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Investigation of the sol–gel transition of electrochemically prepared acrylamide bisacrylamide gels

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Abstract

A novel technique based on the chronoamperometric measurements was developed to study the sol–gel transition for the solution free radical cross-linking co-polymerization of acrylamide and *N*, *N′*-methylene bisacrylamide. The gels were synthesized electrochemically at room temperature in the presence of an initiator, ammonium persulfate. No chemical activator was used for accelerating the reaction; instead a direct voltage was applied by means of a silver-working electrode placed in the reaction mixture. It is found that the current measured during the gelation process monitors the change in the concentration of radicals, which are free to move in the reacting sample. The current due to these free radicals measures the weight average degree of polymerization and gel fraction around the gel point. Observations around the gel point, for low polymerization voltages, show that the gel fraction exponent β and the weight average degree of polymerization exponent γ agree with the mean-field results for low acrylamide concentrations. The samples synthesized above a certain voltage do not show self-similarity at the critical point. This is due to the increase in the local density, so does the heterogeneity, of the gel around the silver electrode, therefore, they do not obey the scaling behavior near the critical point.

Keywords: Acrylamide; Sol–gel transition; Critical exponents

1. Introduction

Polymeric gels are important materials because of their technological and scientific interests. A polymer at its gel-point is in a transition state between liquid and solid; it behaves neither as a liquid nor as a solid at the critical point. Furthermore, polymers around the gel-points are of interest for some applications including gel processing, reactive processing and the development of new polymeric materials such as adhesives, absorbents, porous catalysts, vibration dampers and membranes [1]. Because of the ability to absorb many times their dry weight of solvent and retain their durability, acrylamide (AAm) gels, in particular, have diverse application. They are widely used as absorbents in medical, chemical and agricultural applications [2]. The polymers around the gel point are of interest also for testing the existing theoretical approaches modeling the sol–gel transition, like mean-field (Flory–Stockmayer) [3,4] or percolation theory [5,6].

Flory and Stockmayer made first theoretical considerations on the sol–gel transition for cross-linked polymerizations, where the gelation was modeled on a special type of lattice on which the closed loops were ignored. This approach is independent of the dimensionality. Later, more realistic model, so-called static percolation model, was given on two or three-dimensional lattices. According to the percolation theory the gel point is preceded by the formation of finite clusters, which eventually link up and form the gel. The predictions of these two theories about the critical exponents for the sol–gel transition are different from the universality point of view.

Consider, for example the exponents γ and β for the average cluster size, *S*, and the gel fraction, *G*, near the gel point, are defined as,

$$S \propto |p-p_c|^{-\gamma}, \quad p \to p_c^- \tag{1}$$

$$G \propto |p-p_c|^{\beta}, \quad p \to p_c^+ \tag{2}$$

where the mean-field theory gives $\beta=\gamma=1$, while the percolation studies based on computer simulations give γ and

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β around 1.7 and 0.43, respectively, in three-dimension [5–10].

After 1940s, the scientists involved both in the areas of Chemistry and Physics have extensively studied the formation and physical properties of gels (like swelling and volume phase transition), thus several experimental techniques have been employed to study the gelation processes for many different polymeric systems. These include rheological measurements [11–14], dynamic light scattering [6,15], volume measurements [16,17], fluorescence measurements [18–20], and dielectric measurements [21,22].

Recently, some investigations on the kinetics of the polymerization were made by means of dielectric measurements [21,22] and electron spin resonance [23]. A maximum in dielectric constant, consistent with the gel point, was observed during the gelation of bulk polymers, and at the same point the dielectric loss switched from a linear decrease to a relatively constant behavior [21]. The radical concentration for bulk polymers, i.e. for diffusion-controlled reactions, increases from the onset of polymerization due to the trapping of the charge carriers in local viscosities [23]. The Trommsdorff effect (evident only for the bulk polymers) occurs due to the rapid increase in the free radical concentration as a result of the increase in the viscosity of the reaction mixture [23,24]. The acrylamide (AAm)/*N*,*N*′-methylene bisacrylamide (BIS) gelation (a solution polymerization) was studied by time dependent measurement of real and imaginary parts of the complex dielectric permittivity, where a strong relaxation behavior was observed in all dielectric spectra during the transformation from the sol to the gel state [22]. In this study, the gel point was found as the maximum in the imaginary part of dielectric constant for low frequencies. These studies clearly indicated that the change in the concentration of the radicals should be totally different for the bulk and solution polymerizations. A relation between the kinetics of the reaction and the evolution of electrical properties was also established by Warfield and Petree [25], and Kagan [26].

However, due to the experimental difficulties, the critical point behavior at the sol–gel transition (especially measuring the critical exponent for testing the theories underlying the sol–gel transition) has not been investigated thoroughly so far in the literature except for a recent study where the critical point behavior of sol–gel transition for AAm/BIS polymerization was investigated via fluorescence measurements [20].

In this work, we study the sol–gel transition for AAm/BIS system via a novel experimental technique based on the in situ measurements of the change in free radical (i.e. capable of moving freely in the sol and gel state of the system) concentration as a function of the reaction time. The current due to these free radicals measures the weight average degree of polymerization and gel fraction around the gel point. The universality class of the sol gel transition is discussed through the critical exponents β and γ. We show that sol–gel transition for low concentrated AAm gels belongs to the mean-field class of the universality, consistent with Ref. [20].

2. Experimental

The electrochemical method for initiating AAm polymerization is very straightforward and can be performed at room temperature in the presence of an initiator only, without using chemical activator. The gel formation starts on the silver electrode and extends into the cell by means of stirring magnet which determines, at the same time, the gel point of the polymerization as a result of the slowing down of its mobility. AAm–BIS gels were previously prepared electrochemically and optimal range for the reaction voltage was determined in Ref. [27].

AAm (Sigma), BIS (Sigma) and APS (Merck) were used as supplied. The gels were prepared with a 50 ml solution having 0.62 M of AAm, 9×10^{-2} M of BIS and 5×10^{-3} M APS. The solution was deoxygenated by nitrogen bubbling for 15 min prior to the experiments. In all experiments the solution was stirred continuously using a magnetic stirrer at constant speed. The experiment was repeated for 0.5, 0.6, 0.7 and 0.8 V preparation voltages. The reactions monitored chronoamperometrically at each potential during polymerization.

Electrochemical experiments were carried out with an Autolab PGSTAT 30 (Eco Chemie) potentiostat. Electrolytic solutions were prepared from ultra pure water (Millipore MilliQ System). 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 cm^2.

Gelation times were determined visually from the motion of a magnetic stirrer in the electrochemical cell. The gel point was defined to be the time at which a slowing down of the magnet was first seen, and observed that they coincide with the maxima of the current-time curves.

3. Results and discussions

The silver electrode starts to be ionized and loses electrons as

$$\mathrm{Ag} \rightarrow \mathrm{Ag}^{+} + \mathrm{e}^{-} \tag{3}$$

when the potential is applied between the working and reference electrodes. At the same time, the free radicals start to form via persulfate dissociation on the silver electrode surface as [27],

$$^{-\cdot}\mathrm{OS{-}O{-}O{-}SO}^{\cdot-} \rightarrow {}^{-}\mathrm{OS{-}O}^{\cdot} + \mathrm{SO}_4^{2-}, \tag{4}$$

where SO_4^{2-} ions contribute to the conductivity of the polymeric solution.

Then, the free radicals attack the silver electrode,

$$^{-}\mathrm{OS{-}O}^{\cdot} + \mathrm{Ag} + \mathrm{H_2O} \rightarrow \mathrm{Ag_2O} + \mathrm{SO}_4^{2-} + 2\mathrm{H}^{\cdot} \tag{5}$$

thus, the silver electrode starts to be oxidized and a secondary free radical $\mathrm{H}^{\cdot}$ is produced.

At the same time oxidized silver is soluble in water

$$\mathrm{Ag}^{+} + \mathrm{H_2O} \rightarrow \mathrm{Ag} + \mathrm{H}^{+} + {}^{\cdot}\mathrm{OH} \tag{6}$$

As seen from the above relations, polymerization can be initiated via $^{-}O_3S–O^{\cdot}$, $H^{\cdot}$ or $^{\cdot}OH$ radicals, with corresponding probabilities.

In these experiments three parameters affect the current measured during the electrochemical reaction. One is the value of the voltage applied between working and reference electrodes, second is the number (or the concentration) of the charge carriers, and third is the mobility of the charge carriers. The radicals, although neutral, are highly electrophylic and act as charge carriers [21]. In general two populations of radicals may exist. Those on the cross-linked clusters may be slow or still depending on the stage of the gelation. Those on the linear chains will be mobile during the gelation process; these will be called 'free radicals' during this paper. The fact that the process is a solution or bulk polymerization changes the radical mobility and concentration completely. In solution polymerizations the final concentration of the radical goes to zero at the end of the reaction, whereas in the bulk polymerization the radical concentration increases continuously due to the trapping of the radicals in glassy regions [23].

In our case, the process is the solution polymerization of AAm/BIS system. Therefore, when the reaction is performed under a constant voltage both free electrons and free radicals will contribute simultaneously to the current as charge carriers.

Fig. 1 shows the evolution of the total current, I_{fe}, during the gelation time for different reaction voltages, at room temperature. A small decrease in the current appears in the initial period of the polymerization for low voltages. As the voltage is increased the decrease in the current gets smaller and disappears above 0.6 V, and also the initial period (in which the current decreases or remains constant) becomes shorter. Gelation times determined visually from the motion of a magnetic stirrer coincide with the maxima of the current-time curves.

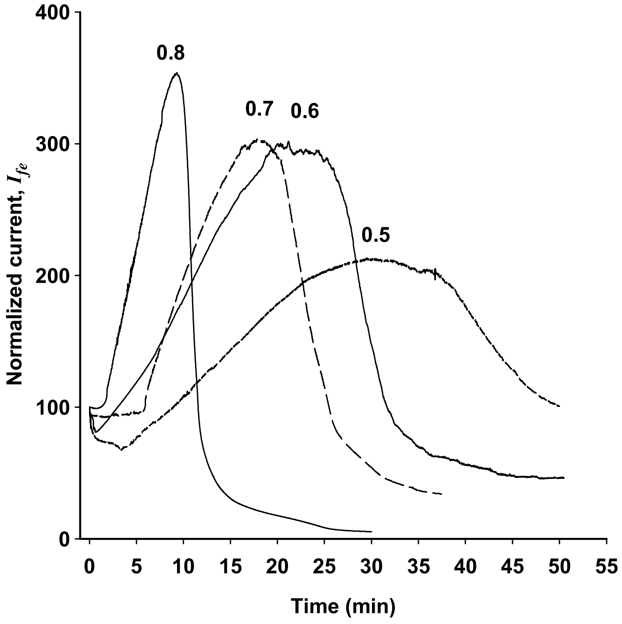

Fig. 1. Normalized current, I_{fe}, against the reaction time, during the AAm–BIS cross-linking co-polymerizations for different polymerization voltages. The numbers on the curves represent corresponding polymerization voltages.

The decrease or unchanging in current in the initial part of the reaction may be due to the decreasing mobility of the charge carriers because of the increasing viscosity throughout the medium. Another possibility for this decrease is that it may be due to formation of a blocking layer on the surface of the silver electrode (increasing viscosity in the close proximity of the silver electrode), at the first step of the reaction. This blocking layer of gel may not be able to diffuse into the solution in the case of low rotation speed of the magnetic stirrer in the solution. The subsidiary experiments, which will be introduced in the following paragraphs, showed that the blocking layer effect plays a crucial role upon the decrease or unchanging in the initial part of the curves in Fig. 1.

Having crossed the initial period discussed above, the currents first increase with time passes through a maximum and then decreases, for each voltage. This may indicate that the concentration of free radicals increases as the persulfate molecules turn into the free radicals, therefore, the current increases and goes through a maximum. The rate constants for initiation and termination of the free radicals change and overwhelm 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, while the termination rate constant overwhelms 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. [23]. The maximum for each curve corresponds to the slowing down of the stirrer, and shifts to longer times as the voltage is decreased. The maximum of the currents can thus be identified as the gel points, t_{gel}.

Some more experiments are needed to show surely that the change in the currents is mainly due to the change in the free radical concentration. Therefore, in the second part of the experiments, we measured the current for the samples including only APS dissolved in pure water. Fig. 2 shows the variation of the current due only to the free electrons, I_e, for different voltages as function of the time, where the concentration of APS was kept fixed for each voltage. As seen from the Fig. 2, the current for each voltage increases almost linearly with time. As the voltage is increased the slope of the curves increases, since more electrons are produced in the course of time, on account of Eq. (3).

We also performed additional experiments on the low concentrated polymers without cross-linker. The concentration of APS was kept fixed for each sample, 5×10^{-3} M, the same with the gelation experiments. The AAm concentration was changed up to 0.4 M for fixed reaction voltage, 0.6 V. The change in the currents for linear polymers is depicted in Fig. 3, for different concentrations. As seen from this figure, the intensity of the current, at any instant of the reaction, increases as the concentration of the monomer is increased. When the concentration of APS is zero nothing is measured.

The following points can be deduced as consequence of the above outcomes: (i) Free radicals contribute to the current, (ii) the concentration of the free radicals increases as

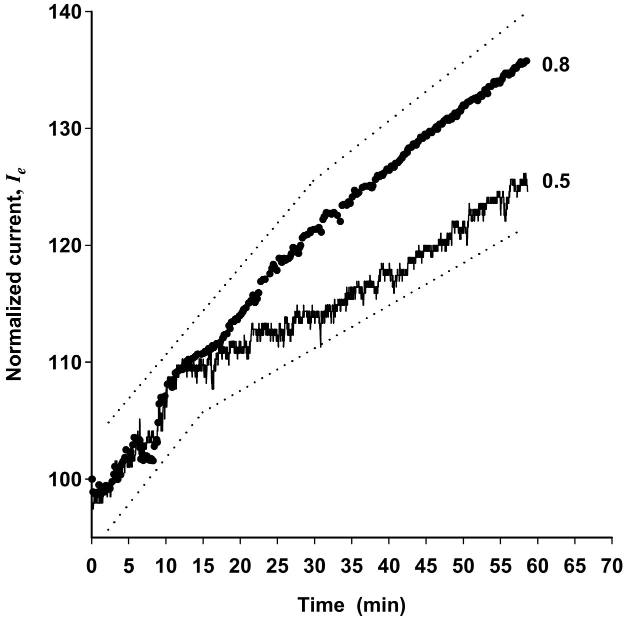

Fig. 2. Normalized currents, I_e, against the time, during the dissociation of persulphate on the silver electrode surface. The numbers on top of the curves represent corresponding polymerization voltages. The dotted lines are for eyes to show the points at which the trend of the currents starts to change.

the polymerization voltages and concentration of the monomers are increased. (iii) The fact that the decrease in the current for the initial period of the reaction was also observed for very low concentrated samples (see 0.2 M AAm in Fig. 3), indicates that this decrease is not due to the increasing viscosity throughout sample, but due to blocking layer formed in the close proximity of the silver electrode by polymer chains just at the beginning of the reaction, as pointed out above. The driving force on the charge carriers may be insufficient for relatively low voltages. Therefore, the high driving forces for the voltages above 0.6 V, may compensate the decreasing mobility effect of the charge carriers in the blocking layer. This is why the intensity decreases for low voltages and keeps constant for high voltages in the initial stage of the reaction. As more of the electrons and free radicals are produced, this initial effect is concealed. Therefore, the appearing effect of the initial period, for later times, will be just some shift in the total reaction time. Here it should be noted that this blocking effect may be reduced or disappeared as the effect of the convection increased by means of high stirring rates. (iv) The fact that the peaks appeared in Fig. 1 was also seen in the case of the linear polymers (sample of 0, 4 M in Fig. 3) where final form of the samples are viscous liquid in which the charge carriers can move freely, proves that the peaks are not due to Trommsdorff effect but due to the increasing free radical concentration upon the increased monomer concentration or reaction voltage. Especially for bulk polymerizations like poly (methylmethacrylate) and polystyrene [18,28–30], it is known that Thrommsdorf effect plays a major role upon the mobility of the free radicals [23]. Since the final gels, including 0.62 M AAm in our case, include 96% (w/w) of water, it can easily be concluded that change in the viscosity of the gel should not considerably affect the mobility of the charge carriers, free radicals and free electrons. Therefore, the main parameters determining the current during the polymerization, for a fixed voltage, are the numbers of free electrons and free radicals. (v) The rate of the production of the electrons on the silver electrode changes after some certain times (15 min for 0.5 V, and 30 min for 0.8 V, see Fig. 2) at which the oxidation of the silver may have been reached to the equilibrium with the competition of the processes given in relations (5) and (6).

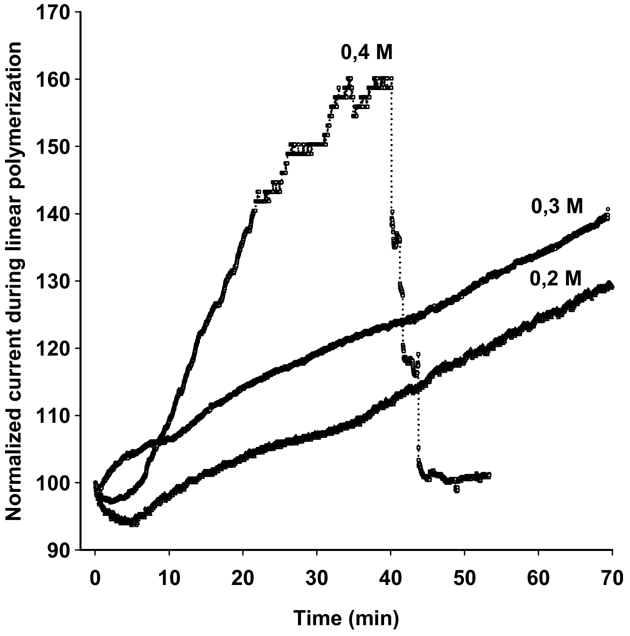

Fig. 3. Variation of the normalized currents during the low concentrated AAm polymerization (linear polymerization), at 0.6 V. The numbers on the curves represent corresponding AAm concentrations.

Here, we are going to argue that the current just due to the free radicals can be calculated using Figs. 1 and 2 together. Under the above conclusion (item iv), that the mobility of the charge carriers should not be affected considerably by monomer conversion, the contribution to current just due to free electrons during the polymerization should be in the same manner as in Fig. 2. Thus, the effect of the free radicals on the current can be obtained subtracting the data in Fig. 2 from the data in Fig. 1.

Fig. 4 shows the subtracted curves, $I_f = I_{fe} - I_e$, for the voltages 0.5, 0.6, 0.7 and 0.8 V. These curves for each voltage represent the current, I_f, just due to the free radicals created and annihilated during the polymerization process. The same behavior was recently observed by low frequency dielectric measurements [22].

Now, we would like to argue, using some similar arguments with Ref. [20], that the average cluster size, S of the polymers in the sol state (below t_{gel}), and the gel fraction, G in the gel state (above t_{gel}) are proportional to the current I_f due to free radicals, depicted in Fig. 4.

As stated above and also in Ref. [27] the Trommsdorff effect cannot be seen in our experiments. Therefore, it may be expected that average length of the polymer chains, and thus, the free radicals should obey a random distribution during the whole course of the polymerization under assumption that

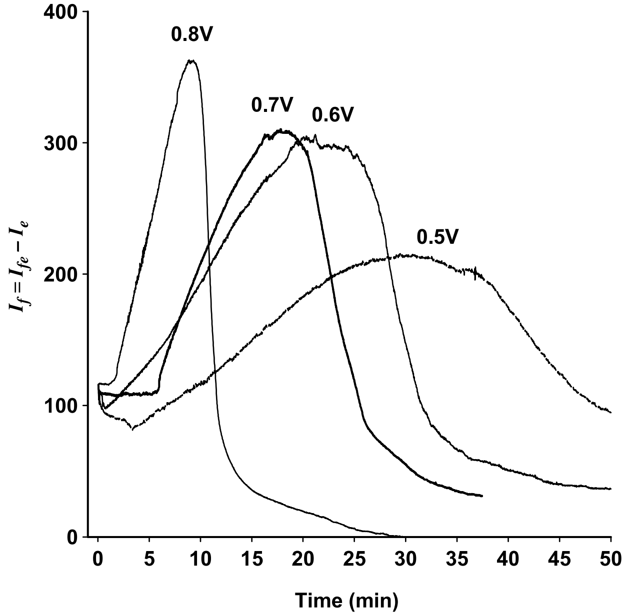

Fig. 4. Subtracted normalized currents, $I_f = I_{fe} - I_e$. I_f determines the contribution to the current just due to the free radicals.

the creation and annihilation of the free radicals occur randomly. Fig. 5 shows the fits of the Gaussian functions to curves in Fig. 4. As seen from the figure the data fits much more good to a Gaussian function if the voltage of the reaction is small, for 0.5 V. As the voltage is increased the data deviate considerably from the Gaussian behavior, especially after the gel point.

Another observation is that the equilibrium swelling behavior of the AAm gels [31], synthesized for the same concentrations and by the same way as in our case, is different for different voltages, so that the equilibrium degree of swelling is being less as the reaction voltage is increased. This behavior together with Fig. 5 can be evaluated as follows. As the voltage is increased the reaction is accelerated especially near the silver electrode, under the same stirring rate, and thus the resultant gel becomes more dense near the silver electrode. It may be assumed that, in that case, the gels will be, partially, more compact as get closer to the silver electrode. Therefore, the degree of the equilibrium swelling of these gels is being less as the voltage is increased. And, at the same time, the free radicals in this dens region may sense—up to some degree—the effect of increasing viscosity which may cause the concentration of the free radicals deviate from the Gaussian behavior.

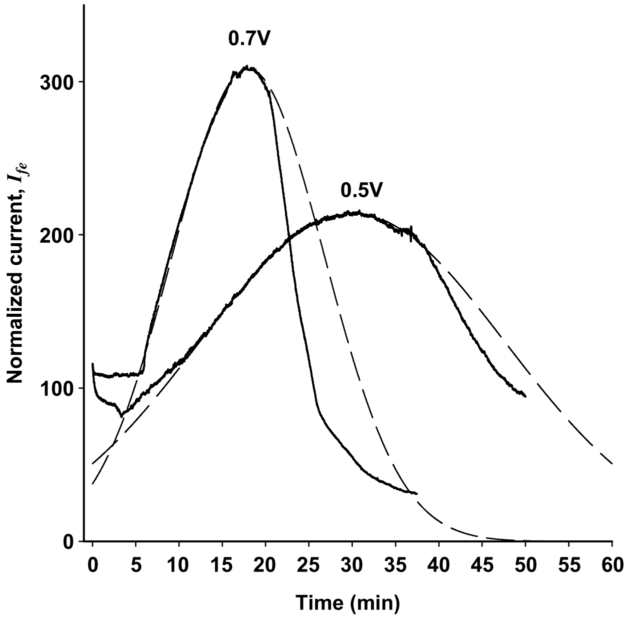

Fig. 5. Examples for fitting, I_f's to the Gaussian functions. The dashed lines represent the Gaussian functions fitted to the corresponding current data.

The total current just due to free radicals, I_f, is proportional to the total number of the free radicals, N_f at time t, $I_f \propto N_f$. Below the gel point, N_f can be interpreted as a summation over the number of the free radicals, N_s, existing in the clusters of size s (s is the total number of the units belonging to the cluster).

$$N_f(t) = \sum_s N_s. \tag{7}$$

We will take a cluster to be a set of occupied points on the lattice, which are nearest neighbor to at least one other member of the set [6]. Therefore, such nearest-neighbor occupied sites may be considered as belonging to the same cluster, regardless of whether they are chemically connected (i.e. belong to the same chain) or not. Here it should be noted that, especially below the gel point, some of the free radicals might not be included in any cluster. In this case, they form the clusters themselves in different sizes depending on the number of the units belonging to the chain of the free radical considered. We then argue that the free radicals contributing to current are precisely those which are trapped within interstitial regions of these clusters or they that form the clusters themselves. Since, below t_{gel}, there is no percolating cluster, the total normalized fluorescent intensity will be proportional to the average cluster size S. To see this, we argue as follows.

The probability that a site of a three-dimensional lattice belongs to a cluster of size s is given by $n_s s$, where n_s is the number of s-cluster (number of clusters including s sites) per lattice site [6]. Thus, the probability, w_s that a cluster contains exactly s site is,

$$w_s = \frac{n_s s}{\sum_s n_s s} \tag{8}$$

and thus the average cluster size, S is calculated by the following relation [6]

$$S = \sum_s w_s s = \frac{\sum n_s s^2}{\sum n_s s} \tag{9}$$

Now, let N_m be the total number of molecules in the reaction vessel (AAm, BIS, Water, and APS) except for the free radicals. Thus, the total lattice site, N is given as

$$N = n_{av} N_f + N_m \tag{10}$$

where n_{av} is the average number of the monomer that belong to each of the free radicals. This approximation could be appropriate especially in a narrow region near the gel point, where the standard deviation of the length of free radicals will be less enough as compared the whole reaction period.

The probability, P_{mf}, that an arbitrary monomer is an element of a free radical is simply $n_{\mathrm{av}}N_{\mathrm{f}}/N$. The probability, P_{fs}, that an arbitrary monomer both is an element of a free radical and this free radical is belongs to the s-cluster, can be calculated as a product of w_s and P_{mf},

$$P_{\mathrm{f}s} = P_{\mathrm{mf}} w_s = \frac{P_{\mathrm{mf}} n_s s}{\sum n_s s} \tag{11}$$

Thus, $P_{\mathrm{f}s}s$ will be the total number of free radicals in each cluster including s sites. The total current, I_{f}, which is proportional to the total number of free radicals localized in the finite clusters, can be calculated as a summation over all s-clusters

$$I_{\mathrm{f}} \sim \sum_s P_{\mathrm{f}s} s = \sum_s \frac{P_{\mathrm{mf}} n_s s}{\sum n_s s} s = \frac{\sum P_{\mathrm{mf}} n_s s^2}{\sum n_s s}$$

$$= \frac{n_{\mathrm{av}}}{N} \frac{\sum N_{\mathrm{f}} n_s s^2}{\sum n_s s}. \tag{12}$$

N_{f} in above relation can be taken out of the summation under the assumption that the total number of free radical do not change so much, at least in a narrow region around the gel point.

$$I_{\mathrm{f}} \propto \left(\frac{n_{\mathrm{av}} N_{\mathrm{f}}}{N}\right) S, \quad t \to t_{\mathrm{gel}}^{-} \tag{13}$$

Thus, the last expression shows that the total normalized current, I_{f}, is proportional to the average cluster size S, below t_{gel}. Note that the proportionality factor $n_{\mathrm{av}}N_{\mathrm{f}}/N$ is simply the fraction of the monomers belonging to the total free radicals in the sample cell, which could be accepted that it remains nearly constant around the gel point as seen from Fig. 5 (especially for sample of 0.5 V).

As the current starts to decrease above the gel point some of the free radicals will be terminated by joining the infinite network, therefore the gel fraction of the sample will increase as inversely proportional to the current I_{f},

$$G \sim I_{\mathrm{f}}^{-1}, \quad t \to t_{\mathrm{gel}}^{+} \tag{14}$$

Thus, the relations (1) and (2) take the following forms,

$$I_{\mathrm{f}} \propto S = A(t - t_{\mathrm{gel}})^{-\gamma}, \quad t \to t_{\mathrm{gel}}^{-} \tag{15}$$

$$\frac{1}{I_{\mathrm{f}}} \propto G = B(t - t_{\mathrm{gel}}), \quad t \to t_{\mathrm{gel}}^{+} \tag{16}$$

where the reduced concentrations $|p - p_{\mathrm{c}}|$ around the critical point was approximated as proportional to the $|t - t_{\mathrm{gel}}|$ [20,29–32]. A and B are the proportionality constants.

Using Eqs. (15) and (16), and the values for t_{gel} we calculated γ and β exponents as function of voltage for fixed AAm concentration of 0.62 M. Fig. 6 represents the log–log plots Fig. 5, for some typical current-time data above and below the gel point, where the slope of the straight lines, close to the gel points, give β and γ exponents, respectively. β and γ exponents agree best with the mean-field theory for low reaction voltages and deviates considerably from both mean-field and percolation results for higher voltage values, as seen in Table 1, together with corresponding t_{gel} values.

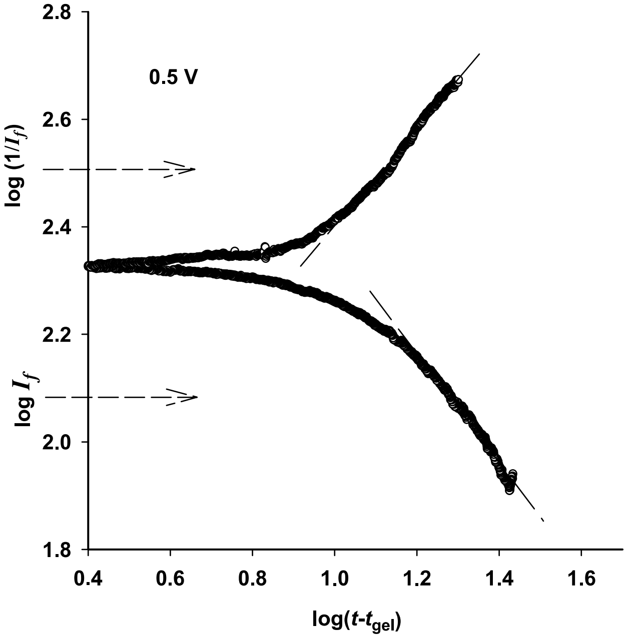

Fig. 6. Representative double logarithmic plot of the data in Fig. 4 for 0.5 V (a) and 0.8 V (b), log I_{f} versus log $(t - t_{\mathrm{gel}})$. γ and β exponents were determination from the slopes of the straight lines near the gel points. As seen, the scaling region comes closer to the critical point but the exponents differ from the mean-field values, as reaction voltage is increased.

Table 1
Experimentally measured critical exponents, β and γ, versus polymerization voltage

Voltage (V)	t_{gel} (min)	β	γ
0.5	30	1.0±0.1	1.0±0.1
0.6	22	1.4±0.2	1.1±0.1
0.7	17.9	1.2±0.2	–
0.8	9.4	1.2±0.2	–

4. Conclusion

In this study we argue that the current during the chronoamperometric measurements monitors the change in the free radical concentration, at least for loosely formed gels, during the free radical polymerization of AAm–BIS system. The number of the free radicals belonging to the clusters increases during the course of the polymerization below the gel point, and decreases above it. This variation in the free radical concentration—under the assumption that the fraction of the monomers belonging to the total free radicals in the sample cell do not varies considerably—obeys a Gaussian type of the distribution when the reaction voltage is chosen appropriate so as to not modify the local density of the gel around the silver electrode.

The values of the exponents deviate from the mean-field values for high voltages (see Table 1) because the local density of gel around the silver electrode differs drastically from the remaining part of the gel. Therefore, the samples for high voltages are driven out of the self similarity at the gel point, thus, they do not obey the scaling behavior about the critical point (especially below the gel point), for γ exponent, as can be seen form the Fig. 6 and Table 1.

It seems that we are able only to approach the critical point, for β exponent, to $|(p-p_c)/p_c| \geq 0.25$, and for the γ exponent to $|(p-p_c)/p_c| \geq 0.5$, for 0.5 V, as can be calculated easily from the Fig. 6a. The same calculations for 0.8 V gives the range of the critical region for β exponent as $|(p-p_c)/p_c| \geq 0.1$. The fact that $|(p-p_c)/p_c|$ decreases for high voltages means that we are coming more close to the gel point as the voltage is increased. This proves that the internal lower cutoff decreases near the silver electrode as the voltage is increased [20], but self similarity disappears (β exponents deviates considerably from both mean-field and percolation results, and γ exponents do not scales with time) due to local density differences comparable, most probably, to the macroscopic size of the gel.

Thus, it seems that the range of the scaling region $|(p-p_c)/p_c|$ is roughly in the mean-field class for low voltages, and modeled by the Flory–Stockmayer theory as previously discussed in a recent study [20].

The another important point for this study is that this technique may be a model for the directed percolation picture on which the events like the imbibitions in porous media, fluid–fluid displacement, bacterial colony growth, fire front motion, and the motion of flux lines in superconductors, for the researchers involved in this part of the problem.

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