Kinetics of Mesophase Transitions in Thermotropic Copolyesters. 4. Pendant Side-Group Effect

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ABSTRACT: A series of five poly(phenyl-*p*-phenylene terephthalate)-*co*-(1-phenylethyl-*p*-phenylene terephthalate) copolyesters having different compositions of *p*-benzenedicarboxylic acid (TPA), phenylhydroquinone (PHQ), and (1-phenylethyl)hydroquinone (PEHQ) have been studied via wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC). A systematic analysis of the crystal unit-cell parameters indicates that they change continuously with composition. Nonisothermal DSC experiments lead to a complete phase diagram of both solidus and liquidus lines as a function of PHQ (or PEHQ) composition in the copolyesters. The phase diagram indicates solid solution behavior of the isodimorphic type in this series of copolyesters. Isothermal crystallization kinetics reveals two transition processes when the experiments were conducted below the solidus line: a fast transition process occurs during quenching; and a slow transition process takes place during subsequent annealing. The influence of the composition, and, therefore, the pendant side-group effect, on the transition kinetics can be observed.

Introduction

We have been studying the mesophase transition behavior in thermotropic copolyesters based on wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) experimental observations.[1-3] When the copolyesters consist of comonomers with different monomer lengths and solid kinks, the regularity along the chain direction (usually defined as the *c*-axis) is disturbed. As long as the ring groups (phenylene and/or naphthylene) in the chains are randomly oriented, a hexagonal packing is possible, allowing relatively large chain mobility.[2] On the other hand, the regularity of the lateral packing can be disturbed if one introduces pendant side groups.[3] In our study of a poly(phenyl-*p*-phenylene terephthalate)-*co*-(1-phenylethyl-*p*-phenylene terephthalate) copolyester consisting of *p*-benzenedicarboxylic acid (TPA), phenylhydroquinone (PHQ), and (1-phenylethyl)hydroquinone (PEHQ) (TPA/PHQ/PEHQ, 50/25/25), we found that the WAXD pattern of this copolymer shows periodic *c*-axis order since it contains comonomers with equal lengths.[3] Surprisingly, this copolymer is still highly crystalline. The quenched and annealed crystal forms both have monoclinic lattice structures but show different unit-cell sizes.[3] Kinetics of both the fast crystallization and the slow annealing processes can be traced, indicating the different transition mechanisms.[3] Recently, studies of the crystal structure, chain conformations in the crystal lattice, and thermal transitions of the TPA/PHQ/PEHQ copolyesters have also been conducted by Blackwell's and Porter's research groups.[4-6] Nevertheless, the effect of these pendant side groups in this copolyester is still largely unknown.

We have synthesized a series of TPA/PHQ/PEHQ copolyesters with different comonomer compositions, namely, TPA/PHQ/PEHQ in the following compositions: 50/50/0, 50/37.5/12.5, 50/25/25, 50/12.5/37.5, and 50/0/50. From WAXD experiments, their crystal structures can be determined. The change of these parameters with composition leads to a clear indication of the effect of these pendant side groups. Thermal characterization of these copolyesters reveals their mesophase transition behavior. Both thermodynamic and kinetic effects can thus be discussed. In this paper, we report our experimental observations and describe our understanding of the effect of these pendant side groups in this series of copolyesters.

Experimental Section

Materials and Samples. Copolyesters consisting of TPA/PHQ/PEHQ with different compositions of PHQ and PEHQ were synthesized in our laboratory. The synthetical procedures for (1-phenylethyl)hydroquinone (PEHQ) and the copolymers were followed as described in the literature and patents.[7] In order to further increase the molecular mass, solid-state polymerization was carried out by heating these polymers to 550 K for 16 h under a nitrogen atmosphere. The detailed compositions in terms of the amounts of TPA/PHQ/PEHQ are 50/50/0, 50/37.5/12.5, 50/25/25, 50/12.5/37.5, and 50/0/50. The statistical molar masses of the repeating units are 316.3, 323.3, 330.3, 337.3, and 344.3 g/mol, respectively (if one counts each comonomer unit as the basic unit, the statistical molecular masses for these copolyesters have to be divided by 2).

Powder samples were prepared and put into DSC pans. The sample weights were controlled in a range of 15-20 mg. All pan weights were within a deviation of ±0.002 mg.

In order to study the crystal unit-cell structures in the copolyesters, melt-spun fibers from their nematic phases were prepared in our laboratory. The diameter of a single fiber was about 1 denier. The draw ratio of the fiber was about 50× during spinning. The fibers were annealed at 580 K for 4 h at fixed lengths. Specimens for X-ray analysis were prepared as parallel bundles of ~50 fibers.

Wide-Angle X-ray Diffraction (WAXD). X-ray experiments were carried out on a Rigaku X-ray generator with a 12-kW rotating anode as the source of the incident X-ray beam. The point-focused beam was monochromatized with a graphite crystal. X-ray fiber diagrams were recorded on a vacuum camera. The *d*-spacings were calibrated with silicon powder (325-mesh size).

Differential Scanning Calorimetry (DSC). DSC measurements were carried out on a Perkin-Elmer DSC-2. The DSC was carefully calibrated for temperature and heat flow following the standard procedures we apply in our laboratory.[1] Bulk samples were used to study nonisothermal and isothermal transition kinetics. For the nonisothermal experiments, the samples were heated to 10 K above their transition temperatures and held for

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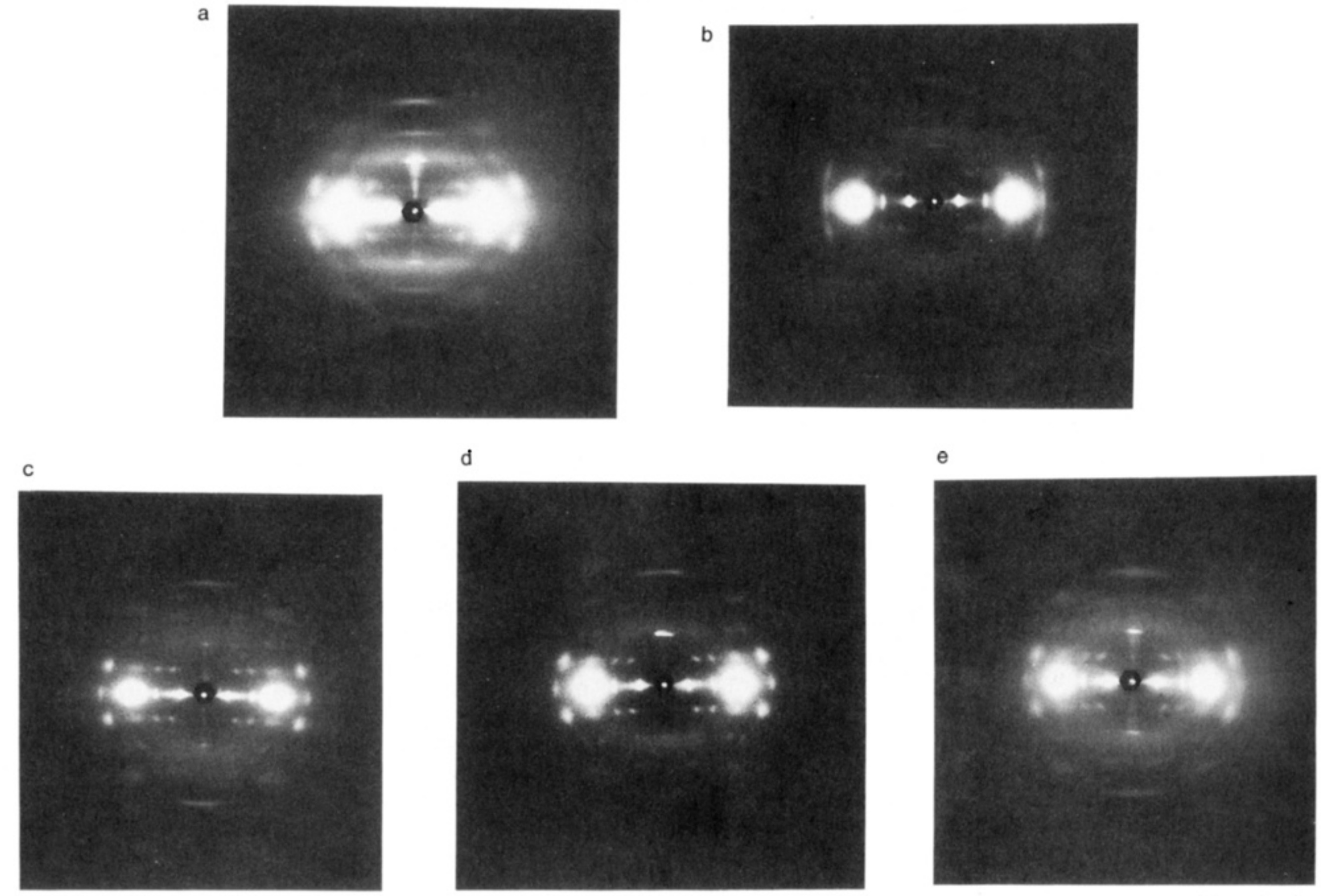

Figure 1. Wide-angle X-ray diffraction photographs of the TPA/PHQ/PEHQ copolyester fibers with compositions of (a) 50/50/0, (b) 50/37.5/12.5, (c) 50/25/25, (d) 50/12.5/37.5, and (e) 50/0/50.

1 min. Then the samples were cooled to room tempeature at different rates. The samples were subsequently reheated to above their transition temperatures again at 10 K/min. For the isothermal experiments, the samples followed the same initial heating procedure. Then the samples were quickly cooled to the predetermined crystallization temperature, T_c, and kept there for different fixed time periods, t_a. The samples were reheated to above their transition temperatures at a 10 K/min heating rate.

Peak temperatures were used as T_d. When two transition peaks were observed during heating, their temperatures were distinguished to be T_d(h) for the high-temperature peaks and T_d(l) for the low-temperature peaks. In order to avoid any influence of previous thermal history, every sample was used only once.

Results and Analysis

Determination of Crystal Unit Cells. Figure 1a shows a typical fiber diagram of the crystal diffraction photograph for the annealed TPA/PHQ/PEHQ (50/50/0) copolyester. Along the equator, there are five diffraction spots that can be identified. Along the meridian, periodic diffraction spots can be clearly observed up to four layers. Both the odd- and even-numbered layers show diffraction spots, but the spots on the even layers are stronger than those on the odd layers. On the quadrants, there are three spots along the first and second layers and one along the third layer. This leads to a total of 16 diffraction spots as shown in Figure 1a. Note that one may also find additional diffraction spots, which appear farther away from the center of the incident beam spot. However, they represent the crystal planes with large Miller indices (i.e., small *d*-spacings), and, therefore, those spots were not taken into account. A detailed listing of the 16 experimental 2θ angles, *d*-spacings, and their corresponding intensities of the diffraction spots is given in Table I.

Table I
Experimental and Calculated Crystallographic Parameters of a Monoclinic (Pseudoorthorhombic) Crystal Unit Cell for Annealed TPA/PHQ/PEHQ (50/50/0) Copolyester Fibers[a]

	2θ, deg		*d*-spacing, Å		
(*hkl*)	exptl	calc	exptl	calc	intensity[b]
(100)	6.689	6.646	13.21	13.30	vs
(200)	13.39	13.31	6.613	6.650	s
(210)	16.56	16.51	5.353	5.369	s
(300)	20.22	20.03	4.392	4.433	vs
(400)	26.93	26.81	3.311	3.325	m
(001)	7.160	7.157	12.35	12.35	w
(101)	9.766	9.773	9.056	9.050	w
(201)	15.10	15.13	5.867	5.855	m
(401)	27.75	27.78	3.215	3.211	m
(002)	14.39	14.34	6.155	6.175	s
(102)	15.88	15.82	5.582	5.600	w
(202)	19.80	19.62	4.483	4.525	w
(122)	25.37	25.22	3.511	3.531	w
(003)	21.59	21.59	4.116	4.116	w
(213)	27.60	27.30	3.232	3.267	w
(004)	29.15	28.92	3.064	3.087	s

[a] The calculated data listed are based on a monoclinic (pseudoorthorhombic) unit cell with $a = 13.30$ Å, $b = 9.100$ Å, $c = 12.35$ Å, and $\gamma = 90.0°$. [b] The intensities are semiquantitatively estimated via a microdensitometer. The intensities are classified as very strong (vs), strong (s), medium (m), and weak (w).

To determine the size and shape of the crystal unit cell for the fiber diagram as shown in Figure 1a, the starting point was to find an *hk*0 reciprocal lattice net, namely, a parallelogram with edges a^* by b^* that accounts for the values determined from the equatorial diffractions. The smallest distance between the center of the X-ray incident

Table II
Experimental and Calculated Crystallographic Parameters of a Monoclinic Crystal Unit Cell for Annealed TPA/PHQ/PEHQ (50/0/50) Copolyester Fibers[a]

	2θ, deg		d-spacing, Å		
(hkl)	exptl	calc	exptl	calc	intensity[b]
(100)	6.993	6.992	12.64	12.64	vs
(200)	14.02	14.01	6.317	6.321	s
(120)	18.30	18.30	4.847	4.847	vs
(300)	21.14	21.08	4.201	4.214	vs
(400)	28.20	28.23	3.164	3.160	m
(001)	7.206	7.210	12.27	12.26	w
(011)	11.90	12.00	7.436	7.374	m
(111)	15.26	15.34	5.805	5.776	m
(221)	21.48	21.27	4.137	4.176	m
(311)	26.93	26.85	3.311	3.320	m
(002)	14.28	14.45	6.201	6.130	s
(102)	16.17	16.07	5.482	5.516	w
(122)	23.00	23.40	3.867	3.802	w
(202)	25.67	25.65	3.470	3.473	w
(003)	21.88	21.75	4.063	4.087	w
(103)	22.97	22.87	3.872	3.888	w
(123)	28.67	28.57	3.114	3.124	w
(004)	29.04	29.13	3.075	3.065	m

[a] The calculated data listed are based on a monoclinic unit cell with $a = 13.30$ Å, $b = 9.710$ Å, $c = 12.26$ Å, and $\gamma = 71.9°$. [b] The intensities are semiquantitatively estimated via a microdensitometer. The intensities are classified as very strong (vs), strong (s), medium (m), and weak (w).

beam and the diffraction spot corresponds to the lowest index. The l index of each diffraction can also be determined by the layer line on which the diffraction lies, and the c crystallographic axis is readily determined from the layer line spacings. After the least-squares refinements via computer, it was found that the crystal unit cell of the annealed TPA/PHQ/PEHQ (50/50/0) copolyester was monoclinic with $a = 13.30$ (±0.05) Å, $b = 9.100$ (±0.04) Å, $c = 12.35$ (±0.05) Å, and $\gamma = 90.0°$ (±0.04°). This crystal lattice can also be recognized as a pseudoorthorhombic lattice structure. The unit-cell parameters lead to a calculated volume of 1495 Å^3. In each unit cell four chains are contained. The calculated crystallographic density is thus 1.406 g/cm^3.

For the TPA/PHQ/PEHQ (50/0/50) copolyester, the crystallographic unit-cell parameters were determined for annealed fibers using the WAXD fiber diagram shown in Figure 1e. Table II lists detailed experimental and calculated 2θ angles, d-spacings, and intensities for the fibers. The unit cell of this sample was monoclinic with $a = 13.30$ (±0.05) Å, $b = 9.710$ (±0.04) Å, $c = 12.26$ (±0.05) Å, and $\gamma = 71.9°$ (±0.3°). Similarly, the unit cells of the annealed TPA/PHQ/PEHQ (50/37.5/12.5) and (50/12.5/37.5) fibers were determined. Their WAXD fiber diagrams are shown in parts b and d of Figure 1, respectively. These values are combined with the unit-cell data of the TPA/PHQ/PEHQ (50/25/25) copolyester reported in our previous publication (see Figure 1c)[3] and are given in Table III, which lists all the unit-cell parameters (a, b, c, and γ), crystallographic volume (V_c), and crystallographic densities (ρ_c) for the annealed fiber samples of this series of copolyesters. It is evident that the a-axes of these unit cells are essentially unchanged, while the b-axes expand with an increase of the PEHQ composition of up to 50% and then stay constant with any further increase of the PEHQ composition. The c-axes correspondingly decrease. Of special interest is the change of the angle γ in these monoclinic lattices from 90° at 50% and 37.5% PHQ compositions to 71.9° at 0% PHQ composition (or 50% PEHQ composition). Furthermore, the crystallographic volume of the unit cell reaches a maximum at a PEHQ composition of 25% and then decreases with further increase of this component. The crystallographic density, on the other hand, initially varies with the PEHQ compositions and increases with any further increase of the PEHQ composition (>25%).

Table III
Crystallographic Unit-Cell Parameters for the Annealed TPA/PHQ/PEHQ Copolyester Fibers with Different Compositions[a]

	TPA/PHQ/PEHQ				
	50/50/0	50/37.5/12.5	50/25/25	50/12.5/37.5	50/0/50
a, Å	13.30	13.30	13.30	13.30	13.30
b, Å	9.100	9.200	9.719	9.700	9.710
c, Å	12.35	12.32	12.35	12.29	12.26
γ, deg	90.0	90.0	78.0	72.3	71.9
V_c, Å^3	1495	1508	1562	1511	1505
ρ_c, g/cm^3	1.406	1.425	1.405	1.484	1.520

[a] The unit-cell data of TPA/PHQ/PEHQ (50/25/25) are quoted from ref 3.

Nonisothermal Transition Behavior. After the copolyester samples were heated to above their transition temperatures (T_ds), they were cooled to room temperature at a cooling rate of 10 K/min. During the cooling, exothermic crystallization processes occurred. The temperatures where exothermic peaks appear vary with the composition. It is interesting to find that with an increase of the PEHQ composition, the exothermic transition temperature monotonously decreases up to 37.5% of PEHQ composition. Further increase of PEHQ in the composition leads to an increase of the transition temperature. For example, the transition temperature during cooling for TPA/PHQ/PEHQ (50/0/50) is at 574 K at a 10 K/min cooling rate. This temperature decreases to 565 K for TPA/PHQ/PEHQ (50/25/25) and further reduces to 559 K for TPA/PHQ/PEHQ (50/12.5/37.5). For TPA/PHQ/PEHQ (50/0/50), this temperature increases to 575 K. The subsequent heating of these copolyester samples at a heating rate of 10 K/min shows an endothermic process, indicating the crystal to liquid crystal phase transition. The change of this temperature with composition more or less corresponds to that during cooling. Both sets of the transition temperatures observed from cooling and heating may serve as solidus and liquidus lines in the phase diagram of the copolyesters, as shown in Figure 2. Nevertheless, it has to be noted that this phase diagram does not represent thermodynamic equilibrium and contains kinetic effects (nucleation during the crystallization, small crystal sizes, and existence of defects in the crystals[3]). When the transition temperatures are extrapolated to zero cooling rate, the solidus line in this phase diagram is closer to the liquidus line when compared with that at a cooling rate of 10 K/min (dashed line in Figure 2). The basic shape of the phase diagrams, however, is essentially unchanged.

Isothermal Kinetic Studies. Figures 3–6 show four sets of DSC heating traces for the TPA/PHQ/PEHQ compositions of (50/50/0), (50/37.5/12.5), (50/12.5/37.5), and (50/0/50) crystallized at 565, 557, 550, and 563, respectively. Two transition processes are clearly shown, as indicated in our previous publications.[1-3] The fast transition process is characterized by a constant or slow decrease of the heat of transition and transition temperature as the annealing time is increased, while the slow transition process shows continuous increases in these two parameters. Figures 7 and 8 represent the relationships between the heats of transition and logarithmic time at

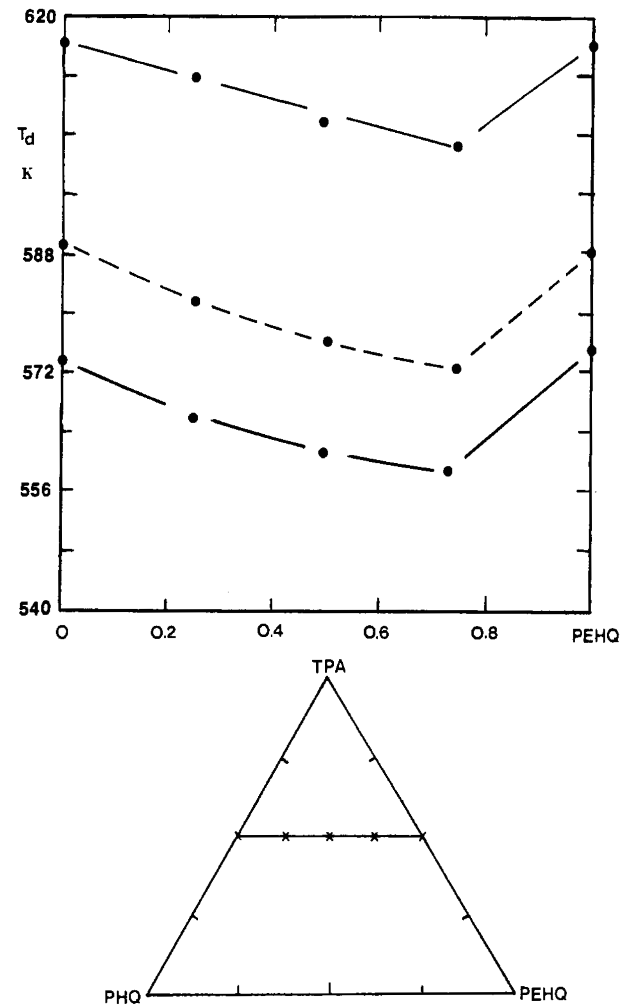

Figure 2. Phase diagram of the TPA/PHQ/PEHQ copolyesters. Since the composition of TPA is not changed in the samples, a two-dimensional phase diagram can be plotted. The top curve is the liquidus line a 10 K/min heating rate, the bottom curve is the solidus line at 10 K/min cooling rate, and the dashed line is the solidus line extrapolated to 0 K/min cooling rate (see text).

different temperatures for both the fast and slow transition processes of all the copolyesters studied. The crystallization temperatures for each copolyester have been purposely chosen to keep the same temperature difference between extrapolated crystallization temperatures during cooling at 0 K/min and crystallization temperatures in the isothermal experiments. For example, the isothermal crystallization temperature of (50/0/50) was 563 K, which is 25 K from its extrapolated crystallization temperature during cooling (588 K); namely, ΔT_c = 25 K. All of the other four copolyesters were held at a crystallization temperature by using the same ΔT_c. It is evident that from Figure 7 the initial heats of transition of the fast processes for these five copolymers range between 2.8 and 4.0 kJ/mol. The sequence of the heats of transition (from largest to smallest) for these copolyesters is TPA/PHQ/PEHQ (50/0/50), followed by (50/12.5/37.5) and (50/25/25), then (50/37.5/12.5), and finally (50/50/0). Furthermore, the heat of transition of the fast process in the case of (50/50/0) decreases with increasing time. For example, it is only about 50% of the initial value after annealing for 8 h. With an increase of the PEHQ composition, a decrease of these heats of transition gradually ceases, as shown in Figure 7. It is clear that after the composition TPA/PHQ/PEHQ (50/25/25) little decrease of the heats of transition for the fast process can be observed. On the other hand, the slow transition processes exhibit increases of their heats of transition with time as shown in Figure 8. Among them, TPA/PHQ/PEHQ (50/0/50) shows the fastest increase. It is followed by (50/12.5/37.5), (50/25/25), and (50/37.5/12.5). Finally, (50/50/0) has the slowest increase in the heat of transition of its slow transition process.

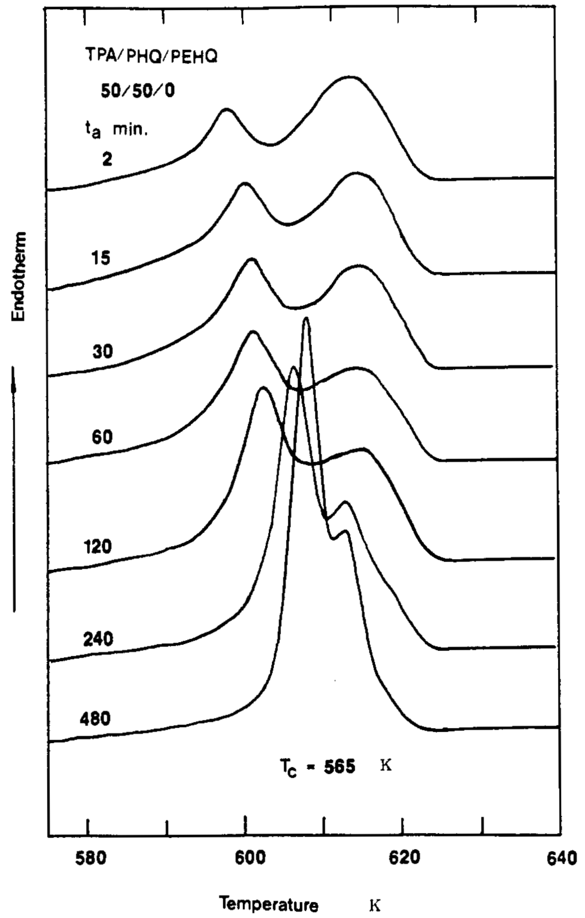

Figure 3. Set of DSC heating traces for the TPA/PHQ/PEHQ copolyester (50/50/0) after isothermal crystallization at T_c = 565 K for different times.

Figures 9 and 10 represent the relationships between the transition temperatures and logarithmic time for both fast and slow processes of all the copolyesters. It is evident that, for the fast transition processes, their transition temperatures (T_d(h)) keep constants within experimental errors (±1 K) for the 25% PEHQ composition and above. The transition temperature of TPA/PHQ/PEHQ (50/50/0) slightly decreases after t_a = 2 h, while that of (50/37.5/12.5) decreases after t_a = 4 h. The transition temperatures of the slow transition processes for these copolyesters exhibit a linear increase with logarithmic time, as shown in Figure 10. Among these, TPA/PHQ/PEHQ (50/0/50) has the fastest increase (steepest initial slope in Figure 10). It is followed by the sequence (50/12.5/37.5), (50/25/25), (50/37.5/12.5), and (50/50/0). Please note that in the cases of (50/50/0) and (50/37.5/12.5) there are slope changes at t_a = 2 and 4 h, respectively.

Discussion

This set of TPA/PHQ/PEHQ copolyesters with different PHQ/PEHQ ratios has provided a unique opportunity to study the pendant side-group effect on the crystalline structure and the mesophase transition behavior. Our discussion focuses on two questions. First, what structural information can be provided by our WAXD

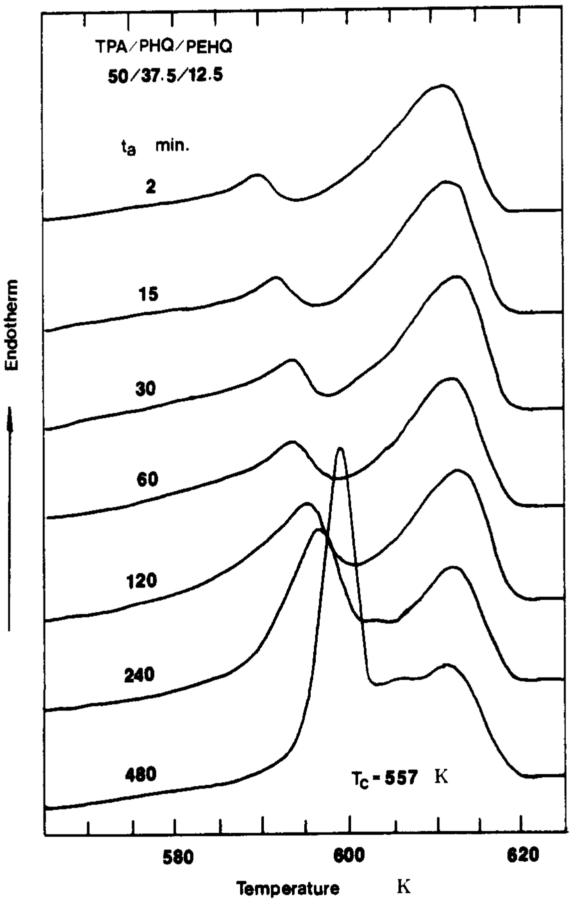

Figure 4. Set of DSC heating traces for the TPA/PHQ/PEHQ copolyester (50/37.5/12.5) after isothermal crystallization at T_c = 557 K for different times.

results and the phase diagram (Figure 2)? Second, how does the pendant side group affect the kinetics of the mesophase transition in these copolyesters?

From Figure 2, it is quite evident that this phase diagram is an indication of solid solution behavior of the isodimorphic type. This implies that both PHQ and PEHQ comonomer units are totally mixed with TPA in the melt, as well as in the crystalline state. This should not be too surprising since these comonomers are chemically linked by covalent bonds. No matter whether they prefer to associate with each other or not (i.e., are compatible or not), these comonomers cannot get away from each other as long as they are randomly distributed along the chains. It is interesting to compare this phase diagram with those of other copolyesters, such as poly(ethylene terephthalate-*co*-*p*-oxybenzoate) (PET/PHB) and poly(oxy-1,4-phenylenecarbonyl-*co*-oxy-2,6-naphthaloyl) (HBA/HNA). For the PET/PHB copolyesters it has been reported that two glass transition temperatures coexist in a wide composition region between about 25 and 80% of PHB composition.[8-14] The two T_g s differ by about 100 K. The melting transition also shows signs of a eutectic phase separation or isodimorphism with a minimum in melting temperature at about 60–70% PHB composition, 60 K below the melting temperature of PET. Recently, it has been reported that the PET/PHB system shows phase separation in the solid states. Furthermore, even in the "liquid" states above their crystal melting transitions, these two components still behave as a dual chemdomain system.[15-19] It is now a common understanding that in this series of copolyesters the segmental composition significantly deviates from randomness. Therefore, it is a chemically complicated system.

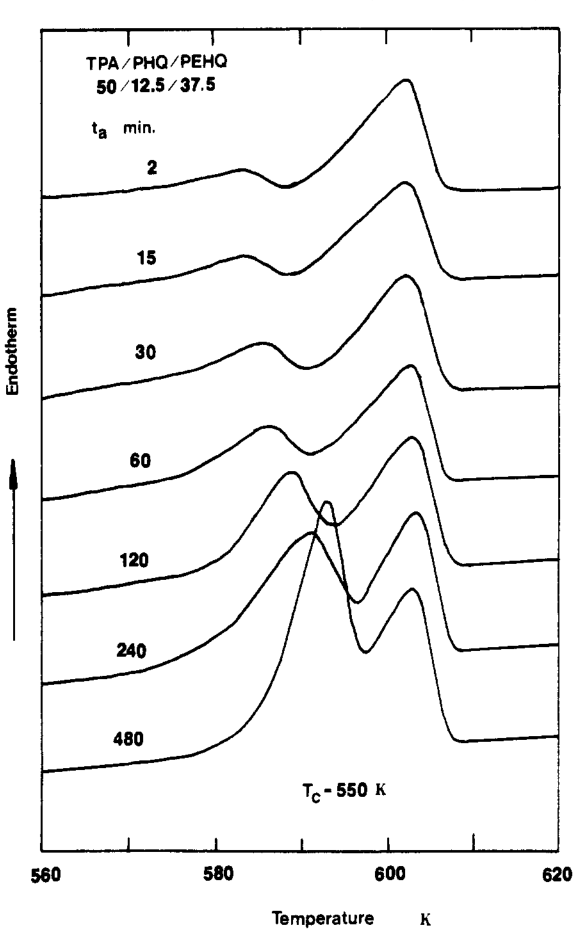

Figure 5. Set of DSC heating traces for the TPA/PHQ/PEHQ copolyester (50/12.5/37.5) after isothermal crystallization at T_c = 550 K for different times.

On the other hand, in the case of HBA/HNA copolyesters only one glass transition temperature seems to exist for each composition although these glass transitions sometimes are rather broad.[20] For the transitions from solid to nematic liquid states, isodimorphism can apparently be obtained[20-22] with a minimum transition temperature at around 58% composition of HBA (liquidus line). The transitions from their nematic to solid states can be observed through the changes of the exothermic peak transition temperatures with compositions (solidus line). The solidus line has been found to be more or less parallel to the change of the transition temperatures along the liquidus line.[1] This indicates that the HBA/HNA copolyesters seem to follow a mixed-crystal phase diagram of isodimorphism although this phase diagram again does not represent thermodynamic equilibrium. It has also been pointed out that this series of copolyesters shows random distribution sequences for these two comonomers.[23-27] The question still largely remains: how do these copolyesters crystallize? Hanna and Windle have proposed a chain-packing model in the mesophase structure, which is based on a matching of order of the monomer units between adjacent molecules.[28] The tendency for further ordering by interchain transesterification at higher temperatures leads to domains with greatly increased chain registration.[29]

Turning back to the TPA/PHQ/PEHQ copolyesters, the phase diagram itself has indicated a mixed crystal of the isodimorphic type. Our WAXD results show that TPA/PHQ and TPA/PEHQ units can coexist in a single phase in both liquid and solid states. The two structural units, TPA/PHQ and TPA/PEHQ, are cocrystallized into a single crystallographic unit cell. From Table III, it is evident that the unit-cell sizes and angles (γ) continuously

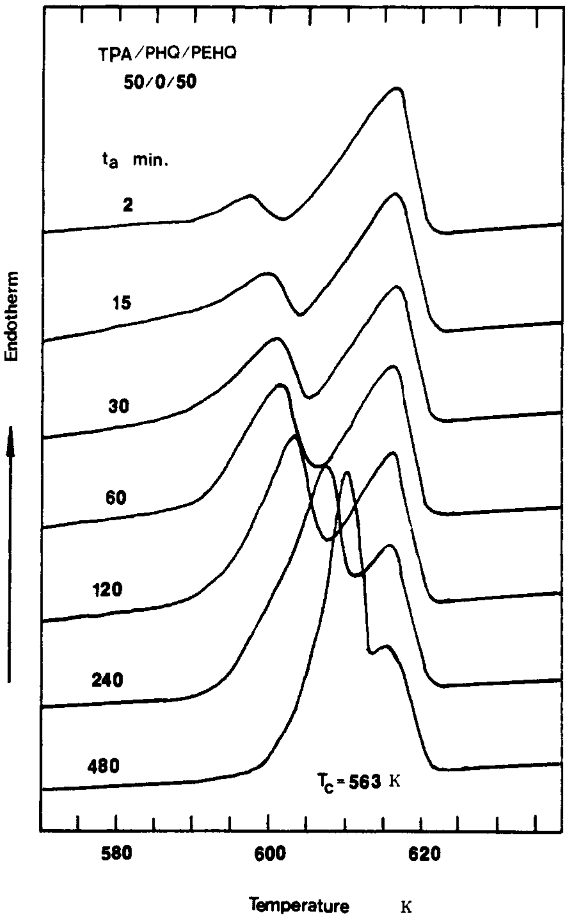

Figure 6. Set of DSC heating traces for the TPA/PHQ/PEHQ copolyester (50/0/50) after isothermal crystallization at T_c = 563 K for different times.

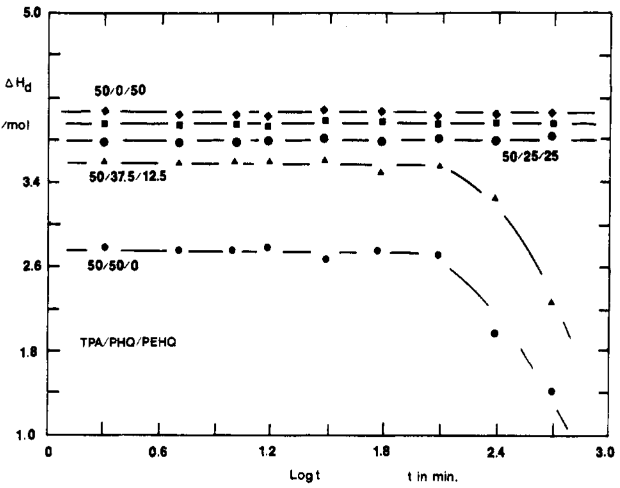

Figure 7. Relationships between the heat of transition of the fast transition process and logarithmic time for the TPA/PHQ/PEHQ copolyesters with different compositions crystallized at the same ΔT_c (see text).

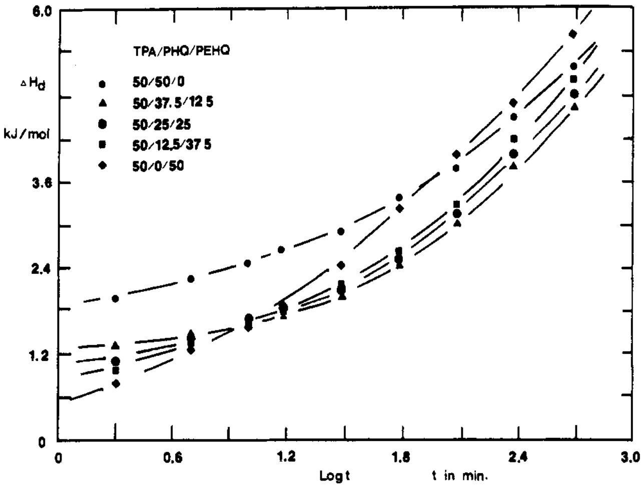

Figure 8. Relationships between the heat of transition of the slow transition process and logarithmic time for the TPA/PHQ/PEHQ copolyesters with different compositions crystallized at the same ΔT_c (see text).

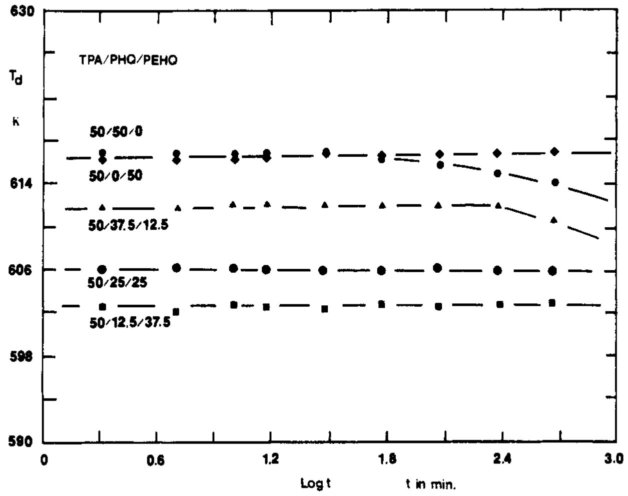

Figure 9. Relationships between the transition temperature of the fast transition process and logarithmic time for the TPA/PHQ/PEHQ copolyesters with different compositions crystallized at the same ΔT_c (see text).

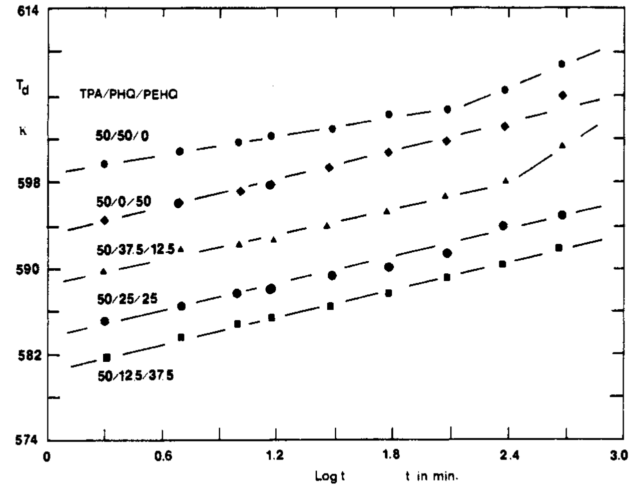

Figure 10. Relationships between the transition temperature of the slow transition process and logarithmic time for the TPA/PHQ/PEHQ copolyesters with different compositions crystallized at the same ΔT_c (see text).

change with composition. For the cases of TPA/PHQ/PEHQ (50/50/0) and (50/37.5/12.5), monoclinic crystal lattices with γ = 90° (pseudoorthorhombic) have been found. The former is in agreement with the results reported by Hong and Blackwell, although detailed sizes are slightly different.[4] As the amount of the PEHQ comonomer unit is increased in the composition from 0 to 25%, the angle γ decreases from 90 to 78°. This indicates that at a certain composition the amount of the PEHQ component signficantly effects a change in the angle γ. Further increasing the PEHQ component leads to a gradual reduction of the angle γ. The a-axes in the unit cells of the copolyesters are essentially unchanged. However, the b-axes expand from 9.100 Å for (50/50/0) to 9.200 Å for (50/37.5/12.5). This again indicates the effect of introducing the PEHQ component. In fact, when the PEHQ component exceeds 25%, the *b*-axes remain essentially constant. The *c*-axes show a slight decrease, perhaps because increasing the PEHQ component may lead to a twisting of their conformations in order to achieve close packing. When one looks at the change of crystallographic volumes of these copolyesters, it is clear that for any introduction of a third monomer unit the crystallographic volume increases, revealing that the comonomer units affect the crystal packing. It must be asked, can we rule out any possibility of phase separation in these copolyesters? Since both the TPA/PHQ/PEHQ (50/50/0) and (50/0/50) show different crystalline structures, we would expect to detect the coexistence of more than one crystal unit cell if phase separation had occurred. Nevertheless, this is not observed in our WAXD experiments. In addition, only one glass transition temperature can be found throughout the composition range.[30] Therefore, we conclude that the cocrystallization of the PHQ and PEHQ components does happen in these copolyesters.

To answer the second question, as far as we can tell, there has been no systematic report on the transition kinetics of the copolyesters in general. The only hint was that in the HBA/HNA copolyesters the overall transition kinetics of HBA/HNA (75/25) is somewhat faster than that of (30/70) (see Figure 7 in ref 1). The difficulties in interpretation are due to not only the supercooling (not temperature) dependence of the transition kinetics but also other effects such as nucleation density, molecular mass, etc., in addition to variation in chemical composition. We have thus defined a new quantity of ΔT_c, the temperature difference between the extrapolated crystallization temperature at 0 K/min and the isothermal crystallization temperature. We only compare the transition kinetics under the same ΔT_c. The syntheses of these copolyesters were controlled by using the same conditions for their preparation. They were annealed (solid-state polymerization) in one vacuum oven at the same time. We hope that these controlling procedures may lead to a meaningful comparison of the transition kinetics of these copolyesters.

Figure 7 indicates clearly that the copolyester that contains only TPA/PEHQ shows a quicker development (larger heat of transition) of the fast transition process. With increasing PHQ composition, the heats of transition decrease monotonously. Furthermore, below 25% of PEHQ in the composition, the copolyesters show a decrease in the heats of transition for the fast processes at longer annealing times. Similar changes in transition temperatures for the fast transition processes of those copolyesters can be observed (Figure 9). This may be attributed to the different chain mobilities along the *c*-axes among these copolyesters. The chain mobilities are determined by two facts: the sizes of pendant side groups and the unoccupied volume in the crystal lattices. It is evident that the pendant side group of the PHQ component is smaller than that of the PEHQ component. On the other hand, the unoccupied volume of the TPA/PHQ/PEHQ having less than 25% PEHQ in the composition should be larger than those with greater than 25% PEHQ. As a consequence, the copolyesters with below 25% PEHQ should have relatively larger chain mobilities along their *c*-axes. It is also interesting that from Figure 8 the slow process of TPA/PHQ/PEHQ (50/50/0) shows the biggest initial heat of transition after $t_a = 2$ min (2.0 kJ/mol) but the slowest subsequent growth, while (50/0/50) shows the smallest one (0.81 kJ/mol) but the fastest later development. Both initial values in the fast and slow transition processes have opposite corresponding sequences (Figures 7 and 8). However, the sequence for the subsequent development in the slow process is the same as that of the initial development in the fast transition processes. The absolute values of the heats of transition at prolonged annealing times for the slow processes show that the two copolyesters with the extremes of (50/0/50) and (50/50/0) have the largest values. This should not be surprising since any introduction of the third monomer leads to an expansion of the crystallographic volume (Table III). This monomer acts as a "defect" in the crystal structures and, therefore, weakens the chain packing (decreases the interactions). However, it is important to note that how fast the development of the crystals occurs in those copolyesters is different from the final absolute values of the heats of transition. The former is a kinetically controlled process, and the latter is a representative of a thermodynamic property.

Conclusions

(1) In this series of TPA/PHQ/PEHQ copolyesters with different PHQ/PEHQ compositions, a complete phase diagram of both solidus and liquidus lines with varying PHQ (or PEHQ) composition can be obtained. Our WAXD and DSC experimental results indicate that they show solid solution behavior of an isodimorphic type. Both TPA/PHQ and TPA/PEHQ structural units are cocrystallized.

(2) The WAXD analyses show a change of the angle γ from 90.0° (a monoclinic or pseudoorthorhombic crystal lattice) for TPA/PHQ/PEHQ (50/50/0) to 71.9° (a monoclinic crystal lattice) for TPA/PHQ/PEHQ (50/0/50). Introduction of the PEHQ component gradually lowers the angle γ and expands the *b*-axes in these copolyesters.

(3) The development of the fast transition processes in these copolyesters is dependent upon the content of the PEHQ component. A higher content of this component leads to a larger heat of transition. The same sequence can be found for the subsequent development of the slow transition processes in these copolyesters.

References and Notes

(1) Cheng, S. Z. D. *Macromolecules* **1988**, *21*, 2475.
(2) Cheng, S. Z. D.; Janimak, J. J.; Zhang, A.-Q.; Zhou, Z.-L. *Macromolecules* **1989**, *22*, 4240.
(3) Cheng, S. Z. D.; Zhang, A.-Q.; Johnson, R. L.; Wu, Z.-Q.; Wu, H.-H. *Macromolecules* **1990**, *23*, 1196.
(4) Hong, S.-K.; Blackwell, J. *Polymer* **1989**, *30*, 225.
(5) Hong, S.-K.; Blackwell, J. *Polymer* **1989**, *30*, 780.
(6) Ghanem, A. M.; Porter, R. S.; Dickinson, C.; Zachariades, A. E. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(7) U.S. Patents 4,661,645 and 4,614,791 assigned to Owens-Corning Fiberglas Co.
(8) Jackson, W. J., Jr.; Kuhfuss, H. F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2043.
(9) Viney, C.; Windle, A. H. *J. Mater. Sci.* **1982**, *17*, 2661.
(10) Joseph, E.; Wilkes, G. L.; Baird, D. G. *Polymer* **1985**, *26*, 689.
(11) Menczel, J.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1433.
(12) Messiri, W.; Menzel, J.; Gaur, U.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 719.
(13) Krigbaum, W. R. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 883.
(14) Lenz, R. W.; Feichtinger, K. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1979**, 20, 114.
(15) Zachariades, A. E.; Economy, E. J.; Logan, J. A. *J. Appl. Polym. Sci.* **1982**, *27*, 2009.
(16) Sawyer, L. C. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 347.
(17) Nicely, V. A.; Dougherty, J. T.; Renfro, L. W. *Macromolecules* **1987**, *20*, 573.
(18) Sun, T.; Bhattacharya, S. K.; Lenz, R. W.; Porter, R. S. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(19) Quach, L.; Hornbogen, E.; Volksen, W.; Economy, J. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 775.

(20) Cao, M.-Y.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 521.

(21) Blundell, D. J. *Polymer* **1982**, *23*, 359.

(22) Calundann, G. W.; Jaffe, M. *Welch Foundation Lecture Conf.* **1982**, *26*, 247.

(23) Blackwell, J.; Gutierrer, G. A.; Chivers, R. A. In *Polymeric Liquid Crystals*; Blumstein, A., Ed.; Plenum: New York, 1985; p 167.

(24) Chivers, R. A.; Blackwell, J.; Gutierrez, G. A.; Stamatoff, J. B.; Yoon, H. In *Polymeric Liquid Crystals*; Blumstein, A., Ed.; Plenum: New York, 1985, p 153.

(25) Blackwell, J.; Cheng, H.-M.; Biswas, A. *Macromolecules* **1988**, *21*, 39.

(26) Biswas, A.; Blackwell, J. *Macromolecules* **1988**, *21*, 3146, 3152, 3168.

(27) Muhlebach, A.; Johnson, R. D.; Lyerla, J.; Economy, J. *Macromolecules* **1988**, *21*, 3117.

(28) Hanna, S.; Windle, A. H. *Polymer* **1988**, *29*, 207.

(29) Economy, J.; Johnson, R. D.; Muhlebach, A.; Lyerla, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (2), 505.

(30) Johnson, R. L. Ph.D. Thesis, Department of Polymer Science, The University of Akron, Akron, OH, 1991.

Registry No. (TPA)(PHQ) (copolymer), 67203-03-6; (TPA)(PHQ) (SRU), 67256-36-4; (TPA)(PHQ)(PEHQ) (copolymer), 125109-67-3; (TPA)(PEHQ) (copolymer), 85797-71-3; (TPA)(PEHQ) (SRU), 85854-82-6.