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Syntheses of Vinyl Sulfoxide/Vinyl Acetate-Type Copolymers

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ABSTRACT

The homopolymerization of a series of alkyl vinyl sulfoxides (CH_2=CHSOR; R = CH_3 (MVSO), C_2H_5 (EVSO), t-C_4H_9 (BVSO)) and their copolymerization with vinyl acetate (VAc) with 2,2'-azobisisobutyronitrile (AIBN) as initiator at 60°C was attempted. MVSO was found to homopolymerize radically, but EVSO and BVSO were not. Poly-MVSO is soluble in chloroform, methanol, DMSO, and water, but insoluble in acetone and benzene. MVSO and EVSO were found to copolymerize with VAc, but BVSO was not. The copolymerization parameters obtained for both systems were as follows; r_1(MVSO) = 2.23, r_2 (VAc) = 0.09, and r_1(EVSO) = 3.40, r_2 (VAc) = 0.11, respectively. MVSO/vinyl alcohol (VA) copolymers were obtained through the saponification of MVSO/VAc copolymers by sodium hydroxide in methanol. The solubility of MVSO/VAc and of MVSO/VA copolymers toward various sol-

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vents was examined, and it was observed that the sulfoxide comonomer has a tendency to give amphiphilicity to poly(vinyl acetate) and poly(vinyl alcohol). The 24 mol% MVSO containing VAc copolymer is soluble in both benzene and water.

INTRODUCTION

Sulfoxide-modified polymers are considered to be potentially attractive for functional polymer materials, since DMSO and other sulfoxide compounds have shown increasing application possibilities by exploitation of their unique behavior as solvent and reagent. Thus, the methacrylate derivative with a sulfoxide group was synthesized [1] and shown to be useful as a polymeric drug carrier [2]. Styrene derivatives containing a sulfoxide group have recently been synthesized [3, 4] and used as phase transfer catalysts [5] and polymeric chelating reagents [4].

Alkyl vinyl sulfoxide is another facile monomer used to introduce sulfoxide moiety onto the polymer chain, but vinyl sulfoxide was reported to fail to homopolymerize [6, 7]. The study of the copolymerization of vinyl sulfoxide has been restricted to a limited number of conjugated monomers such as styrene and methyl methacrylate [6, 7].

The present paper reports the radical homopolymerization of a series of alkyl vinyl sulfoxides and the copolymerization of vinyl sulfoxides with vinyl acetate, a nonconjugated monomer. The saponification of the vinyl sulfoxide/vinyl acetate copolymer was used to prepare the vinyl sulfoxide/vinyl alcohol copolymer.

EXPERIMENTAL

Reagents

Methyl vinyl sulfoxide (MVSO) was synthesized by $NaIO_4$ oxidation at 0°C [8] of methyl vinyl sulfide (prepared in 90% yield from 2-methyl thioethanol according to Price and Gillis [9] in 79% yield (bp 50-50.5°C/4 mmHg; 52°C/3 mmHg in Ref. 6). Ethyl vinyl sulfoxide (EVSO) was prepared similarly from ethyl vinyl sulfide (in 95% yield from commercial 2-ethyl thioethanol) in 76% yield (bp 54°C/2 mmHg; 54-54.5°C/2 mmHg in Ref. 7). tert-Butyl vinyl sulfoxide (BVSO) was obtained by $NaIO_4$ oxidation at 15°C from tert-butyl vinyl sulfide [9] (in 95% yield from 2-tert-butyl thioethanol) in 61% yield (bp 68-70°C/4 mmHg; IR: C=C 1599 cm^{-1}, S–O 1058 cm^{-1}; ^{1}H-NMR (CCl_4, TMS): δ = 1.20 (s, 9H) 5.83 (dd, 1H), 6.05 (dd, 1H), 6.61 (dd, 1H)).

Vinyl acetate (VAc) was purified by distillation under reduced pressure in the presence of AIBN just before use. Dimethyl sulfoxide (DMSO) was distilled under reduced pressure and stored under dry nitrogen. 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol.

Homopolymerization

A definite amount of vinyl sulfoxide, AIBN, and solvent was charged in a Pyrex ampule tube and the mixture solution was flushed with dry nitrogen. The sealed tube was then placed in a bath thermostated at 60°C. After an appropriate period the reaction mixture was poured in CCl_4. The polymer obtained was purified by reprecipitation from methanol/CCl_4 system.

Copolymerization

The copolymerization of vinyl sulfoxide with vinyl acetate was performed either in bulk or in solution by keeping the reaction medium homogeneous. The copolymer obtained was isolated by pouring the reaction mixture into petroleum ether and purified by reprecipitation from the methanol/petroleum ether system.

Saponification of MVSO/VAc Copolymer

The saponification of MVSO/VAc copolymers was carried out by using methanolic NaOH as reported previously [10]. The resulted MVSO/VA copolymer, with a MVSO content of less than 27 mol%, was isolated by filtration and washed with methanol. The copolymer, which had a sulfoxide content of more than 27 mol%, was isolated by precipitation into acetone and purified by reprecipitation from the methanol/acetone system.

Measurements

The ^{1}H-NMR spectrum was recorded with a JEOL FX-270 apparatus. The IR spectrum was observed by a Hitachi Model 260-10 infrared spectrophotometer. Viscosity measurements were carried out by using an Ostwald viscometer at 30°C.

RESULTS AND DISCUSSION

Homopolymerization of Alkyl Vinyl Sulfoxides

Contrary to previous reports [6, 7] that the radical homopolymerization of alkyl vinyl sulfoxides is too sluggish to produce isolatable

TABLE 1. Polymerization of Alkyl Vinyl Sulfoxides (RVSO)[a]

RVSO	Solvent	Time, h	Yield, wt%	$(\ln \eta_r)/C$,[b] dL/g
MVSO	None	30	6	0.05
MVSO	H_2O[c]	30	7	0.07
EVSO	None	30	0.1	-
BVSO	None	30	0	-

[a] At 60°C, AIBN: 0.4 wt%.
[b] In DMSO at 30°C.
[c] $MVSO/H_2O = 1/1$ (mol/mol).

polymer, MVSO was found to homopolymerize by AIBN either in bulk or in H_2O as shown in Table 1. EVSO and BVSO failed to homopolymerize under these reaction conditions. The poly-MVSO obtained was soluble in chloroform, methanol, DMSO, and water but insoluble in benzene and acetone.

Copolymerization of Alkyl Vinyl Sulfoxides with Vinyl Acetate

The copolymerization of VAc with a series of alkyl vinyl sulfoxides was attempted since the copolymerizability of alkyl vinyl sulfoxide with a nonconjugated monomer such as vinyl acetate has not been examined previously.

MVSO was found to copolymerize with VAc in a wide range of initial comonomer ratios, while EVSO copolymerized with VAc in the limited initial comonomer composition. BVSO showed no copolymerizability with VAc.

The copolymerizations of MVSO/VAc and EVSO/VAc systems were carried out at various initial comonomer compositions in order to determine the monomer reactivity ratios. The results are summarized in Tables 2, 3, and 4. The ^{1}H-NMR spectrum of a typical MVSO/VAc copolymer is shown in Fig. 1. The comonomer unit ratio in the copolymers obtained was determined from ^{1}H-NMR peak area for each comonomer component. Sulfur elementary analysis was carried out for some samples. Both analyses showed good agreement, as shown in Table 2. DMSO as the solvent appeared to have no effect on the comonomer composition in these systems.

Monomer reactivity ratios for the MVSO/VAc and EVSO/VAc systems were calculated according to the method described by Kelen and Tüdős [11] as shown in Fig. 2. Monomer reactivity ratios for the MVSO/VAc and EVSO/VAc systems were thus obtained as follows;

TABLE 2. Copolymerization of Methyl Vinyl Sulfoxide with Vinyl Acetate in Bulk at 60°C

Monomer feed, mol%					MVSO in copolymer, mol%	
MVSO	VAc	AIBN, wt%	Time, h	Yield, wt%	From sulfur analysis	NMR
1.0	99.0	0.1	3	4	7.2	9.1
1.9	98.1	0.1	4	2	14.7	18.3
2.9	97.1	0.1	9	4	17.6	20.3
3.8	96.2	0.1	9	3	22.4	23.8
4.8	95.2	0.2	8	4	-	27.4
6.7	93.3	0.2	10	3	-	37.3
9.6	90.4	0.2	10	2	-	44.7

TABLE 3. Copolymerization of Methyl Vinyl Sulfoxide with Vinyl Acetate in DMSO[a]

Monomer feed, mol%					
MVSO	VAc	AIBN, wt%	Time, h	Yield, wt%	MVSO in copolymer, mol%
4.8	95.2	0.2	4	4	25.8
14.4	85.6	0.4	9.5	4	47.9
24.1	75.9	0.4	10	3	57.4
33.9	66.1	0.4	10	3	64.3
48.9	51.1	0.4	11	3	74.5
63.9	36.1	0.4	11	1	82.6
74.2	25.8	0.4	11	1	86.6

[a] At 60°C, DMSO: 50 wt%.

TABLE 4. Copolymerization of Ethyl Vinyl Sulfoxide with Vinyl Acetate[a]

Monomer feed, mol%		Time, h	Yield, wt%	EVSO in copolymer, mol%
EVSO	VAc			
1.1	98.9	15	2.8	8.5
2.0	98.0	15	1.7	13.9
4.2	95.8	24	0.4	26.7
8.4	91.6	24	0.1	39.5
12.6	87.4	24	-[b]	48.6
16.8	83.2	24	-[b]	51.1
21.0	79.0	24	-[b]	56.0

[a] At 60°C, AIBN: 0.2 wt%.
[b] Below 0.1 wt%.

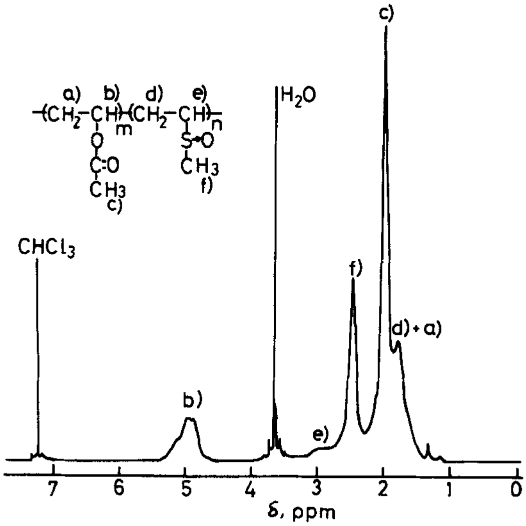

FIG. 1. 270 MHz ^{1}H-NMR spectrum of methyl vinyl sulfoxide/vinyl acetate copolymer (in $CDCl_3$, MVSO 37 mol%).

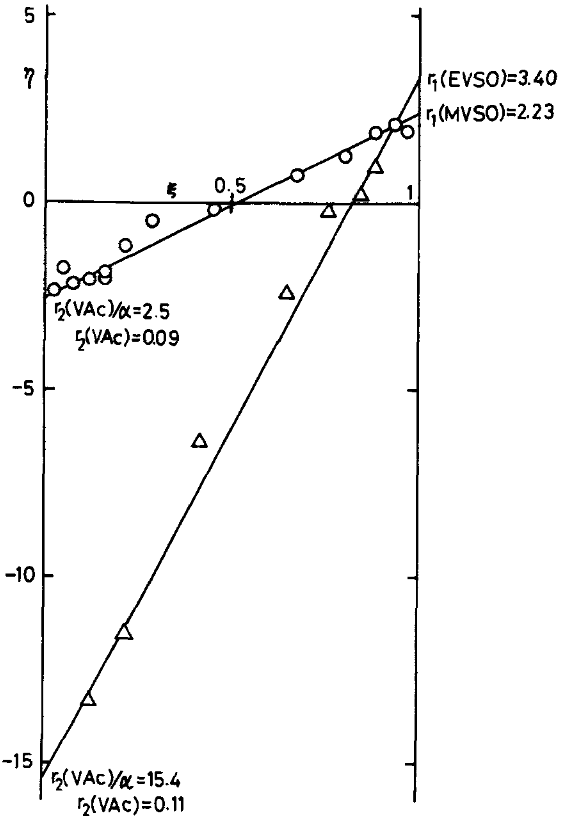

FIG. 2. Kelen-Tüdős plots for (○) methyl vinyl sulfoxide/vinyl acetate and for (△) ethyl vinyl sulfoxide/vinyl acetate systems.

r_1(MVSO) = 2.23 and r_2(VAc) = 0.09

r_1(EVSO) = 3.40 and r_2(VAc) = 0.11

The calculated monomer copolymer composition curves reproduce satisfactorily the experimental points for both systems as listed in Figs. 3 and 4.

From the monomer reactivity ratios for the MVSO/VAc and EVSO/VAc systems, the resonance stabilization factor Q and the electrical factor e [12] were calculated, using the Q and e values of VAc as 0.03 and -0.3 [13], respectively. As listed in Table 5, Q and e values for both MVSO and EVSO are consistent with the reported

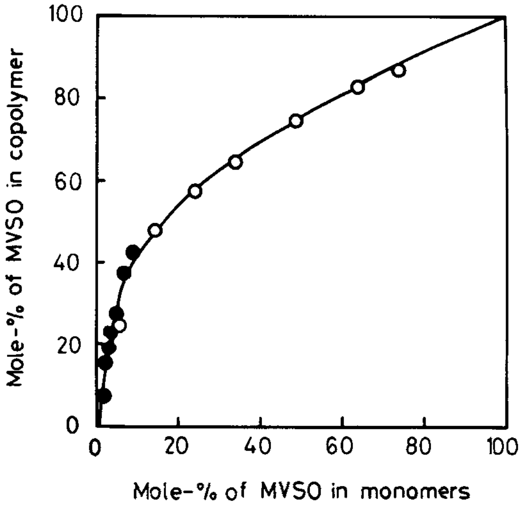

FIG. 3. Monomer-copolymer composition curve of methyl vinyl sulfoxide and vinyl acetate: (●) in bulk, (○) in solution.

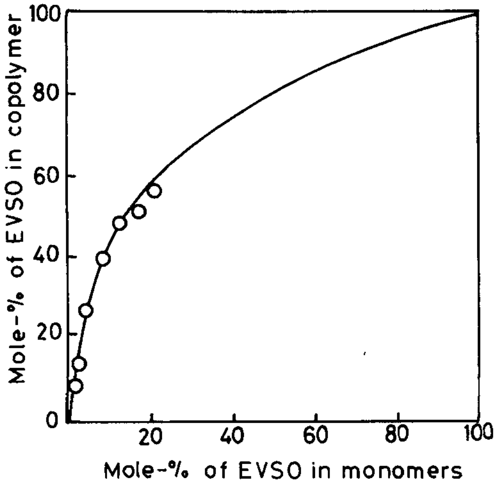

FIG. 4. Monomer-copolymer composition curve of ethyl vinyl sulfoxide and vinyl acetate.

TABLE 5. Copolymerization Parameters of Methyl Vinyl Sulfoxide and Ethyl Vinyl Sulfoxide at 60°C

M_1	M_2	r_1	r_2	Q_1	e_1	Ref.
MVSO	VAc	2.23	0.09	0.2	1.0	Present study
MVSO	St	0.01	4.2	0.1	0.9	6
EVSO	VAc	3.40	0.11	0.2	0.8	Present study
EVSO	St	0.02	7.0	0.1	0.6	7

ones, which were estimated from copolymerization with styrene [6, 7]. Both vinyl sulfoxides are considered to be modestly conjugated and electron deficient monomers because of the electron-withdrawing character of the sulfoxide group.

Preparation of MVSO/VA Copolymer

MVSO/VA copolymer was obtained through the saponification of MVSO/VAc copolymer by methanolic sodium hydroxide. The IR spectroscopic analysis of MVSO/VAc and MVSO/VA copolymer, given in Fig. 5, shows the absence of the carbonyl band at 1740 cm^{-1} for the latter copolymer, indicating that complete saponification of the VAc component in the copolymer was attained.

The MVSO content in the MVSO/VA copolymers was estimated from the ^{1}H-NMR spectrum of the copolymer (Fig. 6) and compared with those of the starting MVSO/VAc copolymers. The results are shown in Table 6. The copolymer composition was found to be intact during the saponification reaction. Table 6 shows that the copolymer viscosity decreases with increasing MVSO content, suggesting some lowering of the molecular weight.

Solubility of MVSO/VAc and MVSO/VA Copolymers

The solubility of MVSO/VAc and of MVSO/VA copolymers against various solvents was examined. As summarized in Tables 7 and 8, the introduction of vinyl sulfoxide groups to VAc or VA polymers strongly affects the solubility of the copolymers obtained. It should be noted that MVSO/VAc copolymer is soluble in water and also soluble in a wide variety of organic solvents. As a typical example, MVSO/VAc copolymer (24/76 mol%) is soluble in benzene, acetone, chloroform, DMSO, and water. MVSO/VA copolymer becomes soluble in methanol by increasing the MVSO content up to 28 mol%.

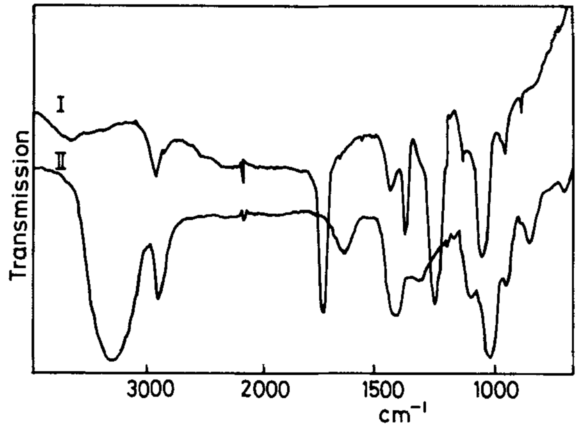

FIG. 5. IR spectra of (I) methyl vinyl sulfoxide/vinyl acetate copolymer and (II) methyl vinyl sulfoxide/vinyl alcohol copolymer.

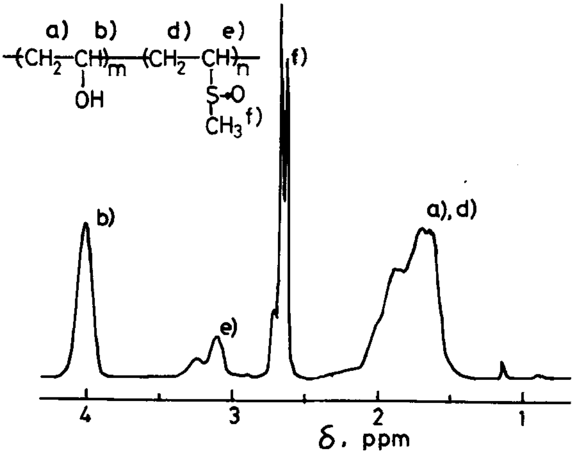

FIG. 6. 270 MHz ^{1}H-NMR spectrum of methyl vinyl sulfoxide/vinyl alcohol copolymer (in D_2O, MVSO 37 mol%).

TABLE 6. Comonomer Composition and Inherent Viscosity of Methyl Vinyl Sulfoxide/Vinyl Acetate and Vinyl Alcohol Copolymers

MVSO/VAc copolymer		MVSO/VA copolymer	
MVSO, mol%	$(\ln \eta_r)/C$,[a] dL/g	MVSO, mol%	$(\ln \eta_r)/C$,[b] dL/g
9.1	0.35	10.9	0.52
20.3	0.15	20.5	0.26
27.4	0.10	28.2	0.15
37.3	0.08	33.7	0.12

[a] In acetone at 30°C.
[b] In water at 30°C.

TABLE 7. Solubility of Methyl Vinyl Sulfoxide/Vinyl Acetate Copolymer[a]

MVSO in copolymer, mol%	Solvent					
	C_6H_6	CH_3COCH_3	$CHCl_3$	CH_3OH	DMSO	H_2O
0	○	○	○	○	○	×
20.0	○	○	○	○	○	△
23.8	○	○	○	○	○	○
37.3	△	○	○	○	○	○
47.9	×	×	○	○	○	○
57.9	×	×	○	○	○	○
100	×	×	○	○	○	○

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

TABLE 8. Solubility of Methyl Vinyl Sulfoxide/Vinyl Alcohol Copolymer[a]

MVSO in copolymer, mol%	Solvent					
	CH_3COCH_3	CH_2Cl_2	C_2H_5OH	CH_3OH	DMSO	H_2O
0	x	x	x	x	o	o
20.5	x	x	x	x	o	o
28.2	x	x	x	o	o	o
43.9	x	x	x	o	o	o
56.2	x	x	x	o	o	o

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

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