Self-assembly of Crosslinked Polyimides Templated by Block Copolymers for Fabrication of Porous Films

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Crosslinked porous polyimide films were fabricated by a soft-template method using the microphase-separated structure based on a template block copolymer. A trifunctional amine, 1,3,5-tris(4-aminophenyl)benzene (TAPB), was used as a crosslinkable monomer of the poly(amic acid) (PAA) to achieve the well-ordered and flexible films. The crosslinking by TAPB improved the thermal stability of the nanostructures of the PAA/polystyrene-b-poly(2-vinyl pyridine) composite films without reduction of the ratio of polyimide. A porous polyimide film was successfully fabricated by thermal treatment of a PAA composite film that has porous lamella structures and disordered porous structures with approximately 50 nm gaps based on the nanostructure of the PAA composite films before thermal treatment.

Keywords: Polyimide, Block copolymer template, Self-assembly, Porous polyimide, Crosslinked polyimide

1. Introduction

Polyimides have outstanding mechanical strength, heat resistance, and chemical stability and are applied to aerospace materials and electronic material fields [1]. Among them, porous polyimides have both excellent properties of polyimides as well as features of porous polymers. Therefore, they are expected to advance the development of functional materials such as gas separation membranes, low dielectric materials, thermal insulators, and separators for fuel cells [2–7]. Well-defined porous polyimides especially have gathered attention because of their excellent properties and controlled pore structure. The fabrication of the well-defined porous polyimides has been reported using the breath figure method [3,8–12], silica-particle template method [13–15], and covalent organic frameworks [16–18]. In the mesoporous range, only a few cases have been reported by the silica sphere template method, which uses hydrofluoric acid to remove the silica template for the pore-forming, and is associated with chemical hazards. Therefore, a much simpler method was strongly desired to fabricate well-defined mesoporous polyimide films.

Based on such background, the fabrication of ordered mesoporous polyimide films by the soft-template method has been reported [19–26]. In this method, an amphiphilic block copolymer with a narrow polydispersity and a well-defined composition ratio is used as a template to form ordered microphase-separated structures. The hydrophilic domain of the block copolymer is miscible with poly(amic acid) (PAA) selectively. The PAA/block copolymer composite co-assembles and forms into an ordered microphase-separated structure. The imidization of PAA is carried out by heating. Subsequently, the composite film is processed by thermal treatment, reactive ion etching, or ozonolysis to decompose the template block copolymer selectively and create an ordered mesoporous structure. This method allows the fabrication of ordered mesoporous polyimide films by facile and safe processes. Furthermore, this method has potential to form various morphologies such as spheres, cylinders, lamellae, and bicontinuous structures by controlling the volume fractions. In those previous works, however, decomposing the template block copolymer at high temperatures (~380 °C) resulted in the collapse of the nanostructure. Although the addition of resol
improved the thermal stability of the nanostructure, the use of excess amounts of resol might cause less flexibility of the film. Therefore, the fabrication of mesoporous polyimide films with both of well-ordered pores and flexibility is still challenging.

In this context, we hereby novel fabrication method of mesoporous polyimide films using a soft template and crosslinkable polyimide instead of the use of crosslinkers such as resol (Fig. 1). A trifunctional amine, 1,3,5-tris(4-aminophenyl)benzene (TAPB), was used as a crosslinkable monomer of the PAA to achieve both order and flexibility of the films. The use of TAPB allows crosslinking of the polyimide without other crosslinkers such as resol. Polystyrene-b-poly(2-vinyl pyridine) (PS-b-P2VP) was used as a template block copolymer. Well-ordered microphase-separated structures are expected to be formed by strong segregation between the hydrophobic domain: PS and the hydrophilic domain: P2VP. The microphase-separated structures of the composite films were characterized by small-angle X-ray scattering (SAXS) and Transmission electron microscopy (TEM). Furthermore, promising PAA composite films were treated in sequential processes, thermal imidization of PAA, and the thermal degradation of PS-b-P2VP. The successful fabrication of the mesoporous polyimide film was demonstrated by SAXS, field emission scanning electron microscopy (FE-SEM), and Fourier Transform-Infrared spectroscopy (FT-IR).

2. Experimental

2.1. Materials

Oxidiphthalic anhydride (ODPA), 1,3-bis(3-aminophenoxy)benzene (BAPB), 1,3,5-Tris(4-aminophenyl)benzene (TAPB), styrene, 2-vinylpyridine (2VP), were purchased from Tokyo Chemical Industry Co., Ltd (Tokyo, Japan). ODPA and BAPB were purified by sublimation at 270 °C and recrystallization from water/methanol = 1/1 (v/v), respectively. TAPB was used as received.

N,N-dimethylformamide (DMF) was purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan) and was stirred over calcium hydride (CaH₂, Nacalai Tesque) overnight then distilled under reduced pressure. Styrene and 2VP were stirred with CaH₂ overnight and distilled under reduced pressure. The monomers were redistilled immediately prior to use over a small amount of di-n-butylMagnesium (Aldrich) and CaH₂, respectively, respectively. Sec-Butyllithium (sec-BuLi, 0.99 M in 95 % cyclohexane and 5 % n-hexane), tetrahydrofuran (THF, >99.5 %, dehydrated and stabilizer free), n-hexane, ethanol, and methanol were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan), and used as received.

2.2. Characterization

The inherent viscosity of the PAA was measured using an Ostwald viscometer with 0.5 g dL⁻¹ of N,N-Dimethylacetamide solutions at 30 °C. Nuclear magnetic resonance (NMR) was acquired on a JEOL JNM-ECS 400 spectrometer (JEOL, Tokyo, Japan) at 400 MHz for ¹H and 100 MHz for ¹³C. The number-average molecular weight (Mₙ) and dispersity (Mₘ/Mₙ) were measured on a ShodexGPC-101 with a ShodexLF804 column using THF as an eluent. Thermogravimetric analysis (TGA) was performed with an EXSTAR TG/DTA 7300 (Seiko Instrument Inc., Tokyo, Japan) at a heating rate of 3 °C min⁻¹. SAXS were measured with a Bruker NanoSTAR (Bruker AXS K.K., Kanagawa, Japan, 50 kV per 50 mA, CuKα radiation) with a 2D-PSPC detector (camera length 1055 mm). TEM was performed using an H-7650 Zero A (Hitachi, Ltd., Tokyo, Japan) microscope at an accelerating voltage of 100 kV. The TEM specimens with 80 nm thickness were prepared with an ultramicrotome (EM UC7, Leica, Wetzlar, Germany) and stained by iodine. FE-SEM was performed on an SU-9000 microscope (Hitachi High-Technologies Corporation, Tokyo, Japan) at 3 kV accelerating voltage. The cross-section of FE-
SEM specimens was prepared by breaking a bulk sample in liquid nitrogen. FT-IR was measured with a JASCO FT/IR-4100 plus spectrophotometer by the KBr pellet method.

2.3 Synthesis of PS-b-P2VP

PS-b-P2VP was synthesized via living anionic polymerization (Fig. 2). 80 mL of dehydrated THF was transferred to a 100 mL Schlenk flask and cooled to -78 °C in a cool bath. Approximately 0.8 mL of sec-BuLi was added and the solution turned yellow. After 10 min, the Schlenk flask was returned to room temperature and the solution became colorless. The Schlenk flask was cooled to -78 °C in a cool bath again. Subsequently, 110 μL of sec-BuLi solution (118 μmol) and 2.65 mL of styrene (23.0 mmol) were added immediately, which turned the solution reddish-brown. After 30 min of stirring, 1.64 mL (15.2 mmol) of 2VP was added to the solution and the color turned to a deep red. After 30 min of stirring, 10 mL of dry methanol was added to quench the reaction and the solution became colorless. The obtained proton-terminated polymer was precipitated in hexane, vacuum filtered, then dried in a vacuum oven at 40 °C for 24 h to obtain a white powder of PS-b-P2VP (3.29 g, 82% yield, $M_n = 17,500$ g mol$^{-1}$, $M_n/M_w = 1.25$, PS$_{91}$-P2VP$_{77}$).

$^1$H NMR (CDCl$_3$, 400 MHz) δ (ppm): 1.42-2.05 (br, CH$_2$, 4H), 2.32 (br, CH$_2$, 2H), 3.23 (br, CH$_2$, 1H), 2.88 (br, CH$_2$, 1H), 6.35-7.07 (br, Ar, PS, Ar P2VP, 8H), 8.08-8.40 (br, Ar P2VP, 1H). $^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm): 40.3, 42.9, 120.6, 125.6, 127.9, 135.3, 145.1, 148.6, 164.3.

2.4. Preparation of crosslinked PAA composite films

The synthesis of crosslinked PAA and the fabrication of PAA/PS-b-P2VP composite films were performed continuously as follows. PAA oligomer terminated with dicarboxylic anhydride was prepared by mixing BAPB and an excess amount of ODPA in DMF for 3 h at 25 °C. The solution was mixed with PS-b-P2VP and stoichiometric TAPB and was stirred for 5 min to obtain a homogeneous solution. The crosslinked PAA composite film was cast on a silicone mold from the solution of 10 wt% polymer mixture through a membrane filter (pore diameter: 0.2 μm), followed by solvent evaporation and crosslinking of PAA at 50 °C for 24 h.

2.5. Preparation of porous polyimide films

Porous polyimide composite films were fabricated by thermal treatment of the crosslinked PAA composite films at 380 °C for 3 h under nitrogen flow (50 mL/min). The imidization of PAA and decomposition of PS-b-P2VP were confirmed by TGA and FT-IR. The resulting porous polyimide films were characterized by SAXS and FE-SEM.

Table 1. Preparation conditions and characterization of the PAA composite films and porous polyimide films.

| Sample | Preparation ratio of PAA monomers (ODPA BAPB TAPB) | Weight fraction of PAA composite films (PAA [%] PS-b-P2VP [%]) | Phase separated structure of PAA composite films | Porous structure of polyimide films |
|--------|--------------------------------------------------|---------------------------------------------------------------|-------------------------------------------------|-----------------------------------|
| 1      | - - -                                           | 0 100                                                         | 21.0 Lamella                                   | N/A N/A                           |
| 2      | 1.00 0.95 0.03                                 | 25 75                                                         | 33.0 Cylinder                                  | N/A N/A                           |
| 3      | 1.00 0.95 0.03                                 | 50 50                                                         | 25.4 Sphere                                    | N/A N/A                           |
| 4      | 1.00 0.95 0.03                                 | 75 25                                                         | 31.1 Sphere                                    | N/A N/A                           |
| 5      | 1.00 0.95 0.03                                 | 25 75                                                         | 33.0 Cylinder                                  | - -                               |
| 6      | 1.00 0.70 0.20                                 | 25 75                                                         | 37.8 Cylinder                                  | - -                               |
| 7      | 1.00 0.30 0.47                                 | 25 75                                                         | 29.3 Lamella/Disordered                        | 28.2 Slit/Disordered             |

$^a$ The domain spacings ($d_0$) were estimated by SAXS.
$^b$ The morphologies were estimated by SAXS and TEM.
$^c$ The morphologies were estimated by SAXS and SEM.
3. Results and discussion

3.1. Self-assembly of crosslinked PAA composite films

The nanostructure of the PAA/PS-b-P2VP composite films was studied by investigating several PAA composite films with different composition ratios using SAXS and TEM. The composite films were prepared by solution casting as follows (Fig. 1 and Table 1). A solution of polymers in DMF/THF co-solvent was cast on a polytetrafluoroethylene (PTFE) block, and then the solvent was slowly evaporated at 50 °C for 24 h. The obtained film was dried under reduced pressure at 50 °C for 24 h.

The SAXS profile of pristine PS-b-P2VP film Sample 1 (Fig. 3 (a)) showed the first scattering peak, indicating the formation of a microphase-separated structure with domain spacing of 21.0 nm. The TEM image (Fig. 3 (b)) showed dark and brighter linear patterns, suggesting the formation of a well-ordered lamellar structure. The average center-to-center distance of the brighter lines was 16 nm.

The SAXS profile of PAA/PS-b-P2VP composite film Sample 2 (Fig. 3 (a)) showed higher-order scattering peaks with \( q/q^* \) ratio of 1:2:√7, indicating the formation of ordered nanostructures with domain spacing of 33.0 nm, where \( q^* \) was the position of the first-order scattering peak. The TEM image (Fig. 3 (c)) showed a pattern of brighter dots and lines in a darker matrix which corresponds to a PS cylinder domain in a P2VP+PAA matrix.

The SAXS profile of PAA/PS-b-P2VP composite film Sample 3 (Fig. 3 (a)) showed higher-order scattering peaks with \( q/q^* \) ratio of 1:2:√7:√12:√21, indicating the formation of an ordered nanostructure with domain spacing of 25.4 nm. The TEM image (Fig. 3 (d)) showed a pattern of brighter dots in a darker matrix which corresponds to a PS sphere domain in a P2VP+PAA matrix.

The changing of morphology from the lamella structure of the pristine PS-b-P2VP film to PS cylinder or sphere structures of the PAA/PS-b-P2VP composite film indicates an increase in the volume fraction of the hydrophilic domain because PAA is miscible with the P2VP segments selectively.

3.2. Self-assembly of PAA composite films

The effect of crosslinking by TAPB on the nanostructure of the composite films was studied by investigating three kinds of samples with different TAPB molar ratios: Sample 5, Sample 6, and Sample 7 (Table 1) with SAXS and TEM. The composition ratio for all the samples was (PAA/PS-b-P2VP = 75/25 wt%), which is the same as that of Sample 2.

The SAXS profiles of Sample 5 and Sample 6 (Fig. 4 (a) top and middle) showed higher-order scattering peaks with \( q/q^* \) ratio of 1:2:√7 with domain spacing of 37.8 nm and 1:√3:√7 with domain spacing of 33.0 nm, respectively. This result indicates that cylinder structures were formed. The TEM images (Fig. 4 (b) and (c)) showed PS cylinder structures that were similar to Sample 2.
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Polytetrafluoroethylene (PTFE) block, and then the polymers in DMF/THF co-solvent was cast on a composite films were prepared by solution casting composition ratios using SAXS and TEM. The composite films was studied by investigating three kinds of samples with different TAPB molar ratios: Sample 5, Sample 6, and Sample 7 (Table 1) with SAXS and TEM. The nanostructure of the composite films was studied by investigating three kinds of samples with different copolymer compositions: Sample 1 (Fig. 3 (a)) showed the first scattering position of the first-order scattering peak. The TEM image (Fig. 3 (b)) showed darker and brighter linear patterns, suggesting the formation of ordered nanostructures with center-to-center distance of the brighter lines was 16 nm. The SAXS profile of pristine PS- b-P2VP film (Fig. 4 (a) top and middle) showed higher-order scattering peaks with q* ratio of 1:2:3, indicating the formation of a lamella structure with domain spacing of 29.3 nm. The TEM image (Fig. 4 (d)) indicated a mixture of areas where brighter and darker lines form clear stripes (near the center of the image) and areas where short line-shaped brighter areas are distributed in the darker area matrix (left and upper right of the image).

Compared Fig. 4 (b) with Fig. 4 (c), a less ordered cylinder structure was obtained in Fig. 4 (c). Also, partly less ordered lamellar areas were observed in Fig. 4 (d). These could be attributed to the rearrangement of the polymer chains being limited by many crosslinking points because Sample 6 and Sample 7 had relatively higher TAPB contents. These results suggest that the nanostructures based on the self-assembly of the template block copolymer could be retained even with relatively high TAPB contents.

3.2. Self-assembly of PAA composite films

Porous crosslinked polyimide films were fabricated by the thermal treatment of crosslinked PAA films at 380 °C for 3 h under a nitrogen flow. The imidization of PAA and degradation of PS-b-P2VP were confirmed by TGA and FT-IR.

The TGA profile of the PAA/PS-b-P2VP composite film Sample 7 is shown in Fig. 5. The TGA curve showed 15.6 % of weight loss at 250 °C, corresponding to the dehydration of the PAA during imidization and evaporation of the residual solvent.

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Also, the weight loss corresponding to the degradation of the template block copolymer began at approximately 350 °C. The final weight of the sample was 21.1 % after heating at 380 °C for 3 h, indicating that the degradation of the template block copolymer successfully completed.

The FT-IR spectra of Sample 7 before and after the thermal treatment are shown in Fig.6. On the FR-IR spectra, the peaks at 1779 cm⁻¹ (C=O) and 1371 cm⁻¹ (C-N) due to polyimide appeared, and the peaks at 1670 cm⁻¹ (C=O) and 1542 cm⁻¹ (C-N) due to PAA disappeared, which indicate that the complete imidization of the PAA. Moreover, the peaks from 2800 cm⁻¹ to 3100 cm⁻¹ disappeared, suggesting the degradation of PS-\textit{b}-P2VP.

3.4. Fabrication and characterization of porous crosslinked polyimide film

The effect of crosslinking on the thermal stability of the nanostructure of PAA composite films was studied by investigating three kinds of porous polyimide film: Sample 5, Sample 6, and Sample 7 using SAXS and FE-SEM.

The SAXS profiles of the porous polyimide films are shown in Fig. 7 (a). Sample 5 and 6 (Fig. 7 (a) top and middle) showed no scattering peaks, indicating the collapse of the ordered nanostructures in the PAA composite films. Sample 7 showed only the first peak, indicating that the nanostructures still remained after the thermal treatment.

The FE-SEM images of Sample 6 (Fig. 7 (b) and (c)) showed both the areas with no pores (Fig. 7 (b)) and the area with pores with several hundred nm of diameter (Fig. 7 (c)). This result indicates that the ordered cylindrical nanostructure collapsed, probably due to some fluidity of the polyimide because of lack of crosslinking.

The FE-SEM images of Sample 7 showed that porous lamella structures (Fig. 7 (d)) and disordered porous structures (Fig. 7 (e)) with approximately 50 nm gaps. These porous structures are likely derived from the lamella structures and disordered structures of the PAA composite film, Sample 7 (Fig. 4 (d)).

Thus, it could be concluded that crosslinked mesoporous polyimide films have been successfully obtained via the soft template method using a crosslinkable monomer, TAPB. The porous polyimide films have both well-ordered nanostructures and flexibility.

4. Conclusion

Porous polyimide films were fabricated via the soft-template method using co-assembly of PAA and PS-\textit{b}-P2VP and crosslinking by a trifunctional amine, TAPB. The resulting films exhibit both flexibility and thermally stable nanostructures. The crosslinked PAA composite films formed various microphase-separated structures such as lamella, cylinder, and sphere, depending on the composition ratio of PAA and PS-\textit{b}-P2VP, and the TAPB content. The thermal treatment of the PAA composite films gave porous polyimide films based on the microphase-separated structures. Further studies will be done to expand this methodology to develop various porous and high-performance polymer films.
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