A Thermotropic Main-Chain Random Copolyester Containing Flexible Spacers of Differing Lengths. 1. Synthesis and Characterization

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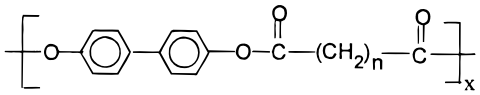
ABSTRACT: A thermotropic main-chain random copolyester containing flexible spacers of differing lengths (hereafter referred to as PSHQ6-12) was synthesized, via condensation polymerization in solution, by first preparing 2-(phenylsulfonyl)-1,4-hydroquinone (A), 4′,4″-bis(chloroformyl)-1,6-diphenoxyhexane (B6), and 4′,4″-bis(chloroformyl)-1,12-diphenoxydodecane (B12). Using differential scanning calorimetry we found that PSHQ6-12 exhibits only two thermal transitions: (i) a glass transition at ca. 90 °C and (ii) a nematic−isotropic transition at ca. 192 °C. The absence of crystalline structure in PSHQ6-12 at room temperature, which was also confirmed by wide-angle X-ray diffraction (WAXD), is attributable to the lack of an orderly packed structure, which originated from the large differences in the length of CH_2 units between monomer B6 having 6 CH_2 units and monomer B12 having 12 CH_2 units. That is, the coexistence of CH_2 units of greatly differing lengths apparently prevented the crystallization of PSHQ6-12, forming only a glassy nematic phase. This is in contrast with the situations for homopolyesters, poly[(phenylsulfonyl)-*p*-phenylene 1,6-hexamethylenebis(4-oxybenzoate)] (PSHQ6) and poly[(phenylsulfonyl)-*p*-phenylene 1,12-dodecamethylenebis(4-oxybenzoate)] (PSHQ12), which were found via WAXD to have highly ordered structure at room temperature and undergo three thermal transitions: (i) a glass transition, (ii) a crystalline−nematic transition, and (iii) a nematic−isotropic transition. Using polarized optical microscopy we found that both copolyester PSHQ6-12 and homopolyesters PSHQ6 and PSHQ12 exhibit Schlieren texture in the nematic region. PSHQ6-12 enabled us to prepare, using *p*-chlorophenol as solvent, lyotropic solutions at concentrations of 60 wt % and higher until the solution becomes a glassy state. The lyotropic solutions were also found to exhibit Schlieren texture under quiescent conditions and form banded structure under shear.

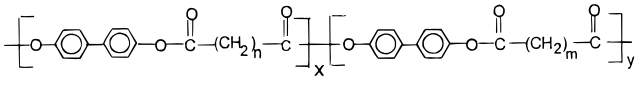
During the past two decades numerous thermotropic liquid-crystalline polymers (TLCPs) have been synthesized. Owing to the practical difficulties with processing some of the TLCPs having very high melting temperatures that arise from highly stiff chains, in the 1970s attempts were made to decrease the melting temperatures of TLCPs by synthesizing copolymers. Some early attempts made in this direction were due to Jackson and Kuhfuss[1] and Calundann,[2] which subsequently led to commercialization.[3] Specifically, Jackson and Kuhfuss[1] synthesized thermotropic copolyesters of *p*-hydroxybenzoic acid (HBA) and poly(ethylene terephthalate) (PET), and Calundann[2] synthesized thermotropic copolyesters of HBA and 6-hydroxy-2-naphthoic acid (HNA).

Starting in the early 1980s, the synthesis of TLCPs having flexible spacers in the main chain, hereafter referred to as main-chain semiflexible thermotropic polymers (MCSTP), emerged and subsequently received wide attention by polymer scientists. There are too many references to cite them all here, so the readers are referred to the review articles[4−7] and references therein.

In the 1980s some very interesting attempts were made to synthesize thermotropic random copolymers by introducing two different lengths of flexible spacers in the main-chain.[8,9] The primary motivation behind such attempts was to decrease anisotropic−isotropic transition temperature(s) and at the same time to broaden the range of temperatures over which a mesophase may reside. The first successful attempt was reported by Watanabe and Krigbaum[8] who synthesized copolyesters based on the 4,4′-dihydroxybiphenyl rigid unit with chemical structure,



which was reported to form a smectic mesophase. Interestingly enough, however, they reported that *no* cocrystallization occurred in the copolyester PB6-12 consisting of flexible spacers having 6 CH_2 units and 12 CH_2 units, whereas the copolyester PB5−7 containing 5 CH_2 units and 7 CH_2 units, and the copolyester PB10−12 containing 10 CH_2 units and 12 CH_2 units cocrystallized. They noted that as the difference in the length of flexible spacer between two 4,4′-dihydroxybiphenyl rigid units becomes larger, the greater the depression of the crystalline melting temperature in a given copolyester. No melting of crystals was observed in the copolyester PB6-12 because the random distributions of two greatly different lengths of CH_2 units interfered with the formation of a well-packed, ordered structure. It should be mentioned that in their study, the copolymers were prepared by melt transesterification using equimolar amounts of 4,4′-dihydroxybiphenyl and diacid. On the basis of this method, Watanabe and Krigbaum[8] postulated the structure shown schematically below.



Using 1,5-dibromopentane, 1,7-dibromoheptane, and 4,4′-dihydroxy-α-methylstilbene (HMS), Percec and coworkers[9] synthesized random copolyethers with the following chemical structure:

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Chart 1

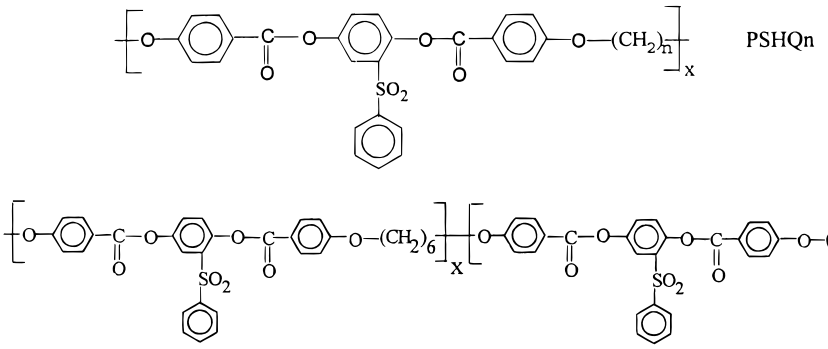
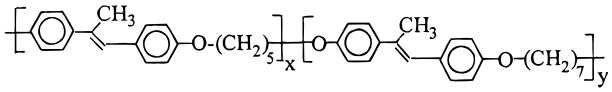


Table 1. Summary of the Molecular Weights and Transition Temperatures for PSHQ6, PSHQ12, and PSHQ6-12

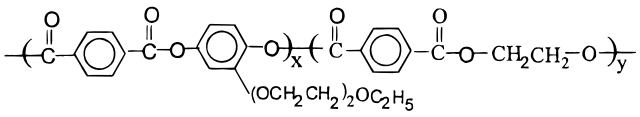
sample code	M_w	M_w/M_n	T_g (°C)[a]	T_{m2} (°C)[b]	T_{m1} (°C)[c]	T_{NI} (°C)[d]	annealing condition for DSC measurement
PSHQ6	23 900	1.98	112.6	164.4	193.4[e]	231.5	at 170 °C for 1 h
PSHQ12	31 900	1.74	82.7	118.9	151.3[f]	168.3	at 130 °C for 1 h
PSHQ6-12	24 300	2.02	93.4	–	–	193.9	at 130 °C for 1 h

[a] Glass transition temperature. [b] Crystal melting temperature. [c] Temperature at which an intermediate endothermic peak appears by further annealing at a temperature between T_{m2} and T_{NI}. [d] Nematic−isotropic transition temperature. [e] There is a range of temperatures (180.8−200.6 °C) over which this transition takes place. [f] There is a range of temperatures (143.1−151.3 °C) over which this transition takes place.



While this copolyether yielded a broad isotropization temperature as compared to the homopolyether HMS-C5 containing 5 CH_2 units and the homopolyether HMS-C7 containing 7 CH_2 units, it had a distinct melting temperature of crystals. This observation is in agreement with the earlier study by Watanabe and Krigbaum.[8]

More recently, Tendolkar et al.[10] synthesized a series of thermotropic random copolyesters, based on ethoxydiethyleneoxyhydroquinone, ethylene glycol, and terephthaloyl chloride moieties, with the following chemical structure:



The purpose of their study was to investigate the effect of the flexible pendent oxyethylene group on the thermal and liquid crystalline properties of the copolyesters synthesized. It turned out that all the copolyesters synthesized in their study were semicrystalline and thus had melting crystals.

Previously, Han and co-workers[11−13] synthesized a thermotropic main-chain homopolyester poly[(phenylsulfonyl)-*p*-phenylene 1,10-decamethylenebis(4-oxybenzoate)] (PSHQ10) (n = 10), shown in Chart 1, and investigated its thermal transition behavior, domain texture, and rheological behavior.

Very recently we synthesized a thermotropic main-chain random copolyester PSHQ6-12 (Chart 1) which contains two different lengths of flexible spacers, 6 and 12 CH_2 units. We have found via differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD) that the copolyester PSHQ6-12 does not cocrystallize and thus offers us a unique opportunity to prepare lyotropic solutions, whereas homopolyesters, poly[(phenylsulfonyl)-*p*-phenylene 1,6-hexamethylenebis(4-oxybenzoate)] (PSHQ6) and poly[(phenylsulfonyl)-*p*-phenylene 1,12-dodecamethylenebis(4-oxybenzoate)] (PSHQ12), crystallize, preventing us from preparing lyotropic solutions at room temperature. In this paper we report the highlights of our findings.

Experimental Section

Polymer Synthesis. By following the procedures described elsewhere,[11] three monomers were prepared, namely 2-(phenylsulfonyl)-1,4-hydroquinone (monomer A) and 4′,4″-bis(chloroformyl)-1,6-diphenoxyhexane (monomer B6), and 4′,4″-bis(chloroformyl)-1,12-diphenoxydodecane (monomer B12).

Copolyester PSHQ6-12 was prepared, via condensation polymerization in solution, by using equimolar amounts of monomer A and monomers B6 and B12; namely, monomer A and an equal molar ratio of B6 and B12 were added into a flask (hereafter referred to as the reactor) under pure argon atmosphere. Then a predetermined amount of pyridine was directly transferred into the reactor, using a double-end deflected needle. The reactor was stirred magnetically in an ice bath in order to reduce the initial rate of polymerization until all three monomers were totally dissolved in dichloromethane as a solvent. Then the ice bath was removed and argon gas was kept flowing (for ca. 24 h) until no more hydrochloric acid was detected at the tip of the bubbler which was connected to the outcoming argon gas line. The reactor was then sealed, and the reaction was allowed to continue under magnetic stirring for two more days to achieve a maximum yield. The product in solution was diluted with additional dichloromethane and precipitated several times in methanol. The precipitate was filtered and dried in a vacuum oven for three days.

Also polymerized were, for comparison, homopolyester PSHQ6 with 6 CH_2 units as flexible spacers, and homopolyester PSHQ12 with 12 CH_2 units as flexible spacers. The details of the synthesis procedures are described in a previous paper.[11]

Intrinsic Viscosity and Molecular Weight Measurements. We measured the intrinsic viscosity [η] at 30 °C of each polymer dissolved in 1,1,2,2-tetrachloroethane and found that [η] = 0.877 dL/g for PSHQ6, [η] = 1.003 dL/g for PSHQ12, and [η] = 0.765 dL/g for PSHQ6-12. The weight-average molecular weight (M_w) of the three polymers were measured

via gel permeation chromatography using polystyrene standards, and Table 1 summarizes the results.

Sample Preparation. Solvent-cast specimens for DSC and WAXD measurements were prepared by dissolving PSHQ6-12 and PSHQ12, respectively, in dichloromethane and by dissolving PSHQ6 in 1,1,2,2-tetrachloroethane, in the presence of an antioxidant (Irganox 1010, Ciba-Geigy Group) and then slowly evaporating the solvent at room temperature for a week. The as-cast films with the thickness of 1 mm were further dried at 90 °C for one week and then in a vacuum oven to remove any residual solvent. Specimens for optical micrograph were prepared by dissolving each polymer in 1,1,2,2-tetrachloroethane in the presence of an antioxidant (Irganox 1010, Ciba-Geigy Group) and then slowly evaporating the solvent for a week and in a vacuum oven to remove any residual solvent. Also prepared were fibers by melt drawing, which were later employed for WAXD and polarized optical microscopy.

We further prepared solutions of copolyester PSHQ6-12, and homopolyesters PSHQ6 and PSHQ12, by using *p*-chlorophenol (mp = 43−45 °C; bp = 220 °C) as solvent. Specific procedures employed are as follows: (i) a predetermined amount of polymer was first placed in a glass tube immersed in an oil bath at 90 °C; (ii) the polymer was then dissolved by adding *p*-chlorophenol as solvent into the glass tube, where the amount of the solvent varied depending upon the initial concentration specified; (iii) after about 12 h in the oil bath, the glass tube was taken out of the oil bath and it was cooled down to room temperature, and the amount of solvent evaporated was determined gravimetrically, enabling us to determine the final concentration of the solution prepared. The concentration was varied to determine the threshold concentration, if applicable, for an onset of mesophase formation in solutions of PSHQ6, PSHQ12, or PSHQ6-12.

Differential Scanning Calorimetry. Thermal transition temperatures of the solvent-cast films of each polymer were determined by differential scanning calorimetry (DSC) (du Pont 9900). All DSC runs were made under a nitrogen atmosphere with heating and/or cooling rates of 20 °C/min, and the thermal histories (namely, annealing temperature and the duration of annealing) of the specimens were varied.

Wide-Angle X-ray Diffraction (WAXD). WAXD experiments were conducted at room temperature on both melt-drawn fibers and as-cast films, using a General Electric X-ray generator (Model XRD-6) operating at 30 kV and 30 mA (Cu Kα radiation, filtered by a Ni foil). The diffraction patterns were recorded with a camera, which was placed at a distance of 52.48 mm from the specimen. The exposure time for each measurement was 4 h.

Polarized Optical Microscopy (POM). A hot-stage (TH-600 type, Linkham Scientific Co.) microscope (Nikon, Model Optiphoto polXTP-11) with a camera, programmable temperature controller, and photomicrographic attachment was used to take pictures, under cross-polarized light, of as-cast films which were placed on a slide glass, and of melt-drawn fibers which were placed between two slide glasses. To take micrographs of the polymer solutions prepared, the following procedures were employed: (i) a solution prepared was first transferred from the glass tube to a slide glass and then the specimen was covered by another slide glass; (ii) the specimen was placed on the microscope and then heated to a temperature, giving rise to homogeneous solution, at which point the solution looked dark under a polarizing microscope, and then the edges of the two slide glasses were sealed using an epoxy adhesive to prevent further evaporation of the solvent; (iii) the specimen was kept at room temperature for 3 days to achieve an equilibrium morphology; (iv) finally the specimen was placed on a polarized optical microscope to take pictures.

Results and Discussion

Thermal Transitions of PSHQ6-12, PSHQ6, and PSHQ12 as Determined by DSC. Figure 1 gives traces of DSC thermograms during the first heating cycle at a rate of 20 °C/min for as-cast PSHQ6-12 specimens, which were first dried at 90 °C for 3 days and then annealed at 130 °C for 30, 50, 100, or 150 h. This annealing experiment was conducted to observe whether or not solid crystals may be formed during annealing. It is of interest to observe in Figure 1 that PSHQ6-12 exhibits only two thermal transitions, namely, the glass transition temperature (T_g) at ca. 92 °C and the nematic−isotropic transition temperature (T_{NI}) at ca. 193 °C, and the annealing for a period up to 150 h has not changed the thermal transitions of PSHQ6-12. The DSC experimental results suggest that PSHQ6-12 has no solid crystals, i.e., it has a glassy nematic phase. The significance of this particular characteristic of PSHQ6-12 will be elaborated on after presenting other evidence which supports this conclusion. Before presenting our view on the origin of the glassy nematic phase in the copolyester PSHQ6-12, let us look at, for comparison, thermal transitions of two homopolyesters PSHQ6 and PSHQ12.

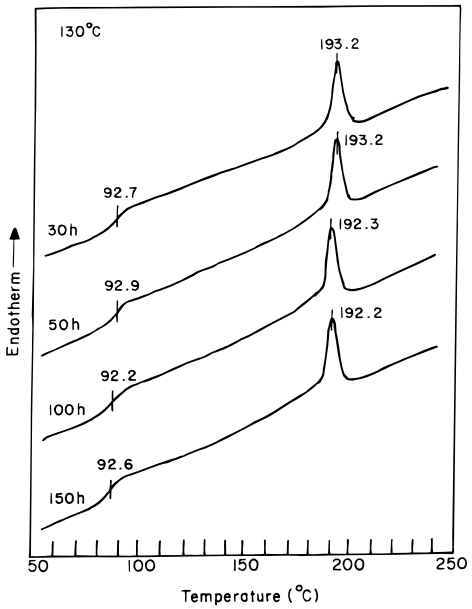


Figure 1. DSC traces during the first heating cycle for as-cast PSHQ6-12 specimens which were dried at 90 °C for 3 days and then annealed at 130 °C for different periods, as indicated on the plot. A fresh specimen was used for each run, and the heating rate used was 20 °C/min.

Figure 2 gives traces of DSC thermograms during the first heating cycle at a rate of 20 °C/min for as-cast PSHQ12 specimens, which were first dried at 90 °C for 3 days and then annealed for 1 h at 110 °C, 130 °C, or 150 °C. The following observations are worth noting in Figure 2. When annealed at 150 °C for 1 h, PSHQ12 exhibits three thermal transitions: (i) at ca. 89 °C representing the T_g, (ii) at ca. 119 °C representing the melting point (T_{m2}) of solid crystals, and (iii) at ca. 169 °C representing the T_{NI}. Below we will show a polarized optical micrograph which indicates that PSHQ12 has only a nematic mesophase (i.e., Schlieren texture) at temperatures between T_{m2} and T_{NI}. However, when annealed at 110 °C for 1 h, PSHQ12 exhibits an intermediate endothermic peak at ca. 143 °C between the T_{m2} of ca. 121 °C and the T_{NI} of 167 °C. It is of interest to observe in Figure 2 that the area under the intermediate endothermic peak (i.e., the enthalpy ΔH_1 associated with the intermediate endothermic peak) becomes very large as the annealing temperature is increased from 110 to 130 °C, and then disappears completely as the annealing temperature is increased further to 150 °C. According to a previous study of Han

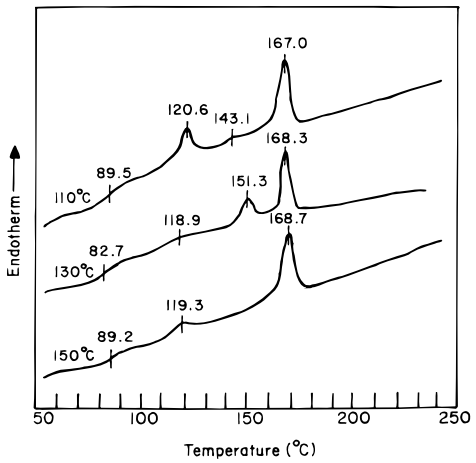


Figure 2. DSC traces during the first heating cycle for as-cast PSHQ12 specimens which were dried at 90 °C for 3 days and then annealed for 1 h at various temperatures, as indicated on the plot. A fresh specimen was used for each run and the heating rate used was 20 °C/min.

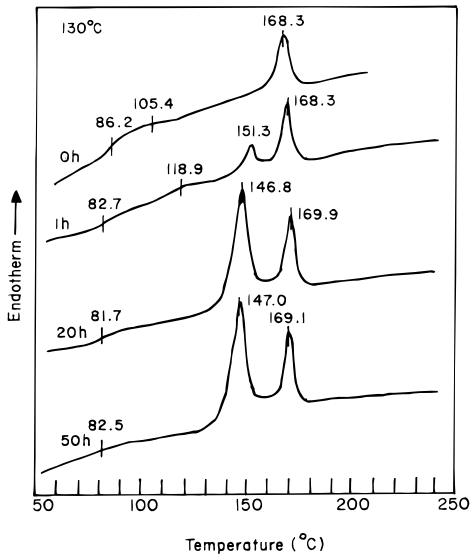


Figure 3. DSC traces during the first heating cycle for as-cast PSHQ12 specimens which were dried at 90 °C for 3 days and then annealed at 130 °C for different periods, as indicated on the plot. A fresh specimen was used for each run, and the heating rate used was 20 °C/min.

et al.,[14] the intermediate endothermic peak at a temperature (T_{m1}) between T_{m2} and T_{NI} represents the melting point of high-temperature melting crystals which were formed via recrystallization during the annealing of the low-temperature melting crystals. This can now explain why in Figure 2 an intermediate endothermic peak did not appear when a PSHQ12 specimen was annealed at 150 °C, because the annealing temperature of 150 °C was very close to the melting point (T_{m1}) of the high-temperature melting crystals.

Figure 3 gives traces of DSC thermograms during the first heating cycle at a rate of 20 °C/min for as-cast PSHQ12 specimens, which were first dried at 90 °C for 3 days and then annealed at 130 °C for 1 h, 20 h, or 50 h. Also given in Figure 3 are, for comparison, traces of DSC thermogram for a PSHQ12 specimen without annealing (the top trace). We observe in Figure 3 that when a PSHQ12 specimen was not annealed, no intermediate endothermic peak appears between the T_{m2} of ca. 105 °C and the T_{NI} of ca. 168 °C, but as the annealing period was increased from 1 to 20 h, the area under the

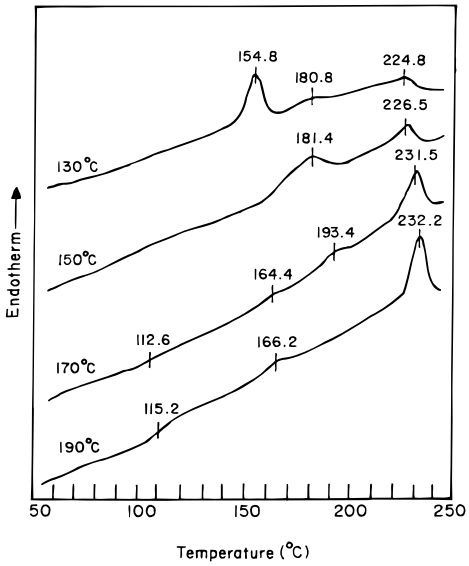


Figure 4. DSC traces during the first heating cycle for as-cast PSHQ6 specimens which were dried at 90 °C for 3 days and then annealed for 1 h at various temperatures, as indicated on the plot. A fresh specimen was used for each run, and the heating rate used was 20 °C/min.

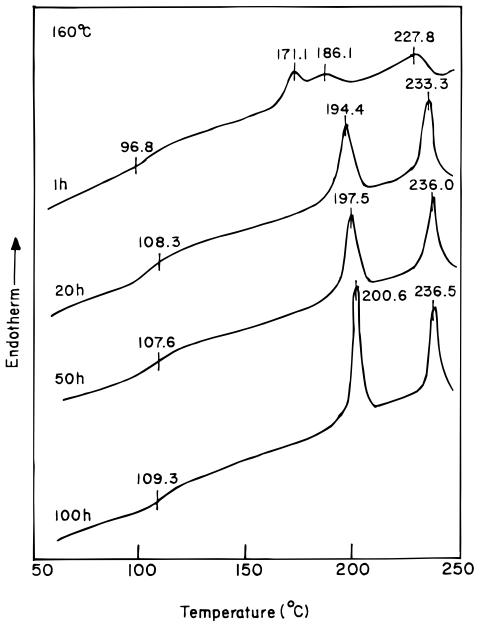


Figure 5. DSC traces during the first heating cycle for as-cast PSHQ6 specimens which were dried at 90 °C for 3 days and then annealed at 160 °C for different periods, as indicated on the plot. A fresh specimen was used for each run, and the heating rate used was 20 °C/min.

intermediate endothermic peak (i.e., ΔH_1) grew considerably, becoming even greater than the area associated with the nematic−isotropic transition (ΔH_{NI}), and then ΔH_1 remains constant as the annealing period was increased further from 20 to 50 h. This observation is very similar to that reported earlier[14] for PSHQ10.

Figure 4 gives traces of DSC thermograms during the first heating cycle at a rate of 20 °C/min for as-cast PSHQ6 specimens, which were first dried at 90 °C for 3 days and then annealed for 1 h at 130 °C, 150 °C, 170 °C, or 190 °C. When annealed at 130 °C for 1 h, a PSHQ6 specimen exhibits an intermediate endothermic peak (T_{m1}) at ca. 181 °C between the T_{m2} of ca. 155 °C and the T_{NI} of ca. 225 °C, and the area under the intermediate endothermic peak (i.e., ΔH_1) grew larger

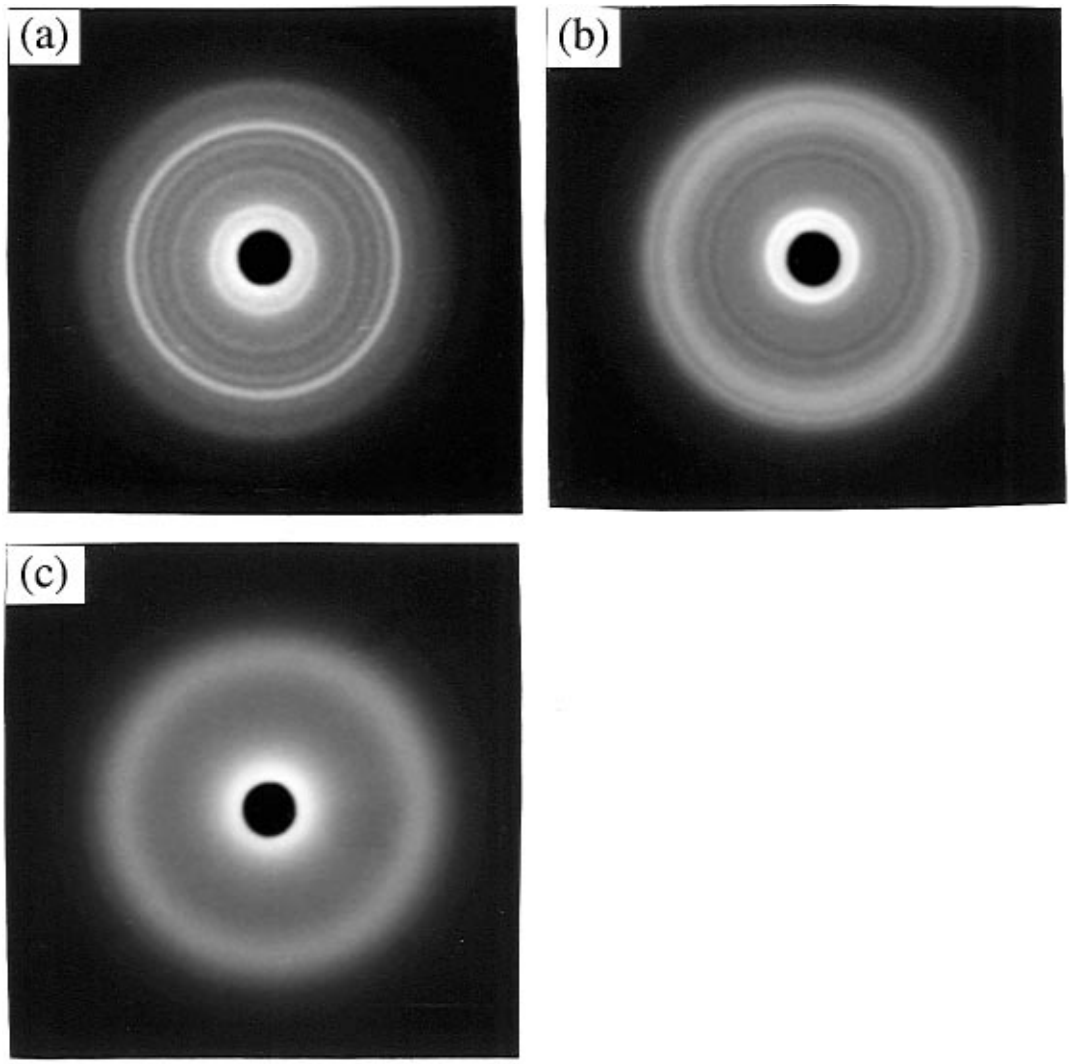


Figure 6. X-ray diffraction patterns at room temperature of (a) an as-cast PSHQ6 specimen annealed at 130 °C for 1 h, (b) an as-cast PSHQ12 specimen annealed at 130 °C for 20 h, and (c) an as-cast PSHQ6-12 specimen annealed at 130 °C for 150 h.

as the annealing temperature was increased to 150 °C, but it became smaller as the annealing temperature was increased from 150 to 170 °C and disappeared completely as the annealing temperature was increased further to 190 °C, which is attributable to the fact that 190 °C is very close to the melting point (T_{m1}) of high-temperature melting crystals, an observation very similar to that made above in reference to Figure 2 for PSHQ12.

Figure 5 gives traces of DSC thermograms during the first heating cycle at a rate of 20 °C/min for as-cast PSHQ6 specimens, which were first dried at 90 °C for 3 days and then annealed at 160 °C for 1, 20, 50, or 100 h. When a PSHQ6 specimen was annealed for a period of 20 h and longer, only two endothermic peaks, representing T_{m1} and T_{NI}, respectively, appear. This observation is very similar to that made above in reference to Figure 3 for PSHQ12. Table 1 summarizes the thermal transition temperatures of copolyester PSHQ6-12 and two homopolyesters PSHQ6 and PSHQ12, as determined by DSC.

Structure of PSHQ6-12, PSHQ6, and PSHQ12 as Determined by WAXD. Figure 6 gives WAXD patterns for as-cast specimens of two homopolyesters PSHQ6 and PSHQ12, and copolyester PSHQ6-12. These specimens, before being subjected to WAXD measurements, had the following thermal histories: (a) PSHQ6 was annealed at 130 °C for 1 h, (b) PSHQ12 was annealed at 130 °C for 20 h, and (c) PSHQ6-12 was annealed at 130 °C for 150 h. Note that, for comparison, the same annealing temperature of 130 °C was employed to the homopolyesters PSHQ6 and PSHQ12 and copolyester PSHQ6-12. The following observations are worth noting in Figure 6. (1) The WAXD patterns for PSHQ6 show very sharp diffraction peaks (0.475 and 1.164 nm) with several weak diffractions, indicating that a highly-ordered crystalline structure was formed in the specimen. (2) The WAXD patterns for PSHQ12 show sharp diffraction peaks (0.398 and 2.413 nm) with several weak diffractions, indicating that a highly-ordered crystalline structure was formed in the specimen.

(3) The WAXD patterns for PSHQ6-12 show very diffuse lateral spacing ranging from 0.38 to 0.48 nm even after the specimen was annealed for a period of 150 h. This then suggests that PSHQ6-12 has no crystals, confirming the DSC results presented in Figure 1. The absence of crystalline structure in PSHQ6-12, even after being annealed for a period of as long as 150 h, is believed due to the random distributions of flexible spacers with greatly differing lengths, thus hindering the formation of a well-packed structure. It is of further interest to note in Figure 6 that (i) the WAXD diffraction patterns for the homopolyester PSHQ12 specimen, even after being annealed for 20 h, are not as sharp as those for the homopolyester PSHQ6 specimen which was

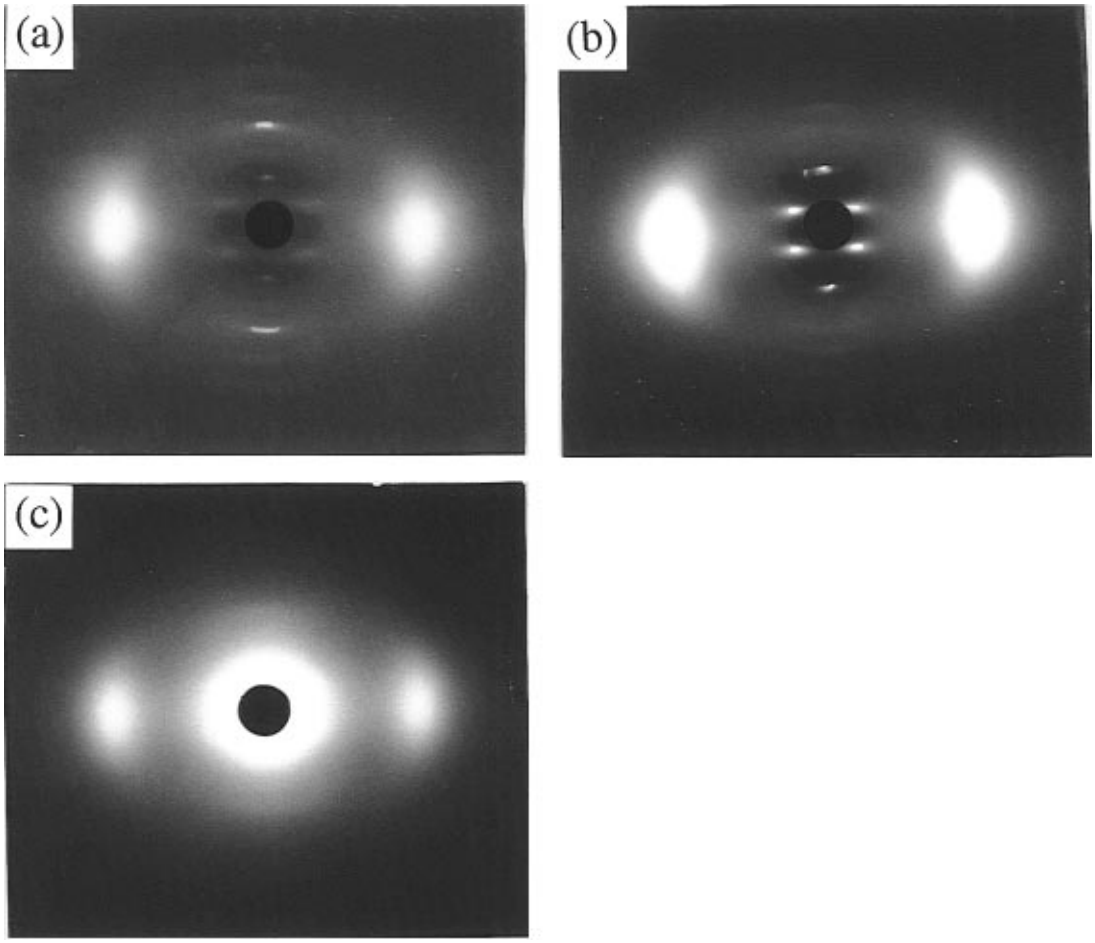


Figure 7. X-ray diffraction patterns at room temperature of (a) an unannealed melt-drawn PSHQ6 fiber, (b) an unannealed melt-drawn PSHQ12 fiber, and (c) an unannealed melt-drawn PSHQ6-12 fiber.

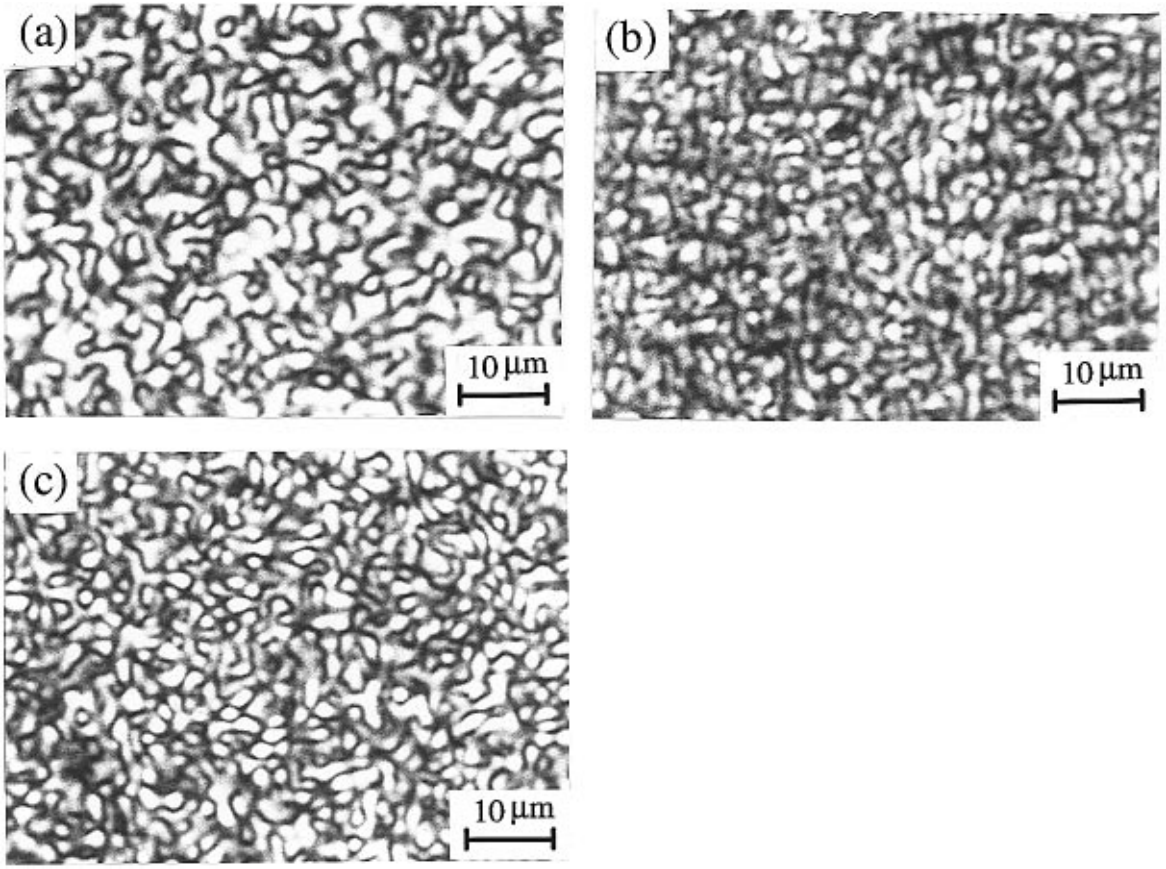


Figure 8. Cross-polarized optical micrographs for (a) an as-cast PSHQ6 specimen at 200 °C, (b) an as-cast PSHQ12 specimen at 140 °C, and (c) an as-cast PSHQ6-12 specimen at 170 °C. All three specimens have Schlieren textures in the nematic region.

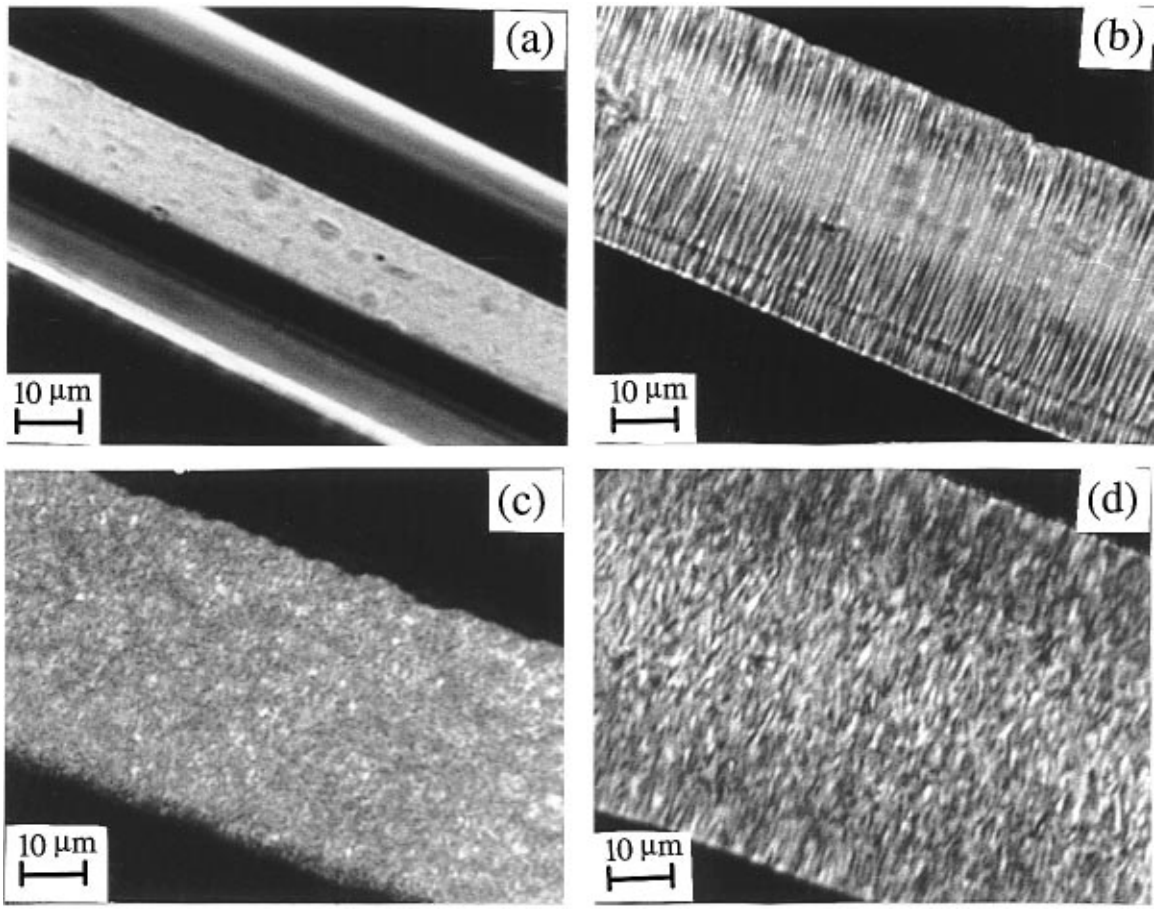


Figure 9. Cross-polarized optical micrographs describing the domain texture of a melt-drawn PSHQ12 fiber which had the following thermal histories: (a) at 130 °C without annealing, (b) after being annealed at 130 °C for 1 h, (c) after being annealed at 130 °C for 72 h, (d) after being annealed at 130 °C for 72 h and then heated to 160 °C.

annealed only for 1 h. Notice further that the lateral spacing (0.475 nm) for PSHQ6 is greater than that (0.398 nm) for PSHQ12, suggesting that PSHQ6 has a larger crystal lattice spacing in the lateral direction than PSHQ12. This can be explained by the fact that the crystals in PSHQ6 having 6 CH_2 units are expected to be less compact than PSHQ12 having 12 CH_2 units. Note, however, that the d-spacing of the inner diffraction ring (1.164 nm) in PSHQ6 is less than that (1.413 nm) in PSHQ12, which is related to the chain periodicity of each polyester.

Figure 7 gives WAXD patterns for melt-drawn fibers of unannealed (a) PSHQ6, (b) PSHQ12, and (c) PSHQ6-12. Fiber specimens were obtained by melt drawing in the nematic state followed by a rapid quenching to room temperature. From the equatorial diffraction patterns in Figure 7a for PSHQ6 and Figure 7b for PSHQ12 we observe very diffuse lateral spacings, indicating that the melt-drawn fibers of PSHQ6 and PSHQ12 have *no* highly ordered lateral spacing. However, both homopolyester specimens show four-point spots with a few meridional diffraction patterns, an indication of the presence of reflection planes from the solid crystal structures. From the four-point spots we obtain the chain periodicity of 2.48 nm in PSHQ6 and 3.24 nm in PSHQ12, which agree with the fully extended states of chain conformation. On the other hand, from Figure 7c for the copolyester PSHQ6-12 we observe very diffuse meridional and equatorial diffractions, suggesting that PSHQ6-12 has virtually perfect amorphous structure in the solid state. This observation is consistent with the DSC results presented in Figure 1.

Domain Textures of Thermotropic Copolyester PSHQ6-12 and Homopolyesters PSHQ6 and PSHQ12. Figure 8 gives polarized optical micrographs for (a) PSHQ6 at 200 °C, (b) PSHQ12 at 140 °C, and (c) PSHQ6-12 at 170 °C, which were taken during the cooling cycle from the isotropic state. All three polymers exhibits Schlieren texture in the nematic state. It should be remembered that according to the DSC traces given in Figures 1−5, nematic texture is expected at temperatures of ca. 100−190 °C for PSHQ6-12, at temperatures of 120−165 °C for PSHQ12, and at temperatures of ca. 170−230 °C for PSHQ6.

Figure 9 gives a series of polarized optical micrographs taken of a melt-drawn PSHQ12 fiber (a) at 130 °C without being annealed, (b) after being annealed at 130 °C for 1 h, and (c) after being annealed at 130 °C for 72 h, and (d) after being annealed at 130 °C for 72 h and then heated to 160 °C. The following observations are worth noting in Figure 9. (1) The oriented melt-drawn fiber (Figure 9a), when annealed at 130 °C for 1 h, exhibits banded structure (Figure 9b). (2) As the annealing continues at 130 °C for 72 h, the banded structure disappears and then crystalline structure appears (Figure 9c). This can be explained by the DSC results given in Figure 3, indicating that high-temperature melting crystals were formed during the annealing at 130 °C for 72 h and thus the appearance of newly formed high-temperature melting crystals overshadowed the banded structure present in the specimen. (3) However when the melt-drawn fiber, which had been annealed at 130 °C for 72 h, was heated to 160 °C, banded structure reappears (Figure 9d). This can be

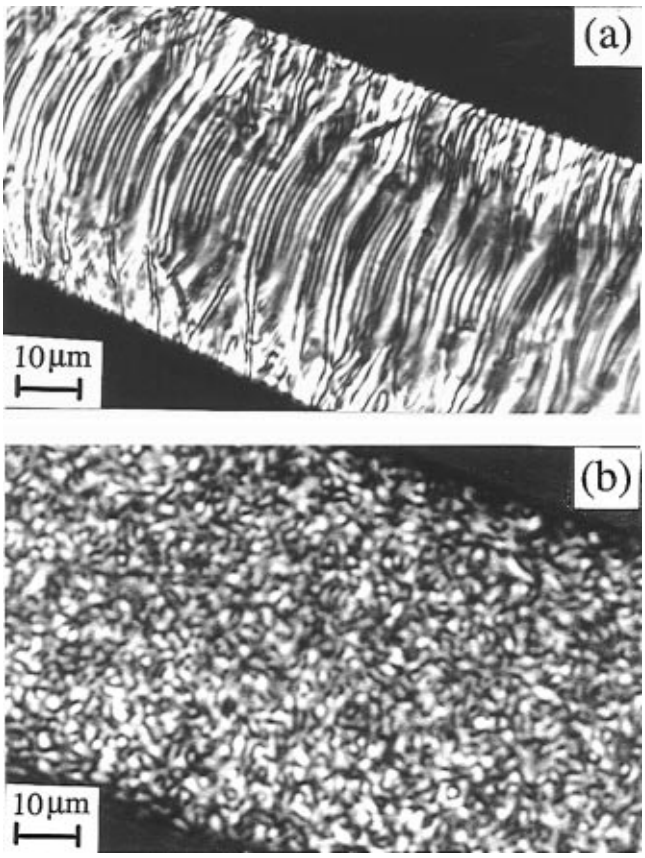


Figure 10. Cross-polarized optical micrographs describing the domain texture of a melt-drawn PSHQ6-12 fiber which had the following thermal histories: (a) after being annealed at 130 °C for 100 h and then heated to 150 °C and (b) after being annealed first at 130 °C for 100 h, heated to 200 °C in the isotropic region, and finally cooled down to 150 °C in the nematic region.

explained by the fact that the high-temperature melting crystals, which were formed during the annealing at 130 °C for 72 h, have the melting point of ca. 150 °C, and thus they melt away at 160 °C, allowing the banded structure to reappear in the melt-drawn fiber specimen. This seems to suggest to us that the orientation patterns present in the banded structure of the melt-drawn fiber specimen remained during the formation of the high-temperature melting crystals.

In the case of PSHQ6, little change in domain texture was observed during annealing at various temperatures. This seems to indicate that PSHQ6 has very long relaxation times, thus delaying the formation of well ordered structure during the period of experiment.

Figure 10 gives polarized optical micrographs of (a) a melt-drawn PSHQ6-12 fiber which was annealed at 130 °C for 100 h and then heated to 150°C, and (b) a melt-drawn PSHQ6-12 fiber which was annealed at 130 °C for 100 h and then heated to 200 °C in the isotropic state followed by slow cooling down to 150 °C. It is of interest to observe in Figure 10a that the banded structure persists in the melt-drawn fiber even after being annealed at 130 °C for 100 h and then heated to 150 °C. This means that *no* high-temperature melting crystal was formed during the annealing of PSHQ6-12, an observation quite different from that made for a melt-drawn PSHQ12 fiber (see Figure 9c). Figure 10b indicates that once the banded structure is destroyed by raising the temperature of a specimen above its T_{NI}, it can never be recovered when its temperature is lowered to the nematic region.

Domain Texture of Lyotropic Solution of Copolyester PSHQ6-12. Micrographs of a 60 wt % solution of PSHQ6-12 in *p*-chlorophenol at room temperature are given in Figure 11, in which the micrograph on the left-hand side describes Schlieren texture, almost identical to that observed in the thermotropic state (see Figure 8c), and the micrograph on the right-hand side describes banded structure that was generated by sliding by hand two glass plates, holding the specimen between the two. The micrographs given in Figure 11 demonstrate clearly that indeed lyotropic solutions can be prepared from the thermotropic copolyester PSHQ6-12 using *p*-chlorophenol as solvent. Isotropic solutions were obtained when the concentration of PSHQ6-12 in *p*-chlorophenol was less than ca. 50 wt %, and biphasic solutions were obtained when the concentration of PSHQ6-12 in *p*-chlorophenol was ca. 50−60 wt %. On the other hand, by dissolving homopolyester PSHQ6 or homopolyester PSHQ12 in *p*-chlorophenol we obtained isotropic solution when its concentration was less than ca. 40 wt % and semicrystalline solution when its concentration exceeded ca. 40 wt %, i.e., we could not obtain lyotropic solutions using homopolyesters PSHQ6 and PSHQ12. This can be explained by the fact that being a semicrystalline polymer, when dissolved in an appropriate solvent (*p*-chlorophenol in the present study), PSHQ6 or PSHQ12 crystallizes first before liquid crystalline phase can set

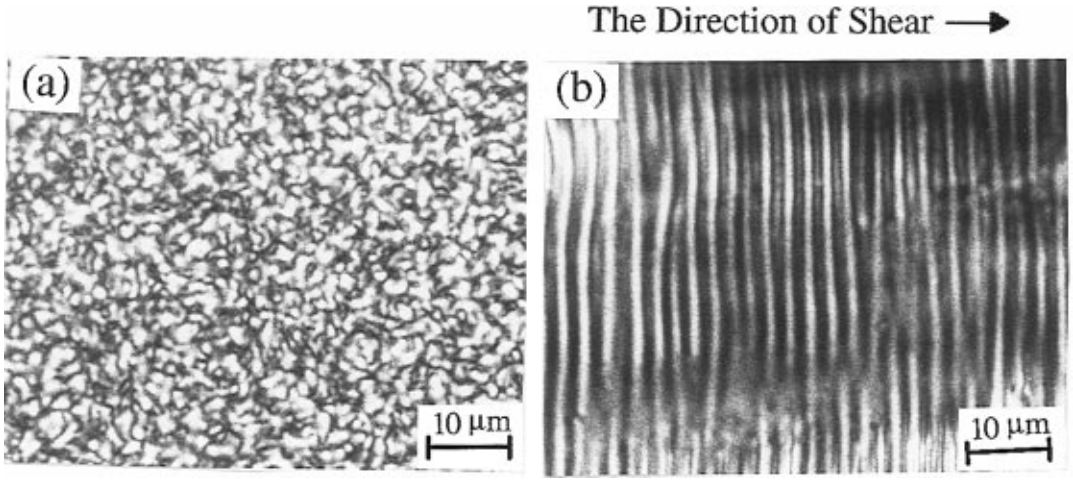


Figure 11. Cross-polarized optical micrographs of a 60 wt % lyotropic solution of PSHQ6-12 in *p*-chlorophenol: (a) Schlieren texture under quiescent condition; (b) banded structure after the specimen was sheared by hand between two glass plates.

in. This is expected to be true for other semicrystalline TLCPs.

Concluding Remarks

In this paper, using DSC, WAXD, and POM we have shown that a thermotropic main-chain random copolyester (PSHQ6-12) having a glassy nematic phase was synthesized via condensation polymerization in solution. We believe that this was realized owing to the fact that a well-packed molecular structure would be very difficult to obtain, if not impossible, when monomers having flexible spacers of greatly differing lengths coexist during copolymerization, i.e., random distributions of 6 CH_2 units and 12 CH_2 units within polymer chains hinder structural regularity, preventing the formation of a well-packed structure. In other words, the random copolyester PSHQ6-12 with flexible spacers of greatly differing lengths apparently suppressed the formation of a well-ordered structure. We believe that the extent of effectiveness of suppressing the formation of a well-ordered structure would increase as the difference in the length of flexible spacers is increased.

We have successfully prepared lyotropic solutions of PSHQ6-12 using *p*-chlorophenol as solvent, while we were not able to prepare lyotropic solutions of homopolyester PSHQ6 or homopolyester PSHQ12 using the same solvent. The possibility of having both thermotropic melt and lyotropic solution from the same chemical structure, PSHQ6-12, opens an exciting opportunity for us to investigate, in the future, the effect of concentration of lyotropic liquid-crystalline polymer solution on rheological behavior. We shall address this problem in the future.

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