Electroinduced Dispersion Polymerization of Acrylonitrile in the Presence of Poly(acrylic acid) and Catalytic Amount of Ce(IV)

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ABSTRACT: Electroinduced dispersion polymerization of acrylonitrile initiated by Ce(IV) was performed in an electrolytic cell in the presence of poly(acrylic acid) (PAA). Micron-size polyacrylonitrile (PAN) particles were stabilized with PAA by electrostatic interaction or by a PAA–Ce(III)–PAN ternary complex formation. A PAA–PAN stable polymer was formed in the cathodic compartment, and the reduced initiator was reoxidized in the anode, thus allowing for the continuation of the process. A possible mechanism of polymerization is suggested. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 723–728, 2002; DOI 10.1002/app.10076

Key words: electroinduced polymerization; dispersion polymerization; polyacrylonitrile; polyacrylic acid; cerium (IV)

INTRODUCTION

Several reports have appeared on the mechanism and kinetics of polymerization involving ceric ion alone[1] and also in combination with reducing substrates such as alcohols,[2,3] 1,2 diols,[4] ketones,[5] and amino acid,[6] and poly(aminocarboxylic acid).[7–10] The same systems were also used as initiators for graft copolymerization of acrylonitrile (AN) and acrylamide[11] and a block copolymer of ketonic resin–polyacrylonitrile.[12]

Under electrolytic conditions and by electrogeneration of metal ion, using Ce(IV)–carboxylic acid, KMnO$_4$–carboxylic acid, or Ce(IV)–EDTA redox systems, water-soluble polyacrylamides containing the carboxylic acid end group were synthesized recently in our laboratory.[13–15]

Recently, polymerization of acrylamide was investigated in an aqueous solution in the presence of a Ce(IV) salt–oxalic acid initiator system in an electrochemical cell with and without separation of the anolyte and the catholyte with the purpose of better understanding the electrochemically induced redox mechanism of acrylamide and to obtain a high yield of the polymer at low initiator concentrations.[16]

The same idea was applied to the polymerization of *N*-vinylcarbazole (NVCz) in an anodic compartment in the presence of a catalytic amount of a ceric salt as an oxidant during the electrochemical polymerization of NVCz in a divided electrochemical cell.[17]

Electroinduced polymerization of AN in the presence of Ce(IV) was recently performed effectively under electrolytic conditions. The precipitated polymer was obtained in the cathode compartment and the reduced initiator was reoxidized in the anode, thus allowing for the continuation of the process. In contrast to previous cases, in the case of AN, simultaneous reduction of Ce(IV) to Ce(III) at the cathode eases the electron transfer from the electrode to the species in solution, resulting in higher yields compared to chemical methods.[18]
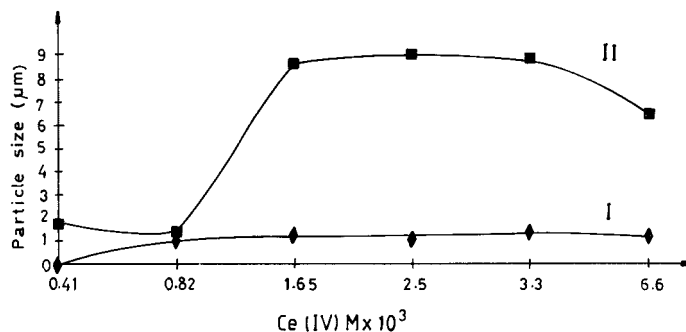
Figure 1 Effect of Ce(IV) concentration on the particle size of the reaction products in (I) the chemical and (II) the electrochemical synthesis. [AN] = 0.4M; [PAA] = 0.12M; [H_2SO_4] = 0.13M; T = 30°C; t = 120 min.

Due to its high oxidation power and clean stoichiometry, Ce(IV) salts are used effectively in the oxidative[19] and matrix[20] polymerization of pyrrole, resulting in a very small size of particles in the latter case, depending the conditions which allow polypyrrole to become almost soluble in the poly(acrylic acid) (PAA) matrix. The effect of the molecular weight of PAA on the polymerization products was also studied and the necessity of a critical chain length for the stability effect of PAA was reported.[21] Now, we report a novel method of obtaining micron-size particles by electroinduced polymerization of AN in the presence of a catalytic amount of Ce(IV) salt and PAA, known as an effective stabilizer,[22] which plays an important role in the particle-formation stage.

EXPERIMENTAL

Materials

Ceric sulfate [$Ce_2(SO_4)_4 \cdot 4H_2O$] (CS), AN, H_2SO_4, and PAA were all Merck-grade chemicals of the highest purity and were used without further purification.

Polymerization Procedure

Electrochemical and Chemical Polymerization

Electrochemical polymerization was carried out in a cell divided into two compartments using a sintered disc of porosity 264. Platinum gauze electrodes of 5 × 4 and 4 × 10 cm area were used as the anode and the cathode, respectively. The cell assembly was connected to a thermostat, and the reaction mixture containing the required amounts of the monomer or the monomer/PAA mixture and Ce(IV) in the aqueous solution of H_2SO_4 was stirred continuously for 1 h in the cathode compartment while the anolyte contains only a H_2SO_4 solution.

Electrolysis was carried out using a constant potential of 3 V using a Thurlby Thander PL 320 DL source. The polymerization product was obtained in the cathode compartment. Under the same conditions, electrochemical polymerization gave no conversion in the absence of Ce(IV).

For comparative purposes, the chemical polymerization was carried out in a round-bottomed flask equipped with a stirrer by the addition of a Ce(IV) sulfate solution to an aqueous solution of the monomer. The polymerization time was 90 min.

Table I Effect of PAA Concentration on the Solid Content and Particle Size of PAN Obtained in Chemical and Electrochemical Polymerization of AN in the Presence of PAA

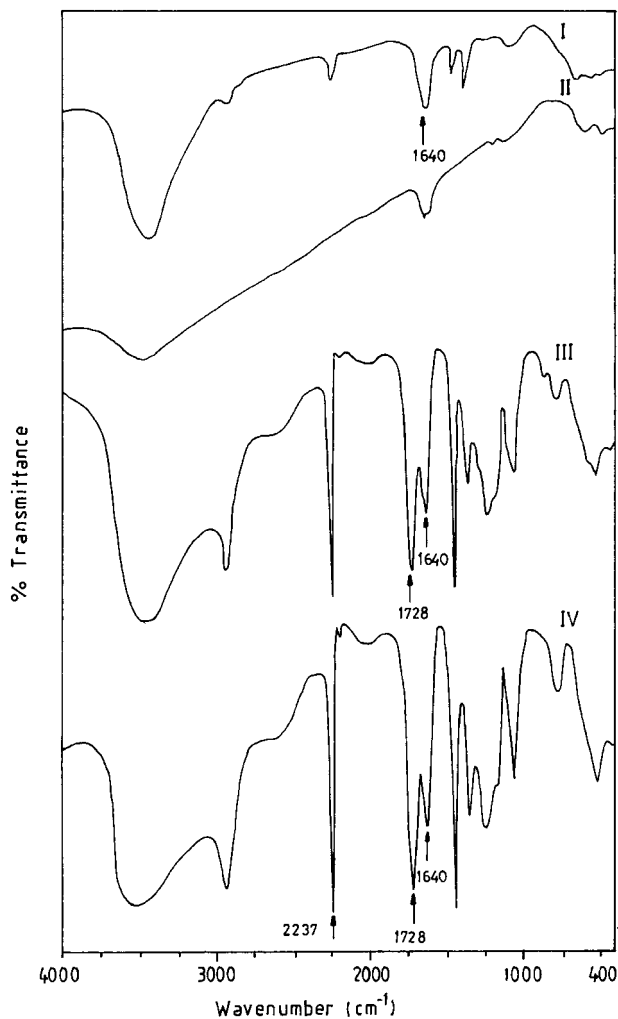| No. | PAA (M) | n_{CS}/n_{PAA} | Chemical | | Electrochemical |
			Solid Content (%)	Particle Size (μm)	Particle Size (μm)
1	0.06	0.02	4.11	3.19	2.59
2	0.12	0.01	2.82	1.39	2.97
3	0.24	0.005	6.02	8.89	4.60
4	0.40	0.003	5.01	2.36	5.98

Figure 2 FTIR spectra of (I) chemically prepared PAN obtained by the reaction of AN with CS; (II) PAA, (III) chemically prepared PAN–PAA obtained by the reaction of AN with CS in the presence of PAA, and (IV) electrochemically prepared PAN–PAA.

An insoluble metal complex precipitation [PAA–Ce(III)] occurred at about the mol ratio of ceric sulfate to PAA (n_{CS}/n_{PAA}) = 0.1, so the ratio of (n_{CS}/n_{PAA}) = 0.021 was chosen for the reaction of AN with CS in the presence of PAA in the electrolytic condition.

Polymer Characterization

FTIR spectra of the polymers were taken on a Mattson 1000 FTIR spectrophotometer. KBr pellets were used for spectral analysis. Polymerization reactions were followed by UV-visible spectrophotometric measurements (Schimadzu UV-160A). The resulting stable particle sizes were obtained by a Counter-type multisizer and an Ocule 250h polarized light microscope.

RESULTS AND DISCUSSION

The effect of temperature, time, and H$^+$ concentration in the chemical and electrochemical polymerizations of AN in the presence of PAA was investigated and suitable conditions were selected as 30°C, 180 min, and 0.13M, respectively. The effect of the monomer concentration on the solid content in chemical and electrochemical polymerizations of AN in the presence of PAA was investigated in the range of a 0.1–0.4M AN concentration. While the AN concentration does not affect the particle size and the solid content in chemical polymerization, the 2% solid content increased by increasing the AN concentration from 0.1 to 0.4M in the electrochemical polymerization might be due to regeneration of Ce(IV), which will continue to polymerize the monomer.

While the Ce(IV) concentration does not affect the solid content of polyacrylonitrile (PAN) in either chemical or electrochemical polymerization and the particle size of PAN in chemical polymerization (Fig. 1), due to the AN radicals presence in the electrochemical polymerization medium (both electroinduced and chemically produced radicals), the particle size increases by increasing the cerium concentration since polymer chains continue to grow as long as AN and Ce(IV) are available.

Table I presents the effect of PAA on the solid content of the electrochemical and chemical polymerization of AN. An increase in PAA results in an increase in the solid content (except for case 2) by giving a maximum at 6.02 (n_{CS}/n_{PAA} = 0.005) and an increase in the particle size by giving maximum at 8.89 μm and then a decrease in the case of chemical polymerization. Although further investigation of the particle size and solid content with the n_{CS}/n_{PAA} ratio is needed, this behavior can be explained by a difference of PAA stabilization and/or stabilization by a PAN–Ce(III)–PAA ternary complex formation due to a change in the n_{CS}/n_{PAA} ratio. In the case of excess of PAA (0.40M), PAA stabilization will be dominant.

In electrochemical polymerization, an increase in PAA resulted in a regular increase in the solid content which could be explained by PAN growth due to regeneration of Ce(III) to Ce(IV) at a constant feed of Ce(IV) [in an electrogeneration system, an increase in Ce(IV) compensates the increase in PAA].
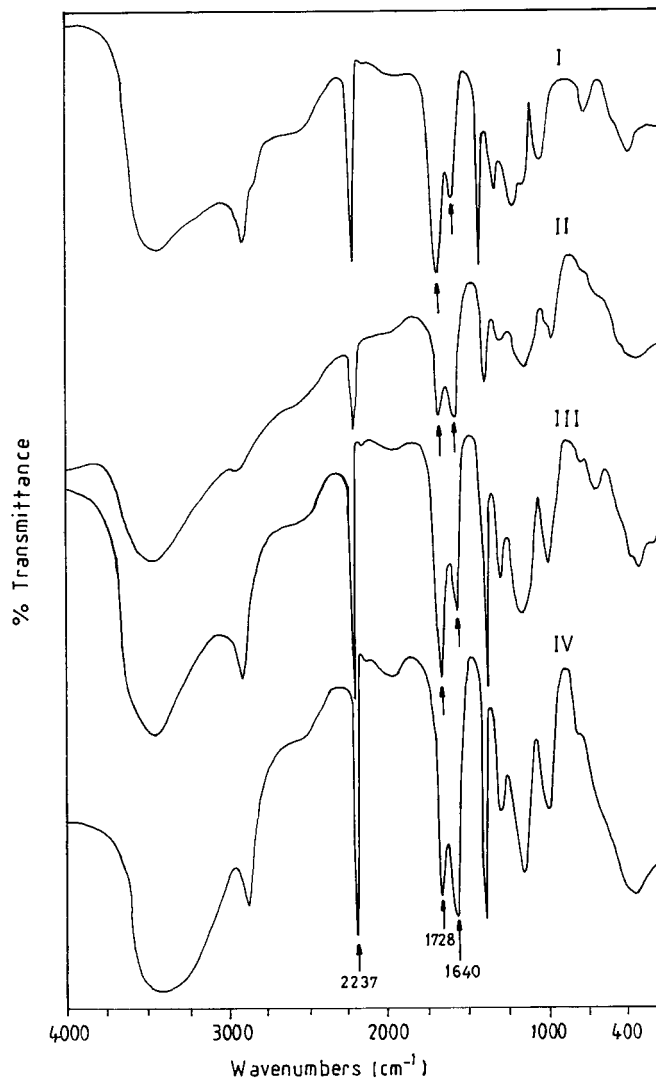
Figure 3   FTIR spectra of chemically synthesized PAN–PAA. (I) [AN] = 0.4M at 30°C and (II) [AN] = 0.4M, (III) [AN] = 0.6M, and (IV) [AN] = 0.8M at 50°C.

FTIR Results

The resulting polymerization products were washed with water to remove the physically adsorbed PAA, dried, and then examined. The characteristic peak at $\lambda = 1100$ cm^{-1} in the FTIR spectra of chemically prepared PAN and chemically and electrochemically prepared PAN–PAA indicates Ce(III) and SO$_4^{-2}$ ligands were incorporated in the polymer [Fig. 2(I, III, and IV)]. The intensity of the peak is the highest in the last case

Table II k Values of the Chemical Polymerization of AN by Ce(IV) in the Presence of PAA

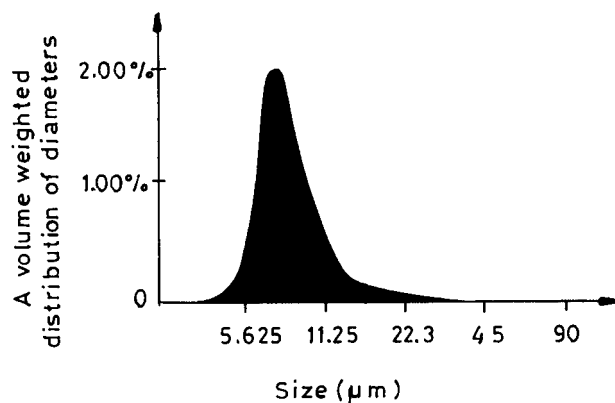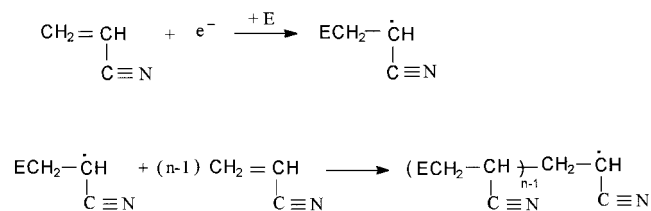| [AN] (M)	[PAA] (M)	[Ce(IV)] (M × 10^3)	[H$_2$SO$_4$] (M)	$k \times 10^3$ s^{-1}
0.8	0.12	3.3	0.13	8.27
0.4	0.12	3.3	0.39	1.27
0.4	0.12	3.3	0.13	6.55

Figure 4 Relationship between the particle size in micrometers and the volume-weighted distribution of diameters. [PAA] = 0.12M; [AN] = 0.4M, [H_2SO_4] = 0.13M; [Ce(IV)] = 2.54 × 10^{-3} M; T = 30°C; t = 120 min. Electrochemical polymerization.

due to production of more Ce(IV) by the electrochemical method (IV). Because there is no Ce(III) interaction in PAA, the corresponding FTIR spectrum (II) does not show any peak at 1100 cm^{-1}.

The peak at λ = 2237 cm^{-1} due to C≡N stretching was seen in I, III, and IV in Figure 2. The PAN–PAA polymer [Fig. 2(III and IV)] shows a peak at 1728 cm^{-1} beside the carbonyl peak of PAA at 1640 cm^{-1}. This new peak at 1728 cm^{-1} indicates the interaction of the carbonyl groups of PAA with the N atom of AN; the carbonyl group becomes more stable and the peak at 1640 cm^{-1} shifts to 1728 cm^{-1}. On the other hand, since all —COOH groups of the PAA chain do not interact with the N atoms of AN, the peak at 1640 cm^{-1} can be still seen. PAA and PAN and do not show any peak at 1728 cm^{-1} [Fig. 2(I and II)].

Figure 3 shows the effect of temperature and AN concentration on the FTIR spectra of the chemically synthesized PAN–PAA polymer. With variation of the AN concentration from 0.4 to 0.6M and, finally, 0.8M, the most intense peak at 1728 cm^{-1} in comparison with the peak at 1650 cm^{-1} was observed in III. The peak intensity ratios of 1728/1640 cm^{-1} were equal to 0.75, 1.33, and 0.94, respectively. These results show that the highest concentration of AN required for obtaining the stable dispersion of PAN is 0.6M. Above this point, due to the absence of enough PAA in the reaction medium, PAN cannot be stabilized on PAA and then precipitates as a PAN homopolymer and the intensity of the peak at 1728 cm^{-1} decreases [Fig. 3(IV)].

Furthermore, if we compare the FTIR spectra of two different products which were obtained at

50 and 30°C, the intensity of the new peak at 1728 cm^{-1} in comparison with the peak at 1640 cm^{-1} for the PAA–PAN polymer obtained at 30°C was higher than in the first case (1728/1640 cm^{-1} = 0.75 and 1.56, respectively). The experiments also support this result that the highest solid content and the particle size in both the chemical and electrochemical polymerization are obtained at the lowest temperature tested (30°C). The bands in the regions 1460–1440, 1370–1350, and 1270–1220 cm^{-1} were assigned to the C—H vibrations of different modes.[23]

Since AN and PAA are in excess relative to Ce(IV), the initial pseudo first-order kinetics is followed by decrease of the Ce(IV) peak in the UV–visible spectra of the reaction mixture during polymerization and was found to be k = 8.27 × 10^{-3} to 1.27 × 10^{-3} depending on the conditions (Table II). Particle sizes of the resulting stable dispersion polymer of AN in the presence of PAA were in the range of 5.8 μm (90% of total), as shown in Figure 4.

CONCLUSIONS

To understand the possibility of the graft copolymerization of AN onto PAA by Ce(IV), the Ce(IV)

E = An Electrophile (H$^-$, Ce(IV), or Ce(III).
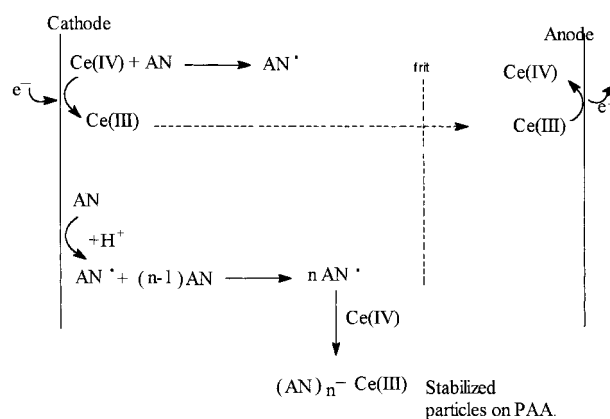
Scheme 1

Scheme 2
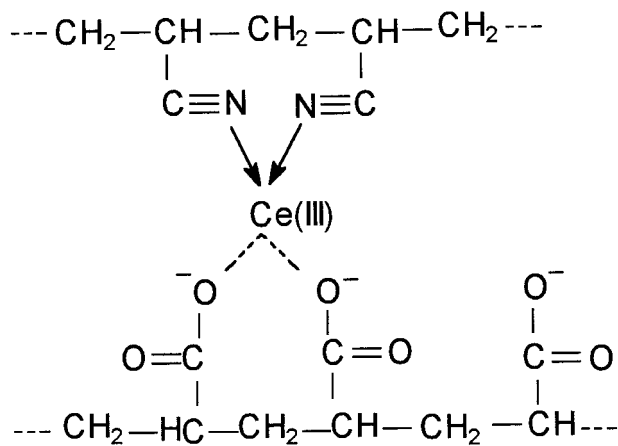
Structure 1

solution was added to the PAA solution, under the experimental conditions, and the absorbances of the mixture were measured as function of time. During the polymerization period, no decrease of absorbance of Ce(IV) at 250 nm was observed, indicating that the graft copolymerization of AN with PAA is not possible.

Because of the electrostatic interaction of PAA and polyvinylpyridine[24] and PAA–PAN[25] reported in the literature, the possibility of interaction between PAA and PAN is high. The results can be used to extend previously reported mechanisms[18] describing the electroinduced polymerization of AN in the presence of Ce(IV) and to confirm a proposed mechanism for both the electrochemical and chemical polymerization of AN.

Polymerization of AN proceeds by oxidation of AN with Ce(IV) to form a radical. In addition to this, AN can be reduced on the cathode surface by forming an AN radical anion which reacts with H^+ in a fast step. AN radicals can be terminated by Ce(III) or electrochemically and final PAN polymer particles are stabilized with PAA by electrostatic interaction or by a PAN–Ce(III)–PAA ternary complex formation.

Physicochemical results of this study support our conclusions on a novel electroinduced dispersion polymerization system of AN in the presence of PAA and catalytic amount of ceric salt for obtaining a PAN–PAA stable polymer of micron size. From these results, in the presence of PAA, a possible mechanism and a structure of a complex formation are shown in Schemes 1 and 2 and Structure 1, respectively.

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