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# Self-assembly of coil-rod-coil molecules into bicontinuous cubic and oblique columnar assemblies depending on coil chain length

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ABSTRACT

Coil-rod-coil molecules **1–3**, consisting of four biphenyls and a *p*-terphenyl unit linked together with ether bonds as a rod segment and poly(propylene oxide) (PPO) with a degree of polymerization (DP) of 7, 12, 17 as coil segments were synthesized. These molecules contain lateral methyl groups at 2 and 5 positions of the middle benzene ring of *p*-terphenyl. The self-assembling behavior of molecules **1–3** was investigated by means of DSC, POM and SAXS in the bulk state. Molecule **1** self-organizes into a lamellar structure in the bulk state and transfers into a bicontinuous cubic structure in the liquid crystalline phase. While, molecules **2**, **3** containing longer coil chains than **1** self-assemble into the hexagonal perforated lamellar (HPL) structures and the oblique columnar structures in the solid state and liquid crystalline phase, respectively. These results reveal that self-organizing behavior of such molecules is dramatically influenced by the length of the coil chains connected with the rod building block, as well as the lateral methyl groups incorporating in the middle of the rod segment.



## 1. Introduction

The correlation between the structures of molecules and self-assembly properties is one of the research topics in supramolecular chemistry. The various ordered nanostructures could be constructed through the appropriate selection of chemical composition and the reasonable design of molecules with recognition and self-assembly functions [1–6]. In diverse self-assembly systems, rod-coil molecules containing phenylene rigid building block have strong tendency to self-assemble into nano-scale supramolecular aggregations [7–12]. It has been reported that the supramolecular nanostructures can be accurately controlled into 1-D lamellar, 2-D columnar, cylinders, discrete bundles, ribbons, solid-state scrolls and so on, through manipulating parameters of driving forces from microphase separation of the covalently connected coil segments and the anisotropic rod segments [13–15]. These parameters include volume fraction of coil to rod segment [16], cross-sectional area of coil segment [17], the side groups at the center of rod segment [18–20] and the shape of the rod segments [21].

Recently, we have reported on the synthesis and self-assembly of rod-coil molecules consisting of four biphenyls and a *p*-terphenyl unit, which contains lateral methyl or ethoxymethyl groups at 2 and 5 positions of the middle benzene ring, linked together with ether bonds as a rod segment [20]. The results exhibit that the capacity of

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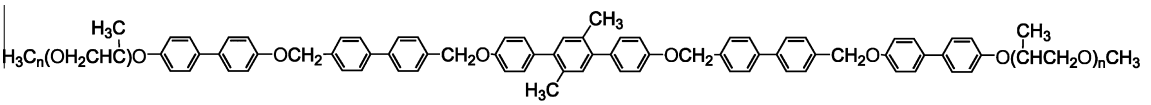


1 n = 7 2 n = 12 3 n = 17

**Scheme 1.** Molecular structures of coil-rod-coil triblock molecules **1–3**.

self-aggregation dramatically decreases as the increase of the length of lateral chains in the middle of rigid segments of the molecules whose compositions have constant coil to rod volume fraction. In addition, hexagonal perforated lamellar and oblique columnar nanostructures are spontaneously formed from the self-assembly of rod-coil molecules with methyl groups in the middle of rigid rod segments and propylene oxide repeat unit of 12 as coil chains (molecule **2** in Scheme 1). In order to elucidate the impact of the length of flexible poly(propylene oxide) chains on self-assembly behavior of such molecular system so as to form ordered supramolecular nanostructures which are expected to be applied widely into the field of catalytic, biomimetic or photoelectric materials, we design and synthesize molecules consisting of four biphenyls and a *p*-terphenyl unit linked together with ether bonds as a rod segment and PPO with different degrees of polymerization (DP) of 7, 17 as coil segments (molecules **1** and **3**). The self-assembling behavior of these molecules was investigated by means of differential scanning calorimetry (DSC), thermal polarized optical microscopy (POM), and X-ray diffraction (XRD) in the bulk state.

## 2. Experimental sections

### 2.1. Materials

Poly (propylene glycol) (Mw = 425, 725, 1000), 1,4-dibromo-2,5-dimethylbenzene, cuprous iodide, tetrakis(triphenylphosphine) palladium(0), 4-hydroxyphenylboronic acid (all from Aldrich) and conventional reagents were used as received.

### 2.2. Techniques

$^1$H NMR spectra were recorded from $CDCl_3$ solutions on a Bruker AM 300 spectrometer. A Perkin Elmer Pyris Diamond differential scanning calorimeter was used to determine the thermal transitions, which were reported as the maxima and minima of their endothermic or exothermic peaks, the heating and cooling rates were controlled to 10 °C/min. X-ray scattering measurements were performed in transmission mode with synchrotron radiation at the 1W2A X-ray beam line at Beijing Accelerator Laboratory, China and at the 5C2 X-ray beam line at Pohang Accelerator Laboratory, Korea. A Nikon Optiphot 2-pol optical polarized microscope, equipped with a Mettler FP82 hot-stage and a Mettler FP90 central processor, was used to observe the thermal transitions and to analyze the anisotropic texture. MALDI-TOF-MS was performed on a perceptive Biosystems Voyager-DE STR using a 2-cyano-3-(4-hydroxyphenyl) acrylic acid (CHCA) as matrix.

### 2.3. Synthesis of coil-rod-coil molecules *1* and *3*

Coil-rod-coil molecules **1** and **3** were synthesized using the same procedures according to the reference described elsewhere [20].

**Molecule 1** $^1$H NMR (300 MHz, $CDCl_3$, δ, ppm) 7.44-7.67 (m, 24Ar–H, *o* to $OCH_2$*phenyl*, *m* to $OCH_2$*phenyl*, *o* to $CH_2Br$, *m* to $CH_2Br$, *m* to $CH_2O$*phenyl* and *m* to *phenyl*$OCH(CH_3)CH_2$-O), 7.32 (d,4ArH, $H_2$,$H_6$,$H_{2''}$,$H_{6''}$ of *p*-terphenyl), 7.15 (s,2ArH, $H_{3'}$,$H_{6'}$ of *p*-terphenyl), 7.04–7.09 (dd, 8Ar–H, *o* to $CH_2O$*phenyl*, *o* to *phenyl*$OCH(CH_3)CH_2O$), 6.96 (d,4ArH, $H_3$-,$H_5$,$H_{3''}$,$H_{5''}$ of *p*-terphenyl), 5.15 (d, 8H, ph$OCH_2$ph), 4.54 (m, 2H, ph$OCH(CH_3)CH_2O$), 3.74 (t, 4H, ph$OCH(CH_3)CH_2O$), 3.38–3.60(m, 42H, –$OCH(CH_3)CH_2O$– and $OCH_3$), 2.29 (s,6H,ph$CH_3$), 1.34 (d,6H,–$OCH(CH_3)CH_2O$–), 1.14 (d,36H, –$OCH(CH_3)CH_2O$–). MALDI-TOF-MS *m/z* $(M)^+$ 1859, $(M+ Na)^+$ 1882.

**Molecule 3** $^1$H NMR (300 MHz, $CDCl_3$, δ, ppm) 7.44–7.66 (m, 24Ar–H, *o* to $OCH_2$*phenyl*, *m* to $OCH_2$*phenyl*, *o* to $CH_2Br$, *m* to $CH_2Br$, *m* to $CH_2O$*phenyl* and *m* to *phenyl*$OCH(CH_3)CH_2$-O), 7.33 (d,4ArH, $H_2$,$H_6$,$H_{2''}$,$H_{6''}$ of *p*-terphenyl), 7.15 (s,2ArH, $H_{3'}$,$H_{6'}$ of *p*-terphenyl), 7.04–7.08 (dd, 8Ar–H, *o* to $CH_2O$*phenyl*, *o* to *phenyl*$OCH(CH_3)CH_2O$), 6.98 (d,4ArH, $H_3$-,$H_5$,$H_3$,$H_{5'}$ of *p*-terphenyl), 5.16 (d, 8H, ph$OCH_2$ph), 4.54 (m, 2H, ph$OCH(CH_3)CH_2O$), 3.74 (t, 4H, ph$OCH(CH_3)CH_2O$), 3.37–3.60(m, 102H, –$OCH(CH_3)CH_2O$– and $OCH_3$), 2.29 (s,6H,ph$CH_3$), 1.34 (d,6H,–$OCH(CH_3)CH_2O$–), 1.13 (d,96H, –$OCH(CH_3)CH_2O$–). MALDI-TOF-MS *m/z* $(M)^+$ 3020, $(M+ Na)^+$ 3043.

## 4. Results and discussion

### 4.1. Synthesis

The coil-rod-coil triblock molecules **1, 3** consisting of four biphenyls and a *p*-terphenyl unit linked together with ether bonds as a rod segment and poly (propylene oxide) as the coil segment were synthesized through similar synthetic procedures of molecule **2** [20]. Molecular structures of **1** and **3** were characterized by $^1$H NMR spectroscopy and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy (see Supporting information). All the results were shown in full agreement with the structure presented in Scheme 1.

### 4.2. Structure analysis in the bulk state

The self-assembling behavior of molecules **1, 3** was investigated by DSC, POM and small-angle X-ray scatterings (SAXS). Fig. 1 shows the DSC heating and cooling traces of molecules **1**, **3**. The transition temperatures and the corresponding enthalpy changes of **1** and **3** obtained

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