

Polymer Coatings by Electropolymerization of Some Vinyl Monomers

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SYNOPSIS

Electroinitiated polymerization coatings are uniform, thin, tightly adherent, conformal, and economical to produce. This article describes use of a novel (for electropolymerization) persulfate initiator to rapidly polymerize a moderate T_g , crosslinked acrylic coating. Polymer coatings derived from the monomers acrylamide, acrylonitrile, and N,N' -methylenebisacrylamide were synthesized on an aluminum cathode by persulfate electroinitiated polymerization at room temperature. The crosslinked polymer was brittle ($T_g = 239^\circ\text{C}$) but thermally stable (degradation temperature = 310°C). The coatings were spongy and contained some small cracks when polymerized at low current density (0.1 mA/cm^2). However, thicker coatings with fewer cracks were obtained at higher current densities. Persulfate was found to be an effective initiator for polymerization in this system, and the initiation mechanism was confirmed to be free radical. In general, it appears possible to produce thin, uniform coatings on aluminum by this route. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Electropolymerization results from the process of passing current through a monomer-containing cathode compartment in an electrochemical cell. Only a small amount of current is needed to initiate chain growth, and monomers are added to the growing chain without a further current requirement. The mechanism of the process can be cationic, anionic, free-radical, or radical-ionic, depending upon the type of monomers, solvent, and electrolyte used. High adhesion between metal and polymer coating typically occurs¹ because monomers wet the metal surface more easily than do polymers and can introduce polymerization in the crevices of the metal surface, locking the polymer chains in place firmly. Another advantage is that the process can be carried out in an aqueous system and does not necessarily involve the evaporation of solvents. In addition, a uniform and defect-free coating is obtained through the electropolymerization process; polymerization is

favored at thin or "pinhole" areas since the electrical resistance is lower there. Polymerization can occur on edges and in holes and corners, so the surface does not have to be flat. Usually, only mild conditions such as room temperature, low current density, and low voltage are required for the electropolymerization process.¹⁻⁶ Also, better control of molecular weight and molecular weight distribution of the polymer can be obtained.¹

Basically, there are two methods to facilitate electropolymerization. The first method is to directly reduce or oxidize the monomer to an active species, which then interacts with monomers nearby the electrode and thereby initiates polymerization. Reduction of the monomer occurs at the cathode, and the active species may be free radical or radical-anion. Oxidation of the monomer occurs at the anode, and the resulting active species may be free radical or radical-cation. However, this type of initiation is not general and is limited by the ease of reduction or oxidation of the monomer.

The second method to electroinitiate polymerization is to reduce or oxidize a deliberately added electrochemical initiator. Initiation is controlled by the number and type of species from the initiator reduction and oxidation. This method can generally

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be applied to different monomer systems, since the initiating species is produced independently. Although there are some reports discussing the use of electrochemical production of initiating species for vinyl polymerization,⁷⁻⁹ the fraction of the initiating species that reacts with the monomer to start chains is reported to be low, and the overall rate of polymerization appears slow (hours).

In this work, persulfate, a potential initiator for electropolymerization, was investigated in a polymerization system containing acrylamide, acrylonitrile, and *N,N'*-methylenebisacrylamide monomers. The coating was electropolymerized onto an aluminum cathode in water at room temperature. The electrosynthesized polymer coating was characterized and the initiation mechanism was determined.

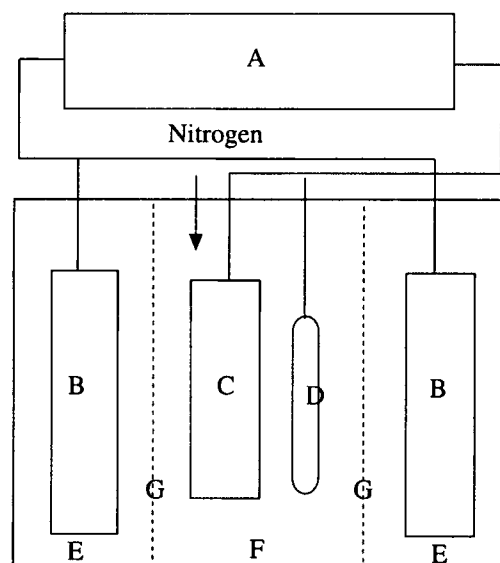
EXPERIMENTAL

Materials

Acrylamide (AM) was used for the research as received from Fisher Scientific Co. Acrylonitrile (AN) was obtained from Aldrich Chemical Co., and the inhibitor was removed by passing it dropwise through an inhibitor-removal column (DHR-4) purchased from Polymer Scientific Co. *N,N'*-Methylenebisacrylamide (MBA) from Sigma Chemical Co. was used as purchased.

Electrochemical Cell

The electrochemical cell used for the research was composed of a 21.5 × 14.5 × 6 cm glass chromatographic tank from Fisher Scientific Co., into which a Delrin® tank, 10 × 9 × 4.5 cm, was placed. The Delrin tank was perforated with many 2 mm-diameter holes, which were covered by polypropylene membranes (0.4 microns pore size, SEPA membrane from Osmonics, Inc.) on both sides of the compartment. The most important advantage of a three-compartment cell is that the polymer coating can be coated evenly on both sides of the metal substrate. The metal substrate was placed inside the central cathode compartment, while the counterelectrodes, stainless-steel plates, were placed in the outer compartments. Constant direct current or voltage was supplied by a Princeton Applied Research potentiostat Model 363. A schematic description of the electrochemical cell is shown in Figure 1.



- A: Galvanostat
- B: Stainless Steel (Anode)
- C: Aluminum (Cathode)
- D: Saturated Calomel Electrode
- E: 0.025M Sulfuric Acid
- F: AM/AN/MBA Solution
- G: Polypropylene Membrane

Figure 1 Schematic description of electrochemical cell.

Treatment of Aluminum Alloy Electrode

An aluminum alloy 5182, provided by the Aluminum Co. of America Research Center, had the following composition in wt %:

Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Other	Al
0.20	0.35	0.15	0.50	5.0	0.10	0.25	0.10	0.15	Remainder

The aluminum alloy 5182 was prepared for coating according to a standard alkaline etching treatment.¹⁰ The aluminum alloy was first etched in a 1.5M sodium hydroxide solution at 65°C for 5 min. Prior degreasing of the aluminum was optional because the etching removed organics as well as the surface oxide very efficiently. The etched aluminum was then rinsed in tap water at room temperature thoroughly and desmutted by dipping for 5 min in 10 vol % nitric acid at room temperature. It was rinsed thoroughly in distilled water at room temperature and air-dried in the hood. The sample was used within less than 5 h after it was judged dry.

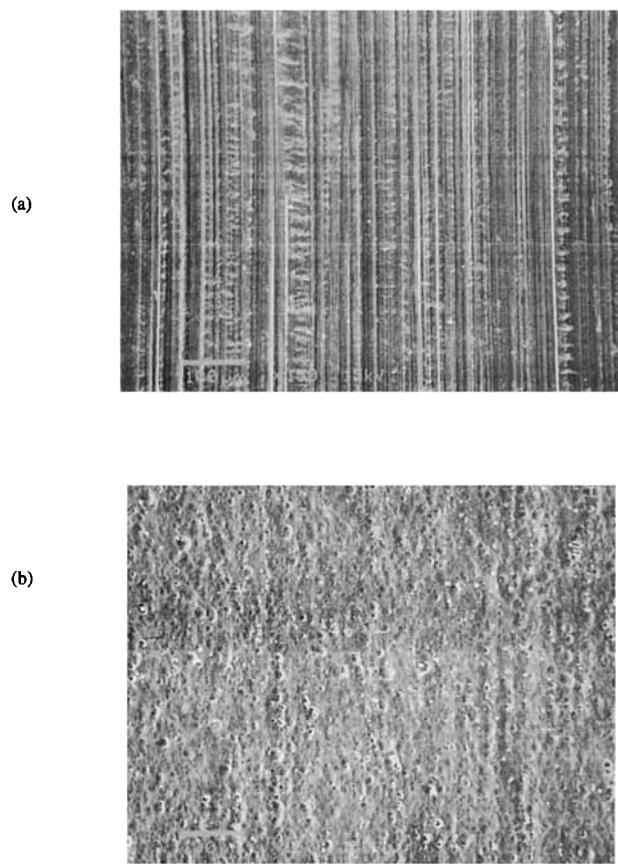


Figure 2 The surface morphology of (a) unetched surface and (b) etched surface at magnification $\times 150$.

Electropolymerization Conditions

Appropriate amounts of the monomers, initiator, and any inert electrolyte were dissolved in distilled water and the resulting solution, with a total volume of 200 mL, was deaerated with nitrogen gas for 30 min; oxygen reacts with the free radicals formed during initiation. The solution was poured into the Delrin tank which composed the center compartment of the three-compartment cell. The chromatographic tank was stored containing 160 mL 0.025M sulfuric acid, which also functioned as the solution for the two outer anode compartments. Nitrogen gas was then purged across the surface of the cell solution for 15 min to form an inert blanket before the current was switched on. After the process was completed, the coated aluminum electrode was carefully rinsed with copious distilled water to remove any trapped monomers and initiator present in the swollen crosslinked copolymer. The coated aluminum was then air-dried at room temperature overnight. It was further vacuum-dried at 150°C until the weight was constant. The weight of the

coating was measured from the weight difference of the aluminum electrode before and after the electropolymerization/drying process. The polymerization process was carried out at 0.10, 0.20, 0.30, and 0.40 mA/cm² for 10, 16, 23, and 30 min.

Infrared Analysis of Coatings

A Nicolet 60SX Fourier transform spectrometer was used to obtain Fourier transform infrared spectra (FTIR) from the coatings for functional group analysis. The coating was carefully removed by scraping from the Al surface and then was vacuum-dried at 150°C for 2 h to remove any absorbed moisture. The polymer was then mixed with KBr to form a pellet for analysis.

Thermal Analysis of Coatings

The glass transition temperature (T_g) of the coatings was determined using a Perkin-Elmer differential scanning calorimeter (DSC) Model 7. Sample heating was done in a nitrogen atmosphere in two cycles. The first heat, at a rate of 40°C/min, was to erase any thermal history of the polymer. The T_g was measured from the second heat scan, which was carried out at a rate of 10°C/min. The thermal stability of the polymer was studied on a Perkin-Elmer thermogravimetric analyzer (TGA) Model 7 at a heating rate of 20°C/min in a nitrogen atmosphere.

Coating Surface Observation

Scanning electron microscopy (SEM, Amray 1000A) was used to characterize the morphology and quality of the electropolymerized polymer coatings. Each sample was coated with gold-palladium to reduce electrical charging. The effects of two major parameters, time and current density, on the morphology and quality of the polymer were studied.

Cyclic Voltammetry

The electroactivity of the monomers, initiator, and electrolyte in the cathode solution were investigated using a cyclic voltammetry (CV) technique with a BAS-100 electrochemical analyzer from Bioanalytical Systems, Inc. The counterelectrode (anode) was a pure platinum coil, while the working electrode (cathode) was a glassy carbon electrode. The working potential was scanned from 0.00 to -3.00 V with respect to a saturated calomel electrode (SCE) with a reversal sweep rate of 250 mV/s. Any reduction or oxidation taking place in the cell during the po-

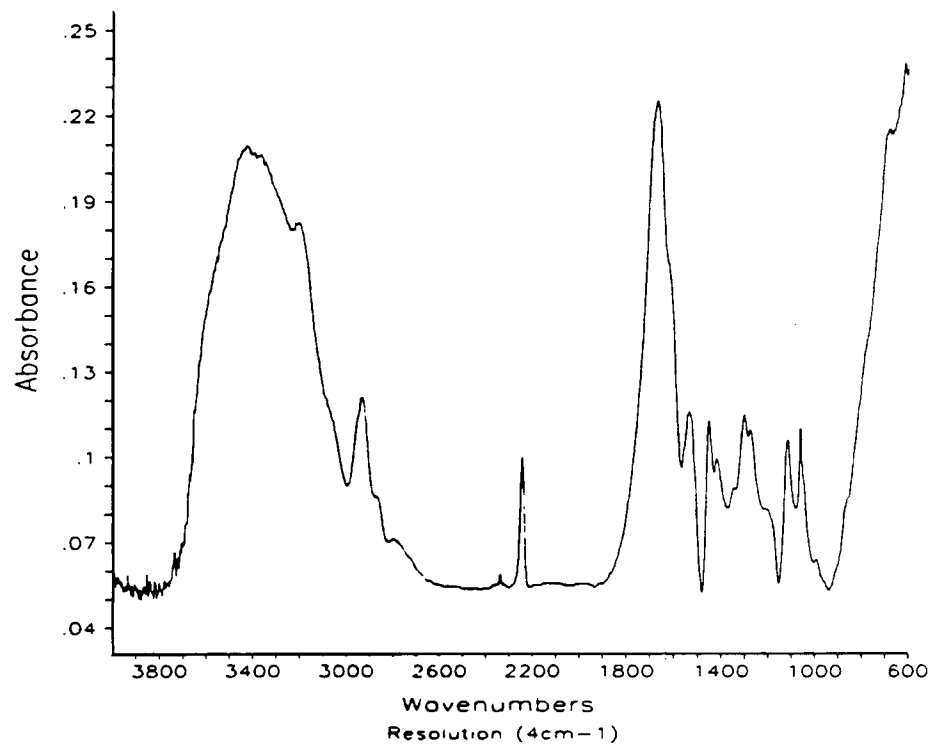


Figure 3 FTIR spectrum for electropolymerized AM/AN/MBA polymer.

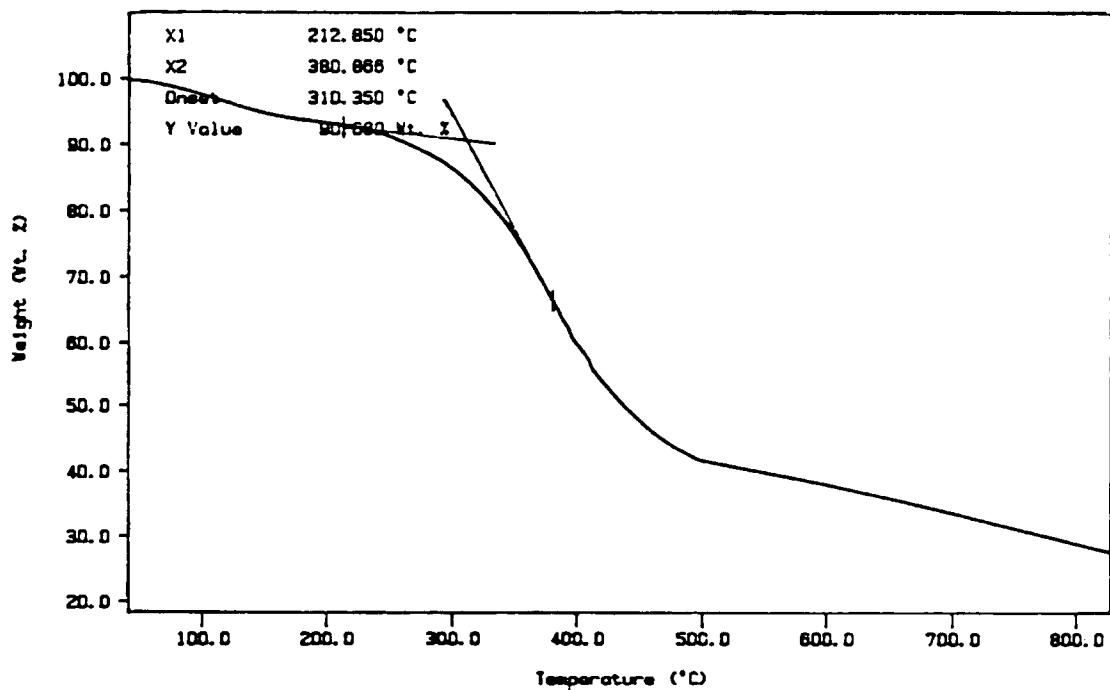


Figure 4 TGA thermogram for electrosynthesized AM/AN/MBA polymer in nitrogen at 20°C/min.

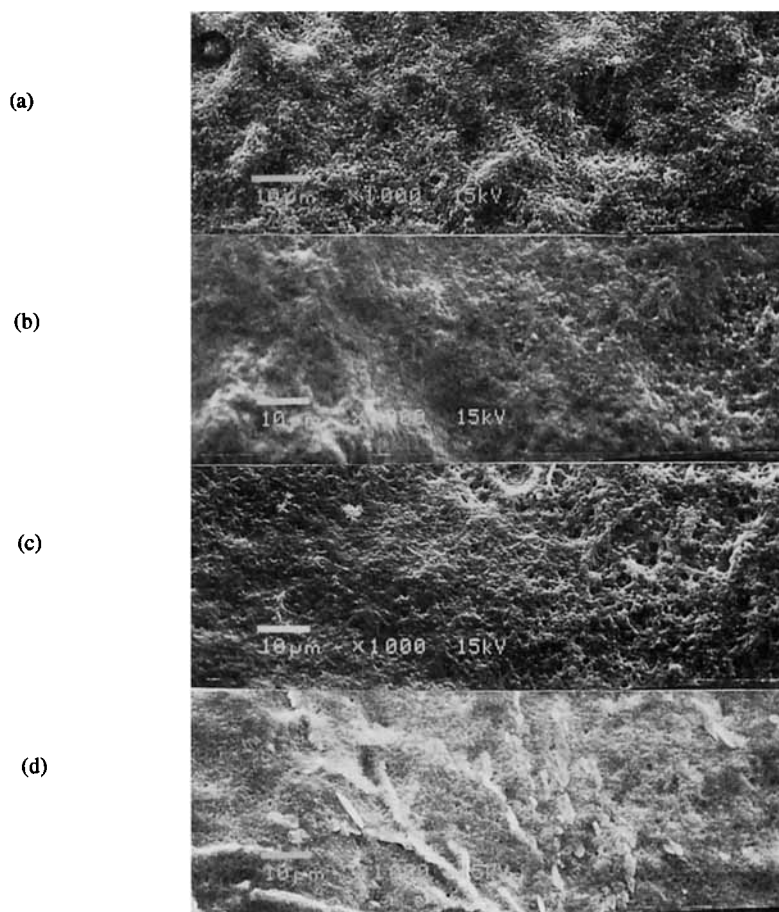


Figure 5 SEM micrographs for the polymer-coated Al at (a) 0.10 mA/cm², (b) 0.20 mA/cm², (c) 0.30 mA/cm², and (d) 0.40 mA/cm² for 16 min (×1000).

tential sweep was indicated by the presence of a peak.

RESULTS AND DISCUSSION

The SEM micrographs in Figure 2 indicate that the etched surface is rougher than is the unetched surface and contains ridges. It is known that the rough etched surface has the protrusions formed from the oxide base which enhance the interlocking between the metal substrate and the adhesive, resulting in better adhesion.¹¹

Infrared Analysis of Coatings

A broad amide peak, which is a mixture of primary amide and secondary amide, is present between 3000 to 3500 cm⁻¹, as shown in Figure 3. The primary amide, —CONH₂—, is due to the AM, and the secondary amide, —CONH—, is due to the MBA. In

the spectrum, there is an obvious nitrile peak located at 2242 cm⁻¹, indicating the presence of AN in the polymer. The presence of MBA is also shown by the —NH— bending at 1550 cm⁻¹, and the sharp carbonyl group from both AM and MBA is at 1675 cm⁻¹.

Thermal Analysis of Coatings

DSC Results

The *T_g* of the polymer formed from the 0.50 M AM/0.50 M AN/0.05 M MBA was 239°C, which is higher than that of polyacrylamide (215°C) and acrylonitrile (99°C). This is probably due to the high crosslinking of the polymer by the addition of MBA. Evidence for crosslinking is also provided by the observed brittleness of the dried polymer on the aluminum electrode. The crosslinking causes shrinkage of the polymer on the Al, and small cracks are observed on the surface. In addition, extra crosslinking can occur between two amine groups in the same

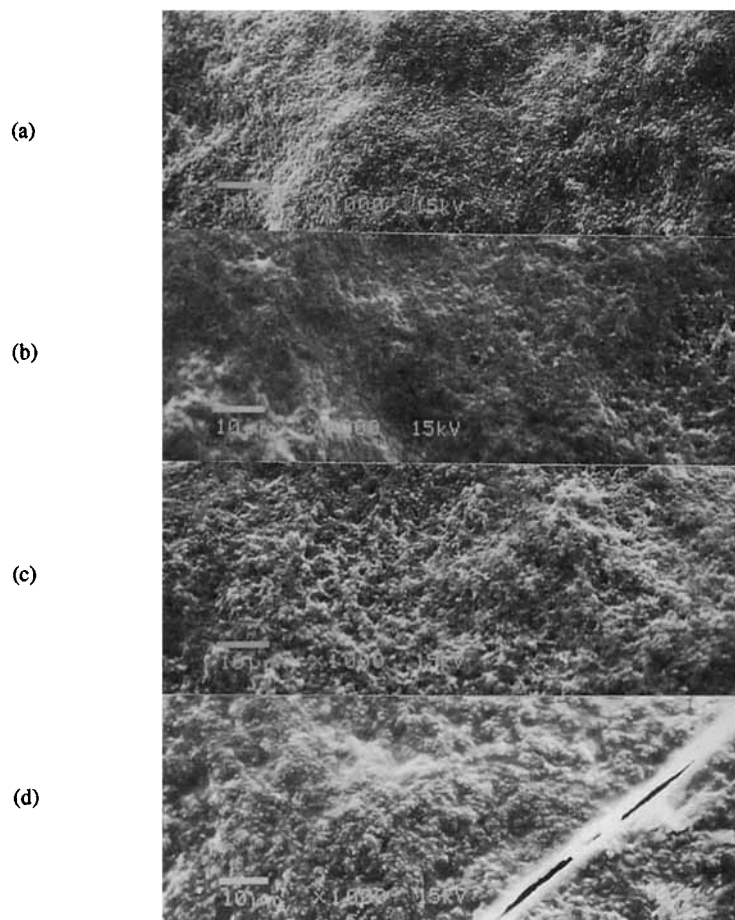


Figure 6 SEM micrographs for the polymer-coated Al at 0.20 mA/cm^2 for (a) 10 min, (b) 16 min, (c) 23 min, and (d) 30 min ($\times 1000$).

chain during polymerization and between two amine groups in two different chains during drying.¹²

TGA Results

For a $0.50 \text{ M AM}/0.50 \text{ M AN}/0.05 \text{ M MBA}$ monomer system, the electropolymerized coating had a

decomposition temperature of 310°C (Fig. 4). The decomposition of the crosslinked polymer is comparable to that of polyacrylonitrile (314°C) but higher than that of polyacrylamide (231°C). It is believed that the crosslinking helps to enhance the thermal stability of the polymer.

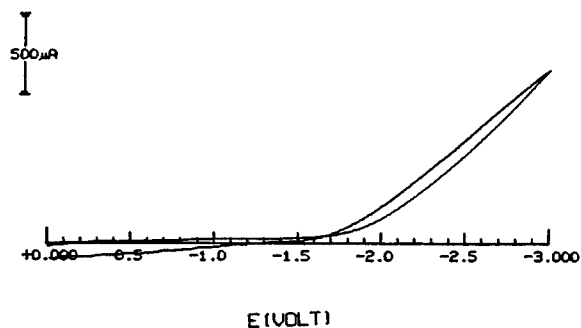


Figure 7 Cyclic voltammogram for 0.01 M KCl solution (background) (W.E. = glassy carbon electrode; scan rate = 250 mV/s).

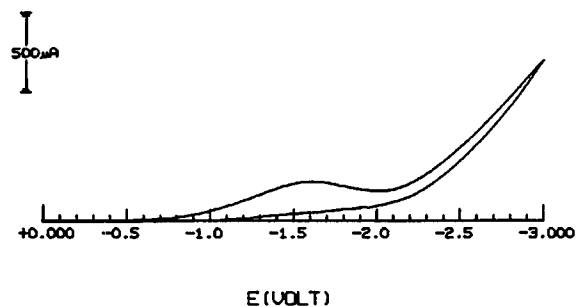


Figure 8 Cyclic voltammogram for $0.01 \text{ M potassium persulfate}$ in water (W.E. = glassy carbon electrode; scan rate = 250 mV/s).

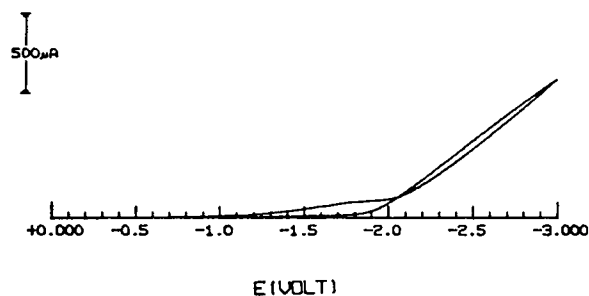


Figure 9 Cyclic voltammogram for 0.1M AM + 0.1M AN + 0.05M MBA + 0.01M potassium persulfate in water (W.E. = glassy carbon electrode; scan rate = 250 mV/s).

SEM Results

Effect of Current Density on the Coating Morphology

Figure 5 presents the SEM micrographs of the electrosynthesized coatings on the Al electrode at 0.10, 0.20, 0.30, and 0.40 mA/cm² for 16 min reaction time. At low current density, 0.10 mA/cm², many bubbles were observed during the process. The rate of polymer coating thickness development becomes slower relative to water reduction, which is a competition reaction in the system. Therefore, it takes a longer time to have an appreciable amount of polymer formed on the electrode. The thin spongy coating at 16 min shows quite obvious small cracks due to the gas liberation and drying process. As current density increases, the rate of polymer coating thickness development becomes faster relative to water reduction.¹³ Thicker coatings were formed, and fewer gas bubbles were apparent. This is because the polymer coatings formed on the Al electrode have an inhibition effect on water reduction. The coatings were more uniform with fewer cracks and small "holes," but after drying, a thick swollen coating leaves a "flaky" texture on the metal substrate, as shown in Figure 5(d).

Effect of Time on the Coating Morphology

Figure 6 shows the SEM micrographs of the electrosynthesized polymer coatings on the Al electrode at 0.20 mA/cm² for 10, 16, 23, and 30 min. A spongy coating structure was found in all the samples. As reaction time increases, the coating thickness also increases. This depresses the efficiency of water reduction, as observed by less gas evolution. A very thick coating was produced in long time periods, and a large amount of water was trapped in the swollen coating. Drying of water from the coatings leaves some obvious large cracks, especially in the sample at 30 min [Fig. 6(d)].

Cyclic Voltammetry (CV) Results

The CV response of the background cell solution, 0.1M KCl solution, is given in Figure 7. The monomers are stable from 0.00 to -3.00 V vs. SCE; only water reduction takes place beyond -1.50 V. In the case of 0.01M potassium persulfate in water (Fig. 8), the persulfate reduction peak occurs in the range of -1.50 to -1.70 V vs. SCE. With the addition of the monomers (Fig. 9), the persulfate reduction shifts to -1.70 to -1.90 V vs. SCE, and there is a drop in the reducing current. This drop is due to the increased resistance of the solution system in the presence of the monomers. The CV results clearly show that potassium persulfate is the only species responsible for initiating polymerization.

Effect of the Addition of Benzoquinone

Hydroquinone and benzoquinone are commonly used as free-radical inhibitors. In this system, potassium persulfate, which is a good oxidizing agent, can efficiently oxidize hydroquinone to benzoquinone. Therefore, benzoquinone was chosen to determine the polymerization mechanism. It was found that the polymerization completely stopped after the addition of 0.01M benzoquinone (Fig. 10). This confirms that the electropolymerization follows a free-radical mechanism.

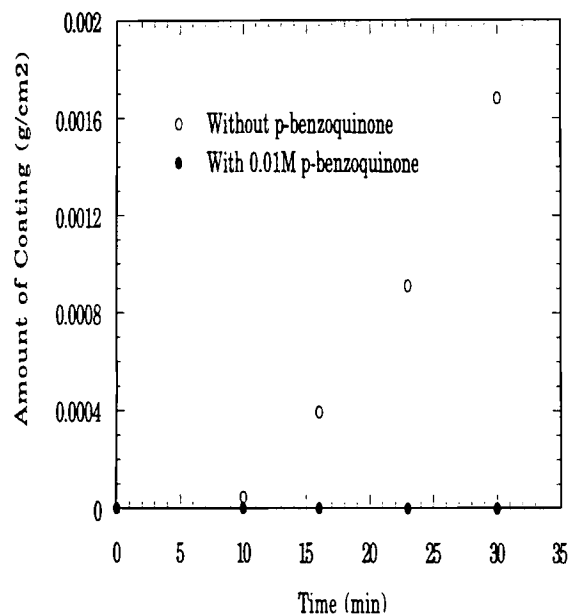
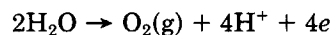


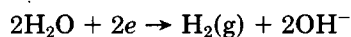
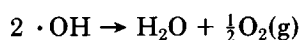
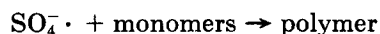
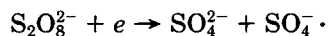
Figure 10 Effect of benzoquinone on the coating amount in the early stages of electropolymerization ([AM] = [AN] = 0.5M; [MBA] = 0.05M, [persulfate] = 0.05M; current density = 0.2 mA/cm²).

The actual reactions taking place on the cathode and the anode are

Anode



Cathode



CONCLUSIONS

The aqueous persulfate electroinitiated polymerization of acrylamide, acrylonitrile, and *N,N'*-methylenebisacrylamide was successfully carried out on the aluminum cathode in a three-compartment cell at room temperature. The polymer coating was thick and swollen but brittle after drying, owing to cross-linking. The FTIR results confirmed that the polymer coating is a copolymer of AM and AN cross-linked by MBA. The electrosynthesized crosslinked copolymer has a high T_g of 239°C and degradation temperature of 310°C. At low current density (0.10 mA/cm²), the polymer coating was uniform but has some small cracks due to water reduction and to the

drying process. Thicker and flaky coatings with fewer cracks are observed at higher current densities. Large cracks appear on the coatings formed in the longer reaction time periods. The proposed initiation is a free-radical mechanism carried out by the sulfate radical, which results from the reduction of persulfate in the potential range of -1.50 to -1.70 V, measured by the CV technique at 250 mV/s scan rate.

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