Surface Fabrication of Block Copolymer-Templated Polyimide Films by Reactive Ion Etching

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In this study, we demonstrated fabrication of polyimide composite films with periodic nanostructure on the surface by oxygen plasma reactive ion etching (RIE). Poly(2-vinylpyridine)-block-poly(methyl methacrylate) (P2VP-b-PMMA) was used as a template for formation of periodic nanostructure. The templating block copolymer formed self-assembled structure including the poly(amic acid) (PAA), as a precursor of polyimide, in only the P2VP domain. After the imidization of PAA, PMMA domain was etched selectively by RIE. Thereby, well-ordered hexagonally-packed pores with a d-spacing of approx. 50 nm and a diameter of approx. 25 nm were obtained on the surface of the film.

Keywords: Polyimide, Self-assembly, Block copolymer-template, Nanofabrication, Reactive ion etching

1. Introduction

Polyimides (PIs) are known as super-engineering plastics due to their superior thermal stabilities, mechanical toughness and dielectric properties [1,2]. Hence, PIs have been adopted in advanced engineering fields such as microelectronics, aerospace and medicine. However, since PIs are generally synthesized via the sequential polymerization of diamines and tetracarboxylic anhydrides, it is difficult to obtain well-defined primary structures. As such, there has been little research focusing on the fabrication of PI films with well-ordered and periodic nanostructures. Fabrication of the PI with well-ordered nanostructure can be expected to be applied to high performance materials such as adsorbents and separation membranes for the next generation.

Recently, we reported the fabrication of PI films with well-ordered nanostructures using amphiphilic block copolymers (BCPs) as a template [3,4]. The template system consists of a blend containing an amphiphilic templating BCP, a thermosetting resol crosslinker, and poly(amic acid) (PAA), a precursor of PI. As PAA is hydrophilic, the BCP forms self-assembled structures including the PAA in only the hydrophilic domain. Furthermore, the resol crosslinker stabilizes the periodic nanostructure during the sequential imidization and pyrolysis of the PAA and the BCP template, preventing the collapse of the nanostructure at high temperatures. On the other hand, removing the resol crosslinker from the composite film is preferable as the addition of the resol decreases the total composition of the PI in the film. Therefore, to prevent structural collapse during the decomposition of the BCP template, a milder BCP removal technique is required.

Herein, we demonstrated the use of oxygen plasma reactive ion etching (RIE) to etch the BCP template, allowing for the fabrication of a well-ordered nanostructure on the PI film surface under milder conditions than thermal decomposition (Fig. 1). In this report, poly(2-vinylpyridine)-block-poly(methyl methacrylate) (P2VP-b-PMMA) was selected as the templating BCP as PMMA can be selectively etched by RIE to obtain pores on the composite film surface.
2. Experimental

2.1. Materials

1,3-Bis(3-aminophenoxy)benzene (BAPB), 4,4’-oxydiphthalic anhydride (ODPA), styrene, 2-vinylpyridine (2VP) and methyl methacrylate (MMA) were purchased from Tokyo Chemical Industry Co., Ltd. BAPB was recrystallized from a water/ethanol=50/50 (vol%) co-solvent. ODPA was sublimated at 260 °C to remove impurities before use. Styrene, 2VP and MMA were distilled under vacuum and three freeze-pump-thaw cycles were carried out prior to anionic polymerization. N,N-dimethylformamide (DMF) was obtained from Godo Co., Ltd and distilled under vacuum before use.

2.2. Synthesis

PAA was synthesized via the polyaddition of BAPB and ODPA using DMF as the solvent. The inherent viscosity of the PAA solution was 0.39 g dL⁻¹ (at a concentration of 0.5 g dL⁻¹ at 30 °C, Ostwald viscometer).

Polystyrene (PS) ($M_n= 20.7$ kg mol⁻¹, PDI=1.27), P2VP ($M_n= 27.3$ kg mol⁻¹, PDI=1.23), PMMA ($M_n= 65.7$ kg mol⁻¹, PDI=1.18), and P2VP-b-PMMA copolymer ($M_{n, P2VP} = 31.9$ kg mol⁻¹, $M_{n, PMMA} = 42.0$ kg mol⁻¹, PDI=1.12, 43 wt% P2VP, 57 wt% PMMA) were synthesized via anionic polymerization using sec- butyllithium as an initiator and THF as a solvent at -78 °C.

2.3. Etching rate test of each homopolymer

PS, PAA and PMMA were dissolved in THF for the tests. P2VP was dissolved in chloroform. These 3 wt% homopolymer solutions were spin-casted onto silicon wafers at a speed of 3000 rpm for 30 s to obtain thin films with a thickness around 150 nm. PI thin films were obtained upon the thermal imidization of the PAA thin films at 190 °C for 12 hours in vacuum. Oxygen plasma RIE was then carried out on the thin films (Oxygen flow rate: 40 sccm, pressure: 30 Pa, output: 20W).

2.4. Preparation of the PAA/P2VP-b-PMMA composite film

PAA and P2VP-b-PMMA were dissolved in DMF with a weight ratio of PAA/P2VP-b-PMMA of 40/60. The DMF solution was drop-casted onto a silicone sheet at 50 °C for 24 hours. Then, the films were dried in vacuum oven at 50 °C for 24 hours.

2.5. Analytical measurements

The molecular weights were determined by size-exclusion chromatography (SEC) (Showa-Denko GPC-101 (Carrier solvent; THF)). The small angle X-ray scattering (SAXS) measurement was performed by Bruker AXS NANOSTAR. The scanning electron microscopy (SEM) images and the transmission electron microscopy (TEM) images were obtained by Hitachi High-Technologies Corporation SU-5500 and Hitachi, Ltd. H-7650 Zero A respectively. The thermal degradation behavior was observed by a SII EXSTAR TG/DTA 7300 thermogravimetric analyzer (TGA) under nitrogen gas flow. Fourier Transform-Infrared (FTIR) Spectroscopy was taken with a JASCO FT/IR-4100 plus spectrophotometer. The thin film thicknesses were determined through Filmetrics Filmmeasure F20.

3. Results and discussion

3.1. Etching rate test of each homopolymer

To investigate the suitable template BCP for the RIE, we carried out the etching test of some homopolymer thin films. Fig. 2 shows the etching rates of each homopolymer by oxygen plasma RIE. PS, PAA and P2VP were mostly same etching rate. In other hand, PMMA was approximately 2.8 times etching rate as much as P2VP. Etching rate of PI was a little slower than P2VP. Based on these result,
since P2VP-\(b\)-PMMA assured enough etching contrast by RIE, we selected P2VP-\(b\)-PMMA as a template BCP for PAA.

3.2. The morphologies of the PAA/P2VP-\(b\)-PMMA composite films

To investigate the morphology of the bare templating BCP and the PAA/P2VP-\(b\)-PMMA composite films, we carried out SAXS measurements and TEM observations. The SAXS profiles of the composite films with different weight ratio are shown in Fig. 3. The SAXS profiles show that the pure BCP film exhibited Bragg reflection at \(q^{*}\), \(2q^{*}\) and \(3q^{*}\), whereby \(q^{*}\) is the position of the first-order scattering peak, thus indicating the formation of lamellar domains. Based on the position of the \(q^{*}\) peak, the \(d\)-spacing was estimated to be 36.5 nm. In addition, a linear pattern could be observed in the TEM image (Fig. 4(a)). The TEM images were not stained as there was sufficient contrast. The dark and bright areas correspond to the P2VP and PMMA domains, respectively.

The SAXS profile of the PAA/BCP=40/60 wt% composite films exhibited Bragg reflections at \(q^{*}\), \(\sqrt{3}q^{*}\), \(\sqrt{7}q^{*}\), and \(4q^{*}\), indicating the formation of cylindrical domains. Based on the position of the \(q^{*}\) peak, the \(d\)-spacing was estimated to be 49.4 nm. Moreover, a characteristic dot and linear pattern was observed in the TEM image (Fig. 4(b), (c)), thus showing that a cylindrical morphology with PMMA in the minor domain had formed. These results indicated that PAA was miscible with only the P2VP domain, as the segment volume of the P2VP domain had increased, leading to the destabilization of the lamellar domain and an increased stability of the cylindrical domain.

The SAXS profile of the PAA/BCP=75/25 wt% composite films exhibited Bragg reflection at \(q^{*}\), \(\sqrt{3}q^{*}\), \(\sqrt{7}q^{*}\), and \(4q^{*}\), indicating the formation of cylindrical domains. Contrary to the SAXS results, a well-ordered hexagonally-packed cylindrical structure could not be observed in the TEM image (Fig. 4(d)). Instead, disordered dark spheres could be observed, indicating that there was excess PAA in the system, leading to the inability to form well-ordered BCP nanostructures.

Based on these result, we conducted further studies using a film with a composition ratio of PAA/P2VP-\(b\)-PMMA=40/60 wt% as it formed well-ordered self-assembled cylindrical structures.

3.3. Imidization of the PAA in the composite films

\textit{In-situ} imidization of PAA in the composite films (PAA/P2VP-\(b\)-PMMA= 40/60 wt%) were carried out during TGA measurements from r.t. to 150 °C (program rate: 10 °C min\(^{-1}\)). The sample was kept under nitrogen gas flow 50 mL/min, and held at 150 °C for 4 hours. To confirm the formation of PI, FTIR measurements were taken before and after thermal treatment (Fig. 5). The peaks at 1780 cm\(^{-1}\)(C=O) and 1384 cm\(^{-1}\)(C-N-C) corresponding to the peaks of PI appeared and the peaks at 1669 cm\(^{-1}\)(C=O) and 1541 cm\(^{-1}\)(C-N-C) corresponding to the peaks of PAA disappeared after thermal treatment.

3.4. RIE treatment of the PAA/P2VP-\(b\)-PMMA composite films after imidization

![Fig. 3. The SAXS profiles of P2VP-\(b\)-PMMA film and PAA/P2VP-\(b\)-PMMA composite films.](image-url)

![Fig. 4. TEM images of PAA/P2VP-\(b\)-PMMA composite films (a) 0/100, (b), (c) 40/60, (d)75/25 (wt%). (All images were not stained.)](image-url)
We carried out oxygen plasma RIE on the PAA/P2VP-b-PMMA composite films which thicknesses were 56 μm after thermal treatment to introduce nanostructures onto the film surface. The thermal and the RIE treatment conditions were the same as in section 3.3 and 3.1, respectively. Figure 6 shows the SEM images of the composite films after RIE treatment of varying times. The surface of the composite film before RIE was perfectly flat (Fig. 6(a)). No obvious structure could be observed. Disordered holes could be observed from a RIE treatment time of 60 s (Fig. 6(b)). A porous structure with a hexagonally-packed dot pattern could be observed with 90 s of RIE treatment (Fig. 6(c)). The diameter and depth of the pores are both approximately 25 nm, and the $d$-spacing is approximately 50 nm. This $d$-spacing is in good agreement with the $d$-spacing obtained from the SAXS analyses. Therefore, these results indicate that the dot pattern achieved stems directly from the self-assembled BCP structure. Although periodic structures could also be observed with 90 s and 120 s of RIE treatment, the periodic holes were enlarged due to the long etching treatment times, resulting in partial connections with adjacent pores (Fig. 6(d), (e)). Therefore, the RIE treatment times must be optimized to yield well-ordered nanopatterns on the PI composite film surface.

4. Conclusion
We successfully fabricated well-ordered hexagonally-packed nanostructures on the surface of a PI composite film with a $d$-spacing of approximately 50 nm and a diameter of approximately 25 nm using milder conditions than thermal decomposition of the BCP template. The use of P2VP-b-PMMA as the templating BCP allowed for the selective etching of the PMMA domain via relatively mild conditions such as oxygen plasma RIE to obtain a nanopatterned surface. However, further optimization of the oxygen plasma RIE treatment conditions are required to obtain an increasingly well-ordered nanopatterned PI surface.

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References
1. D.-J. Liaw, K.-L. Wang, Y.-C. Huang, K.-R. Lee, J.-Y. Lai, and C.-S. Ha, *Prog. Polym. Sci.*, 37 (2012) 907.
2. A. Georgiev, D. Dimov, E. Spassova, J. Assa, P. Dineff, and G. Danev, “High Performance Polymers - Polyimides Based - From Chemistry to Applications”, intech, Croatia (2012) p65.
3. Y. Liu, K. Ohnishi, S. Sugimoto, K. Okuhara, R. Maeda, Y. Nabae, M. Kakimoto, X. Wang, and T. Hayakawa, *Polym. Chem.*, 5 (2014) 6452.
4. L. Gao, K. Azuma, Y. Kushima, K. Okuhara, A. Chandra, and T. Hayakawa, *J. Photopolym. Sci. Technol.*, 29 (2016) 247.