Pulsed-Current Electropolymerization and Postelectropolymerization of Acrylamide in Sulfuric Acid

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ABSTRACT: When electropolymerization of acrylamide in aqueous sulfuric acid solution using graphite fibers as the working electrode was conducted using short current pulses (~1 s), there was no significant change in the polymer yield as compared to the conventional continuous process. The acrylamide radical lifetime is estimated to be about 5 s. However, the molecular weight of the polymer (measured at low conversion) was somewhat higher than that obtained under steady-state conditions and decreased with increasing pulse length. After the current is switched off, postelectropolymerization continues for a significant length of time. For example, more than a 25% weight gain of the graphite-fiber working electrode was obtained when a 2 M acrylamide solution electropolymerizing at 50 mA/g of fiber for 20 min was interrupted by switching off the electric current.

Introduction

Although aqueous and nonaqueous continuous-current electrochemical polymerization of acrylamide has been investigated by several groups,[1-6] little attention has been focused on modulating such an electrochemical process by appropriately applied pulse sequences, nor in examining the extensive postpolymerization which occurs once the current ceases. Clearly, chain propagation would be expected to occur in an electropolymerization after the initiation has occurred by electron transfer from or to the working electrode. The lifetime and the growth of the chain during the current off time are not well understood. But the possibility of reactivity and reaction control, particularly as it might apply in a copolymerization or the design of a polymeric coating, need to be explored. Pulsed-current electrolysis may also be a valuable tool in the design of electropolymerized coatings. Both molecular weight and molecular weight distribution of an electropolymerized sample might be controlled by judicious choice of current pulse length and current pulse sequence.

In aqueous sulfuric acid solution, electropolymerization of acrylamide is believed to proceed by the addition of acrylamide monomer onto the growing chain radical. The potential advantage of controlling electrochemical polymerization and the product of such reaction by applying a controlled current pulse sequence can be fully realized when one can predict with a high degree of accuracy the lifetime of the chain radical.[7] The possibility of continuing electropolymerization of acrylamide after the electric current is switched off and the extent of such postelectropolymerization raise the question of how best to optimize and control the process. Bhadani et al.[7] reported significant postelectropolymerization of acrylamide in aqueous zinc chloride/zinc nitrate solution using a platinum metal working electrode. They stated that anodic electropolymerization of acrylamide in zinc nitrate solution continued after the electric current was switched off and resulted in about 80% conversion during 80 min of postelectrolysis. They also reported significant cathodic postelectropolymerization of acrylamide in an acrylamide/zinc chloride system.

There are a few other studies of discontinuous-current electropolymerization of acrylamide.[8-13] Ogumi et al.[8] studied anodic pulsed electropolymerization of acrylamide in an aqueous acetate solution using a platinum working electrode. They confirmed postelectropolymerization of acrylamide in their system. They further stated that at very short pulse lengths (~3 ms), the rate of electropolymerization and the molecular weight of the resulting oligomers (MW ~ 500) were independent of the current pulse length. In the present study, we report the pulsed-current cathodic electrolysis and postelectropolymerization of acrylamide in aqueous sulfuric acid solution using graphite fibers as the working electrode.

Experimental Section

Materials. High-purity acrylamide (>99%) purchased from Aldrich Chemical Co. was used without further purification. The supporting electrolyte solution was dilute sulfuric acid or a 1:1 mixture of 2-propanol and 0.05 M sulfuric acid. A three-compartment cell (Figure 1) was used for the electrolysis. Each of the two side anodic chambers contained sulfuric acid supporting electrolyte and a stainless steel counter electrode. The graphite-fiber working electrode consisted of an AS-4 graphite fiber bundle (3K), supplied by Hercules Inc., wound onto an H-shaped polypropylene frame. Contact to the external circuit consisted of aluminum foil and alligator clips. Details as to the nature of the working electrode have been previously reported.[14] The catholyte was separated from the anolyte by means of a fritted glass disk. The distance between the working and the counter electrodes was about 6.5 cm. A three-chamber polypropylene cell was also used in the electropolymerizatin of acrylamide.

The source of electric current was a Princeton Applied Research potentiostat/galvanostat Model No. 363. The stainless steel counter electrodes and the graphite fiber working electrode were connected to the positive and the negative terminal of the potentiostat, respectively. Electropolymerization of acrylamide was initiated by passing adequate current through the monomer-electrolyte solution. At the end of the experiment, the coated fibers were immediately withdrawn from the solution, rinsed with methanol, and dried at 110 °C to constant weight. The amount of polymer coatings formed on the surface of the graphite fiber working electrode was measured gravimetrically from the weight difference between the coated and the uncoated fibers. Postelectropolymerization was accomplished by permitting the working electrode to remain in the cell for a predetermined period of time after the passage of current. Linear pulsed-current electropolymerization of acrylamide was accomplished by connecting the working electrode through a modified electronic timer/controller purchased from Fisher Scientific Co. Except when otherwise stated, the ratio of current on and off time is one. Current pulse lengths of 1, 15, 30, and 300 s were used. In each case the graphite-fiber working electrode remained in the solution for a total time (current on time + current off time) equal to that expended during a reference continuous electropolymerization.

Results and Discussion

Pulsed-current electropolymerization of a 2.0 M acrylamide solution in 0.025 M sulfuric acid/2-propanol (1:1) was performed at pulse lengths of 1-300 s. Table I

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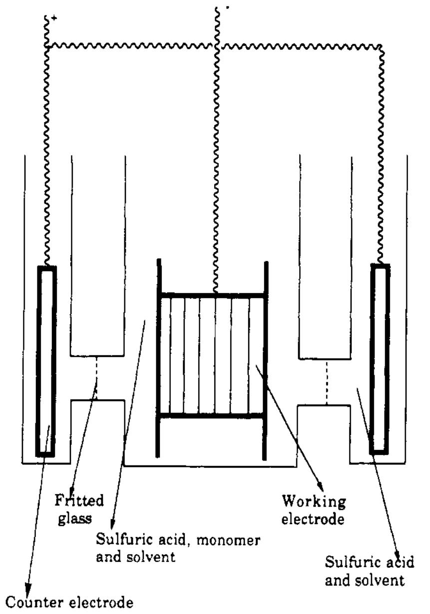

Figure 1. Three-compartment electrochemical cell.

Table I
Effect of Current Pulse Length on the Electropolymerization of 2 M Acrylamide in Sulfuric Acid Solution (0.0125 M) at a Current Density of 20 mA/g

pulse length (s)	total current (on + off) time (s)	total current on time (s)	total no. of pulses	weight of fibers (g)	weight of coatings (g)	weight gain of fibers (g)
5	600	300	120	1.22	0.95	0.78
10	600	300	60	1.23	0.96	0.78
60	600	300	10	1.22	0.90	0.73
300	600	300	2	1.24	0.81	0.65

Table II
Reproducibility of Pulsed Electropolymerization of Acrylamide in Sulfuric Acid Solution

pulse time (s)	total electrolysis time (s)	weight of fibers (g)	weight of coatings (g)	weight gain of fibers (g)
1	600	1.045	0.91	0.87
1	600	1.054	0.96	0.91
1	600	1.044	0.94	0.90
80	600	1.058	0.90	0.85
80	600	1.037	0.82	0.79
80	600	1.036	0.86	0.83

indicates that for short pulse lengths of 5 and 10 s, the weight gain of the fibers was comparable (95%). However, the amount of polymer coating deposited on the graphite fibers decreased by about 16% at longer pulse lengths. It is reasonable to assume that at long pulse lengths the radical concentration decays significantly between pulses.

The reproducibility of these data is demonstrated in Table II for experiments at pulse lengths of 1 and 80 s. The total weight gain on the fibers dropped about 8% when the current pulse length was increased from 1 to 80 s, though the same total current was applied in both cases.

It should be noted that the data presented in Tables I and II were obtained by electropolymerizing 250 mL of 2 M acidified acrylamide solution contained in the monomer chamber (catholyte) and 250 mL of 0.0125 M sulfuric acid solution in the counter electrode chambers (anolyte). A conversion of less than 5% is acceptable for the determination of the initial rates. Table III shows the effect of current pulse length on viscosity average molecular weight of polyacrylamide. The viscosity average molecular weights of the electropolymerized coatings drops from about 22 000 to 16 000 as the pulse length increases from 1 to 600 s.

Table III
Variation of Molecular Weight with Current Pulse Length for Polyacrylamide Synthesized in (1:1) 0.125 M Sulfuric Acid/2-Propanol Solution Containing 2 M Acrylamide

pulse length (s)	concn (g/dL)	intrinsic viscosity (dL/g)	mol wt	total time (min)
600	0.366	0.403	15 907	60
150	0.359	0.406	1 600	60
30	0.410	0.474	20 322	60
1	0.761	0.500	21 600	60
continuous	0.421	0.473	20 000	60

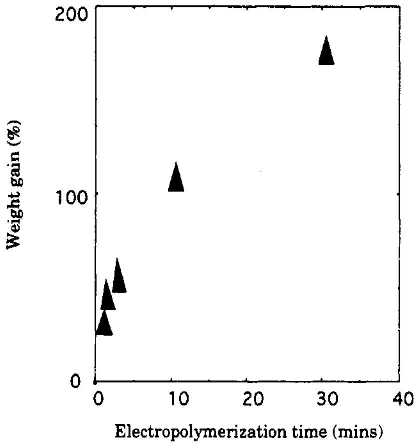

Figure 2. Continuous electropolymerization of acrylamide (2 M) in 0.0125 M sulfuric acid solution.

Table IV
Postelectropolymerization of Acrylamide in a Glass-Chamber Electrolysis Cell Containing 2 M Acrylamide Solution and 0.025 M Sulfuric Acid Solution Using a Graphite-Fiber Working Electrode

weight of fibers (g)	weight of coatings (g)	current off time (min)	current on time (min)	$W_{\mathrm{coating}}/W_{\mathrm{fiber}}$	current (mA)
0.0171	0.036	0	20	2.11	588
0.0147	0.056	20	20	3.81	592
0.0160	0.096	40	20	6.00	589
0.0163	3.180	856	20	195	626

The weight gain of fibers in the continuous-current electropolymerization at a constant initial monomer concentration, current density, and supporting electrolyte concentration increased monotonically with electropolymerization time (Figure 2). For a starting monomer concentration of 2 M, current density of 100 mA/g of fiber, and a sulfuric acid concentration of 0.025 M, about 100% weight gain of fibers is obtained after 10 min of electrolysis. Table IV shows the effect of postelectropolymerization on the weight gain of fibers for two sets of runs performed using 2 M acrylamide solution, 0.025 M sulfuric acid solution, and a current density of 10 mA/g fiber, for a duration of 20 min. In the first case the fibers were withdrawn from the solution immediately after 20 min of continuous electrolysis. This was followed by another run performed under the same experimental conditions except that the fibers were retained in the solution for an additional 20 min after the passage of current was stopped. The weight gain of fibers increased from 211% to 381% when the fibers were kept in the solution for an additional 20-min period. When the above experiment was repeated for a current on time of 20 min followed by a 40-min current off period, about 600% weight gain was obtained. The control experiment here was a continuous electropolymerization under the same experimental conditions, except that the coated fibers were withdrawn from the solution immediately after the current was turned off. The additional polymerization occurring after the termination of electric current was as a consequence of postelectropolymerization.

Figure 2 shows the plot of the weight of polymer coatings deposited onto a graphite-fiber surface as a function of electropolymerization time. The plot is characterized by an initial sharp rise followed by a gradual change, typical of radical electropolymerization. The effect of postelectropolymerization is more pronounced at longer current-off periods. As shown in Figure 3, a significant weight gain increase >25% was observed after 20 min of postelectrolysis. Unusual postelectropolymerization occurred during the polymerization of acrylamide in a 1:1 dilute sulfuric acid solution/2-propanol solution containing 2 M acrylamide solution, using a two-compartment electrochemical cell. About 400% weight gain increase was obtained after 40 min of postelectropolymerization (Table IV).

Radical Lifetime (τ). Aqueous electropolymerization of acrylamide in sulfuric acid solution has been shown to proceed by a radical mechanism. Initiation of electropolymerization occurs by the interaction of hydrogen radicals H* with acrylamide monomer M.

$$H^* + M \rightarrow M^*$$

Further addition of acrylamide to the growing chain results in the formation of the macroradical M_{n+1}* which may terminate by either recombination, disproportionation, or chain transfer. The rate of radical consumption during the current-off time $d[M^*]/dt$ is related to the radical concentration [M*] as follows:

$$d[M^*]/dt = -2K_t[M^*]^2 \qquad (1)$$

$$1/[M^*] - 1/[M^*]_I = 2k_t t \qquad (2)$$

where k_t is the rate constant for termination and $[M^*]_I$ is the radical concentration after a current pulse length of time t. Multiplying eq 2 by the steady-state radical concentration $[M^*]_s$ gives a relationship between the radical lifetime τ and the radical concentration [M*] and $[M^*]_I$ as follows:

$$[M^*]_s/[M^*] - [M^*]_s/[M^*]_I = t/\tau_s \qquad (3)$$

$$\tau_s = 1/2k_t[M^*]_s \qquad (4)$$

The rate of polymerization R_p is related to the radical lifetime τ_s as follows:

$$(R_p)_s/R_p - (R_p)_s/R_{pI} = t/\tau_s \qquad (5)$$

$(R_p)_s$ is the rate of electropolymerization under steady-state conditions as represented by continuous-current electropolymerization. It is calculated from the weight gain data for continuous–current electropolymerization. R_p is the rate of electropolymerization at different current pulse lengths while R_{pI} is the rate of electropolymerization at the start of current off period.

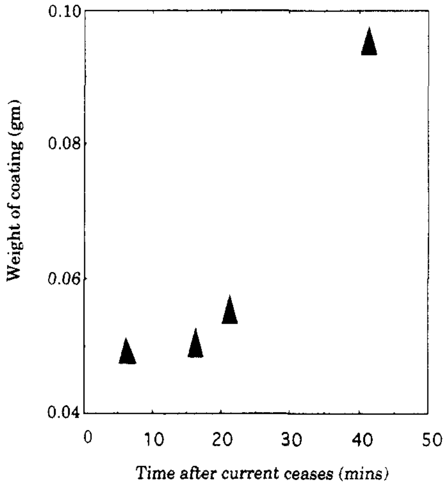

Figure 3. Postelectropolymerization of acrylamide (2 M) in 0.0125 M sulfuric acid solution using a graphite-fiber working electrode.

Table V
Rate of Electropolymerization of Acrylamide onto Graphite Fibers in Sulfuric Acid/2-Propanol Solution

pulse length (s)	log t	R_p weight gain (g/s)	R_{p_s} weight gain (g/s)	R_p/R_{p_s}
1	0	0.775	0.781	0.992
15	1.18	0.578	0.781	0.739
30	1.48	0.498	0.781	0.637
150	2.18	0.468	0.781	0.599

Table V shows values of the rate of electropolymerization R_p obtained for pulsed-current electrolysis at different current pulse lengths. The R_p obtained for runs performed using very short pulse lengths are very high and approach the values for that calculated for a system polymerizing under steady-state conditions. The R_p values at long pulse lengths are significantly lower. The disparity in the R_p values for the different pulse lengths may be rationalized as follows: during slow pulsed-current electropolymerization, the radical concentration may decay to a near-zero value during the current off interval, followed by a gradual return to a steady-state value in the subsequent current on time. This fluctuation in the radical concentration is partly responsible for the lower rate of electropolymerization obtained with long current pulses. At very short current pulses, the radical concentration appears to be maintained at a constant value.

The acrylamide radical lifetime was calculated from the slope of the plot of $(R_p)_s/R_p$ vs log t. A value of 5 s was obtained in agreement with the range of values suggested by other authors.[15-17]

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Registry No. Sulfuric acid, 7664-93-9; acrylamide (homopolymer), 9003-05-8; acrylamide, 79-06-1.