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. XIV. Radical Polymerizations and Copolymerizations of Vinyl Mercaptobenzazoles

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

To cite this Article Otsu, Takayuki and Ohnishi, Hiroshi(1978) 'Sulfur-Containing Vinyl Monomers. XIV. Radical Polymerizations and Copolymerizations of Vinyl Mercaptobenzazoles', Journal of Macromolecular Science, Part A, 12: 10, 1477 — 1490

To link to this Article: DOI: 10.1080/00222337808069412

URL: http://dx.doi.org/10.1080/00222337808069412

J. MACROMOL. SCI.–CHEM., A12(10), pp. 1477-1490 (1978)

Sulfur-Containing Vinyl Monomers. XIV.* Radical Polymerizations and Copolymerizations of Vinyl Mercaptobenzazoles

TAKAYUKI OTSU and HIROSHI OHNISHI

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

ABSTRACT

Vinyl mercaptobenzazoles [thiazole (VMBT), oxazole (VMBO), and imidazole (VMBI)] were prepared through dehydrochlorination of the respective β-chloroethyl mercaptobenzazoles. These monomers were found to undergo vinyl polymerization in the presence of light or radical initiator, α,α'-azobisisobutyronitrile, to give relatively high molecular weight homopolymers. From the results of radical copolymerizations of these monomers with various monomers, the copolymerization parameters were determined as follows: VMBT(M_2)-styrene(M_1): $r_1 = 2.12 \pm 0.09$, $r_2 = 0.336 \pm 0.028$, $Q_2 = 0.75$, $e_2 = -1.38$; VMBO(M_2)-styrene(M_1): $r_1 = 2.61 \pm 0.13$, $r_2 = 0.274 \pm 0.03$, $Q_2 = 0.61$, $e_2 = -1.38$; VBMI(M_2)-styrene(M_1): $r_1 = 4.0$, $r_2 = 0.2$, $Q_2 = 0.37$, $e_2 = -1.17$. The polymerization reactivities of these monomers obtained from these parameters were compared with those of other vinyl sulfide monomers and discussed.

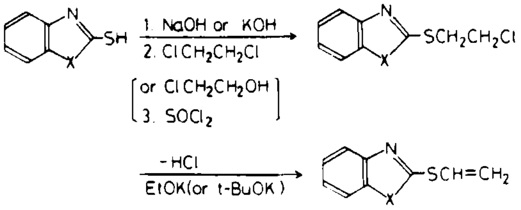
---

*For Part XIII of this series see H. Inoue and T. Otsu, J. Polym. Sci. Polym. Chem. Ed., 14, 845 (1976).

INTRODUCTION

In previous studies, it was found that various alkyl [1, 2] and p-substituted phenyl sulfides [3] could easily undergo homopolymerization and copolymerization with vinyl monomers in the presence of radical initiator. From the observed Q and e values, i. e., $Q = 0.3\text{-}0.5$ and $e = -1.1$ to -1.7, these vinyl sulfide monomers were found to belong an electron-donating conjugative monomer. These findings indicated that the electron-sharing 3d orbital resonance between the growing radical of the vinyl sulfide and its adjacent sulfur atom was important in the transition state of radical polymerization.

On the other hand, some vinyl monomers containing a heterocyclic ring have been noted to obtain their polymers and copolymers with functionalities each as catalysis, chelate formation and ion exchange [4]. Mercaptobenzothiazole is known to have been used as a mastication and vulcanization accelerator in the rubber industry and to be easily transformed to its vinyl derivatives [5, 6]. Therefore, the present paper will describe the results of the preparations of vinyl mercaptobenzazoles such as vinyl mercaptobenzothiazole (VMBT), vinyl mercaptobenzoxazole (VMBO), and vinyl mercaptobenzimidazole (VMBI) from the respective mercaptobenzazoles according to Eq. (1), and their homopolymerization and copolymerization behavior in the presence of radical initiator, α,α'-azobisisobutyronitrile (AIBN).



(1)

VMBT: X = S

VMBO: X = O

VMBI: X = NH

The preparations of these monomers have been made through the reaction of the respective mercaptobenzazoles with acetylene [5, 6] and the free radical addition and oxidation reactions [7] with these azoles have been reported. However, detailed polymerization behavior of these monomers has not been studied, except for a paper of Kern [8] regarding the radical polymerization and copolymerization of VMBT.

EXPERIMENTAL

Preparation of VMBT

VMBT was prepared by the reaction of sodium 2-mercaptobenzothiazole with 1,2-dichloroethane in water, followed by dehydrochlorination according to Eq. (1). To a mixture of 167 g (1 mole) of mercaptobenzothiazole dissolved in 450 ml of aqueous solution containing sodium hydroxide (45 g, 1.1 mole), 300 g (3 mole) of 1,2-dichloroethane was added dropwise at 60°C under stirring, and subsequently this mixture was allowed to stir at 60°C for 5 hr. After separation of the lower layer from the mixture, washing with water and drying over anhydrous sodium sulfate, dichloroethane was distilled off under reduced pressure. Then β-chloroethyl mercaptobenzothiazole was obtained from the resulting oily material by using an alumina column; yield 198 g (86%).

To a solution of 198 g of β-chloroethyl mercaptobenzothiazole and 200 ml of absolute ethanol, 80 ml of 50% potassium hydroxide as the ethanol solution was added dropwise under stirring at 40°C for 3.5 hr. The ethanol was subsequently distilled off, and the residue was washed with water, followed by drying. VMBT was obtained by distillation under reduced pressure: yield 122 g (73%); bp 97.5-98.0°C/0.1 Torr (lit. [6] bp, 135°C/3 Torr); n_D^{20} 1.6871 (lit. [6] 1.6866); d_4^{20} 1.2619 (lit. [6] 1.2629).

ANAL. Calcd for $C_9H_7NS_2$: C, 55.92%; H, 3.65%; N, 7.25%; S, 33.17%. Found: C, 55.75%; H, 3.38%; N, 7.30%; S, 32.80%.

Preparation of VMBO

VMBO was prepared by a method similar to that described for VMBT, except that the dehydrochlorination procedure was carried out with potassium tert-butoxide in tetrahydrofuran-butanol (4:1) mixed solvent at -30°C. The total yield was 80%; bp 89°C/2 Torr (lit. [7] bp, 97-99°C/3 Torr), n_D^{20} 1.6221 (lit. [7] 1.6221), d_4^{20} 1.2001 (lit. [7] 1.2142).

ANAL. Calcd for C_9H_7NOS: C, 60.99%; H, 3.98%; N, 7.90%. Found: C, 60.54%; H, 4.07%; N, 7.91%.

Preparation of VMBI

β-Chloroethyl mercaptobenzimidazole was prepared by the reaction of potassium mercaptobenzimidazole with β-chloroethanol in water at 20°C for 10 hr, followed by chlorination with thionyl chloride. The yield of crude material was 80% and recrystallized from an ethanol-water mixture: mp 122-123°C. This compound was then dehydrochlorinated with potassium tert-butoxide in tetrahydrofuran-butanol mixed solvent at 50°C for 5 hr. The pure VMBI was obtained by recrystallization from ethanol. The total yield was 70%; mp 171-172°C (lit. [7] mp, 156-161°C).

ANAL. Calcd for $C_9H_8N_2S$: C, 61.34%; H, 4.58%; N, 15.9%; S, 18.19%. Found: C, 61.11%; H, 4.32%; N, 16.0%; S, 18.2%.

Other Reagents

Other monomers were distilled just before use. Solvents and precipitants were used after purification by ordinary methods. AIBN was recrystallized twice from methanol.

Polymerization

Polymerizations and copolymerizations were carried out in a sealed tube with shaking in the absence of light. The required amounts of monomer and initiator were charged into a glass ampoule which was then degassed under vacuum by a conventional freezing and thawing technique, and finally sealed off under vacuum. After polymerization for a given time, the tube was opened and its contents poured into a large amount of methanol to precipitate the polymer. The resulting homopolymers and copolymers were purified by reprecipitating their benzene solutions into excess methanol. Conversions were calculated from the weight of the dried polymer obtained.

The composition of the copolymers was calculated from elemental analyses of carbon, and the monomer reactivity ratios (r_1 and r_2) were determined by a nonlinear least-squares method based on an integration equation [8].

RESULTS AND DISCUSSION

Properties of Monomers

As was shown in the preceding section, the physical properties of these three monomers were in good agreement with those reported,

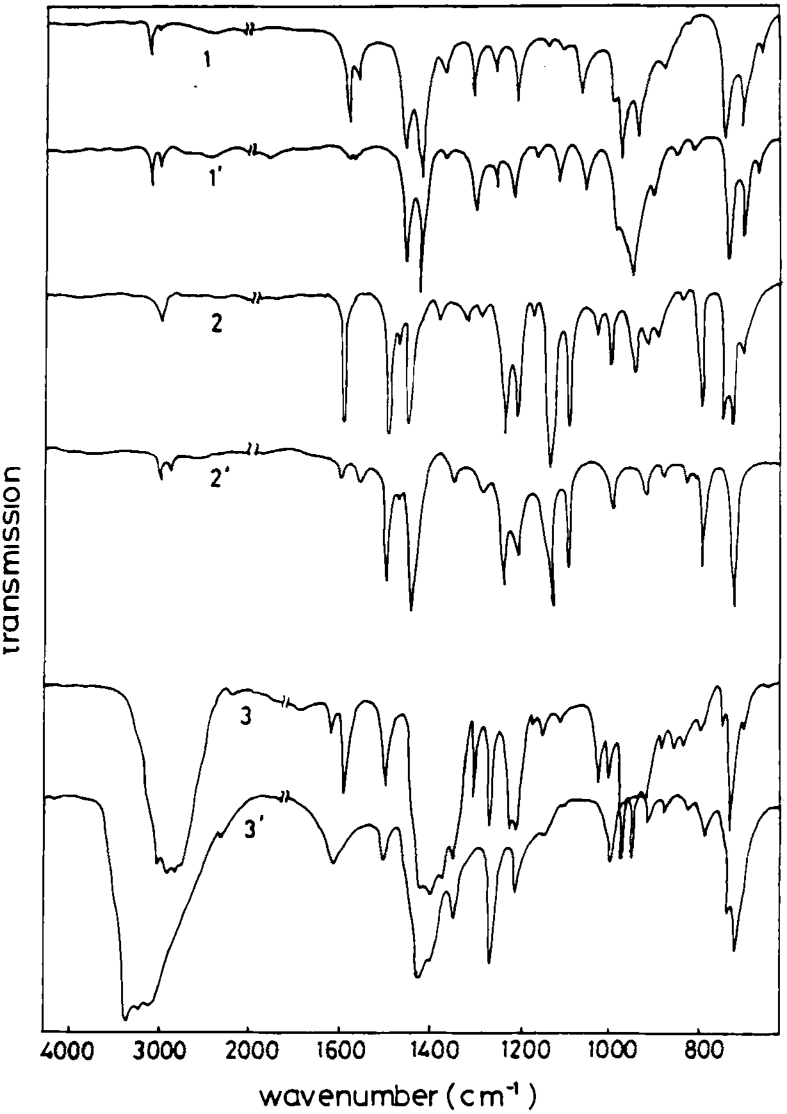


FIG. 1. IR spectra of monomers and their radical polymers: (1) VMBT; (2) VMBO; (3) VMBI; (1') poly(VMBT); (2') poly(VMBO); (3') poly(VMBI).

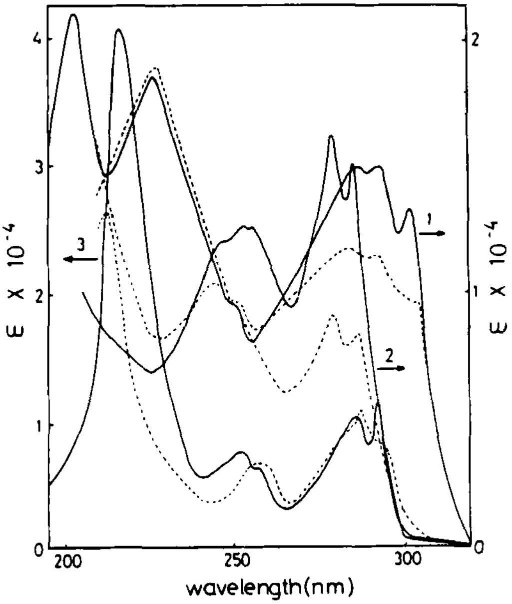


FIG. 2. UV spectra of (—) monomers and (----) their radical polymers: (1) VMBT; (2) VMBO; (3) VMBI.

and their elemental analyses also coincided with the calculated values. Therefore, it is obvious that these monomers are pure monomers.

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 (1580, 1590, 900, and 990 cm^{-1}) and benzazole groups.

Figure 2 shows the UV spectra of these monomers; the characteristic λ_{max} and ϵ are summarized in Table 1. Figure 3 shows the NMR spectra. Absorption bands are present at 5.3-5.8 and 6.8-7.0 ppm due to vinyl protons and at 7.0 ~ 8.0 ppm due to the protons on benzazole rings.

VMBT and VMBO are almost colorless, viscous liquid, and VMBI is in the form of colorless needles. These monomers were found to polymerize easily by a radical mechanism.

TABLE 1. UV Data for VMBT, VMBO, VMBI, and their Radical Polymers

	Monomer in EtOH		Polymer in THF	
	λ_{max} (nm)	ε	λ_{max} (nm)	ε
VMBT	203.0	19,000	-	-
	226.0	17,000	226,0	17,500
	248.0	8,420	249,0	8,240
	285.5	13,800	284,5	10,300
	293.5	13,800	294,5	9,940
	303.5	12,000	303,0	8,310
VMBO	245.0	12,700	245,0	10,500
	253.0	12,900	-	-
	260.0	11,800	258,5	7,570
	279.0	16,400	280,0	9,280
	286.0	15,200	287,5	8,540
VMBI	216.0	41,000	213,0	27,800
	252.0	7,550	254,0	6,850
	277.0	6,510	260,0	6,680
	286.0	10,800	287,0	11,300
	293.0	11,700	294,0	9,250

Homopolymerization

Table 2 shows the results of radical polymerization of VMBT, VMBO, and VMBI under various conditions. These monomers polymerize easily with AIBN in the presence or absence of light to give relatively high molecular weight polymers. These findings are in good agreement with the results that vinyl sulfides could homopolymerize by a radical mechanism, as reported in our previous papers. Although the former two monomers could also polymerize under irradiation of UV light, VMBT did not give polymer in the absence of AIBN, even at 150°C.

From Table 2, it is found that the radical homopolymerization

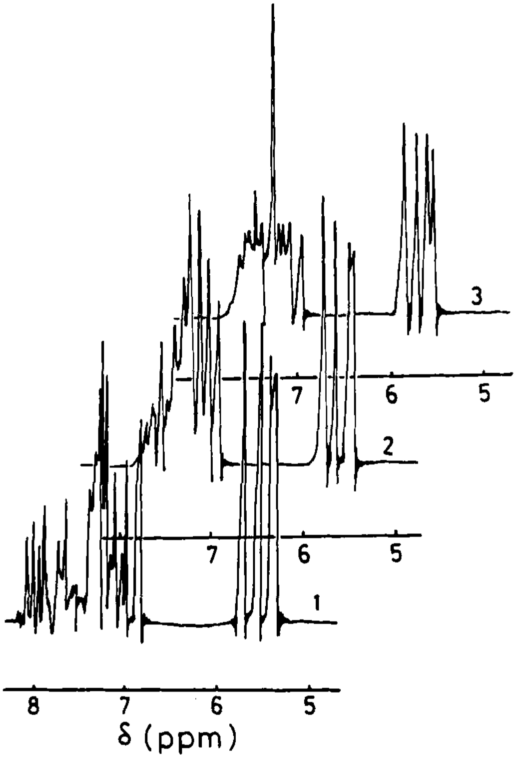


FIG. 3. NMR spectra of monomers: (1) VMBT; (2) VMBO; (3) VMBI.

reactivities of these monomers increase in the order: VMBI < VMBT < VMBO. As is shown later, the polymers obtained at 60°C were found to consist of the ordinary vinyl polymerized structure. A detailed kinetic study of radical polymerization of VMBT will be described in the next paper [9]. These monomers did not homopolymerize in the presence of cationic initiator, boron trifluoride diethyl etherate, in dichloroethane at 0°C for 24 hr.

Copolymerizations with Styrene

Table 3 shows the results of radical copolymerizations of VMBT, VMBO, and VMBI (M_2) with styrene (M_1) initiated by AIBN at 60°C.

TABLE 2. Radical Polymerizations of VMBT, VMBO and VMBI under Various Conditions

Polymer	Initiator (I)	$[I] \times 10^3$, (mole/liter)	Temp, (°C)	Time (hr)	Conversion (%)	$[\eta]$ (dl/g)[a]	$\overline{M}_n$[b]
VMBT in Bulk	None (thermal)	0	150	20	0	-	-
	AIBN	5.0	30	720	16.0	-	25700
	AIBN	4.8	60	12	6.0	0.12	29600
	UV	0	0	7	3.6	0.11	-
	UV, AIBN	4.8	0	7	18.7	0.17	-
VMBO in Bulk	AIBN	10.7	30	3 months	46.9	-	-
	AIBN	10.7	60	12	40.0	-	69700
	UV	0	15	15	1.9	-	-
	UV	0	30	10	17.9	-	-
	UV, AIBN	4.8	15	15	30.3	-	-
	UV, AIBN	10.7	30	10	40.2	-	-
VMBI in DMF	AIBN (3.08)[c]	323	60	9	54.2	-	-
	UV (0.59)[c]	0	0	9	0	-	-
	UV, AIBN (0.55)[c]	17.4	0	9	9.6	-	-

[a] Intrinsic viscosities were measured with Ubbelohde viscometer in benzene solution at 30°C.

[b] Number-average molecular weight ($\overline{M}_n$) was determined by membrane osmometer in benzene at 25°C.

[c] Monomer concentration (mole/liter in DMF).

TABLE 3. Radical Copolymerizations of VMBT, VMBO and VMBI (M_2) with Styrene (M_1) Initiated by AIBN at 60°C[a]

M_2	$[M_2]$ in comonomer (mole %)	Time (min)	Conversion (%)	Copolymer C (%)	Copolymer $[M_2]$ (mole %)
VMBT	7.69	65	4.2	90.01	3.43
	15.8	65	4.3	86.85	8.60
	33.3	65	4.5	81.48	18.5
	42.8	65	4.8	78.54	24.6
	52.9	65	5.1	75.08	32.6
	63.6	65	4.0	70.83	43.6
	75.0	65	5.4	67.52	53.4
	87.1	65	3.2	62.15	72.2
VMBT[b]	15.8	30	8.0	88.24	6.28
	33.3	30	9.3	83.19	15.2
	52.9	10	4.4	75.66	31.2
	75.0	10	5.6	67.07	54.9
	87.1	10	4.3	61.12	76.4
VMBO	16.3	90	4.1	89.23	5.7
	34.2	90	4.4	84.52	15.6
	43.8	90	4.8	81.79	22.0
	53.9	90	5.2	79.17	28.6
	64.5	90	5.6	75.71	37.6
	87.5	90	4.8	67.87	64.4
VMBI	7.67	318	8.7	91.59	1.22
	19.2	360	9.6	89.71	4.75
	30.7	582	12.2	87.97	8.18
	42.7	582	11.1	85.06	14.3
	50.8	750	14.2	82.40	20.3
	71.1	522	9.8	75.29	38.9

[a] Copolymerization conditions: [AIBN] = 5.0×10^{-3} mole/liter in bulk.

[b] Copolymerization at 30°C: [AIBN] = $5\text{-}7 \times 10^{-2}$ mole/liter in bulk.

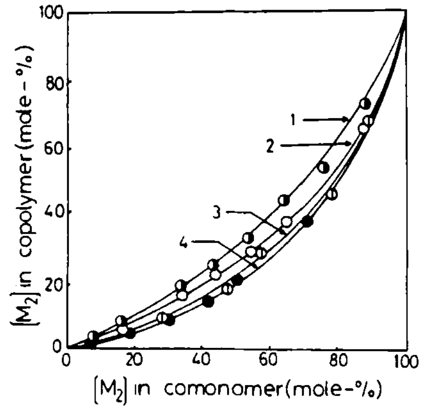


FIG. 4. Copolymer composition curves for radical copolymerizations of styrene (M_1) with (1) VMBT, (2) VMBO, (3) PVS, and (4) VMBI at 60°C.

All copolymerizations take place readily and their rates are almost independent of the monomer feed.

The monomer-copolymer composition curves derived from Table 3 are shown in Fig. 4, in which the curve observed for the copolymerization of phenyl vinyl sulfide (PVS) with styrene is also drawn as comparison. The monomer reactivity ratios for these copolymerizations are shown in Table 4, from which the reactivities of these monomers toward the polystyryl radical is observed to be in the order: VMBT > VMBO > PVS > VMBI.

It is of interest to compare the observed Q, e values with those for the other vinyl sulfides. The e values of all monomers are quite similar and highly negative. These results are understandable from the fact that the alkylthio group in vinyl sulfide shows an excellent electron-releasing nature due to 2p-3p conjugation between carbon-carbon double bond and sulfur atoms. On the other hand, the Q values are almost equal, indicating that these monomers belong to a conjugative monomer, and that the following 3d orbital resonance between the growing radical and the adjacent sulfur atom [Eq. (2)] is important:

$$\sim\!\sim CH_2\text{-}\dot{C}H\text{-}SR \longleftrightarrow \sim\!\sim CH_2\text{-}CH{=}\dot{S}R \qquad (2)$$

Therefore, these monomers are concluded to be an electron-donating conjugative monomers.

TABLE 4. Copolymerization Parameters of Vinyl Sulfides (M_1 = St)

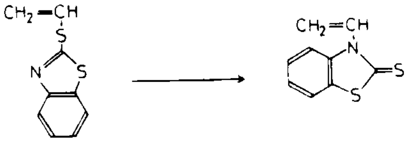
M_2	r_1	r_2	$1/r_1$	Q	e
VMBT	2.12 ± 0.09	0.336 ± 0.028	0.472	0.75	-1.38
VMBO	2.61 ± 0.13	0.274 ± 0.032	0.383	0.61	-1.38
VMBI	4.1	0.20	0.25	0.37	-1.17
PVS	3.27	0.258	0.308	0.22	-1.20
PVS[a]	3.71	0.30	0.27	0.45	-1.3
MVS[b]	5.0	0.15	0.20	0.31	-1.3

[a] Results of Tsuda et al. [3].
[b] Results of Otsu and Inoue [2].

Properties of Polymers

The IR and UV spectra of the homopolymers obtained at 60°C are shown in Figs. 2 and 3, respectively. When both spectra are compared with those of the respective monomers, characteristic absorption bands except the band due to carbon-carbon double bond in the monomers were observed. Especially, as shown in Table 1, λ_{max} and ϵ in the UV spectra of both monomers and polymers were quite identical. Therefore, it was clear that these polymers were obtained through ordinary polymerization of azole monomers.

Previously Kern [6] found that VMBT could isomerize to its N-vinyl derivative at rather high temperature [Eq. (3)], and this monomer then participated in radical polymerization of VMBT to yield a copolymer.



(3)

However, as stated above, it was concluded that such copolymers were not produced from VMBT and other azole monomers under these conditions. Such a conclusion is strongly supported by the fact that no thermal isomerization of VMBT to its N-vinyl derivative was observed, even at 150°C, by means of gas chromatography.

TABLE 5. Thermal Properties of Poly(vinyl Mercaptobenzazoles) and Poly(phenyl Vinyl Sulfide)

Polymer from	Appearance	Softening point (°C)	Degradation temp (C°)		Residue at 500°C (%)
			Initial	Maximum	
VMBT	Pale yellow powder	122-124	200	273	14.0
VMBO	Pale green powder	128-130	155	257	13.8
VMBI	Colorless powder	220-223	221	305	14.4
PVS	Colorless powder	82-84	280	365	7.0

*Conditions of thermogravimetric analysis: nitrogen gas, 25 ml/min, heating rate 10°C/min.

The properties of the resulting polymers are shown in Table 5; those of PVS are also shown for comparison. All of these polymers were colorless or pale colored powders whose molecular weight were above 25000. These polymers were also soluble in benzene, chloroform, dioxane, tetrahydrofuran, dimethylformamide, dimethyl sulfoxide, and concentrated hydrochloric acid, but insoluble in water, methanol, acetone, carbon tetrachloride, diethyl ether, and n-hexane.

The results of thermogravimetric analyses of these polymers are shown in Table 5. In general, all of these polymers were not so thermally stable, but the approximate order of their thermal stabilities was PVS $<$ VMBI $<$ VMBT $<$ VMBO.

REFERENCES

[1] C. C. Price and J. Zomlefer, J. Am. Chem. Soc., 72, 14 (1950).
[2] T. Otsu and H. Inoue, J. Macromol. Sci.–Chem., A4, 35 (1970).
[3] K. Tsuda, S. Kobayashi, T. Otsu, J. Macromol. Sci.–Chem., A1, 1025 (1967).
[4] K. Takemoto, J. Macromol. Sci.–Rev., C5, 29 (1970).
[5] M. F. Shostakovskii et al., Izv. Akad. Nauk SSSR Otd. Khim. Nauk, 1958, 1250.
[6] R. J. Kern, J. Polym. Sci., 43, 549 (1960).
[7] E. N. Prilezaeva and L. I. Shimonia, Izv. Akad. Nauk SSSR, Ser. Khim., 1969, 670.
[8] B. Yamada, M. Itahashi, and T. Otsu, J. Polym. Sci. Polym. Chem. Ed., 16, 1719 (1978).
[9] H. Ohnishi and T. Otsu, J. Macromol. Sci.–Chem., A12, 1491 (1978).

Accepted by editor July 12, 1978
Received for publication August 24, 1978