This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Aqueous Polymerization of Methyl Methacrylate

J. S. Shukla[a]; R. K. Tiwari[a]
[a] Department of Chemistry, Lucknow University, Lucknow, India

To cite this Article Shukla, J. S. and Tiwari, R. K.(1981) 'Aqueous Polymerization of Methyl Methacrylate', Journal of Macromolecular Science, Part A, 16: 5, 1047 — 1060

To link to this Article: DOI: 10.1080/00222338108056459

URL: http://dx.doi.org/10.1080/00222338108056459

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. MACROMOL. SCI.–CHEM., A16(5), pp. 1047-1060, 1981

Aqueous Polymerization of Methyl Methacrylate

J. S. SHUKLA and R. K. TIWARI

Department of Chemistry
Lucknow University
Lucknow Pin 226007, India

Downloaded At: 07:48 25 January 2011

ABSTRACT

Aqueous polymerization of methyl methacrylate (MMA), initiated by the potassium bromate-thioglycollic acid (TGA) redox system, has been studied at 30 ± 0.2°C under positive pressure of nitrogen. The rate is given by $K[MMA][TGA]^0[KBrO_3]^x$ where $x = 1$ for lower $KBrO_3$ concentrations and 0.5 for higher $KBrO_3$ concentrations. The reaction has been studied over the 20-45°C range. The activation energy was found to be 65.72 kJ/mol (15.71 kcal/mol) in the investigated range of temperature. Inorganic electrolytes except $MnSO_4 \cdot 4H_2O$ and $Na_2C_2O_4$ depress both the rate of polymerization and the maximum conversion. All the alcohols (viz., MeOH, EtOH, iso-PrOH, tert-BuOH) and acetone depress the rate of polymerization as well as the maximum conversion.

INTRODUCTION

In an earlier communication [1-3] we used $KBrO_3$ with thiourea and TGA for the free radical initiated polymerization of acrylamide and methacrylamide. Palit et al. [4] used $KBrO_3$ with cysteine hydrochloride for the polymerization of MMA in aqueous medium.

A literature survey reveals that so far $KBrO_3$ with TGA has not been used for a detailed study of aqueous polymerization of MMA.

Copyright © 1981 by Marcel Dekker, Inc.

It therefore seemed interesting to study the role of the $KBrO_3$-TGA redox system on the polymerization of MMA under different conditions. In the present communication we report the results of such a study.

EXPERIMENTAL

Chemicals

The monomer MMA, obtained from N.C.L. Poona, India, was purified by the method of Palit et al. [5] and stored at 0-5°C. Potassium bromate, thioglycollic acid, and other chemicals used were of analytical grade. Double distilled water, freed from organic matters and metal ions, was used in the preparation of the solutions. A freshly prepared solution of TGA (to avoid atmospheric oxidation) was used.

Polymerization and Estimation

The polymerization was carried out in a 250-mL conical flask fitted with airtight standard joints for passing nitrogen and injecting other ingredients. TGA solution followed by monomer solution was added to the flask. The purified nitrogen [6] was passed. After 15 min of deaeration, a calculated quantity of potassium bromate was added. The polymerization reaction started immediately without any induction period, and a stable sol of the colloidal phase remained throughout.

At definite intervals 10 mL of hydroquinone solution (1%) was introduced into the reaction mixture followed by 10 mL of potassium hydroxide (1.5% w/v) to inhibit the reaction. A sufficient quantity of $MgSO_4$ was added to break the colloidal phase. The polymer thus obtained was separated immediately by filtration and washed thoroughly with hot distilled water. It was dried at 40-50°C overnight and weighed. The results of duplicate runs are generally within the range of ±1.0-3.5% conversion.

Downloaded At: 07:48 25 January 2011

RESULTS AND DISCUSSION

Rate Dependence of Initiator Concentration (Potassium Bromate)

The effect of potassium bromate at a fixed monomer concentration (9.474×10^{-2} mol/L) is shown in Fig. 1. The study was made in the range of 3.0-20.0 mmol/L potassium bromate concentration. It was observed that on increasing the initiator concentration, the initial rate of polymerization increased up to the whole range of initiator

Downloaded At: 07:48 25 January 2011

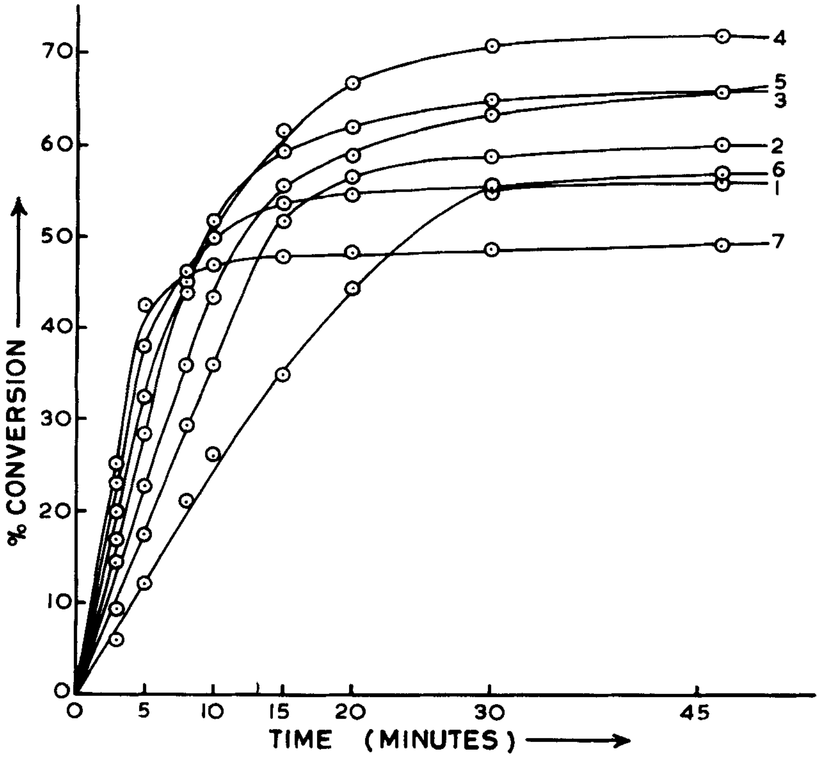


FIG. 1. Rate dependence of initiator potassium bromate concentration on the aqueous polymerization of MMA with TGA-$KBrO_3$ redox system under a nitrogen atmosphere at 30 ± 0.2°C [MMA] = 9.474×10^{-2} mol/L; [TGA] = 1.0×10^{-2} mol/L; [$KBrO_3$] for Curve 1 = 3.0 mmol/L, Curve 2 = 4.5 mmol/L, Curve 3 = 6.0 mmol/L, Curve 4 = 7.5 mmol/L, Curve 5 = 10.0 mmol/L, Curve 6 = 15.0 mmol/L, and Curve 7 = 20.0 mmol/L.

concentration, while maximum conversion above the 7.5 mmol/L $KBrO_3$ concentration tended to decrease.

The order of reaction with respect to the initator has been determined graphically from a double logarithmic plot (Fig. 2). The rate dependence of initiator concentration is interesting and unusual. There is a transition in the order of reaction with respect to initiator from first-order at lower initiator concentrations to half-order at higher initiator concentrations. This is in agreement with the result obtained by Palit et al. [5]. The change in order takes place at 7.5 mmol/L $KBrO_3$ concentration. This indicates that at lower initiator concentration unimolecular termination takes place and at higher initiator

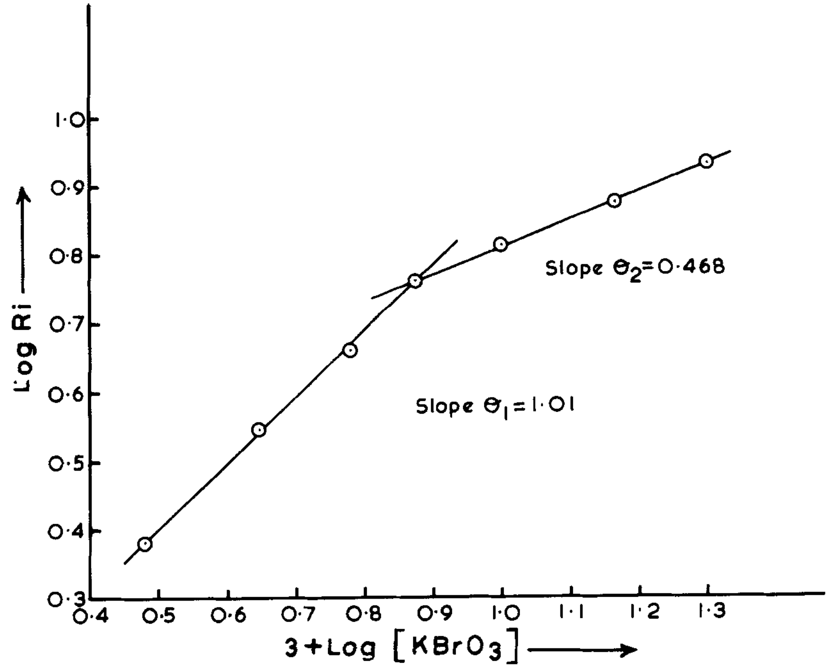


FIG. 2. Double logarithmic plot of the initial rate of polymerization (R_i) (in % conversion/min) vs the concentration of initiator $KBrO_3$.

concentration termination is due to the usual bimolecular. Shukla and Mishra [1] have also reported the first-order dependence on initiator concentration. It can be concluded that the change in the order with respect to initiator depends on the density of polymer particles in the reaction mixture. When low termination takes place unimolecularly and at higher values, the probability of binary collision increases. The termination is governed by the collision of two chain radicals. This idea of unimolecular termination has wide support [7, 8]. Dainton [9] has pointed out that if polymerization is rapid in the aqueous phase, the termination may be mutual or linear. Morgan [10], Whitby et al. [11], Biswas [12], and others [13, 14] have reported the half-order dependence on initiator concentration.

Rate Dependence of Activator Concentration (TGA)

The results of the polymerization of MMA at different concentrations of TGA are recorded in Table 1 and shown in Fig. 3. The observations indicate that with increasing concentration of TGA, the

Downloaded At: 07:48 25 January 2011

Downloaded At: 07:48 25 January 2011

TABLE 1. Rate Dependence of Activator Thioglycollic Acid Concentration on the Aqueous Polymerization of Methyl Methacrylate with TGA-$KBrO_3$ Redox System under Nitrogen Atmosphere at 30 ± 0.2 °C. [MMA] = 9.474×10^{-2} mol/L; [$KBrO_3$] = 6.0×10^{-3} mol/L

No.	[TGA] × 10^{-2} (mol/L)	% concentration in time (min)							
		3	5	8	10	15	20	30	45
1.	0.6	-	14.5	23.57	27.57	34.31	39.53	40.52	41.51
2.	0.8	11.14	17.63	25.00	32.14	39.44	45.91	49.58	51.67
3.	1.0	14.67	22.46	35.81	43.38	54.39	57.89	63.77	65.87
4.	1.2	13.15	20.22	30.26	39.61	48.24	53.67	55.16	56.43
5.	1.4	10.19	15.28	24.62	30.73	36.28	41.25	44.69	46.03

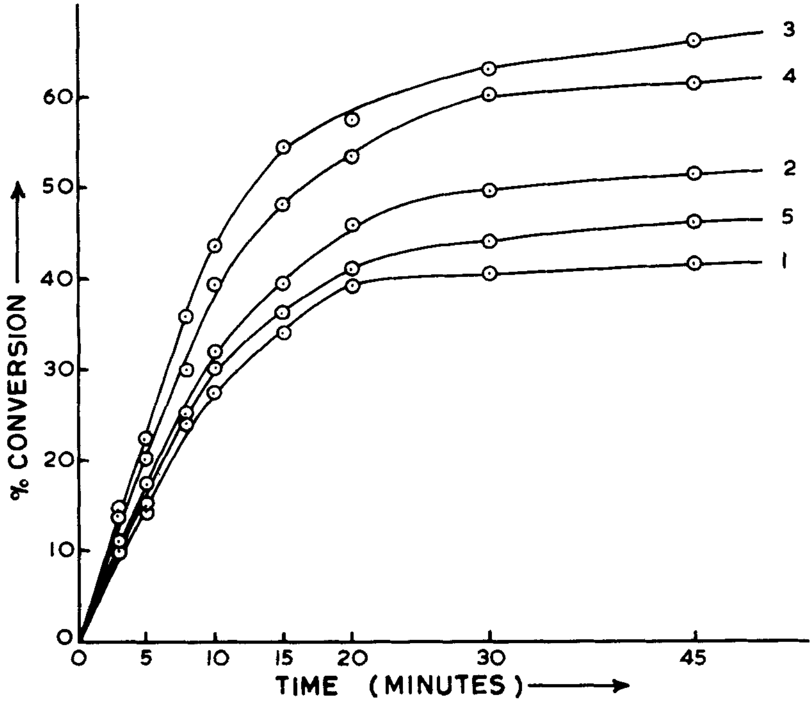


FIG. 3. Rate dependence of activator TGA concentration on the aqueous polymerization of MMA with TGA-$KBrO_3$ redox system under nitrogen atmosphere at 30 ± 0.2°C. [MMA] = 9.474×10^{-2} mol/L; [$KBrO_3$] = 6.0 mmol/L; [TGA] for Curve 1 = 0.6×10^{-2} mol/L, Curve 2 = 0.8×10^{-2} mol/L, Curve 3 = 1.0×10^{-2} mol/L, Curve 4 = 1.2×10^{-2} mol/L, and Curve 5 = 1.4×10^{-2} mol/L.

initial rate as well as maximum conversion increases up to an activator concentration of 1.0×10^{-2} mol/L and above this both of them decrease. In the common redox initiated vinyl polymerization an increase in activator concentration usually results in a corresponding increase in the population of primary free radicals. However, in this case an abrupt result is observed. This fact may be explained as follows.

At higher concentrations of the activator TGA, potassium bromate tends to generate inhibitory oxygen appreciably in the presence of excess hydrogen ions (H_3O^+) given by TGA. Thus, beyond a TGA concentration of 1.0×10^{-2} mol/L, the growing chain radicals are ruptured and suppress the initial rate of polymerization and also maximum conversion. This trend is not unique and it is supported by

Downloaded At: 07:48 25 January 2011

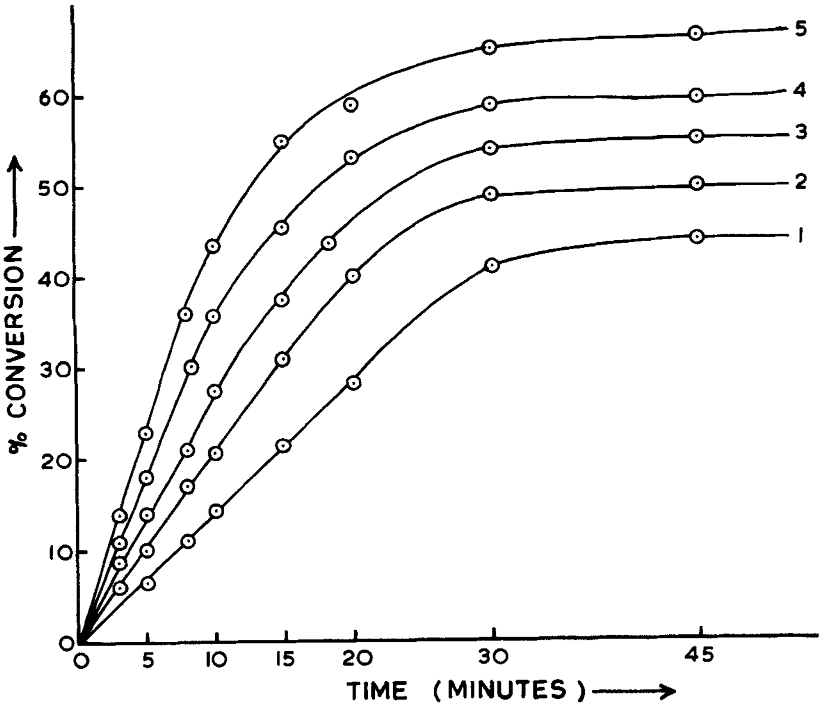


FIG. 4. Rate dependence of monomer MMA concentration of the aqueous polymerization of MMA with TGA-$KBrO_3$ redox system under a nitrogen atmosphere at 30 ± 0.2° C. [$KBrO_3$] = 0.6 mmol/L; [TGA] = 1.0×10^{-2} mol/L; [MMA] for Curve 1 = 1.894×10^{-2} mol/L, Curve 2 = 3.788×10^{-2} mol/L, Curve 3 = 5.682×10^{-2} mol/L, Curve 4 = 7.576×10^{-2} mol/L, and Curve 5 = 9.474×10^{-2} mol/L.

earlier workers [2, 3, 15, 16] in the domain of other redox polymerizations of several monomers.

Rate Dependence of Monomer Concentration

Variation of the rate of polymerization with monomer concentration at 30 ± 0.2° C and at a fixed concentration of $KBrO_3$ (6.0 mmol/L) and TGA (1.0×10^{-2} mol/L) is shown in Fig. 4. It shows that the initial rate of polymerization as well as the maximum conversion increases with increasing monomer MMA concentration. However, the initial rate increases linearly, and the extent of polymerization attains a constant value after a certain period as has been reported by other investigators [17].

Downloaded At: 07:48 25 January 2011

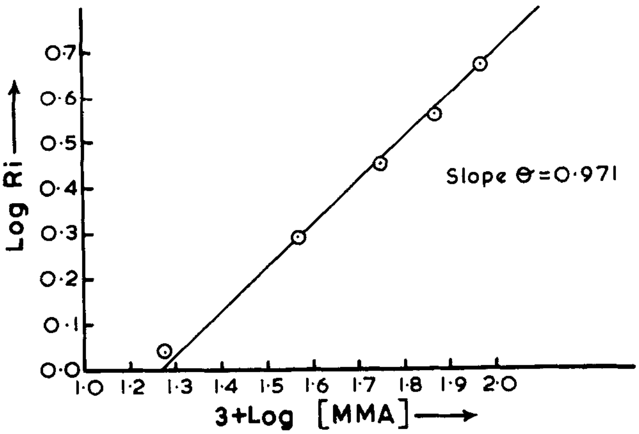


FIG. 5. Double logarithmic plot of the initial rate of polymerization (R_i) (in % conversion/min) vs the concentration of monomer MMA.

Downloaded At: 07:48 25 January 2011

Log R_i (initial rate of polymerization) and log [MMA] are related linearly as shown in Fig. 5. Although in some cases a typical behavior was reported by Palit et al. [18], in other communications Palit et al. [17, 19] have reported this linear behavior also for the polymerization of MMA by Fe^{2+}-$KBrO_3$ and by N-bromosuccinamide-vanadyl sulfate systems. This linear relationship suggests that the termination rate is proportional to the monomer concentration in the aqueous phase. However, the monomer exponent is found to be unity. For a monomer such as MMA having a higher affinity for its insoluble polymer than for water, the general observation is of a first-order dependence of rate on the initial monomer concentration [20].

Rate Dependence of Temperature

The effect of temperature on this system is rather complicated as shown in Fig. 6. The initial rate of polymerization and the maximum conversion increase attain a maximum value at 40°C, and then fall at higher temperatures. The overall activation energy has been calculated in the temperature range 20-40°C from the Arrhenius plot (Fig. 7) of log R_i against 1/T K. It is found to be 65.72 kJ/mol (15.71 kcal/mol) which is in quite good agreement with other observations [1, 15, 21]. Above 40°C it is also observed that the physical nature of the aqueous polymerization media changes from the sol or colloidal phase to the precipitation phase which is likely to affect the rate of polymerization [20]. Therefore, studies at temperatures higher than

Downloaded At: 07:48 25 January 2011

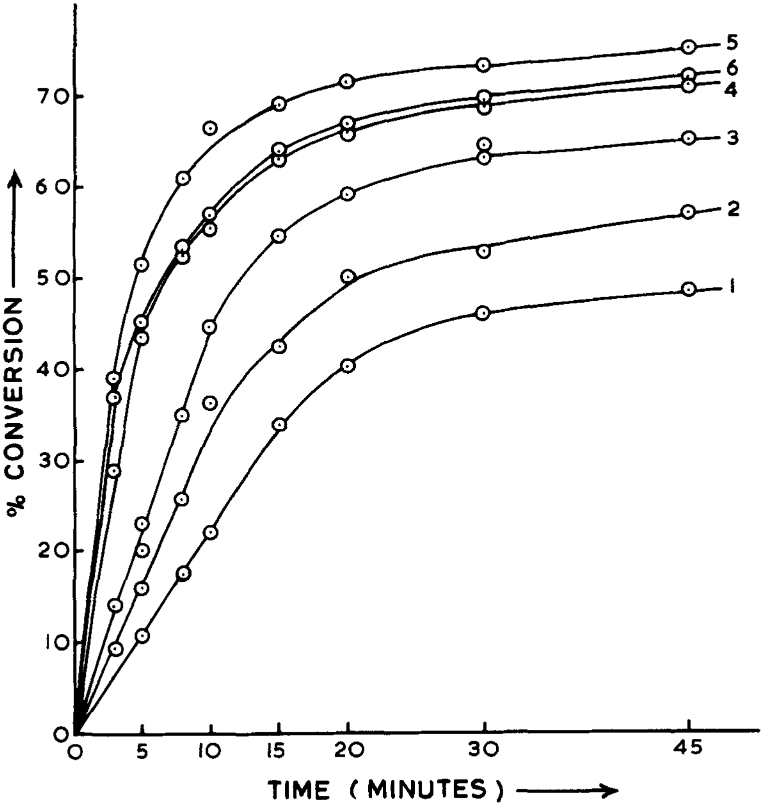


FIG. 6. Rate dependence of temperature on the aqueous polymerization of MMA with TGA-$KBrO_3$ redox system under nitrogen atmosphere at 30 ± 0.2°C. [MMA] = 9.474×10^{-2} mol/L; [$KBrO_3$] = 6.0 mmol/L; [TGA] = 1.0×10^{-2} mol/L. Temperature for Curve 1 = 20°C, Curve 2 = 25°C, Curve 3 = 30°C, Curve 4 = 35°C, Curve 5 = 40°C, and Curve 6 = 45°C.

45°C have not been undertaken. Palit et al. [17, 20] have reported that, for the same monomer, the limiting temperature after which initial rate begins to decrease is also dependent on the rate of initiating systems.

Effect of Inorganic Electrolytes on Rate of Polymerization

The effect of several mono- and dibasic salts, viz., $MgSO_4$, $MnSO_4 \cdot 4H_2O$, NaCl, and $Na_2C_2O_4$, has been studied. Such observations are

Downloaded At: 07:48 25 January 2011

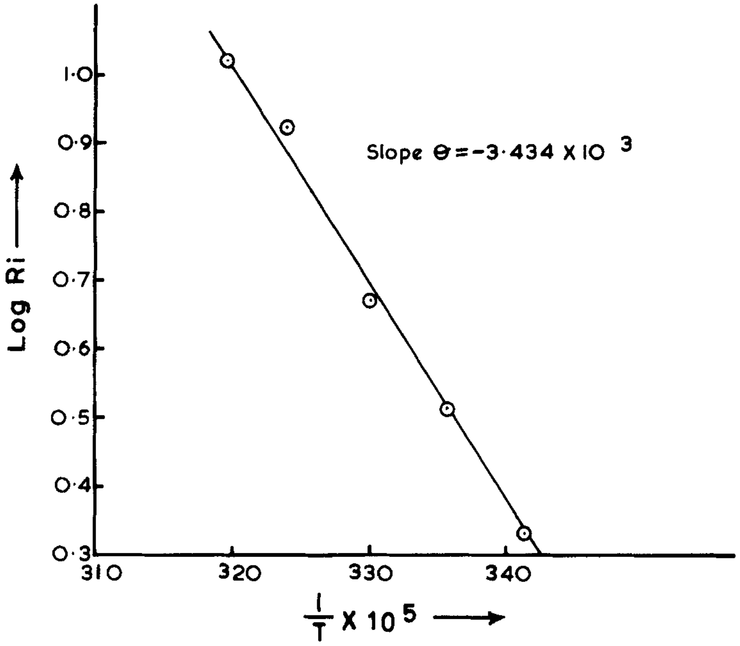


FIG. 7. Arrhenius plot of the initial rate of polymerization (R_i) (% conversion/min) vs 1/T × 10^{-5} K.

amply demonstrated in Fig. 8. Polyvalent cations, except $MnSO_4.4H_2O$, are more effective in bringing down the initial rate as well as the maximum conversion than the monovalent cations [19] except $Na_2C_2O_4$. The higher concentration of salt decreases the rate more. The higher efficiency of polyvalent ions is due to their stronger coagulating power (Schulz-Hardy rule).

Manganese salts are, however, exceptions and increase the initial rate because Mn^{2+} ions are known to autocatalyze the initiating reaction. However, maximum conversion decreases with $MnSO_4.4H_2O$. Abnormal results are observed with sodium oxalate. Sodium oxalate increases the initial rate of polymerization and the maximum conversion, both probably due to the fact that this acts as a stabilizer for the colloidal phase. This type of result is not available in the literature.

Effect of Water-Miscible Organic Solvents on the Rate of Polymerization

The effects of various water miscible organic solvents, viz., MeOH, EtOH, iso-PrOH, tert-BuOH, and CH_3COCH_3, are shown in Fig. 9.

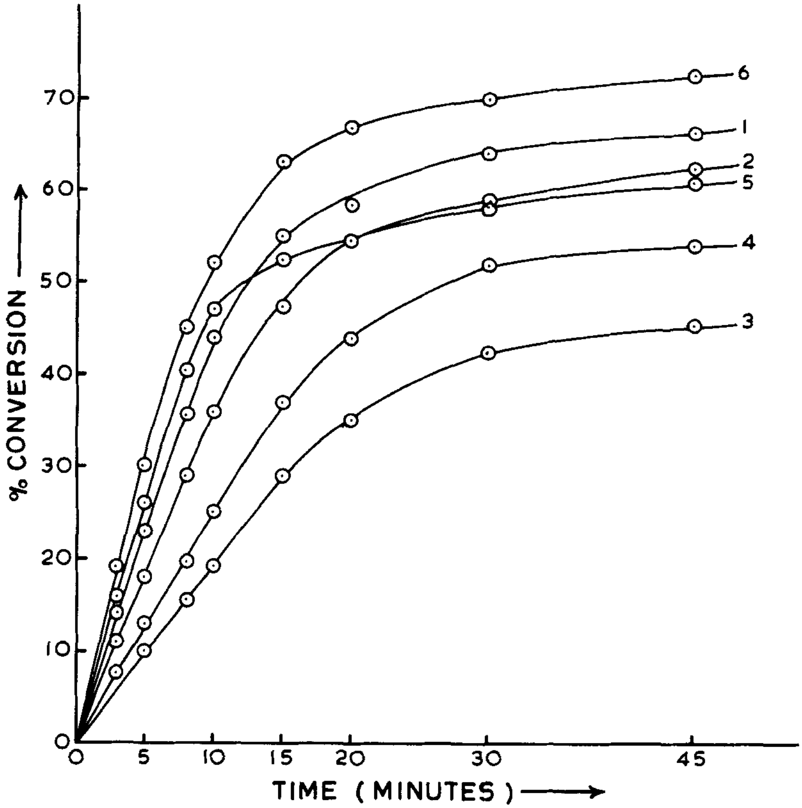


FIG. 8. Effect of various inorganic salts on aqueous polymerization of MMA initiated by TGA-$KBrO_3$ redox system under a nitrogen atmosphere at 30 ± 0.2°C. [MMA] = 9.474×10^{-2} mol/L; [$KBrO_3$] = 0.6 mmol/L; [TGA] = 1.0×10^{-2} mol/L. Salts for Curve 1 = nil; Curve 2 = NaCl, 0.01%; Curve 3 = NaCl, 0.05%; Curve 4 = $MgSO_4$, 0.01%; Curve 5 = $MnSO_4.4H_2O$, 0.01% and Curve 6 = $Na_2C_2O_4$, 0.01%.

All the solvents depress the initial rate and the maximum conversion. The same types of observation were reported by Misra and Narain [21] for vinyl polymerization. The depression caused by tert-BuOH reaches a maximum whereas that due to methanol is a minimum. On introducing more quantity of solvent, e.g., methanol, the rate is depressed more. These results are in agreement with earlier views of radical polymerization. Thus, as usual, the order of depression is dependent on the number of carbon atoms per alcohol molecule. Considering the effect of acetone also, the order of depression in the

Downloaded At: 07:48 25 January 2011

Downloaded At: 07:48 25 January 2011

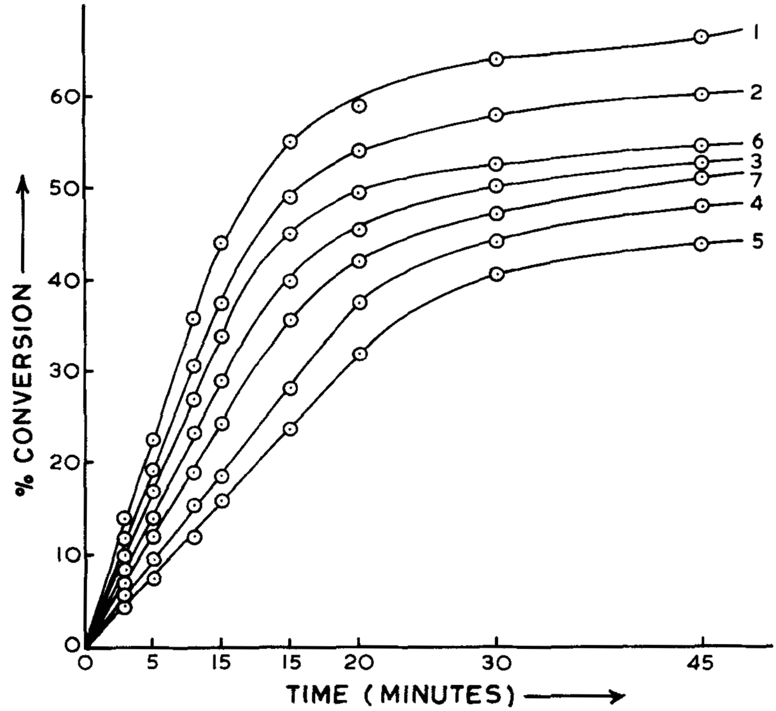
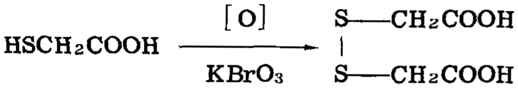


FIG. 9. Effect of various water-miscible organic solvents on aqueous polymerization of MMA initiated by TGA-$KBrO_3$ redox system under a nitrogen atmosphere at 30 ± 0.2°C. $[MMA] = 9.474 \times 10^{-2}$ mol/L; $[KBrO_3] = 0.6$ mmol/L; $[TGA] = 1.0 \times 10^{-2}$ mol/L. Solvents for Curve 1 = nil; Curve 2 = MeOH, 5 mL; Curve 3 = EtOH, 5 mL; Curve 4 = iso-PrOH, 5 mL; Curve 5 = tert-BuOH, 5 mL; Curve 6 = acetone, 5 mL; and Curve 7 = MeOH, 10 mL.

extent of polymerization may be put as $(CH_3)_3COH > CH_3CH(OH)CH_3 > CH_3CH_2OH > CH_3COCH_3 > CH_3OH$.

Mechanism

The mechanism for the formation of free radicals from the $KBrO_3$-TGA system may be represented as



$$HSCH_2COOH \xrightarrow[KBrO_3]{[O]} \begin{array}{l} S\text{—}CH_2COOH \\ | \\ S\text{—}CH_2COOH \end{array}$$

(1) (2)

$$\text{(2)} \xrightarrow[\text{fission}]{\text{homolytic}} \underset{(3)}{\dot{\text{S}}\text{-CH}_2\text{COOH}}$$

TGA (1) readily oxidizes to disulfidoacetic acid (2) which on homolytic fission at the S-S bond produces the free radicals (3) capable of initiating the polymerization of MMA. A similar type of mechanism for the TGA-oxidant system was proposed by Shukla and Singh [2]:

$$\begin{tikzcd}
\underset{\text{monomer}}{\text{M}} + \dot{\text{S}}\text{CH}_2\text{COOH} \arrow[r, "\text{initiation}"] & \dot{\text{M}}\text{-S CH}_2\text{COOH} \arrow[d, "\text{nM}"', "\text{propagation}"] \\
\text{polymer} & \dot{\text{M}}(\text{M})_n\text{-SCH}_2\text{COOH} \arrow[l, "\text{termination}"']
\end{tikzcd}$$

Initiation takes place as soon as the free radical comes in contact with the monomer molecule. The mode of polymer formation may possibly be as given above.

ACKNOWLEDGMENTS

The authors wish to thank the Head of the Chemistry Department for departmental facilities. Inspiration and encouragement from Professor G. S. Misra are also appreciated. One of us (R.K.T.) is thankful to U.G.C., New Delhi, India, for award of J.R.F.

REFERENCES

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

[2] J. S. Shukla and K. Singh, J. Polym. Sci., Polym. Chem. Ed., 17, 531 (1979).

[3] J. S. Shukla and R. K. Tiwari, Ibid., In Press.

[4] S. Maiti and S. R. Palit, J. Polym. Sci., Part A-1, 9, 253 (1971).

[5] S. R. Palit and R. S. Konar, J. Polym. Sci., 57, 609 (1962).

[6] L. F. Fieser, J. Am. Chem. Soc., 46, 2639 (1924).

[7] D. Josefowitz and H. Mark, Polym. Bull., 1, 140 (1945).

[8] P. Hayden and H. Melville, J. Polym. Sci., 43, 215 (1960).

[9] F. S. Dainton, J. Polym. Sci., 34, 227 (1959).

[10] L. B. Morgan, Trans. Faraday Soc., 42, 169 (1946).

[11] G. S. Whitby, M. D. Cross, J. R. Miller, and A. J. Costanza, J. Polym. Sci., 16, 549 (1955).

[12] M. Biswas and S. R. Palit, J. Sci. Ind. Res. (India), 20B, 160 (1961).

Downloaded At: 07:48 25 January 2011

[13] F. A. Bovey and I. M. Kolthoff, J. Polym. Sci., 5, 487 (1950).
[14] A. Katchalsky and G. Blauer, Trans. Faraday Soc., 47, 1360 (1951).
[15] G. S. Misra and H. Narain, Makromol. Chem., 119, 74 (1968).
[16] S. R. Palit and R. S. Konar, J. Polym. Sci., A2, 1731 (1964).
[17] D. Pramanik and S. R. Palit, Kolloid-Z. Z. Polym., 229, 24 (1969).
[18] S. R. Palit and R. S. Konar, J. Polym. Sci., 58, 85 (1962).
[19] A. K. Banthia and S. R. Palit, J. Ind. Chem. Soc., 54, 513 (1977).
[20] S. R. Palit, T. Guha, R. Das, and R. S. Konar, in Encyclopedia of Polymer Science and Technology, Vol. 2, 1965, pp. 229.
[21] G. S. Misra and H. Narain, Makromol. Chem., 113, 85 (1968).

Accepted by editor September 22, 1980
Received for publication October 4, 1980

Downloaded At: 07:48 25 January 2011