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ARTICLES

Critical exponents and fractal dimension at the sol-gel phase transition via *in situ* fluorescence experiments

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Changes in solvent viscosity due to gel formation dramatically enhance the fluorescent yield of aromatic molecules. This effect is used to study the gelation of methyl methacrylate and ethylene glycol dimethacrylate as a function of time, at various temperatures, cross-linker concentrations, and toluene contents. The results are interpreted in view of percolation theory. The gel fraction and average cluster size exponents are found to be $\beta=0.42\pm0.03$ and $\gamma=1.70\pm0.02$, in excellent agreement with percolation results. The fractal dimension of the incipient cluster is determined to be 2.5 ± 0.2. The behavior of the time derivative of the fluorescence intensity is shown to satisfy finite size scaling. [S1063-651X(98)07611-9]

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I. INTRODUCTION

Gelation is the process by which sufficiently many monomers present in a solvent are joined together by chemical bonds such that a spanning network emerges. Once such a macroscopic network is formed, one speaks of the ''gel'' state. The state where no such network is present is called the ''sol.'' The chemical process by which monomers are joined together to form much larger molecules is known as polymerization. The ratio of the actual number of bonds that have been formed between the monomers as the polymerization progresses, to the total possible number of such bonds, is called the ''conversion factor'' p. This ratio is clearly a function of time. While it can also depend on the temperature, the concentration of monomers, or the concentration of crosslinking agents necessary for bond formation, experimentally one usually starts with a fixed composition and monitors the process in time. Thus, under controlled conditions, one observes that there is a sharply defined threshold, the ''gel point,'' where a macroscopic cluster starts to appear, signaled by the sudden, dramatic increase in the viscosity of the sample; this is commonly called the ''sol-gel'' transition.

Percolation [1] offers a particularly simple and yet detailed picture in terms of which one may seek to understand gelation [2]. In the language of percolation, one may think of monomers as occupying the vertices of a periodic lattice, and the chemical bonds as corresponding to the edges joining these vertices at any given moment, with some probability p. Then, the gel point can be identified with the percolation threshold p_c, where, in the thermodynamic limit, the incipient infinite cluster starts to form. Identifying the gel fraction G with the probability P_∞ of an occupied site to belong to the incipient infinite cluster, and the weight average degree of polymerization with the average cluster size S, one can predict the scaling behavior of these and related quantities near the gel point, as a function of $|p-p_c|$.

In spite of its great simplicity and obvious attraction, it has not so far been possible to establish the percolation picture of gelation in a quantitative and unequivocal way. In particular, one would like to measure the values of the critical exponents with sufficient accuracy to determine their universality class, and to verify that they indeed have the nonclassical values for percolation computed from series expansions and Monte Carlo studies as well as renormalization group theory. A main obstacle lies in the precise determination of the gel point and the critical region.

In this paper we would like to report on an *in situ* technique which enables us to surmount this difficulty, and makes it possible to directly measure the critical exponents β and γ for the strength of the infinite cluster and the average cluster size, as well as the fractal dimension of the percolat-

TABLE I. Experimentally determined values of β, γ, and t_c, during the gelation of samples with different crosslinker concentrations and toluene contents. The AIBN content was kept at 0.26 wt. % for all samples.

Sets	Gels	EGDM (10^{-3} Vol%)	Toluene (Vol%)	$T\pm2$ (°C)	t_c (s)	β	γ
1	1	5		75	2183	0.43	1.40
	2	7.5		75	1435	0.41	1.72
	3	10		75	1396	0.43	1.73
	4	12.5		75	1302	0.42	1.75
	5	15		75	1252	0.45	1.77
	6	20		75	1521	0.43	1.78
	7	30		75	873	0.42	1.70
2	8	2.5		85	1609	0.43	1.58
	9	5		85	1395	0.47	1.71
	10	7.5		85	926	0.43	1.43
	11	25		85	791	0.40	1.79
3	12	5		70	3072	0.41	1.82
	13	5		75	2392	0.42	1.54
	14	5		85	1239	0.43	1.59
4	15	10	0.075	75	2065	0.37	1.49
	16	10	0.100	75	1714	0.43	1.77
	17	10	0.130	75	1775	0.43	1.79
	18	10	0.140	75	2725	0.36	0.53
	19	10	0.150	75	1874	0.24	1.77
	20	10	0.180	75	2879	0.35	1.00
	21	10	0.230	75	3035	0.20	0.86

ing cluster. The exponents determined in this way agree, to a few percent, with the best known values for the percolation exponents in three dimensions and rule out the Flory-Stockmayer [3,4] values of $\beta=1$ and $\gamma=1$.

II. STEADY STATE FLUORESCENCE TECHNIQUE

The steady state fluorescence technique is based on the effect of the environment on the fluorescence yield of aromatic molecules. In the sol state, the energy spectrum of the linear and branched polymers in solution provides an energy sink for the rapid vibrational relaxation of the excited aromatic molecules, after the rate limiting transition from the ground state. In the gel, however, this static quenching is much reduced; the change in the absorption spectrum of the matrix due to the formation of the macroscopic polymer network results in a drastic increase in the fluorescence yield [5–9].

The change in the absorption spectra and fluorescence yields in solution can thus be related to the changes in solvent viscosity, and, as we shall demonstrate, provides an elegant way to monitor the sol-gel transition without disturbing the sample in any mechanical way. The effect of viscosity on low frequency, intramolecular vibrational energies of excited naphthalene in swollen poly(methyl methacrylate) (PMMA) latex particles has been reported recently by one of us [10]. In the present paper, we study the sol-gel transition in free-radical crosslinking copolymerization of methyl

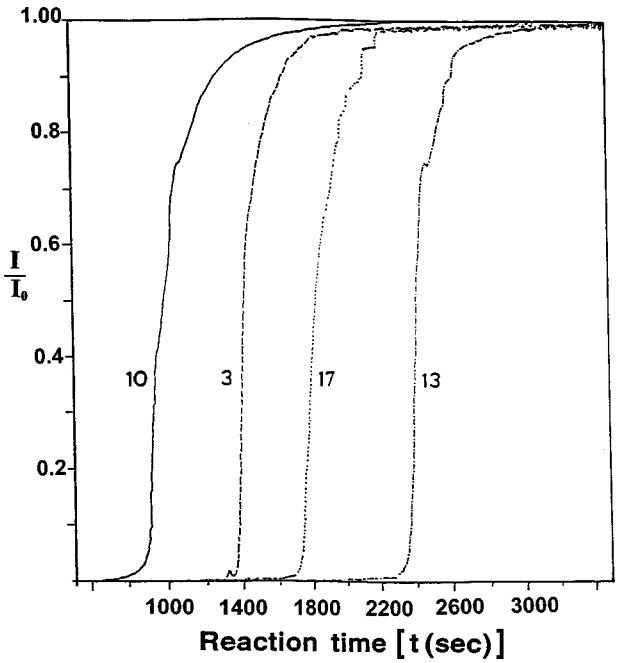

FIG. 1. Plots of pyrene fluorescence intensity I vs reaction time t during polymerization. Each curve has been normalized by its maximum value I_0. The numbers 3, 10, 13, and 17 correspond to samples from the experimental sets 1, 2, 3, and 4 in Table I.

methacrylate (MMA) and ethylene glycol dimethylacrylate (EGDM) using the steady state fluorescence technique.

The experiments with the radical copolymerization of MMA and EGDM were performed in the bulk or in toluene solutions at different temperatures, in the presence of 2,2′-azobisisobutyronitrile (AIBN) as an initiator. The aromatic molecule used as the fluorescent probe was pyrene. EGDM is a commonly used crosslinker in the synthesis of polymeric networks [11]. We freed the monomers MMA (Merck) and the EGDM (Merck) from the inhibitor by shaking with a 10% aqueous KOH solution, washing with water and drying over sodium sulfate. They were then distilled under reduced pressure over copper chloride. The initiator AIBN (Merck) was recrystallized twice from methanol. The polymerization solvent toluene (Merck) was distilled twice over sodium. Details of the sample compositions for all sets of experiments are listed in Table I. The pyrene concentration was the same for all the samples, 4×10^{-4} M. The samples were deoxygenated by bubbling nitrogen for 10 min, and the radical copolymerization of MMA and EGDM was performed directly in the fluorescence accessory of the spectrometer. Steady state fluorescence measurements were performed using the Model LS-50 spectrometer of Perkin & Elmer, equipped with a temperature controller. All measurements were made at the 90° position, i.e., the emitted light was monitored in a direction perpendicular to the existing light beam. The excitation and emission slit widths were both kept at 2.5 mm.

The pyrene molecule was excited at 345 nm, and the variation in the fluorescence emission intensity, I, was monitored with the time-drive mode of the spectrometer, by staying at the 395-nm peak of the pyrene emission spectrum. No shift was observed [12] in the wavelength of the maximum intensity peak during the gelation process. This allowed us to

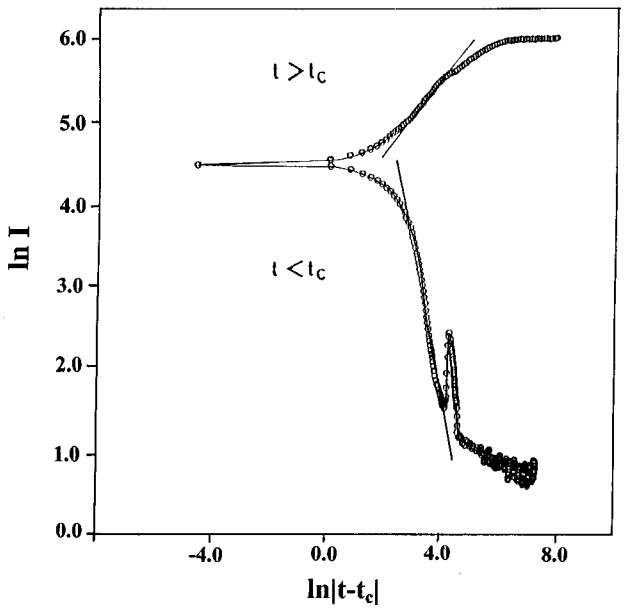

FIG. 2. The first derivative dI/dt of sample 3, against reaction time t. The maximum is consistently greater than the critical time t_c found from the plots in Fig. 3. See text.

take data in the time-drive mode, with a frequency of up to ten points per second, and thus be able to capture the very sharp rise near the critical point with great accuracy. All samples remained transparent throughout the experiment. We monitored the scattered light from the samples in the course of the sol-gel transition, and verified that no appreciable change occurred in the total scattered intensity of the 345-nm light.

III. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 1, we present our results for the normalized pyrene fluorescence intensities as a function of the reaction times, for different concentrations of crosslinking agents, different temperatures, and various degrees of dilution with toluene. The time derivative of the intensity is plotted in Fig. 2, and looks like a typical critical peak [13], with rounding due to finite size effects. Indeed, we will show that we can determine the position of the sol-gel transition on the time axis t_c with great precision, assuming

$$|p-p_c| \sim |t-t_c|, \tag{1}$$

at least in a narrow region about the gel point.

We would first like to argue that for $t>t_c$, the fluorescence intensity I monitors the growing gel fraction G, and for $t<t_c$ it is proportional to the weight average degree of polymerization, S. Before the formation of a macroscopic network, i.e., for $t<t_c$, the pyrene molecules are free to interact with—and be quenched by—the sol molecules. In this sol state, the fluorescence intensity becomes appreciable only to the degree that the pyrene molecules find themselves surrounded by the progressively larger clusters that are formed. The number of pyrene molecules trapped in the interior of a cluster, and therefore contributing to I, increases as the number s of monomers belonging to this cluster. Thus the total normalized fluorescent intensity will be proportional to the

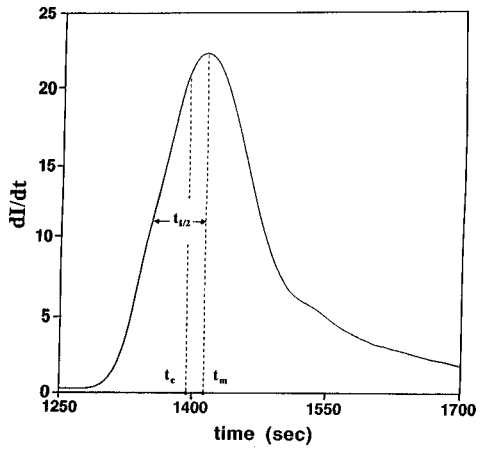

FIG. 3. Double logarithmic plot of data corresponding to sample 3 presented in Fig. 1. The region $10^{-2}<|1-t/t_c|<10^{-1}$ above and below t_c was fitted to the scaling laws given in Eqs. (3) and (4) to obtain the β and γ values; t_c is chosen as that point which yields the best fits in these regions.

average cluster size S. Above the gel point, i.e., for $t>t_c$, most of the pyrene molecules are trapped in the macroscopic network, and I then measures the gel fraction G, the fraction of the monomers that belong to the macroscopic network. In percolation language, the gel fraction can be identified with the ''strength'' [1] of the infinite cluster, in other words, the probability P_∞ that an occupied site on the diluted lattice belongs to the infinite network. In summary, we have

$$I \sim \begin{cases} S, & t<t_c \\ G, & t \geqslant t_c . \end{cases} \tag{2}$$

Now the scaling forms for the quantities S and G around the percolation threshold, together with Eq. (1), yields

$$I \sim G \sim A(t-t_c)^{\beta}, \quad t \to t_c^{+} \tag{3}$$

and

$$I \sim S \sim B(t_c-t)^{-\gamma}, \quad t \to t_c^{-} . \tag{4}$$

Here β and γ are the usual critical exponents for the strength of the infinite cluster and the average cluster size [1]. Notice that we need not subtract the value of $I(t_c)$ from $I(t)$in Eq. (3), since we are assuming that, once the threshold has been crossed, the unquenched fluorescence intensity is being contributed essentially by the monomers trapped in the incipient infinite cluster.

Using Eqs. (2) and (4) it is possible, in principle, to determine the exponents β and γ by making log-log plots of the intensity data. However, such a double logarithmic plot demands that the data be particularly accurate near the gel point. In particular, a small shift in t_c will result in large shifts in the exponents. The way to find the critical point in real experiments is to measure, and to perform the scaling analysis for, more than one quantity. The critical point can then be determined by varying t_c in such a way as to obtain good scaling behavior for both quantities over the greatest range in $|t-t_c|$. In this experiment, we fitted the double logarithmic plots of the fluorescence intensity vs $|t-t_c|$ for $t>t_c$ and $t<t_c$, to determine t_c very accurately. The results

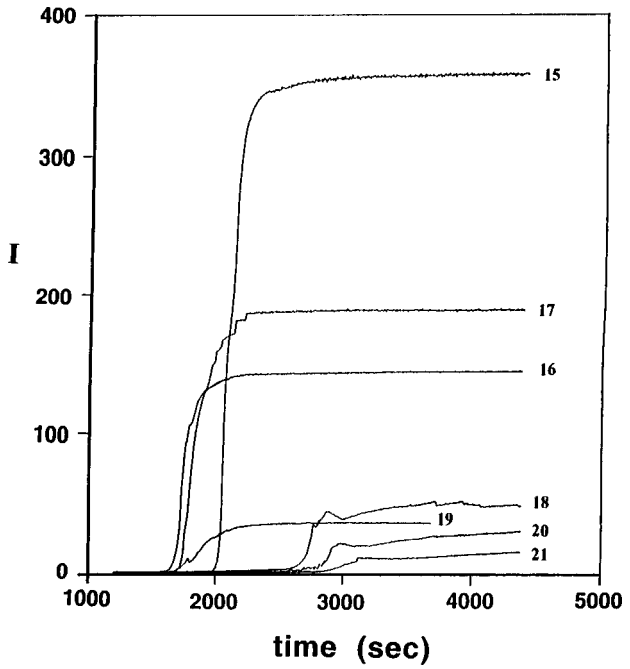

FIG. 4. Plots of pyrene fluorescence intensity I vs reaction time t for samples with different toluene contents. The labels 15–21 correspond to samples in the experimental set 4 in Table I.

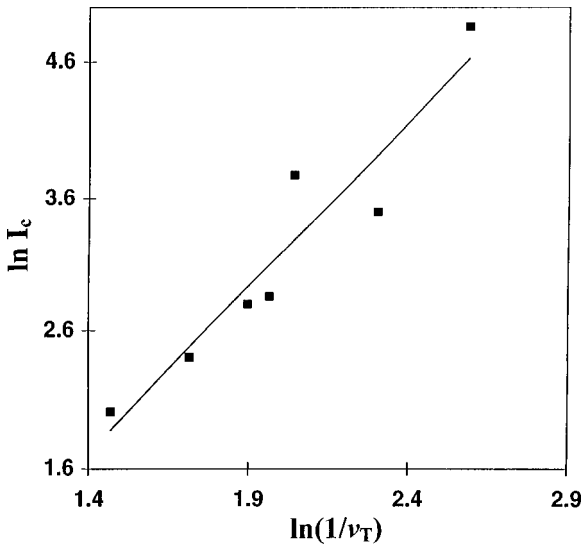

FIG. 5. Double logarithmic plot of the fluorescence intensity at the critical point I_c vs the volume fraction of toluene v_T for data presented in Fig. 4. See Eq. (10) in the text.

are shown in Fig. 3, with the values of the exponents given in Table I. The agreement with the known values ($\beta=0.41$, $\gamma=1.80$) of the percolation exponents in three dimensions is very good, especially over the first three sets, where the concentration is kept constant but the crosslinker density and the temperature are varied. We find $\beta=0.42\pm0.03$ and $\gamma=1.70\pm0.02$. Note that the fourth set of samples shows an increased degree of statistical scatter. This is not difficult to understand, since the voids of random size introduced into the polymer network may be very large, even macroscopic in size. Therefore, the measurements are no longer self-averaging but fluctuate from sample to sample. Improved statistics are needed for a better understanding of this dilute regime.

Naively speaking, one might guess that by taking the derivatives of the $I(t)$ curves, as was done in Fig. 2, the critical point may be obtained from the maxima of these curves. We found that the t_c obtained from the best scaling fits, as above, were consistently smaller than the times t_m at which the maxima of the dI/dt curves appear. Finite size scaling [1] predicts that the difference t_m-t_c vanishes as $L^{-1/\nu}$, where L is the size of the system as measured in units of the lattice spacing, and ν is the correlation length exponent. Moreover, the width of the dI/dt curve (which we argue behaves like the dP_∞/dp curve), measured at half height or any other conveniently chosen point, should be proportional to t_c-t_m and scale with the same power of L [1]. In agreement with finite size scaling, the ratio of t_m-t_c to $t_{1/2}$, the half width at half maximum of the dI/dt curves, was found to be a constant,

$$\frac{t_m-t_c}{t_{1/2}}=0.248\pm0.005, \tag{5}$$

over the whole range of experiments, with varying EGDM concentrations and for different toluene contents.

As can be seen from Fig. 4, there is an overall drop in the fluorescence intensity as the toluene content is increased, because even in the gel state the pyrene molecules are not completely shielded from the solvent, since the network is now more open and can be more easily penetrated by the solvent molecules. Although we have only preliminary results here, and more data points are needed due to the greater scatter, it is still possible to make a rough analysis of the effect of the addition of toluene. Using a Flory-type argument [3], we may estimate l, the expected minimum length of a strand between two branching points on the incipient percolating network, as a function of the toluene volume fraction v_T. This length serves as an effective lattice spacing, or the lower cutoff of the scaling regime of the percolating cluster. We will therefore use it to determine the fractal dimension.

We first compute the branching probability P_B—that is, the probability that not one but at least two monomers attach themselves to a given point on a chain of monomers. Let P_m be the probability of encountering a monomer at a randomly chosen point. Clearly, $P_m=V_m/V$, where V_m is the total volume occupied by the monomers, and V is the total volume of the sample. If $P_{\rm cl}$ is the crosslinker density, then

$$P_B=P_{\rm cl}\sum_{n=0}^{N}P_m^n, \tag{6}$$

where the sum is over all possible linear side chains of length n. Taking the upper limit N to infinity, since in practice N is of the order of the number of monomers in our sample, we find

$$P_B=P_{\rm cl}\left(\frac{1}{1-P_m}\right)=P_{\rm cl}\frac{V}{V-V_m}. \tag{7}$$

Since the crosslinker density is very small, the total toluene content $V_{\rm tol}\simeq V-V_m$. Using $v_T\equiv V_{\rm tot}/V$, we find P_B

$=P_{\mathrm{cl}}/v_T$. If we require that $n_0 P_B = 1$, i.e., that after n_0 links on the monomer chain, a branch point is formed with unit probability, we get $n_0 = v_T/P_{\mathrm{cl}}$; therefore,

$$l = \frac{a}{P_{\mathrm{cl}}} v_T . \tag{8}$$

Since the crosslinker concentration and the monomer size a are constant over all our samples, this result tells us that the toluene volume fraction is simply proportional to the internal lower cutoff.

We now note that the fluorescent intensity just above the gel point (I_c) must be proportional to the number of pyrene molecules effectively surrounded by the percolating network, and therefore, to the number (M) of cells, with linear dimensions of the order of the internal cutoff, contained in the percolating cluster.

This quantity scales with l to the fractal dimension, D_f [14,1], viz.,

$$M \sim l^{-D_f}, \quad t = t_c . \tag{9}$$

Using Eq. (8), we find

$$I_c \sim M \sim v_T^{-D_f}. \tag{10}$$

To determine the fractal dimension, we used relation (8) between the effective lattice spacing of the percolation network and the volume percent of toluene. (See set 4 in Table I.) The double logarithmic plot of I_c vs $(1/v_T)$is shown in Fig. 5. Although there is a large scatter in the data, the fractal dimension D_f was found to be 2.5 ± 0.2, to be compared with the best value [1] of 2.53.

An examination of Table I also shows that for relatively higher toluene contents, with correspondingly larger l, the values of β and γ start to deviate markedly from their expected values. Clearly, for larger l, finite size effects become more pronounced, driving the system further away from the asymptotic critical region. Moreover, the fluctuations in the local environment of the pyrene molecules become so large that even the monotonic behavior of the fluorescent intensity with time is lost for a number of samples as can be seen from Fig. 4.

In conclusion, we have used the steady state fluorescence technique to study the gelation process of methyl methacrylate and ethylene glycol dimethylacrylate, by monitoring the fluorescent light intensity as a function of time. The intensity is proportional to the average size of the polymeric clusters below the gel point, and to the gel fraction above the gel point. Its scaling behavior with respect to time yields the critical exponents β and γ, while, at the gel points, it scales with the fractal dimension D_f with respect to dilution. The values of all the exponents are found to be in close agreement with percolation results.

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