Fabrication of Mesoporous Polyimide Composite Films by a Soft-Template Method Followed by Ozonolysis

Takahiro Komamura, Koei Azuma, Yuta Nabae, and Teruaki Hayakawa*

Department of Materials Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1-S8-36, Ookayama, Meguro-ku, Tokyo 152-8552, Japan
*hayakawa.t.ac@m.titech.ac.jp

Mesoporous polyimide composite films were fabricated by a soft template method using a microphase-separated structure of an amphiphilic block copolymer and porosification by ozonolysis. Poly(1,4-isoprene)-block-poly(2-vinylpyridine) was used as the template block copolymer. Poly(amic acid) (PAA), the precursor of polyimide, and resol, the cross-linker for stabilization of the nanostructure, were miscible into the poly(2-vinylpyridine) domain which is the hydrophilic domain of the template block copolymer. The mixture co-assembled and formed a periodic body-centered cubic nanostructure. The study of ozonolysis condition revealed that the reaction in hexane allowed porosification without the collapse of the nanostructure. Polyimide composite films with well-defined mesopores were successfully obtained by the sequential processes of the PAA composite film, namely, thermal annealing for crosslinking of resol, ozonolysis in hexane for the decomposition of polyisoprene domain, and thermal treatment for imidization of PAA. The domain spacing determined by small-angle X-ray scattering was 28.8 nm, and the average pore size based on scanning electron microscopy was 24 nm.

Keywords: Polyimide, Self-assembly, Block copolymer, Mesoporous polymer, Soft-template method, Ozonolysis

1. Introduction
Polymides are well-known for their outstanding mechanical strength, heat resistance, and chemical stability and are utilized in the aerospace and electronic material fields [1]. Controlling the polyimide morphology is a worthwhile research endeavor to develop their applicability [2–6]. Porous polyimides have expected deployment as functional materials such as low-dielectric (low-k) materials and battery separators [7–12]. Well-defined mesoporous polyimides are especially gaining attention because of the simultaneous existence of their excellent properties and narrow pore distributions. However, the fabrication of well-defined mesoporous polyimide is still a very challenging subject.

There are two typical methods to obtain well-defined mesoporous polymer films [13], a soft-template method that uses self-assembly of the block copolymer [14–19] and a hard-template method that uses the deposition of silica particles [20,21]. However, it was difficult to fabricate the ordered mesoporous polyimide films using the soft-template method in terms of the synthetic challenge that arise. Since polyimides are generally synthesized via step-growth polymerization of poly(amic acid) (PAA) followed by thermal or chemical imidization, it is difficult to control their molecular weight and molecular weight distribution. Namely, it is hard to obtain the block copolymer with a well-defined composition ratio, which results in difficulty in forming ordered microphase-separated structures. As a result, only a few ordered mesoporous polyimide films are reported using the hard-template method [22–28]. However, as the hard-template method uses hydrofluoric acid, it is associated with the chemical hazards. Therefore, a much simpler method was strongly desired to...
fabricate the ordered mesoporous polyimide film.

Given the background, the facile fabrication method of obtaining ordered mesoporous polyimide films by developing the soft-template method was reported [29–36]. In this method, an amphiphilic block copolymer with a narrow polydispersity and a well-defined composition ratio was used as a template to make ordered nanostructure. The hydrophilic segment of the block copolymer was selectively miscible with PAA, a precursor of polyimide, and resol, a cross-linker for stabilization of the nanostructure. The block copolymer mixture was co-assembled and formed into an ordered microphase-separated structure. Subsequently, the composite film was heat-treated to decompose the template block copolymer selectively and created an ordered mesoporous structure. This method allows the fabrication of ordered mesoporous polyimide films easily by facile and safe processes. Furthermore, this method has the potential to form multiple morphologies such as spheres, cylinders, lamellae, and bicontinuous structures by the control of their volume fraction. However, the remaining task of decomposing the template block copolymer at high temperature (~380 °C) might cause a collapse of the nanostructure [36]. Therefore, a much mild porosification method was strongly desired.

In this study, fabrication of the mesoporous polyimide films was performed under a relatively mild temperature by the soft-template method followed by ozonolysis (Fig. 1). The ozonolysis allows the secession of the carbon-carbon double bonds without the heating process [37]. Also, it can decompose polymers including the carbon-carbon double bond in the main chain to the low molecular compound and remove the fragment by a rinse process. Thus, the ozonolysis has been previously used to obtain the ordered mesoporous polymer in the soft-template methods [38–44]. In this study, poly(1,4-isoprene)-block-poly(2-vinylpyridine) (PI-b-P2VP) was used as a template block copolymer that consists of a degradable hydrophobic segment, polyisoprene (PI), and a hydrophilic segment, poly(2-vinylpyridine) (P2VP), which is compatible with PAA and resol. A PAA based on 4,4'-oxydiphthalic anhydride (ODPA) and 1,3-bis(3-aminophenoxy)benzene (MAPB) was used as a source of polyimide because such a flexible primary structure was advantageous for the formation of ordered nanostructures as a result of a previous study [36]. PAA composite films were prepared by mixing of the PAA, the template block copolymer, and resol, and then these nanostructures were characterized by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The optimization of the three different ozonolysis conditions was evaluated by field emission scanning electron microscopy (FE-SEM). Furthermore, promising PAA composite films were treated in sequential processes, thermal annealing of resol, ozonolysis of PI domain, and thermal imidization of PAA. The successful fabrication of the mesoporous polyimide composite film was demonstrated by SAXS, FE-SEM and fourier transform infrared spectroscopy (FT-IR).

2. Experimental

2.1. Materials

Monomers of PAA, ODPA and MAPB were purchased from Tokyo Chemical Industry Co., Ltd. (TCI) and purified by sublimation at 270 °C and recrystallization by water/methanol = 1/1 (v/v), respectively. N,N-dimethylformamide (DMF) and cyclohexane were purchased from FUJIFILM Wako Pure Chemical Corporation and were stirred with calcium hydride (CaH2, Nacalai tesque) for overnight then distilled under partial pressure. Subsequently, cyclohexane was distilled again over n-butyllithium (1.60 M in 75% n-hexane, Kanto

![Fig. 1. Schematic illustration of the fabrication of the porous polyimide films.](image-url)
Chemical Co., Inc.) prior to use. Isoprene (FUJIFILM Wako Pure Chemical Corporation) and 2-vinylpyridine (TCI) were stirred with CaH₂ overnight and distilled under reduced pressure. Immediately prior to use, the monomers were redistilled with small amount of n-butyllithium and CaH₂, respectively. 1,1-Diphenylethene (DPE, >98.0%, TCI) was distilled with n-butyllithium. sec-BuLi (sec-BuLi, 0.99 M in 95% cyclohexane and 5% n-hexane), tetrahydrofuran (THF, >99.5%, dehydrated and stabilizer free), and methanol were purchased from Kanto Chemical Co., Inc. and used as received. PI-b-P2VP (Mₙ = 37,000, Mₘ/Mₙ = 1.07) was synthesized via living anionic polymerization as described in the followed section 2.4 (Fig. 2) [45]. Phenolic resol was synthesized as described elsewhere [31,46].

2.2. Characterization

The inherent viscosity of the PAA was measured with an Ostwald viscometer using 0.5 g dL⁻¹ of N,N-dimethylacetamide solutions at 30 °C. Nuclear magnetic resonance (NMR) were acquired on a JNM-ECS 400 spectrometer (JEOL Ltd.) operating at 400 MHz for ¹H and 100 MHz for ¹³C. Deuterated dimethyl sulfoxide (DMSO-d₆) or chloroform (CDCl₃) was used as a solvent. Tetramethylsilane (TMS) was used as an internal standard for all samples. The number-average molecular weight (Mₐ) and dispersity (Mₘ/Mₐ) were measured on a ShodexGPC-101 with a ShodexLF804 column using THF as a carrier solvent. SAXS measurements were studied with a Bruker NanoSTAR (Bruker, 50 kV per 50 mA) with the 2D-PSPC detector (detector to sample distance 1055 mm). X-ray wavelength (λ) was 1.54 Å using CuKα radiation. TEM was performed using H-7650 Zero A (Hitachi, Ltd.) microscope at an accelerating voltage of 100 kV. TEM specimens 80 nm thick were produced by cryo-ultramicrotomy at -120 °C and stained by osmium tetroxide (OsO₄). FE-SEM was performed with S5500 (Hitachi High-Technologies Corporation) at 3 kV accelerating voltage. The cross-section of FE-SEM specimens was prepared by fracture under liquid nitrogen. FT-IR was taken with FT/IR-4100 plus spectrophotometer (JASCO) using the KBr pellet method.

2.3. Synthesis of PAA

PAA was synthesized via condensation polymerization of diamines and tetracarboxylic dianhydrides. In a 100 mL three-necked flask purged with nitrogen, 2.426 g of BAPB (8.300 mmol) was dissolved in 30.0 mL of DMF at room temperature by a mechanical stirrer. Next, 2.574 g of ODPA (8.300 mmol) was added to the solution, and the mixture was left to stir for 26 h. Subsequently, the solution was diluted with 30.0 mL of DMF and the solution was reprecipitated into an excessive amount of water, vacuum filtered, and dried in a vacuum oven at 50 °C for 24 h to yield a white solid (4.682 g, 94% yield, inherent viscosity ηinh = 0.39). ¹H NMR (400 MHz, DMSO-d₆, δ ppm): 6.76 (s, 1H, -Ar-O-Ar-), 6.83 (dd, J = 5.0, 2.7 Hz, 4H, -Ar-O-Ar-O-Ar-), 7.23-7.54 (m, 11H, -Ar-O-Ar-, -Ar-O-Ar-O-Ar-, -Ar-O-Ar-Ar-, 7.71 (d, J = 9.2 Hz, 1H, -Ar-O-Ar-), 8.03 (d, J = 9.2 Hz, 1H, -Ar-O-Ar-), 10.55 (s, 2H, amide), 12.92 (br, 1H, COOH), 13.31 (br, 1H, -COOH). ¹³C NMR (100 MHz, DMSO-d₆): δ (ppm): 109.2, 109.9, 113.4, 113.8, 114.8, 124.8, 125.2, 130.2, 131.3, 132.6, 141.1, 141.4, 156.4, 158.0, 158.2, 159.0, 162.4, 166.7.

2.4. Synthesis of PI-b-P2VP

PI-b-P2VP was synthesized via living anionic polymerization (Fig. 2). 40 mL of dehydrated cyclohexane was transferred to a 50 mL Schlenk flask and transferred to a second 50 mL Schlenk flask via the trap-to-trap method. 3.10 mL (31.0 mmol) of isoprene was added to the Schlenk flask at room temperature and 95.6 μL (94.6 μmol) of sec-BuLi solution was added at 40 °C. After 4h, cyclohexane was removed under reduced pressure and 40 mL of THF was charged using the trap-to-trap method. The Schlenk flask was cooled to -78 °C and stirred for 18 h until the polymers dissolved

Fig. 2. Synthetic scheme of the PI-b-P2VP via living anionic polymerization of isoprene and 2-vinylpyridine.
completely. 0.10 mL (0.57 mmol) of DPE was added and the solution turned from colorless to deep red. After 0.5 h, the solution was heated to -40 °C. 1.40 mL (13.0 mmol) of 2-vinylpyridine was added to the solution and the color remained deep red. After 4 h, 3 mL of dry methanol was added to quench the reaction and the color changed to colorless. The obtained proton-terminated polymer was precipitated in water, vacuum filtered, then dried in a vacuum oven at 40 °C for 24 h to obtain a white powder of PI-b-P2VP (1.61 g, 75% yield, $M_n$, GPC = 37000 g mol$^{-1}$, $M_w$/M$n = 1.07$). $^1$H NMR (400 MHz, CDCl$_3$, δ, ppm): 8.29 (d, 1H, C$_6$(Ar)), 7.22(t, 1H, C$_4$(Ar)), 6.83(d, 1H, C$_3$(Ar)) 6.35 (d, 1H, C$_4$(Ar)), 5.11 (dd, 1H,-CH$_2$-CH\(=\)C(CH$_3$)-CH$_2$-), 2.04(dd 3H, -CH$_2$-CH=C(CH$_3$)-CH$_2$-), 2.00(dt, 2H, -CH$_2$-CH=C(CH$_3$)-CH$_2$-), 1.43(s, 2H, -CH$_2$-C(CH$_3$)-)1.41 (s, 9H, -O-C-CH$_3$).

2.5. Preparation of PAA composite films

A series of PAA composite films were prepared by solvent casting (Fig. 1 and Table 1). The composite films were cast on a polytetrafluoroethylene (PTFE) block from a DMF/THF mixture of 10 wt% polymer mixture of PAA, PI-b-P2VP and resol, followed by solvent evaporation at 50 °C for 24 h and drying at 50 °C for another 24 h under vacuum. The obtained films were characterized by SAXS and TEM (Fig. 3). The average thickness of the film was 150 μm.

2.6. Optimization of ozonolysis conditions

Optimization of ozonolysis conditions were conducted by following three different methods using an ozone generator SO-03UN-OX04 (Hamamatsu, Intensity: MAX, O$_2$ gas flow: 0.5 L/min) to convert oxygen to ozone. The ozone generator stably generated O$_3$ gas of 15.6 mmol/h from O$_2$ gas of 1.25 mol/h. The ozone concentration of injected mixture gas was 0.52 mol/m$^3$. After

Table 1. List of the PAA composite films before and after the sequential processes.

| Samples | Weight fraction | PAA composite films | Porous polyimide composite films |
|---------|----------------|---------------------|---------------------------------|
| PI-b-P2VP | 100 | 38.6 Cylinder | |
| PAA5/PI-b-P2VP5 | 50 | 33.7 Disordered Sphere | |
| PAA7/PI-b-P2VP3 | 70 | 28.2 BCC Sphere | 36.0 Disordered Sphere |
| PAA6/PI-b-P2VP3/R1 | 60 | 28.2 BCC Sphere | 28.2 Disordered Sphere |

$^a$ Domain spacing ($d_0$) and morphologies were estimated by SAXS and/or TEM.

Fig. 3. (a) SAXS profiles of composite films and TEM images for (b) PI-b-P2VP, (c) PAA5/PI-b-P2VP5, (d) PAA7/PI-b-P2VP3 at $\times$10.0k magnification, and (e) PAA7/PI-b-P2VP3 at $\times$50.0k magnification.
ozonolysis, the composite films were observed by FE-SEM (Fig. 4).

2.6.1. Ozonolysis in the air

Ozone mixture gas flowed into a 100 mL of round-bottom flask for 30 min at ambient temperature. The composite films were put into the flask and the gas flowed continuously for 2 h. The composite films were put out, soaked into 50 mL of hexane in another beaker with sonication for 10 min, and were dried under vacuum at 50 °C for 12 h.

2.6.2. Ozonolysis in water

Ozone mixture gas was bubbled into 100 mL of water in a 100 mL beaker for 30 min at ambient temperature. The composite films were put into the beaker and the gas was bubbled for 2 h. The composite films were put out and soaked into 50 mL of water in another 100 mL beaker with sonication for 10 min and were left for 48 h. Then, those films were dried under vacuum at 50 °C for 12 h.

2.6.3. Ozonolysis in hexane

Ozone mixture gas was bubbled into 100 mL of hexane in a 100 mL beaker for 30 min at ambient temperature. The composite films were put into the beaker and the gas was bubbled for 2 h. The composite films were put out, soaked into 50 mL of hexane in another beaker with sonication for 10 min, and were dried under vacuum at 50 °C for 12 h.

Fig. 4. FE-SEM images of PAA7/PI-b-P2VP3 (a-c) before ozonolysis, (d-f) after ozonolysis by ozone gas (g-i), after ozonolysis in water, and (j-l) after ozonolysis in hexane. (a,d,g,j) View of the top of the surface, (b,e,h,k) view of the edge of the cross-sectional area and surface, and (c,f,i,l) view of the center of the cross-sectional area.
beaker and the gas was bubbled for 2 h. The composite films were put out and soaked into 50 mL of water in another 100 mL beaker with sonication for 10 min and were dried under vacuum at 50 °C for 12 h.

2.7. Preparation of porous polyimide films
Porous polyimide composite films were fabricated by following sequential processes from the PAA composite films, thermal annealing for crosslinking of resol at 100 °C for 24 h under vacuum pressure, ozonolysis for decomposition of PI domain in hexane at an ambient temperature for 2 h, and thermal imidization of PAA at 200 °C for 1 h at a heating rate of 1 °C min⁻¹ as illustrated in the bottom of Fig. 1. The resulting porous polyimide films were characterized by SAXS, FT-IR, and FE-SEM (Figs. 5 and 6).

3. Results and discussion
3.1. Self-assembly of composite films
To determine the viability of PI-b-P2VP as a template to form well-ordered nanostructures was studied by investigating several PAA composite films with different composition ratios. The PAA possesses a polar functional part, the carboxyl and amide groups, were expected to possess a strong interaction with the hydrophilic part of the template block copolymer (P2VP domain), which would result in the formation of well-ordered nanostructure which is segregated from the hydrophobic domain of the block copolymer (PI domain).

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 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 prepared films were characterized by SAXS and TEM. The intensities of the SAXS profile were calculated by azimuthal integration of the scattering pattern, as a function of the scattering vector \( q = 4\sin(\theta/2)/\lambda \), where \( 2\theta \) is the scattering angle and \( \lambda \) is the X-ray wavelength. The TEM samples were stained with OsO₄, which selectively stains PI, to further create better contrast in the images.

The SAXS profile of pristine PI-b-P2VP film (Fig. 3a) showed higher-order scattering peaks with \( q/q^* \) ratio of 1:2:3:4:6:7:8, indicating the formation of lamella structures with domain spacing of 38.6 nm, where \( q^* \) was the position of the first-order scattering peak. The TEM image (Fig. 3b) showed a pattern of white lines and dots in a dark matrix, which likely corresponded to the P2VP cylinder and a PI matrix. This disagreement of the result of SAXS and TEM may be caused that volume fraction of P2VP is 34 vol% which is the border of lamella and cylinder. The average center-to-center distance of the white lines was 35 nm, which agrees with the domain spacing from SAXS measurements.

The SAXS profile of the PAA5/PI-b-P2VP5 composite film (Fig. 3a) showed higher-order scattering peaks having a domain spacing of 33.7 nm, although these scattering peaks could not be assigned to typical known ordered structures. The TEM image (Fig. 3c) showed a pattern of dark dots in a white matrix which corresponds to a disordered PI sphere domain in a P2VP+PAA matrix.

The SAXS profile of the PAA7/PI-b-P2VP3 composite film (Fig. 3a) showed 1:√2: √3:2: √5: √6: √12: √22 in the peaks, indicating a highly ordered body-centered cubic (BCC) structure with a domain spacing of 28.2 nm. The TEM images (Figs. 3d and 3e) showed a pattern of dark dots in a white matrix that corresponds to a BCC PI sphere in a P2VP+PAA matrix. The average center-to-center distance of the dark dots was 27 nm, which agrees with the domain spacing from SAXS measurements.

The SAXS profile of the PAA7/PI-b-P2VP3/R1 composite film (Fig. 3a) was similar to that of which it obtained for the PAA7/PI-b-P2VP3. The TEM image could not be obtained because the composite film with resol was not crosslinked, and was therefore too soft.

The changing of morphology from the lamella structure of the pristine PI-b-P2VP film to PI sphere structure of the PAA/PI-b-P2VP composite film indicates a volume fraction of hydrophilic domain increased because the PAA was miscible into P2VP segment selectively. The composite film PAA7/PI-b-P2VP3 formed a well-ordered nanostructure than the composite film PAA5/PI-b-P2VP5. The result reflects the volume fraction of the hydrophilic domain increased by an increase in the PAA, and the fraction improved to be better for BCC structure. Also, the addition of 10 wt% of resol did not affect the morphology by comparison from the composite film PAA7/PI-b-P2VP3, which indicates resol would be miscible into the P2VP domain with PAA.

3.2. Ozonolysis condition
The condition of ozonolysis was optimized by investigating the composite films PAA7/PI-b-P2VP3 after each three different ozonolysis methods, in the air, in water, and in hexane. The
porous structures of the films were evaluated by FE-SEM observation (Fig. 4). Three different surfaces were observed for each of the films as a top view of the surface, a cross-sectional view around the surface, and a cross-sectional view of the center.

The FE-SEM images of the composite film before ozonolysis (Figs. 4a, 4b, and 4c) showed no porous structure in each image. The FE-SEM images after ozonolysis in the air also showed no porous structure in each image, which indicates that the degradation of the PI domain did not proceed even on the surface of the film.

The FE-SEM images of the composite film after ozonolysis in water were shown in Figs. 4g, 4h, and 4i. The image of the surface (Fig. 4g) revealed an area without pore and an area with uneven pores about 50 nm to 150 nm. The images of cross-section (Figs. 4h and 4i) showed approximately 20 nm of pores which would derive from the microphase-separated structure; however, the structure order collapsed. The result indicates that the degradation of PI proceeded, while the structure order became disorder. The latter could be attributed to the swelling of the film by water because PAA and P2VP are hydrophilic though they are insoluble in water.

The FE-SEM images of the composite film after ozonolysis in hexane (Figs. 4j, 4k, and 4l) showed approximately 20 nm of pores which would derive from the microphase-separated structure; however, the structure order collapsed. The result indicates that the degradation of PI proceeded, while the structure order became disorder. The latter could be attributed to the swelling of the film by water because PAA and P2VP are hydrophilic though they are insoluble in water.

The FE-SEM images of the composite film after ozonolysis in hexane were shown in Figs. 4g, 4h, and 4i. The image of the surface (Fig. 4g) revealed an area without pore and an area with uneven pores about 50 nm to 150 nm. The images of cross-section (Figs. 4h and 4i) showed approximately 20 nm of pores which would derive from the microphase-separated structure; however, the structure order collapsed. The result indicates that the degradation of PI proceeded, while the structure order became disorder. The latter could be attributed to the swelling of the film by water because PAA and P2VP are hydrophilic though they are insoluble in water.

The results of the three types of ozonolysis conditions revealed that the ozonolysis in hexane was an effective method. It was used for the following preparation of porous polyimide films.

3.3. Fabrication and Characterization of porous polyimide film

Porous polyimide composite films were fabricated by following sequential processes of the PAA composite films, thermal annealing for crosslinking of resol, ozonolysis for decomposition of PI domain, and thermal imidization of the PAA as illustrated in the bottom of Fig. 1. The microphase-separated structure of the composite films must be retained during the serial processes to obtain well-ordered mesoporous polyimide films. The nanostructure of the two composite films, PAA7/PI-b-P2VP3 and PAA6/PI-b-P2VP3/R1, after each process were characterized by SAXS, FT-IR, and FE-SEM (Figs. 5 and 6).

The second profile from the top in Fig. 5a is the SAXS profile of PAA7/PI-b-P2VP3 after thermal annealing and shows the weak higher-order peaks, indicating that the nanostructure order became disorder. The third profile from the top in Fig. 5a is the SAXS profile after ozonolysis and shows an almost similar profile to that after annealing. The FE-SEM image after ozonolysis (Fig. 5b) showed a disordered porous structure of approximately 20 nm pore diameter. The results indicate that the ozonolysis process did not disorder the nanostructure during the degradation of the PI domain. Namely, the ozonolysis process is one of the most suitable methods to obtain well-ordered porous structures. The fourth profile from the top in Fig. 5a is the SAXS profile after imidization and shows only a very weak first peak, which indicates the microphase-separated structures had almost collapsed. The SEM image after imidization (Fig. 5c) showed that the pore size increased to 50–100 nm and the order disintegrated which agrees with the SAXS result. The result reflects a relatively low glass transition temperature of the PAA (183 °C) [36]. Optimization of the primal structure of PAA would prevent the collapse of the nanostructure. On the FT-IR spectra (Fig. 5d), the peaks at 1780 cm⁻¹ (C=O) and 1370 cm⁻¹ (C-N) corresponding to the peaks of polyimide appeared and the peaks at 1662 cm⁻¹ (C=O) and 1546 cm⁻¹ (C-N) corresponding to the peaks of PAA disappeared, which indicate that imidization of the PAA composite film proceeded. In this study, the thermal treatment was carried out at 200 °C in terms of stability of the nanostructure. Further thermal treatment of the porous polyimide films at high temperatures may be required to complete imidization of the films.

The second and third profiles from the top in Fig. 6a are the SAXS profiles of PAA6/PI-b-P2VP3/R1 after annealing and after ozonolysis shows higher-order peaks which indicate the microphase-separated structure remained during the processes. The FE-SEM image after ozonolysis (Fig. 6b) showed an ordered porous structure derived from the microphase-separated structure. The average pore size was 18 nm. The fourth profile from the top in Fig. 6a is the SAXS profile after imidization and shows slightly weak higher-order peaks, which suggest the nanostructure based on the microphase-separated structure has remained, but the nanostructure order became slightly disordered. The FE-SEM image after imidization (Fig. 6c) revealed a mesoporous structure with a well-defined pore.
size although the center of gravity of the pores was slightly disordered. The average pore size was 24 nm measured from the FE-SEM image. The FT-IR spectra (Fig. 6d) showed similar results to one of the PAA7/PIₐ-P2VP3, which indicate the imidization taken place. Thus, it was concluded that mesoporous polyimide films had been successfully obtained via the soft template method using PIₐ-P2VP as the template block copolymer followed by ozonolysis under a relatively lower temperature (200 °C) than the temperature reported earlier (380 °C) [36]. Porosification at relatively low temperatures using ozonolysis would reduce the collapse of nanostructures due to heating and would contribute to the development of highly ordered PAA mesoporous films.

4. Conclusion

Mesoporous polyimide composite films were successfully obtained by the soft-template method followed by ozonolysis. PIₐ-P2VP worked well as a templating block copolymer to form ordered microphase-separated structures co-assembled with PAA. As a result of an optimization of ozonolysis conditions, PI domain was selectively decomposed.
by ozonolysis in hexane at an ambient temperature, which results in successful porosification of the PAA composite films without a collapse of the nanostructure. Mesoporous polyimide composite films with well-defined pores based on the microphase-separated structure were successfully obtained by thermal treatment of the PAA composite film PAA6/PI-b-P2VP3/R1 including resol. An addition of 10 wt% of resol played a role as an immobilizer of the nanostructure of the composite film during thermal treatment. The pore size was 24 nm determined by FE-SEM and the domain spacing was 28.8 nm determined by SAXS. In the case of the composite film without resol, PAA7/PI-b-P2VP3, the porous polyimide composite film was obtained with around 100 nm pores by ozonolysis. However, the nanostructure had collapsed during thermal imidization. This problem might be avoided by further optimization of the primary structure of PAA. The soft-template method described in this study allows control of the composite film morphology, pore size, and porosity by optimizing the composition ratio of the template block copolymer and the mixing ration of the components. As a result, polyimides can be developed for functional applications such as absorbents, catalysts, low-dielectric materials, and separator membranes of lithium-ion batteries by this method.

Acknowledgments
We are grateful to Ryohei Kikuchi (Ookayama Materials Analysis Division, Tokyo Institute of Technology) and Prof. Yuji Wada (School of Materials and Chemical Technology, Tokyo Institute of Technology) for the TEM and FE-SEM observations.

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. S. V. Kononova, G. N. Gubanova, K. A. Romashkova, E. N. Korytkova, and D. Timpu, "Scanning Probe Microsc. Prop. Charact. Nanoscale", InTech, (2012) p. 13.
3. A. Irina, I. Stoica, and C. Hulubei, "High Perform. Polym. - Polyimides Based - From Chem. to Appl.", InTech, (2012) p. 13.
4. T. Sawai, K. Wakabayashi, S. Yamazaki, T. Uchida, Y. Sakaguchi, R. Yamane, and K. Kimura, Eur. Polym. J., 49 (2013) 2334.
5. R. Takemori, G. Ito, M. Tanaka, and H. Kawakami, RSC Adv., 4 (2014) 20005.
6. Y. Nabae, S. Nagata, T. Hayakawa, H. Niwa, Y. Harada, M. Oshima, A. Isoda, A. Matsunaga, K. Tanaka, and T. Aoki, Sci. Rep., 6 (2016) 23276.
7. J. L. Hedrick, R. D. Miller, C. J. Hawker, K. R. Carter, W. Volksen, D. Y. Yoon, and M. Trollsás, Adv. Mater., 10 (1998) 1049.
8. H. Yabu, M. Tanaka, K. Jiirou, and M. Shimomura, Langmuir, 19 (2003) 6297.
9. S. Shishatskiy, C. Nistor, M. Popa, S. P. Nunes, and K. V. Peinemann, Adv. Eng. Mater., 8 (2006) 390.
10. G. Li and Z. Wang, Macromolecules, 46 (2013) 3058.
11. E. Aram and S. Mehdipour-Ataei, Int. J. Polym. Mater. Polym. Biomater., 65 (2016) 358.
12. X. M. Tan and D. Rodrigue, Polymers, 11 (2019) 1160.
13. D. Wu, F. Xu, B. Sun, R. Fu, H. He, and K. Matyjaszewski, Chem. Rev., 112 (2012) 3959.
14. C. Liang, K. Hong, G. A. Guiochon, J. W. Mays, and S. Dai, Angew. Chem. Int. Ed., 43 (2004) 5785.
15. S. Tanaka, N. Nishiyama, Y. Egashira, and K. Ueyama, Chem. Commun., 2005 (2005) 2125.
16. F. Zhang, Y. Meng, D. Gu, Y. Yan, Z. Chen, B. Tu, and D. Zhao, Chem. Mater., 18 (2006) 5279.
17. T. Smart, H. Lomas, M. Massignani, M. V. Flores-Merino, L. R. Perez, and G. Battaglia, Nano Today, 3 (2008) 38.
18. I. W. Hamley, Prog. Polym. Sci., 34 (2009) 1161.
19. J. K. Kim, S. Y. Yang, Y. Lee, and Y. Kim, Prog. Polym. Sci., 35 (2010) 1325.
20. X. Hu, Q. An, G. Li, S. Tao, and J. Liu, Angew. Chem. Int. Ed., 45 (2006) 8145.
21. H. Yang and P. Jiang, Langmuir, 26 (2010) 13173.
22. H. Munakata, D. Yamamoto, and K. Kanamura, Chem. Commun., 2005 (2005) 3986.
23. J. Lin and X. Wang, Polymer, 48 (2007) 318.
24. H. Munakata, D. Yamamoto, and K. Kanamura, J. Power Sources, 178 (2008) 596.
25. C. Wang, Q. Wang, and T. Wang, Langmuir, 26 (2010) 18357.
26. Q. Wang, C. Wang, and T. Wang, J. Colloid Interface Sci., 389 (2013) 99.
27. Y. Zhang and L. Ionov, ACS Appl. Mater. Interfaces, 6 (2014) 10072.
28. C. Wang, T. Wang, and Q. Wang, J. Macromol. Sci. Part A, 54 (2017) 311.
29. C. Wang, T. Wang, and Q. Wang, Polymer, 51 (2010) 4836.
30. C. Wang, T. M. Wang, and Q. H. Wang, Express Polym. Lett., 7 (2013) 667.
31. Y. Liu, K. Ohnishi, S. Sugimoto, K. Okuhara, R. Maeda, Y. Nabae, M. Kakimoto, X. Wang, and T. Hayakawa, *Polym. Chem.*, 5 (2014) 6452.
32. L. Gao, K. Azuma, Y. Kushima, K. Okuhara, A. Chandra, and T. Hayakawa, *J. Photopolym. Sci. Technol.*, 29 (2016) 247.
33. Y. Nabae, S. Nagata, K. Ohnishi, Y. Liu, L. Sheng, X. Wang, and T. Hayakawa, *J. Polym. Sci. Part A: Polym. Chem.*, 55 (2017) 464.
34. T. Komamura and T. Hayakawa, *J. Photopolym. Sci. Technol.*, 30 (2017) 173.
35. L. Gao, A. Chandra, Y. Nabae, and T. Hayakawa, *Polym. J.*, 50 (2018) 389.
36. T. Komamura, K. Okuhara, S. Horiuchi, Y. Nabae, and T. Hayakawa, *ACS Appl. Polym. Mater.*, 1 (2019) 1209.
37. P. S. Bailey, *Chem. Rev.*, 58 (1958) 925.
38. J. S. Lee, A. Hirao, and S. Nakahama, *Macromolecules*, 21 (1988) 274.
39. J. S. Lee, A. Hirao, and S. Nakahama, *Macromolecules*, 22 (1989) 2602.
40. A. Avgeropoulos, V. Z. H. Chan, V. Y. Lee, D. Ngo, R. D. Miller, N. Hadjichristidis, and E. L. Thomas, *Chem. Mater.*, 10 (1998) 2109.
41. C. Harrison, *J. Vac. Sci. Technol. B*, 16 (1998) 544.
42. S. Y. Lu, C. H. Chang, C. H. Yu, H. L. Chen, and Y. H. Lo, *J. Mater. Res.*, 20 (2005) 1523.
43. S. Collins, I. W. Hamley, and T. Mykhaylyk, *Polymer*, 44 (2003) 2403.
44. L. Ren, J. Zhang, C. G. Hardy, S. Ma, and C. Tang, *Macromol. Rapid Commun.*, 33 (2012) 510.
45. K. Azuma, T. Komamura, A. Chandra, F. Kato, Y. Nabae, and T. Hayakawa, *J. Polym. Sci. Part A: Polym. Chem.*, 57 (2019) 1105.
46. Y. Meng, D. Gu, F. Zhang, Y. Shi, L. Cheng, D. Feng, Z. Wu, Z. Chen, Y. Wan, A. Stein, and D. Zhao, *Chem. Mater.*, 18 (2006) 4447.