

# Polymerization of Acrylamide Initiated with Electrogenerated Cerium(IV) in the Presence of EDTA

A. SEZAI SARAÇ,\* CANDAN ERBİL, and A. BAHATTIN SOYDAN

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

## SYNOPSIS

Polymerization of acrylamide was carried out with cerium(IV)-EDTA redox initiator system with and without electrolysis. The effect of temperature, time, cerium(IV), and EDTA concentrations on the polymerization yield and molecular weight were studied and compared with electrolytic conditions. At low concentrations of cerium(IV) the electrolytic method continuously supplying Ce(IV) from Ce(III) has an advantage over the nonelectrolytic method for which polymerization did not occur under these conditions. A possible polymerization mechanism is suggested.

## INTRODUCTION

Ceric salts<sup>1,2</sup> or ceric salt-reducing agent systems in aqueous acidic solution are used as initiators of vinyl polymerization. The well-known reaction between ceric (IV) salt and an organic reducing agent such as alcohol,<sup>3,4</sup> glycol,<sup>5</sup> aldehyde,<sup>6</sup> ketone,<sup>7</sup> and carboxylic acid<sup>7,8</sup> is a redox reaction. The oxidation-reduction produces cerous ions and transient free-radical species capable of initiating vinyl polymerization. The mechanism of the ceric-salt-initiated graft copolymerization of vinyl monomers such as acrylamide and acrylonitrile has been studied in detail earlier. Starch,<sup>9</sup> cellulose,<sup>10</sup> and ketonic resins<sup>11</sup> were among the most effective polymeric backbones for grafting.

The rates of oxidation of several chelating agents<sup>12,13</sup> and hydroxy acids<sup>14</sup> with Ce(IV), in acid media, have been determined before. In these systems, Ce(IV) ions are known to form a complex with polyaminocarboxylic acids and hydroxy acids, and this complex acts as source of free radicals which initiates polymer formation. Since polyaminocarboxylic acids are used as chelating agents, in the decontamination of living organisms and as substitutes for phosphates in detergents, it is interesting to study polymerization of acrylamide containing polyaminofunctional groups which might serve as

ion-chelating resin and conducting water soluble polymers.

In this study, the Ce(IV)-EDTA redox system was used to initiate the polymerization of acrylamide. The effects of temperature, time, Ce(IV) and EDTA concentrations on the polymerization yield and molecular weight were studied and compared with the results obtained under the same experimental conditions in the presence of electrolysis. Most of the Ce(IV) in the reaction media is reduced to Ce(III): Ce(III) is not active for polymerization of vinyl monomers and can be recycled electrochemically. This so-called induced chemical-electrochemical process is especially suitable for commercial polymerization of vinyl monomers because of the use of lower Ce(IV) concentrations.

## EXPERIMENTAL

### Reagents

Ceric sulfate  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , ethylenedinitrilotetraacetic acid, EDTA (Titriplex III), acrylamide 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 round-bottomed flask equipped with a stirrer by adding the

calculated amount of Ce(IV) salt solution to an aqueous solution of monomer and titriplex III. After 1 h, the solution was poured into an excess of acetone to precipitate the gross polymer. The conversion of acrylamide was determined by direct weighing of polyacrylamide dried in air.

The molecular weights of the polymers were determined by using an Ostwald viscometer at 30°C for aqueous solutions and were calculated from the viscosity data by using the equation<sup>15</sup>

$$[\eta] = 6.80 \times 10^{-4} M^{0.66}$$

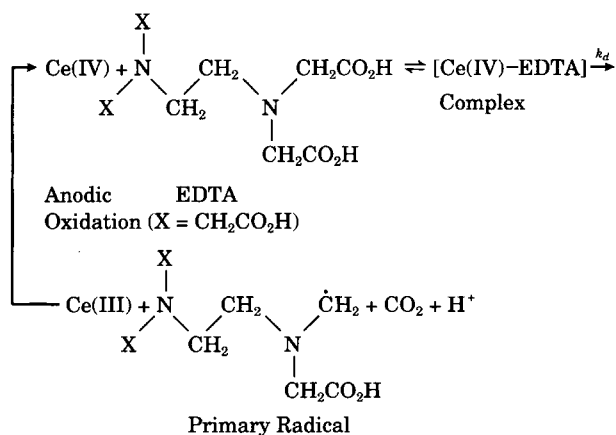
## RESULTS AND DISCUSSION

Under the conditions of this study, it was found that there was no polymerization of acrylamide even after 60 min when ceric sulfate alone was used as an initiator, but with Ce<sup>4+</sup>-EDTA redox initiator it was noticed that the polymerization reaction proceeded without any induction period.

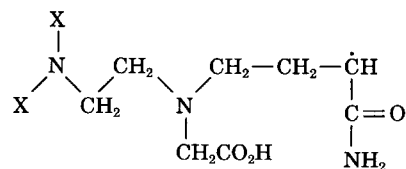
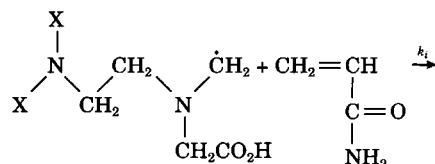
### Reaction Scheme

The following scheme explains the experimental results obtained.

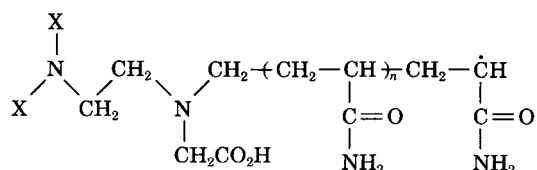
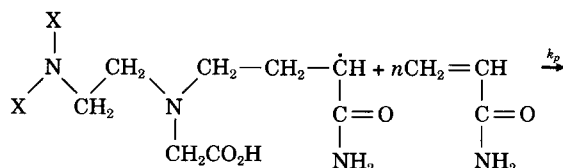
#### Reaction of ceric ion with EDTA:



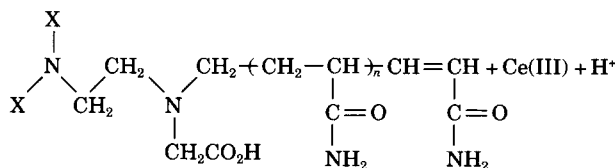
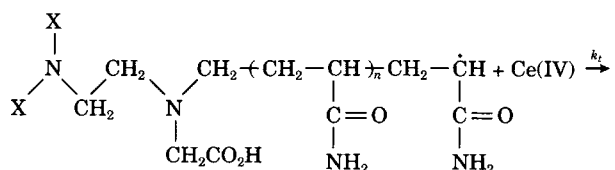
#### Initiation of polymerization by reaction of primary radical with acrylamide:



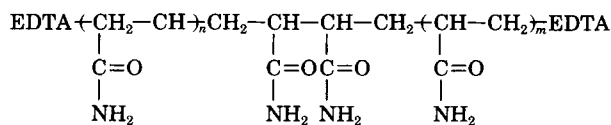
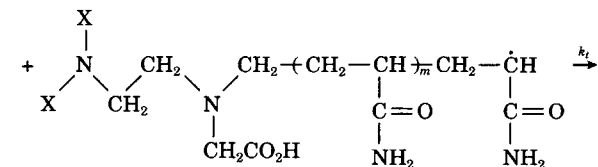
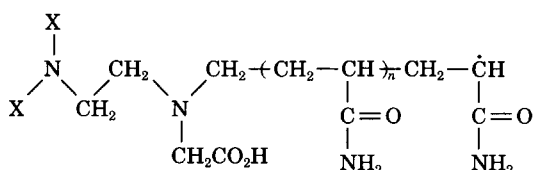
#### Propagation:



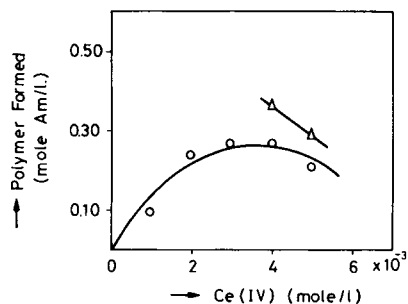
#### Termination by Ce(IV):



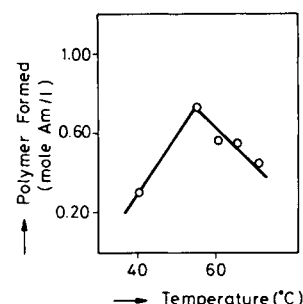
#### Mutual termination:



The reduced polymerization reagent, Ce(III), was reoxidized anodically to assure a certain amount of



**Figure 1** Effect of Ce(IV) concentration on the yield: (O) with electrolysis; (Δ) without electrolysis. [EDTA] =  $2.00 \times 10^{-2}$  mol/L; [acrylamide] = 0.60 mol/L;  $T = 55^\circ\text{C}$ ;  $t = 60$  min; electrode = graphite; voltage = 2.5–3 V; current = 40 mA.

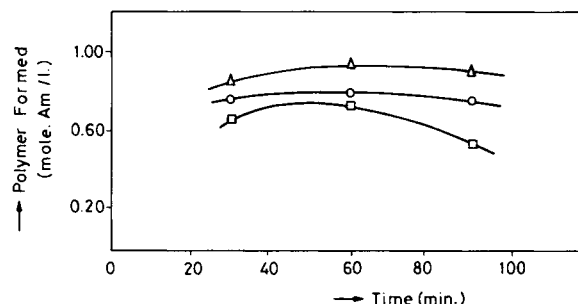


**Figure 2** Plot of polymer yield vs. reaction temperature: [Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O] =  $1.00 \times 10^{-2}$  mol/L; [EDTA] =  $4.00 \times 10^{-2}$  mol/L; time = 60 min.

Ce(IV) present in media. By using this technique, much lower Ce(IV) concentration for redox polymerization of acrylamide was used compared to nonelectrolytic method. The results are shown in Figure 1 and Table I.

The most striking feature is that there is no polymerization at concentrations below  $4 \times 10^{-3}$  M ceric sulfate in the absence of electrolysis. The molecular weights of the polymers in the system with electrolysis also showed a sharp increase at concentrations below  $4 \times 10^{-3}$  mol/L Ce(IV); these results are presumed to be related to the termination reaction by the recombination of polymer radicals.

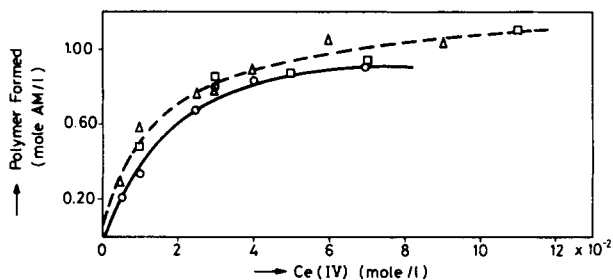
The effect of the electrode type on the conversion was studied and showed that the type of electrode on the polymer yield was significant (Table II). Although molecular weight of polyacrylamide produced with lead electrode system was significantly higher than the others, graphite was the best electrode among metals tried.



**Figure 3** Plots of polymer yield vs. reaction time in the Ce<sup>4+</sup>–EDTA-initiated polymerization of acrylamide. Reaction temperature = 55°C. (O) With electrolysis, [Ce<sup>4+</sup>] =  $3.00 \times 10^{-2}$  M; [EDTA] =  $2.00 \times 10^{-2}$  M. (□) With electrolysis [Ce<sup>4+</sup>] =  $1.00 \times 10^{-2}$  M; [EDTA] =  $4.00 \times 10^{-2}$  M. (Δ) Without electrolysis [Ce<sup>4+</sup>] =  $3.00 \times 10^{-2}$  M; [EDTA] =  $2.00 \times 10^{-2}$  M.

**Table I** Effect of (Ce<sup>4+</sup>) and Electrolysis on Yield and Molecular Weight for the Ceric Ammonium Sulfate–EDTA Redox System in Sulfuric Acid

Ce(IV) (mol/L)	EDTA (mol/L)	With Electrolysis		Without Electrolysis	
		Yield (mol AM/L)	Mol Wt (mol AM/L)	Yield (mol AM/L)	Mol Wt (mol AM/L)
0.0010	0.020	0.096	$6.50 \times 10^4$	—	—
0.0020	0.020	0.240	$7.10 \times 10^4$	—	—
0.0030	0.020	0.268	$1.48 \times 10^5$	—	—
0.0040	0.020	0.267	$1.01 \times 10^6$	0.365	$8.39 \times 10^4$
0.0050	0.020	0.210	$5.98 \times 10^4$	0.290	$1.02 \times 10^6$



**Figure 4** The effect of Ce(IV) concentration on the yield. (O) with electrolysis [EDTA] =  $2.00 \times 10^{-2}$  mol/L; (Δ) without electrolysis [EDTA] =  $2.00 \times 10^{-2}$  mol/L; (□) without electrolysis [EDTA] =  $4.00 \times 10^{-2}$  mol/L. Temperature = 55°C; time = 60 min; electrode = graphite; [acrylamide] = 0.60 mol/L.

**Table II** Effect of Electrode Type on Yield and Molecular Weight<sup>a</sup>

Electrode Type	Yield (mol AM/L)	Mol Weight $\times 10^4$
Graphite	0.661	3.28
Lead	0.599	5.26
Cr/Ni	0.408	2.04

<sup>a</sup> Time = 30 min, [Ce(IV)] = 0.010M, [EDTA] = 0.040M, voltage = 2.5–3 V, current = 40 mA, and temperature = 55°C.

The effect of the polymerization temperature and time on the yield was examined at five different temperatures and two different Ce(IV) and EDTA concentrations under the same experimental conditions with and without electrolysis (Figs. 2 and 3).

The yield rises, attains a maximum at about 55°C, and then falls at higher temperatures. The molecular weight runs parallel with this (Table III). A similar trend in the yield was also observed by Akar et al.<sup>11</sup> and Palit and Konar.<sup>16</sup> This is probably due to a good portion of the initiating species being destroyed at higher temperatures by side reactions.

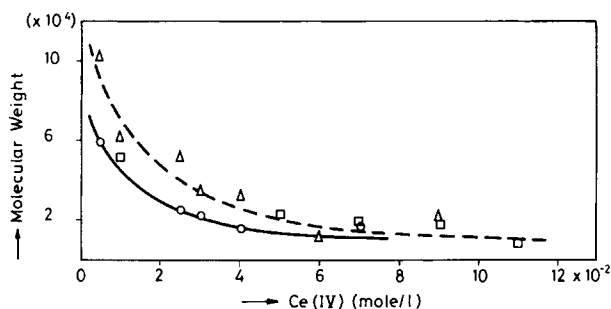
By considering the effect of the polymerization time on the yield, the polymerization was carried out at three different times (Fig. 3). The results clearly show that the polymerization yield in the presence and absence of electrolysis and at two different Ce(IV) and EDTA concentrations was highest after 60 min.

Slightly lower yields and molecular weights obtained at high concentrations of Cerium(IV) for the electrolytic method compared to the nonelectrolytic method might be due to a steady high concentration

**Table III** Effect of Temperature on Yield and Mol Weight<sup>a</sup>

T (°C)	Yield (mol AM/L)	Mol Wt $\times 10^4$
40	0.296	6.31
55	0.737	6.30
60	0.556	4.56
65	0.542	2.99
70	0.450	3.09

<sup>a</sup> [Ce(IV)] = 0.010M, time = 60 min, voltage = 2.5–3 V, [EDTA] = 0.4040M, electrode = graphite, current = 40 mA.



**Figure 5** The effect of Ce(IV) concentration on the molecular weight of polymer formed: (O) with electrolysis [EDTA] =  $2.00 \times 10^{-2}$  M; ( $\Delta$ ) without electrolysis [EDTA] =  $2.00 \times 10^{-2}$  M; ( $\square$ ) without electrolysis [EDTA] =  $4.00 \times 10^{-2}$  M.

of Cerium(IV) produced simultaneously at the anode, which also terminates the polymerization (Figs. 4 and 5). An increase in the polymer yield and decrease in the molecular weight by increasing Ce(IV) concentration was also observed in the presence of dicarboxylic and hydroxy-carboxylic acids instead of EDTA. At high concentrations of Cerium(IV), molecular weight of polymer reaches a minimum constant value, in both electrolytic and nonelectrolytic method (Fig. 5), which is also consistent with the idea of Cerium(IV) termination of polymer.

## CONCLUSION

These results show that the electrolytic method has an advantage over the nonelectrolytic method at very low concentrations of Cerium(IV), which can be continuously regenerated during the electrolytic process. Synthesis of polyaminocarboxylic groups containing polyacrylamides and other polymers might also have a technical importance, because of chelating and conductance properties of these groups.

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