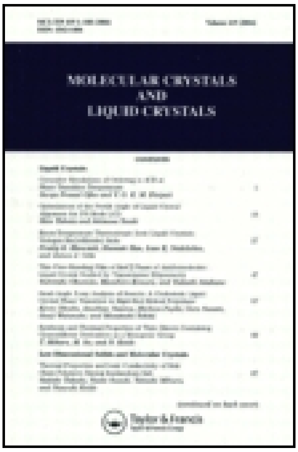

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Gas Permeability of Patterned Polydimethylsiloxane-Grafted Polyimide Membranes Fabricated by Nanocasting Method

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Gas Permeability of Patterned Polydimethylsiloxane-Grafted Polyimide Membranes Fabricated by Nanocasting Method

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We showed a new approach to fabricate separation membranes with enlarged surface areas by nanocasting and investigated the effects of the enlarged surface area on the gas permeability of polydimethylsiloxane (PDMS)-grafted polyimide membranes. A PDMS-grafted polyimide dissolving in solvent was cast onto a patterned nickel (Ni) substrate. The thermal crosslinking reactions occurring among intermolecular PDMS segments allowed the fabrication of insoluble patterned PDMS-grafted polyimide membranes by demolding. The patterned membranes showed higher gas permeability coefficients than the corresponding flat membranes and showed an increasing permeation selectivity for carbon dioxide.

Keywords Gas permeation coefficient; grafted aromatic polyimide; nanocasting; polydimethylsiloxane; separation membrane

Introduction

Crosslinked PDMS membranes, referred to as "silicone membranes," allow the alcohol separation from aqueous solutions by pervaporation [1]. The practical use as separation membranes is restricted owing to their insufficient mechanical strengths and durability to organic compounds. We previously synthesized PDMS-grafted aromatic polyimides by polycondensation of PDMS-containing diamino-terminus macromonomers with 4,4′-hexafluoroisopropylidene diphthalic anhydride [2] to improve the membrane properties. In particular, the flat membrane of a PDMS-grafted polyimide **PI12**, shown in Fig. 1, exhibited high permeation selectivity and mechanical strength and moderate durability, compared with that of a typical silicon membrane. In contrast, the permeability was significantly deteriorated. Nanocasting is one of molding techniques for fabricating patterned polymer surfaces [3]. Here, we fabricated patterned **PI12** membranes by nanocasting and investigated the effects of the increased surface area on the gas permeability.

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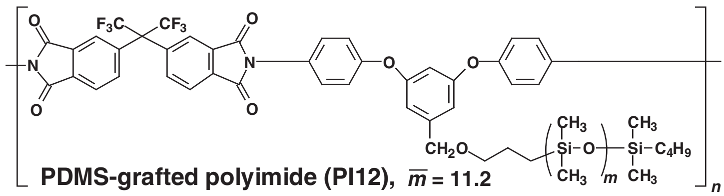

Figure 1. Chemical structure of a PDMS-grafted polyimide (**PI12**).

Experimental

Material

PI12 having an average length of 11.2 dimethylsiloxane units and a weight-average molecular weight M_w of 90,000 g mol^{-1} was prepared according to the previous paper [2]. A patterned Ni substrate (30 × 30 × 0.3 mm) having 85 nm-width convex lines at a pitch of 185 nm and a depth of 130 nm was used for nanocasting. The Ni patterned surface was modified with an antisticking agent Daikin OPTOOL DSX, left to stand at 60°C for 1 h, and rinsed thoroughly with a solvent Daikin OPTOOL HD-ZV, to form a fluorinated release layer. Figure 2 shows the successive steps in fabricating in an insoluble **PI12** patterned membrane. The patterned membrane was prepared by nanocasting from a **PI12** chloroform solution onto the Ni patterned surface, followed by drying at 40°C for 2 h in an oven and then at 80°C for 3 h in a vacuum oven to remove solvent. The **PI12** film was pressed with a silicon substrate modified with OPTOOL DSX under a pressure of 3.3 MPa and annealed at 200°C for 1 h above 150°C at which thermal crosslinking occurs [2]. The **PI12** patterned membrane with a thickness of approximately 85 μm was demolded. The gas permeability coefficients of the patterned membrane were measured for pure gases according to the method described previously [4] and compared with those of the **PI12** flat membrane and a silicon membrane.

Results and Discussion

Figures 3(a) and 3(b) show the atomic force microscope image and height profile of the Ni patterned substrate. As shown in Figs. 3(c) and 3(d) indicating the AFM image and height

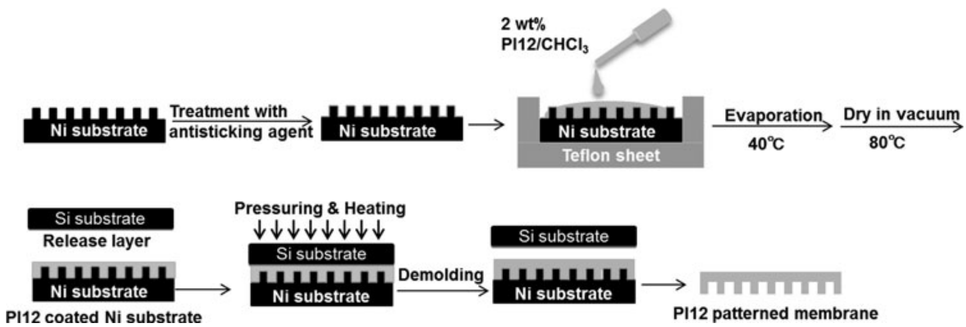

Figure 2. Schematic illustration of the method for preparing an insoluble **PI12** patterned membrane by nanocasting and thermal crosslinking.

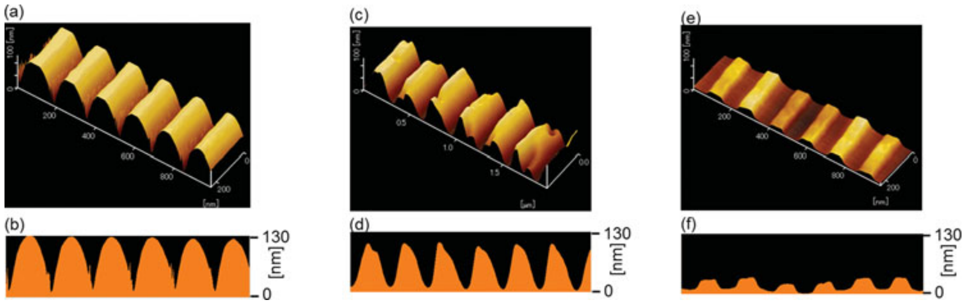

Figure 3. AFM images (a, c, e) and height profiles (b, d, f) of the Ni patterned substrate (a, b) and the **PI12** patterned membrane (c–f).

profile of the **PI12** patterned membrane, the reversed line-and-space patterns with a pitch of 185 nm were observed. The average height was 110 nm, which was slightly smaller than that of the Ni patterned substrate. However, there were several places where the height of the **PI12** patterned membrane significantly decreased to approximately 40 nm as shown in Figs. 3(e) and 3(f).

It was thought that the decreasing heights were attributable to pull-out defects occurring in the demolding step. The fluorinated release layer was insufficient for successful demolding.As summarized in Table 1, the **PI12** flat membrane showed gas permeability coefficients of 101 Barrer for N_2, 226 Barrer for O_2, 275 Barrer for H_2, 1206 Barrer for CO_2, and 886 Barrer for C_2H_6. The **PI12** patterned membrane showed 109 Barrer for N_2, 247 Barrer for O_2, 302 Barrer for H_2, 1349 Barrer for CO_2, and 961 Barrer for C_2H_6. The increased gas permeability coefficients of the **PI12** patterned membrane were attributed to an increase in the surface area by patterning. From the calculation, the nickel patterned substrate has a surface area approximately 2.14 times larger than the flat surface. The increased gas permeability coefficients for N_2, O_2, H_2, and C_2H_6 were approximately 1.08-fold. The presence of pull-out defects in the **PI12** patterned membrane probably causes insufficient increases in the gas permeability. It is worthy of note that the gas permeability coefficient of the **PI12** patterned membrane for CO_2 was 1.12 times as large as that of the **PI12** flat membrane. This result suggested a possibility of improving selective permeation by surface nanopatterning of separation membranes.

Table 1. Gas permeability of **PI12** and silicone membranes

	Gas permeability coefficient, P (Barrer[a])				
Membrane	N_2	O_2	H_2	CO_2	C_2H_6
Flat **PI12**	101	226	275	1206	886
Patterned **PI12**	109	247	302	1349	961
Silicone[b]	243	509	552	2610	2360

a: 1 Barrer = 1×10^{-10} cm^3 (SRP) cm cm^{-2} sec^{-1} cm Hg^{-1}.
b: Crosslinked PDMS membrane as a reference sample.

Conclusions

The PDMS-grafted polyimide membrane with submicrometer line-and-space patterns was fabricated by nanocasting and thermal crosslinking. The gas permeability coefficients were improved by an increase of the surface area. There is a need to further increase the gas permeability by preparing the patterned surfaces with higher aspect ratios using suitable release layers.

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