

Observation of Unprecedented Body Centered Cubic Micellar Mesophase from Rod-Coil Molecules

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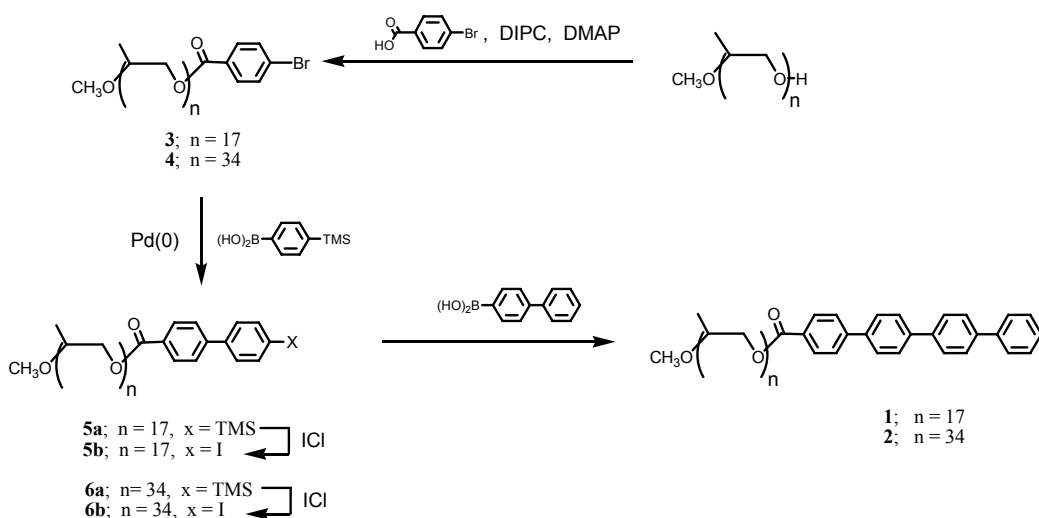
Experimental Section

Materials. 1,3-Diisopropylcarbodiimide (DIPC, 99%), 4-(dimethylamino)pyridine (DMAP, 99%), chlorotrimethylsilane (98%), *n*-butyllithium (1.6M solution in *n*-hexane), tetrakis(triphenylphosphine)palladium(0) (99%), 4,4'-dibromobenzene (98%), triisopropyl borate (98+%), iodomethane (99%), iodine monochloride (1.0M solution in dichloromethane), 4-bromobiphenyl (98%), (all from Aldrich) and the conventional reagents were used as received. 4-Trimethylsilyl phenylboronic acid, 4-diphenylboronic acid, and monomethylated poly(propylene oxide) were prepared according to the procedures described previously.^{1,2}

Technique. ¹H NMR spectrum was recorded from CDCl₃ solutions on 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 analyze the anisotropic texture. Molecular weight distributions were determined by gel permeation chromatography (GPC) with a Water

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, CHCl_3 as solvent (1.0 ml min^{-1}). X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 10C1 X-ray beam line with $\lambda = 0.154 \text{ nm}$ at Pohang Accelerator Laboratory, Korea. In order to investigate structural changes on heating, the samples were held in an aluminum sample holder which was sealed with the window of 8 mm thick Kapton films on both sides. The samples were heated with two cartridge heaters and the temperature of the samples was monitored by a thermocouple placed close to the sample. Background scattering correction was made by subtracting the scatterings from the Kapton. The transmission electron microscope (TEM) was performed at 120kV using JEOL 1020. After sample was annealing at demanded crystalline phase and quenched with liquid nitrogen, ultra-thin sectioning (ca. 50~70 nm thick) of specimens was performed by cryoultramicrotome at -70°C using a RMC PowerTome-XL. Thin sections of specimen were transferred on a carbon-coated copper grid and stained with RuO_4 vapor.

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



Scheme 1. Synthesis of rod-coil molecules.

Compound 3 and 4.

Compounds were synthesized using the same procedure. A representative example is

described for **4**. Poly(propylene oxide) monomethyl ether (5.0 g, 2.5 mmol), 4-bromobenzoic acid (0.75 g, 3.75 mmol) and 4-(dimethylamino)pyridine (DMAP, 0.31 g, 2.5 mmol) were dissolved in 250 ml of dry methylene chloride under nitrogen. And then 1,3-diisopropylcarbodiimide (DIPC, 0.98 ml, 6.25 mmol) was added dropwise to the mixture. The 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, dries 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 3.6 g (yield 66%) of a colorless liquid.

3: $^1\text{H-NMR}$ (250 MHz, CDCl_3 , δ , ppm) 7.84 (d, 2Ar-H, *o* to Br, $J = 8.5$ Hz), 7.54 (d, 2Ar-H, *m* to Br, $J = 8.5$ Hz), 5.26-5.31 (m, 1H, phenyl $\text{COOCH}_2\text{CH}(\text{CH}_3)$ or $\text{CH}_2\text{CH}(\text{CH}_3)\text{OOCphenyl}$), 3.31-3.62 (m, 53H, OCH_3 and $\text{OCH}_2\text{CH}(\text{CH}_3)$), 1.03-1.34 (m, 51H, $\text{CH}(\text{CH}_3)\text{O}$)

4: $^1\text{H-NMR}$ (250 MHz, CDCl_3 , δ , ppm) 7.84 (d, 2Ar-H, *o* to Br, $J = 8.5$ Hz), 7.54 (d, 2Ar-H, *m* to Br, $J = 8.5$ Hz), 5.27-5.31 (m, 1H, phenyl $\text{COOCH}_2\text{CH}(\text{CH}_3)$ or $\text{CH}_2\text{CH}(\text{CH}_3)\text{OOCphenyl}$), 3.32-3.62 (m, 104H, OCH_3 and $\text{OCH}_2\text{CH}(\text{CH}_3)$), 1.02-1.34 (m, 102H, $\text{CH}(\text{CH}_3)\text{O}$)

Compound 5a and 6a

Compounds were synthesized using the same procedure. A representative example is described for **6a**. **4** (3.0 g, 1.36 mmol) and 4-trimethylsilyl-phenyl boronic acid (0.32 g, 1.64 mmol) were dissolved in degassed THF (150 ml). Degassed 2M aqueous Na_2CO_3 (100 ml) was added to the solution and then tetrakis(triphenylphosphine)palladium(0) (17 mg, 13.6 μmol) was added. The mixture was refluxed for 48 hrs with vigorous stirring under nitrogen. Cooled to room temperature, the layers separated, the aqueous layer was washed twice with ethyl acetate. The combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was removed in a rotary evaporator, and the crude products were purified by column chromatography (silica gel, ethyl acetate) to yield 1.94 g (61%) of a colorless liquid.

5a: $^1\text{H-NMR}$ (250 MHz, CDCl_3 , δ , ppm) 8.12 (d, 2Ar-H, *o* to CH_2OOC , $J = 8.4$ Hz), 7.61-7.72 (m, 6Ar-H), 5.28-5.31 (m, 1H, phenyl $\text{COOCH}_2\text{CH}(\text{CH}_3)$ or $\text{CH}_2\text{CH}(\text{CH}_3)\text{OOCphenyl}$), 3.31-3.62 (m, 53H, OCH_3 and $\text{OCH}_2\text{CH}(\text{CH}_3)$), 1.01-1.34 (m, 51H, $\text{CH}(\text{CH}_3)\text{O}$), 0.31 (s, 9H, $(\text{CH}_3)_3\text{Si}$)

6a: $^1\text{H-NMR}$ (250 MHz, CDCl_3 , δ , ppm) 8.12 (d, 2Ar-H, *o* to CH_2OOC , $J = 8.4$ Hz), 7.62-7.72 (m, 6Ar-H), 5.27-5.31 (m, 1H, phenyl $\text{COOCH}_2\text{CH}(\text{CH}_3)$ or

CH₂CH(CH₃)OOCphenyl), 3.32-3.62 (m, 104H, OCH₃ and OCH₂CH(CH₃), 1.02-1.34 (m, 102H, CH(CH₃)O), 0.31 (s, 9H, (CH₃)₃Si)

Compound 5b and 6b.

Compounds were synthesized using the same procedure. A representative example is described for **6b**. To a solution of compound **6a** (1.5 g, 0.64 mmol) in CH₂Cl₂ at -78°C was dropped 1.0M solution of ICl in CH₂Cl₂ (10 ml). The reaction mixture was stirred over 3 hrs under nitrogen. 1M aqueous Na₂S₂O₅ (20 ml) solution was added and stirred over 2 hr. The layers separated, the aqueous layer was washed twice with CH₂Cl₂. The combined organic layer was 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 1.23 g (80%) of a colorless liquid.

5b: ¹H-NMR (250 MHz, CDCl₃, δ, ppm) 8.12 (d, 2Ar-H, *o* to CH₂OOC, *J* = 8.4 Hz), 7.65-7.80 (m, 4Ar-H), 7.37 (d, 2Ar-H, *o* to I, *J* = 8.4 Hz), 5.28-5.31 (m, 1H, phenylCOOCH₂CH(CH₃) or CH₂CH(CH₃)OOCphenyl), 3.31-3.62 (m, 53H, OCH₃ and OCH₂CH(CH₃), 1.01-1.34 (m, 51H, CH(CH₃)O)

6b: ¹H-NMR (250 MHz, CDCl₃, δ, ppm) 8.12 (d, 2Ar-H, *o* to CH₂OOC, *J* = 8.4 Hz), 7.66-7.80 (m, 4Ar-H), 7.37 (d, 2Ar-H, *o* to I, *J* = 8.4 Hz), 5.27-5.31 (m, 1H, phenylCOOCH₂CH(CH₃) or CH₂CH(CH₃)OOCphenyl), 3.32-3.62 (m, 104H, OCH₃ and OCH₂CH(CH₃), 1.02-1.34 (m, 102H, CH(CH₃)O)

Compound 1 and 2.

Compounds were synthesized using the same procedure. A representative example is described for **2**. Compound **6b** (1.0 g, 0.42 mmol) and phenyl boronic acid (0.10 g, 0.82 mmol) were dissolved in degassed THF (30 ml). Degassed 2M aqueous Na₂CO₃ (20 ml) was added to the solution and then tetrakis(triphenylphosphine)palladium(0) (5.2 mg, 4.18 μmol) was added. The mixture was refluxed for 48 hrs with vigorous stirring under nitrogen. Cooled to room temperature, the layers separated, the aqueous layer was washed twice with ethyl acetate. The combined organic layer was 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 0.66 g (64%) of a waxy solid.

1: $\overline{M}_w / \overline{M}_n = 1.03$ (GPC), ¹H-NMR (250 MHz, CDCl₃, δ, ppm) 8.12 (d, 2Ar-H, *o* to

CH_2OOC , $J = 8.3$ Hz), 7.84-7.56 (m, 12Ar-H), 7.24-7.47 (m, 3Ar-H), 5.26-5.31 (m, 1H, phenyl $\text{COOCH}_2\text{CH}(\text{CH}_3)$ or $\text{CH}_2\text{CH}(\text{CH}_3)\text{OOCphenyl}$), 3.31-3.71 (m, 53H, OCH_3 and $\text{OCH}_2\text{CH}(\text{CH}_3)$), 0.88-1.39 (m, 51H, $\text{CH}(\text{CH}_3)\text{O}$)

2: $\overline{M}_w / \overline{M}_n = 1.04$ (GPC), $^1\text{H-NMR}$ (250 MHz, CDCl_3 , δ , ppm) 8.12 (d, 2Ar-H, *o* to CH_2OOC , $J = 8.3$ Hz), 7.85-7.55 (m, 12Ar-H), 7.25-7.48 (m, 3Ar-H), 5.27-5.30 (m, 1H, phenyl $\text{COOCH}_2\text{CH}(\text{CH}_3)$ or $\text{CH}_2\text{CH}(\text{CH}_3)\text{OOCphenyl}$), 3.32-3.70 (m, 104H, OCH_3 and $\text{OCH}_2\text{CH}(\text{CH}_3)$), 0.85-1.38 (m, 102H, $\text{CH}(\text{CH}_3)\text{O}$)

Reference

1. T. Vahlenkamp and G. Wegner, *Macromol. Chem. Phys.*, 1994, **195**, 1933.
2. M. Lee, B.-K. Cho, Y.-G. Jang and W.-C. Zin, *J. Am. Chem. Soc.*, 2000, **122**, 7449.

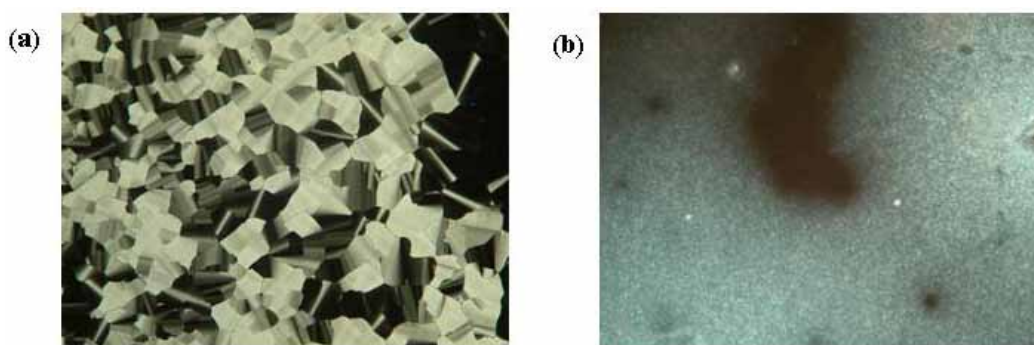


Fig 1. Textures of compound **1** in the col_h at 130 °C (a) and compound **2** at the transition from the body-centered cubic mesophase (dark area) to the crystalline phase (birefringent area).

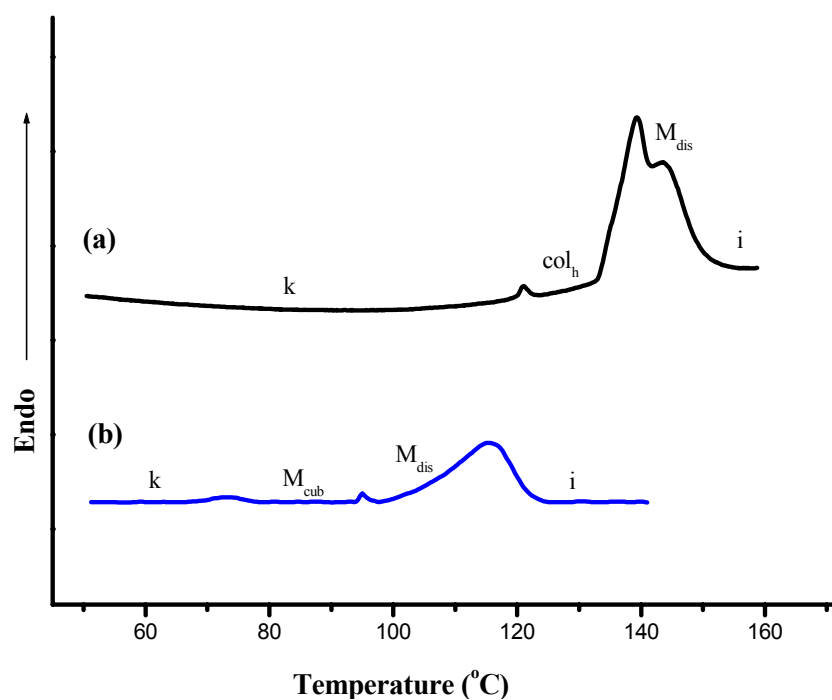


Fig 2. DSC traces ($10\text{ }^{\circ}\text{C min}^{-1}$) recorded during the first heating scan of (a) **1** and (b) **2**.

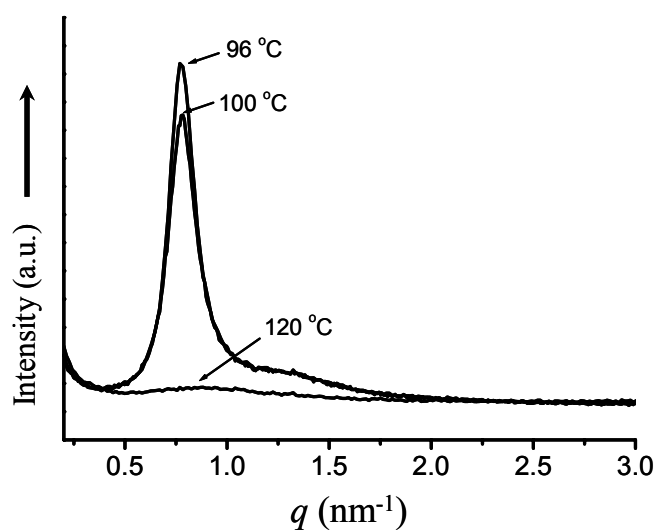


Fig 3. Small angle X-ray diffraction patterns of **2** at different temperatures in the disordered micellar structure.

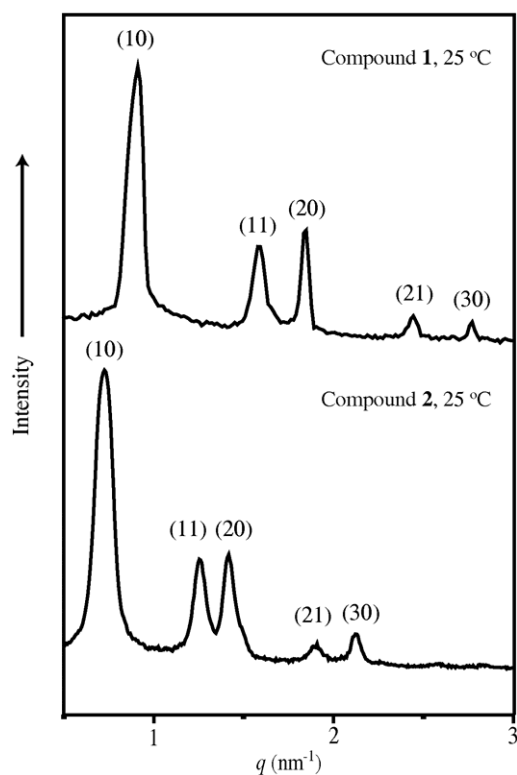


Fig. 4 Small angle X-ray diffraction patterns of **2** and **3** at 25 °C.

Table 1. Small angle X-ray diffraction data for the body-centered cubic mesophase of rod-coil molecule **2**.^a

<i>h</i>	<i>k</i>	<i>l</i>	$q_{\text{calcd}} \text{ nm}^{-1}$	$q_{\text{obsd}} \text{ nm}^{-1}$
1	1	0	0.76	0.76
2	0	0	1.07	1.10
2	1	1	1.31	1.33
2	2	0	1.52	1.54
3	1	0	1.70	
3	2	1	2.01	2.04
4	0	0	2.15	
4	1	1	2.28	

^a q_{calcd} and q_{obsd} are the scattering vectors of the observed reflections, and calculated for the body-centered cubic mesophase with lattice parameters $a = 11.7 \text{ nm}$.

Table 2. Characterization of rod-coil molecules by Small Angle X-ray Scattering.

molecule	liquid crystalline phase					
	hexagonal columnar		body-centered cubic		micellar phase	
	lattice constant		lattice constant		primary peak (nm)	diameter (d) (nm)
	d ₁₀₀ (nm)	a (nm)	d ₁₁₀ (nm)	a (nm)		
1	6.7	7.7			6.9	8.4
2			8.3	11.7	8.2	10.0