Vinyl Polymerization. CXVI.[1] The Effects of Several Sulfides and Oxides on Radical Polymerization

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It is known that some aliphatic disulfides can act as the initiator in radical polymerization.[2,3] Many studies have been made of the reaction and of the mechanism of the radical decomposition of these sulfides. Tobolsky[3] and Otsu et al.,[4] for example, investigated the polymerization of styrene or methyl methacrylate initiated by tetraalkylthiuramdisulfides. On the other hand, little progress has been made in the field of aromatic disulfide, although Pierson[5] and Otsu[6] used some aromatic disulfides, including diphenyl disulfide, as

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[1] Part CXV : T. Nakata, Y. Kinoshita, T. Otsu and M. Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **68**, 864 (1965).

[2] R. J. Kern, *J. Am. Chem. Soc.*, **77**, 1382 (1955).

[3] T. E. Ferington and A. V. Tobolsky, ibid., **77**, 4510 (1955).

[4] T. Otsu, K. Nayatani, I. Muto and M. Imai, *Makromol. Chem.*, **27**, 142 (1958).

[5] R. M. Pierson, A. J. Constanza and A. H. Weinstein, *J. Polymer Sci.*, **17**, 221 (1955).

[6] T. Otsu, ibid., **21**, 559 (1956).

initiators and chain transfer agents of radical polymerization.

The present paper will deal with the polymerization of styrene and methyl methacrylate in the presence of aromatic sulfide or oxide. Some sulfides and oxides of a similar structure were employed in order to see (1) how these compounds act as initiators or chain transfer agents in radical polymerization, and (2) how the differences in structure affect on the radical polymerization.

The compounds used here are:

1) Sulfides: diphenyl sulfide (DPS), diphenyl disulfide (DPDS), dibenzyl sulfide (DBS), and dibenzyl disulfide (DBDS).

2) Oxides: diphenyl ether (DPE), and dibenzyl ether (DBE).

Experimental

Preparation and Purification of Materials.—*Diphenyl Sulfide (DPS).*—Hartman's method[7] was adopted in preparing DPS, and the product obtained was purified by distillation. B. p. 160—161°C/23 mmHg (Found: C, 77.37; H, 5.47; S, 17.39. Calcd. for $C_{12}H_{10}S$: C, 77.37; H, 5.41; S, 17.22%).

Diphenyl Disulfide (DPDS).—This sulfide was obtained by the oxidation of thiophenol with iodine in ethanol. The crude product was recrystallized from dichloroethane. M. p. 58.8—59.0°C (Found: C, 66.33; H, 4.59; S, 29.21. Calcd. for $C_{12}H_{10}S_2$: C, 66.01; H, 4.62; S, 29.37%).

Dibenzyl Sulfide (DBS).—This was prepared by Seriner's process,[8] and the resulting DBS was purified by recrystallization. M. p. 47.5—48.0°C (lit.[8] 49.0°C) (Found: C, 78.43; H, 6.60; S, 14.85. Calcd. for $C_{14}H_{14}S$: C, 78.45; H, 6.59; S, 14.96%).

Dibenzyl Disulfide (DBDS).—Frank's process[9] was adopted for the preparation of this sulfide, and the product was recrystallized from dichloroethane. M. p. 69.0—69.5°C (lit.[9] 69—70°C) (Found: C, 67.96; H, 5.72; S, 25.99. Calcd. for $C_{14}H_{14}S_2$: C, 68.25; H, 5.73; S, 26.03%).

Oxides.—Commercial diphenyl ether was purified by distillation and recrystallization, while dibenzyl ether was purified by distillation alone.

The Purification of the Other Reagents.—Monomers were purified by the standard methods. Azobisisobutyronitrile (AIBN) was recrystallized from alcohol. M. p. 102.0—102.5°C.

Polymerization. — Bulk polymerization by the glass-tube method was employed. Given amounts of the monomer and of sulfide or oxide were charged into a tube and evacuated by the usual method. Thermal polymerizations were carried out at 60°C under shaking. During the polymerization, the outside light was completely excluded. Photo-polymerizations were made at room temperature by applying the ultraviolet rays from a mercury lamp. The conversion of both cases was controlled below 10%. The rate of polymerization was decided by the weight of the polymer obtained after it had been put into a quantity of methanol, let pass through glass filters, and dry.

The Determination of Degree of Polymerization and the Chain Transfer Constants.—The polymer obtained was precipitated again from a benzene solution by pouring it into methanol. The intrinsic viscosity $[\eta]$ was determined in benzene at 30°C by using Ubbelohde's viscometer. The number-average degree of polymerization ($\bar{P}_n$) was calculated by formulas 1 and 2:

For polystyrene[10] $\log \bar{P}_n = 3.205 + 1.37 \log[\eta]$ (1)

For polyMMA[11] $\log \bar{P}_n = 3.420 + 1.13 \log[\eta]$ (2)

The chain transfer constants (C) to sulfides or oxides were determined by Mayo's formula 3:

$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_0} + C\frac{[\mathrm{S}]}{[\mathrm{M}]} \qquad (3)$$

where [S] and [M] are the initial concentrations of the chain transfer agent and the monomer respectively.

Results

The Results of Thermal Polymerization.—The results of thermal polymerization conducted at 60°C in the presence of sulfides or oxides are shown in Table I.

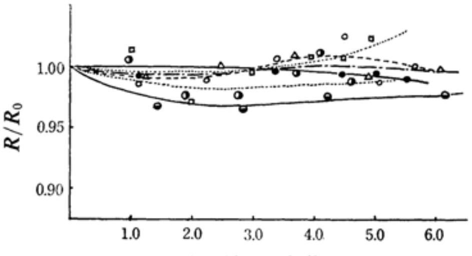

Fig. 1. The effect of sulfides or oxides on styrene polymerization.

--○-- DBS --△-- DBE —◓— DPE
···□··· DBDS —●— DPS ···◑··· DPDS

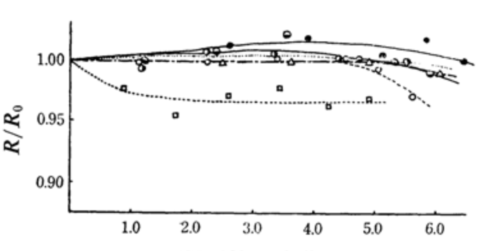

Fig. 2. The effect of sulfides or oxides on MMA polymerization.

Marks are the same as in Fig. 1.

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[7] W. W. Hartman, L. A. Smith and J. B. Dickey, "Organic Syntheses," Coll. Vol. 2, 242 (1948).

[8] R. L. Seriner, H. C. Struck and W. J. Jopison, *J. Am. Chem. Soc.*, **52**, 2066 (1930).

[9] R. L. Frank and J. R. Blegen, "Organic Syntheses," Coll. Vol. 3, 116 (1955).

[10] F. R. Mayo, R. A. Gregg and M. S. Mathieson, *J. Am. Chem. Soc.*, **73**, 1691 (1951).

[11] B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **9**, 171 (1952).

TABLE I. THE RESULTS OF THERMAL POLYMERIZATION IN THE PRESENCE OF SULFIDES AND OXIDES AT 60°C

Initiator	Styrene			MMA		
	$[I]\cdot10^2$ mol./l.	Time min.	Yield %	$[I]\cdot10^2$ mol./l.	Time min.	Yield %
DPS	1.16	730	1.64	1.10	480	1.83
	4.64	730	1.46	4.40	480	1.75
	6.96	730	1.25	6.59	480	1.53
	0	730	1.14	0	480	1.07
DPE	1.18	480	0.26	1.17	330	1.04
	5.90	480	0.26	7.02	330	0.95
	0	480	0.32	0	330	1.36
DBS	2.24	360	0.62	2.24	360	0.65
	5.60	360	0.84	5.60	360	0.49
	0	360	0.57	0	360	0.65
DBDS	2.45	360	0.65			
	4.91	360	0.66			
	0	360	0.53			
DBE	1.21	390	0.67	1.21	240	0.42
	6.05	390	0.89	6.05	240	0.89
	0	390	0.59	0	240	0.50

As may be easily seen from Table I, the concentration of the sulfides or oxides used does not have much effect on the rate of polymerization. As compared with the result in the absence of these compounds, they may safely be said to show little ability either to initiate or to retard.

Figures 1 and 2 show the effect of sulfides or oxides on the polymerizations of styrene and MMA, when AIBN was empolyed as the initiator in the presence and absence of sulfides or oxides.

It may be noted from Figs. 1 and 2 that sulfides or oxides have little effect on the reterdation or acceleration of the polymerization. Thus, the results shown here are much the same as those obtained when sulfides or oxides were employed in thermal polymerization. In order to determine the chain transfer constants to the sulfides or oxides, $1/\overline{P}_n$ was plotted against [S]/[M] according to Mayo's formula 3 as Figs. 3 and 4 show. The linear relationships were observed, but their intercepts did not converge at one point in all cases. The reason for this is not clear at the present time.

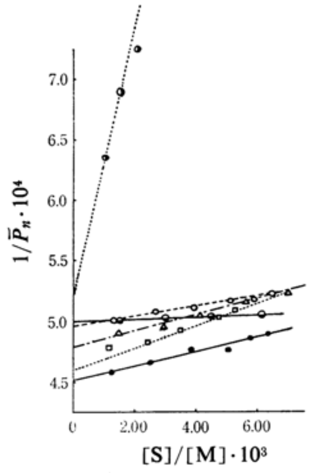

Fig. 3. Mayo's plott on styrene polymerization.
Marks are the same as in Fig. 1.

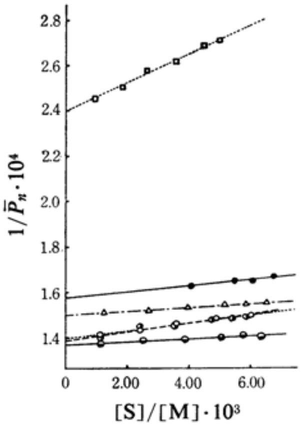

Fig. 4. Mayo's plott on MMA polymerization.
Marks are the same as in Fig. 1.

The apparent chain transfer constants to the sulfides or oxides calculated in terms of the slopes of the lines in Figs. 3 and 4 are given in Table II.

The Results of Photo-polymerization.—The results of the photo-polymerization where sulfides and oxides were used as photo-sensitizers are given in Figs. 5 and 6. Figures 7 and 8 show the results of photo-polymerizations in the presence of AIBN and sulfides or oxides.

TABLE II. APPARENT CHAIN TRANSFER CONSTANTS ($C\cdot 10^3$) IN THE POLYMERIZATION OF STYRENE AND MMA AT 60°C
$[\mathrm{AIBN}]=2.0\times 10^{-3}$

Sulfides or oxides	DPS	DPE	DBS	DBDS	DBE	DPDS
Styrene	5.48	0.786	3.35	8.78	6.24	10.3
MMA	1.32	0.913	1.54	6.27	0.80	1.76

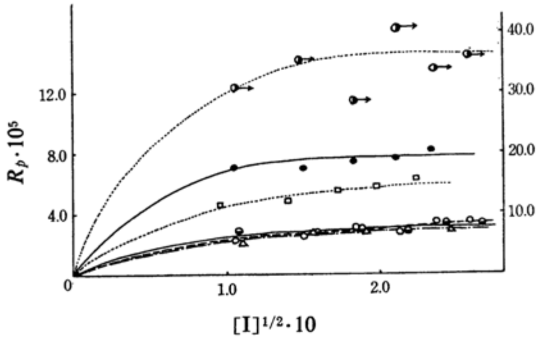

Fig. 5. Photo-polymerization of styrene using sulfides and oxides as photo-sensitizers. Marks are the same as in Fig. 1.

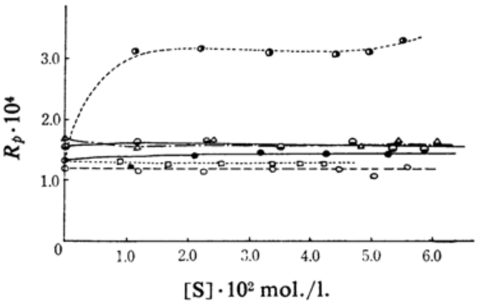

Fig. 8. The effect of sulfides or oxides on photo-polymerization of MMA. $[\mathrm{AIBN}]=2.0\times 10^{-3}$ mol./l. Marks are the same as in Fig. 1.

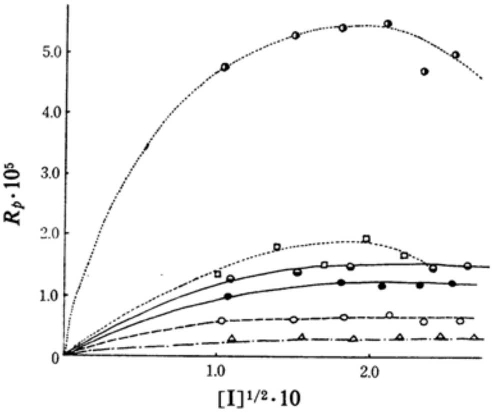

Fig. 6. Photo-polymerization of MMA using sulfides and oxides as photo-sensitizers. Marks are the same as in Fig. 1.

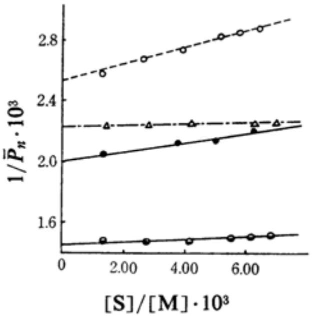

Fig. 9. Mayo's plott on styrene polymerization. (Initiator AIBN) Marks are the same as in Fig. 1.

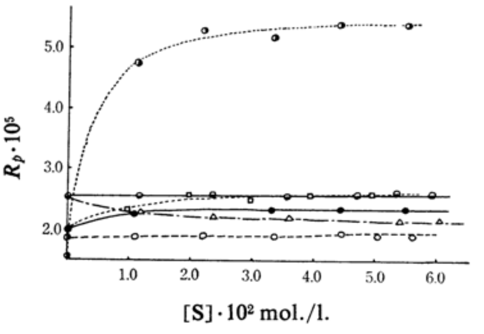

Fig. 7. The effect of sulfides or oxides on photo-polymerization of styrene. $[\mathrm{AIBN}]=2.0\times 10^{-3}$ mol./l. Marks are the same as in Fig. 1.

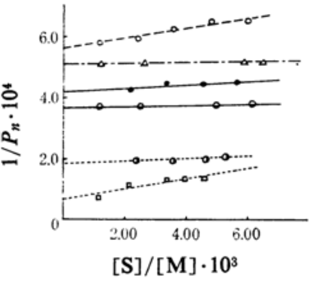

Fig. 10. Mayo's plott on MMA polymerization. (Initiator AIBN) Marks are the same as in Fig. 1.

In all these cases, it may be noted that none of the sulfides or oxides except DPDS affect the rate of polymerization. Figures 9 and 10 show the plots of $1/\bar{P}_n$ with [S]/[M] according to Mayo's formula 3. From the slopes of the line in these figures, the apparent chain transfer constants have been determined to be as shown in Table III.

TABLE III. APPARENT CHAIN TRANSFER CONSTANTS ($C\cdot10^3$) IN THE PHOTO-POLYMERIZATION OF STYRENE AND MMA

$[\mathrm{AIBN}]=2.0\times10^{-3}$

Sulfides or oxides	DPS	DPDS	DPE	DBS	DBDS	DBE
Styrene	32.5	—	0.794	54.8	—	7.16
MMA	5.54	17.4	0.642	18.3	134	1.04

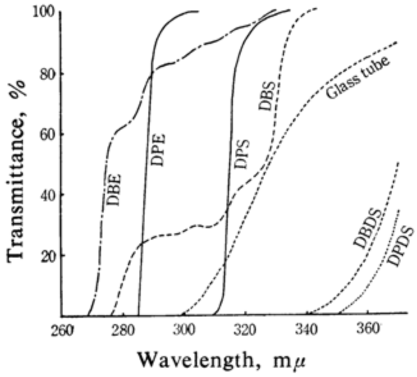

Fig. 11. Absorption spectra of sulfides and oxides.

Discussion

As may be readily seen from Table I, it was found that the sulfides or oxides show little activity as initiators or retarders in the thermal polymerizations of styrene and MMA at 60°C. Accordingly, it may be concluded that the S-S or C-S bonds do not decompose spontaneously at 60°C.

The behavior of the sulfides and oxides as photo-sensitizers, as is shown in Figs. 5 and 6, may be taken to mean that the sulfides are subjected to radical decomposition in contact with light, though they showed no activity in thermal polymerizations. Similar phenomena may be observed from Figs. 7 and 8, which show the results of the experiment in which AIBN was employed as a photo-sensitizer in the presence of sulfides or oxides. Figures 5 and 6 show that DPDS is an excellent photo-sensitizer. It may be of some interest to note, however, that an increase in the concentration of the sulfides used here does not serve to increase the rate of polymerization very much. It is to be inferred that the sulfide radical produced by the application of the light of a mercury lamp starts the initiation, and that at the same time termination occurs; hence, the apparent rate of polymerization begins to decrease. This is why the rate of polymerization here is not in proportion to the square root of the amount of the sulfides or oxides used as the initiators, as Figs. 5 and 6 show.

As may be seen in Table II, when the chain transfer constants to sulfides and oxides as indicated in Table II are compared with the chain transfer constants to benzene ($0.28\cdot10^{-5}$, as determined by Misra et al.12) in the polymerization of styrene and with the constant to benzene of $0.40\cdot10^{-5}$ in the polymerization13) of MMA, the chain transfer constants to the sulfides or oxides are quite large. It may be said, therefore, that the transfer constants of these compounds result from the attack of the polymer radical on the S-S bond or C-S bond. The chain transfer constants to the oxides are much smaller than those to the sulfides of a similar structure.

As is shown in Figs. 5—8, DPDS alone could serve as an effective photo-sensitizer in the sulfides and oxides used. This result may be explained in terms of the transmittance of light under the conditions of polymerization referred to in this work. Figure 11 shows the absorption spectra of the sulfides or oxides at the concentration used and the transparency of the glass tube used. A comparison of the transparency of the glass tube with the light absorption of sulfides has shown that DPDS and DBDS could absorb effective sufficient light under the present conditions, while other sulfides or oxides did not. It may, therefore, be said that the activities of the compounds employed as photo-sensitizers depend more on the transmittance of the glass tubes than on the structure and the absorbancy of the compounds. The characteristic absorptions of these sulfides exist at nearly 243, 249, 255, and 261 mμ. It is to be expected that interesting results may be obtained by applying the lights of these wavelengths.

Summary

A study has been made to see how some sulfides, such as diphenyl disulfide, diphenyl sulfide, dibenzyl disulfide, and dibenzyl sulfide, and such oxides as diphenyl ether and dibenzyl ether affect the radical polymerization of styrene or methyl methacrylate. None of these compounds acted effectively either as an initiator or as a retarder in the thermal

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12) G. S. Misra and R. N. Chadha, *Makromol. Chem.*, **23**, 134 (1957).

13) R. N. Chadha, J. S. Shukla and G. S. Misra, *Trans. Faraday Soc.*, **53**, 230 (1957).

polymerization at 60°C. When employed as photo-sensitizers, the disulfides have been proven to have a remarkable activity of initiation, the monosulfides acting less effectively as initiators. Moreover, the oxides showed no such activity at all. When sulfides were used as photo-sensitizers, the rate of polymerization did not obey the equation of the square root of the concentrations of the sulfides. This may be attributable to the participation of the sulfide radicals in the initiation and termination. The chain transfer constants of these compounds at 60°C were in the order of disulfides>monosulfides>oxides.

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