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Sulfur-Containing Vinyl Monomers. XV. Kinetic Study of Radical Polymerization of Vinyl Mercaptobenzothiazole and Its Copolymerization

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ABSTRACT

A kinetic study of radical polymerization of vinyl mercapto-benzothiazole (VMBT) with α, α' -azobisisobutyronitrile (AIBN) at 60°C was carried out. The rate of polymerization (R_p) was found to be expressed by the rate equation: $R_p = k [AIBN]^{0.5} [VMBT]^{1.0}$, indicating that the polymerization of this monomer proceeds via an ordinary radical mechanism. The apparent activation energy for overall polymerization was calculated to be 20.9 kcal/mole. Moreover, this monomer was copolymerized with methyl methacrylate, acrylonitrile, vinyl acetate, phenyl vinyl sulfide, maleic anhydride, and fumaronitrile at 60°C. From the results obtained, the copolymerization parameters were determined and discussed.

INTRODUCTION

In earlier studies in this series [1, 2], it was reported that alkyl or phenyl vinyl sulfides can homopolymerize in the presence of light or radical initiator. Recently vinyl mercaptobenzazoles (thiazole, oxazole, and imidazole) which consist of vinyl sulfide structure having a heterocyclic ring were also found to undergo radical homopolymerization, and these results were described in the previous paper [3]. However no detailed study of radical polymerization of these monomers has been carried out. Therefore, the present study was attempted to clarify kinetically the course of radical polymerization of vinyl mercaptobenzothiazole (VMBT). The results obtained are described in this paper.

In the previous paper [3], only the copolymerization of VMBT with styrene was investigated, and the copolymerization parameters were determined and compared with those for ordinary vinyl sulfides. In the present study, the copolymerizations of VMBT with various vinyl monomers other than styrene were attempted. These results are also shown in this paper.

EXPERIMENTAL

Materials

VMBT was prepared by the method described in the previous paper [3]. Other vinyl monomers used for copolymerization were purified by ordinary methods. Commercial α, α' -azobisisobutyronitrile (AIBN) were purified by recrystallization twice from methanol. Solvents, precipitants, and other reagents were used after usual purification.

Polymerization

Polymerizations and copolymerizations were carried out in sealed tube in the presence of AIBN, as radical initiator, in the absence of light under shaking. The required amounts of initiator, monomer, and solvent were charged into a hard glass ampoule. Then this ampoule was degassed by ordinary freezing and thawing technique, and finally sealed under vacuum.

After polymerization in a thermostat maintained at the given temperatures, generally 60°C, for an appropriate time, the tube was opened, and its contents poured into a large amount of methanol to precipitate the polymer. In the case of copolymerization with maleic

anhydride, diethyl ether was used as a precipitant. Conversions were calculated from the weight of the dried polymer obtained.

Analyses of Copolymers

The copolymers obtained from low conversion ($< 10\%$) were purified by reprecipitation. The combination of solvent and precipitant was principally benzene and methanol, respectively, except for the copolymers with maleic anhydride and with acrylonitrile, for which tetrahydrofuran-diethyl ether and dimethylformamide-methanol, respectively, were used.

The composition of these copolymers was determined by elemental analyses of their carbon, sulfur, or nitrogen contents. The monomer reactivity ratios for these copolymerizations were calculated by a nonlinear least-squares method based on the integration equation [4].

RESULTS AND DISCUSSION

Kinetic Study of Polymerization

Time-conversion relations for bulk radical polymerization of VMBT initiated by AIBN at 60°C are shown in Fig. 1. This polymerization is found to proceed according to a linear relation with the

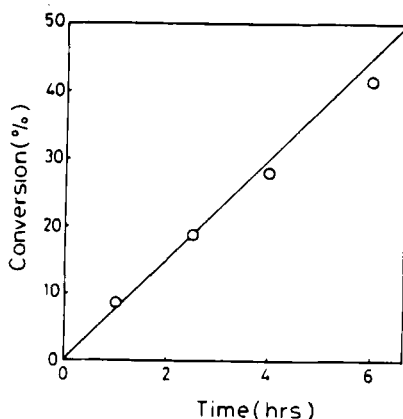


FIG. 1. Time-conversion curve for the bulk polymerization of VMBT at 60°C ; $[\text{AIBN}] = 2.87 \times 10^{-2}$ mole/liter.

TABLE 1. Relations between R_p and Monomer or Initiator Concentration, and Polymerization Temperature^a

$[AIBN] \times 10^3$ (mole/liter)	$[VMBT]$ (mole/liter)	Temp. (°C)	$R_p \times 10^5$ (mole/liter-sec)
1.22	6.53	60	0.42
2.03	6.53	60	0.54
3.38	6.53	60	0.71
5.63	6.53	60	0.89
9.38	6.53	60	1.60
0.63	1.31	60	0.06
0.63	2.61	60	0.20
0.63	3.26	60	0.41
0.63	3.92	60	0.51
0.63	4.57	60	0.59
0.63	5.22	60	0.91
12.8	6.53	55	7.8
12.8	6.53	60	12.0
12.8	6.53	65	13.0
12.8	6.53	70	27.0
12.8	6.53	75	49.0

^a Benzene was used as a diluent when necessary.

reaction time, at least, up to 20% conversion, without an induction period. Therefore the rate of polymerization R_p seems to be determined from the initial slope of this straight line.

Table 1 shows the relationships between R_p and initiator or monomer concentration in the polymerization at 60°C. The log-log plots of R_p with the concentration of initiator are shown in Fig. 2. The slope of the observed straight line indicates that R_p is dependent on the square root of the initiator concentration, suggesting that the termination of this radical polymerization occurs bimolecularly.

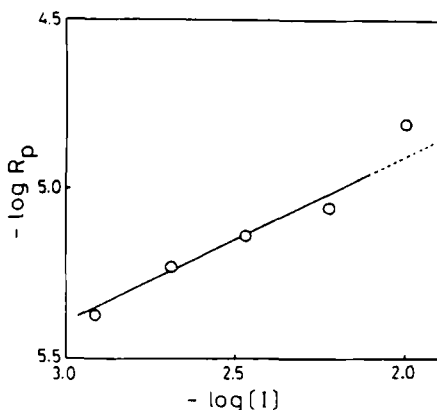


FIG. 2. Log-log plots of R_p with initiator concentration.

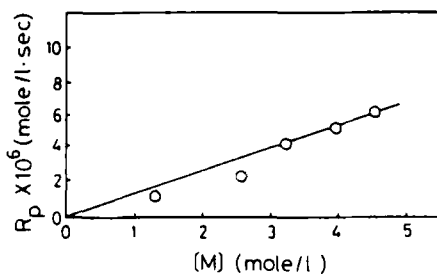


FIG. 3. Relationship between R_p and monomer concentration.

The plot of R_p with the monomer concentration is shown in Fig. 3; R_p is observed to be approximately first-order with respect to monomer concentration. Therefore, the rate equation is expressed as follows:

$$R_p = k [AIBN]^{0.5} [VMBT]^{1.0}$$

A similar rate equation was also observed for the radical polymerization of *tert*-butyl vinyl sulfide initiated by AIBN at 60°C [5].

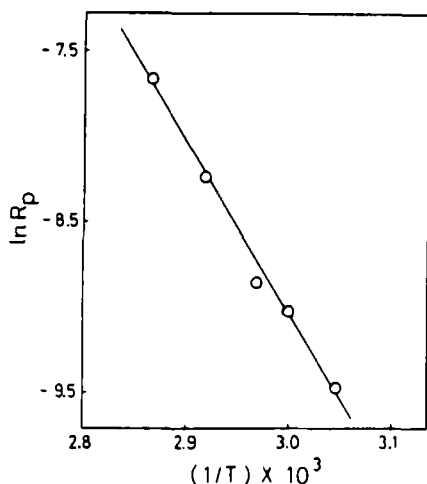


FIG. 4. Arrhenius plots of $\log R_p$ with $1/T$.

Therefore, it is obvious that this polymerization of VMBT proceeds via an ordinary radical mechanism.

Figure 4 shows Arrhenius plots of R_p with the reciprocal of polymerization temperature. From the observed straight line, the apparent activation energy for this overall polymerization is estimated to be 20.9 kcal/mole, which is similar to the value reported in monomers generally initiated by AIBN.

Copolymerizations

Table 2 shows the results of copolymerizations of VMBT (M_2) with methyl methacrylate (MMA), acrylonitrile (AN), vinyl acetate (VAC), and phenyl vinyl sulfide (PVS) (M_1) initiated by AIBN at 60°C.

All copolymerizations are observed to proceed easily under these conditions, and the copolymer yields are almost independent on the feed monomer composition, except the case of the copolymerization with MMA, which shows a maximum yield at about 1:1 feed composition. The copolymers with both St and AN were colorless powders, and those with VAc and PVS were pale yellowish powders independent of the feed monomer composition. However, the copolymers with MMA changed from colorless to pale yellowish powder with increasing VMBT concentration in the feed.

The monomer-copolymer composition curves are shown in Fig. 5,

TABLE 2. Results of Copolymerizations of VMBT (M_2) with Various Monomers (M_1) Initiated by AIBN at 60°C^a

M ₁	[M ₂] in comonomers (mole %)	Time (min)	Conversion (%)	Copolymer		
				C, N, or S (%)	[M ₂] (mole %)	
MMA	7.2	45	5.1	S:	3.48	6.0
	22.9	45	7.2		8.86	16.6
	41.0	45	10.3		15.1	32.1
	51.0	45	10.8		18.8	43.0
	61.8	45	9.9		19.6	45.8
	73.5	45	6.4		24.1	62.1
	86.2	45	2.9		27.7	76.7
AN	4.6	10	2.2	N:	17.91	18.0
	15.6	10	3.6		14.18	32.6
	31.0	10	4.9		12.63	41.3
	39.2	10	2.6		11.87	46.4
	50.1	10	2.1		11.43	49.6
	63.3	10	3.4		10.79	54.8
	79.5	10	2.6		9.88	63.3
VAc	7.2	210	0.34	S:	21.7	49.6
	41.1	180	2.2		27.7	72.5
	52.2	180	2.8		29.5	80.4
	62.0	150	2.9		30.1	83.7
	73.6	105	3.0		30.9	87.8
PVS	8.7	815	3.2	C:	65.81	25.2
	26.8	780	3.2		65.72	38.1
	46.0	750	4.4		60.30	62.2
	66.5	205	3.7		59.05	72.1
	77.3	180	2.5		56.33	79.8
	88.5	50	1.0		58.13	96.1

^aCopolymerizations were carried out in bulk: [AIBN] = 5.0×10^{-3} mole/liter except for PVS, for which [AIBN] = 7.0×10^{-3} mole/liter.

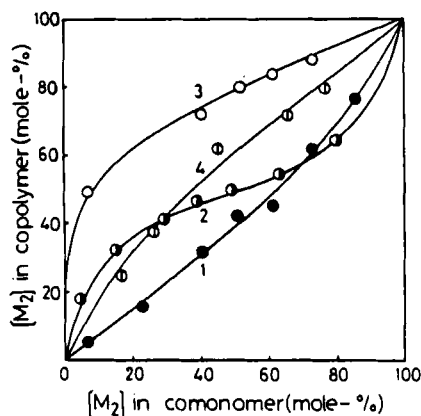


FIG. 5. Copolymer composition curves for radical copolymerizations of VMBT (M_2) with (1) MMA, (2) AN, (3) VAc, and (4) PVS at 60°C .

TABLE 3. Monomer Reactivity Ratios for Copolymerizations of VMBT (M_2) with Various Monomers (M_1) at 60°C

M_1	r_1	r_2	$1/r_1$	$r_1 r_2$
St ^a	2.12	0.336	0.452	0.742
MMA	1.5	0.4	0.67	0.60
AN	0.2	0.2	5.0	0.04
VAc	0.05	3.0	20	0.15
PVS	0.15	0.95	6.7	0.14

^aResult from previous paper [3].

from which the monomer reactivity ratios shown in Table 3 were calculated. The reactivities ($1/r_1$) of VMBT toward attack of various polymer radicals decrease in the order: VAc > PVS > AN > MMA > St.

In the previous paper [3], the Q , e values of VMBT were evaluated as $Q = 0.75$ and $e = -1.38$ from radical copolymerization with St at 60°C . Therefore, the above order, except for polymer radicals of VAc and PVS, is found to increase with increasing electron-accepting nature in the attacking polymer radicals.

TABLE 4. Results of Copolymerizations of VMBT (M_2) with MAn and FN(M_1) in Benzene at 60°C

M_1	[M_2] in comonomer (mole %)	Time (hr)	Conversion (%)	Copolymer	
				S or N (%)	[M_2] (mole %)
MAn ^a	15.3	11.5	3.0	16.8	34.5
	31.1	11.5	3.8	17.5	36.5
	46.6	9.0	3.9	17.9	37.4
	62.2	9.0	3.1	19.4	41.7
	77.7	4.5	3.0	21.5	48.7
	93.3	4.5	2.8	24.7	59.7
FN ^b	15.3	3.25	1.9	14.35	37.7
	31.1	3.25	3.0	14.04	38.6
	46.6	1.33	1.9	13.22	40.9
	62.2	4.0	1.1	12.82	42.1
	77.7	4.33	3.6	11.96	44.7
	93.3	3.25	3.4	9.83	51.7

^a [$M_1 + M_2$] = 3.0 mole/liter; [AIBN] = 1.04×10^{-2} mole/liter.

^b [$M_1 + M_2$] = 3.0 mole/liter; [AIBN] = 6.7×10^{-3} mole/liter.

This seems to correspond to the result that an electron-accepting AN monomer shows a relatively high alternating copolymerization tendency with VMBT. To clarify this point, the copolymerizations of VMBT with maleic anhydride (MAn) and fumaronitrile (FN) were investigated. The results are shown in Table 4; the monomer-copolymer composition curves on the basis of these data drawn are shown in Fig. 6.

As can be seen from Table 4 and Fig. 6, both copolymerizations proceed with more difficulty than those with other monomers (Table 2), and the composition of VMBT in the copolymers obtained gradually increases with a function of VMBT concentration charged. This finding is quite contrary to the result that various alkyl or phenyl vinyl sulfides easily underwent alternating copolymerization, as reported in the previous papers [6, 7]. Such a difference seems to come from extra interaction between MAn and thiazole ring.

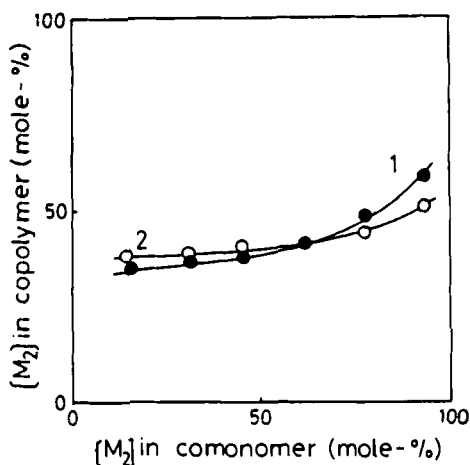


FIG. 6. Copolymer composition curves for radical copolymerizations of VMBT (M_2) with (1) MAn and (2) FN in benzene at 60°C.

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