Orientation Control of the Microphase-separated Nanostructures of Block Copolymers on Polyimide Substrates

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This study aimed to form a perpendicularly orientated lamellar structure with polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA) by its microphase separation on a polyimide substrate. Eight types of polyimides were prepared from different combinations of monomers and tested as the bottom layer for the microphase separation of PS-b-PMMA. The surface free energies of those polyimide substrates were evaluated by the Owens-Wendt method. Thin films of PS-b-PMMA were prepared on the polyimide substrates and the self-assembly was induced by thermal annealing, and the surface architecture was observed by atomic force microscopy. In the tested polyimide substrates, only one from 2,2-bis[4-(3,4-dicarboxyphenoxy) phenyl]propane dianhydride (tetracarboxylic dianhydride) and 1,12-bis (4-aminophenoxy) dodecane (diamine) showed a perpendicularly oriented lamellar structure. This polyimide substrate shows one of the smallest polar components in its surface free energy. Relatively large domain size and long correlation length in the PS-b-PMMA layer were obtained by optimizing the conditions for fabrication of the polyimide substrate, which were prepared by casting the polyimide onto a silicon wafer, followed by thermal annealing. These results suggest that the combination of one monomer with relatively large molecular weight, which will result in a low density of imide groups, and the other monomer with long alkyl chains, which will reduce the polarity of the resulting polyimide, contributes to providing a perpendicular orientation.

Keywords: Block copolymer, Polyimide, Microphase-separated nanostructure, Thin films, Orientation control

1. Introduction

Block copolymer (BCP) lithography is considered to be one of the promising technologies for the next-generation lithography [1–4]. In the BCP lithography, line and dot resist patterns are required to be fabricated by the microphase separation of BCPs, to draw circuit patterns on silicon substrates. For this purpose, the microphase separated lamellar structures are required to be perpendicularly oriented against their substrates, whereas many of BCPs tend to form parallelly oriented lamellae reflecting the interfacial free energy of the interfaces consisting of the BCP domains, the bottom surface, and the top surface (typically air) [5]. In the case of a typical polymer for the BCP lithography, polystyrene-block-poly(methyl methacrylate) (PS-b-PMMA), the strong affinity of the PMMA domain and the silicon substrate results in a parallel orientation [6]. There have been several ways to induce perpendicular orientation as follows: solvent annealing [7], application of an electric field [8], and modification of the substrate by neutral layers [9–20]. The most common method is to cast a random copolymer (RCP) mainly consisting of PS and PMMA, as a neutral layer to balance the interfacial free energies of the PS/substrate and PMMA/substrate interfaces.

On the other hand, the development of flexible devices has recently received a great deal of attention [21]. For this purpose, polyimides (PIs)...
have been considered to be suitable for the flexible substrate due to their mechanical, chemical, and thermal strength. Furthermore, PIs have been proven to be biocompatible [22] and are expected to be applied in the biomedical field recently [23,24]. In this context, technologies for fabricating fine circuit patterns onto PI substrates have been extensively studied [25,26]. The application of the BCP lithography on flexible substrates has also been attempted [13,27–32]. In the typical BCP lithography on flexible substrates, the perpendicular orientation has been achieved by fabricating a neutral layer between the substrate and BCP, which is a similar approach to those on silicon substrates. If the neutral layer becomes unnecessary for the BCP lithography on flexible substrates, these technologies will be more attractive.

In this context, our research group has been motivated to achieve the direct fabrication of perpendicularly oriented lamellae of PS-b-PMMA onto PI substrates without any neutral layers. We assume that this could be achieved if the interfacial free energies of the PS/PI and PMMA/PI interfaces are balanced, and the molecular structure of PI needs to be carefully designed. Considering the fact that PIs can be easily synthesized by polycondensation of tetracarboxylic dianhydrides and diamines [33], an adequate design could be achieved by carefully selecting the molecular structures of the monomers.

The objective of this study is to demonstrate a perpendicularly oriented lamella of PS-b-PMMA on a PI substrate as illustrated in Fig. 1. Eight types of PIs listed in Table 1 were tested as the substrate for PS-b-PMMA. The chemical structures of the monomers for these PIs are shown in Fig. 2. The PI layers were fabricated by casting the solutions of poly(amic acid)s (PAAs) and heating the layers on a silicon wafer for imidization. The surface free energies of the substrates with PIs were evaluated by the Owens-Wendt method for the contact angles [34]. Thin films of PS-b-PMMA were prepared on the PI substrates and thermally annealed to induce the self-assembly. The surface architecture of the obtained films was characterized by atomic force microscopy (AFM). The correlation among the monomer structure for PI, the surface free energy of PI, and the resulting surface architecture of PS-b-PMMA is discussed in terms of comparison against the self-assembly of PS-b-PMMA on a typical neutral layer, a RCP of PS, PMMA, and poly(glycidyl methacrylate) (PS-r-PMMA-r-PGMA).

Fig. 1. Schematic illustration for orientation control of the microphase-separated lamellar nanostructures of block copolymers on a substrate with PI.

Table 1. Combination of the monomers and polymerization conditions

| Label | Tetracarboxylic dianhydride | Diamine | Solvent | Reaction period (h) | η_{inh} (dL g⁻¹) |
|-------|-----------------|--------|--------|-------------------|-----------------|
| PI1   | PMDA            | ODA    | DMAc   | 3                 | 1.27            |
| PI2   | 6FDA            | m-Tolidine | -     | -                 | -              |
| PI3   | 6FDA            | TFMBC  | DMF    | 24                | 0.65            |
| PI4   | 6FDA            | DA5MG  | -      | -                 | -              |
| PI5   | BPDA            | m-Tolidine | -     | -                 | -              |
| PI6   | TAHQ            | DA10MG | NMP    | 24                | 0.91            |
| PI7   | TAHQ            | DA12MG | NMP    | 24                | 0.98            |
| PI8   | BPADA           | DA12MG | NMP    | 3                 | 0.70            |

2. Experimental

2.1. Materials

Styrene, methyl methacrylate (MMA) and glycidyl methacrylate (GMA) were distilled over calcium hydride. The purified styrene and MMA for living anionic polymerization were further distilled over di-n-butylmagnesium and tri-n-octylaluminium, respectively. 1,1-Diphenylethylene was distilled over n-butyllithium. 2,2’-Azobis (isobutyronitrile) was recrystallized from methanol (MeOH). PMDA was recrystallized from acetic anhydride. 4,4’-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) was recrystallized from a solution of acetic acid and acetic anhydride. 1,4-Phenylene bis (1,3-dioxo-1,3-dihydroisobenzofuran-5-carboxylate) (TAHQ) was recrystallized from 1,4-dioxane. 2,2-Bis [4-(3,4-dicarboxyphenoxy) phenyl] propane dianhydride (tetracarboxylic dianhydride) (BPADA) was recrystallized from a solution of toluene and acetic anhydride. ODA was recrystallized from ethanol. 2,2’-Bis (trifluoromethyl) benzidine (TFMB) was recrystallized from MeOH. 1,10-Bis (4-aminophenoxy) decane (DA10MG), 1,12-bis (4-aminophenoxy) dodecane (DA12MG), and all the
other chemicals were used as received without further purification. The substrates with PI2, PI4 and PI5 represent the PI using 4,4'-bipthalic anhydride (BPDA), m-tolidine and 1,5-bis (4-aminophenoxy) pentane (DA12MG), respectively, as shown in Table 1. The substrates coated with these PIs were supplied by a chemical company, and used as received.

2.2. Measurements

$^1$H nuclear magnetic resonance ($^1$H-NMR) for PS-$b$-PMMA and PS-$r$-PMMA-$r$-PGMA were performed at room temperature on a JEOL ECS400 spectrometer. The number-average and weight-average molecular weights ($M_n$ and $M_w$) were determined by the size exclusion chromatography (SEC) using a Shodex GPC-101 system equipped with a refractive index detector and a LF-804 column (Showa Denko) with tetrahydrofuran (THF) as the eluent. Small angle X-ray scattering (SAXS) for the bulk polymer sample was performed using a Bruker NanoSTAR (50 kV/50 mA) with a 2D-PSPC detector (camera length of 1055 mm). The inherent viscosities of the PAA solutions were determined by the viscometry for 0.5 g dL$^{-1}$ of polymer solutions in N,N-dimethylacetamide (DMF), or $N$-methyl-2-pyrrolidone (NMP) at 30 °C using an Ostwald viscometer. The thickness of the polymer films was measured by a FILMTRIES F20-EXR. Contact angles of water and diiodomethane on the PI substrates were measured using a Kyowa DM-501YH. AFM was performed using a JPK NanoWizard Ultra Speed AFM system.

2.3. Polymer synthesis

2.3.1 PS-$b$-PMMA

PS-$b$-PMMA was synthesized via living anionic polymerization. All the polymerization procedures were performed under an argon purge. THF (50 mL) and lithium chloride (11.0 mg, 0.26 mmol) were transferred to a 100 mL schlenk flask and then cooled to $-78$ °C. sec-Butyllithium for drying THF was added until the color changed to light yellow. After treating the flask at room temperature to deactivate the sec-butyllithium for drying, the flask was cooled again to $-78$ °C, and sec-butyl lithium solution in $n$-hexane (50 μL, 0.05 mmol) was added as the initiator. Styrene (1.82 mL, 15.9 mmol) was added and stirred for 30 min, until the color changed to bright orange, followed by the addition of 1,1-diphenylethylene (45 μL, 0.26 mmol), resulting in a
deep red color. After 30 min of stirring, MMA (2.00 mL, 18.8 mmol) was added and further stirred for 30 min, until the solution became colorless. Then, 5 mL of MeOH (excess amount) purged with argon was added to the flask for termination. The polymer was precipitated into an excessive amount of MeOH and filtered. The residue was dried under a reduced pressure overnight to yield whitish powder (2.76 g, 78% yield).

\[ \text{M}_n: 46.3 \text{ kDa}. \quad \text{M}_w/\text{M}_n: 1.13. \]

\(^1\text{H}-\text{NMR} (400 \text{ MHz}, \text{CDCl}_3, \delta, \text{ppm}): 0.70-1.05 (\text{br, } 3\text{H}, \text{C}_3\text{H}_3), 1.20-1.55 (\text{br, } 2\text{H}, \text{back bone C}_2\text{H}_2), 1.70-2.23 (\text{br, } 3\text{H}, \text{back bone CH}_2\text{C}_2, \text{back bone C}_2\text{H}_2\text{C}_2), 3.40-3.84 (\text{br, } 3\text{H}, \text{CH}_3\text{O}), 6.33-6.91 (\text{br, } 2\text{H}, \text{aromatic ortho}), 6.92-7.24 (\text{br, } 3\text{H}, \text{aromatic meta and para}).

2.3.2. PS-r-PMMA-r-PGMA

PS-r-PMMA-r-PGMA was synthesized via free radical polymerization. \(^2,2'\)-Azobis(isobutryonitrile) (0.016 g, 0.1 mmol), styrene (1.145 mL, 10 mmol), MMA (1.04 mL, 9.8 mmol), and GMA (0.021 mL, 0.2 mmol) were added to a 20 mL schlenk tube, and the solution was degassed by three freeze-pump-thaw cycles and backfilled with argon gas. The solution was stirred at 80 °C for 2 h. The polymerization was quenched by rapid cooling in liquid nitrogen. The crude product was diluted with THF, precipitated into an excessive amount of MeOH, and filtered. The residue was dried under a reduced pressure overnight to yield whitish powder (1.59 g, 77% yield). \[ \text{M}_n: 54 \text{ kDa}. \quad \text{M}_w/\text{M}_n: 2.29. \quad ^1\text{H}-\text{NMR}(400 \text{ MHz}, \text{CDCl}_3, \delta, \text{ppm}): 0.24–1.08, 1.10–1.36, 1.37–2.08, 2.09–2.50, 2.62–3.04, 3.10–3.70, 6.40–7.40. \]

2.3.3 PAAs

All PAAs were synthesized via polyaddition of tetracarboxylic dianhydride and diamines. The synthetic scheme, combinations of the monomers, polymerization conditions, and inherent viscosities were presented in Scheme 1 and Table 1. An example of the synthesis is as follows. In a 100 mL three-necked flask purged with nitrogen, ODA (1.00 g, 5.0 mmol) was dissolved in 10 mL of DMAc at room temperature with a mechanical stirrer. Next, PMDA (1.09 g, 5.0 mmol) was added to the solution, and the mixture was left to be stirred for 3 h. Subsequently, the solution was diluted with 30 mL of DMAc and the solution was reprecipitated into an excessive amount of MeOH and filtered. The residue was dried under a reduced pressure at 40 °C overnight to yield yellowish solid.

2.4. Preparation of the bulk sample of PS-b-PMMA

The bulk sample for the morphology study was prepared by slowly evaporating a dilute solution of PS-b-PMMA in chloroform at room temperature, followed by drying under reduced pressure at 170 °C for 24 h.
overnight to yield whitish powder (1.59 g, 77 % residue was dried under a reduced pressure.

excessive amount of MeOH, and filtered. The product was diluted with THF, precipitated into an excessive amount of MeOH and filtered. The residue was dried under a reduced pressure at 40 °C.

degassed by three freeze-pump-thaw cycles and to a 20 mL schlenk tube, and the solution was added to the flask for termination. The polymer was precipitated into an excessive amount of MeOH.

2.3.3 PAAs

δr, ppm): 0.70-1.05 (br, 3H, C₃H₃), 1.20-1.55 (br, 2H, backbone C₃H₂C), 3.40-2.23 (br, C₃H₂CH), 1.70

radical polymerization. 2',2'-

M

400 MHz, CDCl₃.

Fig. 3. Preparation of (a) RCP substrate, (b) PI substrates, and (c) PS-PMMA thin film on each of the substrates.

2.5. Preparation of the substrates

2.5.1. Substrate with a RCP

Silicon wafer was cut into 1 cm² piece, and sonicated in acetone, chloroform, and isopropyl alcohol for 30 min each., and then rinsed with ethanol. Next, the wafer was treated with a mixture of H₂O₂ (30%) and H₂SO₄ (70%) (v/v) at 100 °C for 2 h, and rinsed with water and ethanol. As shown in Fig. 3(a), the RCP layer was fabricated by spin-coating a PS-r-PMMA-r-PGMA solution in toluene (1 wt%) onto the cleaned silicon substrate at 3000 rpm for 30 s using a MIKASA spin coater IH-D7. The spin-coated substrate was treated at 160 °C for 24 h for cross-linking, and the unreacted polymer was removed by sonicating the substrate in toluene.

2.5.2. Substrates with PI layers

An example of preparation is as follows. Silicon wafer was cut and treated in the above-mentioned manner. As shown in Fig. 3(b), a layer was fabricated by spin-coating a 1.5 wt% PAA solution in NMP at 3000 rpm for 30 s, and drying it at 110 °C for 1 min under a nitrogen flow. And then the substrate was treated at 250 °C for 30 min under a reduced pressure for imidization as shown in Scheme 1.

2.6. Preparation of PS-b-PMMA thin films on the substrates

As shown in Fig. 3(c), a PS-b-PMMA thin film was fabricated by spin-coating a 1.2 wt% PS-b-PMMA solution in toluene at 3000 rpm for 30 s onto the substrate prepared in the above-mentioned manner. This condition provided ca. 1.3 L₀ of thickness (1 L₀ is a period of the lamellar domain). The fabricated thin films were annealed under the conditions listed in Table 2.

Table 2. The surface free energies of the substrates and annealing condition for PS-b-PMMA thin films

| Substrate                  | Total surface free energy (mJ m⁻²) | Polar component (mJ m⁻²) | Dispersion component (mJ m⁻²) | Annealing condition of PS-b-PMMA thin film |
|----------------------------|-----------------------------------|--------------------------|-------------------------------|------------------------------------------|
| RCP(PS-r-PMMA-r-PGMA)      | 43.1                              | 0.5                      | 42.6                          | 230 °C, 1 h                             |
| RCP(PS-r-PMMA-r-PGMA)      |                                   |                          |                               | 170 °C, 24 h                           |
| PI1(PMDA/ODA)              | 46.5                              | 1.2                      | 45.3                          | 230 °C, 1 h                             |
| PI1(PMDA/ODA)              |                                   |                          |                               | 170 °C, 24 h                           |
| PI2(6FDA/m-Tolidine)       | 39.3                              | 1.1                      | 38.2                          | 170 °C, 24 h                            |
| PI3(6FDA/TFMB)             | 39.0                              | 0.3                      | 38.7                          | 170 °C, 24 h                            |
| PI4(6FDA/DA5MG)            | 41.5                              | 0.5                      | 41.0                          | 170 °C, 24 h                            |
| PI5(BPDA/m-Tolidine)       | 45.9                              | 1.7                      | 44.2                          | 170 °C, 24 h                            |
| PI6(TAHQ/DA10MG)           | 46.7                              | 1.7                      | 45.0                          | 170 °C, 24 h                            |
| PI7(TAHQ/DA12MG)           | 43.6                              | 1.6                      | 42.0                          | 170 °C, 24 h                            |
| PI8(BPADA/DA12MG)          | 47.1                              | 0.3                      | 46.8                          | 170 °C, 24 h                            |
3. Results and discussion

3.1. Characterization of PS-b-PMMA

PS-b-PMMA was synthesized via living anionic polymerization. The volume fraction of the PS block was determined as 51 vol% based on the $^1$H NMR spectrum and the polymer densities (PS: 1.05 g cm$^{-3}$, PMMA: 1.18 g cm$^{-3}$) [35].

The microphase-separated morphology of the bulk sample was analyzed by SAXS as shown in Fig 4. The scattering pattern clearly suggests the formation of a lamellar structure, and the $d$-spacing was determined as 33 nm based on the first-order scattering peak. Thus, $L_0$ of this polymer was considered to be 33 nm in the following study.

![SAXS 1D profile of a PS-b-PMMA bulk annealed at 170°C for 24 h.](image)

Fig. 4. SAXS 1D profile of a PS-b-PMMA bulk annealed at 170°C for 24 h.

3.2. Orientation property of PS-b-PMMA thin films on the substrates

The surface free energy of each substrate was evaluated via the water and diiodomethane contact angle measurements based on the Owens–Wendt method, and the results are summarized in Table 2.

In comparison against RCP, the polar components of the surface free energies with PI surfaces tend to be higher, but some PI surfaces showed similar values to that with RCP. The correlation between the surface free energy and the resulting microphase separation of PS-b-PMMA is discussed in the following sections.

The AFM images of thin films on the RCP and PI1 substrates are shown in Fig 5(a-h). The images with the RCP substrate clearly showed fingerprint patterns, suggesting the perpendicular orientation of PS-b-PMMA (Fig. 5(d)). In contrast, the images with the PI1 substrate annealed at 170 °C for 24 h (Fig. 5(e)) showed a hole pattern with $1L_0$ depth, which was confirmed by the cross-sectional profile (Fig. 5(i)). This hole pattern is probably derived from the segregation of the PMMA domain on the PI1 substrate, as illustrated in Fig. 5(j) [36–38]. This suggests that the polarity of PI1 is too high to achieve the perpendicular orientation, and PI substrates with less polarity will be of interest.

![AFM images of thin films on the substrates.](image)

Fig. 5. AFM (a) height and (b) phase images (scale: 5 μm × 5 μm) of the PS-b-PMMA thin film on the substrate with RCP annealed at 170 °C for 24 h. AFM (c) height and (d) phase images (scale: 5 μm × 5 μm) of the film on RCP annealed at 230 °C for 1 h. AFM (e) height and (f) phase images (scale: 5 μm × 5 μm) of the PS-b-PMMA thin film on the substrate with PI1 annealed at 170 °C for 24 h. AFM (g) height and (h) phase images (scale: 5 μm × 5 μm) of the film on PI1 annealed at 230 °C for 1 h. (i) The cross-sectional profile of the white line in the image e. (j) Illustration of showing the orientation of e. PS-b-PMMA concentration: 1.2 wt%.
The AFM images of thin films on the PI substrates are shown in Fig. 6(a-p). The film thickness of each thin film was approximately 1.3 \( L_0 \) before annealing. While all the PI substrates showed hole patterns of PS-\( b \)-PMMA, the edges of the holes seem to be different among the samples. While the images in Fig. 6(i-o) show smooth edges for the holes, Fig. 6(p) shows a dotted fringe pattern. This difference could be explained as follows. The PI substrates for Fig. 6(i-o) probably formed lamellar structures as illustrated in Fig. 6(q), and such edges could be quite smooth without any discontinuous dots. In contrast, if the edge region was perpendicularly oriented as illustrated in Fig. 6(r), the AFM image could show some discontinuous dots as seen in Fig. 6(p). This phenomenon is reasonable if one considers that PI8 has shown one of the lowest polar components in Table 2. Introducing a long alkyl chain in the amine monomer, and selecting a relatively large molecular unit for the tetracarboxylic dianhydride monomer might have contributed to lowering the polarity of the resulting polyimide, and provided a suitable interfacial energy for the PS-\( b \)-PMMA/substrate interface.
3.3. Investigation of optimal conditions for perpendicular orientation of microdomains in PS-b-PMMA thin films on PI8 (BPADA/DA12MG)

Since PI8 showed the perpendicular orientation in a quite limited area, the conditions for the film fabrication on the PI8 substrate were further optimized. At first, the rotation speed and the annealing temperature were optimized as shown in Fig. 7(a). Among the tested conditions, 3000 rpm and 230 °C provided the smoothest surface, whereas other conditions resulted in island and hole structures. This rotation speed provided a film thickness of 0.9 \( L_0 \). And then, the annealing time was varied to determine the optimized condition, as shown in Fig. 7(b). In the tested annealing lengths, 30 min provided the best result, showing a clear fingerprint pattern, although its correlation length needs to be further improved.

To the best of our knowledge, this is the first report to demonstrate a direct fabrication of perpendicularly oriented lamellae of PS-b-PMMA onto a PI substrate without any neutral layers. We believe that the present findings are quite promising for the development of various flexible devices in the near future.

4. Conclusion

Aiming for direct fabrication of perpendicularly oriented lamellae of PS-b-PMMA onto a PI substrate, eight types of polyimides were prepared from different combinations of monomers, and tested as the bottom layer for the microphase separation of PS-b-PMMA. Among the tested PI substrates, only the PI substrate prepared from BPADA/DA12MG showed a perpendicular orientation. This PI showed one of the smallest
polar components of the surface free energy, probably owing to the long alkyl chain in the amine monomer and a large molecular unit in the tetracarboxylic dianhydride monomer. Further studies require to be done for obtaining more large domains of the self-assemble structure, and expand this methodology for future applications.

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