Aqueous Polymerization of Acrylamide by Electrolitically Generated KMnO₄ Organic Acid Redox Systems

A. S. SARAÇ,* A. B. SOYDAN, and V. COKA

Technical University of İstanbul, Department of Chemistry, Maslak, 80626, İstanbul, Turkey

SYNOPSIS

Polymerization of acrylamide was carried out with potassium permanganate–malonic acid, potassium permanganate–tartaric acid, and potassium permanganate–citric acid redox initiator systems with and without electrolysis. The effect of potassium permanganate concentration, acrylamide concentration, and temperature on the polymerization yield was studied and molecular weights of polymers were determined and compared with electrolytic conditions. At low concentrations of potassium permanganate, continuously supplying Mn(III) has an advantage over the nonelectrolytic method for which polymerization did not occur under these conditions. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The well-known reaction between permanganate and organic reducing agents is known to involve free-radical intermediates and has been employed as a free-radical initiator of polymerization. The aqueous polymerization of acrylamide by a permanganate-reducing agent system has been investigated in detail.[1-7]

In the aqueous polymerization of acrylamide initiated by a permanganate-reducing agent redox system, it is thought that permanganate first reacts with acrylamide and the solution becomes brownish black which interacts with the reducing agent to produce free-radical (primary radicals) highly reactive Mn(III) ions. Mn(III) ions are supposed to be more reactive in producing free radicals (secondary radicals), capable of initiating polymerization of acrylamide.[7]

In this study, the polymerization of acrylamide initiated with KMnO₄–malonic acid, KMnO₄–citric acid, and KMnO₄–tartaric acid redox systems was studied under electrolytic and nonelectrolytic conditions. At low concentrations of cerium(IV), the

electrolytic method has an advantage over the nonelectrolytic method.[8,9] It is proposed that in the reaction media Mn(IV) ions are reduced to Mn(III) and Mn(II); then, Mn(II) ions can be recycled to Mn(III) by electrochemical means.
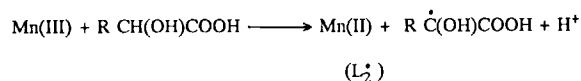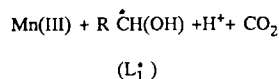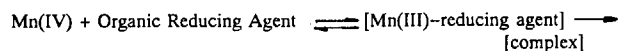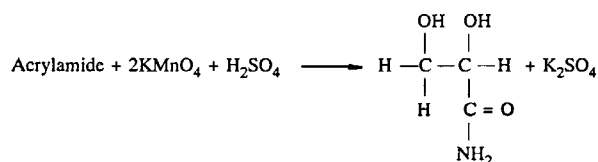
EXPERIMENTAL

Reagents

Potassium permanganate, tartaric acid, citric acid, malonic acid, acrylamide, and sulfuric acid were all Merck reagent-grade chemicals of highest purity and were used without further purification.
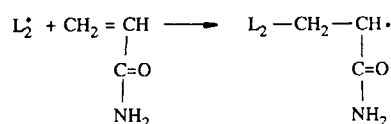
Polymerization Procedure

The polymerization was carried out in a three-necked flask equipped with a stirrer and a funnel for the addition of permanganate solution in a thermostated water bath. The reducing agent and acrylamide were dissolved in $0.05M$ H_2SO_4. The initial concentrations in the reaction mixture were $0.3M$ acrylamide and $0.02M$ of the reducing agent in these studies. The temperature of reaction media varied from 30 to 50°C and the concentration of permanganate varied from 1×10^{-3} to $2 \times 10^{-2}M$ for each
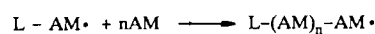
Acrylamide + 2KMnO$_4$ + H$_2$SO$_4$ $\longrightarrow$ H—$\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}$—$\underset{\underset{\underset{\underset{NH_2}{|}}{C=O}}{|}}{\overset{\overset{OH}{|}}{C}}$—H + K$_2SO_4$

Mn(IV) + Organic Reducing Agent $\rightleftharpoons$ [Mn(III)–reducing agent] $\longrightarrow$ [complex]

Mn(III) + R ĊH(OH) +H$^+$+ CO$_2$

(L$_1^\bullet$)

Mn(III) + R CH(OH)COOH $\longrightarrow$ Mn(II) + R Ċ(OH)COOH + H$^+$

(L$_2^\bullet$)

Initiation:

L$_2^\bullet$ + CH$_2$ = CH $\longrightarrow$ L$_2$—CH$_2$—CH$\bullet$
$\quad\quad\quad\quad$ | $\quad\quad\quad\quad\quad\quad\quad\quad$ |
$\quad\quad\quad\quad$ C=O $\quad\quad\quad\quad\quad\quad\quad$ C=O
$\quad\quad\quad\quad$ | $\quad\quad\quad\quad\quad\quad\quad\quad$ |
$\quad\quad\quad\quad$ NH$_2$ $\quad\quad\quad\quad\quad\quad\quad$ NH$_2$

Propagation:

L – AM$\bullet$ + nAM $\longrightarrow$ L-(AM)$_n$-AM$\bullet$

Termination:
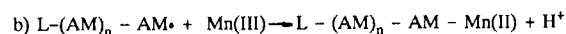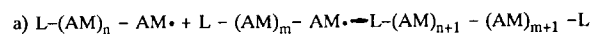
a) L-(AM)$_n$ – AM$\bullet$ + L – (AM)$_m$– AM$\bullet$$\longrightarrow$L-(AM)$_{n+1}$ – (AM)$_{m+1}$ –L

b) L-(AM)$_n$ – AM$\bullet$ + Mn(III)$\longrightarrow$L – (AM)$_n$ – AM – Mn(II) + H$^+$

Regeneration Mn(III) species electrolytically

$\quad\quad\quad\quad\quad\quad\overset{e'}{}$
Mn(II) $\longrightarrow$ Mn(III)

Scheme 1

reducing agent. The electrochemical polymerization was carried out in a three-necked flask; two graphite electrodes were used in a thermostated water bath, and the permanganate solution was added by a funnel for the electrolytic experiment with a d.c. current supplier unit.

Determination of Molecular Weights

For molecular weight determination, the samples of polyacrylamide were purified by twice precipitating from acetone and were dried under vacuum. The intrinsic viscosities of polymers were determined with an Ostwald-type viscometer at 30°C, the relationship of eq. (1) being used[11]:

$$[\eta] = 6.8 \times 10^{-4}\bar{M}_v^{0.66} \quad\quad (1)$$
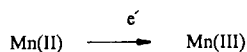
RESULTS AND DISCUSSION

Polymerization of acrylamide was carried out by using potassium permanganate–malonic acid, potassium permanganate–tartaric acid, and potassium permanganate–citric acid redox couples at various reaction temperatures and permanganate concentrations. Under the conditions of this study, it was found that at low concentrations of potassium permanganate there was no polymerization, but in the presence of electrolysis, polymer was obtained. First, the permanganate reacted with
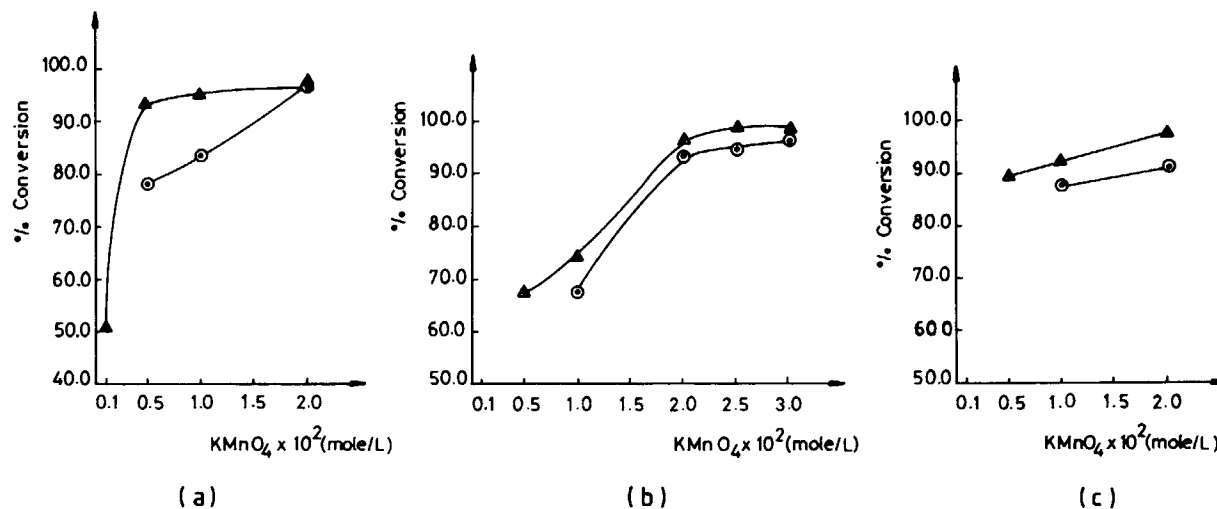

Figure 1 The effect of KMnO$_4$ concentration on the polymerization yield: (a) reducing agent: malonic acid; (b) reducing agent: citric acid; (c) reducing agent: tartaric acid. ($\triangle$) With electrolysis, ($\odot$) without electrolysis. Reducing agent: $2 \cdot 10^{-2}M$; acrylamide: $0.3M$; electrode: graphite; [H$_2$SO$_4$]: $0.05M$; temperature: 50°C; time: 15 min; potential: 2.5 $\mp$ 0.2 V.

acrylamide by producing a brownish solution of MnO_2 which interacted with carboxylic acid to produce corresponding free radicals (L_1). Mn(III) formed by this reaction also produced free radicals (L_2).

The reaction between potassium permanganate and organic reducing agents (tartaric and citric) acids and the polymerization of acrylamide probably proceeded as in Scheme I. For the malonic acid case, reaction proceeded with only secondary radicals.

Beside the termination by combination, there is also the possibility of metal ion termination. According to the atomic absorption measurements, the polymers contain Mn(II) species. "Organic Reducing Agent" indicates malonic, citric, or tartaric acid in Scheme 1. L_1 = primary radicals and L_2 = secondary radicals.

The regenerated Mn(III) ions can again react with organic acids to produce radicals which initiate the polymerization of acrylamide. Blank experiments were carried out either in the absence of reducing agents (malonic, citric, and tartaric acids) or potassium permanganate; there was no polymerization under experimental conditions with and without electrolysis. The effects of reducing agents, potassium permanganate concentration, acrylamide concentration, and temperature on the polymer conversion and molecular weight of polyacrylamide were studied with and without electrolysis.

Relation Between Conversion and Initiator Concentration

The polymerization of acrylamide with malonic, tartaric, citric acid, and potassium permanganate was carried out under similar conditions with and without electrolysis. Low concentrations of permanganate, $5 \cdot 10^{-3}$ mol/1, using electrolysis gave high conversion at about 63%; in the absence of electrolysis, no polymers were obtained (Fig. 1).

Relation Between Conversion and Temperature

Polymerization was carried out in potassium permanganate–malonic acid, potassium permanganate–tartaric acid, and potassium permanganate–citric acid redox systems at different temperatures (Fig. 2). At low temperatures, the conversion increased in the presence of electrolysis, compared to in the absence of electrolysis.

Relation Between Conversion and Acrylamide Concentration

The effect of acrylamide concentration was investigated at $1 \cdot 10^{-2} M$ potassium permanganate and
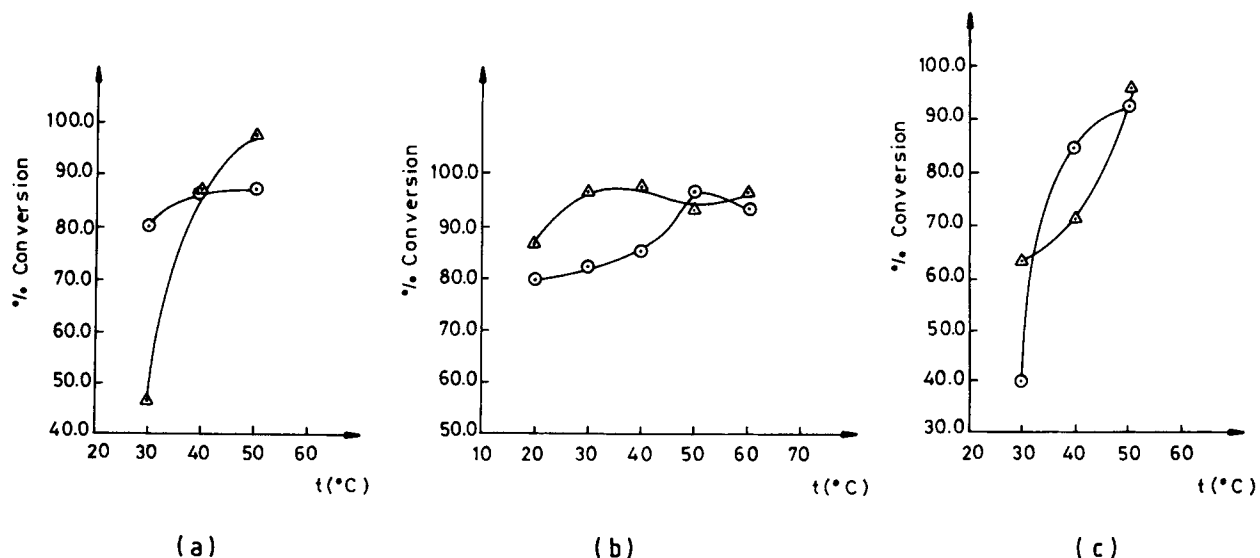

Figure 2 The effect of temperature on the polymerization yield: (a) reducing agent: malonic acid; (b) reducing agent: citric acid; (c) reducing agent: tartaric acid. ($\triangle$) With electrolysis, ($\bigcirc$) without electrolysis. Reducing agent: $2 \cdot 10^{-2} M$; acrylamide: $0.3M$; electrode: graphite; [H_2SO_4]: $0.05M$; [$KMnO_4$]: $5 \cdot 10^{-3} M$; electrode: graphite; time: 15 min; potential: 2.5 ∓ 0.2 V.
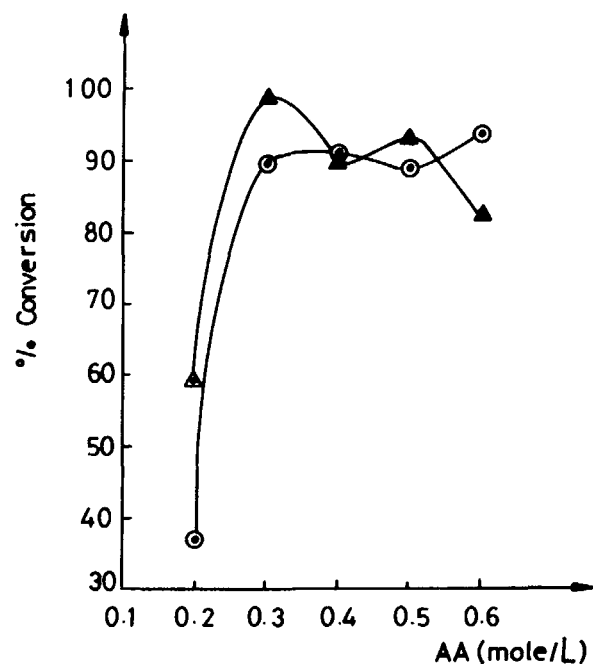
Figure 3 The effect of acrylamide concentration on the polymerization yield: (△) with electrolysis; (⊙) without electrolysis. Reducing agent: citric acid $2 \cdot 10^{-2}M$; [H_2SO_4]: $0.05M$; [$KMnO_4$]: $1 \cdot 10^{-2}M$; electrode: graphite; time: 15 min; potential: 2.5 ∓ 0.2 V.

Table I   Relationship Between Molecular Weights and Acrylamide Concentration

[AM] $\cdot 10^2$ mol dm^{-3}	Chemical Method (M_v)	Electrochemical Method (M_v)
0.2	3412	1296
0.3	18,470	12,547
0.4	23,384	15,893
0.5	26,072	29,561
0.6	Swelling	33,559

$2 \cdot 10^{-2}M$ citric acid concentrations in electrolytic and nonelectrolytic conditions (Fig. 3).

The effect of acrylamide on the yield was examined at five different concentrations under the same experimental conditions with and without electrolysis. A sharp increase was obtained at $0.3M$ acrylamide concentration by both methods and electrolytic conditions showed higher yields at all acrylamide concentrations (Fig. 3).

The molecular weights of polymers were also studied and compared with electrolytic conditions.
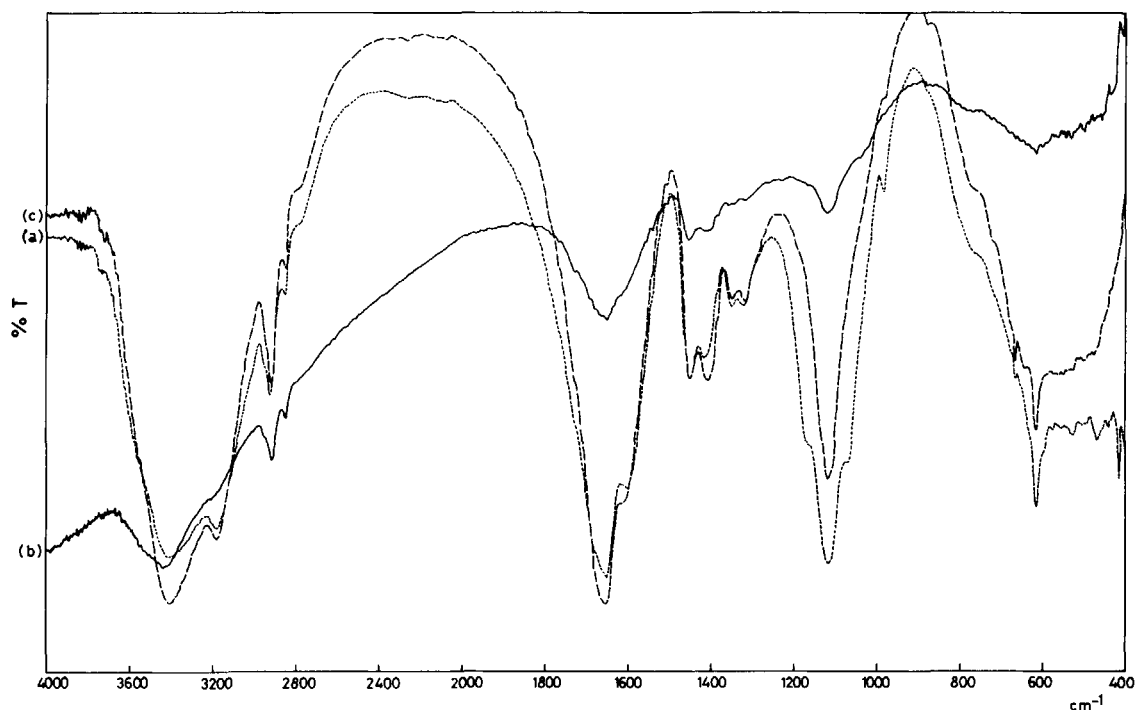

Figure 4   FTIR spectrum of polymers: (a) malonic acid–$KMnO_4$-initiated polyacrylamide; (b) citric acid–$KMnO_4$-initiated polyacrylamide; (c) tartaric acid–$KMnO_4$-initiated polyacrylamide.
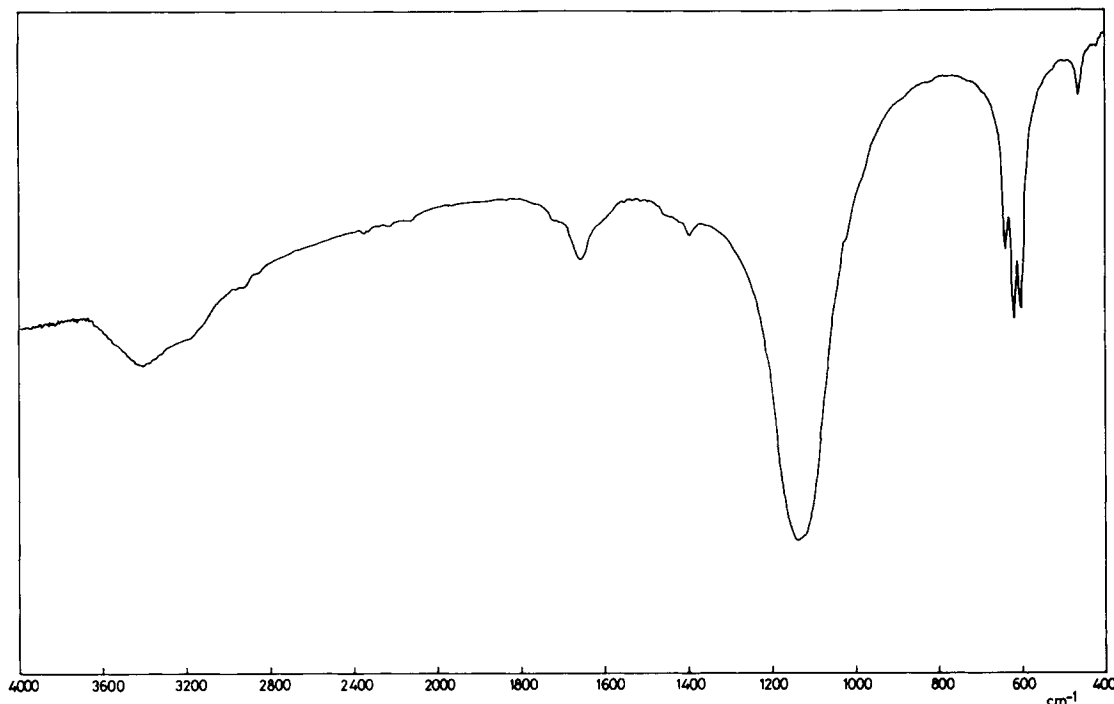
Figure 5   FTIR spectrum of H_2O_2-$KMnO_4$-initiated polyacrylamide.

Results are summarized in Table I. In general, the molecular weight of the polymers obtained increases by increasing the acrylamide concentration, but the molecular weight of polymers obtained by the electrolytic method is lower than by the nonelectrolytic method. The reason for that may be the increase in the number of radicals under electrolytic conditions, which results from the presence of the high concentration of Mn(III) obtained by recycling.

Spectrophotometric Results

FTIR spectra of citric, malonic, and tartaric acid–$KMnO_4$-initiated polyacrylamide show characteristic peaks of both polyacrylamide and carboxylic acid at about 1450 and 1350 cm^{-1} (Fig. 4). For comparison purposes, H_2O_2-$KMnO_4$-initiated polymerization was carried out electrolytically under the same experimental conditions. The FTIR spectrum of H_2O_2–$KMnO_4$-initiated polymer which is carried out in H_2SO_4 indicates the presence of SO_4^{2-} groups in the polymer at about 1100 and 600 cm^{-1} (Fig. 5).[12]

The presence of Mn in these polymers is supported by atomic absorption measurements. The quantity of Mn in the polymers is 3.2, 5, and 2.3% for citric, malonic, and tartaric acid-initiated polymers, respectively.

CONCLUSION

The experimental results indicate that the electrolytic method has an advantage over the nonelectrolytic method. At low concentrations of potassium permanganate, a high yield of polymers were obtained in the presence of electrolysis while no polymer was recovered under the same conditions in the absence of electrolysis. At higher concentrations of potassium permanganate, polymer yield reaches high values compared to nonelectrolytic conditions, due to the increase of Mn(III) ions.

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