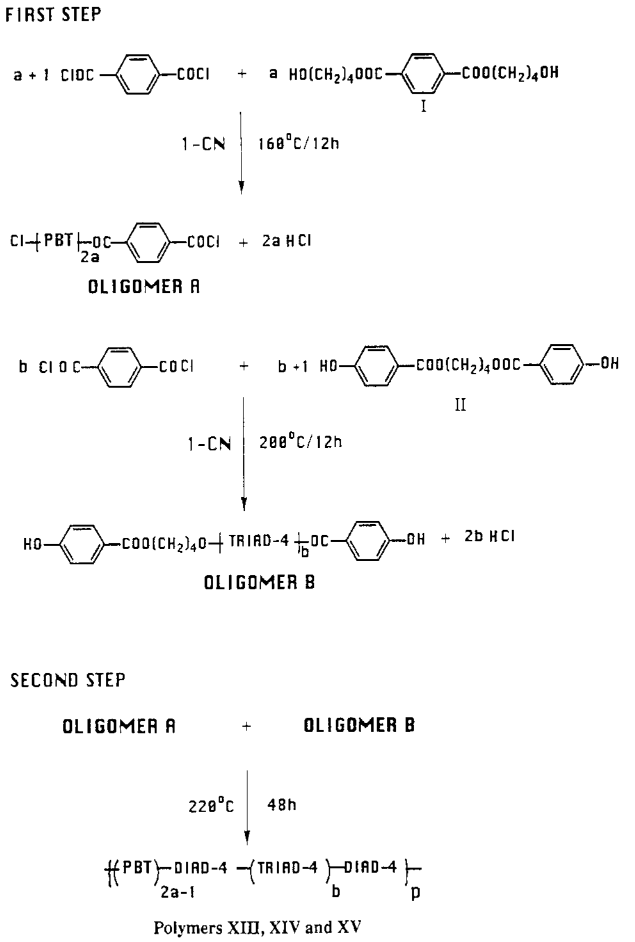


Table 1. Diad-4 Homopolymer and Its Block Copolymer with PBT[a]

polymer	η_{inh} (dL/g)	T_{m} (°C)[b]	$T_{\mathrm{n-i}}$ (°C)[c]	$T_{\mathrm{i-n}}$ (°C)[d]	T_{c} (°C)[e]	LC phase
Diad-4	0.3	219 (25)	258	226 (9)	160 (11.7)	nematic
		201 (10	239	230 (9)	134 (10)	
Diad-4-*co*-PBT[f]	0.72	196 (34)		185 (3.7)	158 (15.6)	nematic
		195 (27)		185 (3.3)	158 (17.4)	

[a] Enthalpy in J/g associated with the transitions is given in parentheses. The two sets of values are given for the first and second thermal cycles, respectively. [b] Crystal-to-nematic transition. [c] Nematic-to-isotropic transition. [d] Isotropic-to-nematic transition. [e] Nematic-to-crystal transition. [f] This block copolymer contains 55 mol % of PBT as determined by ^{1}H NMR which agrees well with the theoretically expected value of 55%.

second segment were added to the same reaction vessel. This is illustrated in Schemes 4 and 5. The stoichiometry of the monomers were carefully selected to obtain high molecular weight block copolymers. Systematic variations of the rod content as well as segment length were made. Table 2 summarizes the block copolymers that were synthesized by the three different schemes. The composition in the tables refers to the expected number of the three moieties, Diad-4, Triad-4, and PBT, present in each repeating unit, based on the stoichiometry of the monomers used in the block copolymer synthesis. For example, an average molar composition identified as 2:4:1, represents a block copolymer having two Diad-4, four Triad-4, and one PBT moieties in each repeating unit. As seen from Table 2, all three schemes yield polymers with high inherent viscosities.

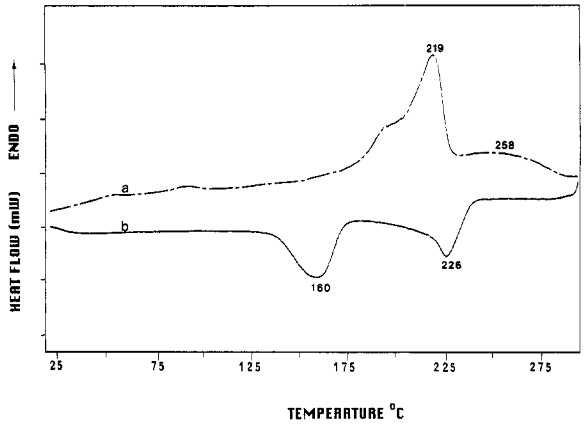


Figure 4. DSC thermogram of the Diad-4 homopolymer: (a) first heating; (b) first cooling.

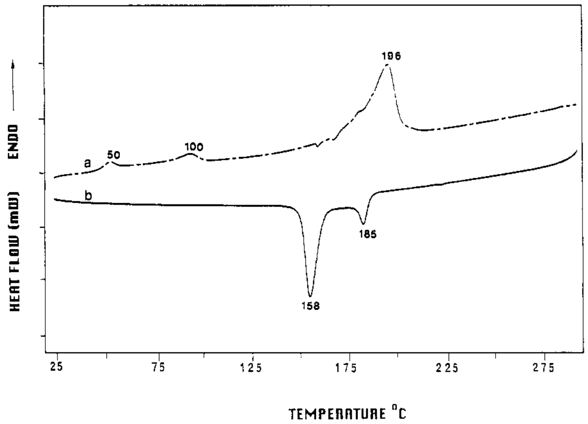


Figure 5. DSC thermogram of Diad-4-*co*-PBT block copolymer obtained during (a) first heating and (b) first cooling.

Block Copolymer Compositions. A typical ^{1}H NMR spectrum of the block copolymer **III** is shown in Figure 2. The peaks were identified by using a comparison with the spectra of PBT and Triad-4 homopolymers. The distinct peak at 8.4 ppm labeled a is characteristic of the terephthaloyl protons present in the Triad-4 moiety, whereas the terephthaloyl protons in PBT appear at 8.1 ppm and are labeled b. The two protons ortho to the oxygen of the oxybenzoyl unit present in both Triad-4 and Diad-4 moieties are identified as c and resonate at 7.35 ppm. The four methylene protons adjacent to the outer oxygens and the other four methylene protons are at 4.5 (d) and 2.0 (e) ppm, respectively. The mole percentages of PBT, Diad-4, and Triad-4 can be calculated from the integrals of the peaks at 8.4, 7.35, and 4.5 ppm, respectively, by using the following equations:

$$X + Y + Z = 1$$

$$4Z \propto \text{integral of protons at 7.3 ppm}$$

$$2Y + 4Z \propto \text{integral of protons at 8.4 ppm}$$

$$4(X + Y + Z) \propto \text{integral of protons at 4.5 ppm}$$

where X, Y, and Z are the mole percentages of PBT, Diad-4, and Triad-4 moieties in the block copolymer.

Table 2 gives a comparison of the molar compositions predicted from the stoichiometry of the starting monomers and those calculated from ^{1}H NMR spectroscopy. There is a qualitative but not quantitative agreement in the variations of compositions regardless of the reaction scheme utilized since the three schemes give similar differences. During the first step involving the synthesis

Table 2. Compositions of Triad-4-*co*-PBT Block Copolymers Synthesized by Three Schemes

				mol % moieties by ^{1}H NMR					
				PBT		Diad-4		Triad-4	
polymer	scheme	composition[a]	η_{inh} (dL/g)	calcd	found	calcd	found	calcd	found
I	4	2:4:1	0.83	14	13	29	42	57	45
II	4	2:4:3	0.80	33	40	22	24	45	36
III	4	2:4:7	0.86	54	50	16	18	30	31
IV	4	2:4:9	0.83	60	53	13	23	27	23
V	4	2:4:11	1.1	65	64	12	15	23	20
VI	4	2:4:21	1.1	78	79	7	10	15	11
VII	4	2:8:17	0.65	63	59	7	22	30	19
VIII	5	2:4:7	0.55	54	64	16	10	30	26
IX	5	2:4:9	0.75	60	62	13	16	27	21
X	5	2:4:21	0.68	78	80	7	9	15	11
XI	5	2:6:11	0.60	58	62	10	13	32	25
XII	5	2:8:17	0.91	63	58	7	17	30	25
XIII	6	2:4:7	0.62	54	52	16	23	30	25
XIV	6	2:2:3	0.68	42	61	29	14	34	30
XV	6	2:8:17	0.95	63	61	7	7	30	32

[a] The numbers represent the number of the Diad-4, Triad-4, and PBT moieties, respectively, per repeating unit of the block copolymer.

of the prepolymer, there is a statistical distribution of oligomers of different molecular weights, in addition to the presence of unreacted monomer used in excess for obtaining reactive end groups. In the second step, when the second set of monomers are added to the system, it becomes harder to predict the probability of these monomers reacting among themselves or with the prepolymers of varying molecular weights. For most of the block copolymers, the clearest general pattern is that the percentages of Diad-4 moieties are generally greater than predicted while the percentages of Triad-4 moieties are generally less.

The presence of transesterification during the polycondensation could account for these random differences between the theoretically predicted and experimentally determined molar compositions. However, Bilibin et al.[15] have established by kinetic study of a similar synthesis also carried out in 1-CN at 245 °C that transesterification is not a major reaction during the process. There are several reports in the literature[16,17,18] regarding the sequence length determination of copolyesters by NMR (^{1}H or ^{13}C) spectroscopy. In all the cases reported, it involved copolyesters formed either from two acids and a diol or from two diols and one acid. In either case, there was sufficient NMR data to estimate the lenths of the sequences formed. The block copolyesters in this study can be considered to be composed of three acids and one diol, from which the three moieties, Triad-4, Diad-4, and PBT, are derived. ^{1}H NMR data were not sufficiently sensitive to give any information regarding the average sequence length of these blocks in the copolyesters.

The ^{13}C NMR of a typical block copolymer **III** is shown in Figure 3. Identification of the peaks was done by comparing with the NMR spectra of PBT,[19] Triad-4,[20] and Diad-4 (Figure 1) homopolymers. The carbonyl carbon of the terephthaloyl group in all three moieties appears as a single peak at 171.9 ppm labeled a. Similarly, the peak at 169.7 ppm is due to the oxybenzoyl carbonyl, h, of both Triad-4 and Diad-4 units. The region 140–124 ppm is interesting since it can distinguish the quaternary carbons belonging to the terephthaloyl group of PBT, Triad-4, and Diad-4 units. Integration of the peaks at 137.3 (f), 136.5 (b), and 136.2 (i) ppm should provide an easy and direct evaluation of this polymer composition. The polymer compositions obtained by this method are very much different from both those theoretically predicted and those calculated from ^{1}H NMR. This must probably be due to the difference in the relaxation times of the different quaternary carbons.

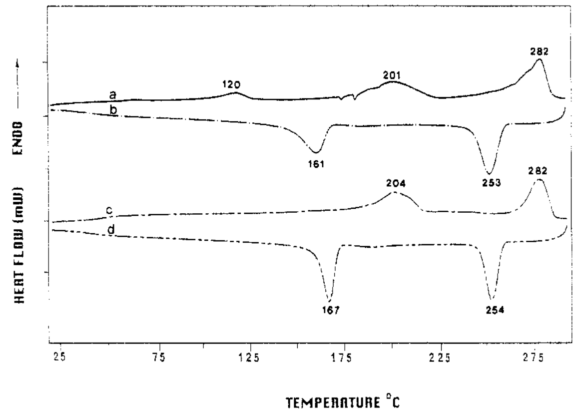


Figure 6. DSC thermogram of **III**: (a) first heating; (b) first cooling; (c) second heating; (d) second cooling.

Thermal Behavior. The thermal behavior of the block copolymers synthesized by Scheme 4 will be discussed in this section, and then the thermal properties of two sets of block copolymers synthesized by the three different reaction schemes will be compared. The DSC trace of the block copolymers **III**, obtained during the first scan, is illustrated in Figure 6. Upon heating from 20 to 310 °C, the block copolymer shows four different transitions: an indication of a glass transition around 50 °C and a minor transition around 120 °C followed by two large endothermic peaks centered at 201 and 282 °C. The glass transition at 50 °C, which is present in all block copolymers having a PBT segment length greater than 7, can be attributed to the T_g of the amorphous PBT domains.

The broad endotherm centered around 201 °C can be associated with the melting of the PBT domains present in the block copolymer. High molecular weight PBT homopolymer shows a sharp melting endotherm at 222 °C when heated at 20 °C/min. It has been shown in the case of segmented block copolymers containing hard and soft segments that the melting point of the PBT hard domains shows a strong dependence on the segment length,[21] increasing continuously from 125 to 200 °C as the segment length increases from 1 to 8 units, above which the melting point starts to level off. As seen from Table 3, for the first DSC heating scan of the block copolymers, the melting point shows a variation as the segment length of PBT varies from 7 to 21. The first two block copolymers **I** and

Table 3. Thermal Properties of Triad-4-*co*-PBT Block Copolymers Synthesized by Scheme 4[a]

polymer	wt % PBT	wt % Triad-4	$T_{k\text{-}k}$ (°C)[b]	ΔH (J/g)[c]	T_m (°C)[d]	ΔH (J/g)[e]	$T_{k\text{-}n}$ (°C)[f]	ΔH (J/g)[g]
Triad-4		100					282	30
							282[h]	12[h]
I (2:4:1)	16	65	130	0.4			282	24
II (2:4:3)	26	49	143	1.6			288	20
					210[h]	7.5[h]	281[h]	9.5[h]
III (2:4:7)	36	45	120	2.9	201	11.4	282	18
					204[h]	12[h]	282[h]	9[h]
IV (2:4:9)	35	37	119	2.9	200	12	282	19
V (2:4:11)	40	34	120	2	205	15	280	15
VI (2:4:21)	62	19	109	1.5	214	29	279	6
PBT	100				222	46		

[a] The values are reported for the first heating scan unless otherwise specified. [b] Crystal-to-crystal transition. [c] Enthalpy associated with $T_{k\text{-}k}$. [d] Melting of PBT domains in the polymer. [e] Enthalpy associated with the melting of PBT domains. [f] Crystal-to-nematic transition of Triad-4 domains. [g] Enthalpy associated with the $T_{k\text{-}n}$ transition. [h] These values are obtained for a second heating scan after cooling the samples at 20 °C/min from 300 °C.

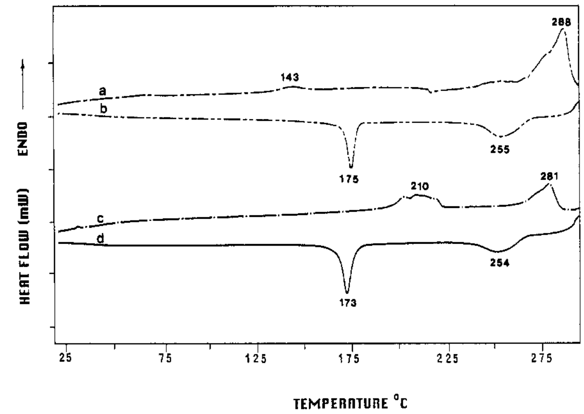


Figure 7. DSC thermogram of **II**: (a) first heating; (b) first cooling; (c) second heating; (d) second cooling.

II, having PBT segment lengths 1 and 3, do not show a first scan melting endotherm in this region. However, polymer **II** has a broad melting endotherm around 210 °C during the second heating scan, as seen in Figure 7. Another interesting feature of the block copolymers having segment lengths higher than 7 is the appearance of multiple endotherms, usually in the second and subsequent heating cycles. The overall area of these multiple endotherms remains the same from one scan to another. The presence of multiple endotherms during the heating of PBT has been reported by several authors, and its origin is still being debated.[22]

The Diad-4-*co*-PBT block copolymer melts in the same temperature region as the PBT phase in the Triad-4-*co*-PBT block copolymers. In spite of the presence of the Diad-4 moiety, all block copolymers in Table 3 show an increase in enthalpy with increasing PBT content. However, the block copolymers **I** and **III**, which have very short PBT segments, do not exhibit a melting endotherm during the first heating scan, although they contained significant amounts of Diad-4 moieties (see Table 2). It is difficult to assess the contribution of the Diad-4 moiety toward the overall enthalpy of this temperature region. Observations from samples **I** and **II** would suggest that the Diad-4 units reduce the overall crystallinity of the PBT segments.

Table 4. Thermal Properties of Triad-4-*co*-PBT Block Copolymers Synthesized by Scheme 4[a]

polymer	wt % PBT	wt % Triad-4	T_c (°C)[b]	ΔH (J/g)[c]	$T_{n\text{-}k}$ (°C)[d]	ΔH (J/g)[e]
Triad-4		100			235	17.5
I (2:4:1)	16	65			259	17
II (2:4:3)	26	49	175	7	255	10
III (2:4:7)	36	45	161	9	253	11
			170[f]	12[f]	225[f]	11[f]
IV (2:4:9)	35	37	166	11	254	9
V (2:4:11)	40	34	167	13	250	8
VI (2:4:21)	62	19	176	21	203	4
PBT	100		163	46		

[a] The values reported are for the first cooling scan after first heating the samples to 300 °C at 20 °C/min. [b] Crystallization of PBT domains. [c] Enthalpy associated with T_c. [d] Nematic-to-crystal transition of Triad-4 domains. [e] Enthalpy associated with $T_{n\text{-}k}$. [f] These values are obtained for the first cooling scan for a sample heated to 320 °C at 20 °C/min and subsequently cooled at the same rate.

The minor endotherm observed around 120 °C, during the first heating scan shown in Figure 6, disappeared in subsequent heating and cooling cycles. Moreover, this endotherm, which is absent in both the Triad-4 and PBT homopolymers, is present in the first heating scan of all the block copolymers, including the Diad-4-*co*-PBT block copolymer (see Figure 5). The peak temperature and enthalpy of this transition are collected in Table 3. The temperature varies with the block copolymer composition from 109 to 143 °C. The enthalpy of this transition is small and varies from 0.4 to 2.9 J/g. The origin of this transition is unknown. In order to check the possibility that this small endotherm forms a part of the multiple endotherms displayed by PBT domains during melting, we studied the effect of heating rate on this small endotherm. Different heating rates of 5, 10, 20, and 40 °C/min were examined. While the enthalpy is unaffected by the heating rate, the peak maximum shows the usual shift with heating rate, but it does not disappear or move very close to the major PBT melting endotherm. Therefore, this endotherm is not associated with the melting endotherm of PBT phases but may be due to some crystal-to-crystal transition which has been observed in the case of dialkyl 4,4′-(terephthaloyldioxy)dibenzoates.[23]

The major peak observed at 282 °C for all block copolymers, irrespective of Triad-4 content, is the same as the one observed for the Triad-4 homopolymer and corresponds to the crystal-to-nematic transition of the Triad-4 domains. As seen from Table 3, the transition temperature is not affected by the length or the amount of the PBT block. The enthalpy of this transition was found to be lower in the second heating scan than in the first, which is the case for all the block copolymers as well as the Triad-4 homopolymer. This behavior is probably due to the incomplete crystallization of Triad-4 domains on cooling from the melt at 20 °C/min. A comparison of the enthalpy of the crystal-to-nematic transition for block copolymers of different composition shows that this enthalpy decreases qualitative but not quantitatively with decreasing Triad-4 content, as would be expected.

As seen in Table 4, the cooling scans for the block copolymers exhibit two distinct exotherms around 254 and 162 °C (see Figures 6 and 7). Crystallization of Triad-4 and PBT homopolymers, under the same conditions, occurs at 235 and 163 °C, respectively. Hence, the two exotherms in the block copolymers are consistent with the crystallization of the Triad-4 and PBT domains. However, these transition temperatures are higher than expected for block copolymers with such short segments. Moreover, the crystallization temperature of Triad-4 domains seems to be very susceptible to the thermal history. For example, in two separate sets of experiments, samples of polymer **III** were heated to 300 °C or to 320 °C at 20 °C/min, and on cooling at the same rate, crystallization occurs at 254 °C in the former and at 225

Table 5. Comparison of the Thermal Properties of Two Sets of Block Copolymers Synthesized by Different Schemes[a]

polymer	composition	scheme	T_m (°C)	T_{k-n} (°C)	T_{n-k} (°C)	T_c (°C)
III	2:4:7	4	201 (11.4)	282 (18)	225 (11)	170 (9)
VIII	2:4:7	5	206 (12)	270 (19.7)	229 (10.6)	168 (12)
XIII	2:4:7	6	213 (13)	269 (14.2)	222 (11.4)	170 (13.6)
VII	2:8:17	4	206 (13)	276 (10)	233 (9.6)	168 (12.4)
XII	2:8:17	5	204 (13.7)	282 (23.8)	232 (16.4)	172 (9.6)
XV	2:8:17	6	207 (13.2)	281 (16.7)	238 (8.9)	176 (12.4)

[a] All samples were heated from 0 to 320 °C at 20 °C/min. The enthalpy of each transition in J/g is given in parentheses.

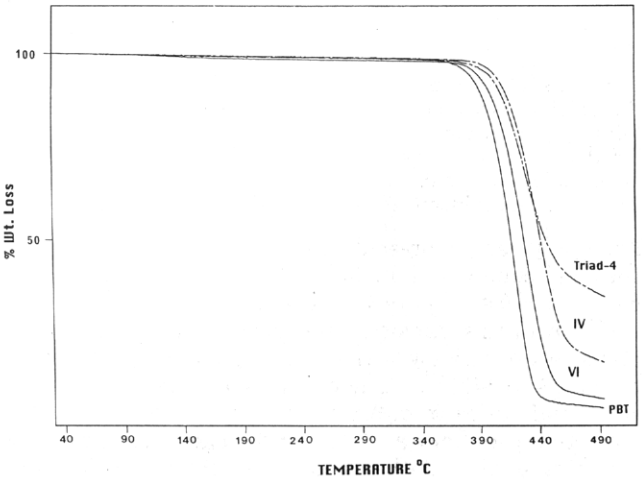


Figure 8. TGA curves of polymers under N_2.

°C in the latter case. Such differences in the crystallization temperature may arise from the fact that, at 300 °C, the polymer chains are in the nematic state, whereas at 320 °C, the low molecular weight fractions might already be in the more disordered isotropic state, making crystallization more difficult, and hence occur at a lower temperature. It is interesting that the enthalpy of crystallization is not affected by these thermal treatments. While the Triad-4 domains in all the samples crystallize around 250–259 °C, polymer **VI**, where the Triad-4 domains are diluted by the presence of longer PBT segments as well as a higher PBT content, shows greater supercooling and crystallizes at 203 °C.

The cooling curves also show sharp crystallization exotherms at about 161–176 °C. The crystallization temperatures are higher than that would expected for a short segment PBT, since high molecular weight PBT crystallizes at 163 °C, under the same experimental conditions. This unexpectedly higher temperature is due to the presence of Triad-4 domains, which can nucleate the crystallization of PBT. All block copolymers show a moderate trend of an increase in crystallization temperature and enthalpy of crystallization with increasing PBT segment length.

The thermal properties of two sets of polymers with theoretically expected compositions 2:4:7 and 2:8:17, synthesized by the three different reaction Schemes 4–6, are summarized in Table 5. As expected from the previous discussions, on heating these block copolymers exhibit two major endotherms corresponding to the melting of PBT domains and the crystal-to-nematic transition of the Triad-4 domains. On cooling these polymers show two exotherms associated with the crystallization of the two separate domains. The transition temperatures and the associated enthalpies for the same overall polymer compositions depend on the method of synthesis. Although the targeted molar composition was the same, the microstructure of the block copolymer is governed by the method of synthesis. The difference in microstructure of the final product accounts for nonsystematic but small variations of the thermal properties of the same composition of the block copolymer obtained by the three different reaction schemes.

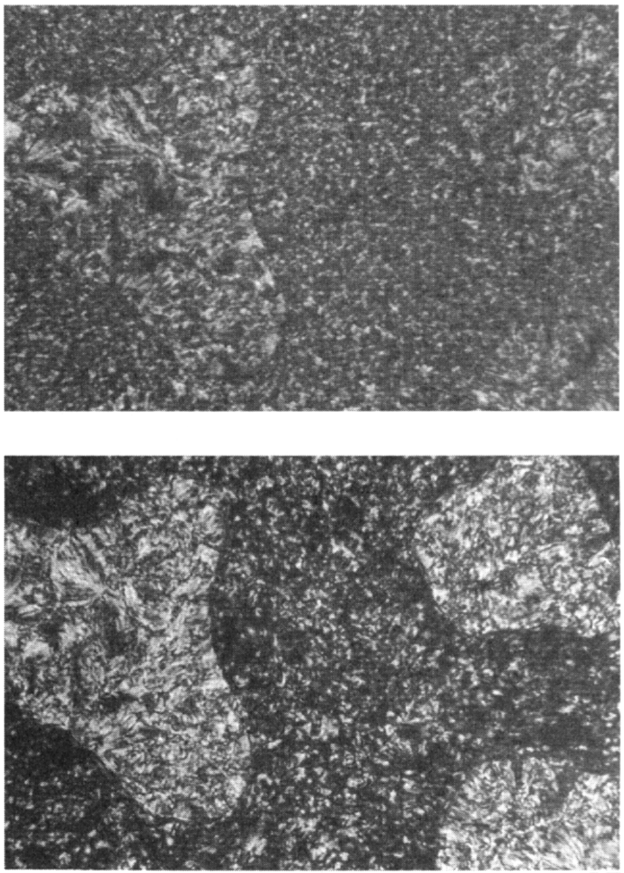


Figure 9. Optical micrographs of polymer **III** (a, top) at RT and (b, bottom) at 210 °C.

Thermal Stability. The thermal stabilities of all block copolymers, and also of PBT and Triad-4 homopolymers, were studied under a N_2 atmosphere at a heating rate of 20 °C/min. Figure 8 presents some typical results. The onset of thermal degradation occurs around 378–400 °C, depending on the block copolymer composition. PBT homopolymer exhibits the least thermal stability, producing a residue of 7% at 500 °C and decomposing at the lowest temperature. On the other hand, Triad-4 homopolymer gives 37% residue at 500 °C. However, it starts to degrade at a slightly lower temperature than the block copolymer **III**, probably induced by the presence of a higher concentration of end groups in the Triad-4 polymer. The amount of residue left by the different block copolymers at 500 °C depends on the polymer composition and is in between those of the pure homopolymers. As expected, the polymers with higher aromatic content give the higher residue.

Polarizing Optical Microscopy. Polarizing optical microscopy was used to identify the liquid crystalline phases and to complement the phase transitions observed

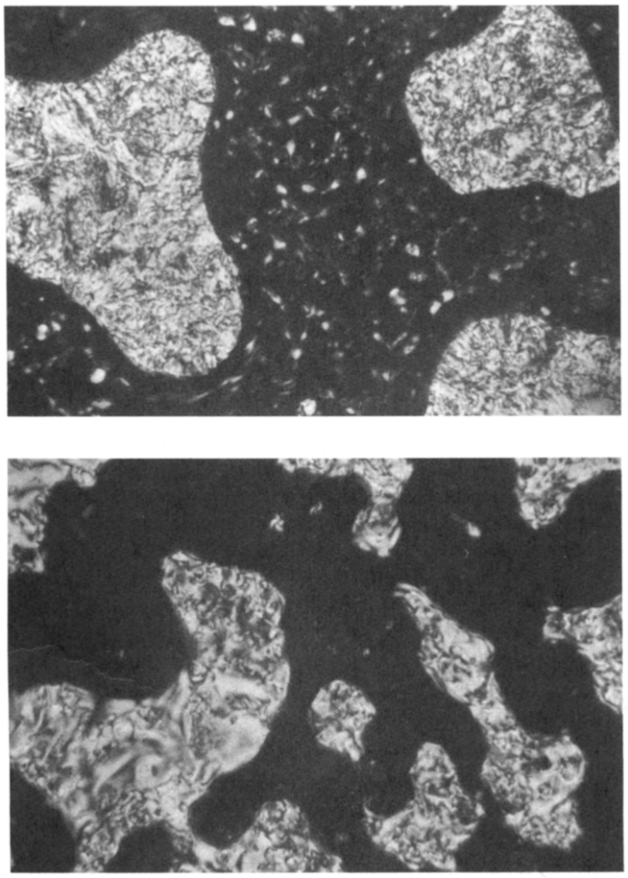


Figure 10. Optical micrographs of polymer **III** (a, top) at 250 °C and (b, bottom) at 300 °C.

by DSC. All samples were heated to 300 °C, between two microscope slides on a Fisher-Johns melting point apparatus. The melts exhibited strong stir-opalescence, when heated above 290 °C, indicating their liquid crystalline nature. The samples were quenched, were transferred to the hot stage of a microscope, and were heated at a rate of 10 °C/min. A more detailed study was undertaken for polymer **III**, but the observations are generally valid for all Triad-4-*co*-PBT block polymers. When observed under the microscope with crossed polars, all samples reveal a highly threaded nematic texture (Figure 9a). Upon heating at 10 °C/min at 200 °C, certain regions melt to become dark, as opposed to the highly birefringent regions, as shown by Figure 9b. This corresponds to the melting of the PBT-rich domains, consistent with the DSC results. On continued heating to 250 °C, the PBT domains completely melted to dark regions (Figure 10a). These dark regions were examined under the polarizer alone to ascertain that they contained polymer and not air bubbles. When the sample is further heated to 300 °C (Figure 10b), the birefringent domains start to flow and break up into smaller particles. Upon cooling from 300 °C, at around 250 °C, the polymer ceases to flow, and birefringent crystallites appear in the isotropic PBT melt phase. At 170 °C, the crystallization of PBT is complete as observed by the appearance of birefringence in the previously dark regions. The polymers behaves similarly during subsequent heating and cooling cycles. The complete disappearance of liquid crystallinity occurs above 340 °C, which was the working limit of the hot stage.

Conclusions

Syntheses of novel thermotropic liquid crystalline block copolymers containing Triad-4 and PBT moieties were carried out in 1-chloronaphthalene at high temperature in the absence of catalysts. Three different reaction schemes were examined. High molecular weight polymers were obtained in all cases. The average molar compositions of the block copolymers calculated from ^{1}H NMR data were not in complete agreement with the theoretically predicted values. The differences arise from the presence of more than expected diad moieties in the block copolymers. Although the average sequence lengths of the moieties in the block copolymers could not be calculated from NMR data, the presence of two distinct melting transitions associated with the PBT and Triad-4 domains and the variation of enthalpy of each transition with block copolymer composition prove the blocky nature of these block copolymers. Synthesis and characterization of copolymers containing the Triad-4 and PBT moieties but in alternating or random arrangement are being investigated and will be the subject of a forthcoming publication.

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