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Sulfur-Containing Vinyl Monomers. XIX.* Radical Polymerization of 2-Mercaptobenzothiazolyl Methacrylate

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ABSTRACT

2-Mercaptobenzothiazolyl methacrylate (MBTM) was synthesized by the reaction of 2-mercaptobenzothiazole and methacrylyl chloride in tetrahydrofuran at -18°C. MBTM was found to polymerize in the presence of 2,2'-azobisisobutyronitrile (AIBN), n-BuLi, and UV light. From the kinetic studies of radical polymerization of MBTM with AIBN in benzene at 60°C, the overall activation energy was determined to be 18.9 kcal/mole, and the rate of polymerization (R_p) was expressed as $R_p = k[\text{AIBN}]^{0.5}[\text{MBTM}]$, where k is the overall polymerization rate constant. From these results this polymerization was confirmed to proceed via an ordinary radical mechanism. This monomer (M_2) was also copolymerized radically with styrene (M_1) at 60°C, and the resulting copolymerization parameters

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*For Part XVIII of this series, see H. Ohnishi and T. Otsu, J. Macromol. Sci.–Chem., A14(7), 1015 (1980).

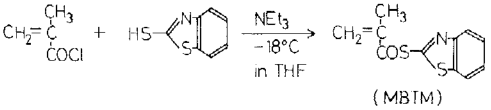
were determined as $r_1 = 0.042$, $r_2 = 0.20$, $Q_2 = 4.09$, and $e_2 = 1.39$. The thermal stability and the photodegradation behavior of the polymers were examined, and they were compared with those of the related polymers.

INTRODUCTION

2-Mercaptobenzothiazole (MBT) was discovered to be useful as an organic vulcanization accelerator in 1921 independently by Bedford [1] and Brunni [2], and its derivative, benzothiazole-2-sulfene morpholide [3] is widely used in the rubber industry. In previous papers some vinyl monomers containing azole rings (vinyl 2-mercaptobenzothiazole [4, 5], vinyl 2-mercaptobenzoxazole [4], vinyl 2-mercaptobenzimidazole [4], vinyl mercapto-4-methylthiazole [6], and β-(2-mercaptobenzothiazolyl) ethyl vinyl ether [7]) were prepared and found to be polymerized by radical initiator. The resulting polymers and copolymers were observed to show photodegradable properties.

Contrary to these results, Saidov et al. [8] reported that the copolymers of methyl methacrylate or vinyl chloride with a small amount of allyl monomers containing azole rings showed excellent thermal and photostabilities. To clarify further this point, 2-mercaptobenzothiazolyl methacrylate (MBTM), which is more polymerizable than the above azole monomers, was prepared, and the polymerization reactivity and the polymer properties were compared. The results obtained will be described in this study.

Sumrell et al. [9] reported that MBTM was not prepared by the direct reaction of methacrylyl chloride with alkaline solution of MBT, because Michael-type addition occurred preferentially. In the present study, however, MBTM was successfully prepared through a similar reaction by using tetrahydrofuran and triethylamine.



EXPERIMENTAL

Reagents

Methacrylyl chloride was prepared by the reaction of methacrylic acid with thionyl chloride in the presence of a small amount of pyridine, followed by distillation. Commercially available MBT and triethylamine were used after recrystallization from acetone and distillation, respectively. AIBN was purified by recrystallization twice from methanol, and n-BuLi was used without further purification.

Other reagents and solvents were purified by conventional methods.

The Preparation of MBTM

A solution of MBT (100 g, 0.6 mole) in 300 mL of tetrahydrofuran (THF) was placed in a 1-L four-necked round-bottom flask equipped with a dropping funnel, thermometer, condenser, and stirrer. After the flask was cooled to -18°C, to this solution with stirring was added dropwise methacrylyl chloride (63 g, 0.6 mole) and then triethylamine (61 g, 0.6 mole) while maintaining the temperature at -18°C. Stirring was continued for an additional hour. Then the reaction mixture was filtered and concentrated under reduced pressure. The product was solidified, washed well with aqueous sodium hydroxide and potassium bicarbonate solutions and finally washed with distilled water. Then the product was recrystallized twice from n-hexane: yield 82.4 g (35%); mp 102.0 ~ 102.5°C; λ_{max} 226 (1.9×10^4), 247 (9×10^3), 280 (1.2×10^4), 295 (1×10^4), and 305 nm (8×10^3).

Analysis: Calculated for $C_{11}H_9NOS_2$: C, 56.14%; H, 3.86%; N, 5.95%. Found: C, 56.28%; H, 3.87%; N, 5.97%.

Polymerization Procedure

Polymerizations were carried out in a sealed glass tube with shaking in a thermostat maintained at constant temperature. The charging of the reagents into an ampule and its sealing were undertaken according to a similar method reported previously [4, 5].

After polymerization for a given time, the tube was opened and its content poured into a large amount of methanol to precipitate the polymer formed. The resulting polymer was purified by reprecipitating from benzene solution into excess methanol. Conversion was calculated from the weight of the dry polymer obtained.

Characterization of the Polymers

The structure of the polymers was checked by IR and NMR determinations. NMR spectra were obtained with 100 MHz NMR spectrometer in 5% deuterochloroform solution. IR spectrum of monomer and polymer was taken as KBr disk and a thin film from benzene solution, respectively.

The viscosity of the polymers was measured in dilute THF solution at 30°C with an Ubbelohde viscometer. The copolymer composition was calculated from the carbon contents on the basis of elementary analysis, and the monomer reactivity ratios were determined by a nonlinear least-squares method based on a differentiation equation [10].

Thermal- and Photostabilities

Thermogravimetric analysis (TGA) of the polymers was determined with a Shimazu TGA-20B model thermobalance at a heating rate of 10°C/min in nitrogen atmosphere.

The photodegradation of the polymers was carried out in THF in a hard glass tube connected with a viscometer under irradiation of a high-pressure mercury lamp at room temperature.

RESULTS AND DISCUSSION

Preparation and Identification of MBTM

The MBTM monomer, which is colorless needle, was obtained from the above-mentioned reaction in 35% yield. From elementary analysis this monomer seemed to be pure. This point was checked by the following spectral determinations.

IR spectrum is shown in Fig. 1 with characteristic absorption bands observed at 1660 ($\nu_{C=O}$ of thiol ester), 1625 ($\nu_{C=C}$), and 890 cm^{-1} (δ_{CH} of terminal methylene). Figure 2 shows the NMR spectrum with absorption bands at 2.0 (methyl proton), 5.7 and 6.1 (vinyl proton), and 7.3 and 7.8 ppm (1,2-disubstituted benzene proton). From these observations this monomer was confirmed to be pure MBTM.

Sumrell et al. [9] reported that the reaction of methacrylyl

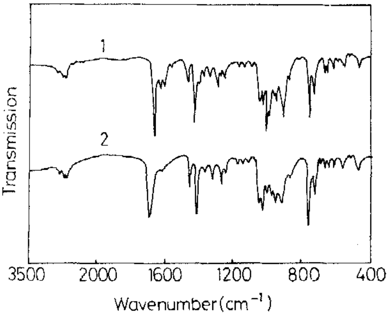


FIG. 1. IR spectra of (1) MBTM and (2) poly(MBTM).

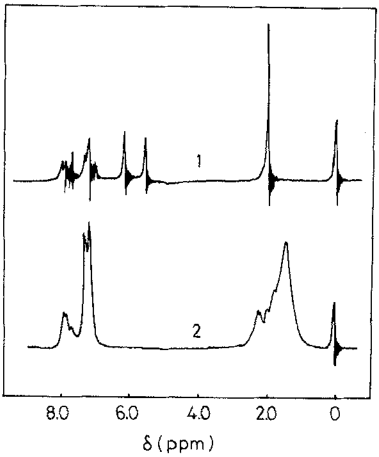


FIG. 2. NMR spectra of (1) MBTM and (2) poly(MBTM).

chloride with sodium MBT gave only the Michael-type addition product. To prevent this side reaction, the THF solution of MBT and triethylamine was used, and a lower reaction temperature (-18°C) was selected for the present work. However, the yield of MBTM was still low (35%), and some Michael-type product, which is easily removed by washing with aqueous sodium bicarbonate solution, was obtained.

Polymerizations of MBTM

The polymerizations of MBTM were carried out with various initiation conditions, and the results are shown in Table 1. MBTM polymerizes with AIBN at 60°C to yield a colorless powder with 0.14 dL/g of intrinsic viscosity, which dissolves in benzene, THF, and chloroform. IR and NMR spectra of the polymers are also shown in Figs. 1 and 2, respectively.

In the IR spectrum, only the characteristic absorption bands at 1625 and 890 cm^{-1} based on the vinyl group disappeared. Further, in NMR spectrum the peaks at 5.72 and 6.12 ppm based on olefinic proton disappeared, and a new peak at 2.25 ppm based on methylene proton was observed. Accordingly, it is clear that this polymer was produced via an ordinary vinyl polymerization mechanism.

MBTM was also photopolymerized and the photosensitization by AIBN was observed. Thermal polymerization at 80°C was found, but it seemed to be induced by diffused light. With the anionic polymerization initiator n-BuLi, anionic polymerization was performed at a slow rate.

TABLE 1. Polymerization of MBTM in Solution[a]

Initiator (mole/L)	Solvent	Temperature (°C)	Time (hr)	Yield (%)
-	Benzene	80	22.7	11.6
AIBN (5.0×10^{-3})	Benzene	60	1.0	12.3[b]
UV	Benzene	20	0.75	4.8
UV/AIBN (8.1×10^{-3})	Benzene	20	0.75	6.1
n-BuLi (2.1×10^{-2})	THF	30	29.0	5.6

[a] Polymerization conditions: [MBTM] = 1.36 mole/L.
[b] $[\eta]$ = 0.14 dL/g (THF, 30°C).

Kinetic Study of Radical Polymerization

To clarify whether the radical polymerization of MBTM proceeds through an ordinary radical mechanism, the kinetic study of polymerization was carried out in benzene with AIBN in the absence of diffused light. Polymerization was performed with a straight line relationship between the conversion and the time conversion at 40 ~ 80°C. From the slopes of these lines the rate of polymerization (R_p) was determined, and their logarithms were plotted with the reciprocal of the absolute polymerization temperatures. The results are shown in Fig. 3. The apparent activation energy for this polymerization was calculated to be 18.9 kcal/mole. This value was in good agreement with that of methyl methacrylate.

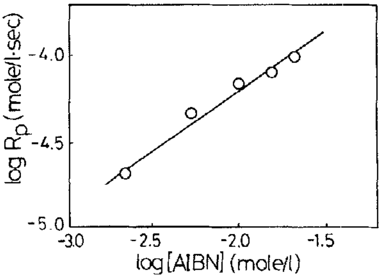


FIG. 3. Relation between log R_p and the logarithms of the concentration of AIBN initiator: [MBTM] = 1.36 mole/L in benzene at 60°C.

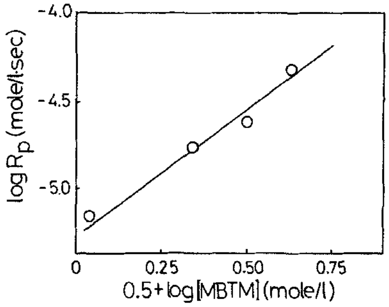


FIG. 4. Log-log plots of R_p with the monomer concentration: [AIBN] = 5×10^{-3} mole/L in benzene at 60° C.

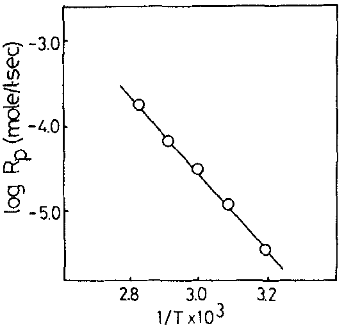


FIG. 5. Arrhenius plots of log R_p vs 1/T.

The effect of AIBN concentration on R_p in the polymerization of MBTM at 60°C was investigated with the monomer concentration kept constant (1.36 mole/L). The results are shown in Fig. 4. It is found from this figure that R_p is proportional to the square-root concentration of AIBN, indicating that this polymerization proceeds via a radical mechanism.

Figure 5 shows the relationship between log R_p and the MBTM concentration when the AIBN concentration was fixed at 5×10^{-3} mole/L. From the results of Fig. 5 a straight line relationship between log R_p and log [MBTM] with a slope of 1.0 was observed. Therefore, the rate equation of this polymerization is expressed as

$$R_p = k[\mathrm{AIBN}]^{0.5}[\mathrm{MBTM}]$$

TABLE 2. Results of Copolymerization of MBTM (M_2) with Styrene (M_1) Initiated by AIBN at 60°C

$[M_2]$ in comonomer (mole %)	Time (min)	Conversion (%)	Copolymer C (%)	Copolymer $[M_2]$ (mole %)
6.25	30	2.1	70.14	36.9
12.5	30	3.0	67.25	44.4
25.0	30	4.7	65.29	50.1
50.0	30	6.2	64.30	53.2
75.0	30	5.7	62.21	60.2
87.5	30	6.0	57.37	71.0

[a] Copolymerizations were carried out in benzene; $[M_1] + [M_2] = 2.5$ mole/L, $[\text{AIBN}] = 2.5 \times 10^{-3}$ mole/L.

where k is the overall polymerization rate constant. It is concluded that this polymerization is initiated by the 2-cyano-2-propyl radical and terminated by an ordinary bimolecular reaction.

Copolymerization with Styrene

To evaluate the copolymerization reactivity of MBTM, radical copolymerization with styrene (M_1) was carried out with AIBN in benzene at 60°C. The results are shown in Table 2. All of the copolymers obtained were colorless powder.

According to this table the copolymer yield slightly increases with an increase of the feed MBTM concentration. The monomer copolymer composition curve obtained is shown in Fig. 6, from which the monomer reactivity ratios are determined as shown in Table 3. The Q, e values for MBTM were calculated as $Q_2 = 4.09$ and $e_2 = 1.39$. In Table 3 the copolymerization parameters of the related monomers are also shown as comparison.

From this, the product of r_1 and r_2 for this copolymerization was 0.008, indicating that this system shows a high alternating tendency, contrary to related monomers. The relative reactivities ($1/r_1$) of these monomers toward the attack of the polystyryl radical are in the order MBTM > PhTM EtTM > PhMA > MMA. The reactivities of thiolmethacrylates are generally higher than those of methacrylates, and MBTM is the most reactive monomer among them. A similar reactivity order was found for the observed Q values.

In a previous paper [11] it was reported that there was a linear

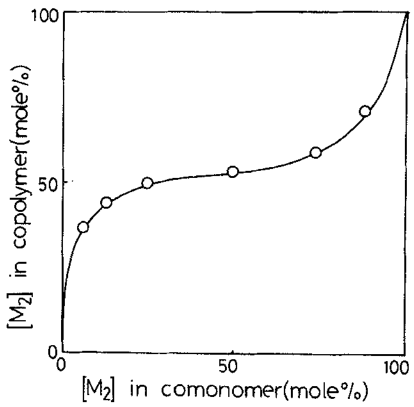


FIG. 6. Copolymer composition curve for the copolymerization of MBTM (M_2) with styrene (M_1) initiated by AIBN in benzene at 60°C: $[M_1] + [M_2] = 2.5$ mole/L, $[\text{AIBN}] = 2.5 \times 10^{-3}$ mole/L.

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

M_2[a]	r_1	r_2	$1/r_1$	Q_2[b]	e_2[b]
MBTM	0.042	0.20	23	4.09	1.39
PhTM	0.11	0.45	9.1	2.34	0.94
EtTM	0.18	0.58	5.6	1.67	0.71
MMA	0.57	0.46	1.8	0.74	0.40

[a] PhTM: phenyl thiolmethacrylate. EtTM: ethyl thiolmethacrylate.
[b] Calculated by assuming that $Q_1 = 1.0$, $e_1 = -0.80$.

relationship between log Q and λ_{max} for the π-π^* transition of vinyl monomers. These plots, including the result of MBTM, are shown in Fig. 7, from which the observed data are found to be nicely set on the straight line. Therefore, it seems that substitution of the mercaptobenzothiazole group in methacrylate monomer make MBTM more reactive than the related monomers.

Thermal- and Photodegradations

The results of TG analysis of the poly(MBTM) is shown in Fig. 8, where those of poly(PhMA) and poly(MMA) are also indicated. The

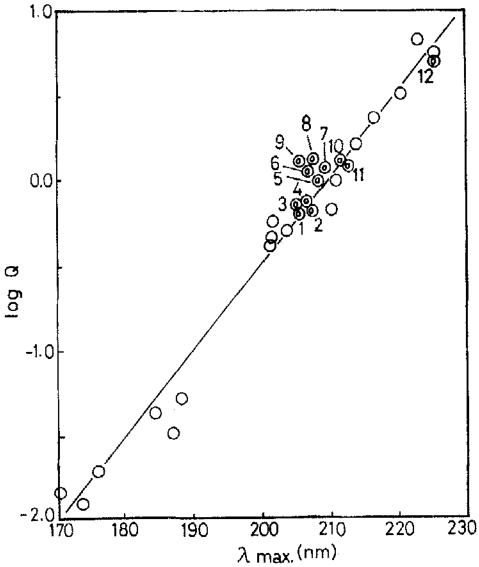


FIG. 7. Relationship between log Q and λ_{max} of methacrylate monomers: (1) n-butyl, (2) isobutyl, (3) methyl (MMA), (4) benzyl, (5) β-chloroethyl, (6) phenyl (PhMA), (7) p-methylphenyl, (8) p-methoxyphenyl, (9) p-chlorophenyl, (10 m-chlorophenyl, (11) p-nitrophenyl, and (12) MBTM. The other points are for various vinyl monomers (see Ref. 11).

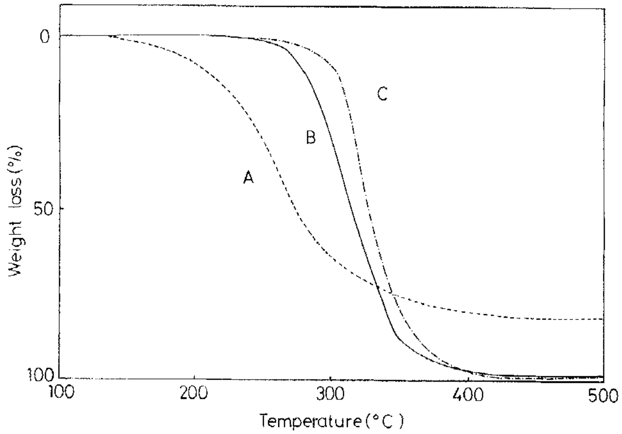


FIG. 8. TGA curves for polymers: (1) poly(MBTM), (2) poly(PhTM), and (3) poly(MMA). Heating rate, 10°C in nitrogen gas.

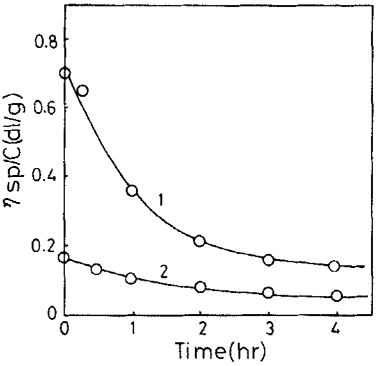


FIG. 9. Relationship between reduced viscosities and irradiation time at room temperature in the photodegradation of polymers in dilute THF solution: (1) copoly(MBTM-styrene and (2) poly(MBTM).

observed initial and maximum decomposition temperatures of poly-(MBTM) are 130 and 259°C, respectively, and the weight loss at 500°C is 81.2%. These initial and maximum temperatures are lower than those of poly(PhTM) (265 and 327°C) and poly(MMA) (258 and 338°C), indicating that poly(MBTM) is less stable than the related polymers. Moreover, the finding that the residue at 500°C for poly(MBTM) is 18.8%, contrary to the other polymers which decompose completely into monomer, seems to account for the unstability of the mercaptobenzothiazole group. Such observations are quite a contrast to the results of Saidov et al. [8] who reported that a thermally stable polymer was obtained from the copolymerization of allyl mercaptobenzothiazole with MMA or its graft copolymerization onto vinyl chloride.

Figure 9 shows the relationship between the reduced viscosities of poly(MBTM) and copolymer with styrene and the irradiation time for photodegradation in dilute THF solution at room temperature. From this figure the photodegradation of the main chain scission is found to occur easily for both polymer solutions, indicating that these are excellent photodegradable polymers. This result is also in contrast to that of Saidov et al. [8]. The mechanism of photodegradation will be described in a future paper.

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