Effect of Ultrasound on Electrochemically Initiated Acrylamide Polymerization

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ABSTRACT: Acrylamide was polymerized under different voltages with ammonium persulfate as the initiator at room temperature. The polymerization reactions were performed in two different ways. In one case, the reaction was performed in a classical, three-electrode electrochemistry cell, and in the other, the cell was placed in an ultrasonic bath, and ultrasound was applied during the reaction. Both reactions were performed at room temperature. The conversion was rapid; even in the normal electrochemical case, the composite rate constant was comparable to the case with free-radical polymerization of acrylamide at 50–70°C. When ultrasound was applied, the conversion values increased more. The heterogeneity index and molecular weights of the polymers produced with and without ultrasound were measured with size exclusion chromatography. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 84: 83–89, 2002; DOI 10.1002/app.10233

Key words: ultrasound; electrochemistry; polymerization; free-radical polymerization; kinetics

INTRODUCTION

Polyacrylamide is a readily water-soluble polymer over a broad range of conditions. It has strong hydrogen bonding and can be obtained in linear high-molecular-weight polymers. These properties have enabled polyacrylamide to find diverse applications from drag reduction to adhesives and from the paper industry to mining.[1] Most polyacrylamide is produced by free-radical polymerization by thermal initiation. However, electrochemical initiation for polymerization is very simple to perform and can be done at room temperature too.

Electrolysis of acrylamide solutions is known to produce two products: polyacrylamide dissociates on the anode and soluble Nylon 3 on the cathode.[2] Ogumi et al. worked the electro-initiated polymerization of acrylamide in an aqueous solution of trifluoroacetic acid and potassium trifluoroacetate.[3] In that work, an oligomer molecular weight of 4000–6000 was obtained, and a platinum electrode was used. Tashiro et al. investigated the initiation of 4-vinylpyridine polymerization by a free-radical mechanism with a silver cathode.[4] The electropolymerization of acrylamide/bisacrylamide in the formation of cross linked polymer films in the presence of $ZnCl_2$ was reported by Collins and Thomas.[5] In their experiment, a cross-linking reaction occurred on the metal cathode surface. Yildiz et al.[6] prepared electrochemically initiated acrylamide/bisacrylamide copolymer gels in bulk.

Ultrasound (US) has been used in polymerization for a long time. It increases the initiation rate[7–10] and also causes the scission of long chains, thus reducing the polydispersity (heterogeneity index).[7–13] The heterogeneity index is defined as the ratio of weight-average molecular weight to number-average molecular weight.
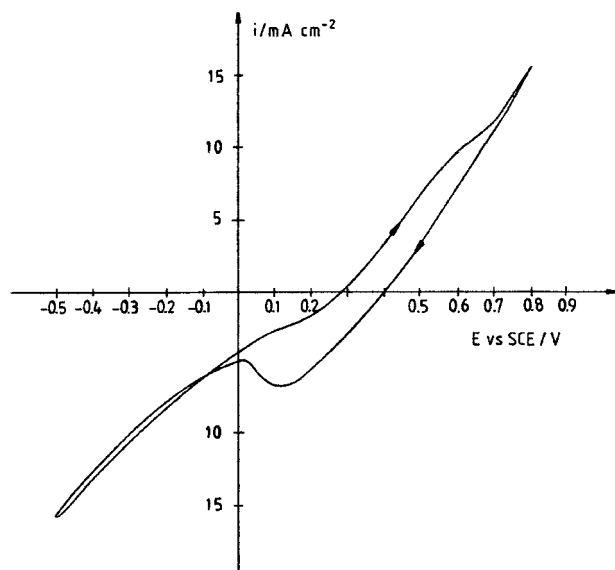
Figure 1 Cyclic voltammogram of Ag electrode in $0.1M$ $(NH_4)_2S_2O_8$ (sweep rate = 50 mV/s).

In this work, acrylamide polymerization was performed electrochemically at different voltages, and in parallel experiments, US was applied during the electropolymerization. The composite rate constants of electro-initiated polymerization with and without US were compared with pure chemical cases. The molecular weights and heterogeneity indexes of polymers produced at 0.6 V with and without US application were measured with size exclusion chromatography (SEC).

EXPERIMENTAL

Equipment

Electrochemical experiments were carried out with a Autolab PGSTAT 30 (Eco Chemie, Holland) potensiostat. Electrolytic solutions were prepared from ultrapure water (Millipore Milli Q system, USA). All experiments were performed in a classical three-electrode cell with a platinum wire as a counterelectrode and a calomel electrode as a reference. The working electrode was a silver wire with a geometric surface of 1.5 cm^2.

Materials

Acrylamide (Aldrich, Switzerland) was used after recrystallization from methanol. Ammonium persulfate (Merck, Germany) was used as supplied.
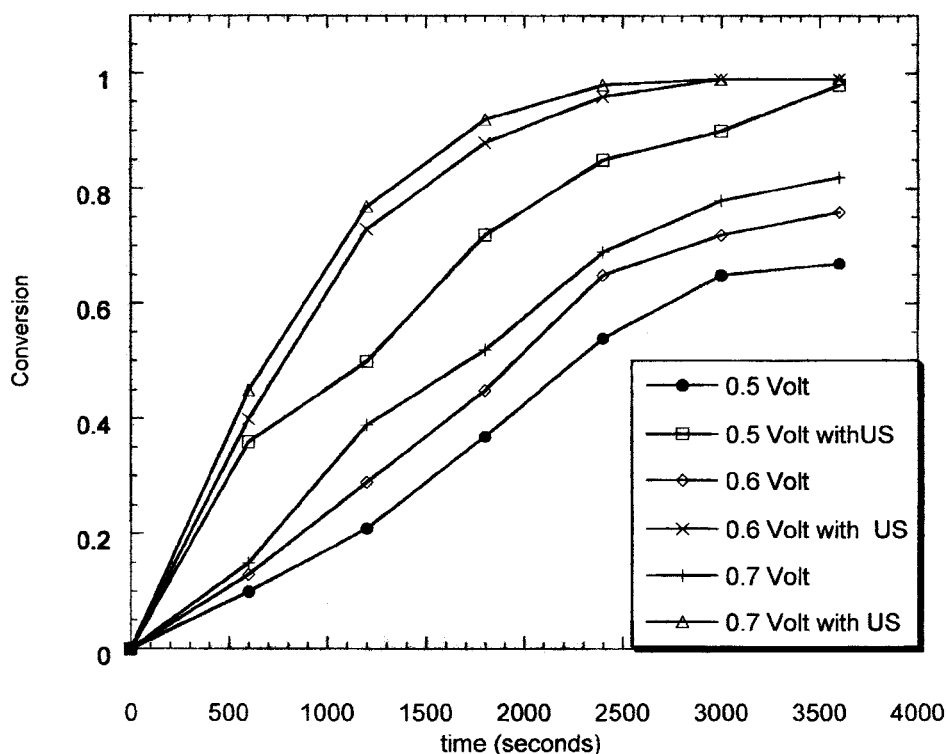

Figure 2 Conversion versus time values in electrochemically initiated acrylamide polymerization ($0.56M$ acrylamide and $0.0044M$ ammonium persulfate in water) at 0.5, 0.6, and 0.7 V with and without US applied during the polymerization.
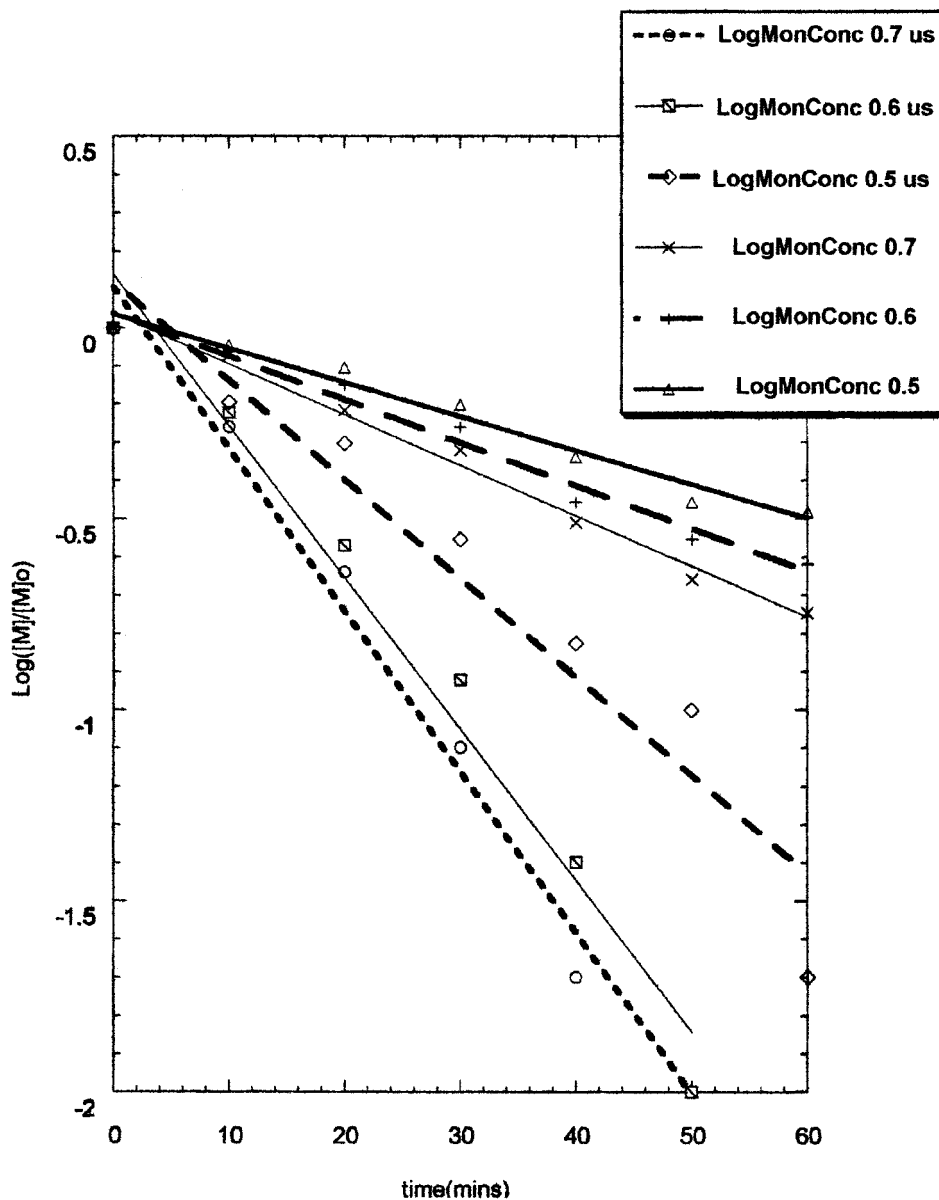
Figure 3   Log($[M]/[M]_0$) versus time for cases with and without US applied.

Polymerization Procedure

The polymers were prepared with a 50-mL solution of $0.56M$ acrylamide and $0.00438M$ ammonium persulfate. The solution was deoxygenated by nitrogen bubbling for 15 min prior to application of the voltage. In all voltammetric experiments, the solution was stirred continuously with a magnetic stirrer at a constant speed. In parallel experiments, the electrochemistry cell was placed in the US bath, and US was applied during the reaction. We stopped the reaction by pouring the cell contents into methanol at the desired time (10, 20, 30, 40, 50, and 60 min), and conversion was determined gravimetrically. To verify that the reaction was electrochemical, an identical mixture of the monomer and the initiator was prepared and kept at the same temperature (20°C). No polymerization occurred in this mixture in 24 h.

RESULTS AND DISCUSSION

The cyclic voltammogram of the Ag electrode in $0.1M$ ammonium persulfate is shown in Figure 1.

Table I κ and K Values in Electrochemical Polymerization $[I]_0 = 0.0438M$ at 20°C

Applied Voltage (v)	κ Without US	κ With US	K Without US	K With US
0.5	3.42×10^{-4}	9.91×10^{-4}	5.18×10^{-3}	15.0×10^{-3}
0.6	4.31×10^{-4}	15.21×10^{-4}	6.53×10^{-3}	23.0×10^{-3}
0.7	5.07×10^{-4}	16.20×10^{-4}	7.68×10^{-3}	24.5×10^{-3}

During the positive going-sweep, oxidation began at 0.3 V/SCE, giving a step rise at 0.6 V. This step was due to the formation of Ag_2O and AgO. The presence of this powerful oxidizing agent (persulfate) oxidized the Ag (pH $\approx$ 4). AgO and Ag_2O dissolved in the water, and the electrode was not pacified. After dissolution, these oxides are unstable and decompose water with the formation of hydroxide radicals.[14] Oxygen evolution was observed beyond 0.8 V. During the negative going-sweep, a positive current occurred up to 0.4 V. This corresponds to the dissolution of oxides. The reduction of the silver surface gave a maximum in the negative current at 0.1 V, a negative current observed from 0 to -0.5 V due to the reduction of persulfate.
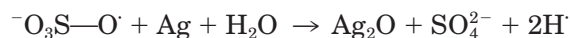
Voltages of 0.5, 0.6, and 0.7 V were chosen as polymerization voltages, and polymerization reactions were performed at these voltages with and without US application during the polymerization.
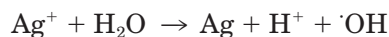
Polymerization

Acrylamide polymerization was initiated by the persulfate dissociation on the silver electrode surface, as follows:[15]

$$^-O_3S—O—O—SO_3^- \; \rightarrow \; ^-O_3S—O^. + SO_4^{2-}$$
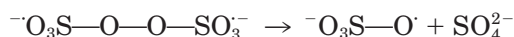
The radical then attacked the silver electrode.

$$^-O_3S—O^. + Ag + H_2O \; \rightarrow \; Ag_2O + SO_4^{2-} + 2H^.$$

Oxidized silver is soluble in water:

$$Ag^+ + H_2O \; \rightarrow \; Ag + H^+ + {}^.OH$$

Radicals formed in all these three reactions and initiated free-radical polymerization[16–18] of the acrylamide system as follows: The initiation step was considered to involve two reactions. The first was the production of the free radicals with rate constant k_d:

$$I_2 \xrightarrow{k_d} 2I^* \tag{1}$$

where I_2 is the initiator and I^* is the primary radical formed by initiator decomposition.

The second step of the initiation was the production of the first monomer radical R_1, with rate constant k_i:
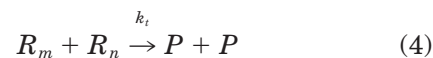
$$I^* + M \xrightarrow{k_i} R_1 \tag{2}$$
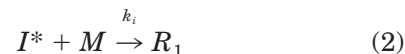
where M is the monomer.

Propagation involves the usual steps, with rate constant k_p (assumed equal for all chain lengths):

$$R_1 + M \xrightarrow{k_p} R_2 \tag{3}$$

Termination occurs mainly by disproportionation in the acrylamide polymerization:[1]

$$R_m + R_n \xrightarrow{k_t} P + P \tag{4}$$

The initiator concentration, $[I_2]$, disappears according to the first-order expression

$$[I_2] = [I_2]_0 \exp(-k_d t) \tag{5}$$

The rate equations for the monomer concentration, $[M]$, and propagating radical, $[R]$, are given by

$$d[R]/dt = 2Fk_d[I_2] - k_t[R]^2 \tag{6a}$$

Table II   K Values for Acrylamide Polymerization in a Chemical-Initiated Nonelectrochemical Case at 50, 60, and 70°C

	Temperature		
	70°C	60°C	50°C
K	2.92×10^{-4}	1.11×10^{-4}	2.08×10^{-5}

where F is the fraction of radicals that lead to chain propagation. Here, it is assumed that eq. (1) is the rate-limiting step in the production of the propagating radical, not eq. (2). Otherwise

$$d[R]/dt = k_i[I^*][M] - k_t[R]^2 \qquad (6b)$$

Here, the termination constant adheres to the definition used by Dotson et al.[16] and Bamford[15] and is twice the value used by Odian.[18] The rate equation for monomer concentration is [when eq. (6a) held]

$$d[M]/dt = -2Fk_d[I_2] - k_p[R][M] \sim -k_p[R][M] \qquad (7)$$

The quasi-steady-state approximation is

$$d[I^*]/dt = d[R]/dt = 0 \qquad (8a)$$

Under this approximation, radical concentrations are given by

$$0 = d[R]/dt = 2Fk_d[I_2] - k_t[R]^2 \qquad (8b)$$

so that

$$[R] = (2Fk_d[I_2])^{1/2}k_t^{-1/2} \qquad (9)$$

The monomer then disappears in a first-order process:

$$[M] = [M]_0 e^{-\kappa t} \qquad (10)$$

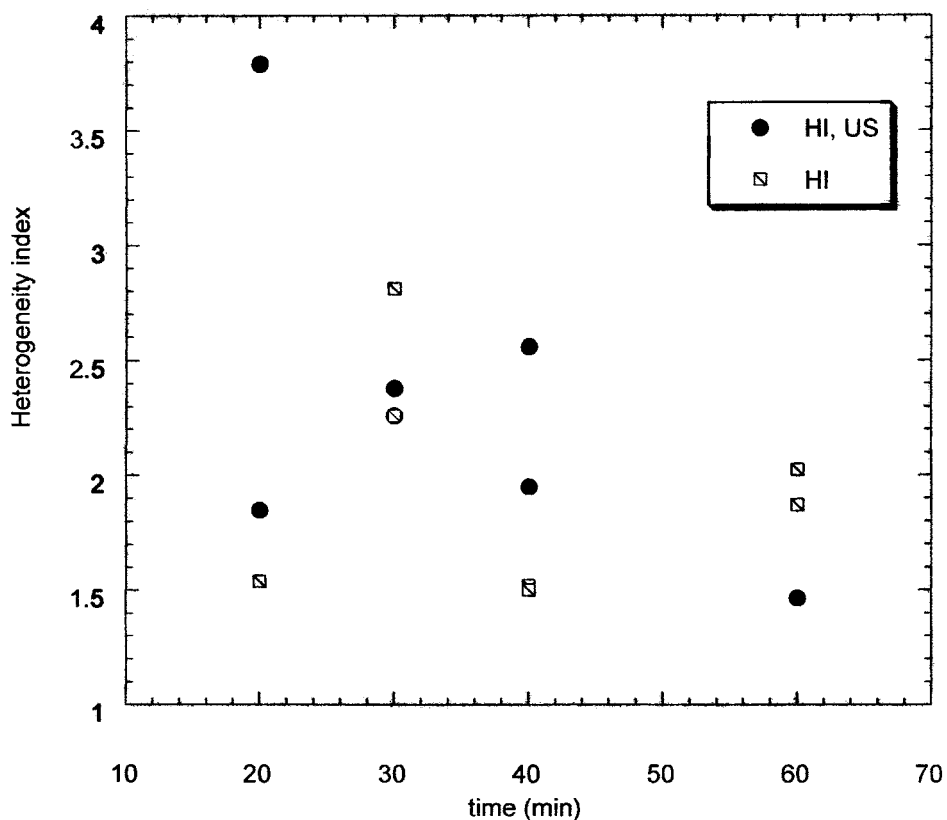where the rate constant κ is given by

Figure 4   Time versus heterogeneity index for polymers synthesized at 0.6 V with and without US.
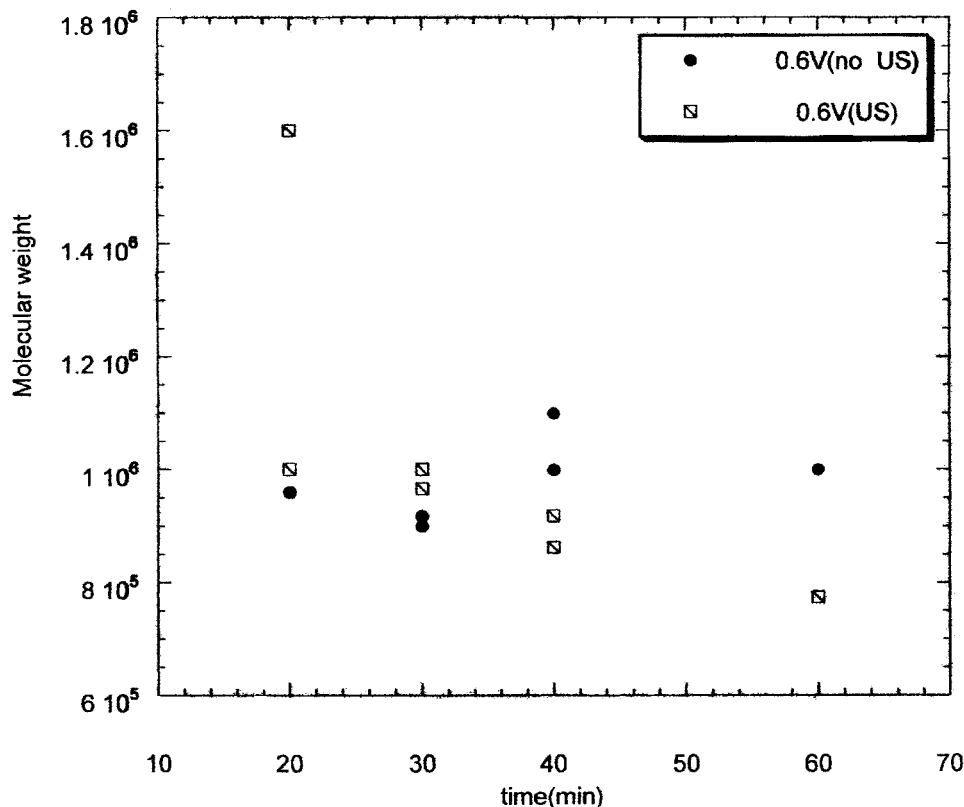
Figure 5 Molecular weight versus time data for polymers synthesized at 0.6 V with and without US.

$$\kappa = k_p[R] \tag{11}$$

$$\kappa = k_p(2Fk_d/k_t)^{1/2}[I_2]^{1/2} = K[I_2]^{1/2}$$

Figure 2 shows the monomer conversion f ($f = 1 - [M]/[M]_o$), versus time for polymerizations initiated at different voltages with and without US application. In electrochemically initiated acrylamide polymerization, there was a big difference between cases where US was applied and where it was not. The curves in Figure 2 can be treated approximately as first order over a significant portion of the reaction. Fits of the form

$$f(t) = 1 - e^{-\kappa t} \tag{12}$$

$$\ln(1 - f(t)) = -\kappa t$$

are also shown in Figure 3, where κ is the first-order decay rate defined by eq. (11), and the K values are given in Table I. The K values for the free-radical polymerization of acrylamide at 50, 60, and 70°C calculated in ref. 19 are given in

Table II. Although the electrochemical initiation was performed at room temperature, it had a comparable rate with the free-radical polymerization performed at 50, 60, and 70°C. This is a very promising result for electrochemical polymerization.

In the lower left corner of the Figure 2, it is shown that US application increased the initial polymerization rate significantly (by a factor of two to three) compared to polymerization at the same temperature and voltage. Because electrode poisoning is not expected to be significant this early in the reaction, the reaction rate can be higher due to increased initiator efficiency. The turbulence created by US can suppress the cage effect by causing the primary radicals to separate from each other rapidly. At the later stages of the reaction, after 50–60% conversion, in the experiments with no US the reaction slowed down. This slowing down can be attributed to electrode poisoning.

Heterogeneity index versus time plots are given in Figure 4. The effect of US on the heter-

ogeneity index was rather complex. Because US breaks the long polymer chains but the short chains are immune to its effect, over sufficiently long times it reduces heterogeneity. Chain-length evolution takes some time, too. On the other hand, in short time scales, the dominant effect is the increase of the initiation rate. Due to the extremely nonuniform and turbulent environments, this increase is not uniform. The fluctuation of the macro radical concentration causes fluctuation of the termination rate and tends to increase the heterogeneity. That is why at the beginning of the reaction (up to 40 min), the rate-increasing effect of US was dominant and heterogeneity with US was higher than the heterogeneity without US. In the later stages of the reaction, a chain scission effect dominated, and the heterogeneity with US decreased. A molecular weight versus time plot is given in Figure 5. The previous discussion is valid for the molecular weight, too, and the decrease in the molecular weight in the US case can be attributed to chain scission by US.

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