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Vinyl Polymerization. CXLVI.[1] The Influence of Dibenzoyl Disulfide Derivatives on Radical Polymerizations

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In order to study the effects of aromatic sulfur derivatives on radical polymerizations, dibenzoyl disulfide (DBDS) and its derivatives were prepared and used as initiators or chain transfer agents for the polymerizations of styrene and methyl methacrylate. All of these derivatives failed to act as initiators of thermal polymerizations, but they did prove effective photosensitizers. The rates of polymerizations were found not to be proportional to the square-root concentration of the initiator (DBDS) used. The sulfur radical derived from the photo-dissociation of DBDS affected not only the initiation reaction, but also the termination reaction. The chain transfer constants to DBDS derivatives in the polymerization of styrene and methyl methacrylate showed no linear relationship with Hammett's equation ($\log C/C_0 = \rho\sigma$), but a linear relationship was obtained when a modification of Hammett's equation ($\log C/C_0 = \rho\sigma + \gamma E_R$) was applied. From the plot obtained by the use of $\log C/C_0 = \rho\sigma + \gamma E_R$, the γ value, which indicates the extent of resonance stabilization in the transition state was found to be 6.0 upon the polymerization of styrene at 60°C. Under similar conditions, however, the γ-value for benzoyl peroxide was calculated as 3.0 from the results of Cooper. This difference may be explained from an increased 3d-orbital resonance stabilization of DBDS in the transition state.

Several studies of the decomposition of organic peroxides have been made in order to clarify the relation between the structure of the peroxides and the abilities of their spontaneous and induced decompositions into free radicals. Not many systematic studies have yet been made, however, of the radical decomposition of organic peroxides. Pierson[2,3] reported the influence of several aromatic disulfides on the polymerization of styrene initiated by 2, 2'-azobisisobutyronitrile. Further studies were carried out by Otsu[4] on the use of diphenyl disulfide derivatives as chain-transfer agents in the polymerization of styrene. Tsuda et al.[5] have studied the influence of several sulfur compounds, which correspond to oxygen compounds, on radical polymerizations of styrene and methyl methacrylate.

The present paper will deal with the effect of the structure of di-substituted DBDS on their spontaneous decomposition (initiating activity) and induced decomposition (chain transfer ability) in the thermal or photo-polymerization of styrene and methyl methacrylate.

The nuclear-substituted DBDS substances used in this study have the following substituents: *p, p'*-OCH_3, *p, p'*-CH_3, *p, p'*-H, *p, p'*-Cl, *p, p'*-Br, *p, p'*-CN and *p, p'*-NO_2.

Experimental

The Preparation of *p, p'*-Disubstituted DBDS.—*Dibenzoyl Disulfide (DBDS).*—The preparation of DBDS was carried out according to the method of Frank and Blegen,[6] m. p. 128.0—128.5°C. (Found: C, 61.21; H, 3.80; S. 23.38. Calcd. for $C_{14}H_{10}O_2S_2$: C, 61.28; H, 3.67; S, 23.37%.)

p, p'-Dibromodibenzoyl Disulfide (Br-DBDS).—Br-DBDS was prepared from *p*-bromobenzoic acid which had been obtained from *p*-nitrotoluene,[7] the same as in the case of DBDS; m. p. 146.0—147.0°C. (Found: C, 39.05; H, 1.97; S, 14.90; Br, 37.15. Calcd. for $C_{14}H_8O_2S_2Br_2$: C, 38.91; H, 1.87; S, 14.84; Br, 36.83%.)

p, p'-Dichlorodibenzoyl Disulfide (Cl-DBDS).—Cl-DBDS was prepared from *p*-chlorobenzoic acid which had been obtained by the oxidation of *p*-chlorotoluene,[8] the same as in the preparation of DBDS; m. p. 122.5—123.0°C. (Found: C, 49.26; H, 2.45; S. 18.39; Cl, 20.60. Calcd. for $C_{14}H_8O_2S_2Cl_2$: C, 48.99; H, 2.35; S, 18.68; Cl, 20.65%).

p, p'-Dimethoxydibenzoyl Disulfide (MeO-DBDS).—Commercial anisic acid was recrystallized (m. p. 183.0—183.5°C), and MeO-DBDS was obtained by the same manner as DBDS. The MeO-DBDS thus obtained was light pink in color; m. p. 119.0—120.0°C. (Found:

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[1] Vinyl Polymerization. CXLV: S. Aoki, T. Otsu and M. Imoto, *Makromol. Chem.*, in press.

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

[3] A. J. Costanza, R. J. Coleman, R. M. Pierson, C. S. Marvel and C. King, ibid., **17**, 319 (1955).

[4] T. Otsu and H. Motooka, *J. Chem. Soc. Japan, Ind. Chem. Sect. (Kogyo Kagaku Zasshi)*, **62**, 287 (1959).

[5] K. Tsuda, S. Kobayashi and T. Otsu, This Bulletin, **38**, 1517 (1965).

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

[7] L. A. Bigelow, ibid., Coll. Vol. I, 136 (1941).

[8] C. S. Marvel and S. M. McElvain, ibid., Coll. Vol. I, 170 (1941).

C, 57.38; H, 4.30; S, 18.97. Calcd. for $C_{16}H_{14}O_4S_2$: C, 57.47; H, 4.22; S, 19.18%.)

p, p′ - Dimethyldibenzoyl Disulfide (Me - DBDS). — *p*-Toluic acid, an oxidation intermediate of *p*-xylene to telephthalic acid, was recrystallized first from toluene and then from benzene; m. p. 178.5—179.0°C. Me-DBDS was prepared from *p*-toluic acid by the same manner as DBDS; m. p. 118.0—119.0°C. (Found: C, 63.30; H, 4.70; S, 21.09. Calcd. for $C_{16}H_{14}O_2S_2$: C, 63.55; H, 4.67; S, 21.15%.)

p, p′-Dinitrodibenzoyl Disulfide (NO_2-DBDS). — According to the method mentioned above, NO_2-DBDS was prepared from *p*-nitrobenzoic acid. This material was yellow in color and was an amorphous substance; m. p. 183.0—183.5°C. with decomp. (Found: C, 46.40; H, 2.40; S, 17.47; N, 7.64. Calcd. for $C_{14}H_8O_6N_2S_2$: C, 46.15; H, 2.22; S, 17.60; N, 7.68%.)

p, p′-Dicyanodibenzoyl Disulfide (CN-DBDS).—From *p*-cyanobenzoic acid,[9] CN-DBDS was prepared by the same manner as DBDS. The CN-DBDS thus obtained was orange in color and was an amorphous material; m. p. 179.5—180.0°C with decomp. (Found: C, 58.87; H, 2.59; S, 19.15; N, 8.47. Calcd. for $C_{16}H_8O_2N_2S_2$: C, 59.24; H, 2.49; S, 19.77; N, 8.64%.)

The Purification of Materials.—It was rather difficult to remove impurities from the DBDS derivatives thus obtained, so recrystallization was repeated from 5 to 10 times in dichloroethane or ethyl acetate.

The 2, 2′-azobisisobutyronitrile (AIBN) which was used as the initiator was purified by recrystallization three times from ethanol; m. p. 102.0—102.5°C.

Styrene (St) and methyl methacrylate (MMA) were purified by the ordinary method.

Polymerization Procedure.—Bulk polymerization by the ordinary glass-tube method was employed. In the case of NO_2-DBDS, however, benzene solution polymerization was adopted, because this disulfide was not dissolved in these monomers.

Thermal polymerizations were conducted at 60°C, under shaking and in the absence of light. Photopolymerizations were done at 25°C, using ultraviolet-ray irradiation. None of the polymerizations were allowed to proceed beyond 10% conversion. It was noted that the addition of NO_2-DBDS or CN-DBDS caused the mixture to grow yellowish-white during the polymerization. After polymerization, the polymer was precipitated by the addition of an excess of methanol, washing with methanol, and then drying under a vacuum. A trace of a yellow substance similar to sulfur was obtained when the polymer, monomer and methanol precipitant were removed. No further examination of this substance was made.

The Determination of the Chain Transfer Constant.—The intrinsic viscosity $[\eta]$ was determined in benzene at 30°C by using Ubbelohde's viscometer. The number-average degree of polymerization $(\overline{P_n})$ was calculated by Eqs. 1 and 2;

For polystyrene[10]: $\log \overline{P_n} = 3.205 + 1.37 \log [\eta]$ (1)

For polymethyl methacrylate[11]:

$$\log \overline{P_n} = 3.420 + 1.13 \log [\eta] \qquad (2)$$

The chain transfer constants (C) to DBDS derivatives were calculated by Mayo's equation (3):

$$1/\overline{P_n} = 1/\overline{P_0} + C \cdot [S]/[M] \qquad (3)$$

where [S] and [M] are the initial concentrations of the DBDS derivatives and the monomers respectively.

Results

DBDS Derivatives Used as Initiators in Thermal Polymerization.—Table I shows the results of the thermal polymerization of St and MMA when DBDS derivatives were employed as initiators at 60°C.

As is shown in Table I, it may safely be said that DBDS derivatives do not act as initiators in the thermal polymerizations of St and MMA. Recently, it has been found that DBDS derivatives also do not act as initiators of the thermal polymerization of St and MMA at 80°C and 100°C.[12]

TABLE I. THERMAL POLYMERIZATION IN THE PRESENCE OF DBDS DERIVATIVES (60°C)

Concn. of DBDS mol./l.	3.1×10^{-3}	1.0×10^{-2}	3.0×10^{-3}	1.0×10^{-2}
Subst. of DBDS	Rate of polymerization, %/hr. St		MMA	
MeO	0.10	0.10	0.14	0.14
Me	0.10	0.10	0.10	0.10
H	0.10	0.10	0.19	0.19
Cl	0.11	0.10	0.13	0.13
Br	0.10	0.10	0.13	0.13
CN	0.16	0.16	0	0.06
NO_2	0	0	0	0
None*	0.12	0.11	0.13	0.13

* Absence of DBDS.

DBDS Derivatives as Chain-transfer Agents in Thermal Polymerizations Initiated by AIBN.—Thermal polymerizations were conducted by adding DBDS derivatives to the systems whose initiator was AIBN. R_0 and R stand for the rate

TABLE II. CHAIN-TRANSFER CONSTANTS TO DBDS AT 60°C

Subst. of DBDS	St	MMA
MeO	9.60×10^{-3}	1.46×10^{-3}
Me	4.63×10^{-3}	1.10×10^{-3}
H	3.60×10^{-3}	1.00×10^{-3}
Cl	1.96×10^{-2}	1.00×10^{-3}
Br	7.45×10^{-2}	1.67×10^{-3}
CN	3.19×10^{-1}	2.90×10^{-2}
NO_2	(6.65×10^{-1})	(6.94×10^{-2})

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[9] E. P. Valby and H. J. Lucas, *J. Am. Chem. Soc.*, **51**, 2718 (1929).

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

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

[12] K. Tsuda, N. Kita and T. Otsu, *Memoires of the Faculty of Engineering, Osaka City University*, **7**, 103 (1965).

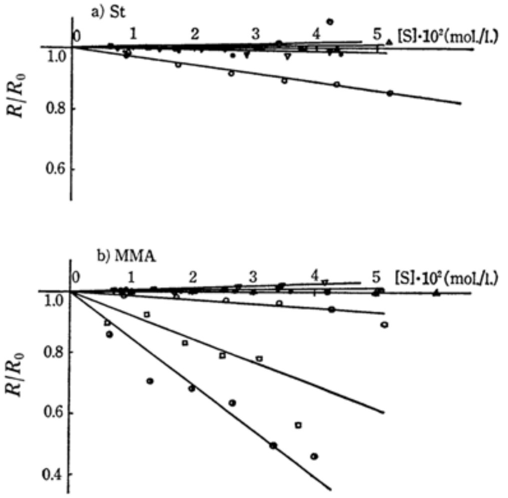

Fig. 1. Effects of DBDS derivatives on the rate of polymerization of St and MMA initiated by AIBN (3.1×10^{-3} mol./l.) at 60°C.
-●- H -△- Cl -▽- Br -◑- NO_2
-◓- MeO -○- Me -□- CN

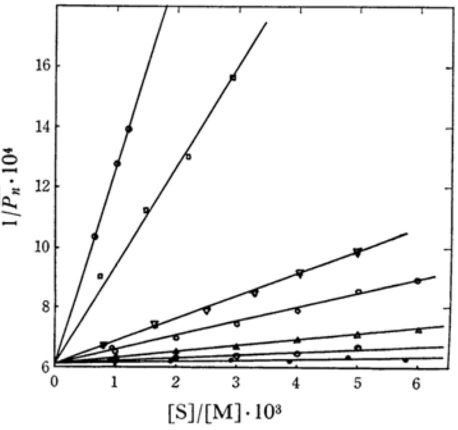

Fig. 2. Relationship between $1/\overline{P_n}$ and [S]/[M] in the polymerization of St initiated by AIBN at 60°C. Marks are the same as in Fig. 1.

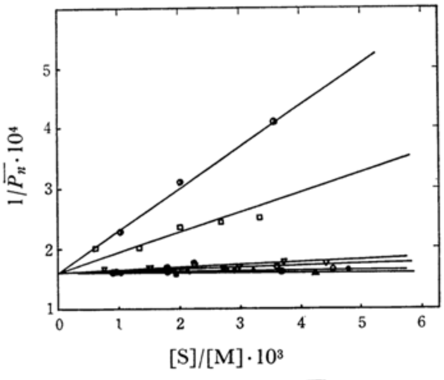

Fig. 3. Relationship between $1/\overline{P_n}$ and [S]/[M] in the polymerization of MMA initiated by AIBN at 60°C. Marks are the same as in Fig. 1.

of polymerization in the absence and in the presence of DBDS derivatives. Figure 1 shows the correlation between R/R_0 and the concentration of the DBDS derivatives. It may be seen that CN-DBDS and NO_2-DBDS remarkably retard the polymerization of MMA. These facts agree with the results shown in Table I. In order to estimate the chain transfer constants of DBDS derivatives, the plots obtained by Eq. 3 are shown in Figs. 2 and 3. The chain transfer constants to DBDS derivatives are shown in Table II.

The Photo-polymerization of DBDS Derivatives. — The results of the photo-polymerization of St and MMA conducted using DBDS derivatives as photo-sensitizers are shown in Table III.

TABLE III. PHOTO-POLYMERIZATION USING DBDS DERIVATIVES AS PHOTO-SENSITIZERS AT 25°C
[DBDS]=1.0×10^{-2} mol./l.

Subst. of DBDS	Rate of polymerization, %/hr. St	MMA
MeO	0.95	3.83
Me	0.95	3.91
H	0.81	3.84
Cl	0.98	3.55
Br	0.99	—
CN	0.97	3.09
NO_2	0	0
None*	0.08	0.23

* Absence of DBDS

As may be clearly seen from Table III, the DBDS derivatives employed here were effective sensitizers in the photo-polymerizations of both monomers. The relations between the concentrations of the DBDS derivatives employed as sensitizers and the rates of polymerizations are shown in Fig. 4. Unlike as in the ordinary radical polymerizations, the rate of polymerization had no linear relationship depending on the square-root concentration of the DBDS derivatives; it gave a maximum, indicating that the sulfur radical produced by the photo-decomposition of DBDS derivatives acts as both initiator and terminater of the polymerization.

Similar phenomena were observed in the photo-polymerization of these monomers in the presence of AIBN. The results are shown in Fig. 5.

Discussion

As is clear from Table I, DBDS derivatives do not serve as initiators of the thermal polymerization of St and MMA. It is obvious from this finding that DBDS derivatives, unlike benzoyl peroxide, do not decompose into free radicals under the present conditions. This may be attributable to the difference between the bond-dissociation energy

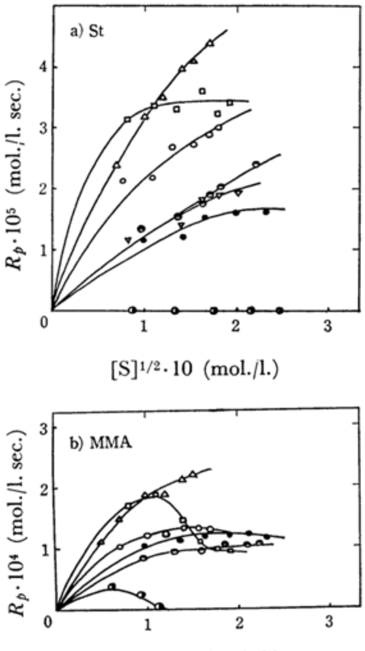

Fig. 4. Effects of DBDS on the rate of photo-polymerization of St and MMA at 25°C.
Marks are the same as in Fig. 1.

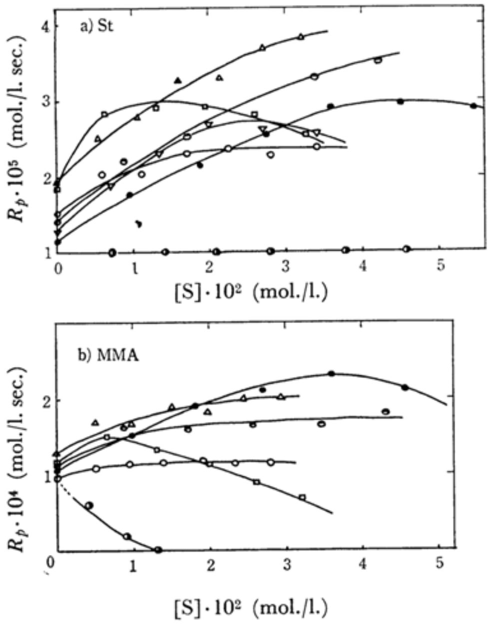

Fig. 5. Effects of DBDS on the rate of photo-polymerization of St and MMA sensitized by AIBN at 25°C.
Marks are the same as in Fig. 1.

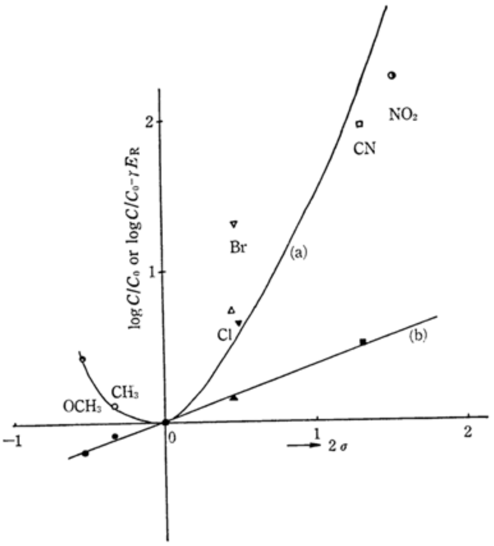

Fig. 6. Plots by Eqs. 4 and 5 for the chain transfer to DBDS in the polymerization of St.

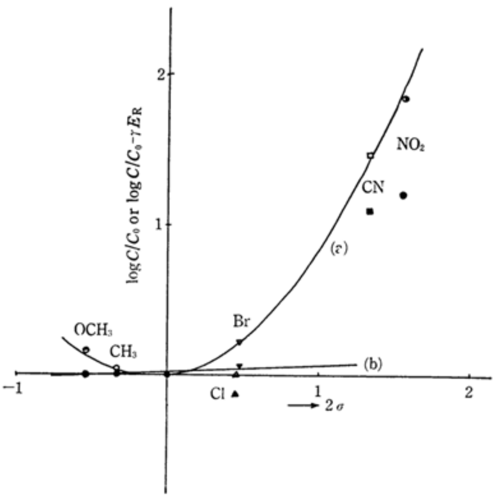

Fig. 7. Plots by Eqs. 4 and 5 for the chain transfer to DBDS in the polymerization of MMA.

of the –O–O– linkage in benzoyl peroxide (about 30 kcal./mol.) and that of the –S–S– linkage in alkyl disulfide (about 70—73 kcal./mol.). As shown in Table III, all DBDS derivatives except NO$_2$-DBDS could act as effective sensitizers of the photo-polymerization of these monomers. NO$_2$-DBDS was found to inhibit thermal and photo-polymerizations.

Contrary to the ordinary kinetic behavior, an abnormal correlation between the rate of polymerization and the concentration of DBDS derivatives in the photo-polymerizations was observed, as is shown in Figs. 4 and 5. These results can be explained by noting that the sulfur radical produced by the application of ultraviolet rays can not only initiate but also terminate the polymerization. Almost the same behavior was observed in

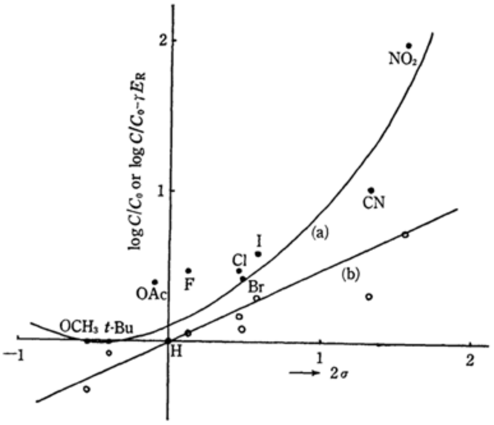

Fig. 8. Relationship between log C/C_0 or log $C/C_0 -\gamma E_R$ and σ constants calculated from the chain transfer to benzoyl peroxide derivatives in the polymerization of St:
a) plotted by Eq. 4, b) plotted by Eq. 5.

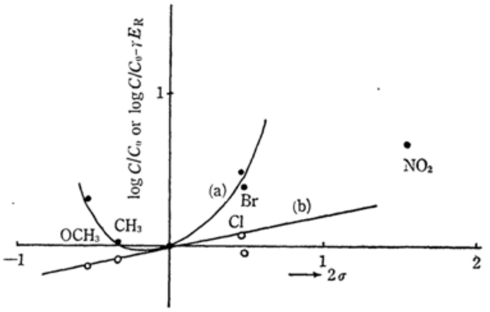

Fig. 9. Relationship between log C/C_0 or log $C/C_0 -\gamma E_R$ and σ constants calculated from the chain transfer to diphenyl disulfide derivatives in the polymerization of St:
a) plotted by Eq. 4. b) plotted by Eq. 5.

the polymerization of MMA initiated by tetraethyl thiuram disulfide.[13]

In order to clarify the relation between the reactivites of DBDS derivatives toward the attack of radicals and their structures, especially those of their substituents, the chain-transfer constants of those derivatives were plotted with the σ values, according to Hammett's equation (4);

$$\log C/C_0 = \rho\sigma \qquad (4)$$

were C and C_0 are the chain-transfer constants of substituted and of unsubstituted DBDS, respectively, σ is Hammett's substituent constant, and ρ is the reaction constant. The results are shown in Figs. 6 and 7; they do not give a straight line. Such parabola-type relations have been observed in many radical reactions.[14,15]

Recently, Yukawa and Tsuno[16] have derived a modified Hammett's equation by considering the resonance contribution in electrophilic ionic reactions. On the other hand, Yamamoto et al.,[17] who are now working in our laboratory, have proposed another modified Hammett's equation (5) for radical reactions:

$$\log C/C_0 = \rho\sigma + \gamma E_R \qquad (5)$$

where the γ value is the extent of the resonance stabilization and E_R is the resonance substituent constant, as was estimated by Yamamoto et al.[15,17] ρ is the reaction constant, and σ is Hammett's polar term. It was then shown that Eq. 5 could be nicely applied in various types of radical reactions (over 120 examples).

When Eq. 5 was applied to the present chain-transfer reactions of DBDS derivatives, the fairly good straight lines illustrated in Figs. 6 and 7 were obtained. From these figures, the values of γ and ρ were obtained as follows:

For St: $\gamma = 6.0$ $\rho = 0.36$
For MMA: $\gamma = 1.5$ $\rho = 0.07$

In 1952, Cooper[18] determined the chain-transfer constant to substituted benzoyl peroxides in the polymerization of St. When Cooper's results are plotted by Hammett's equation (4) and Yamamoto's equation (5), Fig. 8 is obtained. Figure 9 is obtained by the same plots of the chain-transfer constants to substituted diphenyl disulfides.[4] The ρ and γ values from Figs. 8 and 9 are summarized in Table IV.

TABLE IV. γ, ρ VALUES FOR CHAIN TRANSFER REACTION

Attacking radical	Chain transfer agent	γ	ρ
PSt	DBDS	6.0	0.36
PMMA	DBDS	1.5	0.07
PSt	BPO*	3.0	0.38
PSt	DPDS**	4.0	0.23

* BPO: Benzoyl peroxide
** DPDS: Diphenyl disulfide

The value of DBDS toward the attack of a polystyryl radical is larger than that of benzoyl peroxide, because the resonance stabilization of sulfur is exceedingly strong. As has been pointed out by Oae,[19] the resonance stabilization in the reactions involving a sulfur compound may be considered

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[13] T. Otsu, ibid., **3**, 201 (1961).

[14] Y. Yukawa and T. Tsuno, "Progress in Organic Reaction Mechanisms," Ed. by M. Murakami, Vol. I, Maki, Tokyo (1958), p. 1.

[15] T. Otsu and T. Yamamoto, *J. Soc. Org. Synth. Chem. Japan,* **23,** 643 (1965).

[16] Y. Yukawa and T. Tsuno, This Bulletin, **32,** 972 (1960); Y. Yukawa, *J. Soc. Org. Synth. Chem. Japan,* No. 232, p. 69 (1963).

[17] T. Azumi and T. Yamamoto, *Reports of Himeji Institute of Techn.,* **11,** 152 (1960).

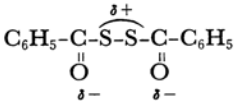
[18] W. Cooper, *J. Chem. Soc.,* **1952,** 2408.

[19] C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York (1962); S. Oae, *Chemistry,* **18,** 1028 (1963); W. Tagaki, *Kagaku-no-Ryoiki,* **17,** 349 (1963).

to be made greater by the existence of the 3d orbital resonance of the sulfur atom in the transition state than those involving an oxygen compound.

The decrease in γ values for the attack of the PMMA radical compared with that of the PSt radical may be considered to reflect the difference in the degree of contribution of the resonance effect in their transition states, but this point is not clear at the present time.

The ρ values obtained are positive, indicating that the –S–S– linkage in DBDS is $\delta+$ as is shown below;



$$\mathrm{C_6H_5{-}}\underset{\underset{\delta-}{\mathrm{O}}}{\underset{\|}{\mathrm{C}}}{-}\overbrace{\mathrm{S{-}S}}^{\delta+}{-}\underset{\underset{\delta-}{\mathrm{O}}}{\underset{\|}{\mathrm{C}}}\mathrm{{-}C_6H_5}$$

This is also true in benzoyl peroxide, as was pointed out by Imoto et al.[20] The fact that almost the same ρ values were obtained in both DBDS and benzoyl peroxide (Table IV) might indicate that the polar contribution of the two compounds in their transition states did not differ from each other.

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[20] M. Imoto and S. Choe, *J. Polymer Sci.*, **15**, 485 (1955).