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Studies on Vinyl Polymerization: Polymerization of Methyl Methacrylate by Permanganate-Malonic Acid Initiator System

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ABSTRACT

Aqueous polymerization of methyl methacrylate initiated by the permanganate-malonic acid redox pair has been studied under atmospheric conditions in the temperature range of 35 to 45°C. The effect of monomer, permanganate, and malonic acid concentrations and temperature on the rate of polymerization was studied. The effect of various water-soluble salts and solvents has been investigated. The rate of polymerization of the permanganate-malonic acid system was compared with the rates involved in various other systems consisting of oxalic acid, citric acid, and tartaric acid coupled with permanganate under similar conditions. The end-group of the polymer has been characterized by IR spectra. A suitable kinetic scheme has been proposed, and appropriate rate expressions have been derived on this basis and explained in the light of experimental findings.

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INTRODUCTION

Permanganate is one of the most versatile oxidizing agents. It cannot alone initiate polymerization of vinyl monomers in aqueous medium, but when coupled with a suitable organic substrate (reducing agent), it acts as a powerful initiator for the polymerization of vinyl monomers, e.g., acrylic acid, methacrylic acid, acrylonitrile, methyl acrylate, methyl methacrylate, acrylamide. A large number of organic substrates, e.g., oxalic acid, citric acid, tartaric acid, isobutyric acid, glycerol, and ascorbic acid, have been coupled with permanganate by different groups of workers [1-17] to utilize them as the initiator systems. Palit et al. [1, 2], Misra et al. [3, 4], Konkhim et al. [7], and Matsuzawa et al. [8] have extensively studied the polymerization of different vinyl monomers by the permanganate-oxalic acid redox system. Literature survey shows that very little work has been done on other redox systems. In this laboratory we have an ambitious research program to carry out the chemical modification of such natural macromolecules as wool, silk, and jute through grafting of vinyl monomers by using $KMnO_4$-organic substrate initiator systems. As a part of the research program, this communication presents the results of studies on the vinyl polymerization of methyl methacrylate initiated by the permanganate-malonic acid redox system in aqueous medium.

EXPERIMENTAL

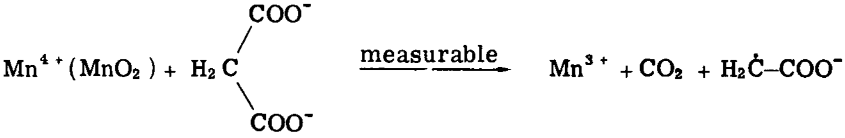
Methyl methacrylate was washed with 5% NaOH solution, followed by dilute orthophosphoric acid, and finally with distilled water and dried over anhydrous $CaCl_2$. Potassium permanganate was a BDH AnalaR grade product. All other reagents, e.g., malonic acid and ferrous ammonium sulfate, were AnalaR grade. The conductivity water used to prepare all solutions was obtained by redistilling distilled water with a small quantity of alkaline permanganate. The polymerizations were carried out in Corning glass vessels fitted with ground joint heads carrying inlet and outlet tubes.

Appropriate quantities of the reaction mixture containing conductivity water, monomer, and malonic acid were taken in the reaction vessel and kept in a thermostat at the desired temperature. Finally, an appropriate amount of permanganate solution, freshly prepared in conductivity water (0.05 M), was added. The polymerization reaction was heterogeneous with the polymers precipitating continuously. After a specified time interval the reaction was arrested by the addition of a known excess of ferrous ammonium sulfate solution. The vessels were kept in ice-cold water for some time. The polymer was filtered off, washed with water, and dried to constant weight. The rate of polymerization was calculated from the slope of a plot of yield versus time.

RESULTS AND DISCUSSION

Mechanism

In the aqueous polymerization of methyl methacrylate initiated by the $KMnO_4$-malonic acid system, the permanganate first reacts with methyl methacrylate to produce MnO_2, which then dissolves in the reaction mixture containing malonic acid and produces highly reactive Mn^{3+} ions:

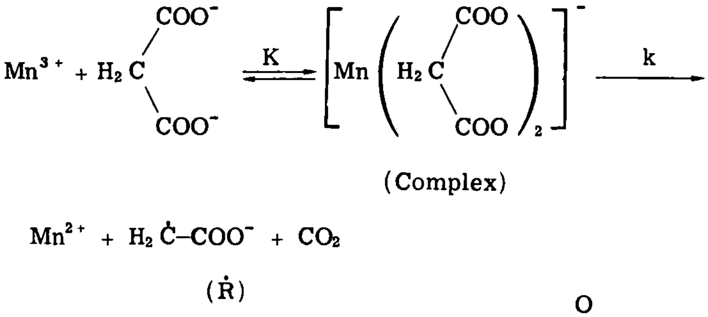


$$Mn^{4+}(MnO_2) + H_2C\begin{smallmatrix} / COO^- \\ \backslash COO^- \end{smallmatrix} \xrightarrow{\text{measurable}} Mn^{3+} + CO_2 + H_2\dot{C}\text{–}COO^-$$

These Mn^{3+} ions react with malonic acid to produce highly active free radicals which are capable of initiating the polymerization of methyl methacrylate. The following mechanism is put forth to explain the experimental facts.

Radical formation

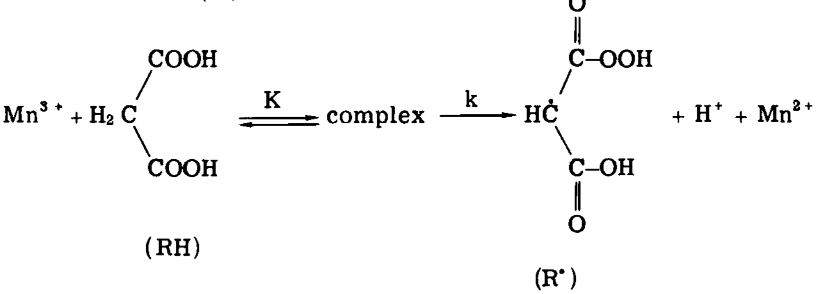
(i)



$$Mn^{3+} + H_2C\begin{smallmatrix} / COO^- \\ \backslash COO^- \end{smallmatrix} \overset{K}{\rightleftharpoons} \left[Mn\left(H_2C\begin{smallmatrix} / COO \\ \backslash COO \end{smallmatrix}\right)_2\right]^- \xrightarrow{k} Mn^{2+} + \underset{(\dot{R})}{H_2\dot{C}\text{–}COO^-} + CO_2$$

(Complex)

(ii)



$$Mn^{3+} + \underset{(RH)}{H_2C\begin{smallmatrix} / COOH \\ \backslash COOH \end{smallmatrix}} \overset{K}{\rightleftharpoons} \text{complex} \xrightarrow{k} \underset{(R^{\bullet})}{H\dot{C}\begin{smallmatrix} / C(=O)\text{–}OOH \\ \backslash C(=O)\text{–}OH \end{smallmatrix}} + H^+ + Mn^{2+}$$

The free radical formed in Step (ii) is more probable because its formation is facilitated by its stabilization through resonance due to the presence of two adjacent carbonyl functions. However, either of the radicals can explain the mechanism satisfactorily. At higher temperatures the radical $H_2\dot{C}–COO^-$ is most probably formed because of the ready escape of CO_2 from malonic acid.

Initiation and Propagation

$$R^\bullet + M \xrightarrow{k_i} R–M_1^\bullet$$

$$RM_1^\bullet + M \xrightarrow{k_p} R–M_2^\bullet$$

$$\vdots$$

$$RM_n^\bullet + M \xrightarrow{k_p} R–M_{n+1}^\bullet$$

Termination

$$\text{(i)}\quad R–M_{n+1}^\bullet + Mn^{3+} \xrightarrow{k_t} \text{polymer} + Mn^{2+} \quad \text{(linear)}$$

$$\text{(ii)}\quad R–M_{n+1}^\bullet + R–M_{n+1}^\bullet \xrightarrow{k_t} \underset{\text{(Polymer)}}{R–M_{n+1}–M_{n+1}–R} \quad \text{(mutual)}$$

Oxidation

$$R^\bullet + Mn^{3+} \xrightarrow{k_o} \text{oxidation product} + Mn^{2+}$$

On applying the steady-state principle to the primary radical as well as to the growing radical and assuming that linear termination predominates over mutual termination, we arrive at the following expression:

$$R_p = \frac{k_p[M]^2}{k_t}\left(\frac{kK[RH]}{[M] + (k_o/k_i)[KMnO_4]}\right) \qquad (1)$$

Equation (1) reduces to

$$\frac{[M]^2}{R_p} = \frac{k_t[M]}{k_p kK[RH]} + \frac{k_o k_t}{k_p k_i kK}\,\frac{[KMnO_4]}{[RH]} \qquad (2)$$

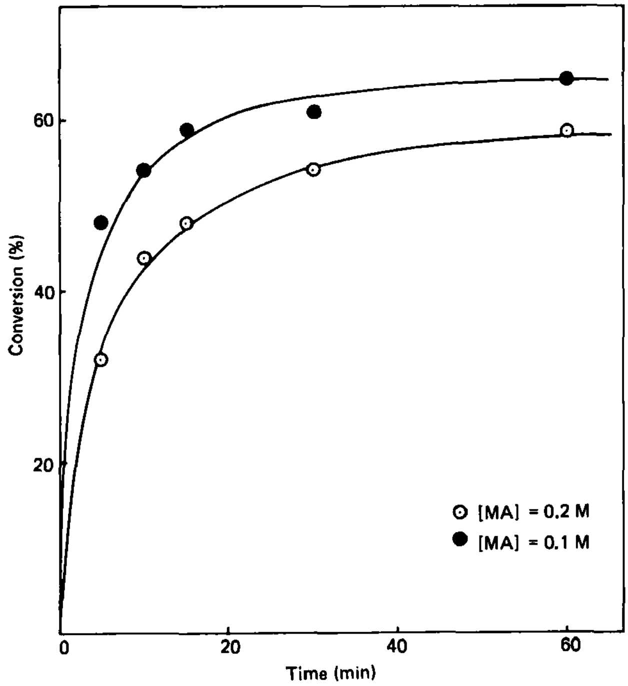


FIG. 1. Time-conversion plot. [$KMnO_4$] = 0.0075 mol/L, [MMA] = 0.093 mol/L, (○) [MA] = 0.2 M, (●) [MA] = 0.1 M.

Relation between Conversion and Reaction Time

Methyl methacrylate was polymerized in aqueous medium in the temperature range from 35 to 45°C and in the presence of the $KMnO_4$-malonic acid redox system. Time conversion curves at two different malonic acid concentrations (0.1 and 0.2 mol/L) and a constant concentration of permanganate (0.0075 mol/L) are shown in Fig. 1. Limiting conversion is attained within half an hour. A considerable percentage of conversion within a very short time period is the most striking feature of the present investigation.

Rate Dependence on Initiator Concentration

$KMnO_4$ coupled with malonic acid constitutes the initiator system in our present work. $KMnO_4$ alone cannot initiate polymerization of vinyl monomers in aqueous medium, but $KMnO_4$ in the presence of malonic acid initiates polymerization, indicating the formation of re-

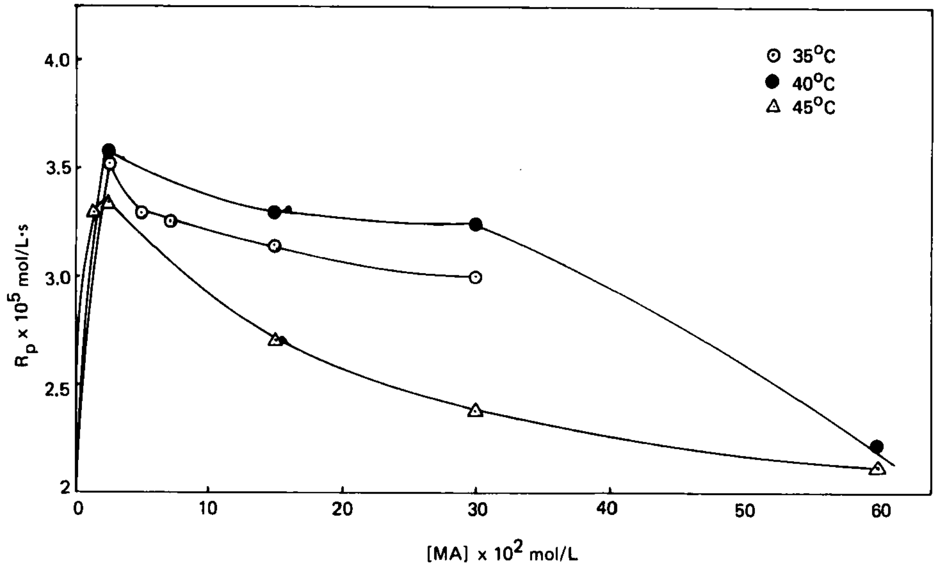
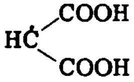


FIG. 2. R_p vs [malonic acid] plot. $[KMnO_4]$ = 0.0075 mol/L, [MMA] = 0.093 mol/L, (○) 35°C, (●) 40°C, (△) 45°C.

active free radicals produced by the reaction between $KMnO_4$ and malonic acid.

The initial rate of polymerization and percentage conversion have been found to increase with an increasing concentration of malonic acid up to a limiting concentration of 0.025 mol/L. Beyond this concentration there is a consistent decrease in the rate. This can be attributed to primary radical (R$^\cdot$) termination at higher concentrations of malonic acid. Figure 2 shows the relation between R_p and malonic acid concentrations at three different temperatures. An unusual observation made here is that the R_p value increases from 30 to 40°C but decreases considerably at 45°C. This is probably due to the decreasing concentration of the initiating free radicals  $\mathrm{H\dot{C}(COOH)_2}$ because of the easy escape of CO_2 molecules from the radicals at higher temperatures.

The relation between R_p and $[KMnO_4]$ at three different temperatures is shown in Fig. 3. The rate increases up to 0.00125 mol/L and thereafter decreases consistently. This indicates that at higher concentrations (the conditions under which the present investigation has

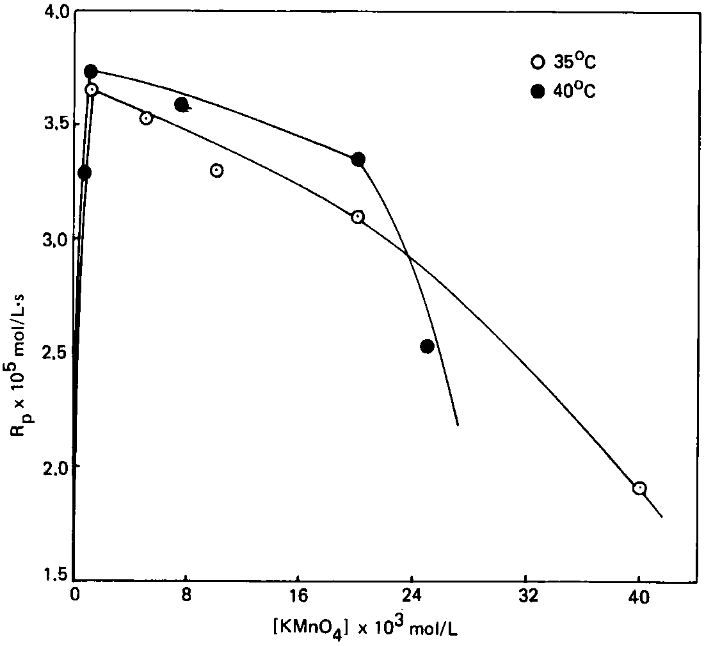


FIG. 3. R_p vs $[KMnO_4]$ plot. [MMA] = 0.093 mol/L, [MA] = 0.025 mol/L, (○) 35°C, (●) 40°C.

been carried out) linear termination predominates over mutual termination. The opposite is true at lower concentrations. The increase of R_p from 30 to 45°C is extremely small, and it is suggested that the rate of polymerization is independent of temperature in the range from 35 to 45°C with respect to $[KMnO_4]$.

Rate Dependence on Monomer Concentration

The initial polymerization rate and the percentage conversion were found to increase with increasing monomer concentration (0.0469 to 0.1773 mol/L). According to rate equation (2), which has been obtained on rearrangement of the equation based on the suggested mechanism, values of $[M]^2/R_p$ have been plotted against [M] for various temperatures (Fig. 4). Reasonable straight lines are obtained, the slopes and intercepts of which throw light on the composite rate constants involved in the polymerization steps.

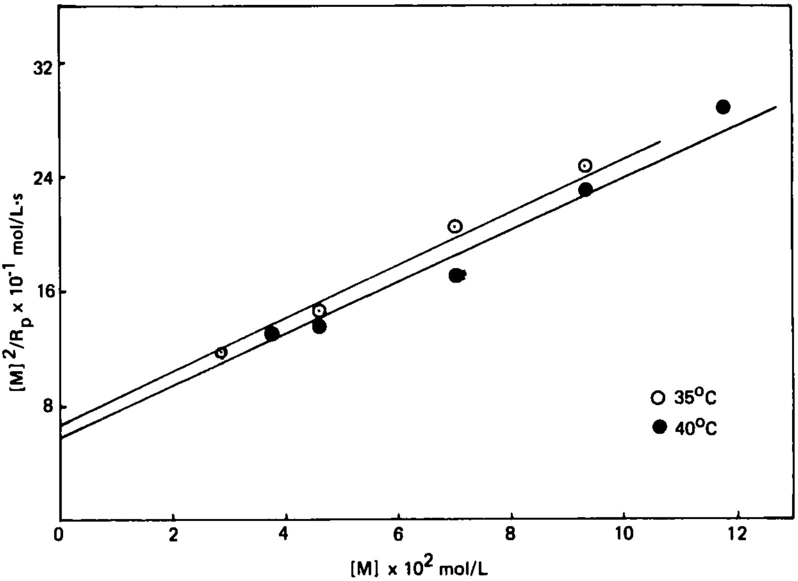


FIG. 4. $[M]^2/R_p$ vs [M] plot. $[KMnO_4]$ = 0.0075 mol/L, [MA] = 0.025 mol/L, (○) 35°C, (●) 40°C.

Comparison of $KMnO_4$-Malonic Acid Redox System with Other Systems

A comparison of the rate of polymerization of the $KMnO_4$-malonic acid redox system with $KMnO_4$-oxalic acid, $KMnO_4$-citric acid, and $KMnO_4$-tartaric acid redox systems in the presence of methyl methacrylate was made in order to measure the effectiveness of the present initiator system. The results of the rates of polymerization and the percentage conversion are given in Table 1. From these it has been suggested that the $KMnO_4$-malonic acid system is the best redox system so far reported. We have, therefore, decided to study this system for the grafting of MMA to natural macromolecules (wool, silk, jute, etc.) in order to improve their useful properties.

Effect of Temperature

The effect of temperature on this system is very interesting. A marked increase of the rate and of maximum conversion is noted with

TABLE 1. $[KMnO_4] = 0.00125$, $[MMA] = 0.093$, and $[MA] = 0.025$ mol/L

Substrates	$R_p \times 10^5$	% Conversion
Malonic acid	3.65	70.21
Oxalic acid	3.33	64.36
Citric acid	1.90	36.70
Tartaric acid	3.23	62.12

an increase of temperature from 35 to 40°C. A further increase from 40 to 45°C either decreases the rate or does not produce an appreciable change in the rate. The increasing and decreasing trend of R_p with an increase of temperature from 35 to 45°C have been reported by many workers, e.g., the former by Palit et al. [1, 2] and the latter by Singh et al. [17]. The optimum temperature for the maximum initial rate of polymerization and maximum conversion is found in this investigation to be 40°C.

Rate Dependence on Additives

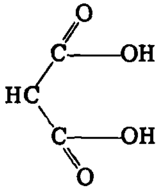
The use of water-soluble solvents and inorganic salts gives information about the influence of the medium on polymerization.

The effect of organic solvents added in the same proportion (5% v/v) is in the order: acetic acid > DMF > methanol > control > dioxane. The effect of such neutral salts as $MnSO_4$, K_2SO_4, NaCl, and $CuSO_4$ on the rate of polymerization was investigated. All the neutral salts except $MnSO_4$ depress the rate of polymerization, and $CuSO_4$ depresses it considerably. This can be attributed to ionic dissociation of the added electrolyte which interferes with normal polymerization, resulting in premature termination of the growing polymer chains. The increase of rate by the addition of $MnSO_4$ can be explained by the disproportionation reaction occurring between Mn^{2+} and Mn^{4+} to generate Mn^{3+}.

$$Mn^{4+} + Mn^{2+} \longrightarrow 2Mn^{3+}$$

Mn^{3+} ion is responsible for the enhancement of the rate of polymerization. Similar observations have been made by Misra et al. [3, 4] and Singh et al. [17].

IR Spectra

The IR spectra of the isolated polymer shows aliphatic $-\overset{O}{\overset{/\!/}{C}}-O^-$ absorption and many peaks at the fingerprint region characteristic of CH-bending vibrations along with peaks characteristic of the homopolymer. This shows that the polymer contains $H_2C-\overset{O}{\overset{/\!/}{C}}-O^-$ or  residue as an endgroup, thus confirming the proposed mechanism.

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