

# Electroinduced Copolymerization of Acrylonitrile–Polyethylene Glycol Compared with Chemical Copolymerization

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**ABSTRACT:** Electroinduced copolymerization of acrylonitrile (AN)–polyethylene glycol (PEG-400) initiated by Ce(IV) was performed in aqueous solution and compared with chemical copolymerization, which allowed Ce(III) to be converted to Ce(IV) electrochemically during the polymerization. The polymer that was insoluble in water was formed in the cathodic compartment. The effect of Ce(IV), H<sub>2</sub>SO<sub>4</sub>, monomer, PEG-400 concentration, temperature, time, and potential on the yield were studied and compared with similar effects under nonelectrolytic conditions. The role of Ce(IV) salt on the copolymerization was followed by spectrophotometric methods during the reaction period. Polymers were characterized by FTIR, UV-visible spectrophotometry, and NMR. Intrinsic viscosities of polymers were determined. Possible polymerization mechanisms are suggested in the case of electrolytic and nonelectrolytic conditions. The electrolytic process has a demonstrable advantage over the nonelectrolytic method. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1410–1419, 2001

## INTRODUCTION

Free-radical initiation of vinyl monomers by redox couples is an effective method that can be applied to the generation of free radicals under mild conditions.<sup>1</sup> In the presence of very low (catalytic) amounts of initiator concentrations ( $10^{-3}$  or even less), electrochemically induced polymerization of vinyl monomers was successfully performed, resulting in higher yields under a variety of conditions in an electrolytic cell. We previously reported work on several redox-initiating systems involving the ceric ion coupled with EDTA, polyaminocarboxylic acid, and amino acids,<sup>2–4</sup> and for the polymerization of acrylamide by electrolytically generated Ce(IV) redox systems in an undivided cell.<sup>5,6</sup> Polymerization of acrylamide was

also studied by a Ce(IV)–oxalic acid (redox couple) initiator system in an electrochemical cell both with and without separation of anolyte and catholyte.<sup>6</sup> Polymerization was initiated by a free radical formed by the fast reaction of oxalic acid and Ce(IV). The polymerization of acrylamide, in a divided electrochemical cell having two compartments, showed that acrylamide was also not polymerized under these conditions in anodic and cathodic compartments in the presence and absence of Ce(IV). However, it was recently shown that, without having a reducing agent, the polymerization of acrylonitrile can be performed successfully by the presence of only catalytic amounts of Ce(IV) with electrolysis in the cathode region.<sup>7</sup>

In the electroinduced polymerization of AN, the presence of Ce(IV) is a necessity for the progress of polymerization because it seems that it behaves like an electrophile and, in addition, it keeps the electrode surface clean for electron

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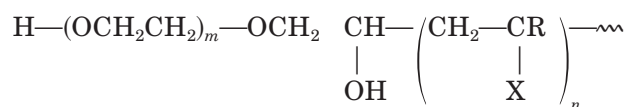
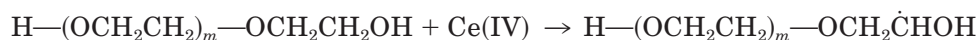
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transfer. In the absence of Ce(IV), attributed to polymer diffusion and grafting onto the cathode to a certain extent, it will inhibit electron transfer from cathode to monomer. It was found that the presence of Ce(IV) was a necessity for the continuation of the polymerization of AN.<sup>7</sup>

Nagarajan et al.<sup>8-10</sup> investigated and reported on the kinetics of the chemical polymerization of

AN and methyl methacrylate (MMA) in the presence of PEG, that is, Ce<sup>4+</sup>-PEG-AN,<sup>8</sup> Mn<sup>3+</sup>-PEG-AN,<sup>9</sup> and Ce<sup>4+</sup>-PEG-MMA.<sup>10</sup> The following *block*-copolymerization mechanism was proposed:



In this study, the chemical and electrochemical polymerization of AN with PEG-400 was carried out comparatively in the presence of a catalytic amount of Ce(IV), called the electroinduced polymerization system, and performed in a separate cathode compartment. The effects of Ce(IV), monomer, sulfuric acid concentration, temperature, time, and potential on the polymerization yield were investigated and the yields compared with those of chemical polymerization to show the efficiency of the method.

## EXPERIMENTAL

### Materials

Cerium(IV) sulfate [Ce(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O; Carlo Erba, Italy], acrylonitrile (AN; Fluka, Sigma-Aldrich Chemie, Germany), polyethylene glycol (PEG-400) (Purum, Fluka), H<sub>2</sub>SO<sub>4</sub>, *N,N'*-dimethylformamide (DMF; Carlo Erba) were used without further purification. Distilled and deionized water was used for preparing solutions. Ce(IV) solutions were freshly prepared before each experiment.

### Polymerization Procedure

#### *Electrochemical Polymerization of AN with PEG-400*

Platinum-plate electrodes (area = 2.6 cm<sup>2</sup>) were used as anode and cathode. The cell assembly was connected to a thermostat and the reaction mixture, containing required amounts of monomer

and Ce(IV) in the aqueous solution of H<sub>2</sub>SO<sub>4</sub>, was stirred continuously in the cathode compartment, whereas the anolyte contained only H<sub>2</sub>SO<sub>4</sub> solution.

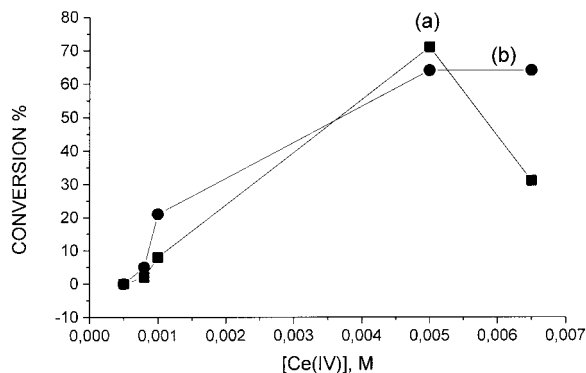
Electrolysis was carried out using a constant potential of 3.0 V by using a Thurlby Thander PL 320 DC source. Polymerization started in water within 5 min of electrolysis, and complete precipitation occurred after about 90 min. The precipitate was filtered off and dried to a constant weight at room temperature or under vacuum.

#### *Chemical Copolymerization of AN with PEG-400*

For comparative purposes, the polymerization was carried out in a cell with a stirrer by the addition of Ce(IV) salt solution to an aqueous solution of monomer and PEG-400. Polymerization started within 5 min, and after 90 min of polymerization, the precipitate was filtered off and dried to a constant weight at room temperature or under vacuum.

### Equipment

Spectrophotometric measurements were made by a Shimadzu UV-160 A UV-visible recording spectrophotometer (Shimadzu, Japan) in a quartz cell. The UV light source used in the polymerization process was provided using a 300-W mercury lamp. FTIR spectra were obtained by a Mattson 1000 spectrometer, preparing KBr disks. NMR spectra were obtained by a Bruker AC 250 model NMR spectrometer (Bruker Instruments, Billerica, MA). A Ubbelohde viscometer was used for determining molecular weight in DMF at 30°C.



**Figure 1** The effect of Ce(IV) concentration on the (a) chemical and (b) electrochemical copolymerization of AN with PEG-400. ([PEG-400] = 0.15M, [AN] = 0.9M, [H<sub>2</sub>SO<sub>4</sub>] = 0.6M, *t* = 40°C, applied potential = 3 V (electrodes: Pt), time = 90 min.)

## RESULTS AND DISCUSSION

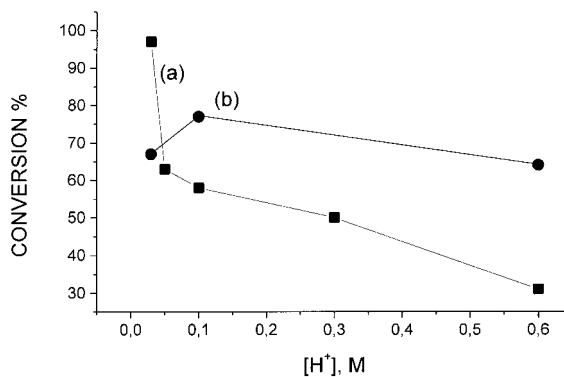
The polymerization of AN with PEG-400 by cerium sulfate was carried out under similar conditions both with and without electrolysis. The conversions can be obtained according to the amount of monomer, and amount of monomer and polyethylene glycol.

$$\text{Conversion \%} = \frac{\text{[amount of polymer (g)]}}{\text{amount of monomer (g)}} \times 100$$

All of the conversions were calculated from this equation.

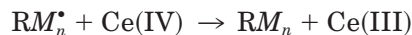
### Effect of Initiator Concentration on Conversion

The relation between the electrochemical and chemical polymerization yield on cerium(IV) sulfate concentration is shown in Figure 1. Ce(IV) concentration was varied from  $5 \times 10^{-4}$  to  $6.5 \times 10^{-3}$  M. The conversion increased up to a concentration of  $5 \times 10^{-3}$  M and, beyond this point, the conversion decreased as a result of the termination by Ce(IV). Considering the linear type of termination by Ce(IV) as the effective process un-



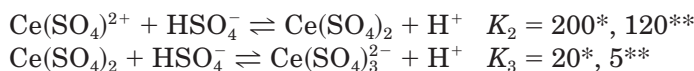
**Figure 2** The effect of acid concentration (H<sub>2</sub>SO<sub>4</sub>) on the (a) chemical and (b) electrochemical copolymerization of AN with PEG-400. ([PEG-400] = 0.15M, [AN] = 0.9M, [Ce(IV)] =  $6.5 \times 10^{-3}$  M, *t* = 40°C, applied potential = 3 V (electrodes: Pt), time = 90 min.)

der the experimental conditions previously reported,<sup>10</sup> the yield of the polymer that was obtained by the chemical polymerization method was about 71% Ce(IV), and the yield for the electrochemical polymerization was about 64% at  $5 \times 10^{-3}$  M.

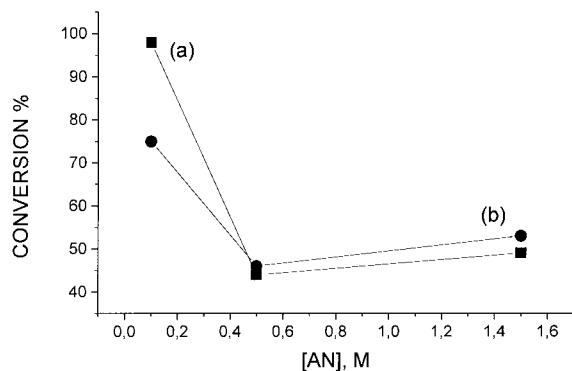


### Effect of Sulfuric Acid Concentration on Conversion

The relation between the conversion and the concentration of sulfuric acid in the system is shown in Figure 2. In chemical polymerization, the conversion passes through a minimum by increasing the acid concentration. The decrease in the conversion, with further increases in the sulfuric acid concentration, may be explained by the distribution of species present in solution: it is well established that the trisulfate complex increases and is known as a less reactive species among the others because of the heavy complexation of Ce(IV) coordination sites that prevents the electron transfer from monomer to Ce(IV).

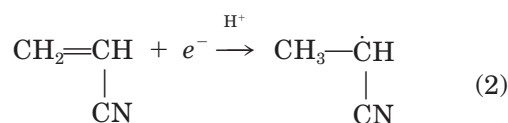
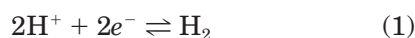


$$[*I \text{ (ionic strength)} = 2, t = 25^\circ C] \quad [**I = 1]$$



**Figure 3** The effect of monomer concentration on the (a) chemical and (b) electrochemical copolymerization of AN with PEG-400. ([PEG-400] = 0.15M, [H<sub>2</sub>SO<sub>4</sub>] = 0.6M, [Ce(IV)] = 5 × 10<sup>-3</sup> M, t = 50°C, applied potential = 3 V (electrodes: Pt), time = 90 min.)

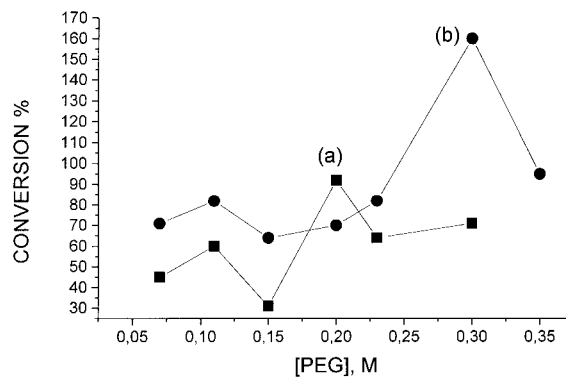
In the electroinduced polymerization, the conversion passes through a maximum by increasing the acid concentration. The increase in the conversion, with the increase in sulfuric acid concentration from 0.03 to 0.1M, might be attributed to the presence of sulfuric acid, which behaves as a strong electrolyte and allows higher currents to pass through the electrolyte, thus increasing the formation of H<sub>2</sub>. The monomer in the reaction medium reacts with H<sup>+</sup> by an electron transfer from the cathode, in addition to the H<sup>+</sup> reduction reaction on the cathode.



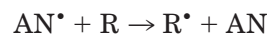
In the electrochemical process, reactions (1) and (2) proceed together. For this reason, the conversion reaches an almost constant value with the increase in acid concentration.

#### Effect of Monomer and PEG-400

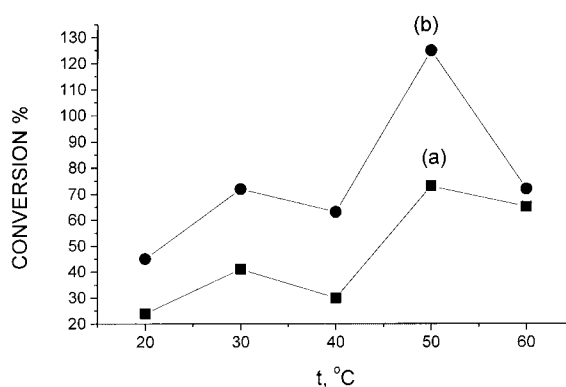
The effect of monomer concentration on conversion was examined for different concentrations of AN, while the other components were kept constant under the same conditions with and without electrolysis (Fig. 3). The conversion decreased in the presence of PEG-400 (attributed to the transfer reactions by AN) to solvent or PEG.



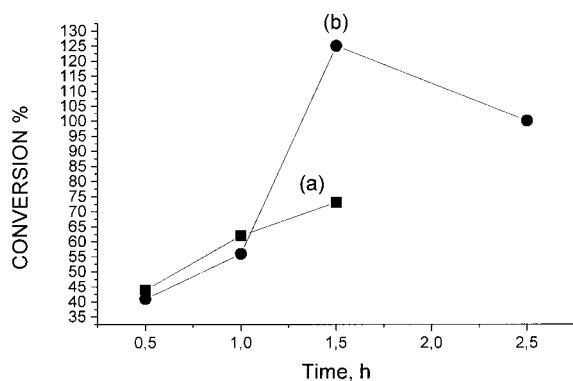
**Figure 4** The effect of polyethylene glycol concentration on the (a) chemical and (b) electrochemical copolymerization of AN with PEG-400. ([AN] = 0.9M, [H<sub>2</sub>SO<sub>4</sub>] = 0.6M, [Ce(IV)] = 6.5 × 10<sup>-3</sup> M, t = 40°C, applied potential = 3 V (electrodes: Pt), time = 90 min.)



In the chemical polymerization, the conversion was generally increased by the increase of PEG concentration, except for the 0.15M PEG concentration (Fig. 4). The maximum yield was obtained at 0.2M PEG concentration. This conversion is higher than 100%, indicating that it includes PEG. If the conversion is calculated from conversion % = {amount of polymer (g)/[amount of monomer (g) + PEG (g)]} × 100, it gives 70% conversion. Beyond 0.2M, the conversion decreased as a result of the constant Ce(IV) concentration, whereas the concentration of PEG increased. The electrochemical polymerization yield was increased by increasing PEG resulting from



**Figure 5** The effect of temperature on the (a) chemical and (b) electrochemical copolymerization of AN with PEG-400. ([PEG-400] = 0.15M, [AN] = 0.9M, [H<sub>2</sub>SO<sub>4</sub>] = 0.6M, [Ce(IV)] = 6.5 × 10<sup>-3</sup> M, applied potential = 3 V (electrodes: Pt), time = 90 min.)

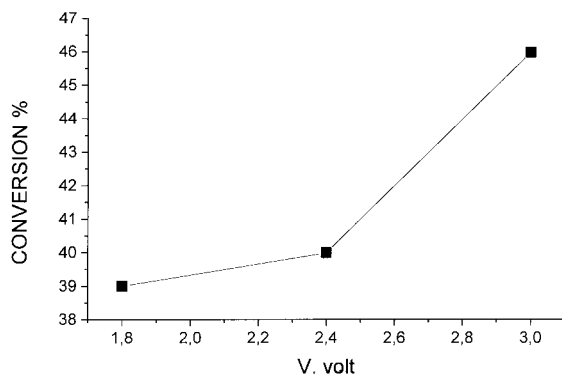


**Figure 6** The effect of time on the (a) chemical and (b) electrochemical copolymerization of AN with PEG-400. ([PEG-400] = 0.15M, [AN] = 0.9M, [H<sub>2</sub>SO<sub>4</sub>] = 0.6M, [Ce(IV)] = 6.5 × 10<sup>-3</sup> M, *t* = 50°C, applied potential = 3 V (electrodes: Pt).)

the Ce(IV) ion, which can be electrochemically regenerated from Ce(III) to Ce(IV) in the anode compartment. Ce(IV) obtained by this process can continuously oxidize PEG and, thus, many more PEG radicals can be obtained by the electrochemical method. The yield of polymer obtained by the electroinduced polymerization method at 0.3M PEG concentration is higher than that obtained by the chemical method.

#### Effect of Temperature, Time, and Potential

The effect of temperature on the conversion is shown in Figure 5. Temperature was varied from 20 to 60°C. In both cases, the polymerization yield increased with increasing temperature up to



**Figure 7** The effect of potential on the electrochemical copolymerization of AN with PEG-400. ([PEG-400] = 0.15M, [AN] = 0.9M, [H<sub>2</sub>SO<sub>4</sub>] = 0.05M, [Ce(IV)] = 5 × 10<sup>-3</sup> M, *t* = 50°C, applied potential = 3 V (electrodes: Pt), time = 90 min.)

**Table I** Specific Viscosities and the Molecular Weight ( $M_w$ ) of the Polymers

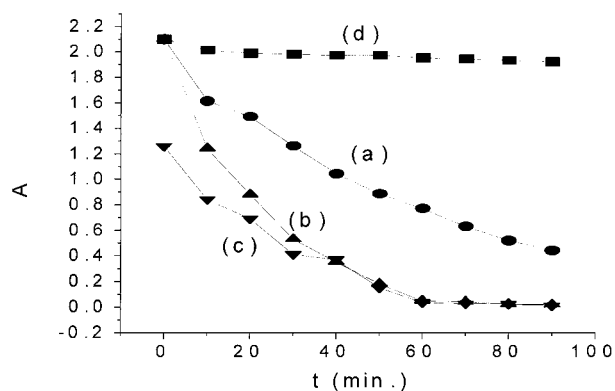
[PEG] (M)	Polymerization Method	$[\eta] \times 10^{-2}$	$M_w^a$
0.15	Chemical (1 h)	4.50	540,000
0.15	Chemical (1.5 h)	1.75	146,000
0.30	Chemical (1.5 h)	2.50	239,000
0.11	Electrochemical (1.5 h)	8.10	1,200,000
0.15	Electrochemical (1 h)	1.55	123,000
0.15	Electrochemical (1.5 h)	6.90	980,000
0.30	Electrochemical (1.5 h)	4.45	533,000
—	Electrochemical (1.5 h)	3.28	350,000 <sup>b</sup>

<sup>a</sup> To see the differences between homo- and copolymer, the  $M_w$  was calculated from the following equation, which is for the homopolymer of AN:  $[\eta] = 33.5 \times 10^{-3} M^{0.72}$  (in DMF at 30°C).

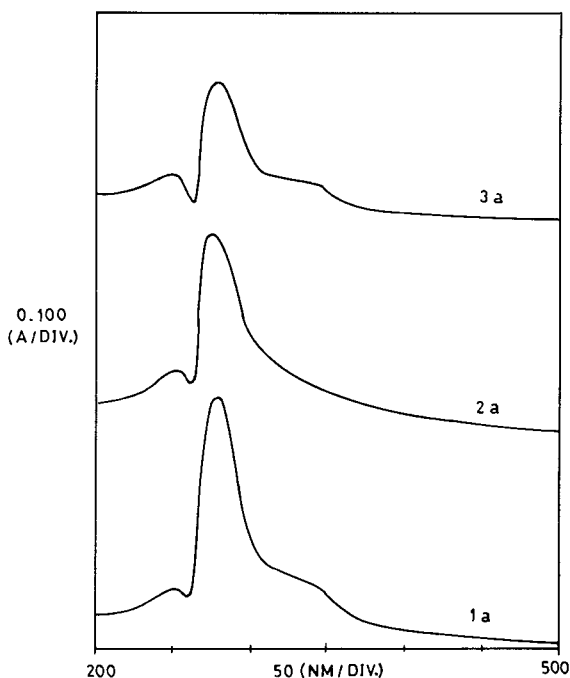
<sup>b</sup> Molecular weight of homopolymer (PAN).<sup>11</sup>

50°C. The electrochemical polymerization yield is higher than the chemical polymerization yield at all of the temperatures used in this study [Fig. 5, curves (a) and (b)]. The conversion by the electrochemical polymerization method is 72% at 30°C, whereas the polymer obtained by the chemical polymerization method reached a yield of only about 73% at 50°C. A further increase of temperature did not increase the conversion because of the increase in the secondary reactions (more H<sub>2</sub> formation, etc.).

At 50°C chemical polymerization showed a lower conversion of 73%, whereas electroinduced



**Figure 8** UV-visible results of Ce(IV) in the reaction period in the absence of monomer (a), in the presence of monomer (b), and in the presence of monomer and PEG-400 (c); and in the chemical polymerization in the absence of monomer and PEG (d) at 306 nm in H<sub>2</sub>O. ([AN] = 0.9M, [Ce(IV)] = 5 × 10<sup>-3</sup> M (CAN), *t* = 50°C, applied potential = 3 V (electrodes: Pt), polymerization period: 90 min.)



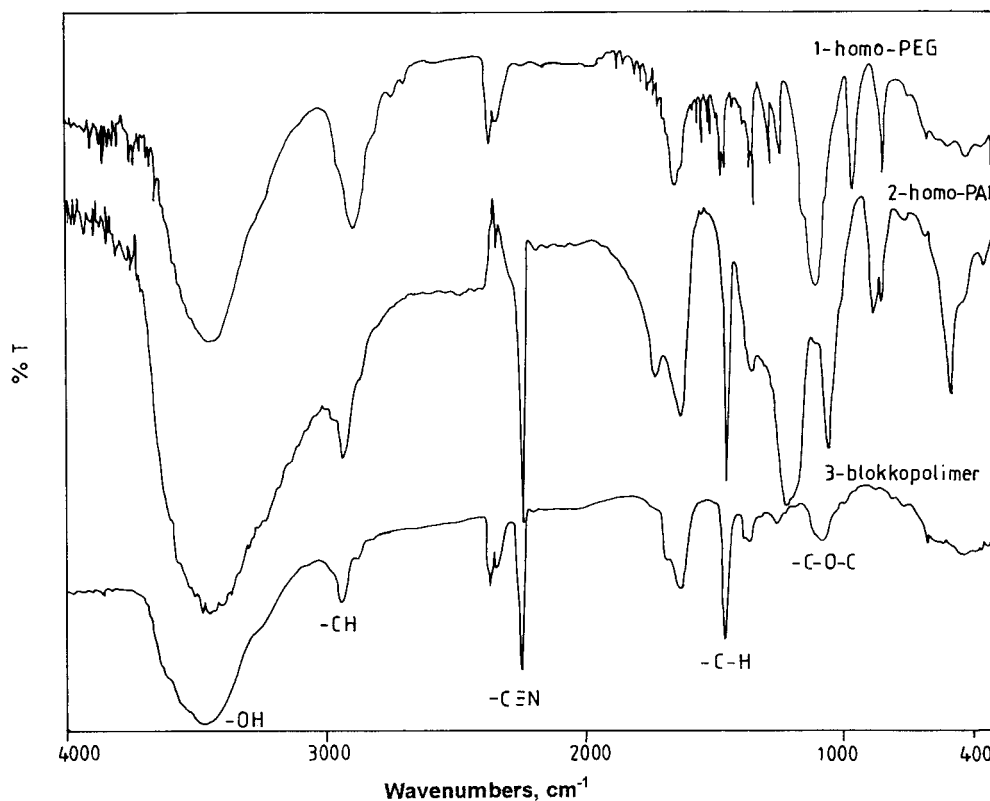
**Figure 9** The UV-visible spectra of copolymers obtained by chemical polymerization. ([PEG-400] = 0.15M, [AN] = 0.9M, [H<sub>2</sub>SO<sub>4</sub>] = 0.6M, *t* = 40°C, [Ce(IV)] = 6.5 × 10<sup>-3</sup> M, applied potential = 3 V (electrodes: Pt), time = 90 min.)

polymerization of AN with PEG-400 gave the polymerization yield of 127% in 90 min (Fig. 6). Under the same conditions in the absence of Ce(IV), electrochemical polymerization gave no conversion.

The effect of the applied potential on the conversion showed that the highest yield could be obtained at 3.0 V in the electrochemical polymerization and this potential was applied for other experiments (Fig. 7). A potential lower than 1.8 V did not allow enough current to pass through the electrolyte, which caused practically no polymerization in the reaction period of 1.5 h. Some low percentage of the yield difference between 3.0 and 1.8 V (which is about 5%) could be attributed to the H<sub>2</sub> reduction increasing with increase in potential, in addition to the increase in Ce(IV) concentration by higher current.

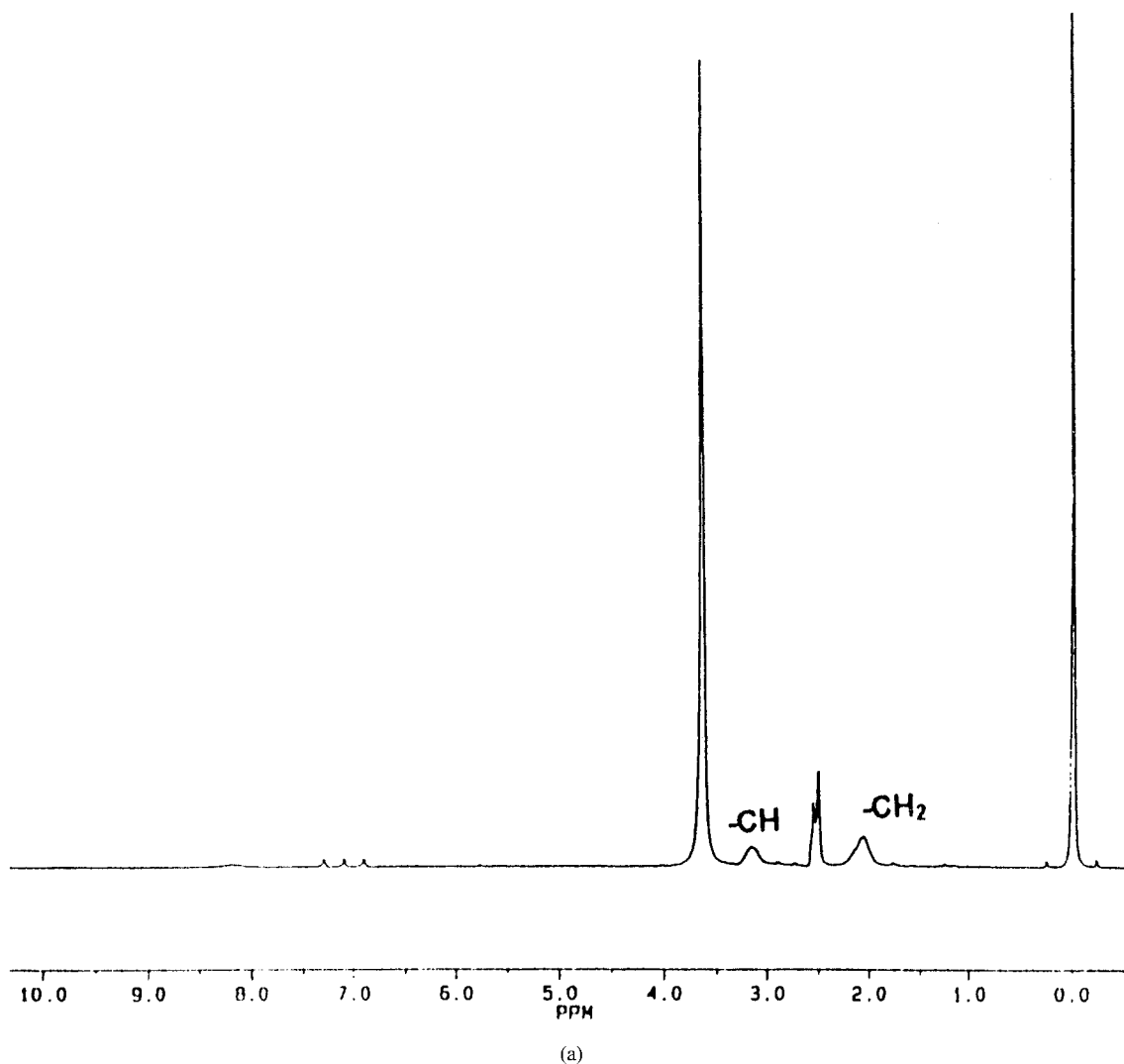
#### Viscosities of Polymers

The viscosities [η] of the polymers that were produced chemically and electrochemically at different PEG concentrations were obtained by a viscometric method (Ubbelohde) at 30°C. The results are presented in Table I.



**Figure 10** FTIR spectra of (a) homo-PEG, (b) homo-PAN, and (c) *block*-copolymer.





**Figure 11** (a) NMR spectra of PAN obtained by the electrochemical method. (b) NMR spectra of copolymer obtained by the electrochemical method.

### UV-Visible Spectra

Because the monomer is soluble under our conditions, the decrease of absorbance of Ce(IV) was followed spectrophotometrically. The decrease in the maximum absorbance value at Ce(IV) at 317 nm was followed in the presence of monomer, monomer and polyethylene glycol, and in the absence of the monomer in the reaction period under electrolytic conditions [Fig. 8, curves (a)–(c)]. In the absence of the monomer (AN), the absorption of Ce(IV) decreased about fourfold (from 2.10 to 0.53); in the presence of the monomer (AN), it also decreased about fourfold (from 1.54 to 0.41) after 30 min at 317 nm. In the chemical polymerization there was not much change in the absorbance

value of Ce(IV) [Fig. 8, curve (d)]. In the presence of AN and polyethylene glycol (PEG), the absorption of Ce(IV) decreased from 1.27 to 0.32 after 30 min at 317 nm. In this case the conversion is lower than that of the electrochemical polymerization.

A pseudo-first-order rate constant ( $k_f$ ) [consumption of Ce(IV) produces free radicals in the initiation step] was obtained from  $\log(A_t - A_\infty)$  versus  $t$  plots, indicating a first-order reaction in the system Ce(IV)–AN–PEG-400, which is in excess. Rate constants were obtained for the decrease of absorbance of Ce(IV):  $k_i = 1.63 \times 10^{-2} \text{ min}^{-1}$  (correlation coefficient  $r = 0.990$ ) in the absence of the monomer;  $k_i = 4.88 \times 10^{-2} \text{ min}^{-1}$

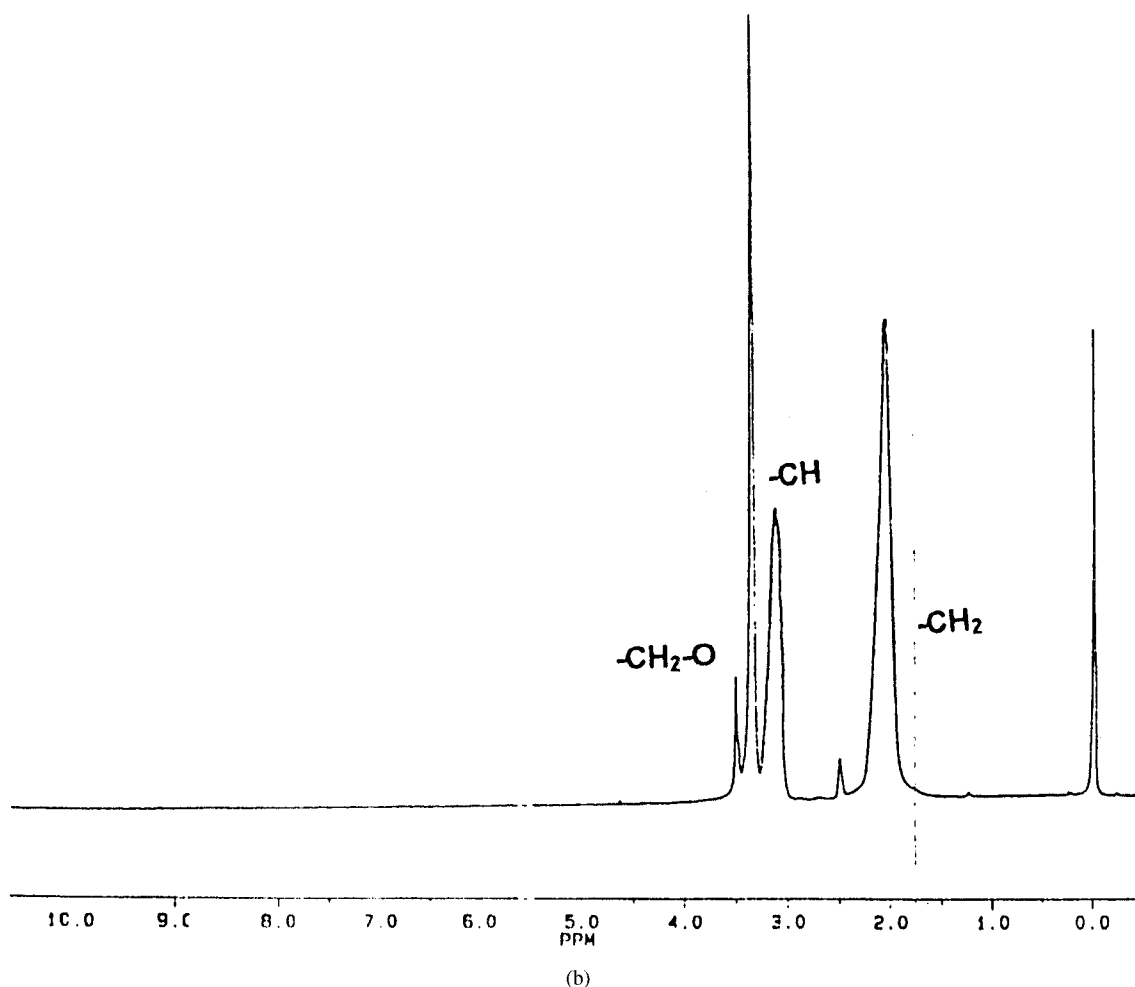


Figure 11 (Continued from the previous page)

( $r = 0.991$ ) in the presence of the monomer; and  $k_i = 4.3 \times 10^{-2} \text{ min}^{-1}$  ( $r = 0.92$ ) in the presence of monomer and PEG.

These  $k$  constants can be taken for comparison purposes because, in the electrolytic process, Ce(IV) is continuously produced, and this amount is not taken into account in the kinetic expression, which could be the reason for the low values of correlation coefficients.

#### UV-Visible Spectra of Resulting Polymers

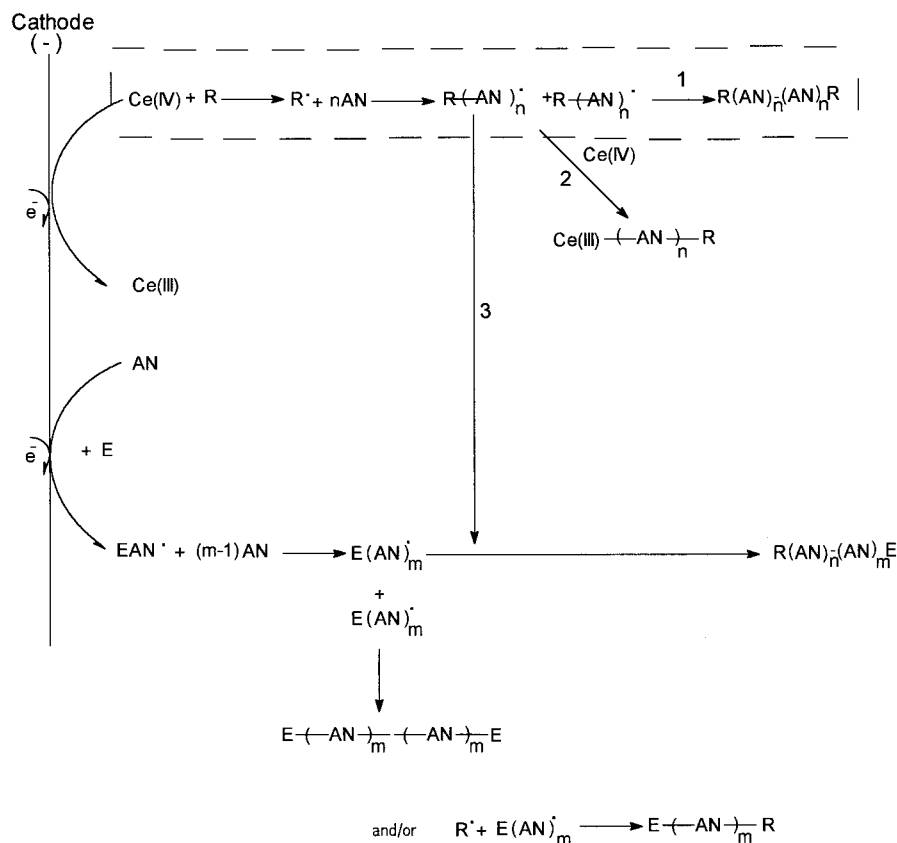
The UV-visible spectra of polymers, obtained for the chemical polymerization method, are shown in Figure 9. Because the solubility of copolymers is low in water, DMF was selected for UV measurements in this medium. UV absorbance curves of Ce(IV) sulfate and PAN, obtained by the electrochemical method, showed a peak at 278.5 nm that belongs to  $-\text{CN}$  ( $n-\pi^*$  excitation). The UV-

visible spectra of copolymers that were obtained chemically showed a peak at 278 nm. Those peaks belonging to  $-\text{CN}$   $n-\pi^*$  excitation in PAN absorption were decreased by increasing the PEG/AN ratio (Fig. 9). The UV-visible spectra of copolymers obtained by the electrochemical method contained a peak at 278.5 nm. This peak's absorption decreased with the increase in PEG concentration in the preparation of polymer. The ratio of PAN decreased as a result of the increase of PEG concentration in the copolymer formation.

#### FTIR Spectra

The FTIR spectra of PEG, PAN, and *block*-copolymer are shown in Figure 10, curves (a), (b), and (c), respectively. The polymer formed showed peaks corresponding to both PEG and PAN, indicating *block*-copolymer formation. The bands at 2953 and 1472  $\text{cm}^{-1}$  are attributed to  $-\text{CH}$  str.

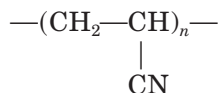




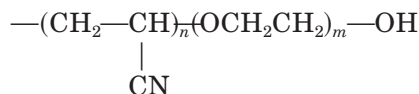
Scheme 1

and  $-\text{CH}$  vib. of the oxyethylene group, respectively. Absorption at  $1114\text{ cm}^{-1}$  is attributed to  $-\text{C}=\text{O}$  str. of the PEG chain. A sharp peak at  $2263\text{ cm}^{-1}$ , corresponding to  $-\text{CN}$  str., is a clear indication of the presence of acrylonitrile segments in the *block*-copolymer.<sup>8</sup> These results support the formation of the *block*-copolymer.

### NMR Spectra



The NMR spectra of the copolymer and PAN, obtained by the electrochemical method, are shown in Figure 11(a) and (b), respectively. The methylene group appears as a broad band at about 2 ppm and the methine absorbance is observed at about 3.1 ppm [the band at 2.5 ppm represents the solvent impurity  $\text{DMSO}-d_5$  (PAN)], similar to the previous report.<sup>12</sup> The peak at 3.72 ppm belongs to DMSO because  $\text{DMSO}-d_5$  contains a little DMSO.



In the NMR spectra of copolymer [Fig. 11(b)], the proton appears as a sharp peak that represents all of the methylene groups belonging to the PEG in the chain, at about 3.5 ppm. The methylene groups appear as a sharp peak at about 2.1 ppm. The methine groups are observed at about 3.1 ppm. The NMR results show that the structure of copolymer contains PEG.

### CONCLUSIONS

In this study the electroinduced polymerization method, previously applied for the homopolymerization of vinyl monomers,<sup>2-7</sup> was successfully applied for the copolymerization of AN and PEG with higher yields (about twofold) than those for the chemical method.

The reaction of  $\text{Ce(IV)}$  with PEG is fast compared to that of  $\text{Ce(IV)}-\text{AN}$ , so radicals can be

easily formed. Reaction radicals are formed from PEG with more Ce(IV) consumption observed during the polymerization period of about 30 min (Fig. 8) in the presence of monomer and PEG, rather than of monomer itself. So both PEG<sup>•</sup> and AN<sup>•</sup> can initiate AN polymerization and these chains can combine with each other, as well as termination of chain radicals by Ce(IV), depending on the experimental conditions. The increase in Ce(IV) concentration attributed to electrochemical regeneration results in more Ce(IV) being present in solution, which would generate more radicals by reaction with AN and PEG. This could be the reason for the high  $M_w$  and higher yields of polymers being obtained by the electrochemical process than those obtained by the chemical method.

Reduction of AN at the cathode, which was allowed by Ce(IV)/Ce(III) conversion at the cathode, and oxidation of the AN radical by direct chemical oxidation of AN, together seem to be an effective initiation mechanism, in addition to the effect of regeneration of Ce(III) to Ce(IV) at the anode (**Scheme 1**), which allows higher yields than those obtained by the chemical method.<sup>7</sup>

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