Separation of H$_2$ and CO through Poly(sulfone-amide) Membranes III. Changes of Gas Permeability and Membrane Structure in the Process of Solvent Removal

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ABSTRACT: Slightly dried cast films of poly(sulfone-amide) synthesized from isophthaloyl dichloride and the mixed diamine which consisted of bis[4-(4-aminophenoxy)phenyl]sulfone and *m*-phenylenediamine (4:6) were thermally treated and the permeabilities of H$_2$ and CO through them were measured. Though the permeability coefficient for H$_2$ (P_{H_2}) was not affected by thermal treatment, the permeability coefficient for CO (P_{CO}) decreased with increasing temperature of the thermal treatment. As a result, the permeability ratio for H$_2$ relative to CO (P_{H_2}/P_{CO}) increased from 50 to 139, when the temperature of the thermal treatment was elevated from 30°C to 220°C. Changes of the membrane structure by thermal treatment were evaluated from measurements of density, thermomechanical analysis (TMA), thermogravimetric analysis (TG), and dynamic viscoelasticity. A decrease of a residual solvent in the membrane and a rearrangement of the polymer chains made the membrane structure more compact and increased P_{H_2}/P_{CO}.

KEY WORDS   Poly(sulfone-amide) / Membrane / Permeability / Hydrogen / Carbon Monoxide / Diffusion / Permeability Ratio / Thermal Treatment / Solvent / Density /

Stiff chain glassy polymers have been studied for the purpose of separating small molecules, such as hydrogen and helium, from larger molecules, such as carbon monoxide and nitrogen.[1-3]

The authors have studied hydrogen separation membranes made from aromatic polyamide containing sulfone linkages in the main chain [this polymer is called poly(sulfone-amide)]. In previous papers,[4,5] the permeabilities of H$_2$ and CO through the poly(sulfone-amide) membranes (structure 1 and 2) were reported.

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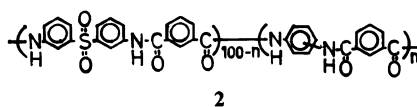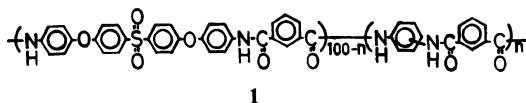
Under definite conditions for preparing membranes, the permselectivity of the poly(sulfone-amide) membranes was affected by the polymer composition. The increase of P_{H_2}/P_{CO} was mainly caused by decrease of the diffusion coefficient for CO (D_{CO}). Therefore, the permselectivity was correlated to the packing character of the polymer chains. The results in the previous papers[4,5] showed that a compact structure was created by a balance between stiffness and crookedness of the polymer chain. The former increased with concentration of the amide linkages in the main

chain, and the latter increased with introduction of *m*-catenation into the main chain.

The poly(sulfone-amide) membranes are prepared by the casting method with their polymer solutions. The packing character of the polymer chains changes not only by the polymer structure, but also by the conditions of membrane preparation. Thermal treatment after the cast induces removal of the cast solvent and rearrangement of the polymer chains, and plays an important role in the determination of membrane character. In this study, this phenomenon was studied in connection with gas permeability. Density was measured to evaluate the packing character of the polymer chains, and some analytical methods were used for evaluating structural changes of the membrane. On the basis of the obtained data, relationships between gas permeability and membrane structure are discussed.

EXPERIMENTAL

Preparation of Polymer

The poly(sulfone-amide) (4SMI-60, structure **3**) was prepared by low-temperature solution condensation as described in the previous paper.[4] The reduced viscosity of the

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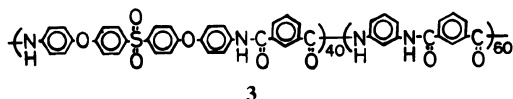
polymer obtained was 0.81 at a concentration of 0.5 g dl^{-1} in *N,N*-dimethylacetamide at 30°C.

Preparation of Membranes

4SMI-60 (4 g) was dissolved in *N*-methyl-2-pyrrolidone (NMP) (20 ml). The solution was filtered and the filtrate was cast on a polypropylene film at room temperature. By evaporating the NMP at 80°C for an hour, the membrane of 10—20 µm thickness was obtained. The thermal treatment was carried out by keeping the membrane at various temperatures

under reduced pressure (*ca.* 0.5 mmHg) for 17 h.

Permeability Measurements

Permeabilities of H_2 and CO were measured with a permeation apparatus made by Rika Seiki Kogyo, and an MKS Baratron pressure transducer was used for detection of pressure increase in the downstream gas reservoir. Gas samples of purity exceeding 99.9% were used. All measurements were carried out at 30°C.

Permeation of a gas through a glassy polymer is usually explained by the dual-mode theory. In this study, however, the permeability coefficient was determined from the steady-state permeation rates at a constant pressure of upstream gas, and only the apparent diffusion coefficient of CO was determined using the time-lag method.[6] The apparent diffusion coefficient (D_{app}) was calculated by the following equation,

$$D_{app} = \frac{l^2}{6L}$$

where L is the time lag and l, the thickness of the membrane.

Analysis of Membrane

The density of the membrane was measured by use of a density gradient tube which consisted of *n*-heptane and carbon tetrachloride at 30°C.

The amount of residual solvent was measured by use of a thermogravimetric analyzer (Shimadzu TG-30). Difference of the sample weight between 160°C and 310°C was measured at a heating rate of 10°C min^{-1} in air. The weight loss in this region has no relation to evaporation of the water adsorbed in the polymer or decomposition of the polymer, and hence is attributable to the evaporation of the NMP.

Thermomechanical analysis (TMA) was carried out on the films with a Shimadzu TMA-30. Change in length of the sample was measured by the elongation mode at a heating rate

of $10°C \, min^{-1}$ in air.

Dynamic viscoelastic property was measured at $110 \, Hz$ and a heating rate of $10°C \, min^{-1}$ in air with a Toyo Baldwin Rheovibron DDV-2E.

RESULTS AND DISCUSSION

Permeability

The 4SMI-60 membrane, dried at 80°C for an hour, was thermally treated for 17 h at various temperatures under reduced pressure. Then, P_{H_2} and P_{CO} were measured at 30°C. Figure 1 shows changes in P_{H_2} and P_{CO} by the thermal treatment. Regardless of the temperature of the thermal treatment, P_{H_2} kept a constant value near $3 \times 10^{-10} \, cm^3 \cdot cm \cdot cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$. On the other hand, P_{CO} decreased with increasing temperature of the thermal treatment from, 6.0×10^{-12} to $2.3 \times 10^{-12} cm^3 \cdot cm \cdot cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$, when the temperature changed from 30°C to 220°C. As the result, P_{H_2}/P_{CO} increased from 50 to 139 as shown in Figure 2.

Figure 3 shows that $D_{app. CO}$ decreased from 7.3×10^{-9} to $5.5 \times 10^{-10} \, cm^2 \cdot s^{-1}$ treatment from at 30°C to at 220°C. The apparent solubility coefficient for CO ($S_{app. CO}$) can be calculated from the following equation

$$P_{CO} = S_{app. CO} \cdot D_{app. CO}$$

As shown in Figure 3, the calculated $S_{app. CO}$ showed a tendency to increase with thermal treatment. No definite comments can be made based on these measurements. However, the results suggest that the decrease in P_{CO} was dominated by decrease in $D_{app. CO}$.

Density

The degree of packing of the polymer chains was evaluated from the densities of the membranes.

In general, the packing character of polymer chains is affected by the crystallinity of a polymer. The X-ray diffraction patterns showed that the poly(sulfone-amide) mem-
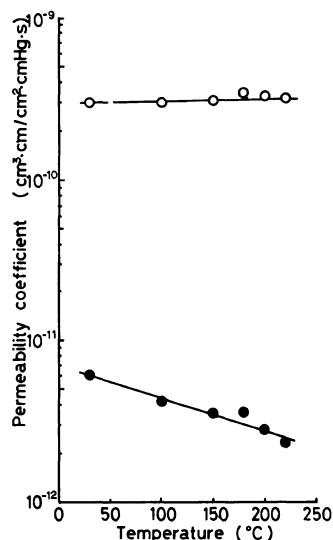

Figure 1. Effects of the thermal treatment on permeability coefficients for H_2 and CO through the 4SMI-60 membrane at 30°C: ○, P_{H_2}; ●, P_{CO}.

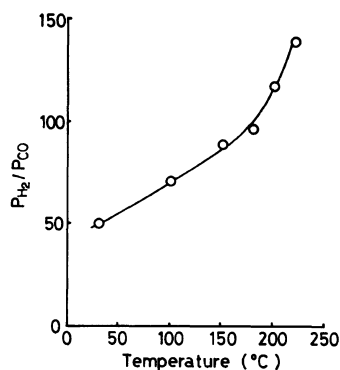**Figure 2.** Effect of thermal treatment on the permeability ratio for H_2 relative to CO of the 4SMI-60 membrane at 30°C.

branes were amorphous regardless of thermal treatment (Figure 4 shows the X-ray diffraction photograph of a membrane treated at 220°C). Therefore, it is not necessary to consider the influence of crystallinity on membrane density.

A trace of the residual NMP used as a casting solvent was detected in the membranes. However, no change in the amount of residual NMP was found before and after the gas permeation experiments, so it is concluded
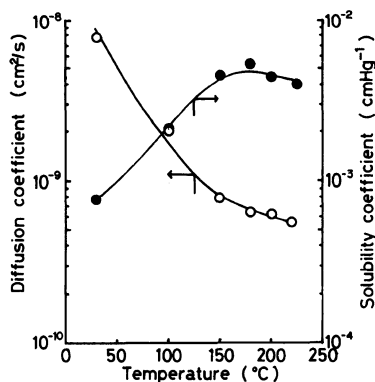
Figure 3. Effect of thermal treatment on $D_{app.CO}$ and $S_{app.CO}$ of the 4SMI-60 membrane at 30°C.
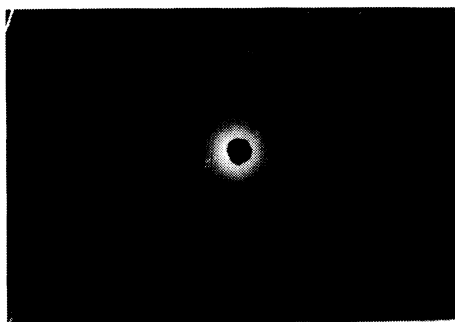

Figure 4. X-Ray diffraction pattern of the 4SMI-60 membrane thermally treated at 220°C.

Table I. Thermal treatment effects on 4SMI-60 membrane

Thermal treatment temperature	Density[a]	Residual NMP[b]	P_{H_2}/P_{CO}[c]
°C	g dl^{-1}	wt%	
30	1.311	11.8	50
150	1.326	4.3	89
200	1.337	1.2	118
220	1.339	1.1	139

[a] Measured at 30°C with a density gradient tube.
[b] Determined by thermogravimetric analysis.
[c] Measured at 30°C.

that NMP was fixed tightly in the membrane. Some investigators have reported that some solvents, like NMP and hexamethylphosphoramide, make a complex with aromatic polyamide.[7-9] This can be understood in relation to the complexation between a solvent and an amide group in the polyamide by hydrogen bonding.

Table I shows the density and amount of residual NMP in the thermally treated membranes. As found in the table, the increase of density with rise in temperature of the thermal treatment was affected not only by rearrangement of the polymer chains but also the amount of residual NMP. It is necessary to estimate influence of the solvent in the membrane on the apparent density of the membrane.

Here, it is assumed that the density of the polymer itself and the density of the NMP contribute to the apparent density of the membrane independently. The apparent density is expressed by a following equation,

$$d = d_p \cdot (1 - v_N) + d_N \cdot v_N \qquad (1)$$

where d_p and d_N are the densities of the polymer itself and NMP respectively v_N is volume fraction of the NMP in the mixture of the polymer and the NMP. The following equation also can be written,

$$v_N = d \cdot w_N / d_N \qquad (2)$$

where w_N is the weight fraction of NMP in the mixture. Substituting eq 2 in eq 1 yields the following equation.

$$(d_p - d_N) \cdot w_N + d_N = d_p \cdot d_N / d \qquad (3)$$

If d_p and d_N remain constant without being affected by thermal treatment, a plot of $1/d$ vs. w_N gives a straight line. Figure 5 shows a plot of the experimental results. A deviation from the straight line at low w_N region was considered due to change in d_p, because it is unlikely that d_N changes with thermal treatment. When the membrane was thermally treated at high temperature, the density of the polymer itself became higher and made the slope of this line higher.

From the intercept of the extrapolated line to $w_N = 1$, d_N was determined as 1.15. This value is not the same as the density value for
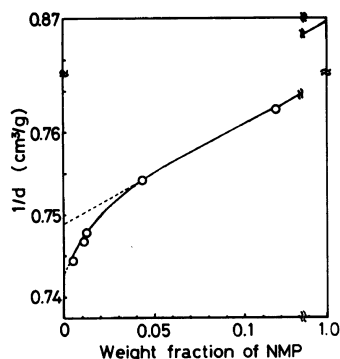
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Figure 5. Relation between the apparent density of the 4SMI-60 membrane and the weight fraction of NMP in the membrane.
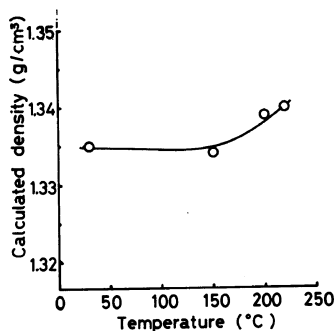

Figure 6. Calculated density of the 4SMI-60 itself as a function of the thermal treatment temperature.

Figure 7. Effect of the thermal treatment on the TMA curves of the 4SMI-60 membranes. The thermal treatment temperatures are: a, 30°C; b, 100°C; c, 150°C; d, 180°C; e, 200°C.

Figure 8. Comparison of the effect of thermal treatment on the shrinking temperature and the permeability ratio for H_2 relative to CO of the 4SMI-60 membrane.

the liquid state at 30°C. Assuming the density of NMP to be 1.15 in the membrane, the density of the polymer itself is calculated as shown in Figure 6. In this figure, it is found that the increase of calculated density occurs by treatment around 180°C or higher temperature. Corresponding to this, the treatment in the same temperature region gave a high permselectivity remarkably.

Thermomechanical Analysis and Dynamic Viscoelasticity Measurements

In addition to the measurement of density, thermomechanical analysis (TMA) and dynamic viscoelasticity were measured to evaluate structural change in thermally treated membranes. Figure 7 shows TMA curves of membranes thermally treated at various tem-
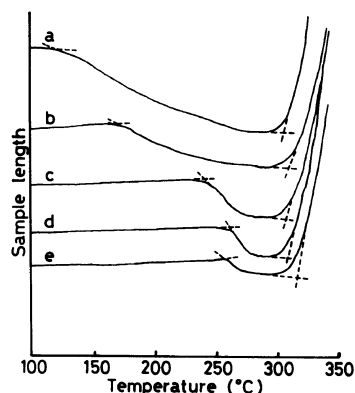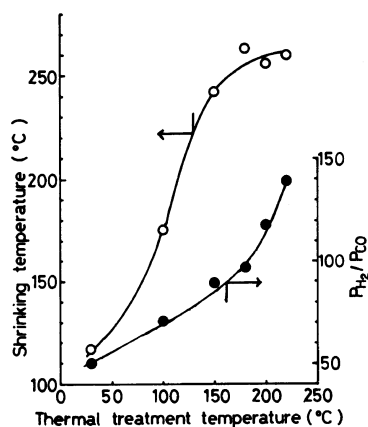
peratures. In the TMA curves of poly(sulfone-amide), the membranes shrank at first with increasing temperature, and then elongated with further increasing temperature. The elongation temperature did not change significantly with thermal treatment. However, the shrinking temperature increased with temperature of the thermal treatment.

Figure 8 compares the change in the shrinking temperature with change in P_{H_2}/P_{CO} by thermal treatment. When the membrane has a lower shrinking temperature, it is considered
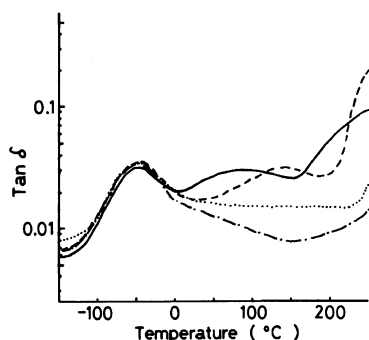
Figure 9. Temperature dependence of $\tan \delta$ for the thermally treated 4SMI-60 membranes. The thermal treatment temperatures are: ——, 30°C; ————, 150°C; ------, 200°C; —·—, 220°C.

that some rearrangement of the polymer chains can take place. When the membrane was thermally treated above 180°C, the shrinking temperature reached around 260°C. At the same time, P_{H_2}/P_{CO} became remarkably high. This shows that the membrane having a tightly fixed structure gives high permselectivity.

Figure 9 shows $\tan \delta$ change of the membrane by thermal treatment. A $\tan \delta$ peak around $-50°C$ was independent of the temperatures of the thermal treatment. A $\tan \delta$ peak for the glass transition was above 250°C. Between these two peaks, there was another peak affected by thermal treatment. This peak temperature increased with temperature of the thermal treatment until near 150°C, then, this transition disappeared by treatment at higher temperature. The disappearance of this transition suggests that fixing of the membrane structure has progressed.

The effective fixation of polymer chains by thermal treatment around 200°C was ascertained by dynamic viscoelastic measurement as well as by density and TMA measurements. This fixation was related to both the removal of residual NMP and rearrangement of the polymer chains.

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