Multiple Nanoscale Templates by Orthogonal Degradation of a Supramolecular Block Copolymer Lithographic System

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T he self-assembly of block copolymers is a promising platform for the "bottom-up" fabrication of nanostructured materials and devices. In designing such nanostructures, the molecular characteristics of the block copolymers dictate the self-assembly process and are therefore critical in the formation of lithographic templates by controlled degradation.[1−4] The emerging role of block copolymer lithography in the fabrication of various devices has led to a significant challenge in the creation of low symmetry, nontraditional arrays of patterned nanostructures. Traditional array patterns such as hexagonally packed spherical or cylindrical nanostructures have been extensively studied, but their integration into microelectronic devices is limited due to potential incompatibility with the rectilinear system typically used in integrated circuit design.[5−7] While more desirable, the formation of rectilinear or square arrays of nanostructures is energetically less favorable; for example, packing of cylinder-forming diblock polymer chains in a square lattice requires significant non-uniform chain stretching leading to packing frustration.[8] As a result, the formation of square or rectangular nanostructures is not possible using a purely covalent diblock copolymer system, and more complex directed self-assembly routes[9] or the use of a triblock copolymer system is required.[10,11] To address this challenge, we have recently reported a modular and hierarchical self-assembling strategy which combines noncovalent supramolecular interactions between blends of H-bonding polymers[12,13] with diblock co-

polymer self-assembly to obtain ordered square arrays of cylindrical nanostructures.[14] This approach involves blending of poly(ethylene oxide)-*b*-poly(styrene-*r*-4-hydroxystyrene) (PEO-*b*-P(S-*r*-4HS)) and poly(styrene-*r*-4-vinylpyridine)-*b*-poly(methyl methacrylate) (P(S-*r*-4VP)-*b*-PMMA) diblock copolymers with the H-bonded styrenic domains forming the matrix. By design of the molecular weight and volume fraction for the PEO and PMMA segments, these domains are expected to form individual cylinders within separate square lattices. In the original design, only the poly(methyl methacrylate) (PMMA) domains were degradable, which leads to a single nanotemplate (square array of cylinders) that could be used for lithographic[15−22] patterning of the underlying silicon wafer. While promising for integrated circuit design, it is extremely difficult with this new strategy to selectively remove the corresponding square-packed PEO domains,[23,24] thus limiting the diversity and tunability of these supramolecular block copolymer systems.

ABSTRACT An orthogonal approach to the creation of multiple nanoscale templates from a single supramolecular block copolymer system is presented. The enabling feature of this strategy is the design of block copolymers that incorporate independent degradation chemistries which permits each block copolymer to be addressed individually and sequentially. By blending a block copolymer containing H-bond donor groups and a UV-degradable domain with the complementary copolymer containing H-bond acceptor groups and an acid-cleavable segment, diverse and tunable nanoporous thin films with different pore sizes and array patterns can be obtained. This robust strategy demonstrates the potential of combining orthogonal chemistry with the inherent tunability of supramolecular systems.

KEYWORDS: block copolymer lithography · templates · supramolecular assembly · thin films
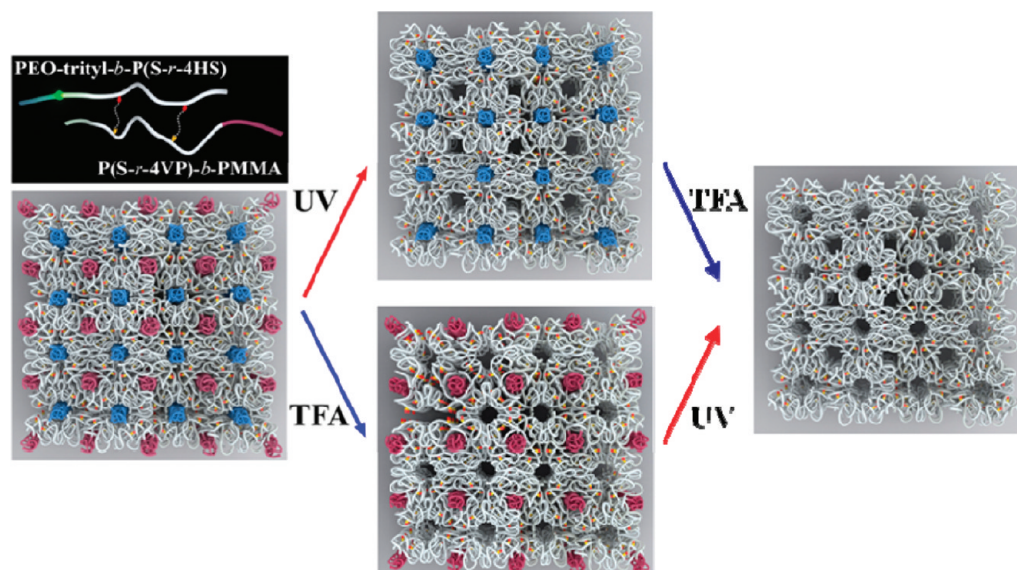
Figure 1. Schematic representation of an orthogonal degradation approach to three different templated square arrays from the blending of supramolecular block copolymers (PEO-trityl-*b*-P(S-*r*-4HS)/P(S-*r*-4VP)-*b*-PMMA) and selective removal of PEO (with trifluoroacetic acid) and/or PMMA domains (with UV).

In conceiving an approach which overcomes these limitations, our attention was drawn to the increasing importance of orthogonal chemistry in materials research. Synthetic strategies are now being developed that allows a single polymeric scaffold to be orthogonally functionalized through the use of cascade or simultaneous strategies to achieve a range of desirable properties/materials from a single starting system and/or introduce multiple functional groups.[25−27] This ability to obtain a library of different materials from a single platform is extremely efficient from a design perspective. To address this challenge, we report a modular approach to the synthesis and processing of orthogonally degradable, supramolecular diblock copolymer blends which allows for the formation of ordered square arrays of nanostructures that are individually addressable and degradable. As a result, this strategy enables tuning of pore size and nanostructure by selective etching of either the PMMA or PEO domains through the incorporation of an acid-sensitive trityl ether linker between the PEO and PS segments in one block copolymer and coupling of this degradation system with diblocks containing photodegradable PMMA segment (Figure 1). This new strategy therefore provides a powerful route to molecularly designing an array of nanoporous polymer films with tunable porosity from a single starting supramolecular copolymer system.

RESULTS AND DISCUSSION

In selecting an orthogonal chemistry to the traditional photodegradation of PMMA domains, acid-catalyzed cleavage was identified as a promising candidate. In particular, the trityl ether linker has been reported to be cleaved under mild acid conditions,[28] and

Zhang *et al.* have further demonstrated that highly ordered nanoporous templates can be obtained from PEO-*b*-PS diblock copolymer thin films by introducing an acid-cleavable trityl ether juncture between PS and PEO segments.[29] Incorporating this design motif into the supramolecular diblock copolymer system then leads to the cleavable diblock copolymers PEO-trityl-*b*-P(S-*r*-4HS) **6** (Scheme 1). Starting from the chloromethyl-substituted alkoxyamine, **1**, alkylation with 4-hydroxybenzophenone followed by addition of phenylmagnesium bromide gives the trityl alcohol, **2**, in an overall yield of 80%. Reaction of **2** oxalyl chloride followed by coupling with 3-azidopropanol using pyridine as the base and silver triflate as the catalyst then affords the alkoxyamine, **3**, which contains both a cleavable trityl linker as well as a reactive azide group. Introduction of the poly(ethylene glycol) chain was achieved by coupling with an acetylene-terminated PEO, **4**, using standard Huisgen cycloaddition conditions mediated by Cu(I) and pentamethyldiethylenetriamine. Generally, formation of a chain end trityl ether unit from an end-functionalized polymer requires long reaction times and high temperature and proceeds with poor yields.[28] In this case, click reaction between **3** and **4** occurs at room temperature to give the macroinitiator, **5**, in essentially quantitative yield, which is fully consistent with the reported efficiency of click coupling reactions. Synthesis of diblock copolymer **6** was then achieved by nitroxide-mediated polymerization[30] of styrene and 4-acetoxystyrene from **5** followed by hydrolysis of acetoxy groups using hydrazine.

In order to test the degradation of the diblock copolymer, **6**, in the solid phase, a solution of **6** was drop cast onto a glass plate and exposed to trifluoroacetic acid (TFA) vapor for 2 h. The cleavage of the trityl ether
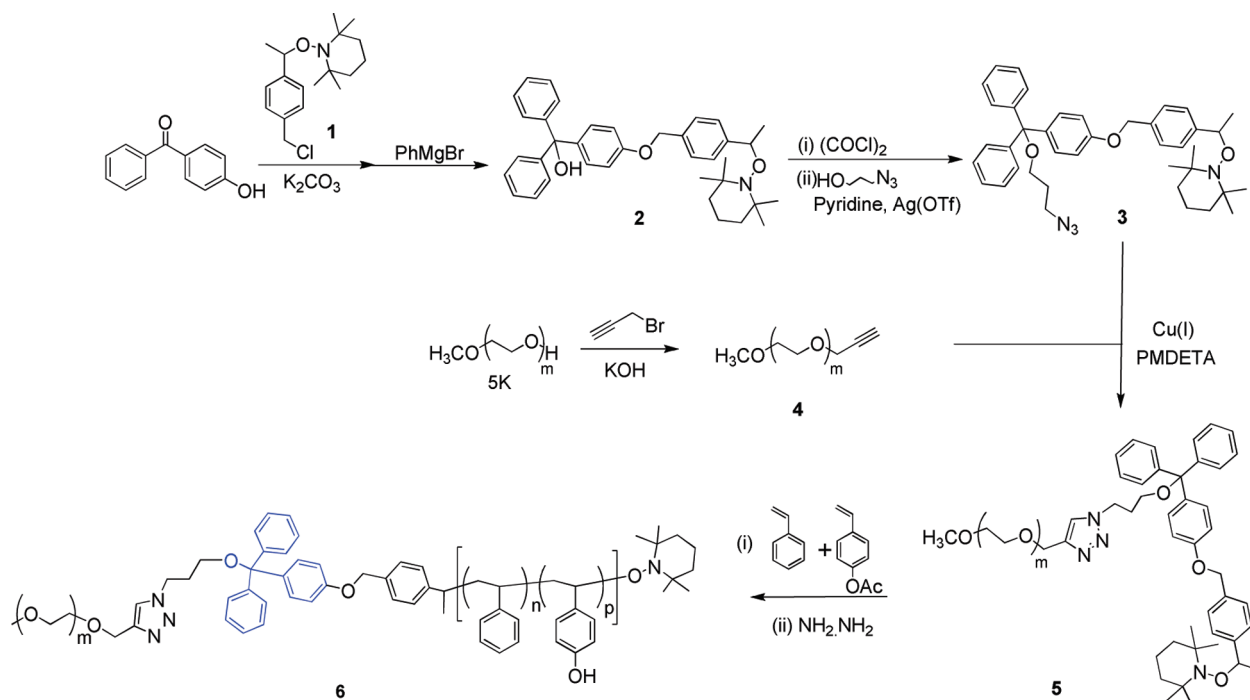
Scheme 1. Synthesis of acid-cleavable diblock copolymer PEO-trityl-*b*-P(S-*r*-4HS), 6, from the alkoxyamine, 1.

group was evident through comparison of the size exclusion chromatography (SEC) traces for the starting macroinitiator and PEO-trityl-*b*-P(S-*r*-4HS) diblock copolymer with the SEC trace for the products isolated after TFA treatment. As can be seen in Figure 2, low polydispersity, monomodal peak was observed for the macroinitiator, **5**, which increases in molecular weight after formation of the diblock copolymer, **6**, but still maintains its monomodal characteristics. However, reaction with TFA results in a lower molecular weight bimodal trace being observed with peak molecular weights corresponding closely to that expected for the cleaved P(S-*r*-4HS) block and starting PEO chain. Separation of these materials by solvent extraction and analysis by SEC and ^{1}H NMR further confirmed the absence of diblock copolymer and full cleavage of the trityl linker.

After demonstrating the efficiency of trityl ether cleavage, a 45 nm thick film of the diblock copolymer,

6 PEO-trityl-*b*-P(S-*r*-4HS), was prepared and solvent annealed under controlled high humidity.[31−34] This results in the expected hexagonally packed cylinders with a high degree of long-range order (Figure 3a).[29] Subsequent exposure to TFA followed by aqueous washing maintains the hexagonal, long-range order; however, full removal of the PEO chains/domains is observed, and highly ordered nanoporous films were produced as evidenced by transmission electron microscopy (TEM) (Figure 3b) and cross-section scanning electron microscopy (SEM) image (Figure 3c). This further demonstrates that cleavage of the trityl ether linkage by TFA is very efficient, yielding nanoporous films, and complete removal of PEO chains from the pores could be achieved.

The ability of the functional diblock copolymer, **6**, incorporating a cleavable trityl group as well as phenolic, H-bond donor units, to form square arrays by supramolecular blending was then examined. Accordingly, PEO-trityl-*b*-P(S-*r*-4HS) (EO$_{113}$S$_{150}$4HS$_5$) was combined with the complementary diblock copolymer, P(S-*r*-4VP)-*b*-PMMA (S$_{195}$4VP$_8$MMA$_{120}$), in a 1:1 molar stoichiometry and spun cast onto silicon wafers. The block copolymer thin films were subjected to solvent annealing under controlled high humidity conditions as described previously[14] and were observed to form highly ordered square arrays of cylinders with a periodicity of ∼55 nm (Figure 4a). The supramolecular thin films were then irradiated with UV light, leading to the degradation of the PMMA domains and partial cross-linking of the PS matrix. SEM images of UV-irradiated films (Figure 4b) indicated the formation of highly ordered square arrays of nanopores (dark domains) with a diameter of ∼12−15 nm and a periodicity of 55 nm. These cylindri-
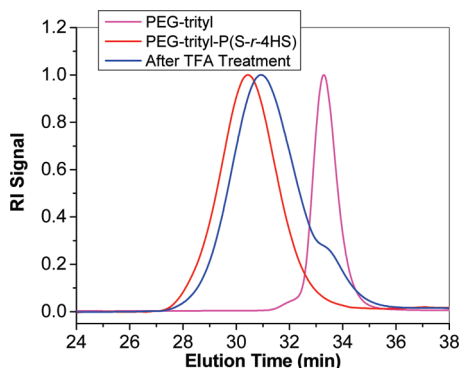

Figure 2. Comparison of SEC traces for the starting PEO macroinitiator, 5, diblock copolymer, 6, and the reaction product after treatment of 6 with TFA
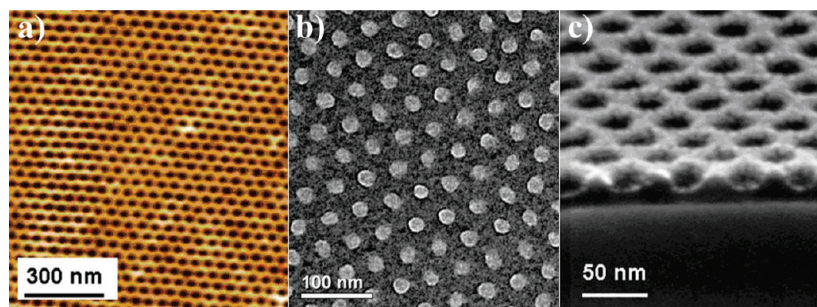
Figure 3. Morphologies of solvent-annealed films of the acid-cleavable diblock copolymer, PEO-trityl-*b*-P(S-*r*-4HS) **6** (SFM height, a), and nanoporous films after trifluoroacetic acid treatment (TEM, b; SEM, c).

cal holes are the result of the photodegradation of the PMMA blocks, while the nondegraded PEO domains could not be observed due to poor contrast between the PEO domains and the PS matrix. To visualize the PEO domains, the UV-degraded films were subsequently immersed in a TFA solution, resulting in cleavage of the trityl ether linkers and solubilization of the PEO chains. This two-step procedure results in a significantly different nanostructure when compared to the initial array formed after irradiation. In this case, two overlapping, highly ordered square arrays of cylindrical pores with different diameters were clearly observed by SEM (Figure 4c). The smaller nanopores were found to have a diameter of $13-15$ nm, consistent with the nanostructure obtained after irradiation and removal of the PMMA cylinders, while a second array of larger nanopores ($23-25$ nm in diameter) was clearly visible and is due to the acid-catalyzed cleavage of the trityl group and removal of the PEO domains. It is postulated that the larger pore size derived from the PEO do-

mains is due to swelling of the PEO cylinders under the high humidity environment of the solvent annealing process, which is in direct contrast to the negligible swelling of the hydrophobic PMMA domains.[31−33] Significantly, both sets of nanopores were found to have a periodicity of 52 nm, which corresponds with the periodicity value for the single square pore array obtained from the films after UV irradiation only. The basic unit cell with tetragonal packing of these two sets of nanopores has a periodicity of 37 nm, exactly $1/\sqrt{2}$ of 52 nm, further indicating that the PEO and PMMA blocks form two separate and overlapping arrays, both with tetragonal lattices.[14]

Additional experiments were then carried out to examine the orthogonality of the two-step process. In the reverse strategy, the films were first exposed to a TFA solution to cleave the PEO followed by UV irradiation to degrade the PMMA. SEM images showed that TFA treatment produced square arrays of large nanopores, which from the previous results correspond with the expected removal of the PEO cylinders (Figure 4d). Subsequent UV irradiation led to the formation of two sets of square arrays of nanopores (Figure 4e), the structure of which is very similar to that obtained from the reverse strategy, UV irradiation followed by treatment with a TFA solution (Figure 4c). The reversibility of the process clearly demonstrates the orthogonality of the degradation reactions combined with the unique ability to create multiple templates from a single block copolymer nanostructure.

In conclusion, we have demonstrated a unique strategy for the generation of multiple nanoscale templates from a single supramolecular block copolymer lithographic system using orthogonal degradation reactions. By exploiting the blending of diblock copolymers based on an acid-cleavable, H-bond donor, PEO-trityl-*b*-P(S-*r*-4HS), and a photodegradable, H-bond acceptor, P(S-*r*-4 VP)-*b*-PMMA, ordered square arrays of both PMMA and PEO cylinders were obtained in which the individual PMMA and PEO domains could be chemically addressed. This allows three distinct nanoscale templates: cylindrical pores from the PMMA domains, cylindrical pores from the PEO domains, or a combined nanostructure with nested arrays of both pores to be obtained from the same starting system. More signifi-
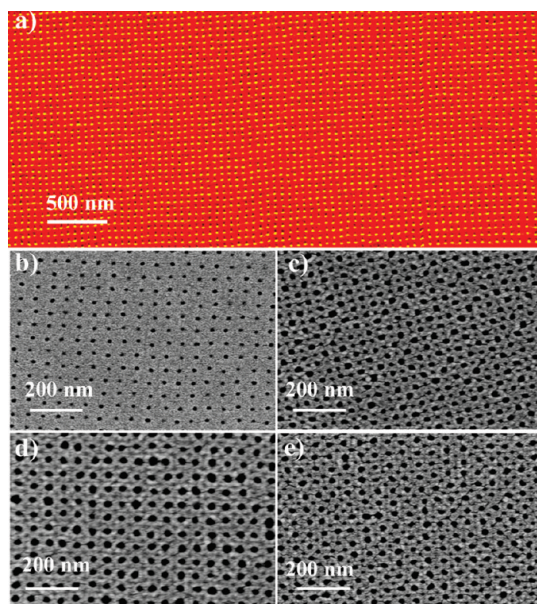

Figure 4. (a) SFM phase image of solvent-annealed films from supramolecular block copolymers; (b) SEM image of UV-irradiated films; (c) SEM image of trifluoroacetic acid treated films after UV irradiation; (d) SEM image of trifluoroacetic acid treated films; (e) SEM image of UV-irradiated films after trifluoroacetic acid treatment.

cantly, the chemically distinct nature of the blocks leads to cylindrical holes of different diameters with the orthogonality requiring no specific order for the degrada-

tion reactions. This strategy provides a convenient route toward diverse and tunable nanoscale templates having nontraditional square arrays of features.

METHODS

The reagents and starting materials were purchased from commercial sources and used as received unless otherwise noted. Compositions of block copolymers were characterized by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy on a Bruker DMX 500 MHz spectrometer using the residual proton resonance or carbon signal of the deuterated solvent of the solvent as internal standard. Mass spectral data were collected on a Micromass QTOF2 Quadrupole/time-of-flight tandem mass spectrometer (ESI-MS). Size exclusion chromatography (SEC) was performed in THF on a Waters chromatograph equipped with four 5 μm Waters columns (300 × 7.7 mm) connected in series with increasing pore size (100, 1000, 10 000, and 1 000 000 Å). Waters 410 differential refractometer index (DRI) and 996 photodiode array detectors were employed. Molecular weight of the polymers was calibrated based on linear PMMA or PS standards.

Synthesis of Trityl Alcohol (2): A mixture of 4-hydroxybenzophenone (1.10 g, 5.57 mmol), the chloromethyl-functionalized alkoxyamine[35] **1** (1.73 g, 5.58 mmol), K$_2$CO$_3$ (1.54 g, 11.1 mmol), and 18-crown-6 (73.0 mg, 0.27 mmol) were dissolved in THF (30 mL) and refluxed for 12 h under argon atmosphere. After completion of the reaction, the THF was evaporated under reduced pressure and the reaction mixture dissolved in CH$_2$Cl$_2$ (100 mL) and washed with water (3 × 50 mL). The combined washings were then extracted with CH$_2$Cl$_2$ (50 mL), dried with anhydrous magnesium sulfate, and filtered. Evaporation of the solvent afforded the crude product that was subjected to high vacuum and taken to the next step without purification. A solution of phenylmagnesium bromide (2.33 mL, 3.0 M, 7.00 mmol) in diethyl ether was added dropwise to a solution of the alkylated benzophenone (1.10 g, 2.33 mmol) in THF (20 mL) at room temperature. The reaction was allowed to proceed for 24 h under argon atmosphere, and after completion of the reaction, the THF was evaporated under reduced pressure and the crude product was dissolved in CH$_2$Cl$_2$ (100 mL) and washed with water (3 × 50 mL). The combined washings were then extracted with CH$_2$Cl$_2$ (50 mL), dried with anhydrous magnesium sulfate, and filtered. Evaporation of the solvent afforded the crude trityl alcohol that was purified by silica gel column chromatography eluting with ethyl acetate/hexane (7:93) to give **2** as a colorless solid in an overall yield of 1.26 g (80%): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45−7.15 (m, 16H), 7.00−6.90 (m, 2H), 5.06 (s, 2H), 4.84 (q, J = 6.6 Hz, 1H), 2.82 (s, 1H), 1.70−0.60 (m, 21H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 157.9, 147.0, 145.6, 139.3, 135.2, 129.5, 129.1, 127.9, 127.8, 127.8, 127.8, 127.7, 127.3, 127.1, 126.7, 120.6, 115.2, 114.1, 82.7, 81.7, 69.9, 59.6, 40.2, 23.5, 17.1; EI/MS (m/z, ri) 549.3 (M$^+$, 0.1), 142.1 (14), 118.1(12), 117.1(100), 105.0 (13).

Synthesis of Trityl Ether (3): To a solution of the trityl alcohol **2** (3.20 g, 5.80 mmol) in dry hexanes (30 mL) was added oxalyl chloride (2.5 mL, 29 mmol), and the resulting reaction mixture was refluxed under argon atmosphere for 2 h. Hexanes and excess oxalyl chloride was removed under reduced pressure, and the crude trityl chloride was taken to the next step without further purification (note that the trityl chloride is highly sensitive to moisture). 3-Azidopropanol[36] (0.64 g, 6.40 mmol), pyridine (1.55 mL, 19.2 mmol), and Ag(OTf) (1.5 g, 5.8 mmol) were then dissolved in freshly distilled THF (15 mL) under an argon atmosphere, and to this mixture was added a solution of the trityl chloride (3.3 g, 5.8 mmol) in THF (10 mL) dropwise. The reaction was allowed to stir at room temperature under argon atmosphere for a period of 2 h, and after completion of the reaction (monitored by TLC), the reaction mixture was filtered, concentrated, and the crude product purified by column chromatography eluting with ethyl acetate/hexane (3:97) to give the azido derivative, **3**, as a colorless solid: yield 2.6 g (70%); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.50−7.15 (m, 16 H), 5.03 (s, 2H), 4.80 (q, J = 6.6 Hz, 1H), 3.45 (t, J = 6.9 Hz, 2H), 3.18 (t, J = 6.02, 2 H), 1.86 (qt, J = 6.2 Hz, 2H), 1.65−0.50 (m, 18H); ^{13}C NMR (125 MHz, CDCl$_3$) δ

157.8, 145.6, 144.5, 135.9, 135.2, 130.2, 128.2, 128.2, 127.7, 127.7, 127.7, 127.3, 126.8, 126.7, 113.8, 86.2, 82.7, 69.9, 60.2, 59.6, 48.7, 40.3, 29.4, 23.5, 17.4; ESI/TOF 633.42 (M$^+$ +1).

Synthesis of Acetylene-Terminated PEG (4): To a solution of poly-(ethylene glycol) monomethyl ether (M_w = 5000 Da) (2.0 g, 0.4 mmol) in toluene (15 mL) was added crushed KOH (0.16 g, 4.0 mmol), and the reaction mixture was allowed to stir at 50 °C for 30 min under an Ar atmosphere. Propargyl bromide (1.78 g, 12.0 mmol) was added to the reaction mixture, and heating continued for 16 h. The hot reaction mixture was then passed through Celite, the Celite washed with excess of acetone, and the combined organic layer concentrated under vacuum, and the crude product was precipitated in diethyl ether. The solid polymer was filtered, dried, and transferred to a Soxhlet thimble, where it was extracted with diethyl ether to ensure removal of excess propargyl bromide. The acetylene-terminated PEG, **4**, was obtained as a white solid: yield 2.0 g (99%); ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.20 (d, J = 2.4 Hz, O-C**H**$_2$-acetylene), 3.80−3.45 (m, PEG CH$_2$), 3.37 (s, C**H**$_3$-O-PEG), 2.43 (t, J = 2.32 Hz, acetylene proton).

Synthesis of Alkoxyamine-Functionalized PEG (5): A mixture of the acetylene-functionalized PEG, **4**, (2.0 g, 0.4 mmol), **3** (1.27 g, 2.00 mmol), and PMDETA (0.013 g, 0.08 mmol) was dissolved in freshly distilled THF. To this solution was added CuBr (0.005 g, 0.04 mmol), and the reaction mixture was allowed to stir at room temperature for 24 h under Ar. The reaction mixture was then passed through a short plug of silica gel, concentrated under vacuumm and the crude product was precipitated in diethyl ether. The solid polymer was filtered, driedm and transferred to a Soxhlet thimblem where it was extracted with diethyl ether to ensure complete removal of excess azido alkoxyamine initiator. The alkoxyamine-functionalized PEG, **5**, was obtained as a white solid: yield 2.0 g (88%); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.45−7.15 (m, aromatic protons), 6.96 (triazole proton), 6.90 (m, aromatic protons), 5.01 (s, C$_6$H$_5$-O-C**H**$_2$-C$_6$H$_5$), 4.78 (q, J = 6.6 Hz, C$_6$H$_5$-C**H**(CH$_3$)-O-), 4.60 (s, PEG-O-C**H**$_2$-triazole), 4.49 (t, J = 7.0 Hz, -CH$_2$-C**H**$_2$-triazole), 3.80−3.45 (m, PEG CH$_2$), 3.37 (s, C**H**$_3$-O-PEG), 3.13 (t, J = 5.6 Hz, -C**H**$_2$-O-trityl), 2.15 (m, -CH$_2$-C**H**$_2$-CH$_2$-O-), 1.62−0.50 (m, TEMPO protons).

Synthesis of PEO-b-P(S-r-4AS) Diblock Copolymer: PEO-b-P(S-r-4-acetoxystyrene) (PEO-b-P(S-r-4AS)) diblock copolymers were synthesized using nitroxide-mediated polymerization (NMP) procedures. PEO nitroxide-mediated macroinitiator, **5** (M_n = 5500, PDI = 1.06) (0.65 g, 0.14 mmol) was dissolved in a mixture of styrene (7.86 g, 75.6 mmol) and 4-acetoxystyene (215 mg, 1.33 mmol) and purged with N$_2$. The polymerization mixture was then stirred at 120 °C for 6 h, dissolved in THF, and precipitated into hexane. The crude product was then redissolved in a minimum amount of THF and reprecipitated into hexane to give the diblock copolymer as a white solid: yield 75%; M_n = 21 400, PDI = 1.15; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.22−7.43 (m, Ar**H**), 3.41−4.05 (s, OC**H**$_2$), 2.23−2.43 (s, C**H**$_3$), 1.20−2.12 (m, C**H**$_2$, C**H**).

Synthesis of PEO-b-P(S-r-4HS) and PMMA-b-P(S-r-4VP) Diblock Copolymers: PEO-b-P(S-r-4HS) and PMMA-b-P(S-r-4VP) diblock copolymers were synthesized according to our earlier report.[14]

Preparation of Thin Films. Supramolecular block copolymers were spin coated from benzene solutions onto silicon substrates with the film thickness being adjusted by controlling the solution concentration. The films were annealed overnight under saturated toluene vapor supplied by a neighboring solvent reservoir in a sealed chamber in controlled high humidity conditions.[32,33] After the solvent annealing process, films were exposed to deep UV light (254 nm) at a dose of 25 J cm^{-2} (XX-15S, UVP Inc.) under vacuum for 15−20 min. Some of the above films were further immersed in trifluoroacetic acid or exposed to TFA vapor for 2−4 h.

Microscopy Imaging: Tapping mode scanning force microscopy experiments were carried out using a Multimode Nanoscope III system (Digital Instruments (now Veeco), Santa Barbara, CA). The

measurements were performed using commercial Si cantilevers with a nominal spring constant and resonance frequency equal to 48 N/m and 190 kHz, respectively (ACL, Applied Nanostructures, Santa Clara, CA). Top-view and cross-section experiments of scanning electron microscopy were carried out with an FEI XL30 Sirion FEG microscope operating at an acceleration voltage of 5 kV. The secondary electron image was collected in ultrahigh-resolution mode at a working distance of about 5 mm. Transmission electron microscopy was further used to image polymer thin films. Block copolymer films on silicon wafers covered by a 100 nm thick layer of oxide were immersed in a 10 wt % HF solution and transferred to a water bath, floated off of the substrate, and placed on a Cu grid. Measurements were conducted with a FEI Tecnai G20 operating at 200 kV.

Supporting Information Available: Additional experimental details. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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