Frustrated Crystallization of a Rod−Coil Block Copolymer from Its Liquid Crystalline State

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Block copolymers offer a variety of one-, two-, or three-dimensional periodic nanostructures through microphase separation of chemically distinct macromolecular blocks.[1] If the block copolymers contain semicrystalline blocks, their microstructures develop with changing concentration or temperature via two competing organizing processes, crystallization and microphase separation.[2−5] If the crystallization occurs above the order−disorder transition temperature (T_{ODT}), the point of microphase separation of the dissimilar blocks, the copolymer chains become frozen into the crystalline matrix, resulting in a disordered microdomain morphology even if the copolymer is cooled below T_{ODT}. If the crystalline block has a melting temperature lower than T_{ODT}, folded lamellar crystals of semicrystalline block can grow but as is confined to the well-defined block copolymer microdomains.

However, if the incorporated crystalline block of the crystalline−amorphous diblock copolymer is a rodlike chain, it cannot crystallize into a folded chain lamella. Since the interfacial area offered by a stiff rodlike chain is much smaller than that of a coil or folded semicrystalline block, the self-assembly of the block copolymers containing a rodlike block and a flexible block results in unique morphologies distinct from the conventional crystalline−amorphous block copolymers.[6−9]

The copolymers containing a rodlike block are called rod−coil block copolymers. Self-organization of the rod−coil copolymers is oftentimes carried out in solution so as to avoid the loss of chain rigidity caused by chemical degradation or conformational change at high temperature. However, the presence of a third component (solvent) during the self-assembly process adds additional complexity to the already complicated phenomena of rod−coil self-assembly because of multiple ordering transitions that occur with changing concentration of rods in solution. Of particular difference from that of a rodlike polymer from a semicrystalline polymer is the intermolecular ordering of the chains into nematic or two- dimensional liquid crystalline phases before they crystallize.[10,11] In the solution of rod−coil block copolymers, the liquid crystalline rod-rich microdomains phase-separates from the isotropic coil-rich microdomains, in which the rod blocks arrange in a smectic A or smectic C-like fashion whose rodlike backbones align normal or tilted with respect to the interfaces between rod and coil microdomains.[12−15] Upon further removal of solvent from the liquid crystalline state, subsequent crystallization of the rods must occur under the confined environment of the liquid crystalline microstructure.

Since the packing density of the rods in the crystalline phase is higher than that in the lyotropic liquid crystalline phase, the crystallization tends to frustrate the interfacial balance that has been established in the micro- and macroscopic structure of the liquid crystalline state. Little has been studied about the effect of such frustration by the prior liquid crystalline state on the morphology of the subsequent crystals.

Here we report a unique morphology of rod−coil block copolymer crystals grown from lyotropic liquid crystalline precursors. A rod−coil block copolymer with the coil block as a majority allowed monitoring the transformation of the intermediate lyotropic LC state to the crystalline state with evaporation of solvent. We demonstrate that the orientation, the shape, and the size of block copolymer crystals are closely related to the microstructure of the prior liquid crystalline states and that the rod−coil packing frustration plays a unique role in the formation of crystalline morphology of the microphase-separated copolymer. The results emphasize the importance of the intermediate liquid crystalline structure in understanding the morphology of copolymers which develops via multiple ordering transitions occurring with the change of concentration or temperature.

The rod−coil copolymer investigated is a diblock copolymer of poly(3-(triethoxysilyl)propylisocyanate) (PIC) ($M_{\mathrm{n}} = 23\,000$) and polystyrene (PS) ($M_{\mathrm{n}} = 39\,000$) with the polydispersity index of 1.25. The synthesis of the copolymer is described elsewhere.[16] The PIC is a stiff rodlike polymer, whose persistence length is known to be above 40 nm.[17,18] Toluene was chosen as a solvent of study because it can dissolve the copolymer without causing gelation over the entire range of concentration.

The liquid crystalline order of the PIC block was identified using wide-angle X-ray diffraction (XRD), polarized optical microscopy (POM), and atomic force microscopy (AFM) of the solution-cast copolymer films before they are completely dried. First, we monitored the intermolecular order of the PIC blocks changing during the late stage of solvent evaporation. The copolymer solution in toluene with a concentration of 5% was cast on a slide glass that is mountable in the XRD sample holder. The copolymer films solidified as the amount of the remaining solvent reached about 10−20% of the total weight. While varying with different samples, approximately 10−20% of the total sample weight was lost with further drying after the XRD measurement. XRD measurement run on these samples gave rise to sharp scattering peaks with q_n/q_1 ratios of $1{:}\sqrt{3}{:}2{:}\sqrt{7}{:}3$, as shown in Figure 1a. This corresponds to a two-dimensional hexagonal lattice of the rodlike PIC chains. The lattice parameter of the hexagonal columnar phase was ∼1.5 nm, while varying slightly with different samples, likely due to different amounts of residual solvent. Interestingly, as the samples were dried further under atmospheric conditions, the intensity of hexagonal order peaks decreased, and instead a new set of XRD peaks appeared (Figure 1a, curve B). The new XRD peaks include two peaks in the smaller angle region centered at *d* spacings of 1.7 and 1.1 nm. These are attributed to an oblique two-dimensional lattice resulting from the segregation of the bulky side groups from the rodlike backbones as solvent molecules continue to escape from the intermolecular space between PIC chains. Two-dimensional columnar phases with hexagonal and oblique lattices are known to occur in the rodlike polymers containing aliphatic side chains.[11,19] Several new peaks

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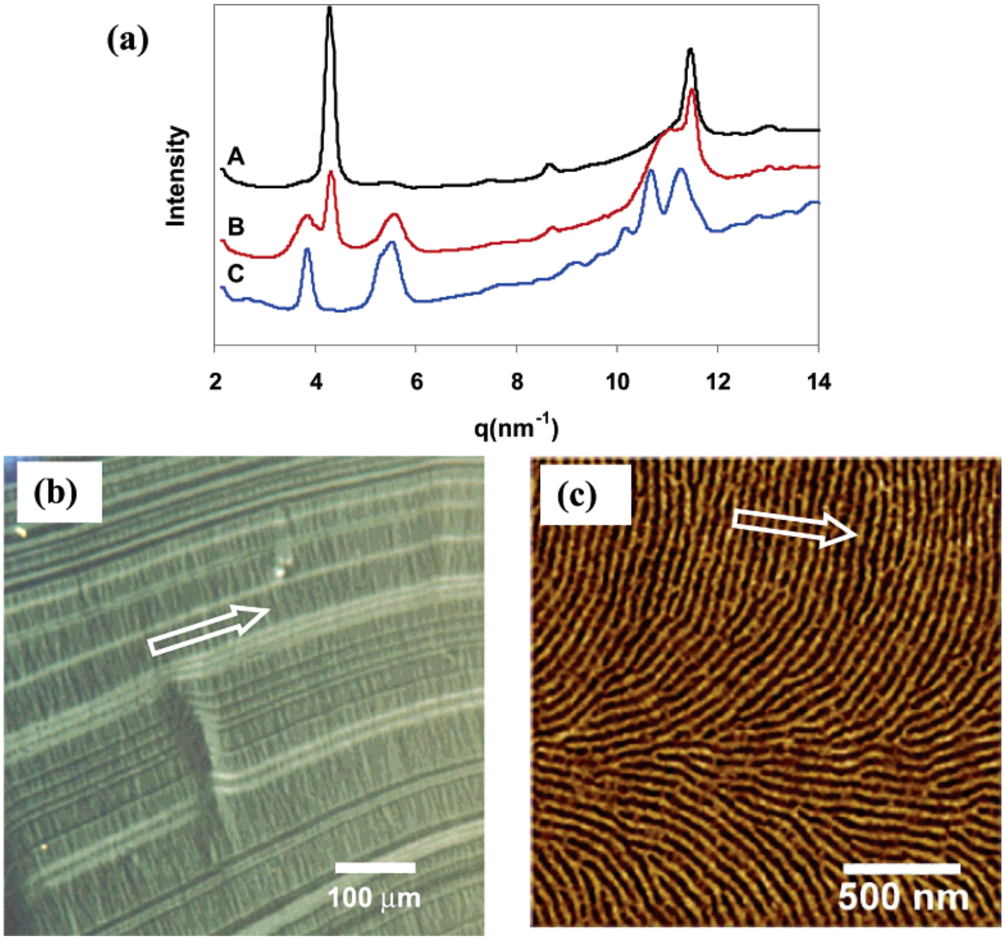

Figure 1. Liquid crystalline microstructure of PSPIC(39/23) captured in the presence of residual solvent: (a) XRD curves of a sample wet with toluene (A), then dried for 1 day in an ambient condition (B), and after a brief heat treatment at 90 °C for 2 min (C); (b) a POM image of a 200 micron thick film exhibiting domain wall patterns; (c) phase contrast AFM image of a wall region. Brighter domains correspond to PS regions. The arrow indicates the direction of solvent evaporation.

in the higher *q* range appeared in the fully dried sample, indicating the formation of 3-d crystals by the PIC chains. The hexagonal scattering peaks remained until the sample was heated above the glass transition temperature (77 °C) of the PS block that had been measured by DSC (see Supporting Information) (Figure 1a, curve C). The rubbery PS blocks above T_g must have allowed the relaxation of the hexagonal-ordered PIC blocks to a more stable oblique order.

The liquid crystalline nature of the copolymer was also revealed by POM and AFM images. Figure 1b shows the POM image often observed while the PSPIC(39/23) films are being dried. The particular sample exhibiting Figure 1b had a dry state thickness of about 100 μm. The banded textures indicate the formation of Neél domain walls over which the director orientations change.[20] Wall-to-wall distances are in the range from a few to 100 μm. AFM images of the surface of the solution-cast film revealed the microdomain morphology comprising the wall pattern. It shows that the copolymer microphase-separates to alternating stripes of PS and PIC microdomains, of which the layer normal in the Neél wall region is perpendicular to the direction of solvent evaporation, as reported previously.[21] The results shown in Figure 1 indicate that the transition from the hexagonal mesophase to the crystalline rods occurs near completion of solvent evaporation at which the copolymer has already microphase-separated into the liquid crystalline PIC and the isotropic PS microdomains.

The micro- and macroscopic structures of the liquid crystalline state become frozen in the samples with further drying under atmospheric conditions. The hexagonal order of the PIC chains persistent in the dry PSPIC sample can be accounted for by vitrification of PS regions prohibiting the formation of close-packed crystals of the PIC chains.

To see how crystallization of PIC chains proceeds further from the liquid crystalline microstructure, the copolymer sample was annealed under solvent-saturated atmosphere for a prolonged time. We prepared a 5% copolymer solution in toluene in a small crucible contained in a closed vessel, and the solvent was slowly evaporated until the sample lost apparent fluidity, which took about 3−5 days. Then the sample was annealed in a toluene-saturated atmosphere for 3 weeks followed by fracturing the crucible in liquid nitrogen to yield about 1 mm thick pieces of the copolymer films. Tapping mode AFM images of the surface of the resulting crystalline sample are shown in Figure 2, where many crystalline grains with multilayered, tapered geometries are uniformly distributed over the sample. The length of the grains in the direction of layer normal was in the range 0.5−1 μm, as estimated from the AFM images. In the low-magnification image shown in Figure 2c, the orientation of the crystal grains varies similarly to the director pattern in the Neél walls.[21−24] This suggests that the morphological structure in the crystalline state is templated by the microscopic and macroscopic structure of the prior liquid crystalline state. The region not showing the layered texture in the phase contrast AFM image has disordered dark and bright microdomains, most likely to be disordered aggregates of micelles formed by crystallization of the rod−coils.[25] The banded texture of the

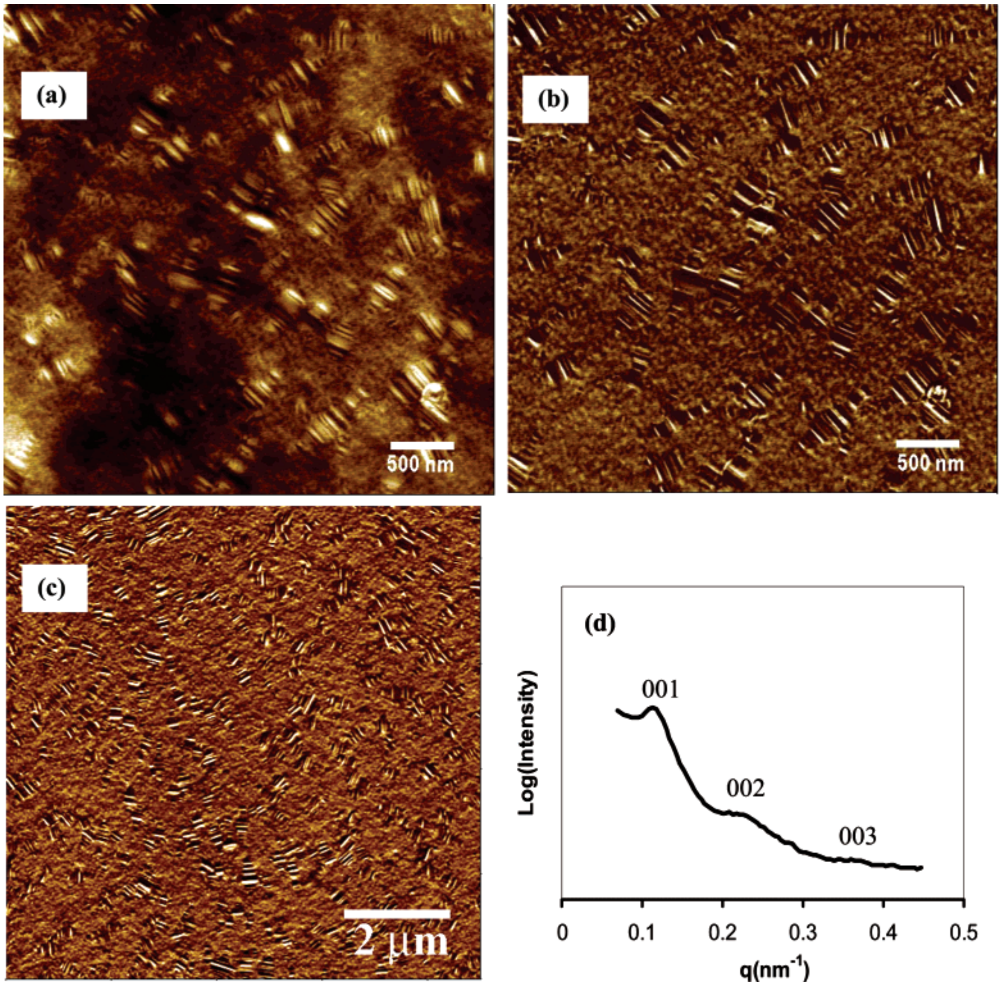

Figure 2. Tapered, multilayered crystals of the PSPIC(39/23) block copolymer grown from its lyotropic LC state: (a, b) height and phase contrast tapping mode AFM images; (c) phase contrast AFM image of the region showing Neél wall-like director pattern; (d) a SAXS profile of the sample. Background was not subtracted from the SAXS data.

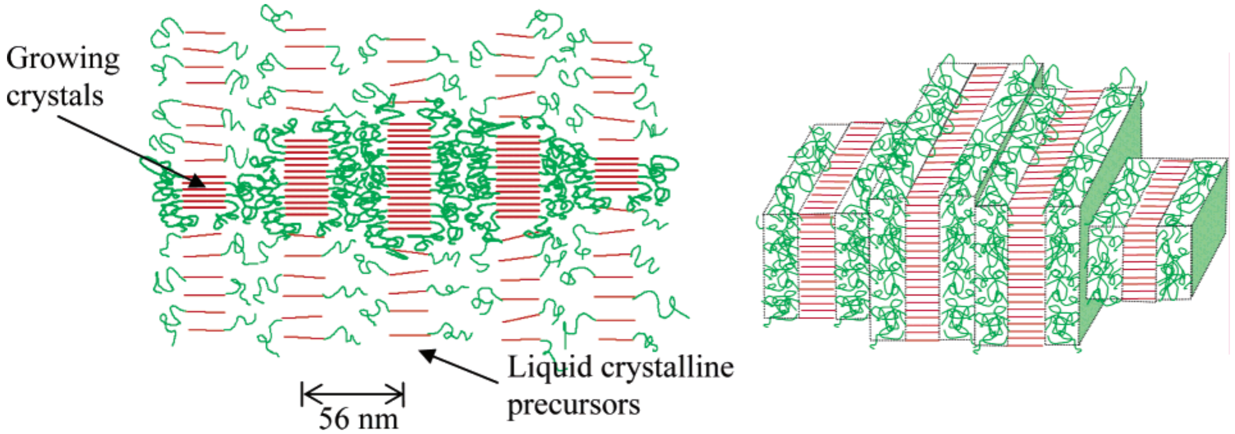

Figure 3. Schematic diagram for the crystallization of rod−coils from the liquid crystalline structure. The crystals can grow laterally within each layer, and new crystalline layers are added to the preformed ones in the direction of layer normal. A postulated 3-dimensional shape of a crystalline grain is shown on the right.

grainy crystals in the AFM image is likely to be indicative of alternating rod−coil layers. The layer periodicity appearing in the AFM image was ∼50 nm, varying significantly with the degree of tilt or elevation of each mutilayered grain from the surface. Attempted transmission electron microscopy (TEM) for microtomed sections did not yield useful information due to the damage caused by the microtoming process and the electron beam. Instead, synchrotron SAXS (Brookhaven National Lab, X27C) exhibited scattering peaks centered at $q = (4\pi \sin \theta)/\Lambda = 0.11$, 0.22, and 0.33 nm^{-1} (Figure 2d), evidently showing that the copolymer has a layered structure with a periodicity of about 56 nm. The broad higher order peaks suggest poor long-range order of layer stacking, consistent with the grainy crystal structure shown by the AFM image.

The orientation of the layered block copolymer crystals observed in the AFM image can be accounted for by the nucleation and growth mechanism under the influence of the lyotropic LC structure. The growth of the crystals is schematically illustrated in Figure 3. We postulate that the tapered geometry observed over many crystals is caused by the rod−coil packing frustration, which occurs due to disparate interfacial areas per chain of the rod and coil blocks at the rod−coil junction when rod blocks are closely packed.[13,15] PIC crystals are nucleated within the liquid crystalline microdomain, and the crystallization propagates in the lateral direction of each PIC layer. As the rods crystallize in the PIC domains, volume shrinkage must occur laterally, whereas the PS domains shrink isotropically. Approximate change in the cross-sectional areas upon transition from the hexagonal packing to oblique packing of the rodlike chains can be estimated using a 120° rhombus with a side of 1.5 nm for the hexagonal and a 120° parallelogram with $a = 1.7$ nm, $b = 1.1$ nm for the oblique. The resulting cross-sectional area of the hexagonal unit cell, 1.9 nm^2, is about 20% larger than that of the oblique (1.6 nm^2). Abrupt decrease of interfacial area per rod at the rod−coil junctions increases repulsive interactions between crowded coil blocks, limiting the number of laterally packed rod chains in each crystal. Here the coils at both edges of a crystallized layer have greater conformational freedom[12,14] and therefore are less available for the crystallization of the adjacent layers in the longitudinal direction. As multiple layers stacked over one by one, the adjacent crystalline layer grows laterally smaller than its previous layer, resulting in the tapered morphology. The tapering helps to expose more coils to the edges, effectively relieving the packing stress caused by the rod−coil packing frustration. Although the 3-dimensional structure of the crystals is still to be investigated, the anisotropic nature of the oblique lattice determined from the XRD data (Figure 1) and the elevated surface of the crystals in the height contrast AFM image (Figure 2a) suggest the morphology of stacked prisms, as shown in Figure 3.

In conclusion, we report that the morphology of a solution-cast rod−coil block copolymer varies with different pathways of crystallization from its microphase-separated liquid crystalline precursor. The orientation, shape, and nanoscopic structure of the crystals are guided by the microstructure of the prior liquid crystalline state. We suggest that the formation of tapered, multilayered rod−coil crystals by solvent annealing is caused by the rod−coil packing frustration occurring during the transition from the microphase-separated, liquid crystalline state to the microphase-separated, crystalline state. The result indicates that the self-assembled structure of the system showing multiple ordering transitions is greatly influenced by the structure of intermediate ordered states and processing conditions.

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Supporting Information Available: DSC thermogram of the PSPIC(39/23) block copolymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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