

Electro-Induced Polymerization of Acrylamide Initiated by the Potassium Permanganate–Titriplex VI Redox System

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ABSTRACT: The polymerization of acrylamide (AAM) was carried out with a potassium permanganate–Titriplex VI redox initiator system with and without electrolysis. Because of the high metal-ion concentration in general, low-molecular-weight polymers were obtained (weight-average molecular weight = 2600–4000). The effect of potassium permanganate and AAM concentrations and temperature on the polymerization yield was studied and compared with results obtained under the same experimental conditions used for electrolysis. The results of Fourier transform infrared spectroscopy, atomic absorption spectrometry, and scanning electron microscopy (SEM) results are given. SEM micrographs of the polymer obtained by electrochemical methods exhibited smoother surfaces than those obtained by nonelectrolytic methods. In the absence of potassium permanganate, there was no polymerization under experimental conditions. A possible reaction mechanism is suggested. The electro-induced system resulted in about a 50% increase in the yield. Manganese content in the electro-induced and chemical polymerization systems were 2.7 and 8.2%, respectively, supporting the yield increase in the electro-induced system. A graphite electrode was used and resulted in a high yield and a fibrous polymeric structure. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1526–1534, 2001

Key words: electroinduced polymerization; acrylamide; Titriplex VI; redox polymerization

INTRODUCTION

The electro-induced cerium (IV) reducing-agent (EDTA) polymerization of acrylamide (AAM) has been studied, and the parameters have been well established.¹ In the electrochemical polymerization of acrylamide, Ce(IV) salt malonic acid or citric acid² and oxalic acid³ redox couples were used. The chemical polymerization by Ce(IV)-poly(amino carboxylic acids) [i.e., EDTA, diethylene triamine penta acetic acid (DTPA), ethylenedioxybis(ethylenenitrilo) tetraacetic acid (EGTA), and nitriloacetic (NTA), which have strongly chelating properties] was studied with different H⁺

concentrations, initiator concentrations, and reaction times.⁴ The initiation of polymerization proceeded through the formation of the free radical after decarboxylation of the carboxyl group of poly(amino carboxylic acid). Results indicate that the termination of the polymerization reaction was mainly mutual termination.

The reaction between permanganate and organic reducing agents is known to include free-radical intermediates and has been employed as a free-radical initiator of polymerization. The aqueous polymerization of AAM by permanganate-reducing-agent systems has been investigated in detail.^{5–11}

In the aqueous polymerization of AAM initiated by a permanganate-reducing-agent system, it is thought that permanganate first reacts with

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AAm and produces immediately a brownish black solution that interacts with the reducing agent to produce free radicals (primary radicals), highly reactive Mn(III) ions. Mn(III) ions are supposed to be more reactive to produce free radicals (secondary radicals), which are capable of initiating the polymerization of AAm.¹²

In this study, the polymerization of AAm was carried out with a potassium permanganate–Titriplex VI (EGTA) redox initiator system with and without electrolysis to demonstrate the advantage of an electro-induced system over chemical methods.

EXPERIMENTAL

Reagents

Potassium permanganate, AAm, and sulfuric acid were all Merck reagent-grade chemicals of the 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 a permanganate solution in a thermostated water bath. The reducing agent and AAm were dissolved in 0.25M H₂SO₄. The initial concentrations of the reaction mixtures were 0.3M for AAm and 2 × 10⁻² M for the reducing agent in this study. The temperature of the reaction media varied from 20 to 60°C, and the concentration of permanganate varied from 1 × 10⁻³ to 5 × 10⁻² M. 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 via a funnel for the electrolytic experiment with a direct current supplier unit. Then, a calculated amount of the permanganate solution was added dropwise for 6–7 min while the mixture was stirred. After 30 min, the polymers were precipitated with a large amount of acetone to free them from any residual monomer and dried under vacuum at room temperature for 2–5 days.

The molecular weights of the polymers were determined with an Ubbelohde-type viscometer at 30°C; the equation used was the following:¹³

$$[\eta] = 68 \times 10^{-3} \cdot M_n^{0.66}$$

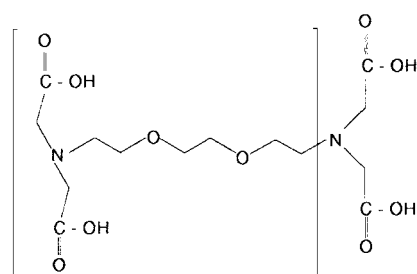
Characterization

The infrared spectra of the products were recorded with a Jasco 5300 Fourier transform infrared (FTIR) spectrophotometer with KBr discs. A JEOL JSM T840 scanning electron microscope was used for morphological studies.

RESULTS AND DISCUSSION

AAm polymerization was carried out at various reaction temperatures and permanganate concentrations with potassium permanganate–Titriplex VI redox couples. Under the conditions of this study and on the basis of the findings of a previous study,¹² we can tentatively propose that permanganate first reacts with AAm by producing a brownish black solution of MnO₂ in addition to a reaction of permanganate with water [Mn(IV)], which interacts with carboxylic acid to produce corresponding free radicals (L₁ ·) and hydroxyl radicals. The Mn(III) formed by this reaction produces free radicals (L₂ ·).

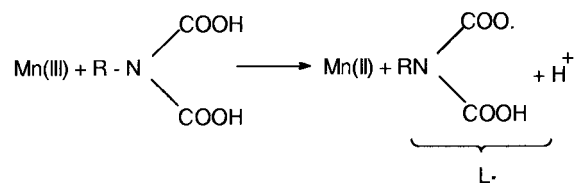
The reaction between potassium permanganate and the organic reducing agent (Titriplex VI) and the polymerization of AAm probably proceeded as in Scheme 1. In the reaction medium, Mn(III) reacts with EGTA to give a radical by hydrogen abstraction or decarboxylation but most probably breaks the R—O—R band.



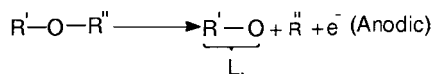
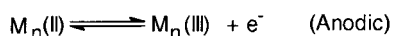
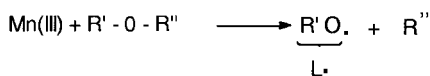
Titriplex VI

Besides the termination by combination, there is also the possibility of metal-ion termination. According to the atomic absorption measurements, the polymers contained Mn(II) species.

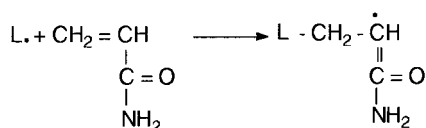
The regenerated Mn(III) ions can again react with the organic reducing agent to produce radicals that initiate the polymerization of AAm. Blank experiments were carried out in the absence of potassium permanganate. There was no polymerization under experimental conditions



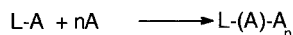
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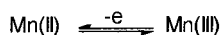
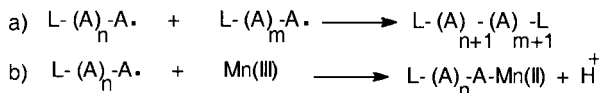
Initiation :



Propagation :

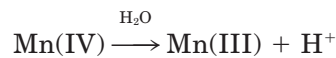


Termination:



Scheme 1

with or without electrolysis, but in the absence of the organic reducing agent, there was no polymerization under experimental conditions with or without electrolysis. At $5 \times 10^{-2} M$ potassium permanganate and $0.25M$ H_2SO_4 with electrolysis, the reaction gave a much higher conversion, about 133%; without electrolysis, the conversion was about 77%. The conversion was calculated with the following equation: (polymer weight/monomer weight) \times 100. Mn(III) and Mn(II) formation in the reaction mechanism was thought, in addition to the direct oxidation of AAm by the metal ions Mn(VII) to Mn(IV) and the reduction of metal ions by the solvent, to play a role in terms of the following reaction:¹⁴



The effects of the reducing agent, potassium permanganate concentration, AAm concentration, and temperature on the polymer conversion, the type of electrode, and the molecular weight of the polymer were studied with and without electrolysis.

Relation Between Conversion and Initiator Concentration

The polymerization of AAm was carried out with the potassium permanganate–Titriplex VI redox system at different permanganate concentrations (Fig. 1). At a low concentration of permanganate ($5 \times 10^{-3} M$), conversion was about 52%, but the high concentration of permanganate conversion was about 68.5%.

Relation Between Conversion and Temperature

The effect of temperature on the yield was examined at six different temperatures under the same experimental conditions, with and without electrolysis. A sharp increase was obtained at 50°C without electrolysis, and a yield of about 80% was observed (Fig. 2).

Relation Between Conversion and AAm and Titriplex VI Concentration

The effect of AAm concentration was investigated at $5 \times 10^{-2} M$ potassium permanganate and $2 \times 10^{-2} M$ Titriplex VI concentrations under electrolytic conditions (Fig. 3). An increase in the polymer yield obtained by an increase in the AAm concentration was observed. It seems that within the limit of experimental errors, Titriplex VI does not have much effect on the conversion.

Relation Between Conversion and Electrode Type

The effect of the electrode type on conversion was studied, and it was found that the effect of the

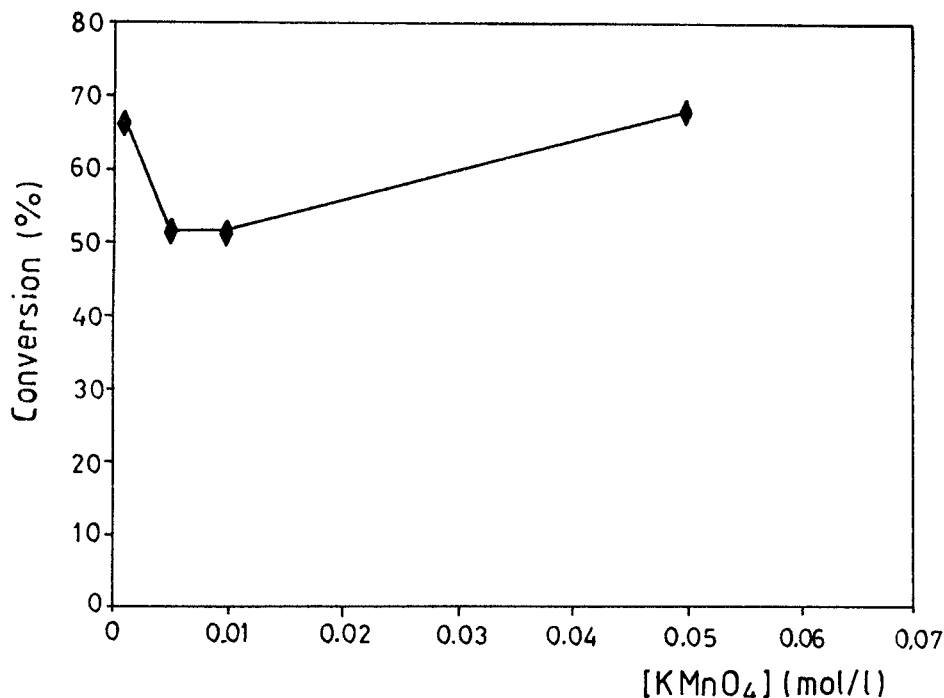


Figure 1 Effect of potassium permanganate concentration on the yield. The electrode was graphite. $[AA] = 0.3M$; $[Titriplex\ VI] = 2 \times 10^{-2} M$; $[H_2SO_4] = 0.25M$; $T = 60^\circ C$; $t = 30\ min$; potential = 4.0 V; $I = 140-143\ mA$.

electrode type on the polymer yield was significant (Fig. 4). In all these experiments, three types of electrodes were used: graphite, platinum, and Cr—Ni. The graphite electrode showed a higher yield than other metal electrodes and was used the most. In experiments in which Cr—Ni electrodes were used, the product was red-brown in color, and the yield was low. Metal ions that dissolved formed complexes with the functional groups of the polymer.

Relation Between Conversion and Acid Concentration

The relationship between the conversion of polymers and the concentration of H_2SO_4 is shown in Figure 5. At a high concentration of H_2SO_4 , conversion fell, probably because of the acidity of the medium acting as an inhibiting agent for the formation of the polymer, and the two peaks observed could have been caused by the presence of different amounts of several oxidation states of manganese ions. At a lower acid concentration, the manganese ion complex governed the generation of primary radicals and led to an increase in the conversion.

Effect of Applied Potential

The potential was changed from 1.2 to 2.0 V. We increased the current passing through the electrolyte by increasing the potential, so the conversion increased (Fig. 6). The conversion was increased by the increase of potential, which was caused not only by a current increase according to Ohm's law but also by the formation of more radicals by the formation of more Mn(III).

The molecular weight of the polymer was also studied and compared under electrolytic and nonelectrolytic conditions. By the nonelectrolytic method, the molecular weight of the polymer obtained was 4000, but by the electrolytic method, the molecular weight of the polymer obtained was 2600. The molecular weight of the polymer obtained by the electrolytic method was lower than that obtained by the nonelectrolytic method. The reason for this was termination by Mn(III); under electrolytic conditions, high concentrations of Mn(III) were obtained by recycling. However, some of the polymers were not soluble in water because of gel formation, so the molecular weight of these polymers could not be determined.

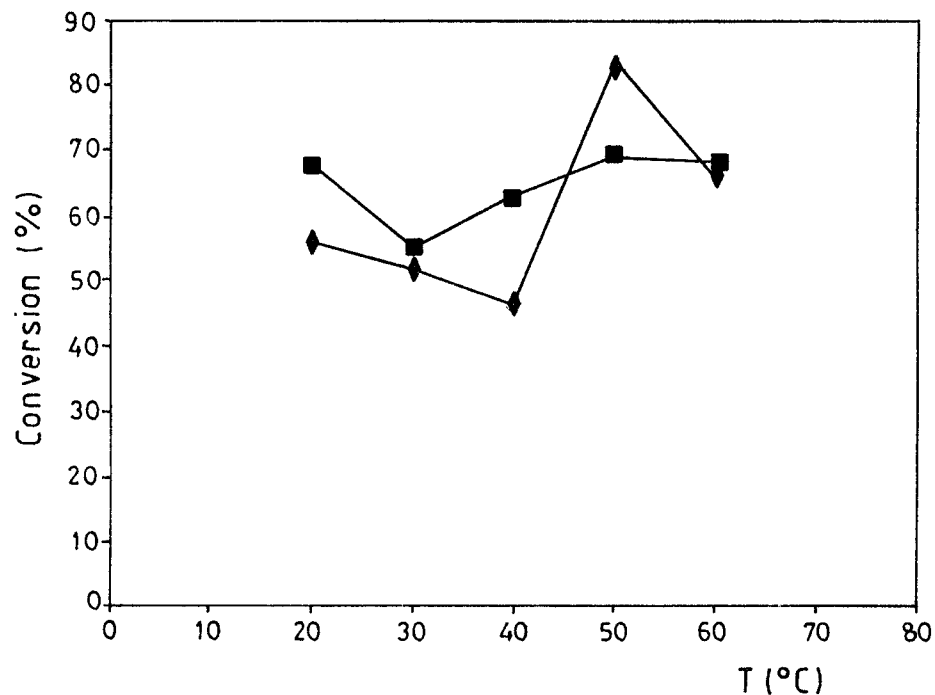


Figure 2 Effect of temperature on the yield without electrolysis (♦) and with electrolysis (■). The electrode was graphite. [AA] = 0.3M; [Titriplex VI] = 2×10^{-2} M; [KMnO₄] = 5×10^{-2} M; [H₂SO₄] = 0.25M; *t* = 30 min; potential = 4.0 V; *I* = 110–114 mA.

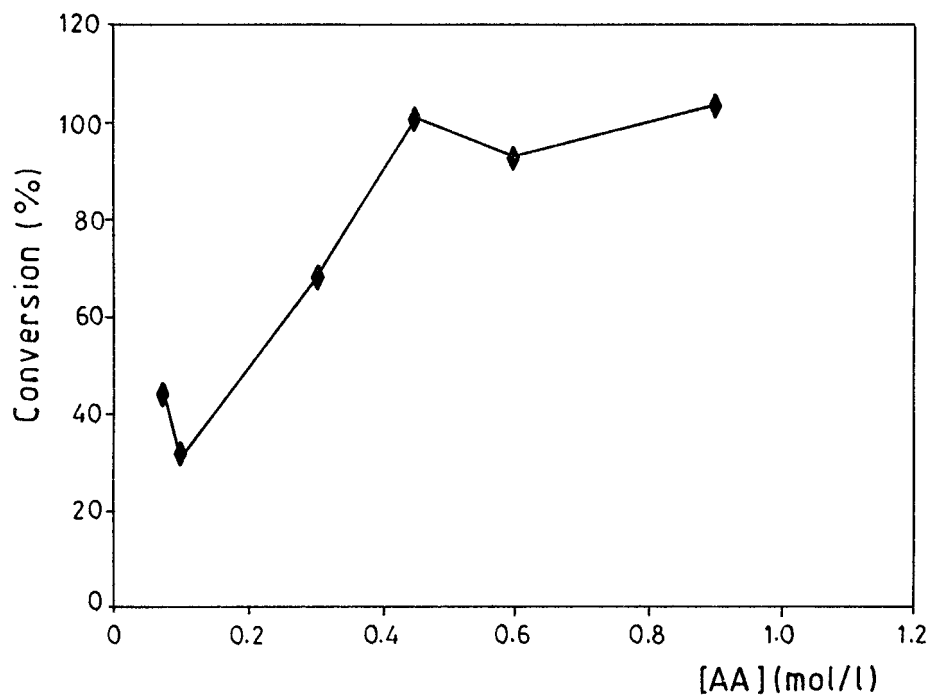


Figure 3 Effect of AAm concentration on the yield. The electrode was graphite. [Titriplex VI] = 2×10^{-2} M; [KMnO₄] = 5×10^{-2} M; [H₂SO₄] = 0.25M; *T* = 60°C; *t* = 30 min; potential = 4.0 V; *I* = 100–101 mA.

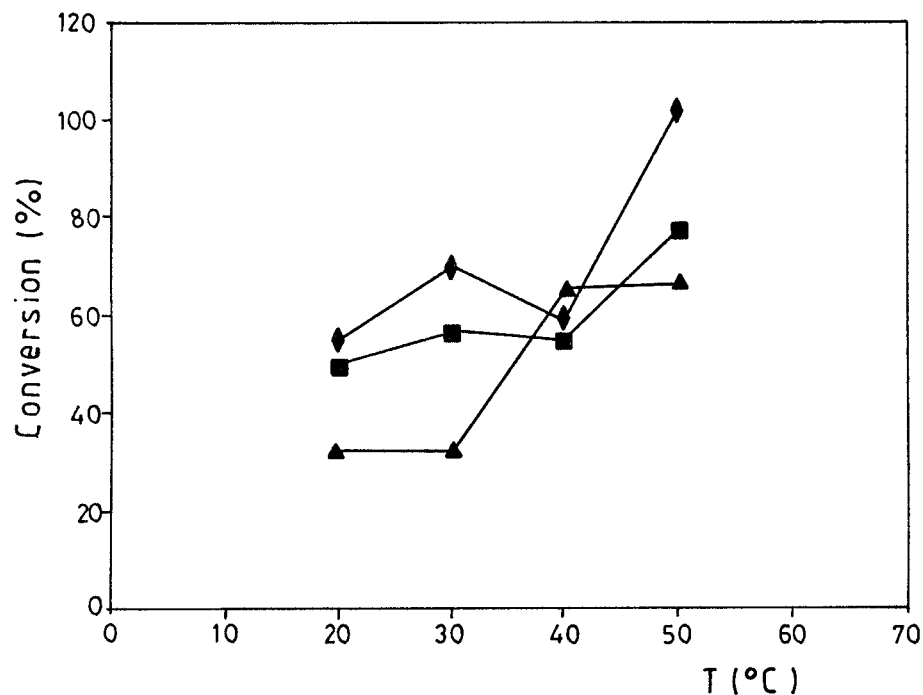


Figure 4 Effect of electrode type on the yield with graphite (♦), platinum (■), and Cr-Ni (▲) electrodes. [AA] = 0.3M; [Titriplex VI] = 2×10^{-2} M; [KMnO₄] = 5×10^{-2} M; [H₂SO₄] = 0.25M; T = 60°C; t = 30 min; potential = 2.0 V.

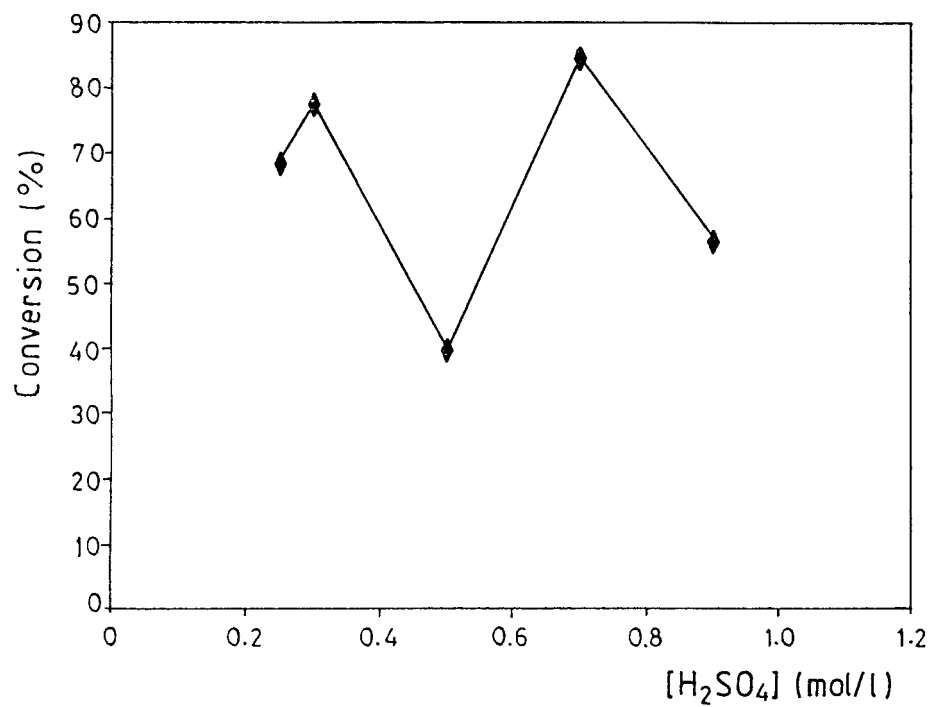


Figure 5 Effect of acid concentration on the yield. [AA] = 0.3M; [Titriplex VI] = 2×10^{-2} M; [KMnO₄] = 5×10^{-2} M; T = 60°C; t = 30 min; potential = 4.0 V; I = 130 mA.

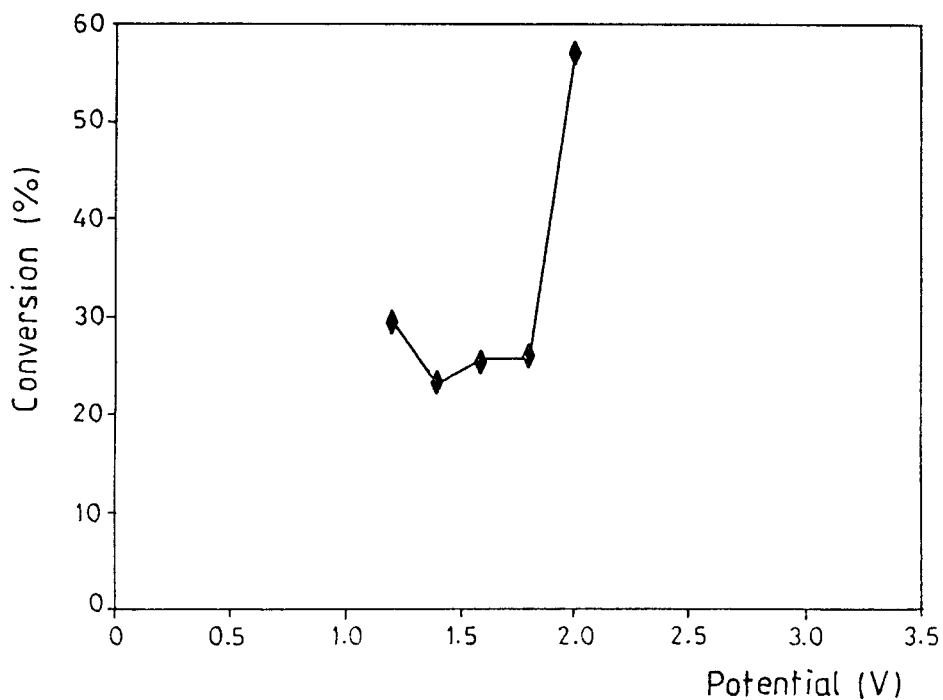


Figure 6 Effect of potential on the yield. [AA] = 0.3M; [Titriplex VI] = 2×10^{-2} M; [H₂SO₄] = 0.25M; T = 60°C; t = 30 min.

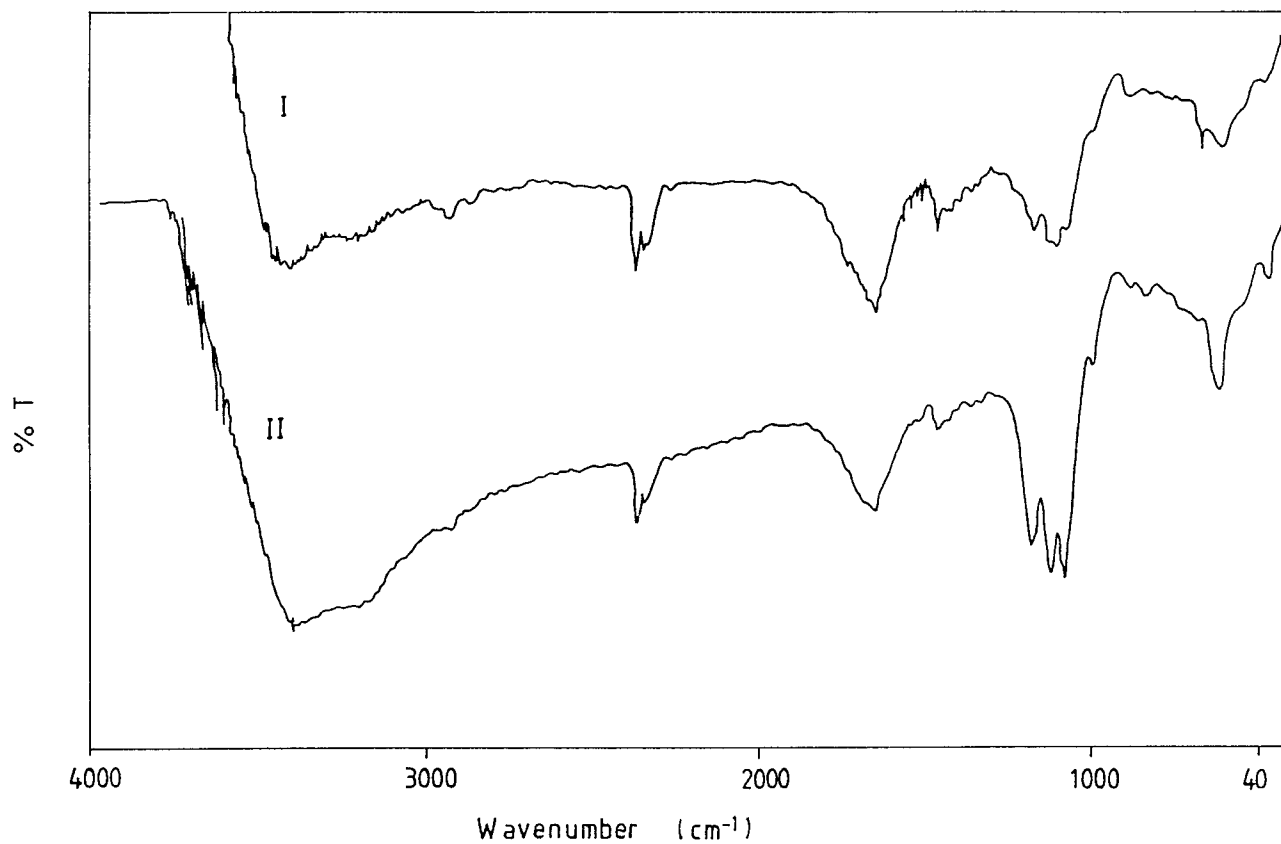


Figure 7 FTIR spectra of the polymers with electrolysis (I) and without electrolysis (II).

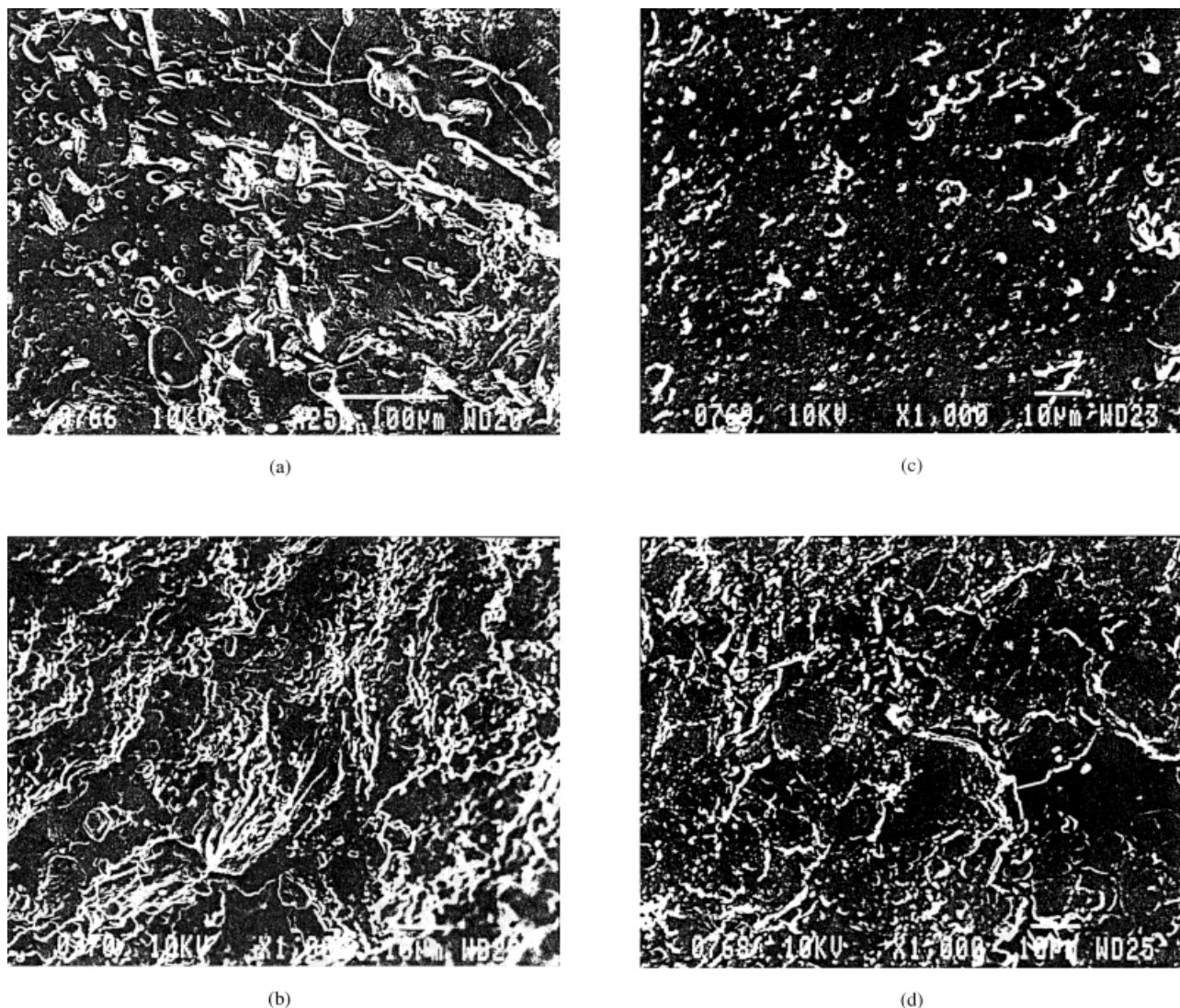


Figure 8 SEM micrographs of the polymers (a) without electrolysis, (b) with electrolysis by the graphite electrode, (c) with electrolysis by the platinum electrode, and (d) with electrolysis by the graphite electrode.

FTIR and Atomic Absorption Spectrometric Results

The FTIR spectra of polymers obtained by the permanganate–Titriplex VI redox system by the electrolytic and nonelectrolytic methods are shown in Figure 7. The FTIR spectra of the polymers showed characteristic peaks of polyacrylamide at about 1650 cm^{-1} , and C—N stretching and C—H stretching were seen at around 1430 and 2950 cm^{-1} , respectively.

The amount of manganese ions in polyacrylamide obtained with the potassium permanganate–Titriplex VI redox system was determined

with atomic absorption measurements. Atomic absorption spectrometric results indicated the presence of Mn in the polymer structure, which could have been caused by an interaction between polyacrylamide containing Titriplex VI end groups and manganese ions. For the initial $5 \times 10^{-3}\text{ M}$ permanganate concentration, the quantity of Mn in the polymer was 0.43% by the electrolytic method, and at a $5 \times 10^{-2}\text{ M}$ KMnO_4 concentration, the quantity of Mn in the polymer was 2.7% by the electrolytic method and 8.2% by the nonelectrolytic method. This

was determined by atomic absorption measurements

That a higher molecular weight polymer was obtained with the nonelectrolytic method rather than with the electrolytic method indicated that the termination in the electrochemical method was favored because of higher metal-ion (in the high valance state) and electrochemical termination.

Scanning Electron Microscopy Results

The difference in the structures of polymers formed in the presence and absence of electrolysis was also seen in the results of scanning electron microscopy (SEM; Fig. 8). The polymers produced by the nonelectrolytic method [Fig. 8(a)] in general had smooth surfaces, and the electrolytic method showed some differences [Fig. 8(b)]. Actually, their physical appearance and properties were flexible. A polymer produced by platinum electrodes [Fig. 8(c)] had more pores. However, polymers produced with a graphite electrode had smaller pores and a cracked structure. Also, polymers produced by graphite electrodes showed some fibers in their structure [Fig. 8(d)].

CONCLUSIONS

A greater increase in the yield was obtained with an electro-induced system than with the chemical polymerization method, probably because of direct electron transfer from EGTA to anode-forming initiating radicals for the polymerization. Manganese content, which was determined by atomic absorption spectrometry, for electro-induced and chemical polymerization methods also indicated the possibility of anodic oxidation of EGTA in addition to electrogeneration of the metal ion [Mn(II) to Mn(III)].

The electro-induced system seems to be a more effective method than the chemical initiation method because of environmental reasons; in the

meantime, high yields were obtained with this procedure. High yields were also obtained previously with the electro-induced polymerization of AAm by Ce(IV). Because of termination by metal ions present in a high concentration, generally low molecular-weight polymers were obtained for the electrolytic (2600) and nonelectrolytic (4000) methods, respectively. Among the working electrodes that were used in this study (i.e., Pt, Cr—Ni, and graphite), the use of graphite resulted in higher yields than the use of the others and also resulted in a fibrous polymeric structure.

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