

Aqueous Electropolymerization of Polyacrylamide onto AS-4 Graphite Fibers

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SYNOPSIS

Constant current electropolymerization of acrylamide was initiated on the surfaces of AS-4 graphite fibers. Electropolymerization was performed using an aqueous solution of acrylamide dissolved in dilute sulfuric acid solution. The progress of electropolymerization was followed by measuring the weight of polyacrylamide deposited onto the surfaces of a unit weight of graphite fiber per unit time. The rate of electropolymerization was obtained from the slope of the linear region of the polymer weight gain vs. electropolymerization time curve. The rate of electropolymerization onto AS-4 graphite fiber surfaces was found to depend on the initial monomer concentration, sulfuric acid concentration, and current density raised to the powers of 1.67, 0.02, 0.54, respectively. Molecular weight measurements on the electropolymerized polyacrylamide were done by solution viscometry. Number average molecular weights of 430,000, 220,000, and 193,000 were obtained for polyacrylamide, electropolymerized at 1 mA/g, 50 mA/g, and 100 mA/g respectively, consistent with classical radical polymerization kinetics.

INTRODUCTION

Graphite fibers have excellent strength/weight and modulus/weight properties. They are therefore in great demand in composite technology as reinforcements for advanced polymeric composites. To serve as effective reinforcements, graphite fibers are surface treated to enhance their wettability and adhesion with the polymeric matrix. Typical surface treatment techniques include surface oxidation, which is usually done in concentrated nitric acid solution or is done electrochemically.

Previous authors, such as Subramanian et al.,¹⁻³ MacCallum and MacKerron,^{4,5} and Bell et al.,⁶⁻⁹ have electropolymerized a wide range of polymeric coatings onto graphite fibers, with the objective of attaining enhanced interfacial properties and improved composite toughness. For example, AS-4 graphite fibers, pretreated by electropolymerized thin poly(glycidyl acrylate-co-methyl acrylate) interlayer ($\sim 0.15 \mu\text{m}$ thick), in an epoxy resin matrix,

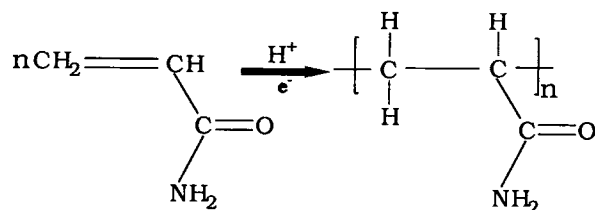
have shown 15–25% simultaneous improvement in both the impact toughness and the interlaminar shear strength of the composite.⁷

Advantages of the electropolymerization technique over the other methods of surface treatment of graphite fibers include: excellent wettability of the individual fibers in a 3000 filament bundle, easy control of the properties of the coatings through selective control of monomer functionality, monomer feed ratio, and electropolymerization parameters such as current density, monomer concentration, supporting electrolyte concentration, and electropolymerization time. Electropolymerization is a simple, easy-to-control technique, and when judiciously applied, the technique should minimize processing cost. Recently, electropolymerization has been extended to the production of thick ($\sim 3.0 \mu\text{m}$) thermoplastic coatings onto graphite fiber reinforcements as a new route to making thermoplastic "prepregs" for advanced graphite fiber/polymeric composites applications.⁸

Several authors have studied the solution, emulsion, and bulk radical polymerization of acrylamide.¹⁰⁻²⁵ However, the different polymerization techniques have resulted in different mechanisms of

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acrylamide polymerization. In the present work, aqueous electropolymerization of polyacrylamide onto AS-4 graphite fibers, acting as the cathode, has been done in aqueous sulfuric acid-acrylamide solution.



Acrylamide

Polyacrylamide

While the resistance of this polymer to solvent is low for use in composites, we hoped to obtain additional information about electropolymerization kinetics and mechanism. An attempt was made to derive a kinetic equation to describe the electropolymerization process from the experimental data.

EXPERIMENTAL

High purity acrylamide from Polysciences Inc., was used as received. Reagent grade sulfuric acid from May and Baker was diluted with distilled water to 0.0125 M and was used as the supporting electrolyte.

Unsize AS-4 graphite fibers, from Hercules Inc., were wound on an H-shaped, 7.6 × 3.8 cm polypropylene frame, and were used as the working electrode (cathode). The counter electrodes were two 12.7 × 3.8 × 0.15 cm rectangular stainless steel plates. Electropolymerization was carried out in a 3-chamber electropolymerization cell (Fig. 1), whose two side compartments contained each of the counter electrodes and sulfuric acid supporting electrolyte solution (0.0125 M). The middle compartment contained both the graphite fiber working electrode and the monomer-supporting electrolyte solution. A Princeton Applied Research Potentiostat, model 363, was used as the source of direct current.

Both the catholyte and the anolyte were saturated with nitrogen before electropolymerization. Current was initially applied to the cell containing the monomer solution and/or the electrolyte, for one min, by means of a dummy (ruthenium) working electrode to activate the cell. The dummy working electrode was then replaced by graphite fiber bundles wound on H-shaped polypropylene frames. The graphite fiber working electrode was immersed in

Electropolymerization cell

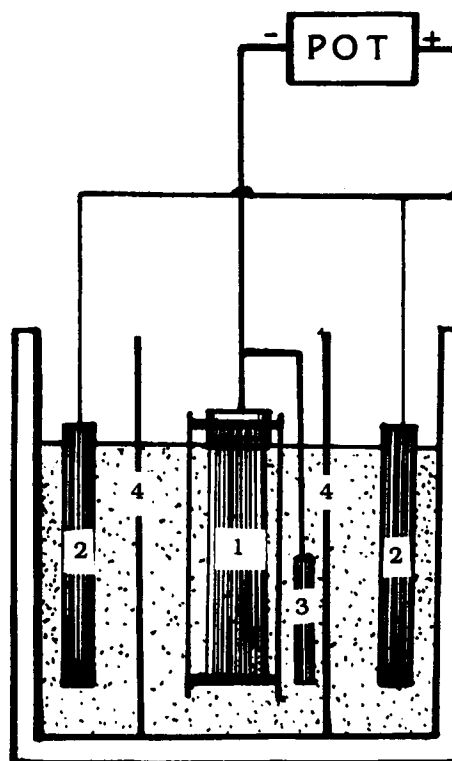


Figure 1 Schematic representation of the electrochemical cell showing: (1) working electrode, (2) counter electrode (3) SCE reference electrode, (4) polypropylene membrane.⁹

the monomer solution for about one min before commencing each electropolymerization run. The monomer-electrolyte solution was not stirred during electropolymerization. The weight of polymer formed is calculated as the difference between the weight of the uncoated and the dried coated fibers. For a typical electropolymerization, performed with an initial monomer concentration of 2 mol/L, at a current density of 20 mA/g of fiber, about 7% of the monomer is converted into polyacrylamide after about 10 min of electropolymerization (Table I).

The effect of initial monomer concentration on the rate of electropolymerization was estimated by measuring the fractional weight of polymer coatings deposited per unit time onto the surfaces of the graphite fiber working electrode, at constant current density and supporting electrolyte concentration. Four different monomer concentrations, 1 M, 2 M, 3 M, and 4 M were studied.

To evaluate the effect of current density on the rate of electropolymerization, the initial monomer

Table I Conversion of Monomer During Electropolymerization of Acrylamide ([M] = 2.0 M, Cd = 20 mA/g, and [H₂SO₄] = 0.0125 M)

Weight of Graphite Fiber (g)	Weight of Polymer Formed (g)	Weight Gain of Fiber (%)	Initial Monomer Conc. (g/250 mL)	Monomer Reacted (%)	Time (min)
2.200	.4902	22.28	35.5	1.38	1.00
2.061	1.413	68.56	35.5	3.98	2.50
2.167	1.841	85.20	35.5	5.19	5.00
2.124	2.436	114.7	35.5	6.86	10.0

concentration and sulfuric acid concentration were kept constant, while the current density was varied. Current densities used were 1 mA/g, 20 mA/g, 50 mA/g, and 100 mA/g. The weight of polymer coating formed per unit weight of fiber per unit time for the different current densities was measured.

To determine electropolymerization rates, the slopes of the linear region of the gms polymer/gm graphite fibers vs. electropolymerization time curves were used. The effect of sulfuric acid concentration on the rate of electropolymerization was studied at four different concentrations, 0.005 M, 0.01 M, 0.05 M, and 0.25 M, keeping the initial monomer concentration and the current density constant.

Thermal analysis of the electropolymerized polyacrylamide coatings was done with the use of a DuPont 9900 Series differential scanning calorimeter and thermogravimetric analyzer, operated at a 10°C/min heating rate under nitrogen atmosphere. Functional group analysis of the coatings was done with a Mattson FT-IR Spectrophotometer Cygnus 100. KBr pellets were used. Measurement of the number average molecular weight (\overline{M}_n), of the electropolymerized polyacrylamide was accomplished in distilled water with a Ubbelohde viscometer at 23°C. Electropolymerized coatings for solution viscometry were Soxhlet extracted in hot water for 48 h. Only about 55% of the electropolymerized coating was extractable. The number average molecular weight, \overline{M}_n , was calculated using the Mark-Houwink equation as modified by Dainton and Tordoff^{19,26}:

$$[\eta] = 6.8 \times 10^{-4} (\overline{M}_n)^{0.66}$$

The polyacrylamide formed deposited onto the surfaces of the graphite fiber working electrodes in very short electropolymerization times (4 min < t < 10 min) and was recovered by withdrawing the electrocoated fibers from the solution. It was then rinsed in a methanol-water solution (2:1), and dried

at ambient temperature for 5 h, followed by drying under vacuum at 150°C for 10 h. The amount of polymer electropolymerized onto the graphite fiber surface was measured as the difference between the weight of the coated and the uncoated fibers.

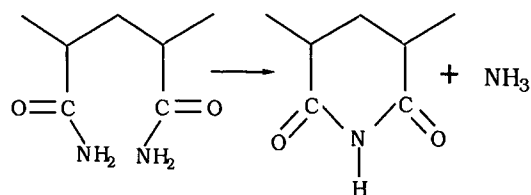
The progress of electropolymerization was followed by measuring the fractional weight gain of polymer coating per unit weight of AS-4 graphite fiber as a function of electropolymerization time.

RESULTS AND DISCUSSION

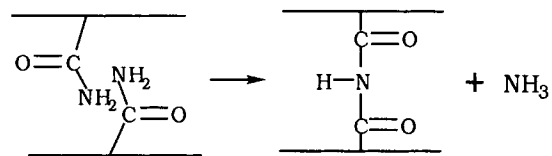
Characterization of Electropolymerized Polymer

The DSC curve for the electropolymerized polyacrylamide is shown in Figure 2.

The glass transition temperature was taken as 240°C from the point of greatest slope on the heat flow vs temperature curve. The high T_g of the electrocoated polyacrylamide may be due to crosslinking and to stiffening of the chain by cyclization of the side chain, as shown in Schemes I and II below:



Scheme I Chain cyclization.



Scheme II Crosslinking.

It should be noted that only about 50% of the poly-

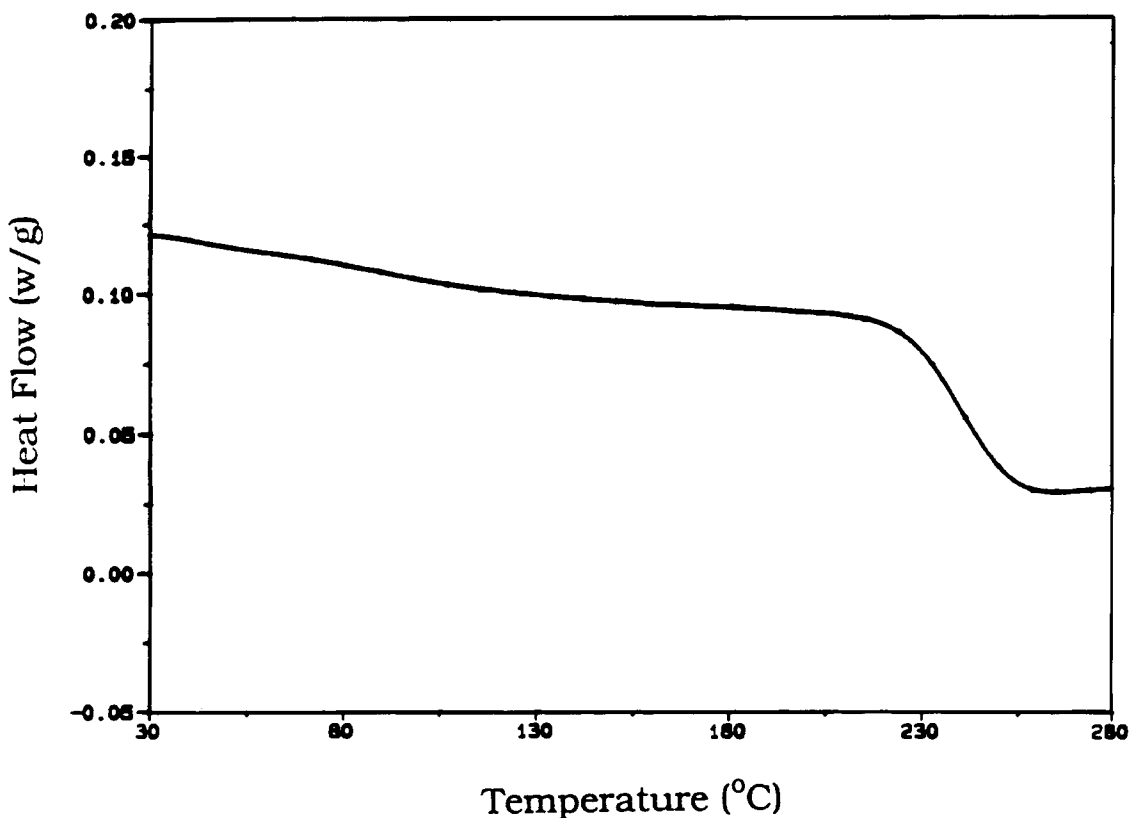


Figure 2 A DSC thermogram for electropolymerized polyacrylamide in nitrogen at 10°/min.

acrylamide electropolymerized onto AS-4 graphite fiber was extractable in hot water after 48 h immersion, consistent with a crosslinking hypothesis.

A typical TGA thermogram of the electrocoatings is shown in Figure 3. The electropolymerized polyacrylamide shows small loss up to approximately 350°C, after which it degraded rapidly. Figure 4 shows FTIR spectra of the electropolymerized polyacrylamide coatings. A broad amide (NH_2) absorption peak is present between 3500–2850 cm^{-1} , and a strong amide carbonyl absorption is shown at 1689 cm^{-1} . Hydrogen bonding interactions and side chain cyclization are associated with the shift in the carbonyl peak absorption from 1700 cm^{-1} . Table I shows the number average molecular weight (\overline{M}_n) of the electrocoated polyacrylamide at different current densities. Polymers formed at current densities of 1 mA/g, 50 mA/g and 100 mA/g, showed number average molecular weights of 430,000, 220,000, and 193,000 respectively, in agreement with the inverse relationship between the number average molecular weight (\overline{M}_n) and the initiator concentration (analogous to current density in electropolymerization) in radical chain polymerization.²⁴ The low number

average molecular weight of the electrosynthesized polyacrylamide at very high current densities is due to the higher probability of chain termination because of the generation of excess amount of hydrogen radicals, which may act as chain terminators. This leads to lower molecular weight values and a broader molecular weight distribution.²⁴

Effect of Initial Monomer Concentration on the Rate of Electropolymerization

Figure 5 shows the weight gain of polymer coatings per unit weight of graphite fibers for different initial monomer concentrations at constant current density (~ 20 mA/g) and electrolyte concentration (~ 0.0125 M), plotted as a function of the electropolymerization time. The amount of monomer electropolymerized per unit time increases with increasing initial monomer concentration. The rate of aqueous electropolymerization, measured from the slope of the linear region of the polymer weight gain vs. electropolymerization time curves, is plotted as a function of initial monomer concentration in Figure 6. The rate of electropolymerization increased

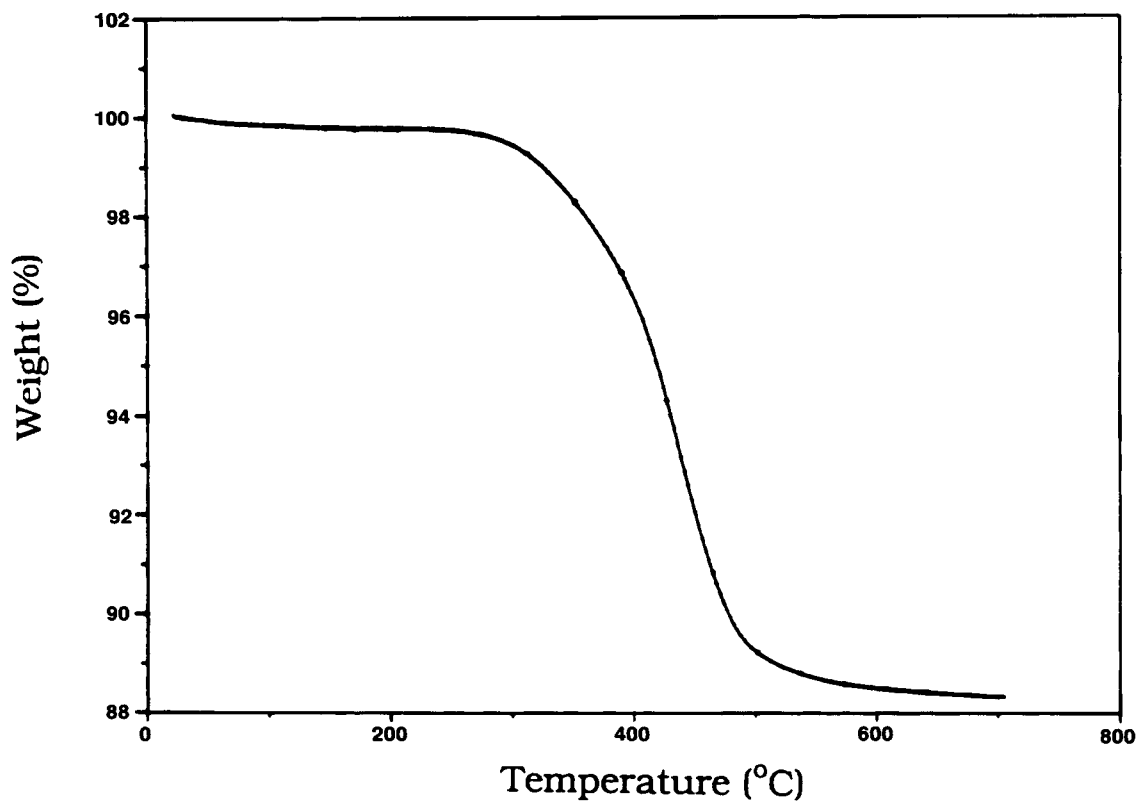


Figure 3 A TGA trace for electropolymerized polyacrylamide in nitrogen at 30°/min.

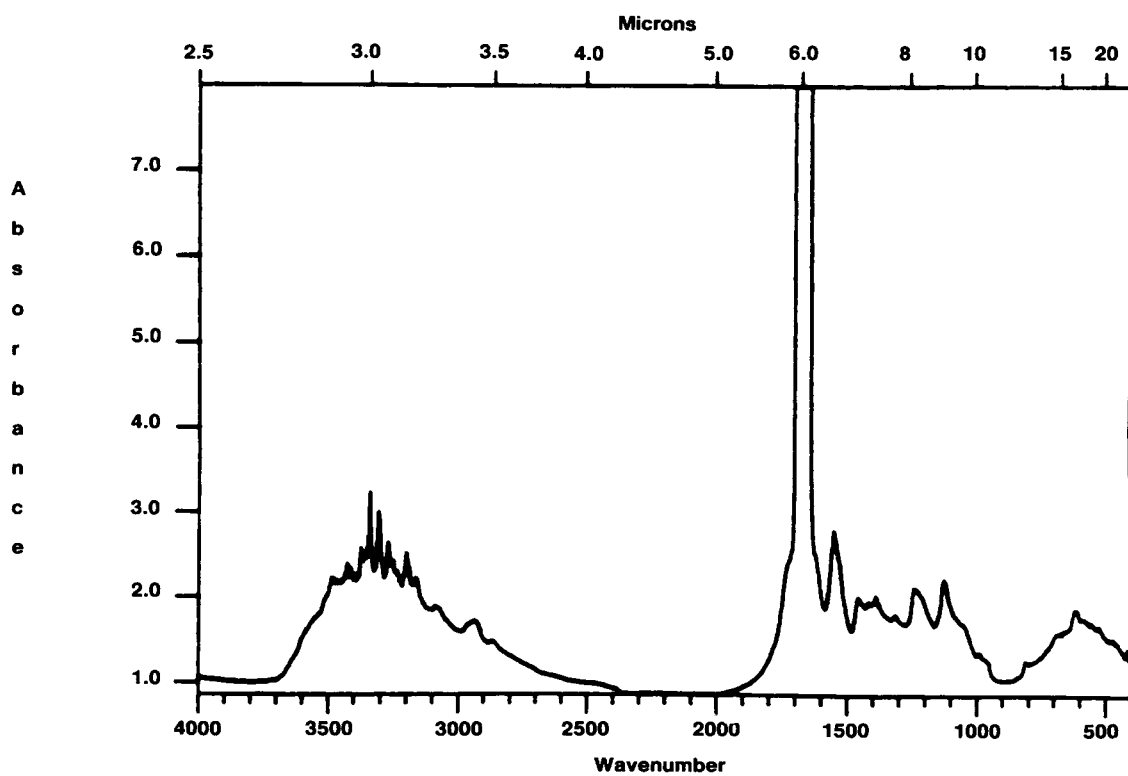


Figure 4 FTIR spectra for electropolymerized polyacrylamide.

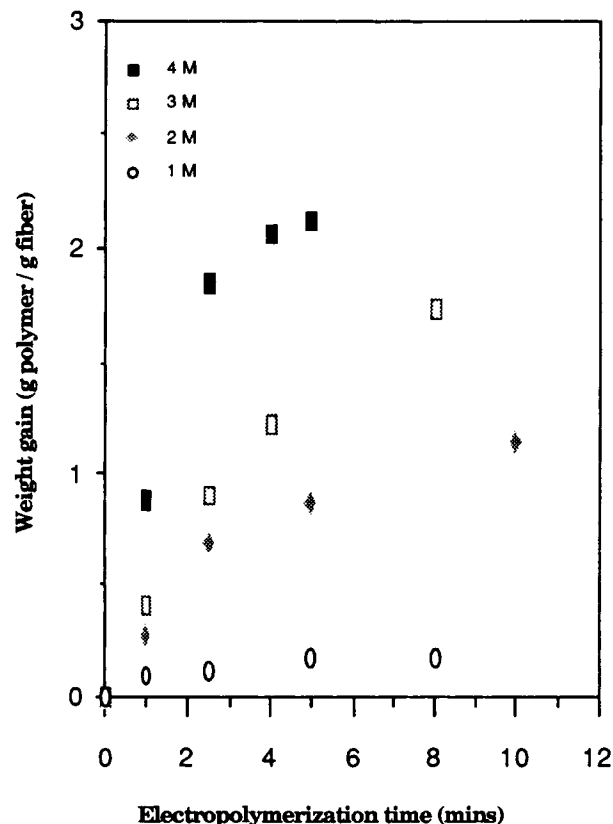


Figure 5 Weight gain of fibers as a function of time for: 1 M, 2 M, 3 M, and 4 M acrylamide solution ($C_d = 20$ mA/g, $[H_2SO_4] = 0.0125$ M).

in an accelerating manner with monomer concentration. Figure 7 shows that the rate of formation of polyacrylamide coatings onto graphite fiber surfaces, at constant current density and supporting electrolyte concentration, is directly proportional to the monomer concentration raised to 1.67 power; that is, $R_p \propto [M]^{1.67}$

Effect of Current Density on the Rate of Electropolymerization

The amount of polymer coating formed per unit weight of graphite fiber was examined at four different current densities: 1 mA/g, 20 mA/g, 50 mA/g, and 100 mA/g. The data are plotted as a function of electropolymerization time on Figure 8. Figure 9 shows the dependence of the electropolymerization rate (from the initial slopes on Fig. 8) on the current densities. Increasing the current density increases the amount of polymer coating formed per unit time, at constant monomer concentration (2 M) and sup-

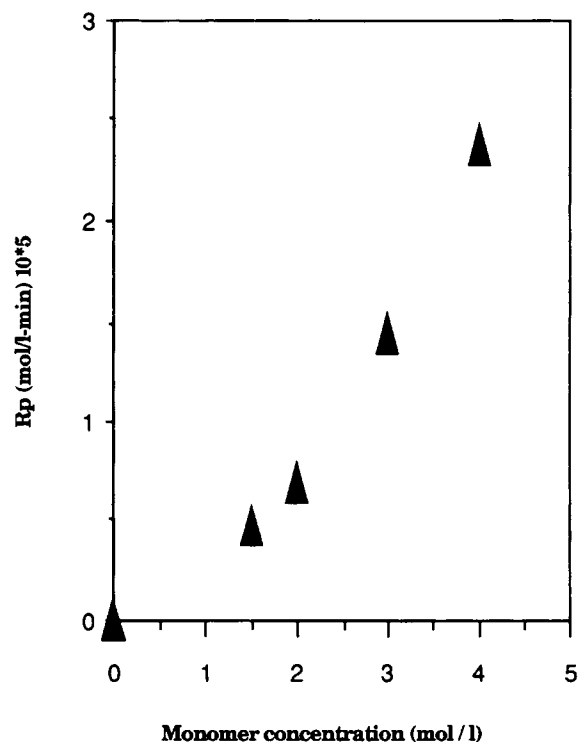


Figure 6 Rate of electropolymerization of acrylamide as a function of initial monomer concentration ($C_d = 20$ mA/g, $[H_2SO_4] = 0.0125$ M).

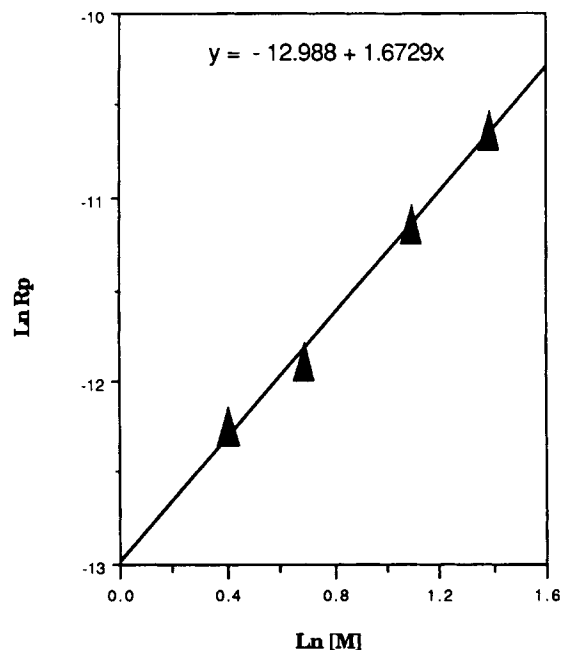


Figure 7 Determination of monomer concentration exponent.

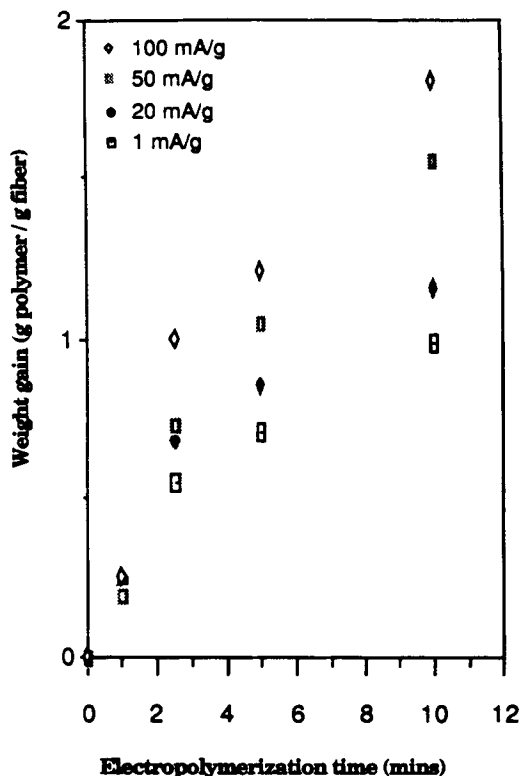


Figure 8 Weight gain of fibers as a function of time for: 1 mA/g, 20 mA/g, 50 mA/g, and 100 mA/g ($[M] = 2 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.0125 \text{ M}$).

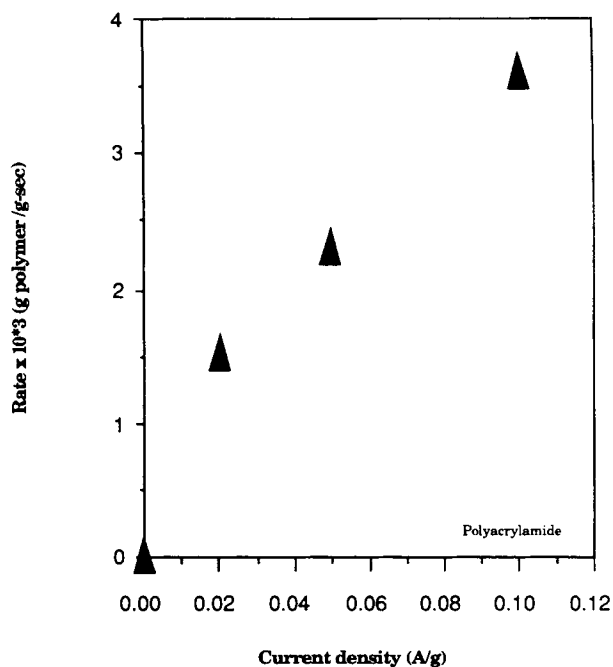


Figure 9 Dependence of electropolymerization of acrylamide on the current density ($[M] = 2 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.0125 \text{ M}$).

porting electrolyte concentration (0.0125 M). However, the number average molecular weight and the number average degree of polymerization decreased from 430,000 and 6000 to 193,000 and 2700, respectively, when the current density was raised from 1 mA/g to 100 mA/g. This means that as the current density increases, the molecular weight decreases. For this system, moderate to low current densities of about 1–10 mA/g are recommended if a number average molecular weight $> 100,000$ is desired. The current exponent was measured from the slope of the LnRp vs. $\text{Ln}(\text{Current density, Cd})$ curve (Fig. 10), and a value of 0.54 was obtained ($\text{Rp} \propto \text{Cd}^{0.54}$).

Effect of Sulfuric Acid Concentration on the Rate of Electropolymerization

The effects of supporting electrolyte concentration on the rate of electropolymerization at constant monomer concentration (2 M) and current density (20 mA/g of fiber), are shown on Figures 11 and 12. The rate of electropolymerization remained relatively unchanged for sulfuric acid concentrations of 0.01 M, 0.025 M, 0.05 M, and 0.25 M respectively, but below 0.01 M the rate of electropolymerization dropped sharply. Sulfuric acid participates in aqueous electropolymerization by producing hydrogen ions H^+ via a dissociation reaction:

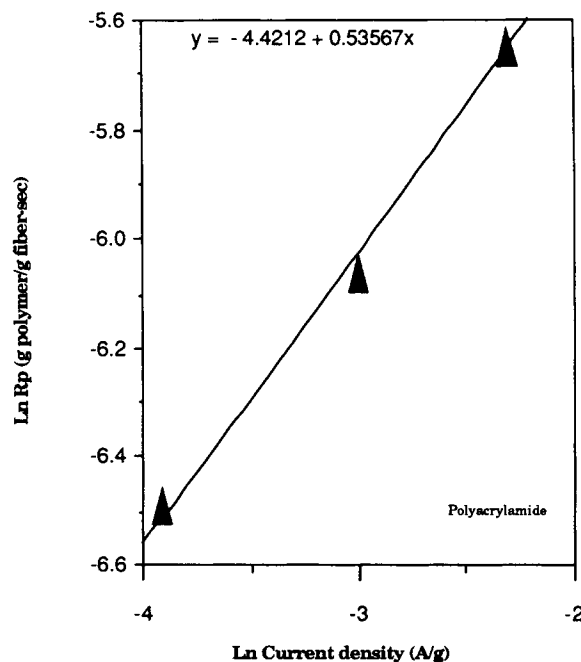


Figure 10 Current exponent determination for polyacrylamide.

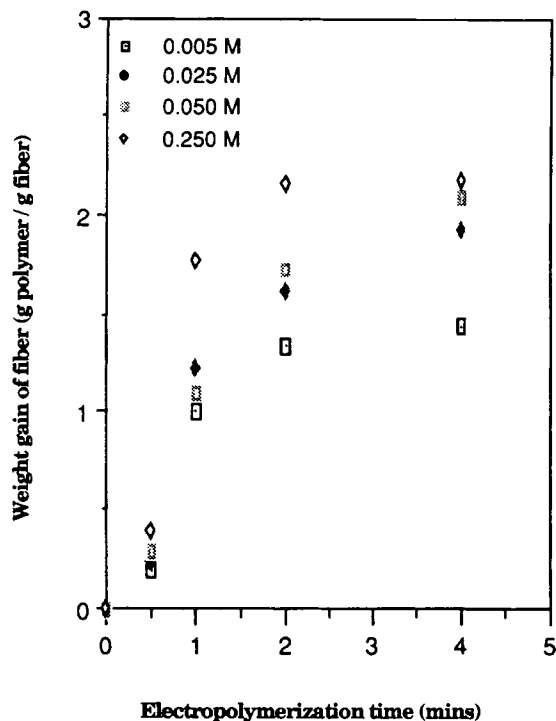
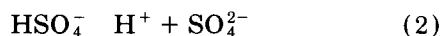


Figure 11 Weight gain of fibers as a function of time for: $[H_2SO_4] = 0.005\text{ M}, 0.025\text{ M}, 0.05\text{ M},$ and 0.25 M ($[M] = 2\text{ M}, Cd = 20\text{ mA/g}$).

Dissociation of Sulfuric Acid

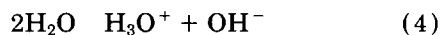


Hydrogen ions undergo a one electron reduction to produce hydrogen radicals



Hydrogen protons and hydroxonium ions are also produced by ionization of water.

Ionization of Water



The cyclic voltammograms of 0.025 M sulfuric acid solution (Fig. 13a) show a reduction peak of hydrogen ions at about -2.1 V vs. SCE (eq. 3). In a system containing distilled water, with tetrabutyl ammonium perchlorate (TBAP) as the carrier electrolyte, an oxidation peak associated with the oxidation of water occurred at about $+2.0\text{ V}$ vs. SCE (Fig. 13b).

A solution acrylamide (1 M) in sulfuric acid (0.025 M) showed a shift in the reduction peak of hydrogen ions to -2.5 V and a significant drop in the current passing through the system due to increased resistance of the cell (Fig. 13c). This effect is associated with the coating of the working electrode surface with polyacrylamide. Repeated cyclic voltammetric scans of acidified acrylamide solution (Fig. 13d) also show that the reduction peak height (current) decreased as the number of scans increased, consistent with the postulation of increased resistance of the cell as polyacrylamide is formed on the electrode surface. Figure 13e shows the cyclic voltammogram of acrylamide in a system containing carrier electrolyte TBAP dissolved in DMAc; no redox peak was observed, confirming that no electrochemical reaction similar to that when acid was present had occurred. Graphite fiber bundles were used as the working electrode in these experiments.

Overall Modelling of Electropolymerization

The rate of precipitation of electropolymerization R_p is related to the monomer concentration $[M]$, current density Cd , and sulfuric acid concentration $[HX]$, as follows;

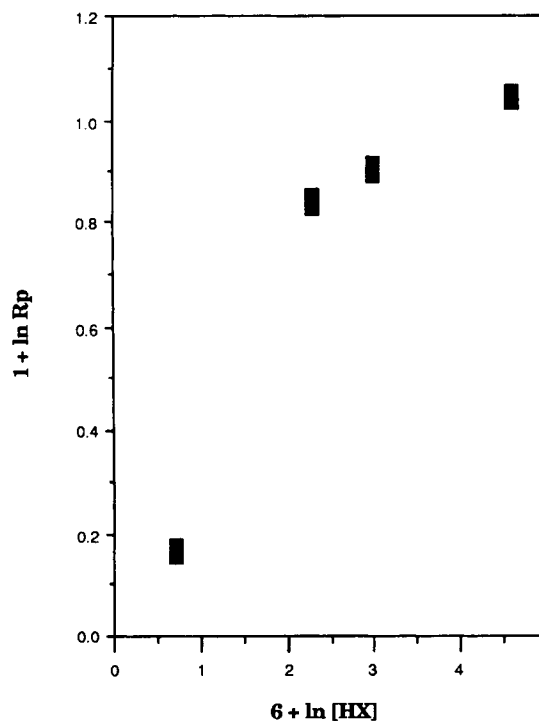


Figure 12 Determination of sulfuric acid concentration exponent.

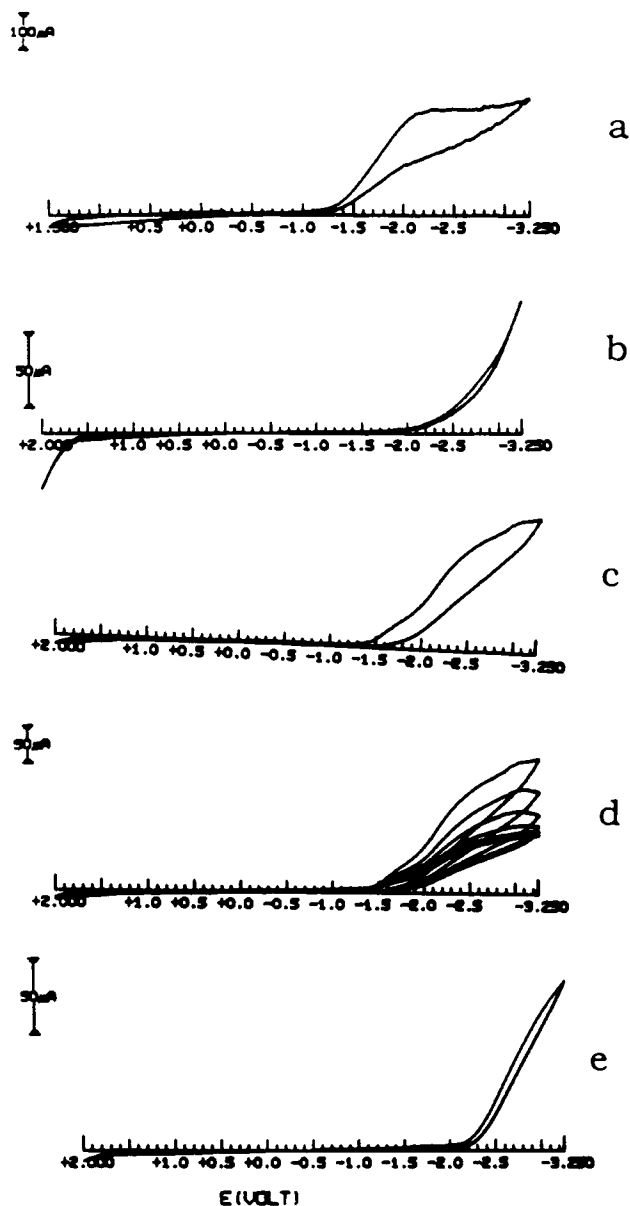


Figure 13 Cyclic voltammograms vs. SCE of: (a) 0.025 M sulfuric acid solution, (b) 0.3M TBAP in water, (c) 1.0 M acrylamide in 0.025 M sulfuric acid solution, (d) Repeated scans of c, (e) 1.0 M acrylamide solution in DMAc and 0.3M TBAP.

$$R_p \propto [M]^a [Cd]^b [HX]^c \quad (6)$$

$a = 1.67, b = 0.54, c = 0.025$ (experimental data).

$$R_p \propto [M]^{1.67} [Cd]^{0.54} [HX]^{0.02} \quad (7)$$

Let proportionality constant = $K \sim K_p (fki/kt)^{0.54}$

$$R_p = K_p [M]^{1.67} (fki Cd/kt)^{0.54} \quad (8)$$

where K_p , K_i and K_t are the rate constants for propagation, initiation, and termination respectively and f is the efficiency of initiation of polymerization.

In previous free radical polymerization work, Tai, Caskey, and Allison reported a 2.16 dependence of the rate of acrylamide polymerization on the monomer concentration.¹⁹ Also Kishore and Bhanu¹⁵ reported a value of 2. Others^{12-14,16-18,20-24} have obtained values ranging from 1 to 2. Further discussion of the meaning of these exponents will be given below.

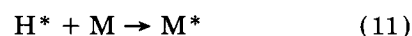
Anodic Reactions

Hydroxyl ions resulting from the ionization of water are anodically oxidized into water and oxygen as shown in eq. (9).



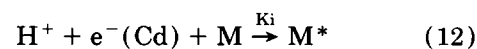
Cathodic Reaction

The reduction of hydrogen ions into neutral radicals takes place on the surface of the graphite fiber working electrode, which is placed in the monomer chamber containing dilute sulfuric acid (0.01 M), and acrylamide monomer (1–4 M) and serves as the cathode. The hydrogen ions produced react with the monomer to produce monomer radicals which grow into macroradicals (M^*) by further reacting with neutral monomers (eqs. 10–13).



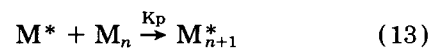
Eqs. (10) and (11) can be combined to give eq. (12).

Initiation



We will neglect the very small acid concentration dependence (0.02 exponent) since the flow of current (Cd) will force the formation of some sort of radical. We will consider the monomer concentration as having an effect on f , the fraction of radicals effectively initiating chains, rather than treating monomer concentration as a separate independent variable in initiation.

Propagation



Eqs. (14) and (15) show the rates of initiation and

propagation derived from eqs. (12) and (13) respectively, with the above assumptions:

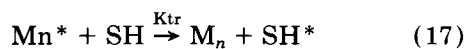
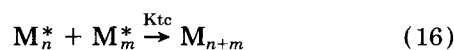
$$R_i = K_i f C_d \quad (14)$$

$$R_p = K_p [M^*][M] \quad (15)$$

where R_i and R_p are the rates of initiation and propagation, and K_i and K_p are the rate constants for initiation and propagation respectively. C_d is the current density. The number of radicals produced on the surface of the working electrode is directly proportional to the C_d , f is the efficiency of electroinitiation (the fraction of the radicals generated which actually initiate chains), and $[M]$ is the molar concentration of the monomer.

Termination Reactions

Termination of the electropolymerization takes place by combination (eq. 16), chain transfer to solvent (eq. 17) or by interaction with primary radicals (eq. 18).



Where SH represents solvent (water in this case). Chain transfer to monomer is presumed to be low because of the much lower monomer concentration. The rate of termination for the different modes of termination can be derived from eqs. (16-18) as follows:

$$R_{tc} = 2K_{tc}[M^*]^2 \quad (19)$$

$$R_{tr} = K_{tr}[M^*] ([SH] \gg [M^*]) \quad (20)$$

$$R_{tp} = K_{tp}[Mn^*] ([H^*] \gg [Mn^*]) \quad (21)$$

To simplify these equations we assumed that the solvent concentration is very high and therefore remains constant during the reaction. Also the concentration of growing chains $[Mn^*]$, relative to hydrogen radical concentration $[H^*]$, is assumed to be very small, so that $[H^*]$ can be assumed constant.

R_{tc} , R_{tr} , and R_{th} are the rates of termination by combination, chain transfer to solvent, and by primary radicals. K_{tc} , K_{tr} , and K_{tp} are the apparent rate constants, containing the effects of $[SH]$ and $[H^*]$ for termination by combination, chain transfer to solvent, and by primary radicals.

The rate of electropolymerization for termination

by combination and by chain transfer can be derived from eqs. (15, 19-21) and by making the steady-state assumption ($R_i = R_t$) such that $[M^*] = ([K_i f C_d]/2K_{tc})^{0.5}$, from eqs. (14) and (19), and also $[M^*] = K_i f C_d$ from eqs. (17) and (21) as follows:

$$R_i = R_{tc}; [M^*] = \{(K_i/2K_{tc}) f C_d\}^{0.5} \quad (22)$$

$$\text{Also } R_i = R_{tr}; [M^*] = (K_i/K_{tr})(f C_d) \quad (23)$$

$$R_i = R_{tp}; [M^*] = (K_i/K_{tp})(f C_d) \quad (24)$$

Next, substituting the values for $[M^*]$ into the propagation rate equation $R_p = K_p[M][M^*]$, we find:

$$\text{Coupling } R_p = K_p[M]\{(f K_i C_d)/K_{tc}\}^{0.5} \quad (25)$$

Transfer termination

$$R_p = K_p[M](f K_i C_d)/K_{tp} \quad (26)$$

Primary radical termination

$$R_p = K_p[M](f K_i C_d)/K_{tp} \quad (27)$$

Note that f may be dependent upon both C_d and $[M]$, and that K_i is not a true rate constant, but rather more a conversion factor for the units of C_d .

One can obtain an estimate of the magnitude of f by use of the polymer molecular weight data presented earlier. We would guess that the highest current efficiency would be found at low current density where recombination of H^* to form $H_2(g)$ is minimized. For example at a C_d of 1 mA/gm, and since a coulomb is one A/sec, we have;

$$\{(0.001 \text{ coulombs/sec})/(96,500 \text{ coulombs/equiv})\} \\ \times \{430,000 \text{ g/equiv}\} = 4.46 \times 10^{-3} \text{ g/sec}$$

That is, one milliamper/g at $f = 1.0$ should produce 4.46×10^{-3} g polymer/g fiber. The experimentally observed amount is 1.23×10^{-3} g/g \times sec, giving an estimated value for f of $(1.23/4.46) = 0.27$, which seems reasonable.

At much higher C_d , say 100 mA/g of fiber, we know that hydrogen bubbles are formed and we would expect the process to be much less efficient. A calculation like that above gives $f = 0.018$, or a fifteen-fold change in f for an 100-fold change in C_d . If we plot $\ln f$ as a function of $\ln C_d$ we find a slope of 0.6, or $f \propto 1/(C_d)^{0.6}$. Substituting this into eq. (25) for coupling,

$$R_p = K_p[M]\{(f_0 K_i C_d)/C_d^{0.6}\}^{0.5}$$

$$\text{or } R_p \propto C_d^{0.2}. f_0 \text{ is independent of } C_d \left(f = \frac{f_0}{C_D^{0.6}} \right).$$

Using eqs. (26) or (27) for transfer or primary radical termination, $R_p \propto C_d^{0.4}$, which is close to the 0.54 actually observed, leads to the deduction that termination by transfer or by primary radicals is more probable. Similar experiments using poly(N,N'-dimethylacrylamide) give an experimental exponent for Cd of 0.4. These results will be discussed in a later article.

One also expects that monomer concentration should have an effect on f, since polymerization is initiated near the fiber surface and diffusion of monomer to the surface is important. The effect of an f dependence on monomer concentration will be to raise the experimental exponent for M in eq. (8) above the theoretical value of 1.0 in eq. (25-27). An experimental value for the exponent of 1.67 was observed. The effect of M would be expected to be greater when polymerization is rapid, as with polyacrylamide. In another system, we are investigating (poly(3-carboxyphenyl) maleimide-co-styrene), which polymerized more slowly, and the exponent for M is close to one.²⁷ Other factors could influence the exponent, as in free radical solution polymerization.

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