Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Sulfur-Containing Vinyl Monomers. XVIII. Preparation and Polymerization of Vinyl Mercapto-4-methylthiazole and Properties of Its Polymers

Hiroshi Ohnishi[a]; Takayuki Otsu[a]
[a] Department of Applied Chemistry Faculty of Engineering, Osaka City University Sugimotocho, Osaka, Japan

To cite this Article Ohnishi, Hiroshi and Otsu, Takayuki(1980) 'Sulfur-Containing Vinyl Monomers. XVIII. Preparation and Polymerization of Vinyl Mercapto-4-methylthiazole and Properties of Its Polymers', Journal of Macromolecular Science, Part A, 14: 7, 1015 — 1027

To link to this Article: DOI: 10.1080/00222338008056726

URL: http://dx.doi.org/10.1080/00222338008056726

J. MACROMOL. SCI.–CHEM., A14(7), pp. 1015-1027 (1980)

Sulfur-Containing Vinyl Monomers. XVIII.* Preparation and Polymerization of Vinyl Mercapto-4-methylthiazole and Properties of Its Polymers

HIROSHI OHNISHI and TAKAYUKI OTSU

Department of Applied Chemistry
Faculty of Engineering
Osaka City University
Sugimotocho, Sumiyoshi-ku
Osaka 558, Japan

ABSTRACT

Vinyl mercapto-4-methylthiazole (VMMT) was prepared by the reaction of sodium 2-mercapto-4-methylthiazole with 1,2-dichloroethane, followed by dehydrochlorination. This monomer was easily polymerized in the presence of light or radical initiator to give a relatively high molecular weight homopolymer (15,000-55,000). The radical copolymerizations with various monomers (M_1) were also performed readily, and the following copolymerization parameters were obtained: $r_1 = 2.39$, $r_2 = 0.338$, $Q_2 = 0.605$, $e_2 = -1.26$ for VMMT (M_1)-styrene (M_2) at 60°C. The resulting homo-and copolymers were photodegradable. The reactivity of radical polymerization, and the thermal- and photodegradation behavior of the polymer were also discussed.

---

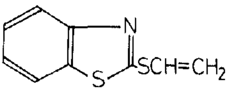
*For Part XVII of this series see: T. Otsu, H. Ohnishi, and M. Koyama, J. Macromol. Sci.–Chem., A14(6), 853 (1980).

INTRODUCTION

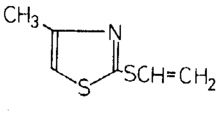
In previous papers, vinyl mercaptobenzazoles [1, 2] (i. e., thiazole, oxazole and imidazole) were prepared and found easily to undergo vinyl polymerization in the presence of light or a radical initiator. From the copolymerization with styrene, the Q and e values were obtained as Q = 0.37-0.75 and e = -1.17 to -1.38, indicating that these monomers are classified as electron-donating and conjugative monomers, similarly to other alkyl vinyl sulfides [3, 4].

It was found in previous papers [1, 5] of this series that polymers having mercaptobenzazole goups were less thermally and photochemically stable than those having the usual aromatic rings such as benzene ring, and these polymers and copolymers showed an excellent photodegradability. These observations seemed indicative of application of these polymers as photodegradable polymer and a trunk polymer for photo-induced graft polymerization.

To check these points and further to clarify the effect of the condensed benzene ring in the above mercaptobenzothiazole monomer on the polymerization reactivity, vinyl mercapto-4-methylthiazole (VMMT) was prepared and polymerized, and the stability of its polymer obtained was determined and compared with those of vinyl mercaptobenzothiazole (VMBT).



VMBT

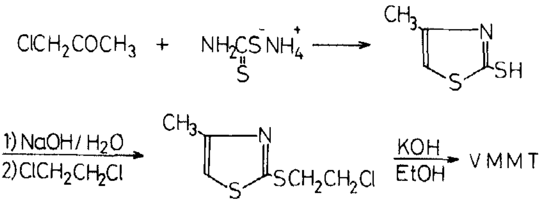


VMMT

EXPERIMENTAL

Preparation of VMMT

This monomer was prepared by the reaction of sodium 2-mercapto-4-methylthiazole which was obtained by the reported method [6] with 1,2-dichlorothane in water, followed by dehydrochlorination.



A mixture of 131 g (1 mole) of 4-methylthiazoline-2-thione and 200 ml of aqueous solution of sodium hydroxide (45 g; 1.1 mole) was added dropwise to 300 g (3 mole) of 1,2-dichloroethane at 60°C under stirring, and subsequently this mixture was allowed to stir at 60°C for 6 hr. After separation of the lower layer from the mixture, washing with water three times and drying over anhydrous sodium sulfate, the dichloroethane was distilled off under a reduced pressure. The 2-chloroethyl-2-mercapto-4-methylthiazole was obtained from the resulting oily material by passage through an alumina column; yield 155 g (80%).

To a solution of 155 g of 2-chloroethyl-2-mercapto-4-methylthiazole in 200 ml of absolute ethanol, 80 ml of a 50% ethanol solution of potassium hydroxide was added dropwise under stirring at 55°C for 6 hr. The ethanol was distilled off, and the residue was collected and washed with water, followed by drying. VMMT was obtained by distillation under reduced pressure; yield 127 g (70%). The product was a colorless liquid, bp 74.5-76.5°C/3 Torr, n_D^{20} 1.5971, d_4^{20} 1.1706.

ANAL. Calcd for $C_6H_7NS_2$: N, 8.91%; S, 40.78%. Found: N, 8.85%; S, 40.65%.

From IR, UV, and NMR determinations (see Tables 1-3), this monomer was also confirmed to be pure.

Other Materials

The monomers used for copolymerization were purified by ordinary methods and distilled just before use. Solvents and precipitants were used after the usual purification. α,α'-Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol.

Polymerization

The radical polymerizations were carried out in sealed tube with AIBN in bulk. The photopolymerization was also performed in bulk under irradiation of 100 W high pressure mercury lamp at 0°C. The charging of reagents into the polymerization tube, and the subsequent degassing and sealing were done according to the method described previously [1, 2].

After polymerization for a given time, the tube was opened and its contents were poured into a large amount of methanol to precipitate the polymer. The resulting polymer was then purified by reprecipitating its benzene solution into methanol, followed by drying under reduced pressure.

The monomer reactivity ratios for the copolymerizations were determined by nonlinear least-squares method based on the integration equation [7].

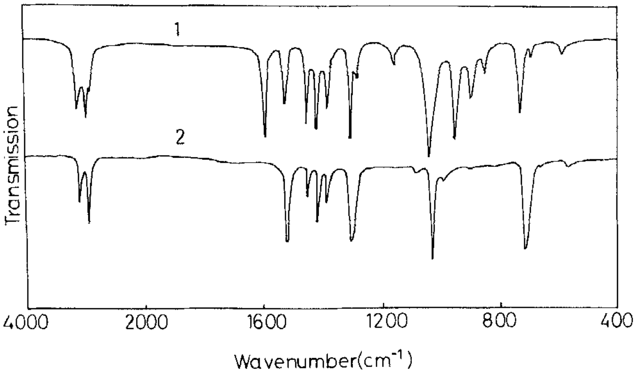


FIG. 1. IR spectra of (1) VMMT monomer and (2) radical polymer.

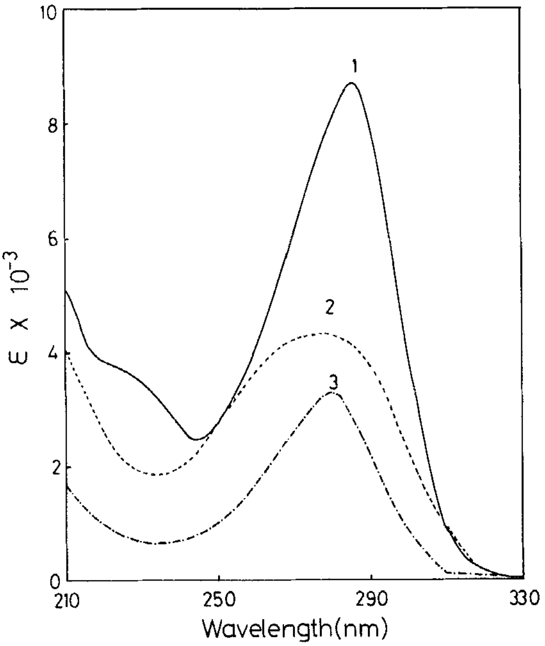


FIG. 2. UV spectra of (1) VMMT monomer, (2) radical polymer, and (3) ethyl mercapto-4-methylthiazole.

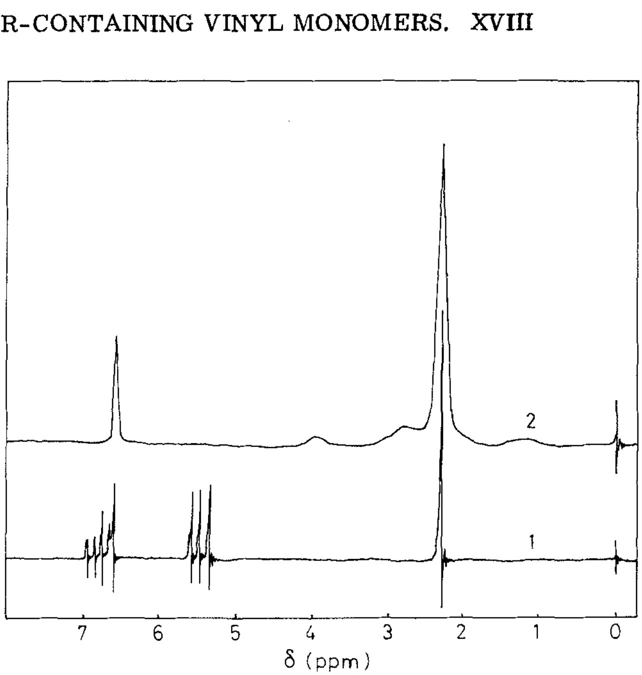


FIG. 3. NMR spectra of (1) VMMT monomer and (2) its radical polymer.

Analyses of Polymer

The composition of the copolymers was determined from elemental analyses of their carbon or sulfur content. The intrinsic viscosity ([η]) was measured in tetrahydrofuran (THF) at 30°C, by using an Ubbehlode viscometer. The number- and weight-average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) were calculated by computer from the GPC curve (Toyo Soda HLC-802UR) determined in THF at 40°C.

Thermal stability of the polymers was evaluated from thermogravimetric analysis (Shimazu TGA-20B). Photochemical stability was estimated from [η], $\overline{M}_n$, and $\overline{M}_w$ changes of the THF-polymer solution (0.7 g/dl) at 30°C during irradiation with UV light (Toshiba 100-W high-pressure mercury lamp).

RESULTS AND DISCUSSION

Properties of VMMT Monomer

This monomer, which was a colorless liquid, was prepared by the above-mentioned reaction route in good yield. The results of elemental

TABLE 1. Homopolymerization of Vinyl Mercapto-4-methylthiazole[a]

Initiation	$[I] \times 10^3$ (mole/liter)	Temp. (°C)	Time (hr)	Conversion (%)	$[\eta]$ (dl/g)[b]	$\overline{M}_n$[c]
Thermal	0	60	15	0	-	-
AIBN	6.0	60	15	6.9	0.08	16,000
UV	0	0	15	4.3	0.19	39,200
UV-AIBN	7.0	0	15	10.7	0.20	54,300
BF_3OEt_2[d]	630	0	25	0	-	-

[a] Polymerization was carried out in bulk ([M] = 7.44 mole/liter) except for cationic initiator.

[b] Intrinsic viscosity was measured in tetrahydrofuran at 30°C.

[c] Number-average molecular weight (M_n) was determined by GPC in tetrahydrofuran at 40°C.

[d] Dichloroethane was used as solvent; [M] = 4.47 mole/liter.

analysis were in good agreement with the calculated values. Figure 1 shows the IR spectrum of this monomer. There are characteristic absorption bands due to both the carbon-carbon double bond and the thiazole group. The UV spectrum is also shown in Fig. 2, from which two characteristic absorption peaks, λ_{max} 220 nm (ϵ = 4050) and λ_{max} 278 nm (ϵ = 8740), were observed. Since the former peak was not found in the saturated compound and the polymer derived from VMMT, it seems to be due to the π-π^* transition of the carbon-carbon double bond in VMMT. The latter peak is based on the thiazole group.

Figure 3 shows the NMR spectrum determined in $CDCl_3$ at 20°C. There are absorption bands at 5.3, 5.6 and 6.1 ~ 6.9 ppm due to vinyl protons, 6.6 ppm due to the protons on thiazole ring, and 2.6 ppm due to the methyl protons. From these results, this monomer is concluded to be pure.

Homopolymerization of VMMT

The results of polymerization of VMMT are shown in Table 1. VMMT is found to polymerize easily in the presence of AIBN radical initiator and under irradiation with UV light. However, no cationic polymerization is observed, probably due to the interaction between boron trifluoride diethyletherate catalyst and the heteroatoms on thiazole ring. Similar results were also found for the polymerization behavior of VMBT [1].

TABLE 2. Results of Radical Copolymerizations of VMMT (M_2) with Various Monomers (M_1)[a]

				Copolymer	
M_1	M_2 in comonomers (mole %)	Time (hr)	Conversion (%)	C or S (%)	M_2 (mole %)
St	9.7	2	5.3	C: 89.49	4.0
	17.6	2	4.1	86.81	8.7
	36.3	2.5	6.3	80.16	18.9
	56.2	2.5	5.0	72.25	33.4
	77.4	6	8.5	61.03	57.7
	88.5	8.5	6.5	54.40	74.5
MMA	8.1	2	8.6	S: 4.13	6.7
	25.4	2	9.6	10.80	18.7
	44.2	2	5.9	16.73	30.7
	54.3	2	2.1	19.76	37.4
	64.9	2	4.2	22.20	43.2
	76.0	2	5.9	26.60	54.4
	87.7	2	3.7	32.71	72.1
AN	5.2	1	1.2	S: 18.86	22.5
	17.4	1	1.1	26.10	37.5
	32.9	1	2.9	28.47	43.8
	42.4	1	3.1	29.35	46.4
	53.3	1	3.2	31.01	51.7
	66.2	1	2.9	31.78	54.4
	81.5	1	6.1	34.69	65.8
PVS	9.7	4	1.9	C: 65.94	16.5
	19.5	9	2.0	63.32	26.3
	29.4	9	1.8	60.80	36.0
	39.3	9	2.0	58.54	45.0
	49.3	9	1.9	54.92	54.8
	69.4	6	2.7	51.25	75.5
	89.7	4	2.4	47.72	91.3

[a] Copolymerizations were carried out in bulk; [AIBN] = $3.6\ 9.0 \times 10^{-}$ mole/liter.

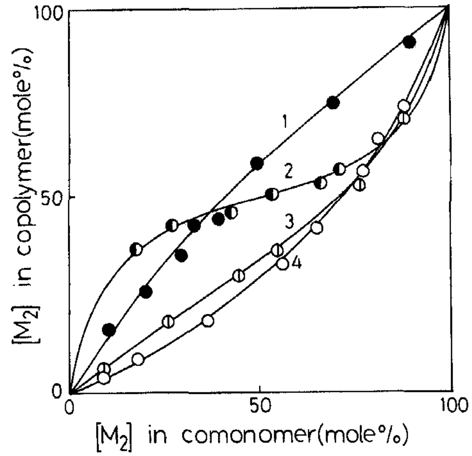


FIG. 4. Copolymer composition curves for radical copolymerizations of VMMT (M_2) with (1) PVS, (2) AN, (3) MMA, and (4) St at 60° C.

All of the resulting homopolymers are pale yellow-orange powders. As the polymerization temperature increases, the color of the polymers intensifies. The polymers, which were of rather high molecular weight ($\overline{M}_n$ = 15,000-55,000), are soluble in most organic solvents except water, methanol, and ethyl acetate.

The observed elemental analyses of the polymer (C, 45.56%; H, 4.55%; N, 8.74%) are in good agreement with the calculated values (see experimental part). From Figs. 1-3, only the absorption band due to carbon-carbon double bond was observed to disappear from the absorption of the VMMT monomer. Therefore, it is clear that this polymer was formed through an ordinary vinyl polymerization mechanism.

Copolymerization

To evaluate the radical polymerization reactivity, the copolymerizations of VMMT (M_2) with styrene (St) methyl methacrylate (MMA), acrylonitrile (AN), and phenyl vinyl sulfide (PVS) (M_2) were carried out with AIBN in bulk at 60° C. The results are shown in Table 2, from which the monomer-copolymer composition curves were derived (Fig. 4).

As is seen from Table 2, all copolymerizations except that with PVS are performed easily under these conditions, and the copolymer yield are almost independent of the feed monomer compositions.

TABLE 3. Copolymerization Parameters for the Copolymerizations of VMMT (M_2) with Various Monomers (M_1) at 60°C.

M	r_1	r_2	$1/r_1$	Q_2	e_2
St	2.4	0.34	0.417	0.61	-1.26
MMA	1.3	0.22	0.769	-	-
AN	0.17	0.19	5.88	-	-
PVS	0.66	0.13	1.52	-	-

From Table 2 and Fig. 4, the monomer reactivity ratios r_1 and r_2 were calculated as shown in Table 3, in which the Q, e values of VMMT calculated from the copolymerization results with styrene as the reference monomer (Q = 1.0, e = 0.8) are also indicated. The relative reactivities ($1/r_1$) of VMMT toward attack of various polymer radicals decreased in the following order: poly(AN) > poly(PVS) > poly(MMA) > poly(St). This order, except for poly(PVS), was in agreement with that of PVS or VMBT observed in previous papers [2, 4].

The calculated Q, e values (Q = 0.61, e = -1.26) of VMMT were almost identical to those reported previously: Q = 0.22 and e = -1.20 for PVS [4] and Q = 0.75 and e = -1.38 for VMBT [2], indicating that VMMT is a strong electron-donating, conjugative monomer.

All copolymers changed from colorless to pale-yellow powders with an increase in VMMT concentration in the feed.

Thermal and Photostabilities

The results of TG analysis of the polymers of VMMT are shown in Fig. 5 and Table 4, in which those of poly(VMBT) and poly(PVS) are also shown for comparison.

Both polymers of VMMT and VMBT were less stable than poly(PVS), indicating that the thiazole ring was unstable. Moreover, the degradation of poly(VMMT) started at a lower temperature than that of poly(VMBT), and the maximum degradation temperature was also lower about 10°C. This result was in contrast to that reported by Saidov et al. [8], who found that MMA copolymers with a small amount of monomer containing a mercaptobenzthiazole ring became more stable than poly(MMA). As reported in the previous paper [7], when poly(VMBT) was allowed to degrade in nitrobenzene at 200°C for 10 hr, a considerable amount of mercaptobenzothiazole (MBT) was isolated, and a polyene with a small amount of uneliminated BMT side group was produced. In this case, a similar elimination seemed to occur, but because of instability of the resulting 4-methylthiazole corresponding to MBT, further degradation seemed to ensue.

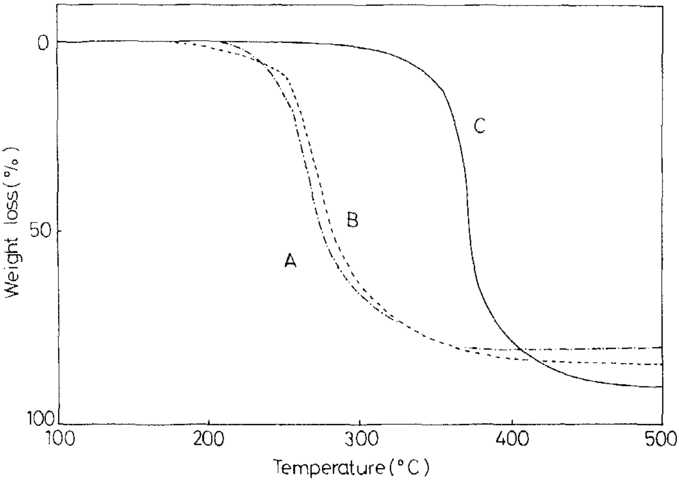


FIG. 5. TG analysis of polymers: (A) poly(VMMT), (B) poly(VMBT), and (C) poly(PVS).

TABLE 4. Results of TG Analysis

Polymers of	$M_n \times 10^{-3}$	Degradation temp. (°C) Initial	Degradation temp. (°C) Maximum	Residue (%) at 500°C
VMMT	16	170	264	19.0
VMBT	24	200	273	14.0
PVS	25	280	363	7.0

Figure 6 shows the results of photodegradation of the homopolymers of VMMT, VMBT, and PVS in THF at 30°C. The viscosities of all polymer solutions decreased gradually as a function of the irradiation time. Similar behavior was also observed for copolymer solutions of MMA and St with VMMT, as is shown in Fig. 7: in both poly(MMA) and poly (St), a decrease in their solution viscosities was not observed under the present irradiation conditions.

Thus, the GPC analyses of the polymers and copolymers isolated after irradiation for 6 hr were carried out, and from the results obtained the values of $\overline{M}_n$ and $\overline{M}_w$ were calculated according to the following equations [9]:

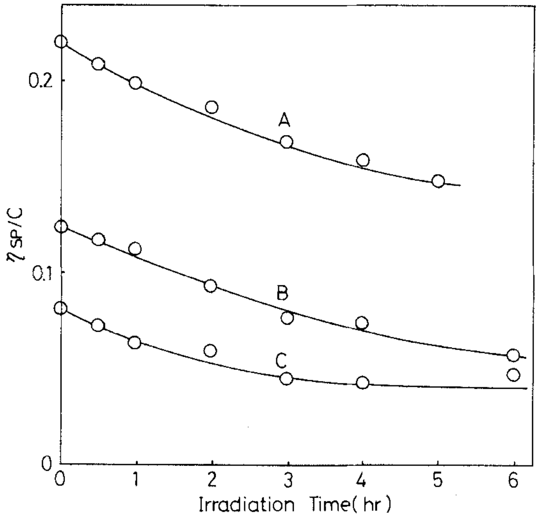


FIG. 6. Relationship between viscosity change of the homopolymers of (A) PVS, (B) VMBT, and (C) VMMT and irradiation time in photodegradation at 30°C in THF (0.7 g/dl).

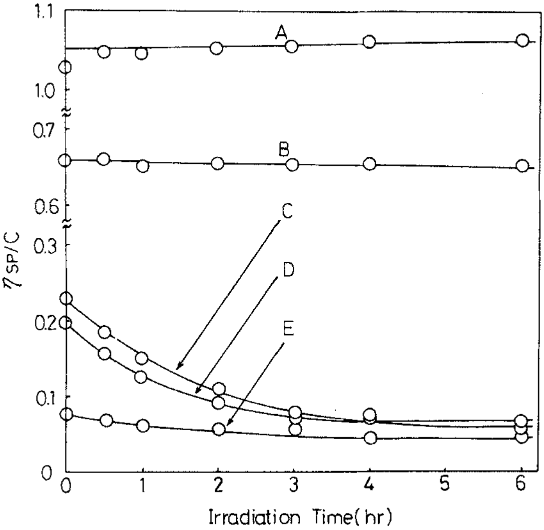


FIG. 7. Viscosity changes of the homo- and copolymers of VMMT: (A) Poly(MMA); (B) poly(St); (C) copoly[St-VMMT (57.6 mole %)]; (D) copoly[MMA-VMMT (54.4 mole %)]; (E) poly(VMMT).

TABLE 5. Results of Photoirradiation of the Polymers in Tetrahydrofuran at 30° C[a]

Polymer	Before irradiation			After irradiation for 6 hr		
	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
Poly(St)	66.9	195	2.9	67.3	150	2.2
Poly(MMA)	146	311	2.1	141	291	2.1
Poly(PVS)	25.4	40.8	1.6	2.8	18.9	6.6
Poly(VMBT)	23.7	53	2.2	0.57	11.5	20
Poly(VMMT)	16	23	1.4	0.23	7.14	31
Copoly[St-PVS (45.6)]	50.9	188	3.7	15.1	61.9	4.1
Copoly[St-VMBT (45.1)]	113	331	2.9	1.06	6.45	6.1
Copoly[St-VMMT (57.6)]	28.7	49	1.6	0.17	2.72	16
Copoly[MMA-PVS (49.5)]	28.4	60.3	2.1	10.4	26.4	2.5
Copoly[MMA-VMBT (45.8)]	125	433	3.5	1.21	10.6	8.8
Copoly[MMA-VMMT (54.4)]	40.3	91.8	2.3	0.14	5.2	35

[a] Experiments were carried out under irradiation of 100W high pressure mercury lamp at 30°C; [polymer] = 0.7 g/dl of tetrahydrofuran.

$$dW/d(\log M) = (dW/dV)\,[dV/d(\log M)]$$

$$\overline{M}_n = \sum [dW/d(\log M)] / \sum \{[dW/d(\log M)]/M\}$$

$$\overline{M}_w = \sum \{[dW/d(\log M)]M\} / \sum [dW/d(\log M)]$$

where M is molecular weight and W is weight fraction of polymer eluted up to elution volume (V). The quantity dW/dV is the ordinate of the normalized elution curve, and dV/d(log M) is the reciprocal of the slope of the usual calibration curve. These two quantities can be determined at any elution volume, and therefore $\overline{M}_n$ and $\overline{M}_w$ can be calculated by using a computer. The results are shown in Table 5.

From Table 5, it was found that all of the starting polymers and copolymers had the normal molecular weight distribution, i. e., their polydispersities ($\overline{M}_w/\overline{M}_n$) were 1.4-3.7. However, the $\overline{M}_w/\overline{M}_n$ values of the polymers irradiated for 6 hr, except those of St and MMA, were observed to increase markedly, indicating that main-chain scission occurred during photoirradiation. Therefore, these mercaptothiazole polymers and copolymers were concluded to be photodegradable polymers.

REFERENCES

[1] T. Otsu and H. Ohnishi, J. Macromol. Sci.–Chem., A12, 1477 (1978).
[2] H. Ohnishi and T. Otsu, J. Macromol. Sci.–Chem., A12, 1491 (1978).
[3] C. C. Price and J. Zomlefer, J. Am. Chem. Soc., 72, 14 (1950).
[4] T. Otsu and H. Inoue, J. Macromol. Sci.–Chem., A4, 35 (1970).
[5] T. Otsu, H. Ohnishi and M. Koyama, J. Macromol. Sci.–Chem., A14(6), 853 (1980).
[6] E. R. Buchman, A. O. Reims and H. Sargent, J. Org. Chem., 6, 764 (1941).
[7] H. Ohnishi and T. Otsu, J. Macromol. Sci.–Chem., A13, 1 (1979).
[8] B. Saidov, E. Shakirova, M. Askarov, and A. Bank, J. Polym. Sci. Polym. Symp. Ed., 40, 199 (1973).
[9] W. W. Yau and S. W. Fleming, J. Appl. Polym. Sci., 12, 2111 (1968).

Accepted by editor June 26, 1979
Received for publication July 24, 1979