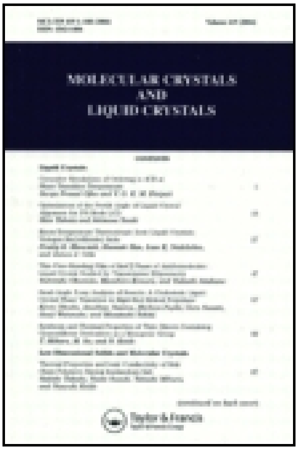

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Self-Organization of Rod-Coil Molecules into a Bicontinuous Cubic Liquid Crystalline Phase

Myongsoo Lee [a], Byoung-Ki Cho [a], Ju-Young Yoon [b] & Wang-Cheol Zin [b]

[a] Department of Chemistry, Yonsei University, Seoul, 120-749, Korea

[b] Department of Materials Science, Pohang University of Science and Technology, Pohang, 790-784, Korea

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Self-Organization of Rod-Coil Molecules into a Bicontinuous Cubic Liquid Crystalline Phase

MYONGSOO LEE[a], BYOUNG-KI CHO[a], JU-YOUNG YOON[b] and WANG-CHEOL ZIN[b]

[a]*Department of Chemistry, Yonsei University, Seoul 120–749, Korea and* [b]*Department of Materials Science, Pohang University of Science and Technology, Pohang 790–784, Korea*

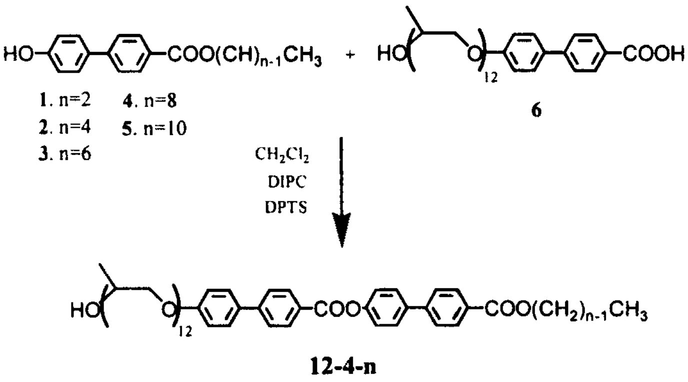
The synthesis and characterization of the rod-coil molecules of alkyl 4-[4-[oxypoly(propyleneoxy)propyloxy]-4'-biphenylcarboxyloxy]-4'-biphenyl carboxylate with alkyl group of ethyl (**12–4–2**), butyl (**12–4–4**), hexyl (**12–4–6**), octyl (**12–4–8**) and decyl (**12–4–10**) are described. The rod-coil molecules **12–4–2, 12–4–4** and **12–4–6** display an enantiotropic bicontinuous cubic mesophase, while **12–4–8** and **12–4–10** show only crystalline phase.

Keywords: rod-coil molecule; bicontinuous cubic mesophase

INTRODUCTION

Manipulation of the order of supramolecular molecular materials is an important goal in chemistry, that can be used to control the physical properties. Building blocks based on calamitic (rod-like) molecular architectures can generate a variety of supramolecular structures in melt state as well as solid state by introduction of long flexible chains.[1] This unique aggregation behavior of rod-coil systems arises from the competition between microphase separation of the coil and rod blocks into ordered periodic structures and the tendency of the rod block to form anisotropic, orientationally ordered structures.[2,3] Recently, we have demonstrated that rod-coil molecules based on poly(alkylene oxide) coil display a remarkable mesomorphism depending on the coil length.[4-6] As an extension of the work with rod-coil system, we have synthesized a series of rod-coil molecules containing poly(propylene oxide) with a degree of polymerization (DP) of 12.

The goal of this paper is to describe the synthesis of a series of rod-coil molecules with different alkyl chains in hydrophobic rod segments and their thermotropic phase behavior characterized by differential scanning calorimetry (DSC) and X-ray scattering experiments.



Scheme 1; The synthesis of rod-coil molecules **12-4-n**.

EXPERIMENTAL

Synthesis

Synthesis of compounds 1-5. Alkyl 4'-hydroxy-4-biphenyl carboxylate **1-5** were all synthesized using the reported procedure.[4]

Synthesis of compound 6. 6 was synthesized as described previously.[6]

Synthesis of compounds 12-4-2, 12-4-4, 12-4-6, 12-4-8, 12-4-10 (12-4-n). The rod-coil molecules were all synthesized using the same procedure. A representative example is described for **12-4-4**. Compound **2** (0.5 g, 1.7 mmol), compound **6** (0.8 g, 0.9 mmol) and, 4-dimethylamino pyridine (0.1 g, 0.8 mmol) were dissolved in dry dichloromethane (20 cm^3) under nitrogen. And then 1,3-diisopropylcarbodiimide (1.7 mmol, 0.27 cm^3) was added dropwise to the mixture. The reaction mixture was stirred at room temperature under nitrogen overnight. The resulting solution was poured into water and extracted with methylene chloride. The methylene chloride solution was washed with water, dried over anhydrous magnesium sulfate, and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel, ethyl acetate) to yield 0.44 g (42 %) of a white solid.

Compound **12-4-2.** Yield 50 %. ^{1}H NMR (CDCl$_3$, δ, ppm) 8.24 (d, 2Ar-$\underline{H}$, *o* to COOphenyl, *J* = 7.8 Hz), 8.12 (d, 2Ar-$\underline{H}$, *o* to COOCH$_2$, *J* = 7.7 Hz), 7.65-7.71 (m, 6Ar-$\underline{H}$, *m* to COOphenyl, *m* to biphenyl carboxylate and *m* to COOCH$_2$), 7.59 (d, 2Ar-$\underline{H}$, *m* to CH(CH$_3$)O, *J* = 8.5 Hz), 7.35 (d, 2Ar-$\underline{H}$, *o* to biphenylcarboxylate, *J* = 8.5 Hz), 7.04 (d, 2Ar-$\underline{H}$, *o* to CH(CH$_3$)O, *J* = 8.6 Hz), 4.58 (m, 1H, OCH$_2$C$\underline{H}$(CH$_3$)), 4.41 (q, 2H, C$\underline{H}_2$CH$_3$, *J* = 7.1 Hz), 3.15-3.91 (m, 35H, OC$\underline{H}_2$C$\underline{H}$(CH$_3$)), 1.34-1.45 (m, 6H, CH$_2$C$\underline{H}_3$ and CH(C$\underline{H}_3$)Ophenyl), 0.90-1.30 (m, 33H, OCH$_2$CH(C$\underline{H}_3$)). Anal. Calcd for C$_{64}$H$_{94}$O$_{17}$: C, 67.70; H, 8.34. Found C, 67.24; H, 8.71.

Compound **12-4-4.** Yield 42 %. ^{1}H NMR (CDCl$_3$, δ, ppm) 8.25 (d, 2Ar-$\underline{H}$, *o* to COOphenyl, *J* = 8.4 Hz), 8.12 (d, 2Ar-$\underline{H}$, *o* to COOCH$_2$, *J* = 8.4 Hz), 7.65-7.72 (m, 6Ar-$\underline{H}$, *m* to COOphenyl, *m* to biphenylcarboxylate and *m* to COOCH$_2$), 7.59 (d, 2Ar-$\underline{H}$, *m* to CH(CH$_3$)O, *J* = 8.4 Hz), 7.34 (d, 2Ar-$\underline{H}$, *o* to biphenylcarboxylate, *J* = 8.4 Hz), 7.04 (d, 2Ar-$\underline{H}$, *o* to CH(CH$_3$)O, *J* = 8.4 Hz), 4.58 (m, 1H, OCH$_2$C$\underline{H}$(CH$_3$)), 4.35 (t, 2H, CH$_3$(CH$_2$)$_2$C$\underline{H}_2$, *J* = 6.6 Hz), 3.35-3.92 (m, 35H, OCH$_2$CH(CH$_3$)), 1.77 (m, 2H, CH$_3$CH$_2$CH$_2$), 1.52 (m, 2H, $CH_3C\underline{H}_2$), 1.05-1.37 (m, 36H, OCH_2CH ($C\underline{H}_3$)), 0.99 (t, 3H, $C\underline{H}_3(CH_2)_3$, *J* = 6.7 Hz). Anal. Calcd for $C_{66}H_{98}O_{17}$: C, 68.13; H, 8.49. Found C, 68.27 ; H, 8.50.

Compound **12-4-6.** Yield 42 %. ^{1}H NMR ($CDCl_3$, δ, ppm) 8.25 (d, 2Ar-$\underline{H}$, *o* to COOphenyl, *J* = 8.4 Hz), 8.12 (d, 2Ar-$\underline{H}$, *o* to $COOCH_2$, *J* = 8.4 Hz), 7.65-7.72 (m, 6Ar-$\underline{H}$, *m* to COOphenyl, *m* to biphenyl carboxylate and *m* to $COOCH_2$), 7.59 (d, 2Ar-$\underline{H}$, *m* to $CH(CH_3)O$, *J* = 8.4 Hz), 7.34 (d, 2Ar-$\underline{H}$, *o* to biphenylcarboxylate, *J* = 8.4 Hz), 7.04 (d, 2Ar-$\underline{H}$, *o* to $CH(CH_3)O$, *J* = 8.4 Hz), 4.58 (m, 1H, $OCH_2C\underline{H}(CH_3)$), 4.34 (t, 2H, $CH_3(CH_2)_4C\underline{H}_2$, *J* = 6.6 Hz), 3.34-3.82 (m, 35H, $OC\underline{H}_2C\underline{H}(CH_3)$), 1.77 (m, 2H, $CH_3(CH_2)_3C\underline{H}_2$), 1.34-1.50 (m, 9H, $CH_3(C\underline{H}_2)_3$ and $CH(C\underline{H}_3)$Ophenyl), 1.08-1.18 (m, 33H, $OCH_2CH(C\underline{H}_3)$), 0.91 (t, 3H, $C\underline{H}_3(CH_2)_5$, *J* = 6.7 Hz). Anal. Calcd for $C_{68}H_{102}O_{17}$: C, 68.55; H, 8.63. Found C, 68.57 ; H, 8.85.

Compound **12-4-8.** Yield 48 %. ^{1}H NMR ($CDCl_3$, δ, ppm) 8.25 (d, 2Ar-$\underline{H}$, *o* to COOphenyl, *J* = 8.4 Hz), 8.12 (d, 2Ar-$\underline{H}$, *o* to $COOCH_2$, *J* = 8.4 Hz), 7.65-7.72 (m, 6Ar-$\underline{H}$, *m* to COOphenyl, *m* to biphenyl carboxylate and *m* to $COOCH_2$), 7.59 (d, 2Ar-$\underline{H}$, *m* to $CH(CH_3)O$, *J* = 8.4 Hz), 7.34 (d, 2Ar-$\underline{H}$, *o* to biphenylcarboxylate, *J* = 8.4 Hz), 7.03 (d, 2Ar-$\underline{H}$, *o* to $CH(CH_3)O$, *J* = 8.4 Hz), 4.58 (m, 1H, $OCH_2C\underline{H}(CH_3)$), 4.34 (t, 2H, $CH_3(CH_2)_6C\underline{H}_2$, *J* = 6.6 Hz), 3.34-3.82 (m, 35H, $OC\underline{H}_2C\underline{H}(CH_3)$), 1.77 (m, 2H, $CH_3(CH_2)_5C\underline{H}_2$), 1.29-1.55 (m, 13H, $CH_3(C\underline{H}_2)_5$ and $CH(C\underline{H}_3)$Ophenyl), 1.07-1.18 (m, 33H, $OCH_2CH(C\underline{H}_3)$), 0.89 (t, 3H, $C\underline{H}_3(CH_2)7$, *J* = 6.7 Hz). Anal. Calcd for $C_{70}H_{106}O_{17}$: C, 68.94; H, 8.76. Found C, 69.24; H, 8.78.

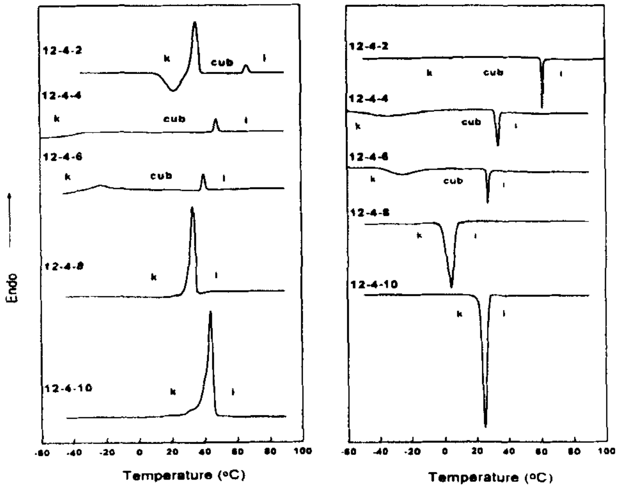
Compound **12-4-10.** Yield 45 %. ^{1}H NMR ($CDCl_3$, δ, ppm) 8.25 (d, 2Ar-$\underline{H}$, *o* to COOphenyl, *J* = 8.5 Hz), 8.12 (d, 2Ar-$\underline{H}$, *o* to $COOCH_2$, *J* = 8.5 Hz), 7.65-7.72 (m, 6Ar-$\underline{H}$, *m* to COOphenyl, *m* to biphenylcarboxylate and *m* to $COOCH_2$), 7.59 (d, 2Ar-$\underline{H}$, *m* to $CH(CH_3)O$, *J* = 8.5 Hz), 7.34 (d, 2Ar-$\underline{H}$, *o* to biphenylcarboxylate, *J* = 8.5 Hz), 7.04 (d, 2Ar-$\underline{H}$, *o* to $CH(CH_3)O$, *J* = 8.5 Hz), 4.58 (m, 1H, $OCH_2C\underline{H}(CH_3)$), 4.34 (t, 2H, $CH_3(CH_2)_8C\underline{H}_2$, *J* = 6.6

Hz), 3.34-3.82 (m, 35H, $OC\underline{H}_2C\underline{H}(CH_3)$), 1.77 (m, 2H, $CH_3(CH_2)_7C\underline{H}_2$), 1.27-1.40 (m, 17H, $CH_3(C\underline{H}_2)_7$ and $CH(C\underline{H}_3)$Ophenyl), 1.07-1.18 (m, 33H, $OCH_2CH(C\underline{H}_3)$), 0.87 (t, 3H, $C\underline{H}_3(CH_2)_9$, J = 6.8 Hz). Anal. Calcd for $C_{72}H_{110}O_{17}$: C, 69.31; H, 8.89. Found C, 69.80; H, 9.07.

RESULTS AND DISCUSSION

The synthesis of rod-coil molecules containing poly(propylene oxide) with a DP of 12 was performed through the procedure outlined in Scheme 1. The rod-coil molecules (**12-4-n**) were obtained by treating (25 ℃, 12 h) **6** with alkyl-4-hydroxy-4'-biphenyl carboxylate (**1-5**) in CH_2Cl_2 in the presence of diisopropylcarbdiimide (DIPC) and 4-dimethylamino pyridinium-p-toluene sulfonate (DPTS). The resulting rod-coil molecules were purified by column chromatography (silica gel) using ethyl acetate as eluent until transition temperatures remain constant.

Figure 1 presents the DSC second heating and the first cooling traces of the rod-coil molecules. The DSC traces obtained during the first and subsequent heating scans are almost identical. The transition temperatures and the corresponding enthalpy changes of all rod-coil molecules obtained from DSC heating and cooling scans are summarized in Table 1. As can be observed from Figure 1, rod-coil molecules **12-4-n** with n = 2-6 exhibit an enantiotropic liquid crystalline phase. In particular, no birefringence between crossed polarizers after melting could be observed. In addition to a crystal melting transition, DSC results indicate an additional phase transition at higher temperature which is accompanied by a sudden significance decrease of viscosity, strongly suggesting the existence of a cubic mesophase.[7] In contrast to the rod-coil molecules with n = 2-6 which exhibit an optically isotropic mesophase, **12-4-8** and **12-4-10** do not display any liquid crystalline phases. This is most probably due to higher



(a) (b)

Figure 1; DSC traces (10 °Cmin^{-1}) recorded during the second heating scan (a) and the first cooling scan (b) of **12-4-n**.

Table 1; Thermal transitions of rod-coil molecules.

Rod-coil molecules	phase transitions (°C) and corresponding enthalpy changes (kJ/mol)	
	heating	cooling
12-4-2	k 38.7 (10.4) cub 69.6 (1.2) i	*i 61.6 (1.1) cub 4.9 (0.1) k*
12-4-4	k -31.2 (1.2) cub 48.2 (1.0) i	i 34.0 (0.9) cub -32.6 (1.5) k
12-4-6	k -23.2 (1.1) cub 39.9 (1.0) i	i 24.7 (0.8) cub -29.1 (1.3) k
12-4-8	k 32.8 (17.6) i	i 4.7 (12.9) k
12-4-10	k 43.9 (21.4) i	i 31.9 (16.9) k

k, crystalline; cub, cubic; i, isotropic.

conformational entropy of long octyl and decyl alkyl chains.

In order to investigate the microstructure of the optically isotropic phase, X-ray scattering experiments have been performed with the rod-coil

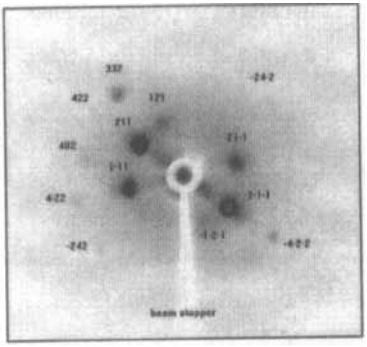


Figure 2; Single crystal diffraction pattern of the cubic mesophase of **12-4-4**.

molecule **12-4-4**. The X-ray diffraction pattern of **12-4-4** in the optically isotropic cubic mesophase, a considerable number of sharp reflection spots in the small angle region are observed as shown in Figure 2. Their relative positions are $\sqrt{6}$, $\sqrt{8}$, $\sqrt{22}$, $\sqrt{24}$. The positions of these reflections can be indexed as the 211, 220, 332 and 442 reflections of $Ia\bar{3}d$ symmetry.[8] From the observed d-spacing of 211 reflection, the best fit values for the cubic lattice parameter for the cubic phase of **12-4-4** is 114 Å. At a wide angle only a diffuse halo remains for all the rod-coil molecules as evidence of the lack of any positional long-range order other than the three dimensional cubic packing of micelles.

On the basis of the X-ray diffraction data described above and the structural similarity with the related rod-coil molecules,[6] the cubic phase can be best described as a bicontinuous cubic phase with $Ia\bar{3}d$ symmetry occurring frequently in lyotropic[9] and thermotropic[10] systems. Thus, a similar model proposed for the lyotropic bicontinuous cubic phase may be used for its description.[11] Assuming that a bicontinuous cubic unit cell with $Ia\bar{3}d$ symmetry consists of interwoven networks of branched cylinders, coils are in the outer part of the aromatic core in a cylinder in which the rods are aligned axially with their preferred direction.

Although a cubic phase is commonly observed in both lyotropic amphiphilic systems and conventional diblock copolymers, it is rare in thermotropic liquid crystalline system and has been observed only a few systems such as amphiphilic glucitol derivatives,[12] polycatenar silver complexes,[13] glycolipid derivatives[14] and calamitic mesogens exhibiting the formerly named "smectic D" phase[15].

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