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Aqueous Polymerization of Methacrylamide Initiated by Glycolic Acid-Ceric Ammonium Sulfate Redox System

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NOTE

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ABSTRACT

The aqueous polymerization of methacrylamide (MA) initiated by the glycolic acid (GA)-Ce(IV) redox system was studied in sulfuric acid medium at $35 \pm 0.2^\circ\text{C}$ under a nitrogen atmosphere. The rate of monomer disappearance was found to be proportional to $[\text{MA}]^1$ $[\text{Ce(IV)}]^{1/2}[\text{GA}]^{1/2}$, and the rate of ceric ion disappearance was proportional to $[\text{GA}]$ and $[\text{Ce(IV)}]$ but independent of $[\text{MA}]$. The rate of polymerization increased with increasing temperature in the 30 to 50°C range. The activation energy was found to be 43 kJ/mol. The effect of increasing $[\text{H}_2\text{SO}_4]$ on the polymerization was also studied. A kinetic scheme involving initiation by free radicals generated from the redox reaction between GA and Ce(IV) and termination by bimolecular reaction of macroradicals has been suggested.

INTRODUCTION

Polymethacrylamide is an industrially important polymer. It is used in the textile, leather, and paper industries. Burfield and Nag

[1] studied the polymerization of methacrylamide initiated by persulfate alone. Bunn [2] carried out polymerization with the $K_2S_2O_8$ - $K_2S_2O_3$ redox pair. Misra et al. [3-5] investigated it by using the persulfate-thiomalic acid [3], $KMnO_4$ -oxalic acid [4] and persulfate-ascorbic acid [5] redox systems, but the polymerization of methacrylamide with ceric ion containing redox pairs has not been studied much. Recently, the Ce^{4+} -malic acid system has been used by Misra et al. [6]. Another redox pair, Ce^{4+} -glycolic acid, has been studied for the aqueous polymerization of acrylamide by the present authors [7]. The kinetics of aqueous polymerization of methacrylamide with the same redox pair has been taken up with a view to comparing the rate of polymerization with that of acrylamide and to evaluating the mechanism of this free radical polymerization.

EXPERIMENTAL

Methacrylamide (E. Merck) was recrystallized from acetone and dried under vacuum over calcium chloride. Glycolic acid (Reidel), ceric ammonium sulfate (Sarabhai M.), and H_2SO_4 (BDH), all AR grade, were used as such. Commercial nitrogen was used after passing through pyrogallol solution and silica gel. The polymerization procedure was similar to that used by Misra et al. [5]. The ceric ion concentration was determined by cerimetry with ferroin as indicator.

RESULTS AND DISCUSSION

Rate of Monomer Disappearance (R_p)

The rate increased with increasing glycolic acid concentration from 0.10 to 0.30 mol/L at fixed concentrations of MA, $Ce(IV)$, and H_2SO_4 (Fig. 1). The order of reaction was found to be nearly half (0.62) from a double logarithmic plot of R_i vs $[GA]$, and this suggests a bimolecular termination mechanism. Increasing the ceric ion concentration increased the rate up to a certain range, above which it decreased. The ceric ion exponent was found to be approximately half (0.53). This shows that bimolecular termination is taking place. Increasing monomer concentration and reaction temperature increased the rate. The monomer exponent was found to be nearly unity (0.82), confirming a bimolecular termination mechanism. The activation energy calculated from the slope of an Arrhenius plot was found to be 10.2 kcal/mol (43 kJ/mol). With increasing H_2SO_4 concentration the maximum conversion increased up to a certain concentration and then decreased.

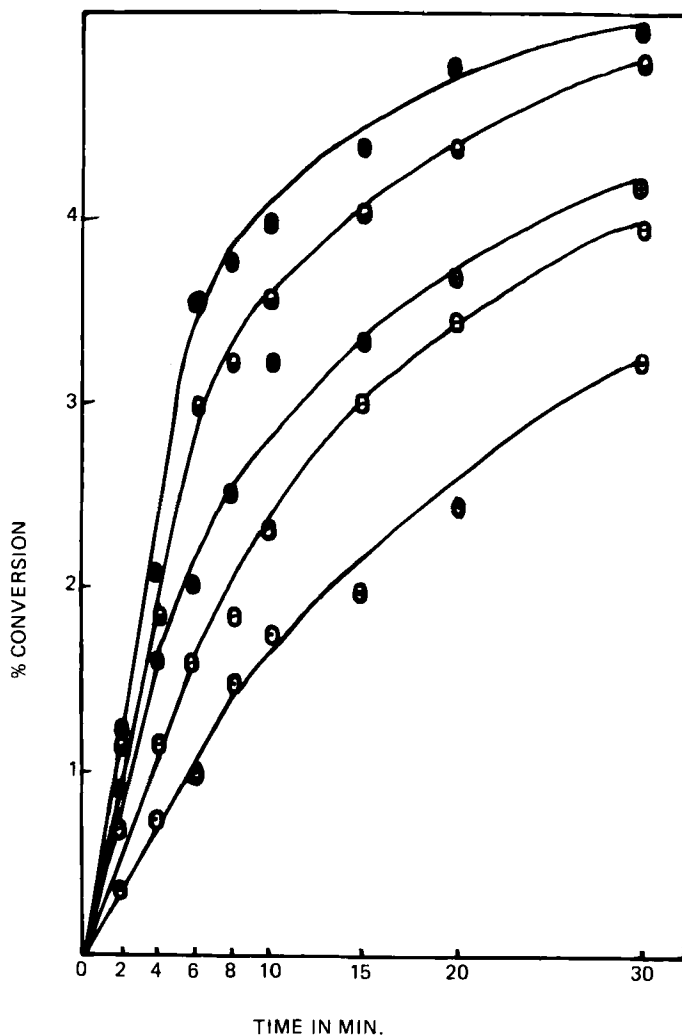


FIG. 1. Time vs conversion curves for the aqueous polymerization of MA with varying $[GA]$ at constant $[MA] = 0.05$ mol/L, $[Ce^{4+}] = 1$ mmol/L, $[H_2SO_4] = 0.0127$ mol/L. $35 \pm 0.2^\circ C$. $[GA]$: (○) 0.10, (⊕) 0.125, (⊖) 0.15, (◐) 0.20, (●) 0.30 mol/L.

Rate of Ceric Ion Disappearance ($-R_{\text{Ce(IV)}}$)

The rate of ceric ion disappearance was directly proportional to $[\text{Ce}^{4+}]$. It was independent of $[\text{MA}]$, showing that the ceric ions are not involved in either initiation or termination reactions. The rate increases linearly with GA at lower concentration, while at higher concentrations it becomes independent. A complex was isolated by mixing the equimolar quantities of the two solutions in the absence of monomer.

The kinetic scheme proposed by Misra et al. [8] fits the kinetic data and leads to expressions for the rate of monomer disappearance and that of ceric ion disappearance which explain all the experimental observations.

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