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Studies on Photopolymerization of Methyl Methacrylate Using Sulfur Dioxide-Halogen Combinations as Initiators

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ABSTRACT

Free radical photopolymerization of methyl methacrylate (MMA) in visible light was studied at 40°C using sulfur dioxide-halogen (Cl_2 , Br_2 , and I_2) combinations as photoinitiators. Of the three SO_2 /halogen systems, only the SO_2 / Br_2 combination formed an interesting initiating system due to 1:1 complexation between the two components resulting in pronounced enhancement of the rate of photopolymerization over those produced by each of the initiator components when used as a lone photoinitiator. Photopolymerization of MMA induced by (SO_2 - Br_2) complex (1:1) as the photoinitiator exhibited a low initiator exponent value, 0.26, and a monomer exponent value of 1.5. Kinetic nonidealities were explained on the basis of (a) monomer-dependent chain initiation and (b) significant initiator-dependent chain termination along with the usual bimolecular mode of chain termination.

INTRODUCTION

The effectiveness of chlorine, bromine, iodine, and sulfur dioxide in individually inducing vinyl photopolymerization and the related

kinetics of photopolymerization of methyl methacrylate (MMA) have been recently reported [1-4]. Interhalogens, IBr and ICl, were also reported [5, 6] to readily induce photopolymerization of MMA. The kinetics of photopolymerization of MMA induced by the interhalogens showed significant deviations from those observed for photopolymerizations induced by the respective halogens. It was therefore considered relevant and interesting to make comparative studies of the kinetics and other aspects of photopolymerization of MMA using combinations of SO₂ and halogens (Cl₂, Br₂, or I₂) as initiator systems. Results of these studies are reported in the present paper.

EXPERIMENTAL

Materials

MMA was purified by the usual procedures [2, 3]. All the solvents used were of reagent grade, and they were distilled once before use in polymerization experiments.

Sulfur dioxide (SO₂) gas and chlorine (Cl₂) gas were generated, purified, and absorbed in carbon tetrachloride following the methods described earlier [1, 4]. SO₂ and Cl₂ contents in the respective solutions in CCl₄ were determined according to standard procedures [1, 4].

A.R. grade (E. Merck) bromine (Br₂) and iodine (I₂) were used in polymerization experiments.

Photopolymerization

Photopolymerization of MMA was studied dilatometrically [1-3] under nitrogen atmosphere at 40°C in presence of a 125-W mercury vapor lamp using three binary initiator systems, viz., SO₂ and Cl₂, SO₂ and I₂, and SO₂ and Br₂. The binary initiator systems were prepared by mixing equimolar proportions of SO₂ and the respective halogen (Cl₂, I₂, and Br₂) in CCl₄. The CCl₄ content in the polymerizations was kept fixed at 0.5% (v/v).

RESULTS

Results of photopolymerizations induced by SO₂-halogen combinations along with those of photopolymerization of MMA under similar conditions using the individual initiator components, viz., SO₂, Cl₂, I₂, and Br₂, as photoinitiators are given in Table 1. Before further considering the results, it would be proper to consider the possible reactions between SO₂ and a halogen when mixed together. It is

TABLE 1. Photopolymerization of MMA at 40°C with SO₂, Halogens, and Their Combination as the Initiating Systems

[SO ₂] (mol/L)	[Cl ₂] (mol/L)	[Br ₂] (mol/L)	[I ₂] (mol/L)	Inhibition period (min)	R _p × 10 ⁵ mol/L·s
0.001	-	-	-	30	2.772
-	0.001	-	-	15	8.120
-	-	0.001	-	10	2.520
-	-	-	0.001	20	10.000
0.001	0.001	-	-	28	6.090
0.001	-	0.001	-	0	12.520
0.001	-	-	0.001	15	3.870

found from a survey of the literature [7-10] that in the dark at room temperature, SO₂ and halogens (Cl₂, I₂, and Br₂ separately) do not react to produce any insoluble product. However, it is known [7, 8] that SO₂ reacts with Cl₂ in the presence of certain catalysts, e.g., camphor, activated charcoal, and acetic acid, to give sulfuryl chloride (SO₂Cl₂), a colorless fuming liquid, but there is little evidence for the formation of SO₂Br₂ or SO₂I₂ from similar reactions between SO₂ and Br₂ or between SO₂ and I₂, respectively.

It is seen from Table 1 that in photopolymerization the initiator combinations SO₂/Cl₂ and SO₂/I₂ have no rate-enhancing effects over those having the respective individual initiator components, but the SO₂/Br₂ combination brings about a pronounced increase in the rate of polymerization over those given by each initiator component of this combination. The other interesting feature of the SO₂/Br₂-induced photopolymerization is the practical absence of an inhibition period.

In order to understand different behaviors among the above three SO₂/halogen combinations, spectral studies of dilute solutions of SO₂, halogens (Cl₂, Br₂, and I₂), and of SO₂-halogen mixtures in CCl₄ in UV and visible regions were carried out, and the absorption spectra are given in Figs. 1 and 2(A).

It is evident from Fig. 1 that the respective spectra of SO₂/Cl₂ and SO₂/I₂ mixtures are just the additions of the spectra of the individual components in each case. However, in the case of the SO₂/Br₂ combination, the mixture shows an absorption spectrum, Fig. 2(A), which is quite different from the summation of the spectra of the individual components, thereby indicating some interaction between SO₂ and Br₂.

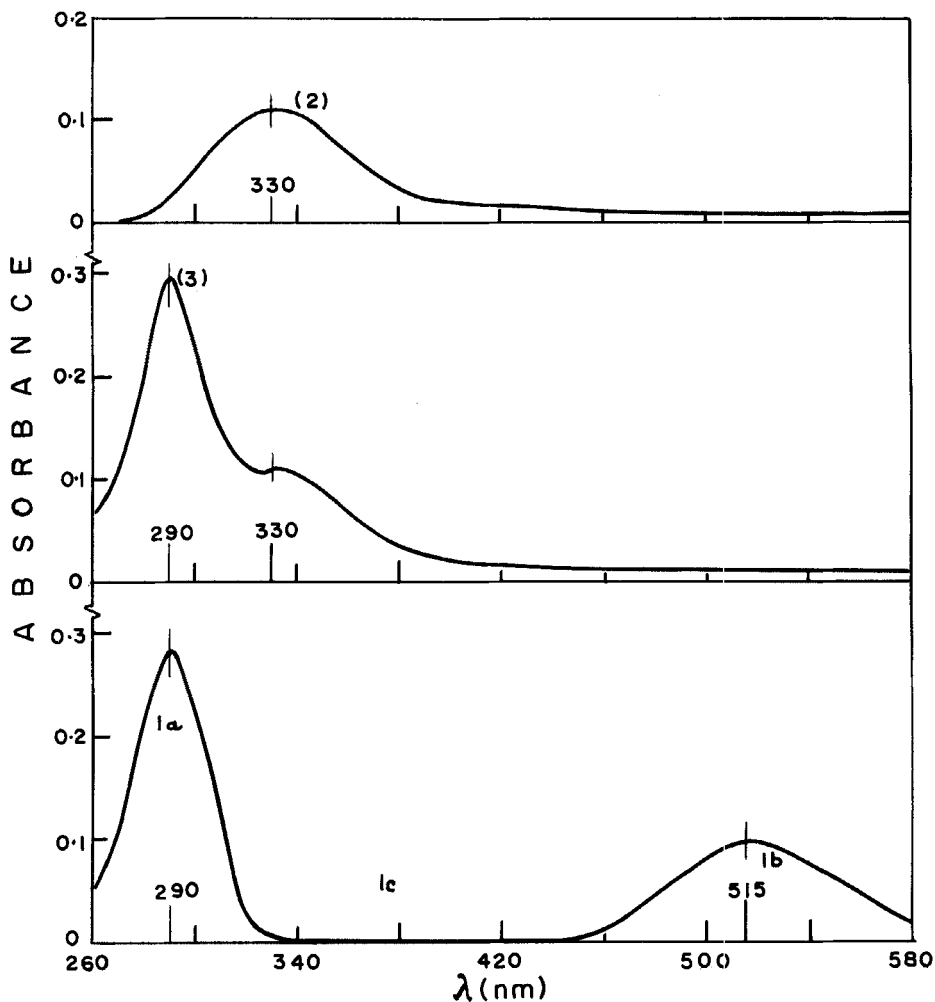


FIG. 1. Absorption spectra of SO_2 , I_2 , Cl_2 and mixtures of SO_2 and I_2 and of SO_2 and Cl_2 in CCl_4 solution using CCl_4 in the reference cell in each case: (1a) $\text{SO}_2 = 0.001 \text{ mol/L}$, (1b) $\text{I}_2 = 0.001 \text{ mol/L}$, (1c) $\text{SO}_2 = 0.001 \text{ mol/L}$ and $\text{I}_2 = 0.001 \text{ mol/L}$, (2) $\text{Cl}_2 = 0.001 \text{ mol/L}$, and (3) $\text{SO}_2 = 0.001 \text{ mol/L}$ and $\text{Cl}_2 = 0.001 \text{ mol/L}$. Spectrum 1c is the summation of 1a and 1b.

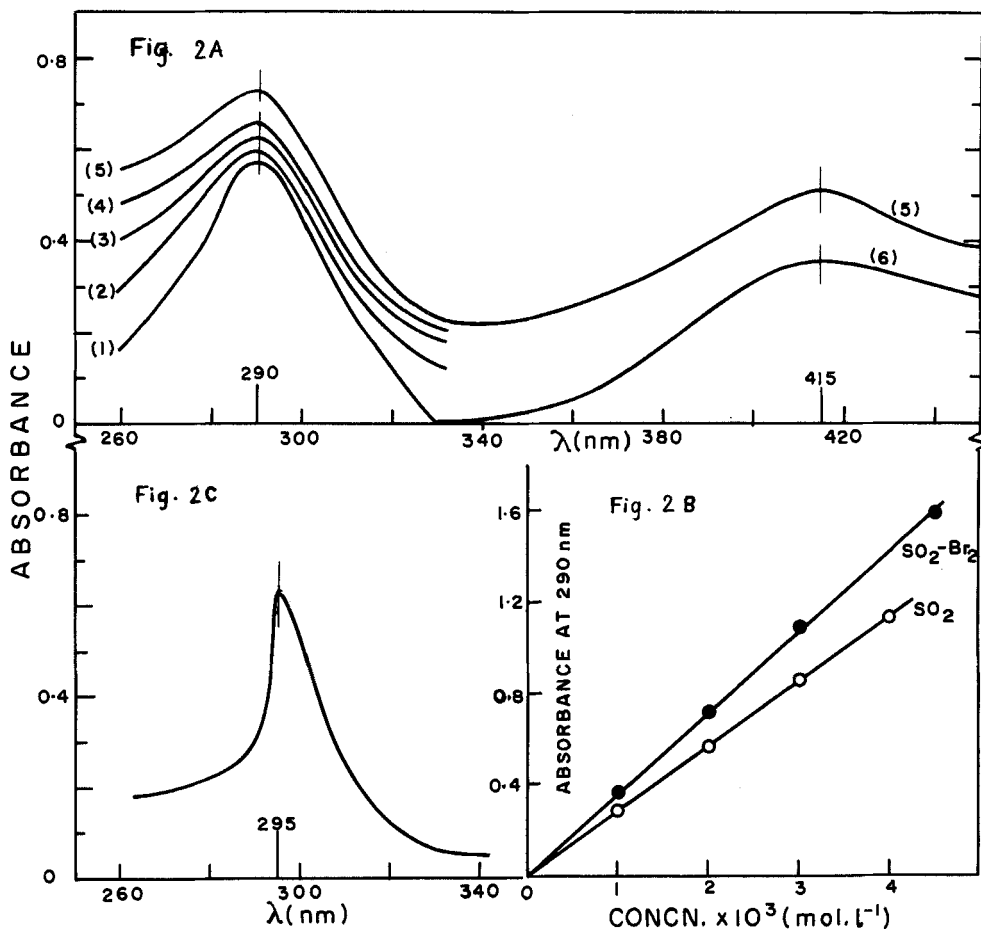


FIG. 2. (A) Absorption spectra of SO_2 , Br_2 , and different mixtures of SO_2 and Br_2 in CCl_4 solution using CCl_4 in the reference cell in each case: (1) $\text{SO}_2 = 0.002$ mol/L, (2) $\text{SO}_2 = 0.002$ mol/L and $\text{Br}_2 = 0.005$ mol/L, (3) $\text{SO}_2 = 0.002$ mol/L and $\text{Br}_2 = 0.001$ mol/L, (4) $\text{SO}_2 = 0.002$ mol/L and $\text{Br}_2 = 0.0015$ mol/L, (5) $\text{SO}_2 = 0.002$ mol/L and $\text{Br}_2 = 0.002$ and 0.004 mol/L, and (6) $\text{Br}_2 = 0.002$ mol/L. (B) Plot of absorbance at 290 nm vs concentration for SO_2 and equimolar mixtures of SO_2 and Br_2 , each in CCl_4 solution (CCl_4 in the reference cell). (C) UV absorption spectra of mixture of SO_2 and Br_2 , each 0.002 mol/L in MMA solution (MMA in the reference cell).

Analysis of the Absorption Spectra of the SO₂-Br₂ System

UV and visible absorption spectra of dilute solutions of SO₂ (0.002 mol/L), Br₂ (0.002 mol/L), and of equimolar mixture of SO₂ (0.002 mol/L) and Br₂ (0.002 mol/L) in CCl₄ are given in Fig. 2(A), Curves 1, 6, and 5, respectively. The spectrum of Br₂ shows an absorption maximum at 415 nm and that of SO₂ shows a peak absorption at 290 nm. The spectrum of SO₂/Br₂ shows two absorption maxima, one in the UV and the other in the visible region, at 290 and 415 nm, respectively. SO₂ has no absorption in the wavelength region 330-450 nm while Br₂ has no absorption in the wavelength region 250-330 nm. For a fixed SO₂-content (0.002 mol/L) in CCl₄, the absorbance at λ_{\max} (290 nm) increased progressively with increasing proportion of Br₂ till the latter was used in equimolar proportion (0.002 mol/L), Fig. 2(A), and with further increase in Br₂ content, no further change in the absorbance of the mixture was visible. The absorption spectra of solutions of SO₂, Br₂, and their mixtures in CCl₄ did not measurably vary with time.

The absorbance values at λ_{\max} (290 nm) for solutions of SO₂ and of equimolar mixtures of SO₂ and Br₂ in CCl₄ at several concentrations were measured. In each case the plot, passing through the origin, is linear, the plot for the SO₂/Br₂ mixture giving a higher slope than the SO₂ plot, Fig. 2(B). The overall absorbance at λ_{\max} (290 nm) for each of the various mixtures of SO₂ and Br₂, Fig. 2(A), is equal to the summation of the absorbances corresponding to the calculated amount of 1:1 SO₂/Br₂ mixture in the system and that of SO₂ present in excess of Br₂. Excess Br₂, wherever present, has little influence on the overall absorbance at 290 nm. The spectral studies therefore indicate instantaneous formation of a 1:1 complex between SO₂ and Br₂ in solution. Therefore, for all practical purposes, molar concentration of either component in an equimolar mixture of SO₂ and Br₂ was taken as the molar concentration of the (SO₂-Br₂) complex.

Thus, of the three SO₂/halogen systems, only the SO₂ and Br₂ combination makes an interesting system due to 1:1 complexation between the components resulting in pronounced rate-enhancing effects in photopolymerization of MMA.

Kinetics of Photopolymerization of MMA Using the SO₂-Br₂ Complex

Polymerization of MMA occurred readily and almost instantly at 40°C in bulk and in solution with the use of SO₂-Br₂ complex as the initiator. Photopolymerization rates R_p , determined in the usual

TABLE 2. Photopolymerization of MMA at 40°C Using (SO₂-Br₂) Complex as the Photoinitiator

$[\text{SO}_2\text{-Br}_2] \times 10^4$ mol/L	$R_p \times 10^5$ mol/L·s	$\frac{R_p}{[M]^2} \times 10^6$	$[\eta]$ (dL/g)	$1/\bar{P}_n \times 10^3$	Initiator exponent	k_p^2/k_t (L/mol·s)
12.88	12.97	1.519	1.145	0.3875		
20.72	14.79	1.730	1.100	0.400		
25.00	16.70	1.956	0.945	0.490		
40.00	18.37	2.151	0.770	0.640	0.26	1.40×10^{-2}
50.00	20.04	2.347	0.670	0.770		
80.00	21.24	2.487	0.580	0.930		
100.00	22.15	2.592	0.445	1.320		
200.00	15.03	1.760	-	-		
400.00	11.70	1.370	-	-		

manner, were, however, higher than the corresponding rates of polymerization done in the dark. The photopolymerization remained practically uninhibited in the presence of air (open dilatometer) but hydroquinone produced inhibitory effects. The polymers gave positive response to the dye partition test for bromine [11] and anionic sulfoxy [12] end groups.

Initiator Exponent

Data on bulk photopolymerization of MMA using different [SO₂-Br₂] (0.001288-0.0400 mol/L) are presented in Table 2. The initiator exponent, usually determined from the initial slope of the plot of log R_p vs log [SO₂-Br₂], is 0.26. Deviation from the square-root dependency of the rate of polymerization on the initiator concentration indicates that some sort of initiator-dependent termination will be significant along with the usual bimolecular termination.

k_p^2/k_t Value

The degree of polymerization \bar{P}_n for the polymers prepared was determined viscometrically [1-3].

The kinetic parameter k_p^2/k_t at 40°C was evaluated from \bar{P}_n and

R_p data, i.e., from the slope of the plot of $1/\bar{P}_n$ vs $R_p/[M]^2$, Fig. 3 (Table 2), in accordance with the Mayo equation

$$\frac{1}{\bar{P}_n} = 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} + \sum \frac{R_{tr}}{R_p} \quad (1)$$

The last term in the right-hand side was included to account for chain transfer effects, assuming that this would not affect the slope of the plot over the low range of initiator concentration. The apparent k_p^2/k_t value, calculated from the slope of the initial linear zone of the plot, is 1.40×10^{-2} L/mol·s. It was assumed in the calculation that any perturbation of the termination process from the usual bimolecular mechanism (85% disproportionation, 15% combination [13, 14]) would not measurably affect the initial slope of the plot in Fig. 3.

Activation Energy

Rates of bulk photopolymerization of MMA at three different temperatures (40, 45, and 50°C) were measured using a fixed $[SO_2-Br_2]$ (0.005 mol/L). Rates of polymerization in the dark, $(R_p)_T$, were also noted in each case, and the observed photopolymerization rates, R_p , were corrected. The corrected photopolymerization rates, $R_{p(\text{photo})} = \sqrt{(R_p)^2 - (R_p)_T^2}$ were used for the calculation of activation energy of true photopolymerization following a graphical plot of $\log R_{p(\text{photo})}$ vs $1/T$, where T is the absolute temperature, Fig. 4. The apparent activation energy, E_a ($E_a = E_p - E_t/2$) for photopolymerization of MMA, calculated from the slope of the plot is 4.30 kcal/mol.

Effect of Polymerization Time (Hence % Conversion) on Intrinsic Viscosity

In the present system of photopolymerization the intrinsic viscosity $[\eta]$ and hence the average chain length of the polymer formed under a given initial set of conditions was found to increase significantly with progressive time of polymerization, i.e., with increasing percent conversion even from very early stages, Fig. 5. The same feature was also observed in the bulk polymerization of MMA and styrene with SO_2 initiator both thermally [14] and photochemically [4].

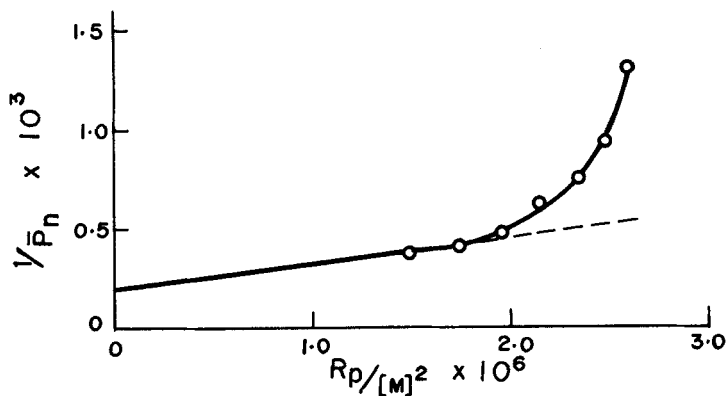


FIG. 3. Photopolymerization of MMA (bulk) at 40°C with (SO₂-Br₂) complex as photoinitiator. Plot of $1/\bar{P}_n$ vs $R_p/[M]^2$.

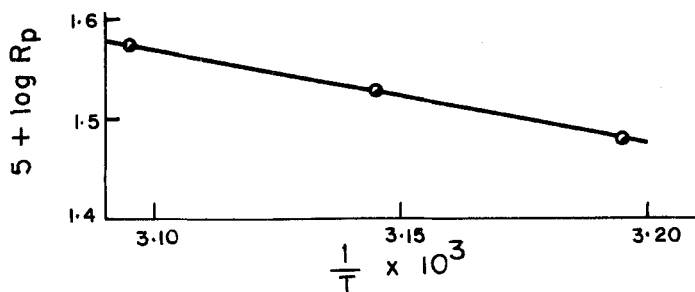


FIG. 4. Photopolymerization of MMA (bulk) with (SO₂-Br₂) complex as photoinitiator. Plot of $\log R_p$ vs $1/T$.

Monomer Exponent

With a fixed [SO₂-Br₂] (0.01 mol/L), photopolymerization of MMA was also studied at 40°C in the presence of different concentrations of several solvents such as benzene, n-hexane, toluene, acetone, chloroform, and carbon tetrachloride. Monomer exponents were calculated from the slope of the respective plots of $\log R_p$ vs $\log [M]$.

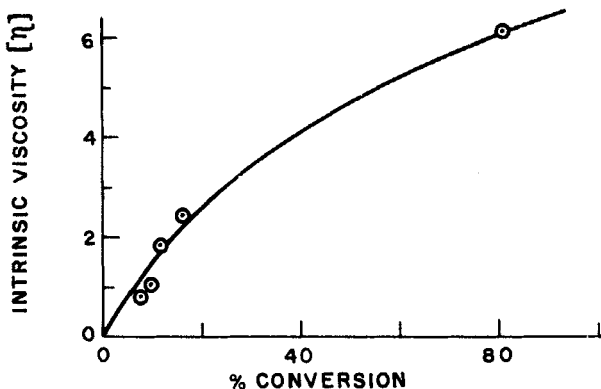


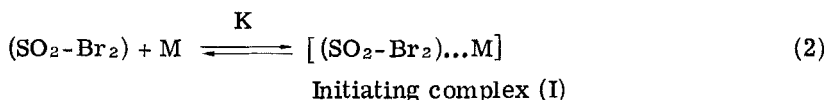
FIG. 5. Photopolymerization of MMA (bulk) at 40°C with (SO₂-Br₂) complex as photoinitiator. Plot of [η] vs % conversion.

In each of the above diluted systems, the monomer exponent was 1.50 or very close to this value.

A monomer order of 1.5 in the present photopolymerization may be understood in terms of involvement of the monomer in the initiation step. Significant initiator-dependent termination via reaction with primary radicals may also partly explain this kinetic feature.

Mechanism

Kinetic data, the inhibitory effect of hydroquinone, and results of endgroup analysis indicate a radical mechanism. The radical generation process may be considered to follow an initial complexation reaction between monomer and initiator molecules:



The idea of complexation between initiator and monomer was supported by the fact that, when taken in MMA solution, the peak absorption of an equimolar mixture of SO₂ and Br₂, i.e., the SO₂-Br₂ complex, shifts slightly to higher wavelength ($\lambda_{\text{max}} = 295 \text{ nm}$, MMA in reference cell), Fig. 2(C).

Initial concentration of the initiating complex (I) can therefore be

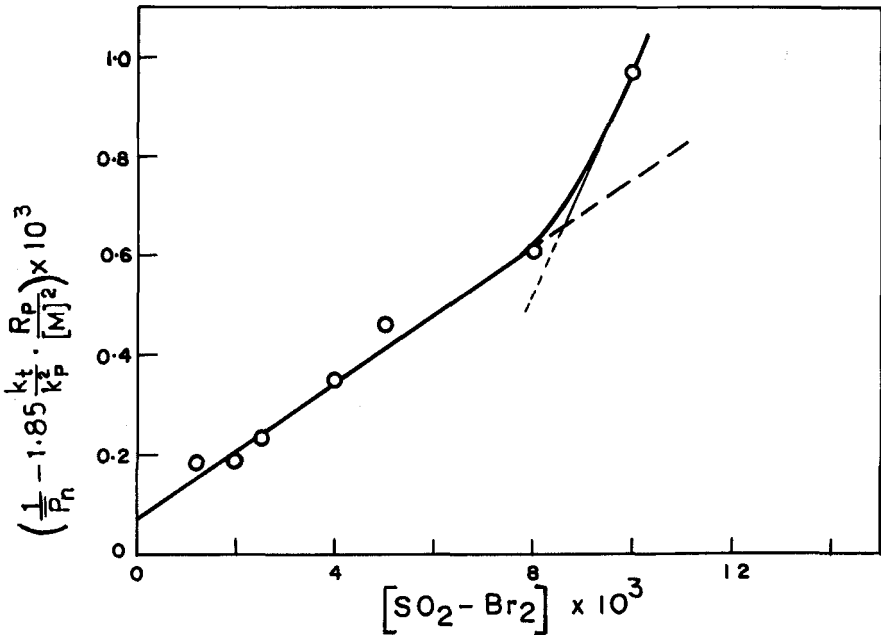


FIG. 6. Photopolymerization of MMA (bulk) at 40°C using (SO₂-Br₂) complex as photoinitiator. Plot of $1/\bar{P}_n - 1.85 k_t/k_p^2 \cdot R_p/[M]^2$ vs $[\text{SO}_2\text{-Br}_2]$.

written as $K \cdot [\text{SO}_2\text{-Br}_2] \cdot [M]$, where K is the equilibrium constant of the initiator monomer complexation reaction envisaged.

Initiator Transfer

The initiator transfer parameter ($C_I K$), where C_I is the initiator transfer constant, can be determined with the help of Eq. (1) expressed in the following form:

$$\frac{1}{\bar{P}_n} - 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} = C_M + C_I K [\text{SO}_2\text{-Br}_2] \tag{4}$$

Here, $[\text{SO}_2\text{-Br}_2]$ is the initial concentration of the SO₂-Br₂ complex and C_M is the monomer transfer constant. A plot of the left-hand side of Eq. (4) vs $[\text{SO}_2\text{-Br}_2]$ is given in Fig. 6, and the initial slope

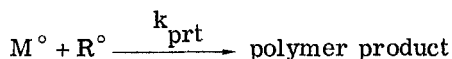
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of the plot, giving the value of $C_I K$, is 6.67×10^{-2} L/mol. A deviation from linearity of this plot, prominent at high $[\text{SO}_2\text{-Br}_2]$, indicates that the transfer process, apparently of the normal kind at low $[\text{SO}_2\text{-Br}_2]$, becomes largely degradative in nature at high $[\text{SO}_2\text{-Br}_2]$.

Termination

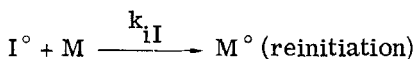
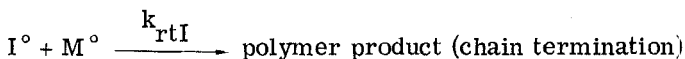
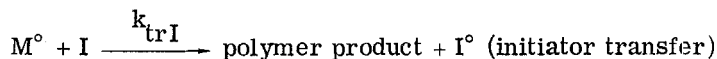
The deviation from square-root dependence of R_p on initiator concentration indicates that some initiator-dependent termination process is significant along with the usual bimolecular termination. Initiator dependent termination of two different kinds may now be considered.

(1) Primary radical termination

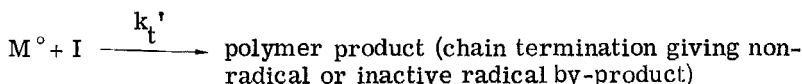


(2) Termination via degradative initiator transfer, which may proceed by two distinctive mechanisms:

(a) With reinitiation effect, such as



(b) With little reinitiation effect, such as



Analysis of Primary Radical Termination Effect

The primary radical termination effect in the absence of any degradative initiator transfer process may be evaluated by using the equation derived by Deb and Meyerhoff [16] which would assume the following form for the present photopolymerization:

$$\log \frac{R_p}{[\text{SO}_2\text{-Br}_2][M]^3} = \log \frac{Kfk_d k_p^2}{k_t} - 0.8684 \frac{k_{prt}}{k_i k_p} \frac{R_p}{[M]^2} \quad (5)$$

The left-hand side of Eq. (5) was plotted against $R_p/[M]^2$, Fig. 7.

The plot gave a straight line with a negative slope, thereby clearly indicating a measurable primary radical termination effect. The value of $k_{prt}/k_i k_p$ calculated from the slope of this plot is $2.33 \times 10^5 \text{ mol}\cdot\text{s/L}$.

Analysis of Degradative Chain (Initiator) Transfer Effect

Degradative Initiator Transfer with Reinitiation Effect

An equation derived by Deb [17] and simplified by Ghosh et al. [18] can be used in the following form for analyzing degradative initiator transfer with the reinitiation effect for the present photopolymerization system:

$$\log \frac{R_p^2}{[\text{SO}_2\text{-Br}_2][M]^3} = \log Kfk_d \frac{k_p^2}{k_t} - 0.434 \frac{k_p^2}{k_t} \frac{k_{rtI}}{k_i k_p} C_I K [\text{SO}_2\text{-Br}_2] \quad (6)$$

A plot of the left-hand side of Eq. (6) against $[\text{SO}_2\text{-Br}_2]$, is shown in Fig. 8. The plot gives a straight line with a negative slope, thereby clearly indicating the occurrence of degradative initiator transfer reaction. The value of $k_{rtI}/k_i k_p$ obtained from the slope of the plot is $1.345 \times 10^5 \text{ mol}\cdot\text{s/L}$.

Degradative Initiator Transfer with Little Reinitiation Effect

This aspect for the present system may be analyzed with the help of the following relationship which may be easily derived according to concepts and approaches derived before [19]:

$$2 \frac{k_t}{k_p^2} \frac{R_p^2}{[M]^3 [\text{SO}_2\text{-Br}_2]} = 2Kfk_d - \frac{k_t'K}{k_p} \frac{R_p}{[M]} \quad (7)$$

The plot of the left-hand side of Eq. (7) against $R_p/[M]$, Fig. 9, gives a straight line with a negative slope, thus giving evidence for the degradative initiator transfer process (without reinitiation effect). The value of $k_t'K/k_p$ obtained from the slope of the plot is 0.15 L/mol .

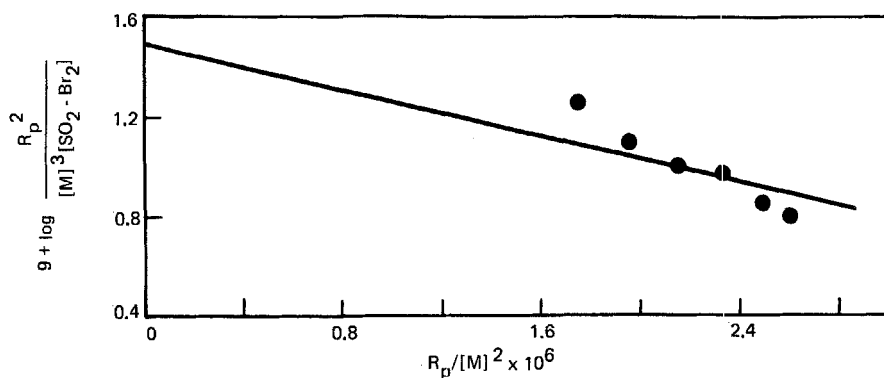


FIG. 7. Photopolymerization of MMA (bulk) at 40°C using (SO₂-Br₂) complex as photoinitiator. Analysis of primary radical termination effect. Plot of $\log R_p^2/[M]^3 [SO_2-Br_2]$ vs $R_p/[M]^2$.

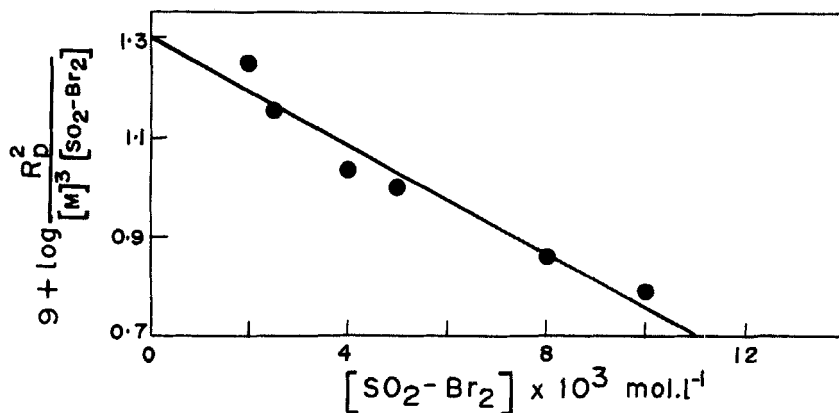


FIG. 8. Photopolymerization of MMA (bulk) at 40°C using (SO₂-Br₂) complex as photoinitiator. Analysis of degradative initiator transfer (with reinitiation effect). Plot of $\log R_p^2/[M]^3 [SO_2-Br_2]$ vs $[SO_2-Br_2]$.

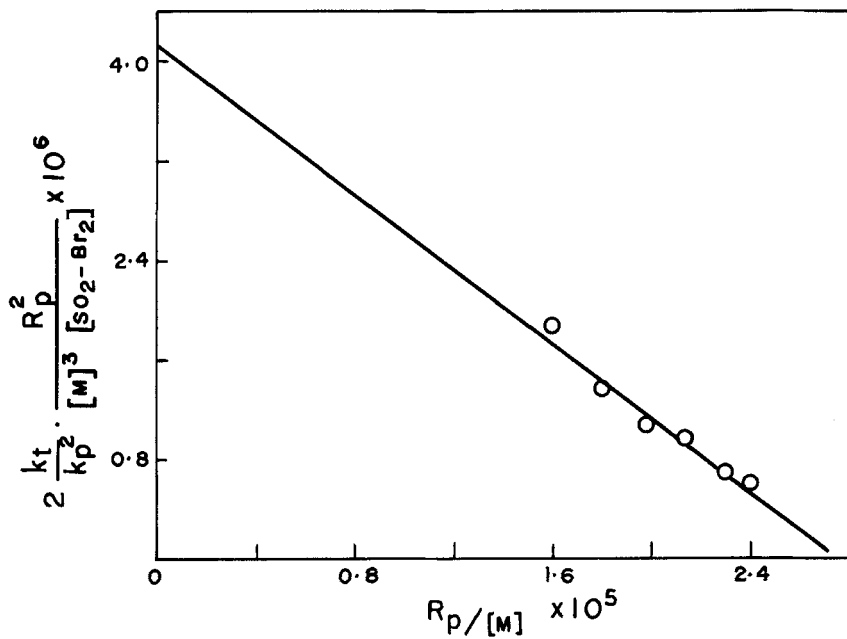


FIG. 9. Photopolymerization of MMA (bulk) at 40°C using (SO₂-Br₂) complex as photoinitiator. Analysis of degradative initiator transfer with no reinitiation effect. Plot of $2k_t/k_p^2 \cdot R_p^2/[M]^3[SO_2-Br_2]$ vs $R_p/[M]$.

It is interesting to note that the $k_t'K/k_p$ value is reasonably close to the value of the final slope of the plot in Fig. 6, corresponding to high [SO₂-Br₂], indicating the degradative nature of the initiator transfer process at high initiator concentration ($k_{trI} \simeq k_t'$). Thus the degradative effect is detectable from both approaches, one primarily considering the degree of polymerization and the other considering primarily the rates of polymerization. From either approach, degradative effects of comparable order are more or less indicated. From consideration of the \bar{P}_n data, the degradative effect becomes apparent only at high [SO₂-Br₂], but from consideration of R_p only, this effect is detectable over the full range of [SO₂-Br₂] studied.

The value of Kfk_d , equivalent to $K\phi\epsilon I_0$ for photopolymerization (where I_0 is the incident light intensity in moles of light quanta per litre second, ϵ is the molar absorptivity of the initiator for the particular wavelength of radiation absorbed, and ϕ is the quantum yield

for radical production in photopolymerization), obtained from the three plots in Figs. 7-9, are in reasonably good agreement, the mean value being 1.86×10^{-6} L/mol·s.

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