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A Surface-Reactive Rod-Coil Diblock Copolymer: Nano- and Micropatterned Polymer Brushes

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Polymers tethered onto surfaces have attracted attention because of their potential uses in many surface-based technologies such as switchable membranes, sensors, cell growth control, or biomimetic materials.[1−5] The bound state of the polymer chains gives thermal and solvent stability in various environments and processing conditions, which can be essential for certain applications. Employing block copolymer structures, which are composed of macromolecular blocks of two or more chemically different monomer units one of which is preferentially adsorbed to the surface, to create polymer brushes offers the ability to tailor surface morphologies at the mesoscopic length scale because of the unique feature dimensions and densities obtainable from block copolymer self-assembly.[6−8] Additionally, combining the self-assembly properties of block copolymers with the current microlithographic techniques will permit a new type of hierarchical surface architecture and properties. We report here a novel approach using a rod-coil diblock copolymer, which consists of a flexible coil and a rigid rod block,[9−13] to synthesize polymer brushes. Using a monomer containing a surface-reactive group for building the rod block, which can anchor to the surface with an in-plane fashion, allows multiple covalent bond formation between a single rod and a surface. This particular structure of the block copolymer gives rise to nanopatterned block copolymer monolayers under various processing conditions such as solution-based immersion coating and solid-state contact printing. The reactivity of the rod-coils in the solid state allows microcontact printing of the polymers directly onto the silicon-based substrates, which is unprecedented.

The rod-coil system of study is a block copolymer of styrene (PS) and 3-(triethoxysilyl)-propylisocyanate (PIC) as shown in Figure 1. The PIC is one of the rodlike helical polymers,[13,14] in which the triethoxysilyl side groups have reactivity to oxidized silicon wafers or to quartz.[15] Figure 1 also describes schematically the geometry of a single rod-coil adsorbed on the surface. The rod has an extended conformation so that the reactive side groups can readily access the resident hydroxyl groups on the substrate surface. For the synthesis of the block copolymers, n-BuLi initiated polystyrene anions were prepared in THF at −78 °C and reacted with 1,1′-diphenylethene before addition of 3-(triethoxysilyl)-propylisocyanate.[16] The molecular weight of the block copolymer, which was mainly used in this study, is $M_n = 62\,000$ with the rod block of 23 000 ($M_w/M_n = 1.25$).

The rod-coil block copolymer brushes can be prepared through three very simple methods: immersion, casting, or contact coating. In the first method, silicon wafers are immersed in the block copolymer toluene solutions with concentrations of 10−500 mg/mL at least for 3 h at room temperature followed by repeated rinsing and ultrasonic washing with toluene. This is analogous to the typical silanization procedure for silica-containing substrates.[15,17,18] Instead of immersion, films can be cast on the substrates and subsequent washing in toluene produces the coatings of the same quality as obtained by the immersion method. The polymer brushes can also be prepared via contact coating using a cross-linked poly(dimethylsiloxane) (PDMS) stamp, on which a film of the rod-coil is cast or pasted from about 1% solution in toluene and then dried briefly. In all cases, any physically adsorbed excess block copolymers are removed by washing with a good solvent for both blocks such as toluene, whereas chemically attached block copolymer monolayers are intact even after the harsh ultrasonic washing. These coatings can be further cured by heating over 120 °C, at which reaction of free triethoxysilyl groups can take place in the absence of solvent.

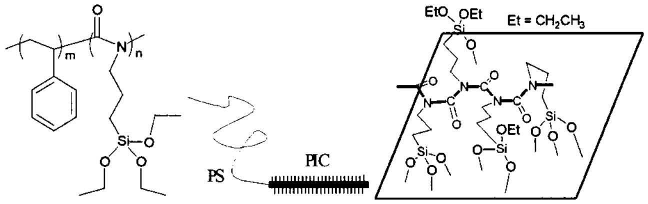

Figure 1. The structure of the block copolymer (left), schematic drawings showing a rod-coil diblock with a reactive hairy rod (center), and a magnified view of the Si−O linkages between a rod and a surface (right). Unlabeled lines from the oxygen atoms designate the bonds to the Si substrate. Many linkages exist between a rod and the substrate because the number of triethoxysilyl groups in a rod is equal to the degree of polymerization of the PIC rod.

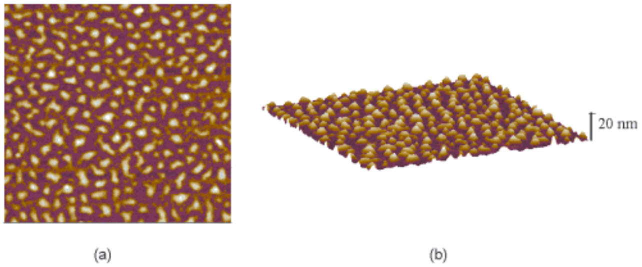

Figure 2. Tapping mode AFM height images for the rod-coil brush prepared on Si wafers immersion-coated from block copolymer solution in toluene (300 mg/mL): (a) plane view and (b) side view (1.0 × 1.0 μm^2).

Tapping mode atomic force microscopy (AFM) of immersion-coated samples reveals the mound patterns as shown in Figure 2. Similar patterns were obtained for the immersion-coated samples for a wide range of block copolymer concentrations. Although the mounds do not exhibit long-range order, Fourier transforms of the image resulted in a broad concentric ring, which corresponds to an average spacing of about 80−90 nm between the elevated domains. The mounds of the heat-treated samples had, on average, a height of 3−5 nm and a diameter of 30−45 nm as estimated from AFM images. Ellipsometry also gave an average film thickness similar to the AFM height values. The base layer was less than 1 nm thick.[19] It is unlikely that the PIC rods form mounds and PS chains stretch over the hydrophilic wafer surface forming a very thin layer. Block copolymers adsorbed in this way would be easily washed off by ultrasonication. Rather we expect the rods to covalently attach to

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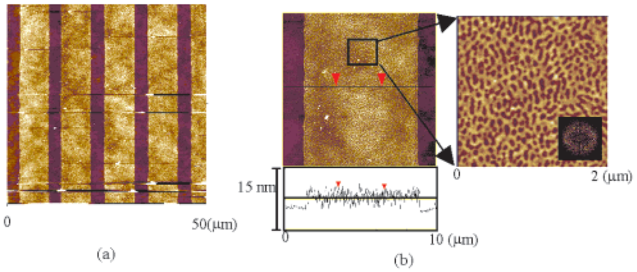

Figure 3. AFM height images of the rod-coil brush patterns prepared by contact printing: (a) $50 \times 50\ \mu m^2$ and (b) $10 \times 10\ \mu m^2$. In part b are shown a height profile and a magnified area ($2 \times 2\ \mu m^2$) with an inset showing the Fourier transformed image.

the surface and the PS blocks to form the mounds. This notion is confirmed by glancing angle X-ray photoelectron spectroscopy (XPS). The ratio of the PIC carbonyl carbon to the total carbon peak intensity was significantly reduced by a factor of about 40% as the takeoff angle was changed from 0° to 70°, implying that the rod backbones are located lower down in the film than the remaining hydrocarbon residues, mainly, PS blocks.

Monomeric triethoxysilyl groups are known to give different coating thicknesses with various immersion times due to intermolecular reaction.[15,18] However, this was not observed for our block copolymer. The size and height of mounds of the sample that was immersion-coated in a solution (30 mg/mL) for 2 weeks were nearly the same as those by the shorter immersion time. In contrast, when a homopolyisocyanate was coated on the Si substrates, thicknesses of 15 and 35 nm were obtained for the immersion times 15 h and 3 days, respectively. It is evident in case of rod-coil block copolymers that a brush layer (dry state thickness of about 5 nm) sets up a self-limiting barrier to prevent further diffusion of rod-coils to the surface.

It is interesting that the molecular arrangements in our dried brush patterns are very similar to those observed in the physical adsorption of poly(styrene-*b*-2-vinylpyridine) (PS-PVP),[8] where PVP chains stretch over the mica surface forming a thin layer. In such type of hydrophobic−hydrophilic copolymer, the penalty in conformational entropy is balanced by the strong adsorption of hydrophilic block onto a polar substrate such as mica. Since this system relies only on physical adsorption, to obtain a monolayer, the polymer concentration of the dipping solution should be sufficiently low to avoid layering of structure normal to the plane.[6,8,20] In contrast, the rod coils can be coated in any concentration and even contact-printed. The excess polymers are easily removable due to the stability of the brush layer given by the covalent rod-surface bonds. A layered domain structure near to the polymer−substrate interface[21] controls the thickness of the covalently attached brushes.

Therefore, we could adapt the contact printing technique to micropattern the rod-coil brushes onto the silicon substrate (Figure 3). About 7.5-μm-wide stripe patterns spaced by about 3.5 μm with an identical thickness (5 nm) were obtained after washing off the excess. Swelling of PDMS could be minimized by rapid solvent evaporation of the polymer solutions on the stamp, which allowed good pattern transfer. Direct contact printing of polymer brushes with a well-controlled thickness onto silicon substrates such as this is unknown, and in most cases, the surface would need to be functionalized to be reactive to the ink materials. Within the micropattern shown in Figure 3, nanostructures with interconnected short wormlike patterns are found. These morphologies are very similar to the surface images of rapidly dried thick films of the rod-coil, which were solution-cast on various substrates, indicating that the preformed domains of the films on PDMS guided the adsorption process. Lateral diffusion barriers were probably set at the interfaces by the block copolymer nanodomains. This approach could lead to a new nanoprinting technique if alignment of the nanopatterns can be better controlled. Higher grafting density than by immersion coating can be attributed to the direct surface contact of the localized block without interdomain diffusion. However, the average film thickness (about 5 nm) and the inter-domain spacing were still close to those by immersion coating indicating these are inherent to the rod-coil.

Water contact angles (advancing/receding) of rod-coil brushes were in the range of 79−84°/75−79°, which were a little lower than the literature values for homopolymer PS (90°/73°)[22] and the measured value for homopolymer PIC (93°/95°). The relation of the resulting contact angles to the nanopatterns may be understood with further study on the response of the nanopatterns to heat or various solvent treatments.[23]

In conclusion, we have demonstrated a new type of polymer brush using a surface reactive rod-coil diblock copolymer. Nano- and micropatterning was successfully performed by various “grafting to” techniques such as immersion, casting, and stamping. The extended conformation of the rods facilitates nanoscale domain formation during the adsorption process. The reactive side groups along the rod backbones covalently link the nanopatterns to the surface. Selecting different types of coil counterpart or variation in the copolymer compositions may produce different patterns or surface functionalities. The simple processing conditions of the rod-coil brushes may be superior to other methods of synthesizing polymer brushes and can be easily employed for many applications. We are trying to improve the ordering of the nanodomains by different processing conditions. Study on the details of the adsorption mechanism is also underway.

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