

Synthesis of Sulfone-Modified Poly(vinyl Alcohol) and Its Application for Permselective Membrane of Sulfur Dioxide

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Synopsis

The Michael type addition reaction of poly(vinyl alcohol) (PVA) with a series of vinyl sulfones, namely methyl vinyl sulfone, ethyl vinyl sulfone, and *t*-butyl vinyl sulfone, was performed with NaOH as catalyst to produce 2-(alkylsulfonyl)ethyl PVA derivatives. The high permselectivity of sulfur dioxide against nitrogen and oxygen was achieved through these sulfone-modified PVA membranes.

INTRODUCTION

The increased concentration of atmospheric sulfur dioxide (SO₂) caused by anthropogenic sources has been blamed for a wide range of environmental dangers, including the widespread incidence of acid rain among industrialized countries. Control techniques for atmospheric SO₂ concentration are currently carried out in two ways: (1) desulfuration of fuels and (2) desulfuration of combustion gas mixtures. The former system can be applied solely to liquid fuel systems and thus cannot be used for solid fuel systems including widely used coal systems. In the latter system, the technique, which involves alkaline absorption of SO₂ from bulk wasted gas mixtures, requires huge operation facilities, limiting its actual use to large combustion plants. Besides, the disposal of the wasted mass may cause another problem.

The development of the membrane technique which may provide a facile and economic way for selective accumulation and separation of SO₂, should be of great importance. There have been, however, surprisingly few studies up to now in the search for suitable membrane materials for the selective separation of SO₂.¹⁻⁴ We have recently reported that sulfoxide-modified poly(vinyl alcohol) (PVA)⁵ and cellulose⁶ can be used as the membrane material for the selective permeation of SO₂. The structure design of these new synthetic membranes was accomplished by taking into account the exceptionally high solubility of SO₂ toward sulfoxides, including dimethyl sulfoxide,⁷ since the permeability property of a synthetic membrane is considered to be governed by the solubility and diffusibility of the gas molecule toward the membrane.

As a continuation and extension of previous studies, we present the synthesis of sulfone-modified PVA derivatives and its application to the membrane

material for the selective permeation of SO_2 . Such sulfone compounds as sulfolane have been used previously as plasticizing additives to poly(vinylidene fluoride), which is thereafter applied for the permselective membrane of SO_2 , because of the exceptionally high solubility of SO_2 into sulfolane.⁸ Also, PVA is known as a membrane material of good mechanical property and having high gas barrier invulnerability. Thus the subsequent modification of PVA with sulfone function is expected to give another membrane material with high permselectivity of SO_2 and high mechanical stability.

EXPERIMENTAL

Reagents

Methyl vinyl sulfone (MVSF) was synthesized by NaIO_4 oxidation at 30°C of methyl vinyl sulfide⁹ in 42% yield (b.p. $73^\circ\text{C}/1.5$ mmHg, lit.¹⁰ $117^\circ\text{C}/17$ mmHg). Ethyl vinyl sulfone (EVSF) was prepared similarly from ethyl vinyl sulfide⁹ in 68% yield (b.p. $82^\circ\text{C}/2$ mmHg, lit.¹¹ $89\text{--}93^\circ\text{C}/3$ mmHg). *t*-Butyl vinyl sulfone (BVSF) was obtained similarly from *t*-butyl vinyl sulfide⁹ in 30% yield (m.p. $69\text{--}70^\circ\text{C}$). Poly(vinyl alcohol) was supplied from Kuraray Co. (PVA-117H, D.P. = 1700). Sodium hydroxide and isopropanol were of reagent grade and used without further purification. Water was used after deionization. The other reagents were purified by the usual methods.

Synthesis of 2-(Alkylsulfonyl)Ethyl Isopropyl Ether

The following is a typical example of the reaction of vinyl sulfones with isopropanol. First, 50 mL of isopropanol solution containing 11.1 g of methyl vinyl sulfone and 0.6 g of sodium hydroxide dissolved in 2 mL of water were mixed and stirred at 30°C for 5 h. The reaction mixture was then neutralized with acetic acid. After adding about 100 mL of water, the reaction solution was extracted with chloroform, and dried over sodium sulfate. The addition product, 2-(methylsulfonyl)ethyl isopropyl ether, $(\text{CH}_3)_2\text{CHOCH}_2\text{CH}_2\text{SO}_2\text{CH}_3$, was isolated by the distillation under reduced pressure (b.p. $79\text{--}81^\circ\text{C}/0.5$ mmHg) in 72% yield. ^1H NMR (CDCl_3); $d = 1.20(d, 6H)$, $3.00(s, 3H)$, $3.18(t, 2H)$, $3.60(q, 1H)$, $3.84(t, 2H)$. In a similar way, 2-(ethylsulfonyl)ethyl isopropyl ether, $(\text{CH}_3)_2\text{CHOCH}_2\text{CH}_2\text{SO}_2\text{C}_2\text{H}_5$, (b.p. $89\text{--}90^\circ\text{C}/0.5$ mmHg) ^1H NMR (CDCl_3); $d = 1.20(d, 6H)$, $1.40(t, 3H)$, $3.08(t, 2H)$, $3.18(t, 2H)$, $3.60(q, 1H)$, $3.84(t, 2H)$ and 2-(*t*-butylsulfonyl)ethyl isopropyl ether, $(\text{CH}_3)_2\text{CHOCH}_2\text{CH}_2\text{SO}_2\text{C}_4\text{H}_9$, (b.p. $100\text{--}101^\circ\text{C}/0.5$ mmHg) ^1H NMR (CDCl_3); $d = 1.20(d, 6H)$, $1.44(s, 9H)$, $3.22(t, 2H)$, $3.60(q, 1H)$, $3.92(t, 2H)$ were obtained in 72% and in 76% yield, respectively.

Synthesis of Sulfone-Modified Poly(vinyl Alcohol) Derivatives

A series of sulfone-modified PVA derivatives was synthesized through the Michael-type addition reaction of PVA with a series of vinyl sulfones. The following example presents a typical reaction procedure. PVA was dissolved in water at 90°C and cooled to the predetermined reaction temperature. Thereupon a required amount of vinyl sulfone and aqueous NaOH were added and the reaction mixture was stirred for the prescribed period. The reaction

mixture was then neutralized by acetic acid. The addition product of vinyl sulfone with PVA was isolated by precipitation into acetone/methanol (4/1 in vol) mixture for products with less than 20% sulfone content or into ethanol for those with more than 20% and then purified by reprecipitation from water or dimethyl sulfoxide (DMSO) solution of the crude products into the above precipitation solvents. The resultant sulfone-modified PVAs were finally dried *in vacuo* at 45°C for 48 h.

Gas Permeation Measurements

The sample membrane of a series of sulfone-modified PVA derivatives was prepared by casting from 10 wt% water solution on a Teflon-coated plate. The casting solvent was evacuated first in a desiccator containing anhydrous calcium chloride and next dried *in vacuo* at room temperature for 24 h and finally dried *in vacuo* at 45°C for 48 h. The gas permeation measurements were carried out using the volume method apparatus described in the previous report.⁵

Other Measurements

¹H nuclear magnetic resonance (NMR) measurements were carried out by a JEOL GX-270 apparatus. Viscosity measurements were carried out using a conventional Ostwald dilution viscometer in DMSO solution at 30°C. Thermoanalyses (TG/DTA) were carried out by means of SEIKO I & E TG/DTA 20 apparatus equipped with SSC/580 thermal controller. The heating rate was 10°C/min.

RESULTS AND DISCUSSION

Synthesis of Sulfone-Modified Poly(vinyl Alcohol) Derivatives

Poly(vinyl alcohol) is known to undergo the Michael-type addition reaction with such conjugated vinyl compounds as methyl vinyl ketone,¹² acrylamide,¹³ acrylonitril,¹⁴ and vinyl sulfoxide.¹⁵ The study on the reaction of vinyl sulfone with PVA, however, has been limited to the patent description using sulfone¹⁶ and divinyl sulfone.¹⁷ Accordingly, the addition reaction of a series of vinyl sulfones with isopropanol was first carried out as a model reaction with PVA. Although it was noticed that the addition reaction of vinyl sulfones with water, used as solvent, proceeds concurrently, vinyl sulfones also reacted with isopropanol in the presence of sodium hydroxide as a catalyst to form the Michael-type addition products, 2-(alkylsulfonyl)ethyl isopropyl ethers.

Based on the model reaction above, the addition reaction of PVA with a series of vinyl sulfones in the presence of sodium hydroxide was carried out. The sulfone-modified PVAs with various sulfone contents were obtained as expected. The ¹H NMR spectra of sulfone-modified PVAs are shown in Figures 1–3, respectively, to confirm the formation of the vinyl sulfone-added PVAs. The sulfone content introduced to the starting PVA was determined by measuring the signal ratio of the corresponding monomer unit in these spectra, which agreed mostly with those obtained by sulfur elemental analysis, as shown in Table I.

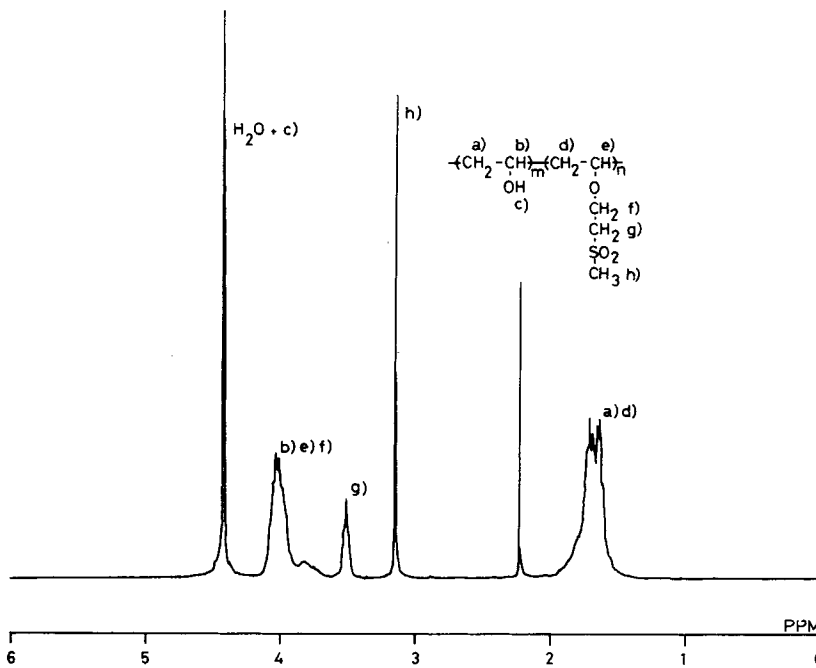


Fig. 1. ^1H NMR spectrum of MVSF-modified PVA in D_2O (sulfone cont. 14.3 mol%, 270 MHz).

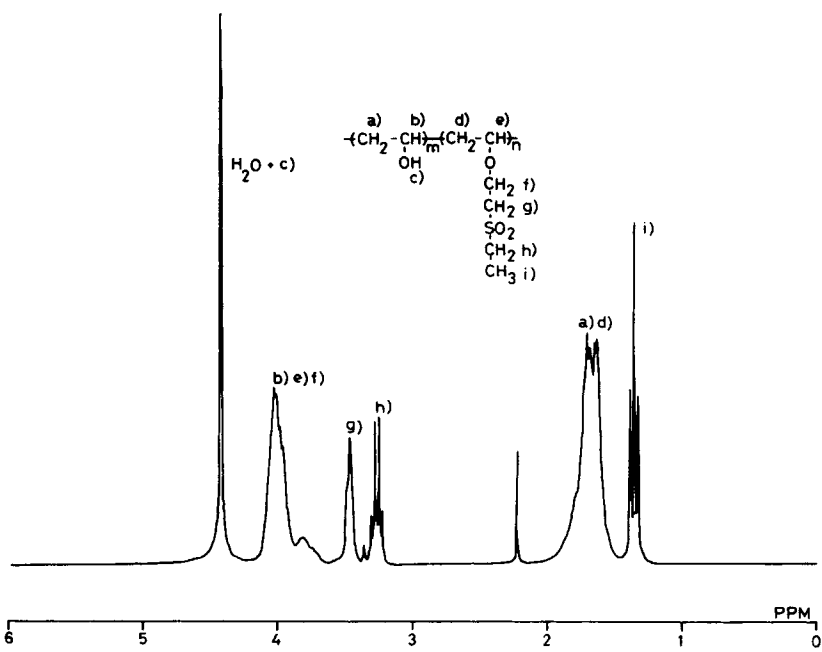


Fig. 2. ^1H NMR spectrum of EVSF-modified PVA in D_2O (sulfone cont. 17.0 mol%, 270 MHz).

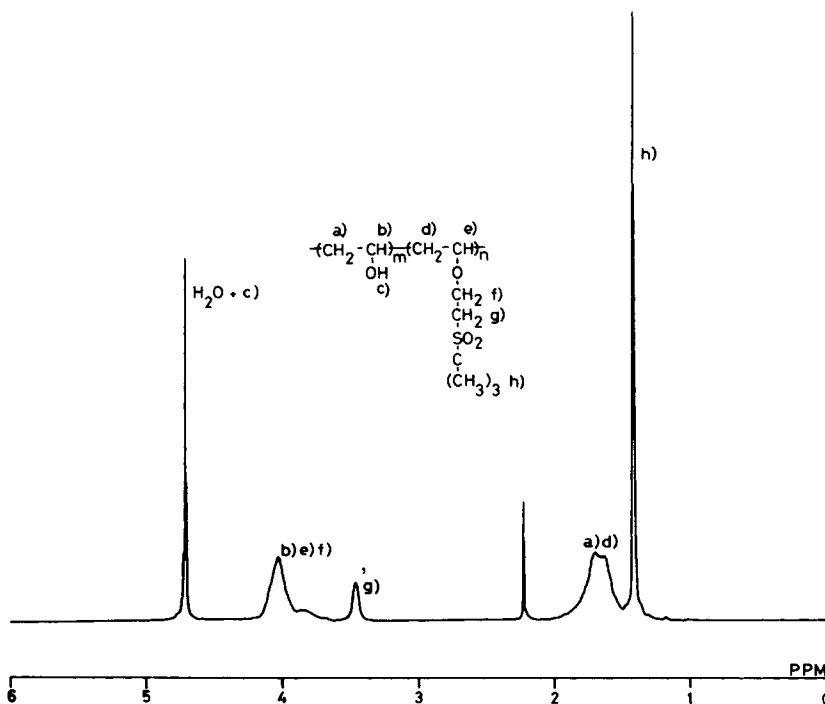


Fig. 3. ^1H NMR spectrum of BVSF-modified PVA in D_2O (sulfone cont. 16.0 mol%, 270 MHz).

The present Michael-type addition reaction was studied in more detail in a search for the optimum condition. A reaction temperature of up to 30°C in the catalyst concentration range of 0.3–0.9 mol/L appeared to be the most suitable for the equimolar reaction of methyl vinyl sulfone and the PVA repeating unit, as seen in Figures 4 and 5.

Although the sulfone content of a series of sulfone-modified PVAs increases with reaction time, it was observed to level off at relatively low value under the present reaction condition (Fig. 6). The ^1H NMR analysis of the reaction mixture revealed that the initially charged vinyl sulfone was completely consumed at the reaction time of 5 h. This is apparently due to the competitive side reaction of vinyl sulfone with water as noted in the model reaction system. Thus, an excess amount of vinyl sulfone compared to PVA repeating unit was required to achieve the high sulfone content in the product. As shown in Figure 7, the sulfone content of every sulfone-modified PVA increases along with the amount of vinyl sulfone charged in the reaction system.

The solubility behavior of a series of sulfone-modified PVAs with various sulfone contents was examined using a number of common solvents (Table I). All sulfone-modified PVAs are soluble in dimethyl sulfoxide. However, with the increase of sulfone content, they become progressively less soluble in water, but solubility in organic solvent is enhanced.

Viscosity measurements of sulfone-modified PVAs were then carried out in dimethyl sulfoxide. As summarized in Table II, the inherent viscosity decreases slightly with the increase of sulfone content. Since the degradation of PVA is not likely under the present reaction condition, the increase of

TABLE I
Solubility of Sulfone-Modified PVA^a

Sample	R	Sulfone Content (mol%)		Solvent						
		NMR	E.A. ^b	C ₆ H ₆	(CH ₃) ₂ CO	CHCl ₃	CH ₃ OH	C ₂ H ₅ OH	(CH ₃) ₂ SO	H ₂ O
M-1		1.9	1.8	×	×	×	×	×	○	○
M-2		12.5	11.3	×	×	×	×	×	○	○
M-3	CH ₃	14.3	14.4	×	×	×	×	×	○	○
M-4		34.7	33.5	×	×	×	△	×	○	○
M-5		42.4	53.3	×	×	×	△	×	○	△
E-1		15.6	16.2	×	×	×	×	×	○	○
E-2	C ₂ H ₅	17.0	15.2	×	×	×	×	×	○	○
E-3		45.9	49.1	×	△	△	△	×	○	△
B-1		11.4	— ^c	×	×	×	×	×	○	○
B-2	<i>t</i> -C ₄ H ₉	16.0	14.3	×	×	×	△	×	○	○
B-3		27.8	30.7	×	×	△	○	△	○	△
B-4		35.0	29.0	×	△	△	○	△	○	△

^aAt room temperature. About 5 wt% solution. (○): Soluble, (△): Partly soluble, (×): Insoluble.

^bCalculated from elemental analysis of sulfur.

^cNot determined.

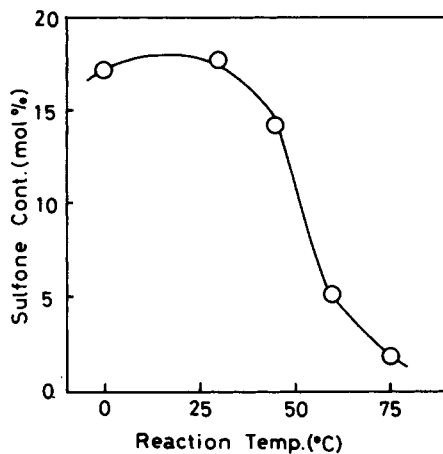


Fig. 4. Sulfone content of MVSF-modified PVA at various reaction temperatures. PVA 0.7 unit mol/L, MVSF 0.7 mol/L, NaOH 0.3 mol/L, 5 h.

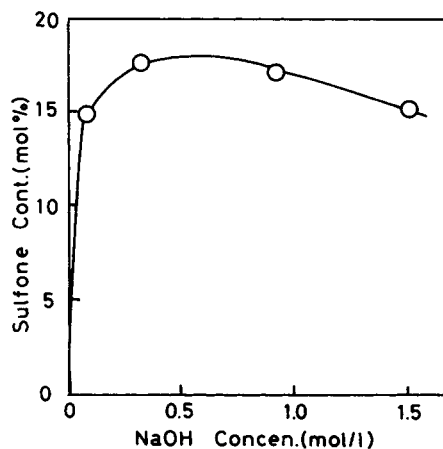


Fig. 5. Sulfone content of MVSF-modified PVA at various NaOH concentrations. PVA 0.7 unit mol/L, MVSF 0.7 mol/L, 5 h, 30°C.

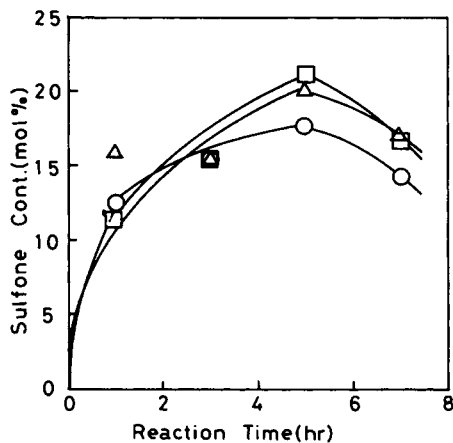


Fig. 6. Sulfone content of sulfone-modified PVA at various reaction times. (○) MVSF, (Δ) EVSF, (□) BVSF, PVA 0.7 unit mol/L, RVSF 0.7 mol/L, NaOH 0.3 mol/L, 30°C.

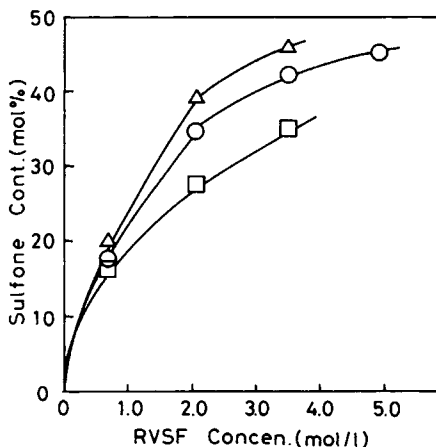


Fig. 7. Sulfone content of sulfone-modified PVA at various RVSF concentration. (○) MVSF, (△) EVSF, (□) BVSF, PVA 0.7 unit mol/L, NaOH 0.3 mol/L, MVSF and EVSF 5 h, BVSF 3 h, 30°C.

TABLE II
Inherent Viscosity of Sulfone-Modified PVA with Various Sulfone Content^a

R	Sulfone Cont. (mol%)	($\ln \eta_r$)/ c (dL/g)
—	0.0	1.35
CH ₃	12.5	1.17
	14.3	1.13
	34.3	0.99
	42.4	0.88
	45.9	0.88
C ₂ H ₅	15.6	1.31
	17.0	1.25
	45.9	0.95
<i>t</i> -C ₄ H ₉	11.4	1.28
	16.0	1.16
	27.8	1.19
	35.0	1.08

^aIn DMSO at 30°C.

2-(alkylsulfonyl)ethyl groups on PVA appears to cause some polymer coil shrinkage.

Thermoanalyses (TG/DTA) of a series of sulfone-modified PVAs were performed and the results are summarized in Figures 8 and 9, respectively. Thermal stability was found to be retained after the introduction of alkylsulfonyl function onto PVA. The melting point peak observed in PVA homopolymer became less intense with the increased sulfone content and was not detectable in methyl sulfone-modified PVA samples with about 14% sulfone content.

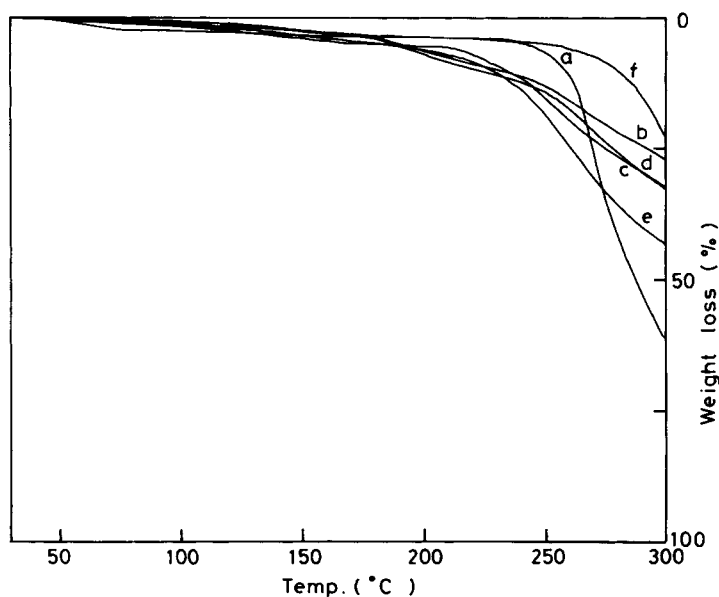


Fig. 8. TGA curves for PVA and sulfone-modified PVA samples. (a) PVA, (b) M-3, (c) M-5, (d) E-2, (e) E-3, (f) B-4. (See also Table I.)

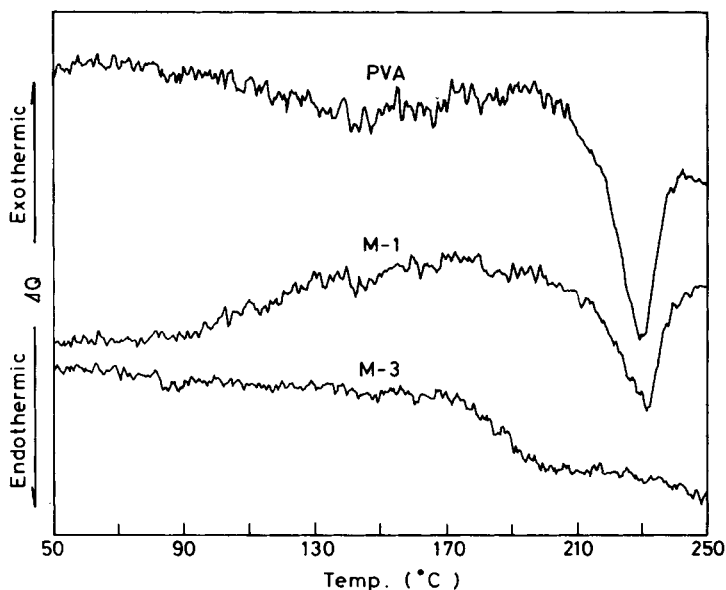


Fig. 9. DTA curves for PVA and sulfone-modified PVA samples. (See also Table I.)

Selective Permeation of SO_2 Through Sulfone-Modified Poly(vinyl Alcohol) Membranes

A series of sulfone-modified PVAs thus obtained was cast to form a membrane and subjected to gas permeation measurements with such gases as SO_2 , N_2 , and O_2 . The permeation coefficient of each pure gas was determined

TABLE III
Gas Permeability of Sulfone-Modified PVA^a

Run No.	Modified PVA		Thickness (μm)	Temperature ($^{\circ}\text{C}$)	Permeability ($\text{cm}^3(\text{STP}) \cdot \text{cm} / (\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}) \times 10^{10}$)					
	Type	Sulfone Cont. (mol%)			$\text{P}(\text{SO}_2)$ (atm)	$\text{P}(\text{N}_2)$ (atm)	$\text{P}(\text{O}_2)$ (atm)	$\text{P}(\text{SO}_2)/\text{P}(\text{N}_2)$ (atm)	$\text{P}(\text{SO}_2)/\text{P}(\text{N}_2)$ (atm)	
1	PVA	0.0	50	24	—	—	0.7	— ^d	— ^e	—
2		12.5	56	20	27	81	350	0.1	0.1	3500
3	MMP ^b	15.3	72	21	6	109	636	0.1	0.1	6390
4		17.7	51	21	7	156	1320	0.2	0.2	6610
5		34.7	45	21	— ^f	— ^f	— ^f	1.0	1.0	—
6	BMP ^c	16.0	51	19	105	492	2900	0.1	0.3	29000
7		21.2	53	20	93	513	2470	0.1	0.1	24700

^aUnit of permeability, $\text{P}; (\text{cm}^3(\text{STP}) \cdot \text{cm}) / (\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg}) \times 10^{10}$.

^bMVSF-modified PVA.

^cBVSF-modified PVA.

^d0.00045 (Ref. 19).

^e0.00052 (Ref. 19).

^fToo weak for permeability measurements.

by means of the volume method,¹⁸ where the rate of gas outflow through the sample membrane was measured until a constant flow rate was attained.

The results of the gas permeation measurements are summarized in Table III, where the result of PVA membrane analysis¹⁹ is also listed for comparison. The sulfone-modified PVA membrane shows a permeability coefficient of SO₂ which is significantly higher than that of PVA membrane and increases markedly with increasing sulfone content. Thus, the introduction of sulfone groups into PVA is proved to be effective for the increase of the permeability of SO₂. The type of alkyl substituent in the sulfone-modified PVA was found also to influence to the permeability of SO₂. The sulfone-modified PVA with the bulkier alkyl substituent, *t*-butyl, attained the higher SO₂ permeability as shown in Table III. On the other hand, the permeabilities of N₂ and O₂ were found to be scarcely affected either by the alkyl substituent or by sulfone content. The permeability coefficient of SO₂ was found to be dependent on the pressure applied to the membrane, as already observed in previous studies.^{1,4-6} At the same time, the swelling of the membrane during the permeation experiment was noticed, indicating the absorption of SO₂ in membrane. This, in turn, weakens the membrane at high applied SO₂ pressure, especially in high sulfone content membranes. The permeability of N₂ and O₂, on the contrary, was found to be independent of the applied pressure, as was observed previously.¹⁸ From these results, the permselectivity of SO₂ versus N₂, $P(\text{SO}_2)/P(\text{N}_2)$, at 2 atm, was found to be as high as 2.9×10^4 for the membrane of BVSF-modified PVA with a sulfone content of 16.0 mol%. For the same membrane, the permselectivity of SO₂ against O₂, $P(\text{SO}_2)/P(\text{O}_2)$, was found to be as high as 1.0×10^4 .

CONCLUSION

A series of sulfone-modified PVA derivatives was produced through the reaction of PVA with various substituted alkyl vinyl sulfones and polymer membranes thus obtained exhibited the high permselectivity of SO₂ against N₂ and O₂.

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