Liquid Crystalline Aromatic Polyesters Containing Isophthalic Acid

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Received June 22, 1993; Revised Manuscript Received October 1, 1993•

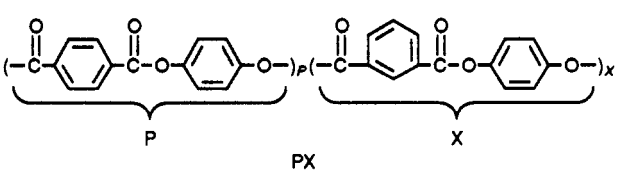
ABSTRACT: We have synthesized a series of copolyesters and terpolyesters containing the isophthalate unit in order to study the implications of nonlinear polymer backbones on liquid crystallinity. Copolyesters were prepared from isophthalic acid, hydroquinone, and terephthalic acid by melt polymerization. Poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate)s with molar percentages of the *p*-phenylene isophthalate repeat unit ranging from 75 to 95 mol % exhibit melting temperatures near 350 °C. The copolyester with 85 mol % of *p*-phenylene isophthalate exhibits a melting temperature of 355 °C and a mesophase range of 30 °C. Thermal properties of terpolyesters composed of four monomer units (isophthalic acid, hydroquinone, terephthalic acid, and *p*-hydroxybenzoic acid) show optimal compositions with melting temperatures below 350 °C and wide mesophase ranges. Our findings show that high contents of nonlinear monomers may be incorporated into polyesters without deleterious effects on liquid crystallinity in a composition range that can be processed at reasonable temperatures.

Introduction

We have recently reconsidered primary/secondary structural influences in thermotropic liquid crystalline polymers (LCPs), especially the role of monomer geometry in liquid crystal formation.[1,2] Our model compound studies reaffirm the long-standing axiom that deviations from molecular linearity decrease mesophase stability and may eliminate the mesophase altogether. More importantly, we discovered that the nonlinear 2,5-thiophene unit with a mesogenic "core angle" of 148°, the angle between the 2,5-exocyclic bonds, is near the critical degree of nonlinearity for mesogenic core units in the class of ester-based model compounds.[1] As excluded-volume interactions are primarily responsible for mesophase formation, when the mesogenic core—the anisometric structural component of liquid crystal (LC) molecules—deviates too far from a prolate (or oblate) ellipsoidal shape, a quasi-parallel arrangement of close-packed molecules is not feasible in the melt. We extended our findings on low molecular mass LC core geometry to LCPs and found that polyesters containing 100% carboxythiophene-2,5-diylcarboxy-*p*-phenylene units are mesogenic.[2] However, in such polymers the 148° angle in the 2,5-thiophene unit disrupts the rectilinear secondary structure of the chain, thereby lowering the melting temperature while retaining mesomorphism. Herein, we consider more closely the notion that a high content of linear monomer units is a structural prerequisite for liquid crystallinity in LCPs. Namely, we investigate how much of the nonlinear isophthalte unit can be tolerated in liquid crystalline polyesters.

Previous work in our laboratory confirms that poly(*p*-phenylene isophthalate) (HQ/IA) prepared from hydroquinone (HQ) and isophthalic acid (IA) melts directly to the isotropic liquid phase.[2] This indicates that the monomer core-angle defect of the isophthalate unit (120°) is too severe for the extensive chain parallelism required for liquid crystallinity. Nevertheless, the recent report[3] of a liquid crystalline polyamide prepared from *p*-phenylenediamine and 2,5-furandicarboxylic acid (which has a core angle of 125°) together with the observation that the 2,5-thiophene-based polyesters exhibit a rather wide mesophase range[2] prompted us to reexamine the limits of mesomorphism in polyesters employing the linear diol HQ and the readily available nonlinear diacid IA. We decided to see if incorporation of varying amounts of linear comonomer (e.g., terephthalic acid or *p*-hydroxybenzoic acid) into the HQ/IA polymer might increase the local anisotropic interchain repulsion sufficiently to induce liquid crystallinity in its melt. For example, Erdemir et al. reported that poly(oxybenzoate-*p*-phenylene isophthalate) (HBA/HQ/IA) forms a liquid crystal phase if the *p*-phenylene isophthalate unit is included at less than 67 mol %.[4] In a 1962 patent, Kantor et al. reported poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate), but they were not aware of the existence of thermotropic LCPs at that time.[5] Also there were several early reports on poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate), but no observations of mesomorphic properties had been reported.[5] A decade later, Goldfarb et al. studied the thermal stability of this copolyester but did not explore the mesomorphic properties.[6] In a 1972 patent, Cottis et al. disclosed a terpolyester containing terephthalic acid, isophthalic acid, hydroquinone, and *p*-hydroxybenzoic acid but did not report liquid crystallinity in this polyester.[7] Hence, it would appear that, in spite of the large amount of work on these systems, correlations between structure and liquid crystalline formation are not extensive.

In order to study monomer structural effects on liquid crystallinity, we reexamined thermal properties and mesomorphic behavior in poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate)s (PX)



PX

where the ratio of the nonlinear bent *p*-phenylene isopthalate unit (X) to the linear *p*-phenylene terephthalate unit (P) is used as a geometric variable to effect the local chain persistence and, ultimately, chain packing in the liquid and solid phase driven by anisotropic

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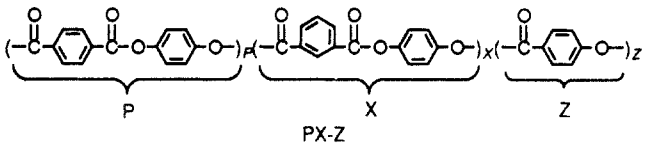
• Abstract published in *Advance ACS Abstracts*, November 15, 1993.

0024-9297/94/2227-0135$04.50/0

excluded-volume interactions. In addition to the PX polyester, we also studied the new terpolyesters based on (HQ/TA/IA/HBA) which incorporate *p*-hydroxybenzoic acid (HBA) into the former copolyester; we designate these terpolymers PX-Z, where *Z* is the molar percentate of HBA.



In PX-Z, we used the para-linked HBA units as a linear segment to increase the percentage of para-substituted units. Moreover, the introduction of HBA alternates the monomer orientation sense and thereby introduces another mechanism for disturbing lateral chain packing which could lead to lowering the melting temperature in these polyesters. Our focus is to locate the critical molar percentage of nonlinear IA units, X_c, which can be incorporated into a polymer and still have it retain liquid crystallinity. Knowledge of X_c may help quantify how monomer geometry effects liquid crystallinity in polymers and ultimately broaden the range of monomers that may be used for designing new engineering LCPs.

Experimental Section

Synthesis. Purified terephthalic acid and isophthalic acid were obtained by the hydrolysis of the crystallized (from CH_2Cl_2) dimethyl esters (Aldrich Chemical Co.). All the diacids were vacuum dried at 60 °C overnight before polymerization. Hydroquinone diacetate was prepared by heating hydroquinone with 10% excess of acetic anhydride and several drops of H_2SO_4 at 100 °C for 10 h. The mixture was slowly poured into ice water, and the precipitate was filtered, dried, and recrystallized from 95% ethanol and then from CH_2Cl_2. The purity of hydroquinone diacetate was checked by a constant melting temperature with differential scanning calorimetry (DSC). *p*-Acetoxybenzoic acid was prepared from *p*-hydroxybenzoic acid and an equimolar amount of acetic anhydride in a 50% CH_2Cl_2 solution. The preparation was carried out at room temperature in the presence of several drops of H_2SO_4 for 10 h. CH_2Cl_2 was removed by rotary evaporation, and the residue was filtered and recrystallized from ethanol three times and vacuum dried. The purity of *p*-acetoxybenzoic acid was checked by a constant melting temperature in DSC traces.

All polyesters were prepared by melt transesterification of the diacetates and the diacids without a catalyst. The reaction apparatus is described in ref 8, and the reaction temperature program was controlled by using the vapor baths of several high-boiling liquids. The polymerizations were carried out in three stages under argon: (1) 1 h at 282 °C (dimethyl phthalate bath); (2) 1 h at 340 °C (anthracene bath); (3) $^1/_2$ h at 380 °C (anthraquinone bath). This last stage of the polymerization was carried out under vacuum (p = 0.5 mmHg).

Characterization. Polarizing microscopy was performed with a Nikon (Microphot-FX) microscope fitted with a Linkam (TMS-90) hot stage. The polymer samples were pressed between a glass slide and a cover slip. Transition temperatures and enthalpy changes were measured with differential scanning calorimetry (Perkin-Elmer DSC-4). DSC thermograms were recorded at heating rates of 40 °C/min under nitrogen. Polymer samples were divided into two classes according to their thermal history: (1) virgin (as-prepared) samples and (2) annealed samples. The virgin samples are the polymers which were taken directly from the reaction tube; the annealed samples were held at 300 °C for 10 h immediately before the measurement. Thermogravimetric analysis was carried out with a Perkin-Elmer TGS-2 at heating rates of 20 °C/min under nitrogen. Softening temperatures were measured with a thermomechanical analyzer (Perkin-Elmer TMA-7) at a heating rate of 20 °C/min under a load force of 100 mN.

Table I. Thermodynamic Properties of Poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate) (HQ/TA/IA)

X (mol %)	X:P	T_m[a] (°C)	ΔH[a] (kJ·mol^{-1})	T_s[b] (°C)	T_m[c] (°C)	T_{NI} (°C)	ΔT[c,d] (°C)
100.0	100:0	392	22.9	396	410		
95.0	95:5	341	12.7	186, 353	350		
90.0	90:10	352	9.1	188, 353	360		
85.0	85:15	348	5.5	346	355	385	30
80.0	80:20	354	7.7	347	360	410	50
75.0	75:25	334	3.3	334	340	420	60
65.0	65:35	416	3.0	403	420	>500	>80
50.0	50:50	437	1.7	442	450	>500	>50

[a] DSC data. [b] T_s is the softening temperature measured by TMA. [c] Microscopy observation. [d] $\Delta T = T_{NI} - T_m$.

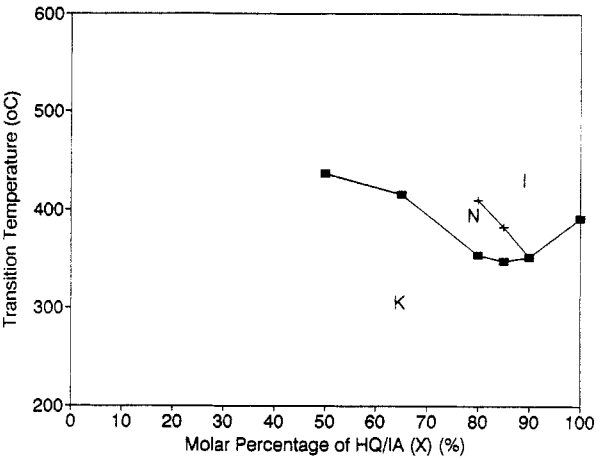


Figure 1. Transition temperatures vs molar percentage of *p*-phenylene isophthalate for poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate) (PX). Abbreviations: K, crystal; N, nematic; I, isotropic melt. The filled squares indicate the melting transition for the as-prepared sample; the crosses indicate the nematic-isotropic transition for the as-prepared sample.

Results

DSC and Optical Microscopy. Poly(*p*-phenylene terephthalate-*co*-isophthalate). First, we consider the PX copolyester consisting of two repeat units, where X is the molar percentage of *p*-phenylene isophthalate and P is the molar percentage of *p*-phenylene terephthalate units ($P + X = 100\%$). The thermal analysis data of copolyester PX are given in Table I. Figure 1 shows a phase diagram of this copolyester in which the transition temperatures are plotted aginst the molar percentage of X, the *p*-phenylene isophthalate repeat unit. Poly(*p*-phenylene isophthalate) (P100, $X = 100\%$) exhibits a melting temperature of 392 °C. The polyester PX with X ranging from 75 to 95% shows a fairly constant $T_m \approx 340$ °C. As X decreases below 75%, the melting temperature of this polyester increases rapidly. For example, the copolymer P50 has a melting temperature of 437 °C, which is near its decomposition temperature. It can be extrapolated from Figure 1 that the PX copolyesters with $X < 50\%$ have melting temperatures above 450 °C.

We could not observe the DSC endotherms corresponding to nematic–isotropic transitions in the PX copolyesters. Therefore, we used optical microscopy to measure the nematic–isotropic transition temperature (T_{NI}). P100 melts directly to the isotropic liquid at 410 °C. Similarly, the P95 and P90 copolyesters form only isotropic melts. However, the copolyester P85 exhibits a T_m of 355 °C and a mesophase range of 30 °C. (There is a discrepancy in T_m between DSC and optical microscopy due to the wide melting range for this transition.) The P85 polyester exhibits a nematic texture (see Figure 2). Optical microscopy shows that all PX copolyesters with X between

Figure 2. Poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate) (P85) with $X = 85\%$ at 362 °C showing birefringement melt (crossed polars, 100×). The magnification has been reduced 80% for publication.

50% and 85% exhibit a nematic phase. In Figure 1, we can extrapolate from the T_m and the T_{NI} curves to predict that the copolyesters PX with $X < 50\%$ also exhibit liquid crystallinity. In summary, it would appear from the literature that previous researchers did not realize that the HQ/TA/IA copolyesters with high percentages of *m*-phenylene rings are in fact liquid crystalline.

Poly(*p*-phenylene terephthalate-*ter*-*p*-phenylene isophthalate-*ter*-oxybenzoate). Encouraged by our findings that HQ/TA/IA copolyesters with a high percentage of the HQ/IA unit exhibit liquid crystallinity, we pursued the possibility of incorporating HBA into these copolyesters to alternate monomer sense and thereby further lower the melting temperature. At the same time, the inclusion of HBA into the polymer increases the linearity of the polymer chain and would, therefore, be expected to stabilize (widen the temperature range of) the mesophase. We investigated terpolyesters PX-Z having four types of monomers and three types of repeat units, where P, X, and Z are the molar percentages ($P + X + Z = 100\%$). The percentage of HBA (Z) was increased systematically from 10% to 35%, and consequently the sum of X and P decreased from 95% to 65%. These terpolymers are designated PX-Z; the previously discussed PX series becomes PX-0 in this notation.

PX-10. Figure 3 shows a plot of the transition temperature vs the molar percentage of HQ/IA (X) in the terpolyesters PX-10 (containing 10% HBA). Table II gives the thermodynamic properties of these polyesters. The polyester P90-10, which is HQ/IA/10% HBA, melts at 370 °C. When X decreases from 90% to 67.5%, the T_m decreases to a minimum value (321 °C) at $X = 67.5\%$ and

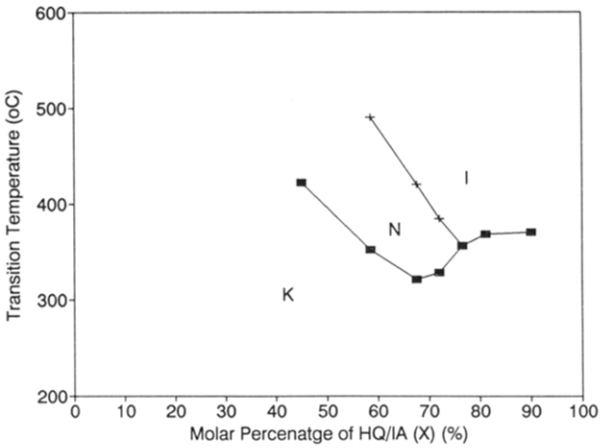


Figure 3. Transition temperatures vs molar percentage of *p*-phenylene isophthalate for terpolyesters containing 10% HBA (PX-10). (See Figure 1 for the definition of the symbols).

Table II. Thermodynamic Properties of HQ/TA/IA/HBA Terpolyester Containing 10 mol % HBA

X (mol %)	X:P	T_m (°C)	ΔH (kJ·mol^{-1})	T_s (°C)	T_m (°C)	T_{NI} (°C)	ΔT (°C)
90.0	100:0	370	6.6	355	360		
81.0	90:10	368	4.7	325	330		
76.5	85:15	356	11.2	321	360		
72.0	80:20	328	4.3	327	340	384	44
67.5	75:25	321	6.7	293	330	420	90
58.5	65:35	352	3.4	370	360	490	130
45.0	50:50	422	2.2	407	440	>500	>60

Table III. Thermodynamic Properties of HQ/TA/IA/HBA Terpolyester Containing 25 mol % HBA

X (mol %)	X:P	T_m (°C)	ΔH (kJ·mol^{-1})	T_s (°C)	T_m (°C)	T_{NI} (°C)	ΔT (°C)
75.0	100:0	350	4.4	330	350		
71.2	95:5	328	4.6	315	325		
67.5	90:10	310	5.0	264	310		
63.7	85:15	315	2.2	289	315	360	45
60.0	80:20	307	3.3	317	310	442	132
56.2	75:25	326	2.9	324	340	470	130
48.8	65:35	330	2.6	306	335	>500	>165
37.5	50:50	415	1.3	409	425	>500	>75

then T_m increases steeply as X decreases below 67.5%. The polyester PX-10 with $X \geq 76.5\%$ forms only an isotropic melt. However, the polyester P72-10 forms a mesophase with a range of 44 °C. When $X < 72\%$, T_{NI} increases as X decreases. The polyester P45-10 melts at 440 °C and exhibits a wide nematic phase.

PX-25. Table III gives the thermal data for the terpolyesters (HQ/TA/IA/25% HBA). Figure 4 shows that the polyester P75-25 melts at 350 °C. The T_m of the PX-25 polymer is fairly constant at about 355 °C when X decreases from 70% to 50%. Additionally, T_m increases steeply when $X < 50\%$; polyester P37.5-25 melts at 415 °C. Optical microscopy shows that polyester P63.7-25 forms a nematic phase with a 45 °C range. The T_{NI} of PX-25 increases as X decreases from 63.7% to 56.2%. The polyester P56-25 HBA has a 130 °C mesophase range. When $X < 56.2\%$, the T_{NI} is above 500 °C.

PX-35. The thermodynamic data of the terpolyesters (HQ/TA/IA/35% HBA) are give in Table IV. Figure 5 shows that the polyester P65-35 melts at 362 °C. When X ranges from 61.8% to 32.5%, the T_m is fairly constant (~375 °C) and the T_{NI} increases as X decreases. For example, the polyester PX-35 forms a nematic phase range of 50 °C when $X = 55.2\%$ and exhibits a 90 °C mesophase range when $X = 52.0\%$. When $X < 48.8\%$, we found that

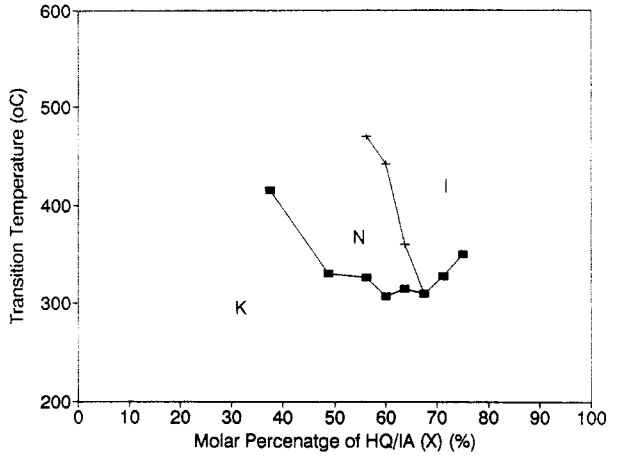


Figure 4. Transition temperatures vs molar percentage of *p*-phenylene isophthalate for terpolyesters containing 25% HBA (PX-25). (See Figure 1 for the definition of the symbols.)

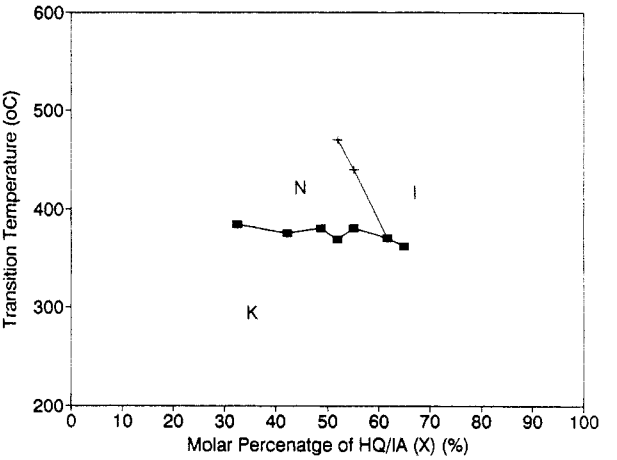


Figure 5. Transition temperatures vs molar percentage of *p*-phenylene isophthalate for terpolyesters containing 35% HBA (PX-35). (See Figure 1 for the definition of the symbols.)

Table IV. Thermodynamic Properties of HQ/TA/IA/HBA Terpolyester Containing 35 mol % HBA

X (mol %)	*X*:*P*	T_m (°C)	ΔH (kJ·mol^{-1})	T_m (°C)	T_{NI} (°C)	ΔT (°C)
65.0	10:0	362	13.9	355		
61.8	95:5	368	9.6	378		
55.2	85:15	380	6.3	390	440	50
52.0	80:20	369	6.8	380	470	90
48.8	75:25	380	7.7	394	>500	>106
42.2	65:35	375	3.6	380	>500	>120
32.5	50:50	384	1.8	398	>500	>102

Table V. Thermodynamic Properties of Annealed Poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate) (HQ/TA/IA)

X (mol %)	*X*:*P*	T_g (°C)	T_m (°C)	ΔH (kJ·mol^{-1})
100.0	100:0	236	396	23.4
95.0	95:5	188	382	20.4
90.0	90:10	189	381	17.4
85.0	85:15	182	380	18.2
80.0	80:20	178	371	16.0
75.0	75:25	176	380	14.6
65.0	65:35	175	421	9.8
50.0	50:50			

T_{NI} is above the decomposition temperature and could not be determined.

Thermal Treatment. Tables V–VII give the thermal analysis data for the annealed polymer samples of copolyester PX and terpolyester PX-Z. The glass transition temperatures for these polyesters are about 180 °C. Figure

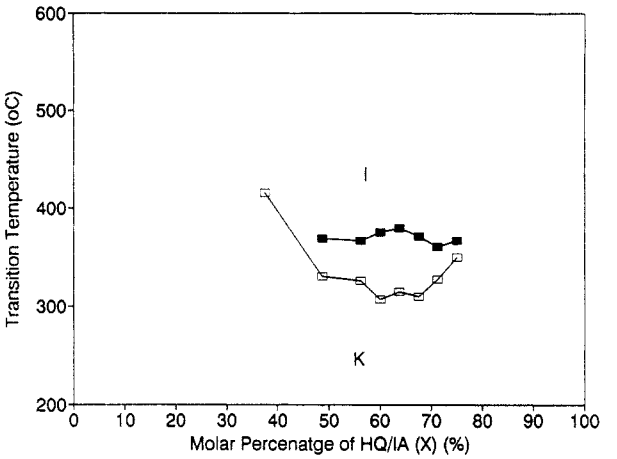


Figure 6. Melting temperature vs molar percentage of *p*-phenylene isophthalate for polyester containing 25% HBA (PX-25). The open squares indicate the melting temperature for the as-prepared sample; the solid squares indicate the melting temperature for the annealed sample.

Table VI. Thermodynamic Properties of Annealed HQ/TA/IA/HBA Terpolyester Containing 10% HBA

X (mol %)	*X*:*P*	T_g (°C)	T_m (°C)	ΔH (kJ·mol^{-1})
90.0	100:0	171	380	15.0
81.0	90:10	169	357	14.1
76.5	85:15	176	375	17.5
72.0	80:20	182	378	14.6
67.5	75:25	172	368	12.2
58.5	65:35	184	378	8.2
45.0	50:50			

Table VII. Thermodynamic Properties of Annealed HQ/TA/IA/HBA Terpolyester Containing 25 mol % HBA

X (mol %)	*X*:*P*	T_g (°C)	T_m (°C)	ΔH (kJ·mol^{-1})
75.0	100:0	181	367	13.2
71.2	95:5	161	360	12.5
67.5	90:10	169	371	12.4
63.7	85:15	163	379	10.4
60.0	80:20	177	375	9.0
56.2	75:25	147	367	9.0
48.8	65:35	150	369	7.7
37.5	50:50			

6 shows a comparison of melting temperatures for the annealed and virgin samples in terpolyesters PX-25. When *X* is greater than 63.7%, the annealed samples have higher T_m's than their respective T_{NI}'s; hence, the mesophase was not observed. Generally, the annealed sample shows a higher T_m than the virgin sample. Moreover, the enthalpy change of the annealed samples is much higher than that in the virgin sample. These results indicate that the annealing process increases the fraction of crystallinity in these polymers.

We demonstrate the annealing effect on the melting temperature by a series of DSC traces for polyester P56.2-25 (Figure 7). Scan a is the first heating for the annealed sample, and scan b is the second heating right after the first measurement. Scan c is the first heating of the virgin sample, and scan d is the second heating of the same sample. It is obvious that the annealed sample has a higher melting temperature and enthalpy change than the virgin sample. On the second heating of the annealed sample, the polyester has the same melting temperature as the virgin sample. A glass transition temperature can be observed on the second heating of the polymer samples. These results suggest that one can melt-process the virgin LC polyester at a somewhat lower temperature and then increase the polyester crystallinity and T_m by annealing.

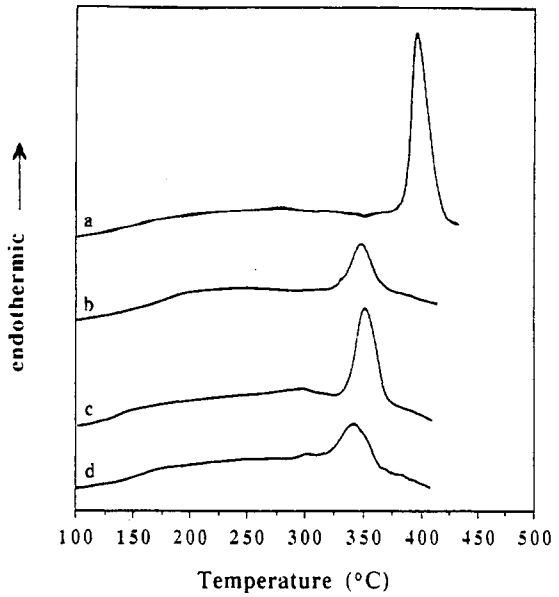


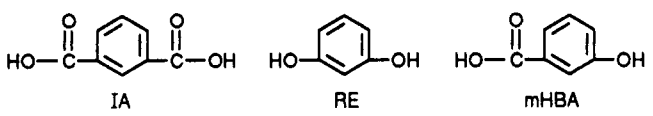
Figure 7. DSC traces of terpolyester P56.2-25 showing the annealing effect and a thermal history dependence: (a) the first heating scan for the annealed sample (annealed at 300 °C for 10 h); (b) the second heating scan for the same annealed sample; (c) the first heating scan for the as-prepared sample; (d) the second heating scan for the same as-prepared sample.

Thermal Stability. All of these polyesters are thermally stable (the 5% weight loss temperatures were found to be higher than 450 °C). These results indicate that the polyesters containing *m*-phenylene units have thermal stabilities similar to those of polyesters containing only *p*-phenylene units.

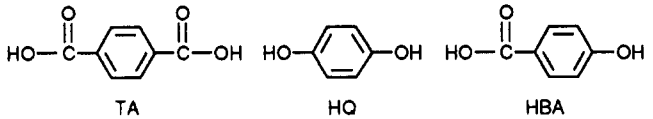
Discussion

Many research groups have incorporated *m*-phenylene units into LCPs to modify physical properties by using basically three *m*-phenylene monomers: isophthalic acid (IA), resorcinol (RE), and *m*-hydroxybenzoic acid (mHBA).[4,9-12] In order to understand the relationships among these known polyesters, we classify the possible combinations obtained from these basic building blocks and the common *p*-phenylene monomers tabulated below:

m-phenylene



p-phenylene



These polyesters are classified into five groups according to the number of *m*-phenylene rings in the polymer chain: (i) three *p*-phenylene units (i.e., TA, HQ, HBA); (ii) two *p*-phenylene units and one *m*-phenylene unit; (iii) one *p*-phenylene unit and one *m*-phenylene unit; (iv) one *p*-phenylene unit and two *m*-phenylene units; (v) three *m*-phenylene units (i.e., IA, RE, mHBA). Jackson studied the group (i) copolyesters (TA/HQ/HBA) and found that this copolyester has a melting temperature greater than 500 °C.[9] The group (iv) and (v) copolyesters contain more than 50 mol % of *m*-phenylene units and are unlikely to form LCPs. Therefore, most LCP research has been focused on the groups (ii) and (iii).

All of the group (ii) and (iii) polymers have been synthesized, and most of them have been studied in order to exploit liquid crystallinity. Erdemir et al. discovered that the IA/HQ/HBA formed only an isotropic melt if the percentage of HQ/IA is greater than 67%.[4] Jin et al. found that TA/RE/HBA loses liquid crystallinity if the percentage of TA/RE units is greater than 33%.[10] Lenz et al. synthesized poly(chloro-*p*-phenylene-*co*-*m*-phenylene terephthalate) and found that, in order to retain liquid crystallinity, the percentage of *m*-phenylene terephthalate cannot exceed 60%.[11] Jackson reported that HQ/TA/mHBA containing more than 50% of mHBA forms isotropic melts.[9] Rosenau-Eichin et al. studied HBA/mHBA and observed that these polyesters with less than 50% HBA form only isotropic melts.[12] These findings indicate that the inclusion of a *m*-phenylene unit in polymer main chain lowers the melting temperature and also decreases the mesophase range. These results lead one to conclude that a high percentage of *m*-phenylene rings in the aromatic polyesters inhibits mesophase formation. However, our results indicate that, in certain circumstances, a high percentage of nonlinear monomer units can be incorporated into LCPs. The poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate) with as much as 85% *p*-phenylene isophthalate exhibits a melting temperature of 355 °C and a mesophase range of 30 °C. The copolyesters with lower percentages of isophthalate exhibit wider mesophase ranges. If—and this is a big uncertainty—we assume that in these polymerizations there are no sequence preferences within this monomer set (random distributions), then these results suggest that a critical local anisotropy of the chain contour is the key to liquid crystal formation in this class of polymers. Exactly how this local anisotropy is connected to other critical characteristics of the chain (e.g., persistence length[13]) is not clear.

In addition to the nonlinear *m*-phenylene units, many viable nonlinear monomers have been exploited to improve the tractability of LCPs. For example, crankshaft 2,6-naphthalene-based LCPs (Vectra) are a commercial success.[14] Our previous work showed that LCPs containing 100% 2,5-thiophene and *p*-phenylene units are thermally stable.[2] The intermediate bend angle in the 2,5-thiophene unit (148°) lowers T_m and maintains a rather wide mesophase range. This result is consistent with the findings here suggesting that isophthalic acid-based LCPs are quite stable. It is noteworthy to point out that the onset of mesophase formation in the polyesters PX and PX-Z is associated with a *X*:*P* of roughly 85:15. As the percentage of HBA increases, the percentage of *p*-phenylene isophthalate repeat units (*X*) naturally decreases and the HBA expands the mesophase range.

Knowing that high contents of nonlinear monomers are compatible with liquid crystallinity, we are able to expand the design window for high-performance LCP materials. The high percentage of isophthalic acid decreases the melting transition dramatically, but it also impairs local chain parallelism and decreases the mesophase range. When the linear AB difunctional monomer *p*-hydroxybenzoic acid is incorporated into the chain, it promotes local chain parallelism and increases mesophase stability. One molecular design objective for LCPs is retention of highly interactive lateral molecular packing to enhance (compressive) mechanical strength. Another is having a reasonable melting temperature for processing without LCP decomposition. It was suggested that the optimal LCP composition would contain a maximum amount of linear monomers, yet still keep the T_m below 350 °C.[14] It

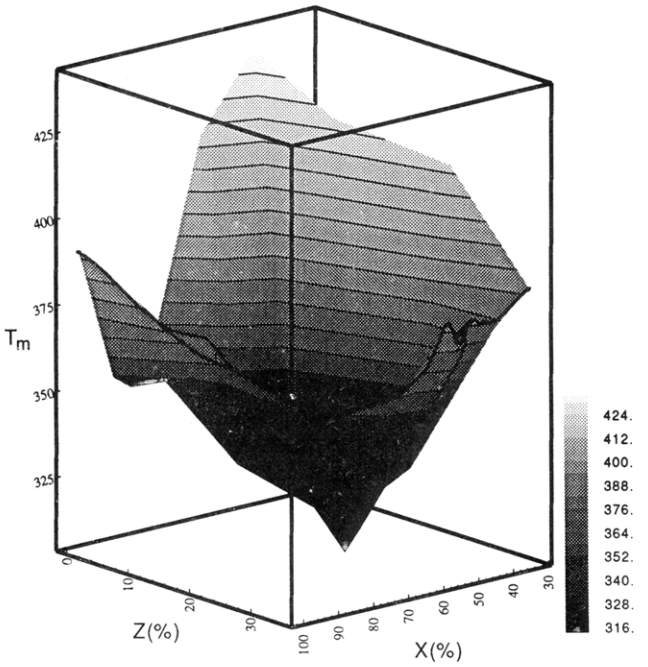


Figure 8. 3D contour phase diagram showing melting temperature vs molar percentages of X and Z in polyesters PX-Z. The magnitude of the melting temperature is represented by the darkness of the contour surface.

is interesting to note that the PX-10 and PX-25 polyesters have lower T_m's than PX. Moreover, the T_{NI} of PX-10 and PX-25 increases more rapidly than that of PX. Therefore, the polyester PX-Z exhibits a wider mesophase range than polyester PX. The incorporation of HBA randomizes the monomer sense distribution and hence lowers the melting temperature presumably without much influence on the local chain parallelism. The PX-35 polyesters have T_m's at about 380 °C and prominent glass transition temperatures. The polyesters PX-Z with lower HBA contents ($Z < 25\%$) show lower T_m's than those with higher HBA percentages. This tractable mesophase domain is summarized in the 3D plot of T_m vs composition in Figure 8. The T_m of PX-Z was plotted against X and Z, and the magnitude of T_m is indicated by the darkness of the contour surface. It is obvious that the minimum T_m appears at P67-25. As PX-Z moves beyond the contour minimum centered at P67-25, its T_m increases and exceeds the optimum processing temperature (350 °C). Therefore, the polyesters PX-Z containing approximately 25% of HBA appear to have the optimal molar percentage of HBA for melt processing in a nematic phase below 350 °C.

Conclusions

Poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate) with molar percentages of *p*-phenylene isophthalate units ranging from 75% to 95% have melting temperatures around 350 °C. The poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate) which contains as much as 85% isophthalate exhibits a melting temperature of 355 °C and a mesophase range of 30 °C. The copolyesters with lower percentages of isophthalate exhibit wider mesophase ranges. These results indicate that copolyesters with high contents of isophthalate units can form liquid crystalline melts. Thermogravimetric analysis results show that poly(*p*-phenylene terephthalate-*co*-*p*-phenylene isophthalate) has good thermal stability up to 450 °C. Terpolyesters composed of terephthalic acid, isophthalic acid, hydroquinone, and *p*-hydroxybenzoic acid exhibit compositions with melting temperatures below 350 °C and wide mesophase ranges. Our findings may have practical implications: liquid crystalline polyesters with high contents of nonlinear monomers can be melt processed near 350 °C. Generally, our findings with various ratios of nonlinear to linear repeat units argue for the concept that a critical local shape anisotropy is a prerequisite for establishing liquid crystalline phases, and a wide combination of monomers may be used to effect this critical anisotropy.

Acknowledgment. The research was supported by subcontracts from the University of Connecticut and the University of Pennsylvania (DARPA/ONR Contract NO. N0014-86-K-0772) and Los Alamos (DOE Subcontract 9-X59-7021-R-1). We thank G. R. Quinting for constructing the 3D contour plot.

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