Synthesis and Characterization of a Combined Main-Chain/Side-Chain Liquid-Crystalline Polymer Exhibiting Both Thermotropic and Lyotropic Characteristics and Its Lyotropic Phase Behavior

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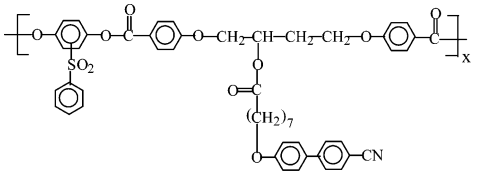
ABSTRACT: A combined main-chain/side-chain liquid-crystalline polymer (PSHQ4−7CNCOOH), which is composed of poly[(phenylsulfonyl-*p*-phenylenene 1,4-tetramethylene bis(oxybenzoate)] (PSHQ4) as the main-chain backbone and 8-[(4-cyano-4′-phenyl)oxy]octanoic acid (7CNCOOH) as the side-chain mesogenic groups, has been synthesized. It has been found that 7CNCOOH has a clearing temperature of 150 °C and exhibits nematic mesophase, and PSHQ4−7CNCOOH exhibits both thermotropic and lyotropic characteristics. The thermotropic characteristics of PSHQ4−7CNCOOH have been investigated using differential scanning calorimetry (DSC), fiber and powder patterns of wide-angle X-ray diffraction (WAXD), and polarized optical microscopy (POM). It has been found that in the thermotropic state PSHQ4−7CNCOOH has a glass transition temperature (T_g) of 85 °C and a nematic-to-isotropic (N−I) transition temperature (T_{NI}) of 172 °C, and it is a glassy polymer. Interestingly, PSHQ4−7CNCOOH is found to exhibit lyotropic characteristics, undergoing isotropic-to-nematic biphasic separation over a wide range of concentrations in *m*-dibromobenzene, *o*-dichlorobenzene, and tetrachloroethane, enabling us to construct a phase diagram. The thermal transitions and phase structures of the main-chain backbone of PSHQ4−7CNCOOH, PSHQ4, were compared with those of PSHQ4−7CNCOOH. It has been found that PSHQ4 has a T_g of ca. 130 °C and a T_{NI} of ca. 260 °C, and it undergoes, during isothermal annealing, crystallization at about 240 °C as determined from DSC. Both the fiber and powder patterns of WAXD indicate that PSHQ4 is a semicrystalline polymer, which is consistent with the findings from DSC. It has been found that, in contrast to PSHQ4−7CNCOOH, PSHQ4 does not exhibit lyotropic characteristics. Both the very large decrease (about 90 °C) in T_{NI} after the attachment of side-chain mesogenic groups (7CNCOOH) onto the main-chain backbone (PSHQ4) and the lyotropic characteristics of PSHQ4−7CNCOOH are attributable to the significant increase in the bulkiness of PSHQ4−7CNCOOH, which apparently cannot pack well, giving rise to a glassy state.

1. Introduction

Beginning in the early 1970s, the synthesis of liquid-crystalline polymers (LCPs) for industrial applications emerged. One notable example is the commercial development of Kevlar fiber,[1] which is based on poly(*p*-benzamide) (PBA) or poly(*p*-phenylene terephthalamide) (PPTA). Kevlar fiber is produced from lyotropic (anisotropic) spinning dopes prepared with sulfuric acid as a solvent because PBA and PPTA are thermally unstable at elevated temperatures. The anisotropic nature of the spinning dope is believed to be a key factor in achieving the unusually strong mechanical properties of Kevlar fiber. Also in that period, the synthesis of rigid-rod-like thermotropic LCPs (TLCPs) for industrial applications emerged, with several having been commercialized.[2−4] One of the great challenges in this area has been the synthesis of TLCPs having reasonably low melting temperature (T_m). When the T_m of a TLCP is too high, a processing difficulty arises in that thermal degradation may occur before reaching T_m. TLCPs having a high T_m would also have a high isotropization (or clearing) temperature (T_{iso}), at and above which they become isotropic liquids and consequently have low melt viscosity. Thus, in the past considerable efforts were made on the synthesis of TLCPs that would have a reasonably low T_m and T_{iso}, by inserting flexible spacers in the mesogenic main-chain backbone and/or by grafting bulky pendent groups onto the main-chain backbone. This resulted in semiflexible (segmented) TLCPs having a much lower T_m and T_{iso} compared to those of rigid-rod-like TLCPs.

During the past three decades, numerous investigators have reported on the synthesis of TLCPs. There are too many studies to cite them all here. Some research groups[5−18] reported on the syntheses of main-chain liquid-crystalline polymers (MCLCPs), while other research groups[19−30] reported on the syntheses of side-chain liquid-crystalline polymers (SCLCPs). Several research groups reported on the synthesis of combined main-chain/side-chain liquid-crystalline polymers (MCSCLCPs). There are two different ways of synthesizing combined MCSCLCPs: one method is to attach mesogenic side groups onto the flexible methylene units of a semiflexible main-chain polymer,[31−36] and another method is to attach mesogenic side groups as lateral substituents onto the mesogenic moieties of a semiflexible main-chain polymer.[37−40] Some research groups[41−47] reported on the structural analysis of MCSCLCPs, while others[48−50] investigated the phase behavior of MCSCLCPs.

Very recently, we synthesized a combined MCSCLCP having the chemical structure (which will be hereafter referred to as PSHQ4−7CNCOOH)



PSHQ4-7CNCOOH

Notice that mesogenic cyanobiphenyl groups with seven

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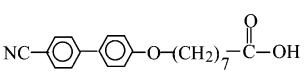
methylene units (which will hereafter be referred to as 7CNCOOH) are attached onto the flexible methylene unit of the main-chain backbone containing mesogenic units. The synthesis of PSHQ4−7CNCOOH was motivated by the desire to investigate how much the presence of the side-chain mesogenic group 7CNCOOH in PSHQ4−7CNCOOH might affect the T_{NI} and mesophase structure of the main-chain backbone. For this, we also synthesized an MCLCP, PSHQ4. Another motivation of this study was to explore the possibility of being able to prepare lyotropic solutions from the thermotropic PSHQ4−7CNCOOH, which was found to be a glassy LCP as will be shown below. Successful preparation of lyotropic solutions from the thermotropic PSHQ4−7CNCOOH would provide us with a very unique opportunity to clarify one of the unresolved issues in LCP rheology to date, namely the sign of first normal stress difference (N_1) in steady-state shear flow.

It is worth mentioning that the preparation of lyotropic solutions from a crystallizable TLCP has been found to be very difficult in general. This is because when a crystallizable TLCP is dissolved in a large quantity of solvent, the dissolved TLCP first crystallizes in the solution as the solvent is evaporated even at a very slow rate, preventing the formation of lyotropes. Such an observation suggests that a desirable situation to obtain lyotropic solutions from a TLCP would be to dissolve a glassy TLCP in an appropriate solvent, so that crystallization would not take place as the solvent is evaporated from a very dilute solution. In the past only a few attempts have been reported on the preparation of lyotropic solutions from TLCPs. Viney et al.[48] reported on the phase behavior of lyotropic solutions over a very wide range of concentrations of a glassy MCSCLCP, and Han and Chang[51] prepared lyotropic solutions over a very limited range of concentrations of a glassy, segmented, thermotropic main-chain copolyester.

In this paper, we report the results of the synthesis and characterization of an MCSCLCP, PSHQ4−7CNCOOH, and the lyotropic characteristics of PSHQ4−7CNCOOH. In doing so, we compare the thermal transition in PSHQ4−7CNCOOH as investigated from differential scanning calorimethry (DSC), the mesophase structure as investigated from wide-angle X-ray diffraction (WAXD), and polarizing optical microscopy (POM) with those of the MCLCP, PSHQ4. The purpose of the comparison is to understand the roles that the side-chain mesogenic groups play in influencing the thermal transition and mesophase structure of PSHQ4−7CNCOOH. We also present images from POM of some representative lyotropic solutions of PSHQ4−7CNCOOH and a phase diagram showing isotropic-to-nematic biphasic separation over a wide range of concentrations. Further, we present our view on the reasons why PSHQ4−7CNCOOH exhibits both thermotropic and lyotropic characteristics, while other combined MCSCLCPs reported in the literature would not exhibit lyotropic characteristics.

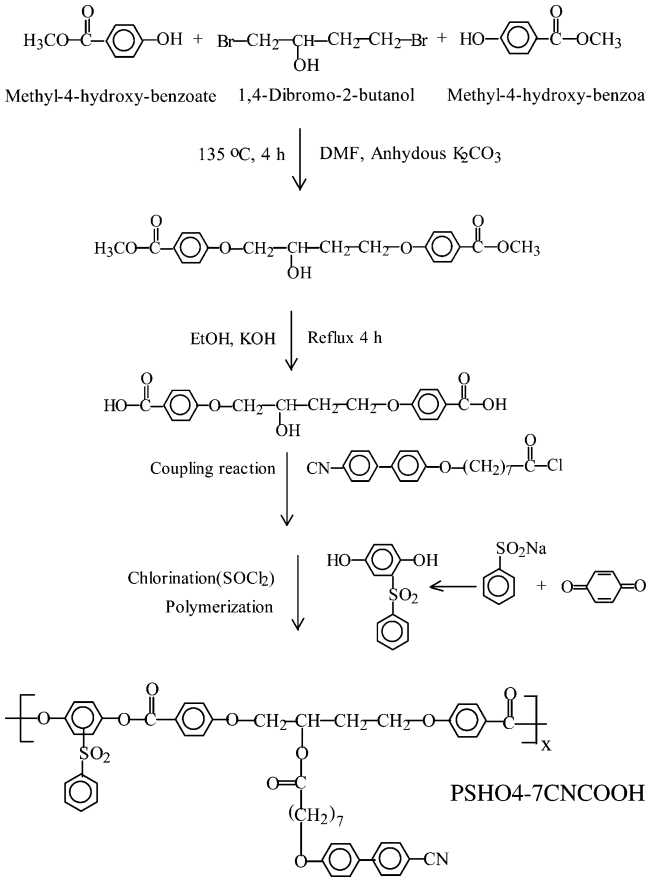
2. Experimental Section

Synthesis of 8-[(4-Cyano-4′-biphenyl)oxy]octanoic Acid (7CNCOOH). We synthesized a liquid crystalline monomer 7CNCOOH with the chemical structure



7CNCOOH

Scheme 1. Synthetic Route for PSHQ4−7CNCOOH

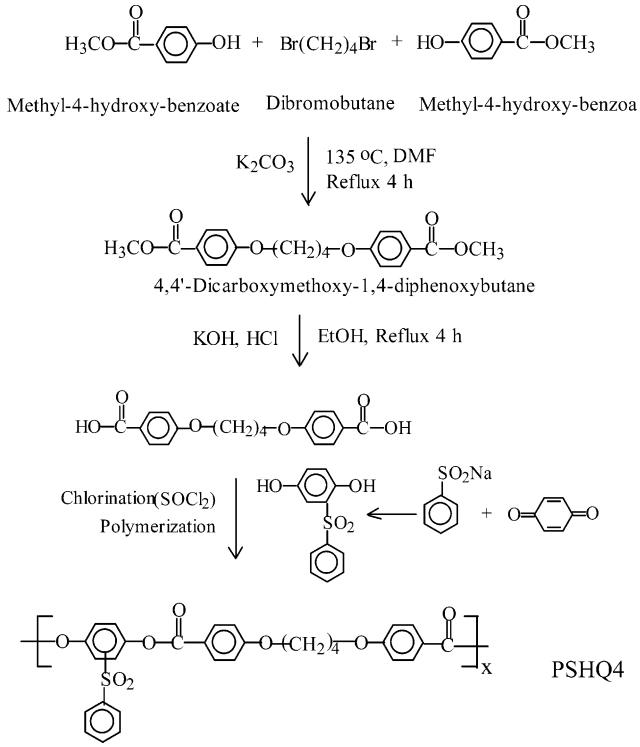


Previously, Lee and Han[52] synthesized 5CNCOOH, which has two fewer methylene units than 7CNCOOH, and described the details of synthesis procedures for 5CNCOOH. Thus, the interested readers are referred to their paper for the synthesis procedures for 7CNCOOH, which are nearly identical.

Synthesis of Polymers. We synthesized PSHQ4−7CNCOOH using the reaction route shown in Scheme 1. We also synthesized an MCLCP, PSHQ4, which forms the main-chain backbone of PSHQ4−7CNCOOH, using the reaction route shown in Scheme 2.

Characterization of the Polymers Synthesized. The chemical structures of both PSHQ4−7CNCOOH and PSHQ4 were characterized using proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy. ^{1}H NMR spectra were obtained using a spectrometer (Varian Gemini-200, 200 MHz). Films suitable for FTIR spectroscopy were prepared by casting 2% (w/v) solution in tetrahydrofuran (THF) or chloroform directly on the KBr salt plate. Film thickness was adjusted, such that the maximum absorbance of any band was less than 1.0, at which the Beer−Lambert law is valid. It was slowly dried for 24 h in a fume hood until most of the solvent evaporated and then dried at 70 °C for a few days in a vacuum oven. Samples were then stored in a vacuum oven until use. FTIR spectra were obtained using a Perkin-Elmer spectrometer (model 16PC FTIR). Spectral resolution was maintained at 4 cm^{-1}. Dry argon gas was used to purge the sample compartment in order to reduce the interference of water and carbon dioxide in the spectrum. Figure 1 shows the FTIR spectra for PSHQ4−7CNCOOH and PSHQ4. The purpose of displaying Figure 1 is to demonstrate that indeed PSHQ4−7CNCOOH has −CN and −$(CH_2)_7$ groups, both coming from the mesogenic cyanobiphenyl groups with seven methylene units, 7CNCOOH, attached onto the flexible methylene units of the main-chain backbone, PSHQ4. Since both PSHQ4−7CNCOOH and PSHQ4 dissolve in tetrachloroethane, but not in THF, we could not determine their molecular weights using gel permeation chromatography against polystyrene standards. Thus, we measured the intrin-

Scheme 2. Synthetic Route for PSHQ4



sic viscosity [η] at 30 °C of each polymer dissolved in tetrachloroethane and found that [η] = 0.675 dL/g for PSHQ4−7CNCOOH and [η] = 0.560 dL/g for PSHQ4. Thus, we conclude that the molecular weight of PSHQ4−7CNCOOH is higher than that of PSHQ4.

Preparation of Lyotropic Solutions of PSHQ4−7CNCOOH. We prepared lyotropic solutions of PSHQ4−7CNCOOH using *m*-dibromobenzene (mp = −7 °C; bp = 218 °C), *o*-dichlorobenzene, (mp = −18 °C; bp = 178 °C), and tetrachloroethane (mp = −43 °C; bp = 147 °C) as solvents. 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 an excess amount of a solvent into the glass tube, for which the amount of the solvent used varied depending upon the initial concentration specified; (iii) the solvent was evaporated to achieve a predetermined concentration, with vigorous stirring, for 12−24 h in the oil bath, and then the glass tube was taken out of the oil bath followed by cooling to room temperature; the amount of solvent evaporated was determined gravimetrically to determine the final concentration of the solution.

Sample Preparation. Thermotropic specimens for DSC, POM, and WAXD were prepared by casting PSHQ4−7CNCOOH from dichloromethane and PSHQ4 from dichloroethane in the presence of an antioxidant (0.1 wt % Irganox 1010, Ciba-Geigy Group), yielding about 2 wt % solution. The as-cast films of about 2−3 μm in thickness were first dried in a fume hood for 2 weeks and then in a vacuum oven for 1 week to remove any residual solvent. Fibers were also prepared by melt drawing of PSHQ4−7CNCOOH and PSHQ4, which were later employed for the WAXD experiment.

Differential Scanning Calorimetry (DSC). Thermal transition temperatures of the solvent-cast films of each polymer were determined by DSC (Perkin-Elmer 7 Series). 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). Two-dimensional WAXD experiments were conducted at room temperature on both melt-drawn fibers and as-cast films of PSHQ4−7CNCOOH and PSHQ4, respectively, using a General Electric X-ray generator (model XRD-6) operated at 30 kV and 30 mA and a Rigaku imaging system with an 18 kV rotating X-ray generator. For the General Electric X-ray generator, the X-ray beam was monochromatized to Cu Kα with a graphite crystal. The X-ray powder and fiber diffraction patterns were recorded with a camera, which was placed at a distance of 52.48 mm from the specimen, and the exposure time for each measurement was 4 h. Variable-temperature WAXD experiments were also conducted on as-cast films of PSHQ4−7CNCOOH and PSHQ4, using a Rigaku X-ray rotating anode (Cu Kα) generator equipped with a diffractometer. The diffraction peak positions and widths were calibrated with silicon crystals of known crystal size in the high-2θ angle region and silver behanate in the low-2θ angle region. The 2θ scanning range employed was 1.3°−35° in reflection. A temperature controller with an accuracy of ±1 °C was used, and the diffraction patterns were measured at various temperatures ranging from 50 to 250 °C.

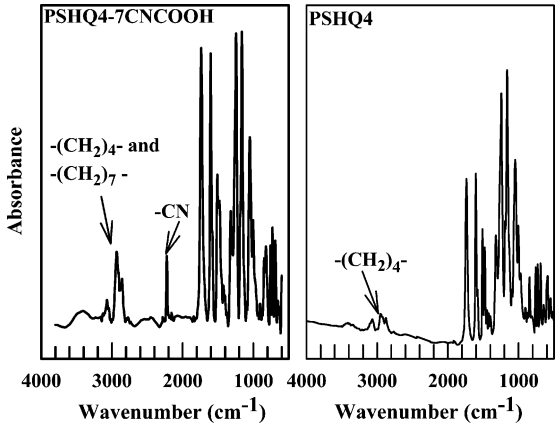


Figure 1. IR spectra for PSHQ4−7CNCOOH and PSHQ4.

Polarizing Optical Microscopy (POM). A hot-stage (TH600 type, Linkham Scientific Co.) microscope (Nikon, model Optiphoto po1XTP-11) with a camera, a programmable temperature controller, and photomicrographic attachment was used to take images under cross-polarized light. To obtain micrographs, an as-cast film sample was placed between two glass slides.

3. Results and Discussion

We will first compare the thermotropic characteristics, in terms of thermal transitions and mesophase structure, of PSHQ4−7CNCOOH with that of PSHQ4 to have a better understanding of the roles that the side-chain mesogenic groups 7CNCOOH play in influencing the phase transition and mesophase structure of the main-chain backbone of PSHQ4−7CNCOOH. Such a comparison has not been reported in the literature[31−36] that dealt with the synthesis of combined MCSCLCPs. Next, we will present the lyotropic characteristics of PSHQ4−7CNCOOH in terms of POM images of some representative lyotropic solutions and a phase diagram over a very wide range of concentrations for three different solvents.

Thermal Transitions in PSHQ4−7CNCOOH and PSHQ4 As Determined by DSC. Figure 2 gives DSC thermograms during the first cooling and the second heating at a rate of 20 °C/min for as-cast PSHQ4−7CNCOOH and PSHQ4 specimens. It is of interest to observe from the left-side panel of Figure 2 that during the second heating PSHQ4−7CNCOOH exhibits only two thermal transitions, namely, a glass transition temperature (T_g) at 85 °C and an isotropization temperature at 172 °C, showing no evidence of crystallinity. On the other hand, the right-side panel of Figure 2

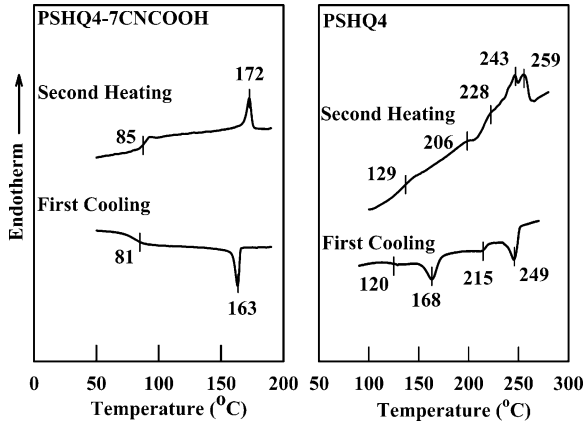


Figure 2. DSC thermograms for as-polymerized PSHQ4−7CNCOOH and PSHQ4 during the first cooling and second heating cycles at 20 °C/min.

shows that during the second heating PSHQ4 undergoes a glass transition at 129 °C and isotropization at 259 °C and has a conspicuous endothermic peak at 243 °C with two small endothermic peaks at 206 and 228 °C. We found that an isothermal annealing at 130 °C for 24 h did not affect the thermal transition in PSHQ4−7CNCOOH, whereas an isothermal annealing of PSHQ4 at 220 °C for 24 h steadily increased the area under the intermediate endothermic peak (i.e., the enthalpy ΔH_1 associated with the intermediate endothermic peak) at ca. 240 °C, signifying that the crystal growth continued during the isothermal annealing, while the upper endothermic peak at 260 °C remained the same. Thus, we tentatively conclude that PSHQ4−7CNCOOH is a glassy TLCP while PSHQ4 is a semicrystalline TLCP. Further, we found that 7CNCOOH has a clearing temperature of 150 °C and has a nematic mesophase. It is then clear that the attachment of the mesogenic 7CNCOOH onto the flexible methylene unit of the MCLCP, PSHQ4, has yielded a combined MCSCLCP, the structure of which has been confirmed by the FTIR spectra given in Figure 1. What is of great interest here is the drastic decrease (ca. 90 °C) in the T_{NI} of PSHQ4 after it was grafted with the cyanobiphenyl mesogenic groups having seven methylene units (7CNCOOH), yielding a combined MCSCLCP, PSHQ4−7CNCOOH.

Mesophase Structures of PSHQ4−7CNCOOH and PSHQ4 As Determined by WAXD. Figure 3 gives X-ray powder diffraction patterns and the intensities of X-ray diffraction patterns in smaller angles (2θ scanning) ranging from 1° to 35° for as-cast specimens of (a) PSHQ4−7CNCOOH and (b) PSHQ4. These specimens, before being subjected to WAXD measurements, had the following thermal histories: (a) PSHQ4−7CNCOOH was annealed at 130 °C for 24 h; (b) PSHQ4 was annealed at 220 °C for 2 h. It is seen in Figure 3a that the WAXD patterns for PSHQ4−7CNCOOH show very diffuse lateral spacing with a broad outer halo with a spacing of 0.45 nm, and the intensity of X-ray diffraction patterns in smaller angles (2θ scanning) has a single peak at 20°, which is attributable to the liquidlike packing of mesogenic groups. In the absence of sharp diffraction peaks in the WAXD patterns, we conclude that PSHQ4−7CNCOOH is a glassy LCP having only a nematic mesophase, confirming the DSC results presented in Figure 2a. The absence of crystalline structure in PSHQ4−7CNCOOH is believed to be due to the disruption of a well-packed structure in the presence of side-chain mesogenic groups 7CNCOOH

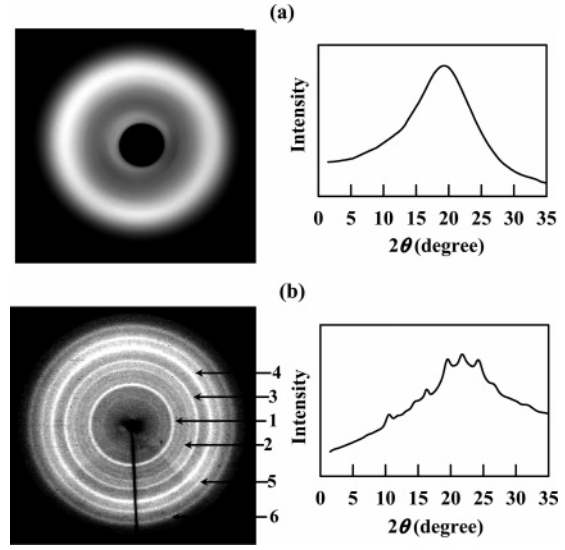


Figure 3. WAXD powder patterns at room temperature of (a) as-polymerized PSHQ4−7CNCOOH specimen annealed at 130 °C for 24 h and (b) an as-cast PSHQ4 specimen annealed at 220 °C for 2 h.

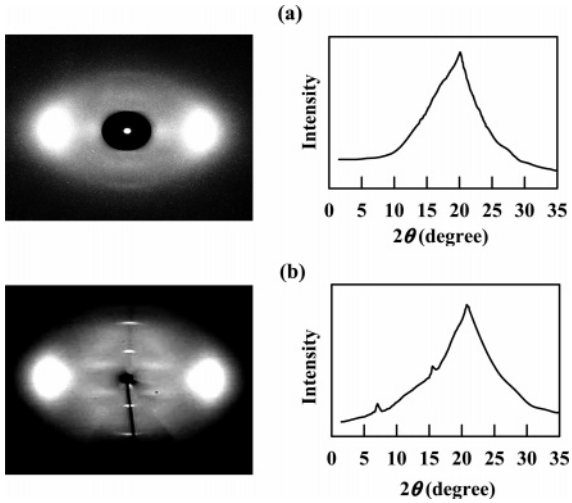


Figure 4. WAXD fiber patterns at room temperature of (a) as-polymerized PSHQ4−7CNCOOH specimen annealed at 130 °C for 24 h and (b) an as-cast PSHQ4 specimen annealed at 220 °C for 2 h.

grafted onto the flexible methylene units of the main-chain backbone. On the other hand, the WAXD patterns for PSHQ4 given in Figure 3b show very sharp diffraction peaks with several weak diffractions and the intensities of X-ray diffraction patterns in smaller angles (2θ scanning) have several peaks, indicating that a highly ordered crystalline structure exists in the specimen. The values of d spacing determined for PSHQ4 from Figure 3b are as follows: (1) $d = 0.84$ nm at $2\theta = 10.5°$, (2) $d = 0.61$ nm at $2\theta = 14.5°$, (3) $d = 0.54$ nm at $2\theta = 16.4°$, (4) $d = 0.45$ nm at $2\theta = 19.5°$, (5) $d = 0.41$ nm at $2\theta = 21.7°$, and (6) $d = 0.34$ nm at $2\theta = 24.5°$. The above observations made for PSHQ4 confirm the DSC results presented in Figure 2.

Figure 4 gives X-ray fiber diffraction patterns and the intensities of X-ray diffraction patterns in smaller angles (2θ scanning) ranging from 1° to 35° for melt-drawn fibers of unannealed (a) PSHQ4−7CNCOOH and (b) PSHQ4. Fiber specimens were obtained by melt drawing in the nematic state followed by a rapid quenching to room temperature. From Figure 4a for

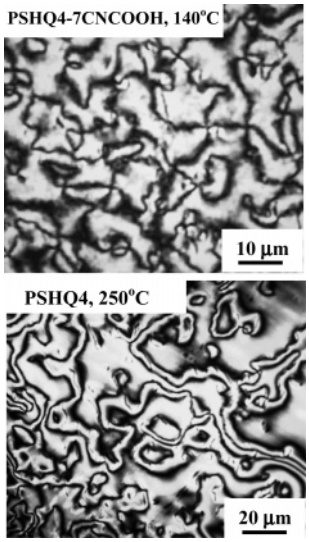


Figure 5. POM images of (a) as-cast PSHQ4−7CNCOOH specimen taken at 140 °C and (b) as-cast PSHQ4 specimen taken at 250 °C.

PSHQ4−7CNCOOH we observe very diffuse meridional and equatorial diffractions, and the intensity of X-ray diffraction patterns in smaller angles (2θ scanning) has a single peak at 20°, suggesting that PSHQ4−7CNCOOH has virtually perfect amorphous structures in the solid state. Again, this observation is consistent with the DSC results presented in Figure 2a and also with the X-ray powder diffraction patterns presented in Figure 3a. On the other hand, the X-ray fiber diffraction patterns given in Figure 4b for PSHQ4 show four-point spots with a few meridional diffraction patterns, and the intensities of X-ray diffraction patterns in smaller angles (2θ scanning) have a large peak at ca. 22° and two additional small peaks, which are indications of the presence of reflection planes from the solid crystal structures. From the four-point spots we obtain the chain periodicity of 2.18 nm in PSHQ4.

We also observed from 2θ scanning of variable-temperature X-ray diffraction patterns, although they are not presented here, that the shape of the main peak for an unannealed PSHQ4−7CNCOOH specimen during the first cooling cycle was almost identical to that during the second heating cycle and the shape of the WAXD patterns changed little over the entire temperatures tested ranging from 90 to 190 °C, whereas many reflections appeared at temperatures between 100 and 230 °C for PSHQ4, indicating that it has a very high rate of crystallization, and the reflection positions in PSHQ4 in the variable-temperature WAXD patterns coincided with those in the X-ray powder diffraction patterns given in Figure 3b.

Mesophase Structure of PSHQ4−7CNCOOH and PSHQ4 As Determined by POM. In obtaining POM images of PSHQ4−7CNCOOH and PSHQ4, the specimens were first heated to a temperature ca. 20 °C above the clearing temperature of the respective polymers to achieve an isotropic state, at which the melt looked dark under a polarizing microscope, and then were cooled at a rate of 2 °C/min down to the measurement temperature (140 °C for PSHQ4−7CNCOOH and 250 °C for PSHQ4). A nitrogen atmosphere was provided to minimize oxidative degradation of the specimens. Figure 5 gives POM images of PSHQ4−7CNCOOH taken at 140 °C and PSHQ4 taken at 250 °C. It is seen in Figure 5 that both PSHQ4−7CNCOOH and PSHQ4 exhibit Schlieren texture in the nematic state. It should be remembered that according to the DSC thermograms given in Figure 2, nematic texture is expected at temperatures of ca. 88−172 °C for PSHQ4−7CNCOOH and at 242−260 °C for PSHQ4.

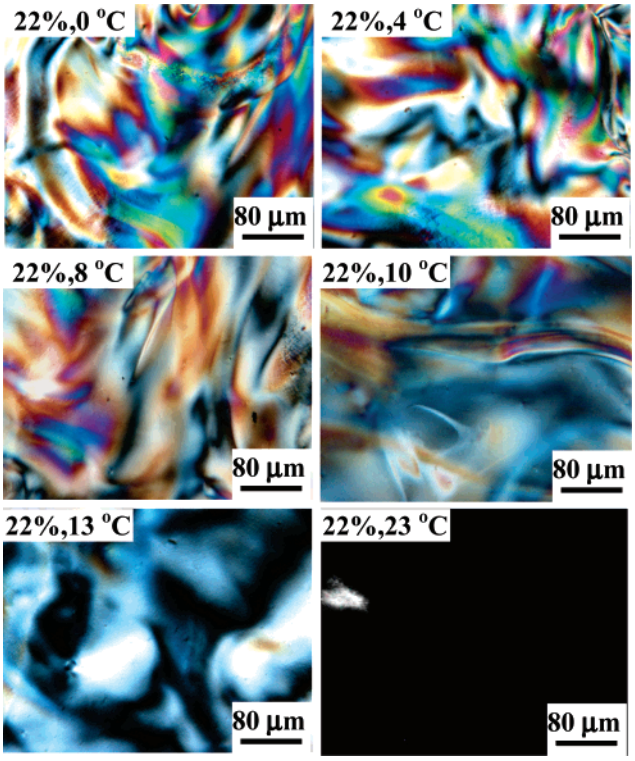


Figure 6. Cross-polarized optical micrographs of 22 wt % solution of PSHQ4−7CNCOOH in *o*-dichlorobenzene at various temperatures in the nematic region, as indicated on each image.

Domain Textures and Phase Behavior of Lyotropic Solutions of PSHQ4−7CNCOOH. Figure 6 gives POM images obtained at temperatures ranging from 0 to 23 °C of 22 wt % lyotropic solution of PSHQ4−7CNCOOH dissolved in *o*-dichlorobenzene. Notice in Figure 6 that the completely dark image at 23 °C represents the isotropic state of the lyotropic solutions. We have also taken POM images at various temperatures for 25, 27, 30, 40, 50, 60, and 70 wt % lyotropic solutions in *o*-dichlorobenzene, 33 and 41 wt % lyotropic solutions in *m*-dibromobenzene, and 50 and 60 wt % lyotropic solutions in tetrachloroethane. For the reason of space limitation we do not present those POM images here. It should be mentioned that we were not able to prepare lyotropic solutions of PSHQ4 because the polymer precipitated out via crystallization from a homogeneous solution of PSHQ4 as the solvent evaporated, a phenomenon commonly observed from supersaturated solutions of crystallizable organic or inorganic materials (e.g., sugar; sodium chloride salt).

Having taken POM images of the lyotropic solutions of PSHQ4−7CNCOOH in *o*-dibromobenzene, *m*-dichlorobenzene, and tetrachloroethane, we have constructed a phase diagram. Figure 7 gives a phase diagram thus constructed, in which the shaded areas represent biphasic region. It can be seen in Figure 7 that the temperature at which the nematic phase persists in a lyotropic solution increases with increasing solution concentration.

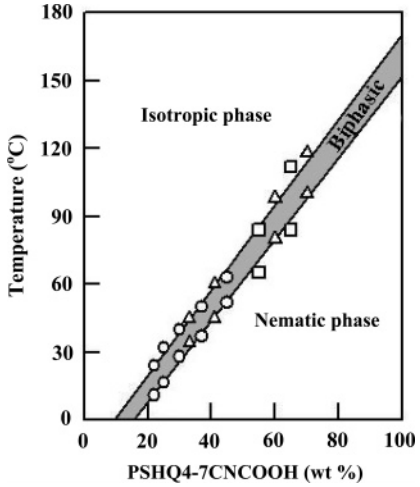
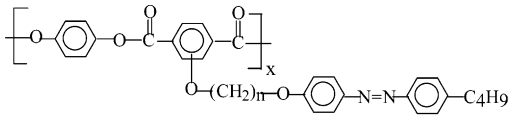


Figure 7. Phase diagram determined by polarizing optical microscopy for lyotropic solutions of PSHQ4−7CNCOOH in three different solvents: (○) *o*-dichlorobenzene, (△) *m*-dibromobenzene, and (□) tetrachloroethane, in which the shaded areas represent the biphasic region.

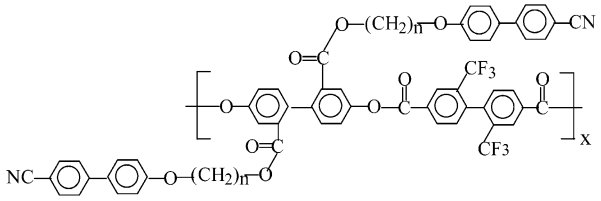
Origin in the Lyotropic Characteristics of PSHQ4−7CNCOOH. Earlier, Piao et al.[39] synthesized a series of combined MCSCLCPs with the chemical structure



PAZO*n*

with n = 3, 4, 5, 6, or 10. According to them, (i) all PAZO*n* synthesized were found to be semicrystalline polymers having melting temperatures (T_m) ranging from 166 to 188 °C depending upon the length (n) of methylene units in the side-chain mesogenic groups and a clearing temperature higher than the thermal degradation temperature, ca. 320 °C, and (ii) PAZO*n* with $n \leq 6$ had nematic mesophase, while PAZO10 had layered mesophase. Being highly crystalline, PAZO*n* would not exhibit lyotropic characteristics.

Ge et al.[40] synthesized a series of combined MCSCLCPs with the chemical structure



PEFBP*n*

having n = 6−12. According to them, all PEFBP*n* synthesized were found to be semicrystalline polymers and exhibited complex morphologies (different crystalline phases) during heating. They carried out detailed structural characterizations of PEFBP*n* using WAXD, POM, and TEM.[47] Again, being highly crystalline, PEFBP*n* would not exhibit lyotropic characteristics.

Referring to PAZO*n* and PEFBP*n*, we have no way of knowing the roles the mesogenic side chains, which were grafted onto the backbone of the main chain, played in controlling the thermal transition temperatures and mesophase structures of the respective MCSCLCPs. In contrast, in the present study we compared the thermal transition temperatures and mesophase structure of the MCLCP, PSHQ4, with those of the MCSCLCP, PSHQ4−7CNCOOH. By doing so, we were able to assess the roles the mesogenic side chain, 7CNCOOH, played in controlling the thermal transition temperatures and mesophase structure of PSHQ4−7CNCOOH.

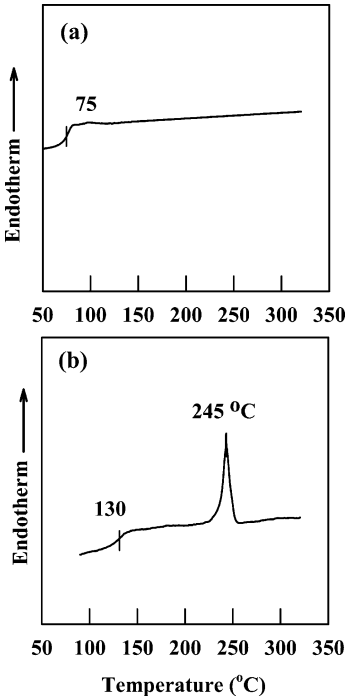
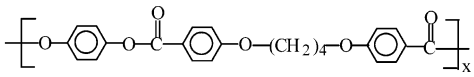
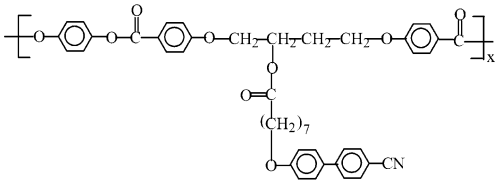


Figure 8. DSC thermograms for (a) PHQ4−7CNCOOH and (b) PHQ4.

To help understand the reason(s) why PAZO*n* and PEFBP*n* are semicrystalline MCSCLCPs, while PSHQ4−7CNCOOH is a glassy MCSCLCP giving rise to lyotropic characteristics, in the present study we synthesized two additional LCPs with the following chemical structures:



PHQ4



PHQ4-7CNCOOH

Notice that PHQ4 and PHQ4−7CNCOOH do not have a phenylsulfonyl pendent group, while PSHQ4 PSHQ4−7CNCOOH have a phenylsulfonyl pendent group in the main-chain backbone.

Figure 8 gives DSC thermograms during the first heating at a rate of 20 °C/min for (a) as-cast PHQ4−7CNCOOH and (b) as-cast PHQ4 specimens. It is seen in Figure 8 that PHQ4−7CNCOOH has a clearing temperature well above its thermal degradation temperature (ca. 340 °C) and PHQ4 has a T_g at 130 °C, a T_m at 245 °C, and a clearing temperature exceeding the highest experimental temperature (320 °C) employed.

Thermogravimetric analysis (TGA) indicates that both PHQ4−7NCOOH and PHQ4 begin to undergo thermal degradation at 340−345 °C, as given in the Supporting Information. Comparison of Figure 8 with Figure 2 reveals the dramatic effect of the presence of phenylsulfonyl pendent group on the thermal transition temperatures of PSHQ4−7CNCOOH and PSHQ4.

Using POM, we found that an as-cast PHQ4−7CNCOOH has a smectic mesophase at 260 °C. A POM image of as-cast PHQ4−7CNCOOH specimen is given in the Supporting Information. We can then conclude that the attachment of phenylsulfonyl pendent group onto the backbone of PHQ4−7CNCOOH has transformed the smectic mesophase of PHQ4−7CNCOOH into a nematic mesophase in PSHQ4−7CNCOOH. On the other hand, we were not able to find a suitable solvent that could dissolve PHQ4, which could then enable us to obtain a POM image of PHQ4 at a temperature higher than 245 °C, an endothermic peak appearing in Figure 8b. To demonstrate that the endothermic peak appearing at 245 °C in Figure 8b is the melting temperature of PHQ4 and it has a mesophase at temperatures above 245 °C, we conducted the following experiment. Namely, a polymerized PHQ4 specimen was first heated to 260 °C and then quenched rapidly into ice water. Subsequently, we took WAXD powder patterns of the quenched specimen at room temperature. The rationale behind this experiment was based on the premise that the quenched PHQ4 specimen would have retained the structure it had at 260 °C before being quenched into ice water. The WAXD powder patterns for the quenched PHQ4 specimen are given in the Supporting Information, showing very sharp diffraction peaks. Also, we took X-ray diffraction patterns in smaller angles (2θ scanning), and they are given beneath the WAXD powder patterns in the Supporting Information. Thus, we can conclude that PHQ4 has a highly ordered crystalline structure at 260 °C, and thus indeed the clearing temperature of PHQ4 exceeds the highest experimental temperature (320 °C) employed.

What is significant here is that the grafting of mesogenic side group 7CNCOOH onto the MCLCP, PHQ4, has transformed the nematic PHQ4 into smectic PHQ4−7CNCOOH. Under such a circumstance we cannot expect that PHQ4−7CNCOOH would be able to form lyotropic solutions. Indeed, we have found that this is the case. Therefore, we conclude that the presence of the bulky phenylsulfonyl pendent group in the main-chain backbone of PSHQ4−7CNCOOH also has played a decisive role in obtaining a glassy, nematic-forming LCP, enabling us to prepare lyotropic solutions from the thermotropic PSHQ4−7CNCOOH.

At this juncture it is worth mentioning a previous study by Kim and Han,[53] who investigated the effect of bulkiness of pendent groups on the mesophase structure and the T_{NI} of segmented MCLCPs having aromatic triads with 10 methylene units as flexible spacer and varying sizes of pendent groups. They found that the bulkier a pendent group, the lower the T_{NI} of the MCLCPs; namely (i) the MCLCP having ethoxy pendent groups undergoes smectic-to-nematic transition at 148 °C and N−I transition at 239 °C, (ii) the MCLCP having *tert*-butyl pendent groups undergoes only N−I transition at 193 °C, and (iii) the MCLCP having phenylsulfonyl pendent groups undergoes only N−I transition at 179 °C. The above experimental observations now explain why the grafting of bulky 7CNCOOH onto the flexible methylene unit of PSHQ4 has decreased its T_{NI} so much (ca. 90 °C) from 260 to 172 °C. Equally significant in the study of Kim and Han[53] is that the grafting of bulky *tert*-butyl or phenylsulfonyl pendent groups onto a segmented LCP yielded nematic mesophase, while the grafting of less bulky ethoxy pendent groups onto the same segmented LCP yielded smectic mesophase. Their study clearly demonstrates that attachment of bulky pendent groups onto the backbone of a segmented MCLCP would hinder the formation of highly ordered packing of the MCLCPs.

4. Concluding Remarks

In this study, we have found that the grafting of mesogenic cyanobiphenyl groups having seven methylene units onto the flexible methylene units of a semicrystalline MCLCP, PSHQ4, decreased its clearing temperature as much as ca. 90 °C, and the resulting combined main-chain/side-chain LCP has become a glassy, nematic-forming mesophase at temperatures between the glass transition temperature and the clearing temperature. We attribute this observation to the fact that the grating of mesogenic cyanobiphenyl groups having seven methylene units (7CNCOOH) onto the flexible methylene units of a semicrystalline PSHQ4 hinders its structural regularity, preventing the formation of a well-packed structure. As a result, we have been able to successfully prepare lyotropic solutions of PSHQ4−7CNCOOH, which was the primary objective of the present study. This will then enable us to investigate the rheological behavior of the lyotropic solutions of PSHQ4−7CNCOOH. The results of such an investigation will be reported in the future.

It is important to point out that the successful preparation of lyotropic solutions of PSHQ4−7CNCOOH presented in this paper was made possible by the fact that PSHQ4−7CNCOOH is a glassy, nematic-forming LCP having a relatively low T_{NI}. Such a low value of T_{NI} (172 °C) for the glassy, nematic-forming PSHQ4−7CNCOOH is attributed to the presence of bulky phenylsulfonyl pendent group in the main-chain backbone.

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Supporting Information Available: TGA traces for PHQ4 and PHQ4−7CNCOOH, POM image of PHQ4−7CNCOOH, and WAXD powder patterns together with X-ray diffraction patterns in smaller angles (2θ scanning) of an as-polymerized PHQ4 specimen. This material is available free of charge via the Internet at http://pubs.acs.org.

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