

Facile Routes to Patterned Surface Neutralization Layers for Block Copolymer Lithography**

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Nanoscale patterning by block copolymer self-assembly is one of the most promising “bottom-up” approaches for nanolithography, and has recently been introduced into large-scale manufacturing environments by IBM for the production of microelectronics based on Air Gap technology.^[1] In contrast to conventional “top-down” photolithography, these materials can generate nanostructures in the sub-25 nm size regime by controlling the polymer molecular weight, architecture, polydispersity, and segmental interactions.^[2–4] Combining the ability to create nanoscale structures with proven compatibility with current top-down lithographic processes, block copolymer thin films have the potential to become a critical feature of semiconductor manufacturing.^[3–16]

One of the key issues for the fabrication of block copolymer nanostructures is controlling the orientation of the microdomains in thin films.^[1,3,4] For diblock copolymers having anisotropic microdomains such as cylinders or lamellae, the preferential interaction of one block with the substrate leads to microdomains that are oriented parallel to the substrate. For example, the PMMA block in poly(styrene)-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymers shows a preferential interaction with silicon substrates and does not lead to useful lithographic structures.^[17] For many applications, the desired orientation of the microdomains is normal to the surface, and for this nanostructure to be stable,

the interfacial interactions of both blocks should be balanced with the underlying substrate. The traditional approach to surface neutralization is anchoring end-functionalized P(S-*r*-MMA) random copolymers to silicon substrates.^[18] By tuning the composition of PS and PMMA in the backbone of the resulting random copolymer brush, the interactions of PS-*b*-PMMA block copolymers with the underlying surface is balanced for a styrene/MMA ratio of ~ 58/42. While this process is effective and compatible with current manufacturing processes, the process is slow and must be optimized for each surface.

To overcome these issues, a more general approach to controlling interfacial and surface interactions via the use of an ultrathin crosslinkable film of a random copolymer was recently developed.^[19] Incorporation of reactive benzocyclobutene (BCB) units into a P(S-*r*-MMA) random copolymer, P(S-*r*-BCB-*r*-MMA), was shown to give crosslinked films on various substrates, such as Au, Al, Si₃N₄, and Kapton, that allowed control of interfacial interactions. However, the BCB unit has the following disadvantages: the BCB monomer is hard to synthesize and not commercially available. Furthermore a significant amount of heat (> 200 °C) is required to effectively crosslink the thin film and the neutralization layer cannot be photochemically patterned. Therefore, an alternative functional group that can be selectively crosslinked without heat and involves facile chemistry is highly desired. In this Communication, we introduce a new type of crosslinkable random copolymer that can be crosslinked by either heat or UV light, and is prepared in high yield from commercially available monomers.

In selecting appropriate chemistry, our attention was drawn to the azido group, which can be easily introduced by nucleophilic displacement of alkyl halides from commercially available monomers such as *p*-chloromethyl styrene and has recently found great use in the synthesis of functionalized materials via copper catalyzed “click” chemistry.^[20] In addition the latent reactivity of the azido group is high and can be activated by either UV irradiation or under thermal conditions. The initial target systems was therefore a P(S-*r*-(S-N₃)-*r*-MMA) random copolymer, containing 3 mole % azide (N₃) units along the backbone, which was synthesized via reversible addition fragmentation chain transfer (RAFT) from styrene, MMA, and *p*-chloromethyl styrene. To avoid complications from the dithioester group during semiconductor processing, the dithioester was removed by treatment with

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2,2'-azobis(2-methylpropionitrile) (AIBN) and the chloromethyl group was displaced by reaction with NaN_3 . This gave the desired azidomethyl random copolymer, **3**, in high yield, the structure of which could be accurately controlled by the initial feed ratio (Scheme 1). The azide group is chemically inert until activated either by heat or UV light and could be easily handled under ambient conditions. Based on the fact that the proportion of styrene/MMA in the P(S-*r*-MMA) random copolymer that results in balanced surface interaction is 58/42, and the azide unit is chemically similar to styrene, the composition of PMMA was kept at 42 % and the others at a total of 58 %. As in the case of P(S-*r*-BCB-*r*-MMA), the molecular weight was controlled between 20000 and 100000 g mol^{-1} to obtain sufficient crosslink density.

Previously, the azide group has been shown to form a highly reactive nitrene on thermolysis or photolysis^[20] which can then undergo reaction with neighboring molecules, resulting in crosslinking.^[21–24] Initially, the photo-crosslinking of the azido copolymer, **3**, was investigated by UV irradiation ($\lambda = 254 \text{ nm}$) under vacuum ($\sim 10^{-2}$ Torr, 1 Torr = 1.333×10^2 Pa) to avoid undesired side reactions. The crosslinking of the azide group was monitored by IR spectroscopy with the peak from the azide group clearly visible at 2100 cm^{-1} before crosslinking which was observed to disappear completely upon photolysis (Fig. 1).

The general procedure to prepare neutralized surfaces by photo-crosslinking is therefore spin coating of a toluene solution of P(S-*r*-(S-N₃)-*r*-MMA) random copolymer (0.4 wt %, 3000 rpm) on silicon substrates to give 11 nm thick films. These thin films were then exposed to deep UV irradiation ($\lambda = 254 \text{ nm}$) to induce the crosslinking. It should be noted that this is the same UV source used to prepare the nanoporous template by photo-degradation of the PMMA block in the PS-*b*-PMMA diblock copolymer thin films.^[12] However, the absence of long PMMA blocks in the random copolymer significantly retards photodecomposition. Various UV intensities (1.4 to 5.3 mW cm^{-2}) and irradiation times (1 to 60 min) were applied and the resulting thickness of crosslinked layers, after washing with a good solvent, are plotted as a function of UV irradiation time at different UV intensities (Fig. 2). At 5.3 mW cm^{-2} , 2 minutes of UV exposure gives crosslinked

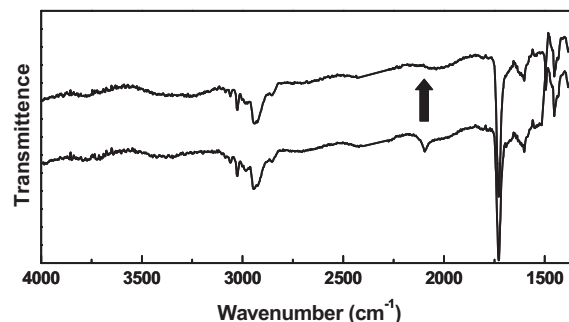
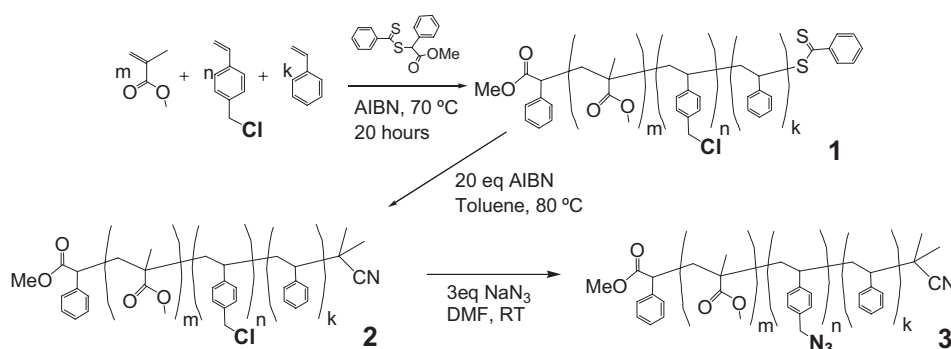


Figure 1. FT-IR spectrum for P(S-*r*-(S-N₃)-*r*-MMA) random copolymer, **3**, and after UV irradiation.

layers of 6.8 nm which reached a constant value of ca. 9–10 nm after 5 minutes. Reducing the UV intensity did not lead to a significant difference in crosslinking efficiency and lower UV intensity (1.4 mW cm^{-2}) was still able to give crosslinked films after short irradiation times. This suggests that the photo-crosslinking of azido groups in these random copolymers is a fast and facile reaction.

To investigate whether these crosslinked layers neutralize the surface as effectively as BCB systems, aligned thin films of PS-*b*-PMMA diblock copolymer were prepared on these layers. After thermal annealing at $170 \text{ }^\circ\text{C}$ for 12 hours, the ordering of diblock copolymer was investigated by SFM. As can be seen in Figure 2, the ordering of PS-*b*-PMMA diblock copolymer depends on the UV irradiation time, i.e., there is an optimal processing time for crosslinking of the underlying layer. For short exposure times ($< 20 \text{ min}$), the diblock copolymer film showed excellent ordering of cylindrical microdomains oriented normal to the surface. After 20 minutes irradiation, the block copolymer films still show perpendicular orientation of cylindrical microdomains, however there were significant defects in the film surface. It can be postulated that the existence of a processing window (defects at longer UV exposure time) is related to side reactions of the random copolymer layer induced by over-exposure to UV irradiation.

As mentioned above, the experimental procedure (blanket irradiation at 254 nm) for the photo-crosslinking of P(S-*r*-



Scheme 1. Synthesis of P(S-*r*-(S-N₃)-*r*-MMA) random copolymer, **3**.

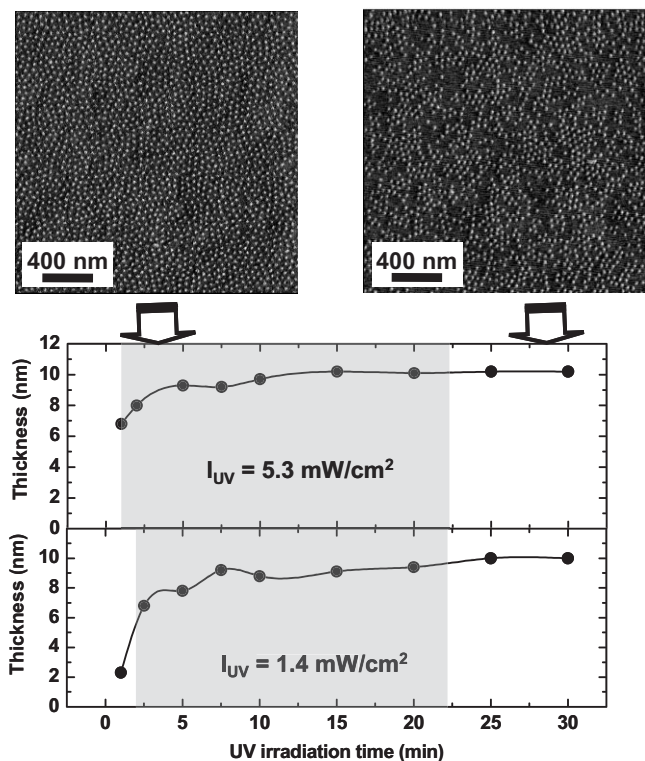


Figure 2. The crosslinked thickness of P(S-*r*-(S-N₃)-*r*-MMA) thin films as a function of UV irradiation time at two different UV intensities (5.3 and 1.4 mW cm⁻²), and the representative SFM phase images of cylinder forming PS-*b*-PMMA diblock copolymers.

(S-N₃)-*r*-MMA) random copolymers is similar to that used to degrade the backbone of the PMMA block in PS-*b*-PMMA thin films. It has been reported that the photo-degradation of the P(S-*r*-MMA) random copolymer is efficiently suppressed by a small fraction of PS in the copolymer.^[25] This was attributed to the screening effect by PS, as the main photo-absorbing species in the P(S-*r*-MMA) is PS. Therefore, to confirm that photo-degradation of the backbone P(S-*r*-MMA) random copolymer does not occur under our experimental conditions, the corresponding hydroxyl terminated P(S-*r*-MMA) random copolymer which does not contain azido groups was spin coated on silicone wafers, then exposed to UV for 10 and 60 minutes. The polymers on the wafer were recovered by washing with a good solvent, dried under vacuum, and then characterized by size-exclusion chromatography (SEC) and NMR. On comparison with a non-irradiated sample, no detectable change in molecular weight, polydispersity, or comonomer ratio was detected. This result strongly supports that the photodegradation of the backbone in the P(S-*r*-MMA) random copolymer does not occur under the employed UV irradiation conditions. Furthermore, it should be noted that even at longer times of UV irradiation, when the ordering of PS-*b*-PMMA diblock copolymer show some defects, backbone degradation of the random copolymer does not occur.

Another issue to consider is the effect of atmosphere on the crosslinking reaction. In the above example, UV irradiation

for either degradation of PMMA blocks or for crosslinking of the azido groups was performed under vacuum ($\sim 10^{-2}$ Torr) to avoid unnecessary side reactions. It was also observed that the random copolymers are crosslinked in air as efficiently as in vacuum. However, after annealing the PS-*b*-PMMA diblock copolymers, the morphology was very different. For samples crosslinked under air, the film surface was not smooth and the ordering of block copolymers was very poor (data not shown). This can be attributed to the presence of oxygen, since the photolysis of oxygen by UV irradiation produces reactive radicals, such as hydroxyl radical, ozone, etc. which can undergo subsequent reaction with the random copolymer layer. For example, these radicals can easily react with nitrenes or other side chain groups to form unwanted oxidative side products, leading to significantly different surface properties. While at a significantly lower concentration, it should be noted that the generation of oxygen derived radicals may also be responsible for defects at longer UV exposure in vacuum. In this case, the over-dosage of UV irradiation also leads to photo-oxidation and a change in surface energy.

In addition to photo-crosslinking, the azide group can be thermolyzed to produce reactive nitrene species, also resulting in the crosslinking. Hence the thermal-crosslinking of P(S-*r*-(S-N₃)-*r*-MMA) random copolymer was investigated, and the efficiency of the crosslinking compared with the corresponding benzocyclobutene (BCB) random copolymer. The experimental condition was the same for both materials; after spin coating of a 0.4 wt % solution of random copolymer in toluene, the coated substrates were heated to 250 °C under a *gentle* flow of nitrogen. Figure 3 shows the crosslinked film thickness as a function of baking time. The crosslinked film thickness reached a constant value of ca. 10 nm after 1 minute

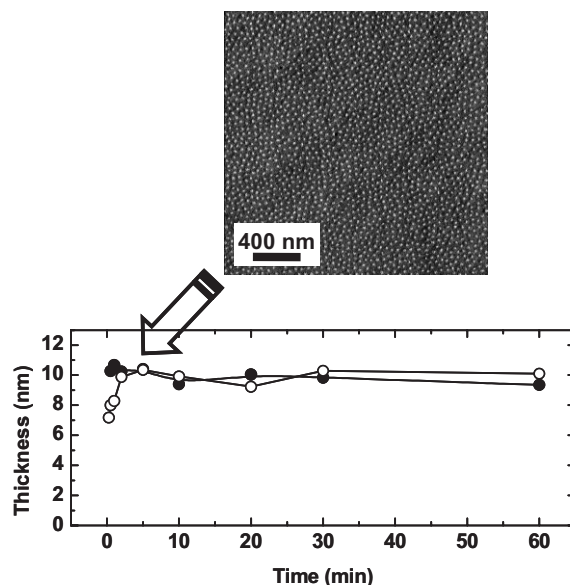


Figure 3. The crosslinked thickness of P(S-*r*-(S-N₃)-*r*-MMA) (filled circle) and P(S-*r*-BCB-*r*-MMA) (open circle) thin films as a function of baking time at 250 °C, and the representative SFM phase image of cylinder forming PS-*b*-PMMA diblock copolymers.

for both materials and it can be concluded that the crosslinking efficiency of P(S-*r*-(S-N₃)-*r*-MMA) is similar to the corresponding P(S-*r*-BCB-*r*-MMA) random copolymer. SFM images in Figure 3 corresponds to the ordering of PS-*b*-PMMA diblock copolymer on P(S-*r*-(S-N₃)-*r*-MMA) after thermal crosslinking for 1 minute, and clearly demonstrates the perpendicular orientation of cylindrical microdomains.

Contrary to the photo-crosslinking case, prolonged processing of the brush layer did not lead to defects in the ordering of PS-*b*-PMMA diblock copolymer, even after thermal-crosslinking for 1 hour. Note that the nitrogen atmosphere in our experimental condition does not guarantee the complete absence of the oxygen and suggests that the presence of oxygen under thermal-crosslinking conditions may not be a crucial factor, while the photo-crosslinking does show oxygen sensitivity.

Another advantage of these azido functionalized materials in comparison with BCB systems is the feasibility of combining bottom-up self-assembly with top-down processing. Since the random copolymers are crosslinked by UV irradiation, they can act as a photoresist and the patterned arrays of random copolymers can be obtained through a photolithographic process. As graphically represented in Figure 4, the random copolymers were spin coated on the substrate, and then irradiated with UV-light through a photo-lithographic mask to produce a patterned layer of random copolymer. Thin films of PS-*b*-PMMA diblock copolymers, having cylindrical and lamellar structures, were then prepared on these patterns and the detailed morphologies of each region were investigated by SFM (Fig. 5) for the ordering of PS-*b*-PMMA diblock copolymer with a cylindrical morphology on a patterned random copolymer layer (8 μm line). In this case, the film thickness is same as the unpatterned samples (~ 35 nm, L_0). The ordering of the block copolymers is significantly affected by the patterning process with the PS-*b*-PMMA block copolymer showing the expected perpendicular orientations on the pattern of the random copolymer layers. In direct contrast, the typical “hole” and “island” morphology of horizontal alignment is observed in the other areas due to the absence of the neutral copolymer layer.

Similar features are also seen in the ordering of lamellar forming PS-*b*-PMMA block copolymer (Fig. 5b), where the film thickness was controlled as ~ 50 nm (1.5 L_0). In the

patterned areas of the crosslinked random copolymer, the block copolymer with lamellar structure exhibits a perpendicular orientation, while a horizontal orientation is evident in the other regions. Minor defects of ordering shown in the pattern of the random copolymer layers can be ascribed to the experimental condition in the mask aligner, as the vacuum level of the contact mode in the mask aligner is relatively low.

In summary, novel functional materials for the fabrication of nanoscopic structures have been developed via the combination of controlled polymerization^[26] and latent side-chain reactivity. Compared to BCB functionalities, it was demonstrated that the use of azide groups offers a number of advantages for tuning the surface interaction. Upon thermolysis or photolysis, the azide group decomposes to form a reactive nitrene, resulting in crosslinking of the random copolymers, which was found to be as efficient as the BCB group, requiring only minutes for complete crosslinking under either thermal or photochemical conditions. Subsequently, thin films of PS-*b*-PMMA block copolymers with cylindrical microdomains oriented normal to the surface were produced on these crosslinked random copolymer layers. The success of this crosslinking strategy, both thermal and photo-crosslinking, coupled with a wide processing window and compatibility with standard processing tools strongly suggests that these materials represent a general approach to modifying surfaces. Furthermore, the P(S-*r*-(S-N₃)-*r*-MMA) random copolymers can be patterned with a conventional top-down lithographic process, which allows subsequently patterning of microdomains in the block copolymers to be accomplished. This use of photo-crosslinkable materials allows the convergence of bottom-up self-assembly of block copolymers and top-down photo-lithographic approaches, which is anticipated to open up new possibilities in the manufacture of various nanomaterials and devices.

Experimental

Analytical TLC was performed on commercial Merck Plates coated with silica gel GF254 (0.24 mm thick). Silica Gel for flash chromatography was Merck Kieselgel 60 (230–400 mesh, ASTM). ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) measurements were performed on a Bruker AC 400 spectrometer at room temperature. SEC was car-

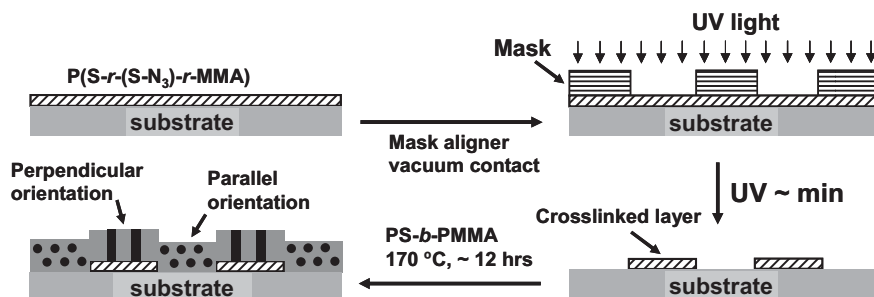


Figure 4. Schematics to prepare PS-*b*-PMMA thin films on the patterned random copolymer layers using a photo-lithographic mask.

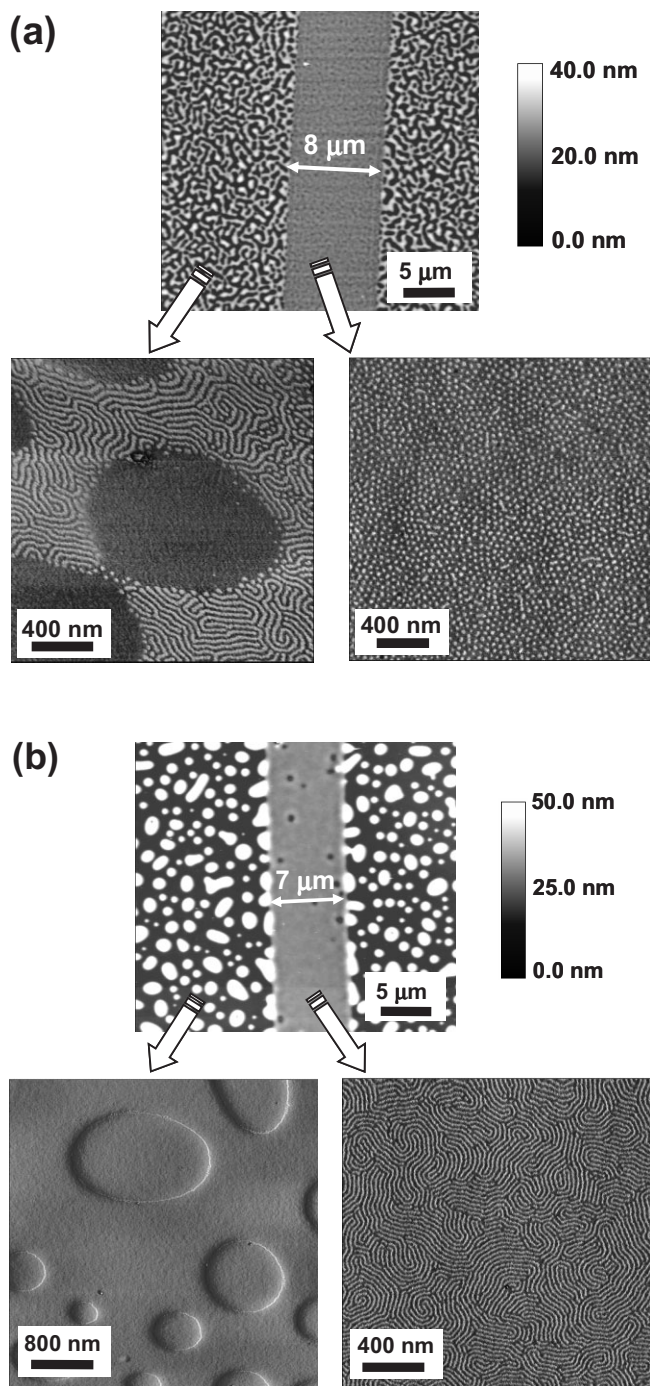


Figure 5. SFM images of a) cylinder, and b) lamellar forming PS-*b*-PMMA thin films on the patterned random copolymer layers. Upper images in (a) and (b) correspond to the height images of the patterns, and lower images show detailed thin film morphologies of indicated regions.

ried out at room temperature on a Waters chromatograph connected to a Waters 410 differential refractometer and six Waters Styragel columns (five HR-5 μm and one HMW-20 μm) using THF as eluent (flow rate: 1 mL min^{-1}). A Waters 410 differential refractometer and a 996 photodiode array detector were employed. The molecular weights of the polymers were calculated relative to linear PS and PMMA standards. Ellipsometry was performed with a AutoEl II

(A9819) automatic ellipsometer from Rudolph Research at a wavelength of 632.8 nm and an angle of 70°. The refractive indexes of the films were set to 1.462 for all the films and at least 5 different measurements were performed. IR spectra were obtained on Perkin-Elmer Spectrum BX FT-IR system. The sample mixture was coated on a KBr pellet. IR spectra were obtained in the transmission mode at a resolution of 4 cm^{-1} and 64 scan.

Synthesis of P(S-*r*-(S-N₃)-*r*-MMA) Random Copolymer: Methyl methacrylate (2.4 g, 24.0 mmol), styrene (3.6 g, 34.6 mmol), 4-vinylbenzene chloride (0.27 g, 1.8 mmol), and RAFT initiator (35.3 mg, 0.12 mmol) were mixed and degassed by performing the three freeze-pump-thaw cycles. The glass ampule was sealed under vacuum, and then heated to 120 °C for 24 hours. The viscous reaction mixture was then dissolved in dichloromethane and precipitated into methanol to give the random copolymer, **1**, as a pink solid. To avoid the coupling during the azidation, the dithioester end group was first removed by the reaction with AIBN in toluene under Argon (80 °C for 4 hours). The solution was precipitated in methanol, and a white powder, **2**, was obtained. The polymer was then dissolved with sodium azide in dimethylformamide, and stirred at the room temperature for 12 hours. The solution was filtered, and precipitated in methanol to yield a white powder, **3**, as a final product. Overall Yield: 67 % (based on unreacted monomer); $M_n = 35,000 \text{ g mol}^{-1}$; PDI = 1.08; $^1\text{H NMR}$ (200 MHz, CDCl_3 , δ): 0.3–2.6 (m, CH_2 , CH , CH_3), 2.60–3.65 (s, OCH_3), 4.10–4.35 (s, ArCH_2N_3), 6.4–7.5 (m, ArH); IR: wavenumbers = 3110–2820, 2100, 1730, 1600, 1490, 1450 cm^{-1} .

Preparation of Thin Films: A 0.4 wt % solution of P(S-*r*-(S-N₃)-*r*-MMA) random copolymer in toluene was prepared and spin coated onto a silicon wafer to yield ~ 12 nm thick films. The thin film was cured by UV irradiation ($\lambda = 254 \text{ nm}$) under vacuum ($\sim 10^{-2}$ Torr). Various exposure time and intensity of UV radiation were applied. Films were then rinsed with toluene several times to remove the non-crosslinked materials. For thermal-crosslinking, the coated substrate was heated to 250 °C under a nitrogen flow for a various baking time, followed by rinsing with toluene. Thin films of PS-*b*-PMMA diblock copolymer with cylindrical microstructure ($M_n = 76000 \text{ g mol}^{-1}$ and PDI = 1.07), ~ 35 nm (L_0) in thickness, were prepared on these substrates. Films were annealed at 170 °C for 12 h under vacuum. The patterned random copolymer layers were prepared with a mask aligner (MJB 3 UV400, Karl Suss America Inc.). The UV light (I-line, $\lambda = 365 \text{ nm}$) was applied to the thin films of the random copolymers through the patterned mask using the vacuum contact mode. A total dose of ca. 10 J cm^{-2} was applied. Uncrosslinked regions were removed by washing with toluene, and then the thin films of PS-*b*-PMMA diblock copolymers, with cylindrical and lamellar ($M_n = 45000 \text{ g mol}^{-1}$ and PDI = 1.07) morphologies, were prepared as above.

Characterization: Scanning force microscopy (SFM) images were obtained in both the height and phase-contrast mode using a Digital Instruments Dimension 3100 scanning force microscope in tapping mode.

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- [1] *IBM's Chip Breakthrough*, Business Week, McGraw-Hill, New York 2007.
- [2] C. J. Hawker, K. L. Wooley, *Science* **2005**, 309, 1200.
- [3] a) R. A. Segalman, *Mater. Sci. Eng.* **2005**, R48, 191. b) C. J. Hawker, T. P. Russell, *MRS Bull.* **2005**, 30, 952. c) S. O. Kim, H. H. Solak, M. P. Stoykovich, N. J. Ferrier, J. J. de Pablo, P. F. Nealey, *Nature* **2003**, 424, 411. d) M. P. Stoykovich, M. Muller, S. O. Kim, H. H. Solak, E. W. Edwards, J. J. de Pablo, P. F. Nealey, *Science* **2005**, 308, 1442. e) R. A. Segalman, H. Yokoyama, E. J. Kramer, *Adv. Mater.* **2001**, 13, 1152. f) K. Shin, K. A. Leach, J. T. Goldbach, D. H. Kim, J. Y. Jho, M. Tuominen, C. J. Hawker, T. P. Russell, *Nano Lett.* **2002**, 2, 933.

- [4] M. J. Fasolka, A. M. Mayes, *Annu. Rev. Mater. Res.* **2001**, *31*, 323.
- [5] M. Bal, A. Ursache, M. T. Tuominen, J. T. Goldbach, T. P. Russell, *Appl. Phys. Lett.* **2002**, *81*, 3479.
- [6] J. Bang, S. H. Kim, E. Drockenmuller, M. J. Misner, T. P. Russell, C. J. Hawker, *J. Am. Chem. Soc.* **2006**, *128*, 7622.
- [7] C. T. Black, K. W. Guarini, K. R. Milkove, S. M. Baker, T. P. Russell, M. T. Tuominen, *Appl. Phys. Lett.* **2001**, *79*, 409.
- [8] J. Y. Cheng, C. A. Ross, V. Z. H. Chan, E. L. Thomas, R. G. H. Lammertink, G. J. Vancso, *Adv. Mater.* **2001**, *13*, 1174.
- [9] J. Y. Cheng, C. A. Ross, E. L. Thomas, H. I. Smith, G. J. Vancso, *Appl. Phys. Lett.* **2002**, *81*, 3657.
- [10] E. Drockenmuller, L. Y. T. Li, D. Y. Ryu, E. Harth, T. P. Russell, H.-C. Kim, C. J. Hawker, *J. Polym. Sci. Part A* **2005**, *43*, 1028.
- [11] D. H. Kim, S. H. Kim, K. Lavery, T. P. Russell, *Nano Lett.* **2004**, *4*, 1841.
- [12] H.-C. Kim, X. Jia, C. M. Stafford, D. H. Kim, T. J. McCarthy, M. Tuominen, C. J. Hawker, T. P. Russell, *Adv. Mater.* **2001**, *13*, 795.
- [13] W. A. Lopes, H. M. Jaeger, *Nature* **2001**, *414*, 735.
- [14] M. Park, C. Harrison, P. M. Chaikin, R. A. Register, D. H. Adamson, *Science* **1997**, *276*, 1401.
- [15] R. A. Segalman, A. Hexemer, R. C. Hayward, E. J. Kramer, *Macromolecules* **2003**, *36*, 3272.
- [16] M. Templin, A. Franck, A. Du Chesne, H. Leist, Y. Zhang, R. Ulrich, V. Schadler, U. Wiesner, *Science* **1997**, *278*, 1795.
- [17] a) G. Coulon, T. P. Russell, V. R. Deline, P. F. Green, *Macromolecules* **1989**, *22*, 4600. b) T. P. Russell, G. Coulon, V. R. Deline, D. C. Miller, *Macromolecules* **1989**, *22*, 2581. c) S. H. Anastasiadis, T. P. Russell, S. K. Satija, C. F. Majkrzak, *Phys. Rev. Lett.* **1989**, *62*, 1852.
- [18] P. Mansky, Y. Liu, E. Huang, T. P. Russell, C. J. Hawker, *Science* **1997**, *275*, 1458.
- [19] D. Y. Ryu, K. Shin, E. Drockenmuller, C. J. Hawker, T. P. Russell, *Science* **2005**, *308*, 236.
- [20] a) E. F. V. Scriven, K. Turnbull, *Chem. Rev.* **1988**, *88*, 297. b) P. Wu, A. K. Feldman, A. K. Nugent, C. J. Hawker, A. Scheel, B. Voit, J. Pyun, J. M. J. Fréchet, K. B. Sharpless, V. V. Fokin, *Angew. Chem. Int. Ed.* **2004**, *43*, 3928. c) J. A. Opsteen, J. C. M. van Hest, *Chem. Commun.* **2005**, 57. d) B. Parrish, R. B. Breitenkamp, T. Emrick, *J. Am. Chem. Soc.* **2005**, *127*, 7404. e) A. P. Vogt, B. S. Sumerlin, *Macromolecules* **2006**, *39*, 5286. f) H. F. Gao, K. Matyjaszewski, *Macromolecules* **2006**, *39*, 4960. g) O. Altintas, B. Yankul, G. Hizal, U. Tunca, *J. Polym. Sci. Part A* **2006**, *44*, 6458. h) O. Altintas, G. Hizal, U. Tunca, *J. Polym. Sci. Part A* **2006**, *44*, 5699. i) R. J. Thibault, K. Takizawa, P. Lowenheilm, B. Helms, J. L. Mynar, J. M. J. Fréchet, C. J. Hawker, *J. Am. Chem. Soc.* **2006**, *128*, 12084. j) H. M. Li, F. O. Cheng, A. M. Duft, A. Adronov, *J. Am. Chem. Soc.* **2005**, *127*, 14518. k) G. Mantovani, V. Ladmiral, L. Tao, D. M. Haddleton, *Chem. Commun.* **2005**, 2089. l) J. F. Lutz, H. G. Börner, K. Weichenhan, *Macromol. Rapid Commun.* **2005**, *26*, 514.
- [21] R. A. Abramovitch, B. A. Davis, *Chem. Rev.* **1964**, *64*, 149.
- [22] J. K. Jorgensen, E. Ommundsen, A. Stori, K. Redford, *Polymer* **2005**, *46*, 12073.
- [23] J. R. Knowles, *Acc. Chem. Res.* **1972**, *5*, 155.
- [24] A. Reiser, F. W. Willets, G. C. Terry, V. Williams, R. Marley, *Trans. Faraday Soc.* **1968**, *64*, 3265.
- [25] A. Torikai, A. Hozumi, K. Fueki, *Polym. Degrad. Stab.* **1986**, *16*, 13.
- [26] a) D. Benoit, C. J. Hawker, E. E. Huang, Z. Q. Lin, T. P. Russell, *Macromolecules* **2000**, *33*, 1505. b) U. M. Stehling, E. E. Malmstrom, R. M. Waymouth, C. J. Hawker, *Macromolecules* **1998**, *31*, 4396. c) J. Dao, D. Benoit, C. J. Hawker, *J. Polym. Sci. Part A* **1998**, *36*, 2161.