Synthesis and Morphology Studies of Polysiloxane-based Triblock Copolymers

Lei Dong, Rin Odashima, Takehiro Seshimo, Yuta Nabae, and Teruaki Hayakawa*

Department of Materials Science and Engineering, School of Materials and Chemical Technology,
Tokyo Institute of Technology,
S8-813, 2-12-1-S8-36, Ookayama, Meguro-ku, Tokyo 152-8552, Japan
*hayakawa.t.ac@m.titech.ac.jp

The directed self-assembly (DSA) behavior of block copolymers (BCPs) has recently been widely studied because of its potential application to the nanofabrication of semi-conductors. In this study, a novel molecular design based on the A-B-C triblock copolymer was developed: polystyrene-*b*-poly(dimethyl siloxane)-*b*-poly(substituted siloxane) (PS-*b*-PDMS-*b*-PMSCXOH, where X = 3 or 6). The high χ parameter between the PS and PDMS segments was expected to effectively reduce line edge roughness (LER) and resulted in a smooth interface with a lamellar nanostructure. The high etching resistance of Si-containing blocks also facilitates the potential pattern transfer to Si substrate. Small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) were used to reveal the self-assembly morphologies of A-B-C triblock copolymers, which are more complex compared to commonly studied binary system of A-B diblock copolymer. The reduced interface roughness in the microphase-separated nanostructures that can lead to reducing LER of patterns observed in bulk.

Keywords: Triblock copolymer, Polysiloxane, Self-assembly morphology, Line edge roughness

1. Introduction

Because of fundamental incompatibility effects between blocks of distinctive chemical structures, the self-assembly of block copolymers (BCPs) can

yield various ordered structures [1]. The self-assembly behavior of BCPs has potential technological applications; thus, the relationship

Fig. 1. Illustration of the molecular design of PS-*b*-PDMS-*b*-PMSCXOH.

between the chemical structure of diblock copolymers and their self-assembly morphology has been widely studied. However, triblock copolymers could exhibit more complex self-assembly morphologies than diblock copolymers [2], but the self-assembly behavior of triblock copolymers, typically A-B-C linear triblock copolymers, has yet to be fully studied.

Based on BCP self-assembly theory, block copolymers with a high Flory-Huggins interaction parameter (χ) are expected to exert a strong microphase separation driving force and minimize the periodic length of assembled morphologies [3-5]. Moreover, based on simulation and experimental results [6,7], BCPs with a high χ parameter could effectively reduce line edge roughness (LER) of formed lamellar patterns by tuning the interfacial region between distinct segments. Generally, BCPs with a high χ parameter, high etching contrast, and perpendicular orientation on thin films are desired for lithography materials [8]. For example, widely used poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) could form a minimized pattern with a 24 nm dimension by using thermal annealing and a neutral layer to tune the affinity between the blocks and the substrate interface. Compared to wholly organic PS-*b*-PMMA, silicon (Si)-containing hybrid BCPs are particularly interesting as they are capable of achieving sub-10 nm feature size and have a higher etching contrast between the organic and inorganic segments. However, perpendicular orientation control of polystyrene-*b*-poly(dimethyl siloxane) (PS-*b*-PDMS), a commonly used Si-containing hybrid BCP, is difficult to achieve because PDMS blocks have low surface free energy (SFE) and SFE determines the extent to which flexible PDMS segments move towards the air interface [9-11].

To solve the orientation problem, our group has recently developed a series of Si-containing hybrid diblock copolymers, namely poly(styrene-*block*-substituted siloxane) (PS-*b*-PMSCXOH, where X = 3 or 6), which are capable of forming a lamellar pattern with sub-10 nm feature size and perpendicular orientation in thin films [12,13]. The introduction of the hydroxy-containing side chain was designed to balance the SFEs of counter-blocks and thus facilitate the formation of perpendicular orientation. However, the LER between the interfaces was insufficiently smooth, because the χ parameter between blocks was sacrificed owing to the introduction of side chain. The suppressed repulsion between blocks indicates the insufficient

driving force for micro-phase separation and results in a relatively broad interfacial region of higher magnitude of LER.

Therefore, this study proposes a new molecular design based on A-B-C linear triblock copolymers, as shown in Fig. 1. The middle PDMS block was hypothesized to increase the χ parameter, smooth the interface, and reduce the LER between the organic PS and inorganic PDMS blocks. Moreover, the PS and two compatible, Si-containing blocks exhibited high etching contrast. The length of the PDMS block was optimized to balance the SFEs of the PS and PMSCXOH blocks and induce a perpendicularly orientated domain in the thin film, which would satisfy the demands of BCP lithographic applications. Thus, the new molecular design aims to combine the advantages of the two Si-containing BCPs: the high χ parameter of PS-*b*-PDMS and the perpendicular orientation control of PS-*b*-PMSCXOH.

2. Experimental

2.1. Materials

Hexamethylcyclotrisiloxane (D3) was sublimated and dissolved in degassed and dehydrated tetrahydrofuran (THF), which was distilled to a calculated concentration. Chlorotrimethylsilane (TMSiCl) was degassed under Ar and 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane (D3v) was distilled over CaH₂. Other reagents and solvents were used as received.

2.2. Methods

The ¹H NMR spectra were recorded with a 400 MHz instrument (JNM-ECS400, JEOL, Japan) using chloroform-*d* as the solvent. The number average molecular weights (M_n) and polydispersity (M_w/M_n) were determined by size exclusion chromatography (SEC; GPC-101, Showa-Denko, Japan) and calibrated with polystyrene. The glass transition temperatures of the polymers were estimated using a differential scanning calorimeter (DSC; DSC 7020, Seiko, Japan). Small angle X-ray scattering (SAXS) measurements were performed using a Bruker SAXS NanoSTAR instrument (Output: 50 kV, 50 mA); CuK α radiation monochromated with a Göbel mirror (wavelength: 1.5416 Å) was applied to the sample, the scattered X-rays were collected by a 2D-PSPC detector. Bright-field transmission electron microscope (TEM) images of the sample structures were obtained using a Hitachi H7650 Zero A (Japan) under an 80 kV accelerating voltage; the samples were subsequently placed onto TEM grids and stained with ruthenium oxide for observation.

Scheme 1. Synthesis routine for PS-*b*-PDMS-*b*-PMSCXOH (X = 3 or 6).

2.3. Synthesis of PS-*b*-PDMS-*b*-PMVS

Polystyrene-*b*-poly(dimethyl siloxane)-*b*-poly(methyl vinyl siloxane) (PS-*b*-PDMS-*b*-PMVS) was prepared by anionic living polymerization; calculated amounts of styrene, hexamethylcyclotrisiloxane (D3), and 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane (D3v) monomers were combined at various temperatures. Following quenching of chlorotrimethylsilane, the resulting precursor copolymer was obtained by precipitation in methanol and dried *in vacuo*.

^1H NMR (CDCl_3 , 400MHz) δ (ppm): 0.06 (s, 6H, CH_3), 0.14 (s, 3H, CH_3), 1.42 (br, 2H, CH_2), 1.84 (br, 1H, CH), 5.76–6.04 (br, 3H, $\text{CH}=\text{CH}_2$), 6.31–6.72 (br, 2H, Ar), 6.89–7.22 (br, 3H, Ar).

2.4. Synthesis of PS-*b*-PDMS-*b*-PMSC6OH

A thiol-ene reaction was used to add the functional side chains to the backbone of the precursor copolymer. In a 10 mL recovery flask, 0.2 g PS₁₄₃-*b*-PDMS₄-*b*-PMSC6OH₁₄ (12.3×10^{-3} mmol), 0.35 mL 6-mercapto-1-hexanol (2.6 mmol), and 4.2 mg 2,2'-azobis(isobutyronitrile) (AIBN; 0.026 mmol) were added to 0.8 mL of degassed THF. The solution was stirred at 65 °C for 3 h under an Ar atmosphere. After heating, the flask was soaked in liquid N₂ for 3 min to freeze the THF solution. After melting at room temperature, the solution was added dropwise to 200

mL of ion exchange water for precipitation. The resulting polymer was washed and isolated by filtration. Ultimately, the white powder was dried overnight *in vacuo* at 50 °C to yield the desired product.

^1H NMR (CDCl_3 , 400MHz) δ (ppm): 0.07 (s, 6H, CH_3 PDMS), 0.15 (s, 3H, CH_3 PMSC6OH), 0.90 (br, 2H, Si- CH_2), 1.41 (br, 2H, CH_2 PS), 1.59 (br, 4H, 3/4- CH_2 PMSC6OH), 1.84 (br, 1H, CH PS; br, 4H, 2/5- CH_2 PMSC6OH), 2.53 (br, 4H, CH_2SCH_2), 3.62 (br, 2H, $\text{CH}_2\text{-OH}$), 6.31–6.72 (br, 2H, Ar), 6.89–7.22 (br, 3H, Ar).

2.5. Synthesis of PS-*b*-PDMS-*b*-PMSC3OH

The synthesis of PS-*b*-PDMS-*b*-PMSC3OH is similar to the synthesis of PS-*b*-PDMS-*b*-PMSC6OH described above.

^1H NMR (CDCl_3 , 400 MHz) δ (ppm): 0.06 (s, 6H, CH_3 PDMS), 0.16 (br, 3H, CH_3 PMSC3OH), 0.90 (br, 2H, Si- CH_2), 1.41 (br, 2H, CH_2 PS), 1.81 (br, H, CH, PS; br, 2H, 3- CH_2 PMSC3OH), 2.61 (br, 4H, CH_2SCH_2), 3.67 (br, 2H, $\text{CH}_2\text{-OH}$), 4.19 (br, 1H, OH), 6.31–6.72 (br, 2H, Ar), 6.89–7.22 (br, 3H, Ar).

2.6. Bulk morphological studies

THF solutions of the investigated BCPs were prepared and filtered through a 0.25 μm pore size PTFE membrane syringe filter. The resulting

Fig. 2. ^1H NMR spectra of (a) PS-*b*-PDMS-*b*-PMSC6OH and (b) PS-*b*-PDMS-*b*-PMSC3OH.

solution was slowly evaporated at 30 °C for 48 h. After evaporation, the bulk samples were thermally annealed for 24 h under vacuum at 110 °C, which was well above the glass transition temperature (T_g) of all segments. To characterize the resulting morphologies, the samples were characterized using SAXS and TEM.

3. Results and Discussion

3.1. Synthesis of PS-*b*-PDMS-*b*-PMVS

The synthesis routine for PS-*b*-PDMS-*b*-PMSCXOH is illustrated in Scheme 1. The monomer feeding rate was tuned to obtain various

compositions of the triblock copolymer PS-*b*-PDMS-*b*-PMVS during polymerization. Five distinct PS-*b*-PDMS-*b*-PMVS copolymers were successfully synthesized and used for the thiol-ene reaction.

The excellent compatibility of the siloxane-based PDMS and PMVS blocks may contribute to the random structure; however, the distinct reactivities of the D3 and D3v monomers, which may be attributed to the stabilizing effects of the vinyl groups in D3v, prevented the formation of random structures among the siloxane-based blocks. Thus, a specific ring-opening polymerization temperature could be applied for each cyclic siloxane-based monomer as the reaction temperatures of the D3 and D3v monomers corresponded to 20 °C and -20 °C, respectively.

Similar two-step sequential reactions were reported for the synthesis of PDMS-*b*-PMVS block copolymers [14]. To verify that the D3 monomer was dormant during polymerization, the D3 monomers were polymerized at -20 °C for 48 h via anionic living polymerization; as expected, PDMS homopolymers could not be obtained under these conditions. Many studies have reported polymerization of D3 above 20 °C via anionic living polymerization [15-19]. The high ring-opening reactivity of the D3v monomer may be attributed to the electron-withdrawing vinyl substituent, which is more reactive than the methyl substituent of D3 during polymerization [20].

3.2. Synthesis of PS-*b*-PDMS-*b*-PMSC3(6)OH

The reaction conditions were optimized to obtain the desired PS-*b*-PDMS-*b*-PMSC3(6)OH with narrow polydispersity indices (PDIs); MVS (1 molar equivalent) was mixed with 15 molar equivalents of either 6-mercapto-1-hexanol or 3-mercapto-1-propanol and 0.15 molar equivalents of AIBN in a minimal amount of THF solvent, and the solution was stirred at 65 °C for 3 h. The characterization data are summarized in Table 1.

Table 1. Characteristics of the synthesized PS-*b*-PDMS-*b*-PMSC6(3)OH copolymers.

No.	Polymer	$M_n^{(a)}$ (g/mol)	PDI ^(a)	Weight fraction ^(b) (%)		
				PS	PDMS	PMSC6(3)OH
A6	PS ₁₄₃ - <i>b</i> -PDMS ₄ - <i>b</i> -PMSC6OH ₁₄	18,700	1.20	82	2	16
B6	PS ₂₂₉ - <i>b</i> -PDMS ₉ - <i>b</i> -PMSC6OH ₄₂	21,900	1.08	72	2	26
C6	PS ₉₅ - <i>b</i> -PDMS ₂₃ - <i>b</i> -PMSC6OH ₄₀	13,400	1.12	50	9	41
D3	PS ₁₀₅ - <i>b</i> -PDMS ₃₆ - <i>b</i> -PMSC3OH ₆₀	16,100	1.16	47	11	42
E3	PS ₁₂₈ - <i>b</i> -PDMS ₉₇ - <i>b</i> -PMSC3OH ₅₃	21,800	1.17	46	25	29

a) Determined by SEC. b) Determined by ^1H NMR spectra.

As shown in Fig. 2, the characteristic peaks of PMVS between 5.76-6.04 ppm completely disappeared and the characteristic peaks of the side chain were observed. The observed peaks in the spectra can be well-attributed to the distinctive protons in the chemical structure of the product. This indicates that PS-*b*-PDMS-*b*-PMSC3(6)OH was successfully synthesized. Furthermore, the SEC results show that the molecular weights of the PS-*b*-PDMS-*b*-PMSC3(6)OH copolymers were reduced during the thiol-ene reaction; this may be attributed to changes to the conformation of the polymer chain in the THF eluent or interactions between polar hydroxyl groups in the polymer side chains and the column substrate.

3.3. Bulk morphological studies

Bulk studies were performed to investigate the thermodynamically stable morphologies of the five BCPs formed in the bulk. The SAXS profiles of the as-prepared and thermally annealed samples are shown in Fig. 3. Except for C6, the BCPs exhibited significant peak scattering after thermal annealing, which suggests the formation of an ordered periodic nanostructure with microphase separation. The morphology of C6 may be disordered because its molecular weight is too low to cause microphase separation.

The morphology types of the BCPs were further investigated by determining the q^* ratios of the scattered peaks. Upon thermal annealing, both A6 and B6 exhibited Bragg reflection at q^* and $\sqrt{7}q^*$, which suggests the formation of a hexagonally packed cylindrical domain. Meanwhile, D3 and E3, which were both 50% PS, had peaks at integer q^* ratios; this indicates ordered lamellar structures in the bulk. Based on these results, morphology type was related to the PS fraction of the polymer and the domain spacing of the ordered nanostructure could be calculated using the position of the primary q^* peak.

Compared to the 20 nm domain spacing reported for PS-*b*-PMSC3(6)OH diblock copolymers [10,11], the domain spacings of the PS-*b*-PDMS-*b*-PMSC3(6)OH triblock copolymers were substantially enlarged, especially when the longitudes of the middle PDMS blocks were relatively high. The larger domain spacing was due to the formation of a complex lamellar structure with three segments, which was verified by TEM characterization. The TEM image in Fig. 4(a) illustrates a distinctive electron density distribution; the dark and light streaks were attributed to the

Fig. 3. SAXS profiles of PS-*b*-PDMS-*b*-PMSC3(6)OH bulk samples: (a) as-prepared and (b) annealed at 110 °C for 24 h.

Fig. 4. (a) TEM images of 430 nm $\times$ 430 nm as-prepared PS₁₀₅-*b*-PDMS₃₆-*b*-PMSC3OH₆₀ bulk samples with ruthenium oxide staining and (b) a proposed macromolecular packing model.

siloxane (PDMS and PMSC3OH) and PS domains, respectively. In theory, PS microdomains could be preferentially stained by ruthenium oxide while PDMS and PMSC3OH remained unstained [21]; however, the stain appeared to be concentrated on 2.0 nm wide regions at the interfaces between PS and the siloxane-based polymers. Remarkably, the aggregation of ruthenium oxide at the interface may cause the observed middle region in TEM [21]. If the contrast observed in Fig. 4(a) was caused by the middle PDMS block, a self-assembled molecular packing model could be proposed as depicted in Fig. 4(b). The self-assembly model in Fig. 4(b) consists of trilayers in which bulky PMSC3OH and PS segments occupy the majority of the space and the PDMS segments function as interface layers

between them, which would result in a sharp edge across the long lamellar stripes.

Furthermore, a comparative study on line edge roughness of micro-domains was conducted. A PS-*b*-PMSC3OH diblock copolymer with similar PS weight fraction (45%) and molecular weight was used as a reference. Obviously the synthesized triblock copolymer revealed a smoother interface with reduced LER (Fig. 5).

Fig. 5. Comparison of TEM patterns of (a) PS₁₀₅-*b*-PDMS₃₆-*b*-PMSC3OH₆₀ and (b) PS₆₉-*b*-PMSC3OH₅₇ with similar pitch size. The yellow curve indicates the line edge.

4. Conclusion

In this study, a series of polysiloxane-based triblock copolymers PS-*b*-PDMS-*b*-PMSCXOH where X = 3 or 6 were synthesized via living anionic polymerization. Hexagonally packed cylinders and lamellar structures were observed in the bulk, and these morphologies were analyzed based on the composition of the copolymer. For the lamellar morphology, the PDMS block between the PS and PMSCXOH blocks was determined to create a smooth interface with minimized edge roughness. Therefore, the triblock copolymers designed in this study exhibited the morphologies and characteristics required for next-generation BCP lithography materials, especially the desired smooth stripe interfaces with reduced edge roughness.

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