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## Radical Copolymerization Behavior of Ethyl Vinyl Sulfoxide

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(Eingegangen am 25. Januar 1971)

### SUMMARY:

The radical copolymerizations of ethyl vinyl sulfoxide (EVSO) with various vinyl monomers were investigated. The copolymerizations of EVSO with styrene, methyl methacrylate and acrylonitrile gave copolymers having minor amounts of EVSO. Vinyl chloride and vinyl acetate, however, did not give any homopolymer and copolymer. From the copolymerization with styrene, EVSO was evaluated as an electron-accepting and non-conjugative monomer:  $Q = 0.13$  and  $e = 0.61$ .

The effects of LEWIS acids ( $\text{LiCl}$ ,  $\text{ZnCl}_2$ ) and proton donors (phenols, alcohols) on the monomer reactivity of EVSO were also investigated. These additives were found to enhance the monomer reactivity of EVSO. From the spectroscopic studies, it was concluded that the rate enhancement in monomer reactivity was attributable to the formation of a complex or to a hydrogen bond formation between the EVSO monomer and these additives.

### ZUSAMMENFASSUNG:

Die radikalische Copolymerisation von Äthylvinylsulfoxid (EVSO) mit verschiedenen Vinyl-Monomeren wurde untersucht. Die Copolymerisation von EVSO mit Styrol, Methylmethacrylat und Acrylnitril führte zu Copolymeren mit sehr geringem Anteil an EVSO. Vinylchlorid und Vinylacetat bildeten jedoch weder ein Homo- noch ein Copolymeres. Aus den Ergebnissen der Copolymerisation mit Styrol folgte, daß EVSO ein Monomeres mit Elektronen-Akzeptor-Eigenschaften und ohne Konjugation darstellt.

Ferner wurde der Einfluß von LEWIS-Säuren ( $\text{LiCl}$ ,  $\text{ZnCl}_2$ ) und Protonen-Donatoren (Phenole, Alkohole) auf die Reaktionsfähigkeit des EVSO untersucht. Es stellte sich heraus, daß diese Zusätze die Reaktionsfähigkeit des EVSO-Monomeren steigerten. Aus spektroskopischen Untersuchungen wurde gefolgert, daß die Steigerung der Reaktivität der Monomeren der Bildung eines Komplexes oder der Ausbildung einer Wasserstoffbrückenbindung zwischen dem EVSO-Monomeren und den Zusätzen zuzuschreiben ist.

### 1. Introduction

In previous papers<sup>1-3)</sup>, the radical polymerizations and copolymerizations of alkyl and *p*-substituted phenyl vinyl sulfides were investigated, and it was found that these vinyl sulfides had to be classified into electron-donating and conjugative monomers.

Vinyl sulfoxide which is a derivative of vinyl sulfide is expected to give an interesting polymer with pendant sulfoxide group by vinyl polymerization. Recently, many organic reactions in which the sulfoxide group can participate have been found, and especially, dimethyl sulfoxide has been used as an important reagent for organic synthesis<sup>4,5</sup>). Thus vinyl sulfoxides can be considered as interesting vinyl monomers, but their polymerization behavior has been little investigated.

In 1952, PRICE and GILBERT<sup>6</sup>) investigated the radical copolymerizations of methyl vinyl sulfoxide with styrene and methyl methacrylate, and they found that the *Q* and *e* values for this monomer were 0.10 and 0.9, respectively. This result indicated that there was a little electronic interaction between the growing radical and the sulfoxide group, which made this monomer electron-accepting. Recently, MULVANEY and OTTAVIANI<sup>7</sup>) synthesized optically active *p*-tolyl vinyl sulfoxide and carried out its radical copolymerization with styrene. KUNIEDA *et al.*<sup>8</sup>) also investigated the anionic polymerization of optically active *p*-tolyl vinyl sulfoxide.

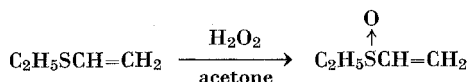
In the present paper, the radical polymerization and copolymerization of ethyl vinyl sulfoxide (EVSO) with various vinyl monomers are investigated. Since the sulfoxide group is known to form a complex with LEWIS acids and to form hydrogen bonds with some proton donors as alcohol or phenol, these effects on the copolymerization of EVSO with styrene are also studied.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Preparation of ethyl vinyl sulfoxide (EVSO)

EVSO used in this study was prepared by oxidation of ethyl vinyl sulfide<sup>3</sup>):



The oxidation of ethyl vinyl sulfide was carried out by the method of PRILEZHAEVA *et al.*<sup>9</sup>) EVSO was purified by repeated distillation in the presence of activated alumina: bp 54.0 to 54.5°C/2 mm Hg (lit.<sup>9</sup>) 54.2°C/2 mm Hg);  $n_D^{20}$  1.4918 (lit.<sup>9</sup>) 1.4900);  $d_4^{20}$  1.0472 (lit.<sup>9</sup>) 1.0422);  $\lambda_{\text{max}}$  in *n*-heptane, 247 m $\mu$ ,  $\epsilon_{\text{max}}$  2540 (lit.<sup>9</sup>)  $\lambda_{\text{max}}$  247 m $\mu$ ,  $\epsilon_{\text{max}}$  2400); stretching frequencies in liquid film, 1601 and 1060 cm<sup>-1</sup> for C=C and S-O bonds, respectively. The chemical shift and coupling constant of the NMR spectrum (neat, tetramethylsilane as internal standard) are shown as follows:

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chemical shift		coupling constant
$\delta_a = 5.98$ ppm	$  \begin{array}{c}  \text{H}^b \quad \quad \text{H}^c \\  \diagdown \quad \diagup \\  \text{C}=\text{C} \\  \diagup \quad \diagdown \\  \text{H}^a \quad \quad \text{S} \rightarrow \text{O} \\  \quad \quad   \\  \quad \quad \text{CH}_2^d \\  \quad \quad   \\  \quad \quad \text{CH}_3^e  \end{array}  $	$J_{ac} = 16.0$ cps
$\delta_b = 6.08$ ppm		$J_{bc} = 10.0$ cps
$\delta_c = 7.06$ ppm		
$\delta_d = 2.82$ ppm		
$\delta_e = 1.17$ ppm		

### 2.1.2. Other reagents

Styrene (St), methyl methacrylate (MMA), acrylonitrile (AN), vinyl acetate (VAc) and vinyl chloride (VC) used as comonomers were purified by usual methods, and used just after distillation.  $\alpha,\alpha'$ -Azobisisobutyronitrile (AIBN) was recrystallized from ethanol. Solvents and additives (*i.e.* benzene, N,N-dimethylformamide (DMF), ethanol and phenol derivatives) were purified by repeated distillations of the commercial materials. The commercial grade lithium chloride and zinc chloride were used after dehydration by heating under vacuum, and stannic chloride was used after distillation.

## 2.2. Polymerization procedure

Polymerizations were carried out in sealed tubes at 60°C. The required amounts of EVSO, comonomer, AIBN, solvent and additive were charged into a hard glass tube. This tube was degassed under vacuum by conventional freeze and thaw technique, and sealed off under vacuum.

All copolymerizations were carried out with shaking, in the absence of external light, to below *ca.* 10% conversion. After an appropriate time, the tube was opened and its content was poured into a large amount of methanol to precipitate the copolymer. The resulting copolymer was then purified by reprecipitation from benzene/methanol system for the copolymers with St and MMA, and DMF/methanol system for the copolymer with AN. When the resulting copolymer was soluble in methanol, the polymerization mixture was poured into a large amount of petroleum ether, and then water was added. The copolymer which had separated out at the interface between petroleum ether and water was collected, and purified by reprecipitation using a benzene/petroleum ether system.

Since there is a possibility for occurrence of cationic polymerization if zinc chloride is used as an additive in the case of the St/EVSO copolymerization, cyclohexane was used as selective solvent to extract the St homopolymer.

The composition of the copolymers was determined from elementary analyses of carbon, sulfur and nitrogen. The monomer reactivity ratios were estimated by a curve fitting method.

## 2.3. Spectroscopic measurements

The IR spectra were measured in carbon tetrachloride with a Jasco IR-G spectrophotometer, using a 0.5 mm NaCl cell. The UV spectra were also measured with a Hitachi EPS-3T spectrophotometer, using a 10 mm quartz cell at room temperature.

## 3. Results and Discussion

## 3.1. Homopolymerizability of EVSO

When EVSO was heated in bulk at 60°C for 40 hrs in the presence of AIBN ( $5 \cdot 10^{-3}$  mole/l.), no polymer was obtained, although the system showed a yellow coloration. Additions of lithium chloride, of zinc chloride, of phenol and of alcohol, which show an effect on the copolymerization, as described later, did not help. This result may be accounted by a degradative chain transfer of the poly(EVSO) radical onto the sulfoxide group

Table 1. Radical copolymerizations of EVSO ( $M_2$ ) with some vinyl monomers ( $M_1$ ) in bulk at 60°C

[M <sub>2</sub> ] in monomers (mole-%)	Time (h)	Conversion (%)	Copolymer obtained	
			C (%)	d [M <sub>2</sub> ] (mole-%)
St (M <sub>1</sub> )/EVSO (M <sub>2</sub> ); [AIBN] = 5·10 <sup>-3</sup> mole/l.				
11.4	2	1.2	91.62	2.2
22.4	3	0.3	90.62	4.2
33.1	6	0.9	89.53	5.9
43.4	10.5	1.0	88.77	7.6
53.5	12	0.8	87.37	10.6
63.4	13	0.8	83.18	19.7
72.9	25.5	1.3 <sup>a)</sup>	82.86	21.4
91.2	18	0.5 <sup>a)</sup>	68.00	52.6
MMA (M <sub>1</sub> )/EVSO (M <sub>2</sub> ); [AIBN] = 1.6·10 <sup>-2</sup> mole/l.				
21.2	3	16.1	(0.81) <sup>b)</sup>	2.6
41.8	3	9.7	(1.68) <sup>b)</sup>	5.6
51.8	4	9.6	(2.56) <sup>b)</sup>	8.3
61.8	4	7.9	(3.53) <sup>b)</sup>	11.5
81.9	7.5	2.9 <sup>a)</sup>	(6.41) <sup>b)</sup>	20.8
AN (M <sub>1</sub> )/EVSO (M <sub>2</sub> ); [AIBN] = 1.6·10 <sup>-2</sup> mole/l.				
6.8	0.3	4.9 <sup>c)</sup>	(22.75) <sup>d)</sup>	6.7
14.1	0.5	2.4 <sup>c)</sup>	(21.97) <sup>d)</sup>	8.5
30.5	0.5	2.0 <sup>c)</sup>	(18.56) <sup>d)</sup>	17.0
49.7	1	0.4	(16.94) <sup>d)</sup>	24.0
60.6	1	0.3	(14.94) <sup>d)</sup>	27.6
72.4	2	0.04	(11.82) <sup>d)</sup>	38.2

<sup>a)</sup> The resulting copolymers are soluble in methanol.

<sup>b)</sup> The values indicate those of the elementary analysis of sulfur.

<sup>c)</sup> The copolymerizations proceeded in heterogeneous system.

<sup>d)</sup> The values indicate those of the elementary analysis of nitrogen.

of EVSO monomer. A similar explanation may be given for the failure of copolymerizations of EVSO and VC or VAc, which give reactive polymer radicals (see 3.2). However, since the chain transfer constants to dimethyl sulfoxide in the radical polymerizations of AN, St, and MMA have been reported to be appreciably small<sup>10,11</sup>, the chain transfer to EVSO in the polymerizations of these conjugative monomers should be less important, differing from reaction of N-oxide with AIBN<sup>12</sup>).

### 3.2. Radical copolymerizations with some vinyl monomers

The results of radical copolymerizations of EVSO ( $M_2$ ) and St, MMA or AN ( $M_1$ ) are shown in Table 1 and the resulting composition curves are shown in Fig. 1. From Table 1, the monomer reactivity ratios obtained are summarized in Table 2.

Table 2. Monomer reactivity ratios for radical copolymerizations of EVSO ( $M_2$ ) and some vinyl monomers ( $M_1$ )

$M_1$	$r_1$	$r_2$
St	7.0	0.02
MMA	10.0	0.01
AN	3.0	0.2

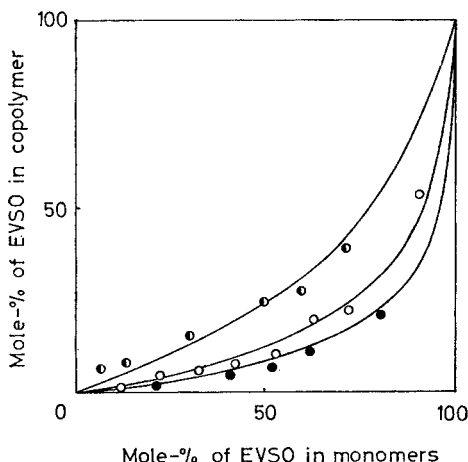


Fig. 1. Monomer-copolymer composition curves for radical copolymerizations of EVSO and some vinyl monomers: (○) St; (●) MMA; (◐) AN

From the results of copolymerization with St, the  $Q$  and  $e$  values for EVSO are evaluated to be 0.13 and 0.61, respectively. These values are almost consistent with those for methyl vinyl sulfoxide reported by PRICE and GILBERT<sup>6</sup>). Although EVSO showed low ability for copolymerizations

with these monomers, the highest content of EVSO in the copolymers was found when AN was used as comonomer. The rate of copolymerization decreased with increasing EVSO content in the monomer mixture, as can be seen in Table 1.

Non-conjugative monomers such as VC and VAc, however, did not yield any homopolymer or copolymers with EVSO, recalling the lack of homopolymerization of EVSO. These results may suggest the importance of the degradative chain transfer reaction to EVSO monomer by the reactive polymer radicals produced from these non-conjugative monomers. The copolymers obtained with St and MMA exhibiting EVSO contents above 30 mole-% and above 20 mole-%, respectively, are soluble in methanol. The AN copolymers are methanol-insoluble, whatever the EVSO content may be.

### 3.3. Effects of additives on the copolymerization of St and EVSO

In general, it has been well established that the sulfoxide bond exhibits 30–50 % of semi-ionic bond character<sup>5)</sup>. Accordingly, the oxygen atom of the sulfoxide group shows a strong basicity, and forms complexes with LEWIS acids and hydrogen bonds with proton donors. These complexes and hydrogen bond formations are expected to induce changes in mono-

Table 3. Radical copolymerizations of EVSO ( $M_2$ ) and St ( $M_1$ ) in the presence of lithium chloride or zinc chloride at 60°C: ( $[M_1] + [M_2]$ ) = 3.3 mole/l.

[M <sub>2</sub> ] in monomers (mole-%)	Time (h)	Conversion (%)	Copolymer obtained	
			C (%)	d [M <sub>2</sub> ] (mole-%)
LiCl ([LiCl]/[EVSO] = 0.5) in DMF; [AIBN] = 1.7·10 <sup>-2</sup> mole/l.				
11.4	2	4.0	91.95	0.7
22.4	3	4.5	91.07	2.6
33.1	12	12.0	90.58	3.7
43.4	13	10.6	89.28	6.4
53.5	20	11.6	87.28	9.6
ZnCl <sub>2</sub> ([ZnCl <sub>2</sub> ]/[EVSO] = 0.3) in benzene; [AIBN] = 1.5·10 <sup>-2</sup> mole/l.				
22.3	5	7.3	88.59	7.9
43.4	15	13.5	82.62	20.9
63.3	16	6.1 <sup>a)</sup>	74.05	39.4
72.9	16	6.0 <sup>a)</sup>	71.53	44.9
82.2	17	4.9 <sup>a)</sup>	68.38	51.7
91.2	17	1.7 <sup>a)</sup>	62.41	64.7

<sup>a)</sup> The resulting copolymers are soluble in methanol.

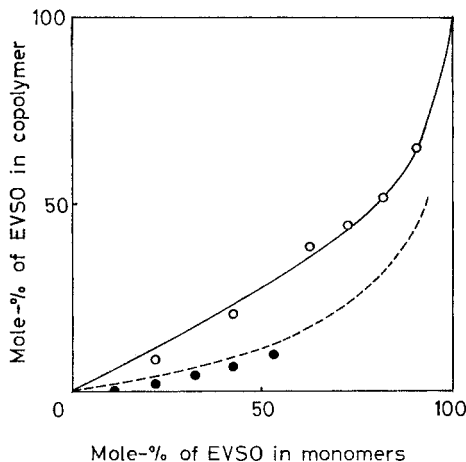


Fig. 2. Monomer-copolymer composition curves for radical copolymerizations of EVSO and St in the presences of LEWIS acids: (○)  $\text{ZnCl}_2$  ( $[\text{ZnCl}_2]/[\text{EVSO}] = 0.3$ ), in benzene; (●)  $\text{LiCl}$  ( $[\text{LiCl}]/[\text{EVSO}] = 0.5$ ), in DMF; (---) none

mer reactivity of EVSO. From such a viewpoint, the effects of LEWIS acids and proton donors on the copolymerization of EVSO with St were examined. Since MMA and AN are known to form complexes with LEWIS acids, affecting their reactivities<sup>13-16</sup>, St was chosen as a reference comonomer. It was also confirmed from the extraction of the resulting polymer mixture with cyclohexane that no cationic polymerization was induced in the presence of zinc chloride under the present conditions.

The results of radical copolymerizations in the presence of lithium chloride in DMF and of zinc chloride in benzene are summarized in Table 3, and the composition curves are shown in Fig. 2.

As shown in Table 3 and Fig. 2, the addition of lithium chloride in DMF does not affect the composition of the copolymer obtained. No effect of DMF solvent on the copolymer composition was observed, either. But the addition of zinc chloride, in benzene, is obviously increasing the EVSO content of the copolymer. The apparent monomer reactivity ratios for this copolymerization are calculated to be  $r_1 = 2.0$  and  $r_2 = 0.05$ , and the apparent  $Q$  and  $e$  values for EVSO are estimated to be 0.15 and 0.72, respectively. It is noted that the  $Q$  and  $e$  values are somewhat larger than those obtained in the absence of zinc chloride. This result is consistent with that found for the effect of zinc chloride on copolymerizations of polar monomers with vinyl chloride<sup>13-16</sup>.

The effects of acetic acid, ethanol and phenol which can form hydrogen bonds with EVSO, on its copolymerization with St are shown in Table 4 and Fig. 3.

Table 4. Radical copolymerizations of EVSO ( $M_2$ ) and St ( $M_1$ ) in the presence of proton donors at 60°C; ( $[M_1] + [M_2]$ ) = 4.0 mole/l. in benzene

[M <sub>2</sub> ] in monomers (mole-%)	Time (h)	Conversion (%)	Copolymer obtained	
			C (%)	d [M <sub>2</sub> ] (mole-%)
Acetic acid ([CH <sub>3</sub> COOH]/[EVSO] = 1); [AIBN] = 1.6·10 <sup>-2</sup> mole/l.				
27.8	8	10.0	89.20	6.6
53.5	15	8.4	85.91	13.7
77.5	30	8.4 <sup>a)</sup>	75.10	37.2
Ethanol ([C <sub>2</sub> H <sub>5</sub> OH]/[EVSO] = 1); [AIBN] = 1.6·10 <sup>-2</sup> mole/l.				
27.8	8	9.6	90.02	4.8
53.5	15	11.4	87.30	10.8
77.5	30	5.0 <sup>a)</sup>	77.90	31.1
Phenol ([C <sub>6</sub> H <sub>5</sub> OH]/[EVSO] = 0.5); [AIBN] = 1.5·10 <sup>-2</sup> mole/l.				
33.1	4	4.9	89.13	6.8
43.3	5	4.9	87.84	9.5
53.5	6	3.8	83.81	18.8
63.3	10	2.5	82.42	21.3
72.9	13	3.7 <sup>a)</sup>	77.33	32.3
82.2	20	3.9 <sup>a)</sup>	71.68	44.6

a) The resulting copolymers are soluble in methanol.

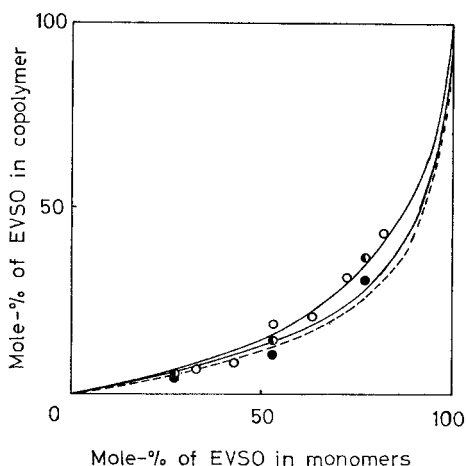


Fig. 3. Monomer-copolymer composition curves for radical copolymerizations of EVSO and St in the presences of proton donors in benzene: (○) phenol ( $[\text{C}_6\text{H}_5\text{OH}]/[\text{EVSO}] = 0.5$ ); (●) ethanol ( $[\text{C}_2\text{H}_5\text{OH}]/[\text{EVSO}] = 1$ ); (◐) acetic acid ( $[\text{CH}_3\text{COOH}]/[\text{EVSO}] = 1$ ); (---) none

From Fig. 3 it follows that the addition of these proton donors slightly increases the EVSO content of the resulting copolymer. The apparent monomer reactivity ratios are estimated to be  $r_1 = 5.3$ ,  $r_2 = 0.1$  when



phenol is added;  $r_1 = 5.0$ ,  $r_2 = 0.05$  for addition of acetic acid; and  $r_1 = 6.8$ ,  $r_2 = 0.05$  for that of ethanol. All proton donors added to the copolymerization system do not always form hydrogen bonds with the sulfoxide group, as can be seen from the values of enthalpy and entropy of hydro-

Table 5. Radical copolymerizations of EVSO ( $M_2$ ) and St ( $M_1$ ) in some proton donors at 60°C; ( $[M_1] + [M_2]$ ) = 4.0 mole/l.

[M <sub>2</sub> ] in monomers (mole-%)	Time (h)	Conversion (%)	Copolymer obtained	
			C (%)	d [M <sub>2</sub> ] (mole-%)
In ethanol; [AIBN] = 1.6 · 10 <sup>-2</sup> mole/l.				
33.1	3	2.2 a)	88.51	8.1
43.4	5	7.1 a)	88.61	7.9
53.5	6	4.0	84.53	16.7
63.3	10	5.5	84.10	17.6
72.9	13	4.2 b)	80.34	25.8
82.2	20	3.5 b)	74.51	38.5
In phenol; [AIBN] = 1.4 · 10 <sup>-2</sup> mole/l.				
11.4	3	6.1	87.11	11.5
22.4	4	8.8	86.82	11.9
43.4	5	6.9	82.31	19.4
53.5	5	5.0 b)	78.75	29.3
63.3	6	6.8 b)	76.92	33.2
82.2	15	5.1 b)	69.46	49.4
91.2	19	2.8 b)	55.32	80.1
In <i>p</i> -chlorophenol; [AIBN] = 1.4 · 10 <sup>-2</sup> mole/l.				
22.4	5	4.3	87.52	10.2
43.4	7	3.6	84.38	17.1
53.5	8	2.9 b)	81.06	24.2
63.3	8	1.6 b)	78.83	29.1
82.2	22	2.5 b)	71.40	45.2
In <i>p</i> -cresol; [AIBN] = 1.4 · 10 <sup>-2</sup> mole/l.				
22.4	5	3.0	87.94	9.3
43.4	7	2.6	84.03	17.8
53.5	8	2.2	83.20	19.6
63.3	8	1.0 b)	79.33	28.0
72.9	15	1.9 b)	76.72	33.7
82.2	22	1.7 b)	73.57	39.9
91.2	27	0.8 b)	61.03	67.7

a) These copolymerizations preceded in heterogeneous system.

b) The resulting copolymers are soluble in methanol.

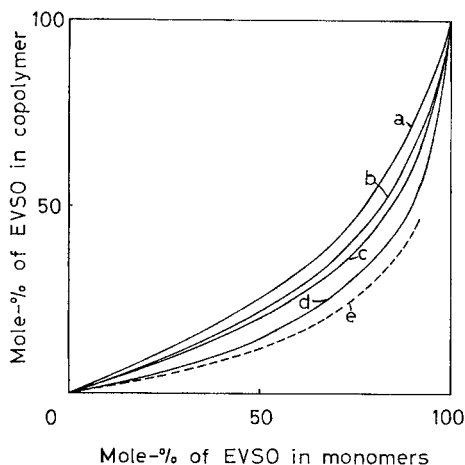


Fig. 4. Monomer-copolymer composition curves for radical copolymerizations of EVSO and St in proton donors; a. in phenol; b. in *p*-chlorophenol; c. in *p*-cresol; d. in ethanol; e. in bulk

gen bond formation, and from the possibility of complex formation of the other bases present in our copolymerization system, as it will be described later.

It is necessary to investigate the copolymerization in the presence of excess proton donors, in order to clarify the variation of the copolymerization parameters. Table 5 and Fig. 4 show the results of radical copolymerizations of EVSO with St, in which alcohol and phenol derivatives are used as solvents.

The EVSO content of the resulting copolymers is found to be higher in such solvents. The monomer reactivity ratios are summarized in Table 6.

Table 6. Variation in monomer reactivity ratios for radical copolymerizations of EVSO ( $M_2$ ) and St ( $M_1$ ) in alcohol and phenol derivatives

Solvent	$r_1$	$r_2$
None	7.0	0.02
Ethanol	6.0	0.1
Phenol	2.8	0.2
<i>p</i> -Chlorophenol	3.2	0.2
<i>p</i> -Cresol	3.5	0.1

The most remarkable effect on the copolymer composition is observed when phenol is used as a solvent. If the addition of LEWIS acids or of proton donors does not affect the homopropagation rate of St, the apparent relative reactivity of EVSO toward the polystyryl radical can be evaluated from  $1/r_1$  as it is shown in Table 7.

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Table 7. Relative reactivity of EVSO toward polystyryl radical

No.	Additive <sup>a)</sup>	Relative reactivity
1	None	1.0
2	LiCl (50 %, in DMF)	1.0
3	ZnCl <sub>2</sub> (30 %, in benzene)	3.5
4	Acetic acid (100 %, in benzene)	1.4
5	Ethanol (100 %, in benzene)	1.0
6	Phenol (50 %, in benzene)	1.3
7	Ethanol (used as solvent)	1.2
8	Phenol (used as solvent)	2.5
9	<i>p</i> -Chlorophenol (used as solvent)	2.2
10	<i>p</i> -Cresol (used as solvent)	2.0

<sup>a)</sup> The values of percent in parentheses indicate the mole-% of the additive based on EVSO.

In all cases, except for the addition of lithium chloride, the relative reactivity of EVSO is observed to increase on addition of these compounds. Since lithium chloride is known to form a complex with DMF<sup>17)</sup>, the absence of variation in relative reactivity may be attributed to the formation of LiCl-DMF complex rather than LiCl-EVSO complex.

The relative reactivities (No. 2–6 in Table 7) observed in the presence of a small amount of additive, may be only apparent values, probably because of the coexistence of complexed and uncomplexed EVSO (or of hydrogen-bonded and non-hydrogen-bonded EVSO) in these systems. On the other hand, the relative reactivities (No. 7–10) observed in the presence of an excess of proton donors may be those of the hydrogen-bonded EVSO species. The extent of increase in relative reactivity is observed to coincide with the increase of the amount of ethanol and phenol added (No. 5, 6 and 7, 8, respectively).

Such a complex formation of the sulfoxide group of EVSO with LEWIS acid does not only affect monomer reactivity, but it may also prevent or

Table 8. Radical copolymerization of EVSO (M<sub>2</sub>) and VC (M<sub>1</sub>) in the presence of stannic chloride in benzene at 60°C. [AIBN] = 1.2 · 10<sup>-2</sup> mole/l., ([EVSO] + [VC]) = 3.7 mole/l., [SnCl<sub>4</sub>]/[EVSO] = 0.8

[M <sub>2</sub> ] in monomers (mole-%)	Time (h)	Conversion (%)	Copolymer obtained	
			S (%)	d [M <sub>2</sub> ] (mole-%)
16.8	6	4.8	1.54	3.1
37.0	6	7.9	14.10	33.7
63.8	6	8.9	12.66	29.5

reduce the degradative chain transfer reaction to the sulfoxide group. Although EVSO can not yield a copolymer with VC, as mentioned above, this copolymerization is observed to proceed if stannic chloride is present in the system. This result is shown in Table 8.

From this table, the monomer-copolymer composition relationship does not follow classical rules, which seems to arise from the fact that the copolymerization proceeds heterogeneously, with the formation of a  $(\text{EVSO})_2 \cdot \text{SnCl}_4$  complex. It is, however, interesting to note that the copolymer of EVSO and the non-conjugative VC monomer can be obtained in the presence of stannic chloride.

### 3.4. Spectroscopic studies on the interaction between EVSO and LEWIS acids or proton donors

The IR spectra of the EVSO-proton donor systems have been measured in carbon tetrachloride to get informations on the variation of stretching frequencies of the O—H and S—O bonds in proton donors and in EVSO, respectively. The results are summarized in Table 9.

Table 9. Variation in stretching frequencies of the O—H and S—O bonds in carbon tetrachloride

Proton donor <sup>a)</sup>	$\nu_{\text{S-O}} \text{ (cm}^{-1}\text{)}$		$\Delta\nu_{\text{O-H}} \text{ (cm}^{-1}\text{)}^{\text{b)}$
None	1070 (1060) <sup>c)</sup>	1047	—
Ethanol	— <sup>d)</sup>	1050	200
<i>p</i> -Chlorophenol	1054	1048	345
Phenol	1056	1048	335
<i>p</i> -Cresol	1059	1048	328

<sup>a)</sup>  $[\text{EVSO}] = 0.05$ ,  $[\text{proton donor}] = 0.06 \text{ mole/l.}$

<sup>b)</sup> The differences in frequency due to hydrogen bonding are represented.

<sup>c)</sup> The value was determined from liquid film.

<sup>d)</sup> The band was not resolved from that of ethanol.

The existence of two S—O stretching vibrations may be attributed to two rotational isomers of EVSO. From Table 9, both the O—H and S—O stretching frequencies have been observed to shift to lower wave numbers, indicating the weakening of both bonds, owing to the formation of hydrogen bonds  $\text{S—O} \cdots \text{H—O}$ . Phenol derivatives exhibit a significant shift in the O—H and S—O stretching frequencies. The order of shift amplitude is essentially the same as that of the acidities of the donors.

JOESTEN and DRACO<sup>18)</sup> derived a linear relationship between the enthalpy and the frequency shift, for phenol-base associations, as shown in the following Eq.:

$$-\Delta H \text{ (kcal/mole)} = 0.016 \Delta \nu_{\text{O-H}} + 0.63$$

According to this Eq., the enthalpy in the EVSO-phenol association can be calculated to be 5.9 kcal/mole, which is slightly smaller than the 6.5 kcal/mole for the DMSO-phenol system<sup>19</sup>, because of the  $\alpha,\beta$ -unsaturated group in EVSO. The equilibrium constant for the EVSO-phenol hydrogen bond formation, in carbon tetrachloride at 60°C, may be slightly lower than 56 l./mole, a value which has been estimated for the DMSO-phenol system by extrapolating the data of DRAGO<sup>19</sup>). When phenol is used as solvent, most of EVSO monomer in the copolymerization system, therefore, may be present as a hydrogen-bonded structure.

The complexes of EVSO with lithium chloride, zinc chloride and stannic chloride were prepared by mixing EVSO with these LEWIS acids. Melting points and elemental analysis of their complexes are as follows:

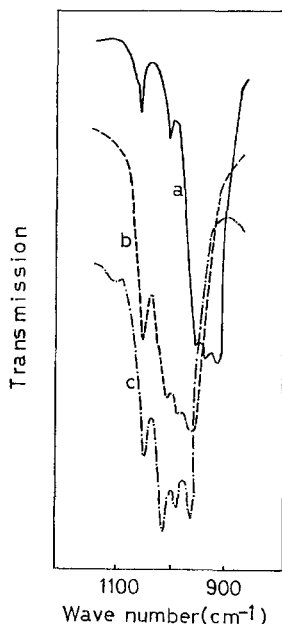


Table 10. The S-O stretching frequencies of the EVSO-LEWIS acid complexes

LEWIS acid	$\nu_{\text{S-O}}$ (cm <sup>-1</sup> )	
LiCl <sup>a)</sup>	1016	1050
ZnCl <sub>2</sub> <sup>b)</sup>	1007	1054
SnCl <sub>4</sub> <sup>a)</sup>	1003	1056

a) KBr disk.

b) Liquid film.

Fig. 5. S-O stretching vibrations of EVSO-LEWIS acid complexes: a. (EVSO)<sub>2</sub>·SnCl<sub>4</sub>; b. (EVSO)<sub>2</sub>·ZnCl<sub>2</sub>; c. EVSO·LiCl

EVSO-LiCl complex: mp 142.5–143.0°C; (EVSO)<sub>2</sub>·ZnCl<sub>2</sub> complex: viscous liquid at room temperature; (EVSO)<sub>2</sub>·SnCl<sub>4</sub> complex: mp 174.5–175.5°C (Analysis, Found: S, 13.67%; Calcd.: S, 13.66%). The complexes with lithium chloride and zinc chloride are very hygroscopic.

The IR charts of these complexes are shown in Fig. 5, from which the S-O stretching frequencies are summarized in Table 10.

From Table 10, the observed shifts in S—O stretching frequencies by complex formations show the weakening of the sulfoxide bond in EVSO, indicating, that the complexing site is the negative oxygen atom of the sulfoxide bond, as reported by COTTON and FRANCIS<sup>20</sup>.

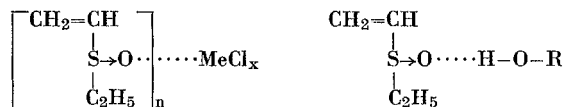
The UV spectra of EVSO in various alcohols were measured to get information on the electronic state of hydrogen-bonded EVSO. The absorption maxima ( $\lambda_{\max}$ ) and extinction coefficients ( $\epsilon_{\max}$ ) are shown in Table 11.

Table 11. The UV spectra of EVSO in various alcohols

Solvent	$\lambda_{\max}$ (m $\mu$ )	$\epsilon_{\max} \cdot 10^{-3}$	Solvent	$\lambda_{\max}$ (m $\mu$ )	$\epsilon_{\max} \cdot 10^{-3}$
<i>n</i> -Heptane	247	2.54	Ethanol	233	2.75
<i>tert</i> -Butanol	237	2.10	Methanol	232	2.21
<i>i</i> -Propanol	235	2.26	Water	225	2.01

As can be seen from Table 11, the shift of the band toward lower wave lengths can be correlated with the decreasing order of  $pK_a$  values of the solvents from *n*-heptane to water. This result is consistent with those obtained for butyl vinyl sulfoxide<sup>21</sup>). In general, this absorption band is ascribed to the  $n\text{-}\pi^*$  electronic excitation of the sulfoxide group, and it shifts to lower wave lengths if hydrogen bonds are formed<sup>22</sup>). The results in Table 11 also prove the existence of hydrogen bonding between EVSO and alcohol. Although the  $\pi\text{-}\pi^*$  band of vinyl group has not been observed in the ultraviolet region, this band is expected to shift to longer wave lengths if hydrogen bonding occurs, as well as in the case of  $\alpha,\beta$ -unsaturated ketones<sup>21</sup>).

It is concluded from these spectroscopic results that EVSO can form complexes with the following structures:



where  $\text{MeCl}_x$  stands for LEWIS acid and  $n$  is 1 or 2. Accordingly, the variation in relative reactivity of EVSO toward the polystyryl radical (Table 7) seems to be attributable mainly to these interactions.

Phenol has also been known to form hydrogen bonds with the benzene ring, and the enthalpy for this process was estimated to be 2.4 kcal/mole<sup>23</sup>). Since the enthalpy for the hydrogen bond formation between phenol and

It is expected to be smaller than that of phenol/benzene system, the change in reaction rate of polystyryl radical towards styrene monomers, which was used as a reference comonomer, may be smaller than that towards EVSO. The rate-enhancing effect of the phenols is found to be the following order: phenol > *p*-chlorophenol > *p*-cresol, which is not the order of increasing acidities. This may be partly attributable to hydrogen bond formation between *p*-chlorophenol and styrene monomer.

It has been reported in the previous papers<sup>13-16)</sup> that the reactivities of polar monomers such as MMA and AN in the radical copolymerizations with vinyl chloride are changed in the presence of various LEWIS acids. Similarly, the change in relative reactivity of complexed (or hydrogen-bonded) EVSO monomer can be explained on the basis of the increase in electrophilicity of EVSO monomer toward polystyryl radical.

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