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Liquid Crystalline Ordering in the Self-Assembled Monolayers of Tethered Rodlike Polymers

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Self-assembled monolayers (SAM), made from a thin molecular film of chemical or biological moieties either in small molecular or polymeric forms, have become essential for tailoring surface properties.[1−3] SAMs with uni- or bidirectional anisotropy may be useful for templated synthesis of organic or inorganic crystals although it is not simple to obtain an anisotropic surface over a practically large area of the surface. This is because the molecules constituting the SAM organize as their long molecular axes oriented normal to the surface to yield structures with rotational symmetry or of short-range order. If rodlike polymers or oligomers with extended chain conformation, such as peptides, are employed, anisotropic SAMs may be obtained by utilizing their tendency to adsorb with their long molecular axes planar to the surface.[4−6] Yet it is desired to find effective methods to control adsorption and ordering of the rodlike chains to produce monomolecular-thick films with uniform chain orientation over a large area. Here we show that rodlike polymer chains as their ends tethered to the surface can be organized into highly oriented, anisotropic SAMs on the substrate surface via lyotropic liquid crystalline ordering in the monolayer.

Surface-tethered polymers, either rod-like or coil-like, are usually synthesized by polymerization from the SAM of the corresponding initiator.[2,7,8] The resulting densely grafted polymer chains are elongated normal to the surface to form polymer brushes. At grafting densities lower than the brush regime, the coils collapse to mushroomlike conformation.[9] In contrast, the rodlike chains maintain their extended chain conformation and instead acquire more freedom to vary the polar anchoring angle (θ) at a lower grafting density (Figure 1a). If θ is unrestricted, the rods would form an isotropic state by random orientation as shown in Figure 1b. If the rods are confined in thin films with a thickness much smaller than their length, the chains would orient planar to the surface with θ approaching 90°. If this is the case, effective concentration of the rods at the surface become sufficiently high for the rods to have liquid crystalline or crystalline order (Figure 1c). This means that a long-range anisotropic monolayer with a thickness of a single chain may be derived from rodlike polymers tethered to solid surfaces at moderate grafting densities.

The polymers investigated for the formation of the tethered rods are block copolymers of poly(*n*-hexylisocyanate) (PHIC) and poly(2-vinylpyridine) (P2VP) whose structures are shown in Figure 1. PHIC is a helical rodlike polymer with its persistence length over 40 nm.[10] P2VP chains are known to adsorb strongly to the polar surface of flat substrates or colloidal particles.[11] Using the methods reported previously,[12,13] we synthesized two triblock copolymers, PHIC$_{331}$-*b*-P2VP$_{342}$-*b*-PHIC$_{331}$ and PHIC$_{165}$-*b*-P2VP$_{172}$-*b*-PHIC$_{165}$, and a diblock copolymer, PHIC$_{661}$-*b*-P2VP$_{343}$, with their polydispersity indices of about 1.1 (Supporting Information). We anticipated that adsorption of P2VP blocks of these rod−coil block copolymers to the substrate surface would result in end-tethered rodlike chains as schematically shown in Figure 1.

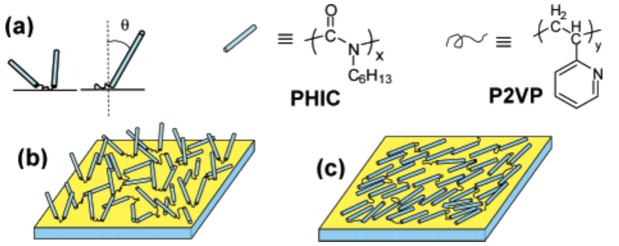

Figure 1. Schematic drawings and chemical structure of the rodlike PHIC chains tethered to the surface by adsorption of P2VP coils: (a) anchoring of rod-coils with di- or triblock architecture on the surface; (b) an isotropic state and (c) a nematic state of tethered rodlike chains at a grafting density lower than the brush regime.

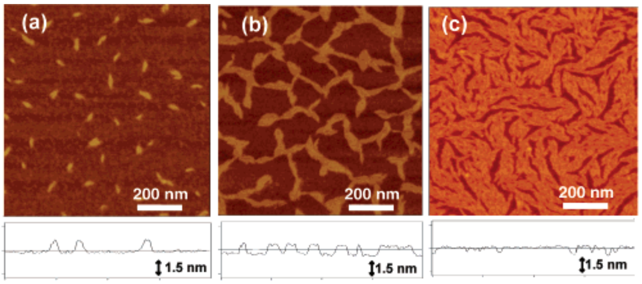

Figure 2. Height contrast AFM images of dry rodlike PHIC chains tethered onto mica through adsorption of P2VP coils. The samples were obtained by the dip-coating of mica plates in toluene solutions of PHIC$_{165}$-*b*-P2VP$_{172}$-*b*-PHIC$_{165}$ with concentrations of (a) 0.001, (b) 0.05, and (c) 0.1 w/v%. Height profiles are given underneath the images.

The block copolymers were grafted to freshly cleaved mica plates by dip-coating in toluene solution. Excess unadsorbed polymers were removed by repeated rinsing with toluene. Grafting density was adjusted by varying the concentrations of dipping solutions in the range of 0.001∼0.5%. Tapping mode atomic force microscope (AFM) images of the PHIC$_{165}$-*b*-P2VP$_{172}$-*b*-PHIC$_{165}$ coatings on mica are shown in Figure 2. Similar morphologies were obtained from all three copolymers investigated. From a low concentration of the dipping solution (Figure 2a), discrete films with the lateral dimension close to the length of an extended PHIC$_{165}$ chain [repeating unit length (∼0.2 nm) multiplied by degree of polymerization (165) ≈ 33 nm] and a thickness of about 1.2∼1.4 nm were obtained as uniformly distributed over the surface. Coverage of the surface increased with increasing concentration of the dipping solution (Figure 2b), and full surface coverage was attained near 0.1% (Figure 2c). The thickness of monomolecular P2VP films as adsorbed to mica is known to be 3∼4 Å.[14] The diameter of a PHIC chain in solution is known to be 1.6 nm which becomes about 1 nm when measured for a dry Langmuir−Blodgett film.[15] AFM-estimated height for the discrete films in Figure 2 panels a and b

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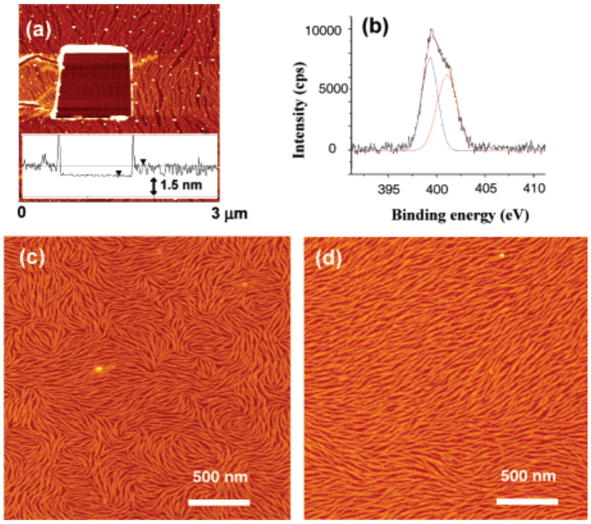

Figure 3. Tapping mode AFM images and XPS data of PHIC$_{331}$-*b*-P2VP$_{342}$-*b*-PHIC$_{331}$ monolayer after annealing under solvent vapor. (a) THF- vapor-annealed monolayer with a central region scratched off by a contact mode AFM for thickness measurement. Inset is a height profile. (b) XPS signal of the N(1s) peak measured for the monolayer on mica surface. Panels c and d show the height contrast images after annealing for 1 h under toluene and THF vapor, respectively.

almost corresponds to the sum of the thicknesses known for the P2VP and PHIC chains. A control experiment with a PHIC homopolymer did not yield the monolayer. Adsorption of the rod blocks to the surface instead of the coils would yield different morphologies as reported previously.[16,17] The structure of the film at full surface coverage was characterized further by AFM and X-ray photoelectron spectroscopy (XPS). The thickness was about 1.4 nm when measured by AFM after a film was partially scratched off using a contact mode AFM tip (Figure 3a). XPS peak of N(1s) was deconvolved to two peaks centered at 399.5 and 401.3 eV (Figure 3b), which correspond to the amide group of PHIC and the mica-adsorbed pyridine, respectively.[18] The binding energy for the N(1s) at 401.3 eV is close to the value for mica-adsorbed pyridine, known to be about 2.3 eV higher than that (398.6 eV) of free pyridine molecules.[14] The strong contribution of the peak near 401 eV indicates that the majority of pyridine groups are adsorbed to the mica surface. All data show consistently that the monolayer comprises PHIC chains that are tethered to the surface through mica-adsorbed P2VP chains.

Liquid crystalline state of the tethered PHIC chains was accessed by exposing the monolayer to solvent vapor. An AFM image of a toluene vapor-annealed monolayer is shown in Figure 3c. Nanoscopic pattern in the height contrast image is attributed to lateral crystallization of planar PHIC chains on drying. The image contains locally ordered domains with various types of defects reminiscent of lyotropic nematic liquid crystalline ordering in the solvent-swollen state. The defect patterns persisted for long annealing times (>10 h) under toluene vapor, indicating that reorganization of the copolymers was effectively suppressed because of strong anchoring of P2VP chains onto mica surface.

In contrast, annealing under THF vapor yielded monolayers of enhanced orientational order with considerably low densities of nematic defects (Figure 3d). Oftentimes unidirectional nematic domains occurred over an area of 10 × 10 μm^2. Dewetting of the monolayer was not observed. We presume that reorganization of PHICs was facilitated by partial segmental desorption of P2VP chains. It is unlikely that the alignment of the long polymer chains was driven by any directional force of drying because the evaporation of solvent occurred from only a few-nanometer-thick monolayer swollen with the solvent.

An approximate grafting density of planar PHIC blocks in the liquid crystalline monolayer of PHIC$_{331}$-*b*-P2VP$_{342}$-*b*-PHIC$_{331}$ was estimated to be 0.01 nm^{-2} assuming the area occupied by a single rod to be the rod diameter (∼1.6 nm) multiplied by its length (∼66 nm). The nematic ordering of the rods at this low grafting density can occur only when they orient planar to the surface. If the chains of the same grafting density stand vertical, it would give a concentration of ∼1% in the solvent-swollen layer as estimated assuming the thickness of the layer is close to the length of a rod, which would be far less than the known concentration range for PHIC solutions to form a lyotropic nematic state.[19]

In conclusion, we have shown that tethering rodlike polymers onto solid surfaces by their chain ends with a moderate grafting density can lead to a liquid crystalline monolayer of planar-oriented rods. The approach to the liquid cryalline SAMs demonstrated here may be utilized in designing well-ordered monolayers of rodlike polymers with various functionalities.

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Supporting Information Available: Synthetic procedure, NMR, and GPC data of the copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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