Precise Synthesis of Fluorine-containing Block Copolymers via RAFT

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1. Introduction

As the demand for increased on-chip density and miniaturized devices is constantly increasing in the microelectronics industry, the ability to precisely engineer patterns in the nanometer scale is critical. Nanopatterning can be realized with conventional photolithography. However, using a top-down approach such as photolithography to produce nanopatterns with sub-10 nm feature sizes is not only costly, but also highly challenging.

Unlike conventional optical lithography, BCP lithography does not face the same intrinsic resolution limits. By exploiting the nanostructures formed by the microphase-separation of BCPs in thin films, the reliable generation of sub-10 nm feature sizes becomes possible. To achieve this, the use of strongly segregating BCPs that exhibit highly repulsive interactions between the two polymer blocks to enable microphase-separation even at very low molecular weights is required [1]. Moreover, in order to obtain patterns with a high aspect ratio, the development of suitable BCPs with highly contrasting etching resistances is essential.

Recently, silicon-containing BCPs have received much attention due to their high etching contrast and small feature dimensions derived from their component incompatibility [2,3]. However, controlling the orientation of such materials is challenging because silicon-containing BCPs with strong segment-segment interaction generally

exhibit disparate polarities and a large difference in the surface free energies between the two blocks. The lower surface free energy of the polymer block results in the tendency for wetting of the block onto the substrate to minimize the interfacial energy. Consequently, thin films of silicon-containing BCPs tend to exhibit a parallel orientation with the silicon-containing layer appearing on the top surface exposed to the air. Some solutions proposed include the use of a top-coat and solvent annealing to control the interfacial affinities of the blocks [4,5]. However, the fact that this is a multi-step process which requires significant amounts of work to find the optimal conditions required for suitable orientation control poses a great challenge for actual industrial use. On the other hand, we recently developed a new class of silicon-containing diblock copolymers, poly(methacrylate polyhedral oligomeric silsesquioxane)-*block*-poly(2,2,2-trifluoroethyl methacrylate), denoted as PMAPOSS-*b*-PTFEMA, that can form perpendicularly oriented structures of lamellae in the thin films by thermal annealing [6].

Not only are the blocks in PMAPOSS-*b*-PTFEMA highly immiscible, but they also display similar surface free energies (γ_{PTFEMA} : 25.1 mN/m, γ_{PMAPOSS} : 28.7 mN/m) and a high etching contrast. This allows for the easy control of orientation in the lamellae morphology with a half pitch size of ca. 10 nm and a thin film with a high aspect ratio. However, PMAPOSS-*b*-PTFEMA with a precisely

controlled primary structure could not be synthesized by anionic polymerization. This is likely a result of various side reactions that occurred. One possibility was that the Lewis basic anion of the propagating chain was reacting with the hydrogens of the methylene moiety between the ester and $-\text{CF}_3$ group of TFEMA. The hydrogens at the methylene group have increased acidities and are activated due to the strong electron withdrawing properties of the ester and $-\text{CF}_3$ groups. This side reaction may lead to the termination of the polymerization reaction.

In this paper, we first report the precise synthesis of PMAPOSS-*b*-PTFEMA via the reversible addition-fragmentation chain transfer (RAFT) mechanism. Radical polymerizations typically have a higher tolerance towards acidic protons compared to anionic polymerizations. Thus, we can expect to circumvent the anticipated side reactions. Finally, we demonstrated the nanopatterning of self-assembled PMAPOSS-*b*-PTFEMA in the thin film.

2. Experimental

2.1. Materials

2,2'-Azobis(isobutyronitrile) (AIBN) and 2,2,2-trifluoroethyl methacrylate (TFEMA) were purchased from Tokyo Chemical Industry (TCI). TFEMA was dried over calcium hydride overnight and distilled under reduced pressure. AIBN was purified by recrystallization from methanol. Methacrylate POSS with ethyl substituents (MAPOSS) was purchased from Hybrid Plastics and recrystallized from methanol. 2-Cyano-2-propyl benzodithioate (CPDB) were purchased from Sigma-Aldrich and used without further purification. Toluene (super dehydrated) was purchased from Wako Pure Chemical Industries (Wako) and used as received.

2.2. Methods

^1H NMR spectra of polymers were recorded on a JEOL 400 MHz nuclear magnetic resonance (NMR) instrument using chloroform-*d* as a solvent. The number average molecular weights (M_n) and molecular weight distributions (M_w/M_n) were measured on an Asahi Technion AT-2002 using THF as a carrier solvent. Small angle X-ray scattering (SAXS) and Grazing incidence X-ray scattering (GISAXS) measurements were carried out using a Bruker NanoSTAR (50 kV/100 mA) to determine the morphologies in the bulk and thin film. Atomic force microscopy (AFM) measurements were performed to observe the

surface architecture of PMAPOSS-*b*-PTFEMA thin film by using a scanning probe microscope (model SPA-400, Seiko) in tapping mode; noncoated silicon etched probes were used in the measurement. The thickness of thin film was measured using F20 (Filmetrics, Inc.).

2.3. Synthesis of macro-RAFT agent

In a typical experiment, MAPOSS (4.05 g, 5.42 mmol), Toluene (11 mL), CPDB (40 mg, 0.181 mmol) and AIBN (14.8 mg, 0.0904 mmol) were weighed into a 20 mL glass sealed tube with a magnetic stir bar, and the solution was degassed by five freeze- evacuate-thaw cycles and sealed. The solution was stirred at 60 °C for 24 h. The reaction was quenched by rapid cooling with liquid nitrogen. The crude product was purified by reprecipitation into excess amounts of methanol twice, and the resulting product was dried under vacuum at 40 °C for 24 h to yield PMAPOSS as a pink powder (65%, 2.61 g). The number-average molecular weight and molecular weight distribution of the product tested by GPC are 7,300 g mol⁻¹ and 1.15, respectively. ^1H NMR (CDCl_3 , 400 MHz): δ 0.61-0.63 (br, 14H, CH_2CH_3), 0.80 (br, 5H, back bone CH_3 , POSS- CH_2CH_2), 0.97-0.98 (br, 21H, CH_2CH_3), 1.72 (br, 4H, back bone CH_2 , POSS- CH_2CH_2), 3.56 (br, 2H, OCH_2). ^{13}C NMR (CDCl_3 , 400 MHz): δ 3.4, 4.0, 4.5, 6.5, 8.2, 17.3, 18.3, 21.7, 44.9, 54.2, 66.8, 126.5, 128.2, 176.3, 177.1, 177.6.

2.4. Synthesis of PMAPOSS-*b*-PTFEMA in the presence of macro-RAFT agent

In a typical experiment, toluene (0.3 mL) was introduced into the reactor as reaction medium. 60 wt% of the monomer (TFEMA, 0.904 g) relative to system, the macro-RAFT agent (PMAPOSS, 0.267 g) and AIBN (3.0 mg, 0.0183 mmol) were dissolved into the reaction medium. The mixture was degassed by three freeze-evacuate-thaw cycles, sealed, stirred at 60 °C for 12 h and quenched by rapid cooling with liquid nitrogen. The product was reprecipitated in an excess methanol/water mixture with a volume ratio of 90/10, then washed by hexane to remove any unreacted macro-RAFT agents and dried in a vacuum oven at 40 °C for 24 h to yield PMAPOSS₁₀-*b*-PTFEMA₁₀₈ as a pink powder (31%, 0.36 g). The polymer had 29,100 g mol⁻¹ and 1.17 as the number-average molecular weight and molecular weight distribution, respectively. ^1H NMR (CDCl_3 , 400 MHz): δ 0.56-0.63 (br, 14H, CH_2CH_3), 0.70-1.35 (br, 29H, back bone CH_3 , POSS- CH_2CH_2 , CH_2CH_3),

1.72-2.28 (br, 6H, back bone CH_2 , POSS- CH_2CH_2), 3.75-3.95 (br, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$ -POSS), 4.02-4.46 (br, 2H, CH_2 - CF_3). ^{13}C NMR (CDCl_3 , 400 MHz): δ 3.4, 4.0, 4.5, 6.5, 8.2, 16.7, 18.5, 21.7, 44.7, 45.0, 45.5, 52.2, 53.4, 53.7, 60.5, 60.9, 61.3, 61.6, 66.8, 118.7, 118.8, 121.5, 121.5, 124.2, 124.3, 126.5, 127.0, 127.1, 128.2, 174.2, 174.6, 175.2, 175.2, 175.6, 175.9, 176.3, 177.1, 177.6.

2.5. Sample preparation

Bulk samples for the investigation of the morphologies and domain spacings of periodic structures in the bulk were prepared by slow evaporation from chloroform solution at ambient conditions. To investigate the surface architectures, thin films with a thickness of 52 nm were prepared. PMAPOSS₁₀-*b*-PTFEMA₁₀₈ was dissolved in chloroform and filtered using a disposable syringe filter with a pore size of 0.20 μm , producing a solution of 1 wt% polymer. This filtered solution was spin-casted onto Si-substrates containing its native oxide at 4500 rpm for 30 s.

3. Results and discussion

3.1. Synthesis of PMAPOSS-*b*-PTFEMA via RAFT

RAFT is a powerful technique for the preparation of block copolymers from a wide variety of monomers. In this study, a PMAPOSS macro-RAFT agent was used for the polymerization of the TFEMA monomer. The PMAPOSS was prepared by the polymerization of MAPOSS in the presence of CPDB. GPC analyses show that the molecular weight and the molecular weight distribution of the macro-RAFT agent is 7,300 and 1.15, respectively. The polymerization of TFEMA was then carried out using the PMAPOSS macro-RAFT agent (Figure 1). After the polymerization reaction, the final product was obtained with a yield of 31 %. The degrees of polymerization for the PMAPOSS and PTFEMA segments were estimated to be 10 and 108 respectively, calculated from the ratios of the ^1H NMR integral intensities of the resonances at 3.9 ppm of the protons of the PMAPOSS segment and 4.3 ppm for the protons of the PTFEMA segment. The volume fraction of the PMAPOSS block was 0.33, calculated using a density of 1.14 g cm^{-3} for PMAPOSS and 1.45 g cm^{-3} for PTFEMA. Figure 2 shows the GPC chromatograms of the macro-RAFT agent and PMAPOSS₁₀-*b*-PTFEMA₁₀₈. The GPC chromatograms of the resulting polymers showed a high symmetry and the molecular weight distributions were approximately 1.2. This implies that the

anticipated side reactions were not occurring. These results indicate that the polymerization of PMAPOSS-*b*-PTFEMA via the RAFT mechanism was successfully and precisely controllable.

Fig. 1. Synthesis of PMAPOSS-*b*-PTFEMA via RAFT.

Fig. 2. GPC curves of the macro-RAFT agent (dashed line) and PMAPOSS₁₀-*b*-PTFEMA₁₀₈ before washing in hexane (solid gray line) and after washing in hexane (solid black line).

Fig. 3. SAXS profile of PMAPOSS₁₀-*b*-PTFEMA₁₀₈ bulk sample.

3.2. Morphological characterization in bulk

Small angle X-ray scattering (SAXS) studies were performed on the bulk sample in order to examine the morphology and feature dimensions of the phase-separated material. The morphology was determined by the ratios of the higher-order scattering peaks to the primary peak (q^*). Figure 3 shows a SAXS profile of the PMAPOSS₁₀-*b*-PTFEMA₁₀₈ that is consistent with a lamellar morphology as indicated by the 1, 2, 3, 4 q/q^* peak scattering ratios. Domain spacing defined by q^* was calculated as $d = 2\pi/q^*$ and is 21.8 nm for PMAPOSS₁₀-*b*-PTFEMA₁₀₈.

3.3. Microphase-separated nanostructure in thin film

To explore the thin film self-assembly characteristic of the aforementioned ordered block copolymer, a polymer thin film was prepared by

spin-coating 1 wt% polymer solution in chloroform for 30 s where the film thickness was adjusted to almost two and a half orders of magnitude higher than the domain spacing in the corresponding bulk sample. It had been previously reported that this block copolymer spontaneously self-assembles in the thin film by simple thermal annealing. Therefore, in this experiment, the thin film was annealed at 130 °C for 3 min under ambient conditions to induce phase-separation. Figure 4 shows the atomic force microscopy (AFM) phase image of the resulting annealed thin film, exhibiting regions with line-like features. Grazing-incidence small angle X-ray scattering (GISAXS) was used to investigate the evolution of the morphology and the orientation of the domains in the thin film. Figure 5 shows the GISAXS pattern and profile of the annealed thin film. A line cut profile of the scattering pattern in the q_y direction shows higher order scattering peak, indicating a highly ordered periodic structure in the plane of the substrate. Moreover, the pattern exhibited two scattering peaks with relative peak position ratios of 1:2, indicative of a lamellar morphology. The periodic length estimated from the position of the first-order peak was 25.2 nm, in good agreement with the domain spacing in the corresponding bulk sample. Thus, these line-like features could be interpreted as lamellae with a perpendicular orientation relative to the substrate.

Although the perpendicular orientation of the lamellar domain in thin films was achieved, the resulting thin film seemingly accommodates appreciable deformation. This is presumably due to the large value of the molecular weight distribution (M_w/M_n : 1.17) or residual macro-RAFT agents that were not completely removed. Future work will focus on the optimization of the polymerization and thermal annealing conditions to preclude the defects and to multiply the areal density of densely packed domain. Larger area demonstrations and epitaxially induced alignments using newly synthesized PMAPOSS-*b*-PTFEMA with the ability to self-assemble into sub-10 nm features, and integration with the directed self-assembly, are also involved in our future work.

In conclusion, lamellar-forming PMAPOSS-*b*-PTFEMA block copolymers with unimodal GPC chromatograms were successfully synthesized by the polymerization of TFEMA in the presence of PMAPOSS as a macro-RAFT agent and AIBN as the initiator via RAFT. The SAXS, AFM and GISAXS data showed the lamellar domain was

perpendicularly oriented to the Si-substrate after atmospheric thermal annealing. These experimental results also show that it is possible to precisely produce PMAPOSS-*b*-PTFEMA quantitatively, impervious to any side reactions. This technique is vital to meet the growing demands of the microelectronics industry for high throughput devices of ever-decreasing sizes.

Fig. 4. AFM phase image of a PMAPOSS₁₀-*b*-PTFEMA₁₀₈ thin film with a thickness of 52 nm after thermal annealing at 130 °C for 3 min.

Fig. 5. (a) GISAXS pattern of a PMAPOSS₁₀-*b*-PTFEMA₁₀₈ thin film and (b) intensity plot with respect to peak position in-plane.

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