Electrochemically Induced Redox Polymerization of Acrylamide

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ABSTRACT: Polymerization of acrylamide (AA) has been studied in aqueous solution in the presence of a Ce(IV) salt-oxalic acid initiator system in an electrochemical cell with and without separation of anolyte and catholyte. For reactions that required the cathode and anode sections to be analyzed individually, a cell whose compartments were divided by a sintered glass disk of the medium porosity was employed. Polymerization was initiated by a free radical that is formed by the fast reaction of oxalic acid and Ce(IV). The electrolysis of the reaction solution results in regeneration of Ce(IV), which can oxidize oxalic acid to produce radicals. The effect of sulfuric acid and cerium (IV) salt concentration and temperature on the yield of electroinitiated polymerization in different cell designs and structural identification of products were performed. Reaction was also followed by cyclic voltametric measurements, and a mechanism was proposed. Results indicated that the electrolysis method with a divided cell (85% conversion) shows advantages, compared with nonelectrolytic (5% conversion) and with undivided electrochemical cell (25% conversion) methods where a high concentration of initiator was used. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 861–869, 1999

Key words: cerium(IV)-oxalic acid redox couple; electro-induced polymerization; acrylamide

INTRODUCTION

Due to its high oxidation power of ceric salts and clean stoichiometry, Ce(IV)-reducing agent redox systems are widely used in polymerization of vinyl monomers in aqueous solution.^{1–8} Acrylamide is one of the most used vinyl monomers that is initiated with different metal–organic compounds for redox coupling.^{9–19} In our previous studies, on redox systems, we reported involving ceric salts coupled with several carboxylic, polyaminocarboxylic, and amino acids.^{20–23} On the other hand, polymerization of acrylamide with Ce(IV)–polyamino carboxylic acid as well as tartaric, malonic, or citric acid in an undivided elec-

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trochemical cell show that polymerization yield was increased compared to chemical polymerization of a very low concentration.^{24–26} The effect of electroregeneration of Ce(IV) to Ce(III) on the polymerization yield of *N*-vinyl carbazole (NVCz) and methyl methacrylate (MMA) in a divided cell was also studied, and the benefit of catalytic advantages of Ce(IV) was made for the preparative electrochemical polymerization of MMA and NVCz^{27,28} and use of a low concentration of metal ion by ecological reasons.²⁹

The aim of this study was to investigate polymerization of acrylamide in a two-compartment divided electrochemical cell with the purpose of better understanding the electrochemically induced redox polymerization mechanism of acrylamide, and to obtain a high yield of the polymer at low initiator concentrations where electrochemical regeneration of the oxidant exhibits ecological

	Conversion %		
Temperature (°C)	Electropolym.	Chemical Polym.	
22	49	42	
35	56	50	
50	62	53	
70	61	66	

Table I The Effect of Temperature on
Conversion in Undivided Cell and
Chemical Polymerization

 $[H_2SO_4] = 0.5 M$, [AA] = 0.5 M, $[Ce(IV)] = 5.10^{-4} M$, $[OA] = 2.10^{-2} M$.

importance by the design of environmentally clean technology.

EXPERIMENTAL

Polymerization Procedure

Electrochemical polymerization of acrylamide has been studied in an aqueous solution in the presence of Ce(IV)-oxalic acid redox initiator systems in a temperature range of 20–70°C.

A two-compartment electrochemical cell was employed, and the compartments were divided by a sintered glass disc to avoid polymer diffusion. Constant magnetic stirring was maintained during current flow, where the cell was placed in a thermostatic bath kept at constant temperature.

A 2-cm² platinum was employed as a working electrode and placed into the anolyte. A 2-cm² Pt electrode was used as a counter electrode. A constant potential supplier was a Thurlby-Thandar PL 320 power supply. To determine the amount of polymers formed, a constant potential was passed through the reaction mixture for the desired time period. At the end of experiment, the anolyte was poured into an excess of acetone, the solution was filtered, dissolved in water again, and reprecipitated with acetone to remove monomer and electrolyte contamination from the polymer. The polymer was dried in a vacuum to a constant weight.

Materials

 $Ce(SO_4)_2 \cdot 4H_2O$ (Fluka), Sulfuric Acid (Merck), acrylamide (Merck), acetonitrile (HPLC grade), and NaClO₄ (Fluka) are all reagent-grade chemicals and used without further purification. The aqueous solutions were prepared in the deionized water obtained from a water purification system.

Measurements

The average molecular weights of the anodic and cathodic polymers were determined from solution viscosity measurements in water at 30°C by an Ubbelohde viscometer using the equation given by ref. 30:

$$[\eta] = 6.8 imes 10^{-4} \cdot M_v^{0.66} \, \mathrm{dLg^{-1}}$$

which gives an approximate mass average molar mass \bar{M}_v .

FTIR spectra were obtained by a Mattson 1000 spectrometer, using KBr disks. UV-Visible spectra were recorded by a Shimadzu 160 A recording spectrophotometer. A POS 73 Model potentiostat with Kipp and Zonen X-Y Recorder was used for cyclic voltametric measurements in a standard electrochemical cell, containing Pt as a working and counter electrode and a saturated calomel electrode (SCE) as a reference electrode.

RESULTS AND DISCUSSION

Effect of Temperature

The effect of temperature on the polymerization yield was investigated for the polymerization in both the anode and cathode compartments and the undivided cell shown in Table I and II. Although the temperature effects are insignificant for the cathode section, for the anode compartment the yield decreased as the temperature increased, while the highest yield was obtained at 22°C. This is different from the conventional chemical method where the free radical regener-

Table I	I The	Effect of	' Temperature	in	the
Anode	Compa	rtment			

		Conversion % In 0.5 M H ₂ SO ₄		
Temperature (°C)	Conversion % In 0.1 M H ₂ SO ₄	Anode	Cathode	
22	61	88	46	
50 70	54	$\begin{array}{c} 67 \\ 49 \end{array}$	$\begin{array}{c} 49\\ 43 \end{array}$	

[AA] = 0.5 M, $[Ce(IV)] = 5.10^{-4} M$, $[OA] = 2.10^{-2} M$.



Figure 1 Effect of H_2SO_4 concentration on polymerization. Yield; (\blacklozenge) for the anode compartment, (\blacksquare) for the undivided cell, (\times) for the cathode compartment, and (\blacktriangle) for chemical polymerization, $T = 22^{\circ}C$, t = 60 min. Applied potential = 1.9 V vs. SCE, $[H_2SO_4] = 0.1 M$ [AA] = 0.5 M, [Ce(IV)] = $5 \times 10^{-4} M$ [OA] = $2 \times 10^{-2} M$.

ation rate was mainly controlled by the temperature. Above 22°C, the conversion showed a decline, which may be due to the side reactions in which primary free radicals are consumed.

$$Ce(IV) + HSO_4^- \rightleftharpoons Ce(SO_4)^{+2} + H^+$$

 $K_1 = 3500^* - 2300^{**}$

Effect of H₂SO₄ Concentration

The yield of polymerization of acrylamide has been studied by varying the concentration of sulfuric acid from 0.05 to 1.38 M (Fig. 1). The results show that increasing the hydrogen ion concentration causes the retardation in the yield of the cathode compartment. This behavior may be due to the direct reduction of Ce(IV) to Ce(III); therefore, the formation of primary free radicals by steps are prevented.

On the contrary, in the anode compartment increasing the acid concentration from 0.05 to 0.5 M increases the conversion, and reached a maximum at 0.5 M. Further increasing the H⁺ concentration maximum conversion showed a decreasing trend by increasing the concentration of sulfuric acid. The increase in the conversion with the increase in sulfuric acid concentration from 0.05 to 0.5 M, and later a decrease in the yield by a further increase in the sulfuric acid concentration may be explained by the distribution of Ce(IV) species present in the solution, which is well defined in the literature^{31,32}:

$$Ce(SO_4) + HSO_4^- \rightleftharpoons Ce(SO_4)_2 + H^-$$

$$K_1 = 200^* \cdot 120^{**}$$

 $Ce(SO_4) + HSO_4^- \rightleftharpoons Ce(SO_4)_3 + H^+$

 $K_1 = 20^* - 5^{**}$

Where Ce(IV) total of the Ce^{+4} , $Ce(OH)^{+3}$, $Ce(OH)_2^{+2}$

*I = 2, **I = 1(I = Ionic Strength) and

 $T = 25^{\circ}C$

A high concentration of mono- and di-sulfate species is present at a low sulfuric acid concentration, which are reported as more reactive species than $Ce(SO_4)_3^{2^-}$ occur at a higher concentration of sulfuric acid.^{33,34} The contribution of an additional redox pair between Ce(IV) and $SO_4^{2^-}$ ions, which produce SO_4^{-} radicals in the systems as well as SO_4^{-} radicals produced by electro-



Figure 2 The FTIR spectra of polyacrylamide obtained (---), (a), in the anode, (---), (b), in the cathode compartment, $[H_2SO_4] = 0.1 M [AA] = 0.5 M [Ce(IV)] = 5 \times 10^{-4} M$, $[OA] = 2 \times 10^{-2} M$.

chemical oxidation, as suggested in the literature, 35 is less probable because no polymerization occurs in the absence of Ce(IV) under these reaction conditions.

Because it is known that the complex between Ce(IV) and oxalic acid is easily decomposed in strong acidic medium,³⁶ at a higher acid concentration, i.e., >0.5 M, the complex decomposes; therefore, the conversion has been found to decrease.

The polymerization of acrylamide in the absence of both ceric ions and oxalic acid was not initiated under these conditions. On the contrary, the polymerization of acrylamide was found to proceed in the coexistence of ceric ions and organic reducing agents. In the cathode compartment polymerization goes through only a chemical reaction, whereas in the anode compartment, because the conversion is higher than both in the case of chemical and electrochemical polymerization alone, Ce(IV) obtained from Ce(III) by electrochemical oxidation is reused and allow to increase the conversion. An increase in the Ce(IV) concentration in the presence of electrolysis increases the conversion, supporting the idea mentioned above.

The FTIR spectra of polymers, formed at the anode, are seen from the curves in Figure 2(a) and (b), respectively. This spectra resemble the spectrum of polyacrylamide reported by earlier workers.^{37–39} Polyacrylamide was obtained both thermally as well as electrochemically by anodic polymerization. Because same polymer structure was obtained from both the anode and cathode compartments, this supposed that the polymerization goes through the same mechanism and agrees with literature findings.

Effect of Ce(IV) Concentration

The effect of Ce(IV) concentration on the polymerization yield are summarized in Table III.

The polymerization of AA in the absence of ceric ions was not initiated either with oxalic acid or monomer under these experimental conditions, and the polymerization of AA was found to proceed in the coexistence of ceric ions and an organic reducing agent. The same yield in the cathodic compartment and for redox polymerization alone, increases in the yield of the anode compartment as the Ce(IV) concentration increases and has higher values than in the cathodic section as well as the undivided cell, and shows the regeneration of Ce(IV), which react again with oxalic acid to produce more radicals initiating the polymerization.

Molecular Weight of Polyacrylamide Obtained in the Anode and Cathode Compartments

The molecular weights of the polyacrylamide obtained with the change of acid concentration in this work are summarized in Table IV.

[Ce(IV)], <i>M</i>	Conversion % (Anode)	Conversion % (Cathode)	Conversion % (Chemically)	Conversion % (Undivided)
$3~ imes~10^{-2}$	121ª	98	63	66
$5~ imes~10^{-4}$	68	43	33	51
$*1~ imes~10^{-4}$	16	9	2	8

Table III Effect of Ce(IV) Concentration on the Yield with a Different Method

^a Higher than 100% conversion is due to inclusion of initiators namely, Ce(IV) and oxalic acid into the polymer. [AA] = 0.5 *M*, [H₂SO₄] = 0.05 *M*, [OA] = $2 \times 10^{-2} M$, *[H₂SO₄] = 0.5 *M*.

Conversion %			M_v	
$[\mathrm{H_2SO_4}], M$	Anode	Cathode	Anode	Cathode
0.05	21	37	33,000	15,000
0.10	61	33	12,000	
0.50	88	48	11,000	
1.38	61	55	13,000	31,000

Table IVMolecular Weight and ConversionValues of Polyacrylamide

[AA] = 0.5 *M*, [OA] = 2×10^{-2} *M*; [Ce(IV)] = 5×10^{-4} *M*; *T* = 22° C; *E* = 1.5 V; *I* = 28 mA, time: 1 h.

The molecular weight of the polymers decreased with increasing the acid concentrations and conversion. This is expected, because increases in the initiator concentration increases the growing chain population, which in turn, enhances the polymerization rate and simultaneously lowers the molecular weight of the polymers formed.



E, V (vs SCE)

Figure 4 Cyclic voltammogram of CAN (1), CAN + OA first cycle (2), second cycle (3): $[OA] = 2 \times 10^{-2}$ *M*, $[Ce(IV)] = 5 \times 10^{-4}$ *M*, Pt electrode, scan rate = 50 mV \cdot s⁻¹, supporting electrolyte = 0.1 *M* NaClO₄ in ACN.



Figure 3 Cyclic voltammogram of $2 \times 10^{-2} M$ OA, Pt electrode, scan rate = 50 mV · s⁻¹, supporting electrolyte = 0.1 M NaClO₄ in ACN.



Figure 5 Repetitive cycling of CAN + OA: $[OA] = 2 \times 10^{-2} M$, $[Ce(IV)] = 5 \times 10^{-4} M$, Pt electrode, scan rate = 50 mV \cdot s⁻¹, supporting electrolyte = 0.1 *M* NaClO₄ in ACN.

Cyclic Voltammograms

Cyclic voltammogram of oxalic acid and CAN are shown in Figures 3 and 4 curve 1, respectively. Although CAN shows reversible behavior, oxalic acid has only one anodic peak. Under these experimental conditions, on the other hand, acrylamide has no peak in the anodic sweeps, showing that there is no direct electron transfer reaction in this scale. When the oxalic acid is added to the CAN solution, the oxidation peak around 1350 mV is greatly decreased, indicating a reaction between CAN and oxalic acid (Fig. 4, curves 1, 2, and 3). By continuous cycling this peak almost disappeared because all CAN is used (Fig. 5). In the presence of acrylamide, the decrease in anodic current is higher, because radical species produced from the reaction between OA and CAN is rapidly used to initiate the polymerization of the acrylamide.

UV-Visible Absorption Measurements

Reaction between Ce(IV) and OA was checked by UV-Visible absorption measurements. The absorption spectrums of the fresh solution of Ce(IV) and OA alone are given in Figure 6(a) and (b), respectively; Ce(IV) shows a maximum absorbance at 300 nm, and OA has two maximum



Figure 6 UV-visible spectra of [Ce(IV)], [OA]; (a) $[OA] = 2 \times 10^{-2} M$, (b) $[Ce(IV)] = 5 \times 10^{-4} M$, (c) OA-Ce(IV).

absorbances at 208 and 251 nm in aqueous 0.5 M acidic solution. When they are reacted, the yellow color disappears to yield an apparently colorless solution in about 60 s, having maximum absorbance at 253 and 241 nm [Fig. 6(c)]. The overall oxidation reaction coefficient between oxalic acid and Ce(IV) was determined, and the rate of consumption of Ce(IV) is given by the following reaction:

$$-\frac{d[\operatorname{Ce}(\mathrm{IV})]}{dt} = k[\operatorname{Ce}(\mathrm{IV})] \cdot \text{ [Oxalic Acid]}$$

k was found as a 0.125 s⁻¹. In addition to CV measurements, these results also suggest that a reaction occurs between OA and Ce(IV). Furthermore, the absorption spectrum of polymers obtained from both the anode and cathode compartments was also taken by dissolving in water [Fig. 7(a)-(c)]. The same maximums that were observed for OA and Ce(IV) were also seen for polymers obtained at the 0.03 M Ce(IV) concentration [Fig. 7(a) and (b)]. The intensity of these absorption peaks decreased with a decrease in polymer obtained at a low concentration of Ce(IV) [Fig. 7(a) and (c)]. These results suggest that radical species produced from the reaction between OA and CAN occurs to initiate the polymerization and inclusion of Ce(IV) into the resulting polymer. An interesting point is that the increase in the Ce(IV) concentration is about two times for the polymerization experiments, results in about a two-time increase in the absorbance value of Ce(III), which probably coordinated to polymer [Fig. 7(a)]. This inclusion might be due to both initiation and as well as termination steps by Ce(IV).

CONCLUSION

The polymerization yield, which is initiated with oxalic acid-Ce(IV) redox coupling, can be considerably increased by electrogenerated Ce(IV) in the anodic compartment.

The increase in H_2SO_4 concentration up to a certain point results in an increase in the polymerization yield, which might also be due to the formation of more reactive $Ce(SO_4)_n$ complexes. Contribution of HSO_4^- and or SO_4^- radical to the initiation of polymerization as suggested in literature³⁵ is less probable under these conditions because no polymerization was observed in this reaction time in the case where Ce(IV) is not present.

In our previous studies²⁵ in undivided cell at lower Ce(IV) concentration, polymerization in the presence of electrolysis gave higher conversion values; at 6.25 $10^{-4} M$ Ce(IV) concentration, conversion is about 25 and 5% with and without electrolysis, respectively. On the other hand, by divided cell design, which is used in this study, it is possible to increase this conversion up to 85% at the same concentration of Ce(IV), due to the prevention of reduction of Ce(IV) at the cathode.



Figure 7 UV-visible spectra of polymers according to Ce(IV) concentration and differences between the anode and cathode compartments: (a) $[Ce(IV)] = 3 \times 10^{-2}$ *M* at anode; (b) $[Ce(IV)] = 3 \times 10^{-2}$ *M* at cathode; (c) $[Ce(IV)] = 5 \times 10^{-4}$ *M* at anode; [AA] = 0.5 *M*, [OA] = 2 $\times 10^{-2}$ *M*, $[H_2SO_4] = 0.5$ *M*.

This method has the advantage of regeneration and reusing of Ce(IV) for further initiation of polymerization more effectively than undivided cell conditions.

According to the results obtained, in this study an oxidation mechanism of oxalic acid by Ce(IV) was proposed:

Redox polymerization

$$\begin{array}{c} cooH \\ cooH \\ cooH \end{array}^{+} Ce(M) \end{array} \Longrightarrow \begin{bmatrix} cooH \\ cooH \\ cooH \end{array} \stackrel{}{\sim} Ce(M) \end{bmatrix}$$

$$\begin{array}{c} Initiation ; \\ \hline \\ cooH \\ cooH \\ cooH \end{array} \stackrel{}{\sim} Ce(M) \end{bmatrix} \xrightarrow{slow} \begin{array}{c} coo \\ cooH \\ cooH \end{array}^{+} H^{+} + Ce(II) \end{array}$$
Propagation ;

$$\begin{array}{ccc} \text{COO} & \text{CONH}_2 \\ \end{array}$$

Termination by Ce(IV)

 $\begin{array}{c} -\begin{pmatrix} \mathsf{CH}_2 - \mathsf{CH}_1 & & \\ & \mathsf{CONH}_2 \end{pmatrix}_n & \mathsf{CH}_2 - \mathsf{CH}_1 + \mathsf{Ce}(\mathsf{M}) & \longrightarrow & \begin{pmatrix} -\mathsf{CH}_2 - \mathsf{CH}_1 & & \\ & \mathsf{CONH}_2 \end{pmatrix}_n & \mathsf{CH}_2 + \mathsf{Ce}(\mathsf{M}) + \mathsf{H} \\ & \mathsf{CONH}_2 \end{pmatrix}_n$

By further reaction the activated complex may decompose to CO_2 , as suggested in the literature.⁴⁰ Although the possibility of different radical formations, i.e., by carboxylation, under these conditions no CO_2 evolution was observed because the concentration of Ce(IV) is low; it seems that only radical formation is possible.

In addition to redox initiation the following reactions are also possible at the electrode surface:

Electrochemical polymerization



I) Redox initiation II) Electroregeneration

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I)+ II) Electroinduced redox initiation

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