

Electrochemical Measurements for Studying the Polymerization Process and Critical Point Behaviors of Hydrogels

Gulcemal Yildiz,¹ Yasar Yilmaz²

¹Department of Chemistry, Istanbul Technical University, Maslak 34469, Istanbul, Turkey

²Department of Physics, Istanbul Technical University, Maslak 34469, Istanbul, Turkey

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ABSTRACT: We propose a new technique based on electrochemical measurements for studying the critical point behaviors of the sol–gel transition of acrylamide-*N,N'*-methylene bisacrylamide hydrogels. In this technique, no chemical activator is used for accelerating the polymerization reaction. However, a potential difference is applied by means of silver and calomel electrodes placed in the reaction mixture. The silver electrode begins to be ionized and loses its electrons. The free radicals, $^{\ominus}O_3S-O^{\bullet}$, H^{\bullet} , and $^{\bullet}OH$, form on the silver electrode via persulfate dissociation. The polymerization is initiated by means of these free radicals. The current measured during the gelation processes passes through a maximum (a Gaussian-like behavior) and varies linearly with the reaction time during linear polymerization. All the parameters (the monomer, initiator, and crosslinker concentrations, the applied volt-

age, and the stirring rate of the reacting mixture) affecting the current have been studied in detail. We show that the maxima appearing in the current–time plots correspond to the gelation thresholds, the so-called sol–gel transition points. We also analytically prove that the current monitors the weight-average degree of polymerization (DP_w) and the gel fraction (G) below and above the threshold, respectively. The scaling behaviors of DP_w and G have been tested near the gelation thresholds, and we have observed that the critical exponents γ and β , defined for DP_w and G , agree with the predictions by mean-field theory. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 754–760, 2009

Key words: degree of polymerization (DP); electrochemistry; gelation

INTRODUCTION

Several experimental techniques have been developed and/or employed to study the gelation processes for many different polymeric systems. These include rheological measurements,^{1–4} dynamic light scattering,⁵ volume measurements,⁶ fluorescence measurements,^{7–10} electron spin resonance,¹¹ and dielectric measurements.^{12,13}

To monitor the variation in the physical nature of polymerization processes during the sol–gel transition, the experimental technique used must be very sensitive to the structural changes. At the same time, it should not disturb the system mechanically. It has been shown^{9,10} that the fluorescence technique used

for *in situ* monitoring of the polymerization of polyacrylamide is particularly useful for the elucidation of detailed structural aspects of the gels. However, the determination of the gel point (or so-called sol–gel transition point) accurately during the polymerization reaction remains so far, to our knowledge, to be one of the main issues of the gelation processes.

Recently, a new technique based on chronoamperometric measurements has been developed to study the sol–gel transition for the solution free-radical crosslinking copolymerization of acrylamide (AAm) and *N,N'*-methylene bisacrylamide (BIS). No chemical activator is used for accelerating the reaction; instead, a direct voltage is applied by means of a silver working electrode placed in the reaction mixture.¹⁴ It has been shown that the current measured during the gelation process has a correlation with the change in the concentration of radicals free to move in the reacting sample. The weight-average degree of polymerization (DP_w) and gel fraction (G) around the gel point have been evaluated with the change in the current measured during the gelation processes. In this study, the gel point is defined as the time at which a slowdown in the vibration of the magnet put in the reacting sample is first seen.¹⁴ In

Correspondence to: Y. Yilmaz (yyilmaz@itu.edu.tr).

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this technique, the vibration of the magnet disturbs the system mechanically. Therefore, it is not easy to determine the time at which the magnet starts to slow down. With the gel points as a rough estimation of the stirring magnet, it has been shown¹⁴ that G , exponent β , and the DP_w critical exponent γ , measured near the gel points, agree with the mean-field results^{15,16} for low AAm concentrations.⁹

In this work, the previously reported technique is discussed in detail for all parameters: the monomer concentration, the initiator concentration, the crosslinker concentration, the applied voltage, and the effect of the stirring of the polymer solution. In addition, we propose a new criterion for the more precise determination of the gel point without a stirring magnet. The scaling behaviors of DP_w and G have also been tested around the gelation thresholds, and it is shown that the critical exponents γ and β , defined for DP_w and G , agree with the predictions of the mean-field theory as discussed in recent studies.^{9,14}

EXPERIMENTAL

AAm (Sigma, St Louis, MO), BIS (Sigma, St Louis, MO), and ammonium persulfate (APS; Merck, Darmstadt, Germany) were used as supplied. The gels and linear polymers were prepared by changes in all the experimental parameters: varying the

AAm, BIS, and APS concentrations and modifying the voltages and stirring rates (i.e., reactions with zero and constant stirring rates). The solutions were deoxygenated by nitrogen bubbling for 15 min. The chemical compositions and conditions for all samples are given in Table I. The currents between the electrodes were measured as a function of the reaction time under an applied voltage.

Current measurements were carried out with an Autolab PGSTAT 30 potentiostat (Eco Chemie, Utrecht, The Netherlands). Electrolytic solutions were prepared from ultrapure water (MilliQ system, Millipore). All experiments were performed in a classical three-electrode cell with a platinum wire as a counter electrode and a calomel electrode as a reference. The working electrode was a silver wire with a geometric area of 1.5 cm².

RESULTS AND DISCUSSION

Figures 1–5 show the currents measured during the linear polymerization and gelation for different parameters: the AAm content, the applied voltage, the stirring rate of the magnet, the initiator (APS) content, and the crosslinker (BIS) content. All experiments were performed at room temperature. The contents of the samples used in the experiments are numbered from 1 to 25 and are listed in Table I.

TABLE I
Chemical Compositions and Voltages of the Samples Used in the Polymerization and Gelation Experiments Together with the t_{gel} Values of the Gel Samples and Calculated Critical Exponents γ and β

	Sample	AAm (M)	APS (mM)	BIS (mM)	Stirrer	Voltage (V)	t_{gel} (min)	γ (± 0.2)	β (± 0.2)
Set I	1	0.20	5	0	Present	0.5			
	2	0.30	5	0	Present	0.5			
	3	0.40	5	0	Present	0.5			
	4	0.50	5	0	Present	0.5			
	5	0.50	5	90	Present	0.5	40.30	0.9	0.6
	6	1.50	5	90	Present	0.5	22.95	1.3	0.9
	7	2.00	5	90	Present	0.5	21.02	1.1	0.9
	8	4.00	5	90	Present	0.5	13.42	1.3	0.5
Set II	9	0.20	5	0	Present	0.5			
	10	0.20	5	0	Present	0.6			
	11	0.20	5	0	Present	0.7			
	12	0.62	5	90	Present	0.5	29.98	1.3	0.9
	13	0.62	5	90	Present	0.6	22.00	1.4	1.1
	14	0.62	5	90	Present	0.7	17.90	1.2	—
Set III	15	0.62	5	90	Absent	0.5			
	16	0.20	5	0	Absent	0.5			
Set IV	17	0.30	3	0	Present	0.5			
	18	0.30	5	0	Present	0.5			
	19	0.30	7	0	Present	0.5			
	20	1.00	1	90	Present	0.5			
	21	1.00	3	90	Present	0.5			
	22	1.00	10	90	Present	0.5	11.95	0.6	0.6
Set V	23	0.62	5	26	Present	0.5			
	24	0.62	5	129	Present	0.5	92.98	1.7	—
	25	0.62	5	257	Present	0.5	82.78	1.3	—

All experiments were performed at room temperature. A dash indicates that the corresponding exponents could not be measured because of the disappearance of self-similarity

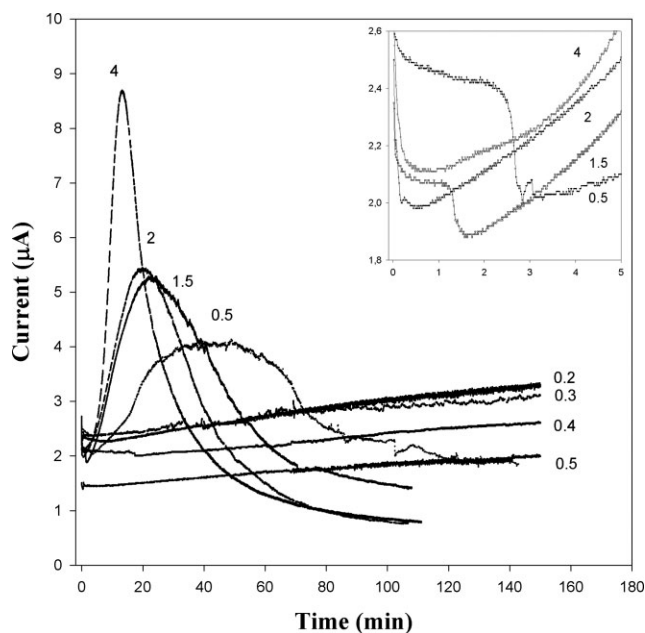


Figure 1 Currents measured during the polymerization (samples 1–4) and gelation experiments (samples 5–8) for various AAm concentrations. The number on each curve indicates the AAm concentration (mM). Each gel sample showed a peak corresponding to the gelation threshold. The inset figure magnifies the initial part of the gelation experiments.

The initial values of Figures 2, 3, and 5 were expected to be the same. However, some small deviations were observed because of the small differences in the positions of the electrodes in the sample cell. Normalization of the currents makes the positions of the electrodes the same for all experiments, and this is required for comparison. The vertical axes in Figures 2, 3, and 5 are the normalized currents for which the initial values of the currents at time $t = 0$ were brought to the same value of 100; all the data in a current–time curve were multiplied by a constant number to bring the initial data of all the curves to the same number, that is, 100.

Figure 1 shows the currents measured during linear polymerization (samples 1–4) and gelation (samples 5–8) for different AAm contents. The currents for linear polymerization change almost linearly with the reaction time. However, the variation of the currents with the reaction time for gelation processes is totally different from that of linear polymerization: a small decrease occurs first in the initial period of gelation, and then it behaves in a Gaussian fashion. The time to reach the maxima of the Gaussians (t_m) is inversely proportional to the AAm content. The intensities corresponding to these maxima of the peaks (I_m 's) also increase with increasing AAm content.

Figure 2 shows the currents measured during the linear polymerization (samples 9–11) and gelation

experiments (samples 12–14) for various voltages. The currents for linear polymerization change again almost linearly with the applied voltage; for the gel samples, t_m decreases and I_m increases when the voltage is increased.

Figure 3 shows the stirring effect on the currents measured during the linear polymerization (sample 9 with and without stirring) and gelation experiments (sample 12 with and without stirring). When the samples were not stirred, the initial decrease in the current became more pronounced for the gel samples, and a very steep decrease appeared in the initial period of the linear polymerization. The shape of the peak deviates from Gaussian-like behavior for the gel samples, and the curves for the linear polymers deviate from linearity when the samples were not stirred.

Figure 4 shows the currents measured during the polymerization (samples 17–19) and gelation experiments (samples 20–22) for various APS concentrations. The peak (Gaussian-like behavior) characterizing the gel formation does not appear below a certain APS content. The peak starts to appear in the observation time and shifts to some shorter times as the APS concentration is increased. The I_m values of the current–time peaks, the initial values of the currents, the average slopes of the current–time plots of the linear polymers, and the effects of the

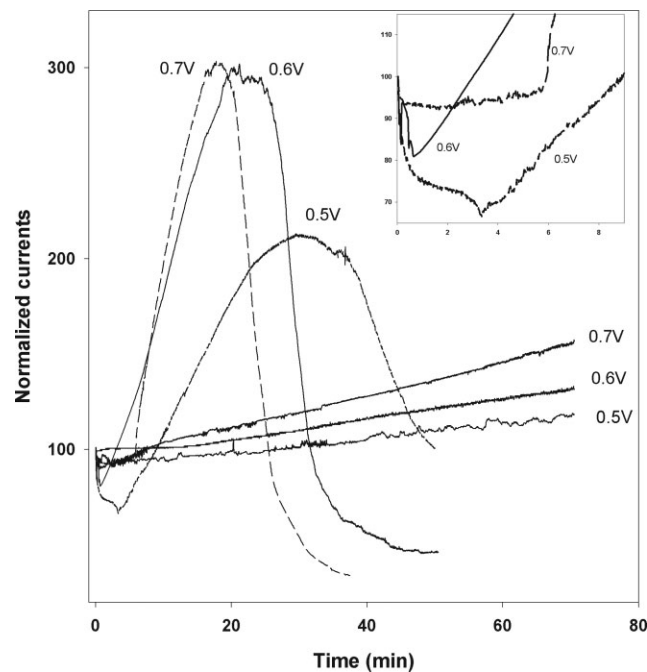


Figure 2 Normalized currents measured during the polymerization (samples 9–11) and gelation experiments (samples 12–14) for various reaction voltages. The number on each curve indicates the corresponding polymerization voltage. The inset figure magnifies the initial part of the gelation experiments.

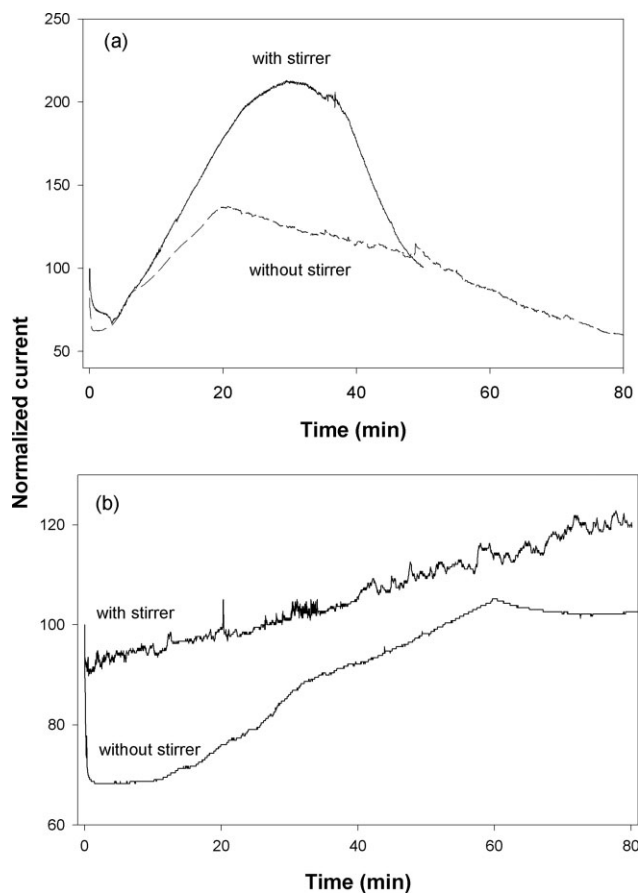


Figure 3 Stirring effect on the currents measured during the (a) gelation (samples 12 and 15) and (b) polymerization (samples 9 and 16) processes.

initial period increase when the APS content is increased. A small deviation from linearity occurs in the initial stage of the reaction only for the highest APS content.

Figure 5 shows the normalized currents measured during the gelation experiments for various crosslinker (BIS) contents (samples 23–25). The reactions take less time when the BIS concentration is increased; that is, the reaction is accelerated with increasing BIS concentration. However, the crosslinker content does not affect the behavior of the current–time curves up to the maxima of the peaks; that is, they show almost the same behaviors below the maxima. On the other hand, the current–time curves become completely different above the maxima as the BIS content is increased.

The following main points can be concluded from the data summarized in Figures 1–5. First, the decreases in the currents in the initial part of the reactions for both linear and gel samples are due to the formation of a blocking layer on the surface of the silver electrode (increasing viscosity in close proximity to the silver electrode due to gel

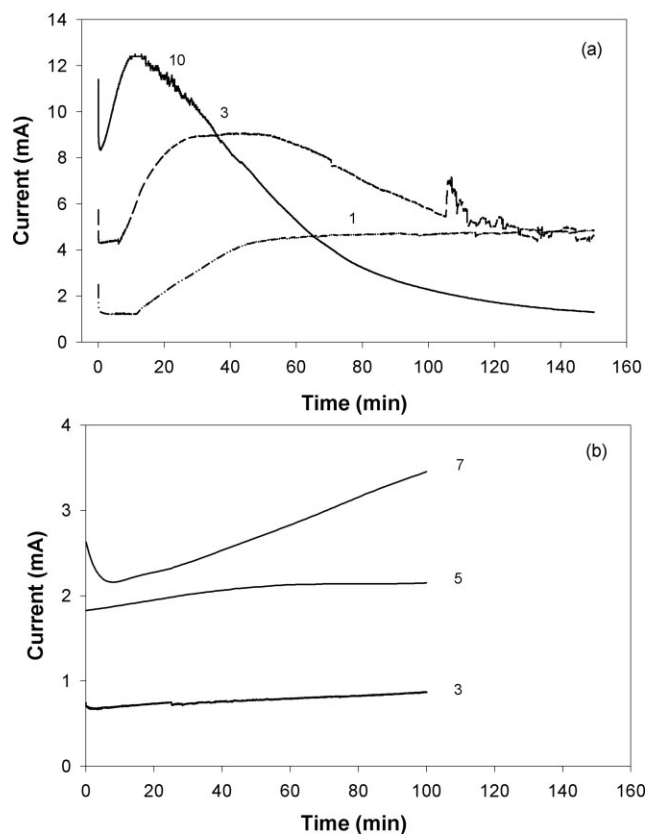


Figure 4 Currents measured during the (a) polymerization (samples 17–19) and (b) gelation (samples 20–22) experiments for various APS concentrations. The number on each curve indicates the APS concentration (mM).

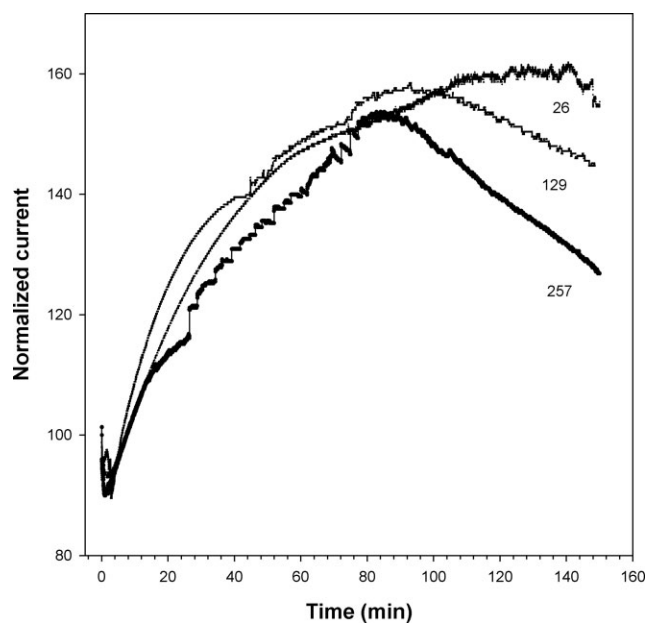


Figure 5 Normalized currents measured during the gelation experiments (samples 23–25) for various crosslinker concentrations. The number on each curve indicates the corresponding BIS content (mM).

formation). When the AAm concentration is increased, the initial periods are shorter (see the inset of Fig. 1). The initial effects observed for the gel samples were not observed for the linear polymers when the APS concentration was not very high. This indicates that only gel formation can cause a considerable blocking layer on the metal surface. This blocking layer of gel cannot be swept away easily at moderate stirring rates. However, the effect of the blocking layer may be reduced if the effect of convection is increased more by means of high stirring rates, as shown in Figure 3(a). However, the blocking layer of the linear polymer diffuses easily into the solution if the sample is stirred [Fig. 3(b)]. The initial period becomes shorter as the voltage is increased. The disappearance of the initial decrease (see the inset in Fig. 2) indicates that the barrier effect for the charge carriers due to the blocking layer decreases as the voltage is increased above a critical value of 0.6 V. The driving force on the charge carriers may be insufficient below this critical voltage. The effect of the decreasing mobility of charge carriers due to trapping in the blocking layer may have been compensated by higher voltages above 0.6 V.

Second, the maxima of the gelation peaks increase when the AAm concentration, APS concentration, and voltage are increased (Figs. 1, 2, and 4). The increasing AAm concentration may lead to an increase in the probability of an initiator meeting a monomer for initiating the reaction. This will cause shorter polymer chains and thus shorter (more mobile) free radicals. Therefore, it can be concluded that the number of free radicals (the charge carriers) increases as the AAm concentration is increased. The voltage also causes an increase in the current of the gels, and this may be due to the increased drifting velocity of the charge carriers. Increasing the APS content will also cause short-length (and thus more mobile) free radicals to form.

Third, for the linear polymers, the currents start from some initial values and increase slightly as the AAm concentration is increased. However, as the AAm concentration is increased, the current starts from lower values.

The current is produced mainly because of the initiators at the beginning of the reaction. The total number of the initiators (APS) as charge carriers will have its maximum value at the beginning of any reaction. Then, it will be reduced rapidly with the reaction time. If the concentration of APS is kept constant, the initial number will be less when the AAm content is increased. Therefore, the initial value of the current becomes lower when the AAm concentration is increased, as shown in Figure 1 for linear polymers. The slightly decreasing slope of the currents as the AAm concentration is increased for

the linear polymers may be due to a slight increase in the viscosity of the samples. As can be seen in Figure 2, the currents for the linear polymers also increase with increasing voltages and fixed AAm and APS contents. This is probably due to the increased driving force.

When the monomer content is kept fixed, the average weight of the free radicals will decrease as the APS content is increased, and thus the number of free radicals will increase. This will readily also cause an increase in the current, as shown in Figure 4(b). The deviation from linearity, especially in the initial stage of the reaction, for the higher APS content sample in Figure 4(b) may be due to the formation of a very dense polymer structure of the blocking layer. A very high polymerization rate and thus the possibility of a very dense entangled polymer structure (showing the gel effect) of the blocking layer might cause this initial decrease in the current of the linear polymer.

Fourth, the maxima of the gelation peaks shift to lower times as the AAm concentration, the voltage, the APS content, and the BIS content are increased (Figs. 1, 2, 4, and 5). Because all these parameters increase the activity of the free radicals (increasing the mobility or decreasing the average size of the moving radicals), this leads to an acceleration of the polymerization reaction.

Fifth, increasing the crosslinker content seems very interesting. As can be seen in Figure 5, gelation takes less time, as expected, when the BIS concentration is increased. However, the increasing BIS content does not considerably affect the behavior of the currents measured before the maxima of the current-time curves. This indicates that almost all free radicals of different sizes are able to move more or less with the same drifting velocity before the maxima, regardless of the local crosslinker density of the polymer clusters, and that there is no Trommsdorff effect in our systems, at least before the maxima. It is well known that the Trommsdorff effect plays a major role in the mobility of free radicals,¹¹ especially for bulk polymerizations, such as those of poly(methyl methacrylate) and polystyrene.^{7,17-20}

Because the final gels are not less than 90 wt % water, it can also be concluded that a change in the viscosity of the gel during the gelation processes should not considerably affect the mobility of the charge carriers. Thus, the gelation experiments indicate that the concentration of free radicals increases as the APS molecules turn into free radicals. Therefore, the current increases and goes through a maximum. The rate constants for the initiation and termination of free radicals change and dominate one another, depending on the time (or monomer conversion). Before the maxima of the current, the initiation rate constant for the free radicals is

dominant, whereas the termination rate constant dominates the initiation after the maxima. Here it should be noted that this behavior may be totally different for the bulk polymers, as discussed in ref. 11. Therefore, the maxima of the current–time curves in Figure 5 may indicate that at these points, the systems transform from one state to another: from the sol state to the gel state!

To prove the last conclusion, we performed swelling experiments for three identical samples, each including 257 mM BIS (sample 25). One of the three identical samples was quenched with an excess amount of methanol just before the reaction time reached the maximum (I), the second sample was quenched at the time corresponding roughly to the maximum (II), and the last one was quenched at the time after the maximum (III). Then, the samples were brought to their maximum swelling stages; later, they were put in ample water one by one and remained there for 3 months. From time to time, the samples were shaken gently, and the water was refreshed. After the samples were dried, the ratio of the total dried mass of the small gel particles (which were broken into pieces during the swelling of the gel) to the dried mass of the biggest part was measured for each of the three samples separately. It was expected that the ratio would be considerably greater for the sample that did not transform into the gel state. The values were found to be around 0.44 for I, 0.07 for II, and 0.04 for III. The ratio for sample I was much larger than those of the others. This result clearly supports our conclusion that the maxima of the gelation peaks are the gelation thresholds, that is, the times corresponding to the sol–gel transition points.

In ref. 14, it is shown that DP_w and G take the following forms near the gelation thresholds:

$$I_f \propto DP_w = A(t - t_{gel})^{-\gamma}, t \rightarrow t_{gel}^- \quad (1)$$

$$\frac{1}{I_f} \propto G = B(t - t_{gel})^\beta, t \rightarrow t_{gel}^+ \quad (2)$$

where I_f is the total current, which is proportional to the total number of free radicals localized in the finite clusters; t is the reaction time; and t_{gel} is the gel point. A and B in the above equations are the proportionality constants. The reduced concentrations ($|p - p_c|$) around the critical point were approximated as proportional to $|t - t_{gel}|$,^{9,10,19–21} where p and p_c are the conversion factors, defined as the ratio of actual number of chemical bonds to total possible number of bonds, at time t and t_{gel} .

Using eqs. (1) and (2) and the values for t_{gel} , we calculated γ and β exponents for the gelating samples. Figure 6 presents log–log plots of the current–

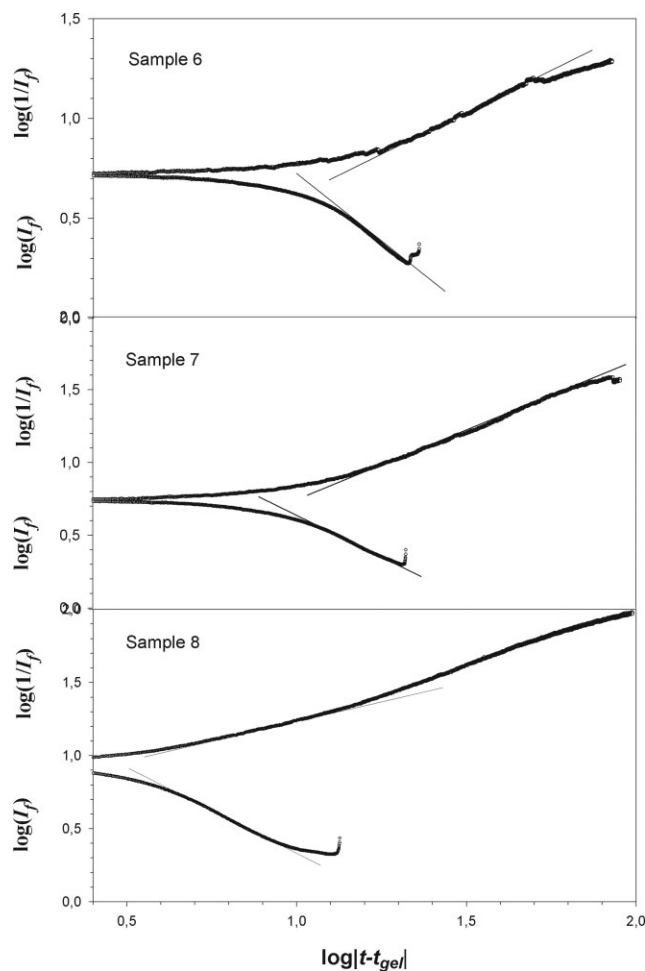


Figure 6 Representative double logarithmic plot of the data for samples 6–8. The γ and β exponents were determined from the slopes of the straight lines near the gel points. The scaling region came closer to the critical point, but the β exponent differed from the mean-field values (coming closer to the percolation exponent) as the AAm content increased.

time plots for some typical current–time data above and below the gel point, at which the slope of the straight lines, close to the gel points, gives the β and γ exponents, respectively. The β and γ exponents are around the mean-field results in the limits of the experimental uncertainties, as shown in Table I, together with the corresponding t_{gel} values (the maxima of the gelation peaks).

CONCLUSIONS

In this study, we have observed that three parameters affect the current measured during the polymerization reaction. One is the value of the voltage applied between the working and reference electrodes, the second is the number (or concentration) of

the charge carriers, and the third is the mobility of the charge carriers. The free radicals, although neutral, are highly electrophilic and act as charge carriers.²¹ Free electrons and free ions produced as byproducts will also contribute simultaneously to the current as charge carriers. Thus, the net current will measure DP_w and G for solution free-radical crosslinking polymerization of AAm.

We have shown that the gelation threshold (t_m) corresponds to the maxima of the current-time peaks measured during the gelation process. The critical exponents γ and β were found to be 1.2 ± 0.2 and 0.8 ± 0.2 , respectively, for the moderate voltage and monomer concentrations. The values of the β exponent deviated from the mean-field values for high monomer and initiator concentrations (samples 8 and 22), and β could not be measured for high crosslinker contents and for high voltages (samples 14, 24, and 25). For these samples, the local density of the gel around the silver electrode differed probably drastically from the remaining part of the gel. Thus, they either deviated from the mean-field values or were driven out of the self-similarity. Therefore, they did not obey the scaling behavior above the critical point. Out of these extreme values of the contents and voltage, the results obey the mean-field or Flory-Stockmayer theory when $\gamma = \beta = 1$.

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