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Aqueous Polymerization of Methyl Methacrylate Initiated by Potassium Peroxydisulfate-Ascorbic Acid Redox System

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ABSTRACT

The aqueous polymerization of methyl methacrylate initiated by the redox system $K_2S_2O_8$-ascorbic acid has been studied at 35°C under the influence of oxygen. The rate of polymerization increases with increasing ascorbic acid concentration at low activator concentration, remains constant within the range 4.375×10^{-3} to 11.25×10^{-3} mole/liter, and at higher ascorbic acid concentration again decreases. The rate varies linearly with monomer concentration. The initial rate and the limiting conversion increase with increasing polymerization temperature. Organic solvents (water-miscible only) and small amounts of neutral salts like KCl and Na_2SO_4 depress the initial rate and the maximum conversion. The addition of small amounts of salts like Cu^{2+} and Mn^{2+} increases the initial rate, but no appreciable increase in the limiting conversion is observed.

INTRODUCTION

Peroxydisulfate ion is a mild oxidizing agent, and the kinetics and mechanism of these processes have attracted attention in recent years. House [1] and Wilmarth and Haim [2] have reviewed the oxidation of various organic and inorganic substrates by peroxydisulfate. The kinetics of the oxidation of a multitude of substrates both under catalyzed and uncatalyzed conditions have been a field of interest for many groups of workers [3-10]. Fukui and co-workers [11] have reported the redox polymerization of acrolein with the potassium persulfate-$AgNO_3$ system. Ikada and co-workers [12] have reported the graft copolymerization of PVA with some vinyl monomers by use of peroxydisulfate ion. Very recently Mushran and co-workers [13] have reported that the reduction of peroxydisulfate by ascorbic acid follows a chain mechanism, which involves the formation of ascorbate, SO_4^-, and OH· free radicals as intermediates. The presence of molecular oxygen in the reaction system, instead of inhibiting autocatalyzes the polymerization rate.

The present work deals with the aqueous polymerization of methyl methacrylate initiated by the redox system $K_2S_2O_8$-ascorbic acid at 35°C under atmospheric oxygen.

EXPERIMENTAL

All reagents used were of AR quality. Methyl methacrylate (Rohm and Haas, USA) monomer was purified by a standard method. Peroxydisulfate and ascorbic acid were of BDH (Analar) grade. Pure distilled water, redistilled over alkaline potassium permanganate and free of carbon dioxide, was used throughout this investigation.

The reactions were carried out in Pyrex tubes (20 × 2.5 cm) fitted with B_{24} sockets and closed by B_{24} cones equipped with gas inlet and outlet tubes. The system in aqueous solution (20 cm) was introduced into the reaction tube and thermostatted at 35°C. A known amount of ascorbic acid (solid) was introduced into the reaction vessel just before the polymerization sets in. The vessel was thoroughly shaken to dissolve the added ascorbic acid completely. The polymerization was initiated with known amounts of a freshly prepared standard solution of $K_2S_2O_8$. Several samples were withdrawn after desired intervals of time and introduced directly into beakers containing 10 ml of cooled 1% hydroquinone solution in 2 N H_2SO_4 to short-stop the polymerization. The polymers were filtered, thoroughly washed with water, and dried in vacuo to a constant weight.

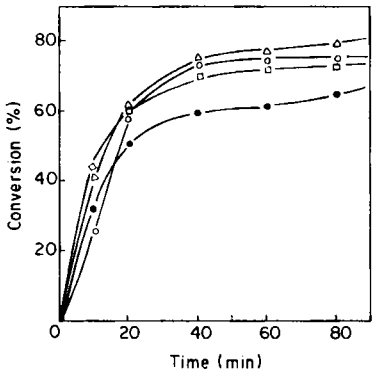

FIG. 1. Effect of activator concentration on relationship of conversion vs. time: (○) [AA] = 0.562×10^{-3} M, (△) [AA] = 4.375×10^{-3} M; (□) [AA] = 15.3×10^{-3} M; (●) [AA] = 20.5×10^{-3} M. [$K_2S_2O_8$] = 1.50×10^{-2} M; [MMA] = 0.0938 M, 35 ± 0.1°C.

Dependence of Rate on Activator Concentration

The initial rate and the limiting conversion have been found to increase with increasing concentration of ascorbic acid, remain constant over a wide range of concentrations (4.375×10^{-3} to 11.25×10^{-3} liter/mole) and at higher concentrations of ascorbic acid (above 11.25×10^{-3} liter/mole); however, an appreciable decrease in the initial rate and in the maximum conversion is observed (Fig. 1). This agrees with the observations made by Morgan [14] and by Guha [15], using $K_2S_2O_8$ as initiator and oxyacids of sulfur as activator. In general, an enhancement in the rate of polymerization in a redox initiated system is expected with increasing concentration of the activator (ascorbic acid) while H^+ ions plays an important role in decreasing the rate of polymerization.

$$AH^{\cdot} + S_2O_8^{2-} \longrightarrow A + SO_4^{2-} + SO_4^{\cdot -} + H^+ \quad (1)$$

$$AH^{\cdot} + SO_4^{\cdot -} \longrightarrow A + SO_4^{2-} + H^+ \quad (2)$$

At higher concentrations of ascorbic acid, the rate of generation as well as the concentration of reactive species is suppressed at an increased concentration of hydrogen ions. At low concentration of ascorbic acid, the concentration of the H^+ ions does not vary

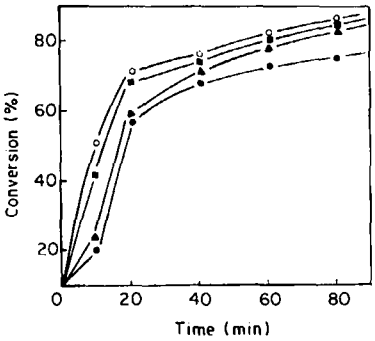

FIG. 2. Effect of catalyst on relationship of conversion vs. time: (●) $[K_2S_2O_8] = 0.5 \times 10^{-2}$ M; (▲) $K_2S_2O_8 = 1.5 \times 10^{-2}$ M; (■) $[K_2S_2O_8] = 2.5 \times 10^{-2}$ M; (○) $K_2S_2O_8 = 3.5 \times 10^{-2}$ M. $[\overline{AA}] = 2.5 \times 10^{-3}$ M; [MMA] = 0.0938 M; 35 ± 0.1°C.

appreciably; the formation of primary radicals is, therefore, balanced, resulting in a constant rate at this range.

Dependence of Rate on Catalyst Concentration

The initial rate and the limiting conversion tend to increase with increasing catalyst concentration at a fixed concentration of the activator and the monomer (Fig. 2). Since ascorbic acid alone is incapable of initiating the polymerization under any circumstance, it is the quantity of the reactive species ($A\dot{H}$, $S\dot{O}_4^-$), produced by the reaction between peroxydisulfate and ascorbic acid (electron donor) which affects the initial polymerization rate. The double logarithmic plot of the initial rate R_i versus [catalyst] is linear with a slope of approximately unity. At higher concentrations of the catalyst, a slight deviation from unit slope is observed. At low concentrations of the catalyst the order is nearly unity, indicating a first-order termination of the growing chain. At relatively higher concentrations of the catalyst, primary radicals are produced, however, at a faster rate. The participation of these radicals in chain termination is, therefore, increased. These results are supported by data of previous workers [16-18], who have shown that the rate of peroxide-catalyzed vinyl polymerization in homogeneous sytems is proportional to the square root of the catalyst concentration. In terms of the generally accepted kinetic interpretation, this means that the initiation reaction is proportional to the catalyst concentration, and that the termination process

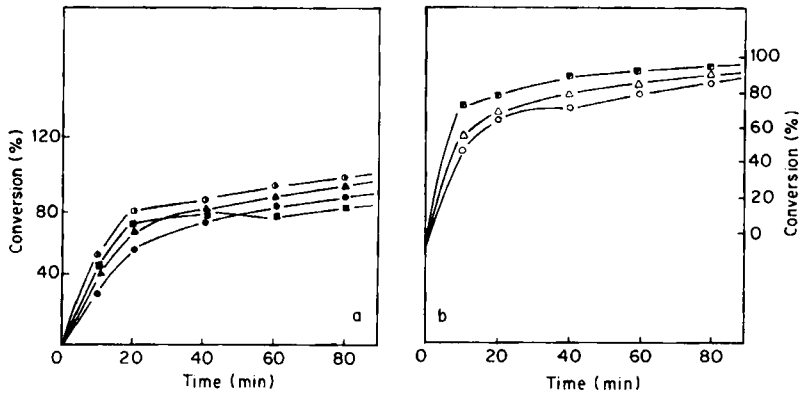

FIG. 3. (a) Effect of monomer on relationship of conversion vs. time: (●) [MMA] = 0.0704 M; (▲) [MMA] = 0.0938 M; (■) [MMA] = 0.1173 M; (◐) [MMA] = 0.1408 M. [$K_2S_2O_8$] = 2×10^{-2} M, [AA] = 2.5×10^{-3} M, temp = 35 ± 0.1°C. (b) Effect of temperature on relationship of conversion vs. time: (○) 35°C; (△) 40°C; (□) 45°C; (◧) 50°C. [$K_2S_2O_8$] = 2×10^{-2} M; [AA] = 2.5×10^{-3} M; [MMA] = 0.0938 M.

occurs by mutual collision of two active centers, and that the steady-state approximation is reasonably well fulfilled.

Dependence of Rate on Monomer Concentration

The conversion curves in Fig. 3 clearly indicate that as the monomer concentration is increased, the maximum conversion is increased correspondingly. The rate of polymerization R_p of methyl methacrylate is linearly proportional to the concentration of the monomer. At higher monomer concentration, deviation from this linearity is observed which might be due to interference of the polymer dissolved in the medium which becomes more viscous due to high extent of conversion [17].

Dependence of Rate on Temperature

The effect of temperature on the polymerization rate of methyl methacrylate is shown in Fig. 3. The initial rate, as well as the limiting conversion, increases with increasing polymerization temperature.

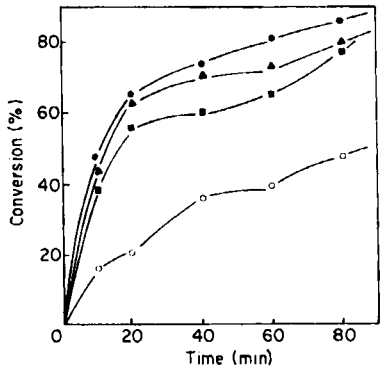

FIG. 4. Effect of water-soluble organic solvents (5%) on relationship of conversion vs. time: (●) Control; (▲) acetic acid; (■) acetone; (○) ethanol. $[K_2S_2O_8] = 2 \times 10^{-2}$ M, $[AA] = 2.5 \times 10^{-3}$ M; [MMA] = 0.0938 M; 35 ± 0.1°C.

Rate Dependence on Additives

Effect of Organic Solvents. Introduction of water-miscible organic solvents like methanol, ethanol, acetone, and acetic acid to the extent of 5% tends to depress the initial rate as well as the limiting conversion (Fig. 4). Similar observations have also been made by several other workers [18-20]. This behavior can be interpreted by assuming that the water-miscible organic solvents can perform three functions: (a) the decrease of the area of shielding of a strong hydration layer in aqueous medium results in the termination of the growing chain; (b) the increase of the regulated rate of production of primary radicals, which renders the termination rate relatively fast compared to the growing rate; (c) the interchain hydrogen bonding, interlocking the polymer chain is not rigid, whereby the tendency of mutual termination of polymer chain increases. These three facts might tend to decrease the degree and the rate of polymerization.

Effect of Inorganic Salts and Catalysts. The addition of small amounts of neutral salts such as KCl and Na_2SO_4 to the system depresses the rate and the maximum conversion, possibly due to the resultant increase in ionic strength of the medium.

The percentage of conversion has also been calculated in the presence of certain other salts like Cu^{2+} and Mn^{2+}. It is noted that these metal cations activate the polymerization process and increase both the rate and the maximum conversion. This activation phenomenon is attributed to the fact that these metal cations form redox pairs

in combination with $K_2S_2O_8$, thus promoting the initiator activity of the redox pair $K_2S_2O_8$-ascorbic acid. The promoting action might be due to some facile reaction path through the intermediacy of the redox system formed by the added metal ion [21].

Mechanism of the Reaction

The reduction of peroxydisulfate by ascorbic acid is a two-electron transfer reaction in which ascorbic acid is oxidized to dehydroascorbic acid. It has already been established by Weissberger [22] and others that ascorbic acid exists as ascorbate ion in aqueous solution which is mainly responsible for the great reducing action.

$$AH_2 \rightleftharpoons AH^- + H^+ \tag{3}$$

Under the present experimental condition, persulfate ion ($S_2O_8^{2-}$) and the monomer form a complex [13], which breaks down, liberating the initiating radical. Under such condition ascorbate (AH^-) and sulfate ion radicals ($\dot{SO}_4^-$) are the active species which initiate the vinyl polymerization. Roskin [23] proposed that hydroxyl radicals ($OH^\cdot$) which might be produced due to the reaction of H_2O with $S_2O_8^{2-}$ might also initiate vinyl polymerization. This predication was not supported by endgroup analysis. The mechanism may be envisaged as shown in Eqs. (4)-(12).

Production of primary radical:

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^- \tag{4}$$

$$\dot{SO}_4^- + H_2O \xrightarrow{k_2} SO_4^{-2} + H + \dot{OH} \tag{5}$$

$$\dot{OH} + AH^- \xrightarrow{k_3} AH^\cdot + OH^- \tag{6}$$

$$\dot{AH} + S_2O_8^{-2} \xrightarrow{k_4} A + SO_4^{-2} + \dot{SO}_4^- + H^+ \tag{7}$$

$$\dot{AH} + \dot{SO}_4^- \xrightarrow{k_5} A + SO_4^{-2} + H^+ \tag{8}$$

Initiation:

$$M + \dot{SO}_4^- \text{ or } AH^\cdot \xrightarrow{k_i} M^\cdot \tag{9}$$

Propagation:

$$M^{\cdot} + M \xrightarrow{k_p} M_1^{\cdot} \tag{10}$$

$$M_{n-1} + M \xrightarrow{k_p} M_n \tag{11}$$

Termination:

$$M_x^{\cdot} + M_y^{\cdot} \xrightarrow{k_t} \text{Dead Polymer} \tag{12}$$

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