Bull. Chem. Soc. Jpn., **54**, *595—599 (1981)*

Photopolymerization of Methyl Methacrylate Using *N*,*N*-Dimethylformamide–Sulfur Dioxide Complex as the Photoinitiator

Premamoy Ghosh,* Samir Biswas, and Subhankar Jana

Plastics and Rubber Technology Division, Department of Applied Chemistry, Calcutta University, 92, A. P. C. Road, Calcutta-700 009, India

(Received August 8, 1980)

Photopolymerization of MMA in visible light was studied at 40 °C using DMF–SO_2 complex as the photoinitiator. Initiator exponent was found to be 0.41 and monomer exponent varied between 1.12 to 1.50 depending on the nature of the solvent. Analysis of data revealed that the photopolymerization was induced by a free radical mechanism. Nonideality of the kinetics was explained on the basis of (a) monomer-dependent chain initiation and (b) initiator-dependent chain termination *via* degradative initiator transfer.

In recent years the role of SO_2 in catalytic concentrations in vinyl polymerization has been studied in detail. It is now well established that SO_2 can act both as an initiator and as a comonomer in vinyl polymerization.[1] SO_2, being a good acceptor, also forms charge transfer complexes with many donor compounds. SO_2 complexes of pyridine and quinoline are reported[2–4] to effectively induce polymerization of methyl methacrylate (MMA). In the polymerization of MMA initiated by pyridine–SO_2 complex, it was found that the presence of such additives as *N*,*N*-dimethylformamide (DMF) greatly accelerated the rate of polymerization[5] probably through participation of DMF in the initiation step. This idea led us to the preparation of the C.T. complex of SO_2 with DMF with the objective of examining its suitability as an independent initiator of vinyl polymerization using MMA as the monomer. Related results and the kinetics of polymerization under photoactivation are reported in the present paper.

Experimental

Materials. Methyl methacrylate (MMA) monomer was purified by usual procedures.[6] *N*,*N*-Dimethylformamide (DMF) obtained from E. Merck and stored over KOH pellets, was purified by distillation. All solvents used were of reagent grade and were distilled once before use in polymerization reaction.

Preparation of N,N-*dimethylformamide–sulfur dioxide Complex.* DMF (5 ml) was taken in a test tube which was then cooled to about −5 °C in crushed ice/salt mixture. Pruified sulfur dioxide gas was bubbled through the cold DMF. SO_2 gas generated by heating fresh copper turnings with reagent grade concentrated sulfuric acid was passed through a scrubber of concentrated sulfuric acid before its final passage in DMF. Bubbling was stopped when the liquid appeared supersaturated with SO_2. Excess SO_2 was allowed to bubble out at room temperature, occasionally aided by slow stirring with a glass rod. The theoretical SO_2-content of 1:1 DMF–SO_2 complex is 46.7%. Analysis by iodimetry showed that the SO_2 content of the prepared complex was 46.92%.

UV absorption spectra of dilute solutions of SO_2 (0.002 mol l^{-1}) and of DMF–SO_2 complex (0.002 mol l^{-1}) in CCl_4 are given in Fig. 1, A, curves 1 and 4 respectively. λ_{max} for each spectrum is 290 nm. DMF itself has no absorption in the wavelength range studied. For a fixed SO_2-content (0.002 mol l^{-1}) in CCl_4, the absorbance at λ_{max} increased progressively with increasing proportion of DMF till the latter was used in equimolar proportion (0.002 mol l^{-1}), Fig. 1, A, and with further increase in DMF content, no further change in the absorbance of the mixture was visible.

The absorbance values at λ_{max} (290 nm) for solutions of SO_2 and of DMF–SO_2 complex in CCl_4 at several concentrations were measured and the data were plotted as in Fig. 1, B. In each case the plot, passing through the origin, is linear, DMF–SO_2 plot giving a higher slope than the SO_2 plot. The overall absorbance at λ_{max} (290 nm) for each of the various mixtures of DMF and SO_2, Fig. 1, A, is equal to the summation of the absorbance corresponding to the calculated amount of 1:1 DMF–SO_2 complex formed *in situ* in the system and that of SO_2 present in excess of DMF.

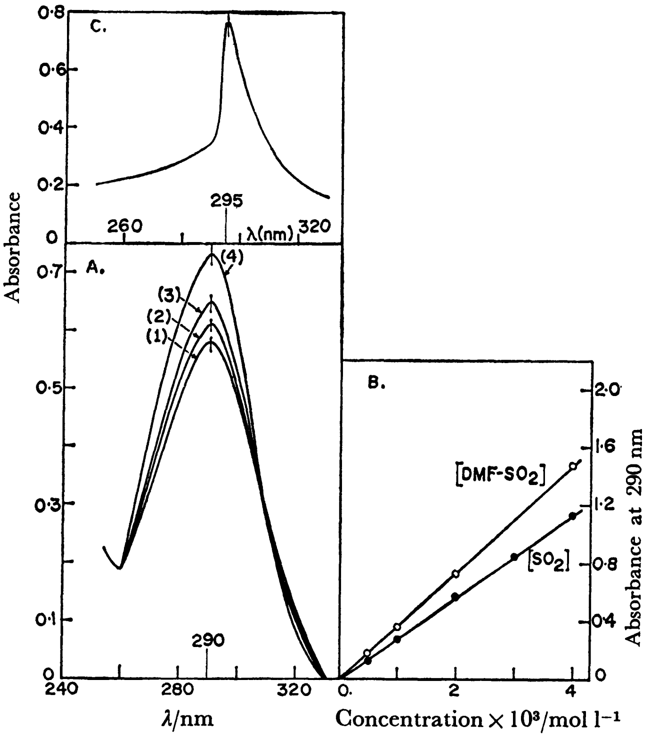

Fig. 1. A) UV absorption spectra of SO_2, (DMF–SO_2), complex and different mixtures of SO_2 and DMF in CCl_4 solution using CCl_4 in the reference cell in each case:
1) SO_2=0.002 mol l^{-1}; 2) SO_2=0.002 mol l^{-1} and DMF=0.0005 mol l^{-1}; 3) SO_2=0.002 mol l^{-1} and DMF=0.001 mol l^{-1}; 4) SO_2=0.002 mol l^{-1} and DMF=0.002 mol l^{-1}, 0.003 mol l^{-1}, 0.005 mol l^{-1}; and DMF–SO_2 complex=0.002 mol l^{-1}.
B) Plot of absorbance at 290 nm *vs.* concentration for SO_2 and DMF–SO_2 complex, each in CCl_4 solution (CCl_4 in the reference cell).
C) UV absorption spectra of DMF–SO_2 complex, 0.002 mol l^{-1}, in MMA (MMA in the reference cell).

Table 1. Photopolymerization of MMA at 40 °C using DMF-SO_2 complex as the photoinitiator

$[DMF\text{-}SO_2]\times 10^4$ / $mol\ l^{-1}$	$R_p\times 10^5$ / $mol\ l^{-1}\ s^{-1}$	$R_p/[M]^2\times 10^7$ / $l\ mol^{-1}$	$[\eta]$ / $dl\ g^{-1}$	$1/\bar{P}_n\times 10^4$	Initiator exponent	$(k_p^2/k_t)\times 10^2$ / $l\ mol^{-1}\ s^{-1}$
2.051	5.400	6.379	2.900	1.120	0.41	1.42
2.56	6.010	7.097	2.690	1.230		
4.85	7.515	8.875	2.300	1.460		
5.82	8.350	9.861	2.22	1.590		
7.25	8.810	10.400	2.125	1.680		
9.70	9.6025	11.340	1.880	1.980		
12.16	10.850	12.810	1.500	2.66		
20.00	9.6129	—	—	—		

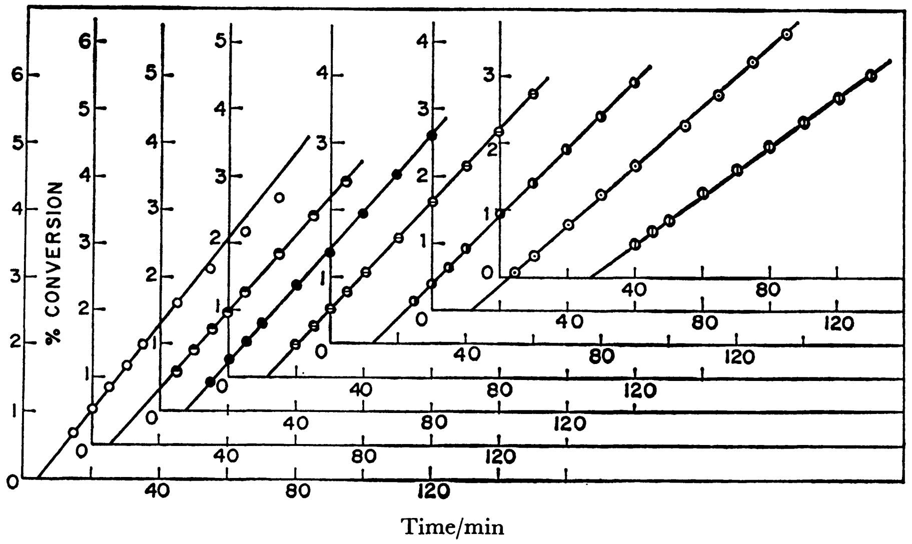

Fig. 2. Photopolymerization of MMA using DMF-SO_2 complex as initiator at 40 °C, for each curve $[DMF\text{-}SO_2]$ in mol l^{-1} is,

◓: 20.00×10^{-4} mol l^{-1} $[DMF\text{-}SO_2]$,
○: 12.16×10^{-4} mol l^{-1} $[DMF\text{-}SO_2]$,
●: 9.70×10^{-4} mol l^{-1} $[DMF\text{-}SO_2]$,
⊖: 7.25×10^{-4} mol l^{-1} $[DMF\text{-}SO_2]$.
◑: 5.82×10^{-4} mol l^{-1} $[DMF\text{-}SO_2]$,
⊙: 4.85×10^{-4} mol l^{-1} $[DMF\text{-}SO_2]$,
⦶: 2.56×10^{-4} mol l^{-1} $[EMF\text{-}SO_2]$,

Excess DMF wherever present has little influence on the overall absorbance. It is, thus, clearly indicated that complexation between DMF and SO_2 takes place almost instantaneously and that the complex is of the 1:1 kind.

When taken in MMA solution, the peak absorption of DMF-SO_2 complex shifts slightly to higher wave length ($\lambda_{max}=295$ nm, MMA in reference cell), Fig. 1, C, indicating further complexation of DMF-SO_2 complex with MMA.

Polymerization. The polymerization of MMA in bulk or in solution was studied dilatometrically in visible light at 40 ± 0.05 °C using DMF-SO_2 complex initiator following usual procedures.[7-9] Polymers formed at low conversions (<10%) in the dilatometers were removed and isolated by precipitation with petroleum ether and drying at 50 °C under vacuum.

Intrinsic Viscosity. Intrinsic viscosity, $[\eta]$ in dl/g of polymers taken in benzene solution were obtained from measurements of solution viscosity at 30 ± 0.05 °C using a Ubbelohde viscometer. Molecular weights ($\bar{M}_n$) of poly(methyl methacrylate) (PMMA) were calculated from the viscosity data using the following equation:[10]

$$[\eta] = 8.69\times 10^{-5}\,\bar{M}_n^{0.76}. \qquad (1)$$

Results and Discussion

In presence of DMF-SO_2 complex, no polymerization of MMA was observed within 2 h at 40 °C in the dark. Polymerization was, however, readily induced in presence of light after inhibition periods (IP) of the order of 5—30 min, lower $[DMF\text{-}SO_2]$ giving higher IP in general. IP is considered to arise due to adventitious impurities (such as, last traces of oxygen) in the polymerization system.

Initiator Exponent. Data on bulk photopolymerization of MMA at 40 °C using different $[DMF\text{-}SO_2]$ (0.000256—0.002 mol l^{-1}) are presented in Table 1. Rates of polymerization, R_p, were calculated from the initial linear zones of % conversion *vs.* time plots, Fig. 2. Initiator exponent determined from the slope of the plot of log R_p *vs.* log $[DMF\text{-}SO_2]$, is 0.41, Fig. 3. Photopolymerization in open dilatometers (in contact with air) produced slightly enhanced inhibition but in presence of dissolved hydroquinone (0.001 mol l^{-1}) there was much pronounced inhibition of polymerization. The polymers gave positive response to

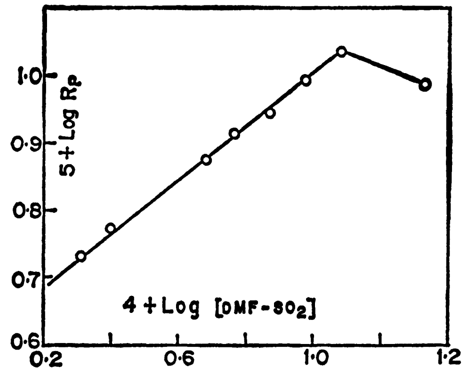

Fig. 3. Photopolymerization of MMA (bulk) using DMF–SO_2 complex as initiator at 40 °C.

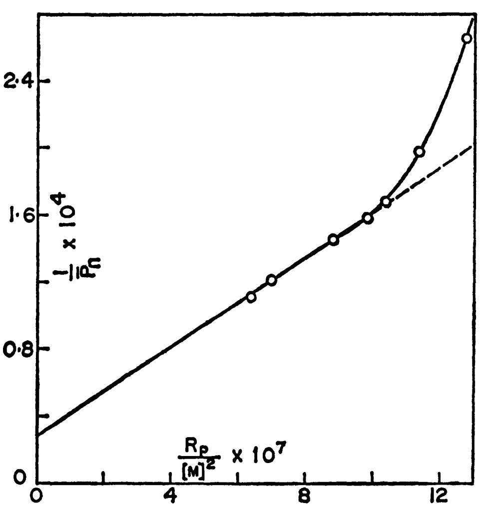

Fig. 4. Photopolymerization of MMA (bulk) using DMF–SO_2 complex as initiator.

dye partition test[11)] for (anionic) sulfoxy end groups.

k_p^2/k_t Value. The kinetic parameter k_p^2/k_t at 40 °C was evaluated from the slope of the plot of $1/\bar{P}_n$ *vs.* $R_p/[M]^2$, Fig. 4 (Table 1), in accordance with the Mayo equation:

$$1/\bar{P}_n = 1.85\frac{k_t}{k_p^2}\cdot\frac{R_p}{[M]^2}+\sum\frac{R_{tr}}{R_p}, \tag{2}$$

where the last term in the right hand side was included to account for chain transfer effects, assuming this would not affect the slope of the plot over 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 $1.42\times10^{-2}\,\mathrm{l\,mol^{-1}}$; it was assumed in the calculation that any perturbation of the termination process from the usual bimolecular mechanism (85% disproportionation, 15% combination)[10,12)] will not measurably affect the initial slope of the plot in Fig. 4.

Monomer Exponent. With a fixed [DMF–SO_2], ($0.000205\,\mathrm{mol\,l^{-1}}$), photopolymerization of MMA was further studied in presence of different concentrations of several solvents such as benzene, toluene, DMF, carbon tetrachloride, pyridine, and tetrahydrofuran (THF). Monomer exponents calculated from the slope of the respective plots of log R_p *vs.* log [M], Fig. 5, range between 1.12—1.50, depending on the nature of the solvent used.

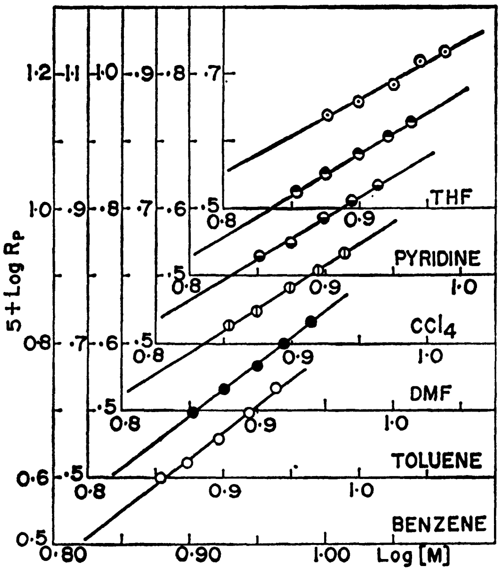

Fig. 5. Photopolymerization of MMA (solution) using DMF–SO_2 complex as initiator.
[DMF–SO_2]=$2.05\times10^{-4}\,\mathrm{mol\,l^{-1}}$ (fixed); data given for each curve are, solvent and slope (monomer exponent).
○: Benzene, 1.50, ●: toluene, 1.50, ⊙: THF, 1.12, ◒: CCl_4, 1.20, ◓: pyridine, 1.20, ⦶: DMF, 1.30.

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

$$\text{DMF–SO}_2 + \text{M} \overset{K}{\rightleftharpoons} \text{DMF–SO}_2\cdots\text{M} \tag{3}$$

Initiating Complex (I)

$$\text{I} \xrightarrow{h\nu} \text{Pair of radicals } (\text{R}\cdot). \tag{4}$$

Initial concentration of the initiating complex (I) is then equal to K[DMF–SO_2][M], where K is the equilibrium constant of the initiator monomer complexation reaction envisaged.

Initiator Transfer. Equation 2 may be used in the following form to determine the initiator transfer parameter (C_IK), where C_I is the initiator transfer constant, in the photopolymerization of MMA in bulk:

$$\frac{1}{\bar{P}_n} - 1.85\frac{k_t}{k_p^2}\cdot\frac{R_p}{[M]^2} = C_M + C_IK\,[\text{DMF–SO}_2]. \tag{5}$$

Here, [DMF–SO_2] is the initial concentration of *N*,*N*-dimethylformamide–sulfur dioxide complex and C_M is the monomer transfer constant. A plot of left hand side of Eq. 5 *vs.* [DMF–SO_2] is given in Fig. 6, and initial slope of the plot, giving the value of C_IK, is $8\times10^{-3}\,\mathrm{l\,mol^{-1}}$. A deviation from linearity of this plot, prominent at high [DMF–SO_2], indicates that the transfer process apparently of the normal kind at low [DMF–SO_2], becomes largely degradative in

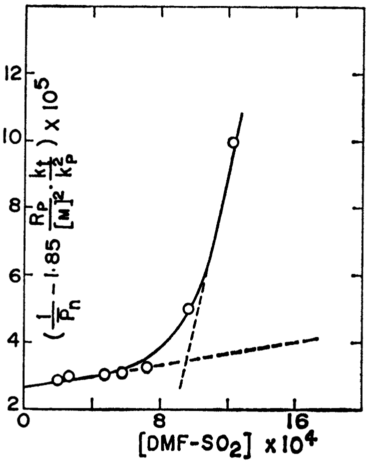

Fig. 6. Photopolymerization of MMA using DMF–SO$_2$ complex as initiator.

nature at high [DMF–SO$_2$].

Termination. The observed initiator exponent of 0.41 indicates that some initiator dependent termination process is significant along with the usual bimolecular termination.

The initiator dependent termination process may be of two different kinds:

1) Primary radical termination

$$\mathrm{M}^{\cdot} + \mathrm{R}^{\cdot} \xrightarrow{k_{\mathrm{prt}}} \text{Polymer product}$$

and

2) Termination *via* degradative initiator transfer, which may be considered to proceed by two distinctive mechanisms:

a) With reinitiation effect, such as:

$$\mathrm{M}^{\cdot} + \mathrm{I} \xrightarrow{k_{\mathrm{trI}}} \text{Polymer product} + \mathrm{I}^{\cdot}\ \text{(Initiator transfer)}$$

$$\mathrm{I}^{\cdot} + \mathrm{M}^{\cdot} \xrightarrow{k_{\mathrm{rtI}}} \text{Polymer product (Chain termination)}$$

$$\mathrm{I}^{\cdot} + \mathrm{M} \xrightarrow{k_{\mathrm{iI}}} \mathrm{M}^{\cdot}\ \text{(reinitiation)}$$

or,

b) With little reinitiation effect, such as:

$$\mathrm{M}^{\cdot} + \mathrm{I} \xrightarrow{k_{\mathrm{t}}'} \text{Polymer product (Chain termination giving non radical or inactive radical by product).}$$

1) *Analysis of Primary Radical Termination Effect.* The equation of Deb and Meyerhoff[13] which would assume the following form for present polymerization, may be used to evaluate primary radical termination effect (in absence of degradative initiator transfer process)

$$\log\frac{R_{\mathrm{p}}^2}{[\mathrm{DMF\text{-}SO_2}][\mathrm{M}]^3} = \log\frac{Kfk_{\mathrm{d}}k_{\mathrm{p}}{}^2}{k_{\mathrm{t}}} - 0.8686\cdot\frac{k_{\mathrm{prt}}}{k_{\mathrm{i}}k_{\mathrm{p}}}\cdot\frac{R_{\mathrm{p}}}{[\mathrm{M}]^2}. \tag{6}$$

Negative slope for the plot of left hand side of Eq. 6 *vs.* $R_{\mathrm{p}}/[\mathrm{M}]^2$, Fig. 7, indicating measurable primary radical termination effect, was obtained for photopolymerization of MMA in bulk at 40 °C. The value of $k_{\mathrm{prt}}/k_{\mathrm{i}}k_{\mathrm{p}}$ calculated from the slope of this plot is 3.135×10^5 mol s l^{-1}.

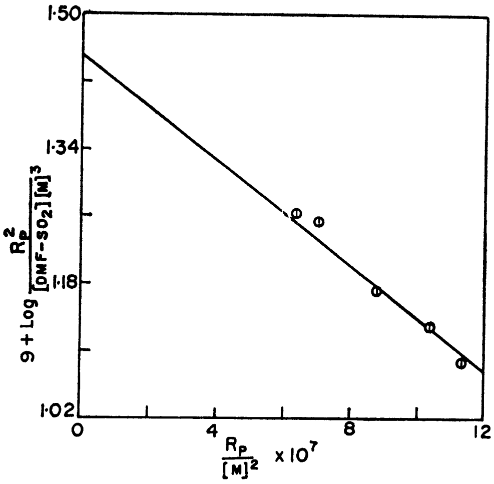

Fig. 7. Photopolymerization of MMA using DMF–SO$_2$ complex as initiator. Analysis of primary radical termination effect.

2) *Analysis of Degradative Chain (Initiator) Transfer Effect.* a) *Degradative Initiator Transfer with reinitiation Effect*: An equation derived by Deb[14] to analyse degradative chain (initiator) transfer with reinitiation effect was simplified by Ghosh *et al.*[15] to the following form:

$$\ln\frac{R_{\mathrm{p}}^2}{[\mathrm{I}][\mathrm{M}]^2} = \ln\frac{fk_{\mathrm{d}}k_{\mathrm{p}}^2}{k_{\mathrm{t}}} - \frac{k_{\mathrm{p}}^2}{k_{\mathrm{t}}}\cdot\frac{k_{\mathrm{rtI}}}{k_{\mathrm{iI}}k_{\mathrm{p}}}\cdot C_{\mathrm{I}}\cdot\frac{[\mathrm{I}]}{[\mathrm{M}]}.$$

In the present case $[\mathrm{I}]=K$ [DMF–SO$_2$][M] and hence we have

$$\log\frac{R_{\mathrm{p}}^2}{[\mathrm{DMF\text{-}SO_2}][\mathrm{M}]^3} = \log Kfk_{\mathrm{d}}\frac{k_{\mathrm{p}}^2}{k_{\mathrm{t}}} - 0.434\frac{k_{\mathrm{p}}^2}{k_{\mathrm{t}}}\cdot\frac{k_{\mathrm{rtI}}}{k_{\mathrm{iI}}k_{\mathrm{p}}}\cdot C_{\mathrm{I}}K[\mathrm{DMF\text{-}SO_2}]. \tag{7}$$

Here, C_{I} is the initiator transfer constant. A plot of left hand side of Eq. 7 *vs.* [DMF–SO$_2$], is shown in Fig. 8. The plot gives a straight line with a negative slope, thereby clearly indicating the existence of degradative initiator transfer process. The value of $k_{\mathrm{rtI}}/(k_{\mathrm{iI}}k_{\mathrm{p}})$ obtained from the slope of the plot is 5.486×10^6 mol s l^{-1}.

b) *Degradative Initiator Transfer with Little Reinitiation Effect*: This aspect may be analysed according to the following approach:

Under steady state condition, we have

$$\frac{R_{\mathrm{i}}}{R_{\mathrm{p}}} = \frac{R_{\mathrm{t}}}{R_{\mathrm{p}}} = \frac{2k_{\mathrm{t}}[\mathrm{M}^{\cdot}]^2 + k_{\mathrm{t}}'[\mathrm{I}][\mathrm{M}]}{R_{\mathrm{p}}} = \frac{2k_{\mathrm{t}}[\mathrm{M}^{\cdot}]^2 + k_{\mathrm{t}}'K[\mathrm{DMF\text{-}SO_2}][\mathrm{M}][\mathrm{M}^{\cdot}]}{R_{\mathrm{p}}}$$

or,

$$R_{\mathrm{i}} = \frac{2k_{\mathrm{t}}}{k_{\mathrm{p}}{}^2}\cdot\frac{R_{\mathrm{p}}{}^2}{[\mathrm{M}]^2} + \frac{k_{\mathrm{t}}'K}{k_{\mathrm{p}}}\cdot R_{\mathrm{p}}[\mathrm{DMF\text{-}SO_2}] = 2\phi\varepsilon I_0K[\mathrm{DMF\text{-}SO_2}][\mathrm{M}]$$

or,

$$2\frac{k_{\mathrm{t}}}{k_{\mathrm{p}}^2}\cdot\frac{R_{\mathrm{p}}^2}{[\mathrm{M}]^3[\mathrm{DMF\text{-}SO_2}]} = 2\phi\varepsilon I_0K - \frac{k_{\mathrm{t}}'K}{k_{\mathrm{p}}}\cdot\frac{R_{\mathrm{p}}}{[\mathrm{M}]}. \tag{8}$$

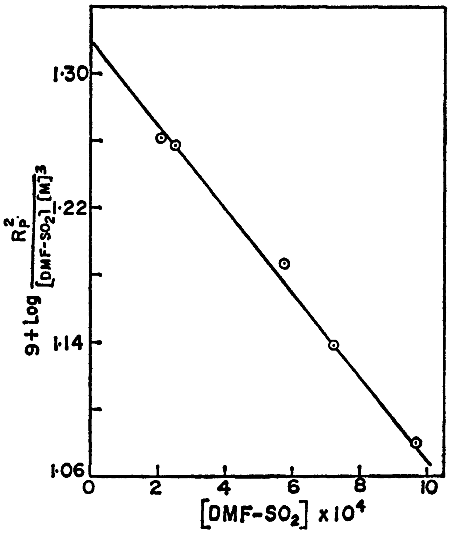

Fig. 8. Photopolymerization of MMA using DMF–SO_2 as initiator. Analysis of degradative initiator transfer (with reinitiation effect).

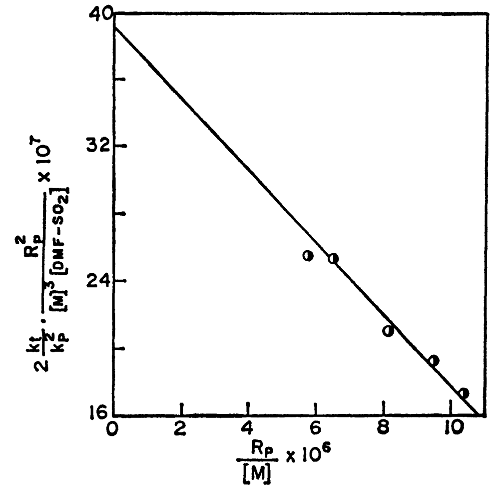

Fig. 9. Photopolymerization of MMA using DMF–SO_2 complex as initiator. Analysis of degradative initiator transfer (no reinitiation effect).

The left hand side of Eq. 8 is plotted *vs.* $R_p/[M]$, Fig. 9. The plot gives a straight line with a negative slope indicating that degradative initiator transfer with no reinitiation effect is significant. The value of $k_t'K/k_p$ obtained from the slope of the plot is 0.23 l mol^{-1}.

It is interesting to note that this value is reasonably close to the value of the final slope of the plot in Fig. 6, corresponding to high [DMF–SO_2], indicating degradative nature of the initiator transfer process at high initiator concentration. Thus, the degradative effect is detectable from analysis of both $\bar{P}_n$ and R_p data and from each analysis degradative effects of comparable order are more or less indicated, particularly for high [DMF–SO_2]. The value of Kfk_d, equivalent to $K\phi\varepsilon I_0$ for photopolymerization (where ϕ is the quantum yield for chain initiation, ε is the molar absorptivity for the active radiation and I_0 is the incident light intensity) obtained from the three plots, Figs. 7—9, are in reasonably close agreement, the mean value being 1.80×10^{-6} l mol^{-1} s^{-1}.

Although, primary radical termination may be considered as a possible cause for non-ideality, consideration of dependence of R_p on [M] predicts it to be of much less consequence. If the present photopolymerization followed the normal kinetics (bimolecular termination) one would expect a value of 1.5 for monomer exponent on the basis of initiation mechanism envisaged; for significant primary radical termination, the expected monomer exponent would be >1.5, the limiting value being 2.0 and for some kind of significant degradative initiator transfer, the expected value of monomer exponent would be <1.5, the limiting value being 1.0. With observed monomer exponent in the range of 1.12—1.50 the non-ideality in the present polymerization appears to be largely due to degradative initiator transfer effect.

Thanks are due to the Council of Scientific and Industrial Research and University Grants Commission, India for supporting this research through Fellowship Grants to S. J. and S. B. respectively.

References

1) *P. Ghosh and S. Chakraborty, Eur. Polym. J.*, **15**, 137 (1979).
2) M. Matsuda, Y. Ishioroshi, and T. Hirayama, *J. Polym. Sic.*, **B-4**, 815 (1966).
3) Y. Ishioroshi and M. Matsuda, Presented at the 19th Symposium on Polymer Chemistry, Kyoto 1970, Preprint p. 315.
4) P. Ghosh, S. Chakraborty, and S. Biswas, *Makromol. Chem.*, **181**, 1331 (1980).
5) Y. Ishioroshi, T. Hirayama, and M. Matsuda, *Kobunshi Ronbunshu*, **34**, 347 (1977).
6) P. Ghosh, P. S. Mitra, and A. N. Banerjee, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 2021 (1973).
7) P. Ghosh and A. N. Banerjee, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 375 (1974).
8) P. Ghosh and P. S. Mitra, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 921 (1973).
9) P. Ghosh and S. Chakraborty, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1531 (1975).
10) T. G. Fox, J. B. Kinsinger, H. F. Mason, and E. M. Shuele, *Polymer*, **3**, 71 (1962).
11) P. Ghosh, S. C. Chandha, A. R. Mukherjee, and S. R. Palit, *Indian J. Polym. Sci.*, **A-2**, 4433 (1964).
12) J. C. Bevington, H. W. Melville, and R. P. Taylor, *J. Polym. Sci.*, **14**, 463 (1954).
13) P. C. Deb and G. Meyerhoff, *Eur. Polym. J.*, **10**, 709 (1974).
14) P. C. Deb, *Eur. Polym. J.*, **11**, 31 (1975).
15) P. Ghosh and P. S. Mitra, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 1743 (1977).