Synthesis of Sulfoxide-Modified Cellulose Derivatives Designed for the Permselective Membrane of Sulfur Dioxide

Kiyokazu IMAI,* Yasuyuki TEZUKA, Tomoo SHIOMI, and Matsunori TAKADA
Department of Material Science and Technology, Technological University of Nagaoka,
Kamitomioka, Nagaoka, Niigata 940-21
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The Michael type addition reaction of cellulose with a series of vinyl sulfoxides, namely methyl vinyl sulfoxide, ethyl vinyl sulfoxide, *t*-butyl vinyl sulfoxide, and phenyl vinyl sulfoxide, was performed with NaOH as a catalyst to produce 2-(alkyl- or arylsulfinyl)ethyl cellulose derivatives. The high permselectivity of sulfur dioxide against nitrogen and oxygen was achieved through these sulfoxide modified cellulose membranes.

The increase of the concentration of atmospheric sulfur dioxide(SO_2) caused by anthropogenic sources has been accused of a wide range of environmental dangers, including widely spreading acid rain among industrialized countries. The control techniques for the atmospheric SO_2 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 SO_2 from bulk wasted gas mixtures, requires huge operation facilities, limiting its actual use to big 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 a selective accumulation and separation of SO_2, 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 SO_2.[1-4] We have recently reported that sulfoxide modified poly (vinyl alcohol) can be used as the membrane material for the selective permeation of SO_2.[5] The structure design of this new synthetic membrane was accomplished by taking into account the exceptionally high solubility of SO_2 toward sulfoxides, including dimethyl sulfoxide,[6] since the permeability property of a synthetic membrane is considered to be governed by the solubility and the diffusivity of the gas molecule toward the membrane.

As the continuation and the extension of the previous studies, this paper presents the synthesis of sulfoxide-modified cellulose derivatives and the application to the membrane material for the selective permeation of SO_2. Cellulose, as well as poly (vinyl alcohol), is considered to be another promising candidate for the membrane material for the present purpose due to its good mechanical property and its high gas barrierity. The subsequent modification of cellulose with sulfoxide function is expected to give a membrane material with high permselectivity of SO_2 and good mechanical property.

Experimental

Reagents. A series of vinyl sulfoxides, i.e. methyl vinyl sulfoxide (MVSO), ethyl vinyl sulfoxide (EVSO), *t*-butyl vinyl sulfoxide (BVSO) was prepared by the method described before.[7] Phenyl vinyl sulfoxide (PVSO) was commercially available and was purified by the fractional distillation. Powdery cellulose was supplied from Asahi Chemical Co. (Avicel, PH 101, D.P. 250). Sodium hydroxide was of reagent grade and used without further purification. Water was used after deionization. Ethyl cellulose (from Nakarai Chem., D.S.=2.5, 80—120 cps) was used as received. Other reagents were purified by the conventional procedures.

Synthesis of Sulfoxide-Modified Cellulose Derivatives. A series of sulfoxide modified cellulose derivatives was synthesized through the Michael type addition reaction of cellulose with a series of vinyl sulfoxides. The following example presents the typical reaction procedure. One gram of cellulose powder was slurried and swelled in 20 ml of aqueous NaOH solution at 26—28 °C. A required amount of vinyl sulfoxide was then added and the reaction mixture was stirred for the prescribed period. The reaction solution became gradually less turbid and, in some cases, turned into almost homogeneous. The reaction mixture was then neutralized by acetic acid and poured into an acetone/methanol (7/3 in volume) mixture to isolate the reaction product, which was washed with the above acetone/methanol mixture and finally dried in vacuo at 45 °C for 48 h.

Gas Permeation Measurements. The sample membrane of a series of sulfoxide modified cellulose derivatives was prepared by casting from either 5 wt% water (for MVSO and EVSO adduct) or DMSO (for PVSO adduct) solution on a Teflon-coated plate. MVSO-modified cellulose with low D.S. (0.83 and 0.92), as well as EVSO- and PVSO-modified cellulose samples gave slightly turbid membranes. The casting solvent was evacuated first either in a desiccator containing anhydrous calcium chloride (for water), or in a thermostatic oven at 35 °C (for DMSO) and finally in vacuo at 60 °C for 2 d. An ethyl cellulose membrane was prepared in a similar way from a dichloromethane solution. The gas permeation measurements were carried out by using the volume method apparatus described in the previous report.[5]

Other Measurements. ^{13}C NMR measurements were carried out by a JEOL JNM GX270 apparatus, in which chemical shifts were calibrated either by using cellulose C_1 carbon (103.0 ppm) or DMSO (43.5 ppm) as an internal standard. Sulfur elemental analysis was carried out with a CALRO ERBA Elemental Analyzer MOD 1106. Viscosity measurements were carried out in water at 30 °C with an Ubbelohde viscometer.

Results and Discussion

1) Synthesis of Sulfoxide-Modified Cellulose Derivatives. The Michael type addition reaction of hydroxyl group to poly (vinyl alcohol), PVA, or cellulose with such vinyl compounds as acrylonitrile, acrylamide, and alkyl vinyl sulfone, has been proved to be a versatile technique to introduce various kinds of functional groups to these polyhydroxy type polymers.[8,9] We have recently adopted this technique to synthesize a series of sulfoxide modified PVA derivatives using a variety of vinyl sulfoxides, i.e. methyl vinyl sulfoxide (MVSO), ethyl vinyl sulfoxide (EVSO) and *t*-butyl vinyl sulfoxide (BVSO).[10]

In the present study, we have carried out the Michael

Table 1. Synthesis of Sulfoxide-Modified Cellulose Derivatives[a]

Run. No.	RVSO	RVSO/Cellulose ratio[b]	React. time	NaOH concn.	Sulfur cont.[c]	D.S.
			h	wt%	wt%	
M-1	MVSO	3.0	1	20	4.60	0.27
M-2	MVSO	3.0	2	20	7.29	0.46
M-3	MVSO	3.0	3	20	9.50	0.66
M-4	MVSO	3.0	5	20	10.45	0.75
M-5	MVSO	3.0	9	20	11.22	0.83
M-6	MVSO	9.0	9	20	14.15	1.19
M-7	MVSO	12.0	9	20	14.50	1.24
M-8	MVSO	9.0	9	15	15.50	1.39
M-9	MVSO	9.0	9	5	13.20	1.06
M-10	MVSO	9.0	9	10	14.20	1.20
M-11[d]	MVSO	9.0+9.0	9+9	10	19.26	2.13
M-12[d]	MVSO	9.0+9.0+9.0	9+9+9	10	20.32	2.40
E-1	EVSO	9.0	9	20	3.45	0.20
E-2	EVSO	27.4	9	20	3.40	0.19
E-3	EVSO	35.7	9	20	2.70	0.14
E-4	EVSO	9.0	9	15	5.79	0.37
E-5	EVSO	9.0	9	10	8.55	0.60
E-6	EVSO	9.0	9	5	4.81	0.29
B-1	BVSO	9.0	9	10	0.54	0.03
P-1	PVSO	9.0	9	10	8.56	0.73
P-2	PVSO	6.0	9	10	6.87	0.51
P-3	PVSO	3.0	9	10	5.40	0.36

a) Reaction conditions: Cellulose 1.0 g, H_2O 20 ml, 26—28 °C. b) Molar ratio between RVSO and hydroxyl group in cellulose. c) Elemental analysis. d) The reaction was continued by adding fresh RVSO repeatedly.

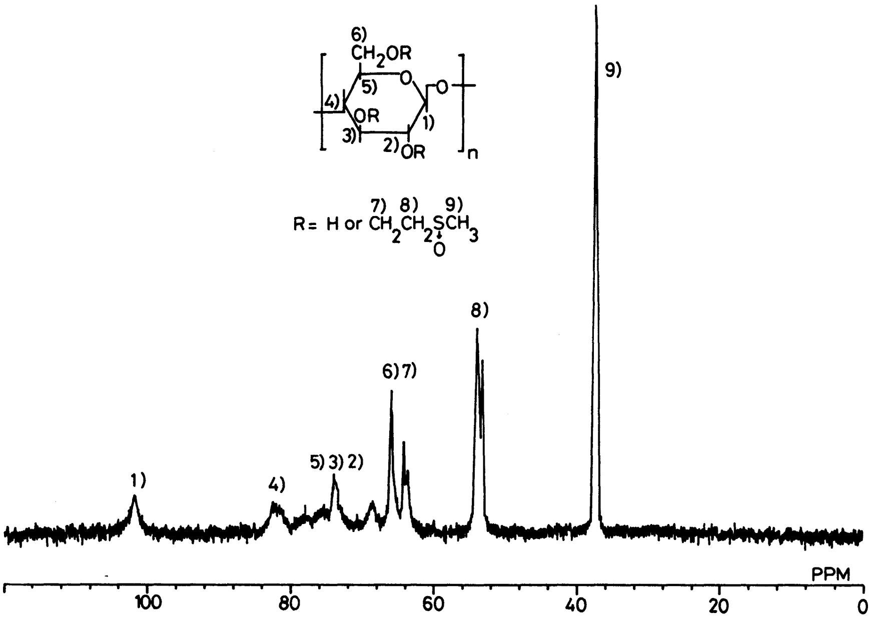


Fig. 1-a. ^{13}C NMR spectrum of MVSO-modified cellulose in D_2O at 40°C (sample M-11 in Table 1).

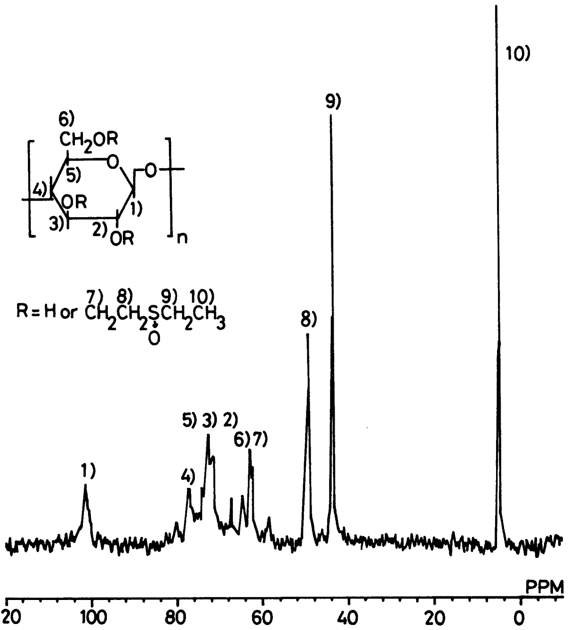


Fig. 1-b. ^{13}C NMR spectrum of EVSO-modified cellulose in D_2O at 40°C (sample E-5 in Table 1).

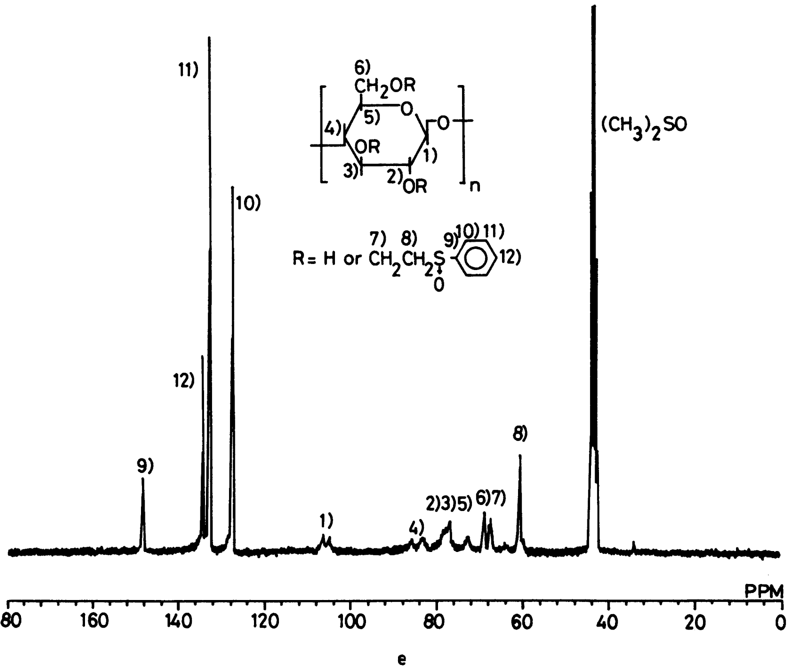
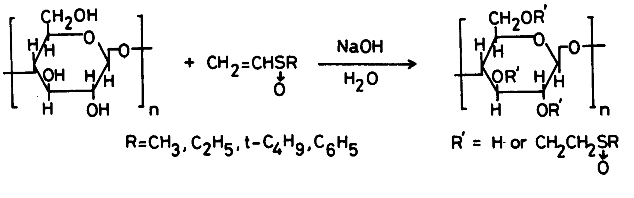


Fig. 1-c. ^{13}C NMR spectrum of PVSO-modified cellulose in DMSO-d_6 at 60°C (sample P-1 in Table 1).

type addition reaction of a series of vinyl sulfoxides against another polyhydroxy polymer, cellulose, in the presence of sodium hydroxide, as a catalyst, to produce various sulfoxide modified cellulose derivatives. As is summarized in Table 1, a series of sulfoxide-modified cellulose derivatives with various degrees of sulfoxide contents, i.e. the degree of substitution (D.S.) for the sulfinylethyl function, was obtained in the reaction with MVSO, EVSO, and PVSO, while BVSO was found to be very sluggish to react with cellulose under these reaction conditions. The formation of sulfoxide-modified cellulose derivatives through the Michael type addition reaction was confirmed evidently by ^{13}C NMR spectroscopic analysis given in Fig. 1-a—c, where the peaks assigned for the 2-(alkyl- or phenylsulfinyl)ethyl group introduced to cellulose appear to



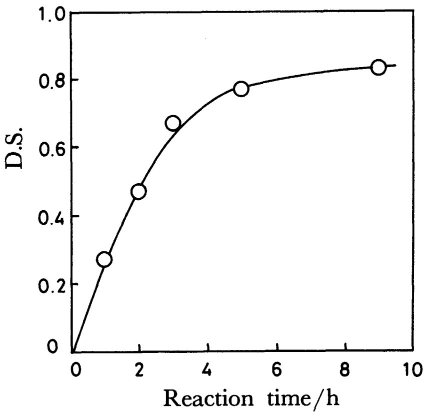


Fig. 2. The degree of substitution of MVSO-modified cellulose at various reaction times. Cellulose 1.0 g(—OH 0.019 mol), MVSO 5.1 g(0.057 mol), NaOH 5.0 g, H_2O 20 ml, 26—28°C.

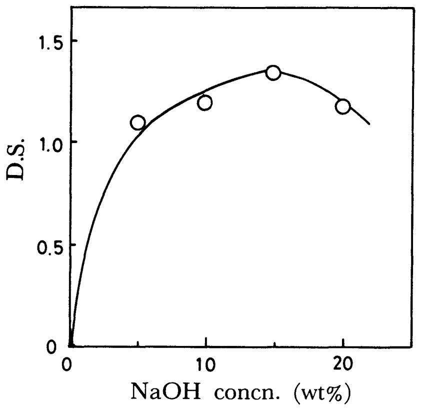


Fig. 3. The degree of substitution of MVSO-modified cellulose at various NaOH concentrations, Cellulose 1.0 g(—OH 0.019 mol), MVSO 15.4 g(0.17 mol), H_2O 20 ml, 9h, 26—28°C.

Table 2. Intrinsic Viscosity of MVSO-Modified Cellulose Derivatives with Various Degrees of Substitution[a)]

D.S.	$[\eta]$ $(\mathrm{dl\,g^{-1}})$
0.83	1.95
1.18	1.81
1.23	1.77
2.01	1.30
2.40	1.25

a) In water at 30°C.

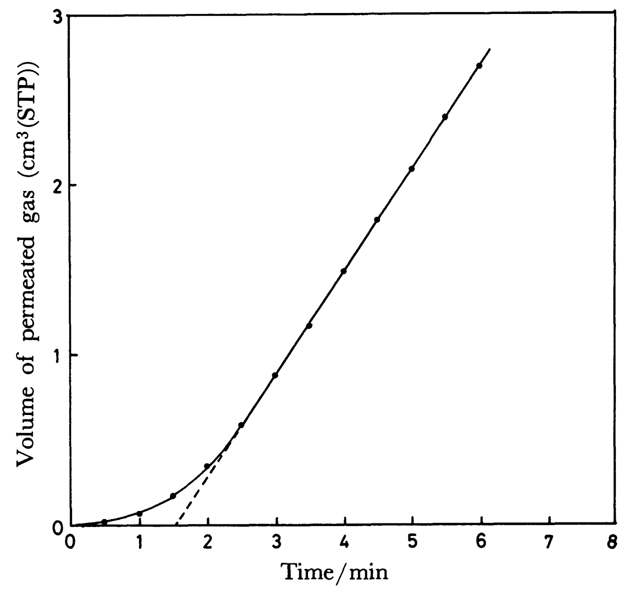


Fig. 4. The permeation measurement of sulfur dioxide through MVSO-modified cellulose membrane (Run 2 in Table 3, 1.0 atm).

be present in addition to those for the glucose ring carbon signals.

As is seen in Table 1, the degree of substitution in the cellulose derivatives failed to exceed around 1.4, far less than the total available hydroxyl group in glucose unit 3.0, even when the reaction was performed either with a large excess of vinyl sulfoxide or with a prolonged reaction time (Fig. 2), or with a higher catalyst concentration (Fig. 3). The undesired side reaction, namely the addition reaction of vinyl sulfoxide with water used as the solvent, was observed to give 2-hydroxyethyl sulfoxide in the presence of sodium hydroxide similar to the reaction with poly (vinyl alcohol).[10)]

The sulfoxide modified cellulose derivatives with the higher sulfoxide content could be obtained by employing the following reaction technique, where an excess amount of fresh vinyl sulfoxide was repeatedly added to the reaction mixture in an appropriate interval as shown in Table 1 (Runs M-11 and M-12). When such a reaction was repeated three times, sulfoxide-modified cellulose with a D.S. value as high as 2.40 was obtained as listed in Table 1 (Run M-12).

The intrinsic viscosity of a series of MVSO-modified cellulose derivatives with various D.S. values was measured as the first-order approximation of the extent of polymer degradation during the sulfoxide-modification reaction. As is summarized in Table 2, MVSO-modified cellulose with the D.S. value of 2.40 was estimated to possess still considerably high molecular weight from its $[\eta]$ value of 1.25, although a slight decrease of $[\eta]$ was actually noticed with the increase in sulfoxide content.

2) Selective Permeation of SO_2 through Sulfoxide-Modified Cellulose Membranes. A series of sulfoxide-modified cellulose derivatives thus obtained was casted to form a membrane and subjected to the gas permeation measurements with such gases as SO_2, N_2, and O_2. The permeation coefficient of each pure gas was obtained through the volume method, where the rate of gas outflow through the sample membrane was measured until a constant flow rate was attained. An example of the permeation experiment for SO_2 by the present system is given in Fig. 4.

Table 3. Gas Permeability of Sulfoxide-Modified Cellulose Derivatives[a)]

Run No.	Modified Cell		Thickness	Temp	$P(SO_2)$			$P(N_2)$	$P(O_2)$	$P(SO_2)/P(N_2)$
	Type	D.S.	(μm)	°C	1.0atm	1.5atm	2.0atm	2.0atm	2.0atm	2.0atm
1	MMC[b)]	0.83	81	20	81	155	356	0.16	0.38	2200
2		0.92	82	17	553	973	2280	0.40	0.16	5700
3		1.06	55	23	722	2150	4090	0.32	0.37	12800
4		2.13	77	18	—[f)]	—[f)]	—[f)]	0.52	0.73	—
5	EMC[c)]	0.66	66	23	284	1080	2210	0.29	0.48	7600
6	PMC[d)]	0.51	92	19	2790	—[f)]	—[f)]	0.14	0.25	19900[g)]
7	EC[e)]	2.50	127	20	1010	1640	2140	3.10	14.20	690

a) Unit of permeability, P: $(cm^3\ (STP)\cdot cm)/(cm^2\cdot s\cdot cm\ Hg)\times 10^{10}$. b) MVSO-modified cellulose. c) EVSO-modified cellulose. d) PVSO-modified cellulose. e) Ethyl cellulose. f) Too weak to permeability measurements. g) 1.0 atm.

The results of the gas permeation measurements for a series of sulfoxide-modified cellulose membranes were summarized in Table 3, where the result of ethyl cellulose membrane was also listed for comparison. The permeation coefficient of SO_2 was found to increase markedly with the increase of the sulfoxide function content in cellulose, while the permeation coefficients of N_2 and O_2 remained almost unchanged. This leads to the high permselectivity of SO_2 against N_2 and O_2 with these sulfoxide-modified cellulose membranes.

With the increase in applied SO_2 pressure, the permeation coefficient of SO_2 for the sulfoxide modified cellulose membrane was found to increase far more significantly compared to that for ethyl cellulose. At the same time, the notable swelling of the sulfoxide-modified cellulose membrane during the permeation experiment was observed especially in high applied SO_2 pressure, indicating the absorption of SO_2 in the membrane. This, in turn, weakens the membrane at high applied SO_2 pressure, especially in high sulfoxide content membranes.

The type of the substituent in vinyl sulfoxide was also found to exercise a prominent influence on the permeation behavior of SO_2, while little effect on the permeation coefficients of N_2 and O_2. The phenyl substituent was found to be the most remarkable effect on the permeation coefficient and permselectivity of SO_2, compared to methyl and ethyl counterpart, nevertheless the membrane tended to become too weak for the measurement at SO_2 pressures higher than 1 atm, even when the D.S. value of this cellulose derivative is 0.51.

Conclusion

A series of sulfoxide-modified cellulose derivatives was produced through the reaction of cellulose with various substituted vinyl sulfoxides and the obtained sulfoxide-modified cellulose membranes exhibited the high permselectivity of SO_2 against N_2 and O_2.

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