Fabrication of Three-Dimensionally Ordered Microporous Membrane by Wet Phase Separation

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ABSTRACT: We report a novel porous fluorinated polyimide membrane with a cylinder structure fabricated by a wet phase inversion process, which is formed by a ternary system, polyimide/solvent/water. The porous polyimide membranes consisted of a thin top porous layer and three-dimensionally ordered cylinder micropores. The porous membrane-forming solvents were *N*-methylpyrrolidone containing nonsolvent additives such as alcohol, and the height and width of the cylinder structure were controlled by the solvents. Water fluxes through the porous polyimide membranes were measured using a stirred dead-end filtration cell, and the fluxes of the porous membrane with the cylinder-type structure were approximately three times greater than those of the membrane with the finger-type structure. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3016–3021, 2004

Key words: porous polyimide membrane; wet phase separation; cylinder micropores; alcohol; water flux

INTRODUCTION

Three-dimensionally ordered micro- or nanoporous membranes are of interest in certain areas because of their wide applications in size- and shape-selective separation, catalysis, optical information processing, and microwave shielding.[1,2] The most current general methods for preparing these porous membranes use template replication by the sol-gel techniques, which have been developed for the purpose of fabricating high-quality inorganic porous membranes.[3,4] However, the challenge remains to fabricate organic microporous membranes that consist of a three-dimensionally ordered structure.

Here, we report a simple and robust method that uses phase separation to form three-dimensionally ordered novel porous fluorinated polymer membranes. We fabricated the polyimide membranes that consisted of a thin top porous layer and cylinder micropores by a wet phase separation process. The structures of the porous membranes were determined from liquid–liquid demixing and polymer–liquid demixing in a polymer/solvent/coagulation system. We controlled the height and width of the cylinder structure using a solvent containing nonsolvent additives such as alcohols. We consider the porous polymer membrane to have some advantages. First, the porous membranes with the cylinder structure may be promising as nanofiltration and microfiltration membranes. The porous membrane consists of a thin porous top layer and ordered high-quality pores, thus indicating the high mass transport properties due to the thin porous layer. Second, if only the thin porous top layer could easily be removed from the porous membrane, the complete straight cylinder pores would be used as unique polymer materials for applications as photonic bandgap materials and catalytic supports. In addition, although it is very difficult to fabricate a large surface area in three-dimensionally ordered inorganic porous membranes, the porous polymer membranes obtained by the phase separation can easily have large surface areas.

In this paper, we report a novel porous fluorinated polyimid membrane with the cylinder structure fabricated by a wet phase inversion process (immersion precipitation), which is formed by the polyimide/solvent/water ternary system. The porous membrane-forming solvents were *N*-methylpyrrolidone (NMP) containing nonsolvent additives such as an alcohol, and the cylinder structure was controlled only by the solvents. The membrane structure was estimated using a scanning electron microscope (SEM). Water fluxes through the porous polyimide membranes were measured using a stirred dead-end filtration cell.

EXPERIMENTAL

Materials

2,2′-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was purchased from the Clariant

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Co. (Japan) and purified by sublimation prior to use. 2,2′-Bis(4-aminophenoxy)hexafluoropropane (6FAP) was purchased from the Central Glass Co. (Japan) and recrystallized twice in ethanol solution prior to use. The dextrans were purchased from Sigma (Japan) and Nacalai Tesque, Inc. (Japan).
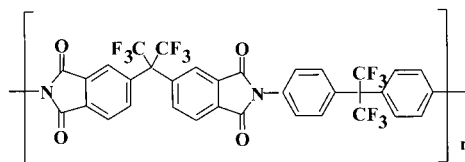
Scheme 1. Structure of 6FDA–6FAP.

Preparation of porous polyimide membrane

6FDA–6FAP polyimide was synthesized by a chemical imidization as reported in the literature.[5,6] The molecular weight (M_w and Mn) of 6FDA–6FAP was determined by gel-permeation chromatography (detector: Jasco 830-RI monitor) with tetrahydrofuran as the solvent. A flow rate of 1.0 mL/min was used, and the polyimide was dissolved in tetrahydrofuran at a concentration of 0.005 wt %. The porous 6FDA–6FAP membranes were fabricated by a wet phase inversion technique. The casting solutions used for the preparation of the membranes were NMP and alcohol. The polymer solution was cast on glass plates with a knife gap of 300 μm. Immediately after casting, the membranes were coagulated in water as a nonsolvent, washed for 15 h, air-dried for 12 h, and finally dried in a vacuum oven at 150°C for 15 h to remove all of the solvents.

Structure of porous membrane

The surface and cross-section of the porous polyimide membranes was observed using a SEM (JXP-6100P, JEOL). The membranes were cryogenically fractured in liquid nitrogen and then coated with Pt/Pd.

Permeability measurements

The stirred dead-end cell filtration system was designed to characterize the filtration performance of the porous membrane.[7] The system consisted of a 50 mL filtration cell (W. R. Grace, Amicon model 8050) connected to a 1-L reservoir that was nitrogen-pressurized from 0.02 to 0.06 MPa. All permeation experiments were conducted at a system temperature of 37°C. The porous membranes were mounted on a permeation cell with a 13.4 cm² surface area.

Prior to the dextran retention experiment, the membrane was thoroughly rinsed with water. The water flux was measured at 0.02 to 0.06 MPa. A standard curve of the dextran solution was obtained using the pure dextran fractions of 10,000 to 800,000. The molar masses of the dextran molecules were determined by gel-permeation chromatography (detector: Jasco 830-RI monitor). The molecular weight cut-off (MWCO) values are given by eq. (1):

$$R(\%) = \frac{C_f - C_p}{C_f} \times 100 \qquad (1)$$

where R is the apparent 90% rejection, C_f is the feed concentration, and C_p is the permeation concentration. The permeation experiments were conducted at a stirring rate of 1,000 rpm.

The diameter ($2r$) of the porous membrane was calculated from the MWCO value of the dextran reported using eq. (2)[8]:

$$r = 0.33 \, (M)^{0.46} \qquad (2)$$

The presence of a defect in the membrane was confirmed from the water permeation and dextran permeation experiments.
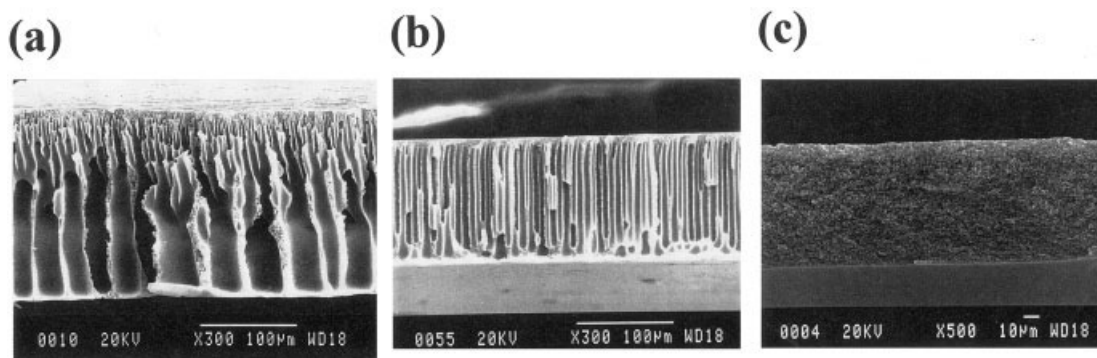

Figure 1 Scanning electron micrographs of the cross-section of porous 6FDA–6FAP membranes prepared from NMP containing butanol. (a) 0% butanol, (b) 25.5% butanol, (c) 42.5% butanol.
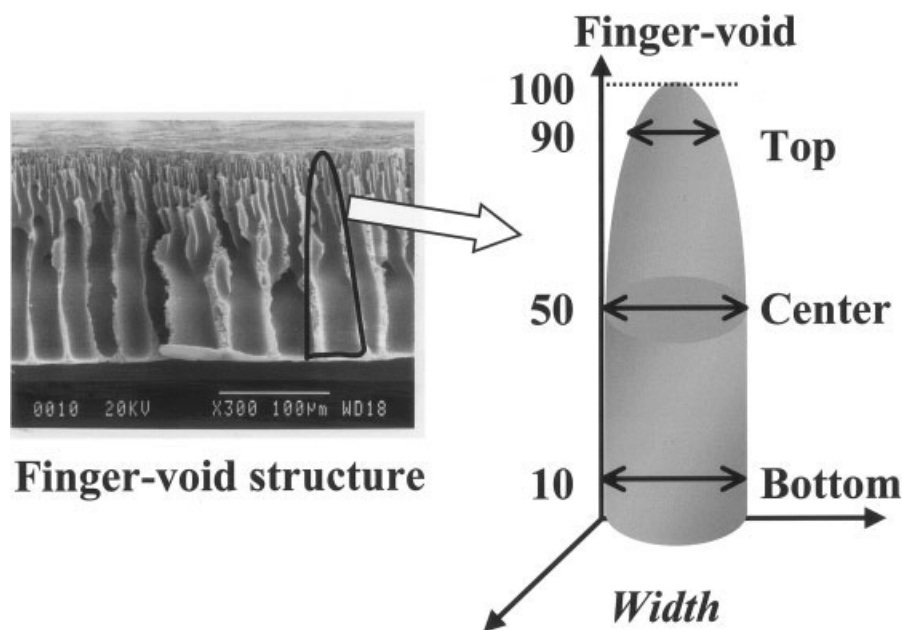
Figure 2 Schematic diagram of width values of finger-void pores calculated from SEM pictures of porous 6FDA–6FAP membranes.

RESULTS AND DISCUSSION

Structure of porous 6FDA–6FAP membranes

The 6FDA–6FAP polyimide had a M_w of 1.5×10^5 with a polydispersity index of 2.0 and the T_g was 332°C. The content of the residual amide groups of poly(amic acid) was followed by monitoring the IR and ^{1}H-NMR spectra. The conversion to the imide determined by the spectroscopies was greater than 99%.

The phase inversion process involves the phase separation of a polymer solution in the polymer-rich and -lean phases, which can be achieved by an immersion–precipitation technique. Both the thermodynamic and kinetic factors among polyimide, solvent, and coagulant have a significant influence on the forming process of the polymer membrane when the membranes are prepared using the phase separation method.[9,10] In particular, the mass transfer, which is expressed by the exchange rate of the solvent/nonsolvent at the interface between the polymer solution and the coagulation bath, determines the membrane structure. The membranes prepared from the wet phase separation generally consisted of a porous top layer and a spongy-type or finger-type structure. In this study, we focused on a porous polymer membrane with a finger-type structure formed in the wet phase separation to fabricate a novel three-dimensionally ordered porous membrane, because we considered that the ordered micropores could be fabricated from the finger structure by controlling the exchange rate of the solvent/coagulate. We reported that the structure of the

6FDA–6FAP membrane prepared from THF or acetone as a solvent clearly consisted of a porous substructure characterized by the presence of a spongy-type structure.[7] In contrast, the membrane prepared from NMP, DMF, or DMSO exhibited a finger-type structure, and, in particular, NMP showed a good solubility for 6FDA–6FAP. Therefore, we selected NMP as the solvent, and, in addition, we added alcohol such as butanol to the NMP solvent to actively control the phase separation.

Figure 1 shows the scanning electron micrographs of the cross-sectional structure of the porous 6FDA–6FAP membranes fabricated from the wet phase inversion process. The membrane structures signifi-
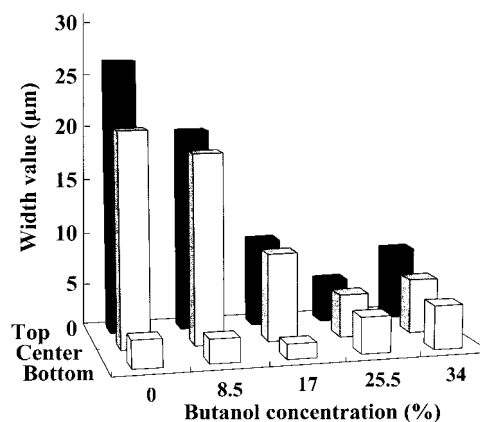

Figure 3 Effect of the butanol concentration on width value of finger-void pore in porous 6FDA–6FAP membranes.

TABLE I
Difference (Δ) Between Bottom and Top Width of Finger-Void of Porous 6FDA–6FAP Membranes Prepared from NMP Containing Butanol

Butanol (wt %)	0	8.5	17	25.5	34
Δ (μm)		25.3	18.3	7.5	0.6	2.9

Δ = Bottom − Top.

cantly depended on the butanol concentration as a nonsolvent additive. The structure of the membrane prepared from NMP without butanol consisted of a porous top layer and a finger-type structure. In contrast, the membrane prepared from NMP containing 42.5 wt % butanol exhibited a sponge-type structure. These results can be explained as follows. In the wet phase inversion process, instantaneous demixing occurs between the solvent and water so that the membrane consists of the porous top layer and a finger-type structure, while delayed demixing occurs so that the membrane consisted of a porous top layer and a spongy-type structure. However, the structure of the membrane prepared from NMP containing 25.5 wt % butanol dramatically changed compared with other membranes and consisted of a porous top layer and a

cylinder-type structure. Although we could not fabricate the porous polyimide membranes with complete straight ordered micropores from the top surface to the bottom, we succeeded in preparing a novel polyimide membrane consisting of a porous top layer and a three-dimensionally ordered structure formed from the cylinder micropores using a wet phase inversion technique.

To quantitatively estimate the width of the cylinder structure, we measured the top, center, and bottom widths of 10 finger-voids as defined by Figure 2 and calculated the average width values. Figure 3 shows the average width values of the finger-void pores calculated from the SEM pictures of the porous 6FDA–6FAP membranes. Table I shows the difference (Δ) between the bottom and top width values of the finger-void pores in the porous 6FDA–6FAP membrane. The Δ values decreased with an increase in butanol concentration, and the Δ at 25.5 wt % butanol indicated a minimum value less than 1 μm. It should be noted that the ordered high-quality single micropores could be fabricated by a simple method such as phase separation. In addition, it was clear that butanol in the NMP solvent had a significant influence on the polyimide structure. To elucidate the alcohol effects on the
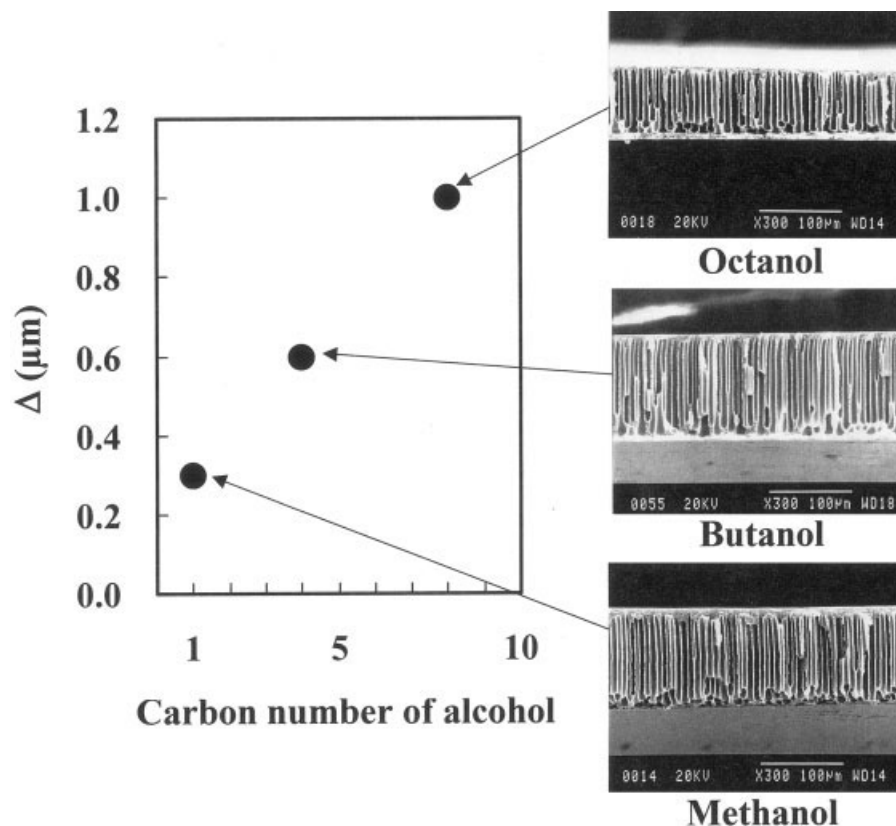

Figure 4 Difference (Δ) between bottom and top width values of finger-void pore in porous 6FDA–6FAP membranes prepared from methanol (29%), butanol (25.5%), and octanol (9%).

polyimide structures, we investigated the cross-sectional structure of the porous 6FDA–6FAP membranes prepared from the different alcohols.

Figure 4 shows the scanning electron micrographs of the cross-sectional structure of the porous 6FDA–6FAP membranes prepared from methanol, butanol, and octanol. The Δ values decreased in the following order: octanol (1.0 μm) > butanol (0.69 μm) > methanol (0.34 μm), and the porous 6FDA–6FAP membranes prepared from the NMP solvent containing methanol indicated the highest-quality single micropores. In addition, we confirmed that the width and height of the cylinder pore could be controlled from about 4 to 10 μm and from about 90 to 200 μm, respectively, using various solvents and alcohols.

It is well known that, during the phase separation, both the thermodynamic and kinetic factors have significant influences on the membrane forming process. In a wet phase inversion process, the thermodynamic properties of the polymer solution provide some information on the overall porosity of the final membrane but none on the pore size and its distribution. In contrast, the pore size and its distribution are mainly controlled by kinetic effects. That is, the mass transfer, which is expressed by the exchange rate of the solvent/coagulation at the interface between the polymer solution and the coagulation bath, determines the membrane structure. In this study, alcohol transport during liquid–liquid demixing clearly plays an important role in determining the membrane structure and, in further research, we will elucidate the formation mechanism of the cylinder structure in the porous 6FDA–6FAP membrane.

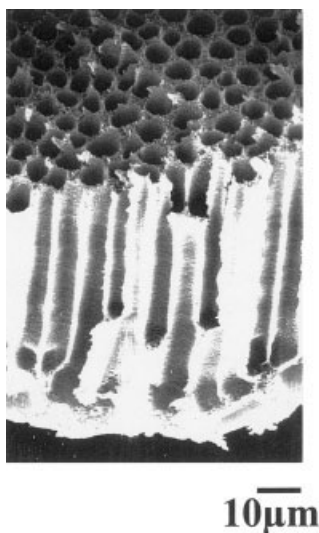In addition, we succeeded in removing only a thin porous top layer from the surface of a porous 6FDA–

Figure 5 Scanning electron micrograph of the cross-section of porous 6FDA–6FAP membrane without top porous layer.

TABLE II
Water Flux of Porous 6FDA–6FAP Membranes

Structure	Apparent diameter (nm)	Water flux 10^{-10} [$m^3/(m^2 \cdot s \cdot Pa)$]
Finger	4.1	46
Cylinder	4.1	99

6FAP membrane with a cylinder structure under liquid nitrogen. Figure 5 shows the 6FDA–6FAP membrane without the top layer. Unfortunately, we could remove only a small part of the top layer from the membrane. However, if only the thin porous top layer could easily be removed from the membrane, the straight cylinder micropores that go through from the top of the membrane to the bottom would be fabricated and be used as unique polymer materials for applications as photonic bandgap materials and catalytic supports. These experiments are currently being carried out.

Flux of water through porous 6FDA–6FAP membranes

The pure water fluxes through the porous polyimide membranes with the pore diameters of 4.1 nm were measured with a stirred dead-end filtration cell. The apparent diameter was determined from the dextran rejection curves for the porous membranes.[8] Table II shows the water fluxes of the porous 6FDA–6FAP membranes. The fluxes of the porous membrane with the cylinder-type structure were approximately three times greater than those of the membrane with the finger-type structure, indicating that the pore size and porosity of the top surface on the membrane with the cylinder-type structure were optimized compared with those of the membrane with the finger-type structure.

CONCLUSION

We fabricated a novel porous fluorinated polyimide membrane with a cylinder structure using a wet phase inversion process. The porous membranes consisted of a thin top porous layer and three-dimensionally ordered cylinder micropores. Unfortunately, we could not fabricate the porous polyimide membrane with the complete straight cylinder micropores that go through from the top of the membrane to the bottom. However, the height and width of the cylinder structure were easily controlled by the NMP solvent containing nonsolvent additives such as alcohols.

This process of forming an ordered porous membrane with the cylinder-type structure is possible for many polymeric systems. We have already confirmed

the formation of the cylinder structure using polysulfone. Additionally, we are starting the fabrication of a three-dimensionally ordered nanoporous membrane having a cylinder structure with dimensions that can be controlled to a nanoorder.

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