

Self-Organized Hierarchical Structure of a Semi-Rod-Coil Diblock Copolymer

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We developed semi-rod-coil diblock copolymers with *tert*-butyl and trifluoromethyl ($-\text{CF}_3$) terminated side groups for constructing highly ordered hierarchical structures by combining individual self-organizing components such as microporous structure, phase-separated nanostructure, and liquid crystalline structure over multiple length scales. It was found that formation of ordered microporous structure is significantly affected by the terminal groups of the rod molecules in the semi-rod-coil diblock copolymer. The block copolymer with *tert*-butyl terminated side groups formed organized structures on three different length scales, ranging from angstroms to micrometers, by simple solvent casting and annealing. Microscopic observations under electron microscope confirmed the formation of hexagonally packed micropores with a narrow size distribution. The phase-separated nanostructures within the microporous structures characterized by layers perpendicular to the substrate with a periodicity of approximately 25 nm. The formation of a liquid crystalline smectic A mesophase within the phase-separated nanostructures was also observed. The order of microporous structure of the $-\text{CF}_3$ diblock copolymer is significantly poorer than that of the *tert*-butyl diblock copolymer. The ease of formation of ordered hierarchical structure is probably related to the relatively poor order of the microporous structure formation of the polymers with $-\text{CF}_3$ end groups.

Key words: hierarchical structure, diblock copolymer, self-organized structure, nanostructure

1. INTRODUCTION

Facile methods for constructing nanometer or micrometer ordered structures or combining them hierarchically have progressed thanks to numerous advances in polymeric materials. Such a structural order over varying length scale is a commonly encountered phenomenon in nature, but achieving this in the synthetic world is a challenge[1,2]. Progress in synthesis and characterization of self-organizing synthetic materials has been astounding, and block copolymers have played a significant role in this process[3-12]. In the last decade, despite studies of self-assembled structures or hierarchies using block copolymers, the applicable length scale remains less than ~ 100 nm[5-9]. In contrast, there have been recent reports on a self-assembly templating process for the creation of micro-sized structures[11-13]. In this templating process using water droplets, some polymers with π -conjugated rod-coil type architectures[12] or amphiphilic molecules[13] in the primary structure form hexagonally packed array of micro-sized holes in a polymer thin film. However, little attention has been paid to the formation of ordered structures on the nanometer-size scale by these approaches. For a wide range of advanced technological devices incorporating organic materials, it is desirable, advantageous, and often necessary that the hierarchical structures and surface structures of these materials can be precisely controlled from the nano- to the micrometer regime[5]. This prompted us to the creation of

hierarchical structures at length scales from molecular to the micrometer scale to combine such the self-organizing principles by the approach of molecular design of block copolymers. Recently, we have been developing a semi-rod-coil type diblock copolymer that self-organize hierarchical structures at length scales from nanometers or angstroms to micrometers over areas in the square centimeter range[14]. In our continuing investigation of the versatility of the semi-rod-coil diblock copolymer, we now report the effect of changing molecular end groups of semi-rod molecules for the formation of hierarchical structures, especially microporous structures. In addition, a successful molecular design of rod-coil type block copolymers was investigated for formation of the ordered microporous structures.

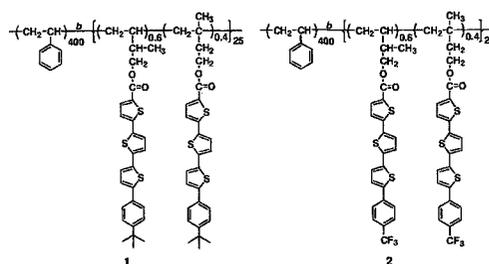


Fig. 1 Chemical structures of semi-rod-coil diblock copolymers 1 and 2.

2. Experimental Section

2.1 Materials. All reagents were purchased from Aldrich, Tokyo Kasei Kogyo Co. (TCI), Wako Pure Chemical Industries (WAKO) and used without further purification unless otherwise noted. 2,2'-Bithiophene was used after through silica gel with *n*-hexane as the eluent. THF was distilled over sodium/benzophenone. Dichloromethane was distilled over CaH₂. Styrene was purified by washing with NaOH aq (1M) to remove inhibitor before stirring with CaH₂ for 24 h, then vacuum-distilled. Isoprene was distilled over CaH₂ after stirring for 24 h. First distilled styrene and isoprene were stirred with dibutylmagnesium for 6 h, and then finally vacuum-distilled into a cold trap of a monomer reservoir.

2.2 Synthesis of Oligothiophenes with *tert*-butyl and trifluoromethyl terminus. Oligothiophenes with *tert*-butyl and trifluoromethyl terminus were synthesized using Stille coupling reactions, respectively[15]. The acid chlorides of the oligothiophenes were synthesized by the reactions of the acids and oxalyl chloride in dichloromethane.

2.3 Synthesis of Semi-Rod-Coil Diblock Copolymers with *tert*-butyl terminated side groups 1 and with -CF₃ terminated side groups 2: A polystyrene-*b*-1,2- and 3,4-polyisoprene was prepared by anionic polymerization of styrene monomers with 400 repeat units and isoprene monomers with 25 repeat units. The polystyrene-*b*-1,2- and 3,4-polyisoprene was modified by hydroboration of the polyisoprene block to yield polystyrene-*b*-poly(hydroxylated isoprene) with hydroxy groups in the polyisoprene block[16]. Poly(styrene-*b*-oligothiophene side-chain modified isoprene) diblock copolymers 1 and 2 were synthesized by esterifying a polystyrene-*b*-modified polyisoprene with oligothiophene acid chlorides, respectively. Details of the molecular synthesis and polymerization studies describe in our previous paper.

2.4 Synthesis of Rod-Coil type polymers, rod-coil 3, coil-rod-coil 4, and rod-coil-rod 5. General procedure: A polystyrene was prepared by anionic polymerization of styrene monomers with 30 repeat units, and quenching by using of 1-bromo-6-*tert*-butyldimethylsilylhexyl ether. Then, the *tert*-butyldimethylsilyl groups was deprotected to give a polystyrene with hydroxy end groups. Esterification of polystyrene with hydroxy end groups and 5'-bromo-2,2'-bithiophene-5-carboxylic acid chloride was carried out in the presence of *N,N*-dimethylamino pyridine in dichloromethane. Stille coupling reaction of the obtained polymer and 5-(*tri-n*-butyl)-2,2'-bithiophene was carried out at 80 °C in dimethylformamide under nitrogen to give a rod-coil type polymer, polystyrene-*b*-quaterthiophene 3 (*M_n*: 3100, PD: 1.08). Polymers, polystyrene-*b*-sexithiophene-*b*-polystyrene 4 (*M_n*: 6900, PD: 1.12) and quaterthiophene-*b*-polystyrene-*b*-quaterthiophene 5 (*M_n*: 3800, PD: 1.08), were also synthesized as a similar procedure of 3.

2.4 Characterizations. Compounds were routinely characterized by IR and NMR spectroscopies, mass spectrometry, and elemental analysis. The molecular weights of polymers were determined by gel permeation chromatography (GPC) with polystyrene standard (THF as eluent, at 40 °C). Thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC)

measurements were used for thermally analyses of polymers. A polarizing microscope was used to observe LC textures of the samples. The microporous structures were characterized by a scanning electron microscope (SEM). Polymer films were prepared from carbon disulfide solutions by casting on glass plates. The films were coated by Au evaporation. X-ray diffraction (XRD) was performed on a Cu K-ALPHA1 (50 kV/200 mA) using RINT2000 vertical goniometer. A leo912 energy-filtering transmission electron microscope (EFTEM), integrating an omega electron spectrometer was operated at an acceleration voltage of 120 kV to observe film cross-sections. To prepare specimens, the polymer solution was cast on a cured epoxy plate, then embedded in the same epoxy resin to be cured at 60 °C overnight. Sections of 50 nm thickness were collected by ultramicrotomy. Energy-filtered images created by unelastically scattered electrons with an energy loss of 100±10 eV giving maximum contrast. To create a sulphur distribution image, we used a three-window power law method, where two energy-filtering images at 100±10 and 130±10 eV are used for background images and an image at 170±10 eV is used for the core loss image.

3. Results and Discussion

The side chain type block copolymers promise form regular nano-scale hierarchical structures through phase separation and intermolecular interactions[5]. Furthermore, the aromatic rigid-rod segments incorporated in rod-coil type block copolymers form micro-sized porous structures unlike the usual coil-coil type block copolymers[12]. The incorporation of π -conjugated rigid-rod molecules in the side chain, thus, can play a role in forming both nano- and micro-sized structures and create the desired hierarchical structures over multiple length scales. In our previous reports, we observed that a semi-rod-coil block copolymer with *t*-butyl terminated side groups, poly(styrene-*b*-oligothiophene side-chain modified isoprene) block copolymers 1, formed organized structures at three different length scales ranging from angstroms to microns by simple solvent casting and annealing[14]. The interesting surface structure on the micropores in the microporous structure was obtained by the characterization of the cross sectional view of transmission electron micrographs. The oligothiophene semi-rod parts in the block copolymer covered on the top-surface of the micropores. The result showed that the semi-rod molecules affect to form the highly ordered microporous structure or the hierarchical structure. Herein, in order to investigate the effect of the terminal groups of the rod molecules in the semi-rod-coil diblock copolymers in forming the microporous structure and hierarchical structure, the semi-rod-coil diblock copolymers with *tert*-butyl and -CF₃ terminated side groups were synthesized. Infrared and ¹H and ¹³C NMR spectroscopy showed that the desired block copolymers were obtained in quantitative yield without a side product. Gel permeation chromatography (GPC) indicated a narrow polydispersity index of ~1.1 of both polymers and a number-average molecular weight *M_n* of 55000 and 58000, respectively (versus polystyrene standard in

tetrahydrofuran).

Films were prepared from 0.2 mL of a 0.25 wt% polymer solutions in carbon disulfide on a variety of substrates such as glass slides, silicon wafers, cured epoxy plates, polyimide films, and water surfaces by casting at room temperature (22 °C) under a moist air flow. The humidity and the flow rate were kept at 85% and 3.0 L min⁻¹, respectively. The solvent completely evaporated within 10-20 seconds, and the films were instantly obtained over an area of ~3 cm².

Observations of the film of **1** under a polarized optical microscope (POM) and a scanning electron microscope (SEM) confirmed the formation of hexagonally packed micropores with a narrow size distribution. The diameter of the open pores on the surface were approximately 1.5 μm, respectively. A cross sectional view shows a single layer with empty spheres, in which spheres with a diameter of 2.5 μm are separated from each other by thin walls of less than 100 nm. In contrast, ordered microporous structure was not obtained from **2**.

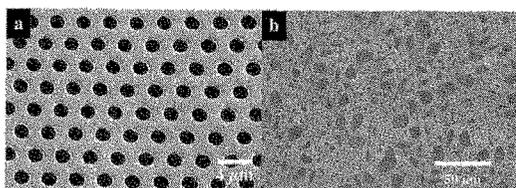


Fig. 2 SEM images of self-organized microporous structures. a) Polymer **1** and b) polymer **2**.

The microporous films were sectioned perpendicular and horizontal to the substrate to give thin specimens which, after embedding in epoxy resin, were observed under a transmission electron microscope (TEM). The film of **1** contains a nanoscale phase-separated structure characterized by layers perpendicular to the substrate with a periodicity of approximately 25 nm. A sulfur-distribution image created by electron spectroscopic imaging on an energy-filtering TEM indicated that the phase-separated PS and POTI blocks aligned layer by layer due to the self-assembly characteristic of the diblock copolymer. On the other hand, the periodic nanoscale phase-separated structure of **2** was not obtained clearly.

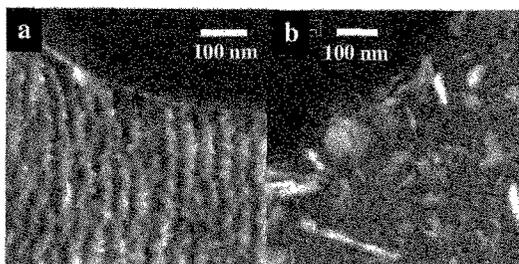


Fig. 3 Self-organized phase-separated nanostructures, TEM images of cross sections of the microporous film (ca. 50 nm thick). a) Polymer **1** and b) polymer **2**.

The mesophase structure of the microporous film of **1** was investigated by differential scanning calorimetry, polarized optical microscopy, and X-ray diffraction. The

XRD pattern after annealing at 170 °C that slightly above the glass transition of POTI block showed a sharp inner reflection corresponding to the phase-separated layer structure, and a very broad outer reflection corresponding to the intermolecular spacing of oligothiophene molecules. The layer spacing and intermolecular spacing within the POTI layer were 39.8 and 4.2 Å, respectively.

In order to investigate the effect of primary structure of the rod-coil type block copolymers for the formation of microporous structure, three different type block copolymers, polystyrene-*b*-quaterthiophene **3**, polystyrene-*b*-sexithiophene-*b*-polystyrene **4** and quaterthiophene-*b*-polystyrene-*b*-quaterthiophene **5**, were synthesized.

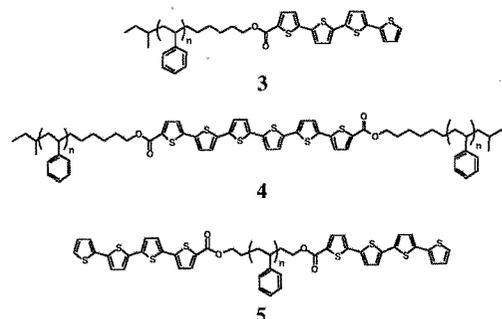


Fig. 4 Chemical structures of rod-coil polymers **3**, **4** and **5**.

The films were prepared from 0.25 wt% polymer solutions in carbon disulfide by casting at room temperature (22 °C) on a glass substrate under a moist air flow. The hexagonally packed microporous structure was obtained from polymers **3** and **5**. The diameters of both films were approximately 2.2 μm. In contrast, the ordered microporous structure was not obtained from polymer **4**. The above results indicate that both molecular end groups and the rod block terminus of the rod-coil polymers play a significantly role to form stable narrow distribution water droplets and the self-assembling during the film preparation process.

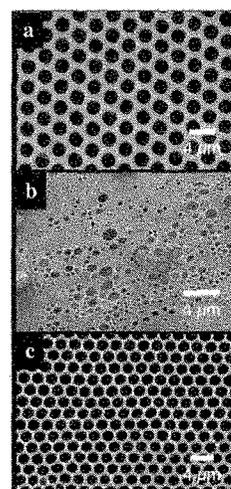


Fig. 5 SEM images of microporous structures. a) Polymer **3**, b) polymer **4**, and c) polymer **5**.

4. Summary

Studies on the effect of molecular changing of end groups on self-assembling behavior for the formation of microporous structure and hierarchical structure were carried out using semi-rod-coil diblock copolymers with *t*-butyl and -CF₃ terminated side groups. The characterization of the microporous film obtained shows that the diblock copolymer with *t*-butyl end groups forms more stable and ordered hierarchical structures over multiple length scales than that of with -CF₃ end groups. In addition, it was found that the rod-coil type block copolymers with rod block terminus form the highly ordered microporous structure. We believe that the rod-coil type polymers play a role of a surface active agent at the interface between polymer solution and water droplets.

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