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Redox-Initiated Polymerization of Methyl Methacrylate

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ABSTRACT

The redox-initiated polymerization of methyl methacrylate (MMA) by the Ce(IV)-malic acid system has been carried out in aqueous medium under an inert atmosphere. The rate of polymerization was found to be proportional to $[MMA]^{3/2}[MA]^{1/2}[Ce(IV)]^{1/2}$ and the rate of ceric ion disappearance was proportional to [Ce(IV)] but independent of [MMA]. The rate increased linearly up to a certain range of [MA], above which it remained constant. Increasing $[H_2SO_4]$ decreased the rate. The activation energy was found to be 57.44 kJ/mol.

INTRODUCTION

In the present paper the heterogeneous, aqueous polymerization of methyl methacrylate initiated by the redox system Ce(IV)-malic acid has been studied. The results have been compared with those obtained for the homogeneous polymerization of acrylamide initiated by the same redox system [1].

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EXPERIMENTAL

Methyl methacrylate (SD'S) was purified by the usual method. Ceric ammonium sulfate (Loba Chemie), malic acid (Riedal) and sulfuric acid, all A.R. or equivalent grade, were used as such. All the solutions were prepared in doubly distilled water.

The technique followed in the present case was similar to that followed earlier by Misra et al. [2, 3] except that the estimation of the polymer formed was carried out gravimetrically. The rate of ceric ion disappearance was calculated by ceremetry. The molecular weights were determined by using the relationship of Baxendale et al. [4].

RESULTS AND DISCUSSION

Rate of Monomer Disappearance (R_p)

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The rate and conversion increased with increasing [MA] up to 6.90 × 10^{-3} mol/L above which both decreased (Fig. 1). At higher [MA] the rate of production of primary radicals is so high that most of them are lost in side reactions which result in a decrease of rate and conversion. The MA exponent of 1.5 indicated a bimolecular termination mechanism. Increasing the ceric ion and monomer concentrations increased the rate and conversion. The ceric ion and monomer exponents were found to be 0.5 and 1.5, respectively, both confirming the bimolecular termination mechanism of two growing macroradicals. In the case of the polymerization of acrylamide by the same redox system, at lower [ceric ion] the ceric ion exponent was 1 but was independent of it at higher concentrations. This shows that this redox pair acts very differently in homogeneous and heterogeneous conditions. This is also confirmed by a monomer exponent of 1 in acrylamide and 1.5 in MMA polymerization, under the same conditions.

Increasing the reaction temperature from 30 to 40°C increased the rate. The rate attains a fairly constant value at and above 45°C. However, conversion is a maximum at 35°C (Fig. 2). This complicated behavior shows that at higher temperatures the occurrence of side reactions is well favored. The activation energy was found to be 63.78 kJ/mol, which is in the normal range. The rate and conversion decreased with increasing [H_2SO_4]. This is due to the formation of a highly sulfated complex of ceric ions. Katai et al. [5] have reported this highly sulfatocerated complex to be less reactive, which decreases the concentration of primary radicals and hence the initial rate and maximum conversion decreased. The molecular weights of the samples increased with increasing [MMA] and decreasing [Ce(IV)].

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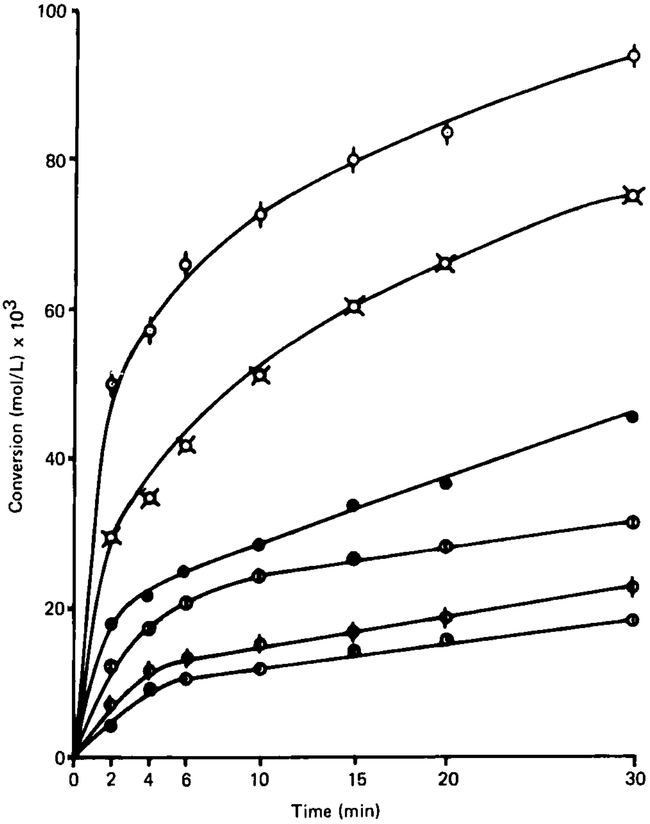

FIG. 1. Time-conversion curves for the aqueous polymerization of methyl methacrylate with varying initial concentration of monomer at constant [MA] = 9.20 × 10^{-3} mol/L, [Ce(IV)] = 4.04 × 10^{-3} mol/L, [H_2SO_4] = 27.86 × 10^{-2} mol/L, 35 ± 0.2°C. [MMA] = (○) 3.76 × 10^{-2} mol/L, (○) 5.64 × 10^{-2} mol/L, (○) 7.52 × 10^{-2} mol/L, (●) 9.40 × 10^{-2} mol/L, (○) 13.16 × 10^{-2} mol/L, (○) 18.80 × 10^{-2} mol/L.

Rate of Ceric Ion Disappearance

The rate of ceric ion disappearance increased with increasing [Ce(IV)]. A plot of rate vs [Ce(IV)] gave a straight line passing through the origin. However, in the case of acrylamide polymerization, the straight line did not pass through the origin at higher [Ce(IV)], showing that ceric ions play some role other than the production of primary radicals. The rate was found to be independent of [MMA]. Both these points suggest that the ceric ions are not involved directly either

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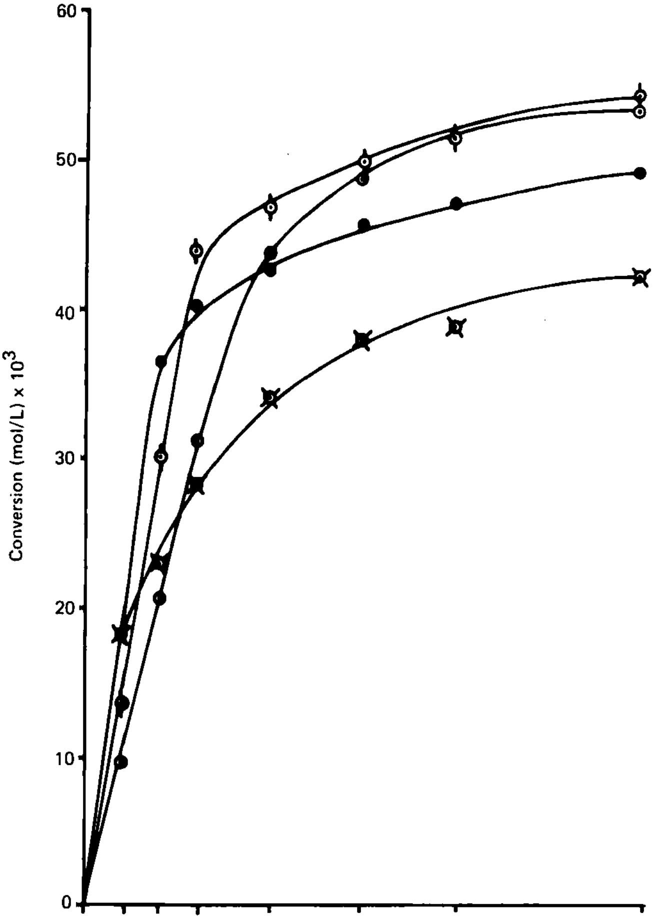

FIG. 2. Time-conversion curves for the aqueous polymerization of methyl methacrylate with varying reaction temperature at constant [MMA] = 9.40 × 10^{-2} mol/L, [MA] = 6.90 × 10^{-3} mol/L, [Ce(IV)] = 32.40 × 10^{-4} mol/L, [H_2SO_4] = 0.225 mol/L. Temperature: (○) 30°C, (○) 35°C, (●) 40°C, (○) 45°C.

in initiation or termination by direct interaction with the monomer or macroradicals. The rate increased very slowly with increasing [MA] up to a certain range above which it remained constant. A plot of rate vs [MA] left an intercept on the ordinate, indicating the formation of a very stable complex between ceric ions and malic acid. A Michaelis-

Menten plot confirms the complex formation between ceric ion and malic acid. The yellowish complex formed was subjected to various studies. IR spectra of the complex gave a peak at 1550 cm^{-1} but no peak was observed at 1725 cm^{-1} which appeared in the spectra of malic acid. This shifted peak and a peak at 650 cm^{-1} show the possibility of metal-oxygen bonding. The pH studies revealed a 1:1 complex formation. A freshly prepared solution of the complex in H_2SO_4 polymerized MMA, which indicated that the decomposition of the complex yields free radicals that initiate polymerization.

KINETIC SCHEME AND RATE EXPRESSION

All the experimental observations can be explained by the following reaction scheme:

$$MA + Ce(IV) \xrightarrow{K} complex \tag{1}$$

$$Complex \xrightarrow{k_r} R^\cdot + Ce(III) + H^+ \tag{2}$$

$$R^\cdot + Ce(IV) \xrightarrow{k_o} products \tag{3}$$

$$R^\cdot + M \xrightarrow{k_i} R\text{–}M^\cdot \tag{4}$$

$$R\text{–}M^\cdot + M \xrightarrow{k_p} R\text{–}M_2^\cdot$$

$$R\text{–}M_{n-1}^\cdot + M \xrightarrow{k_p} R\text{–}M_n^\cdot \tag{5}$$

$$R\text{–}M_n^\cdot + R\text{–}M_m^\cdot \xrightarrow{k_t} polymer \tag{6}$$

where $R^\cdot$ and $R\text{–}M_n^\cdot$ are the primary radical and macro radical, respectively. Applying the steady-state assumption to both $[R^\cdot]$ and $[R\text{–}M_n^\cdot]$, and assuming that $k_p[M] \gg k_i[M]$, the following rate expressions for the rate of monomer and ceric ion disappearance can be derived:

$$-\frac{d[M]}{dt} = R_p = k_p[M]^{3/2}\left\{\frac{Kk_rk_i[MA][Ce(IV)]}{k_t(k_o[Ce(IV)] + k_i[M])}\right\}^{1/2} \tag{7}$$

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and

$$-\frac{d[\mathrm{Ce(IV)}]}{dt} = \frac{2Kk_r[\mathrm{Ce(IV)}]_{\mathrm{Total}}[\mathrm{MA}]}{1 + K[\mathrm{MA}]} \tag{8}$$

Thus all the experimental observations can be explained by Eqs. (7) and (8), which confirms the bimolecular termination mechanism of the two growing macroradicals. Rao et al. [6] have also derived an equation similar to Eq. (7) in the case of the polymerization of acrylonitrile initiated by the same redox system. From all these observations it appears that the malic acid-ceric ion pair acts in two different ways in homogeneous and heterogeneous polymerizations.

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