Mechanism of the Electrocopolymerization of Styrene and *N*-(3-carboxyphenyl)maleimide onto Graphite Fibers in Aqueous Solution

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SYNOPSIS

Electrochemical copolymerization of styrene and *N*-(3-carboxyphenyl)maleimide was performed in an aqueous sulfuric acid solution using AS-4 graphite fibers as the working electrode. Cyclic voltammetric analysis results suggest radical initiation of polymerization via the reduction of the *N*-(3-carboxyphenyl)maleimide and sulfuric acid. Radical chain electrocopolymerization was strongly suggested by the inhibition of chain growth in the presence of hydroquinone and 2,2-diphenylpicrylhydrazyl (DPPH). Compositional analysis of copolymers and reactivity ratios $r_s \sim 0.014$ and $r_m \sim 0.041$ for styrene and *N*-(3-carboxyphenyl)maleimide [*N*-(3-CMI)], respectively, confirmed a 1 : 1 alternating electrocopolymerization. Kinetic analysis shows a first- and 1/2-order dependence of the rate of chain growth on initial monomer concentration and initiator concentration, respectively. A model incorporating these data is presented. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Copolymerization of maleimide and *N*-substituted maleimides with electron-donor monomers, such as styrene, has been shown to yield 1 : 1 alternating copolymers.[1-7] The formation of the 1 : 1 alternating copolymer has been shown to be due to the formation of charge transfer complexes between the electron-acceptor monomer (maleimide or *N*-substituted maleimide) and an electron-donor monomer such as styrene.[1-8] Radical copolymerization of maleimides and styrene has been reported by various authors.[9-18] Florjanczyk and Krawiec performed radical copolymerization of *N*-phenylmaleimide and styrene in toluene at 60°C and obtained a 1 : 1 alternating copolymer. Reactivity ratios of $r_s \sim 0.006$ and $r_m \sim 0.161$ for styrene and *N*-phenylmaleimide, respectively, were calculated.[12] These values are in the range expected for monomers that yield alternating copolymers. Radical copolymerization of *N*-phenylmaleimide and styrene in benzene using AIBN as the initiator was reported to result in a nearly alternating copolymer.[13] Dean also prepared a 1 : 1 alternating copolymer of maleimide and styrene in DMAc using AIBN initiator.[19] Monomers other than electron-donating monomers have also been known to copolymerize with maleimides.[20-27] Elsabee et al. studied the effect of different solvents on the polymerization of maleimides. They reported that the rate of polymerization increased in chloroform, acetonitrile and tetrahydrofuran (THF). They attributed their findings to the ability of these solvents to interact with the π-electrons of the maleimide double bond.[28-30] They further postulated that the overall rate of polymerization increases with increasing ability of the solvents to associate with the maleimides.

Several investigators have studied the electrochemical behavior of maleimide and *N*-phenylmaleimide.[31-34] Barradas et al. showed that electrochemical reduction of maleimide yields monomeric succinimide.[31] They postulated that radical ions are key intermediates in the reduction process. *N*-phenylmaleimide is reported to be reduced polarographically in acid and alkaline solutions to form a dimer and succinamic acid, respectively.[34]

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In a recent publication,[35,36] we showed that the electropolymerization of *N*-(3-carboxyphenyl)-maleimide and styrene onto Hercules AS-4 graphite fibers can be successfully carried out from an aqueous solution containing monomers and dilute sulfuric acid. This is the first successful case of a thermoplastic polymer being made *in situ* directly onto graphite fibers in sufficient quantity to produce polymer impregnated graphite fibers that can be processed directly into a composite. Additional studies have now been carried out to develop an insight as to the mechanism of the electropolymerization process.

EXPERIMENTAL

Materials

High-purity *N*-(3-carboxyphenyl)maleimide [*N*-(3-CMI)] from Mitsui Toatsu Chemical Co. of Japan was recrystallized in ethanol and dried at 100°C under vacuum before electropolymerization. Styrene (99.9%) from Aldrich Chemicals was extracted twice in 10% NaOH solution and washed several times in distilled water to remove inhibitors. A 0.025 *M* sulfuric acid solution in distilled water was the supporting electrolyte. Unsized AS-4 graphite fibers (3000 filament tow) from Hercules and stainless-steel sheets were the working and counterelectrodes used.

Instrumentation

A Princeton Applied Research potentiostat Model 363 was used as the source of constant direct current. By placing the potentiostat in the current control mode, a predetermined flow of electric current was applied through the electrodes. A Hewlett-Packard digital multimeter Model 3438 A was used to monitor the applied current and the cell voltage (Fig. 1). The changes in voltage across the working electrode due to electropolymerization were monitored using a standard calomel reference electrode (SCE).

Electrochemical Cell

A 250 mL three-compartment electrochemical cell[35,36] made of polypropylene was used. The middle chamber, which contains the monomers, sulfuric acid, and graphite fiber working electrode, was separated from the counterelectrode chambers by a 0.4 μm pore-size polypropylene membrane glued onto perforated polypropylene supports. The counterelectrode chambers each contain the sulfuric acid solution and a stainless-steel counterelectrode. Continuous AS-4 graphite fibers wound on H-shaped polypropylene frames were used as the working electrode. The numbers of fiber bundle layers wound on the frames varied between one and two. The graphite fibers were wetted in the reaction mixture for 2 min before electrocopolymerization. The cell was activated by passing electric current through a

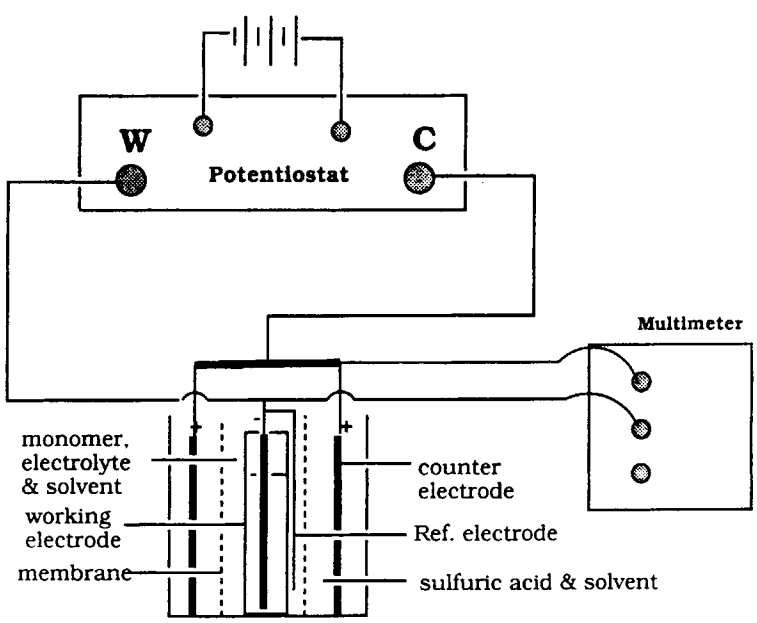

Figure 1 Equipment for batch electropolymerization.

dummy working electrode (stainless-steel plate). The dummy working electrode was withdrawn from the cell and was replaced with the graphite fiber working electrode after 2 min of preelectrolysis.

Electrocopolymerization was started by the passage of current. Copolymer coatings simultaneously polymerized and deposited onto the fiber surfaces. The amount of polymer formed was estimated from the difference between the weight of the coated and that of the uncoated fibers.

Cyclic Voltammetry

The electrochemical activity of the monomers, solvent, and electrolyte was monitored by a cyclic voltammogram (CV). Electroactive species were oxidized and/or reduced during cyclic voltammetric analysis. The presence or absence of reduction and or oxidation peaks is crucial in understanding the mechanism of initiation of electropolymerization. A potential sweep with reversals was applied on a stationary glass carbon electrode and the cell current was recorded as a function of the applied potential on an X-Y recorder. Graphite fiber bundles were also used as the working electrode.

N-(3-CMI) is soluble only in polar solvents such as DMAc, DMF, and DMSO. The CV of the solvents and supporting electrolyte were first measured to determine their electrochemical reactivity. This was followed by the CV of the monomer solution in dilute sulfuric acid solution and tetrabutylammonium perchlorate-N,N'-dimethylacetamide (TBAP-DMAc) solution, respectively. A platinum electrode and saturated calomel electrode (SCE) were also used as the counter- and reference electrodes, respectively. Potential sweep with reversal between −3.0 and +1.0 V was applied at cathodic sweep rates of 100–250 mV/s.

Poly(N-(3-carboxyphenyl)maleimide-*co*-styrene)

A 0.5M solution of N-(3-CMI) was prepared by dissolving about 60 g of the monomer in a 500 mL Erlenmeyer flask using DMAc as the solvent. A 29 mL portion of bulk styrene previously extracted in 10% sodium hydroxide solution and washed in distilled water was dissolved in DMAc. The resulting solution was diluted to 0.5M in a 500 mL flask. A 0.025M solution of sulfuric acid in distilled water was prepared. The monomer–electrolyte–solvent solution was assembled by mixing N-(3-CMI) (0.5M), styrene (0.5M), DMAc, and sulfuric acid (0.025M) in the following volume ratio: 50 : 50 : 20 : 100, respectively. It was introduced into the middle compartment of the electrochemical cell. Sulfuric acid (0.0125M) : DMAc (10 : 1) was placed in the counterelectrode chamber. The electrodes were connected to the potentiostat and electropolymerization was typically performed for 30 min at a constant current density of 20 mA/g of fibers. The resulting copolymer coatings were removed for analysis. The effect of reaction conditions such as the initial monomer concentration, current density, comonomer feed ratio, and electrocopolymerization time of hydroquinone (inhibitor) and 2,2-diphenylpicrylhydrazyl (scavenger) on the rate of electrocopolymerization was determined by varying the selected reaction parameter while keeping the others constant.

The variation of voltage across the cathodic chamber during electrocopolymerization was monitored by SCE reference electrode connected to the graphite fiber working electrode.

Elemental Analysis

Quantitative microanalysis was performed on copolymer samples to determine the percentage of nitrogen, oxygen, hydrogen, and carbon present. These data were used to calculate the copolymer composition. Elemental analysis of the coatings was performed by Galbraith Laboratories. Samples of 1–3 mg were used. The samples were dried to constant weight at 250°C under vacuum and sealed in 10 mL vials before analysis.

Effect of Hydroquinone on Electrocopolymerization

Electrocopolymerization of N-(3-CMI) and styrene in the presence of hydroquinone was performed to determine the extent of radical participation. The reaction was done in the 250 mL three-compartment polypropylene cell. About 50 mL of 0.5M styrene solution, 50 mL of 0.5M N-(3-CMI) solution, 6.5 g hydroquinone, 20 mL DMAc, and 100 mL 0.025M sulfuric acid solution were mixed together and placed in the monomer chamber. Graphite fibers of ~ 1 g wound on the polypropylene frame, ~ 9.5 × 5.5 cm, were positioned in the center of the chamber and connected to the negative terminal of the potentiostat by alligator clips.

Electropolymerization was performed at a current density of 10 mA/g of fibers for 0.5, 1.0, 2.0, and 4.0 min, respectively. At the end of each run, the coated fibers were withdrawn from the cell, rinsed with distilled water, dried, and weighed. The above procedure was repeated with 10 g of hydroquinone. A control experiment was also carried out without hydroquinone.

Effect of 2,2-Diphenylpicrylhydrazyl (DPPH) on Electrocopolymerization

Diphenylpicrylhydrazyl (DPPH) is a radical scavenger. To supplement the information derived from the hydroquinone experiments, DPPH (0.073 g) was dissolved in a monomer–electrolyte solvent solution composed of 50 mL of 0.5*M* solution of *N*-(3-CMI), 50 mL 0.5*M* styrene solution, 20 mL of DMAc, and 100 mL of 0.025*M* sulfuric acid solution. The resulting solution was placed in the working electrode chamber. A graphite fiber cathode was placed in the center of the chamber and connected to the potentiostat, as described previously. Sulfuric acid solution (200 mL of 0.0125*M*) was placed into each of the anodic chambers equipped with a stainless-steel anode. Inert nitrogen gas was bubbled into the solutions to expel dissolved oxygen. The counterelectrodes were connected to the positive terminal of the potentiostat.

Electropolymerization was carried out for 0.5, 1.0, 2.0, and 4.0 min, respectively, using a current density of ~ 10 mA/g of fibers, a monomer concentration of ~ 0.5*M*, and a sulfuric acid solution of ~ 0.0125*M*. A control electrocopolymerization of *N*-(3-CMI) and styrene was performed using similar conditions except that no DPPH was used.

RESULTS AND DISCUSSION

Cyclic Voltammetry (CV)

The cyclic voltammetry (CV) curve of 0.025*M* aqueous sulfuric acid solution using a graphite fiber working electrode is shown on Figure 2(a). Reduction of hydrogen ions associated with the reaction

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

occurred at about −2.1 V against an SCE reference. Replacement of the graphite fiber electrode by a glassy carbon working electrode, in a 1 : 1 aqueous sulfuric acid/DMAc solution, resulted in a shift from −1.5 V vs. SCE to about −2.7 V vs. SCE [Fig. 2(b)]. The CV of styrene is shown in Figure 3(a). An anodic peak associated with the oxidation of the monomer occurred at +0.5 V:

$$M_{\text{styrene}} - e^- \rightarrow \cdot M^+_{\text{styrene}} \qquad (1)$$

Reduction of styrene takes place at about −3.4 V vs. SCE, which is outside the range of voltage covered in this experiment. The CV of a system comprising styrene, sulfuric acid solution, (0.025*M*) and TBAP (0.29*M*) showed a reduction peak at −2.2 V

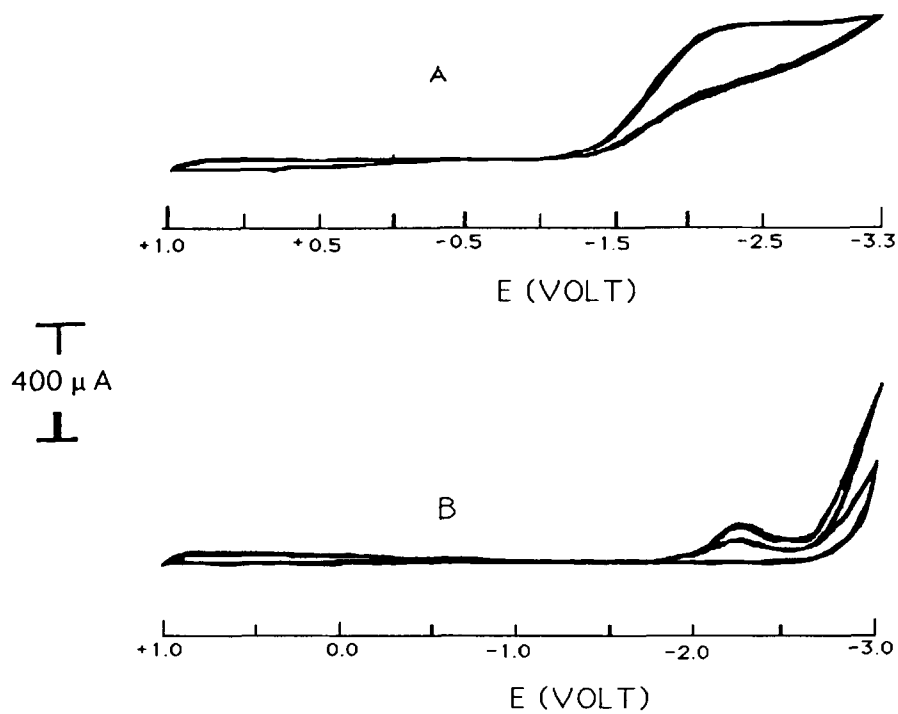

Figure 2 Cyclic voltammograms vs. SCE: (A) 0.025*M* [H_2SO_4] in distilled water (graphite fiber bundle was the working electrode, scan rate = 250 mV/s); (B) 0.025*M* [H_2SO_4] (aq), DMAc: H_2O (1 : 1), 0.29*M* tetraethylammonium perchlorate (TEAP).

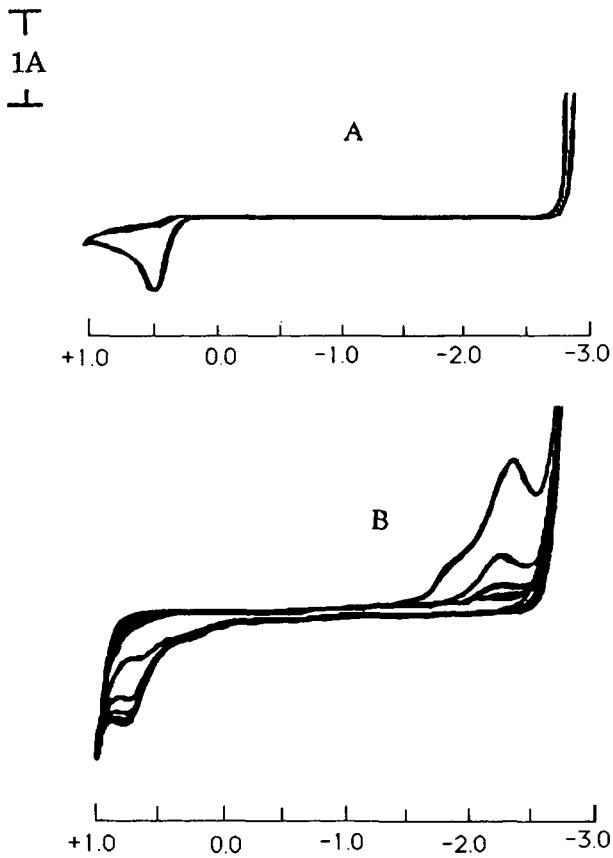

Figure 3 Cyclic voltammograms vs. SCE for (A) 0.5*M* styrene, 0.29*M* TEAP in DMAc and (B) 0.5*M* styrene in DMAc: 0.025*M* H_2SO_4 (1 : 1), using glassy carbon electrode.

and an oxidation peak at +0.8 V [Fig. 3(b)]. These peaks are associated with the reduction of hydrogen ions and the oxidation of styrene monomer, respectively. The oxidation of monomeric styrene was slightly shifted to a more positive potential, probably because of the presence of other species. The height of the redox peaks (relative to that of the first cyclic voltammograph) after subsequent repeated scans indicates how resistive the cell had become as a result of the covering of the electrode surface by insulating organic polymers from the diffusion of the reactants onto the electrode surfaces and consequent electrocopolymerization.

Maleimides are very highly electroactive, showing a distinctive reduction peak. Figure 4 shows the cyclic voltammogram of 0.1*M* *N*-(3-CMI) in DMAc. Only one reduction peak is present at −1.5 V (scan rate of 250 mV/s). A CV scan of freshly prepared *N*-(3-CMI) in DMAc and 0.0125*M* sulfuric acid solution using a glassy carbon working electrode, at a scan rate of 250 mV/s, showed two cathodic peaks, at −1.4 and −2.3 V vs. SCE, respectively.[35,36] The reduction peak height (current) for the reaction (reduction peak at −1.4 V):

$$M_{(3\text{-CMI})} + e^- \rightarrow \cdot M^-_{(3\text{-CMI})} \qquad (2)$$

was of the same magnitude as the peak height corresponding to the reduction of hydrogen ions (reduction peak at −2.3 V):

$$H^+ + e^- \rightarrow \mathrm{H}\cdot$$

The CV (at 250 mV/s) of a typical reaction solution containing 0.5*M* *N*-(3-CMI) in DMAc (50 parts), 0.5*M* styrene in DMAc (50 parts), 0.025*M* sulfuric acid solution in distilled water (100 parts), and DMAc (20 parts) showed two reduction peaks at −1.3 and −2.3 V vs. SCE. No strong oxidative peaks were present.[44] The reduction of hydrogen ions is the predominant reaction at V > −2.3 V (as the voltage gradually rises, long reaction times may favor generation of hydrogen radicals) while the reduction of the *N*-(3-CMI) complex predominates at lower potentials (V < −2.1 V) and short electropolymerization times (t < 45 min).

The variation of weight gain of fibers resulting from electropolymerization as a function of cathodic potential is shown in Figure 5. No significant amount of copolymer coating was formed below −1.4 V, suggesting a threshold voltage below which no polymer is formed. This critical voltage is related to the reduction peak potential for the *N*-(3-CMI)-styrene complex.

Elemental Analysis

The results of microanalysis of copolymer samples containing about 0–100% *N*-(3-CMI) are shown in

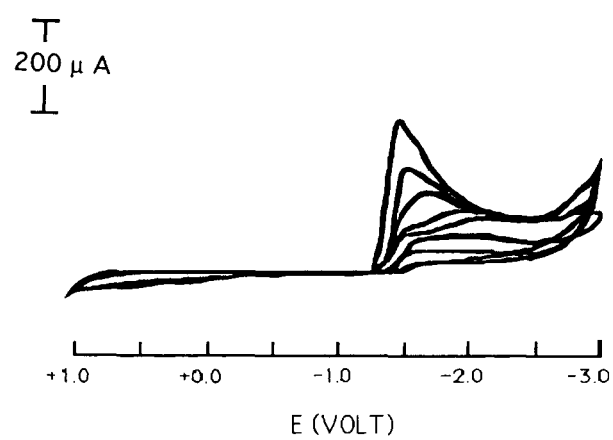

Figure 4 Cyclic voltammogram vs. SCE for *N*-(3-CMI) (0.5*M*) and TEAP (0.29*M*) in DMAc.

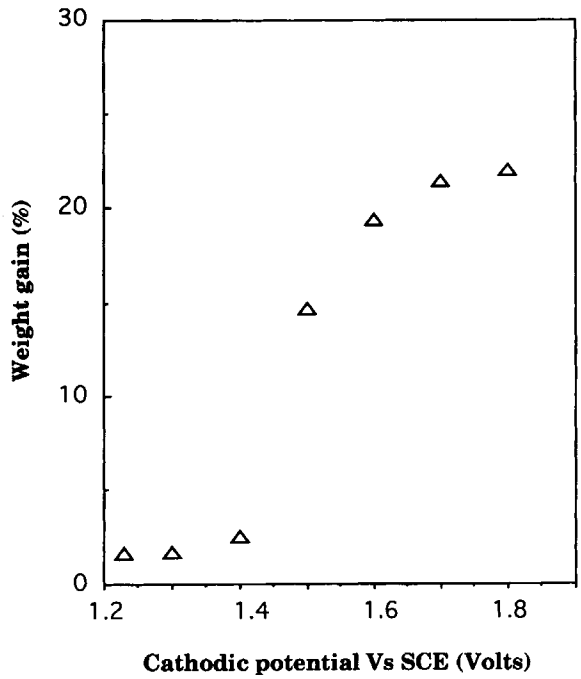

Figure 5 Variation of weight gain of fibers as a function of cathodic potential (vs. SCE).

Figure 6. A plot of the copolymer composition derived from elemental analysis as a function of mol fraction of *N*-(3-CMI) in the feed (Fig. 6) shows that a copolymer containing 50 mol % of *N*-(3-CMI) is always found even though the mol fraction of *N*-(3-CMI) in the feed varied from 20 to 80%. The constancy of the copolymer composition for samples electropolymerized from different comonomer feed compositions suggests a very strong tendency toward 1 : 1 alternation for the system, in agreement with previous findings[13,14,17] on bulk copolymerization of *N*-phenylmaleimide and its derivatives with electron-donor monomers, such as styrene. Residual DMAc or sulfuric acid in the samples analyzed could increase the N, C, and H contents above the values for the copolymer alone. The error in the analysis resulting from the presence of entrapped solvents was minimized by drying the samples to constant weight at 250°C under vacuum. Five hours was sufficient for this purpose. The mol percent of *N*-(3-CMI) in the polymer was calculated from the percent of nitrogen in the samples as follows:

$$\text{Mol \% } N-(3-\text{CMI}) = \{(\%\ N_{\text{exp}})/(\%\ N_{\text{calc}})\}50\% \quad (3)$$

where % N_{exp} and % N_{calc} represent the amount of nitrogen obtained experimentally (determined by elemental analysis) and that from theoretical calculation, respectively. Approximately 50 mol % of *N*-(3-CMI) was found to be present in all the copolymers synthesized from 20 to 80 mol % of the monomer in the feed, in agreement with the previously reported FTIR compositional analysis of the copolymers.[35,36]

A modified Fineman–Ross equation[37,38]:

$$F(1-f) = -r_2 + r_1(F^2 f) \quad (4)$$

(where F is the mol fraction of the comonomer in the feed, f is the corresponding mol fraction of the polymer in the copolymer, and r_1 and r_2 are the reactivity ratios of monomers 1 and 2, respectively) was also used to determine the reactivity ratios (Fig. 7). Reactivity ratio values of −0.014 and 0.041 were obtained for styrene and *N*-(3-CMI), respectively.

Effect of Reaction Conditions on Electrocopolymerization

Electrocopolymerization of *N*-(3-CMI) and styrene was studied as a function of current density (Cd), initial comonomer concentration (M), electrocopolymerization time (t), and comonomer feed composition (feed). Reaction conditions are given in the Experimental section.

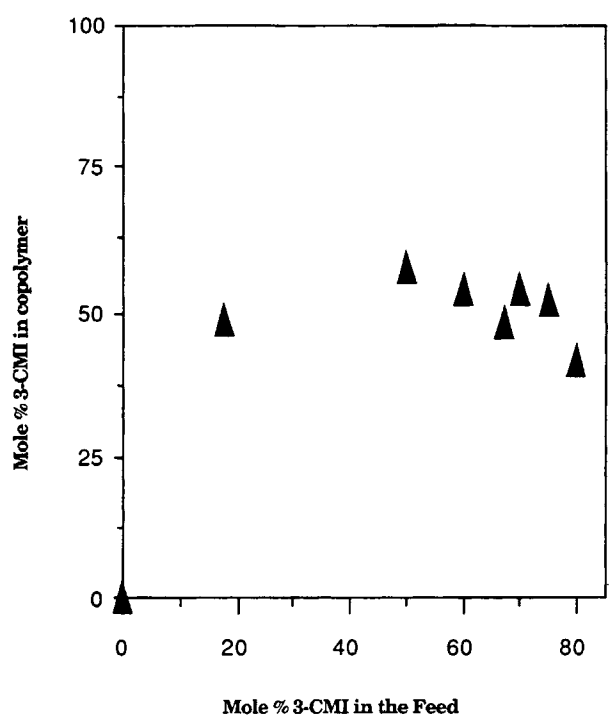

Figure 6 Copolymer composition calculated from microanalysis.

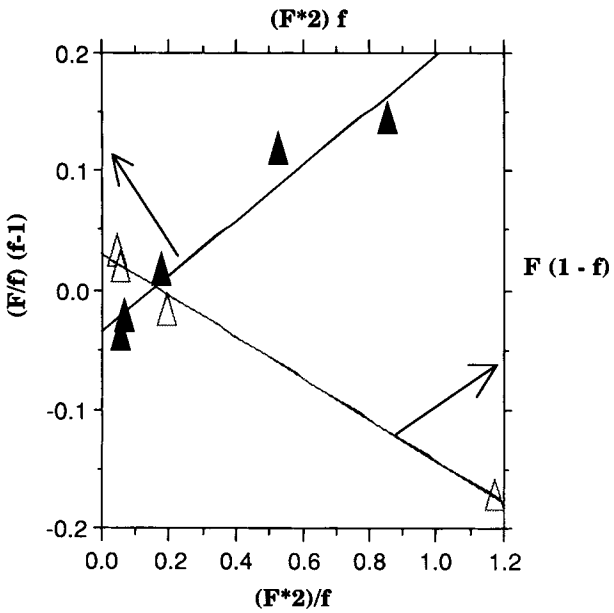

Figure 7 Determination of reactivity ratios by Fineman–Ross method.[37,38]

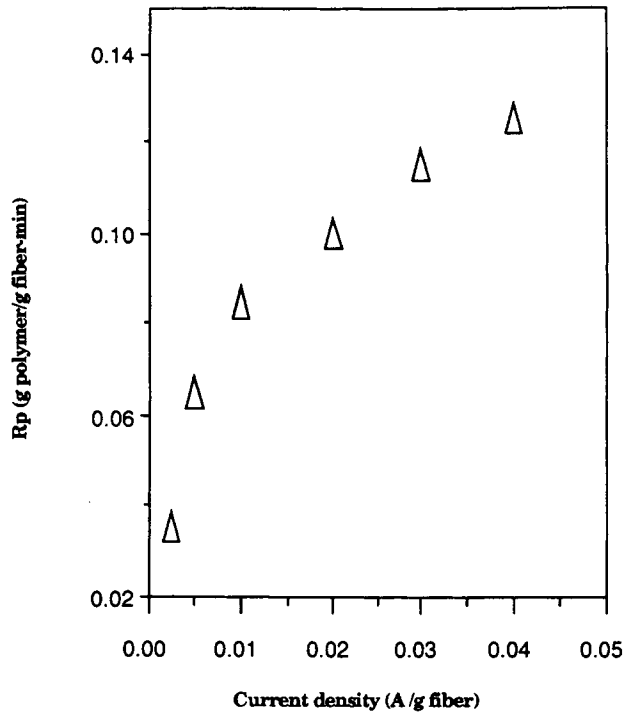

Figure 8 Effect of current density on the rate of electropolymerization (concentrations in the cell $[M] = 0.12M$, $[H_2SO_4] = 0.0125M$).

Current Density

The amount of copolymer coatings formed per unit electropolymerization time increased with increasing current density at a constant initial monomer concentration and sulfuric acid concentration.[35,36] The dependence of the rate of electrocopolymerization (Rp) of N-(3-CMI)/styrene on current density is shown in Figure 8. At a high current density, hydrogen is evolved and also the reaction becomes diffusion-limited. Data from current density < 0.03 A/g fiber were used for a plot of the natural log of the initial rate of electrocopolymerization against the natural log of the current density (Fig. 9), resulting in a slope of 0.5. This corresponds to the exponent on the initiator concentration in a standard free-radical polymerization. Here, initiation is caused by the current. A 0.50 order dependence of rate of polymerization on the initiator concentration is in the range of values found in classical radical chain polymerization. A model can be devised in which current density replaces initiator concentration, as will be discussed later.

Initial Monomer Concentration

The amount of copolymer formed during electrocopolymerization is strongly dependent on the initial monomer concentration.[35,36] At a constant current density of ~ 40 mA/g of fiber and sulfuric acid concentration of ~ $0.0125M$, more copolymer per unit

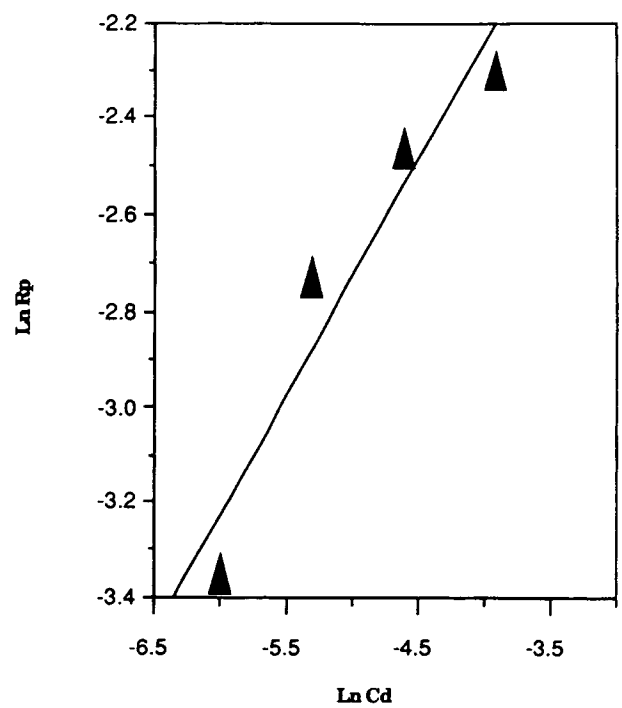

Figure 9 Current exponent determination ($[M] = 0.12M$).

weight of graphite fibers per unit time was deposited as the initial comonomer concentration increased. The relation between the rate of electrocopolymerization (Rp) and initial comonomer concentration (mol/L) is linear, as shown in Figure 10. The exponent on the monomer concentration in a model for this comonomer system can therefore be taken as 1.0.

Effect of Hydroquinone

Figure 11 shows the effect of small amounts of hydroquinone (HQH) on electrocopolymerization of styrene and N-(3-CMI). Incorporation of 6.5 g of hydroquinone (0.06 mol) into the reaction mixture reduced the amount of copolymer coatings formed per unit time on the graphite fiber surfaces by more than 50%. Comparison of reactions performed in the presence of 0.06 (6.5 g) and 0.09 (10 g) mol of hydroquinone with a control experiment without any radical inhibitor (Fig. 11, curves 2, 3, and 1, respectively) showed that while the latter proceeded predictably, the former were drastically retarded due to the termination of electrocopolymerization by abstraction of hydrogen from hydroquinone. A stable quinone radical (HQ·) is created in the process:

$$R\cdot + HQH \rightarrow R{-}H + HQ\cdot \qquad (5)$$

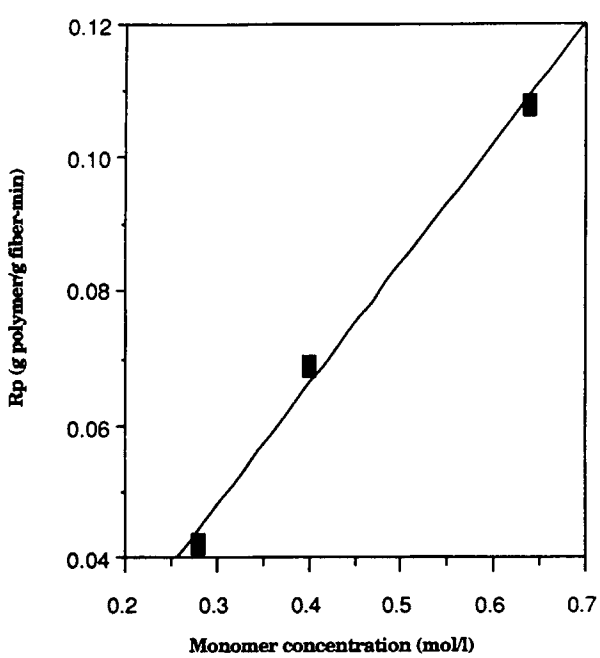

Figure 10 Effect of initial monomer concentration on the rate of electropolymerization (Cd = 0.02 A/g, $[H_2SO_4]$ = 0.0125M).

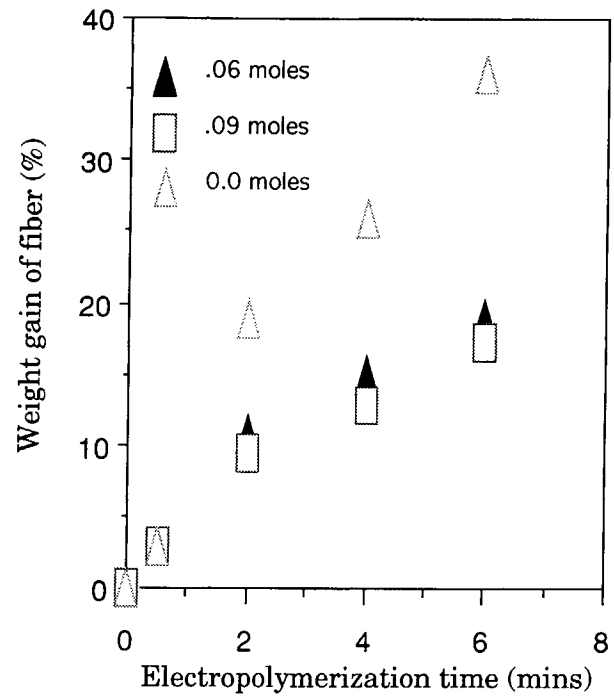

Figure 11 Effect of hydroquinone on electropolymerization.

The above equation describes the reaction of hydroquinine (HQH) with a chain radical (R·). Inhibition of polymerization occurs by abstraction of hydrogen from hydroquinone and results in the formation of a stable quinone radical and a neutral polymer (RH).

Effect of 2,2-Diphenylpicrylhydrazyl (DPPH) on the Rate

Figure 12 shows a plot of weight gain of fiber as a function of electrocopolymerization time for electrosynthesis done with and without DPPH. This experiment clearly shows that aqueous electrocopolymerization of poly[styrene-*co*-N-(3-CMI)] was effectively halted by the radical scavenger. A comparison of the electrosynthesis of N-(3-CMI)–styrene copolymers in the presence of DPPH with a parallel control experiment showed that the weight gain of fibers due to electropolymerization and the consequent rate of electrocopolymerization dropped by more than 300% in the presence of the radical scavenger. The effectiveness of DPPH in terminating radical chain reactions is well established. The inhibition of aqueous electrocopolymerization by hydroquinone and DPPH support a free-radical mechanism for the system.

The inhibition of electropolymerization by 2,2-

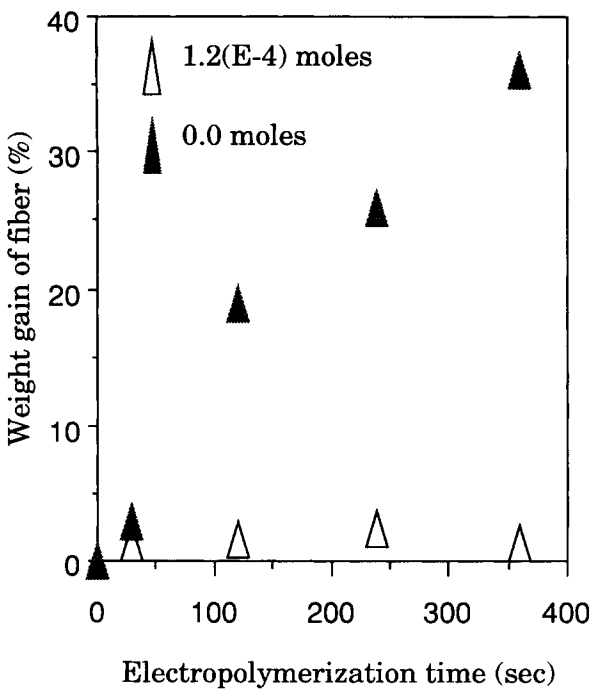

Figure 12 Effect of DPPH on electropolymerization in an unstirred solution (Cd = 0.02 A/g, $[M]$ = 0.1M).

diphenylpicrylhydrazyl (Ph_2—N—NH—R) is accomplished by the abstraction of the tertiary hydrogen. A polymer (M_n) and stable DPPH radical (Ph_2—N—N·—R) are the major products of this reaction:

$$M_n\cdot + Ph_2\text{—N—NH—}\mathbf{R} \rightarrow M_nH + \underset{\textbf{(stable radical)}}{P_2\text{—N—N}\cdot\text{—}\mathbf{R}} \quad (6)$$

Mechanism and Model

A simplified mechanism for aqueous electrocopolymerization is proposed to start with the association of the comonomers into a charge transfer complex [eq. (7)].[12,13,16] Formation of the intermediate charge transfer complex is supported by the chemical shift of the maleimide vinyl protons from δ = 3.33 to 3.38 (Fig. 13). A shift in the UV visible spectra for the comonomer in DMAc and the rapid release of heat on mixing the monomers also support the concept of charge transfer complex formation.

Complex Formation

$$M_{\text{styrene}} + M_{(3\text{-CMI})} \xrightarrow{kc} \underset{\textit{charge transfer complex}}{[M^{\delta+}_{\text{sty}} - M^{\delta-}_{(3\text{-CMI})}]^*} \quad (7)$$

The comonomer charge transfer complex interacts with electrons in the presence of protons or, alternatively, with a hydrogen radical to yield an initiating propagating comonomer radical species:

$$\{M^{\delta-}_{(3\text{-CMI})} - M^{\delta+}_{\text{sty}}\}^* + H\cdot \xrightarrow{ki} \{M_{\text{sty}} - M_{(3\text{-CMI})}\}\cdot \quad (8)$$

It is postulated that in the charge transfer complex formation electrons are donated by styrene to N-(3-CMI). This leaves styrene with a partial positive charge and N-(3-CMI) with a partial negative charge. The initiating radical would have a partial negative charge due to its electron acceptance nature and it would couple with the positive end of the charge transfer complex to initiate the chain. Since complex formation occurs immediately on mixing the styrene and N-(3-CMI) monomers, it is assumed to be present as a reactant comonomer pair before electropolymerization is initiated, and therefore its formation is not involved in the rate of polymerization.

The sequence of reactions leading to the formation of the copolymer can be represented as follows:

Initiation

Interaction of the charge transfer complex with an electron in the presence of a hydrogen proton results in the formation of a comonomer radical. This is the initiation step:

$$[M^{\delta+}_{\text{sty}} - M^{\delta-}_{(3\text{-CMI})}]^* + e^- \xrightarrow{ki} \{M_{\text{sty}} - M_{(3\text{-CMI})}\}\cdot \quad (9)$$

Propagation

Propagation occurs by the coupling of the charge transfer complex with the comonomer radical:

$$M^{\delta+}_{\text{sty}} - M^{\delta-}_{(3\text{-CMI})}{}^* + [M_{\text{sty}} - M_{(3\text{-CMI})}]_n\cdot \xrightarrow{kp} \{M_{(\text{sty})} - M_{(3\text{-CMI})}\}\cdot_{n+1} \quad (10)$$

Termination

If the macroradicals terminate by bimolecular combination,

$$\{M_{\text{sty}} - M_{(3\text{-CMI})}\}\cdot_m + \{M_{\text{sty}} - M_{(3\text{-CMI})}\cdot_n \xrightarrow{ktc} \{M_{\text{sty}} - M_{(3\text{-CMI})}\}_{m+n} \quad (11)$$

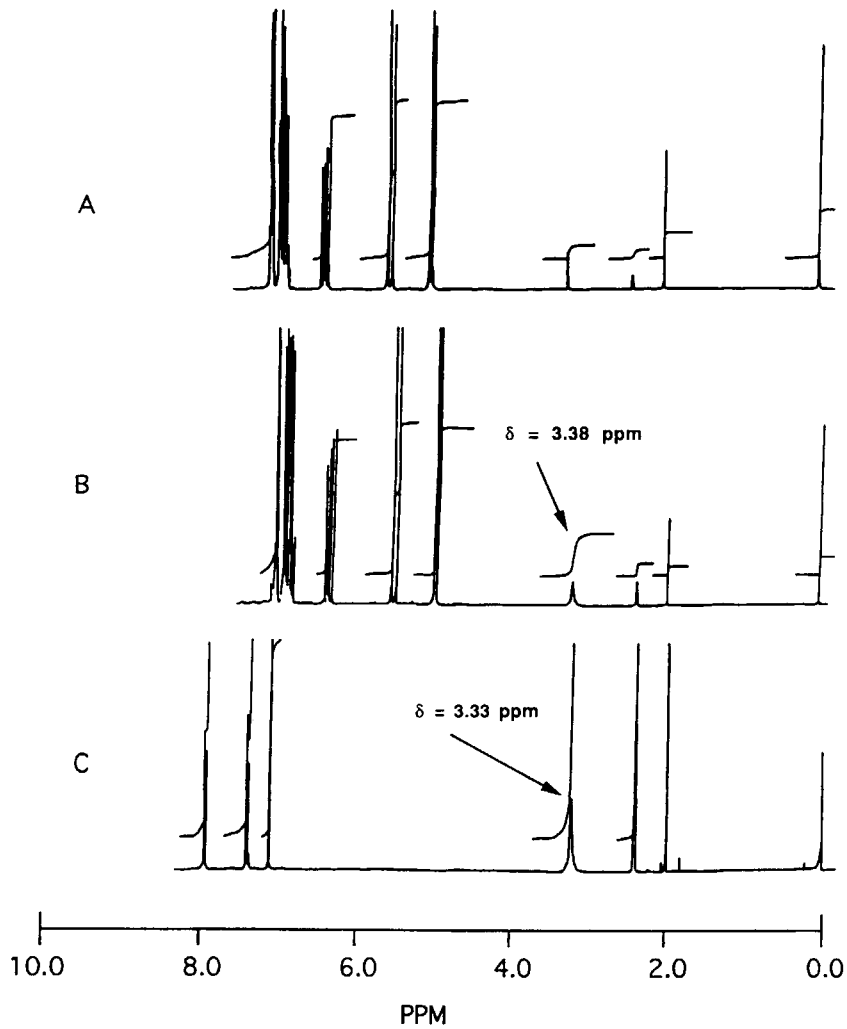

Figure 13 Proton NMR for (A) styrene and (B) styrene-*co*-*N*-(3-CMI) and *N*-(3-CMI).

Equation (11) may be rewritten for termination by transfer to the solvent (SH) [eq. (12)]:

$$\{M_{\text{sty}} - M_{(3\text{-CMI})}\}_n\cdot + \text{SH} \xrightarrow{k_{tr}} \{M_{\text{sty}} - M_{(3\text{-CMI})}\}_n + \text{SH}\cdot \quad (12)$$

and termination by primary radicals (H·) [eq. (13)]:

$$\{M_{\text{sty}} - M_{(3\text{-CMI})}\}_n\cdot + \text{H}\cdot \xrightarrow{k_{tp}} \{M_{\text{sty}} - M_{(3\text{-CMI})}\}_n \quad (13)$$

where K_{tc} is the rate constant for termination by combination; K_{tr}, the rate constant for termination transfer to solvent; and K_{tp}, the rate constant for termination by primary radicals.

Assuming a steady state where $Ri = Rt$, we can simply derive expressions for the rate of polymerization,[43] Rp, depending upon the mechanism of termination:

Coupling $$Rp = kp[M]\{(fki^*Cd)/ktc)^{0.5} \quad (14)$$

Transfer termination

$$Rp = kp[M](fki^*Cd)/ktc \quad (15)$$

Primary radical termination

$$Rp = kp[M](fki^*Cd)/ktc \quad (16)$$

where f is the fraction of radicals generated that actually initiate chains and $[M]$ is the monomer concentration, mol/L; Cd is the current density, in amperes/g fiber; ki^* is here considered as a constant

which, when multiplied by fCd, gives the rate of radical generation; and ki^* is proportional to the ki of standard free-radical polymerization, but because of the units of Cd, $ki^* = ki$.

The rate of polymerization is dependent on the current density Cd (Figs. 8 and 9), which is the equivalent of a constant initiator concentration in a standard free-radical-initiated polymerization. In the present studies, the rate of initiation Ri was found to follow a 0.5 order dependence on the current density.

The initiation efficiency f can be a function of $1/Cd$ and $[M]$. As the current density increases, hydrogen radicals more readily combine to form hydrogen gas and f decreases. Research on electropolymerization of acrylamide[35,36] and dimethylacrylamide[39] indicates $f = fo/(Cd^{0.6})$, where fo is a constant of proportionality, independent of Cd. Thus, for termination by coupling,

$$Rp = kp[M][foki^*(Cd/Cd^{0.6})]^{0.5}$$

giving $Rp\alpha Cd^{0.2}$.

Using eq. (12) or (13) for transfer or primary radical termination, one finds $Rp\alpha Cd^{0.4}$ much closer to the experimentally observed 0.5 for N-(3-CMI) and identical to the experimental exponent of 0.4 for poly(N-dimethylacrylamide). Although this is not conclusive proof, we believe that the weight of evidence to date supports termination of growing chains by primary radicals or chain transfer.

In the above kinetic analysis, it is assumed that the change in the voltage applied to the cell is smaller than the change required (as measured by cyclic voltammetry) to induce reduction reactions other than the reaction described. This was experimentally possible in our measurements.

CONCLUSION

Aqueous electrocopolymerization of N-(3-CMI) and styrene directly onto graphite fibers has been successfully performed in dilute sulfuric acid solution. Electropolymerization was inhibited in the presence of DPPH, suggesting a radical chain polymerization. Copolymer analysis and reactivity ratio calculation suggest a strong tendency toward alternation, consistent with observations from bulk free-radical polymerization. Spectroscopic analysis shows evidence of formation of an intermediate that may be responsible for the 1 : 1 chain propagation. A mathematical model for this type of electropolymerization is proposed analogous to free-radical solution polymerization. Initiation is directly related to the applied current density, and termination appears to be by reaction of the growing chain with primary hydrogen radicals (H·) or possibly by chain transfer.

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