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Anisotropic Micellar Nanoobjects from Reactive Liquid Crystalline Rod−Coil Diblock Copolymers

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Self-assembly of anisotropic particles can provide novel structures with intriguing properties which are not possible to obtain from spherical particles. Because of anisotropy, their self-organization results in liquid crystalline phases[1] or non-fcc lattices. Viruses (0 dimensional), or fibril (1d), or sheetlike (2d) mineral colloids are long-known natural particulate systems. Synthetic methods for nonspherical nanocrystals of minerals or metals have become quite sophisticated in recent years.[2,3] Their organic analogues with sizes up to several nanometers are synthesized by supramolecular assembly or polymerization of small molecular compounds. For example, nanometer-sized nonspherical objects were obtained from directional hydrogen bonding of organic molecules.[4,5] Disklike aromatic nanoparticles were synthesized from polyarylene dendrimers.[6,7] These organic particles offer rich chemistry of functional groups and excellent processability in addition to the anisotropic physical properties.

Compared with the supramolecular assembly of small molecules, the self-assembly of polymers with appropriate architectures gives rise to the anisotropic objects of much lager sizes.[8,9] In particular, microphase separation or micellization of block copolymers offers dimensions up to a few hundred nanometers, and their morphological structures can be adjusted by changing the conformational properties of the constituting blocks as well as their chemical structures and composition.[10,11] The orientation and the shape of microdomains over a large area can be controlled by applying various external constraints or fields to the self-assembling block copolymer systems.[12]

In order for the micellar objects, obtained from the block copolymers that are asymmetric in composition or those dissolved in solvents selective to one of the constituting blocks, to form nonspherical shape and exhibit anisotropic properties, the organization of polymer chains constituting the micelles needs to occur in a highly directional manner. Precisely this type of phase segregation phenomenon occurs in rod−coil block copolymers, which consist of macromolecular blocks of a rigid rod and a flexible coil.[13−15]

For the synthesis of shape persistent objects, one of the microdomains can be selectively cross-linked via reaction of residual vinyl groups[16] or sol−gel chemistry.[17,18] Two-dimensional persistent objects have been synthesized by Zubarev et al.[16] via lateral cross-linking within lamellar microdomains formed by olefin-containing triblock rod−coil oligomers, in which the molecular weight and the shape of the cross-linked objects varied with the reaction time due to the continuity of 2-D lamellar domains, suggesting the need for isolated reactive microdomains to attain regular shapes and sizes of the anisotropic objects.

Here we report the synthesis of anisotropic micellar nanoobjects via self-assembly of rod−coil diblock copolymers with a composition having a large coil-to-rod weight ratio and with rod blocks containing *reactive* side groups. Microphase separation of the two blocks and crystallization of the rod blocks occur as solvent evaporates from the copolymer solution, leading to prism-like rod domains that order into an overall smectic pattern in the coil matrix. Thermal cross-linking of the rod blocks within each micellar nanodomain permanently fixes the individual micellar nanoobjects. The result presents a novel method to form anisotropic organic particles with potential multifacial surface characteristics.

The simplest theoretical model for the self-assembled morphology of rod−coil block copolymers with a minority rod block in coil-selective solvents is the so-called "hockey puck" micellar structure,[19] in which the coil chains emanate as hemispherical bundles from the two end faces of rod bundles surrounding a disklike rod center. The disparate interfacial areas of the two blocks may induce rod tilt and/or interdigitation.[19,20] Needle and platelike morphologies, which result from rod tilt in the micellar regime, have also been predicted theoretically.[21] Although these models have been used to account for many new morphologies of rod−coil block copolymers, none of these anisotropic micellar objects have been directly observed.[22] Moreover, crystallization of the rods, which can occur in many rodlike polymer systems,[23] has not been taken into account in those theoretical models although it may promote the formation of a prism-like microdomain structure rather than disks or cylinders.[21]

The polymer investigated in this work is a block copolymer of poly(3-(triethoxysilyl)propyl isocyanate) (PIC) (M_n = 23K) and polystyrene (PS) (M_n = 200K) with $M_w/M_n = 1.2$. Styrene was polymerized with *n*-butyllithium in THF at −78 °C, followed by the successive addition of 1,1-diphenylethene and 3-(triethoxysilyl)propyl isocyanate.[24] The large coil-to-rod weight ratio ($f_{PS}/f_{PIC} \sim 9$) was chosen in order to maximize the rod−coil packing frustration. A repeating unit of the polyisocyanate backbone consists of a carbonyl and a nitrogen atom, in which steric interaction between the carbonyl group and the side groups attached to the nitrogen atom leads to a stiff helical chain whose persistence length is over 40 nm.[25,26] The polyisocyanate employed here contains bulky 3-(triethoxysilyl)propyl groups as side groups[27] and exhibits melting transitions at 106 and 127 °C in its homopolymer.[28] In PIC/PS block copolymers with high PIC content, the melting transitions were usually observed to be similar to those of the homo-PIC, and the T_g of PS blocks ranged from 75 to 100 °C.[29] The melting points for the 23K PIC block studied here are not clearly identified in DSC thermograms, most likely due to the small weight fraction of the PIC. However, the XRD data discussed below indicate the interchain ordering of the PIC blocks in PIC(23K)/PS(200K) is essentially the same as those with other rod−coil compositions. The T_g of the PS block (200K) was observed near 100 °C.

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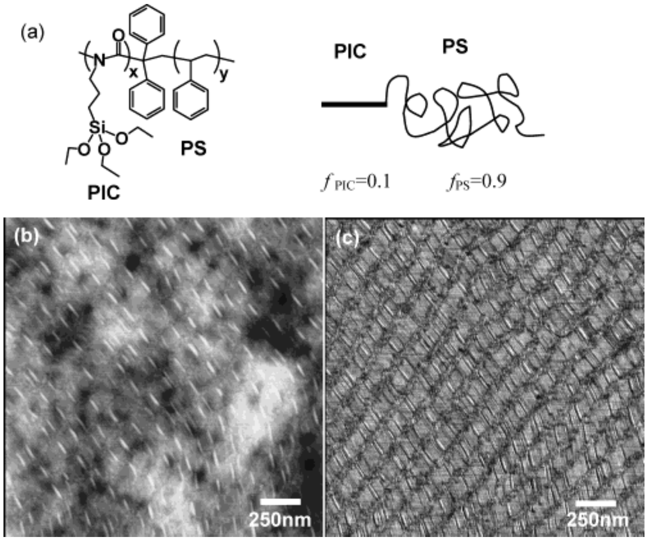

Figure 1. Chemical structure and a schematic drawing of an asymmetric rod–coil diblock copolymer, PIC(23K)/PS(200K), and AFM images of smectic ordered anisotropic features in THF-cast film: (b) height and (c) phse contrast.

Tapping mode atomic force microscope (AFM) images (Figure 1b,c) of THF-cast copolymer films show smectic-ordered anisotropic PIC microdomains. This morphology was observed from samples with range of film thickness (~5–100 μm).[30] No significant change occurred to the initial pattern upon annealing of the films in a THF-saturated atmosphere for a prolonged time (over a week). The rod domains are 80–120 nm long in the AFM height contrast images. Because a single helical PIC chain with a molecular weight of 23K is only about 20 nm in length and its diameter is smaller than 2 nm, the large objects must be bundles of many PIC chains. The smectic-like ordering of these objects is especially evident in the phase contrast image (Figure 1c). The layer structure is a likely indication of a nonuniform density or of a different conformation of the PS chains due to differences in swelling of the PS before complete solvent evaporation. No lateral positional order is observed between the PIC domains within a layer, analogous to small molecule smectic liquid crystals. In a low-magnification image (see Supporting Information), multiple domains differing by the orientations of the PIC domains are observed. The layer periodicity varies in the range 130–170 nm over a large sample area due to variation of the smectic C-like tilt angles of the PIC domains (5–35° from the layer normal).

Wide-angle X-ray diffraction (XRD) at room temperature for a dry PIC(23K)/PS(200K) block copolymer film gave two relatively sharp Bragg peaks in the low-angle region, corresponding to *d* spacings of 1.7 and 1.1 nm, respectively.[31] These can be attributed to an oblique 2-dimensional crystal structure formed by the PIC blocks, where the bulky side groups occupy spaces between the laterally packed PIC backbones. Similar ordering behavior is also observed in other types of rodlike polymers with flexible side groups.[32] The broad amorphous halo in the XRD data is caused by scattering from the majority polystyrene block (see Supporting Information).

The formation of the smectic ordered anisotropic objects was also observed in the films cast from chloroform and methylene chloride. Rapid evaporation of very dilute solutions with polymer concentrations below 0.5% did not yield the structure. It is clear that the formation of the micellar morphologies is related to the association of the copolymers as micellar or liquid crystalline state in solution. Studies on the solution behavior of this copolymer using dynamic light scattering method as a function of concentration and solvent are underway.

The PIC domain can be cross-linked thermally via condensation of triethoxysilyl side groups. The copolymer films were therefore heated for 1–3 days at 120–130 °C. At this temperature, the rod directors remain parallel to each other due to the liquid crystalline order. Since the rod microdomains are well-separated from each other due to the high molecular weight PS blocks, cross-linking across different microdomains does not take place. XRD of the heat-treated film shows a general loss of PIC crystalline order (see Supporting Information) with a new broad peak centered near 0.9 nm evident. This can be attributed to the shrinkage caused by Si–O condensation and the loss of long-range interchain order of the PIC.

The heat-treated PIC(23K)/PS(200K) samples were insoluble in THF but could be dissolved readily in toluene. A 0.02% solution of the cross-linked objects in toluene was deposited onto a carbon substrate for electron microscopy. The TEM images (Figure 2a,b) for sufficiently thin films (of about monolayer of the objects) indeed show prism-like nanoobjects. These objects were not observed in the films cast directly from the toluene solution of the PICPS copolymer. Since the contrast in the unstained bright field TEM image comes from the density and thickness difference between the PIC and PS domains, mainly the PIC rod centers appear dark in Figure 2a. By rapidly evaporating the toluene, the specimens in which the top of the nanoobjects were not covered with aggregated polystyrene chains could be produced. By carefully staining such nanoobjects with ruthenium oxide so as not to over-stain the whole part, we could distinguish the light, unstained rod center from the surrounding dark, RuO_4-statined PS corona in individual objects in the TEM image (Figure 2b). A schematic model of the rod–coil nanoobject is shown in Figure 3. These results clearly present the unique micellar organization of rod–coil block copolymers. To the best of our knowledge, this is the first result showing the theoretically predicted micellar morphology of the rod–coil block copolymer.[19,21]

We also obtained cross-sectional TEM images of a 50 μm thick film to see whether the nanoobjects are formed in the interior of the film (see Supporting Information). Since the thickness of the microtome section (less than 80 nm) is smaller than the periodicity of the smectic layers formed by the copolymers, upon microtoming, the nanoobjects appear less ordered. The variable object orientation gives rise to size and shape variation in the TEM images due to the projections of the objects along the electron beam direction. Nonetheless, the anisotropic nanoobjects are clearly evident in the cross-sectional TEM image, indicating that they are formed as a consequence of the rod ordering and microphase separation in the bulk sample.

The height of the objects was estimated by AFM to be 10–20 nm for a dilute solution deposited on a mica sheet (see Supporting Information). Considering that the AFM estimates the height of the objects covered with PS chains lying on the substrate plane with various possible orientations, the rod blocks can be depicted as thin prisms with thickness much smaller than 20 nm.

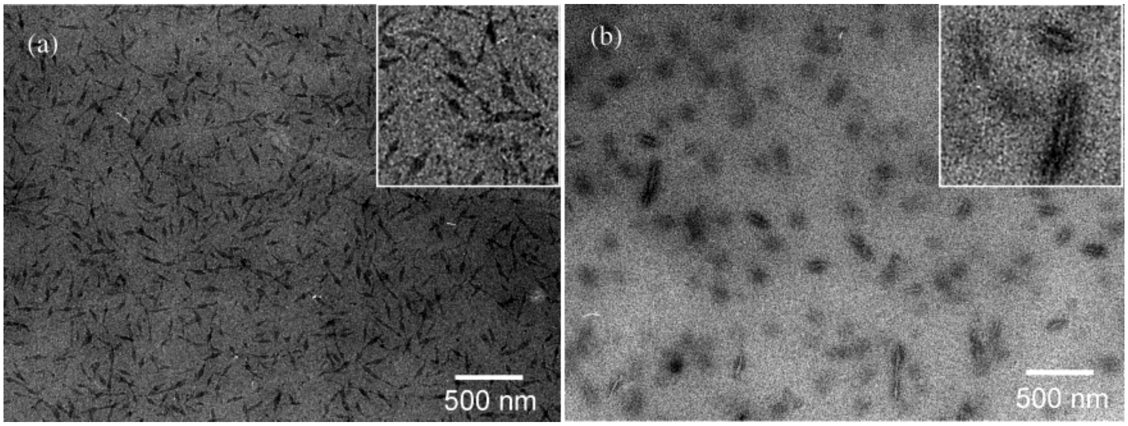

Figure 2. Bright field TEM images of the nanoobjects isolated on a carbon support film: (a) unstained, dark PIC prism; (b) light PIC prisms surrounded by dark, RuO_4-stained PS regions. Insets are high-magnification images for areas of 600 × 600 nm^2.

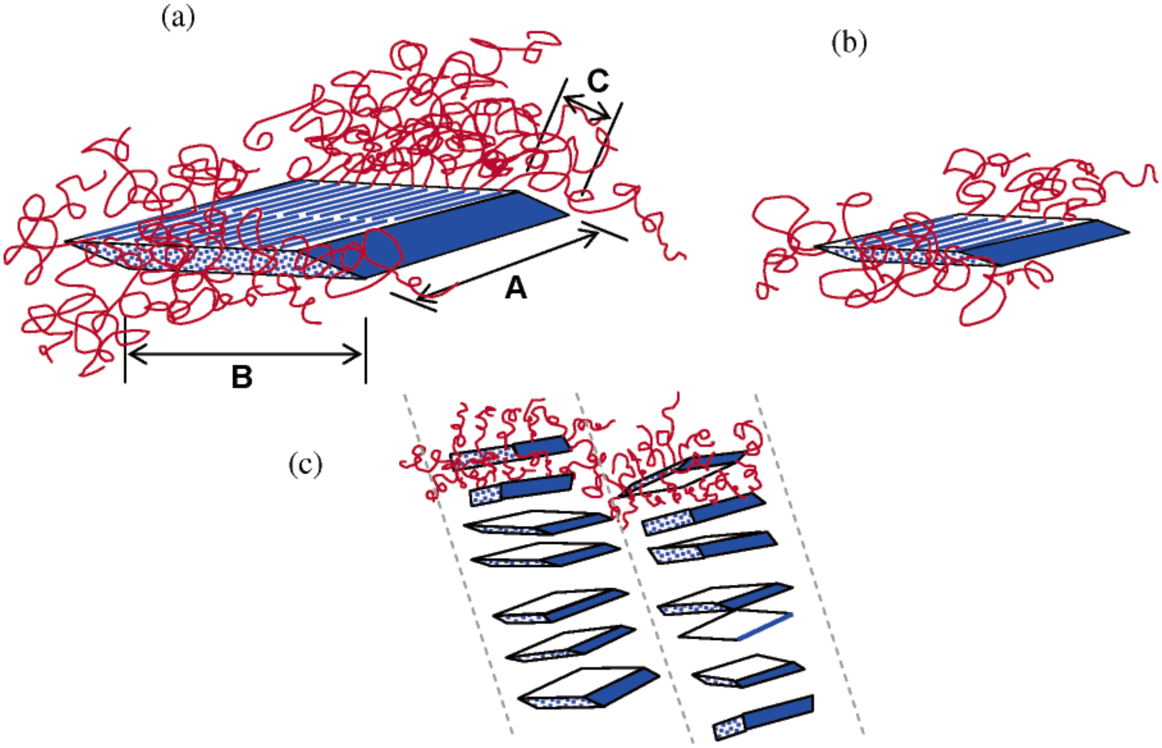

Figure 3. Schematic packing models proposed for the nanoobjects formed from PIC(23K)/PS(200K). In (a) and (b) are shown bilayered and interdigitated packing of the rods within individual micellar objects. In (c) is illustrated the smectic ordering of the anisotropic micelles.

Most objects in the unstained TEM image (Figure 2a) have approximately a parallelogram shape with an acute angle of 25−45° between adjacent sides. Close examination of TEM images of the objects reveals that at least one side of many parallelogram objects is about 45 ± 5 nm. This can be understood using schematic models for the rod packing as illustrated in Figure 3. Since the length of the helical PIC rods is about 20 nm, which can be estimated using its degree of polymerization (∼100) and the projected repeating unit length(∼0.2 nm) of the helical PIC chain,[23] the objects with a side (A) of 45 nm are most likely have a tilted bilayer structure as shown in Figure 3a. While the bilayer packing occurs in the majority of the objects, their geometry can be varied by an alternative interdigitated packing of rods shown in Figure 3b and by the variation of the lateral (B) and thickness (C) dimensions as indicated in Figure 3a. The estimated average aggregation number (N) of the bilayered objects is about 300,[33] corresponding to a molecular weight of $\sim 7 \times 10^7$ g/mol. The smectic ordering of the prisms in the solution cast films is illustrated in Figure 3c. The somewhat irregular orientation of the prisms and the concomitant nonuniform distribution of PS chains probably lead to the loss of lateral positional order between the objects within a layer in the AFM images (Figure 1).

The cross-linking of reactive rodlike blocks in the micellar regime presented here offers a new method to create particles with nonspherical shape, within which the molecular axes are oriented uniaxially with respect to the geometry of the particles. The uniform orientation of rodlike chains within a single particle of anisotropic shape may give new properties as they self-assemble into a periodic structure. Although not investigated here, the anisotropic objects such as those in Figure 3 promise multifacial surface characteristics which may cause nonuniform distribution of solvent molecules around the particles in their solution and potentially yield new lyotropic liquid crystalline materials. These particles can be also used for polymeric nanocomposites.[34] Considering that many rodlike polymers exhibit interesting optoelectronic properties,[35,36] our approach to fabricate the anisotropic nanoobjects utilizing the unique packing behavior of liquid crystalline rod−coil block copolymers, and the incorporated chemical reactivity may open opportunities to create novel functional materials.

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Supporting Information Available: XRD data, large area AFM image of Figure 1, AFM height image of cured objects on mica surface, and cross-sectional TEM images of the cured copolymer films. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) In PIC(23K)/PS(39K) which has a rod fraction of 37%, we observed the glass transition of PS block near 77 °C, two endothermic peaks at 102 and 128 °C and a broad exothermic curve for cross-linking reaction above the second melting through 200 °C.
(30) The films were cast from solution in THF with concentrations of 5−15%.
(31) In the presence of a small amount of solvent, additional peaks corresponding to hexagonal order are also observed in the solution-cast PIC−PS samples. See: Park, J. W.; Thomas, E. L. *Adv. Mater.* **2003**, *15*, 585.
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(33) The aggregation number (N) was estimated for a postulated prism with the sides $A = 45$, $B = 50$, and $C = 10$ nm and the angles 35° between A and B and 60° between B and C, which were obtained from the analysis of TEM and AFM images. Assuming the PIC density is 1.0, N can be obtained by dividing the weight of the PIC prism with that of a single PIC chain with M_w of 23 000 g/mol.
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