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Michael Addition Reaction of Vinyl Sulfoxide with Poly(Vinyl Alcohol)

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ABSTRACT

The Michael addition reaction of a series of alkyl vinyl sulfoxides (CH_2=CH–SO–R; R = CH_3 (MVSO), C_2H_5 (EVSO), t–C_4H_9 (BVSO)) with poly(vinyl alcohol) (PVA) was carried out after investigating the model reaction with isopropyl alcohol. The addition reaction was found to proceed in the presence of sodium hydroxide as catalyst. This sulfinylation of PVA proceeded more easily with MVSO and EVSO than with BVSO, and a polymer containing up to 60 mol% sulfoxide unit was obtained with MVSO and EVSO. The solution viscosity as well as the solubility behavior of the modified PVA's having various types and contents of sulfoxide group were also examined.

INTRODUCTION

Sulfoxide-containing polymers have drawn growing attention in connection with the unique behavior of DMSO and other sulfoxide-containing compounds as solvents and reagents [1]. For example, poly(methyl methacrylate) derivatives containing the sulfoxide group were

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synthesized [2] and used as polymeric drug carriers [3]. Polystyrene derivatives containing the sulfoxide group have been applied to phase transfer catalysts [4] and polymeric chelating reagents [5].

Sulfoxide modification of poly(vinyl alcohol) (PVA) is expected to give an amphiphilic character to this typical hydrophilic polymer and to extend further its application possibilities. In the present paper we describe the synthesis of sulfoxide-modified PVA by a Michael-type addition reaction of vinyl sulfoxide with PVA.

EXPERIMENTAL

Reagents

A series of vinyl sulfoxides, MVSO, EVSO, and BVSO, were prepared by the method described in our previous paper [6]. Poly(vinyl alcohol) was supplied by Kuraray Co. (PVA-117H, DP ≈ 1700 and PVA-105, DP = 500) and purified by reprecipitation into methanol. The other reagents were purified by the usual methods.

Reaction of Alkyl Vinyl Sulfoxide with Isopropyl Alcohol

The typical reaction procedure was as follows. Isopropyl alcohol (0.9 mol/L) and methyl vinyl sulfoxide (3.4 mol/L) were reacted in the presence of aqueous sodium hydroxide (0.4 mol/L) at 60°C for 5 h. The reaction mixture was then neutralized by acetic acid, extracted with methylene chloride, and dried over magnesium sulfate. The addition product, 2-methylsulfinylethyl isopropyl ether, $(CH_3)_2CHOCH_2CH_2SOCH_3$, was isolated by distillation under reduced pressure (bp, 63-64°C/0.5 mmHg) in 69% yield. In a similar way, 2-ethylsulfinylethyl isopropyl ether, $(CH_3)_2CHOCH_2CH_2SOC_2H_5$, and 2-t-butylsulfinylethyl isopropyl ether, $(CH_3)_2CHOCH_2CH_2SOC_4H_9$, were obtained in 64% yield (bp, 78-79°C/0.5 mmHg) and in 30% yield (bp, 91-93°C/0.5 mmHg), respectively.

Reaction of Alkyl Vinyl Sulfoxide with Poly(Vinyl Alcohol)

The reaction of a series of alkyl vinyl sulfoxides with PVA was carried out in a way similar to the model reaction described above. The addition product of vinyl sulfoxide with PVA was isolated by precipitation into acetone and purified by reprecipitation from the water/acetone system.

Measurements

The ^{1}H-NMR spectrum was recorded by means of a JEOL PMX-60 or a JEOL FX-270 apparatus. Viscosity measurements were carried out by using a conventional Ostwald dilution viscometer.

RESULTS AND DISCUSSION

Michael Addition Reaction of Vinyl Sulfoxides with Isopropyl Alcohol

Vinyl compounds such as acrylonitrile [7] or methyl vinyl ketone [8] are known to undergo the Michael-type addition reaction with alcohol. The addition reaction of a series of vinyl sulfoxides with isopropyl alcohol was examined as a model reaction with PVA.

A series of alkyl vinyl sulfoxides were found to react with isopropyl alcohol in the presence of sodium hydroxide as a catalyst. The addition products, alkylsulfinylethyl ethers, were isolated and were subjected to ^{1}H-NMR analysis as shown in Figs. 1-3. All the signals of these spectra are reasonably assigned to those of the addition products. Thus, the Michael addition reaction was confirmed to take place in the present reaction systems.

Besides the expected reaction, a competitive reaction, the addition reaction of water with vinyl sulfoxide, was observed in the present system. This side reaction product, 2-alkylsulfinylethyl alcohol, was isolated from the reaction mixture and characterized by ^{1}H-NMR spectroscopy (Fig. 4).

Michael Addition Reaction of Vinyl Sulfoxides with Poly(Vinyl Alcohol)

Poly(vinyl alcohol) is known to undergo the Michael addition reaction with such conjugated vinyl compounds as methyl vinyl ketone [9],

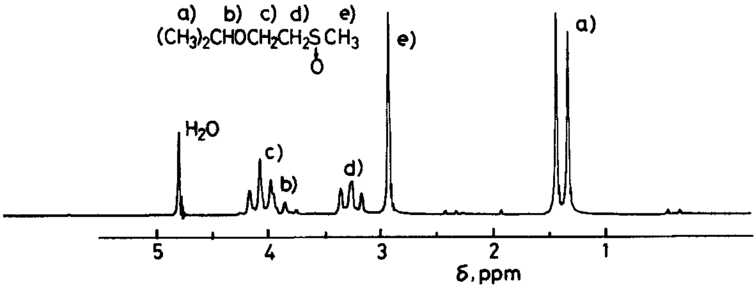

FIG. 1. ^{1}H-NMR spectrum of the addition product between methyl vinyl sulfoxide and isopropyl alcohol (D_2O, 60 MHz).

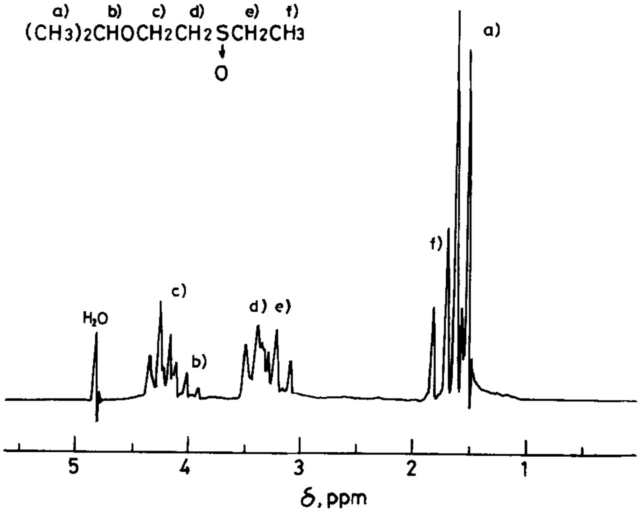

FIG. 2. ^{1}H-NMR spectrum of the addition product between ethyl vinyl sulfoxide and isopropyl alcohol (D_2O, 60 MHz).

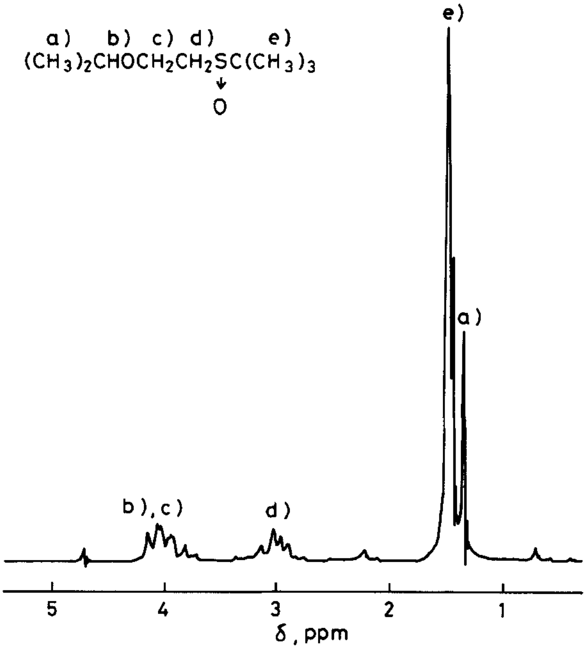

FIG. 3. ^{1}H-NMR spectrum of the addition product between t-butyl vinyl sulfoxide and isopropyl alcohol (D_2O, 60 MHz).

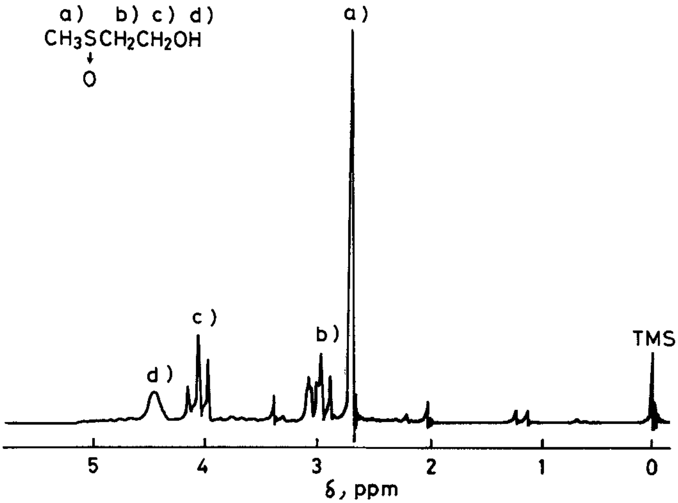

FIG. 4. ^{1}H-NMR spectrum of the addition product between methyl vinyl sulfoxide and H_2O ($CDCl_3$, 60 MHz).

acrylamide [10], and acrylonitrile [11]. The reaction of vinyl sulfoxide with PVA, however, has not been described to date. In the present study this reaction was found to take place in the presence of sodium hydroxide, as expected from the results obtained in the model reaction systems.

The sulfoxide-modified PVA's with various sulfoxide contents were isolated and analyzed by using the ^{1}H-NMR technique as shown in Figs. 5-7. The chemical shifts of each signal for the products obtained were compared with those of the model compounds (Figs. 1-3), and they were satisfactorily assigned to those of the vinyl sulfoxide-added PVA's. The content of sulfoxide introduced to the starting PVA was determined by measuring the signal ratio of the corresponding monomer unit.

The Michael addition reaction of a series of vinyl sulfoxides with PVA was studied in more detail to determine the optimum conditions. A reaction temperature of 60°C and a catalyst concentration of 0.4 mol/L appeared to be the most suitable for the equimolar reaction of vinyl sulfoxide and the PVA repeating unit, as seen in Table 1.

Sulfoxide content saturation along with the reaction time were observed at a relatively early stage regardless of the molecular weight of the starting PVA, as shown in Fig. 8. The sulfoxide content introduced to PVA was observed to remain relatively low under these reaction conditions. NMR analysis of the reaction system revealed that vinyl sulfoxide was completely consumed at this saturation stage. This

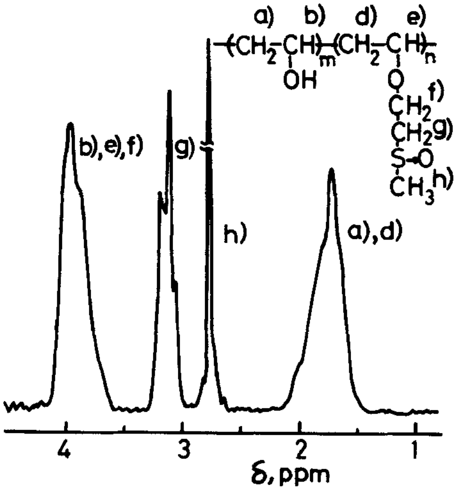

FIG. 5. ^{1}H-NMR spectrum of the addition product between methyl vinyl sulfoxide and poly(vinyl alcohol) (D_2O, 270 MHz, sulfoxide content 60 mol%).

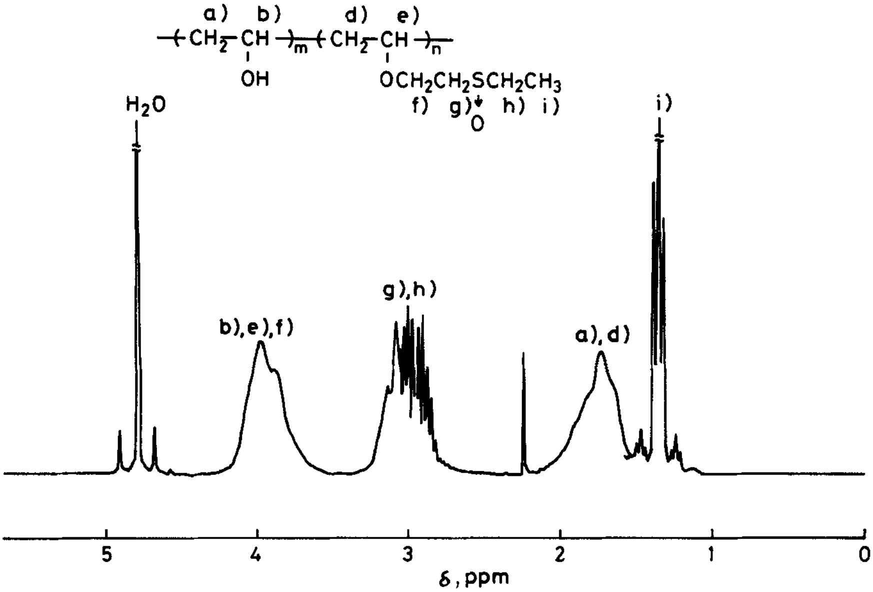

FIG. 6. ^{1}H-NMR spectrum of the addition product between ethyl vinyl sulfoxide and poly(vinyl alcohol) (D_2O, 270 MHz, sulfoxide content 51 mol%).

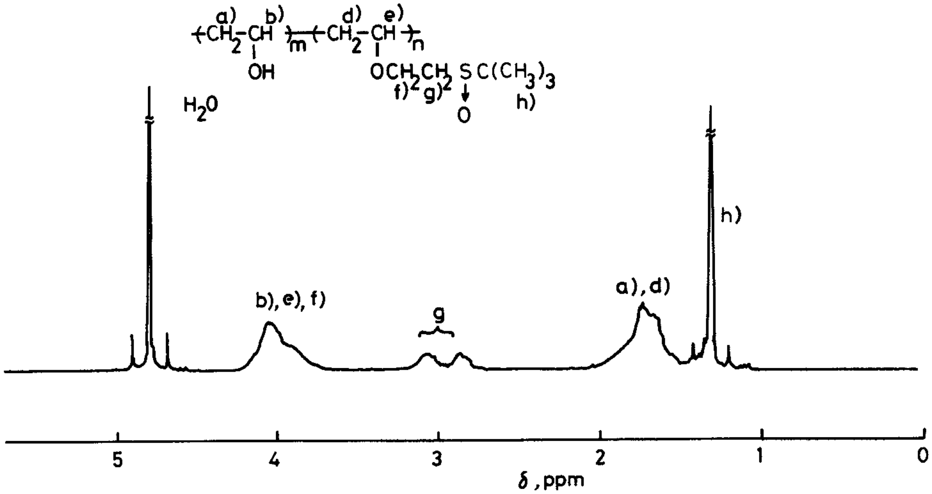

FIG. 7. ^{1}H-NMR spectrum of the addition product between t-butyl vinyl sulfoxide and poly(vinyl alcohol) (D_2O, 270 MHz, sulfoxide content 9 mol%).

TABLE 1. Reaction of Methyl Vinyl Sulfoxide with Poly(Vinyl Alcohol)[a]

NaOH, mol/L	Temperature, °C	Sulfoxide content, mol%
0.9	10	0
0.9	30	6.1
0.9	60	14.3
0.9	80	8.3
0.1	60	7.7
0.4	60	12.9
0.9	60	14.3

[a] PVA, 0.9 unit mol/L; MVSO, 0.9 mol/L, 5 h.

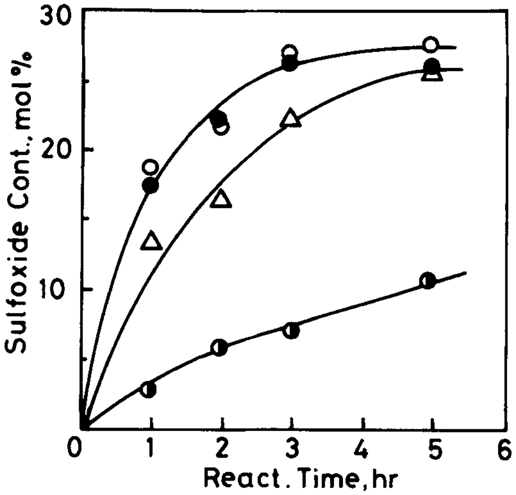

FIG. 8. Time-sulfoxide content plots for the reaction of MVSO (○), EVSO (●), and BVSO (◑) with PVA-117H, and of MVSO with PVA-105 (△). Vinyl sulfoxide, 2.1 mol/L; PVA, 0.7 unit mol/L; NaOH, 0.3 mol/L; 60°C.

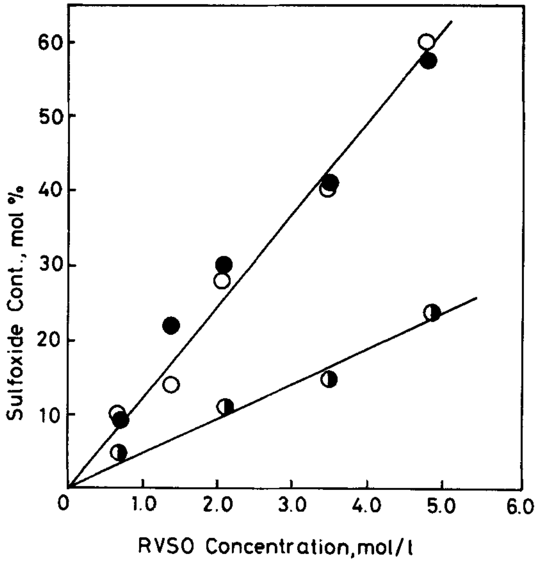

FIG. 9. Sulfoxide content versus vinyl sulfoxide concentration for the reaction of MVSO (○), EVSO (●), and BVSO (◑) with PVA. PVA-117H, 0.7 unit mol/L; NaOH, 0.3 mol/L; 5 h; 60°C.

is apparently due to a competitive reaction, the addition reaction of water with vinyl sulfoxide, as noted in the model reaction systems.

An excess amount of vinyl sulfoxide was required in this addition reaction in order to increase the sulfoxide content on PVA. As shown in Fig. 9, the sulfoxide content increases in proportion to the amount of vinyl sulfoxide charged in the reaction system. A sulfoxide content of up to 60% was obtained when using MVSO and EVSO, while it increases slowly to 25% when using BVSO.

Viscosity measurements of a series of sulfoxide modified PVA's were carried out in aqueous solution in order to examine the effects of the type of alkyl substituent of vinyl sulfoxide on solution properties. As summarized in Table 2, the solution viscosity of PVA's modified with MVSO or EVSO did not change appreciably despite the increase of the sulfoxide content. In contrast, the solution viscosity of PVA's modified with BVSO decreased substantially along with an increase of vinyl sulfoxide content. Since the degradation of PVA is not likely under the present reaction condition, the increase of hydrophobic, bulky t-butyl groups on PVA appears to cause some polymer coil shrinkage in water.

The solubility behavior of a series of sulfoxide-modified PVA's with various sulfoxide contents was examined. The sulfoxide group is expected to affect the solubility of PVA and give it an amphiphilic character. The solubility properties of PVA modified with the sulfoxide group are summarized in Tables 3 and 4. Along with the increase of sulfoxide content, the modified polymer becomes soluble in alcohols and even in methylene chloride, while it remains soluble in water.

TABLE 2. Solution Viscosity of Sulfoxide-Modified Poly(Vinyl Alcohol)s with Various Sulfoxide Content[a]

MPVA		EPVA		BPVA	
Sulfoxide content, mol%	$(\ln \eta_r)/C$, dL/g	Sulfoxide content, mol%	$(\ln \eta_r)/C$, dL/g	Sulfoxide content, mol%	$(\ln \eta_r)/C$, dL/g
0	0.87	0	0.87	0	0.87
10.2	0.82	10.0	0.74	7.1	0.72
14.1	0.82	22.0	0.72	14.5	0.59
27.7	0.84	30.0	0.72	26.1	0.44
40.0	0.82	40.9	0.79	-	-
60.0	0.84	58.3	0.75	-	-

[a] In water at 30°C.

TABLE 3. Solubility of Poly(Vinyl Alcohol) Modified with Methyl Vinyl Sulfoxide[a]

Sulfoxide content, mol%	Solvent[b]					
	CH_3COCH_3	CH_2Cl_2	C_2H_5OH	CH_3OH	DMSO	H_2O
0	x	x	x	x	o	o
14.1	x	x	x	x	o	o
27.7	x	x	x	o	o	o
40.0	x	△	o	o	o	o
60.0	x	o	o	o	o	o

[a] At room temperature.
[b] (o) Soluble, (△) partly soluble, (x) insoluble.

TABLE 4. Solubility of Poly(Vinyl Alcohol) Modified with Ethyl Vinyl Sulfoxide[a]

Sulfoxide content, mol%	Solvent[b]					
	CH_3COCH_3	CH_2Cl_2	C_2H_5OH	CH_3OH	DMSO	H_2O
0	x	x	x	x	o	o
10.0	x	x	x	x	o	o
22.0	x	x	x	△	o	o
30.0	x	x	△	o	o	o
40.9	x	△	o	o	o	o
58.3	x	△	o	o	o	o

[a] At room temperature.
[b] (o) Soluble, (△) partly soluble, (x) insoluble.

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