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## Effect of Bis(6-methylpyridazinyl)-3,3'-disulfide in the Radical Polymerizations of Styrene and Methyl Methacrylate

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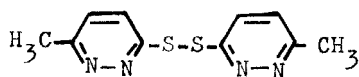
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### ABSTRACT

Thermal and photo polymerizations of styrene (St) have been carried out in the presence of bis-(6-methylpyridazinyl)-3,3'-disulfide (I). I was found to initiate the photo polymerization of St but to retard the thermal polymerization of St. The chain transfer constants of I in the polymerizations of St and methyl methacrylate were determined to be 1.64 and  $1.8 \times 10^{-2}$ , respectively, from which the  $Q_{tr}$  and  $e_{tr}$  values were calculated to be  $5.32 \times 10^{-2}$  and 3.86, respectively.

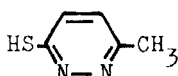
### INTRODUCTION

During the course of our investigation of radical polymerizations of several pyridazinone derivatives [1, 2], we showed that the pyridazinone ring has a rather high resonance stabilizing ability. In this connection, we have now synthesized bis(6-methyl-pyridazinyl)-3,3'-disulfide (I) and investigated the effect of I on the polymerizabilities of styrene (St) and methyl methacrylate (MMA). This paper deals with



I

the effect of I on the spontaneous decomposition (initiating ability) and induced decomposition (chain transfer ability) in the thermal or photopolymerizations of St and MMA.



II

The influences of tetramethylthiuram disulfide [3], diphenyl disulfide [4], and dibenzoyl disulfide [5] were already investigated concerning the initiation or chain transfer mechanism.

## EXPERIMENTAL

### Materials

6-Methyl-3-pyridazinethiol (II) was prepared by the method described elsewhere [6]. A 1-g portion of II was allowed to react with iodine (1.1 g) in 79 ml of 0.1 N sodium hydroxide solution to give 0.5 g (25%) of I (recrystallized from benzene-*n*-hexane); mp 152-154°C. NMR in CDCl<sub>3</sub> (ppm) showed 7.66 (s, 1H), 7.20 (s, 1H), 2.56 (s, 1H). The UV spectrum in ethanol showed bands at 235 nm ( $\epsilon_{\max}$  23,760) and 284 nm ( $\epsilon_{\max}$  5,600).

ANAL. Calcd for C<sub>10</sub>H<sub>10</sub>N<sub>4</sub>S<sub>2</sub>: C, 48.00%; H, 4.00%; N, 22.40%; S, 25.60%. Found: C, 47.86%; H, 4.03%; N, 22.52%; S, 25.35%.

Solvents and monomers were purified by the usual methods.

### Polymerizations

All polymerizations were carried out in degassed glass ampules, into which the required amounts of monomer, solvent, I or 2,2'-azobisisobutyronitrile (AIBN) were placed. Thermal polymerizations were conducted at 60°C, and photopolymerizations were done at 30°C using high pressure mercury lamps. None of the polymerizations

TABLE 1. Thermal Polymerization of St in the Presence of Bis(6-methyl-pyridazinyl)-3,3'-disulfide (I)<sup>a</sup>

[I] × 10 <sup>3</sup> (mole/liter)	Time (hr)	Conversion (%)	$\bar{M}_v \times 10^{-4}$	R <sub>p</sub> × 10 <sup>6</sup> (mole/liter-sec)
0	20	1.84	95.20	1.02
1.20	20	0.94	7.08	0.51
2.60	20	0.64	3.61	0.35
4.19	20	0.46	2.31	0.25
4.87	20	0.39	1.89	0.21
10.18	20	0.19	0.97	0.10

<sup>a</sup>In benzene at 60° C.

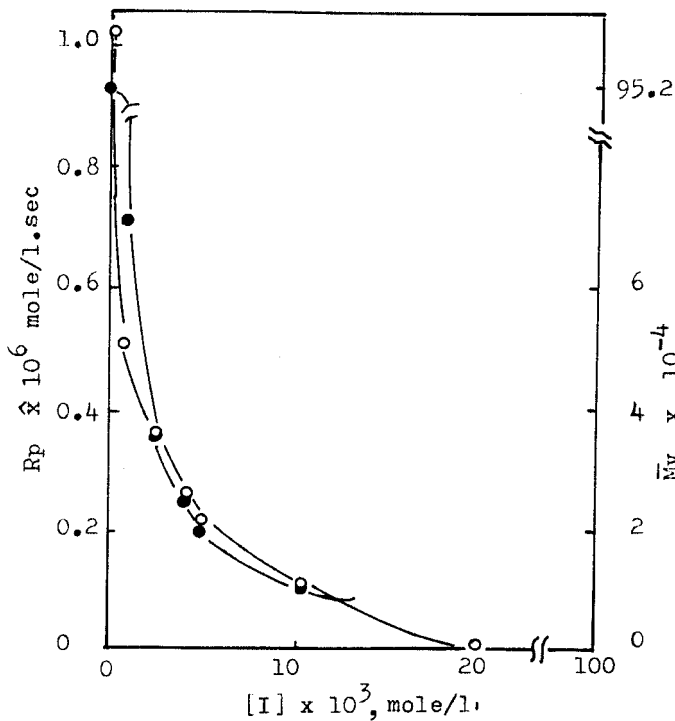


FIG. 1. Effect of bis(6-methylpyridazinyl)-3,3'-disulfide (I) in the thermal polymerization of ST: (○) R<sub>p</sub>; (●)  $\bar{M}_v$ .

TABLE 2. Photopolymerization of St in the Presence of Bis(6-methyl)-3,3'-disulfide (I)<sup>a</sup>

[I] × 10 <sup>3</sup> (mole/liter)	Time (hr)	Conversion (%)	$\bar{M}_v \times 10^{-4}$	$R_p \times 10^6$ (mole/liter-sec)
0	20	3.04	80.54	1.68
1.00	20	7.34	3.25	4.07
2.00	20	9.72	1.89	5.40
3.79	20	8.36	1.63	4.64
5.19	20	5.23	1.03	2.90
9.79	20	4.34	0.75	2.41
19.57	20	2.40	0.38	1.33

<sup>a</sup>400-W mercury lamp in benzene at 30°C.

were allowed to proceed beyond 10% conversions. The polymer was reprecipitated with benzene and methanol and then dried under vacuum.

#### Determination of Chain Transfer Constant

The intrinsic viscosities  $[\eta]$  of the polymers were determined in benzene at 30°C by using an Ubbelohde viscometer.

The number-average degrees of polymerization ( $\bar{P}_n$ ) were calculated by the following equations:

$$\log \bar{P}_n = 3.205 + 1.37 \log [\eta]$$

$$\log \bar{P}_n = 3.42 + 1.13 \log [\eta]$$

for polystyrene [7] and for poly(methyl methacrylate) [8], respectively.

The chain transfer constants (C) were calculated by using Mayo's equation [7].

The resonance factor  $Q_{tr}$  and polar factor  $e_{tr}$  in the chain-transfer reaction were estimated by the Fuhrman equation [9].

### RESULTS AND DISCUSSION

Thermal polymerization of St was carried out in the presence of I at 60°C (Table 1 and Fig. 1). Sharp decreases of the polymerization

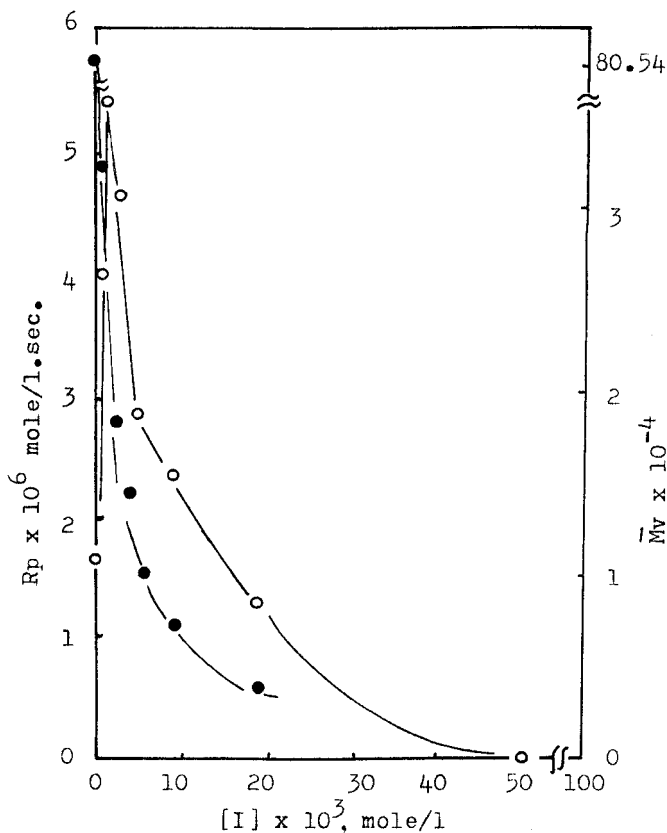


FIG. 2. Effect of bis(6-methylpyridazinyl)-3,3'-disulfide (I) in the photopolymerization of St: (○)  $R_p$ ; (●)  $\bar{M}_v$ .

rate and the molecular weight of the polymer were observed with an addition of a small amount of I, indicating that I does not decompose into a free radical under the present reaction conditions but acts as a terminator in the thermal polymerization of St.

The results of the photopolymerization of St in the presence of I are shown in Table 2 and Fig. 2. Unlike ordinary radical polymerizations, in photopolymerization the rate of polymerization had no linear relationship with the square-root concentration of I, while a maximum value in the polymerization rate was observed, indicating that I acts as both initiator and terminator of the photopolymerization of St. Almost the same phenomenon was observed in the polymerizations St or MMA initiated by tetramethylthiuram disulfide [3] and dibenzoyl disulfide [5].

TABLE 3. Thermal Polymerizations of St and MMA in the Presence of Bis-(6-methyl)-3,3'-disulfide<sup>a</sup>

Monomer	$\frac{[I]}{[M]} \times 10^3$	Time (min)	Conversion (%)	$R_p \times 10^4$ (mole/liter-sec)	$\frac{1}{\bar{P}_n} \times 10^3$
St	0	28	1.22	0.289	1.75
	1	30	0.69	0.154	4.99
	2	31	0.46	0.099	7.70
	3	36	0.41	0.075	8.02
	4	37	0.32	0.050	10.31
MMA	0	18	2.88	1.067	0.416
	1	20	3.19	1.064	0.433
	2	22	3.36	1.017	0.445
	3	24	3.61	1.003	0.451
	4	25	3.70	0.980	0.491

<sup>a</sup> $[AIBN] = 1 \times 10^{-3}$  mole/liter in benzene at 60°C.

In order to evaluate the chain transfer ability of I, AIBN-initiated polymerizations of St and MMA were carried out in the presence of I at 60°C (Table 3). Plots of reciprocal values of  $\bar{P}_n$  versus the concentration of I gave straight lines (Fig. 3); from the slopes of these lines, the C values were calculated (Table 4). The apparent chain transfer constants to I were found to be quite large relative to those of other disulfides listed in Table 4, indicating that the pyridazine ring in I assists in attack of a polymer radical on the disulfide group. The values of  $Q_{tr}$  and  $e_{tr}$  were calculated and are included in Table 4, together with those of other disulfides. It should be noted that the  $Q_{tr}$  and  $e_{tr}$  values of I obtained were also largest among those of the disulfides.

The  $Q_{tr}$  value of I is quite large, larger even than that of dibenzoyl disulfide bearing a rather high resonating group with a radical, i. e., carbonyl group. This observation implies that a radical species in the transition state of the chain transfer reaction is highly stabilized by resonance with the pyridazine ring. In other words, the large C values of I are considered to be mainly caused by the strong resonance ability of the pyridazine ring, perhaps involving a transition state engaging a bond-forming step through a stream of a polymer radical to the disulfide group.

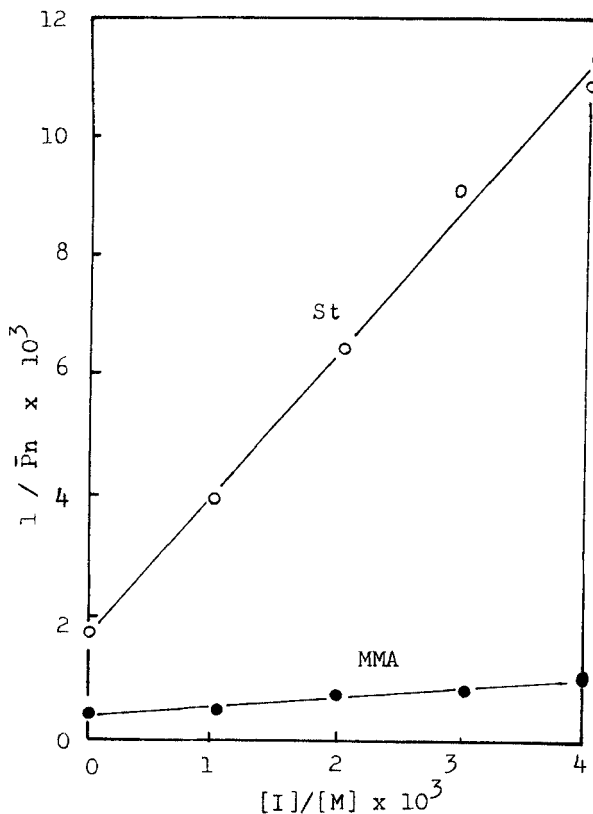


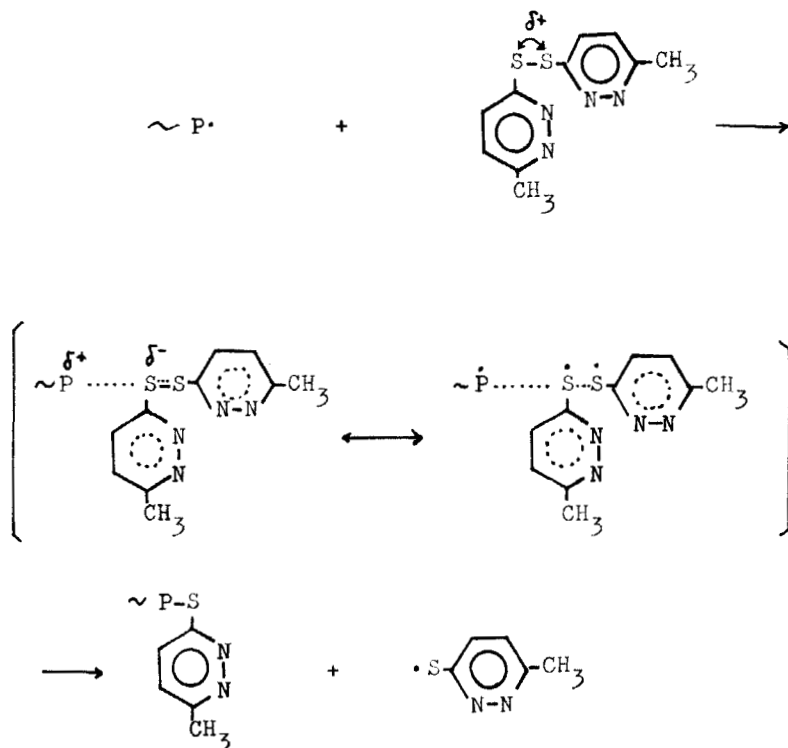
FIG. 3. Plots of  $1/\bar{P}_n$  against the concentration of bis-(6-methylpyridazinyl-3,3'-disulfide (I)).

TABLE 4. Chain Transfer Constants and  $Q_{tr}$  and  $e_{tr}$  Values of Several Disulfides<sup>a</sup>

Disulfides	$C_{MMA}$ $\times 10^2$	$C_{st}$ $\times 10^2$	$Q_{tr}$ $\times 10^2$	$e_{tr}$
$C_6H_5-S-S-C_6H_5$	1.1	11.1	1.41	1.78
$C_6H_5-CH_2-S-S-CH_2-C_6H_5$	0.67	0.88	0.057	0.12
$C_6H_5-C(=O)-S-S-C(=O)-C_6H_5$	0.1	0.36	0.037	2.12
I	1.8	164	5.32	3.86

<sup>a</sup>Data of Tsuda et al. [4, 5].





The large positive  $e_{tr}$  value of I is considered to be caused by the electron-withdrawing effect of the pyridazine ring due to two nitrogen atoms in the ring, which hence accelerates the nucleophilic attack of a rather negative polystyryl radical on I at the transition state. This will result in an enhancement of the  $C_{st}$  values.

#### REFERENCES

- [1] Y. Matsubara, K. Kyoji, M. Yoshihara, and T. Maeshima, Nippon Kagaku Kaishi, 1973, 1992; Chem. Abstr., **80**, 83716p (1974).
- [2] Y. Matsubara, N. Narakino, M. Yoshihara, and T. Maeshima, J. Macromol. Sci.-Chem., **A9**, 1443 (1975); Chem. Abstr., **84**, 31601k (1976).
- [3] T. Otsu, K. Nayatani, I. Muto, and M. Imai, Makromol. Chem., **27**, 142 (1958).
- [4] K. Tsuda, S. Kobayashi, and T. Otsu, Bull. Chem. Soc. Japan, **38**, 1517 (1965).

- [5] K. Tsuda and T. Otsu, Bull. Chem. Soc. Japan, 39, 2206 (1966).
- [6] M. Kumagaya, Nippon Kagaku Kaishi, 81, 1604 (1960).
- [7] F. R. Mayo, R. A. Gregg, and M. S. Matheson, J. Am. Chem. Soc., 73, 1691 (1951).
- [8] B. Baysal and A. V. Tobolsky, J. Polym. Sci., 9, 171 (1952).
- [9] N. Fuhrman and R. B. Mesobian, J. Am. Chem. Soc., 76, 3281 (1954).

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