Self-Assembly of Rod−Coil−Rod Triblock Copolymer and Homopolymer Blends

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ABSTRACT: The self-assembly structures and their transformation of blends of rod−coil−rod triblock copolymers and homopolymers were first detected. Adding coil homopolymers into block copolymers with a lamellar structure resulted in an increase of *d*-spacing. When coil homopolymers were added into triblock copolymer with a rod continuous hexagonally packed-cylinder structure, lamellar structures were obtained, and the lamellar *d*-spacing were smaller than that of the original structure. The addition of rod-like homopolymer into the block copolymers with a lamellar structure also resulted in the increase of the *d*-spacing. As a result of the interdigitation, the rod blocks must rearrange to a larger angle with respect to the interface.

Introduction

Self-assembly of rod−coil block copolymers could produce hierarchically ordered structures, which lead to novel properties and applications in photophysical, electrochemical, or biological fields.[1−4] Such self-assembly is affected by the volume fraction of each block and the Flory−Huggins interaction between blocks. Another key factor is the parallel arrangement tendency of the constitutive rod-like block.[5−7] Because the interaction between rods is strong, flat intermaterial dividing surface is preferentially formed in rod−coil diblock copolymers in order to minimize the interface energy. Layer-like structures are always formed. However, nonlamellar self-assembled structures of block copolymers were also observed in various systems.[8,9] In our previous studies, we discovered hexagonally packed-cylinder (HPC) structures in a rod−coil−rod triblock copolymer, in which rod blocks formed continuous matrix containing hexagonal coil cylinders.[10,11] Besides the factors mentioned above, the topological factor of the copolymer also affected the structure.[12] The rod blocks were connected with each other through the middle coil blocks. The movements of the rod were strongly influenced by the behavior of the other rod in the same polymer chain due to the connectivity. The microphase separated structures might be metastable, because interactions, such as stretching and jamming, existed among the blocks. If homopolymer which was chemically identical to one of the blocks was added into the triblock copolymer, it entered into the corresponding domains.[13] The homopolymer acts as the spacer, helping the block copolymers self-assemble into more stable morphologies.

Meanwhile, adding a homopolymer into a block copolymer is an effective approach to controlling domain spacing and modifying morphology without additional synthesis. Systems of a coil−coil block copolymer solubilizing homopolymer chains have been studied extensively in the past both experimentally and theoretically.[14−18] The blending of rod−coil−rod triblock copolymers with a coil or rod homopolymer, which is more complicated than the coil−coil or rod−coil diblock copolymer systems, has been seldom researched.

Mesogen-jacketed liquid crystalline polymers (MJLCPs) are a kind of rigid or semirigid polymers, which are frequently selected as rod part in rod−coil block copolymers for their ease of modification of the rod length, diameter, and the surface chemistry.[19−22] Up to now, MJLCPs based on 2,5-disubstituted styrene have been synthesized and investigated.[23−26] Recently, we synthesized rod−coil−rod triblock copolymers (see Scheme 1) containing poly{2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene} (PMPCS) as rod block and polyisobutylene (PIB) as middle coil block through combination of living cationic polymerization (LCP) and atom transfer radical polymerization (ATRP). A phase diagram was obtained by investigating the self-assembly structures with different rod volume fractions.[11]

In this article, we added the coil PIB into lamellar and HPC structures of PMPCS-*b*-PIB-*b*-PMPCS, and rod PMPCS into lamellar structure. The self-assembly structures of blends were investigated.

Experimental Section

Materials and Measurements. Materials were synthesized as previously described.[11] Table 1 summarized characteristics of the homopolymers and two block copolymer samples (Tri52 and Tri78) used in this work. Blends of homopolymer and block copolymers were prepared by first dissolving a predetermined amount of PMPCS-*b*-PIB-*b*-PMPCS and PMPCS (or PIB) in THF and then by slowly evaporating the solvent at room temperature under THF atmosphere.

The molecular weights (MWs) and molecular weight distributions of all copolymers were measured by gel permeation chromatography (GPC) with a Waters 2410 instrument equipped with three Waters μ-Styragel columns ($10,^3$ 10^4, and 10^5 Å). THF was the mobile phase at the flow rate of 1.0 mL/min at 35 °C. The calibration curve was obtained by PS standards. The volume fraction of rod blocks was based on the results from their nuclear magnetic resonance spectroscopy (NMR) performed on a Bruker ARX 300 MHz

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Scheme 1. Structure of PMPCS-*b*-PIB-*b*-PMPCS ($x < 5$, Which Is Much Smaller Than m and n)

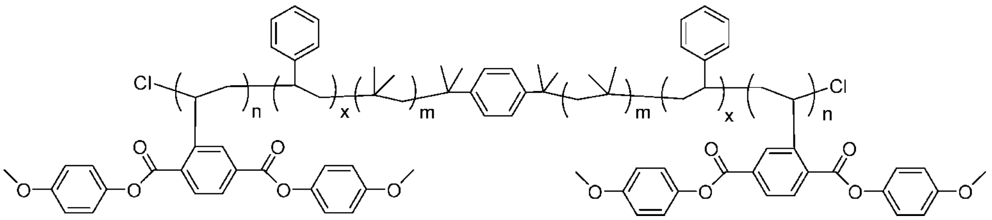

Table 1. Characteristics of Block Copolymers PMPCS-*b*-PIB-*b*-PMPCS (Tri52 and Tri78), PMPCS Homopolymer, and PIB Homopolymer

sample	M_n[a]	PDI[a]	Φ PMPCS[b]	phase[c]
Tri52	19.4k	1.26	0.52	Lam
Tri78	36.7k	1.26	0.78	Hex
PMPCS	8.9k	1.20	1.0	
PIB	9.4k	1.35	0	

[a] Determined by GPC. [b] PMPCS volume fraction calibrated according to ^{1}H NMR. [c] Determined by SAXS and TEM, see ref 11.

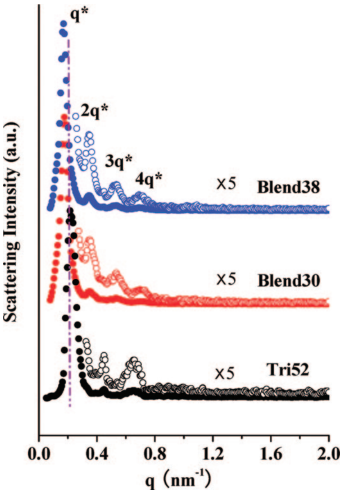

Figure 1. SAXS curves for Blend30 and Blend38, compared with that for Tri52 at room temperature.

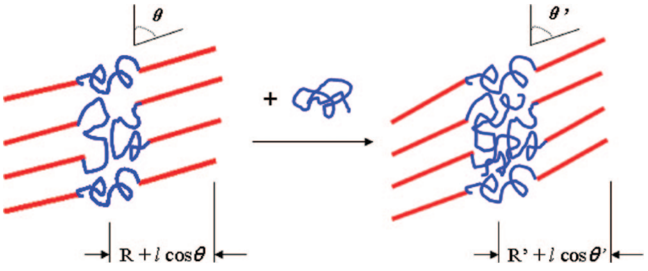

Figure 2. Adding soft PIB into the lamellar structure of rod−coil−rod block copolymers resulting in increased lamellar *d*-spacing.

spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as the reference.

Small angle X-ray scattering (SAXS) experiment was carried out on the SAXSess high-flux small-angle X-ray scattering instrument (Anton Paar) equipped with Kratky block-collimation system. The X-ray was generated using a Philips PW3830 sealed-tube X-ray generator with Cu target. The wavelength was 0.1542 nm. The power of the generator used for measurement was 40 kV and 50 mA. The X-ray intensities were recorded on an imaging-plate detection system with a pixel size of $42.3 \times 42.3\ \mu m^2$. The distance from the sample to detector was 264.5 mm and the exposure time was 300 s. Scattered X-ray at wide angle was also collected. The treatment of original experimental data such as data acquisition, background subtraction, data reduction was handled by Anton Paar SAXSquant 1.01 software and PCG software package. The line smearing effect due to the line-focus X-ray source should be eliminated from experimental curve (desmearing) and this was performed by the desmearing program according to Lake's method.

The microphase separation of samples was observed by transmission electron microscopy (TEM). Samples were embedded into epoxy. Ultrathin sections were cut from a thin film on a ultramicrotome. To enhance the electron density contrast between the PMPCS and PIB phases, the sections were stained by RuO_4 vapor at room temperature for 30 min. TEM studies were performed on a Hitachi H-800 electron microscope.

Results and Discussion

Blends of PIB and Tri52. At middle rod volume fraction, Tri52 formed a lamellar structure.[11] Adding coil PIB homopolymer into lamellar Tri52, PIB was locally swelled into the PIB phase of the triblock copolymer. Two blends were obtained with overall rod volume fractions of 0.38 and 0.30, and they were nominated Blend38 and Blend30, respectively. The self-assembly structures of the blends were first detected by SAXS.

Figure 1 shows the SAXS curves at room temperature of Blend30 and Blend38, compared with that of Tri52. They all

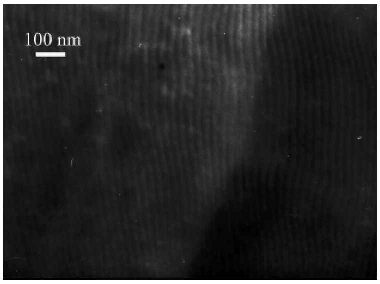

Figure 3. TEM image of Blend60 obtained at room temperature.

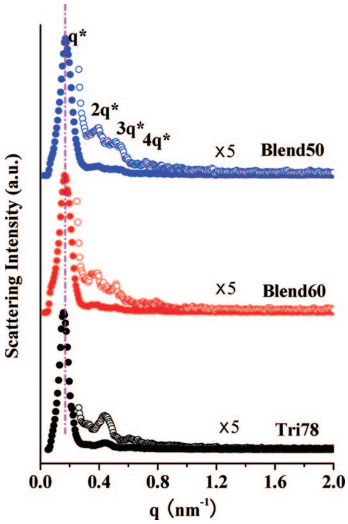

Figure 4. SAXS curves for Blend60 and Blend50, compared with that for Tri78 at room temperature.

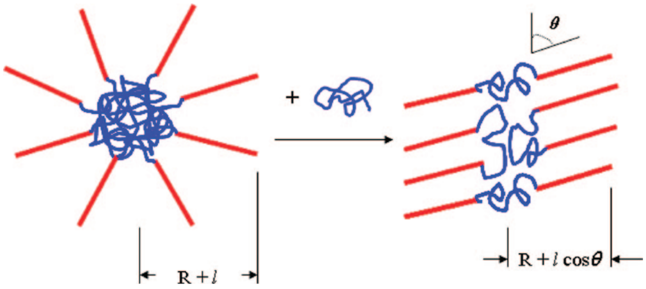

Figure 5. Adding soft PIB into the HPC rod−coil−rod block copolymers resulting in a HPC-to-lamellar transformation.

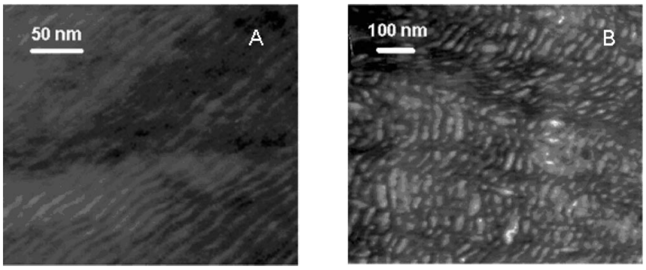

Figure 6. TEM images of Blend62 (A) and Blend72 (B) obtained at room temperature.

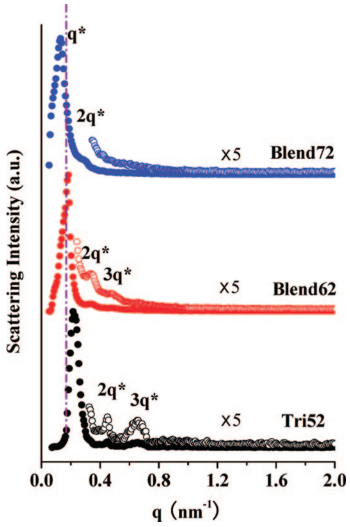

Figure 7. SAXS curves for Blend62 and Blend72, compared with that for Tri52 at room temperature.

formed lamellar structures. The differences were the positions of the primary peaks. The peaks of blends were located at lower angles, indicating higher *d*-spacing. The *d*-spacing of Tri52 was 29.8 nm, while Blend30 and Blend38 were 35.5 and 37.6 nm. Considering the same interfacial area, the thicknesses of coil layer was 14.3 nm in Tri52, which was smaller than those of Blend30 and Blend38, 24.8 and 23.3 nm, respectively. As shown in Figure 2, when the soft PIB was added into the triblock copolymer, the increase of PIB in the PIB layer increased the interfacial area of the lamella. The rod tilted with larger angle to adjust to the extra interface, decreasing the thickness of the rod layer. The more PIB was added, the larger the angle was tilted and the thinner the rod layer.

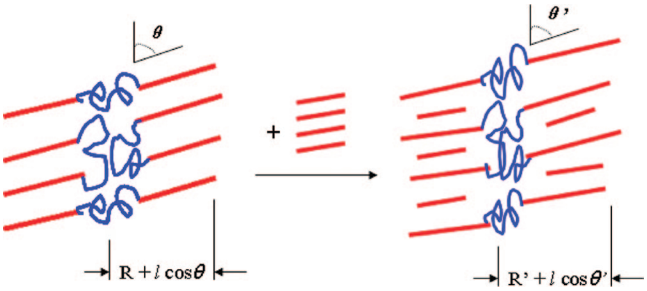

Figure 8. Adding PMPCS into the lamellar rod−coil−rod block copolymers resulted in increased lamellar *d*-spacing.

Table 2. Domain Sizes of Block Copolymers and Blends Obtained from SAXS Results

sample	*d*-spacing (nm)	thickness of rod layer (nm)	thickness of soft layer (nm)
Tri52	29.8	15.5	14.3
Tri78	40.4	22.0[a]	12.4[b]
Blend30	35.5	10.7	24.8
Blend38	37.6	14.3	23.3
Blend50	37.4	18.7	18.7
Blend60	37.8	22.7	15.1
Blend62	36.5	22.6	13.9
Blend72	49.4[c]	35.6[c]	13.8[c]

[a] The length of the rod between two neighboring PIB columns. [b] The average radius of PIB column. [c] Calculated as lamellar structure.

Blends of PIB and Tri78. Previous studies showed that Tri78 self-assembled into hexagonally packed-cylinder (HPC) structures. The PMPCS rod formed the continuous domain, while the middle soft PIB entered into the cylinders. It is an amazing result, because layer-like structures are popular in the rod−coil block copolymer system. As two rigid PMPCS blocks anchored the ends of the coil block, the movements of both PMPCS and PIB were limited. The rods were preferentially jammed, causing the interface to bend. Adding coil PIB homopolymer into HPC-structured Tri78, two blends with the overall rod volume fractions of 0.60 and 0.50, were obtained, which were nominated Blend60 and Blend50, respectively. The phase structures of the blends were distinguishingly different from that of the neat block copolymer.

To confirm the structures of the blends, TEM experiments were carried out. In order to enhance the contrast between the constitutive blocks, RuO_4 was used to selectively stain the PMPCS block. Figure 3 showed the TEM micrograph of Blend60. Alternating black and white layers were clearly seen, which were ascribed to the PMPCS domains and the PIB domains, respectively.

Figure 4 shows the SAXS curves at room temperature of Blend60 and Blend50, compared with that of Tri78. The blends both formed lamellar structures. Interestingly, the primary peaks of blends were located at higher angles, indicating lower *d*-spacing values. The *d*-spacing of Tri78 was 40.4 nm; therefore, the *a* parameter of the HPC structure was 46.7 nm. As shown in Figure 5, in the original HPC structure, the *a* parameter contained the diameter of PIB column and the average length of PMPCS blocks. When the soft PIB was added into the triblock copolymer, the PIB homopolymer swelled the minor PIB domains, resulting in flattened interfacial curves. The *d*-spacing of Blend50 and Blend60 became smaller, 37.4 and 37.8 nm, respectively, because rod blocks in the blends tilted at some angles, resulting in a smaller thickness of the PMPCS layer, although the size of the PIB domains expanded.

Blends of PMPCS and Tri52. Adding rod PMPCS homopolymer into lamellar-structured Tri52, two blends with different overall rod volume fractions of 0.62 and 0.72 were obtained, which were nominated Blend62 and Blend72, respectively. Blend62 formed lamellar structure, confirmed by SAXS and TEM (see Figures 6A and 7). For Blend72, though lamellar structure was also indicated from SAXS results, due to the higher volume fraction of rod component, alternating black layers with discontinuous white layers were observed from TEM micrograph. PMPCS punctuated the PIB layers and formed the perforation. It was a perforated lamellae structure. Previous studies showed that triblock copolymers at the rod volume fraction between 0.69 and 0.79 formed HPC structures.

Figure 7 shows the SAXS curves at room temperature of Blend62 and Blend72, compared with that of Tri52. The primary peaks of blends were located at lower angles, indicating higher *d*-spacing values. When PMPCS was added, as shown in Figure 8, the interfacial area increased by interdigitation of the rods, leading the coils to rearrange to occupy the additional interfacial area. Thus, the thicknesses of PIB layer in the blends were smaller than that of Tri52 (see Table 2). However, this decrease was slight. It must be related with the topological structure of the blocks. Both ends of the coil block were anchored, so the rearrangement would not be too big. On the other hand, the thickness of PMPCS layer became bigger resulting from the rod block rearrange more vertical to the interface. Combining these two factors, rod played a dominant role.

Conclusion

The self-assembly structures of the blends of rod−coil−rod triblock copolymers and homopolymers were all lamellar. Two main factors affected the lamellar *d*-spacing. They were the size of coils and the tilt angle of rods, which were influenced by the topological structure of triblock copolymer. When coil homopolymer was added into lamellar blocks, coil domain swelled with increased thickness, the rod tilted at a larger angle with decreased thickness, the *d*-spacing of the lamella increased. When coil homopolymer was added into the rod continuous hexagonally packed-cylinder structure, lamellar structures were obtained, though the size of coils became larger, and the rods adopted a tilted angle, with decreased lamellar *d*-spacing. When the rod-like homopolymer was added into the lamellar blocks, the size of coil decreased, while rods tilted with a smaller angle, and the total *d*-spacing increased.

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