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### Sulfur-Containing Vinyl Monomers. XVI. Isomerization and Polymerization of Vinyl Mercaptobenzothiazole and Its Related Compounds

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## **Sulfur-Containing Vinyl Monomers. XVI.\* Isomerization and Polymerization of Vinyl Mercaptobenzothiazole and Its Related Compounds**

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### ABSTRACT

In order to assess the possibility of isomerization during radical polymerization of vinyl mercaptobenzothiazole (VMBT), the isomerization of VMBT and its related compounds was investigated in the presence or absence of catalyst. In the absence of catalyst, VMBT was found to polymerize through participation of only its vinyl group at temperatures below 200°C. When VMBT was heated at 200°C in the presence of iodine as a catalyst, mercaptobenzothiazole (MBT) and polymer containing both a double bond and the benzothiazolinethione unit were obtained, but no isomerized N-vinyl monomer (VBTT) was produced. However, ethyl mercaptobenzothiazole (EMBT), a saturated model of VMBT, was easily isomerized to N-ethyl benzothiazolinethione under the same conditions. Therefore,

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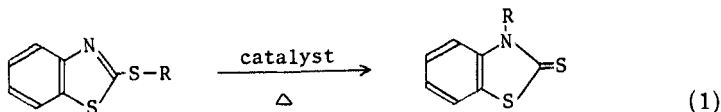
\*Part XV: H. Ohnishi and T. Otsu, *J. Macromol. Sci.-Chem.*, **A12** 1491 (1978).

it was concluded that VMBT was polymerized by the ordinary vinyl polymerization mechanism, even at 200°C without isomerization, but the MBT group in the resulting VMBT polymer underwent isomerization and elimination if isomerization catalyst was present.

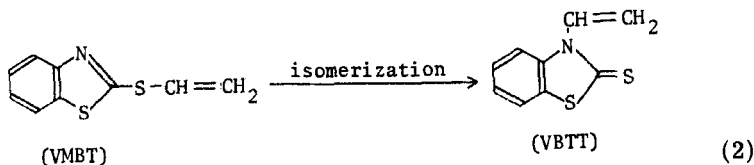
## INTRODUCTION

In previous papers [1, 2], the preparation and polymerization of vinyl sulfides with a benzazole ring were investigated in comparison with the results of alkyl or phenyl vinyl sulfides [3, 4]. For example, vinyl mercaptobenzothiazole (VMBT) was found to homopolymerize easily by a radical mechanism and to be classified as an electron-donating conjugative monomer from copolymerization study with styrene.

However, it has been known that some alkyl and allyl derivatives of mercaptobenzothiazole (MBT) are isomerized to benzothiazolinethione [Eq. (1)] as the result of migration of alkyl or allyl group from sulfur to nitrogen atoms by heating and/or in the presence of iodine [5], alkyl iodide [6], and sodium methoxide [7] as catalyst.



Therefore, there is a possibility that such isomerization occurs in the radical polymerization of VMBT. In fact, Kern [8] reported that when VMBT was polymerized thermally at 120°C for 30 hr, the polymer of N-vinyl benzothiazolinethione (VBTT) which isomerized according to Eq. (2) was probably produced.



Contrary to this, our previous results [1, 2] showed that ordinary homopolymer of VMBT without isomerization from its radical

polymerization at temperatures below 150°C in the presence or absence of radical initiator, azobisisobutyronitrile (AIBN), was formed.

To clarify these discrepancies, the isomerization and polymerization of VMBT in the presence or absence of catalyst were investigated in detail. N-Ethyl mercaptobenzothiazole (EMBT) was used as a saturated model compound of VMBT in order to permit comparisons.

## EXPERIMENTAL

VMBT was prepared by the method described in a previous paper [1]. EMBT was synthesized by the reaction of ethyl bromide with sodium mercaptobenzothiazole in tetrahydrofuran at 20°C for 12 hr according to the method of Moore [5], and purified by distillation; bp 148-150°C/6 Torr (lit. [5] bp 170°C/12 Torr).

Although the preparation of VBTT was reported by Kim et al. [9], our several attempts to prepare this monomer were unsuccessful. N-Ethyl benzothiazolinethione (EBTT) was synthesized by isomerization of EMBT in bulk in the presence of iodine at 200°C and purified by recrystallization from methanol. Colorless needles were obtained; mp 75-76°C (lit. [5] mp 75-76°C).

The polymerization and isomerization reactions were carried out in a sealed tube. The required amounts of VMBT and catalyst were charged into a glass ampoule which then degassed under vacuum by a conventional freezing and thawing technique, and finally sealed off under vacuum. After reaction for a given time at a definite temperature, the tube was opened and diluted with a small amount of tetrahydrofuran. This solution was then poured into excess acetone to precipitate the polymer. After filtration, the resulting solution was concentrated and poured into a large amount of carbon tetrachloride to precipitate MBT. To the concentrated filtrate excess methanol was then added. From the precipitate and filtrate obtained, MBT and unreacted VMBT, respectively, were separated. The identity of each compound isolated was confirmed by IR, UV, and NMR spectral determinations.

The reactions of EMBT with catalyst were carried out by similar manner, but the amounts of products were determined by gas chromatography.

## RESULTS AND DISCUSSION

Table 1 summarizes the results of reactions of VMBT or EMBT in the presence or absence of catalysts, iodine, and sodium methoxide.

TABLE 1. Results of Reactions of VMBT or EMBT in the Presence or Absence of Catalyst<sup>a</sup>

MBT derivative	Catalyst	Temp (°C)	Time (hr)	Product and recovered MBT (%)					
				Polymer	MBT	VMBT	EBTT	EMBT	
VMBT	None	120	20	0	0	~100			
	I <sub>2</sub>	120	20	0	0	~100			
	None	200	10	47.5	(52.5) <sup>b</sup>				
	I <sub>2</sub>	200	5	6.6	44.0	-			
	I <sub>2</sub>	200	10	12.6	81.5	-			
	NaOCH <sub>3</sub>	60	40	0	0	~100			
EMBT	None	200	20		0		0	~100	
	I <sub>2</sub>	200	5				63.1	36.6	
	I <sub>2</sub>	200	15				92.1	6.6	
	NaOCH <sub>3</sub>	60	40				0	~100	

<sup>a</sup>[I<sub>2</sub>] = 3.46 × 10<sup>-2</sup> mole/liter; [NaOCH<sub>3</sub>] = 9.3 × 10<sup>-3</sup> mole/liter in bulk.

<sup>b</sup>Total amounts of VMBT and MBT expected from polymer precipitated.

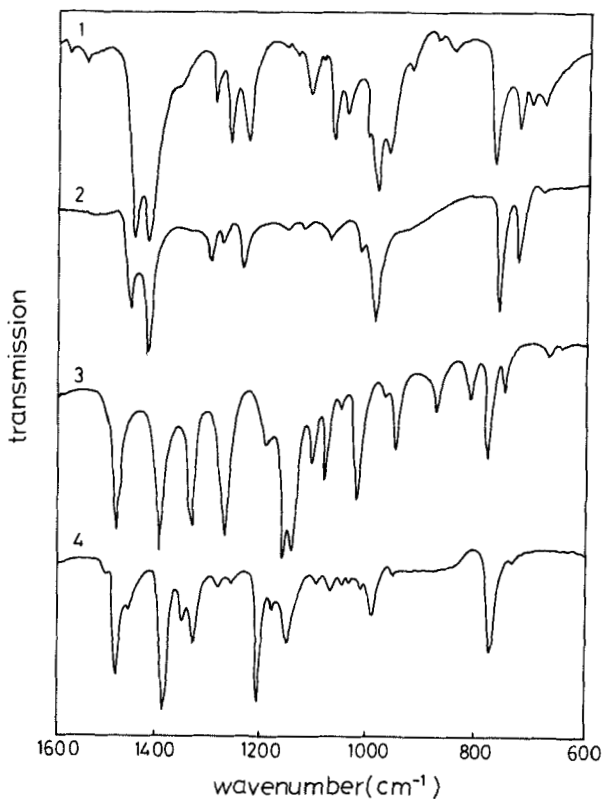


FIG. 1. IR spectra of (1) EMBT, (2) P-60, (3) EBTT, and (4) P-200-I<sub>2</sub>.

When VMBT was heated at temperatures below 120°C in the presence or absence of catalyst, no polymer was obtained, and the VMBT monomer was recovered quantitatively. At 200°C in the presence or absence of iodine, however, VMBT was polymerized to give colored polymer whose yield was lowered by the presence of iodine as a radical inhibitor. After separation of the polymer, VMBT and MBT were isolated from the reaction mixture, but isomerized monomer, VBTT by Eq. (2), was not detected. However, when the reactions of EMBT, a saturated model compound of VMBT, were attempted at 200°C in the presence of iodine, isomerization of EMBT to EBTT according to Eq. (1) was observed (see Fig. 7).

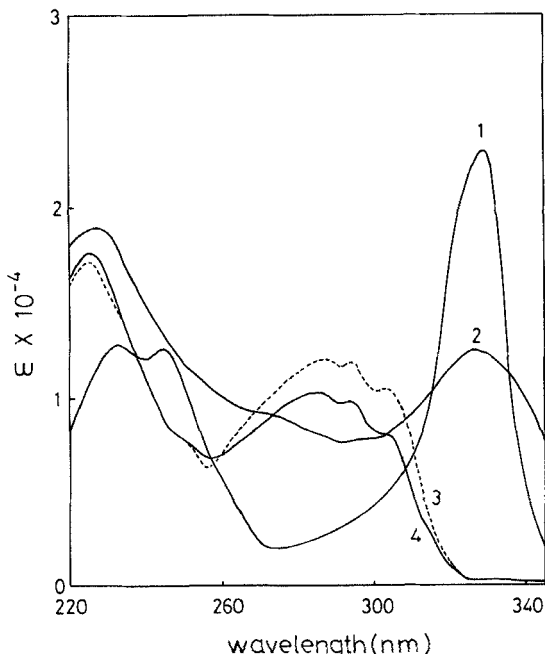


FIG. 2. UV spectra of (1) EBTT, (2) P-200-I<sub>2</sub>, (3) P-60, and (4) VMBT.

From IR spectral determination, the structure of the polymer obtained thermally at 200°C from VMBT was found to be almost identical to that (P-60) obtained through its radical polymerization at 60°C, which consisted of a vinyl-polymerized structure. However, the polymer (P-200-I<sub>2</sub>) obtained at 200°C for 5 hr in the presence of iodine showed different IR and UV spectra from P-60. These IR and UV spectra are shown in Figs. 1 and 2; those of EMBT and its isomerized product, EBTT, are also indicated in these figures.

From the IR spectrum, the P-200-I<sub>2</sub> did not show the absorption bands at 1240 and 1660 cm<sup>-1</sup> which appeared in both EMBT and P-60, but new bands at 1375 cm<sup>-1</sup> due to the -N-C=S group which was found in EBTT and at 980 cm<sup>-1</sup> due to the carbon-carbon double bond appeared. The presence of both groups in P-200-I<sub>2</sub> was also confirmed by UV spectra (Fig. 2), i. e., the absorption maxima ( $\lambda_{\max}$ ) of P-200-I<sub>2</sub> were quite similar to those of EBTT, although they were

TABLE 2. UV Data of VMBT and Related Compounds

Compound	$\lambda_{\max}$ (nm) and (log $\epsilon$ ) <sup>a</sup>			
EMBT	230(4.30)	284(3.97)	293(4.06)	303(3.95)
VMBT	225(4.31)	285(4.21)	293(4.21)	303(4.15)
P-60	226(4.24)	285(4.01)	294(4.00)	303(3.92)
EBTT	233(4.18)	245(4.16)		329(4.44)
P-200-I <sub>2</sub>	231(8.38)			325(8.07)

<sup>a</sup>Determined in tetrahydrofuran.

different from those of EMBT, VMBT, and P-60, as is shown in Table 2. Therefore, it was clear that the P-200-I<sub>2</sub> contained both the carbon-carbon double bond resulting from elimination of MBT from the polymer of VMBT (P-60) and the benzothiazolinethione (BTT) group produced by isomerization of the MBT side group in its polymer.

The NMR spectra of the P-200-I<sub>2</sub> are shown in Fig. 3, from which the characteristic resonance peaks at 1.24, 4.84, and 7.0-7.4 ppm due to the methylene protons adjacent to the double bond, the methine protons, and the protons on the benzothiazole ring, respectively, are observed, indicating the presence of the double bond.

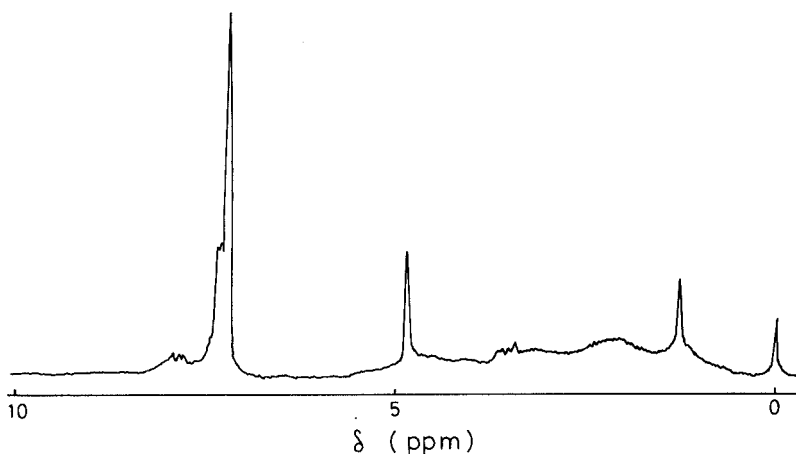


FIG. 3. NMR spectrum of P-200-I<sub>2</sub> in CDCl<sub>3</sub> at 50°C.



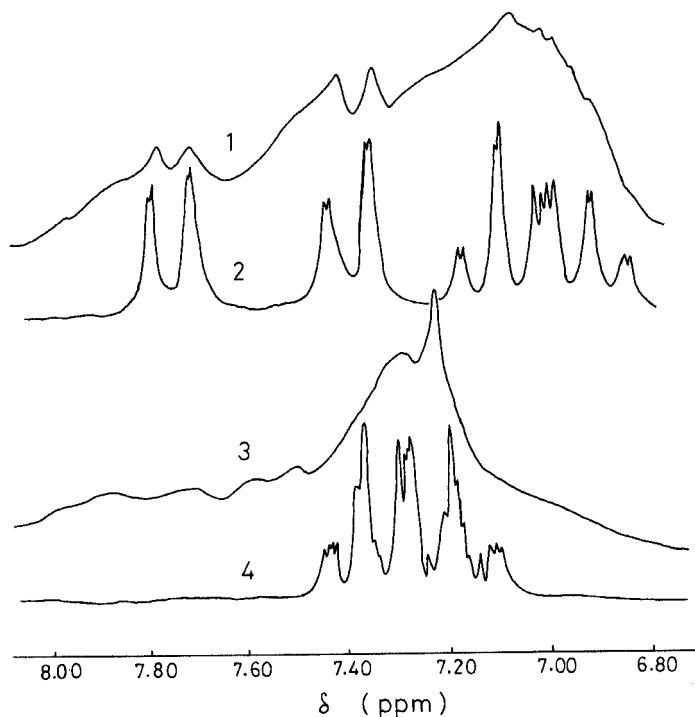


FIG. 4. NMR spectra of (1) P-60, (2) EMBT, (3) P-200-I<sub>2</sub>, and (4) EBTT in CDCl<sub>3</sub> at 50°C.

In order to check further the presence of BTT unit, the NMR spectrum between 6.8 and 7.5 ppm was determined in comparison with that of EMBT and EBTT. The results are shown in Fig. 4. The shape of NMR spectrum for the P-60 was found to be approximately similar to that of EMBT. Contrary to this, the NMR spectrum of the P-200-I<sub>2</sub> was observed to coincide with that of EBTT. Therefore, it was reconfirmed that P-60 consisted of an ordinary vinyl-polymerized structure with the MBT side group, but the P-200-I<sub>2</sub> contained both the carbon-carbon double bond in the main chain and the BTT unit in the side group.

Figure 5 shows the relations between the reaction time and the yields of the polymer and of the MBT in the reactions of VMBT at 200°C in the presence of a small amount of iodine ( $1.43 \times 10^{-3}$  mole/liter). The yields of the polymer increased with reaction time, but

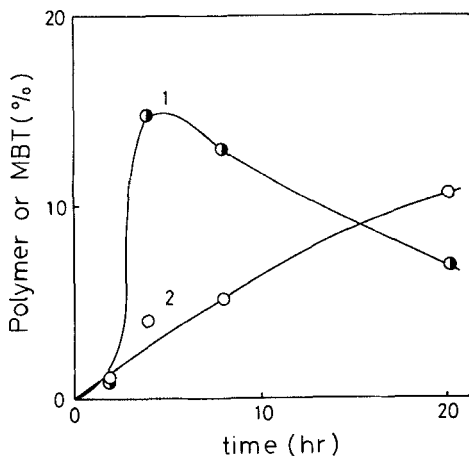


FIG. 5. Relationships between polymer or MBT yield and reaction time in thermal reactions of VMBT in the presence of iodine at 200°C: (1) MBT yield; (2) polymer yield.  $[VMBT] = 6.21$  mole/liter;  $[I_2] = 1.43 \times 10^{-3}$  mole/liter.

those of the MBT produced gave a maximum at an early stage of the reaction. The resulting colored polymer contained the carbon-carbon double bond, but the BTT unit was not found under this catalyst concentration within experimental error.

Similar relations are also shown in Fig. 6, in which the concentration of iodine was used twenty times more than that of the reactions represented in Fig. 5. The yield of polymer decreased, but that of the MBT increase markedly compared with the results of Fig. 5, indicating that iodine acted as both inhibitor of this polymerization and accelerator of elimination of MBT from the polymer.

Unlike the polymers obtained in the reactions described in Fig. 5, the resulting colored polymers contained both the carbon-carbon double bond and the BTT unit, similar to P-200- $I_2$ . As described above, the content of the BTT unit in polymers might be determined from the absorbance at 329 nm in their UV spectra. The plots are also shown in Fig. 6, from which this unit increased with the reaction time. However, VBTT was not detected from all of the reaction mixtures. These results seem to indicate that VMBT polymerizes first at its vinyl group and that the MBT group in the resulting polymer then isomerizes or eliminates to give finally a polymer with BTT group and double bond.

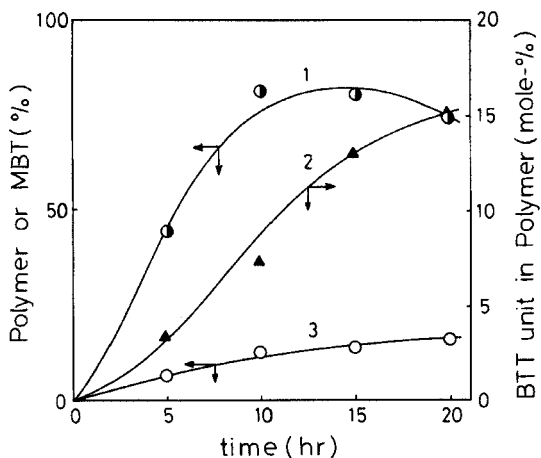


FIG. 6. Relationships between polymer or MBT yield and reaction time in thermal reaction of VMBT in the presence of iodine at  $200^{\circ}\text{C}$ : (1) MBT yield; (2) BTT unit in polymer; (3) polymer yield.  $[\text{VMBT}] = 6.21$  mole/liter,  $[\text{I}_2] = 3.46 \times 10^{-2}$  mole/liter.

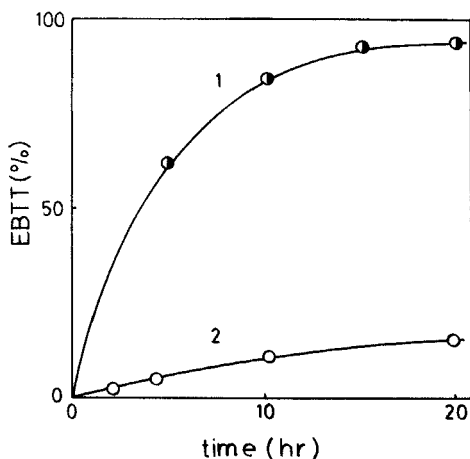
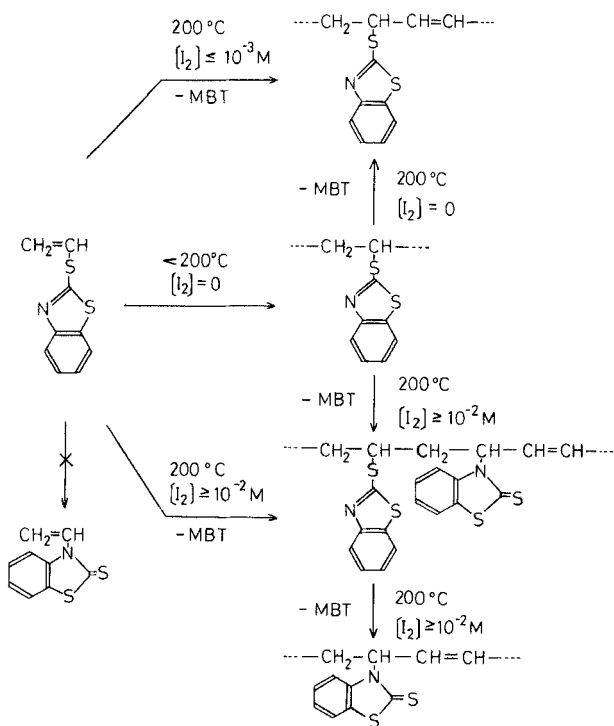


FIG. 7. Thermal reaction of EMBT in the presence of iodine at  $200^{\circ}\text{C}$ ,  $[\text{EMBT}] = 5.97$  mole/liter: (1)  $[\text{I}_2] = 1.43 \times 10^{-3}$  mole/liter; (2)  $[\text{I}_2] = 3.46 \times 10^{-2}$  mole/liter.

To check whether elimination and isomerization of the MBT side group occur from the polymer produced, the polymer (P-60) was heated in nitrobenzene at  $200^{\circ}\text{C}$  in the presence or absence of iodine. After reaction for 5 hr, the reaction mixture was poured into acetone to precipitate the polymer. The polymers recovered were colored powders with both double bond and BTT units, and their yields were 34.8 and 39.4%, when reacted in the absence and presence of iodine, respectively. From the residual acetone solutions, MBT were also isolated.

Figure 7 shows the results of isomerization from EMBT, a model compound of P-60, to EBTT under similar conditions to Figs. 5 and 6. As can be seen from this figure, EMBT isomerized to EBTT depending on the concentration of iodine catalyst used. In these reactions, however, ethylene and MBT were not produced, contrary to the polymer of VMBT (P-60). Such a difference seems to originate from the effect of polymer chain.



(3)

The results described above indicate that the polymerization of VMBT initiated by AIBN in the presence or absence of iodine at elevated temperature seems to follow the scheme shown in Eqs. (3).

## 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 ] T. Otsu and H. Inoue, J. Macromol. Sci.-Chem., A4, 35 (1970).
- [ 4 ] K. Tsuda, S. Kobayashi, and T. Otsu, J. Macromol. Sci.-Chem., A1, 1025 (1967).
- [ 5 ] C. G. Moore and E. S. Waight, J. Chem. Soc., 1952, 4237.
- [ 6 ] A. Robertson and W. A. Sexton, J. Chem. Soc., 1939, 473.
- [ 7 ] W. J. Humphlett, J. Heterocyclic Chem., 5, 387 (1968).
- [ 8 ] R. J. Kern, J. Polym. Sci., 43, 549 (1960).
- [ 9 ] A. A. Kim, L. V. Zavyalova, N. K. Rozhkova, A. S. Bank, and M. A. Askarov, Vysokomol. Soedin., B17, 324 (1975).

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