Rate of Electropolymerization of N,N'Dimethyl Acrylamide in Aqueous Sulfuric Acid Solution

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SYNOPSIS

Electropolymerization of N,N-dimethylacrylamide has been performed in aqueous sulfuric acid solution, using unsized AS-4 graphite fibers as the working electrode. The electropolymerized poly(N,N-dimethylacrylamide) deposited on the surface of the graphite fiber working electrode. The formation of poly(N,N'dimethyl acrylamide) was inhibited by hydroquinone. The addition of about 0.05 moles of hydroquinone to the reaction solution resulted in about a 90% decrease in the weight gain of fibers, in agreement with the proposed free radical mechanism of aqueous electropolymerization. The rate of electropolymerization varied with the initial monomer concentration, current density, and sulfuric acid concentration, raised to the power of 1.3, 0.42, and 0.07, respectively, that is, $R_p \propto [M]^{1.3}$-$Cd^{0.42}[H_2SO_4]^{0.07}$. A mathematical model, based upon free radical polymerization kinetics, is discussed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Electrochemically initiated polymerization of acrylamide in aqueous and nonaqueous solution has been widely investigated.[1-11] Not much attention, however, has been focused on the kinetics and mechanism of electropolymerization of N,N' disubstituted acrylamides. The study of the electropolymerization of disubstituted acrylamide should lead to better understanding of the effect of the primary amide group on the mechanism and kinetics of electropolymerization of acrylamide. It was previously shown that competing side reactions, such as cross-linking and side chain cyclization, occur during the formation of acrylamide.[11] Electropolymerization of vinyl monomers and other systems onto conductive graphite fibers[12-16] has generated much interest lately because of the excellent mechanical properties and lightweight characteristics of polymer–graphite fiber composite systems. The unique combination of light weight, high modulus, and high strength make graphite fibers excellent reinforcements, for both metal and resin matrix composites. Advanced composites and high temperature stable metal matrix composites are in high demand in the aircraft and automotive industries. The excellent electrical conductivity of graphite fibers makes them suitable as electrodes for electropolymerization. Electrochemically initiated polymerization is a versatile and powerful synthetic technique, which can be used in the coating and modification of graphite fiber surfaces.

In an earlier article,[17] we described the electrochemical polymerization of N(3-carboxylphenyl) maleimide and styrene in an electrochemical cell, using graphite fibers as the cathode. The catholyte was comprised of the comonomers, the supporting electrolyte, and N,N'dimethylacetamide. The anolyte was composed of sulfuric acid and N,-N'dimethylacetamide. By this procedure, it was possible to electropolymerize high temperature-resistant ($T_g > 220°C$) thermoplastic coatings onto the fibers in thickness enough that, after washing and drying, 60 vol % fiber composites were fabricated directly from the dried sheets.

The use of graphite fiber electrodes in the electrochemical polymerization of olefinic and stiff backbone monomers confers numerous advantages,

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such as the ability to apply uniform, controlled thickness, and controlled functionality polymer coatings directly onto conducting substrates at reduced cost. The kinetics and mechanism of such syntheses deserve more attention. In this article, we present the results of our investigation on the electrochemically initiated polymerization of N,N'dimethyl acrylamide in aqueous sulfuric acid solution, using a graphite fiber preform as the working electrode.

EXPERIMENTAL

Materials

Reagent grade sulfuric acid, purchased from May and Baker, was used as the supporting electrolyte. It was diluted several times in distilled water. N,N-dimethylacrylamide (DA), 99% pure, was used as purchased from Aldrich Chemical Company. Unsized AS-4 graphite fiber preforms, comprised of continuous graphite fiber bundles wound on an H-shaped 7.6 × 3.8 cm polypropylene frame, were used as the working electrode. 12.7 × 3.8 × 0.15 cm rectangular stainless steel sheets were used as the counter electrodes. EG & G Princeton Applied Research Potentiostat model 362 was the source of DC current.

Electropolymerization

Electropolymerization of N,N'-dimethylacrylamide was performed in a 3-compartment electrochemical cell. The working electrode chamber (middle chamber) was separated from the two side counter electrode chambers by means of a 0.4 μ pore size polypropylene membrane, from Osmonics Inc., glued to perforated polypropylene sheet. The working electrode chamber contained the graphite fiber working electrode, monomer solution (1.5 M–4.0 M), and dilute sulfuric acid solution (0.025 M). The graphite fiber preform (working electrode) was connected to the negative terminal of the potentiostat. The counter electrode chambers each contained dilute sulfuric acid solution (0.025 M) and stainless steel electrode. The stainless steel counter electrodes were connected to the positive terminal of the potentiostat.

Electropolymerization was started by passing 10–50 milliamperes of current through the system. At the end of electropolymerization, the cell was disconnected from the current source, and the coated fibers were withdrawn from the reaction solution, were rinsed with methanol, and were dried at room temperature. The coated fibers were then dried to constant weight at 100°C under vacuum. The amount of polymer coating was determined from the difference between the weights of the coated and uncoated fibers.

Characterization

The intrinsic viscosity of the electropolymerized poly(N,N'-dimethyl acrylamide) was determined by dilute solution viscometry. Viscosity average molecular weights of the coatings, synthesized at different current densities, were calculated by use of the Mark–Houwink equation, with $K = 6.8 \times 10^{-4}$ and $a = 0.66$.[18]

The electrochemical reactivities of the monomer, the solvent, and the supporting electrolyte were determined by cyclic voltammetric analysis. For this purpose, 0.29 M tetraethylammonium perchlorate (TEAP) was used as a carrier electrolyte, a graphite fiber bundle containing about 3 K individual filaments was the working electrode, platinum wire was the counter electrode, and a saturated calomel electrode was used as the reference electrode. Cyclic voltammetry was used to perform the current vs. voltage scans (with reversals) for the different systems between initial and final voltages of +1.0 V and −3.25 V vs. saturated calomel electrode (SCE), respectively.

RESULTS AND DISCUSSION

Electropolymerization of N,N-dimethylacrylamide in sulfuric acid solution occurred in the cathodic compartment of the electrochemical cell, with the electropolymerized coatings depositing on the surface of graphite fiber preform (working electrode). The reacted solution was poured into a beaker of methanol, but no significant amount of polymer was precipitated, suggesting that the electropolymerized poly(N,N'dimethyl acrylamide) was completely deposited onto the surface of graphite fibers. Electropolymerization did not take place in the anodic chamber. This was confirmed by the absence of polymer coatings in both anodic chambers or on the surface of the stainless steel counter electrodes. Electropolymerization of N,N-dimethylacrylamide in aqueous sulfuric acid solution onto graphite fiber working electrode varied with the initial monomer concentration, current density, and the electropolymerization time.

Dilute Solution Viscometry

The viscosity average molecular weight of poly-(N,N'dimethyl acrylamide) was estimated using a modified Mark–Houwink equation of Jai, Caskey, and Allison[18];

$$[\eta] = 6.8 \times 10^{-4} \, (\text{Mv})^{0.66} \qquad (1)$$

Table I(a) shows the number average molecular weights of the electropolymerized coatings and the respective current densities used in their synthesis. Increasing the magnitude of the initiating current resulted in decreased number average molecular weight of the coatings. A plot of the inverse of the number average molecular weight, as a function of the initiating current, is shown in Figure 1, where an approximately linear relationship is observed. A linear dependence of $1/\text{Mn}$ on the initiator concentration, here proportional to the current density Cd, is a well known characteristic of radical chain polymerization.

Effect of Reaction Conditions

Hydroquinone

Figure 2 shows a plot of the weight gain of poly(N,N'dimethyl acrylamide) per unit weight graphite fibers as a function of electropolymerization time. The effectiveness of hydroquinone in inhibiting electrochemical polymerization of N,N'dimethyl acrylamide can be shown by comparing the amount of polymer coating formed when 0.05 moles of hydroquinone was added to 1 liter of the reaction mixture (Fig. 2, curve 1), with the control experiment performed without hydroquinone (Fig. 2, curve 3). Less than 10% weight gain occurred in the reaction solution containing about 0.05 moles of hydroquinone after six minutes of electropolymer-
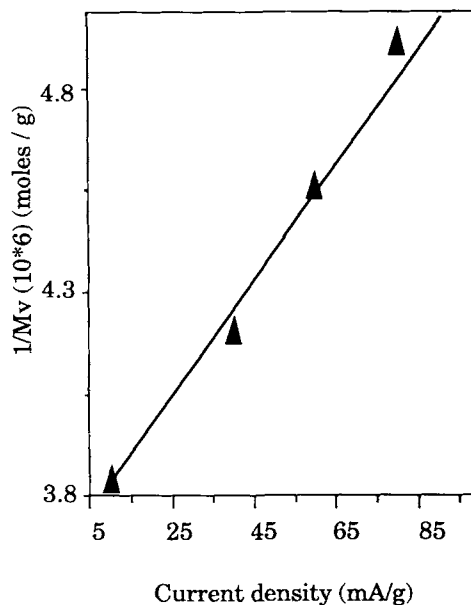

Figure 1 Dependence of viscosity average molecular weight on the current density.

ization. The control experiment resulted in more than 100% weight gain. It was reported earlier that the presence of diphenylpicrylhydrazyl, as radical scavenger in the reaction solution, resulted in zero weight gain of a styrene–maleimide polymer on graphite fibers.[17]
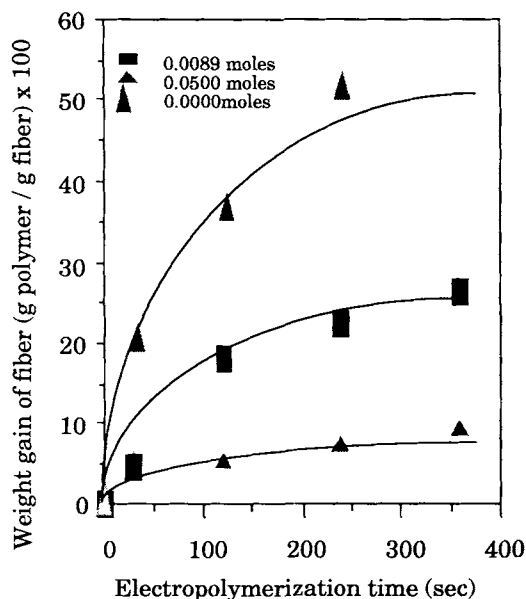
Table I   Variation of Viscosity Average Molecular Weight with the Rate of Electrochemical Polymerization of N, N'Dimethyl Acrylamide in a 0.0125 M Sulfuric Acid Solution

Cd (mA/g)	[M] (mol/L)	$1/M_n$ (mol/g)	R_p (g/g-min)
10	2	3.8×10^{-6}	0.27
40	2	4.2×10^{-6}	0.32
60	2	4.6×10^{-6}	0.33
80	2	4.9×10^{-6}	0.36

Figure 2 Effect of hydroquinone on the electrochemical polymerization of 1.5 M N,N'dimethyl acrylamide (Cd = 20 mA/g).

Initial Monomer Concentration

The weight gain of graphite fibers, due to electro-polymerization of poly(N,N'dimethyl acrylamide), for different initial monomer concentrations at constant current density ($\sim$ 20 mA/g) and supporting electrolyte concentration ($\sim$ 0.0125 M), is plotted as a function of electropolymerization time (Fig. 3). The amount of polymer coatings formed per unit time increases with increasing initial monomer concentration. The rate of electropolymerization of N,N'dimethyl acrylamide in dilute sulfuric acid solution was determined from the slope of the initial linear region of the polymer weight gain vs. electropolymerization time curve. Figure 4 shows that the rate of electropolymerization of N,N'dimethyl acrylamide increased correspondingly with increased initial monomer concentration. A plot of the natural logarithm of the rate of electropolymerization (ln R_p) against the natural log of initial monomer concentration [ln (M)] (Fig. 5), resulted in a slope of 1.3, suggesting a 1.3 order dependence of the rate of electropolymerization on the initial monomer concentration.

Current Density

The quantity of electric current passed during electropolymerization is important in determining the rate of electropolymerization and the properties of the resulting polymer coating, especially those de-
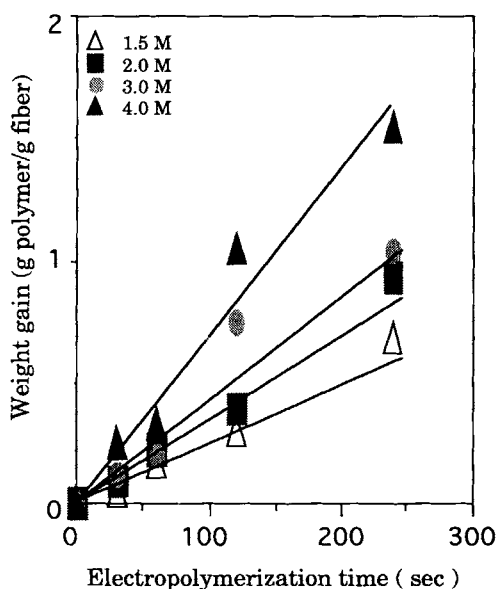

Figure 4   Rate of electropolymerization of N,N'dimethyl acrylamide as a function of initial monomer concentration (Cd = 20 mA/g, [H$_2$SO$_4$] = 0.0125 M).

pendent on the molecular weight. The electropolymerization of poly(N,N'dimethyl acrylamide) onto graphite fibers was studied at four different current densities; 1 mA/g, 10 mA/g, and 40 mA/g. The data are plotted as a function of time in Figure 6. The rates of electropolymerization, at constant initial monomer concentration (2 M) and sulfuric acid

Figure 3   Weight gain of fibers as a function of time for: 1.5 M, 2.0 M, 3.0 M, and 4.0 M N,N'dimethyl acrylamide solution (Cd = 20 mA/g [H$_2$SO$_4$] = 0.0125 M).
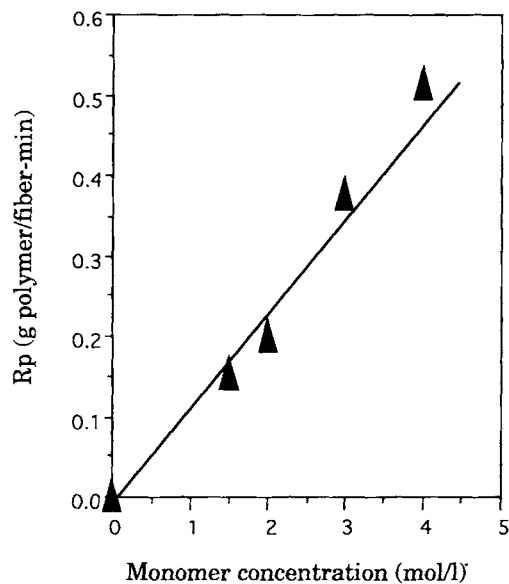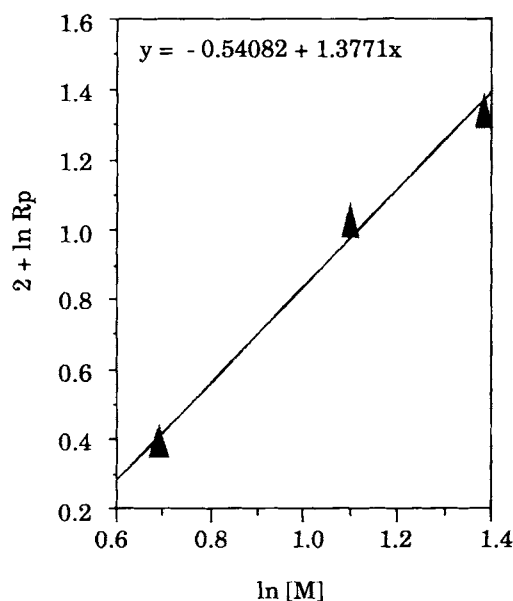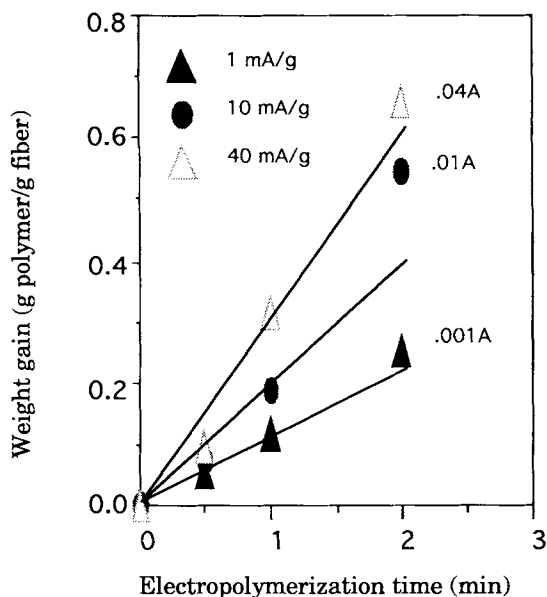

Figure 5   Determination of monomer concentration exponent.

Figure 6 Weight gain of fibers as a function of time for: 1 mA/g, 10 mA/g, and 40 mA/g ([M] = 2 M, [H₂SO₄] = 0.0125 M).

plot (Fig. 8) and a value of 0.4 was obtained. This dependence of the rate of electropolymerization on the initiator concentration (current density) is similar to that found earlier for polyacrylamide.[11,19]

Sulfuric Acid Concentration

The effect of sulfuric acid concentration on the rate of electrochemical polymerization of N,N'dimethyl acrylamide (N,N'DMA), at constant initial monomer concentration (3 M) and current density (20 mA/g), is shown in Figure 9. A double logarithmic plot of the rate of electropolymerization against sulfuric acid concentration was used to estimate a sulfuric acid concentration exponent (Fig. 10). The obtained value of 0.07 suggests little dependence of the rate on the supporting electrolyte concentration. Except at low concentrations, it appears that a certain amount of acid is necessary, and above that amount, the concentration of acid has little effect. The rate of electropolymerization of N,N'dimethyl acrylamide on fiber surfaces remained constant for sulfuric acid concentrations of 0.01 M, 0.025 M, 0.05 M, and 0.25 M, but dropped significantly below 0.005 M.

concentration (0.0125 M), for the different current densities, were measured from the slopes of the linear region of the weight gain of fibers vs. electropolymerization time curves (Fig. 6), and were plotted in Figure 7. The current exponent was measured from the slope of the ln R_p vs. ln Cd (current density)
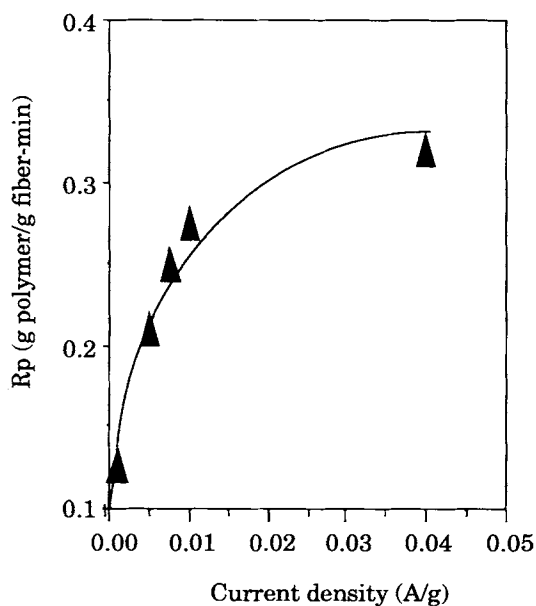
Cyclic Voltammetry

The electrochemical reactivities of 1 M N,N'-dimethylacrylamide solution, 0.025 M sulfuric acid solution, and 0.29 M tetraethylammonium perchlo-
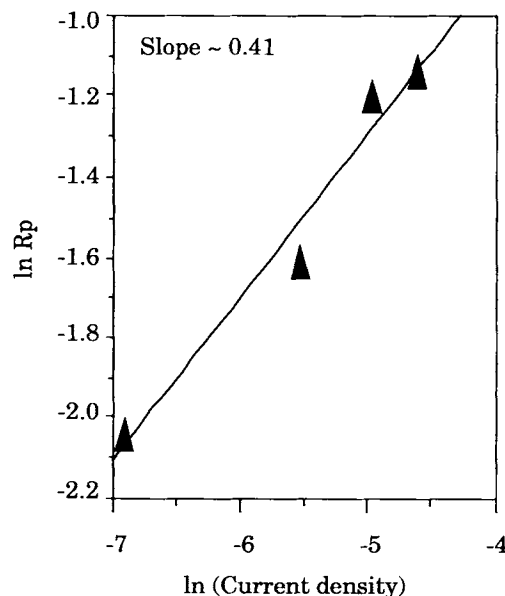

Figure 7 Dependence of electropolymerization of N,-N'dimethyl acrylamide on the current density ([M] = 2 M, [H₂SO₄] = 0.0125 M).

Figure 8 Current exponent determination for poly-(N,N'dimethyl acrylamide).

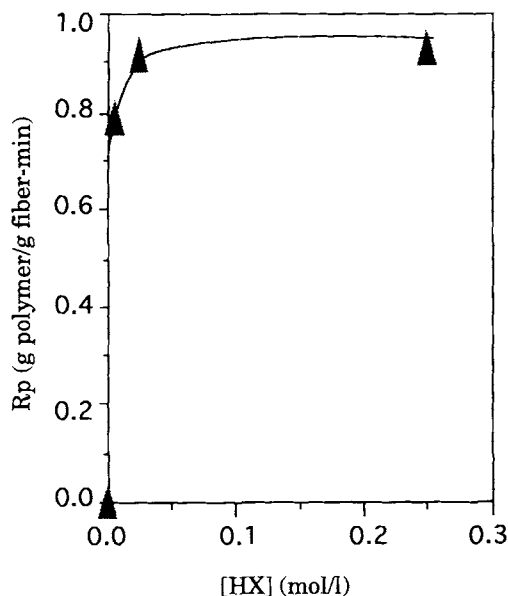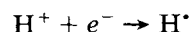**Figure 9** Dependence of the rate of electropolymerization of N,N'dimethyl acrylamide on sulfuric acid concentration ([M] = 3 M, Cd = 20 mA/g).

rate (TBAP) were measured by cyclic voltammetry. The cyclic voltammographs (CV) of 0.025 M sulfuric acid solution were reported earlier.[20] A reduction peak, associated with the electrochemical reaction

$$H^+ + e^- \rightarrow H^\cdot$$

occurred at −2.1 V vs. SCE. A CV for an aqueous solution, containing 1.0 M N,N'dimethylacrylamide, 0.29 M TBAP, and DMAc (1 : 1 by volume) in water, showed no redox peaks and resembled the CV reported previously for acrylamide.[19] A solution of N,N'dimethylacrylamide (1 M), in sulfuric acid (0.025 M), showed a slight shift in the reduction peak potential for a hydrogen ion by 400 mV toward a more negative potential [Fig. 11(a)]. The current (peak height) was reduced to a half its original value, due to increased resistance of the cell, as a result of the coating of the graphite fiber working electrode by insulating organic polymer film. Repeated CV scans of N,N'dimethyl acrylamide–sulfuric acid solution show decreased reduction peak height (current) as the number of scans was increased [Fig. 11(b)].

Experimental Rate of Electropolymerization

The dependence of the rate of electropolymerization Rp of N,N'dimethyl acrylamide on the initial monomer concentration [M], current density Cd, and

sulfuric acid concentration [HX], is represented by the rate equation

$$R_p \ \alpha \ [M]^\beta Cd^\gamma [HX]^\lambda \qquad (2)$$

where β, γ, and λ are the experimentally determined exponents on the initial monomer concentration (1.3), current density (0.4), and sulfuric acid concentration (0.07).

or

$$R_p = \not\!k [M]^{1.3} Cd^{0.4} [HX]^{0.07} \qquad (3)$$

where $\not\!k$ is the proportionality constant.

Mathematical Modelling of Aqueous Electropolymerization

The major chain processes, occurring during the electrochemical polymerization of N,N'dimethyl acrylamide (DA), can be represented as follows:

Initiation

The electrochemical reduction of the hydrogen ion H^+ to form the hydrogen radical $H^\cdot$ is a crucial step in the indirect electrochemical initiation of electropolymerization of DA.

$$H^+ + (Cd)e^- \rightarrow H^\cdot \qquad (4a)$$

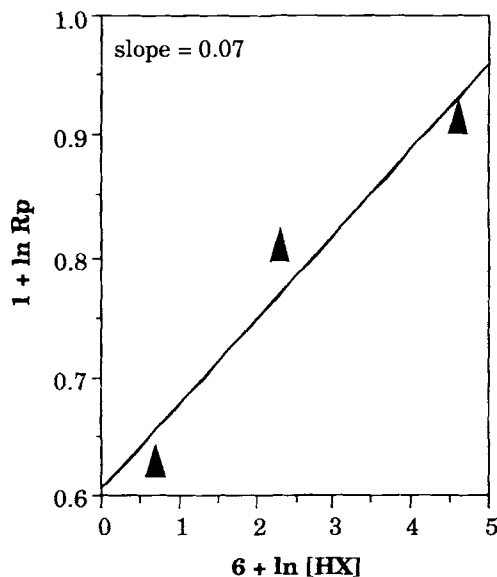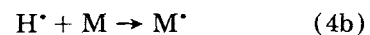$$H^\cdot + M \rightarrow M^\cdot \qquad (4b)$$

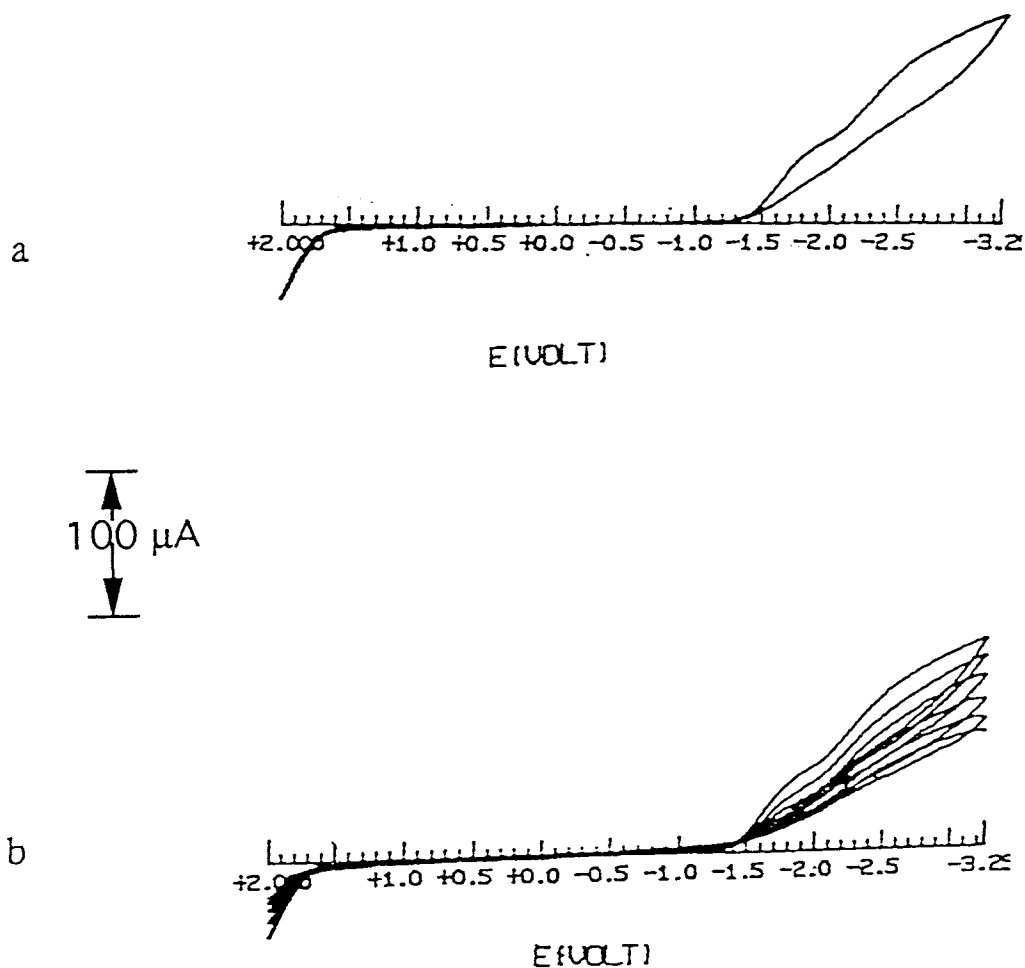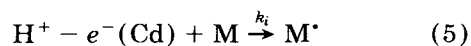**Figure 10** Determination of sulfuric acid concentration exponent.

Figure 11   (a) Cyclic voltammograph for 1 M dimethyl acrylamide and 0.025 M sulfuric acid solution (WE = graphite fiber bundle, scan rate = 250 mV/sec) (b) Repeated scan of (a).

Equations (4) and (5) are combined to form the overall equation for the initiation reaction.

$$H^+ - e^-(Cd) + M \xrightarrow{k_i} M^\bullet \qquad (5)$$

Propagation

The monomer radical $M^\bullet$, produced in eq. (5), propagates into a macroradical by subsequent chain reactions with unreacted monomers M.

$$M + M^\bullet \xrightarrow{k_p} M—M^\bullet \qquad (6a)$$

$$M + M^\bullet_n \xrightarrow{k_p} M^\bullet_{n+1} \qquad (6b)$$
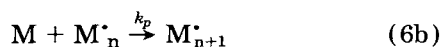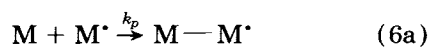
Termination

Termination of electropolymerization can occur when two macroradicals couple to form a dead poly-

mer (coupling) when the macroradical reacts with either the unreacted monomer M (transfer to monomer), or with the solvent SH (transfer to solvent). Termination of electropolymerization by the reaction of macroradical with the hydrogen radical $H^\bullet$ (reaction with primary radical) can also occur.

Termination by Coupling

$$M^\bullet_n + M^\bullet_p \xrightarrow{k_{tc}} M_{n+p} \qquad (7)$$

Termination by Transfer to Monomer (M) and Solvent (SH)

$$M^\bullet_n + M \xrightarrow{k_{tr}} M_n + M^\bullet \qquad (8)$$

$$M^\bullet_n + SH \xrightarrow{k_{tr}} M_n + SH^\bullet \qquad (9)$$
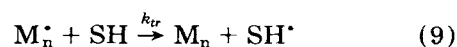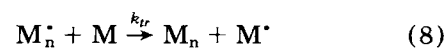
Termination by Reaction with Hydrogen Radical H·

$$M_n^· + H· \xrightarrow{k_{ti}} M_n \tag{10}$$
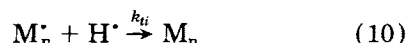
Rate of Electropolymerization

Rate of Initiation

The expression for the rate of initiation of polymerization Ri is derived from eq. (5):

$$H^+ + e^-(Cd) + M \xrightarrow{k_i} M·$$

$$Ri = k_i f [M] Cd \tag{11}$$
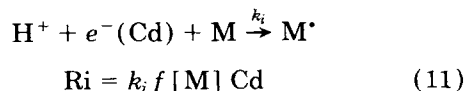
where k_i is the rate constant for initiation, Cd is the initiating current per unit weight of graphite fibers, [M] is the molar concentration of the monomer, and f is the fraction of the hydrogen radicals generated, which actually initiate chains. The number of initiating radicals produced is directly related to the quantity of electricity passed during the process.

Rate of Propagation

The rate of propagation, R_p, is derived from eq. (6). It is assumed that the size of the growing chain does not affect its ability to react with the monomers.

$$R_p = k_p[M][M·] \tag{12}$$

where k_p is the rate constant for propagation and [M] and [M·] are the molar concentrations of the monomer and monomer radical, respectively.

Rate of Termination

Termination of the macroradicals occur by radical coupling, chain transfer to the monomer, chain transfer to the solvent, or by chain transfer to the hydrogen radicals.

The rate expressions for termination of the chain radicals by combination R_{tc}, transfer to the monomer R_{tr}, transfer to the solvent R_{tr}, and transfer to the hydrogen radical R_{ti}, are derived from eqs. (7)–(10), as follows:

Coupling

$$R_{tc} = k_{tc}[M_n^·]^2 \tag{13}$$

Transfer to Solvent

$$R_{tr} = k_{tr}[M_n^·] \tag{14a}$$

Transfer to Monomer

$$R_{tr} = k_{tr}[M_n^·] \tag{14b}$$

Transfer to Hydrogen Radical

$$R_{ti} = k_{ti}[M_n^·] \tag{14c}$$

where [M], [SH], Cd ≫ [M·], and [H·] is assumed to be constant. That is, the concentration of growing chains [M·], relative to the solvent [SH], is small, so that [SH] remained constant and the monomer concentration also remained relatively unchanged during the reaction. k_{tr} includes chain transfer to both monomer and solvent. R_{tc}, R_{tr}, and R_{ti} are the rates of termination by combination, chain transfer to monomer and solvent, and termination by reaction with the initiating species H·. k_{tc}, k_{tr}, and k_{ti} are the apparent rate constants, containing the effects of [M], [SH], and [H·] for termination by combination, chain transfer, and reaction with the initiating species H·, respectively.

The rate of electropolymerization for termination by coupling R_{tc}, chain transfer R_{tr}, and reaction with H· R_{ti}, can be derived from eqs. (12), (13), and (14), and by making the steady state assumption (Ri = Rt), such that:

Coupling

$$k_{tc}[M·]^2 = k_i f \, Cd[M] \tag{15}$$

$$[M·] = \left(\frac{k_i f \, Cd[M]}{2k_{tc}} \right)^{0.5} \tag{16}$$

Transfer to Monomer or Solvent

$$k_{tr}[M·] = k_i f \, Cd[M] \tag{17}$$

$$[M·] = \left(\frac{k_i f \, Cd[M]}{k_{tr}} \right) \tag{18}$$

Transfer to Hydrogen Radical

$$k_{ti}[M·] = k_i f \, Cd[M] \tag{19}$$

$$[M·] = \left(\frac{k_i f \, Cd[M]}{k_{ti}} \right) \tag{20}$$

The rate of electropolymerization is then expressed with respect to the different termination modes by substituting eqs. (16), (18), and (20), respectively, into eq. (12), as follows:

Coupling

$$R_{pc} = k_p[M]^{1.5}\left[\left(\frac{k_i}{2k_{tc}}\right)f\,Cd\right]^{0.5} \qquad (21)$$

Transfer to Monomer or Solvent

$$R_{ptr} = k_p[M]^2 f\,Cd\left(\frac{k_i}{2k_{tr}}\right) \qquad (22)$$

Transfer to Hydrogen Radical

$$R_{pti} = k_p[M]^2 f\,Cd\left(\frac{k_i}{2k_{ti}}\right) \qquad (23)$$

Equations (21) to (23) can be combined to yield a general expression for the rate of electropolymerization for the system:

$$R_p = k_p[M]^2 f\,Cd\left\{\left(\frac{1}{2k_{tc}f\,Cd[M]}\right)^{0.5} + \frac{1}{k_{tr}} + \frac{1}{k_{ti}}\right\} \qquad (24)$$

We have assumed that the efficiency of initiation of electropolymerization f depends upon $[M]$. We recognize the fact that f is also dependent on the rate of generation of the initiating species Cd.[11] At higher $[M]$, the probability of a formed hydrogen radical H· finding a monomer to react with, thus initiating a chain, is also proportionately higher. The probability of an H· reacting with another H· or other species is less at higher monomer concentration $[M]$.

The radical efficiency can be considerd as governed by chain initiation and radical destruction reactions:

$$[H·] + [M] \rightarrow [M·]$$

and

$$[H·] + [H·] \rightarrow H_2$$

$$[H·] + [CTA] \rightarrow H_2 + [CTA·]$$
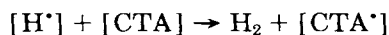
where CTA includes a variety of chain transfer agents. The fraction of [H·] that participates in the desired reaction in eq. (5), namely f, is proportional to $[M]$. As [H·] increases, both the desired initiation reaction and the undesired side reactions increase. Since the H· are generated in close proximity to each other at the electrode surface, the undesired reactions may be more increased near the surface than the desired reaction; hence f may also have a strong

inverse dependence on Cd. Previous data[11] indicate that f may change more than an order of magnitude as the current density is increased. We also assumed that the rate of propagation is independent on the size of the monomer radical, such that reactions in eqs. (6a) and (6b) are equally probable.

Equation (24) suggests that the rate of electropolymerization increases with increasing rate of generation of initiating species. It also predicts that an increase in the initial monomer concentration will result in a corresponding increase in the rate of electropolymerization. The exponent for the monomer concentration and for the initiating current, with respect to the rate of electropolymerization, is related to the mode of termination of electropolymerization. Equation (24) reduces to either eq. (21), (22), or (23) when termination of electropolymerization occurs exclusively by coupling, chain transfer to the solvent, chain transfer to the monomer, or chain transfer to the primary hydrogen radical, respectively.

The relationship between the number average molecular weight M_n of the electropolymerized poly(N,N'dimethyl acrylamide) and the rate of polymerization can be derived from the kinetic chain length $V = R_p/R_t$ and from the equation $M_n = X_n M_o$, as follows:

$$M_n = \frac{R_p M_o}{2\,k_{tc}[M·]^2 + k_{tr}[M·] + k_{ti}[M·]} \qquad (25)$$

Equation (25) can be further simplified to obtain the relationship between the number average molecular weight, the current density, and initial monomer concentration, as follows;

$$M_n = \frac{k_p M_o[M]^{0.5}}{(k_{tc}k_i\,f\,Cd)^{0.5} + k_{tr} + k_{ti}} \qquad (26)$$

where k_p, k_i, k_{tc}, k_{tr}, and k_{ti} have been previously defined. M_o is the molecular weight of the repeat unit.

The relationship between the rate of electropolymerization, R_p, and the number average molecular weight can be derived from eqs. (12) and (21), as follows;

$$[M·] = \frac{R_p}{k_p[M]}$$

$$M_n = \frac{R_p M_o}{2\,k_{tc}\left(\frac{R_p}{k_p[M]}\right)^2 + k_{tr}\left(\frac{R_p}{k_p[M]}\right) + k_{ti}\left(\frac{R_p}{k_p[M]}\right)} \qquad (27)$$

$$M_n = \left[\frac{k_p M_o [\mathrm{M}]}{\left(\dfrac{2 R_p k_{tc}}{k_p [\mathrm{M}]} \right) + k_{tr} + k_{ti}} \right] \qquad (28)$$

where k_p is the rate constant for propagation of chain radicals and R_p is the rate of electropolymerization.

Equations (26) and (28) predict an inverse relationship of the number average molecular weight of the electropolymerized coatings, with the rate of electropolymerization and the current density Cd, respectively. It was shown experimentally that the rate of electropolymerization of N,N'dimethyl acrylamide in aqueous sulfuric acid solution was related to the rate of generation of the initiating species by a 0.4 power [eq. (4)]. Note that the current density is a measure of the rate of radical generation in electroinitiated polymerization. The viscosity average molecular weight of the electropolymerized coatings decreased, as was expected, with increased concentration of the initiating species (Fig. 1, Table I). It is believed that at a high rate of generation of the initiating species (high Cd), the rate of electropolymerization rises significantly, but the rate of chain termination increases correspondingly, resulting in low molecular weight polymers and a wide molecular weight distribution. Production of high molecular weight polymers at a reasonable rate can be accomplished at low to moderate current densities.

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