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Synthesis of Photoacid Generator-Containing Patternable Diblock Copolymers by Reversible Addition−Fragmentation Transfer Polymerization

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Patternable block copolymers have received considerable attention, as they provide two levels of control over nanostructures by combining the self-assembling and lithographic characteristics.[1,2] Some of these systems are based on the widely used polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) where the PS block cross-links and the PMMA block degrades upon exposure to UV or electron beam.[1] Some of the other block copolymer systems include poly(4-hydroxystyrene)-*b*-poly(α-methylstyrene) by Ober et al.[2d−2f] and poly(*t*-butyl (meth)acrylate)-based block copolymers by Gabor[2b] and La et al.,[2g] where suitable additives such as a photoacid generator (PAG) and/or a multifunctional cross-linker can be selectively incorporated into the chemically sensitive block to induce the deprotection or cross-linking reaction by light. The spatial control over the nanostructures in these self-assembled block copolymer resist films is afforded by a top-down lithographic process.

Greater flexibility in design of these patternable block copolymer systems can be attained if a monomeric form of PAG molecule can be incorporated into the polymer backbone by controlled polymerization techniques. The choice of the two blocks in these systems is not limited to polar−nonpolar pairs which is required for selective encapsulation of an added PAG.[2] Furthermore, the morphology can be predictably controlled based on the volume fraction of the two blocks.[2g] Wu et al. have reported the synthesis of a methacrylic monomer having photoacid-generating sulfonium group and its subsequent homo- and random copolymerization using conventional free radical polymerization to create a one-component resist system.[3] Here we report the synthesis of a well-defined, one-component patternable diblock copolymer containing PAG by the controlled polymerization of a highly polar ionic PAG-containing monomer. To our best knowledge, this is the first example of direct incorporation of PAG in one of the blocks. We also report studies on the self-assembling and lithographic characteristics of the newly synthesized material.

Figures 1 and 2 show the synthetic schemes for well-defined photosensitive homopolymer (PSA) and its block copolymer (PMMA-*b*-PSA), respectively. One block (PSA) of the copolymer has photoacid-generating sulfonium groups as well as acid-sensitive ester groups to cause a solubility change, while the other block is poly(methyl methacrylate) (PMMA). The targeted structure contains PAG in every repeat unit of the second block (the ratio of PAG and acid-sensitive ester group = 1:1) (polar−polar block combination). The acrylate monomer (SA) for the PSA block has a highly polar sulfonium ion. We adapted the reversible addition−fragmentation transfer (RAFT) polymerization to carry out the controlled polymerization of SA as it is known to be very effective for polar monomers and is tolerant to a wide range of functionalities.[4] The RAFT polymerization of SA (25 equiv) was carried out in the presence of 2-cyanoprop-2-yl dithiobenzoate as a chain transfer agent (CTA, 1 equiv) with 2,2′-azobis(isobutyronitrile) (AIBN, 0.2 equiv) in acetonitrile at 60 °C to investigate the feasibility of controlled polymerization (Figure 1a). The polymerization was near complete conversion (SA conversion ∼ 88%) within 36 h and proceeded homogeneously without precipitation. The resulting ionic polymer, PSA, was quite soluble in polar solvents such as acetone, acetonitrile, *N*,*N*-dimethylformamide (DMF), and 1-methyl-2-pyrrolidinone (NMP). The ^{1}H NMR (in acetone-d_6) and GPC (using NMP containing LiCl) analysis revealed that the polymer was chemically intact during the polymerization and had narrow molecular weight distribution (M_n = 7.0 kDa and PDI = 1.14). Some of the polymerization mixture was

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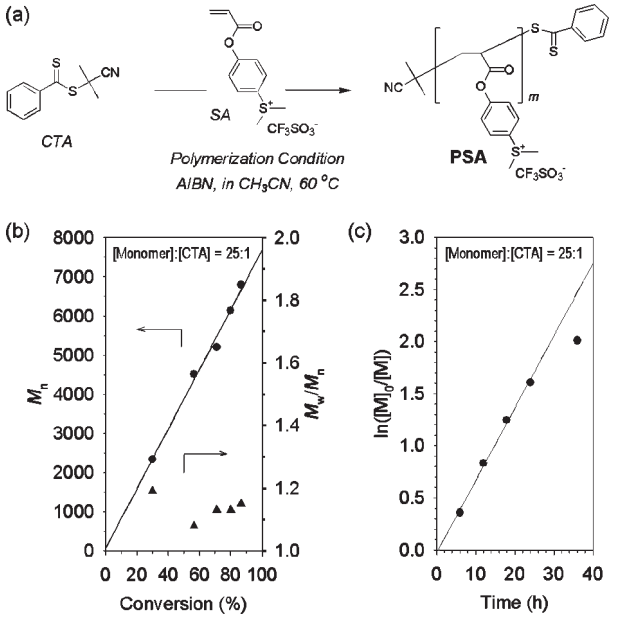

Figure 1. Controlled polymerization behavior of PAG-containing monomer (SA) through RAFT process to produce well-defined photosensitive homopolymer (PSA). (a) Synthetic scheme, (b) kinetic conversion−M_n plot, and (c) kinetic time−conversion plot.

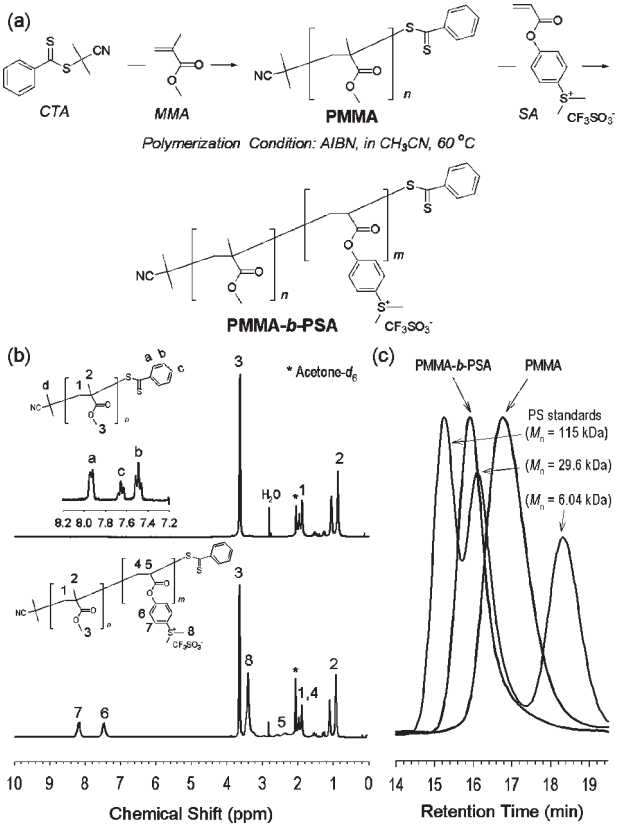

Figure 2. Synthesis and characterization of well-defined photosensitive block copolymer (PMMA-*b*-PSA) through RAFT polymerization. (a) Synthetic scheme, (b) ^{1}H NMR spectra, and (c) GPC traces of PMMA and PMMA-*b*-PSA **2**.

withdrawn at fixed time intervals and subjected to ^{1}H NMR and GPC measurements to monitor the polymerization kinetics. The kinetic plots of M_n (as a function of conversion) and conversion (as a function of time) clearly indicated that the polymerization of the highly ionic SA monomer proceeded in a controlled manner. The M_n of growing PSA polymer increased linearly with conversion, and the PDI values were less than 1.2 (Figure 1b). Even though the polymerization rate is retarded toward the end of the polymerization, the time−conversion ($\ln([M]_0/[M])$) curve obeyed first order kinetics up to ~80% conversion of SA (Figure 1c). Furthermore, the molecular weight of PSA could be controlled by adjusting the feed ratio of SA to CTA.[5]

Table 1. Molecular Weight Data of PMMA-*b*-PSA

	Ratio [MMA]:[SA] Feed	Ratio [MMA]:[SA] NMR	$M_{n,NMR}$ (kDa) PMMA:PSA (total)	$M_{n,GPC}$ (kDa)	M_w/M_n
1	1 : 1	1 : 0.95	15.2 : 51.6 (66.8)	44.4	1.20
2	1 : 0.5	1:0.44	15.2 : 24.0 (39.2)	33.4	1.24
3	1 : 0.1	1 : 0.05	15.2 : 2.9 (18.1)	20.3	1.30

The above optimized polymerization condition enabled the synthesis of the block copolymers (PMMA-*b*-PSA) with controlled molecular weights and narrow polydispersities using RAFT polymerization (Figure 2a). The RAFT block copolymerization generally begins with methacrylates, then styrenics, and finally acrylate monomers for the optimal blocking efficiency.[4] Hence, we carried out the polymerization of MMA first by adjusting the ratio relative to CTA ([MMA]/[CTA]/[AIBN] = 150:1:0.2) to produce PMMA macroinitiator (M_n = 15.4 kDa, M_w/M_n = 1.18). The ^{1}H NMR spectrum of the synthesized PMMA confirmed the presence of the chain-transfer agent at the chain end. The RAFT polymerization of SA was carried out using the PMMA macro-chain transfer agent. The molecular weight fraction of the PSA block compared to the PMMA block was controlled by adjusting the feed ratio of SA. The molecular weight data of all the synthesized PMMA-*b*-PSA block copolymers are summarized in Table 1. A representative ^{1}H NMR spectrum and GPC trace for PMMA-*b*-PSA (entry 2 in Table 1) is shown in Figure 2.[5] The ratio of SA to MMA units determined by NMR (Figure 2b) was 0.44, which was comparable to the feed ratio (0.50). Even though the block copolymer has a lesser number of SA units than MMA units, the M_n (24 kDa) of the PSA block is higher than that (15 kDa) of the PMMA block as the molecular weight of an SA unit is ~3.58 times higher than that of a MMA unit. The molecular weight and PDI measured by GPC (Figure 2c) on the basis of the polystyrene standards were 33.4 kDa and 1.24, respectively. Despite the highly ionic nature of the PAG-containing SA monomer, the resulting block copolymers had well-controlled chemical compositions, molecular weights, and molecular weight distributions.

(5) The detailed data are in the Supporting Information.

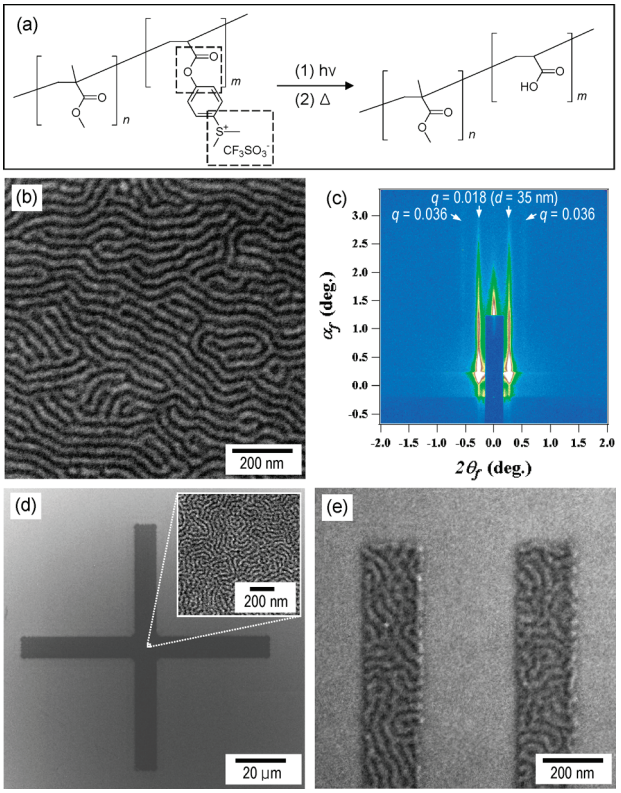

Figure 3. Self-assembling and lithographic properties of PMMA-*b*-PSA. (a) Chemical structure variation of PSA block after the photochemical reaction, (b) SEM image, (c) GISAXS pattern of thin film of **2** showing a lamellar structure in the self-assembled film, and (d and e) SEM images of negative-tone patterns obtained with EUV and electron beam lithography of the nanostructured film of **2**.

The PMMA-*b*-PSA block copolymers had excellent self-assembling capabilities despite the low molecular weights,[5] presumably as a result of increased Flory–Huggins χ parameter resulting from the highly ionic PAG units.[6] The block copolymers underwent a chemical transformation in response to light (Figure 3a). To understand the chemical changes in the photosensitive PSA block, a model compound was synthesized and subjected to the photochemical reaction in solid state.[5] These studies confirmed the hydrolysis of the ester linkage by a small amount of acid, produced from a sulfonium ion, into the carboxylic acid functionality. The reaction was initiated upon exposure and accelerated by the postexposure baking process. PMMA homopolymers are commonly utilized as a resist but require very high dose (>1000 mJ/cm^2 in the case of UV).[7] In our diblock copolymers, we used a dose of <500 mJ/cm^2 of UV (λ = 254 nm), which leaves the PMMA block intact and leads to the deprotection reaction in the PSA block.[5]

The self-assembling and lithographic properties of these block copolymers were further evaluated focusing on the PMMA-*b*-PSA **2** which has comparable molecular weights of the two blocks. The as spin-coated film (thickness = 20 nm) of **2** did not show any discernible morphology, but upon annealing with tetrahydrofuran solvent vapors periodic line arrays of PSA (bright) and PMMA (dark) domains were seen (Figure 3b). Grazing incidence small-angle X-ray scattering pattern (Figure 3c) of the film showed two scattering peaks with the relative q values of 1:2 (d spacing = 35 nm), which is characteristic of a lamellar structure oriented perpendicularly to a substrate.[8] The top-down patterning of the preorganized thin film of **2** was conducted with both EUV and electron beam. Typically the films were preorganized by solvent annealing, soft-baked (at 100 °C for 1 min), exposed (to EUV or electron beam), and postexposure baked (at 120 °C for 1 min). Among several solvents that were tested, DMF gave the best contrast between the exposed and the unexposed areas and acted as a negative-tone developer. Figure 3d shows the negative-tone cross pattern obtained with UV lithography (dose: 180 mJ/cm^2). Morphological analysis by SEM within the patterned area showed that the self-assembled lamellar structure was maintained. With e-beam lithography (dose: 1760 μC/cm^2, Figure 3e), negative-tone line patterns (width = 200 nm) could be also fabricated wherein the self-assembled nanoscale structure of the block copolymer was clearly perceptible.

In summary, we have reported a RAFT polymerization route to well-defined block copolymers (PMMA-*b*-PSA) having photoacid-generating sulfonium and acid-sensitive ester units in one block. Upon exposure the block copolymers underwent chemical changes in the photosensitive block through the cleavage of the ester group by photochemically generated acid. These photosensitive block copolymers could be self-assembled and photopatterned in thin films. It should be noted that the PAG-containing monomer showed excellent copolymerizability with various acrylate monomers. To further demonstrate the structural versatility of this system as a "one-component patternable block copolymer" we are currently investigating block copolymers where a comonomer (*t*-butyl acrylate or phenyl acrylate) having an ester linkage but no sulfonium group is copolymerized with SA in various ratios to create the photosensitive block.

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Supporting Information Available: Details of experimental procedures, model compound studies, NMR, GPC, FTIR, and SAXS patterns of all the synthesized block copolymers (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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