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Effect of Bulky Pendent Side Groups on the Structure of Mesophase in a Thermotropic Main-Chain Liquid-Crystalline Polymer

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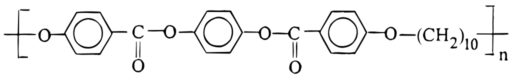
ABSTRACT: We investigated the effect of bulky pendent side groups on the structure of mesophase in a thermotropic main-chain liquid-crystalline polymer, poly[(phenylsulfonyl)-*p*-phenylene 1,10-decamethylenebis(4-oxybenzoate)] (PSHQ10), synthesized in the present study. For comparison, poly(*p*-phenylene 1,10-decamethylenebis(4-oxybenzoate)] (PHQ10) having no pendent side groups was also synthesized. Using wide-angle X-ray diffraction, differential scanning calorimetry, and polarized optical microscopy, we made the following observations: (1) the introduction of phenylsulfonyl side groups into the PHQ10 decreased the isotropization temperature by as much as ca. 140 °C; (2) PHQ10 undergoes three phase transitions, (i) the solid−smectic transition, (ii) the smectic−nematic transition, and (iii) the nematic−isotropic transition; and (3) PSHQ10 undergoes only two phase transitions, (i) the solid−nematic transition and (ii) the nematic−isotropic transition. The absence of a smectic mesophase in the PSHQ10 is ascribed to the presence of bulky phenylsulfonyl side groups, which hinder the molecular packing, thus exerting a steric effect and depressing the smectic properties. The variable-temperature X-ray diffraction patterns indicate further that at temperatures above the melting temperature of crystals, PHQ10 has an ordered structure which is layered and closely packed while PSHQ10 has a less ordered structure, the difference being attributable to the presence of bulky phenylsulfonyl side groups in the PSHQ10. The combined use of low-angle and wide-angle X-ray diffractions taken at various temperatures enabled us to conclude that the PHQ10 has a high-order smectic mesophase. The polarized optical microscopy results reveal that the PHQ10 has a focal conic fan-textured smectic mesophase at temperatures of about 150−260 °C and Schlieren-textured nematic mesophase at temperatures of ca. 260−325 °C, while the PSHQ10 has only a Schlieren-textured nematic mesophase at temperatures of ca. 115−175 °C during the second heating.

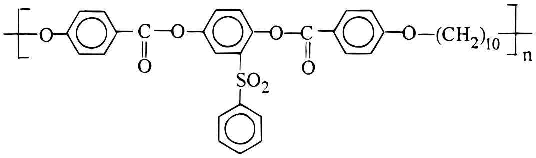
Introduction

During the past decade, numerous studies have been reported on the synthesis of thermotropic main-chain liquid-crystalline polymers (MCLCP), and the readers are referred to the review articles[1−4] for details. Basically, the MCLCP consists of benzene rings interconnected at *para* positions. One such MCLCP, poly(*p*-phenylene 1,10-decamethylenebis(4-oxybenzoate)] (PHQ10), with chemical structure


(PHQ10)

was first synthesized more than a decade ago, and its thermal transition and structure formation were investigated.[5,6] One of the very serious drawbacks of this series of thermotropic MCLCPs lies in their rather high melting temperatures (T_m) and also high clearing temperatures (T_{NI}); thus they are not readily melt processable and may undergo thermal degradation at elevated temperatures (say at 300 °C and above). Therefore some serious efforts[7,8] have been made to lower the T_m and T_{NI} of thermotropic MCLCPs by introducing substituents such as F, Cl, Br, CH$_3$, OCH$_3$, phenyl, or *n*-alkyl groups into or on the mesogenic units.

One such very successful effort was reported by Furukawa and Lenz[7] who introduced bulky phenylsulfonyl side groups onto the mesogenic units of PHQ10 shown above, yielding the structure


(PSHQ10)

This thermotropic homopolyester, poly[(phenylsulfonyl)-*p*-phenylene 1,10-decamethylenebis(4-oxybenzoate)] (PSHQ10), has, although dependent upon molecular weight, a T_m of ca. 110 °C and a T_{NI} of ca. 175 °C and is, in the presence of an antioxidant, thermally very stable at temperatures up to ca. 350 °C as determined by thermal gravimetric analysis. The thermal transition, domain texture, and rheological behavior of PSHQ10 were investigated by various research groups.[9−13]

However, to date few studies have been reported on the effect of bulky pendent side groups on the domain texture of thermotropic MCLCPs with flexible spacers. This subject is of practical importance in the design of MCLCPs that might be melt processable. For this reason, very recently we synthesized both PHQ10 and PSHQ10 in our laboratory and then investigated the effect of thermal history on the domain texture in PHQ10 and PSHQ10, respectively, using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), and polarized optical microscopy (POM). The subject of thermal history is very important to all thermotropic liquid-crystalline polymers (TLCPs) since it greatly affects the domain texture and the rheological behavior (thus processibility) of TLCPs.

In this paper we report the results of our recent investigation, comparing the structure of mesophases in PHQ10 with that in PSHQ10. The purpose of this paper is to describe the role that bulky pendent side

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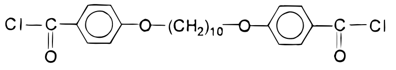
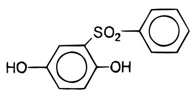
groups play in determining the domain texture in MCLCP, as affected by thermal history.

Experimental Section

In this study both PHQ10 and PSHQ10 were synthesized via solution polymerization in dichloromethane, using a procedure described elsewhere.[7,13] Briefly stated, hydroquinone and 4,4′-bis(chloroformyl)-1,1′-[1,10-decanediylbis(oxy)]bis(benzene) with chemical structure,



which was synthesized in our laboratory using a procedure described elsewhere,[13] were used to synthesize PHQ10, and 2-(phenylsulfonyl)-1,4-hydroquinone with chemical structure



and 4,4′-bis(chloroformyl)-1,1′-[1,10-decanediylbis(oxy)]bis(benzene) were used to synthesize PSHQ10. It should be mentioned that, due to limited solubility in dichloromethane, PHQ10 precipitated out during polymerization. Upon completion of polymerization, the suspension containing precipitated PHQ10 was poured into a nonsolvent, methanol, and the PHQ10 precipitate filtered and dried at 110 °C for 12 h in a vacuum oven. On the other hand, during the polymerization PSHQ10 was solubilized completely in dichloromethane, and the PSHQ10 was fractionated by precipitating several times with methanol and dichloromethane, filtered, and dried in a vacuum oven.

In determining the intrinsic viscosities ($[\eta]$) of PSHQ10 and PHQ10, a mixed solvent consisting of 60 wt % phenol and 40 wt % tetrachloroethane was used; the values of $[\eta]$ determined were 0.686 dL/g for PSHQ10 and 0.213 dL/g for PHQ10, at 40 °C.

For DSC and WAXD measurements with PHQ10, specimens with a thickness of ca. 0.5 mm were prepared by drying the as-polymerized product at 110 °C for 12 h. For WAXD measurement, PHQ10 fibers were also prepared by melt drawing at 260 °C, slightly above the smectic−nematic transition temperature as shown below. For DSC and WAXD measurements with PSHQ10, specimens with a thickness of 0.5 mm were prepared by solvent casting from dichloromethane in the presence of an antioxidant (Irganox 1010; Ciba-Geigy Group) and then slowly evaporating the majority of the solvent first at room temperature for 1 week and then at 80 °C for 3 days to remove any residual solvent. Sample preparation procedures employed for WAXD of melt-spun PSHQ10 fibers are described elsewhere.[14] For taking micrographs using POM, PHQ10 and PSHQ10 specimens were prepared at 70 and 25 °C, respectively, by casting from a 1 wt % solution of 1,1,2,2-tetrachloroethane on a slide glass to make a thin film of about 2−3 μm in thickness.

Thermal transition temperatures of PHQ10 and PSHQ10 were determined by using a differential scanning calorimeter (DuPont 9900), under a nitrogen atmosphere, at heating and/or cooling rates of 20 °C/min. Also used were variable heating and/or cooling rates (5, 20, and 60 °C/min). Thermal histories (namely, annealing temperature and duration of annealing) of the specimens were varied.

WAXD experiments were conducted at room temperature on both melt-drawn fibers and as-polymerized powders of PHQ10 and on as-cast films of PSHQ10, using a General Electric X-ray generator (Model XRD-6) operating at 30 kV and 30 mA (Ni-filtered Cu Kα radiation). The flat plate diffraction patterns were recorded with a 53.3 mm film-to-specimen distance. The exposure time for each measurement was 4 h. Also conducted were variable-temperature WAXD experiments on as-polymerized powder of PHQ10 and as-cast films of PSHQ10, using a Rigaku X-ray generator operating at 40 kV and 30 mA. The X-ray beam was monochromatized to Cu Kα with a graphite crystal. The 2θ scanning range employed was 1.3−45.0° in reflection. A temperature controller with an accuracy of ±1 °C was used, the diffraction patterns being measured at various temperatures ranging from 25 to 280 °C.

A hot stage (TH-600 type; Linkham Scientific Co.), microscope (Nikon, Model Optiphoto polXTP-11) with a camera and a programmable temperature controller, and photomicrographic attachment were used to take pictures, under cross-polarized light, of films solvent cast on a slide glass.

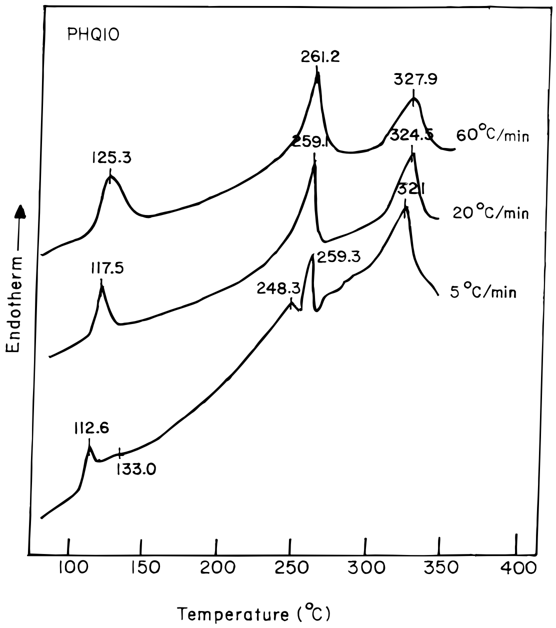


Figure 1. DSC traces for as-polymerized PHQ10 specimens at various heating rates as indicated in the figure.

Results

DSC Results. Figure 1 gives traces of DSC thermograms of as-polymerized PHQ10 at various heating rates, namely, 5, 20, and 60 °C/min. For all three heating rates, the as-polymerized PHQ10 specimens exhibit three major endothermic peaks: (i) a temperature peak at 112−125 °C depending upon the heating rate employed, (ii) an intermediate peak at ca. 260 °C, and (iii) the highest peak at ca. 321−328 °C, again depending upon the heating rate employed. Later in this paper we will show that the endothermic peak at 112−125 °C is attributable to the melting of *unstable crystals*[15] which were formed during solution polymerization. As will be elaborated on below, using WAXD and POM, the peak at ca. 260 °C represents the smectic−nematic transition, while the peak at about 321−328 °C represents nematic−isotropic transition. At the slowest heating rate employed, 5 °C/min, a very small endothermic peak appears at 133 °C, about 20 °C above the lowest endothermic peak, and another small endothermic peak appears at 248 °C, ca. 11 °C below the intermediate endothermic peak. But these two minor endothermic peaks do not appear at higher heating rates, 20 and 60 °C/min. At present we suggest that at a heating rate of 5 °C/min, (i) the peak at 133 °C arose from the melting of the crystals which were formed, via recrystallization, from the *unstable crystals* originally formed during solution polymerization and (ii) the peak at 248.3 °C arose from the melting of some portions of smectic crystals, which recrystallized during the DSC run and then melted again in the main peak at 259 °C.

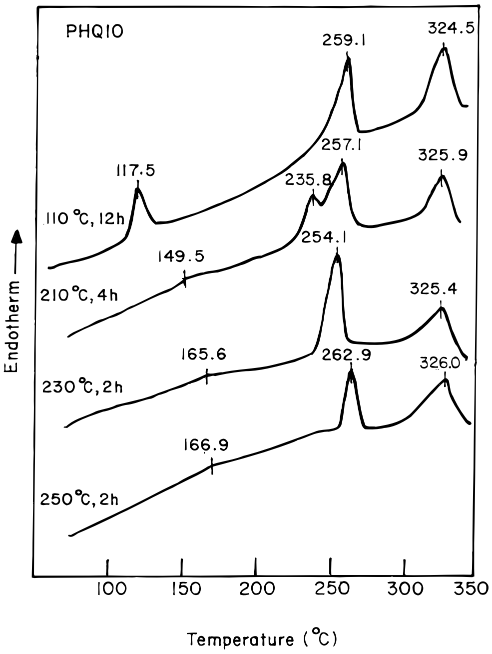


Figure 2. DSC traces for as-polymerized PHQ10 specimens at 20 °C/min which were annealed under isothermal conditions at various temperatures as indicated in the figure.

In order to have a better understanding of the nature of the thermal transitions observed in Figure 1, we conducted further DSC measurements at a heating rate of 20 °C/min by annealing as-polymerized PHQ10 specimens at various temperatures; the results of which are summarized in Figure 2. As the annealing temperature is increased from 110 to 210 °C or higher, the large endothermic peak at 117.5 °C disappears and a very small endothermic peak appears at ca. 150−167 °C depending upon the temperature employed for the isothermal annealing. Notice that this transition temperature is ca. 40−50 °C higher than the lowest transition temperature, 117.5 °C, observed when the specimen was annealed at 110 °C for 12 h. This observation leads us to conclude that the low-temperature endothermic peak (112−125 °C) in Figure 1 represents the melting temperature of the '*unstable crystals*' that were formed during solution polymerization, whereas the very weak endothermic peak at 150−167 °C in Figure 2 represents the melting of the crystals that were formed during cooling after the isothermal annealing. Regardless of the annealing conditions employed, Figure 2 shows two very distinct endothermic peaks: one at ca. 260 °C representing the smectic−nematic transition and another at ca. 325 °C representing the nematic−isotropic transition.

Figure 3 gives traces of DSC thermograms of an as-polymerized PHQ10 specimen at 20 °C/min during (i) the first heating cycle, (ii) the first cooling cycle, and (iii) the second heating cycle. These DSC runs were restricted to temperatures below 280 °C because we were interested in comparing the DSC results with the variable-temperature WAXD results which were obtained using an X-ray instrument that could only be heated to 280 °C. The comparison will be presented later in this paper. The endothermic peak representing the 325 °C nematic−isotropic transition temperature (T_{NI}) (see Figure 1) is not shown in Figure 3.

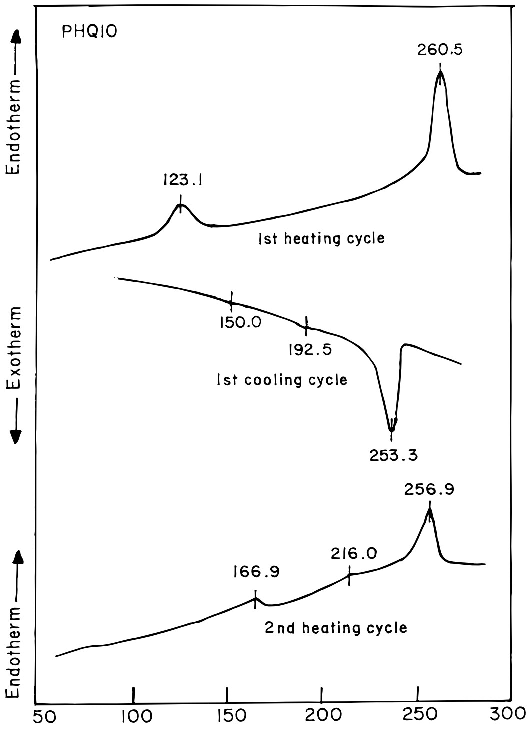


Figure 3. DSC traces for as-polymerized PHQ10 specimens at 20 °C/min during (i) the first heating cycle, (ii) the first cooling cycle, and (iii) the second heating cycle.

The following observations are worth noting for Figure 3. (1) In the first heating cycle the peak at 123.1 °C represents the melting of the '*unstable crystals*' formed during solution polymerization, and the peak at 260.5 °C represents the smectic−nematic transition temperature (T_{SN}). The area of the lower endothermic peak is 5.0 kJ/mol, while the area of the higher endothermic peak is 13.2 kJ/mol. (2) During cooling only one distinct and two very small exothermic peaks are seen. The peak at 253.3 °C represents the nematic−smectic transition temperature (T_{NS}) which is ca. 7 °C lower than that observed during the first heating cycle. This difference is attributable to the supercooling that took place during the cooling cycle. The small peak at 192.5 °C is believed to be associated with an additional chain-ordering process taking place in the smectic mesophase already formed (as will be shown below using the WAXD results), and another very small peak at 150 °C, barely discernible, describes the smectic−crystal transition temperature. (3) In the second heating cycle, three endothermic peaks are seen at (i) 166.9 °C (weak peak), (ii) 216.0 °C (weak peak), and (iii) 256.9 °C (strong peak). The peak at 166.9 °C represents the melting of the crystals which were formed during the cooling cycle, into a well-ordered smectic mesophase, and the weak intermediate peak at 216.0 °C represents the phase transition from a well-ordered smectic mesophase into a less ordered smectic mesophase. Finally, the highest peak at 256.9 °C represents T_{SN}, very close to that observed during the first heating cycle.

For comparison, DSC thermograms obtained at a heating rate of 20 °C/min of an as-cast PSHQ10 specimen are given in Figure 4 with the effect of thermal history on the thermal transition of PSHQ10 reported in some detail in previous studies.[11,14] The specimen was prepared by first removing the majority of the solvent, dichloromethane, at room temperature under the laboratory hood and then the residual solvent in a vacuum oven at 80 °C for 3 days. During the first heating cycle two endothermic peaks appear, (i) a very

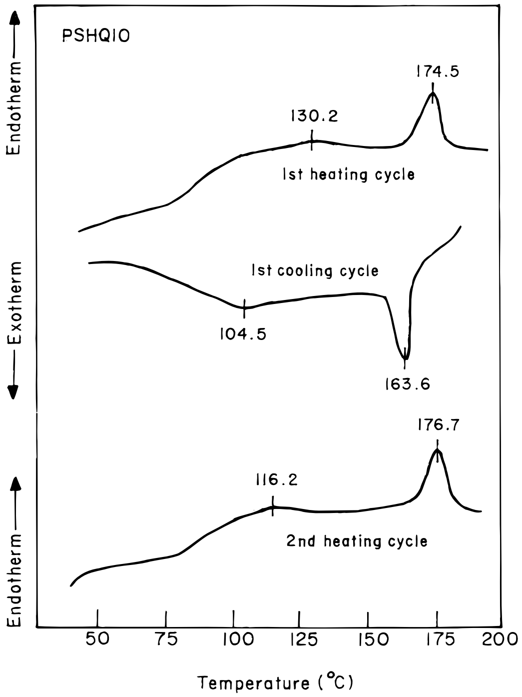


Figure 4. DSC traces for as-cast PSHQ10 specimens at 20 °C/min during (i) the first heating cycle, (ii) the first cooling cycle, and (iii) the second heating cycle.

small peak at 130.2 °C describing the melting of the crystals which were formed via recrystallization (the so-called '*high-temperature melting crystals*,' the origin of which is described in ref 14) and (ii) a large peak at 174.5 °C representing T_{NI}. During cooling, two exothermic peaks appear, one at 163.6 °C representing T_{NI} and another at 104.5 °C representing the nematic—crystal transition temperature. During the second heating cycle two endothermic peaks appear, T_m at 116 °C and T_{NI} at 176.7 °C.

WAXD Results. Figure 5a gives flat plate diffraction patterns, showing two strong peaks, taken at room temperature of an as-polymerized PHQ10 specimen which was annealed at 210 °C for 4 h. The thermal history of this specimen was the same as the one in Figure 2. This seems to suggest that a well-ordered structure is present in the PHQ10 specimen. For comparison, flat plate diffraction patterns of an as-cast PSHQ10 specimen annealed at 130 °C for 80 h is given in Figure 5b. The film thicknesses in both polymer samples were about the same (0.5 mm). The WAXD diffraction patterns of the annealed as-cast PSHQ10 specimen (Figure 5b) are weaker than those of the annealed as-polymerized PHQ10 specimen (Figure 5a), suggesting that the annealed PSHQ10 specimen is less ordered than PHQ10 specimen. In a previous paper,[14] we reported on the effect of annealing on the structure of crystals in PSHQ10, and for more details the readers are referred to the original paper.

In order to obtain more detailed information on the structure formed in PHQ10 and PSHQ10, fiber diffraction patterns of PHQ10 and PSHQ10 were examined. Figure 6 gives WAXD patterns taken at room temperature of (a) an unannealed melt-drawn PHQ10 fiber and (b) an unannealed melt-drawn PSHQ10 fiber, respectively. The melt-drawn PHQ10 fiber in Figure 6a has strong equatorial reflections, while the melt-drawn PSHQ10 fiber has only a diffuse equatorial reflection. Due to the large differences between the diffraction peak intensities, the locations of the meridional and equatorial diffraction peaks were determined by varying the exposure time of a melt-drawn PHQ10 fiber to X-ray. The presence of a high-intensity peak (0.425 nm) and a weak intensity peak (0.246 nm) on the equatorial in the PHQ10 fiber supports a hexagonal structure, and the lattice spacings are summarized in Table 1. However, due to the possibility of additional ordering that might have taken place in the annealed as-cast specimen, we speculate that PHQ10 has an orthorhombic (possibly monoclinic) lattice structure, in which the *d*-spacings of the (100) and (110) planes are 0.425 and 0.246 nm, respectively. In addition to the equatorial diffraction peaks, two meridional peaks, (002) and (004), of medium strength and three very weak peaks, (005), (007), and (009), were obtained.

The WAXD pattern of an unannealed melt-drawn PSHQ10 fiber in Figure 6b shows (a) an equatorial diffraction pattern typical of liquid-crystalline lateral packing (0.3—0.6 nm) and (b) a layer line spacing from highly aligned fibers of 2.89 nm; the first layer line is a symmetric four-point diffraction pattern with the spots elongated horizontally. We suggest that it is due to the reflection planes inclined from the chain axis (distributed about 63°) with the separation along the fiber axis being maintained at chemical repeat unit distance. In addition to the four-point diffraction pattern on presum-

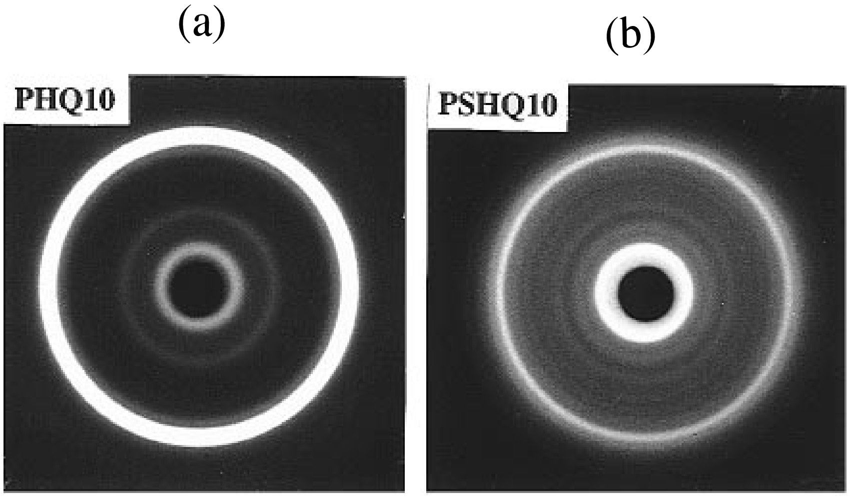


Figure 5. WAXD patterns at room temperature of (a) as-polymerized PHQ10 specimens annealed at 210 °C for 4 h and (b) an as-cast PSHQ10 specimen annealed at 130 °C for 80 h.

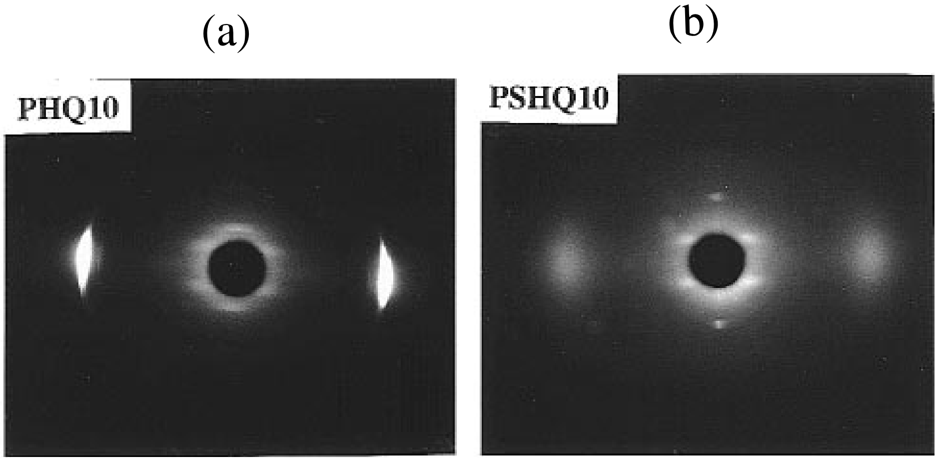


Figure 6. WAXD patterns at room temperature of (a) an unannealed melt-drawn PHQ10 fiber and (b) an unannealed melt-spun PSHQ10 fiber.

Table 1. *d*-Spacings for the Unannealed Melt-Drawn PHQ10 Fiber

2θ (degrees)		d (nm)			
expt	calcd	expt	calcd	(hkl)	comments[a]
Meridional Diffraction					
2.85	2.86	31.00	30.94	(001)	medium
5.71	5.72	15.47	15.47	(002)	medium
11.65	11.46	7.59	7.74	(004)	medium
14.73	14.34	6.01	6.18	(005)	weak
20.41	20.13	4.35	4.41	(007)	weak
26.40	25.97	3.38	3.43	(009)	weak
Equatorial Diffraction					
20.91	20.88	4.25	4.25	(100)	very strong
36.55	36.63	2.46	2.45	(110)	weak

[a] Intensity of the diffraction peak.

ably the first layer line, additional meridional reflections are seen with *d*-spacings of 0.976 and 0.494 nm, thus corresponding to the third and sixth layer line. Normally one would interpret the first layer line spacing as the physical repeat unit distance and the spacing of the first meridional reflection over the first layer line as the chemical repeat unit distance along the fiber axis. However, the extended chemical repeat unit distance has a length of 3.1 nm, while (003) has a 0.976 nm spacing. Since it is unlikely that the molecules are kinked at a sufficient angle to reduce the projected chemical repeat unit length by ca. $^{1}/_{3}$, this suggests that from the streaks and the (003) and (006) reflections axially displaced structure exists due to the bulky pendent phenylsulfonyl groups.

Figure 7 gives a low-angle X-ray scattering pattern taken at room temperature of an unannealed melt-drawn PHQ10 fiber, showing sharp (002) and (004) reflections along the meridional axis, in addition to the two diffuse maxima on the first layer line. The four-point diffraction patterns on the first layer line are connected by a streak, suggesting the presence of a defective layered crystal-like structure,[16] whereas in PSHQ10 they are individual elongated spots. From the first layer line we estimate the chain periodicity in PHQ10 to be 3.1 nm, which is slightly larger than the chain periodicity in PSHQ10. We believe that this difference in chain periodicity between PHQ10 and PSHQ10 can be attributed to the presence of the bulky pendent side groups which hinder the lateral packing in PSHQ10.

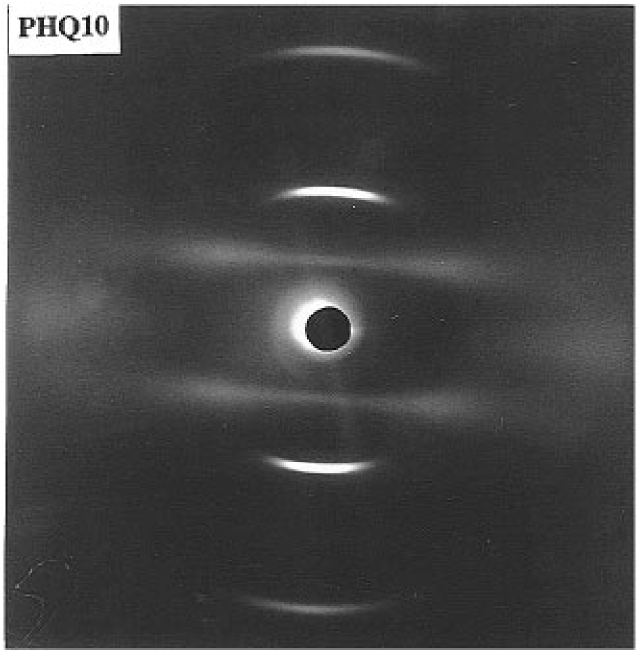


Figure 7. Low-angle X-ray diffraction patterns of an unannealed melt-drawn PHQ10 fiber.

In addition to the structural information on the PHQ10 specimen obtained at room temperature, WAXD patterns were also taken at elevated temperatures. Figure 8 summarizes the variable-temperature X-ray diffraction patterns obtained for an unannealed as-polymerized PHQ10 specimen: (a) first heating cycle, (b) first cooling cycle, and (c) second heating cycle. The selected temperature range used in obtaining the results in Figure 8 was identical with that used in obtaining the DSC thermograms in Figure 3. At 25 °C during the first heating cycle (see Figure 8a), there are five peaks, representing the presence of what we have defined as *unstable crystals* that were formed during solution polymerization. In agreement with the DSC results given in Figure 3, the *unstable crystals* transform at ca. 110−140 °C during the variable-temperature X-ray experiment. Below we will elaborate on this further. As the temperature is increased from 140 to 170 and 240 °C, only one very large and sharp peak is observed, suggesting that a transformation into a less ordered structure occurred in the PHQ10 in this range of temperature. As the temperature is increased further to 270 °C, the peak broadens significantly in agreement with the prior observation via DSC of a transformation to a nematic phase. Such an ordered structure was also

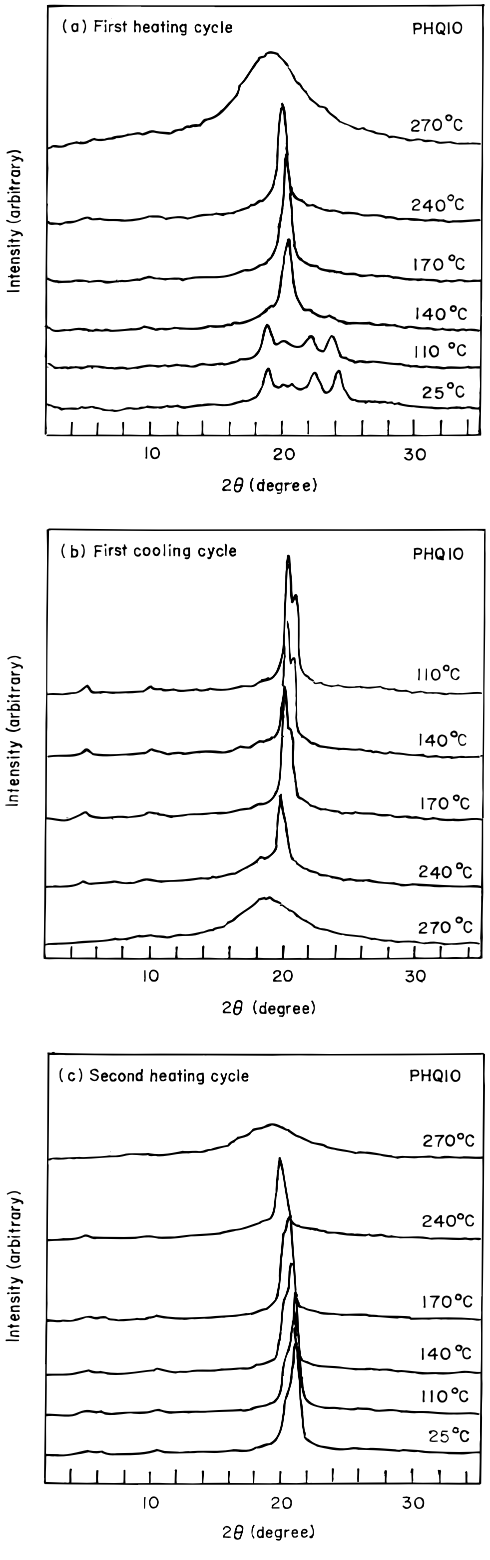


Figure 8. Variation of the X-ray diffraction intensity with scattering angle θ for an as-polymerized PHQ10 specimen during (a) the first heating cycle, (b) the first cooling cycle, and (c) the second heating cycle at various temperatures, as indicated on the plot.

confirmed by POM, which will be presented below. Figure 8b shows the results of the first cooling cycle. The single peak at 2θ of ca. 20° becomes very sharp again, almost reproducing the peak which was observed during the first heating cycle. However, at ca. 170 °C, a second peak appears, indicating the development of the orthorhombic (or possibly monoclinic) packing. This explains the two exothermic peaks, one at 253.3 °C and the other at 192.5 °C, observed in the DSC thermograms during the cooling cycle in Figure 3. Most interestingly, during the cooling cycle at temperatures below 240 °C, additional peaks appear at low scattering angles corresponding to (002) and (004), suggesting that a highly ordered layered structure exists in the PHQ10. On this basis, we suggest that the structure of mesophase in the PHQ10 at temperatures from ca. 110 to ca. 240 °C is some form of smectic. As the temperature is increased once again during the second heating cycle (Figure 8c), the double peak which was observed during the previous cooling cycle is reproduced except that the intensity ratio of the two reflections is reversed. This reinforces our view that an ordered structure exists in PHQ10 at temperatures from ca. 110 to ca. 240 °C. On the basis of the lower 2θ peaks, we conclude that PHQ10 has a layered mesophase, which is believed to be some form of higher order smectic.

Figure 9 summarizes similar variable-temperature WAXD results obtained for an unannealed as-cast PSHQ10 specimen: (a) first heating cycle, (b) first cooling cycle, and (c) second heating cycle. The range of temperatures selected for obtaining the WAXD results in Figure 9 was identical with that used to obtain the DSC thermograms in Figure 4. The shape of the main peak, observed during the two consecutive heating cycles and the cooling cycle, is *virtually* identical, indicating that the structure of the mesophase (i.e., nematic phase) in PSHQ10, which was confirmed independently by POM, changed little from room temperature to 160 °C, becoming somewhat broader in the isotropic region at 190 °C. The peak at large scattering angles for PSHQ10 is rather broad, and there are very weak additional peaks at low scattering angles, suggesting that the ordered structure in the range of 110–175 °C is a one-dimensional liquid-crystalline structure.

POM Results. POM was used to clarify the tentative conclusions about the structures of the mesophases in PHQ10 and PSHQ10 based on the WAXD results. Figure 10 gives representative POM micrographs of an as-polymerized PHQ10 specimen at (a) 240 and (b) 260 °C, taken during the cooling cycle. PHQ10 exhibits (a) a focal conic fan-textured smectic mesophase at 240 °C and (b) a Schlieren-textured nematic mesophase at 260 °C. Thus the smectic–nematic transition temperature is ca. 260 °C. The sample loses all textures at ca. 330 °C, indicating that this is the nematic–isotropic transition (i.e., isotropization) temperature, in agreement with DSC results (see Figure 1). The domain texture observed for PHQ10 at temperatures below 240 °C looked the same as shown in Figure 10a. Accurate determination of the transition from the solid to the smectic mesophase was difficult using POM; there was no obvious change in texture from 240 °C to room temperature. Earlier, using POM, Strzelecki and van Luyen[5] determined the smectic–nematic transition to be ca. 225 °C and the nematic-isotropic transition to be 270 °C in a PHQ10. The differences between the transition temperatures reported by Strzelecki and van Luyen and those determined in the present study are attributable to the differences in molecular weight of the polymers employed. Previously it was reported[9,11] that PSHQ10 has a Schlieren-textured nematic mesophase (very much like that in Figure 10b) at temperatures from ca. 115 to ca. 175 °C; a smectic mesophase was not observed in PSHQ10. This was confirmed in the present study.

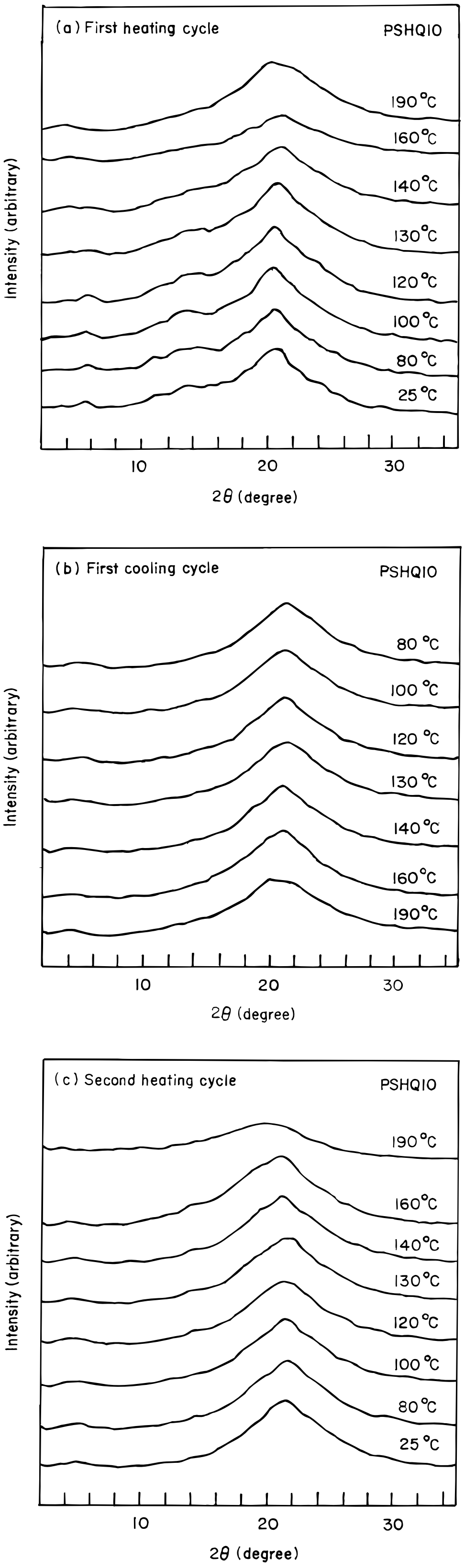


Figure 9. Variation of the X-ray diffraction intensity with scattering angle θ for an as-cast PSHQ10 specimen during (a) the first heating cycle, (b) the first cooling cycle, and (c) the second heating cycle at various temperatures, as indicated on the plot.

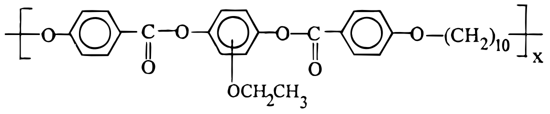
Discussion

Origin of the Unstable Crystals in As-Polymerized PHQ10. The DSC (see Figures 1 and 2) and WAXD (see Figure 8) results suggested that as-polymerized PHQ10 specimens contain *unstable crystals* which were formed during solution polymerization. In order to find the physical origin of the *unstable crystals* present in an as-polymerized PHQ10 specimen, we conducted the following experiments. A small amount of as-polymerized PHQ10 was placed in tetrachloroethane, a better solvent than the dichloromethane used for the solution polymerization. The PHQ10 did not dissolve completely in tetrachloroethane at room temperature but dissolved completely at an elevated temperature (e.g., at 100 °C). After the complete dissolution of PHQ10 in tetrachloroethane at 100 °C, PHQ10 reprecipitated during cooling slowly to room temperature. The reprecipitated PHQ10 was dried in a vacuum oven.

Figure 11 gives WAXD patterns taken at room temperature for (a) an as-polymerized PHQ10 specimen and (b) a reprecipitated PHQ10 specimen. The as-polymerized PHQ10 specimen shows three strong diffraction rings, while the reprecipitated specimen shows only one. It should be mentioned that the presence of the three diffraction rings in Figure 11a is consistent with the presence of the three strong peaks observed at 25 °C during the first heating cycle of the variable-temperature X-ray diffraction experiment (see Figure 8a). We thus conclude that the *unstable crystals* present in as-polymerized PHQ10 specimen were formed during solution polymerization.

Effect of the Size of Pendent Side Groups on the Structure Formation in PSHQ10. Having confirmed in this study the existence of both the smectic and nematic mesophases in PHQ10 while only the nematic mesophase occurs in PSHQ10, we must address the fundamental question as to why *no* smectic mesophase is observed in PSHQ10. According to Gray,[17] lateral substitution resulting in additional molecular twisting (a steric effect) always depresses smectic properties very strongly. Thus, we speculate that the presence of bulky phenylsulfonyl side groups in PSHQ10, which hinders the molecular packing (i.e., exerts a steric effect), greatly depresses smectic properties, giving rise to only the nematic mesophase in PSHQ10. The fact that phenylsulfonyl side groups in PSHQ10 are presumably irregularly positioned along the chain axis would also contribute to the hindrance of molecular packing. If this speculation has merit, the size of the pendent side groups substituted to a PHQ10 must play an important role in determining the types of mesophases in the resulting polymers.

Very recently, Hudson et al.[18] investigated the structure of the mesophases in an ethoxy-substituted poly[phenylene 1,10-decamethylenebis(4-oxybenzoate)] (PEHQ10) with chemical structure



This is simply an ethoxy-substituted PHQ10. According to Hudson et al., this MCLCP (hereafter referred to as PEHQ10) has both smectic and nematic mesophases, as determined by DSC, POM, and WAXD. However, according to the DSC thermograms (see Figure 1 in ref 18) reported by Hudson et al., the area under the DSC endothermic peak representing the smectic−nematic transition in an unannealed PEHQ10 specimen is very small as compared to that representing the nematic−

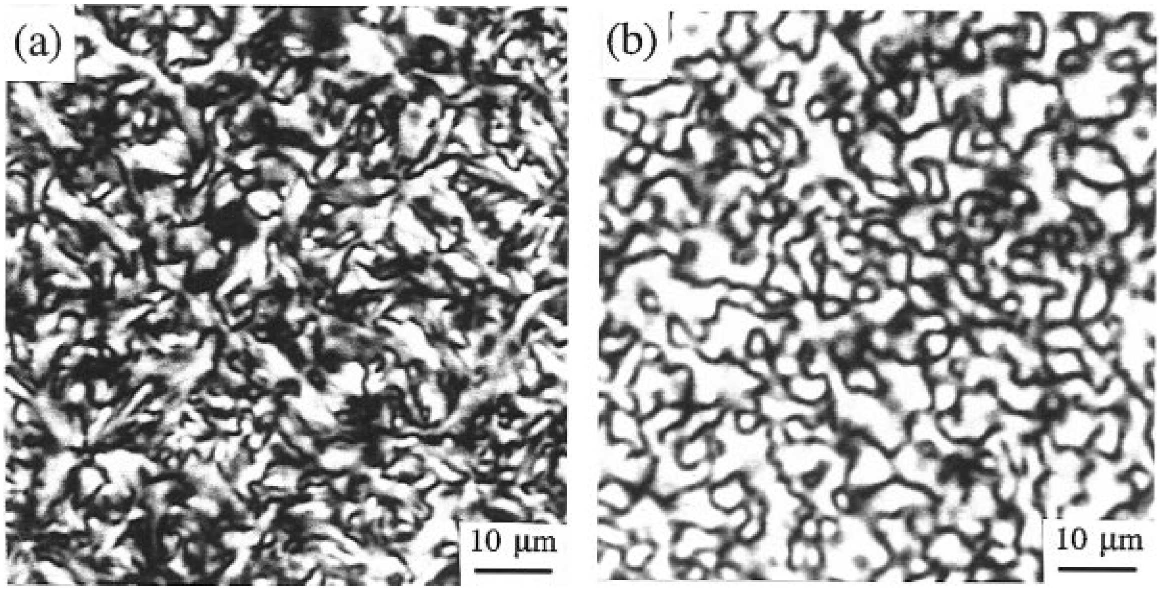


Figure 10. Cross-polarized optical micrographs of an as-polymerized PHQ10 specimen: (a) focal conic fan-textured smectic mesophase at 240 °C and (b) Schlieren-textured nematic mesophase at 260 °C. These micrographs were taken while the specimen was being cooled after it had first been heated to the nematic region at 270 °C. Both DSC and WAXD results indicate that the PHQ10 undergoes the smectic−nematic transition at ca. 260 °C, as may be seen in Figures 1 and 2.

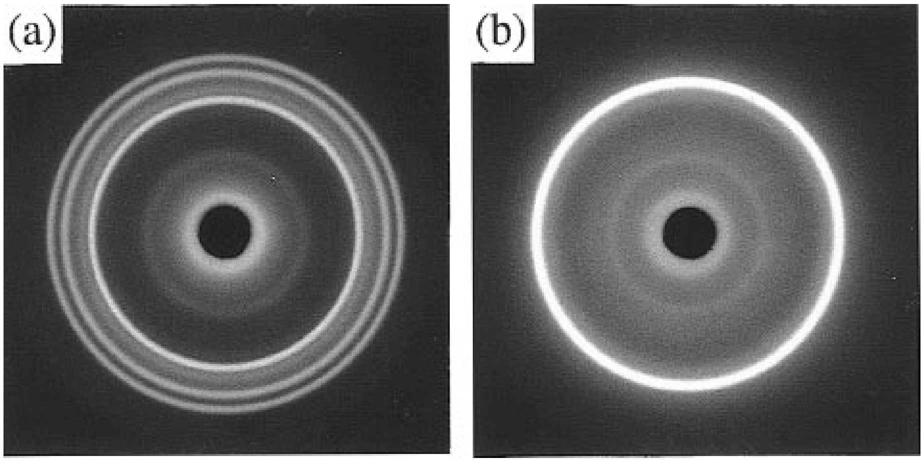


Figure 11. WAXD patterns at room temperature of (a) as-polymerized PHQ10 specimens and (b) a reprecipitated PHQ10 specimen which was prepared by first dissolving in tetrachloroethane at 100 °C and then slowly cooling down to room temperature.

isotropic transition. We have already shown in Figures 1 and 2 that the area under the DSC smectic−nematic endothermic peak in an unannealed PHQ10 specimen, which has *no* pendent side groups, is as large as or larger than that representing the nematic−isotropic transition, while in Figure 4 there is *no* DSC endothermic peak representing the smectic−nematic transition in PSHQ10 having large phenylsulfonyl side groups. The phenylsulfonyl substituent in PSHQ10 is much bulkier than the ethoxy substituent in PEHQ10. This then seems to suggest that the size and shape of pendent side groups that are attached to a PHQ10, and also chemical ordering, play a crucial role in determining whether or not such polymers might have the smectic mesophase. We thus conclude from the above observation that the ethoxy side group in PEHQ10, which was employed by Hudson et al., was not sufficiently large enough to completely depress the smectic properties, while the phenylsulfonyl side groups in PSHQ10 were bulky enough to completely depress the smectic properties.

Previously Cheng et al.[19,20] investigated the kinetics of the mesophase transition in a thermotropic copolyester consisting of *p*-terephthalic acid (TPA), phenylhydroquinone (PHQ), and (1-phenylethyl)hydroquinone (PEHQ) with various molar ratios and concluded, based on WAXD measurements, that the presence of the bulky pendent side groups, phenylethyls, in PEHQ hindered the molecular packing, disturbing the lateral packing in the crystals in the copolyester. The results of the present study corroborate their findings.

Concluding Remarks

We have shown that the introduction of bulky phenylsulfonyl side groups to a thermotropic main-chain liquid-crystalline polyester having decamethylene as flexible spacers, PHQ10, lowered its clearing temperature by as much as ca. 140 °C and has a profound influence on the structure of the mesophases. Specifically, DSC analysis indicated that as-polymerized PHQ10 has *unstable crystals* which melt at ca. 110−125 °C, depending upon the heating rate employed, and undergoes (i) a smectic−nematic transition at ca. 260 °C and (ii) a nematic−isotropic transition at ca. 325 °C. However, when annealed at a temperature ranging from 140 to 250 °C, the *unstable crystals* in PHQ10 transformed and never appeared again during the subsequent cooling or heating cycle, but recrystallization did occur during

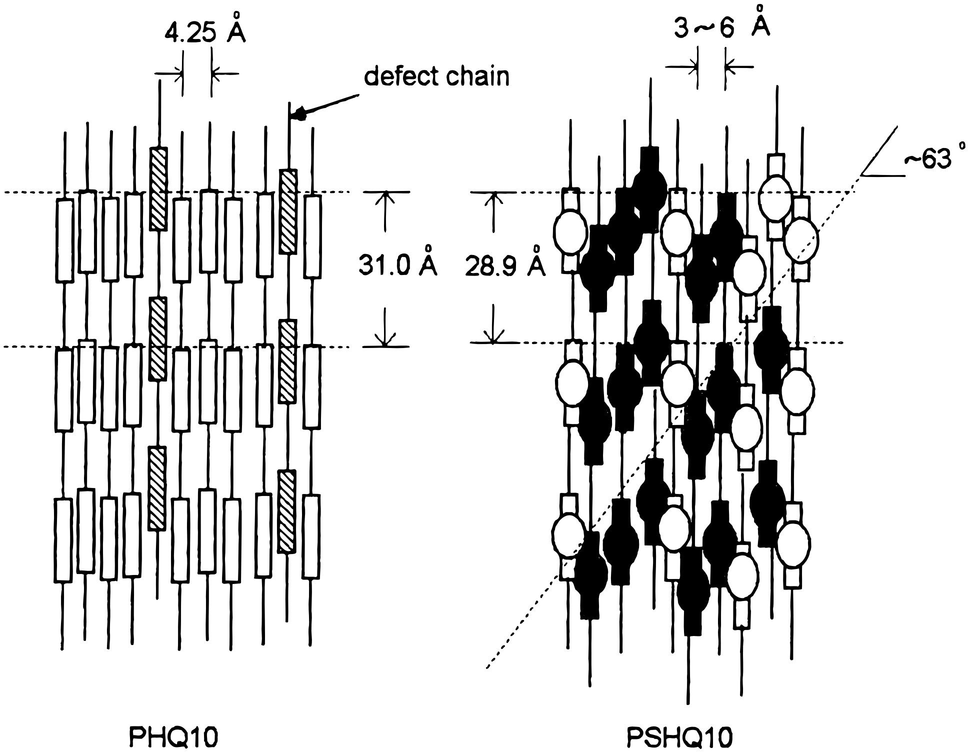


Figure 12. Schematic of the proposed molecular model for (a) PHQ10 that shows regular spacing, which is believed to be responsible for the existence of a high-order smectic mesophase, and (b) PSHQ10 that has phenylsulfonyl side groups (indicated by ellipse). Here the rectangles aligned in the vertical direction represent mesogenic groups and the solid lines between mesogenic groups represent flexible spacers.

the isothermal annealing, forming new crystals which melt at ca. 165 °C (see Figure 2). Isothermal annealing did not change the characteristics of the smectic−nematic and nematic−isotropic transitions in PHQ10. Combined wide- and low-angle X-ray diffractions confirmed the existence of a high-order smectic mesophase in PHQ10 at temperatures ranging from ca. 160 to 250 °C. This was further confirmed by POM. Based on WAXD patterns, as-polymerized PHQ10 at room temperature has a highly ordered crystal structure.

On the other hand, DSC thermograms of PSHQ10, having bulky phenylsulfonyl side groups, show only a solid−nematic transition at ca. 110 °C and the nematic−isotropic transition at ca. 175 °C. WAXD and POM show *no* evidence of the existence of a smectic mesophase in PSHQ10 over the entire range of temperatures (25−190 °C) investigated. We thus concluded that the bulky phenylsulfonyl side groups present in the PSHQ10 hinder the molecular packing, exerting a steric effect, and then depress the smectic properties. The WAXD patterns show only meridional reflections and a broad peak, suggesting that there also is no well-defined crystal structure in PSHQ10 at room temperature. Using variable-temperature WAXD and POM, we confirmed the existence of the nematic mesophase in PSHQ10 at temperatures ranging from ca. 110 to 175 °C.

On the basis of the X-ray diffraction patterns obtained in this study, we postulate the molecular models for PHQ10 and PSHQ10 shown schematically in Figure 12. A layered close packing with a periodicity of 3.1 nm in PHQ10 is suggested. On the other hand, owing to the presence of bulky phenylsulfonyl side groups, this layered structure is greatly suppressed in PSHQ10, and lateral regularity is also interrupted by these groups. Therefore it is suggested that the hindrance due to the presence of bulky phenylsulfonyl side groups yields ~63° axially displaced molecular packing (as indicated by the filled symbols in Figure 12) with a chain repeat unit periodicity of 2.89 nm. Confirmation of the proposed molecular models by using solid-state nuclear magnetic resonance spectroscopy and scanning tunneling microscopy is in progress and will be reported in a future publication.

Most importantly, what remains to be pursued in the future is the development of a theory that will enable one to predict the role that bulky pendent side groups present in a TLCP play in determining the type(s) of mesophase in the polymer. Such a theory, when available, will help in the design of new liquid-crystalline polymers of practical importance.

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