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ABSTRACT

The aqueous polymerization of methyl methacrylate (MMA) initiated by the potassium bromate-thiomalic acid (TMA) redox system was investigated in the presence of atmospheric oxygen at 35 ± 0.2°C. As the monomer MMA concentration and initiator $KBrO_3$ concentration were increased, there was a corresponding increase in both the initial rate and limiting conversion. It was observed that with an increase in activator TMA concentration both the initial rate and the maximum conversion increased up to a certain limit. There was then a fall in initial rate and maximum conversion. The rate of polymerization is given by the relation

$$R_p \propto [KBrO_3]^x[TMA]^0[MMA]^{1.1}$$

where x = 1.06 and 0.06 for lower and higher initiator concentrations, respectively. The energy of activation (E_a) was calculated from an Arrhenius plot and found to be 57.98 kJ/mol (13.36 kcal/mol) under the temperature range investigated (20-45°C).

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INTRODUCTION

Very little work has been done on the aqueous polymerization of vinyl monomers in the presence of atmospheric oxygen. Kharasch et al. [1] reported that atmospheric oxygen probably sets up a co-redox system with thiol and increases the formation of primary free radical concentration and hence the polymerization rate is enhanced. Many workers have reported the aqueous polymerization of MMA using thioacids as activator in inert atmosphere [2-7].

In earlier communications we reported the aqueous polymerization of monomer MMA by different redox couples in an inert atmosphere [8-10]. Aqueous polymerization of MMA has also been carried out in the presence of atmospheric oxygen using different redox systems [11-13]. With a view of studying the effect of atmospheric oxygen on aqueous polymerization activated by thioacids, we have made a detailed kinetic investigation of the aqueous polymerization of MMA initiated by the $KBrO_3$-TMA redox system in the presence of atmospheric oxygen. The results of this study are reported in the present paper.

EXPERIMENTAL

The monomer and other chemicals were purified and the experimental procedure for polymerization and polymer estimation were the same as described earlier [8]. All experiments were carried out at 35 ± 0.2°C except as otherwise mentioned.

RESULTS AND DISCUSSION

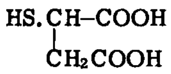
Mechanism

The mercaptan-induced polymerization of vinyl monomers has been studied by Kharasch et al. [1] in the presence of atmospheric oxygen and they have discussed the mechanism involved. According to them, when a positive method of free radical initiated polymerization is involved, the absorption of oxygen forms free radicals. In general anti-Markownikoff's addition takes place, and this results in the formation of active free radicals which initiate polymerization.

In the polymerization reactions taking place in the presence of oxygen, the two actions take place simultaneously.

1. With atmospheric oxygen:

(a) $R{-}SH \xrightarrow[\text{slow}]{O_2\ \text{air}} RS^{\bullet} + HO_2^{\bullet}$ where RSH is

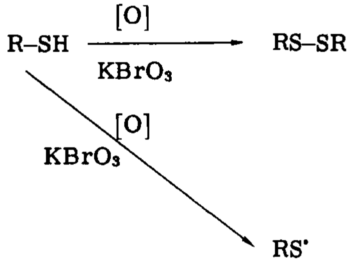


$HS.\underset{\displaystyle CH_2COOH}{\underset{|}{CH}}{-}COOH$

(b) $HO_2^{\bullet} \xrightarrow{RSH} RS^{\bullet} + H_2O_2$

(c) $H_2O_2 \longrightarrow 2\dot{O}H \xrightarrow{\text{deactivation}} H_2O + \frac{1}{2}O_2$

2. With oxidant ($KBrO_3$):



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The following tentative mechanism for the polymerization of vinyl monomers by RS• free radicals is suggested by Misra and Dubey [7]:

$$M + RS^{\bullet} \xrightarrow{\text{initiation}} RSM^{\bullet}$$

$$RSM^{\bullet} + M \xrightarrow{\text{propagation}} RSM_2^{\bullet}$$

$$- - - - - - - - - - - - - - - - - -$$

$$RSM^{\bullet}_{(x-1)} \xrightarrow[M]{\text{propagation}} RSM_x^{\bullet}$$

$$RSM_x^{\bullet} + RSM_y^{\bullet} \xrightarrow[\text{combination}]{\text{termination by}} RSM_{(x+y)}SR$$

$$RSM_x^{\bullet} + RSM_y^{\bullet} \xrightarrow[\text{disproportionation}]{\text{termination by}} RSM_x + RSM_y$$

$$RS^{\bullet} + \dot{S}R \xrightarrow{\text{dimerization}} RS\text{–}SR$$

Rate Dependence of Initiator $KBrO_3$ Concentration

The effect of the variation of initiator $KBrO_3$ concentration at the fixed monomer concentration (9.33×10^{-2} mol/L) and the activator TMA concentration (1.0×10^{-2} mol/L) was studied over a wide range of $KBrO_3$ concentrations (2.5 to 30.0 mmol/L). The results are shown in Fig. 1. These observations indicate that on increasing the initiator concentration from 2.5 to 9.0 mmol/L, both the initial rate and maximum conversion increase. From 9.0 to 15.0 mmol/L $KBrO_3$, only the maximum conversion increased slightly and above that the maximum

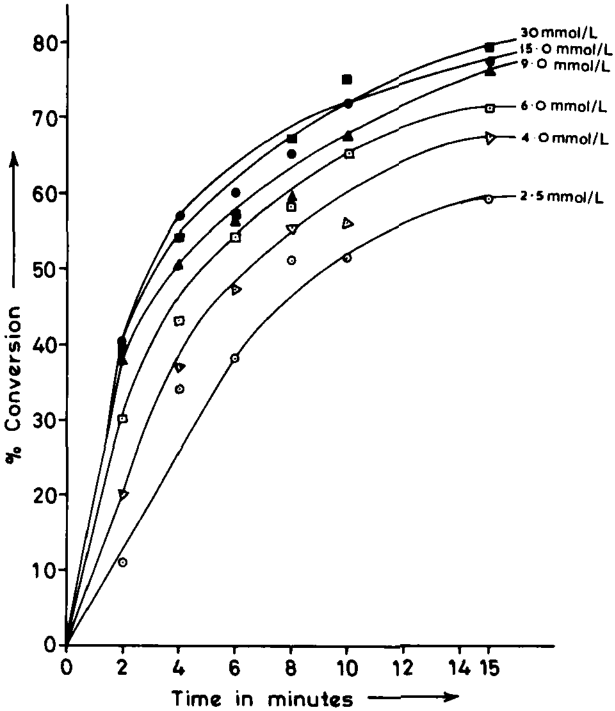

FIG. 1. Rate dependence of initiator concentration. [MMA] = 9.33 × 10^{-2} mol/L. [TMA] = 10.0 × 10^{-3} mol/L.

These results may be explained as follows. At lower initiator concentration there is a sufficient number of activator (TMA) molecules; on oxidation of TMA, free radicals are produced which initiate polymerization. But above a certain initiator concentration the number of activator molecules is insufficient to engage all the initiator molecules for oxidation. At higher $KBrO_3$ concentration, TMA molecules are not left in the reaction mixture, hence termination of growing polymer radicals becomes difficult due to the chain transfer property of thiols which increases the maximum conversion.

The order of polymerization reaction with respect to initiator concentration was determined graphically by plotting a double logarithmic plot of the initiator concentration versus the initial rate of polymerization (Fig. 2). On increasing the initiator concentration above 9.0 mmol/L, there is transition in the order of reaction with respect to the initiator from first order to 0.06 order. This indicates that termination takes place unimolecularly at lower initiator concentration while at higher $KBrO_3$ concentration it is independent of $KBrO_3$ concentration. These results are in the line with the proposed mechanism where $RS^{\bullet}$

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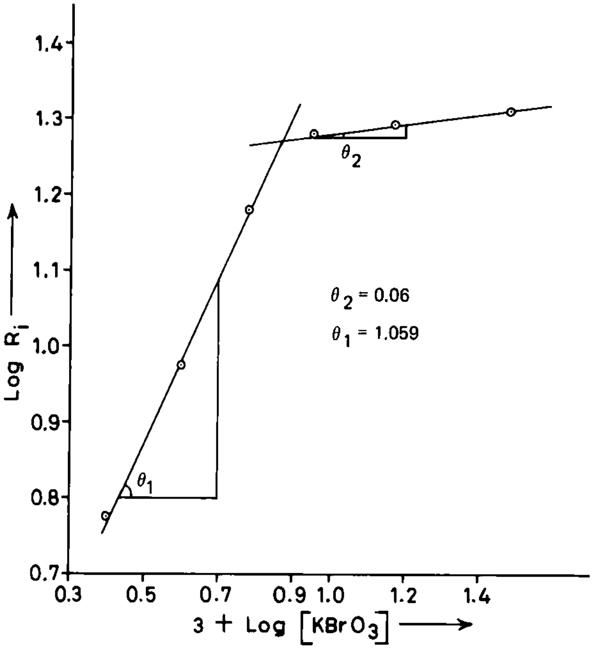

FIG. 2. Double logarithmic plot of R_i vs [KBrO$_3$]. [MMA] = 9.33 × 10^{-2} mol/L. [TMA] = 10.0 × 10^{-3} mol/L.

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free radicals initiate polymerization. The unimolecular termination of growing chain radicals has been reported by Shukla and Mishra [14] and Palit and Konar [15].

Rate Dependence of Activator TMA Concentration

At fixed initiator and monomer concentrations, a variation in the rate of polymerization is observed in the range from 1.0 to 40.0 mmol/L activator TMA concentration. The results are recorded in Table 1. It is observed that TMA alone is incapable of initiating polymerization, even after several hours. A change in activator concentration produces abnormal results. Within the range from 1.0 to 10.0 mmol/L of TMA, there is an increase in both the initial rate and the maximum conversion. Above this TMA concentration the initial rate becomes independent of the activator concentration. At higher activator concentration there is no appreciable change in the initial rate but the maximum conversion falls sharply. This is in line with our previous observations [8-10]. The observations recorded in the present paper indicate that the role of oxygen is not inhibitory as assumed earlier

ABLE 1. Effect of Varying Concentration of TMA on Aqueous Polymerization of MMA by t
BrO$_3$-TMA Redox System[a]

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[TMA] × 10^{-3} (mol/L)	% Conversion with respect to time (min)						
	2	4	6	8	10	15	20
1.0	-	12.04	18.38	22.13	-	34.4	38
4.0	24.04	37.56	46.5	51.36	49.16	65.6	73
7.0	27.56	44.06	51.73	59.58	61.89	71.91	77
10.0	30.52	43.38	54.21	58.84	65.43	71.41	78
20.0	31.31	44.83	55.54	60.22	67.04	73.81	79
30.0	28.9	39.47	47.27	49.8	53.06	55.67	57
40.0	28.1	36.6	35.66	36.86	39.17	42.06	42

[a] Reaction conditions: [MMA] = 9.33 × 10^{-2}, [KBrO$_3$] = 6 mmol/L, 35 ± 0.2°C.

[8-10], but may be attributed to the chain transfer properties of thiols and thioacids.

Rate Dependence on Monomer MMA Concentration

The effect of monomer MMA concentration on the rate of polymerization was investigated over a wide range of concentrations (3.73-11.19 × 10^{-2} mol/L) (Fig. 3). The observations indicate that an increase in monomer concentration up to 9.33 × 10^{-2} mol/L results in a corresponding increase in the initial rate as well as the maximum conversion. At higher monomer concentrations there is a slight decrease in the initial rate but the maximum conversion increases slightly [15-18]. Log [initial rate] and log [MMA] (Fig. 4) are related linearly up to a monomer concentration of 9.33 × 10^{-2} mol/L, but deviation occurs at higher concentrations. This linear behavior of monomer dependence and deviation at higher monomer concentration finds support from Palit et al. [19]. At higher monomer con-

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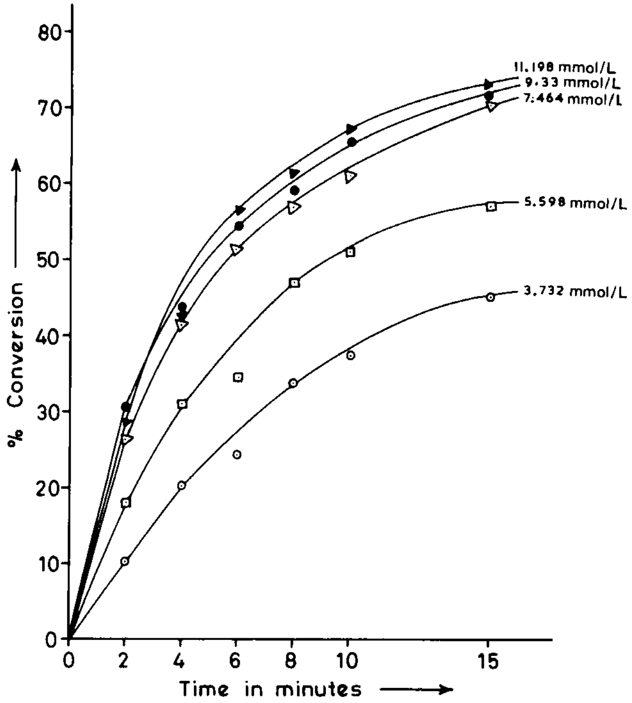

FIG. 3. Rate dependence of monomer concentration. [$KBrO_3$] = 6.0 × 10^{-3} mol/L. [TMA] = 10.0 × 10^{-3} mol/L.

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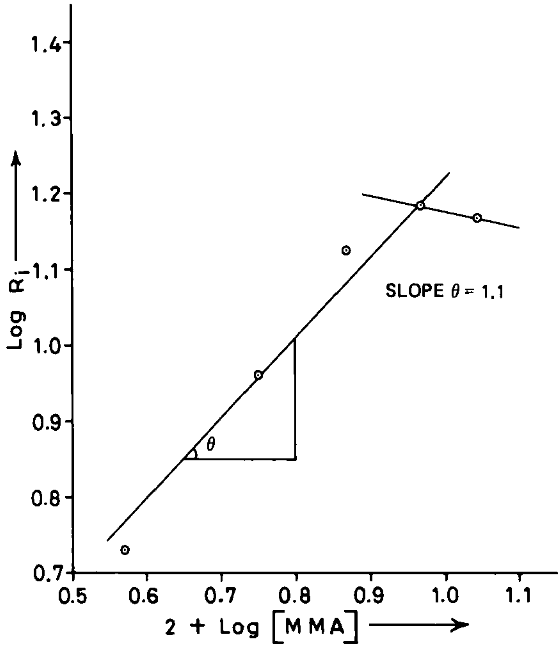

FIG. 4. Double logarithmic plot of R_i vs MMA. [$KBrO_3$] = 6.0 × 10^{-3} mol/L. [TMA] = 10.0 × 10^{-3} mol/L.

centrations the deviation from linear behavior is due to the formation of polymers with which the monomer has some affinity and thus some hindrance is created at an early stage of propagation. Similar observations have been made by others [20-22].

Rate Dependence on Temperature

The dependence of temperature on the rate of polymerization of the monomer MMA at fixed concentrations of initiator, activator, and monomer has been studied over a wide range of temperatures (20-45°C) (Fig. 5). The observations reveal that both the initial rate and the maximum conversion increase as the temperature is raised from 20 to 45°C. This indicates that either there are no radical consuming side reactions or that the side reactions are not significantly altered as a result of the variation in the polymerization temperature [22].

The overall energy of activation was calculated from the slope of the Arrhenius plot (Fig. 6) and found to be 57.98 kJ/mol (13.65 kcal/mol). This value agrees well with other aqueous polymerization reactions [23-25].

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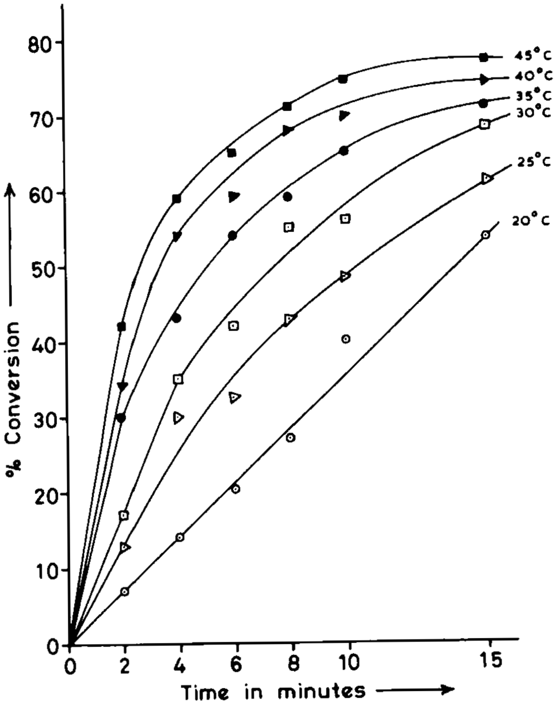

FIG. 5. Rate dependence of temperature. [MMA] = 9.33 × 10^{-2} mol/L. [$KBrO_3$] = 6.0 × 10^{-3} mol/L. [TMA] = 10.0 × 10^{-3} mol/L.

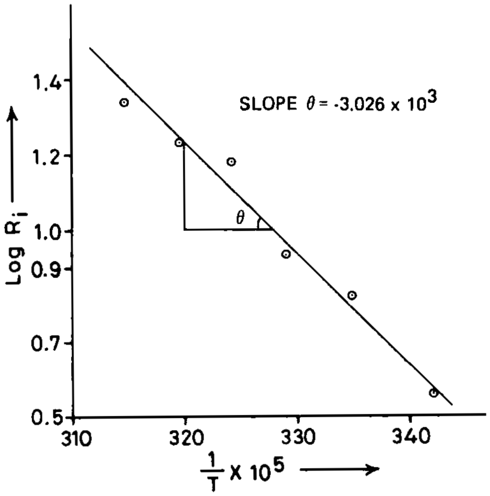

FIG. 6. Arrhenius plot of R_i vs 1/T (°K). [MMA] = 9.33 × 10^{-2} mol/L. [$KBrO_3$] = 6.0 × 10^{-3} mol/L. [TMA] = 10.0 × 10^{-3} mol/L.

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REFERENCES

[1] M. S. Kharasch, W. Nudunberg, and G. J. Mantall, J. Org. Chem., 16, 524 (1951).

[2] A. R. Mukherjee, R. Pal, A. M. Biswas, and S. Naiti, J. Polym. Sci., A-1, 5, 135 (1967).

[3] K. K. Roy, S. R. Palit, and D. Pramanick, Makromol. Chem., 177, 78 (1976).

[4] G. S. Misra and S. L. Dubey, Colloid Polym. Sci., 257, 156 (1979).

[5] D. Pramanick and A. K. Chaterjee, J. Polym. Sci., 18, 311 (1980).

[6] D. Pramanick and A. K. Chaterjee, Eur. Polym. J., 17, 239 (1981).

[7] G. S. Misra and S. L. Dubey, J. Polym. Sci., 17, 1393 (1979).

[8] J. S. Shukla and R. K. Tiwari, J. Macromol. Sci.–Chem., A16, 1047 (1981).

[9] J. S. Shukla and R. K. Tiwari, Ibid., A18, 759 (1982).

[10] J. S. Shukla, R. K. Tiwari, G. K. Sharma, and S. K. Shukla, J. Polym. Sci., Polym. Chem. Ed., In Press.

[11] C. C. Menon and S. L. Kapur, J. Polym. Sci., 54, 45 (1961).

[12] J. Bond and P. I. Lee, Ibid., A-1, 7, 379 (1969).

[13] T. Tanaka, Nippon Kagaku Kaishi, 7, 936 (1979).

[14] J. S. Shukla and D. C. Mishra, Makromol. Chem., 158, 9 (1972).

[15] S. R. Palit and R. S. Konar, J. Polym. Sci., 58, 85 (1962).

[16] J. Abere, G. Goldfinger, H. Naidus, and K. Mark, J. Phys. Chem., 49, 211 (1945).

[17] A. Chapiro, J. Chim. Phys., 47, 747 (1950).

[18] R. G. W. Norrish and R. R. Smith, Nature, 150, 336 (1942).

[19] S. R. Palit, T. Guha, R. Das, and R. S. Konar, in Encyclopedia of Polymer Science and Technology, Vol. 2, 1965, p. 229.

[20] G. S. Misra and J. J. Rebello, Makromol. Chem., 175, 3117 (1974).

[21] G. S. Misra, J. S. Shukla, and H. Narain, Ibid., 74, 1119 (1968).

[22] G. S. Misra and J. J. Rebello, Ibid., 176, 2203-2223 (1975).

[23] W. M. Thomas, E. H. Gleason, and G. Mino, J. Polym. Sci., 24, 43 (1957).

[24] J. M. Baxendale, M. G. Evans, and J. K. Kilhan, Trans. Faraday Soc., 42, 688 (1946).

[25] A. Katchalsky and G. Blauer, Ibid., 47, 1360 (1951).

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