PHYSICAL REVIEW A VOLUME 34, NUMBER 6 DECEMBER 1986

Scattering below the sol-gel transition

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(Received 14 July 1986)

Solutions of tetramethoxysilicon are reacted until very near the sol-gel transition. At this point the sol is diluted and elastic and quasielastic light scattering measurements are made at intermediate momentum transfer. The static scattering exponent for the diluted sol is found to be in good agreement with the percolation prediction of 1.6, and the quasielastic scattering measurements demonstrate the flexibility of the sol clusters.

The phenomenon of gelation dates back to the sulfur vulcanization of India rubber (Cautchouc) by Hayward and Goodyear in 1839.[1] But despite the historical utility of this process, and of gels in general, a solid theoretical and experimental understanding of the connectivity transition near the gel point has eluded researchers. In particular, experimentalists have been troubled by several practical difficulties which make a reliable study of the sol-gel transition more difficult than in other critical systems. First, in chemically cross-linked gels the transition is irreversible, so it is impossible to cycle through the transition. Second, it is difficult to control the time of the sol-gel transition to better than $\approx 5\%$, making a reliable estimate of the time of gelation difficult. Third, the sol-gel transition is characterized by a divergence in the connectivity correlation length, not the spatial correlation length, so studies of the static properties near the transition require dilution of the samples. Since it is possible that this dilution is accompanied by swelling of the clusters, the interpretation of data from diluted samples requires a theory of this swelling.

In this paper we report the results of elastic and quasielastic light scattering measurements on chemical gels formed by acid-, base-, and fluoride-catalyzed condensation polymerization of tetramethoxysilicon (TMOS). The elastic scattering measurements circumvent some of the difficulties described above and provide a simple and direct measurement of a static exponent near the connectivity transition. The inelastic scattering measurements probe more complex, dynamical properties of the sol, which provide information about the flexibility of the clusters.

Before giving the experimental results it is worthwhile to review briefly the theory of dilute gel clusters. The earliest theory which describes the salient features of the sol-gel transition is the mean-field, or tree, approximation of Flory[2,3] and Stockmayer.[4] This theory predicts divergences in the z-averaged radius R_z and the weight-averaged mass M_w as the extent of reaction, p, approaches the extent of reaction at the gel point, p_c. In terms of $\epsilon = p_c - p$, these divergences are

$$M_w \sim \epsilon^{-\gamma}\ ,\qquad R_z \sim \epsilon^{-\nu}\ , \tag{1}$$

where $\gamma = 1$ and $\nu = \frac{1}{2}$. The principle approximation in the mean-field theory is the admission of only purely branched polymers into the ensemble—polymers containing circuits are not admitted. More recently, Stauffer[5] and de Gennes[6] have pointed out that percolation does not suffer this limitation, and might provide a more realistic description of gelation. The percolation exponents, $\gamma = 1.76$ and $\nu = 0.88$, are quite different from mean field, so it would seem a simple matter to distinguish experimentally between these theories.

In a scattering experiment M_w and R_z can be determined from the intercept and initial slope of the intensity versus the square of the momentum transfer, so at first thought it might seem reasonable to use these relations in order to determine the exponents γ and ν directly. In practice, however, it is not possible to determine the gel time, and thus ϵ, accurately and so the errors in this approach can be significant. On the other hand, ϵ can be factored out to yield $R_z^{\gamma/\nu} \sim M_w$, and from a plot of the radius versus the mean cluster mass the exponent γ/ν can be determined. Alternatively, the form of the scattering function at intermediate momentum transfer gives the exponent γ/ν directly. To see this, write the scattered intensity per unit concentration in the standard form $I/c \sim M_w f(qR_z)$ where q is the momentum transfer, which in terms of the wavelength in the scattering medium, λ, and scattering angle, θ, is $q = 4\pi \sin(\theta/2)/\lambda$. On length scales which are small compared to the correlation length ($qR_z \gg 1$) the intensity will become independent of the correlation length, so $I/c \sim \epsilon^0$. This gives[7]

$$I/c \sim q^{-\gamma/\nu} \tag{2}$$

and the exponent γ/ν can be determined directly from a scattering experiment on the sol beneath the gel point.

To perform such a scattering experiment it is first necessary to quench and dilute the reacting mixture. This dilution raises the possibility of the clusters swelling, which could increase the exponent ν. To discuss this possibility it is useful to use the relation[7] $\gamma/\nu = D(3-\tau)$, where D is the fractal dimension of a cluster and τ is the exponent for the number distribution of cluster masses, $N(m) = m^{-\tau}$ for $m \ll m_z$ ($m_z \sim R_z^D$). If the clusters are unswollen the exponent $D(3-\tau)$ is $2-\eta$, where η is an exponent that gives the deviation from Ornstein-Zernike theory. In the mean-field theory $D = 4$ and $\tau = \frac{5}{2}$, giving $\eta = 0$. In percolation theory $D \sim 2.5$ and $\tau \sim 2.2$, so although η is not *identically* zero it is very small. We conclude that an intermediate scattering experiment will not provide a distinction between percolation and mean field in the absence of swelling.

It is important, then, to review the theory of cluster swelling upon dilution of the sol. In 1980 de Gennes[8] applied a Flory-type analysis to calculate the fractal dimension of undiluted clusters. In this approach the free energy is a sum of two terms: a purely elastic (entropic) term and a two-body interaction term. The result, $D=2.5$, is in very good agreement with percolation simulations. The novel feature of this calculation is the inclusion of screening in the two-body interaction term of the free energy. The concept of partial screening, due to Edwards,[9] accounts for the fact that the surrounding sol is a solvent of significant size and so diminishes the excluded-volume interactions of the clusters. The original notion of screening dates back to Flory,[10] who correctly conjectured that in a monodisperse polymeric melt two-body interactions would be *completely* screened.

To compute the fractal dimension for dilute clusters it is simply necessary to omit the screening factor from the two-body interaction term. This swelling calculation was reported by Isaacson and Lubensky[11] in 1980, who found a marked decrease in the fractal dimension, from 2.5 to 2. (It has been observed that 2 is also the lattice animal fractal dimension, giving rise to the description of dilute sol clusters as "lattice animals." This is something of a misnomer, however. Upon dilution the connectivity dimension of the clusters is preserved. Since the connectivity dimension of lattice animals is quite different from percolation clusters it is incorrect to refer to swollen percolation clusters as lattice animals.[12]) This reduction in the fractal dimension gives a concomitant reduction of the scattering exponent from 2 to 1.59 for the diluted percolation clusters.[13] It should be a simple matter to distinguish this exponent from the mean-field result.

Finally, it should be mentioned that a hybrid exponent has been proposed for the mean-field theory.[13] One can combine the swollen cluster fractal dimension, 2, with the Flory-Stockmayer exponent for the size distribution, $\frac{5}{2}$, to obtain $D(3-\tau)=1$. However, it is not entirely clear that this exponent is appropriate. The mean-field theory implicitly assumes that two-body interactions are *completely* screened by the sol. Of course, this does not imply that these interactions are screened by a simple solvent, and indeed, the critical dimension for dilute branched polymers ($d_c=8$) is greater than the critical dimension for percolation ($d_c=6$). But the applicability of this hybrid theory is questionable since it effectively assumes that growth takes place at or above the critical dimension for percolation, and then uses the three-dimensional result for the fractal dimension of the swollen clusters.

A wide variety of silica gels were made by combining a methanol solution which is $4M$ in H_2O with varying amounts of TMOS, ranging from $0.125M$ to $1M$. To these solutions were added either acid (HCl), base (NH_4OH), or ammonium fluoride as catalysts. All chemicals were prefiltered through 0.22-μm filters and the final solution was again filtered through a 0.22-μm filter. Slightly beneath the gel point the reacting mixtures were quenched by diluting with methanol, and elastic and quasielastic scattering measurements were made at three dilutions: 10:1, 50:1, and 250:1. Light scattering measurements were made with both a He-Ne laser, at $\lambda=632.8$ nm, and an argon-ion laser, at $\lambda=457.9$ nm.

Three different methods of catalyzing the hydrolysis and condensation reactions were employed. The first series of samples used a simple one-step base catalysis, the second series used a two-step, sequential acid-base catalysis, and the third series used a concurrent base-fluoride catalysis. The base-catalyzed series spanned a wide range of initial TMOS concentration, from $0.125M$ to $1.0M$, to investigate any dependence of the scattering exponent on initial monomer concentration.

Scattering functions for the $1.0M$ TMOS base-catalyzed gels are shown in Fig. 1. Two salient features of the scattering functions are readily apparent: (1) at higher concentrations the intensity per unit concentration is much smaller than in the more dilute samples, indicating a significant overlap of the clusters; (2) coupled with this lower intensity is a more moderate slope. In the most dilute samples the correlation length ξ was sufficiently large that it was beyond the resolution of the light scattering experiment (>1 um), so scattering exponents could be determined unambiguously, since $q\xi\gg1$. Because of the significant concentration dependence of the scattering exponent, it was necessary to extrapolate the measured scattering exponent to zero concentration, as shown in Fig. 2. The linear extrapolation, which seems to fit the data quite well, yields $D(3-\tau)=1.58\pm0.05$ (average of three preparations), in substantial agreement with the percolation value of 1.59.

As the initial TMOS concentration is reduced, one might expect to see some trend in the scattering exponent, reflecting the increasing importance of diffusion in the ir-

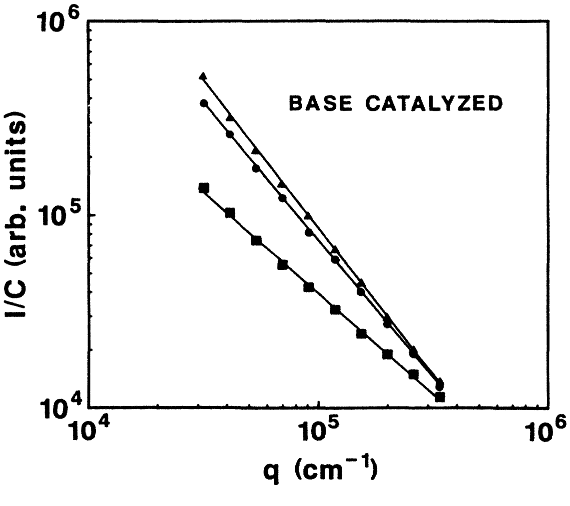

FIG. 1. Elastic light scattering measurements from the $1.0M$ base-catalyzed sol show a strong dependence on concentration. The lowest curve is a 10:1 dilution, the intermediate curve is a 50:1 dilution, and the highest curve is a 250:1 dilution.

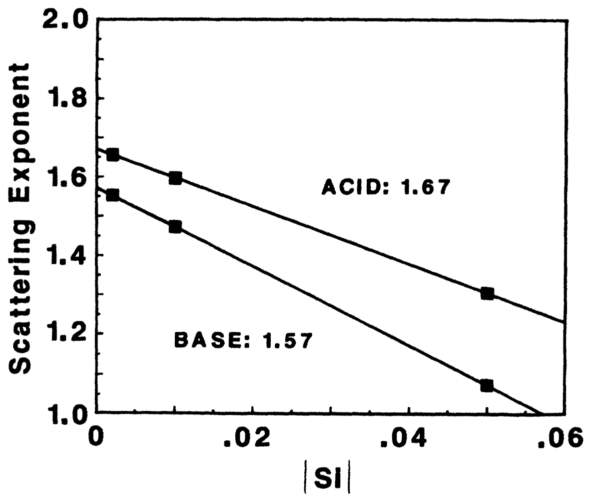

FIG. 2. The elastic scattering exponents derived from the slopes in Fig. 1 are plotted vs concentration. Although the linear extrapolation is without theoretical justification, it fit the data quite well for all samples.

reversible growth process. However, in the entire series of base-catalyzed samples (1.0*M*, 0.5*M*, 0.25*M*, and 0.125*M* TMOS) no significant systematic trends were found in the data, despite the fact that in the 0.125*M* TMOS gel the concentration of SiO_2 was only 0.75%. In fact, the average scattering exponent for all the base catalyzed samples was 1.60±0.05, in good agreement with the values obtained from the 1.0*M* sample.

The base-fluoride–catalyzed gels gave results which were quantitatively similar to the gels catalyzed by base alone, although the time to gelation was greatly diminished. The average scattering exponent in these systems was 1.59±0.05, which is experimentally indistinguishable from the base-catalyzed result.

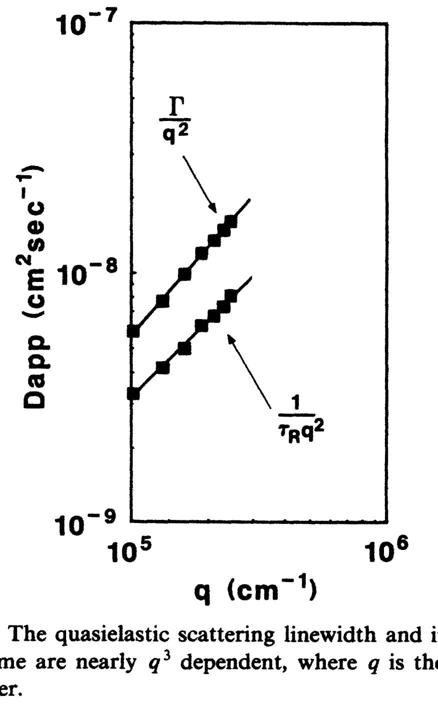

FIG. 3. The quasielastic scattering linewidth and inverse relaxation time are nearly q^3 dependent, where q is the momentum transfer.

The acid-base–catalyzed samples gave results which differed somewhat from the base-catalyzed samples. In these samples the monomeric solution was incubated with acid for a short time, at which point base was added to the reacting mixture. The scattering exponent for these gels was 1.69±0.04, indicating either some slight nonuniversality in gelation, or the presence of some nonasymptotic effect. It should be pointed out, however, that the difference between 1.60 and 1.69 is not large enough to make a strong statement about the difference between these systems.

These intermediate scattering exponents for polycondensates are in reasonable agreement with an exponent reported by Schosseler and Leibler[14] for the γ-radiation–induced "vulcanization" of polystyrene. In these experiments light scattering was used to determine R_z and M_w, and from a plot of R_z versus M_w the exponent $D(3-\tau)$ was extracted and found to be 1.72. This vulcanization exponent is in reasonable accord with percolation, but does not support the mean-field theory.

An earlier study of static exponents for gelation was conducted by Schmidt and Burchardt[15] on the anionic copolymerization of divinylbenzene with styrene. Using light scattering they separately measured the dependence of R_z and M_w on ϵ. These measurements give $\gamma/\nu=2$, which is much larger than percolation, but in excellent agreement with mean-field theory without swelling.

Schaefer and Keefer[16] recently reported small-angle x-ray scattering (SAXS) measurements on the TEOS (tetraethoxysilicon) system and found a scattering exponent of 2.0, which is much larger than the values reported here. One possible reason for this discrepancy is the absence of swelling. The SAXS measurements extended over small length scales, $1<q^{-1}<5$ nm, compared to the light scattering data reported here, where $30<q^{-1}<435$ nm. This difference in length scales is important in the interpretation of data from diluted gel clusters. On large length scales one would expect excluded-volume interactions to be fully developed, as supported by the light scattering data, but on small length scales the excluded-volume interactions would not be fully developed. If the distance between branch points is still smaller than q^{-1} it might be more appropriate to use the theta solvent value,[13] $\frac{16}{7}$, for the fractal dimension of the gel clusters, which would give $D(3-\tau)=1.83$. The absence of swelling thus only partially accounts for the discrepancy between light scattering and x-ray scattering results.

A more plausible explanation is that the SAXS measurements are sensitive only to the early-time structure of the silica polycondensates. It is important to note that the initial reacting mixture is dilute in monomer, unlike a more typical gelation process, where little or no solvent is present. At very early times kinetic effects are important in the irreversible silica system, and the chemistry can be quite complex (quite often dense colloids are formed). In essence, then, the short-range structure is determined far from the critical point, and there is no reason to expect this system to be described by percolation.

In fact, growth may occur in three distinct stages. At early times monomers hydrolyze and condense to form colloids or small branched polymers.[16] In this regime the structures are determined in part by short-range interactions. This dilute solution of "renormalized" monomers may then react via a kinetic process such as reaction-limited cluster-cluster aggregation[17] to form a solution of fractal clusters. Eventually, however, these clusters will overlap as the volume fraction of fractals approaches unity. At this point this dense system crosses over to a universality class that exhibits a sol-gel transition (percolation?) to form the very large clusters observed in the light scattering experiments. Evidence for the change in universality class at the overlap concentration has been presented by Kolb and Hermann[18] for the *diffusion-limited* cluster-cluster aggregation model. In their two-dimensional simulations of this model they found that at low volume fractions of clusters the fractal dimension was 1.4. But as the volume fraction of clusters approached unity, a crossover was found to $D=1.75$. Corresponding results for the *reaction-limited* model are not yet known, but it is possible that at high volume fractions this model crosses over to percolationlike behavior.[19]

The dynamic properties of the sol-gel transition can be probed using quasielastic light scattering on the diluted sol. The quasielastic light scattering experiment measures the autocorrelation function of the scattered field, $S(q,t)=\langle E(q,0)E(q,t)\rangle$, which is determined by the translational, rotational, and configurational modes of the individual scatterers.[20] The simplest scatterers are rigid, spherically symmetric particles which *exhibit* only translational degrees of freedom. In this case the *dynamic* structure factor for a particle of mass m is given by the exponential decay, $S_m(q,t)=S_m(q)e^{-q^2D_tt}$, where $S_m(q)$ is the *static* structure factor for the particle, normalized such that $S_m(0)=1$, and D_t is the translational diffusion coefficient. In the presence of rotational or configurational diffusive modes the structure factor can be written[7]

$$S_m(q,t)=e^{-q^2D_tt}H(qR;\Omega t) , \tag{3}$$

where $H(qR;\Omega t)$ is a function which accounts for the contribution of internal modes to the quasielastic scattering. The characteristic frequency Ω is proportional to D_t/R^2 for both rigid rotations *or* configurational modes of fully flexible scatterers, such as linear polymers.

In a polydisperse system, the observed structure factor is an average over the number distribution $N(m)$;

$$S(q,t)=\frac{\int m^2S_m(q,t)N(m)dm}{\int m^2N(m)dm} . \tag{4}$$

One can determine the arithmetic average relaxation time $\tau_r=\langle\tau\rangle$ from the time integral of $S(q,t)$, and the harmonic average, or Rayleigh linewidth, $\Gamma=\langle 1/\tau\rangle$, from the initial derivative, $-d\ln S(q,t)/dt$, of the dynamic structure factor. These averages will depend on the assumptions made for the function $H(qR;\Omega t)$.

If gel clusters are rigid, the function $H(qR;\Omega t)$ reduces to the static structure factor $S_m(q)$. A monodisperse solution of such scatterers would then have a linewidth and inverse relaxation time equal to q^2D_t. It has recently been shown that an average of these translational modes over the percolation distribution of cluster masses gives much more interesting results. In this case both the linewidth[7] and inverse relaxation time[21] τ_r^{-1} depend on higher powers of the momentum transfer:

$$\begin{aligned}&\Gamma\sim q^d ,\\ &\tau_r^{-1}\sim q^{D+\eta} .\end{aligned} \tag{5}$$

The linewidth result is uninteresting, since the dimension of space, d, is presumably well known. But the result for the inverse relaxation time is potentially useful; the exponent η is nearly zero for percolation, so the inverse relaxation time for *rigid* percolation clusters scales like q^D. Thus it is possible, in principle, to determine the fractal dimension for a single cluster from a single measurement of the dynamics of the polydisperse ensemble.

If the clusters are *flexible* (i.e., the internal configurational modes are independent of the overall size of the scatterer), however, these modes will dominate the dynamics and both the linewidth and inverse relaxation time will scale like q^3 regardless of the polydispersity of the system.[7,21] In fact, this is the experimental observation. Figure 3 shows the experimentally determined dependence of the linewidth and inverse relaxation time on momentum transfer for the diluted sol. Both of these relaxation rates are seen to scale as q^3, indicating that the clusters are fully flexible, in analogy with linear polymers. To some extent this flexibility is surprising, given the large number of circuits sol clusters contain. It may be possible, however, to find a system which exhibits little flexibility, so that D can be measured directly from the dynamics.

In conclusion, static and dynamic light scattering measurements indicate that near the sol-gel transition silica condensation polymers can be described as flexible clusters. Static light scattering measurements from base, base-fluoride, and acid-base catalyzed gels gave $D(3-\tau)=1.60\pm0.05$, 1.59 ± 0.05, and 1.69 ± 0.04, respectively, in good agreement with the percolation value of 1.59. Dynamic light scattering measurements are consistent with the prediction for flexible scatterers, namely that the linewidth and inverse relaxation time are proportional to the cube of the momentum transfer.

Note added in proof. Recently, similar scattering results have been published on polyurethane gels. See E. Bouchaud, M. Delsanti, M. Adam, M. Daoud, and D. Durand, J. Phys. (Paris) **47**, 1273 (1986).

ACKNOWLEDGMENT

Judy Odinek provided invaluable assistance in both sample preparation and in collection of the scattering data.

[1] F. Clouth, *Rubber, Gutta Percha, and Balata* (Maclaren, London, 1903).

[2] P. J. Flory, J. Am. Chem. Soc. **63**, 3083 (1941).

[3] P. J. Flory, J. Phys. Chem. **46**, 132 (1942).

[4] W. H. Stockmayer, J. Chem. Phys. **11**, 45 (1943).

[5] D. Stauffer, J. Chem. Soc. Faraday, Trans. II **72**, 1354 (1976).

[6] P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University, Ithaca, 1979).

[7] J. E. Martin and B. J. Ackerson, Phys. Rev. A **31**, 1180 (1985).

[8] P.-G. de Gennes, C. R. Acad. Sci. **291**, 17 (1980).

[9] S. F. Edwards, Proc. Phys. Soc. London **93**, 605 (1965).

[10] P. J. Flory, *Principles of Polymer Chemistry* (Cornell, London, 1953).

[11] J. Isaacson and T. C. Lubensky, J. Phys. (Paris) Lett. **41**, L469 (1980).

[12] J. E. Martin, J. Phys. A: Math. Gen. **18**, L207 (1985).

[13] M. Daoud, F. Family, and G. Jannink, J. Phys. (Paris) Lett. **45**, L199 (1984).

[14] F. Schosseler and L. Leibler, J. Phys. (Paris) Lett. **45**, L501 (1984).

[15] M. Schmidt and W. Burchardt, Macromoleules **14**, 370 (1981).

[16] D. W. Schaefer and K. D. Keefer, Phys. Rev. Lett. **53**, 1383 (1984).

[17] D. W. Schaefer and K. D. Keefer, *Materials Research Society Proceedings*, edited by C. J. Brinker, D. E. Clark, and D. R. Ulrich (North-Holland, Amsterdam, 1986) Vol. 73.

[18] M. Kolb and H. J. Hermann, J. Phys. A: Math. Gen. **18**, L435 (1985).

[19] P. Meakin and J. E. Martin (unpublished).

[20] B. J. Berne and R. Pecora, *Dynamic Light Scattering* (Wiley, New York, 1976).

[21] J. E. Martin and F. Leyvraz, Phys. Rev. A **34**, 2346 (1986).