

Testing percolation theory in the laboratory: Measuring the critical exponents and fractal dimension during gelation

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Real-time fluorescence measurements have been developed for measuring the fractal dimension d_f and critical exponents γ and β simultaneously during the sol-gel transition of acrylamide bisacrylamide cross-linking copolymerization. We observed that d_f passes through a minimum value of ~ 2.5 at a critical time t_c and crossover to 3 above it. The exponents γ and β , measured at t_c , were found to be around 1.8 and 0.45, respectively. All parameters d_f , β , and γ measured at the critical point t_c agree with three-dimensional percolation results.

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The gelation process was first discussed by Flory [1] and Stockmayer [2] where closed loops were ignored in the percolating picture and the gelation was modeled on a special type of lattice, the so-called Cayley tree. Then more realistic lattice percolation models [3–11], where monomers are thought to occupy the sites of periodic lattices, were used for studying the gelation process. A chemical bond between two monomers is represented by an edge between two neighboring lattice sites. Each bond is formed randomly with probability p . For a certain bond concentration p_c , defined as the percolation threshold, an infinite cluster (gel) is formed in the thermodynamic limit. The polymeric system is in the sol state below p_c .

The predictions of Flory-Stockmayer (mean-field) and percolation theories about the critical exponents for the sol-gel transition are different from the point of universality. Consider, for example, the exponents γ and β for the weight average degree of polymerization, DP_w , and the gel fraction G (average cluster size S and strength of the infinite network, P_∞ , in percolation language [5]) near the gel point. They are defined as

$$DP_w \propto (p_c - p)^{-\gamma}, \quad p \rightarrow p_c^-, \quad (1)$$

$$G \propto (p - p_c)^\beta, \quad p \rightarrow p_c^+, \quad (2)$$

where mean-field theory [1,2] gives $\beta = \gamma = 1$, independent of the dimension (D), while percolation theory gives γ and β around 1.8 and 0.42 for $D=3$ [4–7].

Using percolation theory, it was argued [5–7] that the largest clusters at p_c have a fractal behavior $M \propto L^{d_f}$, defined for the first time by Mandelbrot [12]. Here M is the mass of the cluster and L is the lattice size. The fractal dimension d_f of the infinite cluster formed at $p=p_c$ is about 2.5 [6,7]. The finite clusters formed at p_c have also the same fractal dimension for length scales smaller than or equal to the size of the clusters. Above p_c , both the infinite cluster and the finite clusters are no longer fractal; they form a three-dimensional

object. It is argued [7] on the basis of percolation theory that below p_c , the fractal dimension of the finite clusters is around 2, $d_f \sim 2$, in three dimensions.

The comparison of the percolation picture with real gelation has long remained inconclusive because of the insensitivity and inaccuracy of the experimental methods. The experimental techniques used for studying the sol-gel transition must be very sensitive to the structural changes and at the same time not perturb the system. Furthermore, in close proximity of the critical point, the data must be taken at very short intervals in order to sufficiently probe the critical region and obtain power-law relations. Even if all these conditions were fulfilled, determination of the position of the critical point p_c would be the main difficulty for critical point studies, because there is no unique way that has been discovered so far to determine the exact position of the critical point t_c in real experiments.

In a recent work [13] the free-radical cross-linking copolymerization of acrylamide-bisacrylamide (AAM-BIS) was studied using pyranine as a fluorescence probe, where the pyranine which is added to the prepolymerization solution in trace amounts showed a spectral shift to a short wavelength upon the initiation of polymerization. The pyranine molecules start to bind to acrylamide polymer chains via radical addition upon the initiation of the polymerization. The fluorescence spectrum of the bonded pyranines shifts from 512 nm to 427 nm. Thus, it allows one to monitor DP_w and G as clearly proved in Ref. [13].

In the present study, we have improved the technique used in Ref. [13] so as to measure the fractal dimension of polyacrylamide (PAAm) hydrogel during the gelation process at any instant of the polymerization and tested the percolation picture against real experiments.

Gels were prepared by using 1 M AAm (Merck) as monomer and 6.5 mM of bisacrylamide (Merck) as cross-linker by dissolving them in 25 ml of pure water. The initiator ammonium persulfate (APS, Merck) and the fluorescence probe pyranine concentrations were kept constant at 7×10^{-3} M and 4×10^{-4} M, respectively. The pre-gel samples were deoxygenated by bubbling nitrogen for 15 min. Experiments were performed at room temperature using tetramethylethylenediamine (TEMED) as an accelerator. The fluorescence measurements were performed with a fluorescence spectrom-

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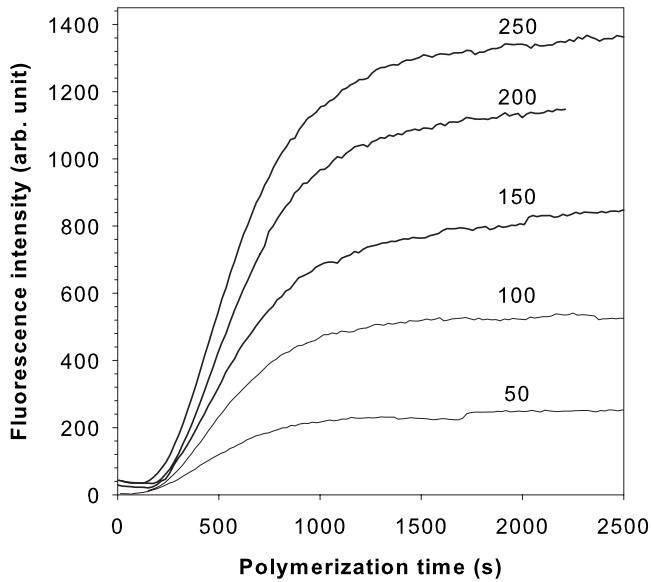


FIG. 1. The fluorescence emission intensities at 427 nm from five identical samples during the gelation processes. The numbers on the curves represent the corresponding slit width of the exciting light.

eter which was built in our laboratory. This instrument allows one to change the slit width of exciting light with a slit regulator that was mounted to the exit of the monochromator. The width of the slit was measured with a comparator that was mounted onto the slit regulator. The emission intensity was collected by means of a charge-coupled-device (CCD) array camera (Ocean Optics, USB2000). Having tested our new spectrometer with a LS50 Perkin & Elmer fluorescence spectrometer, the gelation experiments were carried out for five different slit widths of 50, 100, 150, 200, and 250 μm . The pre-gel samples were excited with 380 nm light, and the emission intensities were collected at 427 nm (corresponding to the maximum of the spectrum of bonded pyranine which increases with the monomer conversion) using the time acquisition mode of spectrometer. The fluorescence intensities presented in Fig. 1 were taken during the gelation of five identical samples each being monitored by different slit widths.

Here we argue that the data presented in Fig. 1 can be used to determine the fractal dimension of the AAm-BIS system *during the gelation process*. As previously discussed in Ref. [13], the fluorescence intensity from the gelling sample is directly proportional to the average cluster size S (or the weight average degree of polymerization, DP_w) at the same instant t , $I(t) \propto S(t)$. Therefore, the intensities given in Fig. 1 will be proportional to the mass M of the average cluster formed at time t , $I(t) \propto M(t)$.

In our experiments, the illuminated region of the samples is a rectangular prism in form. The height and depth of this illuminated region were kept fixed for each sample, and the width was changed by changing the slit width of the slit regulator. Therefore, the relation defining the fractal dimension $M \propto L^{d_f}$ takes the form

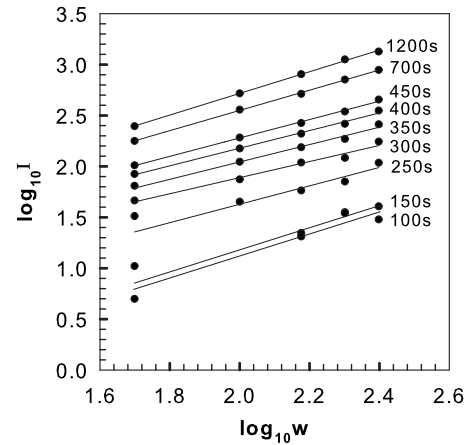


FIG. 2. The log-log plots of Eq. (3) formed, using the data in Fig. 1, for different time steps in between 100 s and 1200 s.

$$I = Aw^{d_f/3}, \tag{3}$$

where w is the width of the slit and A is a proportionality constant. Note that the exponent in Eq. (3) changes to $d_f/3$ since the illuminated region is scaled only in one dimension.

Using the data in Fig. 1, the intensities corresponding to certain times were recorded for each sample and the log-log plots of Eq. (3), $\log_{10} I = \log_{10} A + (d_f/3)\log_{10} w$, were formed for different time steps, as given in Fig. 2. The slope of each curve in Fig. 2 thus gives $d_f/3$ for the corresponding gelation time. The d_f is plotted in Fig. 3 as a function of the gelation time.

At the initial stage of the polymerization the monomer conversion is small and thus the number of pyranines attached to the polymer strands will be small as well, since the number of bonded pyranines increases with increasing monomer conversion [13]. Therefore, the intensities at the beginning of polymerization include large random errors. As the monomer conversion increases, the measured fluorescence intensities increase, and thus the experimental errors on d_f decrease as seen from Fig. 3. In spite of large random errors in the initial stage of the gelation, it is obvious from

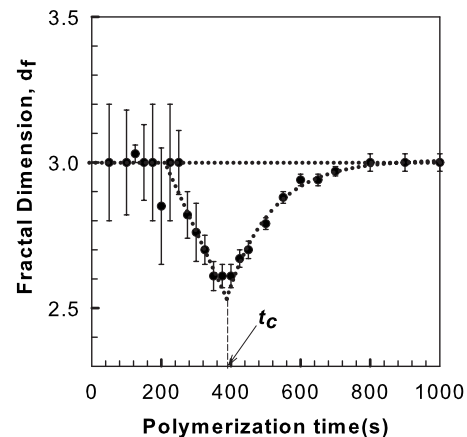


FIG. 3. Measured fractal dimension d_f during the polymerization.

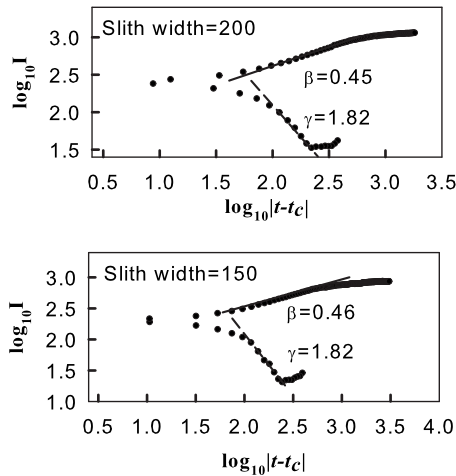


FIG. 4. Typical log-log plots of Eqs. (1) and (2) for the samples carried out for the slits 150 μm and 200 μm .

Fig. 3 that the fractal dimension passes through a minimum value of ~ 2.5 at a critical time t_c .

Here, we would like to report that the time t_c corresponding to the minimum of the d_f-t curve happens to be, at the same time, close to the bond percolation threshold $p_c = 0.2488$ [6] for a three-dimensional (3D) cubic lattice. The critical conversion p_c is defined as the critical ratio of the number of monomers which have been polymerized to the total number of monomers. Since the number of monomers converted to polymers will be proportional to the fluorescence intensity I , p_c can be defined as $p_c = I(t_c)/I(t_{\max})$ in terms of the fluorescence intensities taken from the gel at $t=t_c$ and $t=t_{\max}$. Using the data in Fig. 1 and taking t_c as the time corresponding to the minimum of d_f (Fig. 3), the average value of p_c was found to be 0.254 ± 0.003 , which happens to be very close to the percolation threshold [6].

Using a similar procedure to that given in Ref. [13], we calculated the exponents γ and β defined in Eqs. (1) and (2) near the critical point t_c . Figure 4 represents the log-log plots of Eqs. (1) and (2) where the slopes of the straight lines, near the gel point, give the exponents γ and β . We repeated this procedure for different times thought as the critical points and observed that the average values of γ and β coincide with the percolation results $\gamma=1.8$ and $\beta=0.45$ only if t_c is chosen as the time corresponding to the minimum of the d_f-t curve presented in Fig. 3.

It should also be noted that we are not able to measure the fractal dimension of the polymer clusters formed before the gelation threshold, where d_f is expected to be close to 2 [7],

but it seems that we measure it as 3 as can be seen from the initial part of Fig. 3. This unexpected result can be evaluated as follows: The mean mass M of the infinite cluster scales with the slit width w and the characteristic length (the correlation length) ξ above t_c [6]:

$$M \sim w^{d-\beta/\nu} \left(\frac{w}{\xi}\right)^{\beta/\nu} G(w/\xi). \quad (4)$$

Here, d is the space dimension and ν is the correlation length exponent. The scaling function $G(w/\xi)$ describes the crossover from $w/\xi \ll 1$ to $w/\xi \gg 1$. The expected results for our case in the two limits require that

$$G(w/\xi) \sim \begin{cases} (w/\xi)^{d/\nu}, & (w/\xi) \ll 1 \\ 3, & (w/\xi) \gg 1. \end{cases} \quad (5)$$

The scaling function G is an exponential function between these two limits as can be seen from Fig. 3. For $t < t_c$, the characteristic length scale ξ is of the order of the size of finite clusters. Here we are not able to observe the $(w/\xi) \ll 1$ part of the scaling function due to the insufficiency of our method to measure the fractal dimension of the small clusters formed below t_c . The radius of polymer clusters is roughly 0.05 μm [14] as an average which is smaller than our minimum length of scale, 50 μm . Therefore, we are not able to observe the inside of small clusters. The picture, thus, seems to be a 3D object at the beginning of the polymerization and, thus, we measure d_f as 3 instead of 2. As the clusters grow up and become sensible with our length scales, the crossover in d_f occurs from 3 to ~ 2.5 when the infinite cluster starts to appear. Therefore the minimum of d_f denoted as t_c is the sol-gel transition point or so-called percolation threshold.

In this work we report that steady-state fluorescence measurements can be used for real-time measurements of the fractal dimension and critical exponents γ and β simultaneously during the gelation process. We observed that d_f passes through a minimum value of ~ 2.5 at a critical time t_c and crossover to 3 above it. All parameters d_f , β , and γ measured at the critical point t_c agree with the best 3D percolation results, which may encourage one to use lattice approximations rather than classical approaches (mean-field theory or Flory-Stockmayer approximation) for polymer studies without hesitation.

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