Top-down Meets Bottom up: Block Copolymers with Photoreactive Segments

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The fluorine-containing block copolymers of poly(styrene-*block*-2,2,2-trifluoroethyl methacrylate) (PS-*b*-PTFEMA) and poly(4-hydroxystyrene-*block*-2,2,2-trifluoroethyl methacrylate) (PHOST-*b*-PTFEMA), which both are capable of both top-down and bottom-up lithography were developed. These block copolymers were synthesized by either anionic or ATRP living polymerization methods. Comparison is made to patternable block copolymers of poly(hydroxystyrene-*block*- α -methyl styrene) (PHOST-*b*-PAMS) and poly(hydroxyethyl methacrylate)-*block*-poly(methyl methacrylate) (PHEMA-*b*-PMMA). Thin films of the block copolymers were subjected to lithographic processing using e-beam and DUV radiation combined with vacuum processing to create integrated patterns such as dots in lines. Solvent annealing was used to create long range order.

Keyword: self-assembly, patternable block copolymer, lithography, nanopattern, photoresist

1. Introduction

The use of block copolymer (BCP) materials in thin films has attracted widespread interest for creating dense, periodic arrays of small features. This approach is of interest because it permits bypassing the use of extraordinarily expensive tools, offers the prospects of sub-20 nm features with simple coat and anneal processing and has been shown to be capable of many sub-structures needed for circuit design. [1-3] Using this method to create nanopatterns, the block copolymer can be made to form arrays of lamellar, hexagonal and spherical morphologies with tunable scales of the nanometer size (3-50nm) by controlling the molecular weight and interaction parameter between blocks.[4] Recent progress in BCP lithography has shown it possible to use thin films of the block copolymer on various substrates as a templating tool for transferring its pattern into the underlying substrate. Progress has also been shown in enabling both lateral and vertical ordering of the

microdomains over large areas that are almost defect-free.[5,6] These process advances allow block copolymer lithography to be successfully tested for many applications such as integrated circuits, magnetic materials, patterned media, etc.[7] However, to use BCP lithography and/or templating for fabrication of fully integrated nanostructured devices simple blanket, large scale periodic patterning is insufficient. Controlling the precise location in which nanopatterns are formed and a more complex, wider variety of lithographically defined patterns are required. In order to overcome current limitations, we are focusing on development of “patternable block copolymers”, which have the potential to combine “top-down” and “bottom-up” lithography. A potential strategy for designing “patternable block copolymers” is incorporating both negative-tone and positive-tone resist segments (blocks) into one block copolymer.

In this work, we report the synthesis,

morphological and lithographic characterization of several new series of BCPs which contain both negative-tone and positive-tone segments; PHOST-*b*-PTFEMA and PS-*b*-PTFEMA. PS and PHOST are crosslinkable under deep-UV or e-beam radiation (i.e. negative-tone resist). PTFEMA was selected to be a degradable segment under the same exposure conditions (i.e. positive-tone resist). These BCPs were synthesized via anionic or ATRP methods. Microphase separated structures in either bulk or thin films of the resulting BCPs were studied using TEM, SAXS, and atomic force microscopy (AFM). Comparison is made to patternable block copolymers of poly(hydroxystyrene-*block*- α -methyl styrene) (PHOST-*b*-PAMS) and poly(hydroxyethyl methacrylate)-*block*-poly(methyl methacrylate) (PHEMA-*b*-PMMA).

2. Experimental

2.1. Materials

Chemicals were obtained from Aldrich, Oakwood Products Inc., or Alfa Aesar and used without further purification unless otherwise noted. For anionic polymerization, tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone (deep purple color) under nitrogen and titrated with *sec*-BuLi before polymerization. Monomers styrene, methyl methacrylate (MMA) and 2,2,2-trifluoroethyl methacrylate (TFEMA), were successively stirred and distilled with calcium hydride. These monomers were then distilled again under vacuum over a small amount of di-*n*-butylmagnesium (styrene) and tri-*n*-octylaluminum (MMA and TFEMA) just prior to use. 1,1-Diphenylethylene (DPE) was distilled over 1,1-diphenyl-3-methylpentyllithium. For atom transfer radical polymerization (ATRP), monomers of styrene and TFEMA were passed through an inhibitor remover just prior to use.

2.2 Instrumental studies

Nuclear magnetic resonance (NMR) (^1H , 300 MHz; ^{13}C , 75 MHz) spectra were acquired on a Varian MERCURY 300 NMR spectrometer using CDCl_3 as a solvent and tetramethylsilane (TMS) as an internal standard. Size exclusion chromatography (SEC) of solutions of polymers prepared in THF (1–3 mg/mL) was carried out using four Waters Styragel HT columns operating at 40 °C with Waters 490 ultraviolet (254 nm wavelength) and Waters 410 refractive index detectors. Atomic force microscopy (AFM) was performed on a Veeco Dimension 3100 operated in tapping mode with Olympus tapping mode etched

silicon probes (resonant frequency = 300 kHz, force constant = 42 N/m) under ambient conditions. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500. Measurements were taken by heating from 20 to 550 °C at 10 °C/min. Differential scanning calorimetry (DSC) was performed on a SII NanoTechnology Inc. DSC7020. Measurements were taken within the temperature range from -50 to 210 °C at 10 °C/min. Ellipsometry was performed on a Lastek Nanofilm EP3 Imaging Ellipsometer. Small Angle X-ray Scattering (SAXS) data were taken at the G1 station at the Cornell High Energy Synchrotron Source (CHESS) with typical beam energy of 9.5 keV and flight path length of 2.2 m. 2D scattering patterns acquired from a Flicam CCD detector were azimuthally integrated around the beam center. Transmission electron microscopy (TEM), samples were sectioned with a Leica Ultracut UCT ultramicrotome at room temperature. Sample slices were collected on water and transferred to copper TEM grids. Bright field (BF-TEM) images were taken with a FEI Tecnai T12 Spirit electron microscope equipped with a SIS Megaview III CCD camera, operated at an acceleration voltage of 120 kV. E-beam lithography was written using a JEOL 9300 with a 0.5 nA beam current, 100 kV accelerating voltage, and 5 nm pixel size. In the case of deep-UV exposed films, JBA 1000 was used for blanket-exposure of films; output was measured to be $\sim 14 \text{ mW/cm}^2$ at 250 nm.

2.3 Film preparation

Samples for TEM observation were prepared by casting $\sim 5\text{wt}\%$ solution of the polymers in THF for a week at room temperature. After casting, the polymer films were approximately $0.7 \mu\text{m}$ thick. They were then dried completely under vacuum conditions at room temperature and subsequently annealed in a vacuum oven at 200 °C for 3 days. Samples for AFM observation were prepared as followings. Solutions of 0.6–1.0wt% PS-*b*-PTFEMA in α,α,α -trifluorotoluene were spin-coated onto pre-cleaned silicon wafers at rates of 3000–6000 rpm. After spin-coating, the films were dried under vacuum at room temperature to remove the residual solvent and annealed in an appropriate solvent atmosphere.

2.4 Synthesis of PS-*b*-PTFEMA via anionic polymerization or atomic transfer radical polymerization

PS-*b*-PTFEMA was prepared by either ATRP

or anionic polymerization as described elsewhere.[8]

2.4 Synthesis of poly(4-*tert*-butoxy styrene-*b*-2,2,2-trifluoroethyl methacrylate) (PtBuOS-*b*-PTFEMA) via anionic polymerization

PtBuOS-*b*-PTFEMA was prepared by anionic polymerization.

2.5 Synthesis of PHOST-*b*-PTFEMA

PHOST-*b*-PTFEMA was synthesized by a hydrolysis reaction of PtBuOS-*b*-PTFEMA as described elsewhere.[9]

3. Results and Discussion

3.1. PS-*b*-PTFEMA

A series of block copolymers consisting of a coupled PS block and a PTFEMA was designed as a positive-tone resist and synthesized by either anionic polymerization or ATRP. Polymers had a total molecular weight between 26.2k~44.3k g/mol with volume ratios from 27 to 90 vol-% PS.

In this patternable block copolymer system, PS was designed as a negative-tone segment, and PTFEMA was designed as the positive-tone segment for e-beam or deep-UV lithography. Exposure to deep-UV (~250 nm) and e-beam radiation triggers the crosslinking of PS and degradation of PTFEMA simultaneously.

Figure 1. TEM image of PS-*b*-PTFEMA with a number average of molecular weight of 26.2k.

Bulk copolymer morphology studies were carried out before attempting thin film characterization of the block copolymer. Microphase-separated morphologies were investigated using SAXS in combination with TEM. SAXS and TEM data provided clear evidence of the formation of well-defined microphase separated structures (Figure 1).

Microphase separation behavior of the PS-*b*-PTFEMA polymers in thin films with a thickness of several tens of nanometers on Si wafer were also investigated using AFM. A thin film of PS-*b*-PTFEMA ($M_n=44.3k$) which contains a small volume fraction of PS (27%) was annealed in a α,α,α -trifluorotoluene atmosphere for 2h and showed the formation of well-ordered hexagonally packed spherical structures.

3.2 PHOST-*b*-PTFEMA

The block copolymer, PHOST-*b*-PTFEMA, with a total molecular weight of 64000 g/mol and a PTFEMA weight ratio of 32%, was designed and prepared by anionic polymerization and subsequent hydrolytic de-protection as shown in Scheme 1. GPC showed a narrow polydispersity of 1.16 and the primary structure of the resulting block copolymer was characterized by FT-IR, 1H NMR and ^{13}C NMR spectroscopy.

Scheme 1. Anionic Synthesis of PHOST-*b*-PTFEMA Block Copolymer

AFM height and phase images of spin-cast PHOST-*b*-PTFEMA films were studied. PHOST-*b*-PTFEMA films contain a small volume fraction of a PTFEMA (36%) block that were then annealed in a THF atmosphere for 6h and showed the formation of what is believed to be parallel cylinders. The parallel cylinder domain orientation is expected as THF is a good solvent for both blocks and allows both polymer chains to gain mobility.[19] On the other hand, annealing in THF/DPM (1:1 v/v) mixed solvent causes a well-ordered array of dots occurring over large areas of the sample compared to the as-deposited film as shown. Introducing a small amount of DPM solvent vapor can act to avoid preferential wetting of the PTFEMA cylinders to the polymer/solvent vapor interface. This shows that the choice of solvent used for annealing allows for control of a self-assembled morphology.

3.3 Lithography

Figure 2 shows a SEM image of a PS-*b*-PTFEMA thin film after the e-beam irradiation and its subsequent development by methyl isobutyl ketone/isopropanol (1/3 vol/vol) mixture. An e-beam dose of 413 $\mu\text{C}/\text{cm}^2$ crosslinked the dot arrays of PS and induced degradation of PTFEMA. The block copolymer morphology was retained in the patterned film.

Figure 2. SEM image of PS-*b*-PTFEMA PS-*b*-PTFEMA after exposure of e-beam in a vertical direction followed by the development in methyl isobutyl ketone/isopropanol (1/3 vol/vol mixture).

3.4 Comparison with other BCP resists

In other studies we have examined BCP resists with different composition, but the same strategy, that is, a cleavable segment and a crosslinkable segment. In one material, (PHOST-*b*-PAMS), solvent vapor annealing enabled formation of long range order and we could selectively produce lying cylinders or spherical arrays if the PAMS block was the minority phase. [9, 10] Depending on selection of solvent vapor microstructure was reversible up to the point negative tone patterning was carried out. [11] In another system, as yet unpublished, the (PHEMA-*b*-PMMA) system formed cylinders of the PMMA block in a matrix of PHEMA. Using a mixed solvent vapor and varying the solvent vapor ratio, we have been able to show spherical, cylindrical, lamellar and gyroid phases. These results suggest that the PS-*b*-PTFEMA system may be even more versatile if the correct solvent annealing conditions are identified

4. Conclusions

Patternable BCPs of PS-*b*-PTFEMA and PHOST-*b*-PTFEMA with various volume fractions

of each block were synthesized via living polymerization. PS-*b*-PTFEMA and PHOST-*b*-PTFEMA were both found to have well-defined microphase separation in both the bulk and thin films states. PHOST-*b*-PTFEMA was found to show well-ordered microphase-separated structure in systems with large volume fractions of PHOST. We demonstrated that the choice of solvent used for annealing control of the self-assembled morphology in this material is critical for a well-ordered film with excellent long-range order. Through a combination of block copolymer self-assembly techniques and conventional top-down lithography such as e-beam lithography, integrated structures such as “dots in lines” were successfully obtained from these BCP photoresists.

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