Mechanism and Evaluation in Electroinitiated Copolymerization Coatings of Acrylonitrile and Acrylic Acid

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Synopsis

Adherent films of copolymers on different metal surfaces were formed by an electrolytically initiated polymerization of acrylonitrile (AN) and acrylic acid (AA) in $0.05N$ H_2SO_4 aqueous solution. The electrolysis was carried out under a constant current. Hydrogen overvoltages for five different metals used as the cathode were measured in order to interpret the nature and quality of the coating. Solutions containing varying volume fractions of AN and containing different electrolytes gave rise to coatings of varying film thickness. Based on the analyses of copolymer compositions, it is believed that the polymer was formed at the cathode by a free-radical propagation mechanism. The film hardness and the adhesion between the polymer and the metal surface were measured with an Arco microknife. Furthermore, the scanning electron microscope (SEM) was used to examine the structure of the film surface and cross section. The corrosion rates of the coated and uncoated metals in substitute ocean water were also measured for purposes of evaluation of the coatings.

INTRODUCTION

The successful application of electroinitiated polymerization for formation of coatings on metal surfaces both in stationary cell systems[1-3] and in flow systems using either a packed bed or a fluidized bed cell[4] has been clearly demonstrated. The stationary system involved the monomer–solvent–electrolyte solution being held in a three-compartment cell, the cathode and anode being metallic plates held immersed in the cell contents. In the flow system, the solution flows past a stationary bed of metallic or metal-coated particles or, if the velocity is sufficiently high, also fluidizes the bed; the particles are charged by a current feeder which is connected to an external circuit. Prior work[5-7] on electroinitiated polymerization had the objective of achieving polymerization within the cell solution rather than on the electrode itself.

Our work[1] in a stationary cell system has shown the effect of various metal surfaces and various polymerization voltages on the thickness of poly(AN–CO–AA) coatings formed from a monomer mixture in the ratio of 80% AN to 20% AA, by volume. It seems logical that this ratio in itself should have an effect on the nature and thickness of the film formed. The nature and thickness of the coatings could be evaluated by weight increase, scanning electron microscopy, hardness and adhesion ratings, and corrosion studies. The corrosion studies, carried out in simulated ocean water, should particularly become useful for applications of these coated metals in OTEC programs. Furthermore, it is important that the polarization curves be studied to relate the thickness of the coating formed to the hydrogen overvoltage and thus throw light on the mechanism of the copolymerization occurring on the metal surface.

EXPERIMENTAL

Materials

Acrylonitrile, a pure Aldrich product, is freed of the inhibitor by washing with 5% NaOH and then with 5% H_3PO_4, followed by drying under anhydrous Na_2SO_4 or $CaSO_4$ for several days and finally by fractional distillation under reduced pressure. The middle fraction is collected and used. Acrylic acid, a pure Aldrich product, is fractionally distilled under reduced pressure and the middle fraction used. Concentrated H_2SO_4 (Mallinckrodt analytical grade) is used without additional treatment.

Preparation of Metal Surface For Coating

Different cleaning steps for different metals are followed, as recommended in the literature.[8]

Electrolytic Cell and Polymerization Runs

As described elsewhere,[1] in order to obtain a coating on both sides of the metal cathode, the electrolytic cell used is a three-compartment cell separated by two sintered glass discs. The central compartment of about 500 ml capacity is used as the cathode region, while the two outer compartments of about 250 ml capacity each, one on each side of the cathode, are used as the anode regions with two platinum plates as the anodes. The dimensions of anode and cathode plates are about 4 in. × 0.5 in. × 0.03 in. The use of the monomer is restricted to the cathode compartment since the coating is desired only on the cathode metal surface. The volumes of cathodic and anodic solutions are 400 ml in each compartment for all runs.

The current density through the cell and the cathode voltage with reference to a saturated Calomel electrode (SCE) are recorded on a two-channel potentiostatic chart recorder (Hewlett-Packard, 7128A) in series with the circuit and connected with a 10-ohm-shunt resistor. All electrolysis runs are carried out at room temperature. Nitrogen gas is bubbled through the solution 15 min prior to and during the process. At the end of a run, the coated metal is dipped into distilled water several times and then dried in a vacuum oven at about 40°C for 4 hr.

Evaluation of Dry Film Hardness and Adhesion

The evaluation of the polymer film for hardness and adhesion between the film and the metal surface is carried out with an Arco microknife.[9] The microknife tests dry film hardness by cutting through the film sample with a diamond or a carboloy point. While cutting, these 60° cone-shaped points are under constant pressure from an adjustable weight source. The hardness of a film is expressed as the amount of weight on the point, in grams, required to cut through the sample using two cutting strokes in the same position. The microknife makes a cut 2 in. long through the film sample to the subsurface. A lever carrying a beam with an adjustable weight makes it possible to vary the load on the point. In use, the weight on the point is gradually increased until two strokes of the point

cut through the film just enough to make the subsurface visible to the eye. The weight reading is then recorded in grams and referred to as the "microknife hardness" of the film.

The microknife, when used in adhesion testing, determines the lateral stress that is necessary to dislodge a coating from its subsurface. In operation, the microknife acts as a high-precision engraving machine capable of cutting exactly parallel lines at an adjustable spacing between lines. For testing adhesion, the weight is adjusted so that two strokes cut through the film and a third cut penetrates into the subsurface. Then, a series of parallel three-cut grooves are made. A considerable film area is left between the first two grooves. The space between grooves is then reduced in 1-mil increments in each successive cut. As the grooves come closer together, the point is ultimately reached where the lateral stress on the film sample is great enough to cause it to tear away from its subsurface. The degree of adhesion is then expressed as the distance, in mils, between the last two grooves where the film is dislodged. A high numerical rating indicates poor adhesion. For practical purposes, the best adhesion possible is 4 mils for films about 1.0 mil thick. Adhesion readings below 4 mils are very rare while those over 15 mils are very poor.

Observation of Surface and Cross-Sectional Profiles of Coating Under Scanning Electron Microscope

The SEM instrument used is the ETEC Auto Scan model. A small piece of coated metal is cut and a sputter coating of gold is deposited on the surface and cross section of the above specimen, under vacuum, prior to examination under the SEM.

Corrosion Comparison of Coated and Uncoated Metals in Substitute Ocean Water

The corrosion evaluation is a simple immersion test.[10] The coated and uncoated metals are immersed over the same length of time in the specific substitute ocean water contained in a covered resin flask (1000 ml). The tested ocean water is prepared by following the procedures described in ASTM D1141-52. The chlorinity and pH values of the above corrosive solution are about 19.38 and 8.3, respectively; the dissolved oxygen is in the range 6.6 to 7.2 ppm.

The use of corrosion rates implies that all weight loss is due to general corrosion and not due to localized corrosion, such as pitting or intergranular corrosion. Assuming that localized or internal corrosion is not present, the corrosion rate, expressed as mils penetration per year (mpy), is calculated by the equation

$$\text{corrosion rate (mpy)} = \frac{(\text{wt. loss}) (534)}{(\text{area}) (\text{time}) (\text{metal density})}$$

TABLE I
Density and Composition of Metals Used

Alloy	Composition, wt %	Density, g/cm^3
Aluminum	98.8 Al, 1.2 Mn	2.73
Nickel	99.4 Ni + Co	8.89
Copper	99.90 Cu, 0.01 P	8.91
Carbon steel	0.20 C, Mn, P, S	7.85
Stainless steel	18.0–20.0 Cr, 9.0–12.0 Ni, 0.08 C	7.93

where weight loss is in mg, area is in in.² of metal surface immersed, and time is
in hr exposed; the density and composition of the metals used in the experiments
are listed in Table I.

Elemental Analysis of Coating

The elemental analysis of the copolymer coating is carried out with a Per-
kin-Elmer Model 240 elemental analyzer.

RESULTS AND DISCUSSION

Influence of Cathode Materials

Five different metals—stainless steel, carbon steel, nickel, aluminum, and
copper—are used as cathodes while platinum is the anode in each case.   An equal
volume of AN and AA (22.5 ml each) in $0.05N$ H_2SO_4 aqueous solution is used
as the comonomer feed.   Polarization curves of current density versus cathode
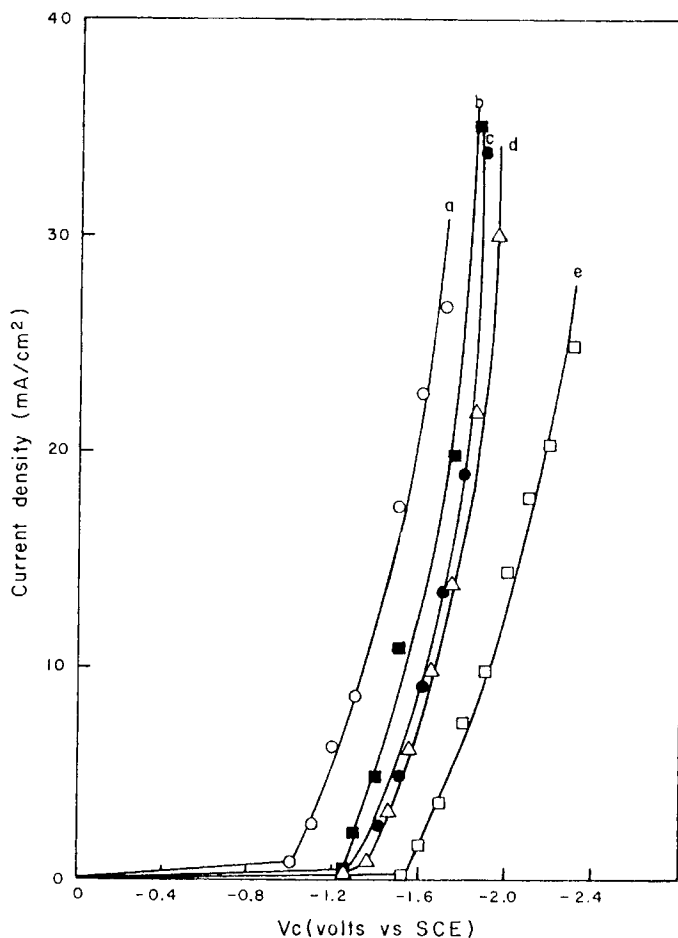voltage for the above metals are shown in Figure 1.   The hydrogen overvoltages

Fig. 1. Polarization curves for (a) copper; (b) S-steel; (c) nickel; (d) C-steel; (e) aluminum in co-
monomer (AB–AA) solution, with $0.05N$ H_2SO_4 as electrolyte.

(η_{H_2}) are reported at the point when sharp current density increase in the polarization curves occurs.[7]

In Table II, the influence of the cathode metals on the coating thickness, hardness, and the adhesion between the coating and the metal surface is reported along with the hydrogen overvoltage determined in the solution used for the polymerization. It is observed that copper, having the lowest hydrogen overvoltage, shows the thinnest coating, i.e., the amount of hydrogen molecules evolved along the copper electrode is more than that for any other metal electrode, and this in turn causes more difficulty in forming the coating onto copper. Hydrogen evolution usually causes the polymer deposition to be difficult and poorly adherent. The hydrogen overvoltage values of S-steel, C-steel, and nickel are all very close, and the coating thickness, hardness, and the adhesion rating are also in the same range. The reason for aluminum having higher η_{H_2} but lower values of film thickness and hardness may be due to the metal oxide being easily formed on the metal surface.[1]

Influence of Volume Fraction of AN in the Feed Solution

Eight different volume percentages of AN (100%, 80%, 65%, 50%, 35%, 25%, 20%, 0%) in the comonomer feed were polymerized in the electrolytic cell with the same cathode (S-steel) and the same concentration of electrolyte (0.05N H_2SO_4) under the same current range. It was found that the film thickness is varying in extremes for different AN fractions in the comonomer feed, and the coating obtained with 50% of AN appears to be 15 times thicker than the coating obtained with pure AN (Table III). The coating surface structure is also different as will be shown subsequently by the SEM pictures.

The kinetic data relating coating thickness to time are shown in Figures

TABLE II
Hydrogen Overvoltage Values of Cathode and Thickness, Hardness, and Adhesion of Coatings[a]

Cathode	$-\eta_{H_2}$ (V_c vs. SCE)	Thickness of coating, mg/in.²	Dry film hardness of coating, g	Microknife[b] reading, mils
S-Steel	1.25	11.8	450	6
C-Steel	1.32	13.2	500	8
Nickel	1.29	7.6	325	8
Aluminum	1.52	2.4	300	9
Copper	1.00	0.6	—[c]	—[c]

[a] Monomer mixture: 50% AN and 50% AA by volume; 22.5 ml of each monomer in 400 ml 0.05N H_2SO_4 aqueous solution.
[b] Arco microknife (Gardner Lab, Inc.)
[c] The coating thickness is too small for reliable measurements.

TABLE III
Influence of Volume Percent of AN in Feed on Coating Thickness[a]

AN concentration, vol-%	100	80	65	50	35	25	20	0
Thickness of coatings mg/in.²	0.8	1.0	2.6	11.2	1.6	0.7	0.5	0

[a] Total monomer volume is 45 ml in 400 ml 0.05N H_2SO_4 aqueous solution, with S-steel cathode.
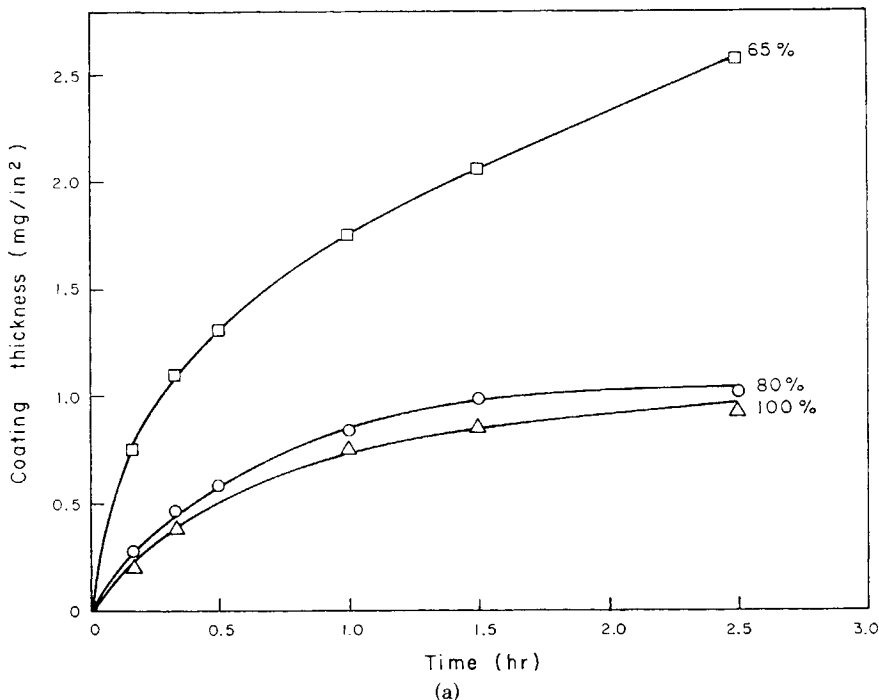
Fig. 2. Coating thickness of poly(AN–CO–AA) vs time for various volume percentages of AN in the feed: (a) 100%, 80%, 65%; (b) 50%; (c) 35%, 25%, 20%.

2(a)–2(c) for each volume fraction of AN in the feed. If the volume fraction of AN in the feed is very high, the kinetic curves show that the maximum polymerization rate occurs at the initial stages and that the rate decreases afterward with time. However, for high volume fraction of AA in the feed, the kinetic curves are S-shaped, the maximum polymerization rate occurring after an initial low. This is due to more initial hydrogen evolution for the case of high fraction of AA in the feed, and this causes difficulty in the polymer depositing onto the metal. It was also noted that no polymer is deposited on the metal surface in the first $1\frac{1}{2}$ hr for the case of 100% AA in the feed

Examination Surface and Cross-Sectional Profiles of Coating Under Scanning Electron Microscope

The film surface photomicrographs of copolymer coatings obtained on the S-steel electrode for various volume percentages of AN in the feed (100%, 80%, 70%, 60%, 50%, 40%, 30%) are shown in Figures 3(a)–3(g). The electrolyte for these runs is a 45 ml comonomer mixture (AN and AA) in 400 ml 0.05N H$_2$SO$_4$ solution. The current density is maintained constant at around 22 mA/cm^2 during the polymerization, and each run lasts for about 90 min.

It was found that the coatings obtained from higher volume fractions of AN in the feed appear more like a powder coating. For example, the grain size for pure PAN is the largest; as the volume fraction of AN decreases, the grain size in the coating decreases, and the coating appears more dense, Figures 3(a)–3(e).
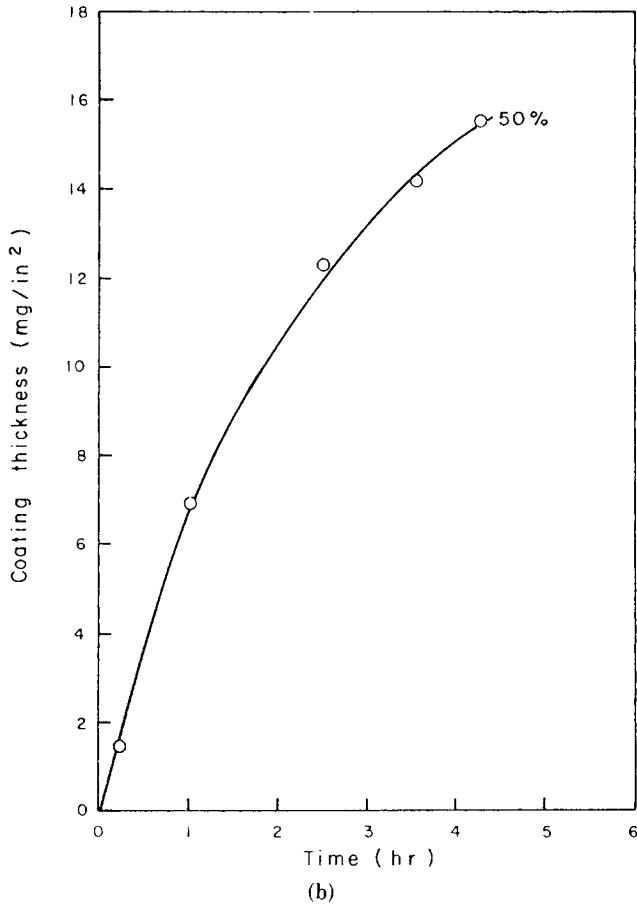
Fig. 2. (*Continued from previous page.*)

It was shown that the coating obtained from 50% of AN is the finest and most dense. If the volume fraction of AN in the feed is less than 50%, the coating surface appears as a continuous film, Figures 3(f) and 3(g).

The cross-sectional structure of coatings of three different thicknesses corresponding to 60%, 50%, and 40% of AN in the feed is shown in Figures 4(a)–4(c). The thickness varies form 8 to 15 microns, and the polymer coating obtained with 50% AN in the feed shows the highest thickness, as mentioned earlier.

Comparison Between Corrosion Rates for Coated and Uncoated Metals Using Weight Loss Method

As discussed earlier, the coated and uncoated metals are immersed in the substitute ocean water over the same time period, and the weight loss is measured to obtain the corrosion rates. The coatings tested are those that are obtained from an equal volume of AN and AA (22.5 ml each) in $0.05N$ H_2SO_4 aqueous solution. The results are given in Table IV.

The corrosion data in the above table show that both the coated and uncoated
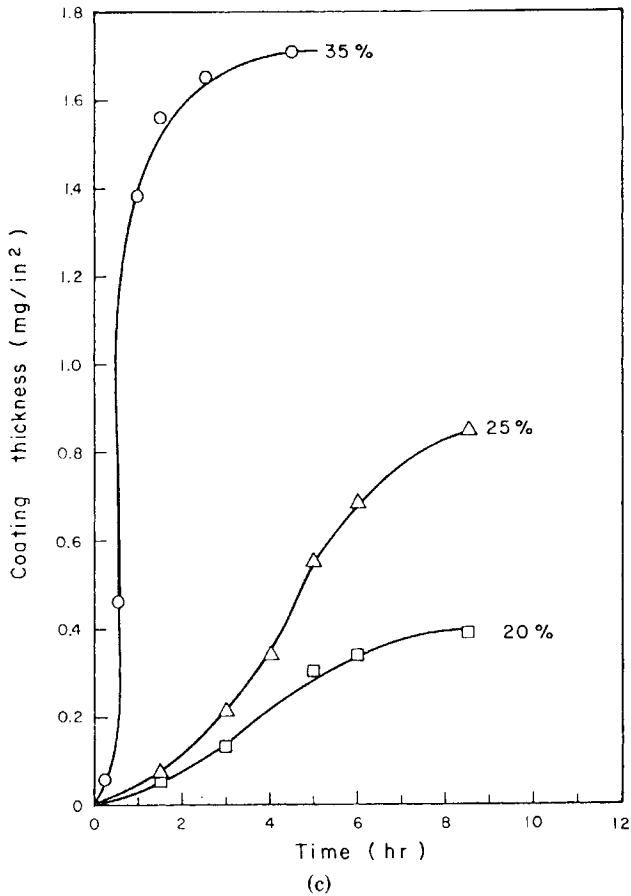
Fig. 2. (*Continued from previous page.*)

S-steel and nickel are not corroded in ocean water.[11]   The coating on the C-steel can prevent corrosion because the coating deposited on the C-steel is the thickest (Table II).   However, in the case of copper and aluminum, the coatings seem to accelerate corrosion.   One of the reasons may be that the coatings are not thick enough to resist the corrosion, the other reason may be that the coatings are not so uniform that there are some exposed metal spots appearing on the coating surface.   Here, the organic-coated metal is portrayed as cathodic to the exposed metal.[12]   Any reduction process which can take place through the polymer coating will stimulate corrosion at the exposed metal anodes.   This also explains why the coated C-steel cannot totally resist corrosion.

Mechanism of Copolymerization

In some instances of electroinitiated polymerization studies, it is conceivable that the polymerization may proceed through a free-radical, an anionic, or a cationic mechanism.   To discriminate among the various propagation mechanisms, the analysis of copolymer compositions is often used.[13,14]
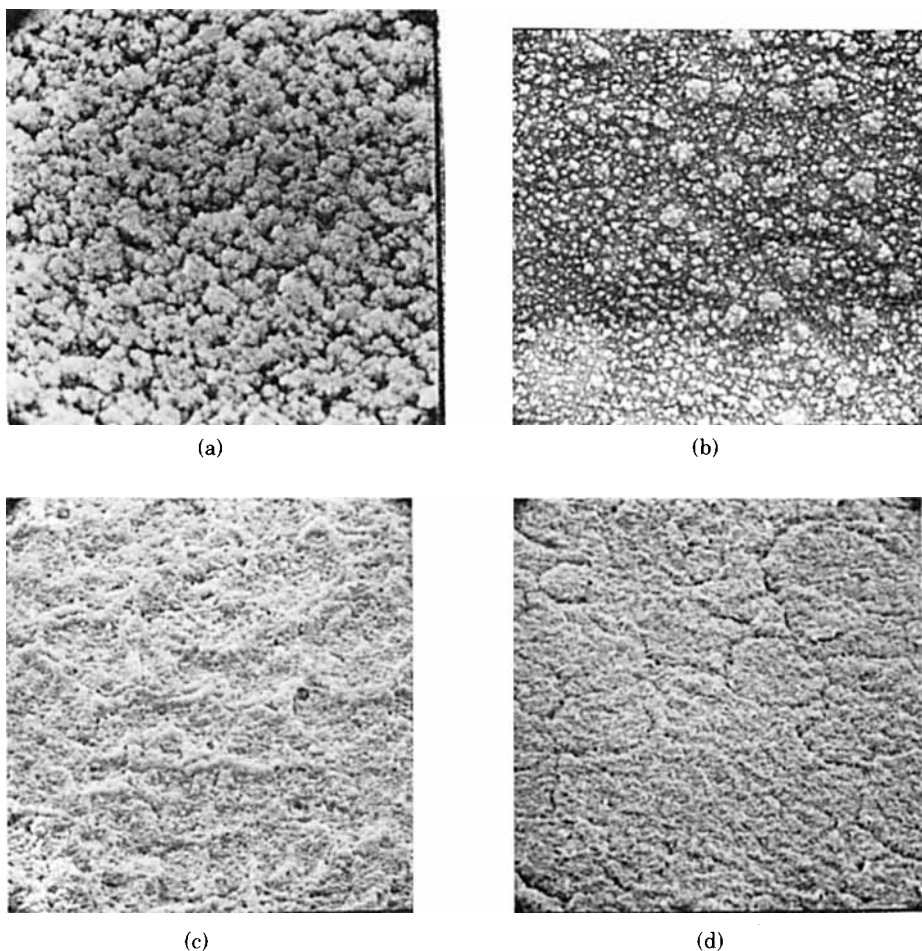
Fig. 3. Surface structure, under SEM at 1000×, of coatings of poly(AN–CO–AA) obtained with various volume percent of AN in the feed: (a) 100%; (b) 80%; (c) 70%; (d) 60%; (e) 50%; (f) 40%; (g) 30%.

Funt and Williams[15] suggest that when an equimolar mixture of AN and methyl methacrylate (MMA) is polymerized through a free-radical mechanism, the resulting polymer contains both species in approximately equal amounts. If, however, the polymerization is anionic, the product mixture will contain predominantly AN, whereas if it is cationically initiated, the polymer will not form readily.

Mixtures of AN and AA containing varying mole fractions of AN are copolymerizd here, and the determination for AN content in the copolymer product is based on the elemental analysis of nitrogen, carbon, and hydrogen. The results are given in Table V. They show that the mole fraction of AN in the copolymer product approximately equals the mole fraction of AN in the comonomer mixture, so the polymerization can be considered to be a free-radical propagation mechanism. Also, it was observed that the bubbling of nitrogen gas through the
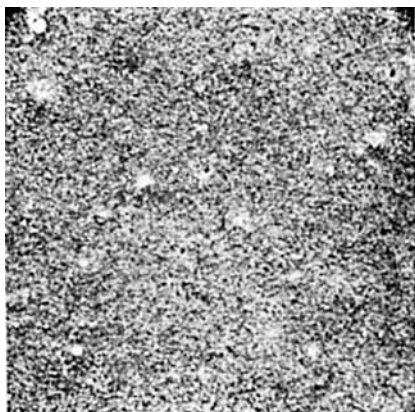
(e)   (f)
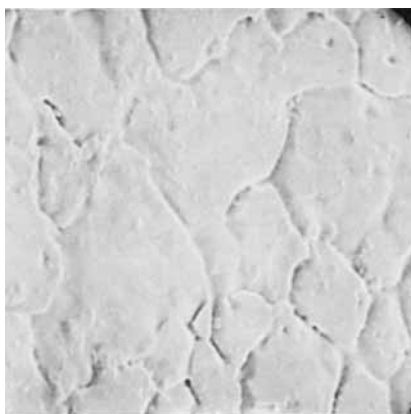
(g)

Fig. 3. (*Continued from previous page.*)

cell improves polymerization by displacing the dissolved oxygen, which usually inhibits free-radical polymerization.

Furthermore, in order to investigate the role of hydrogen ion on the mechanism and thickness of the coatings, different electrolytes were employed. In order to reduce the effect of H^+ which may be relased from the monomer of acrylic acid, only acrylonitrile was used as the monomer. The results are given in Table VI. It was found that thicker coatings can be obtained with strong acids as the electrolyte, e.g., H_2SO_4 and HNO_3. However, the polymer coatings obtained with $NaNO_3$ and $(C_2H_5)_4NCl$ as the electrolytes which do not release hydrogen ions are very thin; the thickness of the coating obtained with CH_3COOH, which is a weak organic acid, is between the above two cases. Thus, the initiation mechanism for the polymerization of acrylonitrile in an aqueous solution is believed to be[16]
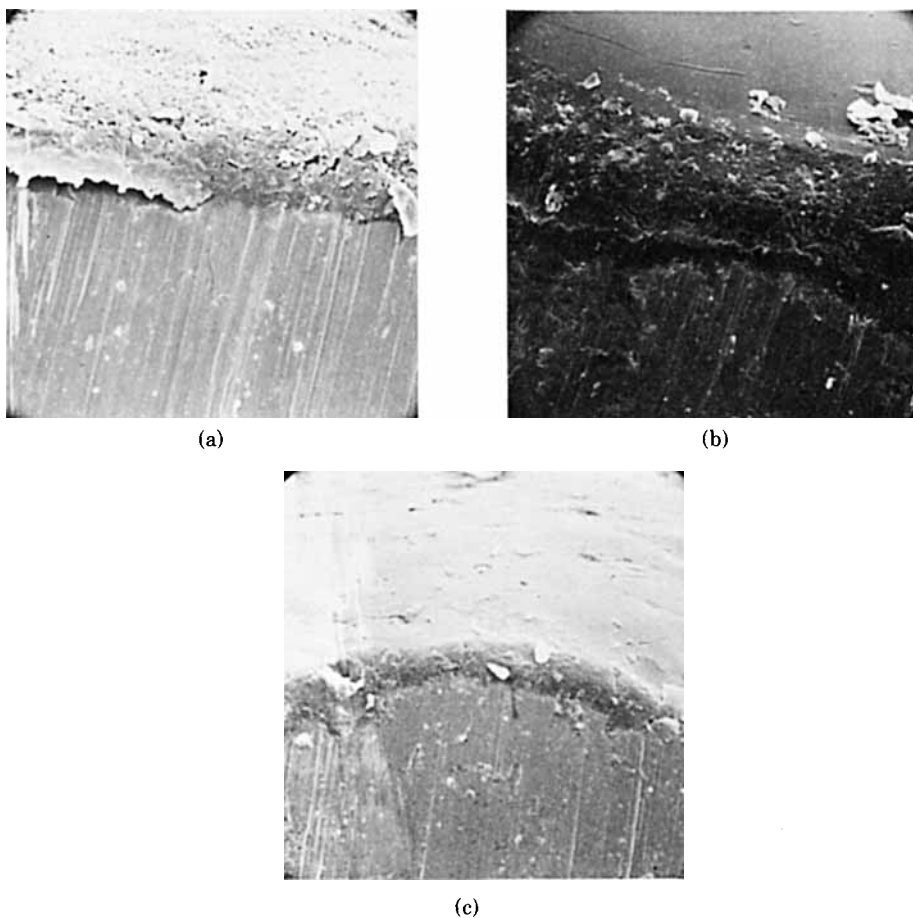
$$H^+ + e^- \rightarrow H\cdot$$
$$H\cdot + M \rightarrow M\cdot$$

(a)

(b)

(c)
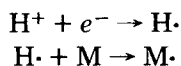
Fig. 4. Cross-sectional profile, under SEM at 1000×, of coatings of poly(AN–CO–AA) obtained with various volume percent of AN in the feed: (a) 60%; (b) 50%; (c) 40%.

where M is the monomer. Also, the reaction of H· + H· → H_2 can occur, which causes difficulties in depositing polymers onto the metal surfaces.

CONCLUSIONS

It was shown that the thickness (yield) of the coatings formed is strongly affected by the AN:AA ratio in the feed. The coating obtained from mixtures containing equal volumes of AN and AA has the maximum thickness, as confirmed by both the weighing and SEM methods. The mechanism proposed is one where a hydrogen atom, formed at the cathode, is added onto the monomer, followed by growth of the resulting free radical by further addition of monomers. However, some of the hydrogen atoms are lost in the hydrogen evolution, and as a result some coatings are thin. Furthermore, hydrogen evolution often causes

TABLE IV
Comparison Between Corrosion Rates for Coated and Uncoated Metals in Substitute Ocean
Water[a]

Specimen[b]	Corrosion rate, mpy	Ratio[c]
Coated S-steel	—[d]	
Uncoated S-steel	—[d]	—
Coated C-steel	3.45	
Unocated C-steel	4.32	1.25
Coated Ni	—[d]	
Uncoated Ni	—[d]	—
Coated Al	3.64	
Unocated Al	3.31	0.91
Coated Cu	3.70	
Uncoated Cu	1.80	0.49

[a] ASTM D1141-52.

[b] The coating poly(AN–CO–AA); concentration of monomers: 22.5 ml each of AN and AA in 400 ml 0.05N H_2SO_4 aqueous solution.

[c] Defined as the corrosion rate of uncoated metal divided by the corrosion rate of coated metal.

[d] Corrosion rate approaches zero value. Area: 2.09–2.60 in.^{2}; time: 24–29 hr.

TABLE V
Copolymerization of AN and AA on Stainless Steel[a]

Mole fraction of AN in feed	Copolymer composition			Mole fraction of AN in copolymer
	N,%	C,%	H,%	
0.90	23.3	64.5	5.5	0.91
0.80	20.2	59.3	8.1	0.81
0.66	17.8	58.9	6.0	0.73
0.51	14.1	56.6	6.0	0.61
0.36	8.5	52.3	5.0	0.39
0.26	5.4	50.0	5.8	0.26

[a] Monomer concentration is 45 ml total monomer in 400 ml aqueous solution, containing 0.05N H_2SO_4 as electrolyte.

TABLE VI
Influence of Various Electrolytes on Coating Thickness[a]

Electrolytes	0.05N H_2SO_4	0.1N H_2SO_4	0.1M HNO_3	0.1M CH_3COOH	0.1M $NaNO_3$	0.1M $(C_2H_5)_4NCl$
Thickness of coatings, mg/in.^{2}	0.99	1.03	0.66	0.42	0.23	0.15

[a] Monomer is 45 ml AN in 400 ml aqueous solution, with S-steel cathode.

the polymer deposit to be poorly adherent. It was also shown that, even if they are hard and adhesive, nonuniform coatings could give rise to galvanic corrosion.

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