Perpendicularly-Oriented Block Copolymers Containing Silicon-Rich Hyperbranched Polymers for High Resistance to O₂-RIE

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The directed self-assembly (DSA) of block copolymers (BCPs) has recently become a viable alternative technique for the nanofabrication of semiconductors. To facilitate pattern transfer onto silicon (Si) wafers from BCP masks, a novel class of Si-rich BCPs with hyperbranched polysiloxane side chains were synthesized in this report. The resistance to oxygen-reactive ion etching (O₂-RIE) was quantified for the linear and modified-hyperbranched polysiloxanes, revealing that the modified-hyperbranched polysiloxanes exhibited increased O₂-RIE resistances. Furthermore, by tailoring the chemical properties on the end-groups of the polysiloxane side chains, atomic force microscopy (AFM) and scanning electron microscopy (SEM) studies revealed that perpendicularly-oriented lamellae could be observed on the thin films.

Keywords: Block copolymer, Hyperbranched polymer, Polysiloxysilane, Perpendicular orientation, Reactive ion etching (RIE)

1. Introduction

The directed self-assembly (DSA) of block copolymers (BCPs) has been an intensive area of research for the nanofabrication of semiconductors due to its potential in fabricating sub-10 nm feature sizes at high throughput and low cost [1]. However, to be used as a next generation lithographic mask, BCPs must possess several important properties such as strongly segregating blocks, facile perpendicular orientation control on thin films, and high etch contrasts [2]. To that end, poly(styrene-block-methyl methacrylate) (PS-b-PMMA) has been well studied by researchers as it can be used to create highly ordered structures with a perpendicular orientation on thin films by using thermal annealing and a neutral layer to tailor the chemical properties of the substrate interface [3-5]. However, as the segregation strength of PS-b-PMMA is relatively weak, the minimum pattern dimension ($L_0$) that can be achieved is approximately 24 nm and thus sub-10 nm feature sizes cannot be obtained [6]. Another potential candidate for BCP lithography is poly(styrene-block-dimethylsiloxane) (PS-b-PDMS) [7]. Silicon (Si)-containing hybrid BCPs such as PS-b-PDMS can increase the etching contrast between the organic and inorganic blocks. However, the perpendicular orientation control of hybrid BCPs is difficult due to the disparate chemical properties of the blocks.

Previously, our group successfully obtained line and space (L/S) structures with sub-10 nm feature sizes using modified poly(styrene-block-methylvinylsiloxane) (PS-b-PMVSs), a class of perpendicular-lamella forming Si-containing BCPs [2]. However, the etching contrast between the modified PS-b-PMVSs is insufficient for pattern transfer. Therefore, in this work, we developed a novel Si-rich BCP of polystyrene-block-polymethylsiloxane-g-hyperbranched polysiloxysilane...
silanes with hydroxyl groups at the termini (PS-\textsuperscript{b}-[PMSi-g-HBPSiOH]) by introducing hyperbranched polysiloxysilanes (HBPSi) \cite{8} to the side chains of PS-\textsuperscript{b}-PMVS to increase the silicon content of the BCPs and improve the etching contrast to oxygen-reactive ion etching (O\textsubscript{2}-RIE). The schematic illustration for the synthesis of PS-\textsuperscript{b}-[PMSi-g-HBPSiOH] is depicted in Fig. 1.

2. Experimental

2.1. Materials

Triethylamine (NE\textsubscript{t}3) was distilled over potassium hydroxide. Diethylether (Et\textsubscript{2}O) was distilled over calcium hydride (CaH\textsubscript{2}). 1,3,5-trimethyl-1,3,5-trivinyl cyclotrisiloxane (MVCtS) was distilled over CaH\textsubscript{2}. Styrene was distilled over dibutylmagnesium. Trimethyl silyl chloride (TMSiCl) was degassed under argon (Ar). Other reagents and solvents were used as received.

2.2. Methods

\textsuperscript{1}H- and \textsuperscript{13}C-NMR spectra of polymers were recorded on a JEOL 400 MHz and 100 MHz nuclear magnetic resonance (NMR) instrument using chloroform-\textit{d} as a solvent, respectively. The number average molecular weights (\textit{M}\textsubscript{n}) and molecular weight distributions (\textit{M}\textsubscript{w}/\textit{M}\textsubscript{n}) were determined by size exclusion chromatography (SEC) (Showa-Denko GPC-101) using THF as a career solvent. The thermal decomposition behavior was investigated with a SII EXSTAR TG/DTA 7300 thermogravimetric analyzer (TGA) under nitrogen flow. The glass-transition temperature (\textit{T}\textsubscript{g}) was determined with a SII EXSTAR DSC 7200 differential scanning calorimeter (DSC). Small angle X-ray scattering (SAXS) measurements were carried out using a Bruker NanoSTAR (50 kV/100 mA) with a 2D-PSPC detector (camera length 1055 nm) to determine the morphologies in the bulk. O\textsubscript{2}-RIE treatments were performed by etching instrument (SATO VAC, Inc.). The oxygen flow rate was set to 40 sccm and the applied power used was 20 W. Atomic force microscopy (AFM) measurements were performed to observe the surface architecture of thin film by using a scanning probe microscope (model SPA-400, Seiko) in tapping mode. The thickness of thin film was measured using F20 (Filmetrics, Inc.).

2.3. Preparation of 1,1,3,5,5-pentamethyl-1,5-divinyltrisiloxane (AB\textsubscript{2} type monomer)

AB\textsubscript{2} type monomer was synthesized via a sequential polymerization based on an existing method \cite{8}. Water (3.33 mL), NE\textsubscript{t}3 (27.2 mL), and Et\textsubscript{2}O (800 mL) were introduced into a reactor at 0 °C under nitrogen (N\textsubscript{2}) flow. Chlorodimethylvinilsilane was slowly added dropwise into the reactor with vigorous stirring. After 15 min, NE\textsubscript{t}3 (22.8 mL) was added. Dichloromethylsilane (7.6 mL) was then slowly added dropwise into the reactor with vigorous stirring. 1 h later, the crude product was washed with 0.3 N hydrochloric acid. The organic layer was dried with magnesium sulfate, filtered and concentrated. After purification by vacuum distillation, a colorless liquid was obtained.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz, \textit{\delta}): 0.11 (d, 3H, \textit{J} = 1.4 Hz, Si-CH\textsubscript{3}), 0.17 (s, 12H, Si-CH\textsubscript{3}), 4.65 (q, 1H, \textit{J} = 1.4 Hz, SiH), 5.73 (q, 1H, \textit{J} = 4.4, 19.4 Hz, SiCH=CH\textsubscript{2}), 5.94 (q, 1H, \textit{J} = 4.4, 14.9Hz, SiCH=CH\textsubscript{2}), 6.11 (q, 1H, \textit{J} = 14.9, 19.4 Hz, SiCH=CH\textsubscript{2}). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz, \textit{\delta}): 0.1, 1.5, 132.0, 138.9.

Fig. 1. Schematic illustration for the synthesis of PS-\textsuperscript{b}-[PMSi-g-HBPSiOH].
2.4. Preparation of homopolymers

PS and polymethylsiloxane with hydroxyl groups at the termini (PMSiOH) were synthesized by anionic polymerization according to the reference [9]. Hyperbranched polysiloxysilanes with hydroxyl groups at the termini (HBPSiOH) was synthesized with the reference [8].

2.4.1. Preparation of the PS

A prescribed volume of sec-butyl lithium (20 µL) and styrene (0.55 mL) were stirred in dehydrated tetrahydrofuran (THF, 15 ml) at -78 °C under argon (Ar) atmosphere. 30 min later, degassed methanol was added and stirred for 15 min. The resulting polymer was precipitated in methanol.

\[^1H\text{NMR (CDCl}_3, 400 MHz, \delta): 1.41 \text{ (br, 2H, CH}_2\text{), 1.84 \text{ (br, 1H, C}_H\text{-CH}_2\text{), 6.45-6.57 \text{ (br, 2H, CH(2,5)), 7.08-7.25 \text{ (br, 3H, CH(3,4,5)).}}\]

\[^{13}C\text{NMR (CDCl}_3, 100 MHz, \delta): 40.6, 43.9, 125.9, 128.0, 128.3, 145.6.\]

2.4.2. Preparation of the PMSiOH

Sec-butyl lithium (2.0 mL) and MVCtS (20.9 mL) were stirred in dehydrated THF (150 mL) at -20 °C under Ar atmosphere for 36.5 h. TMSiCl (6.0 mL) was added and stirred for 2 h. The polymethylvinylsilane (PMVS) was precipitated in methanol. PMVS (0.43 g) was dissolved into THF (2.0 mL) and introduced into a reactor. 2,2’-Azobis(isobutyronitrile) (AIBN) (19.2 mg) and 3-mercapto-1-propanol were added, and the reaction temperature was increased to 60 °C and stirred for 2 h. The obtained product diluted in THF and the resulting polymer was precipitated in water.

\[^1H\text{NMR(CDCI}_3, 400 MHz, \delta): 0.06 \text{ (br, SiC}_H\text{(CH}_3\text{)Si), 0.10, 0.11 \text{ (br, Si-CH}_3\text{), 0.37-0.42(m, SiCH}_2\text{-CH}_2\text{Si), 0.90 (br, SiCH}_2\text{-CH}_2\text{Si), 1.01 (br, SiCH(CH}_3\text{)Si), 1.83 (br, SiCH}_2\text{CH}_2\text{CH}_2\text{OH), 2.55-2.65 (m, CH}_2\text{-S-CH}_2\text{), 3.73 (br, CH}_2\text{-OH).}^{13}C\text{NMR (CDCl}_3, 100 MHz, \delta): -0.9, 0.6, 9.0, 9.6, 18.4, 19.0, 26.5, 27.0, 28.5, 32.2, 61.1.\]

2.4.3. Preparation of HBPSiOH

Dehydrated toluene (1.4 mL) and the AB2-type monomer (1.0 g) were introduced into a reactor at 0 °C under Ar flow. A platinum (0)-1,3-divinyl-1,1,3,3-tetramethylsiloxane complex solution (in xylene, Pt ~ 2%) (Pt(dvs)) was added to the reactor and stirred for 3 h. The hyperbranched polysiloxysilane (HBPSi) was precipitated into methanol two times. HBPSi (0.15 g) was dissolved into THF (1.0 mL) and introduced into a reactor. AIBN (10 mg) and 3-mercaptop-1-propanol were added, and the reaction temperature was increased to 60 °C and stirred for 2 h. The obtained product diluted in THF and the resulting polymer was precipitated in water.

\[^1H\text{NMR(CDCI}_3, 400 MHz, \delta): 0.06 \text{ (br, SiC}_H\text{(CH}_3\text{)Si), 0.10, 0.11 (br, Si-CH}_3\text{), 0.37-0.42(m, SiCH}_2\text{-CH}_2\text{Si), 0.90 (br, SiCH}_2\text{-CH}_2\text{Si), 1.01 (br, SiCH(CH}_3\text{)Si), 1.83 (br, SiCH}_2\text{CH}_2\text{CH}_2\text{OH), 2.55-2.65 (m, CH}_2\text{-S-CH}_2\text{), 3.73 (br, CH}_2\text{-OH).}^{13}C\text{NMR (CDCl}_3, 100 MHz, \delta): -0.9, 0.6, 9.0, 9.6, 18.4, 19.0, 26.5, 27.0, 28.5, 32.2, 61.1.\]

2.5. Preparation of PS-b-PMVS

The main chain polymer, PS-b-PMVS, was synthesized via a sequential polymerization based on an existing method [2,9]. A prescribed volume of sec-butyllithium (0.13 mL) and styrene (2.21 mL) were stirred in dehydrated THF (160 mL) at -
78 °C under Ar atmosphere. 30 min later, MVCtS (2.07 mL) was added and the reaction temperature was increased to -20 °C. After 24 h, TMSiCl was added and stirred for 1 h. The resulting polymer was precipitated in methanol. 1H NMR (CDCl3, 400 MHz, δ): 0.11 (s, 3H, Si-CH3), 1.41 (br, 2H, CH-C2H), 1.84 (br, 1H, CH2-CH2), 5.75-6.03 (m, 3H, SiCH=CH2), 6.45-6.57 (br, 2H, CH(2,5)), 7.04-7.08 (br, 3H, CH(3,4,5)). 13C NMR (CDCl3, 100 MHz, δ): -0.2, 40.6, 44.0, 125.9, 128.0, 128.3, 133.5, 137.0, 145.6.

2.6. Preparation of PS-b-[PMSi-g-HBPSiOH]

PS-b-PMVS (1.0 g) was dissolved into dehydrated toluene (5.0 mL) and introduced into a reactor at 0 °C under Ar flow. Pt(dvs) was added to the reactor. The AB2-type monomer (3.24 g) was then added dropwise and allowed to warm to room temperature and stirred for another 3 h. The polymer was precipitated into methanol three times. PS-b-[PMSi-g-HBPSi] was obtained as a viscous colorless liquid. PS-b-[PMSi-g-HBPSi] (0.5 g) was dissolved in cyclohexane and 3-mercapto-1-propanol was added with stirring. 1 h later, the solution was left to settle until it separated into two phases. The upper colorless layer was separated and purified. PS-b-[PMSi-g-HBPSi] was obtained by precipitation in methanol. PS-b-[PMSi-g-HBPSi] (0.3 g) was dissolved in THF (1.5 mL) and introduced into a reactor. AIBN (25 mg) and 3-mercapto-1-propanol were added, and the reaction temperature was increased to 60 °C and stirred for 2 h. The obtained product was rapidly cooled with liquid nitrogen and the resulting polymer was precipitated in water (Scheme 1).

1H NMR (CDCl3, 400 MHz, δ): 0.06 (br, SiC(CH3)Si), 0.14 (br, Si-CH3), 0.37, 0.43(br, SiCH2-CH2Si), 0.90 (br, SiC2H-CH3), 1.01 (br, SiCH2CH3Si), 1.32 (br, SCH2CH2CH2OH) 1.41 (br,CH2-CH), 1.81 (br, CH2-CH), 2.61 (br, CH2-S-CH2), 3.68 (br, CH2-OH), 5.78-6.06 (m, SiH=CH2), 6.45-6.56 (br, 2H, CH(2,5)), 6.94-7.07 (br, 3H, CH(3,4,5)). 13C NMR (CDCl3, 100 MHz, δ): -0.4, 0.1, 0.5, 18.3, 26.5, 28.6, 31.2, 40.4, 44.0, 61.2, 125.7, 128.0, 134.0, 136.4, 145.4.

3. Results and discussion

3.1. Synthesis of PS-b-[PMSi-g-HBPSiOH]

The AB2 monomer was successfully synthesized through the water-initiated reaction between chlorodimethylvinylsilane and dichloromethylsilane as reported in the literature [8]. PS-b-PMVS was then prepared through the sequential anionic polymerization of styrene and MVCtS, and PS-b-[PMSi-g-HBPSiOH] was synthesized by a Pt-catalyzed reaction with the AB2-type monomer in the presence of PS-b-PMVS. The final product, PS-b-[PMSi-g-HBPSiOH] was synthesized using a simple thiol-ene reaction with 3-mercapto-1-propanol. SEC analyses show that the molecular weight and the molecular weight distribution of the polymers slightly changed from 18,600 g mol-1 and 1.10 for PS-b-[PMSi-g-HBPSiOH] to 20,700 g mol-1 and 1.19 after the introduction of the HBPSi side chains for PS-b-[PMSi-g-HBPSi]. Figure 2a shows the 1H NMR spectrum of PS-b-[PMSi-g-HBPSiOH] in CDCl3. Characteristic peaks were found at 1.00 and 0.39 ppm that were assigned to the methyl and methylene groups of the α- and β-addition, respectively. The 1H NMR spectrum also indicated that approximately 9 units of MVCtS were introduced into the side chains of PS-b-PMVS. This corresponds well with the results of the SEC analysis. SEC analysis of the final polymer after the post-synthesis thiol-ene reaction to change the end-group functionality, PS-b-[PMSi-g-HBPSiOH] showed that the molecular weight and the molecular...
weight distribution were 21,200 g mol\(^{-1}\) and 1.20, respectively. \(^1\)H NMR analysis (Fig. 2b) showed a decrease in the number of terminal vinyl groups and the appearance of the methylene protons at 1.32, 2.61, and 3.68 ppm.

3.2. O\(_2\)-RIE resistance

To quantify the O\(_2\)-RIE contrast between PS and the polysiloxane blocks of the novel BCP, the oxygen plasma etching rate of each homopolymer was measured by plotting the film thickness loss upon O\(_2\)-RIE treatment. Figure 3 shows that Si-containing homopolymers such as PMSiOH and HBPSiOH exhibited higher etch resistances than PS as expected of Si-containing polymers. Furthermore, the difference in the rate of etching between the hyperbranched HBPSiOH and PS, and the linear PMSiOH and PS was significantly higher. This is likely because the introduction of hyperbranched Si-containing side chains increases the density of Si per segment chain volume when compared to the linear analogue \[10\]. The increased Si-content per segment chain volume provides a stable oxide film which increases O\(_2\)-RIE treatment resistance.

![Fig. 3. Oxygen plasma etching rate of homopolymers.](image)

3.3. Bulk morphological studies

Bulk studies were first carried out to determine the stable morphologies of the BCPs. The bulk samples were prepared from THF solution, and after evaporating the solvent, the samples were thermally annealed under vacuum at 70, 90, and 110 °C as the \(T_g\) of the BCP as determined by DSC is approximately 90 °C. Small angle X-ray scattering (SAXS) was then used to determine the morphology. Figure 4 shows that the as-prepared sample exhibited four strong peaks at integer ratios to the first-order scattering peak, suggesting that thermal annealing facilitated the formation of a higher-ordered lamellar structure. Moreover, the SAXS measurements revealed that the domain spacing of PS-b-[PMSi-g-HBPSiOH] was approximately 22.4 nm.

![Fig. 4. SAXS profiles of PS-b-[PMSi-g-HBPSiOH].](image)

![Fig. 5. AFM images of PS-b-[PMSi-g-HBPSiOH] after annealing at 70 °C for 3 min (a) height image (b) phase image before O\(_2\)-RIE, (c) height image (d) phase image after O\(_2\)-RIE. (f) Cross-sectional profile of (c).](image)
nm, 23.9 nm and 23.6 nm when it was annealed at 70, 90, and 110 °C, respectively.

3.4. Thin film studies

Structural analyses of the thin films were carried out by AFM. The thin film samples were prepared by first spin-coating a 1.0 wt% PMMA-r-PMA propylene glycol methyl ether acetate (PGMEA) solution onto a piranha solution-treated Si substrate. The BCP was then spin-coated on top of the neutral layer from a 1.5 wt% PGMEA solution at 7500 rpm for 30 s. The thin films were then annealed at 70 °C for 3 min. Oxygen-reactive ion etching (O2-RIE) treatment was used to selectively remove the PS domain. Scanning electron microscopy (SEM) and AFM analyses of the PS-b-[PMSi-g-HBPSiOH] thin film revealed that when annealed at 70 °C, perpendicularly-oriented lamellae with a well-ordered fingerprint pattern could be observed as shown in Figs. 5a ~ 5d. The cross-sectional profile of the AFM measurements also indicated that a well-ordered lamellar pattern with a perpendicular orientation could be obtained on the thin films (Fig. 5f).

Furthermore, SEM images of the edge of the thin film also evidenced the formation of perpendicularly oriented lamellae. The SEM image shown in Fig. 6b was obtained at an observation angle of 20°. As shown in Figs. 6a and 6b, the lamellar pattern had successfully oriented perpendicularly relative to the substrate throughout the thin film, from the top free interface to the substrate interface. These results indicated that a thick layer of polysiloxane remained even after O2-RIE. Therefore, the Si-rich PS-b-[PMSi-g-HBPSiOH] is a promising candidate that can facilitate pattern transfer for next-generation BCP lithography applications.

4. Conclusion

We successfully synthesized a novel class of Si-rich BCPs via the introduction of Si-containing hyperbranched polymers onto the side chains of modified PS-b-PMVSs. AFM and SAXS analyses indicated that these novel BCPs can form well-ordered perpendicularly-oriented lamellae on thin films. Furthermore, an increase in the O2-RIE etch contrast could be observed in these BCPs due to the increased Si-density of the HBPSi moieties. These results suggest that the addition of Si-containing hyperbranched polymers could be used to allow for further optimization of BCP candidates for the development and tailoring of the physicochemical properties of next-generation BCP lithography materials.

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