Electropolymerization of 2-Methacryloyloxy(ethyl) Acetoacetate on Aluminum Using a Novel Initiation Method

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ABSTRACT: Electropolymerization has been used as a method to form polymers on graphite fibers and metals. Most of the previous studies have involved either the use of sulfuric acid as an initiator or direct reduction or oxidation of monomers to form the polymers. In this article, α -bromoisobutyronitrile (BrIBN) was used as a new electrochemical initiator to form polymer coatings on an aluminum cathode. The reduction of BrIBN on a glassy carbon electrode was examined using cyclic voltammetery. It was found that BrIBN could be reduced to isobutyronitrile radicals at potentials below the reduction potential of water. The reduction behavior of BrIBN was found to be similar in aqueous, semiaqueous, and nonaqueous solutions. 2-Methacryloyloxy(ethyl) acetoacetate was then electropolymerized on aluminum using the BrIBN as the initiator and lithium perchlorate as a supporting electrolyte. Defect-free coatings were formed at half-cell potentials of less than -1.20 V. The effect of various process variables on the polymerization kinetics under potentiostatic conditions is reported. The coating thickness increased with polymerization time, monomer concentration, and initiator concentration. A strong dependence of thickness on monomer concentration was observed. As expected, there was weak dependence on the initiator concentration. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1665-1675, 1999

Key words: electropolymerization; electrochemical polymerization; coating; aluminum; protective coatings

INTRODUCTION

General

Electropolymerization is a process in which polymerization is initiated by passage of an electric current through electrodes placed in a monomer-solvent-electrolyte solution. The reactions occurring at the electrode–solution interface can result in generation of active species that may initiate polymerization. The active species may be anions, cations, or radicals, depending on the conditions applied at the electrode. Polymers were formed electrochemically in solution as early as 1943.^{1,2} Today, a variety of conducting and nonconducting polymers with controlled properties can be formed electrochemically on many different substrates (e.g., graphite fibers, platinum, steel, copper, and aluminum). Many different electro-organic synthesis schemes are discussed by Kyriacou.³

This article describes a method for cathodic electropolymerization on aluminum. Using this method, very thin adherent polymer coatings can be polymerized directly on aluminum.

Initiation Schemes

Electrochemical initiation can be direct or indirect. Direct initiation occurs by reduction or oxidation of the monomers themselves. Reduction of acrylonitrile has been studied extensively. Under rigorously anhydrous conditions, polyacryloni-

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trile can be grafted on iron and nickel by cathodic electropolymerization.⁴ In such conditions, the polymerization mechanism is anionic. 2-Ethylhexylacrylate has been polymerized anionically onto graphite fibers.⁵ The polymer formed exhibited very good adhesion to the fiber surface. Most conducting polymers [such as polyanilines, polythiophenes polypyrrole, poly(oxyphenylenes), and their derivatives] are electropolymerized on the anode by direct oxidation of the monomer. Pyrrole and thiophene have been electropolymerized from bulk on platinum anodes to give conducting polymers and copolymers.^{6,7} Polyanilines have been polymerized on steel for corrosion protection⁸ and on platinum anodes to produce conducting films.⁹ If the polymer formed is electrically conducting, thick coatings can be formed. Extensive studies on the oxidative polymerization of phenol and its derivatives have also been done to form poly(oxyphenylenes) and their substituted forms.¹⁰⁻¹² Such films were formed from bulk monomer and were ~ 50 to 100 nm thick.

Indirect initiation occurs when a species is oxidized or reduced to give a free radical, cation, or anion. These active species then initiate the polymerization. Common examples are sulfuric acid and potassium persulfate, which are reduced to radicals at the cathode.

Some indirect initiation schemes can be shown as¹³:

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{-} + {}^{\bullet}OH$$

$$OH^{\bullet} + M \rightarrow HO - M^{\bullet}$$
(1)
$$R_2O_2 + e^{-} \rightarrow RO^{-} + RO^{\bullet}$$

$$RO^{\bullet} + M \rightarrow RO - M^{\bullet}$$
(2)

In these cases, polymerization is initiated by free radicals that were formed electrolytically. A significant amount of work has been done on cathodic electropolymerization of vinyl monomers on graphite fibers by Bell and colleagues.^{14,15} They reported electropolymerization of high temperature-resistant styrene-maleimide copolymers from partially aqueous solutions using sulfuric acid as an initiator. The initiation scheme can be represented as follows:

$$\mathrm{H^{+}} + \mathrm{e^{-}} \rightarrow \mathrm{H^{\bullet}} \tag{3}$$

Reduction of the proton occurs on the graphite surface, leading to formation of hydrogen radicals, which then initiate the polymerization. A potential greater than about -1.5 V with respect to the saturated calomel electrode (SCE reference electrode) is required for the reaction to proceed, and hydrogen is usually evolved as a side reaction. One of the most extensively studied systems is the electropolymerization of acrylonitrile and other vinyl monomers, such as methyl acrylate on graphite fibers, to improve interlaminar shear strength of fiber-reinforced composites.^{16,17} Metal electrodes (such as platinum, copper, iron, aluminum, and their alloys) have also been used.^{8,10,18–22} In many cases, the nature of the coatings formed depends on the substrate used. Electropolymerization of acrylamide and methyl methacrylate on graphite fibers has been performed using sulfuric acid as the initiator.^{23,24} Other indirect initiators include perchlorates, which oxidize to form the perchlorate radical. Electropolymerization of styrene using fluorene-9one radical-anion lithium cation dimer as initiator has also been conducted on a steel cathode.²⁵ Potassium persulfate, a common thermal initiator, is reduced to persulfate radicals during the polymerization of acrylamide on aluminum.^{18,26} In another study, acrylonitrile was electropolymerized anionically in dimethylsulfoxide (DMSO), also by using potassium persulfate.²⁷ The advantage of indirect initiation is that initiation rates and molecular weight of the polymer can be controlled by varying the initiator concentration. Whereas free radical electropolymerization can be conducted in aqueous systems under moderate conditions, ionic initiation requires anhydrous conditions. Using indirect initiation schemes, many monomers that cannot undergo direct electrolytic reduction or oxidation can be polymerized.

Electropolymerization on Metals

Metals form good candidates for electropolymerization because of their electrical conductivity. Almost all the work on coating metals has been done by cathodic electropolymerization, because metals are relatively inert as cathodes and easily oxidized as anodes. The different electrochemical and surface properties of different metals often have a large influence on the process parameters, such as the type of initiator and electrolyte that can be used, and the reaction kinetics of the polymerization. Liang and Bell²² synthesized styrene-maleimide copolymer coatings on copper using sulfuric acid as the initiator. Such coatings

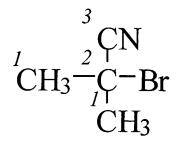


Figure 1 Structure of α -BrIBN.

were conformal in nature and had excellent adhesion to the metal substrate. Vinyl monomers, such as acrylamide and acrylonitrile, have also been polymerized on aluminum from aqueous or semiaqueous solutions.¹⁸ Interestingly, the sulfuric acid initiator did not work on aluminum, as was found by Lee.²⁸ The reasons for this will be discussed later. Lecayon and colleagues^{29,30} have coated nickel with polyacrylonitrile by cathodic electropolymerization in acetonitrile. The solutions had to be anhydrous, and the films obtained were very thin, of the order of 80–100 nm. Overall, this is an area where there are possibilities to form protective polymer coatings that exploit the advantages of the electropolymerization process.

Recently, we have developed a new initiation route for cathodic electropolymerization. The two initiators, sulfuric acid and potassium persulfate described earlier, have some drawbacks. Electropolymerization on aluminum did not occur when sulfuric acid was used. On the other hand, potassium persulfate is thermally unstable and can initiate polymerization of the monomer solution at room temperature. This work involved finding an initiator that could easily generate free radicals on the aluminum surface and initiate polymerization at a reduction potential of less than -1.5 V. A low reduction potential would allow its use in aqueous solutions, without simultaneous reduction of water during electropolymerization. The process can also be applied to other metals, such as steel and copper. Desired properties for the initiator were a low reduction potential, solubility in water, and thermal stability. A study of different classes of compounds was conducted to find a suitable candidate. Alkyl halides were selected as one class of compounds capable of undergoing electrochemical reduction at low potential. Such an initiator would allow cathodic electropolymerization of monomers in aqueous, as well as partly aqueous, environments.

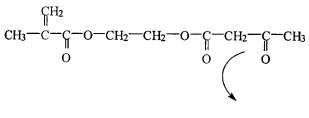
The compound selected for investigation as an electrochemical initiator was α -bromoisobutyronitrile (BrIBN) (Fig. 1). The synthesis of this compound has been described by Stevens.³¹ The reduction behavior of BrIBN is reported herein for various conditions, using cyclic voltammetery. The expected one electron reduction of BrIBN should result in formation of an isobutyronitrile radical. This radical is also obtained by thermal decomposition of 2,2'-azobisisobutyronitrile, a well-known free radical initiator for polymerizations.

In this article, the electropolymerization of 2-methacrylovloxy(ethyl) acetoacetate (MEA) is reported. The structure of the monomer is shown in Figure 2. MEA has a β -diketone moiety in the side group and therefore has the potential to chelate with the aluminum surface, resulting in a strong metal-polymer bond.³²⁻³⁴ As a result, strongly adherent coatings of poly(MEA) were formed on the aluminum cathode. Electropolymerization was conducted on aluminum substrates, and the effects of various process variables (such as initiator and monomer concentration, cathode potential, and polymerization time) were studied. Many advantages offered by electropolymerization have been discussed elsewhere.^{14,26,35} Aluminum was chosen as the cathode with the objective of forming adherent polymer coatings on the surface without use of a phosphate or a chromate pretreatment.

EXPERIMENTAL

Synthesis of BrIBN

Phosphorous tribromide (99%) (PBr₃) was obtained from Acros Chemicals (Pittsburgh, PA), bromine (99.5%) from Aldrich Chemical Co. (Milwaukee, WI), isobutyronitrile (IBN) and sodium bisulfite from Kodak-Eastman Fine Chemicals (Rochester, NY), and petroleum ether from Fisher



ß-diketone linkage Figure 2 Structure of MEA.

Scientific (Pittsburgh, PA); all were used as obtained. BrIBN was synthesized using 25 g (0.36 mol) of IBN, 98 g (0.36 mol) of PBr₃, and 58 g (0.36 mol) of bromine in accordance with the method of Stevens.³¹ Bromine was added very slowly to the PBr₃-IBN mixture, and cooled in an ice bath, since the reaction was extremely exothermic. The mixture was stirred and gently warmed to room temperature. Hydrogen bromide evolved as the side product. BrIBN was isolated by distilling the reaction mixture at 150°C. The entire process was conducted at atmospheric pressure. The BrIBN obtained was kept dissolved in petroleum ether and washed with a sodium bisulfite solution to remove the residual bromine and HBr. This ether solution was redistilled to obtain the final product, which was a clear liquid with a pungent odor. About a 70-80% yield could be obtained by this method.

Characterization of BrIBN

The structure and purity of BrIBN was confirmed by nuclear magnetic resonance (NMR) and gas chromatography/mass spectrometry. The electrochemical behavior of BrIBN was studied using a BAS 100W cyclic voltammeter with a glassy carbon working electrode (GCE), platinum counter electrode, and SCE reference electrode. The GCE was cleaned before every use by polishing with a 0.2 μ m alumina. Lithium perchlorate was used as the supporting electrolyte in all cases. The reduction behavior of BrIBN was performed as a function of scan rate and initiator concentration. Voltammograms were recorded in water, *N*-methyl pyrolidinone (NMP), and water–NMP solutions.

Aluminum Sample Preparation

The commercial aluminum used as the cathode was an Al 5162 (% element, 0.2 Si, 0.35 Fe, 0.15 Cu, 0.2 Mn, 4.0 Mg, 0.1 Cr, 0.25 Zn, 0.10 Ti) or Al 6061 (1.0 Mg, 0.6 Si, 0.2 Cr, 0.27 Cu) alloy. Samples were cleaned using Micro[®], an alkaline laboratory cleaning soap. Samples were then rinsed in water and mildly etched in 5% hydrofluoric acid (HF) for 30 s at room temperature, rinsed in tap water, and air-dried. This treatment resulted in clean aluminum with a very thin layer of aluminum oxide. All samples were used soon after drying in air.

Electropolymerization

Cell Construction

A three-compartment cell was used, which consisted of a glass chromatographic tank into which a $9 \times 7.5 \times 4.5$ cm polypropylene chamber was placed. Two walls $(9 \times 7.5 \text{ cm})$ of this chamber were perforated with many 0.5 cm diameter holes, and covered with a 0.4 μ m pore size polypropylene membrane from Osmonics, Inc. (Minnetonka, MN). The aluminum cathode was placed in the central chamber, whereas the stainless steel plate counter electrodes were placed in the outer chambers. Provisions were also made for purging nitrogen into the cathode chamber to remove oxygen, which inhibits the polymerization. Cathode solution volume varied from 100 to 300 mL, and most metal coupons were only $\sim 50\%$ submerged. An SCE was used as the reference electrode. A schematic of the cell has been presented elsewhere. 35

Materials for Electropolymerization

MEA (Aldrich Chemical Co.) was purified using inhibitor removing columns (Scientific Polymer Products, Ontario, NY; Model DHR-4). DMSO (Aldrich Chemical Co.) and NMP (Fisher Scientific) were used as obtained. Lithium perchlorate (Aldrich Chemical Co.) supporting electrolyte was used as obtained.

Procedure

The power source for the electropolymerization was a Princeton Applied Research Model 363 Potentiostat/Galvanostat. The cathode solution in the central compartment consisted of solvent, electrolyte, monomer, and initiator, whereas the anode solution consisted only of aqueous electrolyte. The cathode solution was purged with nitrogen for 15-30 min in the cell before electropolymerization to remove the dissolved oxygen. Electropolymerization work was done under constant potential mode. The half-cell cathode potential was varied from -1.1 to -1.5 V, using SCE as the reference electrode, and polymerization time varied from 3 to 120 min. After polymerization, coated samples were rinsed with distilled water before drying at 100°-120°C for 3–5 h. The amount of the polymer coating formed on the aluminum cathode was measured by either measuring the weight gain of the aluminum cathode after drying or by thickness measurements using a digital micrometer with at least a count of 0.001 mm (from Mitutoyo, Inc., Paramus, NJ).

RESULTS AND DISCUSSION

Initiator Study

Generally, compounds containing the carbon halogen bond are electrophilic. For a compound of

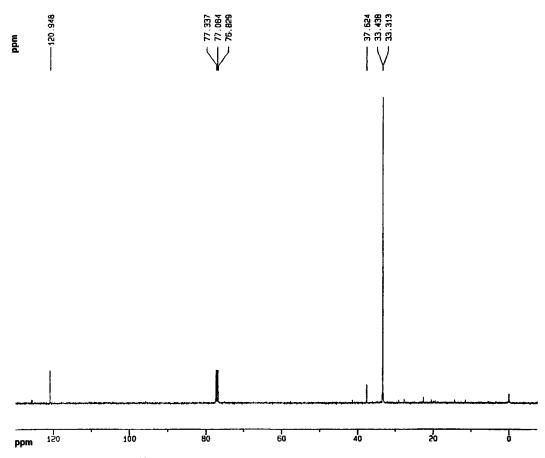


Figure 3 ¹³C-NMR spectrum of α -BrIBN, with broadband decoupling.

type X-IBN, the ease of reduction of the bond follows the order C—F < C—Cl < C—Br < C—I. Of these, the C—Br and C—I bonds fall in the reduction potential range of -1.5 V. I—IBN is unstable and light-sensitive, so it was not studied. The reduction properties of the carbon—halogen bond have been well documented.³⁶

Characterization of BrIBN

The ¹H-NMR of BrIBN in CDCl_3 showed a single proton peak at 2.086 ppm, from the methyl groups. Occasionally, a peak in the range of 12 ppm was also seen from residual HBr produced as a byproduct of the synthesis. The ¹³C-NMR with broad-band decoupling {C1 33.3 ppm, C2 37 ppm, C3 120 ppm} is shown in Figure 3. The spectrum without broadband decoupling shows the splitting of the peak from CH₃ labeled C1 into a quartet as expected for the methyl group (Fig. 4), confirming the structure.

Cyclic Voltammetery

The electrochemical behavior of BrIBN was characterized using cyclic voltammetery. A background scan obtained using DMSO and 0.05MLiClO₄ exhibited no reduction peaks, indicating the solution stability up to -2500 mV (SC reference electrode). Upon addition of 0.002M BrIBN, large reduction peaks appeared, indicating reduction of BrIBN (Fig. 5). The reduction peak is due to the diffusion-limited peak current and is explained by Kissinger and Heineman³⁷ using the following equation:

$$i_p = (2.99 \times 10^5) n (\alpha n_a)^{1/2} A D^{1/2} C^o \nu^{1/2}$$
 (4)

where i_p is the peak current, n is the number of electrons transferred, α is the transfer coefficient, n_a is the number of electrons in the rate-determining step of the electrode process, A is the area of the electrode, D is the diffusion coefficient of the species being reduced, C^o is the bulk concentration of the same species, and ν is the scan rate. Also, the peak potential is also dependent on the scan rate, although a more complex dependence. The peak current and potentials are plotted as a function of the square root of the scan rate in Figure 6. Above a scan rate of 100 mV s⁻¹, linear

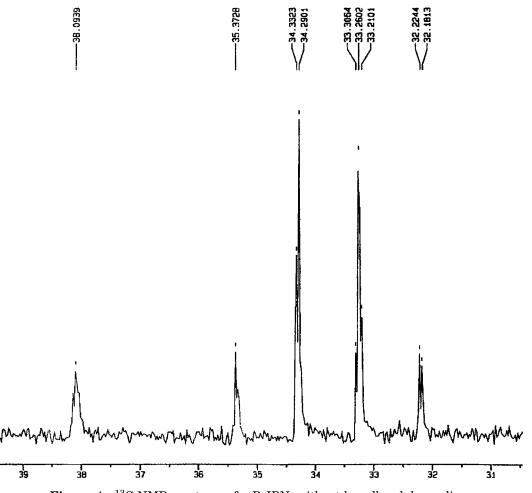


Figure 4 ¹³C-NMR spectrum of α -BrIBN, without broadband decoupling.

dependence of peak current with the square root of the scan rate is seen, which is consistent with eq. (4).

The next step was to run cyclic voltammograms in NMP, NMP/water [20/80 (volume ratio)] mixture, and water to approach the conditions used in the electropolymerization experiments. Figure 7 shows the reduction behavior of BrIBN in pure NMP. A large reduction peak is seen again, with the peak starting at -1200 mV. A possible second electron transfer peak is seen at about -2100 mV. The second electron transfer peak could possibly lead to the formation of an IBN anion. When water is used as a solvent, the first reduction peak is still seen (Fig. 8), following which a large amount of current flows, due to reduction of water. In Figure 9, the background-subtracted data are shown for NMP/water 20/80 solvent. The reduction peaks in this case are very pronounced.

It seems that the electrochemical behavior of BrIBN is similar under all the different solution

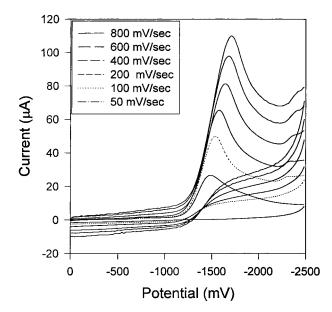


Figure 5 Reduction of BrIBN in DMSO using GCE at scan rates of 50, 100, 200, 400, 600, and 800 mV s⁻¹.

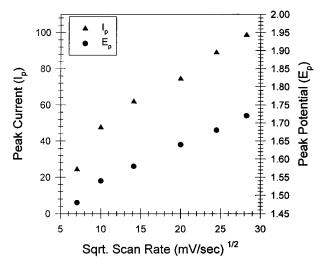


Figure 6 Plot of peak reduction potentials and currents for BrIBN reduction in DMSO, $\text{LiClO}_4 = 0.05M$.

conditions applied. The study of electrochemical reduction behavior of BrIBN and other bromonitriles has been reported previously, where GCE and mercury were used as working electrodes.^{38,39} Among α -, β -, γ -, and δ -bromonitriles, the α -BrIBN was easiest to reduce and was the only one to show a one-electron transfer reduction step. Most similar compounds show a two-electron reduction behavior because the potential required for the first electron transfer is more than that needed for the second.³⁶ In the case of

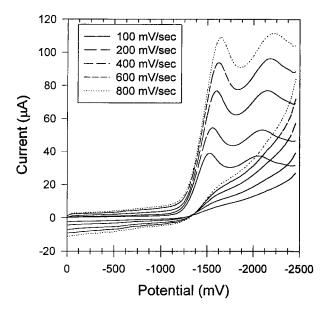


Figure 7 BrIBN reduction in NMP at different scan rates 0.1M LiClO₄ and 0.002M BrIBN, GCE electrode.

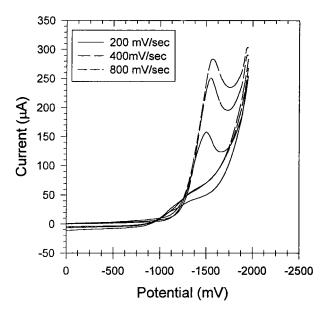


Figure 8 0.006*M* α -BrIBN in water; 0.1*M* LiClO₄.

BrIBN, the first and second electron transfer potentials are well separated. As a result, radicals can be generated by applying the suitable reduction potential. The relatively passive surface of aluminum, due to the presence of aluminum oxide, prevents it from being used effectively in cyclic voltammetery studies.

Electropolymerization of MEA

All kinetic studies described in the following sections were conducted in potentiostatic (constant

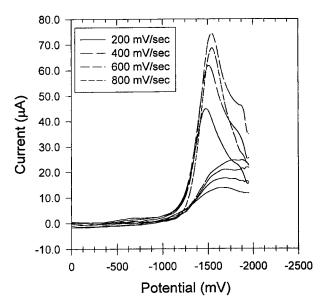


Figure 9 0.002*M* BrIBN in 20/80 NMP/water; 0.1M LiClO₄; background subtracted.

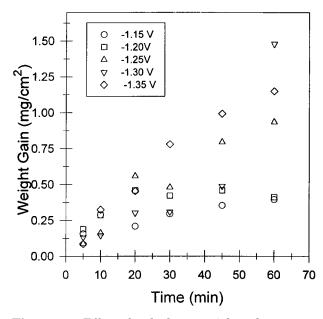


Figure 10 Effect of cathode potential on the amount of poly(MEA) formed at various polymerization times.

voltage) mode. This leads to a constant driving force condition and not a constant initiation rate condition. The potentiostatic mode permits only a qualitative discussion of the electropolymerization kinetics. If polymerization is conducted under the galvanostatic (constant current) mode, the cathode potential increases quickly with polymerization time to overcome the resistance from the nonconducting polymer coating, and significant reduction of water begins to occur. This reduction leads to blister formation and, in some cases, delamination of the polymer coating being formed.

Effect of Cathode Potential

The cathode solution composition was: NMP/water 40/60 (v/v), BrIBN = 0.03*M*, LiClO₄ = 0.1*M*, and MEA = 0.3*M*. The aluminum cathode potential was varied from -1.15 V to -1.35 V relative to SCE. The samples used had a coated (submerged) area of ~ 3.5 cm². Polymerization times were varied from 3 to 60 min. In Figure 10, the weight gain (mg cm⁻²) is plotted as a function of polymerization time for various cathode potentials. A 1 mg cm⁻² weight gain equals ~ 10 μ m coating thickness. At low cathode potentials of -1.15 V and -1.20 V, the amount of polymer formed increased with time, although very slowly. The coatings formed in this case were completely free of defects. At a potential of -1.25 V, the weight gain rate increased significantly, and the coatings formed were still free of defects. At potentials of -1.30 V and higher, the rate of weight gain showed a large increase. The coating formed had a few blisters, indicating some reduction of water. As the polymer coating delaminates in certain areas due to blistering, the aluminum cathode resistance decreases and the polymerization rate increases locally. The rate increase can be at least partially linked to blister formation. The solution stability also depended on the potential. The bulk solution was more stable at lower potentials where no hydrogen formation was observed.

Effect of Monomer Concentration

The cathode solution composition was: NMP/water 40/60 (v/v), BrIBN = 0.1*M*, LiClO₄ = 0.1*M*, and potential = -1.25 V. Figure 11 shows a plot of weight gain vs. polymerization time for different monomer concentrations. The dependence on monomer concentration is clearly seen and seems to increase at longer polymerization times. Whereas only ~ 0.05 mg cm⁻² polymer was obtained at 60-min polymerization time for 0.05*M* MEA concentration, ~ 1.25 mg cm⁻² polymer was obtained using 0.25*M* MEA, under similar conditions. Also, the polymerization rate seems to increase with increasing time. A decreasing rate would be expected due to a decreasing rate of

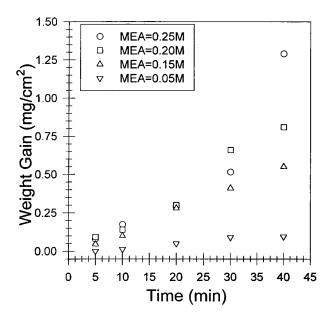


Figure 11 Effect of monomer (MEA) concentration on the amount of poly(MEA) formed at various polymerization times.

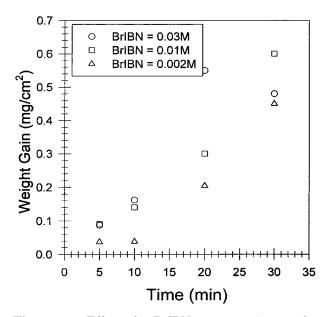


Figure 12 Effect of α -BrIBN concentration on the amount of poly(MEA) formed at various polymerization times.

initiation. This is probably due to the autoacceleration during polymerization.⁴⁰ The autoacceleration herein occurs from the combination of the gel effect and the occlusion effect due to the heterogeneous polymerization conditions. The growing polymeric radicals become coiled up, because they are essentially insoluble, and termination becomes progressively more difficult, whereas propagation may still proceed reasonably well. No measurable weight gain was obtained at concentrations below 0.05M MEA in the cathode chamber, even at long polymerization times. If the monomer concentration is very low, then the molecular weight of the polymer is also low. At very low monomer concentrations, many of the low molecular weight chains may dissolve into the solution, resulting in thinner than expected films. Alternatively, mass transfer to the metal surface may become limiting because of the low surface monomer concentration.

Effect of Initiator Concentration

The solution composition was: NMP/water 40/60 (v/v), $\text{LiClO}_4 = 0.1M$, MEA = 0.2M, and potential = -1.25M. A plot of weight gain vs. polymerization time for different initiator concentrations is shown in Figure 12. Even though the initiator concentration was varied from 0.002M to 0.03M, by a factor of 15, the weight gain increase at any given time seems to have a weak dependence on the BrIBN concentration. These observations are consistent with previous initiator concentration studies using H_2SO_4 by Iroh and colleagues¹⁵ using the sulfuric acid initiator on graphite fibers.

Effect of Solvent Quality

Solvent quality, the ability to dissolve/swell the monomers/polymer, is an important process variable. The limiting monomer concentration and the swelling of the polymer of the polymer formed depend on the solvent quality. The solvent quality itself can be varied by varying the water/DMSO or water/NMP ratio. Increasing water content leads to poorer solvent quality. As a result, the limiting monomer solubility decreases and also the polymer formed does not swell. Under such conditions, only thin polymer coatings can be expected, because diffusion in the coating is slow. As the relative amount of solvent increases, the solubility of the monomers increases and also the polymer formed swells more. A swollen polymer coating permits diffusion of monomers through it, and thicker polymer coatings can be expected. In Table I, the coating thickness obtained by elec-

Water/DMSO (v/v)	$\begin{array}{c} {\rm MEA} \\ {\rm Concentration} \\ (M) \end{array}$	Thickness (µm)	Adhesion	Appearance
100/0	0.1	6–8	Very good	Uniform, white, porous, easily scratched
40/60	0.35	7 - 20	Excellent	Uniform, clear to yellow, hard
31/69	0.57	20 - 25	Excellent	Uniform, yellow, hard
20/80	0.874 (not saturated)	6–10	Excellent	Uniform, clear to yellow

Table I Observations Using $0.01M \alpha$ -BrIBN, Forming Poly(MEA) Coating from Solutions of Different Water/DMSO Ratios

tropolymerizing MEA in different solvent conditions are listed. Other qualitative observations on adhesion and appearance warrant further discussion.

The coating thickness increases as the amount of DMSO is increased up to 69 vol %. At water/ DMSO of 20/80, the thickness obtained decreases. This apparently anomalous behavior is seen because, under good solvent conditions, the polymer formed on the metal tends to dissolve into the solution as it is formed. Thus, it seems that, as the amount of DMSO is increased, the coating thickness obtained increases due to increased diffusion, and then decreases as the polymer formed becomes soluble. The coatings obtained from polymerization in water were white and weak due to the very poor solvent conditions. As the solvent quality was improved, the coatings obtained were clear, smooth, and void-free.

The solvent-water ratio can also influence the stability of the monomer solution. Because the solvent content is increased to a high level, the low molecular weight polymer becomes soluble. Thus, during the electropolymerization process under good solvent conditions, some of the low molecular weight chains may dissolve into the bulk solution while still propagating. This can lead to some amount of polymerization in the bulk solution. There is therefore an optimum amount of solvent in the mixture at which relatively thick polymer coatings can be formed, without compromising the solution stability.

CONCLUSIONS

A new electrochemical initiation scheme, shown herein for polymerization of MEA on aluminum, has been developed. The electrochemical reduction of α -BrIBN occurred by a one-electron transfer, resulting in the generation of an IBN radical. These free radicals were generated on aluminum at potentials lower than the reduction potential of water. By using the above initiation scheme, defect-free polymer coatings were synthesized on aluminum. Polymerization was conducted in aqueous, as well as semiaqueous, conditions. Unlike other electrochemical initiators, such as potassium persulfate, BrIBN is thermally stable and soluble in water as well as polar organic solvents.

The effects of various process parameters (such as monomer concentration, cathode potential, and initiator concentration) were investigated. Although a strong dependence of the kinetics upon monomer concentration and cathode potential was seen, the dependence on the initiator concentration was weak. Defect-free coatings were made at low potentials up to -1.25 V. At higher potentials, of more than -1.30 V, some reduction of water occurred, resulting in defects in the polymer coatings formed. The coating thickness increased with polymerization time in all cases. The thickness and morphology of the polymer coatings obtained were also dependent on the solvent quality. White, powdery coatings were obtained from purely aqueous solution (poor solvent conditions), and thin uniform clear coatings were obtained when the solvent quality was improved. Under very good solvent conditions, very thin or almost no polymer was obtained because the polymer formed was dissolved in the solution. This initiation scheme offers the possibilities of electropolymerizing a variety of other monomers capable of free radical polymerization, on other metals in addition to aluminum.

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