

An Ordered Network Polymer of Bicontinuous Cubic Structure Resulting from Photo-Polymerization of a Coil-Rod-Coil Molecule Self-Assembly

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Introduction

An important research subject in the fields of electronics, biomimetic chemistry, and materials science is the design and preparation of three dimensionally (3-D) ordered nanometer-scale polymers with well-defined shape and size. Specific properties of these polymers are dramatically improved by their self-organization.¹⁻⁵ Generally, 3-D ordered polymers were prepared using an intrinsically cross-linkable Lyotropic Liquid Crystal (LLC) system.⁶⁻⁹ However, this methodology cannot be extended to other systems, such as the ABA type rod-coil molecular liquid crystalline system containing the hydrophobic coil segment or the amphiphilic molecules which don't form LLC at ambient temperatures. A strategy to generate ordered polymers from rod-coil molecule self-assembly incorporating reactive groups at the coil or rod block in the liquid crystalline phase has been developed by Stupp and other laboratories.^{10,11} Lee and Jin have reported the preparation of well-defined 3-D ordered cross-linked bundles from a reactive hexagonal closed-packed coil-rod-coil molecule, whose structure is easily controlled to form lamellar, bicontinuous cubic, hexagonal columnar or other structures through the systematic variation of the volume fraction of the rod and coil part.¹²⁻¹⁵ Herein, we report the results of the synthesis and self-organization behavior of the reactive tri-block coil-rod-coil molecule **4** (Scheme I) and the formation of a 3-D network polymer.

Experimental

Techniques and Materials. X-ray scattering measurements were performed in transmission mode with synchrotron

radiation at the 3C2 X-ray beam line at Pohang Accelerator Laboratory, Korea. 2,2'-Dimethyl-4,4'-biphenol, compound **1**, **2** and **3** were prepared according to the similar procedures described elsewhere.^{12,14}

Compound **2** was obtained in 58% yield as a colorless liquid. ¹H NMR (250 MHz, CDCl₃, δ , ppm) 7.31-7.40 (m, 4Ar-H, m to OH-phenyl, m to CH₂O-phenyl), 6.83-6.94 (m, 4Ar-H, o to OH-phenyl, o to CH₂O-phenyl), 3.31-3.62 (m, 30H, -OCH₂CH₂-OCH₂CH, and CHCH₂O phenyl), 3.34 (s, 6H, OCH₃), 2.44 (m, 1H, phenyl -OCH₂CH (CH₂OCH₂)₂).

Compound **3** was obtained in 75% yield as a wax-like solid. m.p. 86 °C. ¹H NMR (250 MHz, CDCl₃, δ , ppm) 7.43-7.80 (m, 12Ar-H, m to OCH₂phenyl, o to OCH₂phenyl, o to CH₂Br and m to CH₂Br, m to CH₂Ophenyl and m to OCH₂CH) 6.93-7.06 (m, 4Ar-H, o to OCH₂CH, o to OCH₂CH), 5.14 (s, 2H, OCH₂phenyl), 4.55 (s, 2H, phenylCH₂Br), 3.55-4.03 (m, 30H, -OCH₂CH₂OCH₂CH, and -CHCH₂Ophenyl), 3.36 (s, 6H, OCH₃), 2.44 (m, 1H, phenyl OCH₂CH (CH₂OCH₂)₂).

Synthesis of 4. Compound **3** (0.5 g, 0.61 mmol), 2,2'-divinyl-4,4'-biphenol (73.8 mg, 0.31 mmol) and excess K₂CO₃ were dissolved in 30 mL of acetone. The mixture was refluxed for 4 h and then cooled to room temperature. After filtration, the solvent was removed and the crude product was purified by recycle gel permeation chromatography (JAI) to yield 0.32 g (60%) of a wax-like white solid. ¹H NMR (250 MHz, CDCl₃, δ , ppm) 7.28-7.66 (m, 26Ar-H, m to OCH₂phenyl, m to OCH₂CH, o to CH₂Ophenyl and m to CH₂Ophenyl), 6.96-7.10 (m, 12Ar-H, o to OCH₂phenyl, o to OCH₂CH), 6.42-6.44 (m, 2H, CH₂CHphenyl), 5.64-5.67 (d, 2H, cis -CH₂CHphenyl), 5.11-5.20 (m, 10H, trans -CH₂-CHphenyl and OCH₂phenyl), 3.55-3.96 (m, 60H, -OCH₂CH₂-OCH₂CH and CHCH₂Ophenyl), 3.36 (s, 12H, OCH₃), 2.44 (m, 2H, phenylOCH₂CH (CH₂OCH₂)₂). IR (cm⁻¹) 3037, 2870, 1640, 1609, 1567, 1521, 1481, 1380, 1243, 1175, 1110, 995, 918, 806. ¹³C NMR (62.5 MHz, CDCl₃, δ , ppm) 158.3, 157.8, 140.6, 137.7, 136.1, 135.2, 133.2, 128.2, 127.7, 116.5, 115.1, 114.0, 110.7, 71.96, 70.68, 69.4, 59.1, 39.9. Anal. Calcd for C₁₀₄H₁₂₆O₂₂: C, 72.28; H, 7.35. Found: C, 72.39; H, 7.26.

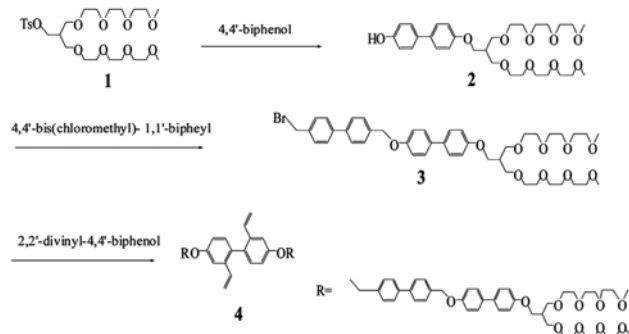
Polymerization of 4. In a nitrogen atmosphere, a thin film of **4** containing a trace of the photo-initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) (molar ratio monomer to DMPA: 200:1) was heated to 130 °C under UV irradiation. Four hours later, a transparent ordered network polymer was obtained. IR (cm⁻¹); 3034, 2922, 2870, 1606, 1567, 1380, 1241, 1175, 1110, 995, 806.

Results and Discussion

A white waxy solid precursor molecule, **3** (see Scheme I), containing bis(triethylene glycol) monomethyl ether and

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two biphenyl units was synthesized in two steps of etherifying reaction, using triethylene glycol monomethyl ether, toluene-*p*-sulfonyl chloride, and methallyl dichloride in the presence of potassium carbonate. In each of the etherifying reactions, an excess of 4,4'-dihydroxybiphenyl or 4,4'-bis(bromomethyl)-biphenyl was added to obtain the target molecules **2** or **3**. Finally, coil-rod-coil macromolecular monomer **4**, consisting of a coil segment of bis(triethylene glycol) monomethyl ether and a rod segment of five biphenyl units linked together by benzyl ether was successfully synthesized via etherification of molecule **3** and 2,2'-divinyl-4,4'-biphenol. The structure of **4** containing a reactive divinyl group as a side group in the center of the rod segment was characterized by ^1H NMR spectroscopy, the presence of vinyl proton signals at 5.11 (d, trans $\text{CH}_2\text{CHphenyl}$), 5.65 (d, cis $\text{CH}_2\text{CHphenyl}$) and 6.44 ppm (m, $\text{CH}_2\text{CHphenyl}$), of $-\text{OCH}_2\text{phenyl}$ protons at 5.20 ppm, of $-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$, and $\text{CHCH}_2\text{Ophenyl}$ protons at 3.5–3.7 ppm, of methine protons at 2.44 ppm and of aromatic protons at 7.28–7.66 and 6.96–7.10 ppm, respectively. This indicated that **4** was synthesized (see Figure 1). The monomer structure was also characterized by ^{13}C NMR, MS spectroscopy and elemental analysis and was shown to be in full agreement with the structure presented in Scheme I.



Scheme I. Synthetic route of monomer **4**.

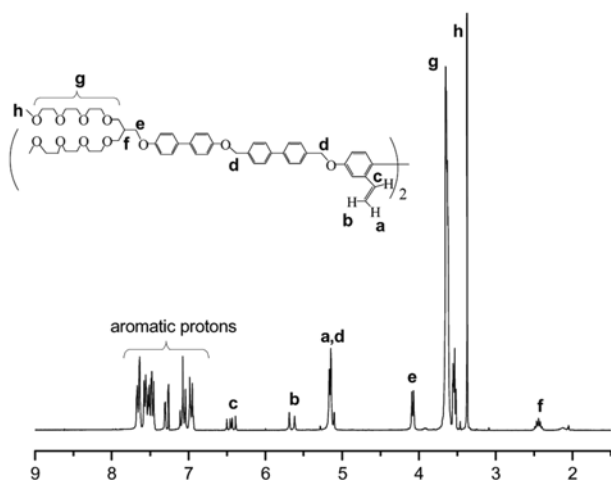


Figure 1. ^1H NMR spectrum of **4** (Solvent CDCl_3).

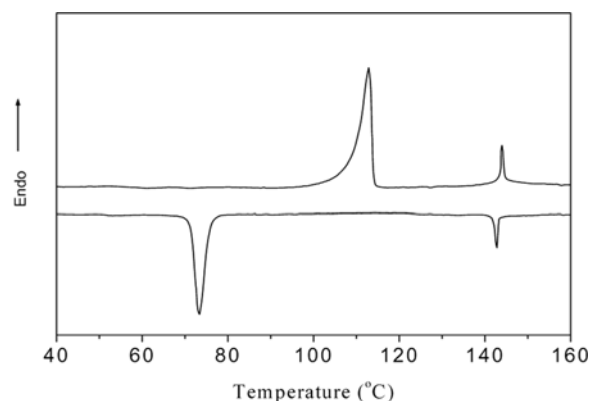


Figure 2. DSC traces ($10^\circ\text{C}/\text{min}$) of **4** recorded during the heating and cooling scans.

The thermal property and the mesophase structure of **4** were investigated by means of differential scanning calorimetry (DSC), thermal optical polarized microscopy and small angle X-ray diffraction scatterings (SAXS). In the DSC study (see Figure 2), **4** exhibited a thermotropic liquid crystalline phase at 112.8°C , and then changed to the isotropic liquid phase at 144°C . Optical polarized microscopy showed no birefringence between crossed polarizers upon slow cooling from the isotropic phase to the solid state phase. This probably suggests the presence of a cubic mesophase phase.^{16,17} To investigate the detailed supramolecular structure of the self-assembled coil-rod-coil molecules, X-ray scattering experiments were performed at various temperatures. Figure 3

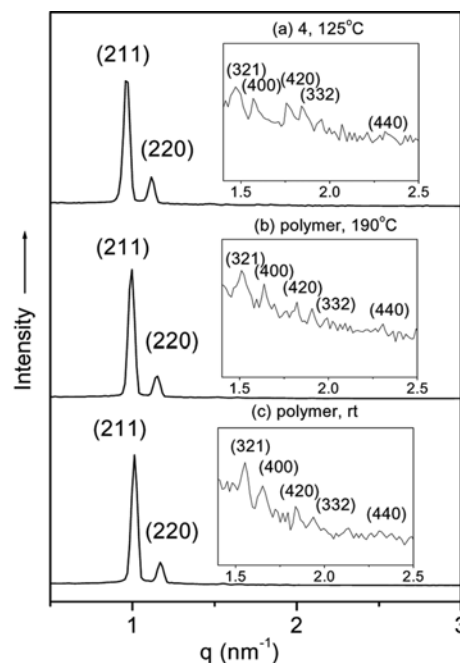


Figure 3. Small-angle X-ray diffraction patterns of (a) **4** at 125°C ; (b) network polymer at 190°C ; (c) network polymer at room temperature.

shows the SAXS pattern of **4**. A considerable number of sharp reflections in the small-angle X-ray diffraction patterns were observed at the liquid crystalline phase. The positions of these reflections at the relative positions of $6^{1/2}$, $8^{1/2}$, $14^{1/2}$, $16^{1/2}$, $20^{1/2}$, $22^{1/2}$, and $32^{1/2}$ can be indexed as the 211, 220, 321, 400, 420, 332, and 440 reflections of a bicontinuous cubic (bcc) phase with $Ia3d$ symmetry (see Table I).¹⁸⁻²⁰ From the observed d spacing of the 211 reflection, the lattice parameter of bcc crystalline phase of **4** is calculated to be 16.1 nm.

The cross-linked network polymer was synthesized by photo-polymerization of **4** using 2,2-dimethoxy-2-phenylacetophenone as the photo-initiator in the liquid crystalline phase to obtain the 3-D ordered polymer.²¹⁻²³ The network polymer exhibited nonsolubility and poor swellability in organic solvents. The FTIR experiment was performed to estimate the extent of the photo-polymerization of **4**. A comparison of the FTIR spectra of the polymer with that of reactive **4** (see Figure 4) clearly shows that the peak assigned to the out-of-plane bending band of C-H in the vinyl group at 918 cm^{-1} and C=C band at 1640 cm^{-1} nearly disappeared after the photo-polymerization procedure. This

Table I. Small-Angle X-Ray Diffraction Data for Bicontinuous Cubic Structure of **4 in the Liquid Crystalline (Measured at 125°C)**

h	k	l	$q_{\text{obsd}}(\text{nm}^{-1})$	$q_{\text{calcd}}(\text{nm}^{-1})$
2	1	1	0.967	0.967
2	2	0	1.113	1.110
3	2	1	1.470	1.466
4	0	0	1.571	1.566
4	2	0	1.755	1.751
3	3	2	1.839	1.836
4	4	0	2.211	2.220

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections for the bicontinuous cubic structure with lattice parameters $a=16.06\text{ nm}$.

Table II. Small-Angle X-Ray Diffraction Data for Bicontinuous Cubic Structure of the Network Polymer

Measured at 190°C					Measured at Room Temperature				
h	k	l	$q_{\text{obsd}}(\text{nm}^{-1})$	$q_{\text{calcd}}(\text{nm}^{-1})$	h	k	l	$q_{\text{obsd}}(\text{nm}^{-1})$	$q_{\text{calcd}}(\text{nm}^{-1})$
2	1	1	0.997	0.996	2	1	1	1.011	1.011
2	2	0	1.153	1.153	2	2	0	1.167	1.167
3	2	1	1.511	1.523	3	2	1	1.553	1.551
4	0	0	1.638	1.637	4	0	0	1.654	1.651
4	2	0	1.823	1.822	4	2	0	1.838	1.850
3	3	2	1.909	1.907	3	3	2	1.922	1.936
4	4	0	2.305	2.306	4	4	0	2.325	2.334

q_{obsd} and q_{calcd} are the scattering vectors of the observed and calculated reflections for the bicontinuous cubic structures with lattice parameters $a=15.41\text{ nm}$ measured at 190°C and 15.21 nm measured at room temperature respectively.

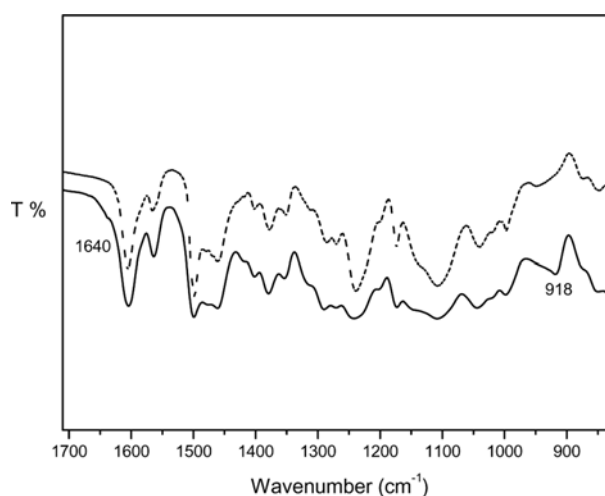


Figure 4. FTIR spectra of **4** (solid line) and its cross-linked polymer (dashed line).

indicated that the polymerization was successfully carried out by free radical photo-polymerization.²⁴

The structure of the network polymer was also investigated by means of the SAXS experiment. Interestingly, the SAXS pattern of the network polymer measured at 190°C exhibited similar relative positions to **4**, measured at the liquid crystalline phase, with sharp reflections characteristic of a bicontinuous cubic phase with $Ia3d$ symmetry (see Figure 3).¹⁸⁻²⁰ The lattice parameter of the cubic liquid crystalline d spacing is 15.4 nm (see Table II), whose value is slightly smaller compared to **4** in the liquid crystalline phase. Another interesting point to be noted is that the SAXS pattern of the network polymer measured at room temperature also exhibited a bicontinuous cubic structure (see Table II), while **4** showed a crystal phase at room temperature. Thus, via photo-polymerization of **4** at the liquid crystalline state, we successfully obtained thermo-stable network polymer materials, and maintained a well-

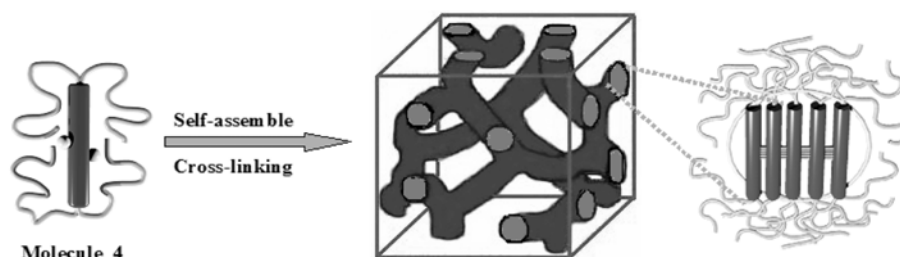


Figure 5. Schematic representation of self-assembly of **4** and conversion to 3-D ordered bicontinuous cubic structural polymer.

defined shape and size of the self-assembled supramolecular structures (see Figure 5).

Conclusions

An unusual strategy to generate an ordered network polymer from the self-assembly of reactive coil-rod-coil molecules was successfully achieved. The bicontinuous cubic structure of molecule **4** was maintained by cross-linking the photo-polymerization self-assembly of **4** in the liquid crystalline state. The result suggests that an approach to control a reactive supramolecular molecule structure and conversion to a polymer allows a novel, highly ordered 3-D nanostructural polymer to be produced.

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