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# Studies on the Aqueous Polymerization of Acrylamide Initiated by the Potassium Permanganate/Glyceric Acid Redox System

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ABSTRACT: The kinetics of the aqueous polymerization of acrylamide has been investigated in an inert atmosphere at 35 ± 0.1 °C by employing the potassium permanganate/glyceric acid redox system. The rate of polymerization is maximum at an optimum concentration of glyceric acid but is directly proportional to the concentration of monomer. The order with respect to potassium permanganate has been found to be 0.5, which shows the bimolecular mode of termination. The energy of activation is found to be 71 ± 2 kJ/mol. The number-average molecular weight and degree of polymerization have been determined viscometrically. The effects of various water-miscible inorganic salts, detergents, and organic solvents have been studied.

## Introduction

Various redox systems[1-5] have been used successfully for the polymerization of acrylamide[1-4] and other vinyl monomers.[5] Permanganate in combination with different reducing agents has been used for the polymerization of acrylamide.[6,7] Recently Misra and Bajpai[8] have studied the aqueous polymerization of acrylamide initiated by the permanganate/lactic acid redox system. However, no attempt has been made to derive the kinetic rate law. This has prompted us to investigate the detailed kinetic study of the polymerization of acrylamide initiated by the permanganate/glyceric acid redox system.

## Experimental Section

Acrylamide (E. Merck) was purified by recrystallization from methanol. Glyceric acid (Fluka) and the other chemicals used were of BDH AnalaR grade. The rate of polymerization has been followed as reported elsewhere.[9]

**Determination of Molecular Weight.** For molecular weight determination the samples of polyacrylamide were purified by twice precipitating from methanol (AR) and were dried under vacuum. The intrinsic viscosity[10] of the polymer was determined at very high dilution (<0.4%) with an Ubbelohde type viscometer at 30 °C.

## Results and Discussion

In the aqueous polymerization of acrylamide initiated by the permanganate/glyceric acid redox system, the permanganate first reacts with acrylamide and produces immediately a brownish black solution of hydrated manganese dioxide, which ultimately interacts with the glyceric acid to produce free radicals ($\mathrm{CH_2OHCHOH\dot{C}OO}$) and highly reactive $\mathrm{Mn^{3+}}$ ions. These $\mathrm{Mn^{3+}}$ ions are supposed to be more reactive to produce the free radical ($\mathrm{CH_2OH\dot{C}HOH}$) instantaneously, which is capable of initiating the polymerization of acrylamide. The following steps have been proposed for the polymerization on the basis of experimental results:

$$3\mathrm{>C{=}C<} + 2\mathrm{MnO_4} + 4\mathrm{H_2O} \xrightarrow{\text{fast}} 3\mathrm{>C(OH){-}C(OH)<} + 2\mathrm{MnO_2} + 2\mathrm{OH^-} \quad (1)$$

$$\mathrm{Mn(IV)} + \mathrm{CH_2OHCHOHCOOH} \xrightarrow{k_1} \mathrm{Mn(III)} + \underset{\mathrm{A}}{\mathrm{CH_2OHCHOHCO\dot{O}}} + \mathrm{H^+} \quad (2)$$

$$\mathrm{CH_2OHCHOHCO\dot{O}} \xrightarrow{\text{fast}} \underset{\mathrm{B}}{\mathrm{CH_2OH\dot{C}HOH}} + \mathrm{CO_2} \quad (3)$$

$$\mathrm{Mn(III)} + \mathrm{CH_2OHCHOHCOOH} \xrightarrow{k_2} \mathrm{Mn(II)} + \underset{\mathrm{B}}{\mathrm{CH_2OH\dot{C}HOH}} + \mathrm{CO_2} + \mathrm{H^+} \quad (4)$$

Initiation:

$$\mathrm{M} + \dot{\mathrm{B}} \xrightarrow{k_i} \dot{\mathrm{M}}_1 \quad (5)$$

Propagation:

$$\dot{\mathrm{M}}_1 + \mathrm{M} \xrightarrow{k_p} \dot{\mathrm{M}}_2$$

$$\dot{\mathrm{M}}_{n-1} + \mathrm{M} \xrightarrow{k_p} \dot{\mathrm{M}}_n \quad (6)$$

Termination:

$$\dot{\mathrm{M}}_n + \dot{\mathrm{M}}_m \xrightarrow{k_t} \mathrm{M}_{n+m} \quad (7)$$

The first step has been assumed to be very fast due to the fact that permanganate attacks very quickly on the ethylenic double bond;[11] therefore step 1 will not appear in the rate law.

On considering the above steps the following rate expression has been derived as

$$-\frac{\mathrm{d[M]}}{\mathrm{d}t} = R_\mathrm{p} = k_\mathrm{p}\left\{\frac{k_1}{k_\mathrm{t}}\right\}^{1/2}[\mathrm{M}][\mathrm{KMnO_4}]_0{}^{1/2}[\mathrm{CH_2CHCHOHCOOH}]^{1/2} \quad (8)$$

The kinetic chain length can be given as follows:

$$\nu = k_\mathrm{p}\frac{[\mathrm{M}]}{2(k_\mathrm{t}k_1[\mathrm{KMnO_4}]_0[\mathrm{CH_2OHCHOHCOOH}])^{1/2}} \quad (9)$$

**Rate Dependence on Initiator.** When the concentration of potassium permanganate is increased from 0.83 × $10^{-4}$ to 10.0 × $10^{-4}$ mol dm$^{-3}$, the initial rate of polymerization and maximum conversion increase substantially (Table I), and thereafter the rate of polymerization and maximum conversion decrease consistently. At higher concentrations of potassium permanganate the rate of polymerization is decreased due to the inhibition action of colloidal manganese dioxide, which is formed by the reaction of permanganate with the monomer (step 1), but in the presence of a sufficient amount of glyceric acid, the manganese dioxide does not exist in the colloidal state and the rate of polymerization increases due to the formation of the free radical through steps 3 and 4. The order with respect to permanganate has been calculated by plotting a graph (Figure 1A) of log $R_i$ (percent conversion per minute for initial 5% conversion) vs. log (initial concentration of permanganate) and has been found to be 0.5. The square root dependence on the initiator concentration throws light on the mode of termination and rules out the

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Table I
Rate Dependence on Varying the Concentration of Initiator[a]

| [KMnO$_4$] × 10$^4$, mol dm$^{-3}$ | % conversion at different times (min) | | | | | | | [η] × 10$^2$ at 60 min, dL/g |
|---|---|---|---|---|---|---|---|---|
| | 2 | 5 | 10 | 15 | 30 | 50 | 60 | |
| 0.83 | 0.62 | 1.47 | 2.90 | 4.62 | 16.17 | | | 155.3 |
| 1.66 | 0.85 | 2.08 | 4.19 | 9.57 | 29.14 | 37.20 | 37.22 | 119.3 |
| 3.33 | 1.20 | 2.92 | 6.24 | 13.98 | 39.46 | 50.02 | 50.08 | 93.1 |
| 5.00 | 1.42 | 3.45 | 7.74 | 16.42 | 44.84 | 54.08 | 55.00 | 79.1 |
| 10.00 | 1.78 | 4.52 | 10.43 | 20.21 | 49.14 | 62.36 | 62.66 | 64.9 |

[a] [Acrylamide] = 1.0 × 10$^{-1}$ mol dm$^{-3}$; [glyceric acid] = 1.25 × 10$^{-2}$ mol dm$^{-3}$.

Table II
Rate Dependence on Varying the Concentration of Activator[a]

| [glyceric acid] × 10$^3$, mol dm$^{-3}$ | % conversion at different times (min) | | | | | | | [η] × 10$^2$ at 60 min, dL/g |
|---|---|---|---|---|---|---|---|---|
| | 2 | 5 | 10 | 15 | 30 | 40 | 60 | |
| 4.16 | 1.05 | 2.82 | 5.27 | 10.75 | 34.62 | 51.62 | 73.98 | 75.7 |
| 6.25 | 1.16 | 3.18 | 6.77 | 13.55 | 39.46 | 55.05 | 72.04 | 70.9 |
| 12.50 | 1.70 | 4.26 | 10.43 | 20.21 | 49.14 | 59.67 | 62.66 | 63.3 |
| 25.00 | 1.78 | 4.48 | 13.33 | 25.50 | 53.97 | 60.00 | 60.64 | 52.3 |
| 45.00 | 1.46 | 3.82 | 12.47 | 23.44 | 49.57 | 53.76 | 55.05 | 42.7 |

[a] [Acrylamide] = 1.0 × 10$^{-1}$ mol dm$^{-3}$; [KMnO$_4$] = 1.0 × 10$^{-3}$ mol dm$^{-3}$.

Table III
Rate Dependence on Varying the Concentration of Monomer[a]

| [acrylamide] × 10$^2$, mol dm$^{-3}$ | % conversion at different times (min) | | | | | | | [η] × 10$^2$ at 60 min, dL/g |
|---|---|---|---|---|---|---|---|---|
| | 2 | 5 | 10 | 15 | 30 | 40 | 60 | |
| 2.5 | 1.18 | 2.80 | 5.58 | 8.32 | 27.07 | 35.16 | 37.40 | 77.6 |
| 3.7 | 1.62 | 4.16 | 8.32 | 12.48 | 32.61 | 41.04 | 46.10 | 84.5 |
| 5.0 | 2.32 | 5.38 | 10.62 | 16.34 | 39.14 | 49.69 | 54.68 | 102.0 |
| 7.0 | 2.61 | 6.32 | 12.58 | 19.23 | 44.22 | 55.12 | 59.09 | 108.0 |
| 10.0 | 2.85 | 6.72 | 13.18 | 20.21 | 49.14 | 59.67 | 62.66 | 140.0 |

[a] [KMnO$_4$] = 1.0 × 10$^{-3}$ mol dm$^{-3}$; [glyceric acid] = 1.25 × 10$^{-3}$ mol dm$^{-3}$.

possibility of metal ion participation in the termination process. In the initial part of the reaction the rate of polymerization is more or less negligible, which has been assumed to be due to the formation of inactive radicals as given in step 2. The 0.5 order with respect to initiator has also been reported by other workers during vinyl polymerization.[6-8,12]

**Rate Dependence on Activator Concentration.** The experimental results given in the Table II indicate that the initial rate of polymerization increases in the concentration range from 4.16 × 10$^{-3}$ to 12.5 × 10$^{-3}$ mol dm$^{-3}$ and remains almost constant in a very short concentration range, i.e., from 12.5 × 10$^{-3}$ to 25.0 × 10$^{-3}$ mol dm$^{-3}$. Beyond this concentration there is a gradual decrease in the initial rate as well as in the maximum conversion. This is due to the fact that on increasing the concentration of glyceric acid from 4.16 × 10$^{-3}$ to 12.5 × 10$^{-3}$ mol dm$^{-3}$, the concentration of active free radicals increases and hence the initial rate of polymerization. But in the concentration range from 25.0 × 10$^{-3}$ to 45.0 × 10$^{-3}$ mol dm$^{-3}$, the opposing side reaction is probably predominant, which prevents the formation of active free radicals due to the direct reduction of manganese(IV) into manganese(II) as given in the following equation:

$$2MnO_2 + 4H^+ \rightarrow 2H_2O + 2Mn^{2+} + O_2 \qquad (10)$$

The order of reaction with respect to glyceric acid has been calculated by drawing a logarithmic plot (Figure 1B) of $R_i$ (percent conversion per minute for initial 5% conversion) vs. the initial concentration of activator. The value of the exponent has been found to be 0.4 in the concentration range from 4.16 × 10$^{-3}$ to 12.5 × 10$^{-3}$ mol dm$^{-3}$ but tends to 0 in the concentration range from 12.5 × 10$^{-3}$ 25.0 × 10$^{-3}$ mol dm$^{-3}$; therefore the rate of polymerization remains more or less constant in this concentration range, which is probably due to the existence of a balance between the free radical formation steps (3 and 4) and the opposing side reaction (10). Similarly, other workers[13,14] have also observed that the rate of polymerization is more or less independent of the concentration of the activator beyond a certain range.

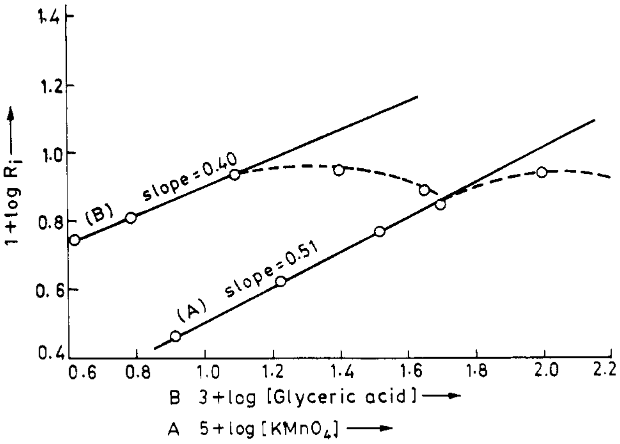

**Figure 1.** Double-logarithmic plot of the initial rate of polymerization $R_i$ (percent conversion per minute for initial 5% conversion) vs. concentration of catalyst and activator at 35 °C: (A) [acrylamide] = 1.0 × 10$^{-1}$ mol dm$^{-3}$, [glyceric acid] = 1.25 × 10$^{-2}$ mol dm$^{-3}$, [KMnO$_4$] = (0.83–10) × 10$^{-4}$ mol dm$^{-3}$; (B) [acrylamide] = 1.0 × 10$^{-1}$ mol dm$^{-3}$, [KMnO$_4$] = 1.0 × 10$^{-3}$ mol dm$^{-3}$, [glyceric acid] = (4.16–45) × 10$^{-3}$ mol dm$^{-3}$.

**Rate Dependence on Monomer Concentration.** Results (Table III) indicate that the initial rate of prop-

Table IV
**Effect of Temperature on the Rate of Polymerization**[a]

| temp, °C | % conversion at different times (min) 2 | 5 | 10 | 15 | 30 | 40 | 60 | $[\eta] \times 10^2$ at 60 min, dL/g |
|---|---|---|---|---|---|---|---|---|
| 25 | 0.66 | 1.64 | 3.20 | 4.98 | 15.80 | 25.20 | 43.70 | 77.2 |
| 30 | 0.78 | 2.30 | 4.30 | 10.60 | 28.10 | 41.10 | 56.10 | 68.1 |
| 35 | 1.65 | 4.15 | 10.40 | 20.20 | 49.10 | 59.70 | 62.60 | 63.3 |
| 40 | 2.60 | 7.60 | 20.00 | 31.40 | 58.60 | 62.00 | 63.20 | 56.2 |
| 45 | 4.05 | 12.10 | 29.30 | 47.60 | 61.20 | 61.60 | 62.20 | 49.2 |

[a] [Acrylamide] = 1.0 × $10^{-1}$ mol $dm^{-3}$; [glyceric acid] = 1.25 × $10^{-2}$ mol $dm^{-3}$; [$KMnO_4$] = 1.0 × $10^{-3}$ mol $dm^{-3}$.

Table V
**Effect of Inorganic Salts on the Rate of Polymerization**[a]

| salt[b] | % conversion at different times (min) 5 | 10 | 15 | 20 | 30 | 40 | 50 |
|---|---|---|---|---|---|---|---|
| blank | 4.3 | 10.4 | 20.2 | 30.4 | 49.1 | 59.7 | 62.7 |
| LiCl | 4.2 | 9.6 | 18.1 | 27.4 | 43.8 | 55.3 | 58.1 |
| NaCl | 4.1 | 9.5 | 18.1 | 27.6 | 43.7 | 55.3 | 58.0 |
| KCl | 4.0 | 8.3 | 17.9 | 26.4 | 43.1 | 54.9 | 57.3 |
| RbCl | 3.8 | 8.9 | 17.4 | 25.8 | 43.0 | 54.7 | 57.1 |
| $NH_4Cl$ | 3.0 | 8.0 | 17.3 | 26.7 | 42.8 | 53.1 | 57.0 |

[a] [Acrylamide] = 1.0 × $10^{-1}$ mol $dm^{-3}$; [glyceric acid] = 1.25 × $10^{-2}$ mol $dm^{-3}$; [$KMnO_4$] = 1.0 × $10^{-3}$ mol $dm^{-3}$. [b] [Salt] = 1.0 × $10^{-2}$ mol $dm^{-3}$.

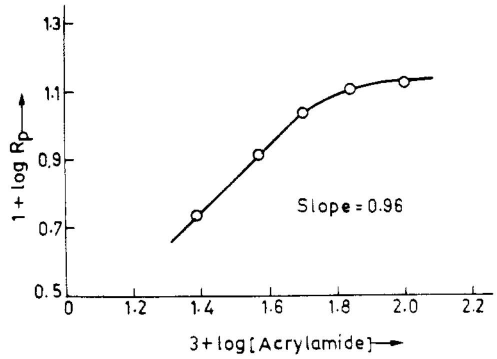

**Figure 2.** Double-logarithmic plot of rate of propagation $R_p$ (percent conversion per minute up to 15% polymerization) vs. initial concentration of monomer at 35 °C: [$KMnO_4$] = 1.0 × $10^{-3}$ mol $dm^{-3}$, [glyceric acid] = 1.25 × $10^{-2}$ mol $dm^{-3}$, [acrylamide] = 2.5 × $10^{-2}$–10.0 × $10^{-2}$ mol $dm^{-3}$.

agation ($R_p$) (where $R_p$ is the percent conversion per minute up to a maximum of 15% polymerization) and maximum conversion increase linearly on increasing monomer concentration from 2.5 × $10^{-2}$ to 5.0 × $10^{-2}$ mol $dm^{-3}$. But at high monomer concentrations, the rate of propagation becomes diffusion-controlled and the water-soluble polyacrylamide formed in the system interferes with the normal course of propagation.[15] The order of reaction with respect to the monomer has been calculated by plotting a graph (Figure 2) of log $R_p$ (percent conversion per minute up to a maximum of 15% polymerization) vs. log (initial concentration of monomer), which is found to be unity. The deviation in the monomer exponent from unity to less than unity at higher monomer concentrations is due to the retardation in the rate of propagation.

**Rate Dependence on Temperature.** The results at various temperatures are given in Table IV. A graph (Figure 3) has been made in order to calculate the energy of activation, which is 71 ± 2.0 kJ/mol. At temperatures above 45 °C the rate of bimolecular interaction of the immature growing chain radicals increased, which resulted in a decrease in the maximum conversion. The decrease in viscosity of the medium at higher temperatures may also increase the mobility of the growing radicals, which therefore increases the frequency of the termination processes.

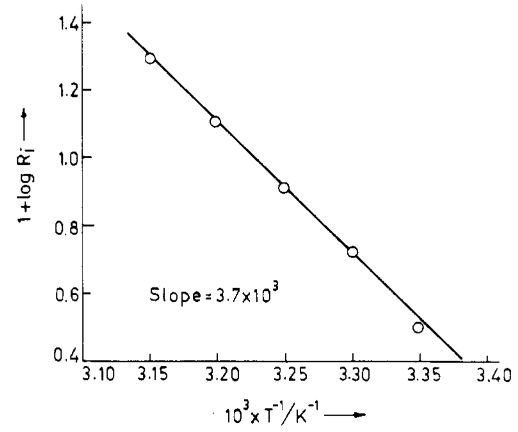

**Figure 3.** Arrhenius plot of the initial rate of polymerization $R_i$ (percent conversion per minute for initial 5% conversion) vs. the reciprocal of the absolute temperature: [acrylamide] = 1.0 × $10^{-1}$ mol $dm^{-3}$, [glyceric acid] = 1.25 × $10^{-2}$ mol $dm^{-3}$, [$KMnO_4$] = 1.0 × $10^{-3}$ mol $dm^{-3}$. Temperature was 25–45 °C.

**Rate Dependence on Additives.** The rate of polymerization of acrylamide has been studied in the presence of various additives, such as inorganic salts, detergents, complexing agents, alcohols, and sulfuric acid. The experimental results (Table V) clearly indicate that the rate of polymerization decreases in the presence of alkali metal chloride. The effect of the ionic radii[16] of the alkali metal ion has been found to be another possible factor in reducing the rate of polymerization; i.e., as the ionic radii increases, the effect of alkali metal chloride increases to suppress the rate of polymerization and the maximum conversion. The rate of polymerization and maximum conversion also decrease in the presence of ammonium chloride. The increase in ionic strength of the medium[17] in the presence of alkali metal chloride may also be another factor in depressing the rate of polymerization. The addition of manganous sulfate (Figure 4) shows an extraordinary behavior by increasing the initial rate of polymerization as well as maximum conversion. This is due to the fact that $Mn^{2+}$ ions react with $Mn^{4+}$ ions and produce the highly reactive $Mn^{3+}$ ions; therefore the production of primary free radicals through reaction step 4 increases, which in turn enhances the rate of polymerization and

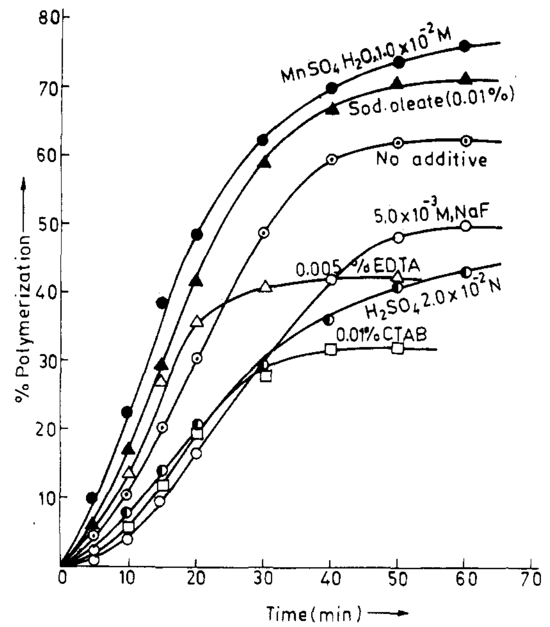

**Figure 4.** Effect of additives at 35 °C: [acrylamide] = $1.0 \times 10^{-1}$ mol dm$^{-3}$, [$KMnO_4$] = $1.0 \times 10^{-3}$ mol dm$^{-3}$, [glyceric acid] = $1.25 \times 10^{-2}$ mol dm$^{-3}$.

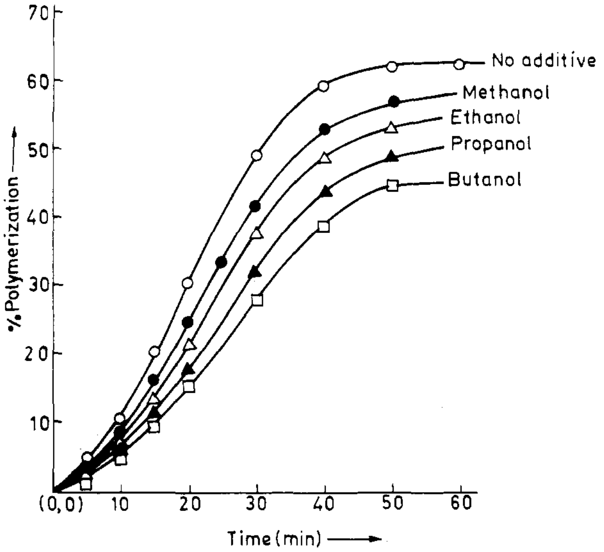

**Figure 5.** Effect of alcohols at 35 °C: [acrylamide] = $1.0 \times 10^{-1}$ mol dm$^{-3}$, [$KMnO_4$] = $1.0 \times 10^{-3}$ mol dm$^{-3}$, [glyceric acid] = $1.25 \times 10^{-2}$ mol dm$^{-3}$, [alcohols] = 5% (v/v).

maximum conversion.

The addition of an anionic detergent, i.e., sodium oleate (Figure 4), above its cmc value enhances the rate of polymerization appreciably. Since the dissociation of anionic detergents provides negatively charged ionic micelles that probably exert a repelling force between the growing polymer chains, it decreases the possibility of bimolecular termination. But the positively charged micelles produced by the cationic detergent cetyltrimethylammonium bromide (CTAB) (Figure 4) favors the orientation of the growing polymer chain for termination; hence the rate of polymerization decreases in the presence of a cationic detergent. The addition of sulfuric acid (Figure 4) decreases the initial rate of polymerization as well as the maximum conversion, which is due to the opposing side reaction (10).

The rate of polymerization decreases in the presence of sodium fluoride (Figure 4) and increases in the presence of ethylenediaminetetraacetic acid. The detailed kinetic investigation of the vinyl polymerization[12,14] shows that the rate of polymerization decreases in the presence of complexing agets like sodium fluoride and EDTA. The exceptional behavior of EDTA in the present system can be explained by assuming that EDTA in combination with permanganate forms a redox system; hence the initial rate of polymerization increases, as reported by Palit et al.[18]

The addition of alcohols such as methanol, ethanol, propanol, and butanol (Figure 5) has a retarding effect on the initial rate of polymerization as well as on maximum conversion. The depression in the rate of polymerization can be supposed to be due to the fact that these solvents[14] decrease the area of shielding of a strong hydration layer in aqueous medium, resulting in the termination of the radical end of the growing chain.

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**Registry No.** LiCl, 7447-41-8; NaCl, 7647-14-5; KCl, 7447-40-7; RbCl, 7791-11-9; $NH_4Cl$, 12125-02-9; $MnSO_4$, 7785-87-7; $KMnO_4$, 7722-64-7; NaF, 7681-49-4; $H_2SO_4$, 7664-93-9; EDTA, 60-00-4; CTAB, 57-09-0; sodium oleate, 143-19-1; methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 1-butanol, 71-36-3; acrylamide, 79-06-1; glyceric acid, 473-81-4.

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