

NOTES

Separation of H₂ and CO through Poly(sulfone amide) Membranes V. Polymer Structure and Gas Permeability

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Gas separation of small molecules such as hydrogen from larger molecules such as carbon monoxide through stiff-chain glassy-polymer membranes is mainly affected by the packing character of the polymer chains, which determines the diffusivity of the gas molecules. Investigation on the relationship between gas-permeation character and polymer structure in aromatic polymers has been actively published in recent years.¹⁻⁸

The authors have been studying hydrogen separation membranes made from aromatic polyamide containing sulfone linkages in the main chain [this polymer is called poly(sulfone amide)].⁹⁻¹² In the case of poly(sulfone amide) membranes, it was found that the permeability ratio of H₂ relative to CO (P_{H_2}/P_{CO}) is controlled by balance between the stiffness induced by the concentration of amide linkages in the backbone and crookedness enhanced with the introduction of *m*-catenation into the main chains. Recently, the same effect, that is, *m*-catenation makes the diffusion of gases through a glassy-polymer membrane slower than *p*-catenation does, has been reported in several papers.¹³⁻¹⁸

In this paper, to clarify the effect of polymer structure in the poly(sulfone amide) on gas permeability, study was focused on series of

copolymers in which the content of *p*- and *m*-catenation and amide-linkage concentration were changed independently.

EXPERIMENTAL

Materials

Bis[4-(4-aminophenoxy)phenyl]sulfone (4SED), bis[4-(3-aminophenoxy)phenyl]sulfone (3SED), bis(3-aminophenyl)sulfone (3DDS) (these three monomers were obtained from Konishi Chemical Ind. Co., Ltd.) and bis(4-aminophenyl)sulfone (4DDS) (Wakayama Seika Kogyo Co., Ltd.) were used as purchased. Isophthaloyl dichloride (IPC) (Mitsubishi Gas Chemical Co., Inc.) was crushed to a powder under nitrogen atmosphere. *N*-Methyl-2-pyrrolidone (NMP) was dried over molecular sieves more than one day before use.

Preparation of Polymers

The poly(sulfone amide)s were prepared by low-temperature solution polycondensation as described in previously.⁹⁾

Preparation of Membranes

The polymers (4 g) were dissolved in 20 ml of NMP. The solutions were filtered and cast on a polypropylene film at room temperature,

and the solvent was evaporated at 80°C for one hour. The membranes were dried under reduced pressure at 150°C for 15 h. Thickness of the films obtained was 10–20 μm .

Permeability Measurement

Permeabilities of H_2 and CO were measured in the same way described in the previous paper.¹¹

In order to analyze gas permeation through a glassy polymer in detail, consideration based on the dual-mode theory¹⁹ is necessary. However, many papers discuss data on permeation and sorption measurements under a certain pressure, and give useful information on the molecular design of gas separation membranes. There are also articles describing agreement between solubility data from sorption experiment and those calculated from

the time-lag method for some polymers. The purpose of this research is to understand permeability change with systematic change of polymer structure and obtain information about the molecular design for gas separation membranes.

The permeability coefficient was determined from the steady-state permeation rate at a constant pressure of upstream gas (1 atm), and the apparent diffusion coefficient of CO was determined using the time-lag method.²⁰ The apparent diffusion coefficient (D_{app}) was calculated by the following equation,

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

where L is the time lag, and, l , the thickness of the membrane. The permeation of H_2 was too fast to determine the time lag accurately, and

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

Polymer	Diamine ratio (molar ratio)		$\eta_{\text{sp}}/c^{\text{a}}$ dl g ⁻¹	T_{g}^{b} °C	TGA ^c °C	Density ^d g ml ⁻¹
	4SED	3SED				
4S3SI-0	100	0	1.25	261	443	1.321
4S3SI-25	75	25	0.89	250	447	1.322
4S3SI-50	50	50	0.67	236	447	1.323
4S3SI-75	25	75	0.65	230	440	1.326
4S3SI-100	0	100	0.46	210	441	1.328
	4DDS	3DDS				
4D3DI-0	100	0	0.77	322	439	1.360
4D3DI-25	75	25	0.66	307	418	1.360
4D3DI-50	50	50	1.13	292	415	1.361
4D3DI-75	25	75	1.15	278	408	1.362
4D3DI-100	0	100	1.01	264	455	1.362
	4SED	4DDS				
4S4DI-30	70	30	1.01	278	456	1.334
4S4DI-50	50	50	0.90	292	416	1.340
	4SED	3DDS				
4S3DI-30	70	30	1.05	262	422	1.331
4S3DI-50	50	50	1.38	262	432	1.351

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

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

^c 5% weight loss temperature determined by thermogravimetry in air at 10°C min⁻¹.

^d Density measured at 30°C with a density gradient column.

the apparent diffusion coefficient of H_2 was not evaluated.

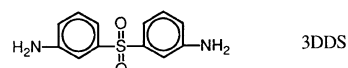
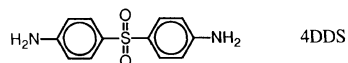
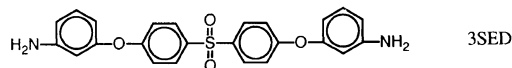
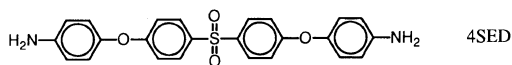
Analysis of Membranes

Reduced viscosity, density, glass transition temperature and thermal decomposition temperature were measured as described in the previous paper.¹¹

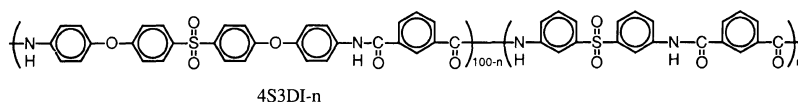
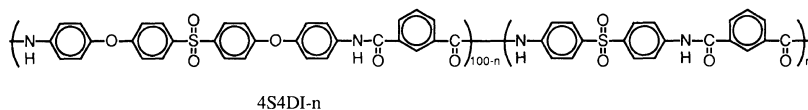
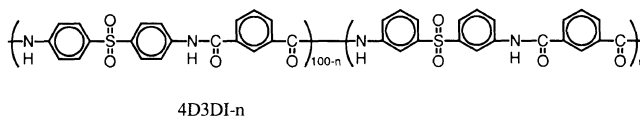
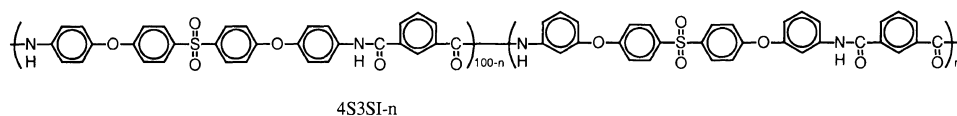
RESULTS AND DISCUSSION

Poly(sulfone amide) copolymers were prepared to clarify the relationships between polymer structure and gas permeability from viewpoints of the influence of catenation and concentration of amide linkage. For this purpose, four diamines shown below were selected to polymerize with isophthaloyl dichloride (IPC); 4SED and 3SED contain ether and sulfone linkages, 4DDS and 3DDS

contain only sulfone linkage and give a polymer with higher concentration of amide linkages.



The polymer structure of four series of poly(sulfone amide) copolymers obtained from these monomers are shown below. The results of preparation and some characterizations of copolymers are shown in Table I.



First, in order to consider the effects of catenation, two series of copolymers, 4S3SI and 4D3DI copolymers were examined. The permeability coefficients of H_2 and CO through the copolymers at 30°C are illustrated in Figure 1. The permeabilities of both gases decreased monotonously with increase of *meta*-diamine content in each copolymer system. The apparent diffusion coefficient of CO also

decreased with increasing *meta*-diamine content (Figure 2), and these orders were in good agreement with the order of density of membranes as shown in Table I. Diffusivity is usually discussed on the basis of packing character: the reciprocal of the free volume which is calculated with measured density and the van der Waals volume for a polymer.^{21,22} In each copolymer system, the polymer

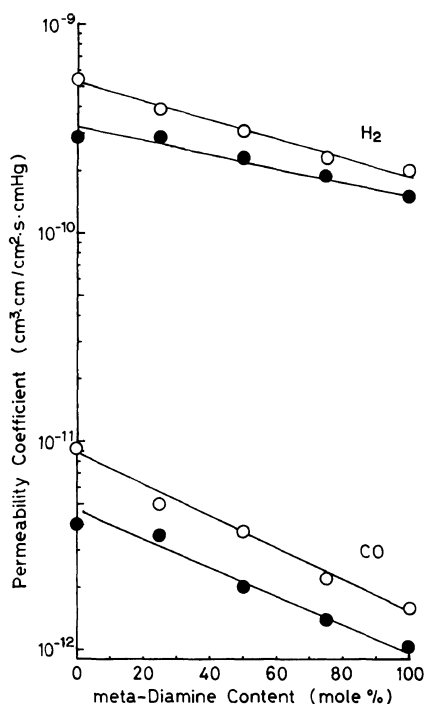


Figure 1. Relation between permeability coefficients and composition of the poly(sulfone amide) copolymers: ○, 4S3SI copolymers; ●, 4D3DI copolymers.

structure is different only in the ratio of *m*- and *p*-catenation. This means each copolymer system has a constant van der Waals volume, respectively. Therefore, the packing character can be compared directly by using density values. They indicate that *m*-catenation contributes to the compact packing of the polymer chains more effectively than that of *p*-catenation. This effect may be induced by the conformational freedom enhanced by *m*-catenation.¹⁸

Although definite conclusions about the solubility coefficient should not be discussed based on these measurements, the decrease of the apparent solubility coefficient for CO ($S_{app,CO}$) with increase of *meta*-diamine content was found in both copolymer systems from the calculation using the relation of $S_{app} = P/D_{app}$. Difference in the chemical structure is negligible, and Langmuir sorption in micro voids is suggested as a cause of the solubility change.

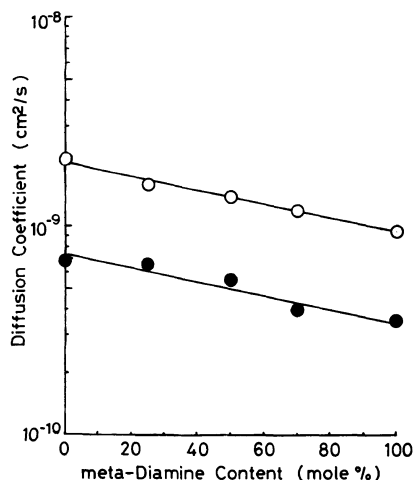


Figure 2. Relation between diffusion coefficient for CO and composition of the poly(sulfone amide) copolymers: ○, 4S3SI copolymers; ●, 4D3DI copolymers.

When *m*-catenation content increased, the permeability of CO decreased more significantly than that of H₂. As a result, the permeability ratio for H₂ relative to CO increased with content of *m*-catenation. This effect is mainly induced by decrease of CO diffusivity, and the influence of decrease in CO solubility is also suggested at the same time.

Comparing 4S3SI and 4D3DI copolymers, the permeability and diffusivity are always larger in the 4S3SI series. Because 4D3DI does not contain ether linkages, the concentration of amide linkages is higher. The amide bonds make the polymer structure stiffer and possibly form intermolecular hydrogen bonds. These effects contribute to the lower gas diffusivity in 4D3DI copolymers. With a combination of the catenation effect and the amide-linkage concentration effect, 3DI showed remarkably high P_{H_2}/P_{CO} , 150.

To consider the hybrid effect of catenation and amide linkage, two series of copolymers, 4S4DI and 4S3DI copolymers, were investigated. Figure 3 shows permeability changes of H₂ and CO with polymer composition. With increase in the DDS content, that is, increase in the concentration of amide linkages, H₂ and

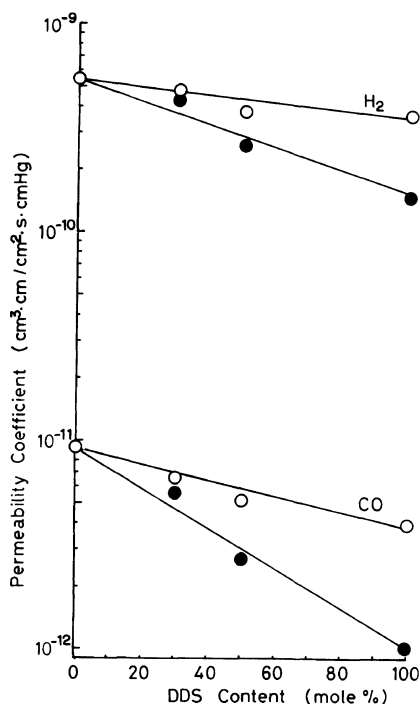


Figure 3. Relation between permeability coefficients and composition of the poly(sulfone amide) copolymers: ○, 4S4DI copolymers; ●, 4S3DI copolymers.

CO permeabilities decreased for both systems. Comparing these two series, the introduction of *m*-catenation instead of *p*-catenation at the same DDS composition decreased the permeability more effectively. Figure 4 shows the diffusivity change of CO with the polymer composition. It coincided with CO permeability change. The apparent solubility coefficient for CO did not decrease so remarkably with polymer composition. As a result, the diffusivity change is considered to dominate gas permeabilities in these systems.

Because the composition of linkage species changes with polymer composition in 4S4DI and 4S3DI copolymers, packing character should be discussed based on free volume. Therefore, the packing density defined by the following equation^{21,22} was used.

$$\text{Packing density} = \frac{\text{Specific volume}}{(\text{Specific volume} - \text{Specific van der Waals volume})}$$

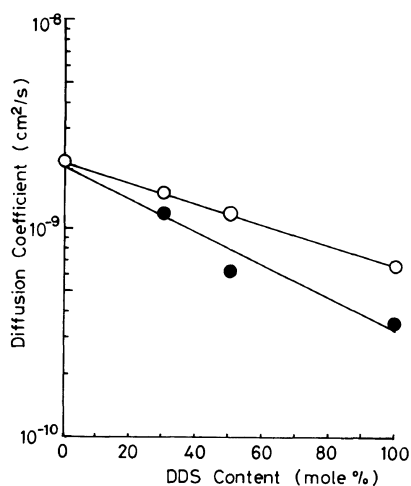


Figure 4. Relation between diffusion coefficient for CO and composition of the poly(sulfone amide) copolymers: ○, 4S4DI copolymers; ●, 4S3DI copolymers.

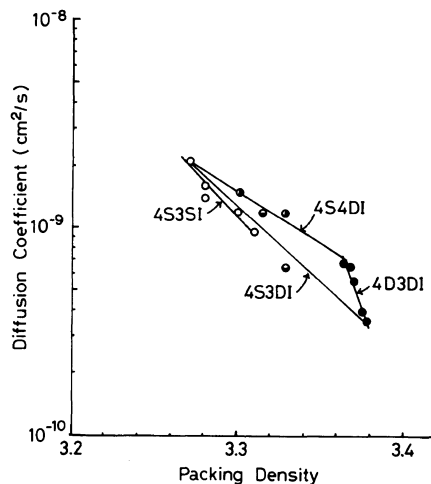


Figure 5. Correlation between packing density and diffusion coefficient for CO in the poly(sulfone amide) copolymers.

Here, the specific van der Waals volume was obtained by using a computer program system "MOL-GRAPH", Daikin Industries, Ltd. The relation between packing density and CO diffusivity is shown in Figure 5. Good correlation of packing density and diffusivity was obtained in all four copolymer series. It was found that the introduction of *m*-catenation and high concentration of the

amide-linkages had increased packing density, and restricted the diffusion of gas molecules.

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