

# Electropolymerization of Monomers on Metal Electrodes

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## Synopsis

The use of electropolymerization to coat metal electrode surfaces with polymers formed *in situ* was investigated in detail. Electrolysis was carried out in a three-compartment cell with fritted disk separators such that polymerization occurred in the middle compartment only. Both anodic and cathodic reactions were utilized to form coating on pretreated metal surfaces. It was shown that polymerization occurred both by vinyl polymerization of olefin monomers as well as by ring-opening reactions of cyclic monomers. The factors that control the coating thickness, the morphology of the polymer deposit, and the adhesion of the polymer formed to the metal substrates were determined. It was found that the growth of the coating on electrode followed the chain polymerization kinetics to a considerable degree. However, increased current did not necessarily lead to increased coating thickness because it also led to increased early termination of growing polymer chains to form soluble low molecular weight products. Water, because of its high surface tension, encourages physical adsorption on metal surfaces of organic monomers dissolved in it. Thus, water was found to be unique as solvent for obtaining coatings with good adhesion to metal substrates. Coatings formed were analyzed by several methods including infrared spectroscopy. Several types of bonding, other than bond formation caused by polymerization reactions, were identified. Finally, the cyclization of polyacrylonitrile was observed when the coating was obtained on aluminum cathode during electrolysis of acrylonitrile-sodium nitrate-DMF solution.

## INTRODUCTION

The electro-initiated polymerization or electropolymerization of vinyl and other monomers has been investigated in considerable detail by now.<sup>1-3</sup> These earlier studies have generally attempted to determine polymerization mechanisms, the effects of process variables on polymer molecular weight, and the polymer yield, and also to establish rate equations in some instances. Thus, when an electric current is passed through a solution of the monomer, solvent, and electrolyte, polymer formation takes place through either free-radical, anionic, or cationic mechanisms or by a combination of these. The initiation of polymerization may be direct, through oxidation or reduction of monomer molecule, or indirect, through formation of an active intermediate from one of the other components in solution and subsequent initiation of polymerization by such species formed *in situ*, or both. The advantages of electropolymerization include the diversity of accessible polymerization reactions, a product free from impurities in many cases, better control of molecular weight and molecular weight distribution, and relatively mild polymerization conditions. The disadvantages of this method include the restrictions placed on the choice of solvent and electrolyte for a particular monomer by the solubility relationships and the requirement of good conductivity of the electrolytic solution.

It should be noted that most electropolymerization studies have been primarily concerned with the formation of polymers in solution. The coating of electrodes, whenever it occurred, has been an unexpected and undesirable side reaction since it changes the electrode potential in an unquantifiable manner making the control of the process or study of the reaction mechanisms difficult. Attempts to overcome this "problem" have included the use of a solvent, that is also a good solvent for the polymer formed, intermittent reversal of polarity, increase in stirring rate, and reduced electrode surface areas.

The objective of the current investigation is to explore the use of electropolymerization to coat metal surfaces with polymers formed *in situ*. This method, which can be regarded as complementing electropolymerization in solution, is recent, and no systematic studies of this process exist. It should also not be confused with the conventional electrocoating methods where a preformed polymer is deposited on substrates from solutions or suspensions of polymer by electrophoretic means. Ross and Kelly<sup>4</sup> obtained submicron-thickness adherent films of poly(*p*-xylylenes) on aluminum cathodes by electrolyzing a solution of *p*-xylylenebis(trimethylammonium salt) in a polar solvent using an undivided cell. Asahara et al.<sup>5-9</sup> have shown formation of polymer films on metals during electropolymerization of several vinyl monomers. They also reported formation of amorphous whiskers with molecular weight of ~1000 during electrolysis of acrylonitrile solutions.

Bezuglyi and Korshikov et al.<sup>10-12</sup> obtained poorly adhering poly(methyl methacrylate) and polystyrene films on steel cathodes by electrolysis of the solutions of corresponding monomers from *N,N*-dimethylformamide (DMF) in an undivided cell. Through use of free-radical inhibitors and anionic inhibitors, the mechanism of polymerization was also established to be mainly anionic. This mechanism was further confirmed by a study of the copolymerization of styrene with methyl methacrylate under identical conditions.<sup>13</sup> Bruno et al.<sup>14</sup> have electropolymerized acrylonitrile from dichloromethane solution on an iron electrode and, using carbon-13 NMR, showed that the polymer obtained had no stereoregularity. Bogenschuetz<sup>15</sup> obtained very thin corrosion-resistant coatings on a variety of metals by electropolymerization of diacetoneacrylamide. Similarly, good poly(arylene oxide) coatings have been obtained by electropolymerization of phenols.<sup>16</sup>

The research reported here is an in-depth study of the electropolymerization method of forming coatings on metal electrodes. Using a divided cell, such coatings were formed from electrolysis of numerous monomer-solvent-electrolyte combinations. The conditions of electropolymerization were also varied. Based on the results, the many factors that govern coating quality, its thickness, and adhesion to substrate were determined.

## EXPERIMENTAL

### Materials

Most of the vinyl monomers were obtained from the Aldrich Chemical Company, Milwaukee, Wisconsin. Additionally, glycidyl methacrylate (Haven Chemical Company, Philadelphia, Pennsylvania), phenyl glycidyl ether (Shell Chemical Corporation, New York, New York), *N*-methylolacrylamide (American

Cyanamid Company, Wayne, New Jersey), and polyfunctional azirdine PFAZ301 (Ionac Chemical Company, Birmingham, New Jersey) were also obtained from their respective commercial suppliers. The inhibitors from vinyl monomers were removed by alkali washing or vacuum distillation as necessary.

The reagent-grade solvents and electrolytes were obtained from the Aldrich Chemical Company, Milwaukee, Wisconsin, the Mallinckrodt Chemical Works, St. Louis, Missouri, and the J. T. Baker Chemical Company, Phillipsburg, New Jersey, and used as received without further purification.

A common aluminum alloy containing 1.2% manganese (alloy 3003) and a low-carbon steel (AISI 1018) were obtained from the Ryerson, Spokane, Washington. Similarly, copper of 99.9+% purity was obtained from the Alaskan Copper and Brass Company, Seattle, Washington. All metals were cut into 2.5 cm-by-10.2 cm strips, and a suitable surface treatment, as described below, was applied to them before use.

### Surface Treatments for Metal Electrodes

In order to obtain efficient bonding between the coating and the metal, surface treatments based upon those commonly employed for obtaining best adhesive bonding with metals<sup>17,24,25</sup> were applied to all metal strips. Thus, for aluminum alloys, the surface treatment was to clean with soap and water, degrease with trichloroethylene at 65°C, and then immerse in chromic acid solution (30 parts water, 10 parts concentrated sulfuric acid of sp. gr. 1.86, and 1 part sodium dichromate) for 10 min at 65–71°C. This was followed with rinsing in water and oven drying at 65°C for 1 hr.

For steel, the surface preparation involved cleaning with soap and water, degreasing with trichloroethylene at 65°C, and immersion in acid solution (1 part concentrated hydrochloric acid of sp. gr. 1.18 and 1 part water) for 10 min at 57–63°C. This was followed with rinsing in water and oven drying at 100°C. Since the steel treated in this manner rusts rapidly, the prepared metal was used immediately.

For copper, the surface treatment was to clean with soap and water, degrease with trichloroethylene at 65°C, and then immerse in etching solution (197 parts water, 30 parts concentrated nitric acid of sp. gr. 1.42, and 15 parts 42% aqueous ferric chloride solution) for 2 min at room temperature. This was followed by rinsing in water and air drying at room temperature.

Sometimes, the only surface treatment used for metals was to clean with soap and water and degrease in trichloroethylene at 65°C. This treatment greatly assisted in separating the coating from the metal, without contaminating it with metal oxides and hydroxides, for further analysis.

### Electropolymerization Apparatus

The electrolytic cell used was a 9-cm-diameter cylindrical glass cell which was divided into three compartments by two circular fritted glass disks. The metal to be coated was placed in the middle compartment while an auxiliary platinum electrode was placed in each of the remaining two compartments. The working electrode was 6 cm from either platinum electrode. Electrolysis could be conducted at constant cell voltage or constant cell current using a dc power supply

(Hewlett-Packard Model 6438 B) with a range of 0–60 volts and 0–5 amps. A two-channel strip chart recorder (Hewlett-Packard Model 7128 A) provided for continuous monitoring of cell voltage and cell current as a function of time.

Occasionally, a 200-ml tall-form electrolytic beaker was used as an undivided cell. The beaker was covered with a circular rigid polyethylene sheet. The anode and cathode were suspended 3 cm apart from this cover into electrolytic solution.

### Electropolymerization Procedure

The desired monomer–solvent–electrolyte solution, 400 ml, and another 400 ml of solvent–electrolyte mixture without the monomer were prepared and deaerated with nitrogen for 15 min. Next, the monomer solution was placed in the middle compartment of the electrolytic cell while the solution containing no monomer was divided into the two end compartments. Nitrogen was bubbled continuously through the monomer solution during electropolymerization. The electrodes were placed in the cell and connected to the power supply so that the reaction of interest, whether anodic or cathodic, would occur in the middle compartment. The solution was first preelectrolyzed for  $\frac{1}{2}$  hr. The middle-compartment electrode was next replaced with a weighed electrode made of the metal to be coated, and the electrolysis was conducted at the desired cell voltage or cell current. After the prescribed electrolysis time, the coated electrode was removed, washed with fresh solvent, dried under vacuum at room temperature or higher temperature as needed, and weighed again. The thickness of the coating was determined from the gain in weight of the electrode and the area coated. The electropolymerization procedure when using an undivided cell was similar, except that only 150 ml of desired monomer–solvent–electrolyte solution was prepared.

### Analysis of Coatings

All coatings were examined with the aid of an American Optical stereo-optical microscope using magnifications of up to 100 $\times$  and the general appearance of the coating was noted. Some of the coatings were further studied using metallogical microscopes and a scanning electron microscope.

Thicker coatings were scraped off from the metal and analyzed by transmission infrared spectroscopy using the Perkin-Elmer spectrophotometer Model 621. Thin coatings were similarly analyzed by multiple specular reflection infrared spectroscopy using Wilks Engineering Model 9 attachment.

Elemental analysis was carried out on some of the coatings using the Perkin-Elmer Model 240 elemental analyzer. Similarly solvent extraction in a Soxhlet extractor was employed to determine soluble and insoluble fractions in the coatings. Finally, in a few cases, the molecular weight of the soluble portion was determined by the solution viscosity method.

## RESULTS AND DISCUSSION

Polymers from vinyl monomers, viz., acrylonitrile, acrylic acid, styrene, N-methylolacrylamide, methyl methacrylate, styrene-maleic anhydride, meth-

acrylic acid-acrylamide, methacrylic acid-*N,N'*-methylenebisacrylamide, glycidyl methacrylate, etc., were formed as coating on aluminum, copper, and steel electrodes by the electropolymerization method. Both protic and aprotic solvents were utilized. Similarly, even though the choice of electrolytes was severely restricted by solubility in the particular monomer-solvent combination chosen, an effort was made to use neutral salts, acids, and tetraalkylammonium salts for each combination as far as possible. Coatings were also obtained by electrolyzing monomer-electrolyte combinations only.

To determine if the electric field of intensity used in the present study was by itself capable of initiating polymerization of monomers on metal electrodes, the neat monomers, viz., acrylonitrile and styrene, were electrolyzed without adding an electrolyte for periods of up to 96 hours. In the absence of a supporting electrolyte, these monomers caused high cell resistances, and, thus, only a negligible measurable current resulted in the case of acrylonitrile monomer and none in the case of styrene monomer. No detectable coating could be obtained in either case. Similarly, the electrolysis for 72 hr of 1:1 styrene-maleic anhydride mixture in benzene with no supporting electrolyte yielded a negligible measurable current and no detectable coating on aluminum electrodes. Hence, it is concluded that in the absence of a measurable electrode reaction as indicated by a measurable current, the electric field obtained under the present experimental conditions does not cause the formation of a polymer coating on metal electrodes.

The general approach adopted in the present study, for determining various factors that control the coating morphology, its thickness, and adhesion to the substrate, was to vary one component of the monomer-solvent-electrolyte system while keeping all other factors constant and to observe changes in the coating formed. The cell voltage, electrolysis time, monomer concentration, electrolyte concentration, and electrode material were also varied. A summary of the representative experiments is given in Table I. From this table, it is concluded that monomers, vinyl as well as cyclic, which can be polymerized by free-radical or ionic mechanisms can be formed as a coating on metal electrodes by electrolysis of their solutions in suitable solvents containing a supporting electrolyte.

### Morphology of the Polymer Coating

The deposit formed on the metal electrode was inspected soon after its removal from the electrolytic cell. After washing and drying, this coating was again examined with the aid of a stereo-optical microscope using magnifications of up to 100 $\times$ . Some of the coatings were examined further at much higher magnification using a metallurgical microscope, and a few were studied using scanning electron microscopy. It was found that the growth of coating was at least superficially uniform, except at the electrode edges where a thicker coating tended to form. In many instances, this uniform coating would delaminate during the process of removal of the electrode from the cell and peel and crack during drying, or break off when electrolysis was continued for a longer period of time, thus leading to a final nonuniform, dried coating. Based upon their physical appearance, the polymer coatings obtained could be generally subdivided into the following three classes:

**Class I.** This class of coatings had a powdery to spongy physical appearance.

TABLE I  
Summary of Selected Experiments in Electropolymerization of Monomers on Metal Electrodes

Composition of solution	Voltage, volts	Current, mA		Remarks
		Initial	Final	
Acrylic acid, 1.39M H <sub>2</sub> SO <sub>4</sub> , 0.051M Water	8	290	270	very thin, translucent, class-III coating in 6 hr; aluminum cathode
Acrylic acid, 1.39M NaNO <sub>3</sub> , 0.059M Water	8	138	120	very thin, translucent, class-III coating in 6 hr; aluminum cathode
Acrylic acid, 1.39M NaNO <sub>3</sub> , 0.059M Methanol	8	64	60	very thin, translucent but wrinkly, class-III coating in 6 hr; aluminum cathode
Acrylic acid, 1.39M NaNO <sub>3</sub> , 0.059M	8	38	37	very thin, transparent, class-III coating in 6 hr; aluminum cathode
N,N-Dimethylformamide Acrylic acid, 1.39M AlCl <sub>3</sub> , 0.047M Water	8	145	122	Thick, greyish white, class-I coating in 23.5 hr; even though superficially smooth, it showed spongy structure under the microscope; aluminum cathode
Acrylic acid, 1.39M N,N'-Methylenebisacrylamide, 0.081M, H <sub>2</sub> SO <sub>4</sub> , 0.051M Water	8	250	125	thick, white, spongy but superficially smooth, class-I coating in 25 hr; aluminum cathode
Acrylic acid, 1.39M NaNO <sub>3</sub> , 0.029M PFAZ 301, 25 g/l. Water	10 <sup>a</sup>	90	124	thick, somewhat grey, class-I coating in 19.5 hr; this coating had a moderately fine powdery surface appearance; aluminum cathode
Acrylonitrile, 2.36M NaNO <sub>3</sub> , 0.044M	5	30	40	thick, orange-yellow class-II coating in 1.5 hr; this coating hardened and cracked extensively upon drying; aluminum cathode
N,N-Dimethylformamide Acrylonitrile, 2.36M NaNO <sub>3</sub> , 0.044M	7	28	27	
	5	16	11	thick, orange-yellow class-II coating in 1.5 hr; this hardened to dark red-brown coating upon drying at 100°C and also cracked; steel cathode

N,N-Dimethylformamide Acrylonitrile, 2.36M NaNO <sub>3</sub> , 0.044M	5	20	14	thick, orange-yellow class-II coating in 1.5 hr; this hardened to dark red-brown coating upon drying at 100°C and also cracked; copper cathode
N,N-Dimethylformamide Acrylonitrile, 1.18M H <sub>2</sub> SO <sub>4</sub> , 0.051M Water	8	260	230	very thin, translucent class-III coating in 5 hr; aluminum cathode
Acrylonitrile, KClO <sub>4</sub> , 0.024M	10	15	3	brown, powdery class-I coating in 24 hr; the undivided cell was used for electrolysis; aluminum cathode
Acrylonitrile, (C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr, 0.032M	3.6	16.4	7.6	thin, yellow class-II coating in 10.5 hr; this coating hardened and cracked extensively upon drying; undivided cell was used for electrolysis; aluminum cathode
Acrylonitrile, neat	15 <sup>a</sup>	0.20	0.20	no detectable coating obtained in 38 hr, even though there was some loss of surface reflectivity of metal; undivided cell used; aluminum cathode
Acrylonitrile, NaClO <sub>3</sub> , 0.031M H <sub>2</sub> O, 1.11M	30	0.40	0.20	
Acrylonitrile, (CH <sub>3</sub> ) <sub>4</sub> NCl, 0.061M	6.5	0.42	0.35	brown, powdery class-I coating in 26 hr; undivided cell used; aluminum cathode
Acrylonitrile, H <sub>2</sub> SO <sub>4</sub> <sup>b</sup> , 0.136M	5	10	10	thin, light-brown class-I spongy coating in 20.5 hr; undivided cell used; aluminum cathode
Acrylonitrile, 1.18M NaNO <sub>3</sub> , 0.044M	12	3.5	3	white class-I coating in 7 hr; undivided cell used; aluminum cathode
Dimethyl sulfoxide N-Methylolacrylamide, 0.619M H <sub>2</sub> SO <sub>4</sub> , 0.051M Water	15	37	30	thin, orange-yellow, soft class-II coating in 0.75 hr; this dried to a hard, translucent, extensively cracked coating; aluminum cathode
N-Methylolacrylamide, 0.619M NaNO <sub>3</sub> , 0.015M	8	300	280	thick, white, powdery, superficially smooth class-I coating in 5.5 hr; aluminum cathode
N,N-Dimethylformamide Methyl Methacrylate, 0.750M MgCl <sub>2</sub> , 0.037M Methanol	5	12	11	thick, white class-I coating in 24 hr; aluminum cathode
	2.5	105	100	thick, white, spongy, poorly adhering class-I coating in 3.5 hr; aluminum cathode

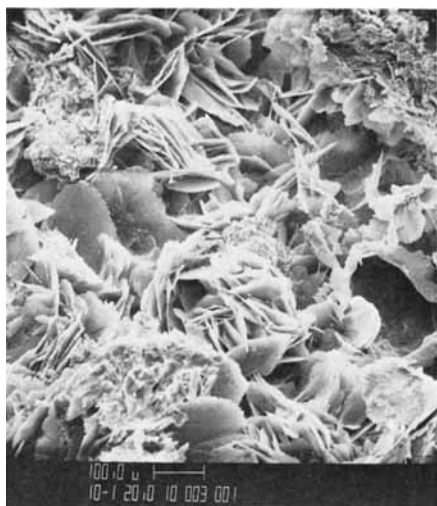
TABLE I  
Summary of Selected Experiments in Electropolymerization of Monomers on Metal Electrodes

Composition of solution	Voltage, volts	Current, mA		Remarks
		Initial	Final	
Methyl Methacrylate, 1.75M CH <sub>3</sub> COOLi, 0.303M Methanol	4	20	18	very thin, barely visible class-III coating in 6 hr; aluminum cathode
Styrene, 0.962M NaNO <sub>3</sub> , 0.029M N,N-Dimethylformamide	10	30	2	thin, brownish-yellow class-II coating in 13 hr; this hardened and cracked extensively upon drying; aluminum cathode
Styrene, 0.962M NaNO <sub>3</sub> , 0.029M Methanol	12	75	69	very thin, barely visible class-III coating in 6 hr; aluminum cathode
Styrene, neat	30	0	0	no detectable coating in 96 hr on either anode or cathode; undivided cell used; aluminum cathode and anode
Maleic anhydride, 0.504M Styrene, 0.504M Benzene	15	0.006	0.003	no detectable coating in 72 hr on either anode or cathode; undivided cell used; aluminum cathode and anode
Glycidyl methacrylate, 0.440M CH <sub>3</sub> COONa, 0.030M Dichloromethane	5	13	11	thick, white, powdery class-I coating in 17 hr; aluminum cathode
Glycidyl methacrylate, 0.440M NaClO <sub>4</sub> , 0.027M Acetonitrile	10	26	4	thin, white, powdery class-I coating in 4 hr; some corrosion (pit formation) of aluminum metal also evident; aluminum cathode
Glycidyl methacrylate, 0.440M (C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr, 0.018M Dichloromethane	12	11	7	thin, greyish, powdery class-I coating in 6.5 hr; a yellow layer between the metal and the coating was also present; aluminum anode
Glycidyl methacrylate, 0.440M KClO <sub>4</sub> , 0.027M N,N-Dimethylformamide	8	37	45	thin, white, powdery class-I coating in 14.25 hr; aluminum cathode
Phenyl glycidyl ether, 0.833M NaClO <sub>4</sub> , 0.036M Acetonitrile	10	130	2	white class-II coating in 19 hr; this coating cracked extensively upon drying; aluminum anode



12	480	480	very thin, barely visible, greyish-white class-III coating in 1 hr; aluminum cathode
Acrylamide, 0.436M Methacrylic acid, 0.436M H <sub>2</sub> SO <sub>4</sub> , 0.051M Water			
12	445	190	thin, white, powdery class-I coating in 12.75 hr; this coating cracked extensively upon drying; copper cathode
Acrylamide, 0.436M Methacrylic acid, 0.436M H <sub>2</sub> SO <sub>4</sub> , 0.051M Water			
12	205	170	very thin, greyish class-III coating in 5 hr; steel cathode
Acrylamide, 0.436M Methacrylic acid, 0.436M H <sub>2</sub> SO <sub>4</sub> , 0.051M Water			
10	195	130	thin, white, powdery class-I coating in 6 hr; aluminum cathode
Methacrylic acid, 0.436M N,N'-Methylenebisacrylamide, 0.145M, H <sub>2</sub> SO <sub>4</sub> , pH 2.0 Water			
10	135	70	moderately thick, white, powdery class-I coating in 15 hr; copper cathode
Methacrylic acid, 0.436M N,N'-Methylenebisacrylamide, 0.145M, H <sub>2</sub> SO <sub>4</sub> , pH 2.0 Water			

<sup>a</sup> Cell voltage was changed to second value after 12 hr. <sup>b</sup> Reagent-grade concentrated sulfuric acid was used.

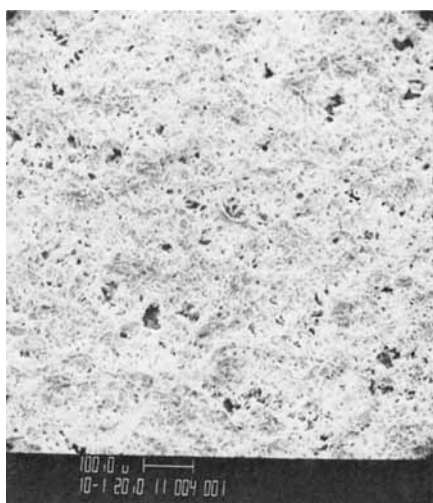


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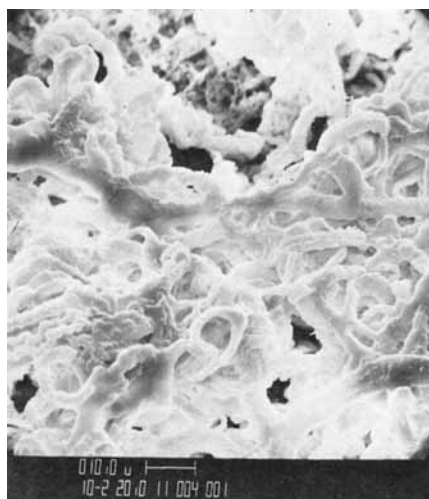


1000X

Fig. 1. SEM of powdery class-I poly(glycidyl methacrylate) coating on aluminum cathode obtained by electrolysis of 0.440M glycidyl methacrylate-0.030M sodium acetate-dichloromethane solution at 5 volts for 17 hr.



100X



1000X

Fig. 2. SEM of spongy class-I crosslinked poly(acrylic acid) coating on aluminum cathode obtained by electrolysis of 1.39M acrylic acid-0.081M *N,N'*-methylenebisacrylamide (crosslinKer)-0.051M concd. sulfuric acid-water solution at 8 volts for 25 hr.

When removed from electrolytic cell, these coatings had a substantial quantity of solvent interlocked in the spaces between the polymer particles, but there was no significant swelling of the polymer as such. The solvent could be removed rapidly under vacuum leaving behind a coating that had essentially the same thickness and physical appearance as a coating freshly removed from the cell. A slight mechanical shock tended to readily separate powdery coatings from the metal, leaving behind a very thin, powdery coating on metal. Figure 1 shows

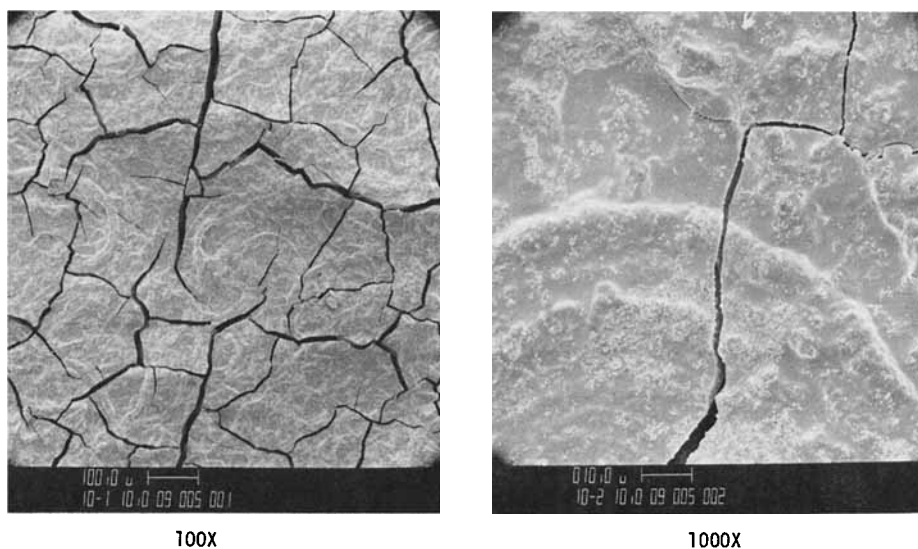


Fig. 3. SEM of class-II polyacrylonitrile coating on aluminum cathode obtained by electrolysis of 2.36M acrylonitrile-0.044M sodium nitrate-DMF solution at 5 volts for 2 hr.

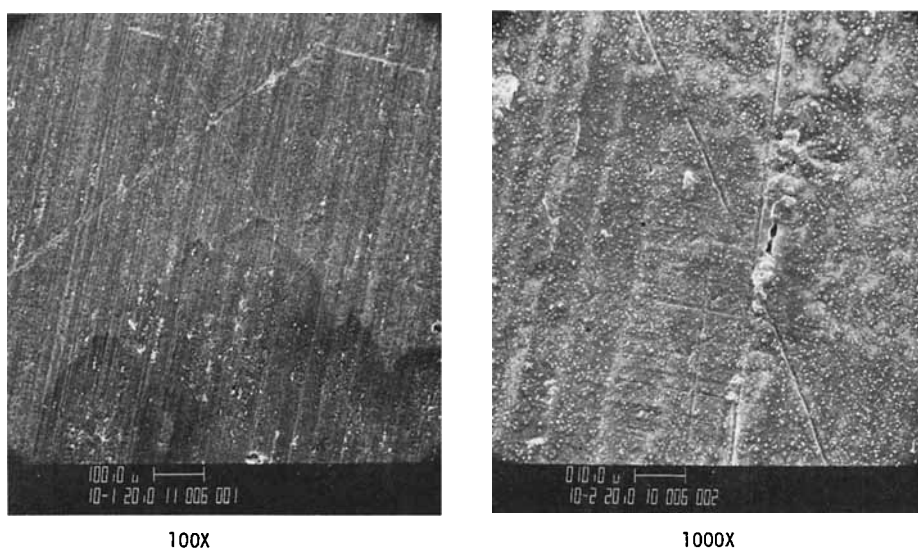


Fig. 4. SEM of class-III poly(acrylic acid) coating on aluminum cathode obtained by electrolysis of 1.39M acrylic acid-0.051M concd. sulfuric acid-water solution at 8 volts for 6 hr.

scanning electron micrographs (SEM), at 100 and 1000 magnifications, of powdery poly(glycidyl methacrylate) coating on aluminum cathode obtained by electrolyzing glycidyl methacrylate-sodium acetate-dichloromethane solution for 17 hr. This highly fragile coating on aluminum always left polymer powder on any surface it came in contact with. Spongy coatings, however, did not delaminate as easily even though there was some cracking and peeling of these coatings upon drying. Figure 2 shows the scanning electron micrographs of

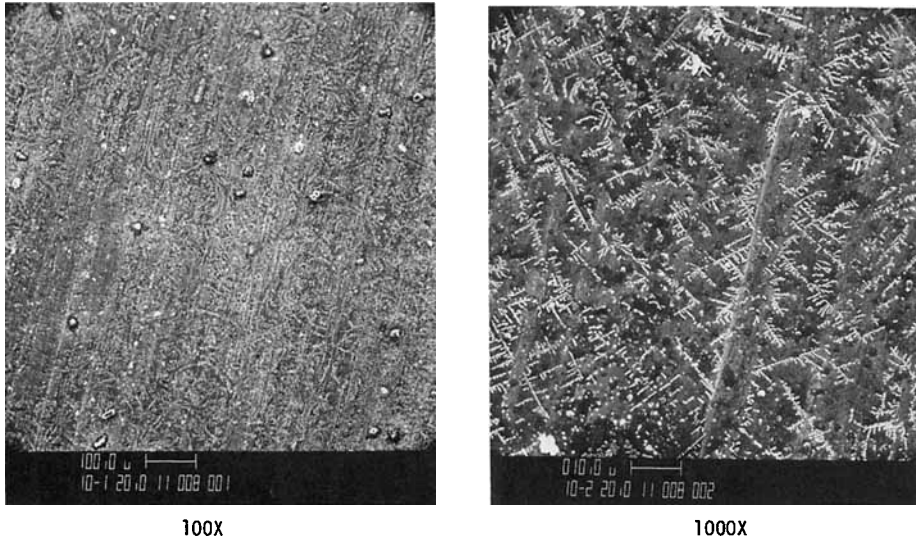


Fig. 5. SEM of class-III poly(acrylic acid) coating on aluminum cathode obtained by electrolysis of 1.39M acrylic acid–0.059M sodium nitrate–water solution at 8 volts for 6 hr.

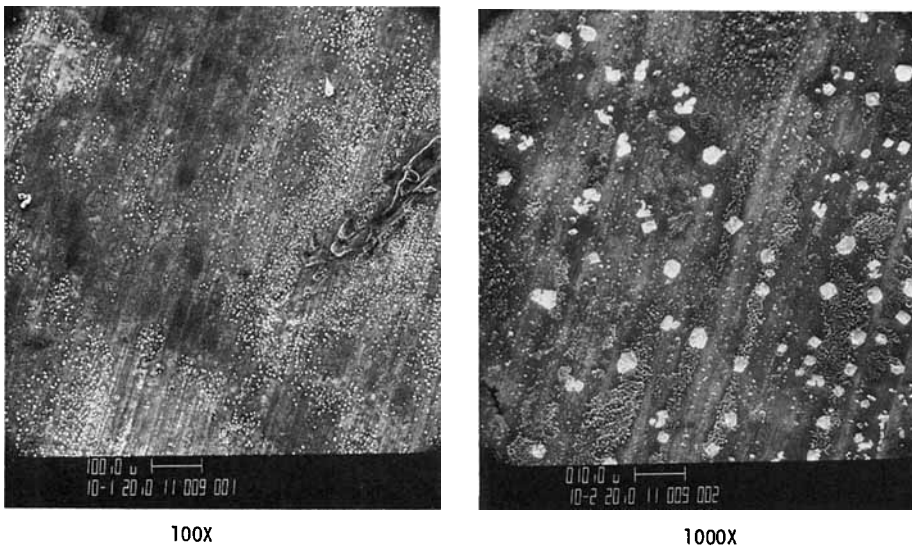


Fig. 6. SEM of class-III poly(acrylic acid) coating on aluminum cathode obtained by electrolysis of 1.39M acrylic acid–0.059M sodium nitrate–methanol solution at 8 volts for 6 hr.

spongy crosslinked poly(acrylic acid) coating on aluminum cathode obtained by electrolyzing acrylic acid–*N,N'*-methylenebisacrylamide (crosslinker)–concentrated sulfuric acid–water solution for 25 hr. The fibrillar appearance of this coating is distinctly noticeable. The class I coatings could be generally made to grow to several hundred micrometers in thickness by continuing the electrolysis for a longer period of time.

**Class II.** This class of coatings had a much more planar surface appearance not unlike that of a painted or sprayed-on coating. Upon removal from the

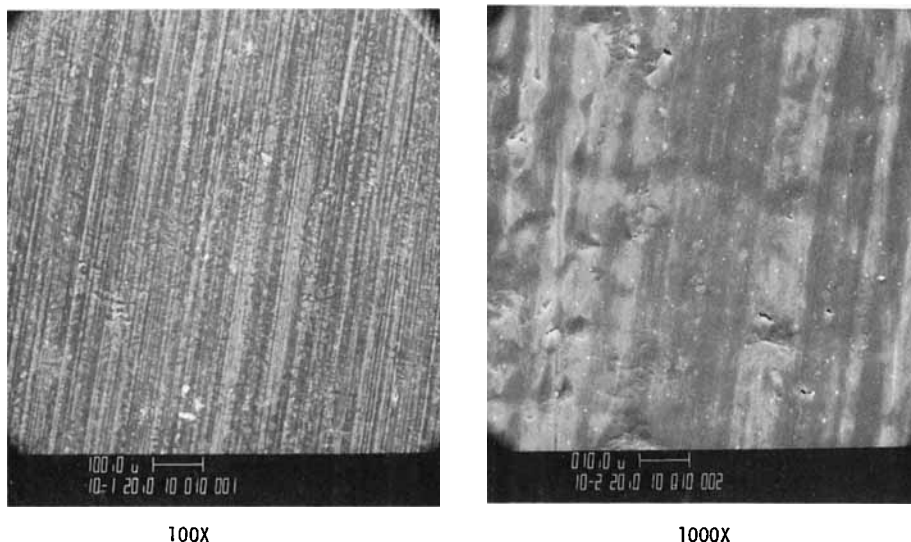


Fig. 7. SEM of class-III poly(acrylic acid) coating on aluminum cathode obtained by electrolysis of 1.39M acrylic acid-0.059M sodium nitrate-DMF solution at 8 volts for 6 hr.

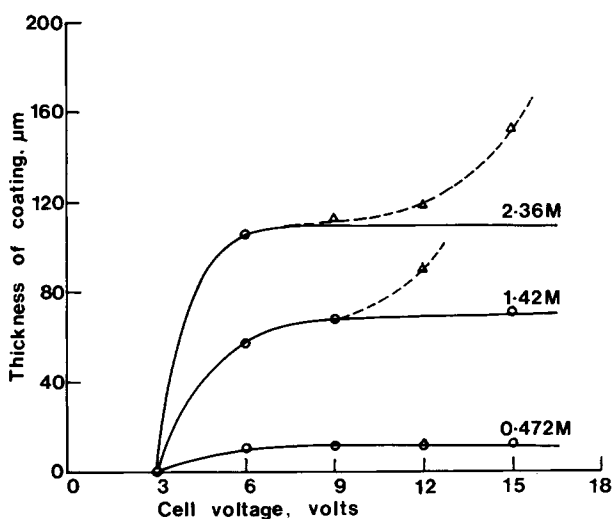


Fig. 8. Thickness of class-II polyacrylonitrile coating formed on aluminum cathode by electrolysis of acrylonitrile-0.044M sodium nitrate-DMF solutions for 30 min, as a function of cell voltage at indicated monomer concentrations: (O) uniform coating; ( $\Delta$ ) whiskers.

electrolytic cell, these coatings were always highly swollen with the solvent and cracked extensively upon drying at room temperature under vacuum. The cracking of the coating generally began during the few minutes between the removal of the electrode from the cell to transferring it to the vacuum chamber. This cracking could not be prevented even when a solvent of low volatility such as N,N-dimethylformamide (bp 153°C) was used. The thickness of the dried coating was always less than one tenth that of the freshly prepared coating. The class II coating could generally be made to grow up to 100  $\mu\text{m}$  in thickness (dry)

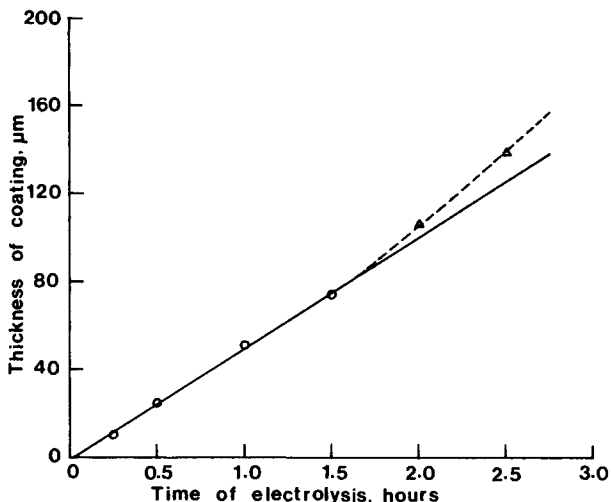


Fig. 9. Thickness of class-II polyacrylonitrile coating formed on aluminum cathode by electrolysis of 0.943*M* acrylonitrile–0.044*M* sodium nitrate–DMF solutions, as a function of the time of electrolysis: (O) uniform coating; (Δ) whiskers.

through continuing electrolysis for a longer period of time. Figure 3 shows the scanning electron micrographs of a class II polyacrylonitrile coating on aluminum cathode obtained by electrolyzing acrylonitrile–sodium nitrate–DMF solution for 2 hr. The extensive cracks can be observed in an otherwise smooth coating even at 1000 $\times$  magnification.

**Class III.** The most distinctive feature of this class of coatings was their extreme thinness, so much so that often the only visual indication of their presence was a change in surface reflectivity of the metal. When removed from the cell, these coatings contained negligible amount of solvent and dried out rapidly, even before application of vacuum. The presence of coating on metal was most difficult to confirm for this class of coatings. Generally, the results of microscopic examination, infrared studies, and weight change measurements were necessary to positively confirm the presence of a coating. The situation was further complicated by the fact that class III coatings were frequently observed when acidic aqueous solutions of monomers were electrolyzed. In such solutions, a significant dissolution of electrode metal occurred initially before application of negative potential, and formation of coating prevented further dissolution. This led to a negative weight gain of the electrode in many cases. The class III coatings could be made to grow up to a thickness of 1.0  $\mu\text{m}$  by continuing electrolysis for a longer period of time. Figure 4 shows the scanning electron micrographs of a class III poly(acrylic acid) coating on aluminum cathode obtained by electrolyzing acrylic acid–concentrated sulfuric acid–water solution for 6 hr.

The effect of changing electrolyte, from concentrated sulfuric acid to sodium nitrate, on the morphology of a class III poly(acrylic acid) coating while keeping all other factors constant is seen from Figures 4 and 5. Growth of polymer particles in dendritic fashion was very appreciable when sodium nitrate was supporting electrolyte (Fig. 5), while use of concentrated sulfuric acid as electrolyte led to random growth of polymer particles on an aluminum surface (Fig. 4).

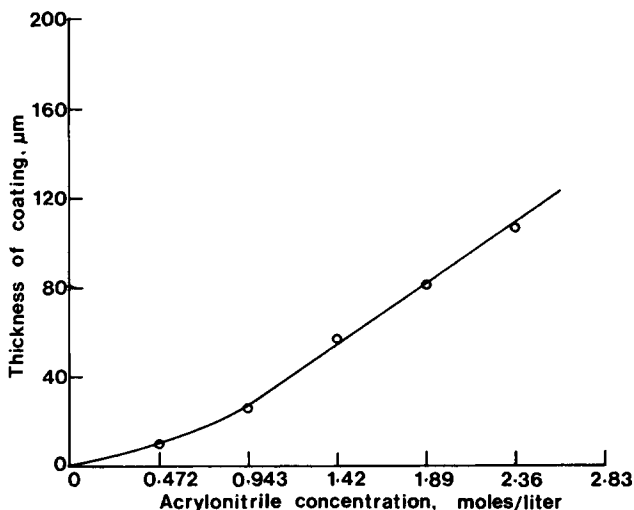


Fig. 10. Thickness of class-II polyacrylonitrile coating formed on aluminum cathode by electrolysis of acrylonitrile-0.044M sodium nitrate-DMF solutions at 6 volts for 30 min, as a function of the monomer concentration.

The effect of changing solvent, from water to methanol to DMF, on the morphology of class III poly(acrylic acid) coating is shown in Figures 5 to 7. From Figure 6, it can be seen that use of methanol as solvent gave rise to a substantial number of lozenge-shaped lamella of poly(acrylic acid) crystals. Use of DMF as solvent led to a coating that was uniform even at 1000 $\times$  magnification, as shown in Figure 7, while use of water as solvent caused formation of polymer particles in dendritic shapes, as shown in Figure 5.

There was a predominant tendency to form powdery to spongy class-I coatings. This tendency is attributed to the polycrystallinity of metal substrate and numerous microscopic irregularities on it, which led to nonuniform tendencies of electrons to escape from the surface as well as provide nuclei for growth of polymer particles. Further, it was found that an increase in the solubility of polymer, formed by electrolysis, in the electrolytic solution counteracted the formation of powdery to spongy coatings and led to the formation of a coating that had a "painted on" appearance. Finally, good solubility of polymer formed *in situ* in the electrolytic solution caused extremely thin class-III coatings to be formed.

### Thickness of Polymer Coating

The dependence of the thickness of a class-II polymer coating formed on aluminum cathodes through electrolysis of acrylonitrile-DMF-sodium nitrate solution was studied as a function of the concentration of monomer, applied cell voltage, time of electrolysis, and initial current. The coating thickness was calculated using gain in weight of electrode, area coated, and a density<sup>18</sup> of 1.18 g/cm<sup>3</sup> for polyacrylonitrile. The results are shown in Figures 8 to 11. In Figures 8 and 9, the formation of whiskers, as reported by Asahara et al.,<sup>7</sup> is also shown. It is apparent that there is a minimum critical thickness of approximately 90  $\mu$ m below which whisker formation does not take place. If a coating is allowed to

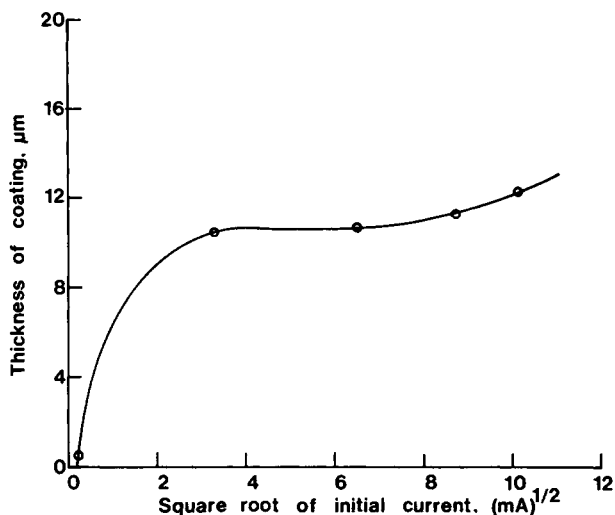


Fig. 11. Thickness of class-II polyacrylonitrile coating formed on aluminum cathode by electrolysis of 0.472*M* acrylonitrile–0.044*M* sodium nitrate–DMF solutions for 30 min, as a function of the square root of initial current. Cell voltage was varied to change current.

grow beyond this thickness, it generally peels, with the peeled sections aligning themselves in the direction of the electric field. The peeled sections do not, however, detach themselves completely from the electrode's surface. Thus, they give the appearance of whisker formation. This behavior was found to be limited to the acrylonitrile–DMF–sodium nitrate system. No such whisker formation took place when styrene–DMF–sodium nitrate solution was electrolyzed to obtain similar class-II coatings. Also, in other systems where coating can be made to grow to large thicknesses, the cracking and peeling of the coating do occur, but without the peeled sections aligning themselves in the direction of the electric field. Generally, these peeled sections separated from the electrode and fell into electrolytic solution in these other cases.

The Figure 8 shows that the cell voltage above a critical value has a negligible effect upon coating thickness. This is in spite of the fact that higher cell voltage does lead to substantially increased current. Therefore, it is suggested that higher cell voltage causes increased charge transfer to species other than monomers which do not initiate polymerization while the charge transfer to monomer remains constant. Thus, beyond a critical cell voltage, the rate of polymerization of monomer is independent of cell voltage. It is also likely that when very large concentrations of initiating radicals are formed at high current, they fail to grow to high polymers and suffer early termination to form soluble low molecular weight products. The concentration of monomer, as expected, had a dramatic effect on coating thickness obtained. From Figure 10, it is apparent that the coating thickness increases linearly with increasing monomer concentration, except at low concentrations of acrylonitrile. Similarly, Figure 9 shows that the coating thickness increases linearly with the time of electrolysis.

Next, one must consider the fact that thick polyacrylonitrile and polystyrene coatings were formed from electrolysis of the solutions of corresponding monomers in DMF even though DMF is a good solvent for both polymers, while only



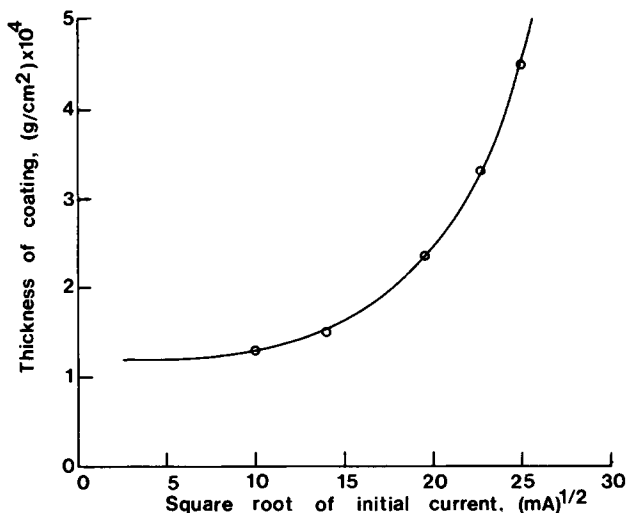


Fig. 12. Thickness of class-I coating formed on aluminum cathode by electrolysis of 0.436*M* methacrylic acid–0.145*M* *N,N'*-methylenebisacrylamide–concd. sulfuric acid–water solutions at 10 volts for 6 hr, as a function of the square root of initial current. The pH of the solution was varied to change current.

thin poly(acrylic acid) coatings could be obtained from electrolysis of its monomer from aqueous solutions. The fact that the coatings form at all during electrolysis of these monomer–solvent combinations indicates that the polymerization in the desolvated layer of monomer near the electrode is strongly favored over solution polymerization under conditions chosen in the present study. It is also suggested that the maximum thickness of coating obtained is a balance between the rate of polymerization and the rate of dissolution of the polymer deposit formed. Further, the rate of anionic polymerization, which predominates in electropolymerizations carried out in DMF, is several orders of magnitude larger than the rate of free-radical polymerization, which is prevalent during electropolymerizations from aqueous solutions. Assuming that the rate of dissolution is comparable in all three monomer–solvent combinations mentioned above, it follows that formation of thicker coatings would be favored when an aprotic solvent is used, even if the polymer formed is soluble in the solvent used.

The maximum obtainable thickness of coating over a long period of electrolysis at constant cell voltage was found to decrease with increasing solubility of polymer deposit in electrolytic solution. Thus, when the acrylic acid–water–sulfuric acid system is electrolyzed, only thin class-III coatings could be obtained. However, when a water-soluble crosslinking agent such as *N,N'*-methylenebisacrylamide or aluminum chloride was added to the electrolytic solution to insolubilize the polymer, thick class-I coatings were obtained. In such coatings, the ultimate coating thickness increased with increasing cell voltage.

### Current–Time and Current–ThicKness Relationships

For most experiments conducted at constant cell voltage, the current as a function of time was continuously recorded for periods up to 1 hr, and then a final reading at the end of electrolysis time was taKen. The current–time relationship

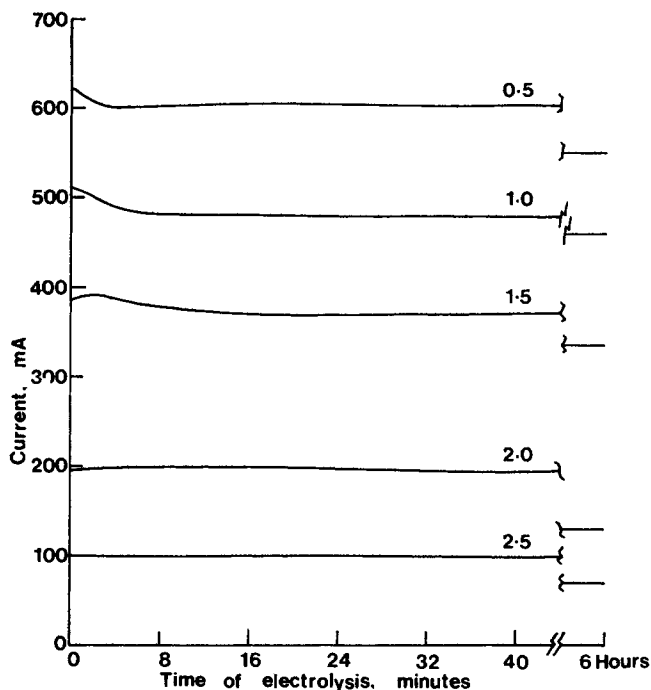


Fig. 13. Current-time relationships for class-I coatings obtained on aluminum cathodes by electrolysis of 0.436*M* methacrylic acid-0.145*M* *N,N'*-methylenebisacrylamide-concd. sulfuric acid-water solutions at indicated pH values and 10 volts.

varied greatly with monomer-solvent-electrolyte combination chosen and considerably with the cell voltage used. Some of the typical current-time and current-thickness curves obtained are shown in Figures 13-15. Generally, there was either a uniform decrease in current with the progress of electropolymerization, as shown in Figures 13 and 15, or a moderate initial increase in current followed by a regular decrease in current when electropolymerization was continued for additional time, as shown in Figure 14, or finally, erratic changes in current with increasing time. The last-mentioned behavior was attributed mainly to the cracking and peeling of the coating during electrolysis.

The steady decrease in current with increasing electropolymerization time was the expected result of formation of an insulating polymer coating on the electrode. Occasionally, this result was also obtained in aqueous solutions, where a very small concentration of the supporting electrolyte had been used, even when no detectable coating had been formed. The final thickness of coatings, for which current-time relationships are shown in Figures 13 to 15, were of the order of a few microns for class-I coatings (Fig. 13), tens of microns for class-II coatings (Fig. 14), and half a micron for class-III coatings (Fig. 15). Since the volume resistivity of vinyl polymers is of the order of  $10^{16}$  ohm-cm, it is obvious that the current drop recorded is much smaller than would be expected. This reduced current drop is attributed to entrapment of solvent and electrolyte between polymer particles (class-I and -II coatings) as well as to swelling of polymer

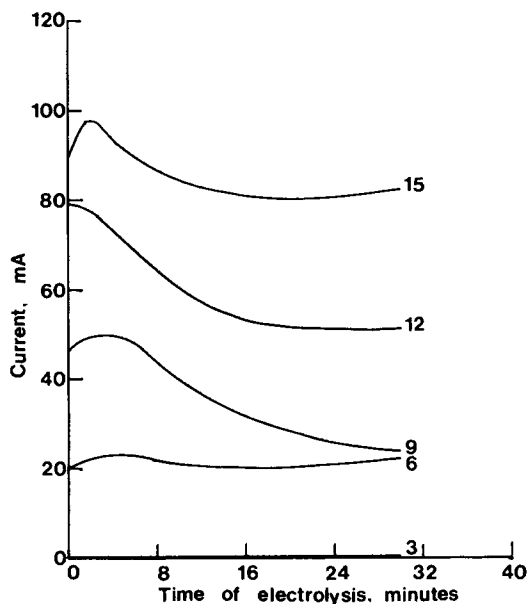


Fig. 14. Current-time relationships for class-II coatings obtained on aluminum cathodes by electrolysis of 1.42*M* acrylonitrile-0.044*M* sodium nitrate-DMF solutions at indicated cell voltages.

(class-II coatings) by solvent permitting free passage of solution components through coating.

The initial increase in current, followed by a regular decline in current, was observed during formation of all three types of coatings in several instances. Such a variation which occurred during formation of class-II polyacrylonitrile coating is shown in Figure 14. The moderate initial increase in current is attributable to changing electrode potential due to the formation of a coating on it, an increase in ionic strength of solution through either formation of anion radicals as in the case of aprotic solution or dissolution of electrode material as in the case of acidic aqueous solutions, and movement of ionizable monomers such as acrylic acid across the cell dividers, thereby leading to an increased conductivity of the cell.

From Figures 13 to 15, it is noted that the rate of change of current is much larger at higher absolute values of current than at lower absolute values of current. This can be explained on the basis of the assumption that higher current leads to a higher rate of polymerization and hence a faster change in current at constant cell voltage. To explore current-thickness relationships further, the coating thickness was plotted against square root of initial current for two cases, as shown in Figures 11 and 12. From these, it can be seen that the linear dependence typical of chain polymerization was not found in these cases. The large variation in the current-thickness relationship with each monomer-solvent-electrolyte combination chosen is also apparent. This nonlinear dependence of coating thickness on square root of current is attributed to the changing initiation mechanisms and changing initiation efficiency with increasing current.

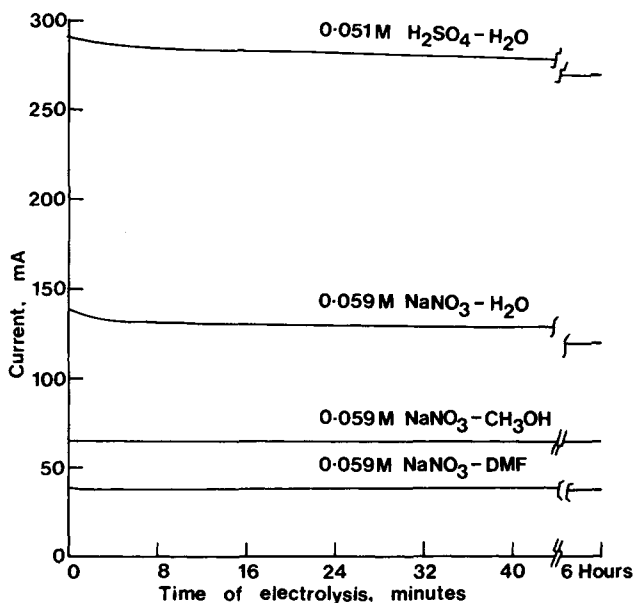


Fig. 15. Current-time relationships for class-III coatings obtained on aluminum cathodes by electrolysis of 1.39M acrylic acid solutions in indicated electrolyte-solvent combinations at 8 volts.

### Adhesion of Polymer Coating to Metal Substrate

The extent of peeling that occurred during the washing and drying of the coating was itself an approximate measure of the degree of adhesion between the polymer film and metal substrate. An attempt was also made to use an Arco Microknife Adherometer (Gardner Laboratory, Bethesda, Maryland) to measure the adhesion between coating and metal. The Adherometer functions by cutting deep parallel lines on the coated metal with the aid of a loaded diamond stylus. The minimum weight on the stylus necessary for the stylus to cut through the coating to metal substrate is taken as a measure of the hardness of coating. Using this load, parallel lines are cut on coated specimen at various distances. The maximum distance between the lines at which the lateral stress exerted by the stylus on the coating is sufficient to detach from the metal the coating strip between the lines is taken as an empirical quantitative measure of adhesion.

When this test was applied to coatings obtained by the electropolymerization method, it gave exceptional adhesion rating to most of the samples tested. Also, the Adherometer tests tended to contradict the estimates of adhesion suggested by the qualitative extent of peeling. Since the Adherometer test is unsatisfactory when used to measure adhesion of porous and/or very thin coatings to metal substrates and since such coatings were obtained predominantly when electropolymerization method was used, it was concluded that extent of peeling was a more realistic measure of adhesion to substrate of the coatings obtained by electropolymerization.

On this basis, it was observed that the polymer coating obtained during electropolymerizations using water as solvent had superior adhesion to metal substrate when compared to coatings obtained from electrolysis of the same mo-

nomers using organic solvents. Thus, it was concluded that for good adhesion, the monomer-solvent-electrolyte system should be devised in such a way as to encourage adsorption of monomer on the electrode. Therefore, based on well-developed principles of physical adsorption,<sup>19</sup> a series of solutions were prepared which contained acrylic acid-sodium nitrate and either water, methanol, or DMF which, because of their decreasing surface tensions, would make it increasingly difficult for acrylic acid to be adsorbed on aluminum electrodes. The adhesion to the substrate of the polymer coatings obtained by electrolysis of these solutions confirmed the importance of the monomer adsorption to subsequent adhesion of polymer film to metal. Since vinyl monomers have low surface tension, their solutions in high surface-tension solvents would favor adsorption of monomer on metal. Therefore, water, because of its much higher surface tension as compared to organic compounds, is a unique solvent whenever it can be used for forming coatings on metals by electropolymerization.

### Analysis of Coatings

The polymer formed on electrodes was analyzed by multiple specular-reflection infrared spectroscopy and frequently also by transmission infrared spectroscopy. In polymer films obtained by electrolysis of the acrylonitrile-sodium nitrate-DMF system, existence of cyclized polyacrylonitrile was shown by absorption at  $1570\text{ cm}^{-1}$  for conjugated  $\text{—C=N—}$  bonds,<sup>20,21</sup> at  $1650$  and  $1635\text{ cm}^{-1}$  for  $\text{C=N}$  bonds, and at  $1220$  and  $1145\text{ cm}^{-1}$  for  $\text{C—N}$  bonds.<sup>22,23</sup> Extraction of the coating with DMF at  $153^\circ\text{C}$  gave a residue of 48% for 48 hr of extraction and 9% for 72 hr of extraction. Further, when the extraction was carried out at room temperature, a residue of 40% was obtained after two weeks of extraction. This shows that the solubility of the product obtained is much less than the solubility of polyacrylonitrile in DMF. Next, using DMF at  $35^\circ\text{C}$  as solvent, the molecular weight of the soluble portions was determined to be  $\approx 20,000$  in each case by solution viscosity method. For this purpose, the parameters of the viscosity-molecular weight relationship for cyclized polyacrylonitrile were assumed to be the same as for linear polyacrylonitrile.<sup>18</sup> The elemental analysis of the coating gave a C:H:N ratio of 3.01:3.03:1.00 against expected values of 3.00:3.00:1.00. Also, the orange-yellow coating obtained continued to darken for a long time after removal from the electrolytic cell. Final coloration was much deeper when drying was carried out at  $100^\circ\text{C}$  than when it was carried out at room temperature. It should be noted that the *thermal* cyclization of polyacrylonitrile does not begin at least until  $250^\circ\text{C}$ .<sup>18</sup> In view of these data, it is concluded that a cyclized polyacrylonitrile coating forms on the cathode when acrylonitrile-sodium nitrate-DMF solution is electrolyzed.

Similarly, the infrared spectra of polymer formed from electrolysis of acrylonitrile-water-sulfuric acid indicated the presence of amine groups. The polymer formed from electrolysis of acrylic acid-water-sulfuric acid, on aluminum cathode, showed the presence of the aluminum salt of acrylic acid.

### SUMMARY AND CONCLUSIONS

It is concluded that most of the vinyl and cyclic monomers can be made to polymerize on metal electrodes through electrolysis of suitable monomer-electrolyte-solvent combinations.

Based upon morphology as determined by light-microscopic and electron-microscopic studies, the superficially uniform polymer coatings obtained could be subdivided into three classes. The class-I coatings had powdery to spongy appearance and could be made to grow to several hundred micrometers in thickness. The class-II coatings had the appearance of a painted-on coating and generally could be made to grow to 100  $\mu\text{m}$  in thickness. These coatings, when removed from the cell, were always highly swollen with solvent. The class-III coatings were extremely thin, and, consequently, their presence on metal electrode was most difficult to confirm. These coatings could be made to grow to 1  $\mu\text{m}$  in thickness by continuing electrolysis for longer periods of time. The polycrystallinity of metal was responsible for the predominant tendency for formation of powdery to spongy coatings, but the greater solubility of the polymer deposit formed tended to counteract it.

During electrolysis of acrylonitrile–sodium nitrate–DMF solution, if the coating formed on the cathode is allowed to grow to 90  $\mu\text{m}$  or more, it generally peels, with the peeled sections aligning themselves in the direction of the electric field. This phenomenon, called whisker formation by others, was not observed during electrolysis of styrene–sodium nitrate–DMF solutions.

For class-II polyacrylonitrile coating, the dependence of coating thickness on cell voltage, initial current, monomer concentration, and time of electrolysis was determined. The results indicated that chain polymerization kinetics were followed to a considerable degree. Further, it was strongly indicated that, at higher current, the increased rate of formation of initiating radicals in localized electrode regions led to increased early termination of growing polymer chains to form soluble, low molecular weight products. Thus, increased current density does not necessarily lead to increased coating thickness.

The current drop observed during formation of the coatings was much smaller than would be expected on the basis of calculated resistivity of uniform polymer coatings. This was attributed to swelling of coating by solvent in some cases and to the entrapment of solvent in the porous coatings.

Water, because of its high surface tension, encourages physical adsorption on metal surfaces of organic monomers dissolved in it. For that reason, water was found to be a unique solvent for obtaining coatings with good adhesion to metal substrates by the electropolymerization method.

The cyclization of polyacrylonitrile was observed, when the coating was obtained on aluminum cathode, during electrolysis of acrylonitrile–sodium nitrate–DMF solution.

This study was supported in part by a grant from the U.S. Army Research Office.

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Received October 14, 1976

Revised November 17, 1976