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Aqueous Polymerization of Methyl Methacrylate Initiated by Ce^{4+} -Glycolic Acid Redox System

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ABSTRACT

The aqueous heterogeneous polymerization of methyl methacrylate (MMA) initiated by the Ce^{4+} -glycolic acid (GA) redox system was studied at $35 \pm 0.2^\circ C$ under a nitrogen atmosphere. The rate of monomer disappearance was proportional to $[MMA]^1 [GA]^1 [Ce^{4+}]^0$, and the rate of ceric ion disappearance was found to be directly proportional to $[Ce^{4+}]$ and $[GA]$ but independent of $[MMA]$. The activation energy was found to be 34 kJ/mol. The molecular weight of polymethyl methacrylate increased with increasing $[MMA]$ and decreased with increasing [oxidant]. The effect of increasing $[H_2SO_4]$ on polymerization was also studied. The results are compared with those obtained for the aqueous homogeneous polymerization of acrylamide with the same redox pair.

INTRODUCTION

The polymerization of methyl methacrylate (MMA) has been investigated with Ce^{4+} as oxidant and various reductants such as malonic acid [1], formaldehyde [2], and amines [3]. In the present study Ce^{4+} has been used with glycolic acid for the aqueous heterogeneous polymeri-

zation of MMA to elucidate the mechanism and kinetics of this system and to compare it with homogeneous polymerization.

EXPERIMENTAL

Materials

Methyl methacrylate (BDH) was distilled under nitrogen. Ceric ammonium sulfate (Sarabhai M.) and glycolic acid (Riedel) were used as such. The water used as solvent in all experiments was prepared by the redistillation of distilled water containing a small amount of alkaline KMnO_4 .

Polymerization Procedure

Polymerization was carried out in glass vessels 6 in. in length and 2 in. in diameter. A reaction mixture containing monomer, glycolic acid, and the requisite amount of water was deaerated for 30 min by passing dry N_2 at the rate of one bubble per second. The polymerization reaction was carried out at $35 \pm 0.2^\circ\text{C}$. Ceric ammonium sulfate solution (in 5 N H_2SO_4) was deaerated separately under the same conditions. The reaction was started by the addition of ceric ion solution and quenched with ice-cold ferrous ammonium sulfate solution (0.1 N) at desired intervals of time. The reaction mixture containing precipitated polymer was filtered. Polymer was estimated gravimetrically. Filtrate was kept for cerimetry using ferroin as indicator.

The polymer was purified by dissolving in acetone and reprecipitating in methanol. The molecular weights were determined by viscometry using an Ubbelohde viscometer at 25°C with acetone as solvent. The following relationships of Schulz and Blaschke [4] (Eq. 1) and Bischoff et al. [5] (Eq. 2) were used for the calculation of the molecular weights

$$[\eta]_{25^\circ} = \frac{\eta_{\text{sp}}/c}{1 + k'\eta_{\text{sp}}} \quad (\text{where } k' = 0.5) \quad (1)$$

$$[\eta]_{\text{g/mL}} = 7.5 \times 10^{-3} \bar{M}_v^{0.70} \quad (2)$$

RESULTS AND DISCUSSION

Rate of Monomer Disappearance (R_p)

Rate dependence on activator. The initial rate (R_{ini}) and maximum conversion increased with increasing glycolic acid concentration in the range $(2 \text{ to } 12.5) \times 10^{-2}$ mol/L at a fixed $[MMA]$, $[Ce^{4+}]$ and $[H_2SO_4]$, (Fig. 1.). Increasing the concentration of activator increases the concentration of active free radicals; hence the rate of polymerization increased. The activator exponent was found to be unity. The aqueous homogenous polymerization of acrylamide with the same redox pair [6] also exhibited a first-order dependence on activator.

Rate and Molecular Weight Dependence on Oxidant

R_{ini} and maximum conversion remained constant in the studied range $(2 \text{ to } 10) \times 10^{-4}$ mol/L at fixed concentrations of MMA, GA, and H_2SO_4 . The independence of rate on $[Ce^{4+}]$ reveals that it takes part in the termination process. A similar behavior has been reported in the Ce^{4+} /alcohol system [7], while in the polymerization of acrylamide with the same redox pair a catalyst exponent of 0.5 was obtained. Molecular weights decreased with increasing ceric ion concentration in MMA. A similar behavior was reported with acrylamide, but the molecular weights of polymethyl methacrylate were higher than those of polyacrylamide.

Rate and Molecular Weight Dependence on Monomer

R_{ini} as well as maximum conversion increased with increasing concentration of monomer in the range $(2.84 \text{ to } 11.36) \times 10^{-2}$ mol/L (Fig. 2). With an increase in monomer concentration the availability of monomer in the propagation step increases, resulting in increases in R_{ini} and maximum conversion. The monomer exponent was found to be unity. In the case of acrylamide a monomer exponent of unity has also been reported. This rules out the possibility of primary radical termination. The molecular weights showed an increase with increasing monomer concentration. A similar behavior was shown by the acrylamide system. An induction period of 10 min was observed at low monomer concentration $(2.84 \times 10^{-2}$ mol/L) in the MMA system.

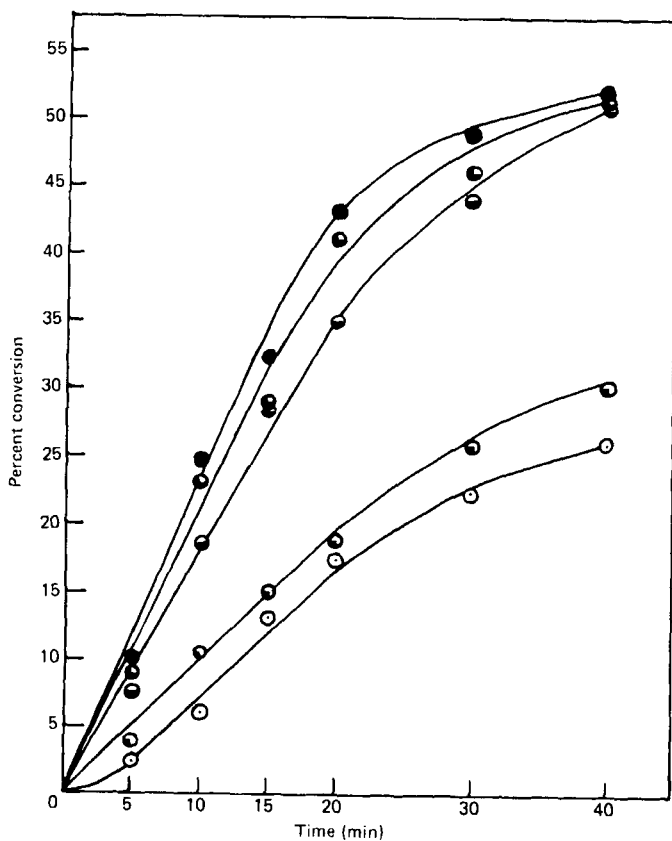


FIG. 1. Time vs conversion curves for the aqueous polymerization of methyl methacrylate with varying initial concentration of glycolic acid at $[MMA] = 5.68 \times 10^{-2}$ mol/L, $[Ce^{4+}] = 10.0 \times 10^{-4}$ mol/L, $[H_2SO_4] = 25 \times 10^{-2}$ mol/L, $35 \pm 0.2^\circ C$: $\odot = 2$, $\circ = 5$, $\ominus = 8$, $\bullet = 10$, $\bullet = 12.5$; all $\times 10^{-2}$ mol/L.

Temperature Dependence

R_{ini} and maximum conversion increased with increasing temperature from 30 to $50^\circ C$. As the temperature increases, the frequency of initiation and propagation increase, resulting in increases in R_{ini} and maximum conversion. The activation energy as calculated from an Arrhenius plot was found to be 34 kJ/mol. In the case of acryl-

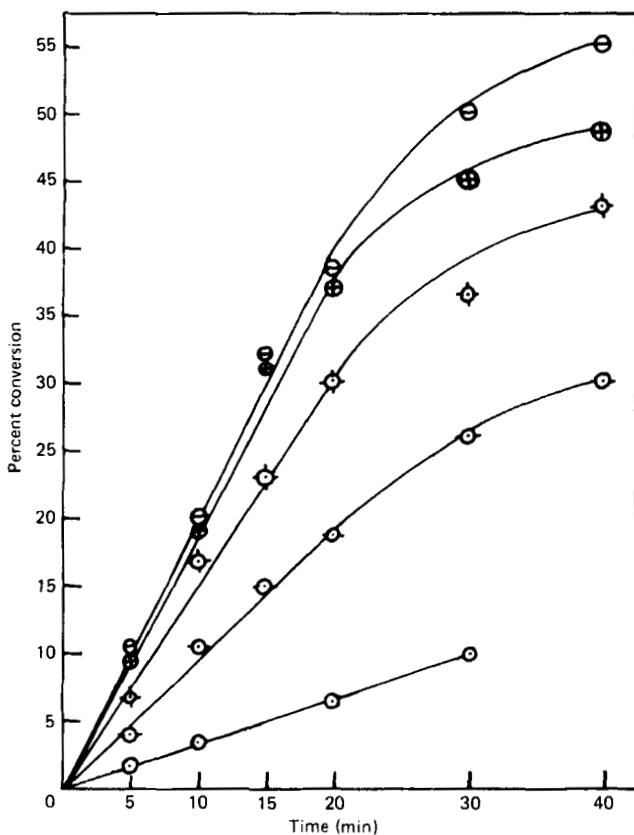


FIG. 2. Time vs conversion curves for the aqueous polymerization of methyl methacrylate with varying initial concentrations of monomer at constant $[GA] = 5.0 \times 10^{-2}$ mol/L, $[Ce^{4+}] = 10 \times 10^{-4}$ mol/L, $[H_2SO_4] = 25 \times 10^{-2}$ mol/L, $35 \pm 0.2^\circ C$: $\circ = 2.84$, $\circ = 5.68$, $\diamond = 7.56$, $\oplus = 8.52$, $\ominus = 11.36$; all $\times 10^{-2}$ mol/L.

amide, an activation energy of 30.2 kJ/mol has been reported with the same redox pair.

H₂SO₄ Dependence

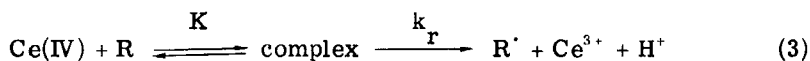
The effect of H₂SO₄ was studied in the range $(25 \text{ to } 75) \times 10^{-2}$ mol/L at fixed concentrations of MMA, Ce⁴⁺, and GA. It was found that

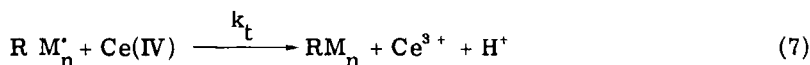
R_{ini} remained constant but the maximum conversion decreased. In the case of acrylamide, both factors showed a decline after a certain $[H_2SO_4]$.

Rate of Ceric Ion Disappearance ($-dCe(IV)/dt$)

The rate of ceric ion disappearance was found to be directly proportional to $Ce(IV)$. At a lower concentration of $Ce(IV)$, a plot of $-d[Ce(IV)]/dt$ vs $[Ce(IV)]$ gave a straight line passing through the origin, while at higher concentrations it showed an intercept on the ordinate. This confirms that $Ce(IV)$ ion at higher concentrations participates in a reaction other than the redox reaction, which is most probably its participation in the termination step as is also shown by the rate of monomer disappearance. The rate increased linearly with $[GA]$. A plot of $-d[Ce(IV)]/dt$ vs $[GA]$ gave a straight line with an intercept on the ordinate. The presence of the intercept in a plot of $[rate]^{-1}$ vs $[GA]^{-1}$ shows complex formation between ceric ion and glycolic acid (Fig. 3). Complex formation has also been reported in the acrylamide system [6].

The following kinetic scheme is proposed, based on the experimental results.





Applying the steady-state assumption to both $[R']$ and $[M']$ for the rate of monomer and ceric ion disappearance, the following expressions have been derived:

$$-\frac{d[M]}{dt} = \frac{Kk_p k_r}{k_t} [MMA]^1 [GA]^1$$

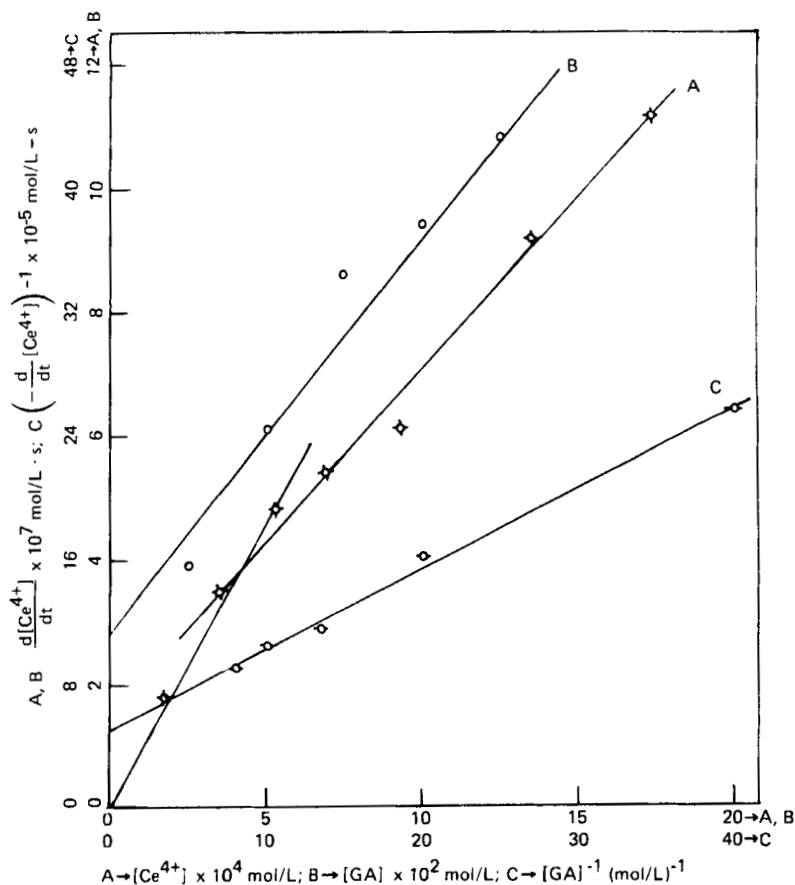


FIG. 3. Rate of ceric ion disappearance in mol/L/s vs (A) $[Ce^{4+}]$, (B) $[GA]$, (C) $[GA]^{-1}$. A (\diamond): $[MMA] = 5.68 \times 10^{-2}$ mol/L, $[GA] = 5.0 \times 10^{-2}$ mol/L, $[H_2SO_4] = 25 \times 10^{-2}$ mol/L. B (\circ) and C (\circ): $[MMA] = 5.68 \times 10^{-2}$ mol/L, $[Ce^{4+}] = 9.3 \times 10^{-4}$ mol/L, $[H_2SO_4] = 25 \times 10^{-2}$ mol/L, $35 \pm 0.2^\circ C$.

$$-\frac{d[Ce(IV)]}{dt} = \frac{2 K k_r [Ce(IV)]_{total} [GA]}{1 + K [GA]}$$

In the case of acrylamide, termination occurs mainly by mutual combination, while in the present case linear termination has been pro-

posed. Thus it can be concluded that the same redox pair behaves differently with different monomers in homogeneous and heterogeneous systems.

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