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

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To cite this Article Shukla, J. S. and Ttwari, R. K.(1982) 'Aqueous Polymerization of Methyl Methacrylate. II', Journal of Macromolecular Science, Part A, 18: 5, 759 — 771

To link to this Article: DOI: 10.1080/00222338208074433

URL: http://dx.doi.org/10.1080/00222338208074433

J. MACROMOL. SCI.–CHEM., A18(5), pp. 759-771 (1982)

Aqueous Polymerization of Methyl Methacrylate. II

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ABSTRACT

Aqueous polymerization of methyl methacrylate (MMA) initiated by potassium persulfate-thioglycollic acid (TGA) redox system has been studied at 30°C under nitrogen atmosphere. The rate of polymerization is expressed by

$$R_p = K[\mathrm{MMA}]^{0.98}[\mathrm{TGA}]^{0}[K_2S_2O_8]^{0.478}$$

The polymerization was studied over the temperature range 20-45°C. The activation energy calculated from an Arrhenius plot was found to be 8.34 kcal/mol (34.9 kJ/mol). The effects of inorganic electrolytes and organic solvents on polymerization were also investigated. Except for manganese sulfate and sodium oxalate, all of them depressed both the initial rate and the limiting conversion.

INTRODUCTION

Thio compounds coupled with permanganate, persulfate, and acidic bromate have been reported as useful redox pairs toward the polymerization of acrylic monomers in aqueous medium [1, 2]. In our previous communications [3-5] the polymerization of acrylamide, methacrylamide, and methylmethacrylate by the TGA-$KBrO_3$ redox pair has been reported. This work has been further extended to investigate the TGA-$K_2S_2O_8$ redox system in the aqueous polymerization of MMA.

EXPERIMENTAL

The chemicals used were of analytical grade. Monomer purification and the rate measurement were followed by the method discussed earlier [4].

RESULTS AND DISCUSSION

Mechanism

The probable mechanism for the formation of free radicals by the TGA-$K_2S_2O_8$ system and the polymer formation was found to be the same as reported earlier [4].

Rate Dependence of Initiator Concentration

The effect of potassium persulfate concentration on the rate of polymerization at fixed monomer concentration (94.47 mmol/L) and activator concentration (10 mmol/L) at 30°C has been investigated over the range 4-40 mmol/L $K_2S_2O_8$ concentration. This is shown in Fig. 1. These observations indicated that on increasing the initiator concentration the initial rate of polymerization and the maximum conversion increased up to 20 mmol/L $K_2S_2O_8$ concentration. Above this concentration the initial rate of polymerization increased while the maximum conversion decreased. These observations are in line with Ref. 5.

To determine the order of reaction with respect to initiator, log R_i (R_i = initial rate of polymerization) has been plotted against log $[K_2S_2O_8]$ (Fig. 2). The exponent value was found to be 0.478. These observations indicated unimolecular termination [6, 7].

Rate Dependence of Activator Concentration

The effect of activator concentration was studied over a range 4-40 mmol/L TGA concentration and is shown in Fig. 3. An unusual decrease in both the initial rate of polymerization and maximum conversion was observed with increasing activator concentration

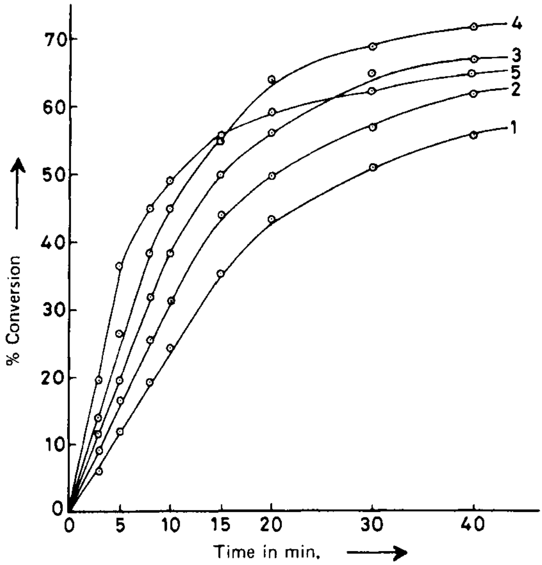

FIG. 1. Rate dependence of the initiator potassium persulfate concentration. [MMA] = 94.74 mmol/L, [TGA] = 10.00 mmol/L, [$K_2S_2O_8$] for Curve 1 = 4.0 mmol/L, Curve 2 = 7.5 mmol/L, Curve 3 = 10.0 mmol/L, Curve 4 = 20.0 mmol/L, and Curve 5 = 40.0 mmol/L.

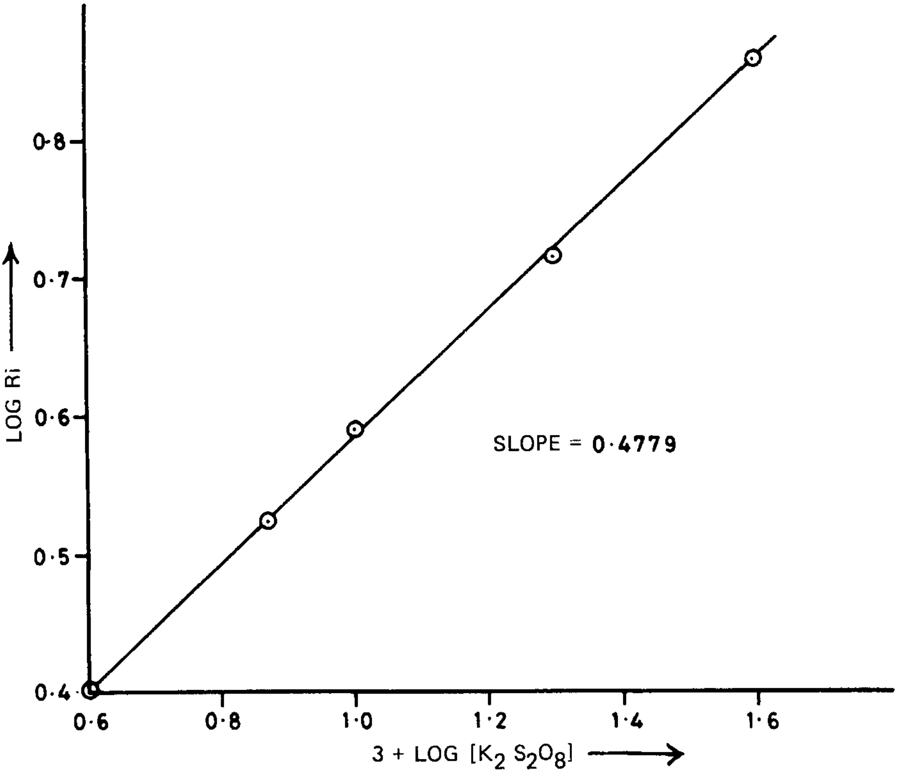

FIG. 2. Double logarithmic plot of the initial rate of polymerization (R_i) (in % conversion/min) vs the concentration of initiator $K_2S_2O_8$.

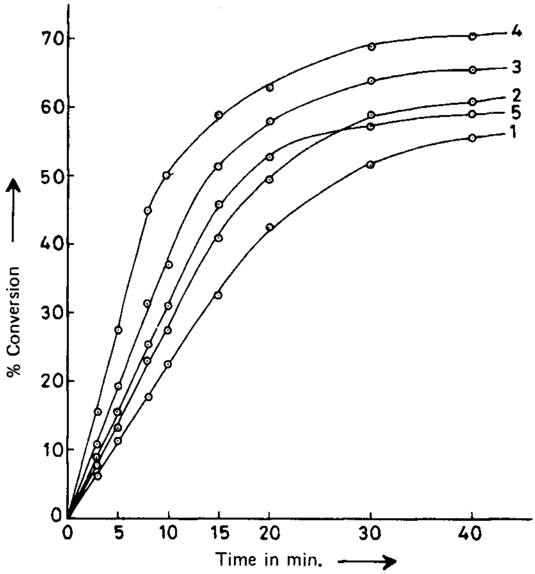

FIG. 3. Rate dependence of activator TGA concentration. [MMA] = 94.74 mmol/L, [$K_2S_2O_8$] 10.0 mmol/L, [TGA] for Curve 1 = 5.0 mmol/L, Curve 2 = 7.5 mmol/L, Curve 3 = 10.0 mmol/L, Curve 4 = 20.0 mmol/L, and Curve 5 = 40.0 mmol/L.

above 20 mmol/L. These observations are in accordance with those of Shukla et al. [4, 5], Patil et al. [8, 9], and Misra et al. [10, 11].

At a relatively higher concentration either persulfate or its lower fragments tend to generate appreciable "inhibitory oxygen" in the presence of excess of H^+ ions derived from TGA. Thus the rate of generation as well as the concentration of the reactive species is suppressed as a consequence of the increased rate of production of inhibitory oxygen. At a lower activator concentration the effect of H^+ ion concentration is sufficient to establish a balance with the opposing effect of a varying rate of generation of free radicals. Thus the concentration of the initiating species probably remains constant at a lower activator concentration [12]. The rate of polymerization, which is dependent only on the concentration of the reactive species, will therefore be independent of TGA concentration at fixed $K_2S_2O_8$ and MMA concentrations.

Rate Dependence of Monomer Concentration

The polymerization reaction was investigated over a wide range of monomer MMA concentrations (37.8 - 113.6 mmol/L). The observations, plotted in Fig. 4, indicate that both the initial rate of

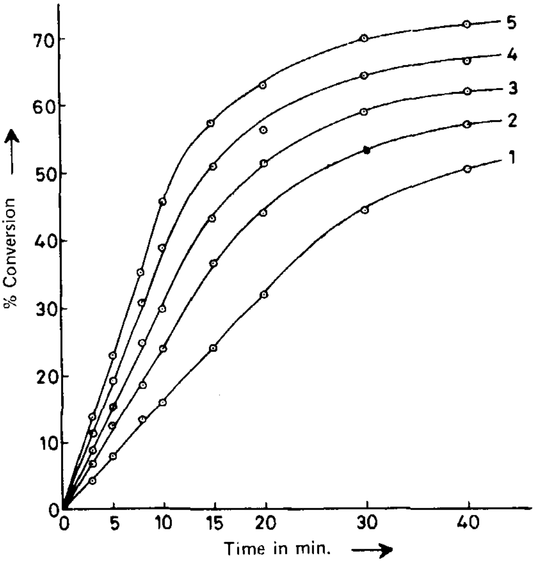

FIG. 4. Rate dependence of monomer MMA concentration. $[K_2S_2O_8]$ = 10.0 mmol/L, [TGA] = 10.0 mmol/L, [MMA] for Curve 1 = 37.88 mmol/L, Curve 2 = 56.82 mmol/L, Curve 3 = 75.76 mmol/L, Curve 4 = 94.74 mmol/L, and Curve 5 = 113.64 mmol/L.

polymerization and the maximum conversion are directly related to the monomer concentration. The initial rate of polymerization increased linearly and after a certain period the extent of polymerization attained a constant value [13].

A double logarithmic plot (log R_i vs log [MMA]) (Fig. 5) shows a first-order dependence on monomer concentration. This suggests that the termination rate is proportional to the monomer concentration in the aqueous phase and is independent of polymer concentration in the colloidal phase. For a monomer such as MMA, which has a higher affinity for its insoluble polymer than water, the general observation is of first-order dependence of the rate of initial monomer concentration [14].

Rate of Dependence of Temperature

The effect of temperature on the rate of polymerization of MMA was investigated over a range of 20-45° C (Fig. 6). The initial rate as well as the maximum conversion increased with temperature up to 40° C. The initial rate further increased but the maximum conversion fell immediately. In our previous communication [4] we observed

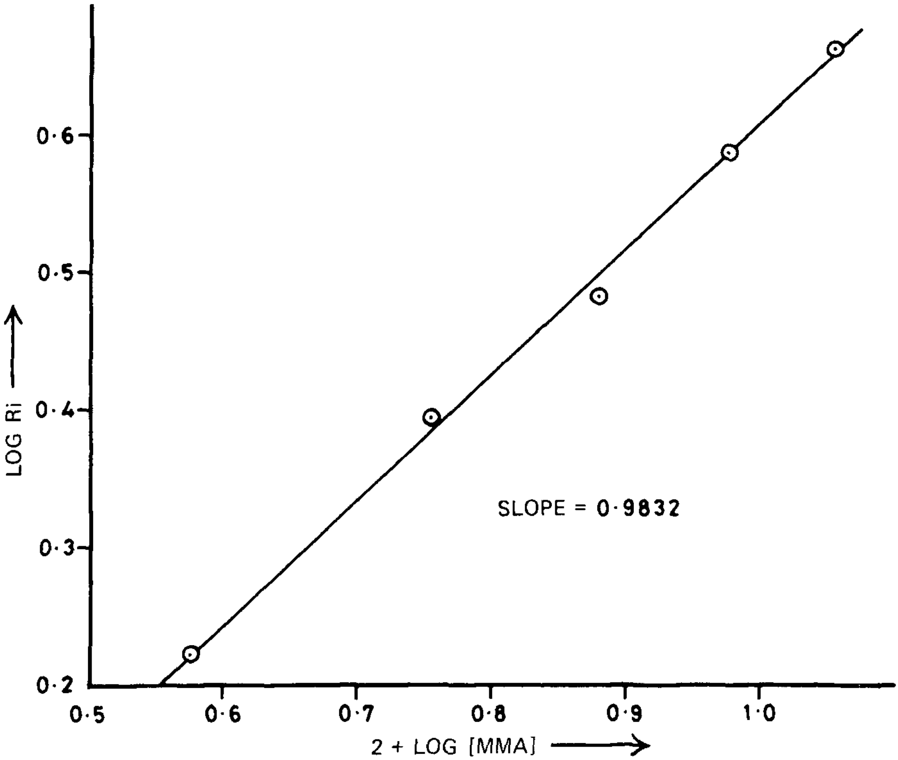

FIG. 5. Double logarithmic plot of initial rate of polymerization (R_i) vs the concentration of monomer MMA.

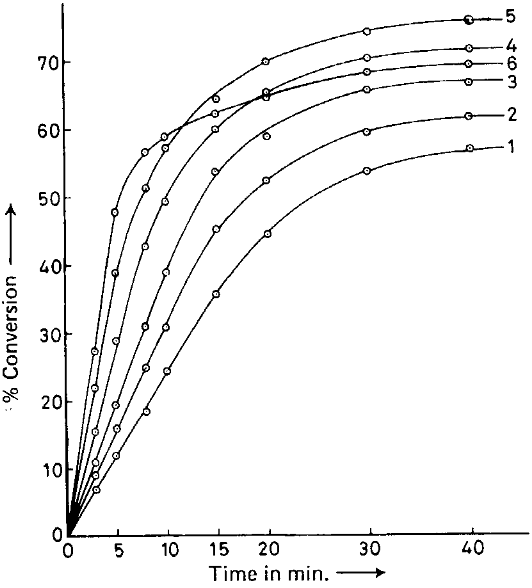

FIG. 6. Rate dependence on temperature. [MMA] = 94.74 mmol/L, [$K_2S_2O_8$] = 10.0 mmol/L, [TGA] = 10.0 mmol/L, temperature for Curve 1 = 20°C, Curve 2 = 25°C, Curve 3 = 30°C, Curve 4 = 35°C, Curve 5 = 40°C, and Curve 6 = 45°C.

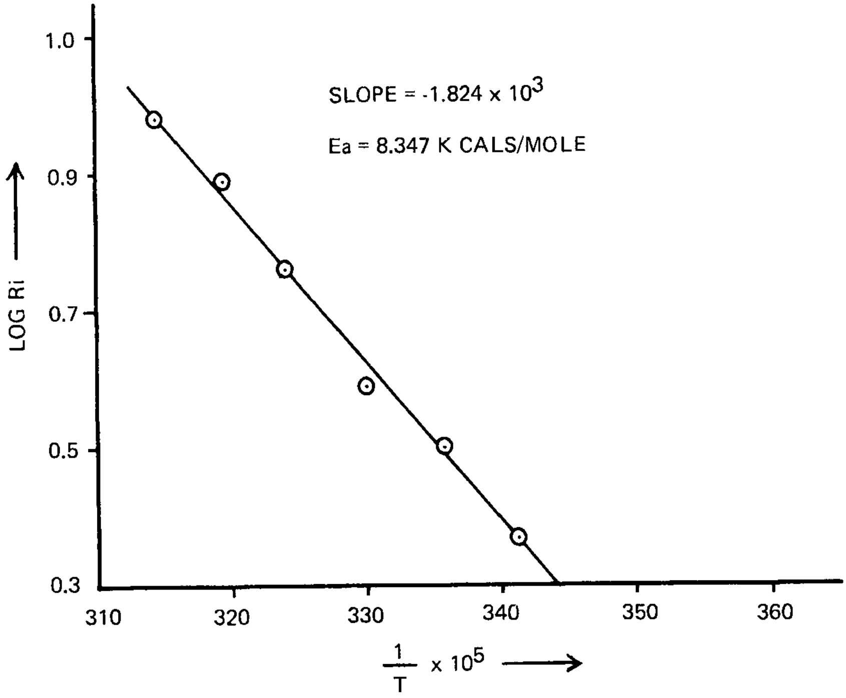

FIG. 7. Arrhenius plot of the initial rate of polymerization (R_i) vs $1/T \times 10^5$ K.

that both of them decreased at 40° C in the polymerization of MMA by the TGA-$KBrO_3$ redox system. This is because at higher temperatures the primary radicals undergo side reactions and their contribution to the production of free radicals is suppressed after a period of initiation and hence the maximum conversion is suppressed [16].

Banthia and Patil [13] have also observed that the limiting temperature, after which initial rate of polymerization begins to decrease, is also dependent on the rate of the initiating reaction and hence will not be the same for different initiating systems [15]. It was also observed that at 45° C the reaction medium changes from a sol or colloidal phase to a precipitation phase after 10 min of initiation. This may also be a cause of the decrease in maximum conversion.

The overall energy of activation has been calculated from an Arrhenius plot (Fig. 7) in the temperature range of 20-45° C, resulting in a value of 8.34 kcal/mol (34.9 kJ/mol) [8, 13, 16].

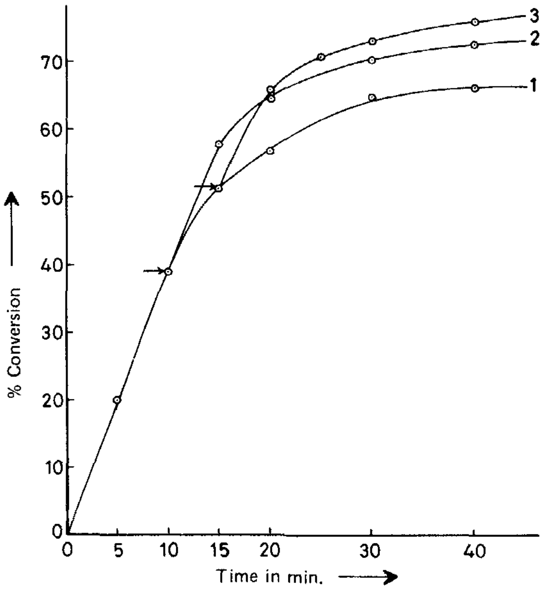

FIG. 8. Initiator injection experiment. Arrows show the time of injection. Same amount of initiator as taken for initiation was injected. [MMA] = 94.74 mmol/L, [$K_2S_2O_8$] = 10.0 mmol/L, [TGA] = 10.0 mmol/L, Curve 1 = nil, Curve 2 = at 10 min, and Curve 3 = at 15 min.

Rate Dependence on Additives

Initiator Injection Experiment

Another point of interest is the effect of the addition of fresh initiator at the intermediate stages of polymerization. Since the separating phase is in the form of a coarse coagulum, injection of initiator late in a run is equivalent to a fresh initiation. This is shown in Fig. 8. It was observed that the injection of initiator late in a run increased both the rate of polymerization and the maximum conversion [8, 17].

Effect of Inorganic Electrolytes

The effect of various inorganic electrolytes on the polymerization reaction has been studied. The observations are demonstrated in Fig. 9. They are of the same pattern as our previous work [4, 5]. KCl and $MgSO_4$ depressed both the initial rate of polymerization and the maximum conversion. Manganese sulfate enhanced the initial rate but brought down the maximum conversion, whereas sodium oxalate enhanced the initial rate of polymerization as well as the

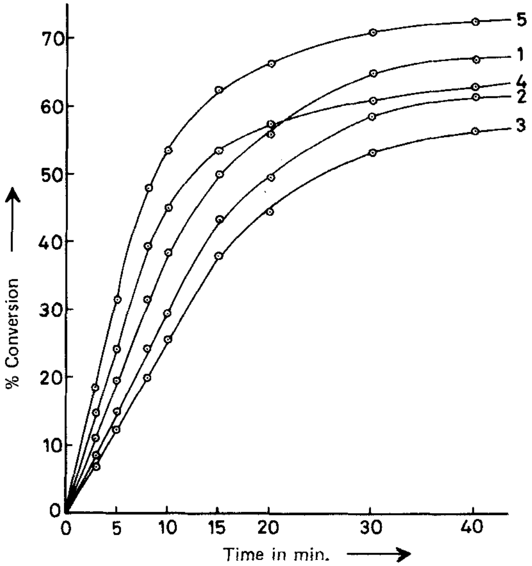

FIG. 9. Effect of various inorganic salts. [MMA] = 94.74 mmol/L, [$K_2S_2O_8$] = 10.0 mmol/L, [TGA] = 10.0 mmol/L, salts for Curve 1 = nil, Curve 2 = KCl 0.01%, Curve 3 = $MgSO_4$ 0.01%, Curve 4 = $MnSO_4 \cdot 4H_2O$ 0.01%, and Curve 5 = $Na_2C_2O_4$ 0.01%.

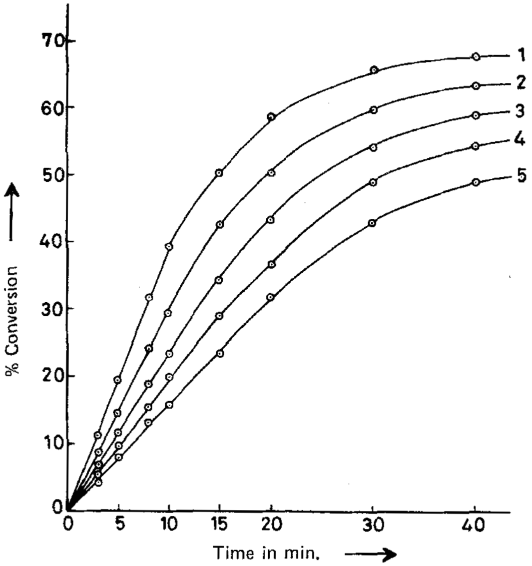

FIG. 10. Effect of various alcohols (5 mL of alcohols were taken). [MMA] = 94.74 mmol/L, [$K_2S_2O_8$] = 10.0 mmol/L, [TGA] = 10.0 mmol/L, alcohols for Curve 1 = nil, Curve 2 = MeOH, Curve 3 = EtOH, Curve 4 = iso-PrOH, and Curve 5 = tert-BuOH.

maximum conversion. These results are supported by other investigators [13].

Effect of Alcohols

All the alcohols, e.g., methanol, ethanol, isopropanol, and tert-butanol, depress both the rate of polymerization and the maximum conversion (Fig. 10). Palit et al. [8] have also found that polymerization of MMA is depressed by organic solvents whether they are good or bad solvents for the polymer. It is also observed that the depression is directly proportional to the number of carbon atoms present in the alcohol molecule.

ACKNOWLEDGMENTS

The authors wish to thank the Head of the Chemistry Department Lucknow University, Lucknow, for providing departmental facilities. R.K.T. is thankful to University Grants Commission, New Delhi, India, for the award of a Junior Research Fellowship.

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Accepted by editor November 6, 1981
Received for publication November 20, 1981