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Block Cooligomers: A Generalized Approach to Controlling the Wetting Behavior of Block Copolymer Thin Films

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The successful demonstration of block copolymer thin films as soft templates for pattern transfer inspired an exciting new research area in nanofabrication.[1,2] Unlike sphere-forming block copolymers, it is critical to finely control the wetting behaviors of lamellae- and cylinder-forming block copolymers in thin films, especially when a perpendicular orientation of domains is desirable. Approaches including chemical nanopatterning,[3−6] self-assembled monolayers,[7−9] organosilicates,[10] random copolymer brushes,[11−16] and blend brushes[17] have been developed to modify substrates in order to achieve a perpendicular orientation of block copolymer domains in films. Among them, chemical modification using random copolymer brushes has been widely used for the self-assembly of block copolymers,[11−16] but for certain block copolymer, synthesis of a random copolymer from the same monomer pair may be difficult or even impossible to practice. Instead of using random compolymers, Ji et al. recently demonstrated the use of ternary blends of low molecular weight block copolymer and two corresponding homopolymers to modify substrates for the self-assembly of larger molecular weight block copolymers.[17] The addition of low molecular weight block copolymers effectively compatiblized the mixing of homopolymers to prevent microphase separation and controlled the grafting ratio of homopolymers in blend brushes. This blend brush approach is especially suitable for block copolymers with monomer pairs that could not be randomly copolymerized; however, the limitation of this approach is that a selective solvent toward the block of higher substrate interfacial energy is typically required to prevent preferential wetting of the other block on substrates and facilitate the grafting process to achieve a sufficiently small length scale of homopolymer domains.

Here we report a block cooligomer approach to controlling the wetting behaviors of block copolymers in thin films (Figure 1). The blocks in cooligomers are small so that microphase separation can be prevented and a chemically homogeneous brush layer with controllable compositions can be easily obtained on substrates. For a given block copolymer, it is always possible to prepare a block cooligomer in an analogous monomer sequence. Incorporation of a reactive group permits covalently grafting or cross-linking the block cooligomer on the substrate surface.[11−13,15] This approach should be generalizable to any block copolymer system.

We demonstrate this concept using block cooligomers, oligo[styrene-*b*-(methyl methacrylate-*r*-hydroxyethyl methacrylate)] [O(S-*b*-M*r*H)] (**3**), as brush layers for the self-assembly of poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) block copolymers. O(S-*b*-M*r*H) was synthesized by two-step sequential nitroxide-mediated polymerization using a nitroxide initiator, *N*-*tert*-butyl-*N*-(2-methyl-1-phenylpropyl)-*O*-(1-phenylethyl)hydroxylamine (**1**, purchased from Aldrich) (Scheme 1).[16] Styrene (S), methyl methacrylate (MMA), and hydroxyethyl methacrylate (HEMA) were purchased from Aldrich and purified by passing through activated alumina prior to use. Styrene (3.12 g, 30.0 mmol) was first polymerized in presence of initiator **1** (0.33 g, 1.0 mmol; purchased from Aldrich) at ~120 °C for 4 h under a nitrogen atmosphere to form oligostyrene (**OS**, **2**: ~75% conversion by ^{1}H NMR analysis; M_n = 2.5 kg/mol, PDI = 1.14 by GPC, relative to a PS standard using THF as eluent). MMA (1.56 g, 15 mmol) was then polymerized at 120 °C using 1.0 g of purified oligostyrene **2** (M_n = 2.5 kg/mol) as the macroinitiator in presence of 44 mg of 2,2,5-trimethyl-4-phenyl-3-azahexane 3-nitroxide (0.2 mmol; purchased from Aldrich);[18] 2 h later HEMA (0.195 g, 1.5 mmol) was added into the polymerization system, and the polymerization proceeded for another 2 h to yield a block cooligomer O(S-*b*-M*r*H) (**3**: 71% conversion by ^{1}H NMR; M_n = 2.5−2.4 kg/mol, PDI = 1.22). O(S-*b*-M*r*H) was purified by precipitation in methanol. The purified O(S-*b*-M*r*H) had ~51 mol % of styrene fraction. Another O(S-*b*-M*r*H) (M_n = 2.5−1.6 kg/mol, PDI = 1.25) that had ~64 mol % styrene fraction was synthesized according to the same procedure. Both cooligomers had an average number of ~1.5 HEMA units per chain. The HEMA units should be at positions close to and randomly distributed at the chain end of the oligo(methyl methacrylate) block.

The brush formation procedure was analogous to the previously published work (Figure 1a).[13,16] Thin films of O(S-*b*-M*r*H)s (~30 nm thick) were deposited by spin-coating from 1 wt % toluene solutions onto clean silicon substrates and annealed at 160 °C for 24 h under vacuum. During annealing, hydroxyl groups in HEMA units reacted with silanol groups of the native oxide through a dehydration reaction to form a brush layer of block cooligomers. Excess unreacted oligomers were stripped off by 5 × 3 min sonication in warm toluene. The brushes from 2.5−2.4 and 2.5−1.6 kg/mol block cooligomers were defined as OSM**2**-**2** and OSM**2**-**1**, resepctively. The thickness was measured to be 3.4 ± 0.2 nm for both oligomeric brushes using a Ruldoph elliposometer. The grafting density of both brushes was estimated to be ~0.4−0.5 chain/nm^2. Atomic force microscopy (NanoScope IIIa multimode AFM, Digital Instruments) measurement revealed that the brushes had no detectable microphase separation. The static water contact angles were 69.8 ± 1.0° and 73.1 ± 1.3° for brushes OSM**2**-**2** and OSM**2**-**1**, respectively (Future Digital Scientific OCA15 video goniometer), and agreed with the contact angles of binary PS/PMMA neutral blend brushes.[17] The contact angle results ruled out the possibility that an OS layer covered on top of an oligo(methyl methacrylate) (OMMA) layer in the brush because the contant angle of PS is ~90°. The combined results from the AFM and contact angle measurement indicated that the two blocks were mixed in small length scale. Previous study on HEMA-containing poly(styrene-*r*-2-vinylpyridine) brushes showed that the brush compositions determined by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy agreed well with their bulk compositions measured by ^{1}H NMR analysis.[16] It may also be reasonable to

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assume that the brush composition is same as the bulk composition of the block cooligomer.

We performed 24 experiments (a combination of 2 block cooligomeric brushes, 3 types of block copolymers, and 4 film thicknesses) to test whether the block cooligomeric brushes were same as the random copolymer brushes[11−16] and blend brushes.[17] The information gathered from the assembly behaviors of three types of PS-*b*-PMMAs with four different film thicknesses on these two block cooligomeric brushes would be sufficient to reach a conclusion. The rationale for choosing O(S-*b*-M*r*H) brushes with 51% (**OSM2-2**) and 64% (**OSM2-1**) styrene fraction is that 64% is within the neutrality window for all three types of PS-*b*-PMMAs, while 51% is at the boundary of neutrality window for both lamellae-forming and PS cylinder-forming PS-*b*-PMMAs and outside the neutrality window of PMMA cylinder-forming PS-*b*-PMMA.[15,17]

Three PS-*b*-PMMAs [M_n = 52−52 kg/mol (**L5252**), 46−21 kg/mol (**C4621**), and 20−50 kg/mol (**C2050**); PDI = 1.05−1.07; purchased from Polymer Source] that form lamellae, PMMA cylinders in PS matrix, and PS cylinders in PMMA matrix, respectively, were used to test the wetting behaviors of block copolymers on these block cooligomer brushes. The periods (L_0) of **L5252**, **C4621**, and **C2050** were measured to be 47.5 nm, 36.5 nm (row-to-row), and 38.2 nm (row-to-row), respectively, on a Rigaku small-angle X-ray scattering instrument. PS-*b*-PMMA films with various film thicknesses were deposited on the oligomeric brushes by spin-coating from toluene solutions and annealed at 190 °C for 24 h before SEM imaging (LEO VP1550, 1 kV accelaration voltage). If a perpendicular orientation of domains is achieved in PS-*b*-PMMA thin films, the interaction between the substrate and both blocks is nearly balanced, and the brush is termed neutral or nonpreferential to PS-*b*-PMMAs.[19]

Figure 2 shows SEM images of the surface morphologies of PS-*b*-PMMA thin films on O(S-*b*-M*r*H)-modified substrates. The compositions of brushes OSM**2-1** and OSM**2-2** were within

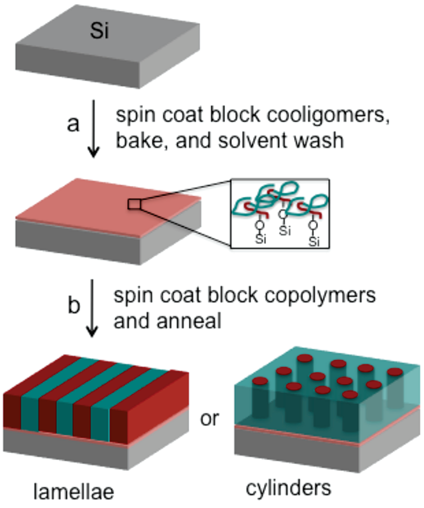


Figure 1. (a) Thin films of block cooligomers are spin-coated from solutions onto silicon substrates and annealed at 160 °C to graft cooligomers onto the substrate surfaces to form a brush layer. Unreacted cooligomers are removed by solvent wash. (b) Block copolymer films with various thicknesses are deposited onto the brushes from solutions and annealed at 190 °C to reach equalibrium structures. Perpendicularly oriented lamellae or cylinders are obtained on neutral brushes.

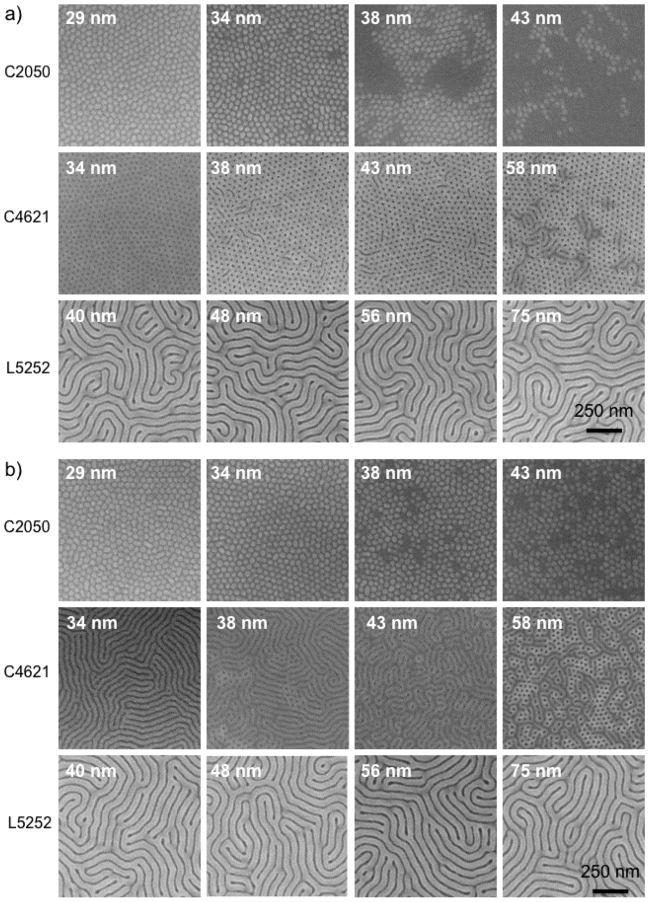
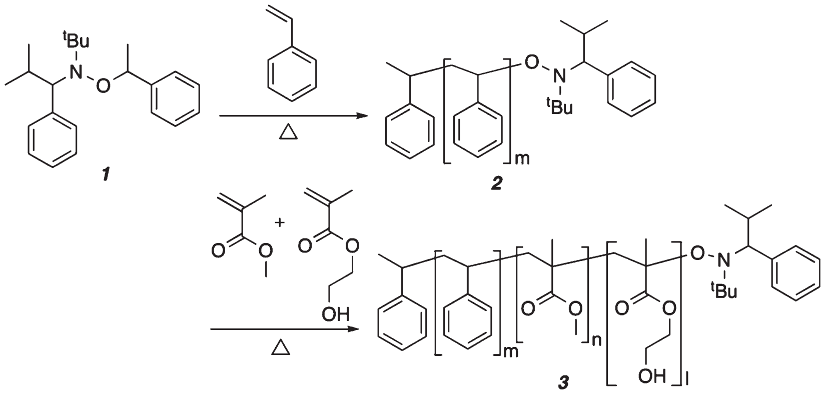


Figure 2. SEM images of thin films of three block copolymers (**C2050**, **C4621** and **L5252**) assembled on (a) OSM**2-1** and (b) OSM**2-2** brushes at 190 °C for 24 h. The film thickness is indicated at the left upper corner of each image.

Scheme 1. Synthesis of O(S-*b*-M*r*H) (3) by Two-Step Nitroxide-Mediated Polymerization



the neutrality window of lamellae-forming PS-*b*-PMMAs on both random copolymer brushes[15] and binary blend brushes.[17] As expected, perpendicular lamellae in a fingerprint pattern, similar to the domain patterns of **L5252** films that were assembled on PS-*r*-PMMA random copolymer brushes[13,15,20] and binary PS/PMMA blend brushes,[17] formed in films with thicknesses (L) of 40−75 nm ($0.84-1.58L_0$) on both brushes. The formation of perpendicular structures indicated that both brushes were neutral toward **L5252** and functioned same as the random copolymer brushes and blend brushes.[11−13,15,16,20]

The domain orientation of **C2050** films on brushes OSM**2-1** and OSM**2-2** had a similar trend with increase of L (Figure 2). Perpendicular PS cylinders formed in films with L = 29 and 34 nm, while parallel structures coexisted with perpendicular PS cylinders when L was $\sim 1L_0$ or thicker, e.g., L = 38 and 43 nm. The percentage of parallel domains increased with L and was larger on OSM**2-1** than that on OSM**2-2**. Both oligomeric brushes were neutral to **C2050**, but their compositions were slightly outside the reported neutrality window of PS cylinders on random copolymer brushes.[15]

The assembly behaviors of **C4621** films were different on brushes OSM**2-1** and OSM**2-2** (Figure 2). A perpendicular orientation of PMMA cylinders formed on OSM**2-1** when the film was slightly thinner than $1L_0$ (L = 34 nm). Defects, e.g. parallel cylinders or loop structures, appeared on the film surface when L = 38−58 nm, and the percentage of parallel cylinders increased with L.[20−22] In comparison, parallel PMMA half-cylinders formed on the surface of the film with L = 34 nm on OSM**2-2**. When L was increased to 38−58 nm, a small fraction of perpendicular PMMA cylinders formed on film surfaces. The percentage of perpendicular PMMA cylinders increased with L. The different assembly behaviors on the two brushes at $\sim 1L_0$ thickness indicated that OSM**2-1** was neutral to **C4621** while OSM**2-2** was preferential to **C4621**. This is consistent with the fact that the composition of OSM**2-1** (64 mol % styrene) was within the previously reported neutrality window of PMMA cylinders while the composition of OSM**2-2** (51 mol % styrene) was not.[15] The surface morphologies of films were almost identical on both brushes when L was further increased to ~110 nm ($\sim 3L_0$, not shown) and similar to that of the 43 nm thick C4621 film on **OSM2-1**, as shown in Figure 2.

The surface morphology of block copolymer films is determined by both the substrate and free surface boundary conditions, but the substrate boundary condition dominates at the thickness range we studied.[23] In thin films ($L < 1L_0$), the substrate effect was sufficient enough to induce a perpendicular orientation of domains throughout the film thickness on neutral surfaces, e.g., **C2050** and **L5252** on both brushes and **C4621** on **OSM2-1**, or a parallel orientation of domains on a preferential surface, e.g., **C4621** on **OSM2-2**. The substrate effect decays with the increase of L, and the free surface boundary condition also contributes to the domain orientation at free surfaces in relatively thicker films. At 190 °C, PS has a slightly smaller surface energy than PMMA.[11] The slight difference in surface energies resulted in the formation of a small fraction of parallel cylinders on surfaces in **C4621** films with L = 38−58 nm on **OSM2-1**.[23] On the other hand, the nearly equal surface energy of both blocks provides the driving force to induce a fraction of perpendicular cylinders on surfaces in relatively thicker **C4621** films with L = 38−58 nm on **OSM2-2** that is preferential to **C4621**. In even thicker films, e.g. $L \approx 110$ nm, the surface boundary condition dominated and determined the domain orientation at surfaces, and there was no noticeable difference in the surface morphologies on both brushes.[23]

The domain orientation of cylinder-forming block copolymers was more sensitive to L than that of lamellae-forming block copolymers on surfaces in thin films. Recent researches have shown that the perpendicular orientation of domains was only achieved in a certain film thickness range on neutral brushes of specific compositions.[20−23] The thickness range for the formation of perpendicular domains was larger on brushes with compositions close to the optimal neutral composition. We also observed a similar thickness-dependent assembly behavior of PS cylinder-forming PS-*b*-PMMA films on the block cooligomer brushes. Analogous to their observations,[20−22] the composition of **OSM2-2** might be closer to the optimal neutral composition than that of **OSM2-1** for PS cylinders since there were more perpendicular fractions in films with L = 38 and 43 nm on brush **OSM2-2**. We did not observe the thickness-dependent assembly behavior in **L5252** films up to L = 75 nm ($1.56L_0$) on both brushes.

In summary, we demonstrated a generalized approach to preparing the wetting brush layers from block cooligomers for the self-assembly of block copolymers. Our results suggest that randomness within a chain is not necessary for the formation of neutral brushes. For any given block copolymer, it is always possible to synthesize a smaller version of itself, the block cooligomer, from the same monomer pair, while random copolymerization might be difficult or impossible. The key concept in our block cooligomer approach lies in that the block sizes are small enough to guarantee the mixing of two blocks into a sufficinently small length scale, compared to the domain size of the block copolymer, to achieve a chemically homogeneous brush layer. This block cooligomer approach is an important extension of the binary homopolymer blend brush work[17] and has advantages over the random copolymer brush[11−16] and blend brush[17] approaches, especially for the formation of brush layers for the self-assembly of multiblock copolymers.

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