Formation of Ultra Narrow Lamellar Structures in POSS-containing Triblock Terpolymers

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An ultra narrow line structure was prepared in the lamellar morphology of polyhedral oligomeric silsesquioxane (POSS)-containing triblock terpolymer in the bulk via the self-assembly. The triblock terpolymers, which comprised polystyrene, POSS-containing poly(methacrylate) (PMAPOSS) and poly(methyl methacrylate), were synthesized by anionic polymerization. The self-assembled structures were studied by using a transmission electron microscopy (TEM) and a small-angle X-ray scattering (SAXS). It was found that a narrow PMAPOSS domain was layered in triple-domain lamellar, which caused by the effect of strongly segregation with the middle PMAPOSS block. The total *d*-spacing was 32 nm, and the smallest width of PMAPOSS domain layer was ca. 4 nm.

Keyword: triblock terpolymer, polyhedral oligomeric silsesquioxane (POSS), self-assembly

1. Introduction

Block copolymer lithography exploits the self-assembled nanostructures formed in block copolymers thin films for producing dense nanopatterns over a large area that may overcome the intrinsic resolution limit of conventional optical lithography [1-3]. For the practical utilization of the block copolymer lithography, the directed self-assembly of block copolymers offers a promising method to form the long range highly ordered nanopatterns such as dots and lines in the thin films based on epitaxial assembly on chemically and/or topographically patterned substrates. The pattern sizes are generally dependent on the domain spacing of the microphase-separated nanostructures [4, 5]. Therefore, achieving the high resolution patterns is required the use of strongly segregating block copolymers that have a relatively low molecular weight

with a high χ parameter.

Recently, we had reported the development of and self-assembly of a novel series of polyhedral oligomeric silsesquioxane (POSS)-containing polymethacrylate (PMAPOSS)-based diblock copolymers such as polystyrene (PS)-*block*-PMAPOSS, poly(methyl methacrylate) (PMMA)-*block*-PMAPOSS for the block copolymer lithography materials [6-8]. They can self-assemble to well-defined features of a 10 nm scale in the thin films because of the strongly segregating ability [9]. Furthermore, the PMAPOSS domains have significantly higher etch resistance compared with the organic domains to oxygen reactive ion etching.

Line patterning in lithography is one of the most important and useful for a wide variety of devices. Creating the single nanometer scale narrow lines with a high resolution is required in the near future of the block copolymer lithography. The line patterns are generally produced by

selective etching of the microphase-separated nanostructures with parallel cylinders or oriented lamellar in the thin films. However, the cylindrical structures that comprise the minor domains of the PMAPOSS segments were not observed in the bulk morphologies of PMAPOSS-containing block copolymers. This was in spite of the fact that the structures of the microphase-separated PMAPOSS-containing polymers could be varied from spheres to lamellae by altering the PMAPOSS volume fraction. On the other hands, the lamellar structures were obtained in a wide range of volume fraction. However, we have not successfully obtained the oriented lamellar in the thin films for PMAPOSS-containing diblock copolymers.

In this study, we propose the ABC triblock copolymer with PMAPOSS as a short middle block (B) in order to build progressively more advanced architecture leading to tailored line patterns based on the oriented lamellar structures. Each A and C block was selected PS and PMMA, respectively, because it is well-known that the PS-*b*-PMMA diblock copolymer can form the oriented lamellar structures in the simple thermal annealing. Therefore, we came up with idea that the ABC triblock copolymers consisting of PS (A), PMAPOSS (B) and PMMA (C), which can basically form the lamellar structures of PS and PMMA, can exploit for creating line patterns by selective etching of PS and PMMA domains in the oriented lamellar structures in the thin films. In this case, we can expect to obtain the narrow lines with a single nanometer width by remaining the strong segregated and the oxidized PMAPOSS domains that exist as an interface layer between the PS and PMMA lamellar structures.

Herein, the procedure for synthesizing a new series of POSS-containing triblock terpolymers, PS-*b*-PMAPOSS-*b*-PMMA, by sequential anionic polymerization is presented in a preliminary account. The self-assembled structures obtained using the triblock terpolymers microphase separated nanostructures in the bulk was studied by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM).

2. Experimental

2.1. Materials

Sec-Butyl lithium (*sec*-BuLi) was purchased from Kanto Chemical Co (Tokyo,

Japan). 3-(3,5,7,9,11,13,15-Heptaisobutylpentacyclo-[9.5.1.^{3,9}1.^{5,15}1^{7,13}]octasiloxan-1-yl)propyl methacrylate (MAPOSS) was purchased from Hybrid Plastics Inc. (USA). The other reagents were purchased from TCI Co. (Tokyo, Japan). Prior to use, tetrahydrofuran (THF) was refluxed over Na wire for 12 h and distilled over LiAlH₄ under nitrogen. It was finally distilled from its sodium naphthalenide solution on a high vacuum line (10⁻⁶ Torr). Styrene was washed with 10% NaOH aq, dried over MgSO₄, and distilled over calcium hydride (CaH₂) under reduced pressures. Prior to use, the monomer was distilled over di-*n*-butylmagnesium (Bu₂Mg) (~5 mol%) on the vacuum line into ampules equipped with break seals that were prewashed with potassium naphthalenide in THF. Methyl methacrylate (MMA) was first distilled over CaH₂ under reduced pressures and then distilled from their 3 mol% (C₂H₅)₃Al solution on the high vacuum line. 1,1-diphenylethylene (DPE) was distilled over *n*-butyllithium, MAPOSS was purified by recrystallization from methanol and dried on the high vacuum line with diphosphorous pentaoxide for over night. Lithium chloride (LiCl) was baked under vacuum at 180 °C for 24 h. The other reagents were used as received.

2.2. Instrumentation and Characterization

IR spectra were recorded on a JASCO FT/IR-460 Plus spectrometer. ¹H, ¹³C and ²⁹Si NMR spectra were recorded on a JEOL JNM-AL 300 spectrometer at 300 MHz, 75 MHz and 59.4 MHz, respectively. Molecular weights and molecular weight distributions were measured on an Asahi Technicon AT-2002 equipped with a Viscotek TDA model 302 triple detector array using THF as a carrier solvent at a flow rate of 1.0 mL min⁻¹ at 30 °C. Three PS gel column (pore size (bead size)) were used: 650 Å (5 µm), 200 Å (5 µm), 75 Å (5 µm). The relative molecular weights were determined by SEC with RI detection using standard polystyrene calibration curve. Thermal analyses of the compounds, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) were carried out using a Seiko SSC/6000 (TG/DTA 6200 and DSC6200) thermal analyzer with ca. 5 mg of samples at a heating rate of 10 °C min⁻¹. Nitrogen was

used as the purge gas at a flow rate of 50 mL min⁻¹ for both the TGA and DSC measurements. For TEM analysis, bulk samples were embedded in epoxy resin and cured at 70 °C for 24 h. The embedded samples were then microtomed using a Diatome diamond knife at room temperature to a preset thickness of 70 nm using Microtome. The sections were placed on TEM grids and viewed directly using a JEOL JEM-200CX at 100 kV. Small angle X-ray scattering (SAXS) measurements on the bulk samples were carried out obtained using a Bruker NanoSTAR (50 kV/100 mA) with a 2D-PSPC detector (camera length 1055 nm).

2.3. Bulk sample Preparation

The sample of PS-*b*-PMAPOSS-*b*-PMMA for investigating the bulk morphology was prepared by slow evaporation from chloroform solution and subsequently annealed at 180 °C in vacuum for 24 h.

2.4. Synthesis of PS-*b*-PMAPOSS-*b*-PMMA by Living Anionic Polymerization

All of polymerizations were carried out under high vacuum (10⁻⁶ Torr) in sealed glass reactors equipped with break-seals. A small portion was always taken to determine the molecular weight (M_n) and molecular weight distribution (M_w/M_n) values prior to the next reaction. The concentrations of monomer and initiator were usually in the ranges 0.4-0.8 and 0.02-0.11 M, respectively. All reactors were prewashed with red-colored 1,1-diphenylhexyllithium (ca. 0.05 M) in heptane after being sealed off from a vacuum line and used.

Polystyryllithium (PSLi) was prepared by the polymerization of styrene (19.0 mmol) in THF solution (22.3 mL) initiated with *sec*-BuLi (0.096 mmol) in heptane solution (1.60 mL) at -78 °C for 10 min. Then, a THF solution (2.01 mL) of DPE (0.301 mmol) was added to the PSLi solution at -78 °C. After the reaction was allowed to stand for an additional 30 min at -78 °C, LiCl (0.359 mmol) dissolved in THF (3.61 mL) was added -78 °C, followed by addition of a THF solution (5.7 mL) of MAPOSS (0.50 mmol) at -78 °C with vigorous shaking, and the polymerization was allowed to stand for 6 h. After 6 h, a THF (21.3 mL) solution of MMA (19.1 mmol) was added with vigorous shaking at -78 °C, and the polymerization allowed to stand for 30 min. The polymer was quenched

with degassed methanol and precipitated in methanol. It was reprecipitated twice from THF to methanol, and freeze-dried from its dry benzene solution *in vacuo* for 24 h. The polymer (4.03 g) was obtained in 93% yield and characterized by SEC, ¹H, ¹³C, and ²⁹Si NMR, and IR spectroscopy. For final triblock terpolymer, SEC gives M_n (SEC) of 44 700 g mol⁻¹ and M_w/M_n of 1.04. IR (KBr, cm⁻¹): 3082, 3060, 3025, 3000, 2951, 2924, 2849, 1731, 1601, 1493, 1452, 1366, 1270, 1231, 1167, 1115, 1028. ¹H NMR (300 MHz, CDCl₃ ppm): δ 7.06-7.03 (m, aromatic, PS), 6.57-6.36 (m, aromatic, PS), 3.81 (br, -OCH₂, PMAPOSS), 3.59 (br, -OCH₃, PMMA), 2.06-1.72 (m, isobutyl -CH (PMAPOSS), main chain -CH₂, -CH, PS, PMAPOSS, PMMA), 1.4-1.39 (m, main chain -CH₂, PS), 1.01-0.94 (br, isobutyl -C(CH₃)₂, PMAPOSS), 0.84 (m, αCH₃, PMMA), 0.60 (br, -SiCH₃, PMAPOSS). ¹³C NMR (75 MHz, CDCl₃): δ 178.0, 177.7, 176.9, 145.9, 145.5, 145.2, 144.9, 127.8, 127.5, 127.2, 125.5, 125.3, 54.0, 52.3, 51.7, 45.3, 44.7, 44.4, 43.6, 42.5, 40.2, 25.5, 23.7, 22.3, 22.2, 18.5, 16.3, 8.3 ppm. ²⁹Si NMR (59.4 MHz, CDCl₃): δ -67.5, -67.8 ppm.

3. Results and Discussion

3.1. Triblock Terpolymer Synthesis by Living Anionic Polymerization

The desired PS-*b*-PMAPOSS-*b*-PMMA triblock terpolymers were prepared by living anionic polymerization in the presence of *sce*-BuLi as initiator, excess of LiCl and DPE at -78 °C. The first block consisted of PS followed by PMAPOSS as the second block and PMMA as the third block (Figure 1).

Figure 1. Synthetic scheme of PS-*b*-PMAPOSS-*b*-PMMA triblock terpolymer.

The polymerization results are listed in the table 1. The chemical structure of the triblock terpolymers were characterized by ¹H, ¹³C, and ²⁹Si NMR and IR spectra. The molecular weight

was measured by SEC. Figure 2 shows ^1H NMR spectrum of PS-*b*-PMAPOSS-*b*-PMMA. The ^1H NMR spectrum of triblock terpolymer clearly show successful incorporation of each block, indicated by the appearance of methylene (-OSiCH₂) protons corresponding to PMAPOSS at 0.60 ppm, PS aromatic protons at 7.06-6.36 ppm and methyl groups protons corresponding to PMMA at 0.84 ppm. Also SEC chromatograms of the polymers show that molecular weights of the polymers increased in a controlled manner reflected by the shift higher molecular weight region (Figure 3). And the SEC analysis showed the molecular weight distribution is narrow (below 1.06). Hence, the composition of PS-*b*-PMAPOSS-*b*-PMMA was ascertained by using the integration ratio's from ^1H NMR spectrum of aromatic protons for PS, methylene protons for PMAPOSS and comparing with the integration of methoxy protons from PMMA along with the M_n values successfully obtained. The volume fraction of each block was estimated from the density of PS (1.05 g cm⁻³), that of PMAPOSS (1.14 g cm⁻³), and PMMA (1.15 g cm⁻³) in combination with the ^1H NMR data.

Figure 2. ^1H NMR spectrum of PS-*b*-PMAPOSS-*b*-PMMA triblock terpolymer in CDCl_3 .

Figure 3. SEC curves of PS-*b*-PMAPOSS-*b*-PMMA (solid line), PS-*b*-PMAPOSS (meshed line), and PS (dashed line).

3.2. Thermal Properties of Triblock Terpolymer

The thermal properties of

PS-*b*-PMAPOSS-*b*-PMMA were investigated using TGA and DSC. We first confirmed that no significant weight loss was observed below 300 °C by TGA analysis. To eliminate the effect of thermal histories of the samples, the samples were heated to 200 °C and held for 10 min at this temperature before cooling to r.t at a rate of 10 °C min⁻¹. DSC data reported was obtained from the second run. Two transitions were observed at 87 °C and 99 °C in the heating cycle, which are corresponding to the T_g of the PMMA and PS, respectively.

Table 1. Characteristics of Triblock Terpolymers
^aMeasured by SEC, relative to PS linear standards in

Run	M_n^a	M_w/M_n^a	wt% ^b	vol% ^c
1	47 100	1.03	30 / 43 / 27	32 / 42 / 26
2	58 800	1.04	28 / 12 / 60	30 / 12 / 58
3	45 000	1.04	34 / 17 / 49	36 / 17 / 47
4	82 000	1.05	32 / 23 / 45	34 / 22 / 44
5	56 000	1.06	31 / 28 / 42	33 / 27 / 40

THF. ^bThe numbers refer to the final composition determined by SEC calibrated against PS linear standard and integrations from ^1H NMR spectrum.

3.3. Bulk Morphological Characterization

The morphologies of the PS-*b*-PMAPOSS-*b*-PMMA in their bulk state were studied using SAXS, and TEM. The samples were prepared by slow evaporation from chloroform at room temperature, then thermal annealed at 180 °C for 24 h in a vacuum oven.

At first, we investigated the micro phase separation structure of the PS-*b*-PMAPOSS-*b*-PMMA **1**, which has the composition creating the three-domain lamella in the reported triblock terpolymer such as PS-*b*-poly(isoprene)-*b*-PMMA and PI-*b*-PS-*b*-poly(ethylene oxide) [10, 11]. The SAXS profile displayed five scattering peaks, which ratio was 1 : 3^{1/2} : 2 : 3 : 5. Figure 4b shows a TEM image of PS-*b*-PMAPOSS-*b*-PMMA **1** sample after staining with RuO₄. In the TEM image, there are bright dots of PMMA with in PMAPOSS phase, which seem to cause the undulation of the lamellae. The SAXS pattern of the solution clearly exhibits the peaks characteristic of a lamellar structure, while this sample the [110] reflection observed. Considering the volume fractions of the blocks, we assume an undulated-lamellar-morphology with PMMA-core surrounded by a PMAPOSS-layer within a

PS-layer. And, the PMMA minority phase forms hexagonally arranged dots within the PMAPOSS sheets of a lamellar phase.

Figure 4. SAXS and TEM results of PS-*b*-PMAPOSS-*b*-PMMA **1**, a)SAXS profile, and b)TEM image.

While, reduction of the PMAPOSS volume fraction, PS-*b*-PMAPOSS-*b*-PMMA **2-4**, the SAXS diffraction profiles exhibited reflections based on lamellar structure. In addition, the TEM images of PS-*b*-PMAPOSS-*b*-PMAHFC **2-4** showed two-domain lamellar nanostructures, which is strongly supported by the SAXS results. In TEM measurement, samples were imaged without staining as the contrast between the POSS-containing block (dark regions), the PS block and the PMMA block (bright regions) was sufficient for achieving high-quality images (Figure 5a). Then, in order to investigate whether the obtained nanostructure is thermodynamically stable structure, we prepared the PS-*b*-PMAPOSS-*b*-PMMA **3** sample extending thermal annealing time for 48 h. As the result of TEM measurement, no change was seen, indicated that the annealing condition could give forming a thermodynamically stable nanostructure (Figure 5b). Moreover, no change was observed in the domain size and contrast image before and after staining with RuO₄ (Figure 5c). Thus, the lamellar morphology of an AB-like block copolymer, in which PS and PMAPOSS form the mixed phase between two PMMA layers.

Figure 5. TEM images of PS-*b*-PMAPOSS-*b*-PMMA **3**, a)thermal annealed at 180 °C for 24h, b)thermal annealed at 180 °C for 48 h, and c)stained with RuO₄ (bright phase PMMA).

Further increasing of the PMAPOSS volume fraction leads to the formation of a three-domain lamellar nanostructure. This can be seen in Figure

6, which shows a TEM micrograph. In this case, all three block components can be distinguished: PMMA appears as white phase, the grey phase assigned to PS, and the very narrow dark phase can be assigned to PMAPOSS. The lamellar *d*-spacing was found to be 34 nm, which is in good agreement with values obtained from the TEM image. And, the width of remarkable narrowly dark domain is 4 nm. The lamellar structure is the layered structure whose repeating unit is -ABCB-, A, B and C is PS, PMAPOSS, and PMMA, respectively (Figure 6b). The ultra narrow PMAPOSS layer, which is not obtained in the PMAPOSS containing diblock copolymer system, was observed in a designed triblock terpolymer, which is the result of the highly repulsive PMAPOSS middle segment.

Figure 6. TEM image and schematic illustration; a)TEM image of PS-*b*-PMAPOSS-*b*-PMMA **5**, b)schematic illustration of three-domain layer.

Conclusion

In conclusion, a new series of POSS-containing triblock terpolymers, PS-*b*-PMAPOSS-*b*-PMMA, was prepared using living anionic polymerization. The use of this method enables control of the molecular weight and the achievement of narrow molecular weight distributions. We also successfully obtained the ultra narrow PMAPOSS layer (4 nm) in the bulk of the PS-*b*-PMAPOSS-*b*-PMMA lamellar morphology. This morphology is expected to be a promising line patterns in the block copolymer lithography.

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