Double-Hexagonal Morphology Formed by Rod-Rich Triblock Copolymer

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The formation of block copolymers are contradictory in that the chemically distinct constituent building blocks have to remain separate just like their blends but cannot because of the covalent linkage in between. So nanoscale microphase separation occurs, producing periodical structures, such as lamellae, cylinders, or spheres. These morphologies are determined by the volume fraction of one component f and the product χN, where χ is the Flory−Huggins interaction parameter and N is the degree of polymerization.[1−3] If the rodlike blocks are connected, they would play a significant role in creating supramolecular architectures. Generally, layerlike morphology is preferentially formed for both symmetric and asymmetric volume fractions in AB rod−coil diblocks in addition to spherical and gyroidal morphologies that are only observed in low molecular mass rod−coil systems.[4−11] This is because the interaction between the rods is relatively strong and the rods are nearly parallel to one another to form the liquid crystalline (LC) phase. Thus, the lower scale LC phase dominates the higher scale microphase separation.[11]

In this article, we describe a contrary process. That is, the lower scale LC phase is dominated by the higher scale microphase separation. We employ mesogen-jacketed LC polymers (MJLCP),[12,13] in which the LC mesogens are attached to the mainchain by short linkages to force the mainchain to adopt an extended conformation for steric factors, as rigid end blocks and low-T_g PDMS as the soft midblock. Different from other rod−coil block copolymers, the ABA type triblock copolymers are MJLCP rich. We choose the well-studied poly-{[2,5-bis-(4-methoxyphenyl)oxycarbonyl]styrene} (PMPCS).

Previous studies show that the PMPCS cast from solution is amorphous; then, the columnar nematic phase gradually develops at elevated temperature.[14] Therefore, the PMPCS-rich triblock might self-assemble into certain ordered structure just like coil−coil blocks at room temperature. When heated to LC temperature, the PMPCS blocks would become ordered under confined conditions.[15]

The triblock copolymer PMPCS−PDMS−PMPCS is synthesized through the atom transfer radical polymerization (ATRP) procedure from α,ω-di(2-bromoisobutyryl) terminated PDMS with a number-average molecular weight (M_n) of 19.8K and polydispersity (PDI) of 1.46. The detailed synthesis procedure is shown in supporting online material. From GPC, the M_n of the triblock copolymer is 62.5K and the PDI is 1.29. The calculated weight fraction of PMPCS blocks is 89.6% by ^{1}H NMR.

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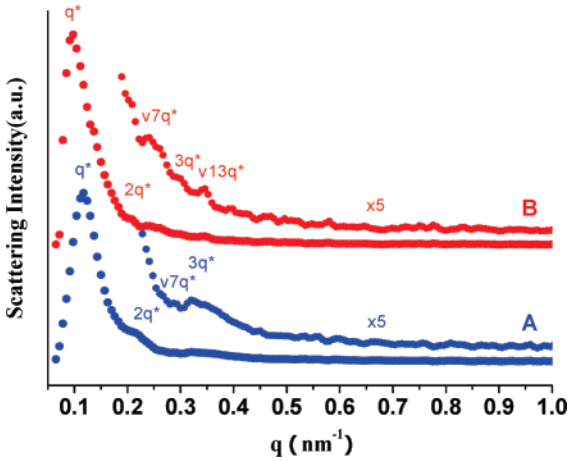

Figure 1. Scattered intensities as a function of scattering vector q at room temperature (A) and at 160 °C (B). Angular positions of higher order peaks with respect to the first-order maximum are labeled for each curve. The maxima angular positions of $\sqrt{3}$ and $\sqrt{7}$ are usually expected for a cylindrical morphology. The patterns were obtained on a high-flux SAXS instrument (Anton Paar) equipped with the Kratky block collimation system. The Cu Kα radiation ($\lambda = 0.154$ nm) was from a Philips PW3830 sealed-tube X-ray generator operating at 40 kV and 50 mA. The X-ray intensities were recorded on an imaging plate detection system.

Their microdomain structure was explored by small-angle X-ray scattering (SAXS) (Figure 1). The dilute solution of the sample in THF was cast onto PTFE substrate, and the solvent was allowed to evaporate under THF atmosphere. In the SAXS pattern of the obtained film at room temperature (Figure 1A), the primary peak is centered around a scattering wave vector q value corresponding to ∼58.5 nm. The higher order reflections are clearly visible at angular positions of 2, $\sqrt{7}$, and 3 of the first-order maximum. This pattern is characteristic of a hexagonal array of cylindrical morphology consisting of PDMS cylinders in the PMPCS matrix as expected for this volume fraction. When the sample was annealed at 160 °C, the PMPCS domain entered into the LC phase, as evidenced by polarized optical microscopy and wide-angle X-ray diffraction (WAXD). In the SAXS pattern of the polymer at 160 °C (Figure 1B), the primary peak is shifted to a lower q value corresponding to ∼70.4 nm and there are higher order reflections at angular positions of 2, $\sqrt{7}$, 3, and $\sqrt{13}$ of this first-order maximum. It is also indicative of a hexagonal array of cylinders.

To confirm the results of the SAXS patterns of a cylindrical morphology, we also examined the samples by transmission electron microscopy (TEM) (Figure 2A). Due to the presence of silicon in PDMS, which causes a difference in the mass thickness contrast, any staining was not necessary. TEM images reveal that the hexagonal PDMS cylinders (dark parts) in the PMPCS matrix (gray parts) are in agreement with the SAXS data. From the results of SAXS and TEM, we know that the subsequent LC phase does not destroy the microstructure regardless of the increase in d spacing. It is an interesting discovery in the rod-governed self-assemble system.

The question is how do the rodlike PMPCS blocks arrange themselves parallel to each other? Electron diffraction (ED) experiments in TEM are carried out to elucidate the ordered LC structure (Figure 2B). A hexagonal lattice is observed, with a measured d spacing of 0.43 nm. Previous studies have shown that the homoPMPCS backbones behave as rodlike chains with

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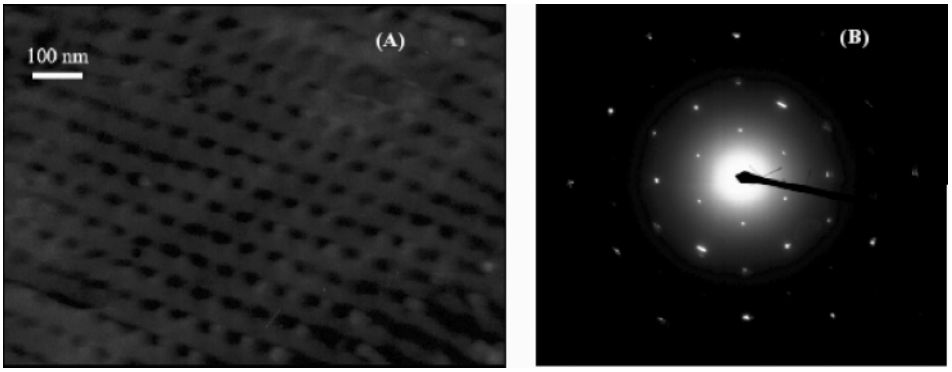

Figure 2. TEM micrographs (A) and ED patterns (B) of the sample. Sample was annealed at 160 °C under N_2 for 24 h and embedded into epoxy. Ultrathin sections were cut from a thin film on a ultramicrotome and were investigated using a Hitachi H-800 electron microscope operated at 100 kV. TEM indicated hexagonally packed PDMS cylinders in the PMPCS matrix with a *d* spacing of ~65 nm. ED patterns showed hexagonal lattice with a *d* spacing of 0.43 nm, indicating LC mesogens to be hexagonally packed.

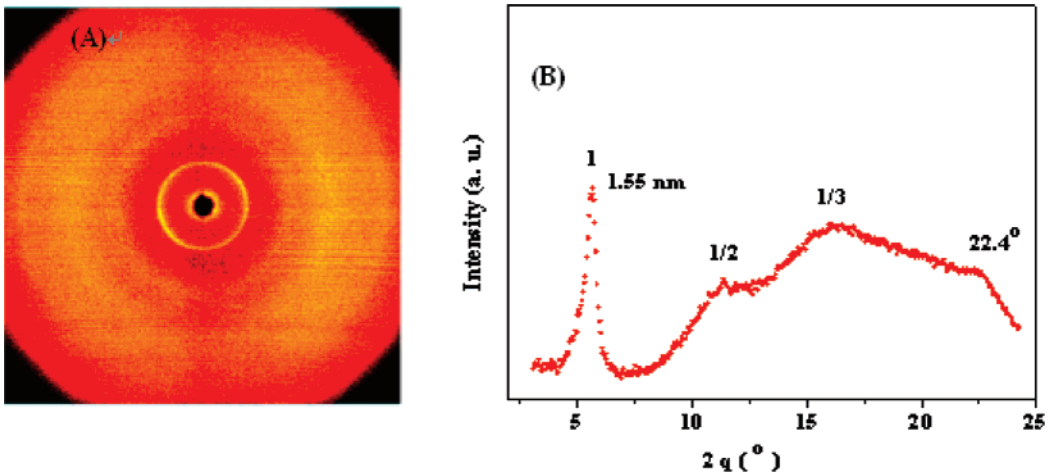

Figure 3. 2D WAXD pattern of the sample annealed at 160 °C (A) and the intensity profiles along the equator (B). Higher orders of diffraction were visible. The scattering vector ratio followed 1:1/2:1/3, indicating a smectic phase, and the *d* spacing was 1.55 nm. The outer ring at 22.4° gave the intermesogen a *d* spacing 0.45 nm. 2D WAXD patterns were obtained on a Bruker D8 Discover diffractometer with GADDS as a 2D detector. Silicon powder and silver behenate were used as standards. Samples were mounted on the sample stage, and the 2D diffraction patterns were recorded in a transmission mode.

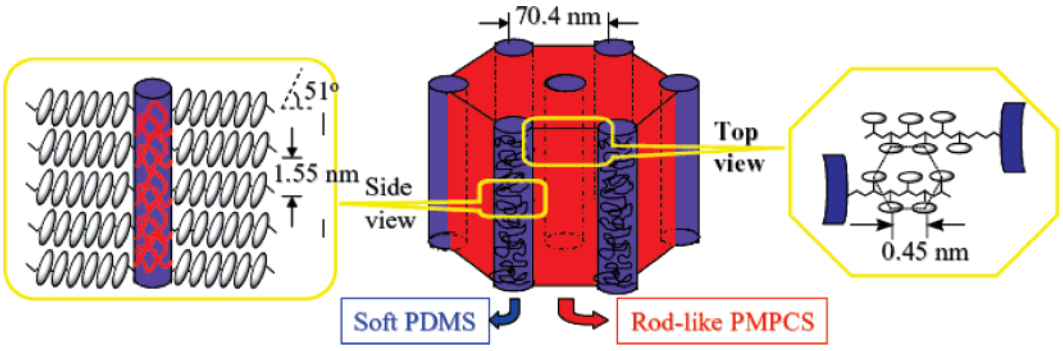

Figure 4. Schematic representation of the double-hexagonal morphology. Triblock copolymer self-assembles into hexagonally packed PDMS cylinders in the PMPCS matrix (right two), with a *d* spacing of 70.4 nm. In the continuous PMPCS domain, the LC mesogens form the SI phase.

the mesogenic groups laterally attached. When heated to LC temperature, the rigid main chains pack hexagonally to form a nematic phase with a *d* spacing of 1.67 nm, corresponding to the diameter of the mesogen-packed mainchain.[14] Here, it is the LC mesogens that arrange into a hexatic pattern (Figure 4). 2D WAXD provide more details (Figure 3). One sharp inner ring and several outer can be seen. From the intensity profile, a *d* spacing of 1.55 nm is obtained and higher order diffractions are at angular positions of 1/2 and 1/3 of the first-order maximum. It is a layered structure. Upon consideration of the length of the LC mesogen to be ~2 nm, it should tilt 51° away from the axis of the mainchain. So, a combination of the ED results and the WAXD results indicate the LC mesogens to form a hexatic smectic phase (SI).[16] The peak at $2\theta = 22.4°$ is the reflection of the hexatic arrangement in one layer, and the calculated *d* spacing is 0.45 nm, which is also in agreement with the ED data.

Finally, a schematic illustration of a packing model is shown in Figure 4. The model is a kind of a "double-hexagonal" organization. At room temperature, the triblocks self-assemble into a cylindrical hexagonal structure. Soft PDMS enter into cylinders, while the amorphous PMPCS form a continuous domain. When temperature is up to LC temperature, the PMPCS segments crawl among the cylinders to form the LC phase.

During the process, the hard PMPCS segments do not destroy the soft PDMS cylinders and the cylindrical hexagonal phase remains intact. In the continuous PMPCS domain, the tilted mesogens adopt a hexatic smectic phase, which is obviously different from that observed for the homoPMPCS. However, in the domains, some array of disinclination lines may exist. Further investigations are in progress.

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Supporting Information Available: Synthetic details and key NMR observations and TEM of the sample. This information is available free of charge via the Internet at http://pubs.acs.org.

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