

Synthesis of liquid crystalline rod-coil dimers based on poly(propylene oxide) coil

Byoung-Ki Cho¹, Ja-Hyoung Ryu¹, Wang-Cheol Zin², Myongsoo Lee^{1*}

¹ Department of Chemistry, Yonsei University, Shinchon 134, Seoul 120-749, Korea

² Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang 790-784, Korea

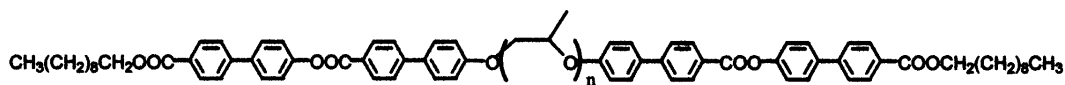
Received: 22 February 2000/Revised version: 21 March 2000/Accepted: 29 March 2000

Summary

The synthesis and characterization of 4-[poly(propyleneoxy)propyloxy]-4'-bis[4-decyloxycarbonylbiphenyl-4'-biphenylcarboxylate] with poly(propylene oxide) coil of seven (**dimer-7**), twelve (**dimer-12**), seventeen (**dimer-17**), twenty one (**dimer-21**) are described. **Dimer-7** with short length of poly(propylene oxide) coil exhibits successively smectic C, smectic A and nematic mesophases, while **dimer-12** and **dimer-17** with longer lengths of coils exhibit a bicontinuous cubic mesophase with *Ia3d* symmetry. Further increasing the length of coil, as in the case of **dimer-21**, suppresses liquid crystallinity.

Introduction

Liquid crystalline rod-coil molecules consist of an elongated rodlike mesogenic group and a flexible chain. These molecules have attracted much interest and not only as a result of their considerable application potential in the range of advanced nanotechnologies but also they provide demanding challenge to understanding of self-organization in molecular systems.^{1,2} A remarkable feature of the liquid crystalline behavior of this class of materials is the dramatic supramolecular structural changes depending on the volume ratio of rod relative to coil. Recently, we have demonstrated that rod-coil molecules based on poly(alkylene oxide) coil show a remarkable mesomorphism depending on the coil volume fraction relative that of rod.³⁻⁵ This is a result of the microphase separation through two immiscible blocks and the spontaneous orientation of the mesogenic rods according to the rod director.



dimer-n

As an extension of this approach, we have prepared a series of liquid crystalline rod-coil dimers in which two rod-like mesogenic units are connected through poly(propylene oxide) coil.

The goal of this paper is to describe the synthesis of a series of rod-coil **dimer-n** molecules with different lengths of poly(propylene oxide) coils where *n* denotes the number of propylene oxide units in the coil block, and their thermotropic phase behavior characterized by differential scanning calorimetry (DSC) and X-ray scattering

* Corresponding author

experiments.

Experimental

Materials

4-Hydroxy-4'-biphenylcarboxylic acid (98%), 1-bromodecane (98%), 1, 3-diisopropylcarbodiimide (DIPC, 99%), toluene-*p*-sulfonyl chloride (98%), 4-dimethylaminopyridine (99%), poly(propylene glycol) of M_w 425, 725, 1000, 1200 (all from Aldrich), and the other conventional reagents were used as received. 4-Dimethylamino pyridinium-*p*-toluene sulfonate (DPTS) was prepared as described previously⁵ and dried under vacuum at 50 °C for 48 h. Ethyl-4-hydroxy-4'-biphenylcarboxylate and decyl-4-hydroxy-4'-biphenylcarboxylate were also prepared as described previously.⁶ Dichloromethane was dried by distillation from calcium hydride and stored over type 4Å molecular sieve. Pyridine was dried by distillation from sodium metal and stored over type 4Å molecular sieve.

Techniques

¹H-NMR spectra were recorded from CDCl₃ 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 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 X) equipped with a Mettler FP 82 hot-stage and a Mettler FP 90 central processor was used to observe the thermal transitions and to analyse the anisotropic texture.⁷ Microanalyses were performed with a Perkin Elmer 240 elemental analyser 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, Korea. In order 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 cartridge 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 (M_w/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, CHCl₃ as solvent (1.0 ml min⁻¹).

Synthesis

The synthesis of molecules with different coil lengths is outlined in Scheme 1 and was performed according to similar procedure described previously.⁵

Synthesis of 4'-[poly(propyleneoxy)propyloxy]-4-bis(biphenylcarboxylic acid) (**1-4**)

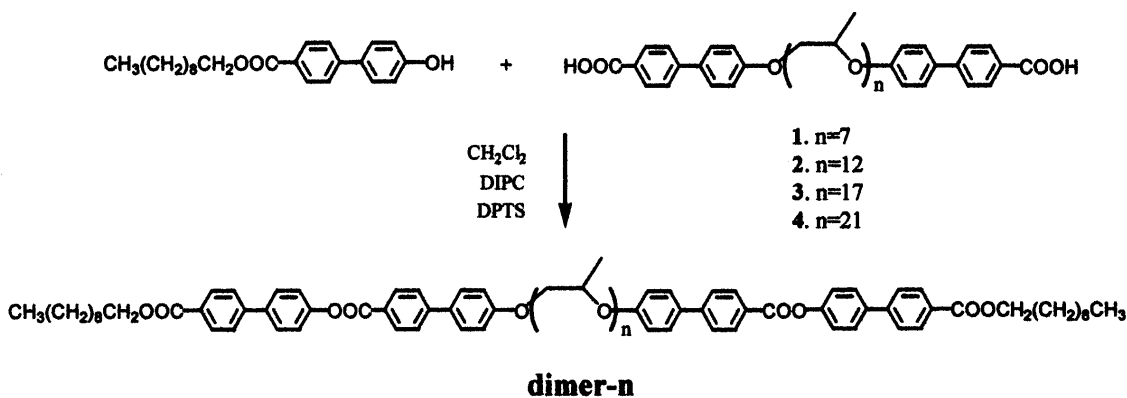
1: yield 53.2 %. ¹H NMR (CDCl₃, δ, ppm) 8.12 (d, 4Ar-H, *o* to COOH, *J* = 8.0 Hz), 7.62 (m, 4Ar-H, *m* to COOH, *J* = 8.0 Hz), 7.53 (d, 4Ar-H, *m* to CH(CH₃)O, *J* = 8.3 Hz), 7.00 (d, 4Ar-H, *o* to CH(CH₃)O, *J* = 8.2 Hz), 4.57 (m, 3H, phenylOCH₂CH(CH₃) and CH₂CH(CH₃)Ophenyl), 3.40-4.00 (m, 18H, OCH₂CH(CH₃)), 0.95-1.35 (m, 21H, CH(CH₃)O).

2: yield 54.0 %. ¹H NMR (CDCl₃, δ, ppm) 8.08 (d, 4Ar-H, *o* to COOH, *J* = 8.1 Hz), 7.59 (m, 4Ar-H, *m* to COOH, *J* = 8.1 Hz), 7.49 (d, 4Ar-H, *m* to CH(CH₃)O, *J* = 8.5 Hz),

6.97 (d, 4Ar-H, *o* to CH(CH₃)O, *J* = 8.1 Hz), 4.54 (m, 3H, phenylOCH₂CH(CH₃) and CH₂CH(CH₃)Ophenyl), 3.15-4.02 (m, 33H, OCH₂CH(CH₃)), 0.87-1.39 (m, 36H, CH(CH₃)O).

3: yield 55.7 %. ¹H NMR (CDCl₃, δ, ppm) 8.12 (d, 4Ar-H, *o* to COOH, *J* = 7.8 Hz), 7.63 (m, 4Ar-H, *m* to COOH, *J* = 7.8 Hz), 7.54 (d, 4Ar-H, *m* to CH(CH₃)O, *J* = 8.4 Hz), 7.02 (d, 4Ar-H, *o* to CH(CH₃)O, *J* = 7.2 Hz), 4.56 (m, 3H, phenylOCH₂CH(CH₃) and CH₂CH(CH₃)Ophenyl), 3.14-3.92 (m, 48H, OCH₂CH(CH₃)), 0.84-1.42 (m, 51H, CH(CH₃)O).

4: yield 58.5 %. ¹H NMR (CDCl₃, δ, ppm) 8.12 (d, 4Ar-H, *o* to COOH, *J* = 7.8 Hz), 7.63 (m, 4Ar-H, *m* to COOH, *J* = 7.8 Hz), 7.54 (d, 4Ar-H, *m* to CH(CH₃)O, *J* = 8.4 Hz), 7.02 (d, 4Ar-H, *o* to CH(CH₃)O, *J* = 7.2 Hz), 4.56 (m, 3H, phenylOCH₂CH(CH₃) and CH₂CH(CH₃)Ophenyl), 3.14-3.92 (m, 60H, OCH₂CH(CH₃)), 0.84-1.42 (m, 63H, CH(CH₃)O).



Scheme 1; Synthesis of dimer-n

Synthesis of 4-[poly(propyleneoxy)propyloxy]-4'-bis[4-decyloxyphenylbiphenyl]-4'-biphenylcarboxylate] (**dimer-n**)

dimer-7: yield 70.4 %. ¹H NMR (CDCl₃, δ, ppm) 8.25 (d, 4Ar-H, *o* to COOphenyl, *J* = 7.6 Hz), 8.12 (d, 4Ar-H, *o* to COOCH₂, *J* = 7.8 Hz), 7.56-7.67 (m, 16Ar-H, *m* to COOphenyl, *m* to biphenylcarboxylate, *m* to COOCH₂ and *m* to CH(CH₃)O), 7.33 (d, 4Ar-H, *o* to biphenylcarboxylate, *J* = 7.6 Hz), 7.03 (d, 4Ar-H, *o* to CH(CH₃)O, *J* = 8.1 Hz), 4.57 (m, 3H, phenylOCH₂CH(CH₃) and CH₂CH(CH₃)Ophenyl), 4.34 (t, 4H, CH₃(CH₂)₈CH₂, *J* = 6.7 Hz), 3.30-3.90 (m, 18H, OCH₂CH(CH₃)), 1.78 (m, 4H, CH₃(CH₂)₇CH₂), 1.13-1.56 (m, 49H, CH₃(CH₂)₇ and CH(CH₃)O), 0.88 (t, 6H, CH₃(CH₂)₉, *J* = 6.8 Hz). Anal. Calcd for C₉₅H₁₁₆O₁₆: C, 74.97; H, 7.85. Found C, 74.95; H, 7.82. M_w/M_n = 1.07 (GPC).

dimer-12: yield 78.1 %. ¹H NMR (CDCl₃, δ, ppm) 8.26 (d, 4Ar-H, *o* to COOphenyl, *J* = 8.1 Hz), 8.12 (d, 4Ar-H, *o* to COOCH₂, *J* = 8.2 Hz), 7.57-7.70 (m, 16Ar-H, *m* to COOphenyl, *m* to biphenylcarboxylate, *m* to COOCH₂ and *m* to CH(CH₃)O), 7.34 (d, 4Ar-H, *o* to biphenylcarboxylate, *J* = 8.4 Hz), 7.04 (d, 4Ar-H, *o* to CH(CH₃)O, *J* = 8.3 Hz), 4.58 (m, 3H, phenylOCH₂CH(CH₃) and CH₂CH(CH₃)Ophenyl), 4.34 (t, 4H, CH₃(CH₂)₈CH₂, *J* = 6.3 Hz), 3.25-3.90 (m, 33H, OCH₂CH(CH₃)), 1.77 (m, 4H, CH₃(CH₂)₇CH₂), 1.12-1.60 (m, 64H, CH₃(CH₂)₇ and CH(CH₃)O), 0.88 (t, 6H, CH₃(CH₂)₉, *J* = 6.8 Hz). Anal. Calcd for C₁₀₈H₁₄₆O₂₁: C, 72.86; H, 8.26. Found C, 72.78; H, 8.29. M_w/M_n = 1.10 (GPC).

dimer-17: yield 68.5 %. ¹H NMR (CDCl₃, δ, ppm) 8.25 (d, 4Ar-H, *o* to COOphenyl, *J* =

8.2 Hz), 8.12 (d, 4Ar-H, *o* to COOCH₂, *J* = 8.1 Hz), 7.57-7.71 (m, 16Ar-H, *m* to COOphenyl, *m* to biphenylcarboxylate, *m* to COOCH₂ and *m* to CH(CH₃)O), 7.34 (d, 4Ar-H, *o* to biphenylcarboxylate, *J* = 8.4 Hz), 7.04 (d, 4Ar-H, *o* to CH(CH₃)O, *J* = 8.2 Hz), 4.58 (m, 3H, phenylOCH₂CH(CH₃) and CH₂CH(CH₃)Ophenyl), 4.33 (t, 4H, CH₃(CH₂)₈CH₂, *J* = 6.4 Hz), 3.25-4.05 (m, 48H, OCH₂CH(CH₃)), 1.77 (m, 4H, CH₃(CH₂)₇CH₂), 1.12-1.65 (m, 79H, CH₃(CH₂)₇ and CH(CH₃)O), 0.88 (t, 6H, CH₃(CH₂)₉, *J* = 6.8 Hz). Anal. Calcd for C₁₂₃H₁₇₆O₂₆: C, 71.34; H, 8.57. Found C, 71.31; H, 8.61. M_w/M_n = 1.10 (GPC).

dimer-21: yield 55.4 %. ¹H NMR (CDCl₃, δ, ppm) 8.25 (d, 4Ar-H, *o* to COOphenyl, *J* = 8.2 Hz), 8.12 (d, 4Ar-H, *o* to COOCH₂, *J* = 8.1 Hz), 7.57-7.71 (m, 16Ar-H, *m* to COOphenyl, *m* to biphenylcarboxylate, *m* to COOCH₂ and *m* to CH(CH₃)O), 7.34 (d, 4Ar-H, *o* to biphenylcarboxylate, *J* = 8.4 Hz), 7.04 (d, 4Ar-H, *o* to CH(CH₃)O, *J* = 8.2 Hz), 4.58 (m, 3H, phenylOCH₂CH(CH₃) and CH₂CH(CH₃)Ophenyl), 4.33 (t, 4H, CH₃(CH₂)₈CH₂, *J* = 6.4 Hz), 3.25-4.05 (m, 60H, OCH₂CH(CH₃)), 1.77 (m, 4H, CH₃(CH₂)₇CH₂), 1.12-1.65 (m, 91H, CH₃(CH₂)₇ and CH(CH₃)O), 0.88 (t, 6H, CH₃(CH₂)₉, *J* = 6.8 Hz). M_w/M_n = 1.05 (GPC).

Results and discussion

The synthesis of rod-coil **dimer-n** molecules is outlined in Scheme 1. The liquid crystalline rod-coil dimers were obtained by treating (25 °C, 12 h) decyl-4-hydroxy-4'-biphenylcarboxylate with 4'-[poly(propyleneoxy)propyloxy]-4-bis(biphenylcarboxylic acid) (**1-4**) in the presence of diisopropylcarbodiimide (DIPC) and 4-dimethylaminopyridine-*p*-toluene sulfonate (DPTS). The waxy solids were purified by column chromatography (silica gel) using methylene chloride and ethyl acetate as eluents, respectively. All of the rod-coil dimers showed a monomodal molecular weight distribution less than polydispersity values of 1.11 determined from GPC, indicative of high purity.

Figure 1 presents the DSC second heating and first cooling traces of rod-coil dimers. The DSC traces obtained during the first and second heating scans are almost identical. The transition temperatures and the corresponding enthalpy changes derived from DSC heating and cooling scans are summarized in Table 1. As can be seen from Figure 1, **dimer-7** exhibits a crystalline phase which melts into a smectic C phase followed by a smectic A phase which, in turn, undergoes transformation into a nematic phase. Optical microscopic observations of this compound are identical to this behavior. Transition from isotropic liquid can be seen by the formation of a schlierene texture at 155 °C, indicating a nematic mesophase.⁷ On further cooling, schlieren texture begins to be transformed into batonnets at 153 °C which merge into a focal conic fanlike texture consistent with a smectic A mesophase.⁷ On successive cooling, focal conic fanlike texture changes to be broken-fanlike texture, which is the characteristic of the transition of smectic A phase into smectic C phase.⁷ To investigate the detailed microstructures, small angle X-ray scattering (SAXS) experiments were performed with this compound at elevated temperatures. In the crystalline phase, sharp reflection is exhibited corresponding to lamellar periodicity of 37 Å which is smaller than a half of fully-stretched molecular length (47 Å)⁸ in Table 2, indicating the fully interdigitated monolayer lamellar structure in which rods are tilted to be 37°. In the smectic C phase, d-spacing appears to be 35 Å, while in smectic A phase, d-spacing is 41 Å. This behavior agrees well with optical polarized microscopic results. According to these lengths, the rod tilt angle in smectic C phase can be estimated to be 31°.

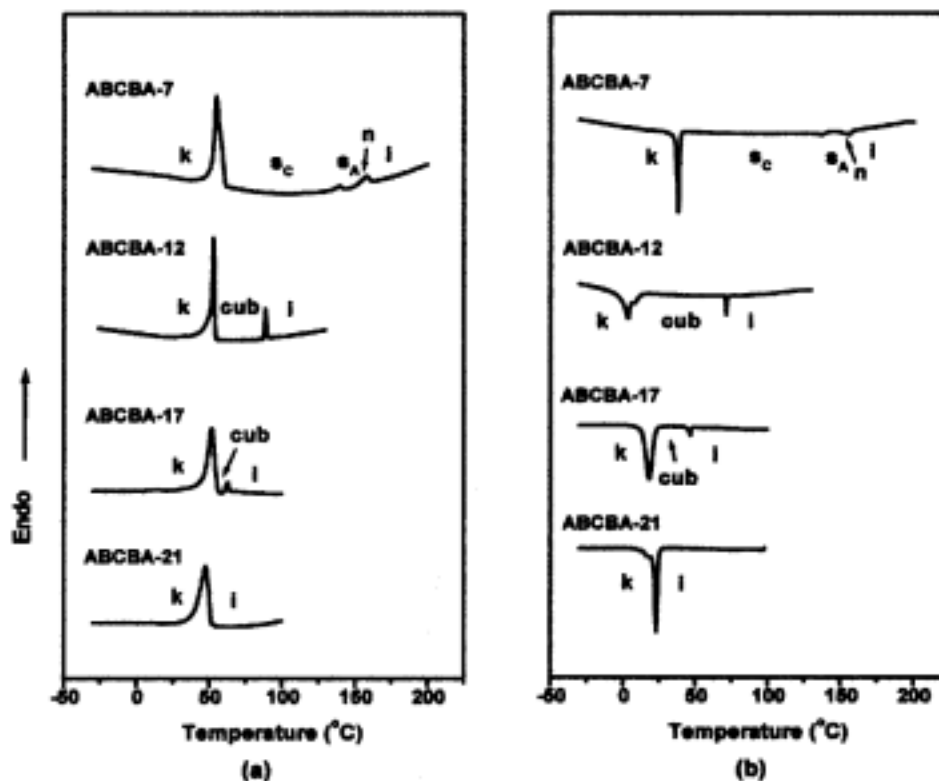


Figure 1: DSC traces exhibited during (a) the second heating scan and (b) the first scan by **dimer-n** with different numbers of repeating units (n) of poly(propylene oxide) coil.

Table 1. Thermal transitions of **dimer-n**.

molecule (dimer-n)	phase transitions ($^{\circ}\text{C}$) and corresponding enthalpy changes (kJ/mol)	
	heating	cooling
dimer-7	k 55 (23.9) s_C 139 (0.8) s_A 154 (a) n 158 (2.2) i	i 155 (2.4) n 153 (a) s_A 137 (1.1) s_C 38 (20.1) k
dimer-12	k 53 (18.1) cub 89 (3.6) i	i 71 (1.8) cub 4 (19.4) k
dimer-17	k 52 (29.2) cub 63 (2.2) i	i 47 (1.4) cub 18 (29.7) k
dimer-21	k 48 (29.2) i	i 23 (26.7) k

k, crystalline; s_C , smectic C; s_A , smectic A; n, nematic; cub, cubic; i, isotropic. ^aOverlap peak.

As can be seen from figure 1, **dimer-12** exhibits a crystalline melting at 53 $^{\circ}\text{C}$, followed by a liquid crystalline phase which turns into liquid phase at 88 $^{\circ}\text{C}$ on heating scan. **Dimer-17** shows a phase behavior similar to that of **dimer-12**, which exhibits crystal melting followed by a mesophase. On the optical microscopy, no birefringence between crossed polarizers after melting could be observed for **dimer-12** and **dimer-17**, strongly suggesting the existence of a cubic mesophase.⁹ In order to investigate the microstructure in the crystalline and liquid crystalline phases, X-ray scattering experiments have been performed. In crystalline phase, diffraction pattern of **dimer-12** exhibits q -spacing ratio of 1:2:3 corresponding to lamellar periodicity of 43.6 \AA .

Table 2. Characterization of dimer-*n* by small angle X-ray scattering

molecule (dimer- <i>n</i>)	Crystalline phase			Smectic phase		Cubic phase	
	Calc. length ^a	d_{001}	Rod tilt angle	d_{001} (s_C)	d_{001} (s_A)	d_{211}	Lattice constant (<i>a</i>)
	(Å)	(Å)	(°)	(Å)	(Å)	(Å)	(Å)
dimer-7	47	37	37	35	41		
dimer-12	58	44	41			40	99
dimer-17	68	50	43			43	105

^aCalculated length is a half of fully-stretched molecular length based on density measurements.

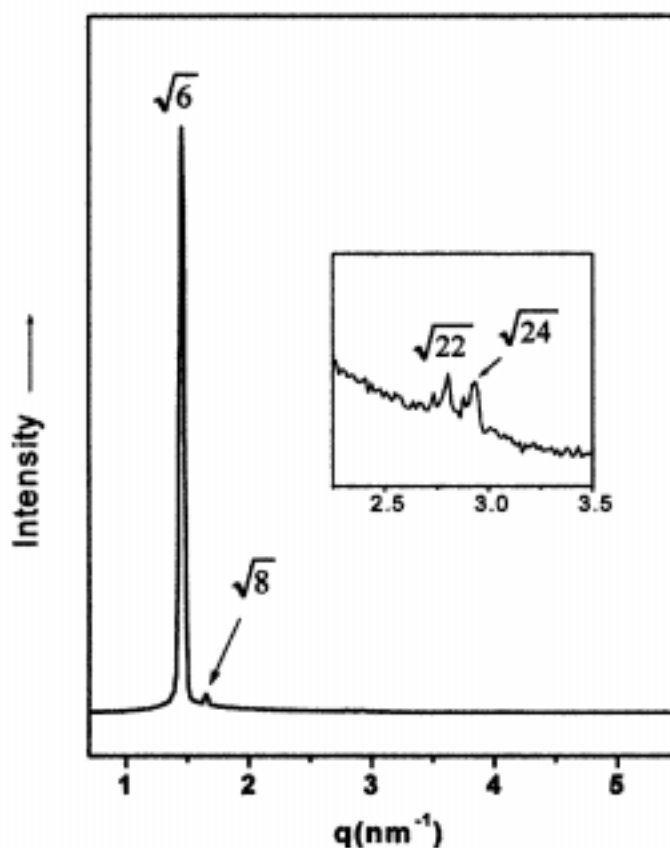


Figure 2: SAX spectrum obtained in the bicontinuous cubic mesophase at 54 °C for **dimer-17** plotted against q ($= 4\pi\sin\theta/\lambda$).

Dimer-17 shows similar diffraction pattern with lamellar periodicity of 50 Å. Considering the half of fully-stretched molecular length⁸ in table 2, rod tilt angle of **dimer-12** and **dimer-17** in crystalline phase are 41 and 43 °, respectively. In liquid crystalline phase, a representative SAX diffraction pattern of **dimer-17** is shown in Figure 2. Two strong and two weak peaks are observed at relative positions $\sqrt{6}$, $\sqrt{8}$, $\sqrt{22}$ and $\sqrt{24}$. The positions of these peaks can be indexed as the (221), (220), (332) and (422) reflections of $Ia\bar{3}d$ symmetry.¹⁰ From the observed *d* spacings of (221)

reflections, the best fit values for the lattice parameters for the cubic phase of **dimer-12** and **dimer-17** could be estimated as 99 and 105 Å, respectively.

Further increasing the length of poly(propylene oxide) coil as in the case of **dimer-21** with the longest poly(propylene oxide) coil suppresses the formation of liquid crystallinity (Figure 1). This is most probably due to higher conformational freedom of long poly(propylene oxide).

As can be observed in table 2, rod tilt angle in crystalline phase increases depending on the length of poly(propylene oxide) coil. This increment of rod tilt angle is most probably due to the energetic penalties associated with chain stretching, illustrated by theories to cause the rod-coil junctions to spread apart, the area per coil increases, and thus, coil stretching penalties are reduced.^{11,12}

On the basis of SAXS data described above and the similar molecular structure with related rod-coil molecule,^{3,5} the cubic phase can be explained as a bicontinuous cubic phase with *Ia3d* symmetry which consists of interwoven networks of branched cylinders occurring frequently in lyotropic¹³ and conventional block copolymer system¹⁴. Considering the bulkiness of coil segment and the stiffness of rod segment, coils are located in the larger outer space of aromatic core domains in which rods are aligned axially with their preferred direction. Such a molecular packing structure which has extensive rod/coil interfacial area is more thermodynamically stable than the layered smectic structure in the point of the entropic reason. Since highly flexible coils could gain more space relative to layered structure, this entropic advantage sufficiently compensate for the enthalpic disadvantage arising from the increase of rod/coil interface area.

Consequently, the main driving forces for organization of bicontinuous cubic network in the molecular rod are believed to be anisotropic arrangement of rods and resulting entropic penalties associated with coil stretching.

Conclusion

Dimer-n series with different lengths of poly(propylene oxide) as coils were synthesized. **Dimer-7** with short length of coil exhibits smectic mesophases in addition to nematic mesophase, while **dimer-12** and **dimer-17** with long lengths of coil exhibit a bicontinuous cubic mesophase. **Dimer-21** with the longest length of coil exhibits only a crystalline phase with a lack of mesophase. The results described in this study suggest that the control of self-assembled liquid crystalline structures is possible in molecular rod system containing poly(propylene oxide) coil depending on the coil length.

Acknowledgment

Financial support of this work by CRM-KOSEF (2000), the Brain Korea 21 Project and the Synchrotron Source Radiation at Pohang, Korea (for the beam time and technical assistance) is gratefully acknowledged.

Reference

1. Tew GN, Li L, Stupp SI (1998) *J. Am. Chem. Soc.* 120: 5601
2. Jenekhe SA, Chen XL (1998) *Science* 279: 1903
3. Lee M, Cho B.-K, Kim H, Zin W.-C (1998) *Angew. Chem. Int. Ed. Engl.* 37: 638
4. Lee M, Cho B.-K, Kim H, Yoon J.-Y, Zin W.-C (1998) *J. Am. Chem. Soc.* 120: 9168
5. Lee M, Lee D.-W, Cho B.-K, Yoon J.-Y, Zin W.-C (1998) *J. Am. Chem. Soc.* 120: 13258
6. Lee M, Cho B.-K (1998) *Chem. Mater.* 10: 1894.
7. Demus D, Richter L (1978) "Texture of Liquid Crystals", Verlag Chemie, Weinheim
8. Molecular length was estimated by calculation based on density measurements. The

densities of each segment were used as ρ (PPO), ρ (decyl) = 1.0 and ρ (rod in crystalline phase) = 1.4 g/cm³.

9. Stauffer G, Schellhorn M, Lattermann G (1995) *Liq. Cryst.* 18: 519
10. Luzzati V, Spegg PA (1967) *Nature* 215: 701
11. Semenov AN (1991) *Mol. Cryst. Liq. Cryst.* 209: 191
12. Halperin A (1991) *Macromolecules* 23: 2724
13. Charvolin J (1991) *Mol. Cryst. Liq. Cryst.* 198: 145
14. Forster S, Khandpur AK, Zhao J, Bates FS, Hamley IW, Ryan AJ, Bras W (1994) *Macromolecules* 27: 6922