

Polymerization of Methyl Methacrylate With H_2O_2 -Thiourea Redox Initiator System

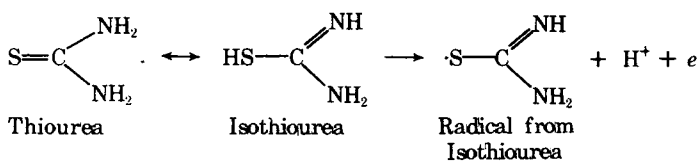
PREMAMOY GHOSH and MADHU SUDAN BANERJEE, *Plastics and Rubber Technology Division, Department of Applied Chemistry, Calcutta University, Calcutta-700009, India*

Synopsis

Polymerization of MMA was done in aqueous media and in a bulk (nonaqueous) system employing a H_2O_2 -TU redox initiator system. Kinetic features differ significantly depending on the nature of the reaction media. The redox system is much more efficient as a chain initiator in aqueous media than in bulk MMA, where conversion to polymer, thermally and even under photoactivated conditions, is very slow and sluggish. In the bulk media, pronounced inhibition and retardation effects appear to be due to formation of unstable reaction intermediate presumably through dimerization of $\dot{S}(:NH)-NH_2$ radical generated in the primary redox reaction.

INTRODUCTION

Use of thiourea or N-substituted thiourea as a component in redox initiator system in aqueous vinyl polymerization is rather recent.¹⁻⁵ Polymerization in solution in nonaqueous media has also been reported. With thiourea as the activator (reductant) in a redox initiator system, it is generally accepted that polymerization takes place, at least in part, through the agency of $\dot{S}-C(:NH)-NH_2$ radical generated in the system by oxidation of isothiurea:



Incorporation of the radical $\dot{S}-C(:NH)-NH_2$ in the polymer as an end group has been indicated and confirmed by end group analysis and other methods.²

We have used hydrogen peroxide-thiourea redox initiator for the polymerization of methyl methacrylate (MMA) in bulk (nonaqueous) and in aqueous media under thermal or photoactivated conditions. Results are reported in the present paper.

EXPERIMENTAL

Materials

Monomer MMA was purified following standard procedures.⁶ Thiourea (TU) and hydrogen peroxide [30% (w/v)] were obtained from E. Merck.

Polymerization

Aqueous polymerization was done in 150-ml conical flasks under nitrogen-flushed conditions at 35°C, using known concentrations of H₂O₂, TU, and monomer. The progress of the polymerization with time was followed gravimetrically.

For bulk polymerization, an MMA extract of hydrogen peroxide was prepared,⁷ and its H₂O₂ content was determined iodometrically. This MMA extract and thiourea dissolved in distilled methanol were used for polymerization experiments, the methanol content in each bulk polymerization was kept fixed at 1% (v/v) unless stated otherwise. Bulk polymerization was done under nitrogen atmosphere at 40°C in the presence of a 125-W mercury vapor lamp. The progress of the polymerization was followed dilatometrically.⁶

Molecular Weight

Molecular weight \bar{M}_n of poly(methyl methacrylate) (PMMA) samples was obtained viscometrically using the following equation⁸ relating intrinsic viscosity $[\eta]$ and \bar{M}_n :

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_n^{0.76}$$

End Group

Polymers prepared by H₂O₂-TU redox initiator system are expected to bear hydroxyl (OH) and amino (-NH₂) end groups in them. Some of the prepared polymers were therefore subjected to sensitive dye partition tests for the detection of -OH and -NH₂ end groups.^{9,10}

Hydroxyl end group detection by the dye partition method required prior transformation of the unreactive -OH end groups to dye responsive -SO₄⁻ end groups by treating the polymers with chlorosulfonic acid in pyridine medium, according to the standard method.⁹ A dye test for the amino end group was done directly on the prepared polymers.¹⁰ The dye reagents for -OH and -NH₂ end group analyses were methylene blue and disulfine blue VN-150, respectively, each being dissolved in aqueous centinormal hydrochloric acid solution. To perform the dye partition tests, polymer samples were taken in chloroform solution and were then shaken well with the reactive aqueous dye reagent. A coloration of the chloroform layer indicated the presence of the said end groups (OH or NH₂) in the polymers.^{9,10}

RESULTS

Variation of Yield of Polymer with TU Concentration

The variations in yield of polymer with thiourea concentration for fixed concentrations of H₂O₂ and MMA and for a fixed time of polymerization in aqueous and bulk polymerization systems are given in Tables I and II. In Table II, data are presented for bulk polymerization of MMA over a wide range of TU concentrations in the dark at 60 ± 1°C and in presence of sunlight at 35 ± 1°C. It is clearly seen that while thiourea in the concentration range of 10⁻³-10⁻⁴ m/liter

TABLE I
Aqueous Polymerization of Methyl Metacrylate with H₂O₂-TU Redox Initiator System^a

Expt. No.	TU (moles/liter × 10 ³)	Inhibition period (min)	% Conversion	[η] (dl/g)
1	0.5	11	43.23	1.32
2	1.0	7	62.63	0.82
3	2.0	5	65.41	0.63
4	10.0	2	85.11	0.15
5	15.0	2	81.59	—
6	25.0	1.5	74.36	—
7	50.0	1	53.92	—

^a H₂O₂ = 1.927 × 10⁻² moles/liter; temperature: 35°C; MMA = 0.092 moles/liter; nitrogen atmosphere; time of polymerization = 2 hr.

TABLE II
Bulk Polymerization of Methyl Methacrylate with H₂O₂-TU Redox Initiator^a

A. Polymerization in dark Temperature: 60 ± 0.1°C H ₂ O ₂ : 0.012 moles/liter Time: 3 hr Nitrogen atmosphere				B. Polymerization in sunlight Temperature: 36 ± 1°C H ₂ O ₂ : 0.015 moles/liter Time: 1 hr Nitrogen atmosphere			
Expt. No.	TU × 10 ⁵ (moles/liter)	% Conversion	[η] in benzene at 30°C	Expt. No.	TU × 10 ⁵ (moles/liter)	% Conversion	[η] in benzene at 30°C
1	Nil	6.42	—	7	Nil	2.81	—
2	1.0	3.29	3.83	8	1.0	2.72	1.41
3	5.0	1.21	3.70	9	5.0	2.57	1.24
4	10.0	0.067	3.63	10	10.0	2.34	1.14
5	100.0	0.017	3.42	11	100.0	1.91	1.03
6	1000.0	0.013	3.19	12	1000.0	1.31	0.95

^a TU was taken in methanol solution. Volume of methanol maintained in each experiment: 2 ml per 100 ml MMA. Retardation effect of TU is much less pronounced in photoactivated systems than in thermal systems. This is probably due to the fact that the retarding intermediate (which is expected to be a disulfide as discussed in the text) also acts as a photoinitiator

easily activates H₂O₂-induced polymerization of MMA in aqueous media, it fails to do so when the polymerization is done in the bulk. On the other hand, thio-urea appears to suppress the bulk polymerization significantly even when present in a concentration of 10⁻⁵ m/liter, and this effect is more pronounced with higher concentrations of TU.

Kinetic Investigation

Aqueous Polymerization

Some representative percentage conversion versus time plots for aqueous polymerization at 35°C are shown in Fig. 1. For the set of experiments shown in Figure 1, plot A, the concentration of H₂O₂ was kept fixed and that of TU was varied, while for those shown in Figure 1, plot B, the concentration of TU was kept fixed and that of H₂O₂ was varied. From the initial steady slope of each plot the respective rate of polymerization R_p was calculated. From slopes of the log R_p vs log [TU] and log R_p vs log [H₂O₂] plots, Figures 2A and 2B corre-

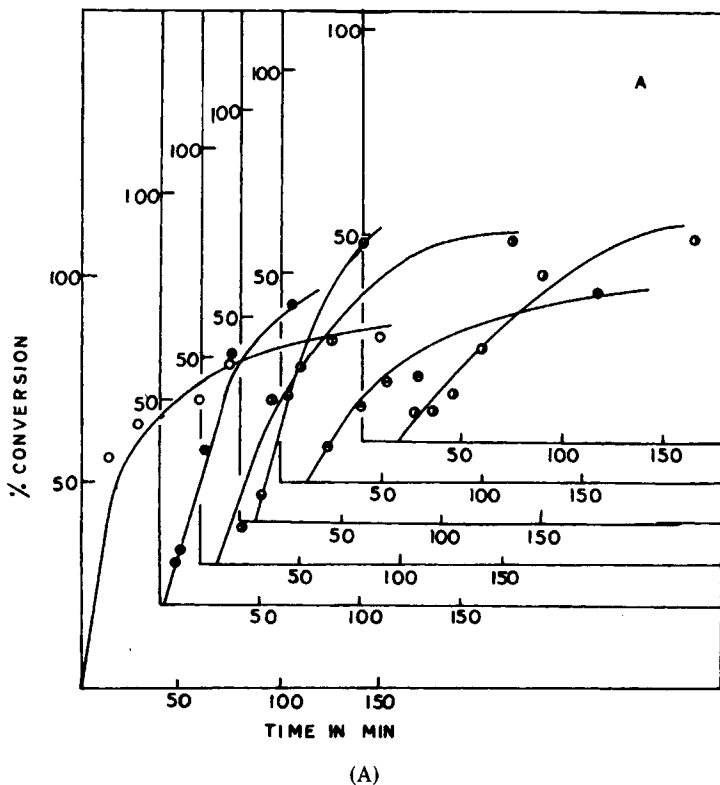


Fig. 1. Aqueous polymerization of MMA at 35°C. Plot of % conversion vs time. (A) For each curve $[H_2O_2]$ is fixed at 1.93×10^{-2} moles/liter and $[TU]$ in moles/liter is \circ , 1×10^{-2} ; \bullet , 2.5×10^{-3} ; \odot , 2×10^{-3} ; \ominus , 1.5×10^{-3} ; \oplus , 1×10^{-3} ; \otimes , 0.5×10^{-3} . (B) For each curve $[TU]$ is fixed at 1×10^{-2} moles/liter and $[H_2O_2]$ in m/liter is \circ , 9.63×10^{-2} ; \bullet , 7.14×10^{-2} ; \odot , 5.11×10^{-2} ; \ominus , 3.082×10^{-2} ; \oplus , 1.93×10^{-2} ; \otimes , 0.51×10^{-2} .

sponding to Figures 1A–1B, a square root dependence of R_p on the concentration of both the redox initiator components is indicated.

The variation of R_p with monomer concentration has also been studied at fixed concentrations of H_2O_2 and TU, and the results are presented in the form of $\log R_p$ vs $\log [M]$ plot in Figure 3. The slope of the linear plot is unity, indicating that R_p is directly proportional to the monomer concentration. The kinetic features for aqueous polymerization of MMA appear to be similar to those reported for aqueous polymerization of acrylonitrile.¹ Usual free radical polymerization with termination by bimolecular mechanism is thus indicated.

Bulk Polymerization

Table II clearly indicates that polymerization in the bulk takes place at a much faster rate under photoactivated conditions than under purely thermal conditions. Hence, kinetic studies of MMA polymerization with H_2O_2 -TU redox initiator were made dilatometrically by irradiating the filled dilatometers with light from a 125-W mercury vapor lamp (Philips India Ltd) at 40°C according to a procedure described elsewhere.⁶ Considering the very pronounced inhibition

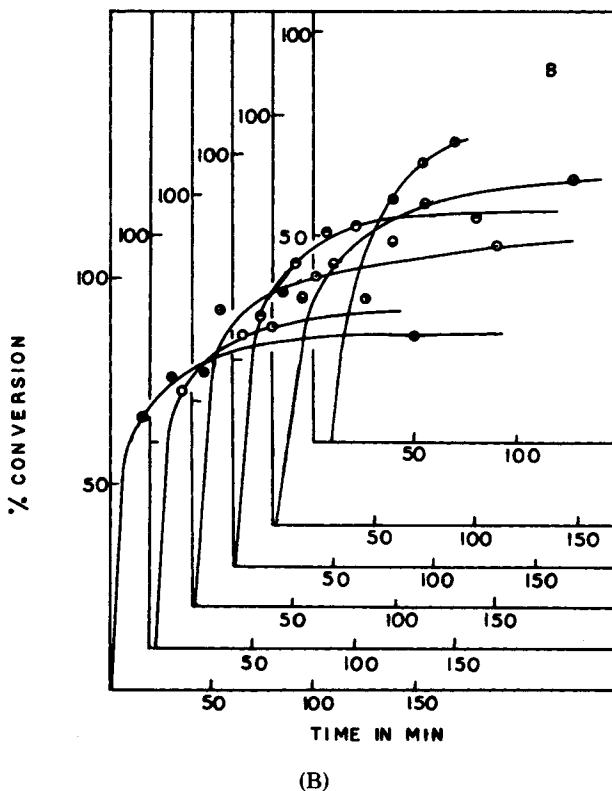


Fig. 1. (Continued from previous page.)

or retardation effect of TU, Table II, a very low concentration of TU (of the order of 10^{-6} m/liter) was used for kinetic investigations in the bulk system.

Some representative percentage conversion vs time plots are shown in Figures 4(A) and 4(B). The inhibition periods (IP) are not all that reproducible, but the general trend is that the IP is slightly higher with higher TU concentration in the 10^{-6} m/liter concentration range. Variation of rate with H_2O_2 concentration and with TU concentration was studied, and the results are presented in graphical plots, $\log R_p$ vs $\log [H_2O_2]$ and $\log R_p$ vs $\log [TU]$, respectively, Figures 5(A) and 5(B). It is clear from the plots that while the H_2O_2 exponent is 0.45 (close to the usual square root dependence), the TU exponent is much lower, i.e., 0.17. The monomer exponent obtained from the slope of the $\log R_p$ vs $\log [M]$ plot in systems diluted with acetone, Figure 6, is found to be 1.5.

DISCUSSION

The kinetic features of aqueous and bulk polymerization are significantly different. Initiator exponents are lower than 0.5 in the bulk system; the TU exponent deviates much more significantly from the square root relationship than the H_2O_2 exponent. Termination in bulk system thus appears to be highly dependent on TU concentration or more precisely on radicals or reaction products derived from it. This is also reflected in a reasonably higher monomer exponent (1.5) in the bulk system than unity, indicating therefore a significant

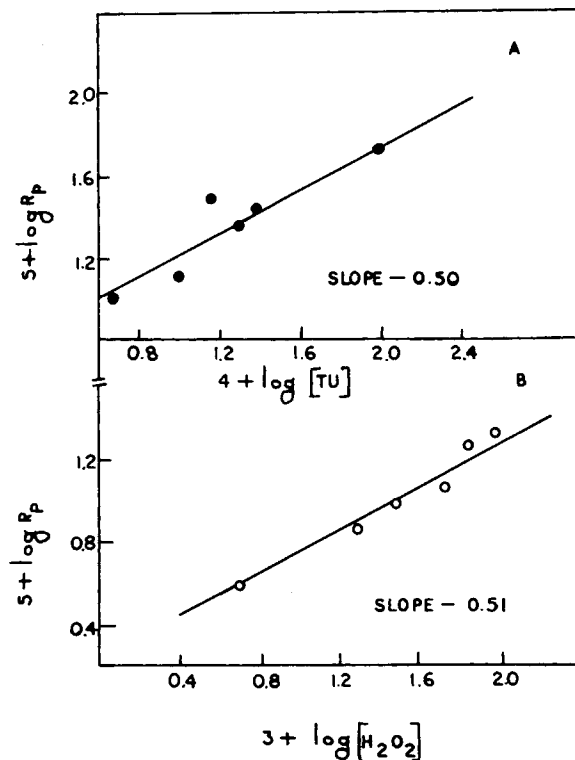


Fig. 2. Variation of rate of aqueous polymerization of MMA with initiator concentration at 35°C. (A) Plot of $\log R_p$ vs $\log [TU]$; (B) plot of $\log R_p$ vs $\log [H_2O_2]$.

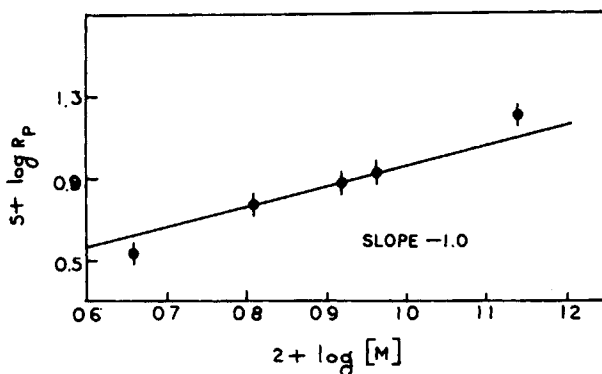


Fig. 3. Variation of rate of aqueous polymerization of MMA with monomer concentration at 35°C. Plot of $\log R_p$ vs $\log [M]$; $[H_2O_2] = 5.11 \times 10^2$ moles/liter; $[TU] = 1 \times 10^{-2}$ moles/liter.

deviation from the bimolecular termination mechanism of a normal free radical polymerization process. In aqueous system, however, termination is indicated to take place by the usual bimolecular mechanism.

The inhibitory effect of TU is very prominent even in the 10^{-5} – 10^{-6} m/liter concentration range in the bulk system, while in the aqueous system, this effect is absent even when TU is present at a much higher concentration range (10^{-2} – 10^{-3} m/liter) and its initiating potential is highly prominent.

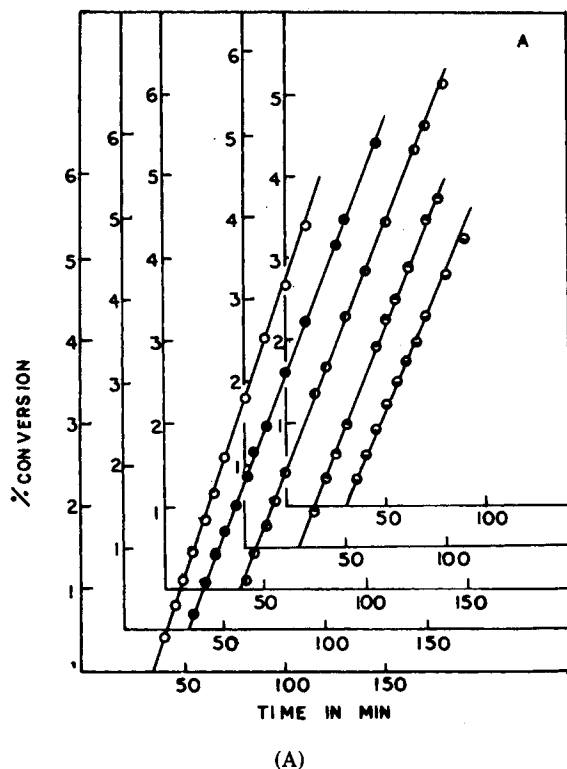
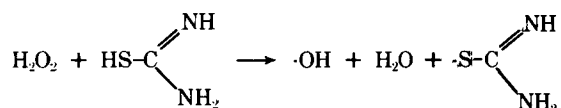
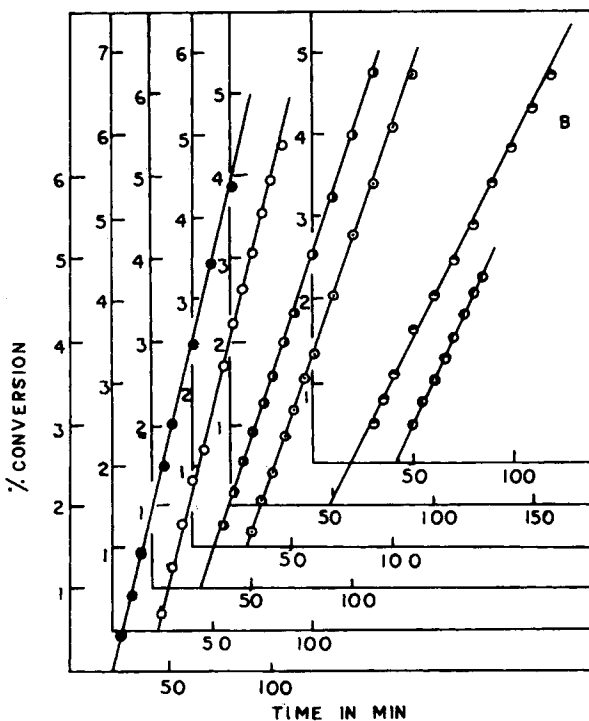


Fig. 4. Photopolymerization of MMA in bulk at 40°C. Plot of % conversion vs time. (A) For each curve $[H_2O_2]$ is fixed at 0.099 moles/liter and $[TU]$ in moles/liter is \circ , 8.26×10^{-6} ; \bullet , 5.51×10^{-6} ; \ominus , 4.13×10^{-6} ; \oplus , 2.75×10^{-6} ; \odot , 2.07×10^{-6} . (B) For each curve $[TU]$ is fixed at 8.26×10^{-6} moles/liter and $[H_2O_2]$ in moles/liter is \bullet , 39.9×10^{-2} ; \circ , 27.95×10^{-2} ; \oplus , 14.72×10^{-2} ; \odot , 11.99×10^{-2} ; \ominus , 7.9×10^{-2} ; \bullet , 5.9×10^{-2} .

In the present H_2O_2 -TU redox system of initiation, the polymers obtained gave positive response for the presence of $-OH$ and $-S-C(:NH)-NH_2$ endgroups as analyzed by the application of dye-sensitive partition techniques, indicating thereby that initiation of polymerization takes place through the agency of $\dot{O}H$ and $\dot{S}-C(:NH)-NH_2$ radicals generated in the system during the reduction activation reaction between H_2O_2 and TU:



In aqueous system, the $\dot{S}-C(:NH)-NH_2$ radicals appear to be efficiently utilized for chain initiation. The inhibition and retardation effect on polymerization in the bulk system therefore does not appear to be due to either TU or the radical derived from it. The effect is probably attributable to some other compounds or intermediates formed *in situ* through side reactions leading to loss of initiating radicals with the formation of unreactive or retarding or inhibiting intermediates. In fact, it was observed that in all experiments done in bulk with TU concentration of 1×10^{-5} m/liter or higher a haziness or turbidity slowly appeared within



(B)

Fig. 4. (Continued from previous page.)

5–15 min of mixing the three components ($\text{H}_2\text{O}/\text{MMA}/\text{TU}$) together, and the turbidity increased with time and with increased TU content. The turbidity appeared both in the absence and in the presence of air or oxygen and no turbidity was found to develop when either of the redox components was absent from the system.

This observation of slow precipitation may obviously raise a question whether the active radicals, being encapsulated and isolated from the active bulk medium, retarded polymerization. When the polymerization was carried out in presence of about 10% (v/v) methanol in the system, appearance of the precipitate (tur-

TABLE III
Variation of Inhibition Period and R_p Under Different Conditions of Polymerization^a

Methanol (ml)	TU $\times 10^6$ (moles/liter)	Nature of the system	$R_p \times 10^5$ (moles/liter/sec)	Inhibition period (min)
0.1	—	Clear	9.46	32
0.1	8.26	Clear	12.12	36
0.1	826.0	Slow appearance of turbidity and ppt.	9.21	47
0.1	8260.0	Slow appearance of turbidity and ppt.	8.95	53
1.1 ^b	826.0	Clear	9.19	112
1.1 ^b	8260.0	Clear	8.75	117

^a MMA = 12 ml; H_2O_2 : 0.099 moles/liter.

^b Extra 1 ml methanol prevented the appearance of turbidity.

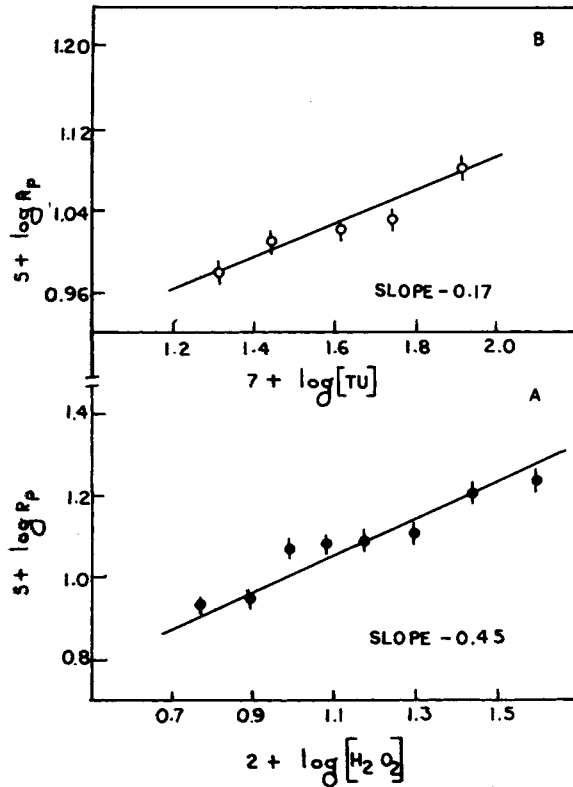


Fig. 5. Variation of rate of bulk photopolymerization of MMA with initiator concentration at 40°C. (A) Plot of $\log R_p$ vs $\log [H_2O_2]$; (B) plot of $\log R_p$ vs $\log [TU]$.

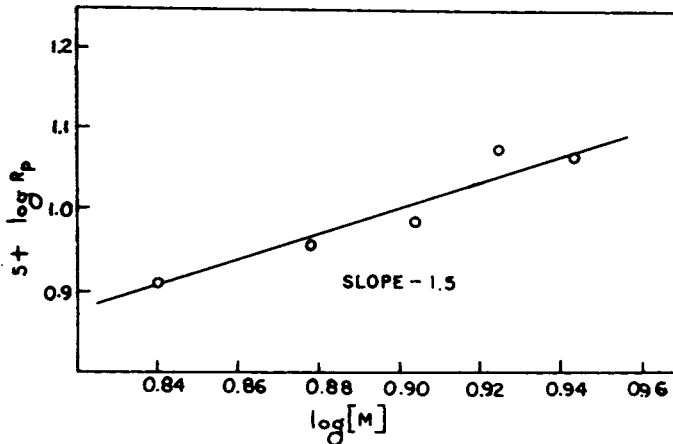


Fig. 6. Variation of rate of bulk photopolymerization of MMA with monomer concentration at 40°C. Plot of $\log R_p$ vs $\log [M]$; $[TU] = 8.26 \times 10^{-6}$ moles/liter; $[H_2O_2] = 0.28$ moles/liter.

bidity) could be completely avoided, methanol being a solvent for the precipitate, but in the homogeneous nonaqueous system in the presence of methanol, the rate of polymerization remained practically the same, but the polymerization was initiated after a much prolonged IP, Table III. Thus the question of active

TABLE IV
Bulk Polymerization of MMA with H₂O₂-TU Photoinitiator System: Effect of Variation of TU Concentration^a

Expt. No.	[TU] × 10 ⁶ (moles/liter)	I = [H ₂ O ₂] [TU] × 10 ⁶	R _p × 10 ⁵ (moles/liter/sec)	R _p ² × 10 ⁴ [I][M] ² (A)	4 + log A	R _p × 10 ⁵ [M] ²
1	8.264	0.818	12.120	2.076	0.3173	0.140
2	5.510	0.545	10.760	2.456	0.3903	0.124
3	4.130	0.408	10.580	3.172	0.5014	0.122
4	2.750	0.272	10.270	4.483	0.6516	0.118
5	2.066	0.204	9.526	5.134	0.7113	0.110

^a [H₂O₂] = 0.099 moles/liter, [MMA] = 9.3 moles/liter.

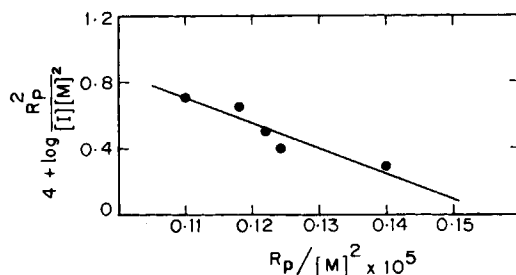


Fig. 7. Plot of $\log R_p^2/[I][M]^2$ vs $R_p/[M]^2$ for bulk photopolymerization of MMA at 40°C. [I] = [H₂O₂][TU]; [H₂O₂] = 0.099 m/liter; [TU] varies

radical encapsulation is not tenable, and the inhibitory effect is much pronounced if the reaction intermediate is allowed to remain in solution instead of being precipitated out.

We are of the opinion that the turbidity appearing in the bulk system is due probably to the *in situ* formation of the disulfide, H₂N·(HN:)C-S-S-C:(NH)·NH₂. Organic disulfides and polysulfides are known to retard vinyl polymerization, presumably through degradative chain transfer.¹¹⁻¹³ So, the possible formation of the above disulfide through dimerization of the radical $\dot{S}-C:(NH)·NH_2$ derived as an intermediate during oxidation of TU, can explain the retardation of polymerization in bulk systems. However, we could not characterize the precipitate on isolation and purification, as it appeared to be highly unstable in nature. In aqueous systems, the formation of the disulfide is not indicated (absence of inhibition or retardation effect); on the other hand, according to Barnett,¹⁴ formation of traces of formamidine sulfinic acid, H₂N·C:(NH)-SO₂H, in the process of oxidation of TU in aqueous system can not be ruled out. Sulfinic acids are known to be good initiators of polymerization and they are not reported to have any retardation effect.

CONCLUSION

Thus, the redox reaction between H₂O₂ and TU seems to have distinctly different features depending on the nature of the reaction media as revealed by polymerization of MMA in aqueous and bulk system. The redox system is much more efficient as a chain initiator in aqueous media than in bulk MMA where

conversion to polymer is very sluggish; and inhibition and retardation effects of unstable reaction intermediates become highly prominent, so much so that even at concentrations of TU close to or higher than about $1 \times 10^{-5} M$, polymerization is significantly retarded. The primary retarding intermediate, which could not be properly characterized for being highly unstable, is presumed to be the disulfide $H_2N-C(:NH)-S-S-(HN:)C-NH_2$.

On analysis of primary radical termination effect in vinyl polymerization, Deb and Meyerhoff¹⁵ have shown that a plot of $\log (R_p^2/[I][M]^2)$ against $R_p/[M]^2$ would give a linear plot with a negative slope in case primary radical termination is significant. With our kinetic data regarding variation of R_p with TU concentration, corresponding to Figures 4(A) and 5(B), and Table IV, a Deb-Meyerhoff plot of the above kind is made and shown in Figure 7. Here, $[I]$ stands for product of concentrations of TU and H_2O_2 . A pronounced negative slope for the linear plot clearly indicates the occurrence of primary radical termination to an appreciable extent in the present polymerization system.

Thanks are due to CSIR, India for supporting this work in the form of a Fellowship Grant to one of us (M.S.B.).

References

1. T. Sugimura, N. Yasumoto, and Y. Minoura, *J. Polym. Sci.*, A 3, 2935 (1965).
2. B. M. Mandal, U.S. Nandi, and S. R. Palit, *J. Polym. Sci.*, A-1, 4, 3115 (1966).
3. A. R. Mukherjee, R. Pal, A. M. Biswas, and S. Maity, *J. Polym. Sci.*, A-1, 5, 135 (1967).
4. B. M. Mandal, U. S. Nandi, and S. R. Palit, *J. Polym. Sci.*, A-1, 7, 1407 (1969).
5. B. M. Mandal, U. S. Nandi, and S. R. Palit, *J. Polym. Sci.*, A-1, 8, 67 (1970).
6. P. Ghosh, P. S. Mitra, and A. N. Banerjee, *J. Polym. Sci., Polym. Chem. Ed.*, 11, 2021 (1973).
7. U. S. Nandi and S. R. Palit, *J. Polym. Sci.*, 17, 65 (1955).
8. T. G. Fox, J. B. Kinsinger, H. F. Mason, and E. M. Shuele, *Polym.*, 3, 71 (1962).
9. P. Ghosh, P. K. Sengupta, and A. Pramanik, *J. Polym. Sci.*, A 3, 1725 (1965).
10. S. Maity, and M. K. Saha, *J. Polym. Sci.*, A-1, 5, 151 (1967).
11. P. Ghosh, *J. Polym. Sci. D*, 5, 195 (1971).
12. T. E. Ferrington and A. V. Tobolsky, *J. Am. Chem. Soc.*, 80, 3215 (1958).
13. T. E. Ferrington and A. V. Tobolsky, *J. Am. Chem. Soc.*, 77, 4510 (1955).
14. E. B. Barnett, *J. Chem. Soc.*, 97, 63 (1910).
15. P. C. Deb and G. Meyerhoff, *European Polym. J.*, 10, 709 (1974).

Received July 7, 1977

Revised March 9, 1978