

Covalent Stabilization of Nanostructures: Robust Block Copolymer Templates from Novel Thermoreactive Systems

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ABSTRACT: Structurally robust block copolymer templates with feature sizes of approximately 10 nm were prepared from functionalized poly(methyl methacrylate)-*b*-polystyrene block copolymers. By the inclusion of benzocyclobutene crosslinking groups in the polystyrene block, the covalent stabilization of thin films to both thermal treatment and solvent exposure became possible. In addition, the crosslinking of the poly(styrene-benzocyclobutene) domains at 220 °C, followed by the removal of poly(methyl methacrylate), provided a robust, crosslinked nanostructure with greater processing and fabrication potential. © 2005 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 43: 1028–1037, 2005

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INTRODUCTION

One of the key attributes of both thermoplastic materials and supramolecular assemblies is the dynamic nature of the molecular organization. This allows the processing of thermoplastic materials¹ or the ability to reform and evolve the supramolecular assembly through the exchange of individual molecules between molecular clusters or phase-separated structures.² This was exploited by Meijer and coworkers³ in the design of a novel family of telechelic polymers bearing hydrogen-bonding termini. These fundamentally new materials are expected to dramatically affect a variety of commercially important applications for which external stimuli, such as heat or dilu-

tion, trigger physically crosslinked polymers to behave as low-viscosity fluids that are easy to process. However, in many applications, it is highly desirable to have a static structure that is not affected by reversibility. To this end, significant effort has been devoted in recent years to the covalent stabilization of self-assembled nanostructures. Such an approach leads to discrete nanoscale objects that have fundamentally different properties and applications than the starting materials or their corresponding supramolecular assemblies.

This concept has been exploited by Wooley and coworkers⁴ and others^{5,6} in the design of copolymers that can be assembled in solution and crosslinked to produce stabilized structures, such as shell-crosslinked nanoparticles. However, the covalent stabilization of the highly ordered, phase-separated morphologies of block copolymers in the solid state has attracted much less attention.⁷ This is unfortunate because a range of industrially important bulk

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nanostructures can be accessed from block copolymers, and it is advantageous to make these structures robust. This is particularly true for thin films of block copolymers, for which surface patterning on a nanometer-size scale can be achieved. These block copolymer templates have been recognized as promising platforms for the fabrication of nanostructured devices for advanced storage and microelectronic applications.^{8–13} Many of these applications require precise control over the microdomain orientation, which is achieved by the balancing of interfacial interactions and removes the preferential interactions of the blocks with the surface. If these interactions can be balanced, or a neutral surface can be created, the desired orientation of the microdomains normal to the surface will occur by spontaneous self-assembly.

For poly(methyl methacrylate)-*b*-polystyrene copolymers, one approach to achieving this neutral surface is the covalent attachment of a random copolymer of styrene and methyl methacrylate (MMA).¹⁴ The ratio of the two monomers in the random copolymer is critical, with a styrene/MMA ratio of 58/42 giving a neutral surface and the desired vertical phase morphology.¹⁵ To enhance the technological relevance of these self-assembled thin-film nanostructures, one of the components of the block copolymer film must be removed to produce a template or scaffold that retains the original dimensions and structure of the microphase-separated block copolymer. Ion-beam etching, UV irradiation, ozonolysis, and chemical etching have each been used to this end.¹⁶ For certain applications, the resulting template suffers from thermal and solvent processing issues because of its noncrosslinked or lightly crosslinked structure. Thus, one strategy for improving the applicability and usability of nanoscale block copolymer templates is covalent stabilization. Here we present the generation of a robust template from a novel poly(methyl methacrylate)-*b*-polystyrene copolymer containing a thermally reactive functional group, benzocyclobutene (BCB), which is incorporated into the polystyrene (PS) block and undergoes selective crosslinking during the processing of the thin-film template.

EXPERIMENTAL

¹H NMR (400 MHz) and ¹³C NMR (100 MHz) measurements were performed with a Bruker AC 400 spectrometer at room temperature with the

residual solvent signal as an internal reference. Size exclusion chromatography was conducted at room temperature on a Waters chromatograph connected to a Waters 410 differential refractometer and five PL gel columns (three mixed B columns, one 10³-Å column, and one 10⁵-Å column; 10-μm particles), with tetrahydrofuran (THF) as an eluant (flow rate = 1 mL/min). A calibration curve obtained from PS standards was used to calculate the weight-average (M_w) and number-average (M_n) molecular weights and the polydispersity index (PDI; i.e., M_w/M_n). Thin films were prepared by the spin casting of 3 wt % toluene solutions of the block copolymer on either random-copolymer-treated silicon substrates or passivated silicon substrates. Passivated surfaces were prepared by the removal of the native silicon oxide layer with a 5% aqueous HF solution under standard conditions. Small-angle X-ray scattering (SAXS) was performed on beam line 1-4 at the Stanford Synchrotron Radiation Laboratory at the Stanford Linear Accelerator Center to determine the characteristic period (L_0) of the block copolymers. A focused, collimated X-ray beam with a flux of 2×10^{10} photons/mm²/s was monochromated with a Si (111) crystal to deliver 1.488-Å X-rays onto the sample. Tapping-mode scanning force microscopy images were obtained in both height- and phase-contrast modes with a Digital Instruments Nanoscope II scanning force microscope with etched silicon tips on cantilevers, with spring constants ranging from 40.0 to 60.0 N/m.

4-Vinylbenzocyclobutene (1)

To a 500-mL, round-bottom flask were added (Ph)₃PCH₃Br (24.3 g, 68.1 mmol) and 110 mL of dry THF, and the solution was cooled to -78 °C. *n*-BuLi (2.5 M in hexane; 26.4 mL, 66.0 mmol) was added dropwise, and the reaction mixture was allowed to warm to room temperature. The yellow-orange solution was cooled to -78 °C, and the aldehyde (**6**; 7.16 g, 54.2 mmol), diluted in 34 mL of dry THF, was added slowly. The reaction mixture was allowed to warm to room temperature, and stirring was continued for 2 h. The reaction was quenched by sequential treatment with saturated NH₄Cl and a saturated NaHCO₃ solution, and the crude product was filtered over Celite, washed with diethyl ether/hexane (1:1), and evaporated to dryness (no heat) to yield the crude product. Further purification by column chromatography with 5% diethyl ether/hexane as

an eluting solvent, followed by Kugelrohr distillation (75 °C, 1.0 mm), gave the pure styrene derivative (**1**) as a colorless liquid (5.50 g, 78%).

IR: 2925, 1627, 1473, 989, 901, 829 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , δ): 7.26 (d, 1H, $J = 7.4$ Hz, ArH), 7.20 (s, 1H, ArH), 7.04 (d, 1H, $J = 7.4$ Hz, ArH), 6.74 (dd, 1H, $J = 17.5$ Hz, $J' = 10.8$ Hz, CH), 5.70 (d, 1H, $J = 17.5$ Hz, CH_2), 5.20 (d, 1H, $J = 10.8$ Hz, CH_2), 3.19 (s, 4H, CH_2). ^{13}C NMR (100 MHz, CDCl_3 , δ): 146.09, 145.75, 137.94, 136.69, 125.71, 122.58, 119.90, 112.38, 29.52, 29.35 ppm. ELEM. ANAL. Calcd. for $\text{C}_{10}\text{H}_{10}$: C, 92.2%; H, 7.80%. Found: C, 92.0%; H, 8.03%.

Dithioester-Terminated Poly(methyl methacrylate) (PMMA) Macroinitiator (**3**)

A mixture of dithio(1-cyano-1-methylethyl)benzoate (**2**; 22.1 mg, 0.10 mmol), ^{17}MMA (2.00 g, 20.0 mmol), and azobisisobutyronitrile (AIBN; 1 mg, 0.005 mmol) was dissolved in benzene (1 mL) and heated at 70 °C under nitrogen for 48 h. The viscous reaction mixture was then diluted with dichloromethane (10 mL) and precipitated into methanol (500 mL). The precipitated solid was redissolved in dichloromethane (10 mL) and reprecipitated into methanol (500 mL) to yield purified **3** as a pink solid.

Yield: 87%. M_n : 18,500. PDI: 1.08. IR: 3050–2850, 1735, 1452, 930 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , δ): 7.7–7.3 (m, ArH), 3.94 (s, OMe), 2.10–1.20 (m, CH_2 , CH, CH_3). ^{13}C NMR (100 MHz, CDCl_3 , δ): 174.1, 55.2, 42.0–44.0, 40.4, 29.2 ppm.

Hydrogen-terminated Poly(methyl methacrylate)-*b*-Poly(styrene-*r*-vinylbenzocyclobutene) (**4**)

3 ($M_n = 18,500$, PDI = 1.08; 2.00 g, 0.11 mmol) was dissolved in a mixture of styrene (4.49 g, 43.2 mmol), **1** (624 mg, 4.80 mmol), and benzene (5.0 mL) and heated at 110 °C under nitrogen for 24 h. The viscous reaction mixture was then diluted with dichloromethane (50 mL) and precipitated into methanol (1500 mL). The solid was redissolved in dichloromethane (10 mL) and precipitated into methanol (1500 mL) to yield the purified thioester-terminated block copolymer (**4**) as a pale pink solid.

Yield: 84%. M_n : 53,000. PDI: 1.12. IR: 3100–2850, 1730, 1601, 1492, 1452, 909, 699 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , δ): 7.24–6.54 (m, ArH), 3.92 (s, OMe), 3.05 (br s, CH_2), 2.04–1.26 (m, CH_2 , CH, CH_3). ^{13}C NMR (100 MHz, CDCl_3 , δ): 173.0,

145.0–146.4, 127.9, 125.5, 121.8, 42.0–44.0, 40.4, 29.2 ppm.

Poly(methyl methacrylate)-*b*-Poly(styrene-*r*-vinylbenzocyclobutene) (**5**): Removal of the Dithioester Chain End

The dithioester-terminated block copolymer (**4**; $M_n = 53,000$, PDI = 1.12; 4.00 g, 0.075 mmol) was dissolved in toluene (50.0 mL), and tri-*n*-butyl tin hydride (290 mg, 1.0 mmol) was added. The reaction mixture was then heated at reflux under nitrogen for 12 h, cooled, and precipitated into hexane (1000 mL). The colorless solid was then redissolved in dichloromethane (50 mL) and reprecipitated into hexane (1000 mL) twice more to yield the purified block copolymer (**5**) as a white solid.

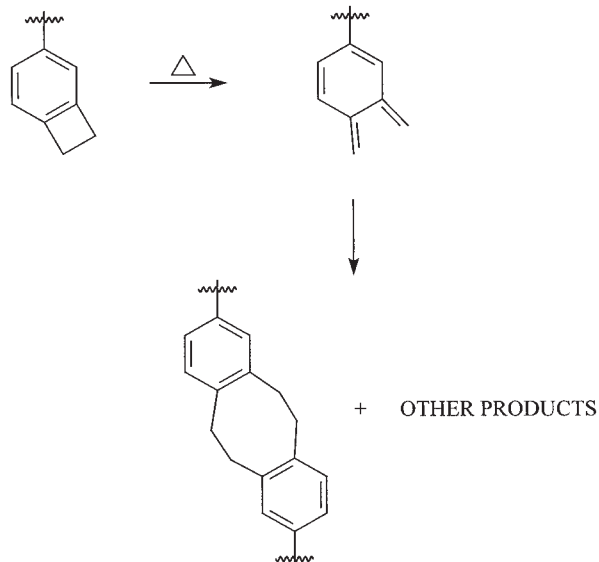
Yield: 91%. M_n : 54,000. PDI: 1.11. IR: 3100–2850, 1730, 1601, 1495, 915, 690 cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , δ): 7.24–6.50 (m, ArH), 3.94 (s, OMe), 3.07 (br s, CH_2), 2.05–1.25 (m, CH_2 , CH, CH_3). ^{13}C NMR (100 MHz, CDCl_3 , δ): 173.5, 145.5–146.5, 127.9, 125.1, 121.9, 42.0–44.0, 40.0, 29.2 ppm.

Preparation of the Thin Films

Thin films of the block copolymers were prepared through the spin casting of toluene solutions (1.0 L_0 , 0.75 wt % at 2000 rpm; 1.5 L_0 , 1.5 wt % at 4000 rpm; and 2.0 L_0 , 1.5 wt % at 2500 rpm) either on passivated silicon substrates or on substrates modified with a random copolymer. The thin films were annealed and cured by heating under nitrogen for 2 h at 170 °C and then for an additional hour at 220 °C. The cured thin films were exposed to deep-UV radiation from a mercury lamp to degrade the PMMA and were washed first with glacial acetic acid and then with methanol. After drying at room temperature under a stream of nitrogen, crosslinked, nanoporous block copolymer templates were obtained.

RESULTS AND DISCUSSION

The BCB group was chosen as the crosslinking unit in this study because of a number of critical factors.¹⁸ First, the low reactivity of the BCB group at temperatures below 150 °C allows it to be readily introduced into a variety of polymer backbones and to be subsequently processed in the presence of air and moisture. In addition, the

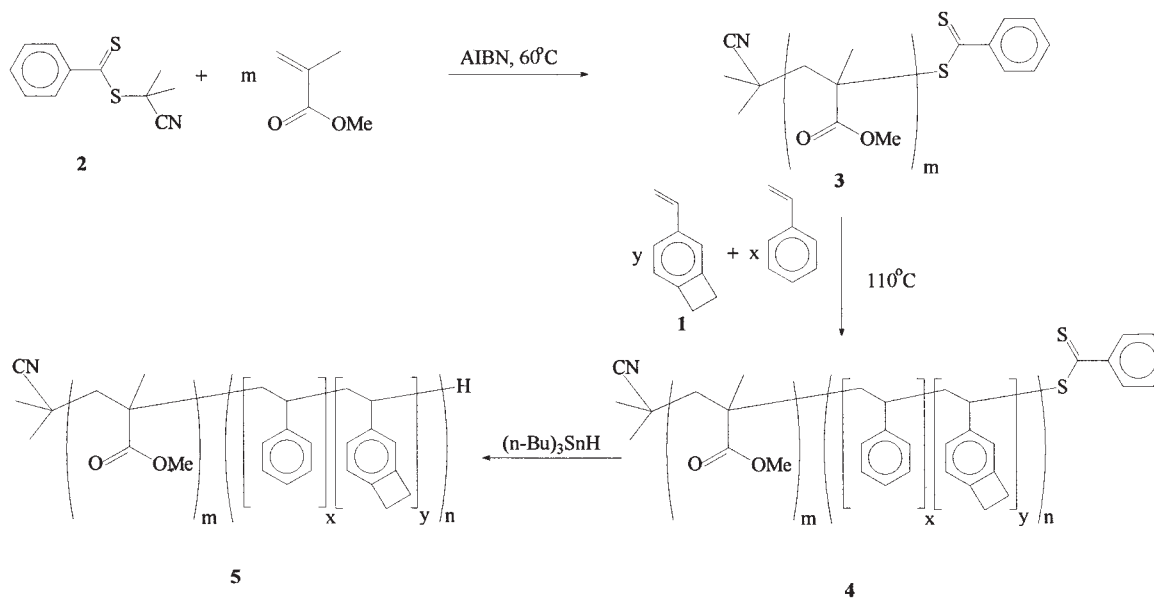


Scheme 1. Ring opening and primary crosslinking reaction for BCB groups.

BCB crosslinking reaction is efficient and occurs between 180 and 250 °C, which is within the normal range of annealing temperatures for the generation of block copolymer assemblies. Finally, the crosslinking reaction results in the formation of ring structures that are etch-resistant and beneficial for the transfer of the block copolymer nanostructure to the underlying substrate (Scheme 1). For these reasons, diblock copolymers

of PMMA coupled with a random copolymer of styrene and **1** were prepared with reversible addition–fragmentation chain transfer (RAFT) procedures.¹⁹ As shown in Scheme 2, the dithioester (**2**) was used to initiate the polymerization of MMA in the presence of AIBN as a coinitiator to yield narrow-polydispersity PMMA homopolymer (**3**), which contained a dormant dithioester group at the chain end. The reaction of **3** with various ratios of styrene and **1** at 110 °C was then found to yield the desired block copolymers (**4**) with accurate control over the molecular weight and polydispersity. To examine the effect of chain ends on the phase separation and self-assembly of these diblock systems, the thioester chain end was removed by the reaction of **4** with tri-*n*-butyl tin hydride to yield the hydrogen-terminated materials (**5**) in essentially quantitative yields.

Two series of block copolymers were prepared with molar fractions of 0.5 MMA and 0.5 styrenic block with 1:9 and 2:8 ratios of BCB to styrene repeat units [**4a**, 21,700 Da (PDI = 1.12), and **4b**, 27,200 Da (PDI = 1.15)]. Asymmetric block copolymers containing approximately 30/70 (mol/mol) MMA/styrenic block were also prepared by RAFT procedures, again with 1:9 and 2:8 ratios of BCB to styrene repeat units [**4c**, 53,000 Da (PDI = 1.12), and **4d**, 48,000 Da (PDI = 1.09)]. ¹H NMR spectroscopy and gel permeation chromatography (GPC) analysis of the block copolymers (**4a–4d**) showed a high degree of purity with little



Scheme 2. Synthesis of **4** and **5** by RAFT polymerization.

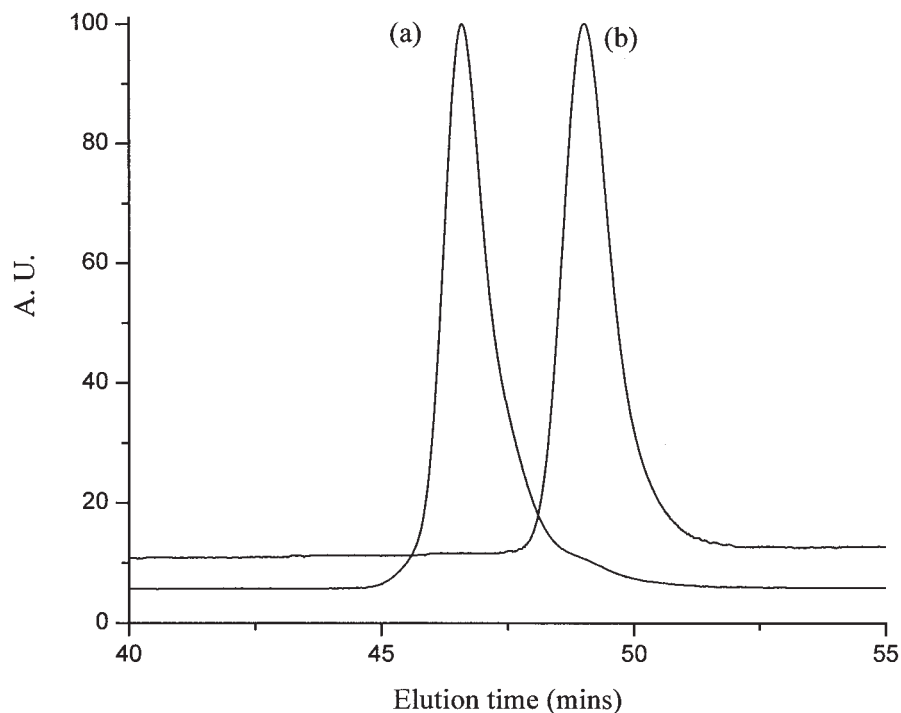


Figure 1. GPC traces for (a) a 30/70 poly(methyl methacrylate)-*b*-poly(styrene-*r*-vinylbenzocyclobutene) block copolymer (**4c**) with 10% BCB units in the backbone and (b) the starting PMMA macroinitiator (**3**).

homopolymer contamination, and in all cases, the broad singlet at 3.0–3.2 ppm confirmed the addition of the BCB unit. A representative GPC chromatograph for **3d** and **4c** is shown in Figure 1. On the basis of the bulk polymer morphology, **4a** and **4b** should impart a lamellar structure, whereas **4c** and **4d** should lead to cylinders of PMMA in a PS matrix with L_0 's of approximately 24 and 26 nm, respectively, as determined by SAXS.

The phase separation of the block copolymers and the reactivity of the BCB groups were investigated with differential scanning calorimetry (DSC). As shown in Figure 2 for block copolymers **4a** and **4b**, two distinct glass-transition temperatures (T_g 's) at approximately 96 and 115 °C, corresponding to the styrenic and methacrylate blocks, respectively, were observed in the first heating. The thermal crosslinking of the BCB groups, evidenced by the strong exothermic peak, was observed during the first heating for both copolymers and was much more pronounced for the 20% copolymer, as expected. These results demonstrated that the block copolymers underwent phase separation and, more importantly, allowed the processing window for the crosslinking reaction to be determined. In these block co-

polymer structures, the ring opening and crosslinking of the BCB group started to occur at approximately 180 °C, with the exotherm reaching a maximum at approximately 250 °C. This suggested that an annealing temperature of 200–250 °C would be effective in crosslinking thin films formed from the BCB-functionalized PS–PMMA block copolymers. Significantly, after they were heated to 300 °C to ensure complete crosslinking, T_g of the PMMA block could still be observed. This suggested that phase separation was still present and that the PMMA domains were not destroyed during the thermal crosslinking reaction. The disappearance of T_g for the PS block was also consistent with earlier work on statistical BCB–styrene copolymers in which the T_g of the copolymer was observed to shift to much higher temperatures (120–130 °C) and become much broader with increasing BCB content.

A schematic representation of the generation of nanoscopic patterns is shown in Figure 3. The silicon substrate was either passivated or treated with a polystyrene-*r*-poly(methyl methacrylate) random copolymer prepared by nitroxide-mediated procedures to balance interfacial interactions.²⁰ The BCB-functionalized block copolymer

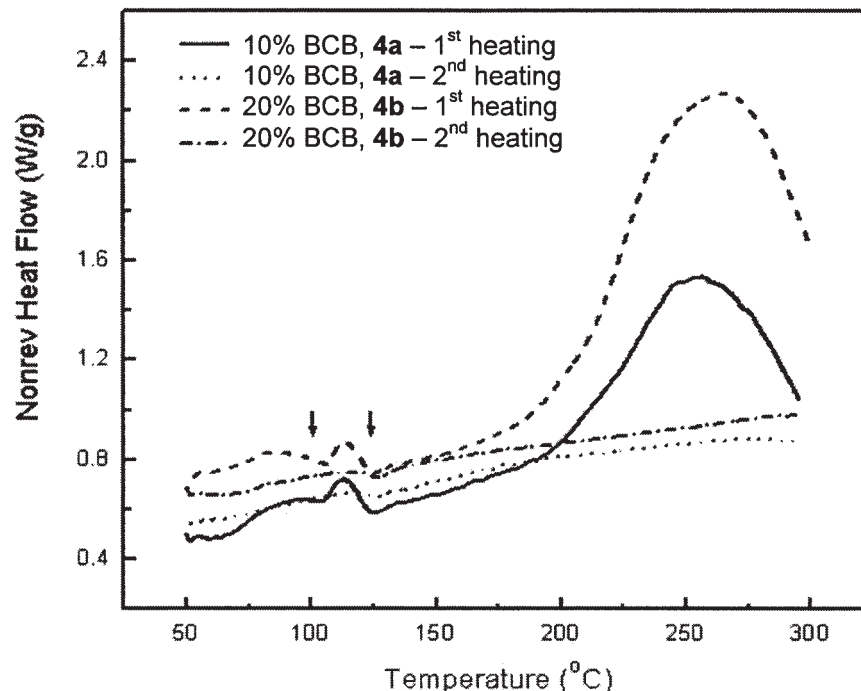


Figure 2. DSC thermograms of approximately 50/50 poly(methyl methacrylate)-*b*-poly(styrene-*r*-vinylbenzocyclobutene) block copolymers (**4a** and **4b**).

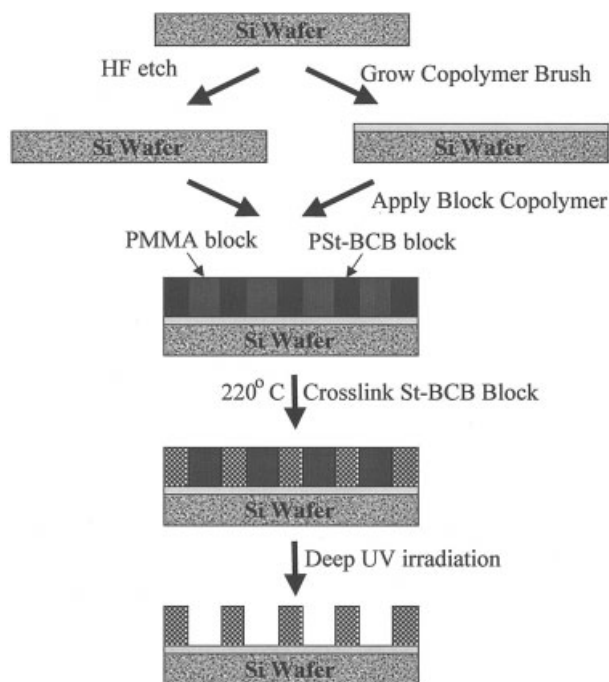


Figure 3. Schematic representation of the process for generating crosslinked nanostructures with poly(methyl methacrylate)-*b*-poly(styrene-*r*-vinylbenzocyclobutene) block copolymers.

was then spin-coated onto the substrate, annealed to orient the microdomains normal to the surface, and then heated to 220 °C to crosslink the PS matrix. A dependence of the morphology on the film thickness was observed for the 30/70 poly(methyl methacrylate)-*b*-poly(styrene-*r*-vinylbenzocyclobutene) cylindrical morphologies and was in agreement with the process optimization results obtained by Black and Guarini.²¹ The retention of structure and order after crosslinking at 220 °C (Fig. 4) demonstrated that microphase separation occurred either before or during the thermal crosslinking of the BCB groups (Fig. 4). For copolymers **4a** and **4b**, the orientation of the microdomains normal to the film surface was seen when the films were $(n + 1/2)L_0$ thick, where n is an integer. For a lamellar morphology with asymmetric wetting [a condition expected here because of the similarities in the chemical structures of PS and poly(styrene-*r*-benzocyclobutene) (PSBCB)], maximal frustration occurred when the film thickness was approximately L_0 . However, the microdomains orient normal to the surface when the film thickness was equal to $(n + 1/2)L_0$, and this suggested that the introduction of the BCB groups into the PS block altered the surface and interfacial energies significantly. A normal orien-

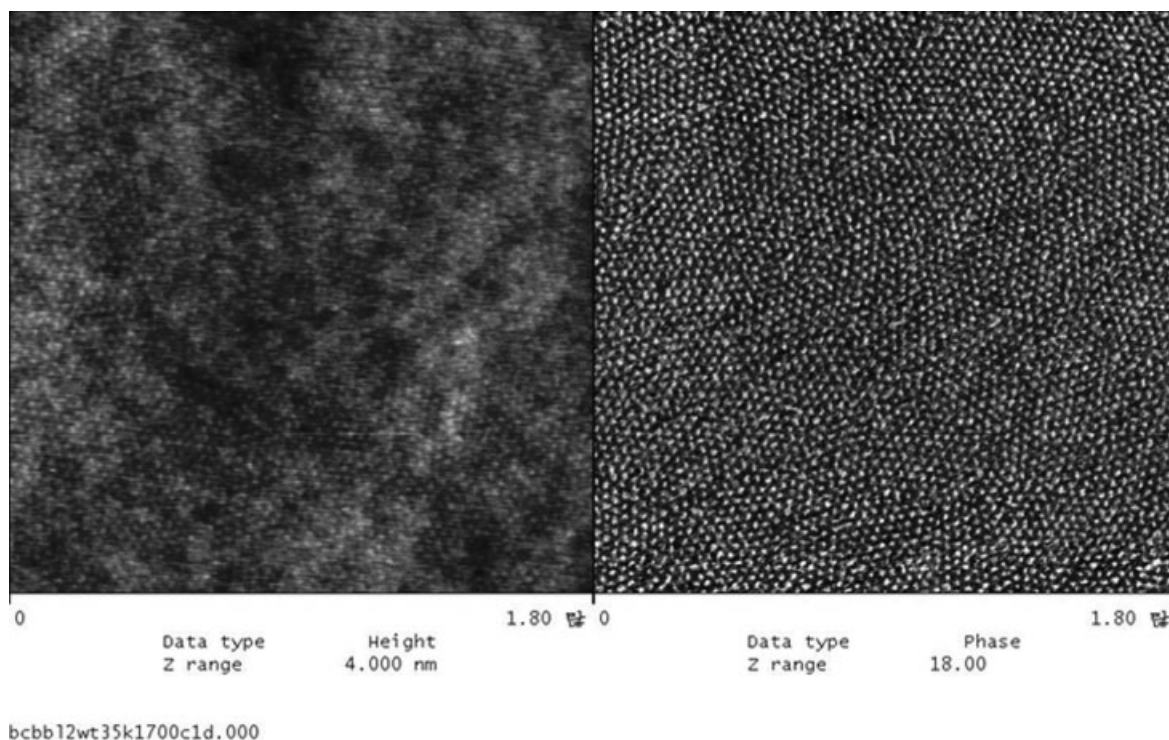


Figure 4. Height-contrast and phase-contrast AFM images of thin films of a block copolymer (**4c**) with 10% BCB units in the backbone after annealing at 180 °C for 12 h. The images are 1.8 μm \times 1.8 μm and have a height range of 4 nm.

tation of the microdomains was observed for a film thickness of $3.5L_0$ or less, and this indicated that the air interface was nonpreferential to both methacrylate and styrene-BCB blocks. The width of the microdomains of each block was measured to be 10–15 nm from a section analysis of atomic force microscopy (AFM) images, which was expected from the molecular weights of each block. The influence of the dithioester chain end on the morphology and alignment of the block copolymer thin films was then studied by the selective removal of the dithioester by a reaction with tri-*n*-butyl tin hydride (Scheme 2). In each case (**4a–4d**), the dithioester could be removed quantitatively, as determined by UV-vis and NMR analyses, to yield the hydrogen-terminated derivative (**5a–5d**), with no observable change in the molecular weight or polydispersity. An examination of these derivatives under the same conditions described previously revealed thin-film nanostructures that were identical to those for the chain-end-functionalized derivatives. This demonstrated that the influence of the dithioester chain end was minimal in this case.

The final step in the generation of a nanoscopic template is the selective removal of one compo-

nent; in this case, that was the PMMA block. To achieve this selective removal, the crosslinked block copolymer thin film was exposed to deep-UV radiation followed by washing with glacial acetic acid. Figure 5 shows a field emission scanning electron microscopy image of a template produced from an approximately 50/50 block copolymer with 20% BCB incorporation (**4b**). The surface and cross section of the sample were imaged by the tilting of the sample by approximately 10° with respect to the incident electron beam, and from the images it can be seen that the PMMA microdomains were removed, the orientation of the microdomains was normal to the surface, and the orientation spanned the entire film. Similar results were also observed for 70/30 PSBCB/PMMA block copolymers, for which hollow cylinders about 15 nm in diameter were observed to extend through the entire films.

It was critical to examine the thermal and environmental stability, both before and after the crosslinking of the BCB residues, to demonstrate the covalent stabilization of these nanostructures. For both the cylindrical (**4c** and **4d**) and lamellar (**4a** and **4b**) structures, for which 10 and 20% BCB groups had been incorporated into the

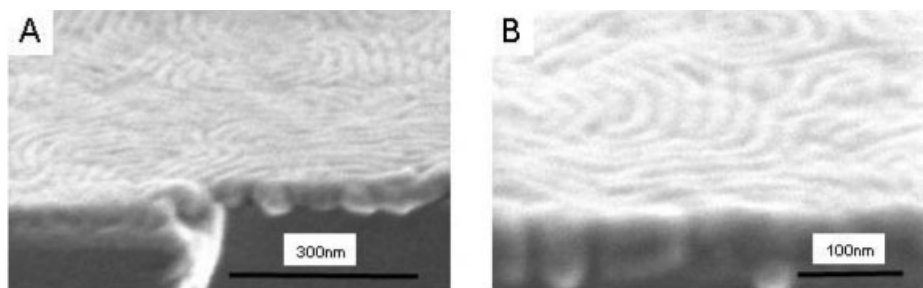


Figure 5. Field emission scanning electron microscopy images of a template prepared from a block copolymer (**4b**) with 20% BCB in the backbone. The film ($1.5L_0$ thick) was annealed at 200 °C for 2 h. The PMMA microdomain was removed by deep-UV exposure followed by an acetic acid rinse. Image B is a higher magnification of image A.

PS block, the nanopatterned surfaces proved to be extremely robust. The solvent resistance was initially examined for continuous thin films before the removal of the PMMA blocks. Figure 6(A) shows the height-contrast AFM image of a thin film of 50/50 poly(methyl methacrylate)-*b*-poly(styrene-*r*-vinylbenzocyclobutene) with 10% BCB groups after annealing at 250 °C and soaking in toluene for 24 h. The nanoscopic pattern remained on the surface without any disturbance even after the film was soaked in toluene, a very good solvent for both blocks. This retention of the structure could only be due to covalent stabilization of the PS matrix by the crosslinking of the BCB groups. In direct contrast, the exposure of the same films to toluene after annealing to only 150 °C, below the temperature required for the ring opening of the BCB units, resulted in the complete dissolution of the film. Similarly, the

annealing of an unfunctionalized PS–PMMA thin film containing no BCB groups to 250 °C, followed by soaking in toluene, resulted in the rapid dissolution of the thin film. The nature of the crosslinking reaction was then probed by an examination of the surface morphology of a similar unfunctionalized PS–PMMA thin film after exposure to deep-UV radiation and development with glacial acetic acid. Although exposure to deep-UV radiation was shown to lead to the crosslinking of the PS domains, the crosslinking reaction was poorly controlled, and the extent of crosslinking was low. It was therefore not surprising that the stability of the resulting nanostructures was also poor. As shown in Figure 6(B), the surface morphology of approximately $1.0L_0$ -thick, unfunctionalized block copolymer films, ordered on a neutral random copolymer brush, showed no features after exposure to deep-UV radiation, washing with

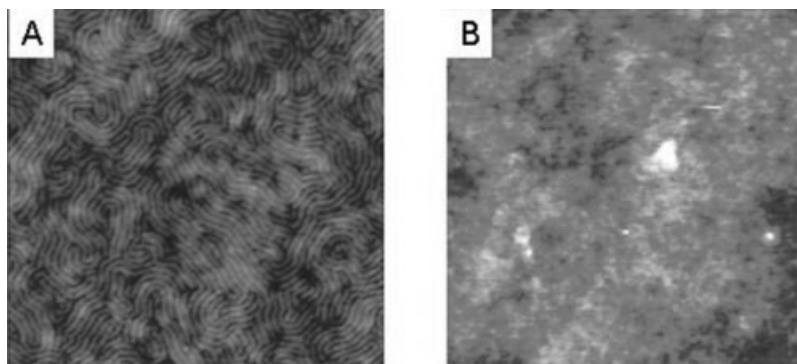


Figure 6. Height-contrast AFM images of diblock copolymer surfaces after they were soaked in toluene for 24 h: (A) a $1.5L_0$ -thick block copolymer thin film (**4a**) with 10% BCB in the backbone after annealing at 250 °C for 2 h followed by soaking in toluene for 24 h and (B) an approximately $1.0L_0$ -thick unfunctionalized block copolymer ordered on a neutral random copolymer brush soaked in toluene for 5 h after deep-UV exposure followed by an acetic acid rinse. For both images, the scan size is $2 \mu\text{m} \times 2 \mu\text{m}$, and the height is 10 nm.

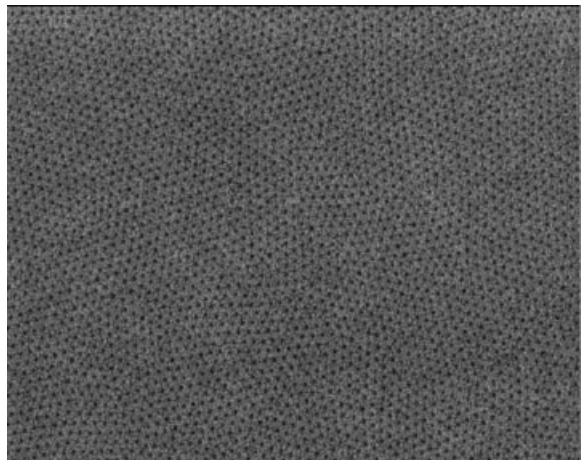


Figure 7. AFM image of the template formed from a 30/70 block copolymer (**4c**) with 10% BCB units in the backbone after annealing at 150 °C for 2 h. The image is 1.4 μm \times 1.0 μm .

glacial acetic acid, and soaking in toluene for 5 h. Unlike the previous examples, the thin film was still present, and so the random crosslinking of the styrene block induced by deep-UV radiation was sufficient to retard dissolution but did not provide sufficient crosslinking to stabilize the nanostructure.

The thermal stability of the block copolymer template was then studied through the annealing of either the cylindrical or lamellar templates at 150 °C for 12 h under nitrogen after the removal of the PMMA domains. This was at least 20–30 °C above T_g for the PS domains, and so linear or lightly crosslinked features were expected to undergo flow, and the structure was expected to be lost. For 0% BCB incorporation, annealing at 150 °C led to rapid destruction of the nanostructure and the loss of all features, and the incorporation of 10% BCB significantly increased the template stability. The 20% BCB samples showed excellent retention of structural features. As shown in Figure 7, the height-contrast AFM image of the template derived from the cylindrical poly(methyl methacrylate)-*b*-poly(styrene-*r*-vinylbenzocyclobutene) (10%) block copolymer (**4c**) after thermal treatment shows the preservation of the vertical nanostructures with a high degree of fidelity.

CONCLUSIONS

Reactive functional groups, such as BCB units, were successfully incorporated into styrene/MMA

block copolymer structures, and the vertical alignment of these systems on silicon substrates was demonstrated. Of particular importance was the ability to thermally crosslink the PS domains during the processing of these thin films by the ring-opening reaction of the BCB groups. This crosslinking reaction resulted in a dramatic improvement in the dimensional stability of the nanoscopic patterns, and after the removal of the PMMA domains, the resulting templates were significantly more stable to both solvent and thermal treatments.

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