Hydrogen-Bonding-Mediated Formation of Supramolecular Rod−Coil Copolymers Exhibiting Hexagonal Columnar and Bicontinuous Cubic Liquid Crystalline Assemblies

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ABSTRACT: The preparation and characterization of the supramolecular rod−coil copolymers directed by molecular recognition of 4,4′-bipyridine and 4-[poly(propyleneoxy)propyloxy]-4′-bis(biphenyl carboxylic acid) with degrees of polymerization (DP) of poly(propylene oxide) coil of eight (**P-8-HP**), 10 (**P-10-HP**), 15 (**P-15-HP**), 17 (**P-17-HP**), 21 (**P-21-HP**), 27 (**P-27-HP**) and 34 (**P-34-HP**) are described. The introduction of poly(propylene oxide) (PPO) coils with different lengths into the rodlike polymeric system induces a rich variety of self-assembled microstructures. In the crystalline phase, the supramolecular rod−coil copolymers with DP of PPO 8−17 organize into a microphase-separated monolayer lamellar structure. In contrast, the supramolecular rod−coil copolymers with DP of PPO 21−34 exhibit a hexagonal columnar crystalline phase. A dramatic phase change after crystalline melting of the polymers is observed with the variation of the coil length. The supramolecular rod−coil copolymers **P-8-HP** and **P-10-HP** display a bicontinuous cubic mesophase with *Ia*3*d* symmetry, while the supramolecular rod−coil copolymers **P-15-HP**, **P-17-HP**, and **P-21-HP** with a medium length of PPO coil exhibit a hexagonal columnar mesophase. Further increasing the length of coil, as in the case of **P-27-HP** and **P-34-HP**, suppresses liquid crystallinity and induces only crystalline polymers.

Introduction

Self-organizing materials, which include liquid crystalline polymers, block copolymers, hydrogen-bonded complexes, and many biological polymers, have been widely studied and observed to have great potential for various functional materials.[1] Manipulation of supramolecular nanostructure in self-organizing materials is of critical importance to achieving desired functions and properties in solid state and liquid crystalline state molecular materials. Thus, diverse molecular architectures are being explored as a means to manipulate the supramolecular structure, which has dramatic effects on the physical properties of polymers. Three-dimensional dendrimers with controlled surface and interfacial properties,[2] rod−coil diblock copolymers with a variety of supramolecular assemblies resulting in multifunctional properties,[3] and a small triblock copolymer based on a rod with spontaneous noncentrosymmetric organization[4] are typical examples.

Main chain liquid crystalline polymers are a class of self-assembling materials, which are conventionally prepared by coupling a rodlike mesogenic unit to a polymeric backbone through a flexible spacer. This polymeric architecture can also be constructed by noncovalent interactions such as ionic force and hydrogen bond which generate liquid crystalline polymeric properties. For example, molecular recognition process through hydrogen bond between dicarboxylic acids or tetracarboxylic acids and bipyridines has been employed for the induction of main chain linear polymeric liquid crystalline complexes.[5] Polymeric complexes through triple hydrogen bonds between uracil and bis(acylamino)pyridines have also been reported to lead to formation of supramolecular liquid crystalline strands.[6]

Because of the molecular shape of the rigid anisotropic unit, however, their assembly is generally shown to be nematic or lamellar smectic types of supramolecular structures in which the rodlike units are arranged with their long axes parallel to each other.[7] In remarkable contrast, block copolymers consisting of incompatible coil segments self-organize into a variety of supramolecular structures through mutual repulsion of each segment.[8] These design concepts can be extended to generate polymeric rod−coil block systems, which may be an attractive way of creating novel self-assembling materials since they share general characteristics of both liquid crystalline polymers based on rodlike mesogens and block copolymers. Such rod−coil multiblock copolymer systems are expected to induce a wide range of microphase-separated supramolecular structures due to the chemical incompatibility of the dissimilar blocks and the resulting entropic penalties associated with chain stretching. It is in this context that we have prepared supramolecular rod−coil copolymers from complementary components of diacids and bipyridine.

The design of supramolecular rod−coil multiblock copolymers was based on a 4′-biphenylcarboxylic acid functionalized poly(propylene oxide) coil which would introduce block segregation character into supramolecular liquid crystalline copolymers. The extended mesogenic rod blocks would be formed through intermolecular hydrogen bonding between bis(4′-biphenylcarboxylic acid) and 4,4′-bipyridine, since the lone pairs of the 4,4′-bipyridine are directed along the molecular axes of the rod. Therefore, these supramolecular rod−

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coil copolymers can be considered as either main chain liquid crystalline polymers or segmented copolymers, taking into account their supramolecular chain architecture.

Experimental Section

Materials. 4-Hydroxy-4′-biphenylcarboxylic acid (98%), toluene-*p*-sulfonyl chloride (98%), poly(propylene glycol)s of ({DP}) 8, 17, 21, and 34 (all from Aldrich), and the other conventional reagents were used as received. Poly(propylene glycol)s of ({DP}) 10, 15, and 27 were synthesized according to the procedure described previously.[9] 4,4′-Bipyridine (98%, from Aldrich) was used after purification by recrystallization from toluene. Ethyl-4-hydroxy-4′-biphenyl carboxylate was prepared as described previously.[9] Dichloromethane was dried by distillation from calcium hydride and stored over type 4 Å molecular sieves. Pyridine was dried by distillation from sodium metal and stored over type 4 Å molecular sieves.

Techniques. ^{1}H NMR spectra were recorded from $CDCl_3$ solutions on a Bruker AM 250 spectrometer. The purity of the products was checked by thin-layer chromatography (TLC; Merck, silica gel 60). A Perkin-Elmer DSC-7 differential scanning calorimeter equipped with a 1020 thermal analysis controller was used to determine the thermal transitions, which were reported as the maxima and minima of their endothermic or exothermic peaks. In all cases, the heating and cooling rates were 10 °C min^{-1}. 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 Korea Research Institute of Chemical Technology. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 3C2 and 4C2 X-ray beam line at Pohang Accelerator Laboratory, Pohang, Korea. To investigate structural changes on heating, the sample was held in an aluminum sample holder which was sealed with the window of 7 μm thick Kapton films on both sides. The sample was heated with two catridge heaters and the temperature of the samples was monitored by thermocouple placed close to the sample. Background scattering correction was made by subtracting the scatterings from the Kapton. Molecular weight distributions ($\bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) with a Waters R401 instrument equipped with Stragel HR 3, 4, and 4E columns, M7725i manual injector, column heating chamber, and 2010 Millennium data station. Measurements were made by using an UV detector, with $CHCl_3$ as solvent (1.0 mL min^{-1}). Infrared (IR) spectra were recorded on a Nicolet Impact 400 FT IR spectrophotometer using KBr pellet or NaCl cell.

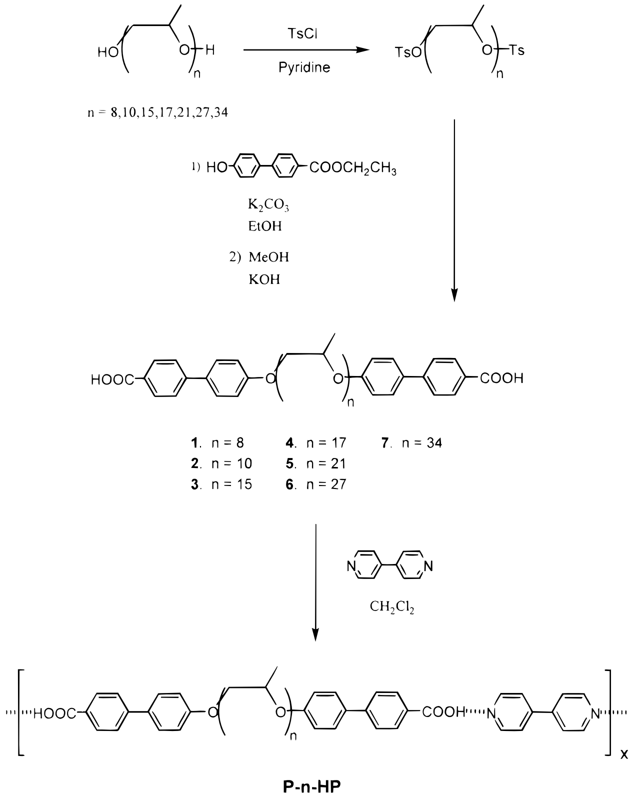
Synthesis. The synthesis of supramolecular rod–coil copolymers containing poly(propylene oxide) coils with various degrees of polymerization is outlined in Scheme 1.

Synthesis of 4-[Poly(propyleneoxy)propyloxy]-4′-bis(biphenyl carboxylic acid)s, 1–7. The synthesis of bis(4′-biphenylcarboxylic acid) hydrogen-bond donors based on poly(propylene oxide)s **(1–7)** was performed through a similar procedure described previously.[9]

1: yield 56.2%. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 8.12 (d, 4Ar–H, *o* to COOH, J = 8.0 Hz), 7.62 (m, 4Ar–H, *m* to COOH, J = 8.0 Hz), 7.53 (d, 4Ar–H, *m* to $CH(CH_3)O$, J = 8.3 Hz), 7.00 (d, 4Ar–H, *o* to $CH(CH_3)O$, J = 8.2 Hz), 4.56 (m, 3H, phenyl$OCH_2CH(CH_3)$ and $CH_2CH(CH_3)$Ophenyl), 3.40–4.00 (m, 21H, $OCH_2CH(CH_3)$), 0.88–1.35 (m, 24H, $CH(CH_3)O$). Anal. Calcd for $C_{50}H_{66}O_{13}$: C, 68.63; H, 7.60. Found: C, 68.64; H, 7.57. $\bar{M}_w/\bar{M}_n$ = 1.14 (GPC). IR (KBr): $\bar{\nu}$ = 1685 cm^{-1} (C=O str).

2: yield 50.5%. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 8.12 (d, 4Ar–H, *o* to COOH, J = 8.0 Hz), 7.62 (m, 4Ar–H, *m* to COOH, J = 8.0 Hz), 7.53 (d, 4Ar–H, *m* to $CH(CH_3)O$, J = 8.3 Hz), 7.00 (d, 4Ar–H, *o* to $CH(CH_3)O$, J = 8.2 Hz), 4.56 (m, 3H, phenyl$OCH_2CH(CH_3)$ and $CH_2CH(CH_3)$Ophenyl), 3.42–4.05 (m, 27H, $OCH_2CH(CH_3)$), 0.87–1.35 (m, 30H, $CH(CH_3)O$). Anal. Calcd for $C_{56}H_{78}O_{15}$: C, 67.86; H, 7.93. Found: C, 67.84; H, 7.92. $\bar{M}_w/\bar{M}_n$ = 1.14 (GPC). IR (KBr): $\bar{\nu}$ = 1685 cm^{-1} (C=O str).

Scheme 1. Synthesis of Supramolecular Rod–Coil Copolymers P-*n*-HP.



3: yield 58.0%. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 8.12 (d, 4Ar–H, *o* to COOH, J = 8.2 Hz), 7.63 (d, 4Ar–H, *m* to COOH, J = 8.1 Hz), 7.54 (d, 4Ar–H, *m* to $CH(CH_3)O$, J = 8.5 Hz), 7.02 (d, 4Ar–H, *o* to $CH(CH_3)O$, J = 8.1 Hz), 4.56 (m, 3H, $CH_2CH(CH_3)$Ophenyl and $(CH_3)CHCH_2$Ophenyl), 3.14–3.92 (m, 42H, $OCH_2CH(CH_3)$), 0.84–1.42 (m, 45H, $OCH_2CH(CH_3)$). Anal. Calcd for $C_{71}H_{108}O_{20}$: C, 66.54; H, 8.49. Found: C, 66.86; H, 8.29. $\bar{M}_w/\bar{M}_n$ = 1.11 (GPC). IR (KBr): $\bar{\nu}$ = 1685 cm^{-1} (C=O str).

4: yield 48.7%. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 8.12 (d, 4Ar–H, *o* to COOH, J = 7.8 Hz), 7.63 (d, 4Ar–H, *m* to COOH, J = 7.8 Hz), 7.54 (d, 4Ar–H, *m* to $CH(CH_3)O$, J = 8.4 Hz), 7.02 (d, 4Ar–H, *o* to $CH(CH_3)O$, J = 7.2 Hz), 4.56 (m, 3H, $CH_2CH(CH_3)$Ophenyl and $(CH_3)CHCH_2$Ophenyl), 3.14–3.92 (m, 48H, $OCH_2CH(CH_3)$), 0.84–1.42 (m, 51H, $OCH_2CH(CH_3)$). Anal. Calcd for $C_{77}H_{120}O_{22}$: C, 66.17; H, 8.17. Found: C, 66.46; H, 8.62. $\bar{M}_w/\bar{M}_n$ = 1.18 (GPC). IR (KBr): $\bar{\nu}$ = 1685 cm^{-1} (C=O str).

5: yield 55.4%. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 8.12 (d, 4Ar–H, *o* to COOH, J = 8.3 Hz), 7.63 (d, 4Ar–H, *m* to COOH, J = 8.3 Hz), 7.54 (d, 4Ar–H, *m* to $CH(CH_3)O$, J = 8.4 Hz), 7.02 (d, 4Ar–H, *o* to $CH(CH_3)O$, J = 8.5 Hz), 4.56 (m, 3H, $CH_2CH(CH_3)$Ophenyl and $(CH_3)CHCH_2$Ophenyl), 3.25–3.95 (m, 60H, $OCH_2CH(CH_3)$), 0.84–1.43 (m, 63H, $OCH_2CH(CH_3)$). Anal. Calcd for $C_{89}H_{144}O_{26}$: C, 65.58; H, 8.90. Found: C, 65.48; H, 8.64. $\bar{M}_w/\bar{M}_n$ = 1.11 (GPC). IR (NaCl): $\bar{\nu}$ = 1687 cm^{-1} (C=O str).

6: yield 40.3%. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 8.12 (d, 4Ar–H, *o* to COOH, J = 8.2 Hz), 7.63 (d, 4Ar–H, *m* to COOH, J = 8.2 Hz), 7.54 (d, 4Ar–H, *m* to $CH(CH_3)O$, J = 8.3 Hz), 7.02 (d, 4Ar–H, *o* to $CH(CH_3)O$, J = 8.3 Hz), 4.56 (m, 3H, $CH_2CH(CH_3)$Ophenyl and $(CH_3)CHCH_2$Ophenyl), 3.24–3.95 (m, 78H, $OCH_2CH(CH_3)$), 0.82–1.43 (m, 81H, $OCH_2CH(CH_3)$). Anal. Calcd for $C_{107}H_{180}O_{32}$: C, 64.95; H, 9.17. Found: C, 64.92; H, 9.22. $\bar{M}_w/\bar{M}_n$ = 1.15 (GPC). IR (NaCl): $\bar{\nu}$ = 1685 cm^{-1} (C=O str).

Table 1. Thermal Transitions of the Supramolecular Rod−Coil Copolymers[a]

polymer (**P-*n*-HP**)	f_{coil}[c]	phase transitions (°C) and corresponding enthalpy changes (kJ/mru[b])	
		heating	cooling
P-8-HP	0.52	k 105.2 (17.9) cub 153.2 (2.1) i	i 141.3 (1.9) cub 87.3 (16.1) k
P-10-HP	0.57	k 94.3 (23.9) cub 134.9 (2.5) i	i 124.3 (2.3) cub 72.3 (19.2) k
P-15-HP	0.67	k 77.2 (16.0) col 89.6 (2.0) i	i 85.2 (2.0) col 63.9 (11.2) k
P-17-HP	0.69	k 71.4 (16.3) col 86.0 (2.6) i	i 82.3 (2.5) col 50.9 (15.6) k
P-21-HP	0.74	k 54.8 (14.4) col 68.9 (2.3) i	i 63.9 (2.1) col 31.4 (12.8) k
P-27-HP	0.78	k 44.7 (17.3) i	i 35.3 (16.6) k
P-34-HP	0.82	k 35.4 (16.5) i	i 27.5 (16.3) k

[a] Data are from second heating and first cooling scans. k = crystalline, cub = cubic, col = hexagonal columnar, and i = isotropic. [b] mru = mole repeat unit. [c] f_{coil} = coil volume fraction.

7: yield 54.7%. ^{1}H NMR (250 MHz, $CDCl_3$, δ, ppm): 8.12 (d, 4Ar−H, *o* to COOH, J = 8.3 Hz), 7.63 (d, 4Ar−H, *m* to COOH, J = 8.3 Hz), 7.54 (d, 4Ar−H, *m* to $CH(CH_3)O$, J = 8.4 Hz), 7.02 (d, 4Ar−H, *o* to $CH(CH_3)O$, J = 8.5 Hz), 4.56 (m, 3H, $CH_2C\mathit{H}(CH_3)$Ophenyl and $(CH_3)CHC\mathit{H}_2$Ophenyl), 3.25−3.96 (m, 99H, $OC\mathit{H}_2C\mathit{H}(CH_3)$), 0.80−1.43 (m, 102H, $OCH_2CH(C\mathit{H}_3)$). Anal. Calcd for $C_{128}H_{222}O_{39}$: C, 64.46; H, 9.38. Found: C, 64.55; H, 9.33. $\bar{M}_w/\bar{M}_n$ = 1.15 (GPC). IR (NaCl): $\bar{\nu}$ = 1685 cm^{-1} (C=O str).

Preparation of Supramolecular Rod−Coil Copolymers (P-*n*-HP). The supramolecular rod−coil copolymers were prepared in the methylene chloride solution of diacid and an equimolar amount of 4,4′-bipyridine. The mixture was stirred at room temperature under nitrogen for 2 h, followed by slow evaporation of the solvent in rotary evaporator. The resulting supramolecular rod−coil copolymers were dried in a vacuum at 25 °C for 6 h.

Results and Discussion

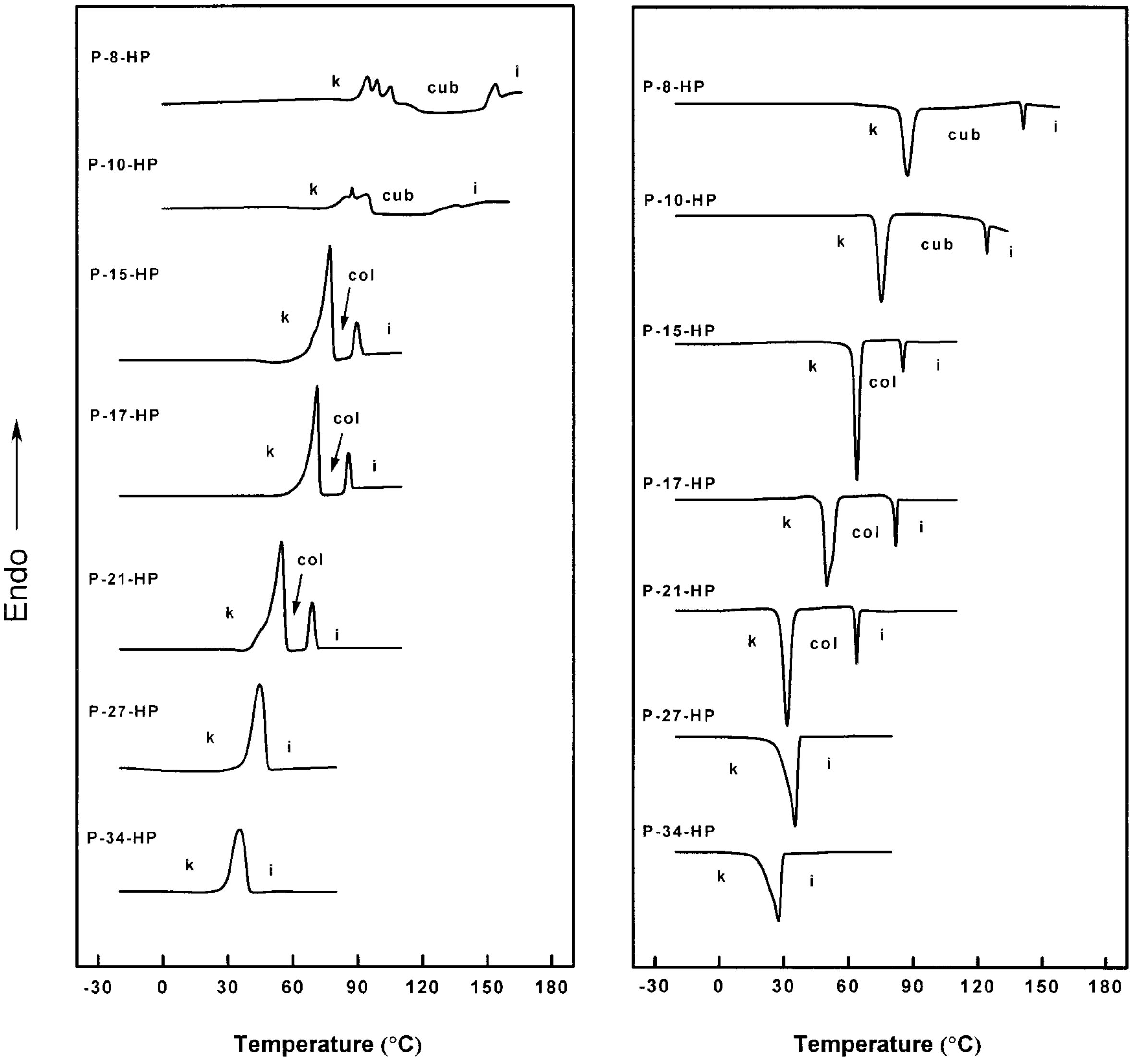
Synthesis and Thermal Characterization. The synthesis of bis(4′-biphenylcarboxylic acid) hydrogen-bond donors based on poly(propylene oxide)s **1**−**7** was performed through a similar procedure described previously (Scheme 1).[9] All analytical data of hydrogen-bond donor molecules are consistent with expected structures. Molecular weight distributions of these molecules determined by GPC appear to be less than 1.18. Degrees of polymerization (DP) of the poly(propylene oxide) unit of the molecules determined from the ratio of the aromatic protons (ortho to alkoxy) to the ethylene protons of poly(propylene oxide) unit shown in the ^{1}H NMR spectra were in good agreement with the expected values.

The resulting bis(4′-biphenylcarboxylic acid)s were complexed with equimolar amount of 4,4′-bipyridine to obtain supramolecular rod−coil copolymers. Formation of the complexes was confirmed by infrared spectroscopic experiments showing the characteristic stretching bands (two bands centered around 2500 and 1900 cm^{-1}) resulting from self-association of carboxylic acid and pyridine through intermolecular hydrogen bonding.[5] The obtained supramolecular rod−coil copolymers were observed to form a fiber which could be drawn from the liquid crystalline melt. This observation suggests that the complexation of a diacid and a bipyridine can give rise to the formation of a linear chain-extended polymeric structure with sufficient chain length to achieve the mechanical coherence necessary to form fibers.

The thermotropic phase behavior of the resulting supramolecular rod−coil copolymers was investigated by a combination of techniques consisting of differential scanning calorimetry (DSC), thermal optical polarized microscopy, and X-ray scattering experiments. Figure 1 presents the DSC second heating and first cooling curves of the supramolecular rod−coil copolymers. The transition temperatures and the corresponding enthalpy changes of all polymers obtained from DSC are summarized in Table 1. In contrast to the bis(biphenylcarboxylic acid) precursors which exhibit only a crystalline phase, all the supramolecular rod−coil copolymers exhibit a thermotropic liquid crystalline phase. As can be observed from Figure 1 and Table 1, **P-8-HP** exhibits a crystalline melting at 105.2 °C, followed by a liquid crystalline phase which undergoes isotropization at 153.2 °C. **P-10-HP** shows a phase behavior similar to that of **P-8-HP**, which exhibits crystal melting followed by a mesophase. On the optical microscope, no birefringence between cross polarizers after melting of **P-8-HP** and **P-10-HP** could be observed, strongly suggesting the existence of an optically isotropic cubic mesophase.[10]

The supramolecular rod−coil copolymer **P-15-HP** based on poly(propylene oxide) with a DP of 15 exhibits a crystalline melting at 77.2 °C, followed by a mesophase which, in turn, undergoes transformation into isotropic liquid at 89.6 °C. Optical microscopic observations of this compound are consistent with this behavior. 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 exhibited by conventional discotic mesogens.[11] Both supramolecular rod−coil copolymers **P-17-HP** and **P-21-HP** also show phase behavior similar to that of the polymer **P-15-HP**, which exhibits a crystalline melting followed by a hexagonal columnar mesophase. Figure 2 shows a representative texture exhibited by the hexagonal columnar liquid crystalline phase of **P-15-HP**. Further increasing the length of flexible coil as in the case of **P-27-HP** and **P-34-HP** suppresses the formation of liquid crystallinity.

The thermal behavior of the supramolecular rod−coil copolymers determined from heating and cooling DSC curves as well as thermal optical polarized microscopic observations is presented in Figure 3. As shown in Figure 3, the transition temperatures associated with both the crystalline−melting and the mesomorphic−isotropic phases decrease with increasing DP of poly(propylene oxide) coil. However, the slope of the $T_i - n$ is steeper than that of $T_m - n$. Consequently, at a certain number of repeating units of PPO, the $T_i - n$ dependence intercepts the $T_m - n$ dependence, and therefore, the liquid crystalline phase becomes virtual above this number of repeating units as in the case of **P-27-HP** and **P-34-HP**. A notable feature in this figure is the existence of a cubic phase in the range of smaller DP of coil. Similar to lyotropic and conventional block copolymer systems, the topology in this region should be a bicontinuous cubic phase since such a structure can attain a smaller interfacial area than that of a columnar structure.[12] Therefore, we assume that the polymers



(a) (b)

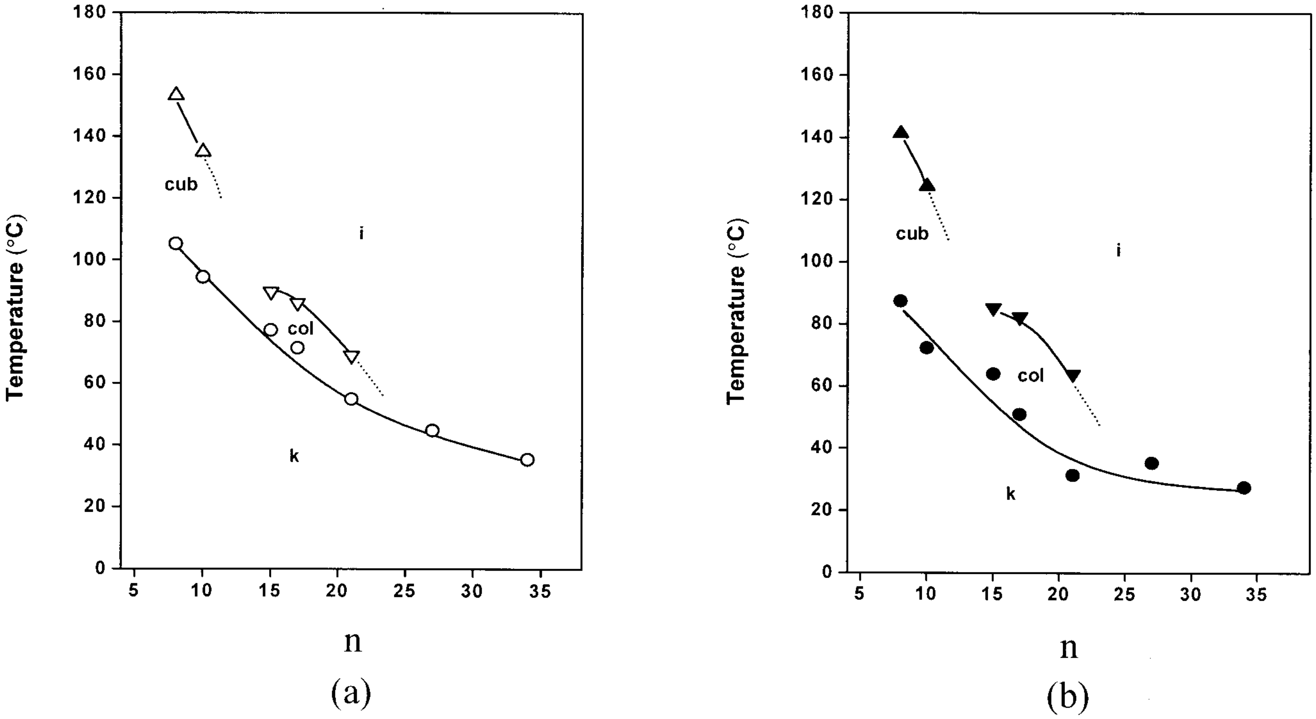
Figure 1. DSC traces exhibited during (a) the second heating scan and (b) the first cooling scan by **P-*n*-HP** with different numbers of repeating units (*n*) of poly(propylene oxide) coil.

Figure 2. Representative optical micrograph (100×) of texture exhibited by the hexagonal columnar mesophase of **P-15-HP** at 80 °C on cooling scan.

with DP of poly(propylene oxide)s 8 and 10 exhibit a bicontinuous cubic mesophase.

X-ray Diffraction Studies. To investigate the microstructures in the self-assembled crystalline and liquid crystalline states, X-ray scattering experiments have been performed with the supramolecular rod−coil copolymers at various temperatures. The *d* spacings and the lattice constants determined by small-angle X-ray diffractions are summarized in Table 2. In the crystalline state, the X-ray diffraction patterns of the supramolecular rod−coil copolymers from **P-8-HP** to **P-17-HP** display three reflections in the spacing ratio of 1:2:3 in the small-angle region, while two sharp reflections are observed in the wide-angle region, indicative of a lamellar structure consisting of microphase-separated crystalline rod domains and the amorphous coil domains. The layer spacings are close to the corresponding estimated repeating unit length of the supramolecular rod−coil copolymers, indicative of a monolayer lamellar structure.

In contrast, **P-21-HP**, **P-27-HP** and **P-34-HP** display three reflections in the ratio of 1:$\sqrt{3}$:2 in the small-angle region, characteristic of a two-dimensional hex-



(a)

(b)

Figure 3. Dependence of the transition temperatures of the supramolecular rod–coil copolymers on the number of repeating units (*n*) of poly(propylene oxide) coil. (a) Data from the second heating scan: ○, T_{m}; △, $T_{\mathrm{cub-i}}$; ▽, $T_{\mathrm{col-i}}$. (b) Data from the first cooling scan: ●, T_{m}; ▲, $T_{\mathrm{cub-i}}$; ▼, $T_{\mathrm{col-i}}$.

Table 2. Characterization of the Supramolecular Rod–Coil Copolymers by Small-Angle X-ray Scattering

	crystalline phase			liquid crystalline phase			
		columnar		cubic		columnar	
polymer (**P-*n*-HP**)	lamellar d_{001} (Å)	d_{100} (Å)	lattice constant (*a*) (Å)	d_{211} (Å)	lattice constant (*a*) (Å)	d_{100} (Å)	lattice constant (*a*) (Å)
P-8-HP	36.6			43.9	107.5		
P-10-HP	42.1			48.7	119.3		
P-15-HP	44.2					48.0	55.4
P-17-HP	47.2					49.7	57.4
P-21-HP		54.6	63.0			52.5	60.6
P-27-HP		59.8	69.1				
P-34-HP		64.8	74.8				

agonal columnar structure. Considering two-dimensional hexagonal columnar structure, the plot of the squared diameter of a column (a^2) vs molecular volume (V_{m}) should be linear and pass through the origin. As shown in Figure 4, a^2 shows a linear dependence on molecular volume and the extrapolation of this plot gives the origin where a^2 and V_{m} are zero. This plot is believed to provide further support for formation of a hexagonal columnar structure in the crystalline state of these polymers.

The X-ray diffraction patterns of **P-8-HP** and **P-10-HP** in their liquid crystalline state display several sharp reflections in the small angle region are observed as shown in Figure 5. The relative positions of these reflections are $\sqrt{6}$ and $\sqrt{8}$, which can be indexed as the 211 and 220 reflections of a body-centered cubic phase with *Ia*3*d* symmetry.[13] From the observed *d* spacing of the 211 reflection, the best fit values for the lattice parameter for the cubic phase of **P-8-HP** and **P-10-HP** are 107.5 and 119.3 Å, respectively. At a wide angle, only a diffuse halo remains for both the supramolecular rod–coil polymers as evidence of the lack of any positional long-range order other than the three-dimensional cubic packing of supramolecular units (Figure 6).

On the basis of the X-ray diffraction data described above and its position in the phase diagram, located between lamellar crystalline and hexagonal columnar liquid crystalline structures, the cubic phase can be best described as a bicontinuous cubic phase with *Ia*3*d* symmetry, occurring frequently in coil–coil block copolymer systems.[12,13] Thus, a similar model proposed for the bicontinuous cubic phase of coil–coil block copolymers may be used for its description.[12] Assuming that a bicontinuous cubic unit cell with *Ia*3*d* symmetry consists of a 3D-periodic minimal surface dividing the space, rods may be forming a monolayer whose center is fixed on the surface. The resulting monolayer sheet is continuous throughout the space with 3-dimensional periodicity.

Although a bicontinuous cubic phase with *Ia*3*d* symmetry has been observed in several thermotropic low molar mass liquid crystalline systems such as amphiphilic glucitol derivatives,[14] polycatenar silver complexes,[15] and glycolipid derivatives,[16] it is extremely rare in liquid crystalline polymeric systems based on mesogenic units. Previously, only a thermotropic micellar cubic mesophase has been observed in the liquid crystalline polymers based on dendritic side groups in which molecular shape can easily adopt spherical assembly.[17]

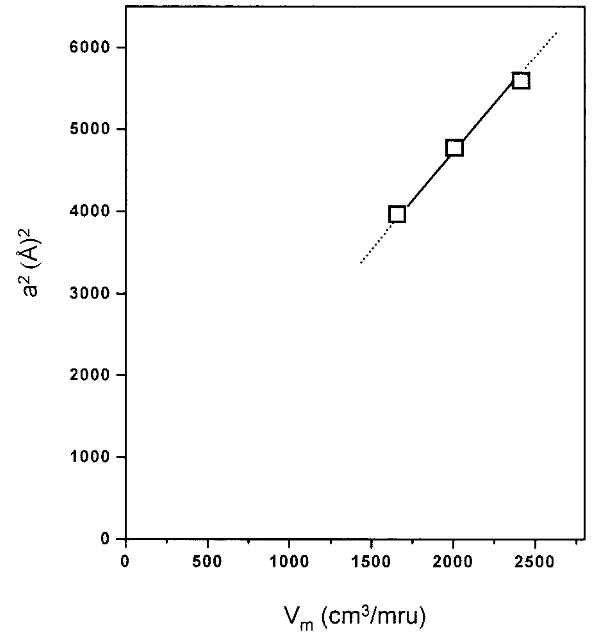


Figure 4. Dependence of the squared diameter of column (a^2) on the molar volume (V_m) of supramolecular rod–coil copolymers.

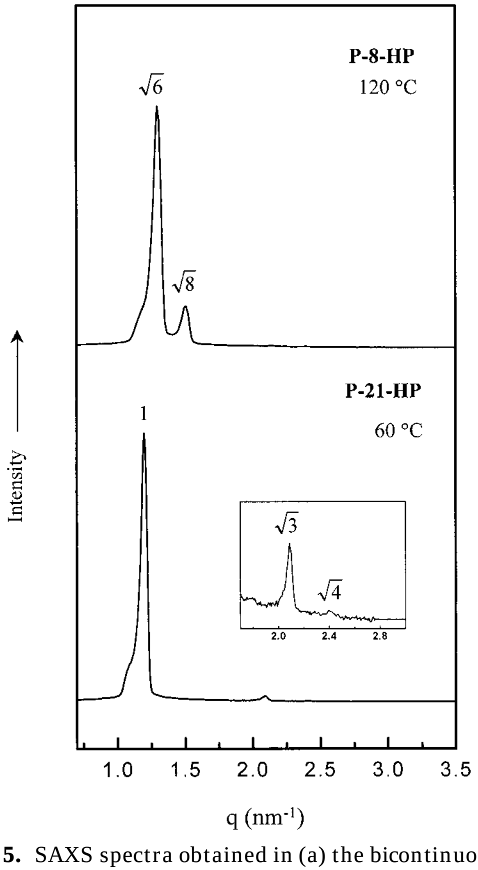


Figure 5. SAXS spectra obtained in (a) the bicontinuous cubic mesophase at 120 °C for **P-8-HP** and (b) the hexagonal columnar mesophase at 60 °C for **P-21-HP** plotted against q (=$4\pi(\sin\theta)/\lambda$).

The X-ray diffraction patterns of the birefringent mesophase of **P-15-HP**, **P-17-HP**, and **P-21-HP** display three sharp reflections with the ratio of 1:$\sqrt{3}$:2 in the small-angle region, characteristic of the two-dimensional hexagonal structure (hexagonally packed array of cylindrical micelles). The observed d spacings and the lattice constants are given in Table 2 and a representative small angle X-ray diffraction pattern of **P-21-HP** is shown in Figure 5. At the wide angles only a diffuse halo remains as evidence of a lack of any positional long-range order other than the two-dimensional hexagonal packing of supramolecular columns. These results together with optical microscopic observations indicate that these supramolecular rod–coil copolymers display a disordered hexagonal columnar mesophase.

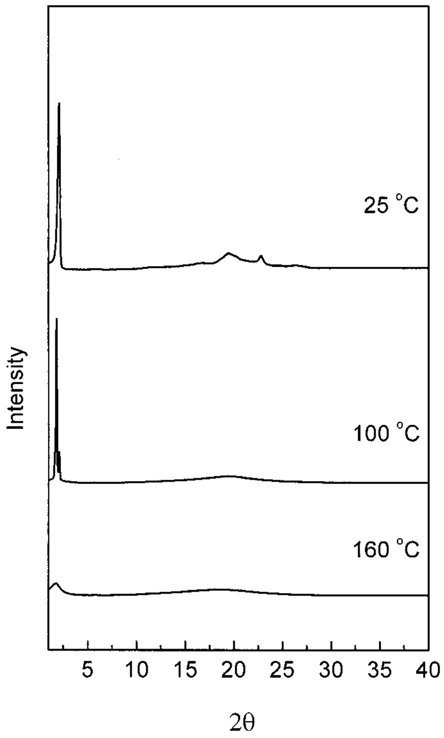


Figure 6. Wide-angle X-ray diffraction patterns of **P-10-HP** measured at various temperatures.

The phase behavior of the supramolecular rod–coil copolymers exhibiting a hexagonal columnar phase is in significant contrast to that of main chain liquid crystalline polymers based on rodlike mesogens which generally exhibit nematic or smectic liquid crystalline phases. The molecular organization of the supramolecular rod–coil copolymers into the columnar structure is also remarkably different from that usually observed in columnar phases of liquid crystalline polymers based on disk-[18] and taper-shaped mesogens[19] since their mesogenic architecture is rodlike rather than disklike.

A notable feature of our system is the ability of the supramolecular main chain polymers based on a rod building block to self-assemble into ordered structures with curved interface in their crystalline and liquid crystalline states. Formation of bicontinuous cubic and hexagonal columnar assemblies in the supramolecular rod–coil copolymers is in marked contrast to general behavior of conventional liquid crystalline polymers based on rigid mesogenic units.[7] The molecular organization of the supramolecular rod–coil copolymers into the bicontinuous cubic or the columnar structures is also remarkably different from that usually observed in those of block copolymers based on immiscible coil blocks[8,13,20–21] since the rods consisting of a core domain favor the anisotropic aggregation with their long axes even in the melt state rather than isotropic aggregation. The results described in this paper demonstrate that systematic variation in the length of coil in the supramolecular rod–coil system can change the self-assembled structure from lamellar, bicontinuous cubic to hexagonal columnar phases.

Conclusion

We have prepared supramolecular rod−coil copolymers directed by molecular recognition of hydrogen bond acceptor and hydrogen bond donor components. The resulting supramolecular rod−coil copolymers were characterized by DSC, thermal optical microscopy, and X-ray scattering measurements. In the crystalline state, the supramolecular rod−coil copolymers with DP of poly(propylene oxide) 8−17 have been observed to organize into a microphase separated monolayer lamellar structure, while the polymers with DP of poly(propylene oxide) 21−34 to organize into a hexagonal columnar structure. In the liquid crystalline states, the supramolecular rod−coil copolymers with DP of poly(propylene oxide) 8−10 self-assemble into an optically isotropic cubic mesophase. This phase has been identified by X-ray scattering method to be a bicontinuous cubic phase with *Ia*3*d* symmetry. Increasing the length of coil induces a hexagonal columnar mesophase as exhibited by **P-15-HP**, **P-17-HP**, and **P-21-HP**. Further increasing the length of coil as in the case of **P-27-HP** and **P-34-HP** suppresses liquid crystallinity and gives rise to only a crystalline polymer. These results demonstrate that a rich variety of self-assembled supramolecular structures can be induced in the rodlike polymeric systems through introduction of long flexible coil.

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