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Preparation and Free-Radical Polymerizations of Methyl-4-vinylphenylsulfoxide and Methyl-4-vinylbenzylsulfoxide

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ABSTRACT

Methyl-4-vinylphenylsulfoxide (1) was prepared by the selective oxidation of 4-methylthiostyrene with sodium metaperiodate in 87% yield. This monomer was readily homopolymerized in DMSO by AIBN at 60° C. The polymer obtained is soluble in ethanol, chloroform, DMSO, and DMF, but insoluble in water, benzene, and petroleum ether. The inherent viscosity of this polymer was 0.33 dL/g in DMSO. This sulfoxide monomer (1) was copolymerized with styrene, methyl methacrylate, acrylonitrile, and acrylamide under radical conditions. From the copolymerization with styrene, copolymerization parameters were obtained as follows; $r_1 = 0.56$, $r_{St} = 0.26$, and $Q_1 = 1.19$, $e_1 = 0.58$. Similarly, methyl-4-vinylbenzylsulfoxide (2) was prepared, and the polymerizability of (2) was also investigated.

INTRODUCTION

Dimethylsulfoxide (DMSO) is potentially a very valuable reagent and solvent for organic syntheses. In 1967, Oda et al. [1] tried to prepare a polymer containing DMSO structure and obtained poly(methylsulfinylethyl acrylate), which is soluble in water. After that, Ringsdorf et al. [2] found that this polymer worked as a pharmaceutical agent. Further, sulfoxide polymer membrane was found to have high degree of permeation for polar molecules [3]. Thus sulfoxide polymers have attracted much attention as functional polymers.

Recently Kakiuchi et al. [4] reported that polymeric phosphoramides catalyzed phase-transfer reactions more efficiently than their monomeric analog (HMPA). HMPA, as well as DMSO, is known as a useful dipolar aprotic solvent. Considering their work, it might be expected that sulfoxide polymers play the same role as polymeric phosphoramide in organic reactions. Unfortunately, most of the reported polymers have another functional group, such as carbonyl or hydroxy group, together with the sulfinyl group [1-3]. Therefore, these polymers are not suitable for catalyst use under basic conditions because of their stability.

Meanwhile, Price [5] and Otsu [6] studied the radical polymerizability of vinylsulfoxides independently and found that these monomers scarcely homopolymerize and that the reactivity of copolymerization is very low. The same results were obtained in the preparation of optically active sulfoxide polymer [7]. From these results, polymers which have the sulfinyl group in high concentration could not be obtained by the polymerization of vinylsulfoxides.

Therefore, in order to study the relationship between structure and function, a new monomer which readily polymerizes and does not have another functional group except for the sulfinyl group is required. We report here the preparation of 4-vinylphenylsulfoxide (1) and of methyl-4-vinylbenzylsulfoxide (2), and the free-radical copolymerization of these monomers.

EXPERIMENTAL

Preparation of Methyl-4-vinylphenylsulfoxide (1)

A solution of sodium metaperiodate (27.8 g, 0.13 mol) in water (100 mL) was added slowly to a solution of methyl-4-vinylphenylsulfide (15 g, 0.1 mol) in methanol (450 mL) and water (100 mL) at 0°C. Then the sodium iodate produced was filtered off, and the filtrate was diluted with water (300 mL), extracted three times with chloroform (100 mL), and dried with sodium sulfate. Evaporation of the solvent gave a white solid which was recrystallized by n-hexane. The yield was 12 g (72%), mp 42-43°C. IR (KBr): 3050, 2980, 1622, 1492, 1394, 1304, 1149, 1082, 1040, 991, 927, 833 cm^{-1}. NMR ($CDCl_3$): 2.70 (s, 3H), 5.33 (dd, 1H), 5.79 (dd, 1H), 6.76 (dd, 1H), 7.55 ppm (m, 4H). UV: λ_{max} = 262 nm (ϵ = 21500) in ethanol.

Analysis: Calculated for $C_9H_{10}OS$: 65.06; H, 6.02; S, 19.28%. Found: C, 64.54; H, 6.20; S, 19.40%.

For hydrogen peroxide oxidation, a solution of methyl-4-vinylphenylsulfide (10 g, 0.067 mol) and 30% hydrogen peroxide (7.5 g, 0.067 mol) in acetic acid (100 mL) was stirred for 24 h at room temperature. After neutralization with a 20% aqueous solution of sodium hydroxide, the product was extracted with chloroform and dried. Evaporation of the solvent and recrystallization with n-hexane gave the desired product (1.1 g, 10%).

Preparation of Methyl-4-vinylbenzylsulfide

4-Chloromethylstyrene [8] (53.1 g, 0.35 mol) was added to a solution of sodium methylmercaptide (30 g, 0.43 mol) in 400 mL of ethanol at room temperature. After stirring for 5 h at 60°C, the reaction mixture was cooled and poured into a large amount of water. It was then extracted with ether and dried with sodium sulfate. The desired product was obtained by distillation, bp 95-98°C/3 torr (Ref. 9, 93-99°C/3 torr). The yield was 38 g (66%).

Preparation of Methyl-4-vinylbenzylsulfoxide (2)

The same procedure as described for (1) was used on a half scale. The yield was 16.3 g (85%), mp 60-61.5°C. IR (KBr): 2900, 1622, 1500, 1405, 1300, 1105, 1025, 985, 940, 915, 842 cm^{-1}. NMR ($CDCl_3$): 2.45 (s, 3H), 3.95 (s, 2H), 5.25 (dd, 1H), 5.70 (dd, 1H), 6.72 (dd, 1H), 7.35 ppm (m, 4H). UV: λ_{max} = 283 nm (ϵ = 11400) in ethanol.

Analysis: Calculated for $C_{10}H_{12}OS$: C, 66.67; H, 6.67; S, 17.78%. Found: C, 66.27; H, 6.70; S, 17.83%.

Other Reagents

Styrene, methyl methacrylate, and acrylonitrile used as comonomer were purified by ordinary methods and distilled under nitrogen just before use. Acrylamide was purified by recrystallization from ethanol. 2,2'-Azobisisobutyronitrile (AIBN) used as an initiator was recrystallized twice from methanol. Other reagents and solvents were used after purification.

Polymerization of Methyl-4-vinylphenylsulfoxide (1)

A solution of (1) (0.50 g, 3 mmol), AIBN (8.2 mg, 0.05 mmol), and freshly distilled DMSO was charged into a polymerization tube. The tube was degassed by the freezing and thawing technique, and sealed under vacuum. After 8 h at 60° C, the tube was opened. The reaction mixture was poured into 100 mL of ether to precipitate the polymer. The solvent was decanted, and then the polymer was dissolved in 2 mL of chloroform and reprecipitated with 100 mL of petroleum ether. The polymer was dried for overnight under vacuum. The yield was 0.403 g (80.6%).

Analysis: Calculated for $(C_9H_{10}OS)_n$: C, 65.06; H, 6.02; S, 19.28%. Found: C, 64.77; H, 6.35; S, 19.81%.

The IR spectrum (KBr) showed an absorption at 1040 cm^{-1} (S=O), but did not show at 991 and 927 cm^{-1} (=CH_2).

The inherent viscosity of this polymer was measured in DMSO at 30° C.

Polymerization of Methyl-4-vinylbenzylsulfoxide (2)

The same procedure as described for (1) was used. The yield of the polymer was 58%.

Analysis: Calculated for $(C_{10}H_{12}OS)_n$: C, 66.67; H, 6.67; S, 17.78%. Found: C, 66.13; H, 6.22; S, 17.52%.

The IR spectrum showed a characteristic absorption band of sulfoxide at 1030 cm^{-1}.

Copolymerization of (1) and (2) with Styrene

Copolymerization was carried out by the same method as mentioned previously [8]. After copolymerization for a given time, the tube was opened and its contents were poured into a large amount of ether to precipitate the copolymer. The solvents were decanted, and the copolymer obtained was purified by the reprecipitation of the chloroform solution with petroleum ether.

The composition of the copolymers was calculated from their elementary analysis of sulfur by the Wagner method [10] using arsenazo III as indicator [11]. Monomer reactivity ratios (r_1 and r_2) were obtained by the Fineman-Ross method and confirmed by the curve-fitting method.

Copolymerization of (1) with Some Vinyl Monomers

The general method is as follows. A solution of (1) (3 mmol), each vinyl monomer (3 mmol), and AIBN (0.05 mmol) in DMSO was heated in a sealed tube at 60°C for 20 h. The reaction mixture was poured into a large amount of ether. The copolymer obtained was reprecipitated from the chloroform solution by petroleum ether. Copolymers were confirmed by characteristic absorptions of IR spectra.

Instruments

IR spectra were recorded on a JASCO IRA-2 spectrometer. NMR spectra were recorded in deuteriochloroform on a 60 MHz Hitachi R-20B spectrometer using tetramethylsilane as an internal standard.

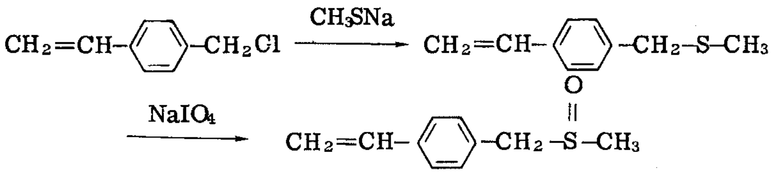
RESULTS AND DISCUSSION

Preparations of Vinyl Monomers Containing Sulfinyl Group

Methyl-4-vinylphenylsulfoxide (1) and methyl-4-vinylbenzylsulfoxide (2) were prepared as follows:

(1)

(1)



(2)

(2)

Though several methods have been developed for the oxidation of sulfide to the corresponding sulfoxide, the oxidation of olefinic sulfide is complicated by the possibility of epoxidation of the double bond and overoxidation to yield sulfone. Fortunately, we obtained methyl-4-vinylphenylsulfoxide (1) by the selective oxidation of the corresponding sulfide using sodium metaperiodate by a modification of the procedure of Leonard and Johnson [12]. The desired sulfoxide monomer was obtained quantitatively by the use of sodium metaperiodate in aqueous methanol at 0°C. An alternative procedure which was employed for the preparation of alkylvinylsulfoxide [5] (that is, treatment with hydrogen peroxide in acetic acid) led to only 10% yield of the desired sulfoxide. Compound (2) was similarly prepared by the use of 4-chloromethylstyrene as the starting material (Eq. 2). The

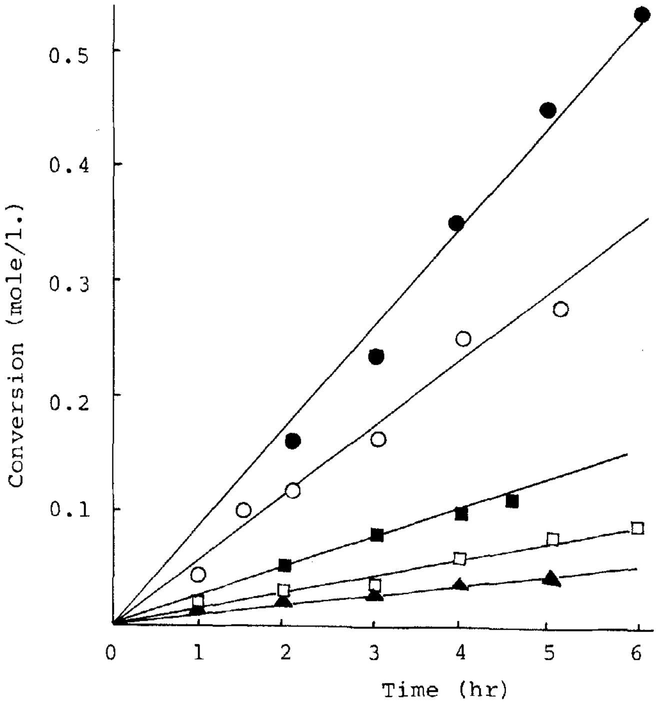


FIG. 1. Time conversions of radical polymerizations of some sulfur-containing monomers. [AIBN] = 10^{-2} mol/L. CH_3CN = 5 mL. (●) Dimethyl-4-vinylphenylsulfonium tetrafluoroborate. (○) Methyl-4-vinylphenylsulfoxide. (■) Methyl-4-vinylbenzylsulfoxide. (□) Styrene. (▲) Methyl-4-vinylphenylsulfide.

TABLE 1. Overall Rates (R_p) of Thermal Polymerization of Several 4-Substituted Styrenes[a]

Substituent	$R_p \times 10^6$ (mol/L·s)
SCH_3	2.22
H	2.60[b]
CH_2SOCH_3	3.61
$SOCH_3$	6.48
$^+S(CH_3)_2$	9.20[b]

[a] [AIBN] = 1×10^{-2} mol/L, CH_3CN = 5 mL.
[b] Ref. 14.

TABLE 2. Copolymerization of Methyl-4-vinylphenylsulfoxide (1) with Several Vinyl Monomers at 60°C (Solvent: DMSO)

Comonomer[a]	Time (h)	Conversion (%)	m_1[b]
Methyl methacrylate	20	90.3	0.42
Styrene	1	5.9	0.66
Acrylamide	20	61.1	0.77
Acrylonitrile	20	73.4	0.79

[a] Equimolecular quantities of (1) and comonomer were used.
[b] Mole fraction of (1) in copolymer.

TABLE 3. Copolymerization of Methyl-4-vinylphenylsulfoxide (1) with Styrene (M_2)

M_1[a]	Time (h)	Conversion (%)	S (%)	m_1[b]
0.202	3	8.41	8.49	0.33
0.301	3	10.80	10.12	0.41
0.422	1	5.38	12.68	0.55
0.499	1	5.92	13.23	0.58
0.695	1	6.72	15.05	0.68
0.791	1	8.48	15.67	0.73
0.891	1	9.04	16.32	0.78

[a] Mole fraction of (1) in monomer mixture.
[b] Mole fraction of (1) in copolymer

structure of these products was determined on the basis of the elementary analysis and spectral data.

Homopolymerization

Monomer (1) was successfully polymerized in DMSO with AIBN as an initiator to give poly(methyl-4-vinylphenylsulfoxide) in high yield in contrast with the case of alkylvinylsulfoxide [5, 6]. The polymer obtained was soluble in ethyl alcohol, chloroform, DMF, and DMSO, but insoluble in water, benzene, and petroleum ether, and had an inherent viscosity of 0.33 dL/g is DMSO solution.

Similarly, monomer (2) was readily polymerized to give poly(methyl-4-vinylbenzylsulfoxide) which had an inherent viscosity of 0.41 dL/g in DMSO solution.

The time-conversion curves of polymerization for these monomers and analogous compounds are shown in Fig. 1, from which the overall rates of these monomers were calculated. The results are summarized in Table 1. These results are in agreement with an earlier report [13] that styrenes carrying electron-withdrawing groups polymerize faster than styrene.

Radical Copolymerization with Some Vinyl Monomers

Methyl-4-vinylphenylsulfoxide (1) was copolymerized with methyl methacrylate, styrene, acrylamide, and acrylonitrile at 60° C in the presence of AIBN. The copolymers obtained were confirmed by their IR spectra. The results are summarized in Table 2.

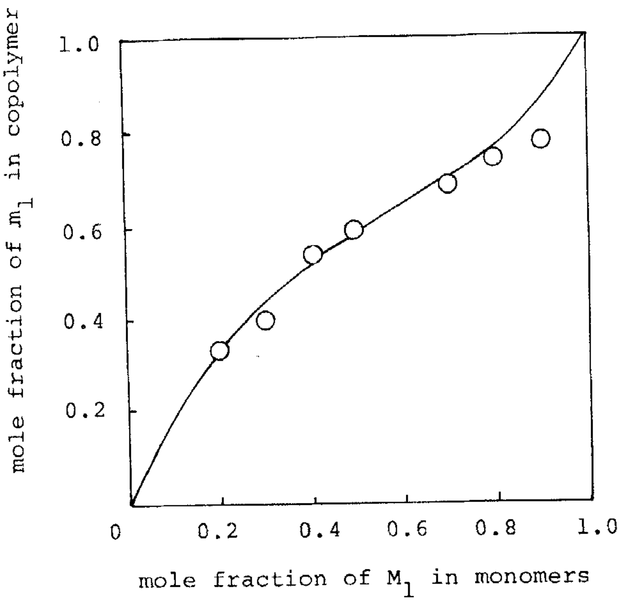


FIG. 2. Monomer-copolymer composition curve of methyl-4-vinylphenylsulfoxide (M_1) and styrene (M_2).

TABLE 4. Copolymerization of Methyl-4-vinylbenzylsulfoxide (2) with Styrene (M_2)

M_1[a]	Time (h)	Conversion (%)	S (%)	m_1[b]
0.103	15	9.97	3.92	0.14
0.202	15	9.64	6.32	0.24
0.301	15	9.97	8.80	0.37
0.422	15	9.90	10.72	0.47
0.499	15	10.80	11.49	0.51
0.604	15	8.85	12.92	0.61
0.695	15	9.55	13.77	0.66
0.791	15	11.96	14.78	0.74
0.891	15	14.90	15.54	0.80

[a] Mole fraction of (2) in monomer mixture.
[b] Mole fraction of (2) in copolymer.

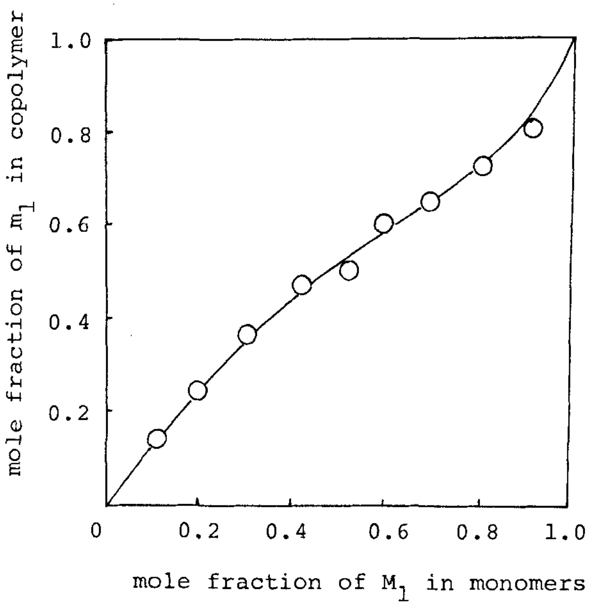


FIG. 3. Monomer-copolymer composition curve of methyl-4-vinylbenzylsulfoxide (M_1) and styrene (M_2).

TABLE 5. Copolymerization Parameters of Several 4-Substituted Styrenes (M_1)

Substituent	M_2	r_1	r_2	Q	e
H				1.0	-0.8
OCH_3 [15]				1.36	-1.48
SCH_3 [14]	Styrene	0.94	0.67	2.58	-1.48
$SOCH_3$	Styrene	0.56	0.26	1.19	0.58
CH_2SOCH_3	Styrene	0.52	0.60	1.03	0.28
$^+S(CH_3)_2$ [14]	Styrene	0.93	0.23	1.61	0.64

In order to clarify the substituent effect of the sulfinyl group in radical polymerization and the copolymerization reactivity of (1), copolymerization of (1) with styrene in DMSO was investigated in detail. The results are shown in Table 3. The composition of the copolymers was calculated from their sulfur content. Figure 2 shows the monomer-copolymer composition curve. The results of copolymerizations of (2) with styrene are shown in Table 4 and Fig. 3.

The monomer reactivity ratio was computed for the copolymerization of (1) and styrene according to the Finemann-Ross method as $r_1 = 0.56$, $r_2 = 0.26$. From these values of the monomer reactivity ratio for this system, the resonance stabilization factor Q and the electrical factor e were calculated [16]. Radical copolymerization parameters of (2) were also calculated. Q and e values of compounds analogous to (1) and (2) are shown in Table 5.

As can be seen from Table 5, the Q value of (1) does not differ from that of styrene and is smaller than that of the corresponding sulfide. The larger Q values of alkylthio- and sulfoniostyrenes than of styrene and alkoxystyrenes were elucidated from the 3d-orbital resonance [14]. Therefore, these results indicate that the sulfinyl group does not participate in the electron-sharing resonance of the propagating species. The same result was obtained in the case of vinyl sulfides and vinyl sulfoxides [5, 6, 17, 18]. The positive e values of these monomers (1) and (2) are reasonable due to the electron-withdrawing character of the sulfinyl group.

A study of the utilization of these polymers for organic synethsis is in progress. The results will be reported elsewhere in the near future.

REFERENCES

[1] T. Ohashi, Y. Hayashi, and R. Oda, Kobunshi Kagaku, 24, 334 (1967).

[2] H. G. Batz, V. Hofmann, and H. Ringsdorf, Makromol. Chem., 169, 323 (1973); V. Hofmann, H. Ringsdorf, and G. Muacevic, Ibid., 176, 1929 (1975).

[3] E. Klein, P. D. May, J. K. Smith, and N. Leger, Biopolymers, 10, 647 (1971).

[4] M. Tomoi, T. Takubo, M. Ikeda, and H. Kakiuchi, Chem. Lett., p. 473 (1976).

[5] C. C. Price and R. D. Gilbert, J. Am. Chem. Soc., 74, 2073 (1952).

[6] H. Inoue, I. Umeda, and T. Otsu, Makromol. Chem., 147, 271 (1971).

[7] J. E. Mulvaney and R. A. Ottaviani, J. Polym. Sci., Part A-1, 8, 2293 (1970).

[8] S. Kondo, T. Ohtsuka, K. Ogura, and K. Tsuda, J. Macromol. Sci.–Chem., A13, 767 (1979).

[9] S. Tanimoto, J. Horikawa, and R. Oda, Kogyo Kagaku Zasshi, 70, 1269 (1969).

[10] H. Wagner, Mikrochim. Acta, p. 19 (1957).

[11] K. Hozumi and K. Umemoto, Microchem. J., 12, 46 (1967).

[12] N. J. Leonard and C. R. Johnson, J. Org. Chem., 27, 282 (1962); J. Am. Chem. Soc., 84, 3701 (1962).

[13] M. Imoto, M. Kinoshita, and M. Nishigaki, Makromol. Chem., 86, 217 (1965).

[14] K. Ogura, S. Kondo, and K. Tsuda, J. Polym. Sci., Polym. Chem. Ed., 19, 843 (1981).

[15] J. Brandrup and E. H. Immergut (eds.), Polymer Handbook, 2nd ed., Wiley, New York, 1975, p. 388.

[16] T. Alfrey, Jr., and C. C. Price, J. Polym. Sci., 5, 10 (1947).

[17] C. C. Price and J. Zomlefer, J. Am. Chem. Soc., 72, 14 (1950).

[18] T. Otsu and H. Inoue, J. Macromol. Sci.–Chem., A4, 35 (1970).

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