

Separation of H₂ and CO through Poly(sulfone-amide) Membranes II. Highly Permselective Membranes Containing Bis(3-aminophenyl)sulfone as a Diamine Component

Yoshimitsu SAKAGUCHI, Masaya TOKAI, Hiroshi KAWADA,
and Yasuo KATO

*Toyobo Research Center, Toyobo Co., Ltd.,
1-1 Katata 2-chome, Ohtsu, Shiga 520-02, Japan*

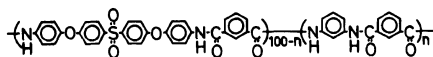
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ABSTRACT: Poly(sulfone-amide) copolymers were synthesized from isophthaloyl dichloride (IPC) and mixed diamines which consisted of various ratios of bis(3-aminophenyl)sulfone (3DDS) and *m*-phenylenediamine (MPD), and permeabilities of H₂ and CO through the polymer membranes were measured at 30°C. The permeability coefficient for H₂ (P_{H_2}) of the poly(sulfone-amide) of which the diamine component is 3DDS was 1.5×10^{-10} cm³·cm cm⁻²·s·cm Hg, and the permeability ratio for H₂ relative to CO (P_{H_2}/P_{CO}) was 150. When the mixed diamines contained 30 mol% of MPD, P_{H_2} was 1.5×10^{-10} cm³·cm cm⁻²·s·cm Hg, and P_{H_2}/P_{CO} was 185, the maximum value for these copolymers. The copolymers derived from *p*-phenylenediamine (PPD) in place of MPD showed decrease in P_{H_2}/P_{CO} . These results suggest that a bent structure is important to obtain a compact structure in the poly(sulfone-amide) membranes.

KEY WORDS Poly(sulfone-amide) / Membrane / Permeability / Hydrogen / Carbon Monoxide / Diffusion / Permeability Ratio / Amide Linkage / Bent Structure /

Recently hydrogen separation membranes have been studied actively,¹⁻³ so it is significant to find polymers which have a superior separation efficiency of hydrogen and carbon monoxide.

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 a previous paper,⁴ permeability of H₂ and CO through poly(sulfone-amide) membranes, which consisted of bis[4-(4-aminophenoxy)phenyl]sulfone (4SED), *m*-phenylenediamine (MPD) and isophthaloyl dichloride (IPC) (structure 1), was



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measured. Their permeability ratios for H₂ relative to CO increased with increase of MPD content in the mixed diamines. This result was explained by the restricted diffusion of CO at a high concentration of the amide linkage in the polymer chain. When *p*-phenylenediamine (PPD) was used in place of MPD, the increase of the permeability ratio was not so remarkable. This suggests that existence of an appropriate number of bends in the polymer chain is also important to obtain a dense structure.

This paper reports the permeation behavior of H₂ and CO through the poly(sulfone-amide) containing bis(3-aminophenyl)sulfone (3DDS) as a main diamine component. 3DDS has no ether linkage, so the poly(sulfone-amide) comprising 3DDS has a higher concentration of amide linkages in the main chain than the

poly(sulfone-amide) comprising 4SED has. Moreover, the amino group of 3DDS is bonded on the *m*-position. This structure introduces a bent structure in the polymer chain. These effects are expected to contribute to high permselectivity.

EXPERIMENTAL

Materials

Three monomers, IPC (Mitsubishi Gas Chemical Co., Inc.), MPD (Nakarai Chemicals Ltd., EP) and PPD (Nakarai Chemicals Ltd., EP) were crushed to powder under nitrogen atmosphere. 3DDS (Konishi Chemical Ind. Co., Ltd.) was used without further purification. *N*-Methyl-2-pyrrolidone (NMP) (Mitsubishi Chemical Ind. Co., Ltd.) was dried over molecular sieves more than one day before use.

Polymerization

The diamine components were dissolved in NMP under nitrogen atmosphere, in such a way that the concentration of resulting polymer solution became 20 wt%. This solution was cooled below 5°C in an ice bath and then an equimolar amount of IPC was added. After the solution was stirred for an hour in the ice bath, the polymerization was continued for another hour at room temperature. The polymer solution was poured into methanol. The precipitated polymer was washed with water several times by use of a blender, and then dried for a period of one day under reduced pressure at 150°C.

Characterization

The reduced viscosities of the polymers were measured at a concentration of 0.5 g dl⁻¹ in *N,N*-dimethylacetamide (DMAc) at 30°C. The glass transition temperature was determined by using a differential scanning calorimeter (DSC) (Perkin-Elmer DSC-1B) at a heating and cooling rate of 20°C min⁻¹ under flowing argon. Thermogravimetric analysis (TGA) was

conducted at a heating rate of 10°C min⁻¹ under flowing air, using a thermogravimetric analyzer (Shimadzu TG-30). ¹H NMR spectra were obtained on dimethyl sulfoxide-*d*₆ solutions with an NMR spectrometer (Varian FT-80A).

Preparation of Membranes

The polymer (4 g) was dissolved in NMP (20 g) and filtered. The solution was cast on a polypropylene film at room temperature, and the solvent was evaporated at 80°C for one hour. Then the membrane was dried under reduced pressure at 150°C for 15 h. The thickness of films was 10–20 μm.

Permeability Measurement

The permeability of H₂ and CO was measured with a permeation apparatus made by Rika Seiki Kogyo, and an MKS Baratron pressure transducer was used for detection of the pressure increase in the downstream-side gas reservoir. All measurements were carried out at 30°C. Gas samples of purity exceeding 99.9% were used.

The permeability coefficient was determined from the steady-state permeation rates, and the permeability ratio was calculated. The apparent diffusion coefficient of CO was determined using the time-lag method⁵ at a constant pressure of upstream gas. The apparent diffusion coefficient (D_{app}) was calculated by the following equation,

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

where L is time lag and l , thickness of the membrane. Time lags for the permeation of CO were in the order of minute. The permeation of H₂ was too fast to determine the time lag accurately, and the apparent diffusion coefficient of H₂ was not evaluated.

RESULTS AND DISCUSSION

Preparation of Poly(sulfone-amide)

Poly(sulfone-amide) copolymers were synthesized from IPC and mixed diamines which consisted of various ratios of 3DDS and MPD (3DMI copolymers, structure 2). The copolymers containing PPD in place of MPD were also synthesized (3DPI copolymers, structure 3).

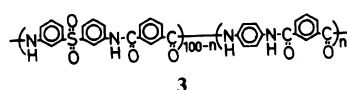
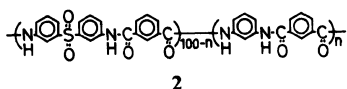


Table I shows the results of polymerization and properties of the resulting polymers. Each polymer had a reduced viscosity in the vicinity of 0.8 to 1.6, and was sufficient to obtain a tough membrane. The polymer composition was determined by ¹H NMR spectra. As an example, ¹H NMR spectrum of the sample

3DMI-30 is shown in Figure 1. The composition of the mixed diamines in the polymers was determined by comparing integral intensities of the amide groups. The obtained polymer composition was the same as the monomer composition for every polymer sample. Each polymer had a high glass transition temperature, and increased with increase of the MPD or PPD content. The decomposition temperatures were similar in these polymers.

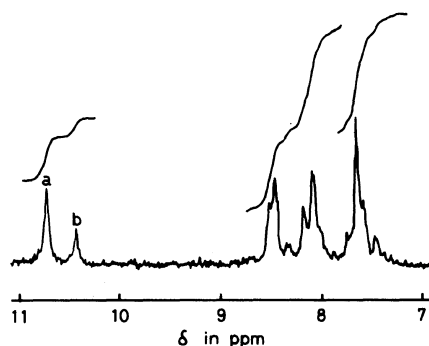


Figure 1. ¹H NMR spectrum of 3DMI-30 in DMSO-*d*₆: a, signal of the amide proton derived from 3DDS and IPC; b, signal of the amide proton derived from MPD and IPC.

Table I. Preparation and properties of poly(sulfone-amide) copolymers

Polymer	Diamine ratio in monomer		3DDS unit ^a content in polymer	η_{sp}/c^b dl g ⁻¹	T_g^c °C	T_d^d °C
	3DDS	MPD or PPD				
Copolymer containing MPD as comonomer						
3DI	100	0	100	1.01	264	403
3DMI-15	85	15	82	0.97	264	395
3DMI-30	70	30	69	0.81	266	396
3DMI-50	50	50	51	1.01	266	383
3DMI-70	30	70	29	1.64	271	391
3DMI-80	20	80	21	1.37	275	372
MI	0	100	0	—	308	357
Copolymers containing PPD as comonomer						
3DPI-30	70	30	67	1.31	272	383
3DPI-50	50	50	49	1.07	277	393

^a Polymer composition determined by ¹H NMR.

^b Reduced viscosity measured at a concentration of 0.5 g dl⁻¹ in DMAc at 30°C.

^c Glass transition temperature determined by DSC in argon at 20°C min⁻¹.

^d Decomposition temperature determined by thermogravimetry in air at 10°C min⁻¹.

Table II. Gas permeability of membranes of poly(sulfone-amide) copolymers^a

Polymer	Permeability ratio		Permeability coefficient ^b		Diffusion coefficient ^c
	P_{H_2}/P_{CO}		P_{H_2}	P_{CO}	$D_{app,CO}$
3DI	150		1.5×10^{-10}	1.0×10^{-12}	6.9×10^{-10}
3DMI-15	164		1.8×10^{-10}	1.1×10^{-12}	6.4×10^{-10}
3DMI-30	185		1.5×10^{-10}	8.1×10^{-13}	5.6×10^{-10}
3DMI-50	158		1.9×10^{-10}	1.2×10^{-12}	6.6×10^{-10}
3DMI-70	146		1.9×10^{-10}	1.2×10^{-12}	7.2×10^{-10}
3DMI-80	162		2.1×10^{-10}	1.3×10^{-12}	7.2×10^{-10}
MI	143		2.0×10^{-10}	1.4×10^{-12}	8.2×10^{-10}
3DPI-30	136		1.9×10^{-10}	1.4×10^{-12}	8.0×10^{-10}
3DPI-50	121		2.3×10^{-10}	1.9×10^{-12}	9.9×10^{-10}

^a Gas permeability measured at 30°C.^b $\text{cm}^3 \cdot \text{cm cm}^{-2} \cdot \text{s} \cdot \text{cm Hg}$.^c $\text{cm}^2 \text{s}^{-1}$.

Gas Permeability through Poly(sulfone-amide) Membranes

The permeability coefficients H_2 and CO (P_{H_2} and P_{CO}) through the membranes of 3DMI and 3DPI copolymers are given in Table II. The permeability ratios for H_2 relative to CO (P_{H_2}/P_{CO}) were higher than those of the poly(sulfone-amide)s derived from 4SED, which were reported in the previous paper.⁴ Especially, 3DMI copolymers had extremely high P_{H_2}/P_{CO} , and 3DMI-30 revealed the maximum P_{H_2}/P_{CO} value, 185. The change of P_{H_2}/P_{CO} with the composition of the copolymers is shown in Figure 2. P_{H_2}/P_{CO} of 3DMI copolymers increased with the content of MPD in the diamines up to 30 mol%, and then decreased. P_{H_2}/P_{CO} of 3DPI copolymers decreased monotonously with the content of PPD.

For the permeation of CO , Table II also shows the apparent diffusion coefficient ($D_{app,CO}$). It is seen that P_{CO} is roughly proportional to $D_{app,CO}$. The apparent solubility coefficient for CO ($S_{app,CO}$) was calculated through the following relation

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

The calculated values of $S_{app,CO}$ were scattered from 1.4×10^{-3} to $1.9 \times 10^{-3} \text{ cm Hg}^{-1}$, and no

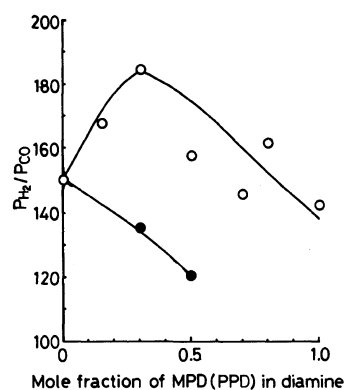


Figure 2. Relation between the permeability ratio for H_2 relative to CO at 30°C and the composition of the poly(sulfone-amide) copolymers: \circ , 3DMI copolymers; \bullet , 3DPI copolymers.

definite relationship between P_{CO} and $S_{app,CO}$ was obtained. The results suggest that the permeation of CO is mainly controlled by the diffusion characteristics.

According to the concept of activated diffusion, diffusion process of a gas molecule through a polymer membrane is related directly to the probability that a hole or passage, of sufficient size for transport of the gas molecule, is created in the polymer medium. Therefore, in the case of glassy polymer, such as poly(sulfone-amide), the packing condition

of the polymer chains plays an important role in determining the diffusion behavior of the gas molecule. In view point of the suggestion described above, the diffusion, accordingly the permeation rate of CO through the poly(sulfone-amide) membranes, may be considered to be determined by the degree of packing of the polymer chains.

The relation between P_{H_2}/P_{CO} and $D_{app,CO}$ is shown in Figure 3. The decrease of $D_{app,CO}$, that is the restricted diffusion of CO, by the dense packing of the polymer chains makes P_{H_2}/P_{CO} higher. Figure 4 shows the relation between P_{H_2}/P_{CO} and P_{H_2} . The dense structure of the membrane seems to affect primarily the diffusion behavior of CO.

The degree of packing of the polymer chains is altered by conditions of preparing a membrane, such as casting, drying and thermal treatment. From the viewpoint of polymer structure, it was explained that the degree of packing of the poly(sulfone-amide) was controlled by both the stiffness brought by the amide linkage and the flexibility brought by the *m*-catenation.⁴ Because of no ether linkage in 3DDS, the poly(sulfone-amide) comprising 3DDS introduces a relatively high concentration of amide linkages in the main chain, and makes the polymer chain stiffer. This may explain the observed fact that the sample 3DI has a high P_{H_2}/P_{CO} value. The bends in the polymer chain of 3DI may also contribute to the densely packed structure. Copolymerization of PPD makes the polymer chains so stiff that dense packing becomes unfavorable in spite of a higher concentration of amide linkages. On the other hand, copolymerization of MPD may introduce an appropriate stiffness to the polymer chains, and the resulting dense structure will make the value of P_{H_2}/P_{CO} higher. Generally speaking, the stiff and dense structure of polymer membrane is favorable to obtain a high permselectivity of hydrogen from other gases. However, the maximum was seen in the plots of P_{H_2}/P_{CO} against the composition of 3DMI copolymers. This

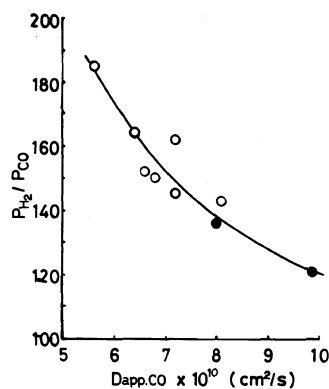


Figure 3. Relation between the permeability ratio for H₂ relative to CO and the apparent diffusion coefficient for CO of the poly(sulfone-amide) copolymers at 30°C: ○, 3DMI copolymers; ●, 3DPI copolymers.

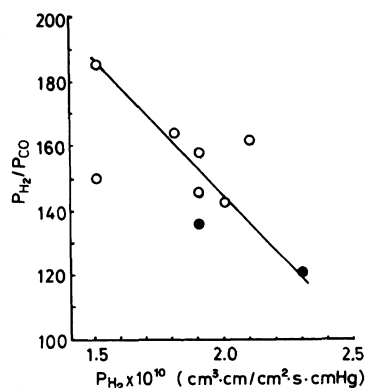


Figure 4. Relation between the permeability ratio for H₂ relative to CO and the permeability coefficient for H₂ of the poly(sulfone-amide) copolymers at 30°C: ○, 3DMI copolymers; ●, 3DPI copolymers.

suggests that there is an optimum point in the balance between the stiffness and crookedness in the polymer chains. A similar tendency that a polymer containing *m*-catenation exhibits lower gas permeability than a polymer containing *p*-catenation was reported for not only polyesters⁶ but also polyimides.⁷

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REFERENCES

1. F. P. McCandless, *Ind. Eng. Chem. Process Res. Dev.*, **11**, 470 (1972).
 2. U. T. Stannett, W. J. Koros, D. R. Paul, H. K. Lonsdale, and R. W. Baker, *Adv. Polym. Sci.*, **32**, 69 (1979).
 3. K. Haraya, K. Obata, T. Hakuta, and H. Yoshitome, *Membrane*, **11**, 48 (1986).
 4. Y. Sakaguchi, H. Kawada, and Y. Kato, *Kobunshi Ronbunshu*, **43**, 755 (1986).
 5. R. M. Barrer, *Trans. Faraday Soc.*, **35**, 628 (1939).
 6. R. R. Light and R. W. Seymour, *Polym. Eng. Sci.*, **22**, 857 (1982).
 7. G. F. Sykes and A. K. St. Clair, *J. Appl. Polym. Sci.*, **32**, 3725 (1986).
1. F. P. McCandless, *Ind. Eng. Chem. Process Res.*