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Sulfur-Containing Vinyl Monomers. XVII.* Preparation and Polymerization of 2-(Mercaptobenzazolyl)ethyl Vinyl Ethers

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ABSTRACT

2-(Mercaptobenzothiazolyl)ethyl vinyl ether (TVE), 2-mercaptobenzoxazolyl)ethyl vinyl ether (OVE), and 2-(mercaptobenzimidazolyl)ethyl vinyl ether (IVE) were prepared from the reactions of the respective mercaptobenzazoles with chloroethyl vinyl ether. These monomers homopolymerized with cationic initiator to give relatively low molecular weight resinous materials, but radical initiator gave no polymer. The radical copolymerizations with vinyl chloride (VC) as M_1 were performed, and the colorless copolymers were obtained when the VC contents were more than ca. 50 mole %. The monomer reactivity ratios and Q, e values were determined as follows: TVE (M_2)-VC: $r_1 = 2.02$, $r_2 = 0.164$, $Q_2 = 0.02$, $e_2 = -1.85$, OVE(M_2)-VC: $r_1 = 1.65$, $r_2 = 0.134$, $Q_2 = 0.02$, $e_2 = -2.03$, IVE(M_2)-VC: $r_1 = 0.05$, $r_2 = 14.0$, $Q_2 = 0.04$, $e_2 = -0.20$. These copolymers were less thermally stable than the ordinary PVC. These monomers could easily undergo alternating copolymerization with maleic anhydride.

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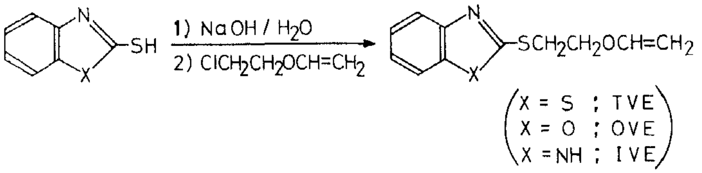
*For Part XVI see: H. Ohnishi and T. Otsu, J. Macromol. Sci.–Chem., A13(1), 1 (1979).

INTRODUCTION

Mercaptobenzothiazole and its derivatives have been used as vulcanization accelerators in the rubber industry, and also as photoinitiators of vinyl polymerization [1, 2]. Thus, if monomers containing these groups are prepared and introduced into the polymer chain, functional polymers with radical-producing ability or the other functionality seem to be obtained.

On the other hand, Saidov et al. [3] reported that copolymers more stable than the homopolymer to heat and light were obtained by radical copolymerization of methyl methacrylate or graft copolymerization of poly(vinyl chloride) with a minor amount ($< 10\%$) of allyl and methacryloyl monomers having mercaptobenzothiazole and benzotriazole rings. In order to assess this point, some vinyl ethers with mercaptobenzazole rings were synthesized and copolymerized with vinyl chloride in this study.

In the previous papers [4, 5], vinyl mercaptobenzazoles were prepared, and their polymerization reactivities were determined in detail by means of radical copolymerization. Since the copolymer of poly(vinyl chloride) with a minor amount of vinyl ether unit has been known to become thermally stable, vinyl ether monomers having mercaptobenzazoles, i. e., 2-(mercaptobenzothiazolyl)ethyl vinyl ether (TVE), 2-(mercaptobenzoxazolyl)ethyl vinyl ether (OVE) and 2-(mercaptobenzimidazolyl)ethyl vinyl ether (IVE) were synthesized according to the reaction shown in Eq. (1).



(1)

Moreover, to evaluate the reactivities of these monomers, the polymerization and copolymerization behavior were also investigated. The results obtained will be described in this paper.

EXPERIMENTAL

Preparation of TVE

TVE was prepared by the reaction of sodium 2-mercaptobenzothiazole with 2-chloroethyl vinyl ether in water. To a mixture of 167 g (1 mole) of mercaptobenzothiazole and 450 ml of aqueous solution of sodium hydroxide (45 g, 1.1 mole), 117 g (1.1 mole) of 2-chloroethyl vinyl ether was added dropwise at 60°C under stirring, and subsequently this mixture was allowed to stir at 60°C for 5 hr. The resulting lower layer was separated and washed with hot water. After standing for a day, this viscous layer became solid. Pure TVE was obtained by recrystallization from methanol: yield, 218 g (92%); mp 42.5-43.0°C.

ANAL. Calcd for $C_{11}H_{11}NOS_2$: C, 55.67%; H, 4.67%; N, 5.90; S, 27.02%. Found: C, 55.44%; H, 4.55%; N, 5.80%; S, 26.92%.

Preparation of OVE

OVE was prepared by similar method described for TVE: yield, 71.0%; bp 108-109°C/Torr; n_D^{20} 1.5881; d_4^{20} 1.2006.

ANAL. Calcd for $C_{11}H_{11}NO_2S$: C, 59.71%; H, 5.01%; N, 6.33%; S, 14.49%. Found: C, 59.43%; H, 4.08%; N, 6.25%; S, 14.50%.

Preparation of IVE

IVE was prepared by a method similar to that described for TVE: yield, 92%; mp 129.0-129.5°C.

ANAL. Calcd for $C_{11}H_{12}N_2OS$: C, 59.98%; H, 5.49%; N, 12.77%; S 14.55%. Found: C, 59.87%; H, 5.19%; H, 12.76%; S, 14.51%.

Other Reagents

Vinyl chloride (Mitsubishi Monsanto Co.) was distilled just before use. Maleic anhydride was recrystallized twice from chloroform. Solvents and precipitants were used after purification by ordinary methods. α,α'-Azobisisobutyronitrile (AIBN) and α,α'-azobis-2,4-dimethylvaleronitrile (AVN) were recrystallized from methanol.

Polymerization

Polymerizations and copolymerizations were carried out in a sealed tube under shaking in the absence of light. The radical polymerization procedure was the same as that reported in the previous papers [4, 5]. A similar method was used for cationic polymerization, except that boron trifluoride diethyl etherate was used as a catalyst.

Analysis of the Polymer

The composition of the copolymer was calculated from elemental analyses of carbon and/or sulfur, and the monomer reactivity ratios

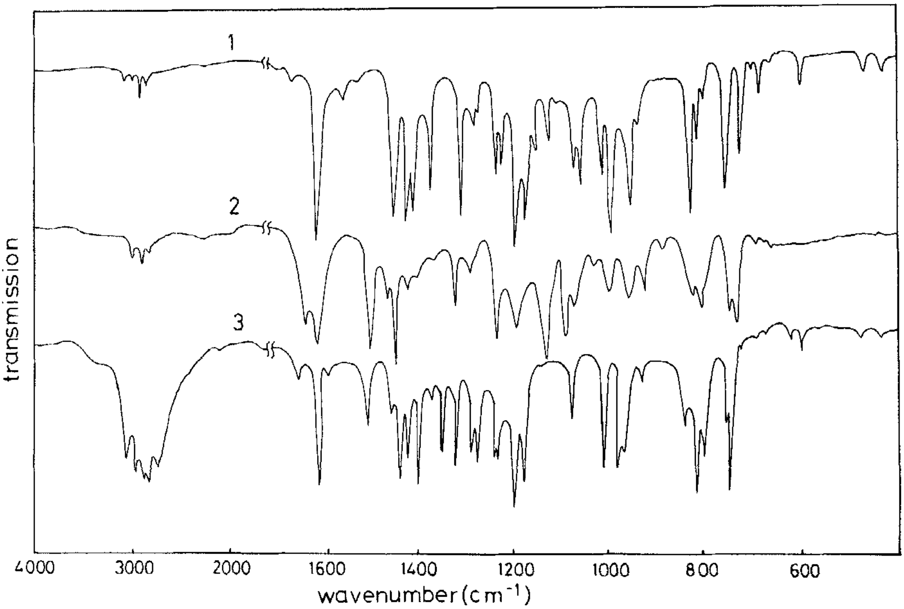


FIG. 1. IR spectra of (1) TVE; (2) OVE; (3) IVE.

(r_1 and r_2) were determined by a nonlinear least-squares method based on a differential composition equation [6].

The molecular weight of the polymers was determined by GPC (Toyo Soda HLC-802UR) using tetrahydrofuran. The thermal stability of the polymers was measured by TG analysis (Shimazu TGA-20B).

RESULTS AND DISCUSSION

Properties of Monomers

As shown in the preceding section, it was found that these three monomers were obtained in good yield through Eq. (1). The resulting TVE and IVE monomers were pale yellow and colorless needles, respectively, but OVE was a colorless, viscous liquid.

The IR spectra of these monomers are shown in Fig. 1. It is seen from this figure that there are characteristic absorption bands due to both the carbon-carbon double bond (1610, 1600, 950, and 990 cm^{-1}) and benzazole groups.

The UV spectra of these monomers are shown in Fig. 2, from which the caracteristic λ_{max} and log ϵ are summarized in Table 1.

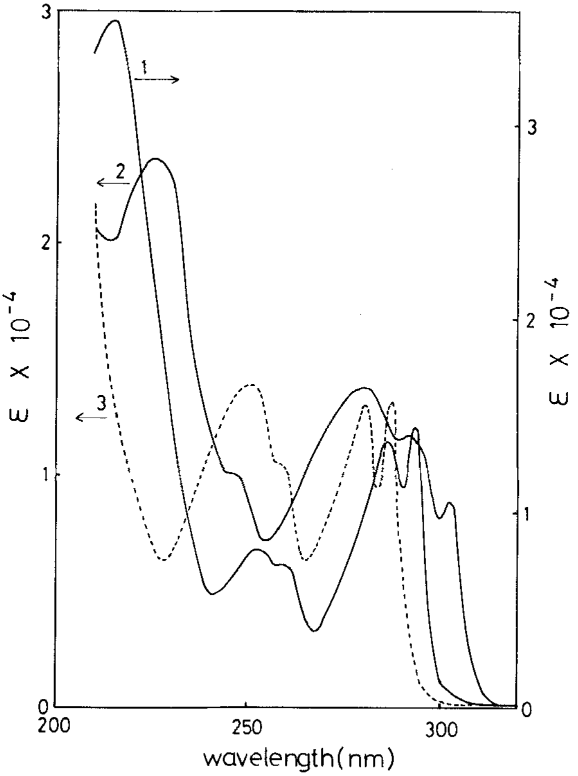


FIG. 2. UV spectra of (1) IVE; (2) TVE; (3) OVE.

Figure 3 also shows their NMR spectra. An absorption band seen at 3.3-4.0 ppm is due to the protons on benzazole rings. From these results and the elemental analysis data described before, the resulting monomers were confirmed to be pure.

Homopolymerization

Table 2 shows the results of radical and cationic polymerizations of these monomers. The data in Table 2 indicate that these monomers do not polymerize with AIBN, but polymerize with $BF_3 \cdot OEt_2$ to give relatively low molecular weight polymers ($\simeq$ 10000). These findings are in agreement with the well known observation that vinyl ethers could homopolymerize only by a cationic mechanism. From Table 2, the cationic homopolymerization reactivities of these monomers are observed to increase in the order: TVE $<$ IVE $<$ OVE.

TABLE 1. UV Data of Monomers[a]

Monomer	λ_{max} (nm)	log ϵ
TVE	225	4.37
	247	4.01
	280	4.14
	291	4.07
	302	3.96
OVE	250	4.15
	258	4.03
	272	3.96
	280	4.12
	287	4.13
IVE	215	4.55
	252	3.92
	259	3.87
	286	4.15
	294	4.17

[a] Determined in tetrahydrofuran.

The homopolymers obtained were pale-yellow resinous materials, and their IR spectra showed no bands attributable to the carbon-carbon double bond which appeared in the monomers. Therefore, these polymers seem to consist of vinyl-polymerized structures.

Copolymerization with Vinyl Chloride (VC)

Table 3 shows the results of radical copolymerizations of these azole monomers (M_2) with VC (M_1) initiated by AIBN at 60°C. According to Table 3, the rates of copolymerizations are almost independent of the monomer feed, except for the TVE-VC system, in which the rate decreased with increasing M_2 monomer in the feed. The resulting copolymers ranged from colorless to pale-yellow powders, the color increasing as the M_2 in the copolymers increased.

The monomer-copolymer composition curves are shown in Fig. 4. The monomer reactivity ratios for these copolymerizations are shown

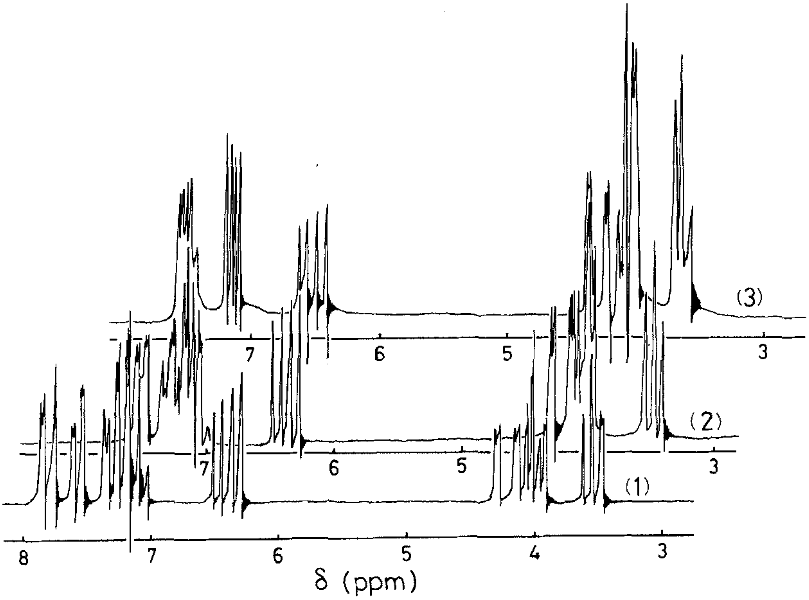


FIG. 3. NMR spectra of (1) TVE; (2) OVE; (3) IVE.

TABLE 2. Homopolymerization of TVE, OVE, and IVE[a]

Monomer	Initiator	Solvent[b]	Temp. (°C)	Time (hr)	Yield (%)	Mol. wt. $\times 10^{-4}$
TVE	AVN	B	60	15	0	-
	BF_3OEt_2	NB	0	40	0.42	1.25
OVE	AVN	B	60	15	0	-
	BF_3OET_2	NB	0	40	9.95	1.45
IVE	AVN	B	60	15	0	-
	BF_3OEt_2	NB	0	40	2.20	-

[a] Polymerization conditions: [M] = 1.8 mole/liter, [AVN = 1.5×10^{-2} mole/liter or [BF_3OEt_2] = 0.159 mole/liter.

[b] B, benzene; NB, nitrobenzene.

TABLE 3. Radical Copolymerizations with Vinyl Chloride (M_1) Initiated by AIBN at 60°C[a]

M_2	$[M_2]$ in comonomer, (mole %)	Time (hr)	Conversion (%)	Copolymer composition	
				C (%)[b]	$[M_2]$ (mole %)
TVE	8.93	1.6	7.4	46.38	5.55
	22.73	7.5	10.8	37.35	12.02
	37.04	15.3	8.8	29.62	19.42
	40.71	15.3	6.4	27.85	21.41
	46.88	15.3	4.7	25.93	23.83
	55.18	15.3	10.5	19.65	33.28
	63.20	15.3	6.1	16.61	38.89
	71.07	15	1.8	15.18	41.89
OVE	11.16	15	1.9	42.40	6.7
	27.36	15	3.4	47.18	16.46
	42.97	15	9.8	49.55	23.59
	53.06	15	18.9	52.61	35.81
	61.09	15	1.7	(18.73)	36.43
	70.47	15	1.9	53.78	42.22
	79.02	15	1.8	(11.79)	51.84
IVE	9.56	15	3.01	40.11	2.33
	24.07	15	13.84	41.23	4.05
	38.80	15	6.74	42.48	6.15
	48.74	15	9.60	42.56	6.29
	66.75	15	2.96	45.31	11.73

[a] Copolymerization condition; [AIBN] = 5.0×10^{-3} mole/liter in benzene (TVE and IVE), and in bulk (OVE).

[b] Values in parentheses indicate the observed sulfur contents.

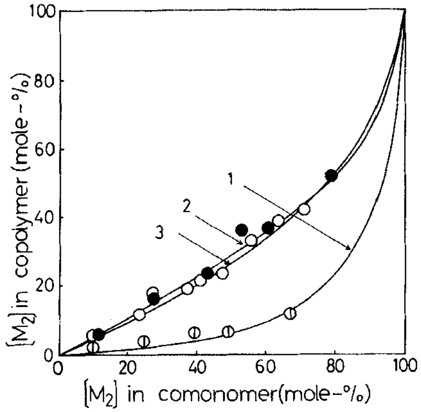


FIG. 4. Copolymer composition curves for radical copolymerization of vinyl chloride (M_1) with (1) IVE, (2) OVE, and (3) TVE at 60°C.

TABLE 4. Radical Copolymerizations of Azoles (M_2) with Maleic Anhydride (M_1) Initiated by AVN at 40°C[a]

M_2	$[M_2]$ in comonomer (mole %)	Time (hr)	Conversion (%)	Copolymer composition S (%)	Copolymer composition $[M_2]$ (mole %)
TVE	18.0	3.5	0.98	19.67	48.0
	44.0	3.5	11.0	19.82	48.6
	55.9	3.5	7.3	19.28	49.2
	67.7	3.5	6.0	19.43	49.9
OVE	20.89	8	12.5	9.72	47.45
	34.77	6	22.3	9.73	47.53
	59.34	5	27.2	9.74	47.58[b]
	64.35	6	25.1	10.01	49.75
	79.73	6	14.9	10.08	50.28

[a] Copolymerization conditions; $[M_2]$ = 0.95 mole/liter in tetrahydrofuran.

[b] $[\eta]$ = 0.12 in tetrahydrofuran at 30°C.

TABLE 5. Copolymerization Parameters for Vinyl Ethers

M_1	M_2	r_1	r_2	Q_2	e_2
VC	TVE	2.02	0.164	0.021	-1.85
	OVE	1.65	0.134	0.023	-2.03
	IVE	14.0	0.05	0.044	-0.20
	n-OVE[a]	1.9 ± 0.2	0.1 ± 0.1	0.061	-0.79
	DVE[a]	1.93 ± 0.15	0.15 ± 0.2	0.033	-0.74
MAn	TVE	0.021	0	-	-
	OVE	0.037	0	-	-
	IBVE	0.040	0	0.023	-1.77

[a] n-OVE: n-octyl vinyl ether, DVE: dodecyl vinyl ether; IBVE: isobutyl vinyl ether. The copolymerization parameters were obtained from the literature [10].

in Table 4, from which the reactivities of these monomers toward the poly(VC) radical are observed to be in the order: IVE < TVE < OVE.

It is of interest to compare the observed Q,e values with those for the other vinyl ethers. From Table 4, the Q and e values obtained were almost identical to those of the ordinary vinyl ethers, but the latter values were more negative, except for the system with IVE.

The results of TG analysis of these polymers are shown in Fig. 5. Initial and maximum decomposition temperatures and the amount of the residue at 500°C are summarized in Table 6.

When the results of the homopolymers obtained were compared with those of poly(vinyl chloride) (PVC) the initial decomposition temperature decreased markedly, while the maximum decomposition temperature somewhat increased, except for poly(IVE). However, both temperatures of the copolymers decreased as a function of the incorporated azole unit. For example, the copolymer containing 2.8 mole % of the TVE unit showed the decreased values of both temperatures to 18°C and 37°C, as compared with those of PVC. These results are quite contrary to those of Saidov et al. [3].

Recently, we have found that polymers and copolymers having the azole groups are excellent as photodegradable polymers similar to vinyl ketone polymers [8, 9]. Therefore, it is unexpected that these copolymers change to products with good photostability. Such a discrepancy seems to originate from the differences in both chain structure and molecular weight.

Since Saidov et al. [3] prepared the graft copolymer of high molecular weight PVC with a pendant azole unit, the susceptibility to main-chain scission by photo- or thermal degradation seems to be

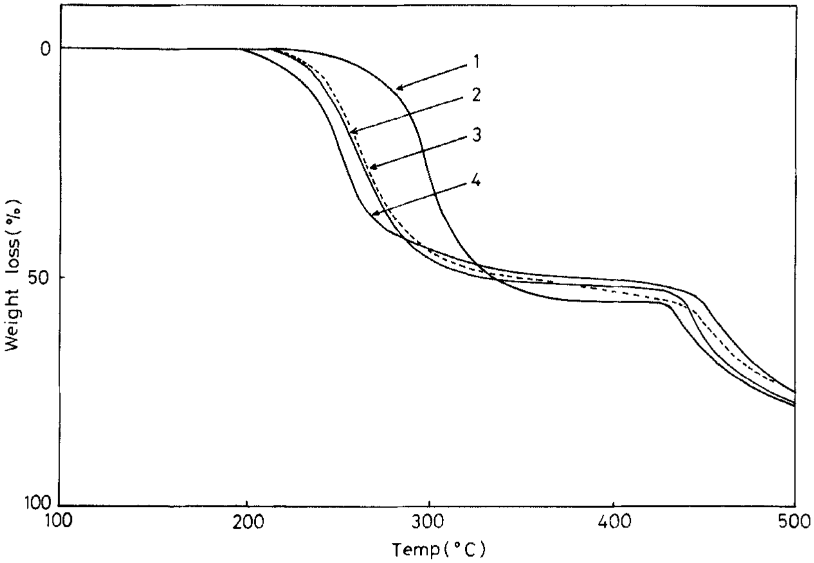


FIG. 5. TGA curves for: (1) (PVC); (2) copolymer of vinyl chloride (VC) with TVE (2.8 mole %); (3) copolymer of VC with OVE (21.9 mole%); (4) copolymer of VC with IVE (18.2 mole %).

TABLE 6. TG Analyses of the Copolymers with Vinyl Chloride[a]

Copolymer M_2 (mole %)	Degradation temp (°C)		Residue at 500°C (%)
	Initial	Maximum	
PVC (0)	223	293	21.8
TVE (2.8)	205	256	22.8
TVE (5.4)	155	252	21.8
TVE (100)	138	340	18.7
OVE (20.9)	151	258	25.5
OVE (34.8)	140	249	23.8
OVE (100)	58	338	22.1
IVE (18.2)	195	250	25.6
IVE (30.8)	193	228	25.0
IVE (100)	46	276	11.4

[a] Conditions for TGA: nitrogen gas, 25 ml/min; heating rate, 10°C/min.

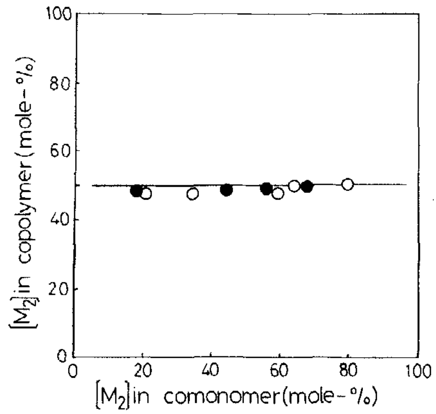


FIG. 6. Copolymer composition curves for radical copolymerizations of Maleic anhydride (M_1) with TVE (●) and OVE (○) at 40°C.

lowered. However, in the present copolymer, which is of relatively low molecular weight (Table 3), the azole-containing unit is located in the main chain. Therefore, it seems to be susceptible to main-chain scission in photo- or thermal degradation.

Copolymerizations with Maleic Anhydride (MAn)

Table 4 also shows the results of radical copolymerization of TVE and OVE (M_2) with maleic anhydride (MAn) (M_1) initiated by AVN at 40°C. The monomer-copolymer composition curves are also shown in Fig. 6. It is clear that these monomers undergo alternative copolymerization with MAn, and their rates gave a maximum when the equimolar mixture of the feed monomers was used. However, these alternating copolymerizations were not induced in the absence of radical initiator. The resulting copolymers were relatively low molecular weight colorless powder and soluble in tetrahydrofuran.

Contrary to these results, IVE did not copolymerize with MAn, probably as the result of interaction between the basic imidazole ring and acidic MAn ring.

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