

## Critical exponents for the sol-gel transition

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Solutions of tetramethoxysilicon were reacted, using both acid and base as catalysts, until near the sol-gel transition. Portions of the reacting mixture were quenched by dilution, and the average cluster mass and correlation length were measured with use of static and dynamic light scattering. Critical exponents describing the divergences of the average mass and correlation length were found to be larger than the predictions of either the percolation or Flory-Stockmayer theory.

### I. INTRODUCTION

The qualitative features of gelation have been understood since the early branching theories of Flory and Stockmayer<sup>1-3</sup> (FS) yet many of the quantitative aspects of the sol-gel transition, such as the critical exponents, are still a subject of controversy.<sup>4</sup> In general it is accepted that gelation can occur in two extreme limits: "weak" (reversible) gelation, where the bonds are sufficiently labile that the system reaches thermodynamic equilibrium and "strong" (irreversible) gelation, where the bonds are stable to annealing. The structure of weak gels is independent of the reaction path, but depends only on the crosslink density, temperature, concentration, solvent quality, etc. For these weak gels a key issue is whether the critical behavior is described by the percolation model or the mean-field (FS) theory.

On the other hand, the structure of strong gels depends on the reaction path, so it is thought that the kinetic aspects of the growth process may be important in describing the final structure. In these strong gels, a central issue is whether a physically reasonable "kinetic gelation" model would exhibit a sol-gel transition in a different universality class than percolation. The answer to this question is not entirely trivial; for example, the Manneville-de Seize model of free-radical-initiated addition polymerization appears to exhibit a very broad crossover to percolation-like behavior near the critical point.<sup>5-7</sup>

A principle prediction of any theory of the sol-gel transition, however, is the exponents which characterize the critical behavior of static quantities such as the average cluster mass and radius, gel fraction, and elastic modulus. In this paper, we use static and dynamic light scattering to measure the exponents  $\gamma$  and  $\nu$  which give the divergence of the weight-average cluster mass and z-average cluster radius, respectively. Measurements were made beneath the gel point on diluted irreversible polycondensates of tetramethoxysilicon (TMOS), using both acid and base to catalyze the hydrolysis and condensation reactions.

Researchers undertaking the measurement of critical exponents for the sol-gel transition are met with the usual variety of difficulties and criticisms. A principle source of these is the uncertainty in determining the gel point and the extent of reaction. For strong gels it is not possible to cycle through the gel point, as one might cycle through

the temperature in a thermal phase transition; instead, the determination of the gel time  $t_{\text{gel}}$  is a one-shot proposal, with a sample-to-sample reproducibility of about 5%. Likewise, it is often not possible to directly determine the extent of reaction  $p$ , so it must be assumed that  $p \sim t$  in the vicinity of  $t_{\text{gel}}$ . Although this proportionality is undoubtedly true "very close" to the gel point, in real experiments the data are taken for nonvanishing  $\epsilon = |t_{\text{gel}} - t|/t_{\text{gel}}$ , and so a weak, nondivergent dependence of  $p$  on  $t$  would reduce the apparent critical exponents from their true values.

Some progress has recently been made by measuring certain ratios of critical exponents which do not require a determination of  $\epsilon$ . For example, the static scattering exponent<sup>8</sup> is  $\gamma/\nu$ , where  $\gamma$  and  $\nu$  describe the divergence of the weight-average cluster mass and z-average cluster radius, respectively. As described below, for *dilute* percolation clusters the scattering exponent is 1.6, whereas the mean-field prediction is 2. This scattering exponent has been reported by Martin and Keefer<sup>9</sup> for tetramethoxysilicon (TMOS) gels, and by Bouchaud *et al.*<sup>10</sup> for polyurethane gels. Both of these measurements are in agreement with the percolation model. In a similar vein, Schlosser and Leibler<sup>11</sup> determined  $\gamma/\nu$  for radiation-crosslinked polystyrene chains by directly plotting the average mass against the average radius, and found  $\gamma/\nu = 1.72$ , again in good agreement with the percolation model. Earlier measurements by Schmidt and Burckhardt<sup>12</sup> on the divinylbenzene/styrene system gave  $\gamma/\nu = 2$ , however, in support of the mean-field theory.

### II. THEORY

The growth of the sol near the gel point was first described by Flory and Stockmayer,<sup>1-3</sup> who found that the average mass and correlation length diverge as inverse powers of  $\epsilon = |p_c - p|$ , where  $p_c$  is the extent of reaction at the gel point. The FS results are

$$\begin{aligned} M_w &\sim \epsilon^{-\gamma}, \\ R_z &\sim \epsilon^{-\nu}, \end{aligned} \quad (1)$$

where the exponents  $\gamma$  and  $\nu$  are 1 and  $\frac{1}{2}$ , respectively. The FS exponents are thought to suffer from several approximations. The model is formulated on an "ul-

trametric" Bethe lattice (making the model dimension independent), so clusters with circuits are excluded, sites within a cluster have equal reactivity, and excluded volume effects are not taken into account. As a result of these approximations, the fractal dimension of a typical cluster is predicted to be 4. In three dimensions this leads to an unphysical divergence of the density  $\rho = M/R^3 \sim R$  of the typical cluster as the gel point is approached.

Stauffer<sup>13</sup> and de Gennes<sup>14</sup> pointed out that since the percolation model avoids these approximations it might improve on the FS theory. In the three-dimensional percolation model the average mass and radius are more strongly divergent than in the FS model, with  $\gamma = 1.76$  and  $\nu = 0.88$ . This value of the exponent  $\nu$  pertains to the percolation model in its *undiluted* state. In order to measure the average mass and radius of the clusters, however, it is first necessary to dilute the sol. Isaacson and Lubensky<sup>15</sup> have used a Flory-type theory to argue that when the sol is diluted the clusters swell. In short, in the concentrated state two-body interactions within a particular cluster are screened by the surrounding sol. The screening diminishes the two-body contribution to the free energy by  $1/N_w$ , where  $N_w$  is the weight-average degree of polymerization of the sol, which depends on  $\epsilon$ . When the system is diluted, however, the surrounding sol is replaced by a simple solvent and the greatly diminished screening is independent of  $\epsilon$ . The net effect of the dilution is to swell the clusters, changing the fractal dimension  $D$  of a single cluster whose radius is smaller than the correlation length from 2.5 to 2.

The magnitude of this swelling is dependent on the cluster radius, and so affects the exponent  $\nu$ . Letting  $\bar{R}_z$  and  $\bar{D}$  denote the correlation length and fractal dimension in the diluted system we have  $\bar{R}_z^{\bar{D}} \sim R_z^D \sim \epsilon^{-\nu D}$ , which gives

$$\bar{R}_z \sim \epsilon^{-\nu D / \bar{D}} = \epsilon^{\bar{\nu}}. \quad (2)$$

The numerical value of  $\bar{\nu}$ , to which our data are to be compared, is then  $0.88 \times (2.5/2) = 1.1$ . Since all of the data we report here are for dilute clusters, we will not continue to explicitly use the symbols  $\bar{R}_z$  etc., in the discussion of results.

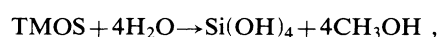
Before giving the experimental results for the TMOS/methanol system, it is worth commenting on the effect of solvent in these experiments, and whether or not one should even expect the percolation model to apply. In practice, the amount of monomer in these gels is small, of the order of 6% by weight, calculated as  $\text{SiO}_2$ . And our own experiments have shown that TMOS gels can be made with less than  $\frac{1}{25}$  of this starting material. At these very low weight fractions of monomer it is very likely that the monomer itself does not site percolate. That is, in the absence of monomer-monomer interactions (an athermal solvent), there is probably not a connected path of infinite extent of neighboring silica monomers, and the system cannot bond percolate without the introduction of spatial correlations in the final, undiluted gel.

This implies that there are two correlation lengths in these low-density silica gels: a connectivity correlation length (the  $z$ -average cluster radius), and a spatial correlation length  $\xi$ . The connectivity correlation length

diverges at the gel point, whereas in a typical clear gel the spatial correlation length is nondivergent at the gel point.<sup>4</sup> Since the elementary percolation model is a transition in connectivity alone, it cannot explain the presence of a finite correlation length in the *undiluted* gel. Therefore, in an experiment such as this it is important to measure the divergence of the connectivity correlation length on length scales which are large compared to the correlation length of the *undiluted* gel. If this elementary condition is not satisfied, then one may be investigating a process which is in a different universality class than the connectivity transition. In the light-scattering experiments described here, this condition is easily satisfied, since the spatial correlation length in the undiluted gels is on the order of 10 nm.

The nature of the spatial correlation length of the undiluted gel is not well understood, particularly since it is not apparent whether an equilibrium or kinetic model should describe the early stages of growth in the silica system. However, it is reasonable to expect a dilute *equilibrium* gel to be described by correlated site percolation,<sup>4</sup> which introduces the bond probability through a nearest-neighbor attractive interaction between sites. The extent of reaction is then increased by reducing the "temperature." If the initial concentration of monomer is sufficiently high, this model gives a sol-gel transition with percolation exponents, and a finite spatial correlation length at the sol-gel transition. On length scales small compared to the spatial correlation length, the pair-correlation function of the undiluted gel will be described by the Ising model, so  $I \sim q^{-2}$  (here  $I$  is the scattered intensity and  $q$  is the momentum transfer).

The silica system, however, is complex, due to the limited solubility of silicic acid in methanol. This silicic acid is formed from the hydrolysis of TMOS,



and is produced in quantities which exceed the solubility of silicic acid in methanol. Under some circumstances this can lead to the nucleation and growth of monodisperse silica particles of radius  $b$ , which then aggregate to form a gel. This kinetic gelation can be thought of as occurring in two stages. In the first stage of gelation silica particles aggregate to form small fractal clusters, of fractal dimension  $D$ . The volume fraction of these clusters,  $\phi = (R/b)^{d_c} \phi_0$ , increases from the initial volume fraction  $\phi_0$  with the average radius raised to the condimension  $d_c = d - D$  ( $d$  is the spatial dimension). Eventually the volume fraction approaches unity, at a radius  $R \sim b/\phi^{1/d_c}$ , and spatial correlations no longer develop.

In the second stage of growth the connectivity correlation length increases as the clusters react to form very large, overlapping clusters, which eventually form a gel. We reiterate that in the experiments we are about to describe, the spatial correlation length of the undiluted gel is very much smaller than the radius of the diluted clusters. Thus we are investigating this second regime of growth, where the clusters are highly overlapped, and *only* the connectivity is diverging.

A kinetic model of this type has been proposed by Kolb and Herrmann,<sup>16</sup> who extended two-dimensional

*diffusion-limited* cluster-cluster aggregation simulations to high initial particle densities. In the second stage of growth they found a fractal dimension of  $1.75 \pm 0.07$ , which is much larger than the low-density value of  $1.42 \pm 0.05$ , and somewhat smaller than the percolation value of 1.89. More importantly, however, for the physically reasonable case where the cluster mobility depends on the inverse radius they did not observe a gel point at finite time. It is possible that even in a kinetic model of gelation this second regime is simply percolation of the clusters which are formed in the first stage of gelation, in much the same way that the Manneville-de Seize model of kinetic gelation appears to eventually crossover to percolation of the chains formed in the first stage of growth.

### III. EXPERIMENTAL

Silica gels were made from solutions of tetramethoxysilicon (TMOS) and water, in a stoichiometric molar ratio of 1:4, using a methanol solvent. The hydrolysis and condensation reactions were catalyzed by two methods; a one-step base catalysis, and a two-step sequential acid/base catalysis. In the two-step catalysis the solutions were incubated with HCl for several minutes to promote the hydrolysis of TMOS to silicic acid. Then an excess of base was added to catalyze the condensation of siloxyl groups to Si—O—Si bonds (bridging oxygens). The detailed recipe for the 1 molar base gels is 14.9 ml TMOS, 7.2 ml H<sub>2</sub>O, and 4 ml of 0.109M NH<sub>4</sub>OH to 100 ml total volume with methanol. The acid/base-catalyzed gels were made in the same molar ratios, except that in the first step 0.10 ml of 0.10M HCl is added, followed by the addition of 4 ml of 0.109M NH<sub>4</sub>OH after 4-min incubation time. These solutions were filtered with 0.2- $\mu$ m Millipore filters immediately after the addition of catalyst. Both catalytic schemes gave gels in approximately 160–170 min.

To determine the hydrodynamic radius of the diluted clusters, dynamic light-scattering measurements were made with a He-Ne laser operating at 632.8 nm, and an argon-ion laser operating at 514.5 nm, giving an accessible length scale regime of  $34 \text{ nm} < 1/q < 440 \text{ nm}$  [in terms of the wavelength in the scattering medium  $\lambda$  and the scattering angle  $\theta$ ,  $q = 4\pi \sin(\theta/2)/\lambda$ ]. A 256 channel Langley-Ford autocorrelator was used to accumulate the intensity autocorrelation functions, on samples diluted a factor of 250:1 with methanol. The intensity, or homodyne, autocorrelation functions were fit using a second-order cumulant analysis, and the initial decay rate of the heterodyne function, obtained as the first cumulant  $\Gamma$ , was used to calculate the *apparent* hydrodynamic radius,  $R_h = q^2 kT / (6\pi\eta\Gamma)$ , where  $\eta$  is the solvent viscosity. This hydrodynamic radius is a z-average quantity and so diverges with the same power of  $\epsilon$  as the radius of gyration.

To determine the average cluster mass and radius of gyration, static light-scattering measurements were made with a commercial Chromatrix KMX-6, operating at 632.8 nm. This instrument covered the range  $900 \text{ nm} < 1/q < 2200 \text{ nm}$ . These light-scattering data were combined with static light-scattering data from the home-built

instrument by calibrating each instrument with a filtered methanol standard. The weight-average cluster mass and the z-average radius were obtained from the intercept and slope of a Guinier plot of  $I/c$  versus  $q^2$ . Extrapolations were made to zero wave vector and concentration, by running 50:1 and 250:1 dilutions at three scattering angles.

In order to calculate the average molecular weight from the light-scattering data, it was necessary to determine the refractive index increment of the sol,  $dn/dc$ , as a function of the extent of reaction. These measurements were made on a commercial Brice-Phoenix differential refractometer. It was found that  $dn/dc$  increased with the extent of reaction, so the data were corrected for this effect.

### IV. RESULTS

#### A. Static light-scattering measurements

For a fractal system the scattering per unit concentration is expected to be of the form  $I/c \sim M_w f(qR_z)$ , where  $f(x) \sim x^{-\mu}$  for  $x \gg 1$ . The scattering exponent  $\mu$  can be defined through the relation

$$R_z^\mu \sim M_w \quad (3)$$

Thus for  $qR_z \gg 1$  the scattered intensity becomes independent of the length scale  $R_z$ ,  $I/c \sim q^{-\mu}$ , and the intensity ultimately does not increase with the extent of reaction. For a simple, monodisperse solution of fractals  $\mu$  is just  $D$ , the fractal dimension of a single cluster. However, for a gelling system, where the distribution of cluster masses is characterized by the slow algebraic decay

$$N(m) \sim m^{-\tau} h(m/R_z^D) \quad (4)$$

the scattering exponent is  $D(3-\tau)^8$  [in the percolation model  $\tau = (d+D)/D$ , where  $D$  refers to a typical cluster in the unswollen state]. From (1) it is thus observed that  $D(3-\tau) = \gamma/\nu \sim 1.6$  for dilute (swollen) percolation clusters.<sup>8,10</sup>

Near the gel point 1-ml aliquots of the reacting solution were withdrawn and diluted 250:1 for light-scattering measurements. The growth of the scattering function is shown in Fig. 1 for the two-step catalysis. It is seen that as the gel is approached, the scattering function crosses over to power-law decay at progressively smaller values of  $q$ , indicating the formation of larger clusters near  $t_{\text{gel}}$ . Near the gel point the observable portion of the scattering function is pure power law, with an exponent of  $1.67 \pm 0.06$ , in good agreement with the swollen percolation cluster prediction of 1.6, and in excellent agreement with the value of  $1.69 \pm 0.06$  reported previously by Martin and Keefer.<sup>9</sup> Measurements on the base-catalyzed gels gave a scattering exponent of  $1.6 \pm 0.06$ , which is only marginally lower than the acid/base exponent.

In Fig. 2 the radius of gyration is plotted versus the cluster mass, as an alternate method of determining the exponent  $D(3-\tau)$ . It should be observed that near the gel point the clusters become quite large, with measured values of the radius exceeding 2000 nm, and molecular weights exceeding  $10^9$ . This value of the radius is essentially at the resolution limit of the light-scattering instru-

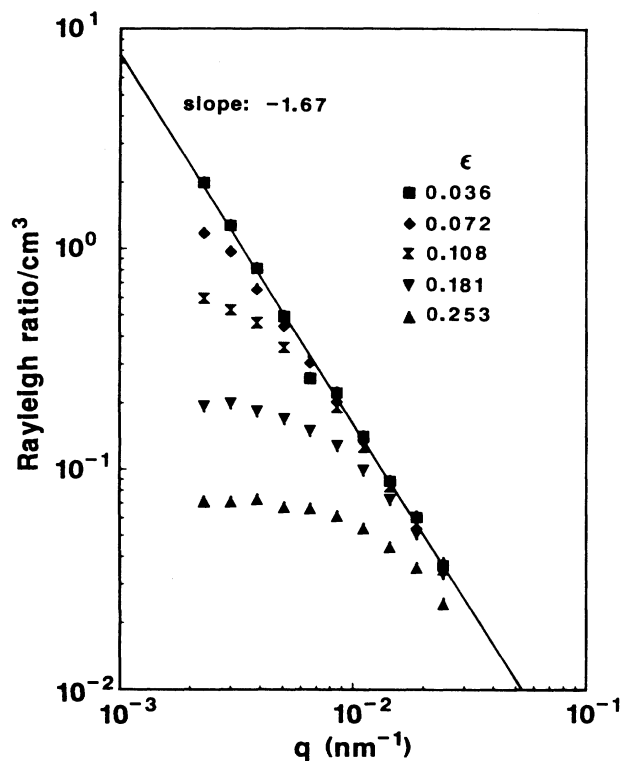


FIG. 1. The scattered intensity approaches a limiting slope of  $1.67 \pm 0.06$  as the acid/base-catalyzed TMOS system approaches the gel point. This agrees with the swollen percolation cluster prediction of  $D(3-\tau) = 1.6$ . At all values of the extent of reaction  $\epsilon = |t_{\text{gel}} - t| / t_{\text{gel}}$  aliquots of the reacting mixture were diluted 250:1 to make these measurements.

ment, so it was not possible to make meaningful measurements closer to the gel point. It is found that  $R_g^{1.79} \sim M_w$ , which agrees reasonably well with the experimentally determined scattering exponent. As seen from the scatter in the data, the errors associated with this determination of  $D(3-\tau)$  are somewhat larger than the error from the

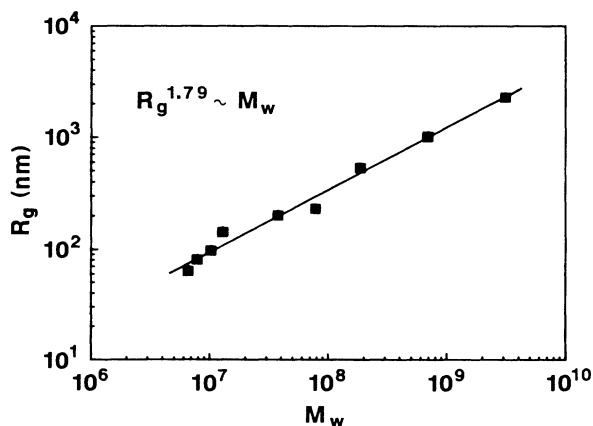


FIG. 2. The z-average radius of gyration is shown to scale as a power of the weight-average cluster mass for an acid/base-catalyzed system. The effective fractal dimension,  $D(3-\tau) = 1.79 \pm 0.12$ , is in good agreement with the value of  $1.67 \pm 0.06$  taken from the intermediate scattering data in Fig. 1.

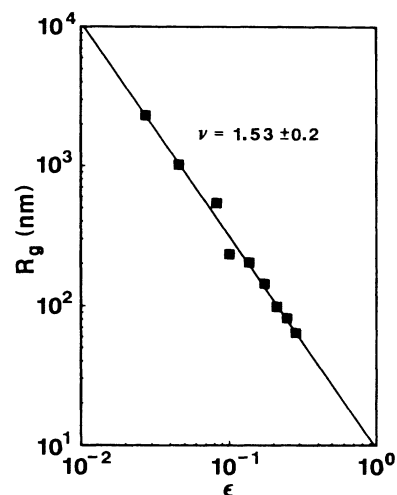


FIG. 3. The z-average radius of gyration is shown to diverge as  $\epsilon^{-1.53 \pm 0.2}$ , where the error of  $\pm 0.2$  reflects the uncertainty in the time of gelation. This value of  $\nu$  is larger than either the swollen percolation cluster prediction of 1.1 or the mean-field prediction of 0.5.

scattering function, so the scattering value of  $1.67 \pm 0.06$  is a more reliable number.

The study of the kinetics of growth is more difficult than the determination of the exponent  $D(3-\tau)$ , since the analysis of growth data depends on an accurate assessment of the gel point. The ability to measure the gel point turned out to be the largest source of error in these measurements, so a discussion of this aspect of the measurements seems worthwhile. In practice, upper and lower bounds were found for  $t_{\text{gel}}$  by extracting a series of

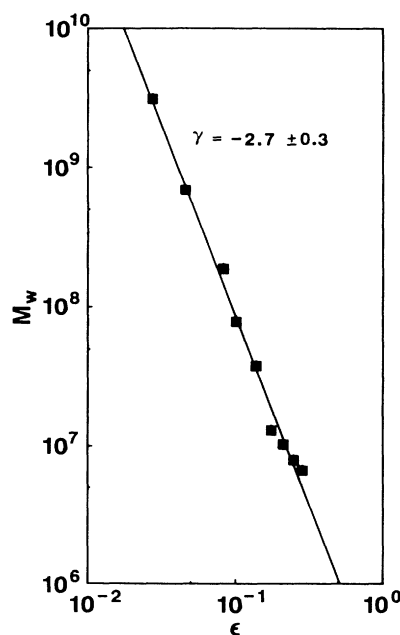


FIG. 4. The critical exponent for the weight-average cluster mass is  $\gamma = 2.7 \pm 0.3$ . This is to be compared with the percolation prediction of 1.76 and the mean-field prediction of 1.

small aliquots of the reacting solution near the gel point, and diluting these with methanol. At some point it was found that the aliquot was insoluble, indicating that the sample was taken beyond the sol-gel transition. This time  $t_{\max}$  was taken as an upper bound for  $t_{\text{gel}}$ , and the time the previous aliquot was taken  $t_{\min}$  was used as a lower bound.

The gel point was nominally taken to be the midpoint of this time interval  $t_{\text{gel}} = (t_{\max} + t_{\min})/2$  and the exponents we report here were obtained by a linear fit to the growth data on log-log axes. However, the errors we report for this exponent are not the errors associated with the linear regression, which are relatively small, but are calculated by repeating the data analysis with both  $t_{\max}$  and  $t_{\min}$  taken as the gel point. This error is much larger than the fitting error, and is a much more realistic determination of the true uncertainties in the critical exponents. Extrapolation methods, discussed in detail below, were also used to find  $t_{\text{gel}}$ , as a check on this direct determination.

The data for the growth of the radius of gyration are shown in Fig. 3. Throughout the entire range of time ( $0.027 < \epsilon < 0.028$ ,  $\delta\epsilon = \pm 0.009$ ) the radius of gyration apparently diverges as  $\epsilon^{-1.53 \pm 0.2}$ , including data which are not very close to the gel point. This broad critical regime is surprising, but is convincingly demonstrated by the hydrodynamic radius data discussed below, where the uncertainties in the measurements are smaller. This value of  $\nu$  is notably larger than the swollen percolation prediction of 1.1, and compares even less favorably with the FS prediction of  $\frac{1}{2}$ .

The result for the divergence of the molecular weight Fig. 4 is similar. The measured value of  $\gamma = 2.7 \pm 0.3$  is much larger than the percolation prediction of  $\gamma = 1.76$  or the FS prediction of  $\gamma = 1$ . Of course, the ratio of  $\gamma/\nu$  is 1.76, in agreement with Fig. 2. Thus, although the effective fractal dimension of the polydisperse ensemble agrees quite well with the swollen percolation model, the measured divergences in the silica system are stronger than the percolation predictions.

### B. Dynamic light-scattering measurements

Since the hydrodynamic radius  $R_h$  is a z-average radius, it will diverge with the same power of  $\epsilon$  as the radius of gyration. This gives us a second, relatively accurate method of determining the exponent  $\nu$ . However, the analysis of these dynamic light scattering data from the diluted sol requires a brief explanation. In the dynamic light-scattering experiment the mean decay rate  $\Gamma$  is obtained from the first cumulant of the intensity autocorrelation function. This decay rate is simply the linewidth of light scattered by the medium. It can be shown that the scattering linewidth from a power-law polydisperse ensemble of rigid or flexible scatterers is of the form<sup>8,17</sup>

$$\Gamma = q^2 D_z F(qR_z) \quad (5)$$

where  $D_z$  is the z-average diffusion coefficient  $D_z = kT/6\pi\eta R_h$ . If the polydispersity exponent is greater than 2, as it is for systems which exhibit a sol-gel transi-

tion at finite time, then  $F(qR_z)$  has the limiting behaviors<sup>8,17</sup>

$$F(qR_z) = \begin{cases} 1, & qR_z \ll 1 \\ qR_z, & qR_z \gg 1 \end{cases} \quad (6)$$

Thus, when  $qR_z$  is small the hydrodynamic radius can be obtained from the linewidth through  $R_h = q^2 kT / (6\pi\eta\Gamma)$ . However, when  $qR_z$  is much larger than 1 the linewidth becomes completely independent of the length scale and  $\Gamma \sim q^3 kT / \eta$ . This can be restated by defining an *apparent* hydrodynamic radius through  $R_{\text{app}} = q^2 kT / (6\pi\eta\Gamma) = R_h / F(qR_z)$ . This apparent radius decreases as  $1/q$  in the asymptotic  $\Gamma \sim q^3$  regime.<sup>9</sup>

To illustrate this effect,  $R_{\text{app}}$  versus  $q$  is plotted in Fig. 5 for a wide range of extents of reaction. At short times (small clusters)  $R_{\text{app}}$  is essentially independent of  $q$ , whereas very near the gel point (large clusters)  $qR$  is greater than 1 and  $R_{\text{app}}$  scales like  $1/q$ . Alternatively, the same effect can be seen by taking measurements on successively larger samples while holding  $q$  constant. The results of these measurements for acid/base- and base-catalyzed gels are shown in Fig. 6. All samples were diluted 250:1 in methanol, and run at a scattering angle of  $10^\circ$  with a He-Ne laser ( $1/q = 440$  nm). Far from the gel point the apparent radius increases, since  $qR_z$  is less than 1 for these small clusters. However, as the system approaches the gel point the apparent radius becomes independent of the length scale, and thus of  $\epsilon$ , since the clusters grow sufficiently large that  $qR_z \gg 1$ . In essence, the instrumental resolution is exceeded when  $R_z$  exceeds the length scale  $1/q$ . Although this is an elementary

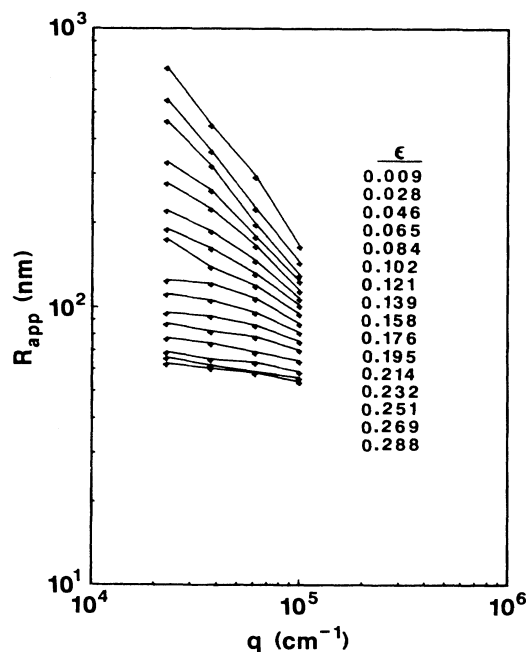


FIG. 5. The  $q$  dependence of the apparent hydrodynamic radius is given for several values of  $\epsilon$ , the highest curve corresponding to the smallest value of  $\epsilon$ . Very near the gel point  $R_{\text{app}}$  is proportional to  $q^{-1}$ , as expected (Ref. 17) for a power-law polydisperse system with  $\tau > 2$ .

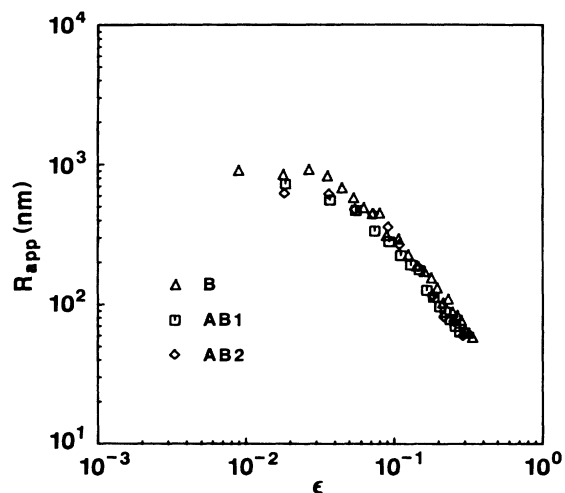


FIG. 6. The apparent hydrodynamic radius, measured at  $q = 2.30 \times 10^{-3} \text{ (nm}^{-1}\text{)}$ , is shown as a function of  $\epsilon$  for two acid/base-catalyzed gels (AB1 and AB2), and a base-catalyzed gel. The saturation of the data very near the gel time is due to a crossover to a dynamical regime where the mean relaxation rate is independent of the length scale, i.e.,  $\Gamma \sim q^3$ . A similar crossover occurs for the statics at small  $\epsilon$ .

point, it is frequently overlooked in experimental work on a wide variety of systems.

To accurately obtain the radius from the dynamic light-scattering data, it is best to exploit the scaling described by (4), which states that the data should collapse to a master curve on the nondimensioned axes  $R_{\text{app}}/R_z$  and  $qR_z$ . The true z-average radius is then simply a shift factor for the collapse. For the base-catalyzed samples this data collapse is shown in Fig. 7. As a practical matter this data collapse has the effect of *extending* the instrumental resolution, but the dynamics data eventually become independent of length scale over the experimentally

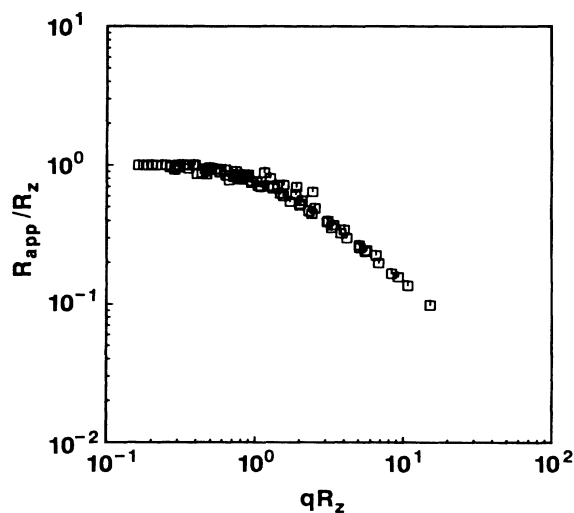


FIG. 7. A master curve is made by plotting the data in Fig. 7 on the dimensionless axes  $R_{\text{app}}/R_z$  versus  $qR_z$ . The z-average radius is the shift factor for the data collapse.

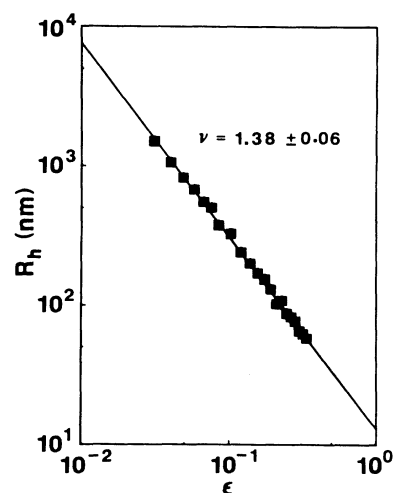


FIG. 8. The z-average hydrodynamic radius for a base-catalyzed gel, taken as the shift factor for the data collapse in Fig. 7, is shown to diverge as  $\epsilon^{-1.38 \pm 0.06}$ . This value of  $\nu$  is in good agreement with the value of  $1.5 \pm 0.2$  found for the radius of gyration of the acid/base-catalyzed gel. The estimated error is smaller, however, since the gel point was determined with greater certitude.

accessible  $q$  regime, and the data collapse then becomes ambiguous.

A plot of the radius of the base-catalyzed gels versus  $\epsilon$  is shown in Fig. 8. The quality of the data is quite good, extending up to a radius of greater than  $1 \mu\text{m}$ . For samples nearer the gel point the data scaling was completely indeterminate since the apparent radius was length-scale independent throughout the entire accessible  $q$  regime of the dynamic light-scattering instrument. The measured

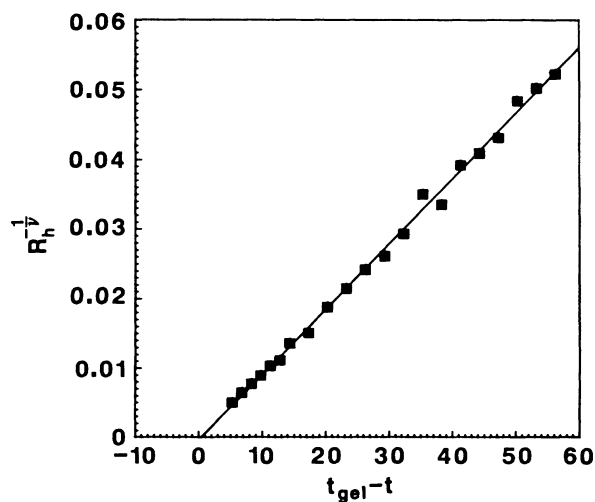


FIG. 9. Thy hydrodynamic radius data in Fig. 8 are linearized using the experimental value of  $\nu = 1.38$ . This allows a linear extrapolation of the data to find the apparent gel point. The data extrapolate to 0.33 min before the estimated gel point ( $\epsilon = 2 \times 10^{-3}$ , which is well with the estimated gel-point error of  $\pm 0.75$  minutes).

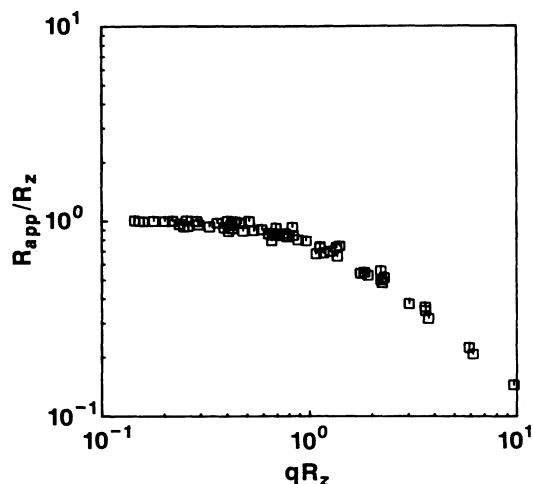


FIG. 10. The data collapse for the apparent hydrodynamic radius of an acid/base-catalyzed gel. These data demonstrate a crossover from  $R_{app} \sim R_z$  to  $R_{app} \sim 1/q$  behavior at  $qR_z = 1$ .

value of  $\nu$  is  $1.38 \pm 0.06$ , ( $0.03 < \epsilon < 0.34$ ,  $\delta\epsilon = \pm 0.004$ ) in satisfactory agreement with the value of  $1.53 \pm 0.2$  obtained for the divergence of the static radius. Again it is observed that critical behavior begins at very early times, so that the entire range of data is very well described by a single exponent. In particular, there is no evidence for a crossover from mean-field to percolation exponents as the critical point is approached.

Since the quality of these dynamics data is quite good, it was thought that an improved estimate of the gel point could be obtained through a linear extrapolation procedure. To this end a linear-linear plot of  $R_h^{-1/\nu}$  versus  $t_{gel} - t$ , shown in Fig. 9, was extrapolated with a linear regression (using the midpoint value  $\nu = 1.38$ ). This gave an extrapolated gel time that was 0.34 minutes ( $\delta\epsilon = 0.002$ ) smaller than the nominal value of  $t_{gel}$ , taken

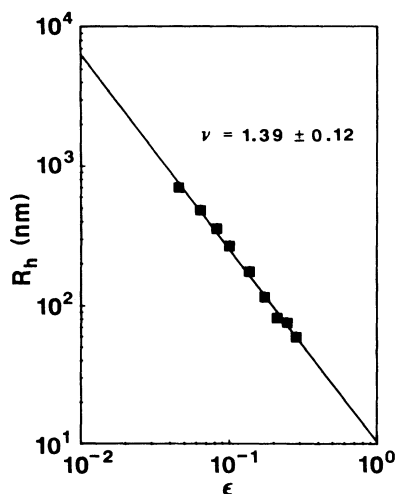


FIG. 11. The exponent  $\nu$  for the first acid/base-catalyzed gel is found to be  $1.39 \pm 0.12$ , in good agreement with the value of  $1.38 \pm 0.06$  found for the base-catalyzed gel.

as the midpoint of  $t_{min}, t_{max}$ . This correction is well within the  $\pm 0.75$  min uncertainty in the measured value of  $t_{gel}$ , and so demonstrates a certain self-consistency in the data analysis. If the exponent  $\nu$  is then recalculated with the extrapolated value of  $t_{gel}$ , a small correction of  $-0.03$  is found.

In Figs. 10–12 the same analysis is applied to two acid/base-catalyzed gels. Once again, the data are well described by critical growth throughout the entire range of  $\epsilon$ . The measured values of  $\nu$  are  $1.39 \pm 0.12$  ( $0.045 < \epsilon < 0.28$ ,  $\delta\epsilon = \pm 0.009$ ), and  $1.22 \pm 0.13$  ( $0.028 < \epsilon < 0.29$ ,  $\delta\epsilon = \pm 0.009$ ), which are within experimental error of the value for the base-catalyzed gels. In fact, no experimentally significant difference could be found in the structure of these base and acid/base-catalyzed gels.

## V. CONCLUSION

In the large-length-scale regime considered in this paper, measurements on the base-catalyzed and acid/base-catalyzed gels reveal no experimentally significant differences between these systems. Our principal observations for these gels are the following:

(1) For the acid/base-catalyzed system the scattering function for the diluted sol is a power law, with an exponent of  $1.67 \pm 0.06$ . This establishes the elementary fact that near the gel point the sol ensemble is fractal, and is in good agreement with the swollen percolation prediction of  $\gamma/\nu = D(3-\tau) = 1.6$  and with the previous measurements of Martin and Keefer, which gave  $D(3-\tau) = 1.69 \pm 0.06$ . In a previous study, the base-catalyzed gels gave a slightly smaller exponent of  $1.58 \pm 0.06$ .

(2) The z-average radius of gyration is found to scale like a power of the weight-average mass,  $R_z^{1.79} \sim M_w$ . Within experimental error this exponent is in agreement

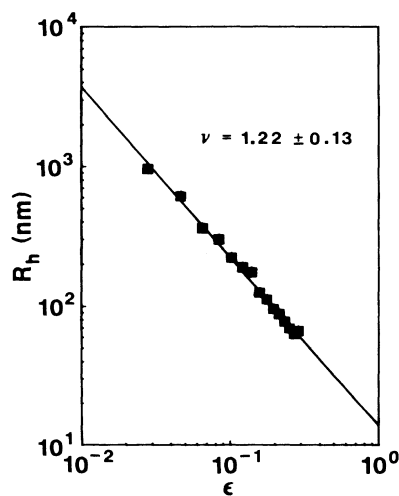


Fig. 12. The second acid/base-catalyzed gel gave a slightly smaller value of  $1.22 \pm 0.13$  for  $\nu$ . Since the stated errors are due to uncertainties in the gel point, this exponent can be combined with  $\nu$  from Fig. 11 to give  $\nu = 1.31 \pm 0.04$ .

the scattering exponent, as it must be for a fractal ensemble.

(3) For the acid/base-catalyzed system the exponent for the divergence of the weight-average molecular weight is  $\gamma = 2.7 \pm 0.3$ . This is larger than the percolation value of 1.76, and much larger than the FS prediction of 1.

(4) The exponent  $\nu$ , as measured by the divergence of the radius of gyration, is  $1.53 \pm 0.2$  for the acid/base-catalyzed gels. Again, this is more strongly divergent than the swollen percolation model, which gives  $\nu = 1.1$ , and is in worse agreement with the FS theory, which predicts  $\nu = 0.5$ .

(5) Measurements of the growth of the hydrodynamic radius give  $\nu = 1.39 \pm 0.12$  and  $\nu = 1.22 \pm 0.13$  for the acid/base-catalyzed gels and  $\nu = 1.38 \pm 0.06$  for the base-catalyzed gels.

Taken as a whole, these results do not lend strong support to either the Flory-Stockmayer theory or the percolation model. And there are no obvious corrections to the experimental data which would improve the agreement with the percolation model. For example, in this experiment the dependence of the extent of reaction on time is unknown. However, one would generally expect the reaction rate to decrease with time, implying that the true critical exponents are *larger* than the measured critical exponents. The same is true for instrumental resolution

effects. The effect of finite instrumental resolution is to more severely underestimate the size of the largest clusters, leading to a measured critical exponent which is smaller than the true critical exponent.

In light of these considerations, it may be that a kinetic growth model is needed to describe the connectivity divergence in strong gels. It seems very reasonable that a cluster-cluster aggregation model might be an appropriate description of the growth in these strong gels. However, we have already noted that in the diffusion-limited simulations of Kolb and Hermann<sup>16</sup> a gel point was not found at finite times, which seems to rule this out as a possible explanation of gelation. Instead, it may be more appropriate to model this system with a *reaction-limited* cluster-cluster simulation. There is already some evidence that the reaction-limited model is weakly gelling in three dimensions. In particular, the homogeneity of the reaction kernel is slightly greater than 1, indicating the emergence of an infinite cluster in finite time.

#### ACKNOWLEDGMENTS

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