*Macromolecules* **1999,** *32,* 7688−7691

# Notes

## Self-Organization of Main-Chain Rod−Coil Copolymers into Columnar and Bicontinuous Cubic Assemblies

**Myongsoo Lee* and Byoung-Ki Cho**

*Department of Chemistry, Yonsei University,*
*Shinchon 134, Seoul 120-749, Korea*

**Yoon-Sok Kang and Wang-Cheol Zin**

*Department of Materials Science and Engineering,*
*Pohang University of Science and Technology,*
*Pohang 790-784, Korea*

*Received April 6, 1999*
*Revised Manuscript Received September 3, 1999*

### Introduction

Control of supramolecular nanostructure in self-organizing materials is of critical importance to achieving desired functions and properties in solid state and liquid crystalline molecular materials. Thus, diverse molecular architectures are being explored as a means of manipulating supramolecular structure which has dramatic effects on the physical properties of polymers.[1−5] Main-chain liquid crystalline polymers are a typical example for self-assembling materials, which are conventionally prepared by coupling a rodlike mesogenic unit to a polymeric backbone through a flexible spacer. Because of the molecular shape of the anisotropic units, however, their assembly is generally restricted to nematic or lamellar smectic supramolecular structures in which the rodlike units are arranged with their long axes parallel to each other.[6]

In marked contrast, block copolymers consisting of two chemically distinct coil segments self-organize into a variety of supramolecular structures through mutual repulsion of each segment.[7] Introduction of this design concept into main-chain liquid crystalline polymers would lead to a novel strategy for manipulating supramolecular structure of self-assembling main-chain polymers. It is in this context that we have prepared main-chain rod−coil copolymers consisting of alternating rigid-rod segments and flexible coil segments which are the two extreme topologies of linear polymeric chains.

The design of rod−coil copolymers was based on three molecularly uniform biphenyl units coupled through a benzyl ether linkage and a poly(propylene oxide) coil which would introduce block segregation character into main-chain liquid crystalline polymers. Therefore, these rod−coil copolymers can be considered as either main-chain liquid crystalline polymers or segmented block copolymers taking into account their molecular architecture. We report herein the results on the thermotropic phase behavior of a series of rod−coil copolymers **5**−**8** (Scheme 1) which represent different coil volume fractions in the polymers.

### Experimental Section

**Materials.** 4,4′-Biphenol, toluene-*p*-sulfonyl chloride (98%), and 4,4′-bis(bromomethyl)biphenyl from Tokyo Kasei were used as received. Poly(propylene glycol)s of (DP$_n$) 8 ($M_w/M_n$ = 1.16), 12 ($M_w/M_n$ = 1.16), and 18 ($M_w/M_n$ = 1.17) and tetrabutylammonium hydrogen sulfate (TBAH, 97%) (all from Aldrich) were also used as received. Poly(propylene glycol) of ({DP}) 15 and poly(propyleneoxy)propyl ditosylates were synthesized according to the procedure described previously.[8]

**Techniques.** $^1$H NMR spectra were recorded from CDCl$_3$ solutions on a Bruker AM 250 spectrometer. A Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a 1020 thermal analysis controller was used to determine the thermal transitions. A Nikon Optiphot 2-pol optical polarized microscopy (magnification: 100×) equipped with a Mettler FP 82 hot-stage and a Mettler FP 90 central processor was used to observe the thermal transitions and to analyze the anisotropic texture. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer at the Organic Chemistry Research Center. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 3C2 X-ray beam line at Pohang Accelerator Laboratory, Korea. Number average molecular weights ($\bar{M}_n$) and molecular weight distributions ($\bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) according to polystyrene standards (Aldrich) with a Waters R401 instrument equipped with Styragel HR 3, 4, and 4E columns, M7725i manual injector, column heating chamber, and 2010 Millennium data station. Measurements were made by using a UV detector and CHCl$_3$ as solvent (1.0 mL min$^{-1}$).

**Synthesis.** A general outline of the synthetic procedure is shown in Scheme 1.

**4-[Poly(propyleneoxy)propyloxy]-4′-bis(phenylphenol)s (1−4).** 4-[Poly(propyleneoxy)propyloxy]-4′-bis(phenylphenol)s (**1**−**4**) were synthesized using a similar procedure described previously.[8]

**1**: Yield 83%. $^1$H NMR (250 MHz, CDCl$_3$, $\delta$, ppm) 7.33−7.39 (m, 8Ar−H, *m* to OH, *m* to OCH$_2$CH, and *m* to OCH(CH$_3$)), 6.85−6.93 (m, 8Ar−H, *o* to OH, *o* to OCH$_2$CH, and *o* to OCH(CH$_3$)), 4.51 (m, 3H, phenylOC$H_2$CH(CH$_3$) and CH$_2$C$H$(CH$_3$)Ophenyl), 3.25−3.85 (m, 21H, OC$H_2$C$H$(CH$_3$)), 0.88−1.35 (m, 24H, CH(C$H_3$)O). Anal. Calcd for $C_{48}H_{66}O_{11}$: C, 70.39; H, 8.12. Found: C, 70.38; H, 8.19. $M_w/M_n$ = 1.06 (GPC).

**2**: Yield 77%. $^1$H NMR (250 MHz, CDCl$_3$, $\delta$, ppm) 7.33−7.39 (m, 8Ar−H, *m* to OH, *m* to OCH$_2$CH, and *m* to OCH(CH$_3$)), 6.84−6.92 (m, 8Ar−H, *o* to OH, *o* to OCH$_2$CH, and *o* to OCH(CH$_3$)), 4.51 (m, 3H, phenylOC$H_2$CH(CH$_3$) and CH$_2$C$H$(CH$_3$)Ophenyl), 3.24−3.85 (m, 27H, OC$H_2$C$H$(CH$_3$)), 0.88−1.35 (m, 30H, CH(C$H_3$)O). Anal. Calcd for $C_{60}H_{90}O_{15}$: C, 68.54; H, 8.63. Found: C, 68.42; H, 8.67. $M_w/M_n$ = 1.16 (GPC).

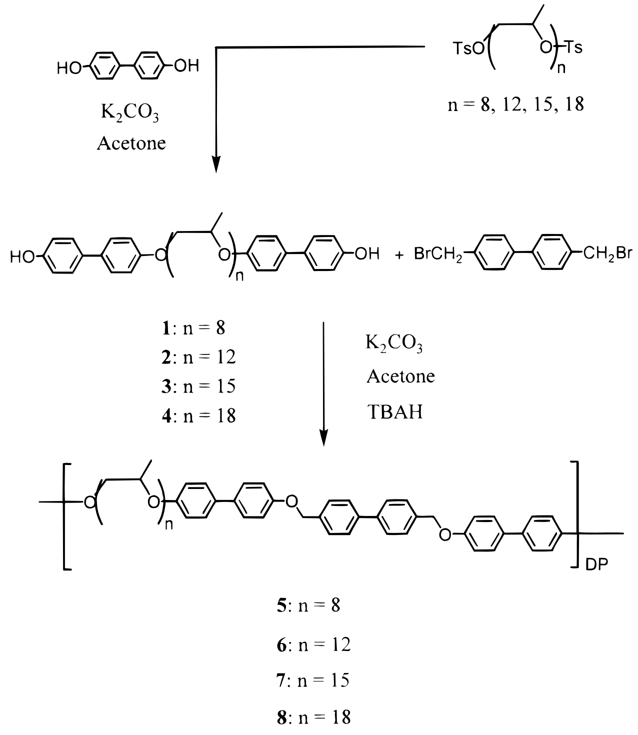
**3**: Yield 81%. $^1$H NMR (250 MHz, CDCl$_3$, $\delta$, ppm) 7.34−7.40 (m, 8Ar−H, *m* to OH, *m* to OCH$_2$CH, and *m* to OCH(CH$_3$)), 6.85−6.91 (m, 8Ar−H, *o* to OH, *o* to OCH$_2$CH, and *o* to OCH(CH$_3$)), 4.51 (m, 3H, phenylOC$H_2$CH(CH$_3$) and CH$_2$C$H$(CH$_3$)Ophenyl), 3.25−3.88 (m, 42H, OC$H_2$C$H$(CH$_3$)), 0.88−1.40 (m, 45H, CH(C$H_3$)O). Anal. Calcd for $C_{69}H_{108}O_{18}$: C, 67.62; H, 8.88. Found: C, 67.68; H, 8.87. $M_w/M_n$ = 1.12 (GPC).

---

* To whom correspondence should be addressed: Fax 82-2-364-7050; E-mail mslee@alchemy.yonsei.ac.kr.

10.1021/ma990515e CCC: $18.00

**Scheme 1. Synthesis of Rod−Coil Copolymers 5−8**



**4**: Yield 75%. $^1$H NMR (250 MHz, $CDCl_3$, $\delta$, ppm) 7.36−7.41 (m, 8Ar−H, *m* to OH, *m* to $OCH_2CH$, and *m* to OCH($CH_3$)), 6.85−6.94 (m, 8Ar−H, *o* to OH, *o* to $OCH_2CH$, and *o* to OCH($CH_3$)), 4.51 (m, 3H, phenylOC*H*$_2$CH($CH_3$) and $CH_2$C*H*($CH_3$)Ophenyl), 3.25−3.90 (m, 51H, OC*H*$_2$C*H*($CH_3$)), 0.85−1.40 (m, 54H, CH(C*H*$_3$)O). Anal. Calcd for $C_{78}H_{126}O_{21}$: C, 66.92; H, 9.07. Found: C, 66.97; H, 9.02. $M_w/M_n = 1.18$ (GPC).

**Synthesis of Rod−Coil Copolymers (5−8).** Rod−coil copolymers **5** and **6**−**8** were all synthesized using the same procedure. A representative example is described for **5**. 4-[Poly(propyleneoxy)propyloxy]-4′-bis(phenylphenol) **1** ($M_w = 819.0$, 0.32 g, 0.39 mmol), 4,4′-bis(bromomethyl)biphenyl (0.13 g, 0.39 mmol), $K_2CO_3$ (0.22 g, 1.56 mmol), and TBAH (tetrabutylammonium hydrogen sulfate, 0.066 g, 0.19 mmol) were dissolved in 5 mL of acetone. The mixture was heated at reflux for 24 h, and then solvent was removed in a rotary evaporator. The resulting mixture was poured into 1 N HCl and extracted with methylene chloride. The organic layer was poured into 20−40 volumes of methanol to give a white precipitate. The filtered polymer was dried and precipitated from methylene chloride solution into methanol until the GPC trace showed no trace of oligomer and monomer. Yield 66%. $^1$H NMR (250 MHz, $CDCl_3$, $\delta$, ppm) 7.44−7.64 (m, 16Ar−H, *m* to $OCH_2$phenyl, *m* to $OCH_2CH$, and *m* to OCH($CH_3$), *o* to $CH_2$Ophenyl and *m* to $CH_2$Ophenyl), 6.96−7.06 (m, 8Ar−H, *o* to $OCH_2$phenyl, *o* to $OCH_2CH$, and *o* to OCH($CH_3$)), 5.13 (s, 4H, OC*H*$_2$phenyl), 4.53 (m, 3H, phenylOC*H*$_2$CH($CH_3$) and $CH_2$C*H*($CH_3$)Ophenyl), 3.20−3.82 (m, 21H, OC*H*$_2$C*H*($CH_3$)), 0.85−1.45 (m, 24H, CH(C*H*$_3$)O). Anal. Calcd for $C_{62}H_{76}O_{11}$: C, 74.67; H, 7.68. Found: C, 74.63; H, 7.71.

**6**: Yield 57%. $^1$H NMR (250 MHz, $CDCl_3$, $\delta$, ppm) 7.44−7.65 (m, 16Ar−H, *m* to $OCH_2$phenyl, *m* to $OCH_2CH$, and *m* to OCH($CH_3$), *o* to $CH_2$Ophenyl and *m* to $CH_2$Ophenyl), 6.96−7.06 (m, 8Ar−H, *o* to $OCH_2$phenyl, *o* to $OCH_2CH$, and *o* to OCH($CH_3$)), 5.13 (s, 4H, OC*H*$_2$phenyl), 4.53 (m, 3H, phenylOC*H*$_2$CH($CH_3$) and $CH_2$C*H*($CH_3$)Ophenyl), 3.20−3.85 (m, 27H, OC*H*$_2$C*H*($CH_3$)), 0.85−1.45 (m, 30H, CH(C*H*$_3$)O). Anal. Calcd for $C_{74}H_{100}O_{15}$: C, 72.28; H, 8.19. Found: C, 72.35; H, 7.97.

**7**: Yield 48%. $^1$H NMR (250 MHz, $CDCl_3$, $\delta$, ppm) 7.43−7.64 (m, 16Ar−H, *m* to $OCH_2$phenyl, *m* to $OCH_2CH$, and *m* to OCH($CH_3$), *o* to $CH_2$Ophenyl and *m* to $CH_2$Ophenyl), 6.95−7.06 (m, 8Ar−H, *o* to $OCH_2$phenyl, *o* to $OCH_2CH$, and *o* to OCH($CH_3$)), 5.13 (s, 4H, OC*H*$_2$phenyl), 4.52 (m, 3H, phenylOC*H*$_2$CH($CH_3$) and $CH_2$C*H*($CH_3$)Ophenyl), 3.20−3.90 (m, 42H, OC*H*$_2$C*H*($CH_3$)), 0.85−1.45 (m, 45H, CH(C*H*$_3$)O). Anal. Calcd for $C_{83}H_{118}O_{18}$: C, 71.01; H, 8.47. Found: C, 71.06; H, 8.42.

**8**: Yield 62%. $^1$H NMR (250 MHz, $CDCl_3$, $\delta$, ppm) 7.44−7.65 (m, 16Ar−H, *m* to $OCH_2$phenyl, *m* to $OCH_2CH$, and *m* to OCH($CH_3$), *o* to $CH_2$Ophenyl and *m* to $CH_2$Ophenyl), 6.95−7.06 (m, 8Ar−H, *o* to $OCH_2$phenyl, *o* to $OCH_2CH$, and *o* to OCH($CH_3$)), 5.14 (s, 4H, OC*H*$_2$phenyl), 4.52 (m, 3H, phenylOC*H*$_2$CH($CH_3$) and $CH_2$C*H*($CH_3$)Ophenyl), 3.20−3.90 (m, 51H, OC*H*$_2$C*H*($CH_3$)), 0.85−1.45 (m, 54H, CH(C*H*$_3$)O). Anal. Calcd for $C_{92}H_{136}O_{21}$: C, 70.02; H, 8.69. Found: C, 70.06; H, 8.64.

## Results and Discussion

The synthesis of monodisperse bis(4,4′-phenylphenol) monomers based on poly(propylene oxide)s **1**−**4** was performed by using a similar procedure described previously.[8] The resulting monomers **1**−**4** were polymerized with an equimolar amount of 4,4′-bis(bromomethyl)biphenyl by etherification to yield rod−coil copolymers as shown in Scheme 1. Therefore, these rod−coil polymers consist of alternating uniform rod segments and monodisperse coil segments, similar to segmented block copolymers. All analytical data are consistent with expected structures. As shown in Table 1, the number-average molecular weights and the molecular weight distributions of the polymers determined by gel permeation chromatography (GPC) appear to be in the range 20 000−30 000 g/mol and 1.8−2.3, respectively, with reference to polystyrene standards.

Phase transition temperatures and associated enthalpy changes of **5**−**8** determined from the DSC scans are summarized in Table 1. All of the rod−coil copolymers exhibit a thermotropic liquid crystalline phase. The polymer **5** containing 52% coil volume ($f_{\text{coil}} = 0.52$) exhibits a solid state at room temperature followed by a mesophase which, in turn, undergoes gradual decomposition from 230 °C, whereas the polymer **6** ($f_{\text{coil}} = 0.62$) shows a transition from a liquid crystalline phase to the isotropic liquid at 137 °C. In contrast to that of conventional liquid crystalline polymers, no birefringence between crossed polarizers could be observed in both the solid and liquid crystalline states of both polymers. The change in viscosity and flow properties of **6** indicates that the transition is from an ordered isotropic mesophase to a disordered liquid, suggesting the existence of a cubic mesophase.[9,10]

In contrast to **5** and **6**, the polymer **7** ($f_{\text{coil}} = 0.67$) exhibits a birefringent solid at room temperature, which melts into a liquid crystal at 89 °C and then an isotropic phase at 130 °C. On the polarized optical microscope, a transition from an isotropic liquid can be seen by the formation of dendritic domains which merge into a pseudo-focal conic texture which is characteristic of a hexagonal columnar mesophase.[11] The polymer **8** ($f_{\text{coil}} = 0.71$) displays a similar phase behavior, which exhibits a crystalline melting into a hexagonal columnar mesophase.

The phases of these polymers were characterized by X-ray diffraction experiments. In the optically isotropic solid and liquid crystalline states of **5** and **6**, a considerable number of sharp reflections in the small-angle X-ray diffraction patterns are observed. A representative small-angle X-ray diffraction pattern of **5** is shown in Figure 1. As can be seen in Figure 1, the sharp reflections are observed at the relative positions of $\sqrt{6}$, $\sqrt{8}$, $\sqrt{14}$, $\sqrt{16}$, $\sqrt{20}$, $\sqrt{22}$, and $\sqrt{32}$. By analogy with lyotropic systems of amphiphilic molecules and flexible

**Table 1. Characterization and Thermal Transitions of the Rod−Coil Copolymers (Data Are from First Heating and Cooling Scans)**[a]

| polymer | $\bar{M}_n$ (GPC) | $\bar{M}_w/\bar{M}_n$ (GPC) | $f_{coil}$[c] | phase transitions (°C) and corresponding enthalpy changes (kJ/mru[b]): heating | cooling |
|---|---|---|---|---|---|
| **5** | 21 800 | 2.23 | 0.52 | g −18.9 k 91.6 (0.8) cub 230.0 dec | dec 230.0 cub −20.9 g |
| **6** | 23 700 | 1.89 | 0.62 | g −29.8 k 86.2 (1.7) cub 136.5 (0.6) i | i 123.8 (0.7) cub −34.4 g |
| **7** | 24 500 | 1.97 | 0.67 | g −48.4 k 88.9 (2.6) col 130.1 (0.3) i | i 109.3 (0.3) col 84.8 (3.1) k −53.6 g |
| **8** | 30 200 | 1.84 | 0.71 | g −56.6 k 85.4 (2.6) col 117.8 (0.5) i | i 104.5 (0.5) col 79.4 (3.2) k −55.2 g |

[a] k = crystalline, cub = cubic, col = hexagonal columnar, i = isotropic, dec = decomposition. [b] mru = mole repeat unit. [c] $f_{coil}$ = coil volume fraction.

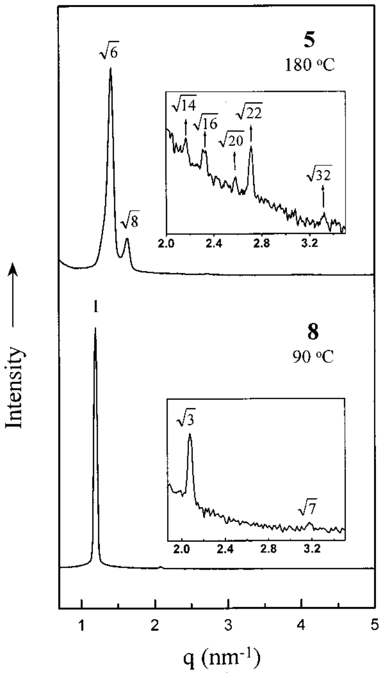


**Figure 1.** SAXS spectra of **5** and **8** plotted against $q$ (= $4\pi \sin \theta/\lambda$). Spectra were measured with synchrotron radiation at the 3C2 beam line ($\lambda$ = 0.1608 nm) at the Pohang Accelerator Laboratory, Korea.

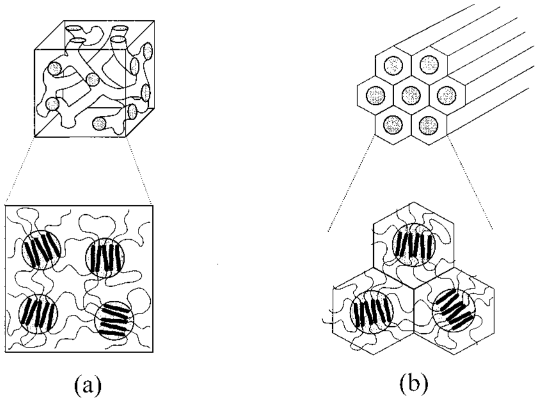


**Figure 2.** Schematic representation of the self-assemblies of rod−coil copolymers in (a) the bicontinuous cubic and (b) the hexagonal columnar phases.

coil block copolymer systems, the positions of these reflections can be indexed as the 211, 220, 321, 400, 420, 332, and 440 reflections of a bicontinuous cubic phase with *Ia*3*d* symmetry.[7,12] From the observed *d* spacing of the 211 reflection, the best fit values for the lattice parameter of the cubic liquid crystalline phase of **5** and **6** are 108 and 124 Å, respectively. These dimensions suggest that the rod units are arranged axially with their preferred direction within a cross-sectional slice of the aromatic core. At a wide angle taken from the liquid crystalline state, only a diffuse halo remains for **5** and **6** as evidence of the lack of any positional long-range order other than the cubic symmetry.

In their solid and liquid crystalline states, small-angle X-ray diffraction patterns display three reflections with Bragg spacings in the ratio of $1:\surd 3:\surd 7$, characteristic of a two-dimensional hexagonal columnar structure (Figure 1). From the observed first-order reflection, the lattice parameters can be estimated to be 58 and 60 Å in the solid state and 57 and 60 Å in the liquid crystalline state for **7** and **8**, respectively, in reasonable agreement with the length of a rod−coil repeating unit. In their liquid crystalline state, only a diffuse halo can be observed in the wide-angle X-ray pattern, indicating that there are only weak liquidlike arrangements of the rods within the column. On the basis of the experimental results, the schematic representation for the molecular organization of repeating units into the bicontinuous cubic and hexagonal columnar liquid crystalline phases can be constructed as shown in Figure 2. Both phases consist of aromatic rod domains in which rods are aligned axially with their preferred direction, surrounded by flexible coils. These results demonstrate that our system can offer a facile strategy to control supramolecular structure from 2-D hexagonal to 3-D cubic structure by simple variation of coil segment length in main-chain liquid crystalline polymers.

A notable feature of our system is the ability of the main-chain liquid crystalline polymers based on a rod building block to self-assemble into ordered structures with curved interfaces. Formation of supramolecular columnar and bicontinuous cubic assemblies in the rod−coil copolymers is in marked contrast to general behavior of conventional liquid crystalline polymers based on rodlike mesogens and segmented copolymers based on alternating rigid and flexible segments.[6,13] To the best of our knowledge, this is the first example of main-chain liquid crystalline polymers based on rodlike mesogens which exhibit hexagonal columnar or bicontinuous cubic phases, formed through aggregation of a rodlike unit into a cross-sectional aromatic core, although liquid crystalline phases with curved interfaces have recently been observed in hydrogen bonding-mediated supramolecules.[14]

Formation of the ordered structures with interfacial curvature from the main-chain rod−coil copolymers can be rationalized by considering entropic penalties associated with coil stretching and anisotropic arrangement of rod segments. Bulky PPO coils induce curvature at the rod/coil interface, arising from the connectivity of the rod and coils, constraint of constant density, and minimization of coil stretching. At the interface separating the rod and coil domains in the layered smectic structure, the relatively smaller area per junction favored by rod block results in chain stretching of the coil block, which is energetically unfavorable. Therefore, the rod−coil copolymers self-assemble into bicontinuous cubic or hexagonal columnar structures with larger interfacial area, instead of a layered smectic structure. These results suggest that introduction of long flexible coils into main-chain liquid crystalline polymeric systems based on rodlike mesogens can provide a powerful strategy to control supramolecular structure in dimensions of a few nanometers.

**Acknowledgment.** Financial support of this work by the CRM-KOSEF (1998), the Korea Science and Engineering Foundation (1999-1-308-002-3), and the Synchrotron Source Radiation at Pohang, Korea (for the beam time and technical assistance), is gratefully acknowledged.

**Supporting Information Available:** Representative optical micrograph of texture exhibited by hexagonal columnar mesophase of **8**, DSC traces obtained from first heating and cooling scans of **5**−**8**, characterization of rod−coil copolymers by SAXS, and wide-angle XRD pattern of **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) Muthukumar, M.; Ober, C. K.; Thomas, E. L. *Science* **1997**, *277*, 1225.

(2) Frechet, J. M. J. *Science* **1994**, *263*, 1710.

(3) Jenekhe, S. A.; Chen, X. L. *Science* **1998**, *279*, 1903.

(4) Widawski, G.; Rawiso, M.; Francois, B. *Nature* **1994**, *369*, 387.

(5) Stupp, S. I.; LeBonheur, V.; Walker, K.; Li, L. S.; Huggins, K. E.; Keser, M.; Amstutz, A. *Science* **1997**, *276*, 384.

(6) Demus, D., Goodby, J., Grey, G. W., Spiess, H.-W., Vill, V., Eds. *Handbook of Liquid Crystals;* Wiley-VCH: Weinheim, 1998; Vol. 3.

(7) (a) Hillmyer, M. A.; Bates, F. S.; Almdal, K.; Mortensen, K.; Ryan, A. J.; Patrick, J.; Fairclough, A. *Science* **1996**, *271*, 977. (b) Khandpur, A. K.; Forster, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen, K. *Macromolecules* **1995**, *28*, 8796.

(8) (a) Lee, M.; Cho, B.-K.; Kim, H.; Zin, W.-C. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 638. (b) Lee, M.; Cho, B.-K.; Kim, H.; Yoon, J.-Y.; Zin, W.-C. *J. Am. Chem. Soc.* **1998**, *120*, 9168.

(9) (a) Demus, D.; Richter, L. *Texture of Liquid Crystals*; Verlag Chemie: Weinheim, 1978. (b) Gray, G. W.; Goodby, J. W. *Smectic Liquid Crystals. Textures and Structures*; Leonard Hill: Glasgow, 1984.

(10) (a) Borisch, K.; Diele, S.; Goering, P.; Mueller, H.; Tschierske, C. *Liq. Cryst.* **1997**, *22*, 427. (b) Borisch, K.; Diele, S.; Goering, P.; Kresse, H.; Tschierske, C. *J. Mater. Chem.* **1998**, *8*, 529.

(11) Destrade, C.; Foucher, P.; Gasparoux, A.; Nguyen, H. T.; Levelut, A. M.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 121.

(12) (a) Luzzati, V.; Spegt, P. A. *Nature* **1967**, *215*, 701. (b) Rancon, Y.; Charvolin, J. *J. Phys. Chem.* **1988**, *92*, 2646. (c) Clerc, M.; Levelut, A. M.; Sadoc, J. F. *J. Phys. II (Paris)* **1991**, *1*, 1263. (d) Alexandridis, P. *Macromolecules* **1998**, *31*, 6935.

(13) (a) Eisenbach, C. D.; Heinemann, T.; Ribbe, A.; Stadler, E. *Macromol. Symp.* **1994**, *77*, 125. (b) Osaheni, J. A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **1995**, *117*, 7389.

(14) Lee, M.; Cho, B.-K.; Kang, Y.-S.; Zin, W.-C. *Macromolecules*, submitted.

MA990515E