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FRACTAL STRUCTURE AND FRACTAL TIME IN SILICA SOL-GELS

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ABSTRACT

Near the gel point, light scattering studies of silica sol-gels reveal fractal clusters whose size diverges as a power law, in accord with the predictions of percolation theory. More surprising is the appearance of a fractal time description of the dynamics of these clusters. This novel dynamics has recently been revealed by quasielastic light scattering from the density fluctuations that occur at the sol-gel transition. Since the relaxation of fluctuations in these branched polymer systems is self-similar, decay processes occur on all time scales (fractal time), and average decay times diverge. An interpretation of this observation will be presented that relies on a length-scale-dependent viscosity and the geometrical self-similarity of the sol-gel transition. The scattering theory is extended to the calculation of time- and frequency-dependent viscoelastic properties, as well as mechanical properties such as the shear modulus, steady state creep compliance, and viscosity. The viscoelastic predictions are found to be in good agreement with experimental data.

INTRODUCTION

Silica gels are technologically important materials with a rich chemistry, yet relatively little is known about the evolution of structure of these complex materials. In part, the complexity of silica gels arises from the wealth of synthetic routes used to produce them. A typical synthetic process depends on such parameters as the pH, concentration of monomer, water, catalyst, salt etc., and these parameters are usually varied in an empirical fashion to produce a suitable gel time, gel density and so forth. That the evolution of structure in these gels is so poorly understood is partially due to the fact that researchers are unable to agree on exactly what is meant by structure. Once a suitable definition of structure is adopted, one might then ask some very basic questions, such as "What structural characteristics are strongly affected by the chemistry and what properties are largely immutable?" Since the most dramatic physical changes occur in the vicinity of the sol-gel transition, this regime would seem to offer the most fruitful initial avenue of investigation.

The investigations we have made on the sol-gel transition include relatively

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straightforward static structure measurements as well as more complex determinations of dynamical properties. To interpret these measurements we have used the well known analogy [1-4] between the sol-gel transition and a second-order thermodynamic phase transition to develop theories of the elastic and inelastic light scattering behavior, and viscoelastic phenomena. In this article we give a overview of the various aspects of the sol-gel transition in silica, and briefly discuss the less universal aspects of growth that occur at early times.

THE SOL-GEL TRANSITION

Length Scales

At the gel point many physical properties have the value o or ∞: for example, the shear modulus is 0, the viscosity is ∞, the gel fraction is 0 and the average cluster mass is ∞. One way to quantify structure is to ascertain exactly how things come to be 0 or ∞. This *critical point* approach to gelation produces a family of exponents that can then be understood in terms of a model of growth that predicts a length scale divergence at a finite time. The obvious practical question thus becomes whether this family of exponents can be affected by the choice of chemistry - the standard lore of critical phenomena would suggest that chemistry is irrelevent. However, the sol-gel transition is more complex than a thermodynamic phase transition and in the presence of solvent there are *two* length scales [5]. One of these length scales, the *spatial* correlation length, is sensitive to chemistry and the other length scale, associated with the connectivity divergence, is not. The spatial correlation length is finite and arises from the aggregation phase of growth that occurs at early time, whereas the connectivity correlation diverges at the gel point.

In a chemical gel bond energies are large compared to kT, so it is not obvious that the *quenched* randomness of the resulting structures can be described by an equilibrium model. However, if the bonding between neighboring monomers is completely random, the structure of the gel will be described by the bond percolation model. As applied to gelation, percolation may be thought of as a kinetic model that generates a frozen equilibrium ensemble. We will consistently use the percolation model as a basis for comparison of our data.

Fractal Dimensions and Scattering

Near the gel point, the percolation model generates a self-similar ensemble of branched polymers. Any single polymer has a fractal dimension [1] $D=2.5$, i.e. the radius R scales with the mass M as $M \sim R^{2.5}$. However, the distribution of cluster masses is also self-similar, in the sense that the mean separation distance between polymers of radius R is proportional to R for all R, implying an ever increasing number of smaller clusters It is easily shown [6] that the number of clusters of mass M is $N(M)=M^{\tau}$ where the *polydispersity exponent*

$$\tau=1+3/D=2.2 \tag{1}$$

Since this relates a critical exponent to the dimension of space (in eq. 1 $d=3$), it is known as a *hyperscaling relation* [1]. A light or x-ray scattering experiment allows us to probe the *net* self-similarity of this *twice fractal* ensemble, which is a combination of the self-similarity of a single cluster and the self-similarity of the size distribution. The combined effects give [7,8]

$$I \sim q^{-D(3-\tau)} \tag{2}$$

where I denotes the scattered intensity and q is the scattering wavevector [$q=4\pi\sin(\theta/2)/\lambda$, where θ is the scattering angle and λ is the wavelength in the scattering medium]. The dimension $D(3-\tau)$ is called the *ensemble fractal dimension* and is a distinct concept from the fractal dimension D of a single cluster. That this point is essential to the existence of a sol-gel transition is not universally appreciated and some investigators [9] have incorrectly assumed that the standard mass fractal scattering behavior $I \sim q^{-D}$ applies near the gel point.

In making comparisons to experiment there is an additional subtlety; gelation is a transition in *connectivity*, and in order to probe the connectivity scattering measurements must be done on diluted samples. Otherwise, the self-similar packing of clusters cancels the scattering. As explained below, clusters swell upon dilution [10,11], reducing the single cluster fractal dimension D from 2.5 to 2. Thus the anticipated scattering behavior from a dilute bath of percolation clusters is $I \sim q^{-1.6}$, since $D(3-\tau)=2(3-2.2)=1.6$. Our light scattering experiments [12,13] on tetramethoxysilicon (TMOS) gels, catalyzed by either acids, bases, or with fluoride ion, give $I \sim q^{-1.60\pm0.06}$ in excellent agreement with percolation. Similar results were obtained on TEOS gels, indicating that this aspect of the structure is insensitive to the chemistry.

The structural evolution that occurs far before the gel point is controlled by aggregation and is therefore much more sensitive to chemistry. By carefully controlling pH and ionic strength a wide variety of structures can be produced, and growth rates can easily be changed over 8 orders of magnitude. In fact, it is possible to observe [5] the exponential growth associated with *reaction-limited aggregation*, as well as the power-law growth [14] associated with *diffusion-limited aggregation*. However, no matter how complex and chemistry-dependent the initial growth is, near the gel point the aggregates percolate to create a universal sol-gel transition.

Polydispersity

An important aspect of the critical approach to the sol-gel transition is the prediction that the polydispersity exponent $\tau=1+3/D$ is greater than 2. In fact, $\tau>2$ is absolutely essential if one is to have a gel point in finite time. The reason is clear enough; at the gel point the average cluster radius diverges to infinity, yet clusters of comparable size cannot overlap. Thus if all clusters were more or less the same size, they would tend to occupy an infinite volume at the gel point. Of course, in reality the volume of the gel doesn't diverge at the gel point. It turns out that the only way in which the average radius can diverge without the total volume diverging is to have the polydispersity algebraically decay as $N(M)\sim M^{-\tau}$ with $\tau=1+3/D$. From lineshape analysis of the intensity correlation autocorrelation function, we have determined [15] $\tau=2.3\pm.15$, in accord with the critical point analogy of the the sol-gel transtion.

Divergence of the Cluster Size

Let us now return to our original point of how things come to be 0 or ∞. In short, all divergences are due in one way or another to the divergence of the average cluster mass, i.e. the appearance of an infinite cluster at the gel point. In the percolation model divergences follow standard critical point formulae [1] $A\sim\varepsilon^{\alpha}$, where in practical measurements ε is the time from the gel point and the critical exponent α may be positive or negative. For example, the percolation model predicts that the average cluster radius and mass diverge as

$$R_z\sim\varepsilon^{-\nu(.9)},\quad M_w\sim\varepsilon^{-\gamma(1.76)} \tag{3}$$

respectively, where the numerical value of the exponent is in parenthesis. Using quasielastic and elastic light scattering we found that [16] $R_z\sim\varepsilon^{-1.1\pm0.06}$ (exponent corrected for swelling) and $M_w\sim\varepsilon^{-2.7\pm0.3}$, in excellent support of the critical point analogy, but only in qualitative agreement with percolation. Data on organic systems are in better agreement with percolation exponents.

These light scattering measurements demonstrate that ~10 min before a gel time of ~170 min, silica cluster radii were already well over 10,000 Å. This observation differs with previous small angle x-ray scattering measurements on TEOS gels [9], where the 'Guinier' radius was reported to be only ~200 Å just 1 min before a gel point of ~500 min. and no critical divergence of the radius was found at the gel point. The lack of a critical divergence in this work is due to the 200 Å resolution of the Kratky SAXS camera and insufficient dilution of the sol-gels. When the 'Guinier' radius exceeds the instrumental resolution the scattering is intermediate, $I \sim q^{-\alpha}$, and no information about the radius can be obtained (a result of mass conservation.) Likewise, when a sample is insufficiently diluted, the 'Guinier' radius of the solution is much smaller than the true cluster size. Thus the study of critical divergences requires high resolution measurements on highly dilute samples.

Swelling of Clusters (Linear-Like Polymers?)

Since the growth that gives rise to branched polymers is a continuous divergence in connectivity, it is not possible to determine the structure in the reaction bath by using techniques that probe spatial correlations (e.g. scattering). Thus we can only measure the ensemble fractal dimension of the branched polymers after significant dilution. In practice it has been necessary to dilute clusters as much as 1000:1.

Theories of branched polymers predict a dramatic swelling upon dilution from the bulk state into a good solvent. In fact, the fractal dimension of a branched polymer is predicted to change from 2.5 to 2 upon dilution [10,11] Since this change cannot be determined directly, we have adopted indirect methods of determining the change in fractal dimension ΔD. The first method is to measure the divergence of the intrinsic viscosity $[\eta]$ near t_{gel}. In terms of the typical cluster mass M_z this divergence depends on ΔD through [2,17]

$$[\eta] \sim M_z^{3\Delta D/D_s} \tag{4}$$

where D_s is the swollen dimension. Thus if the fractal dimension doesn't change upon dilution the viscosity does not diverge as a power law. Using percolation exponents, eq. 4 can be expressed in terms of the weight average cluster mass as $[\eta] \sim M_w^{3/8}$. Preliminary experiments show that the intrinsic viscosity diverges, but that ΔD only changes by about 2/3 of its theoretically predicted value of 0.5. *A technical note: in the silica literature the intrinsic viscosity is sometimes expressed in terms of the number average molecular weight as* $[\eta] \sim M_n^a$. *This is* *correct for linear polymers, but for branched polymers formed near the sol-gel transition this relation is incorrect, since M_n does not diverge at the gel point. In other words, formally the exponent $a=\infty$.*

ΔD can also be determined by using light scattering to measure the concentration dependence of the spatial correlation length ξ which may be thought of as an apparent cluster size in solution (it has nothing to do with the real cluster size, but is merely the radius that is measured in a scattering experiment.) In the reaction bath ξ is small, typically ~200 Å, but when the system is diluted, ξ increases rapidly, eventually becoming the true cluster size (10^4 - 10^5 Å) in the limit of infinite dilution. Physically, the correlation length is the length scale beneath which the solution is essentially dilute. In any case, it can be shown that ξ increases with dilution according to [18,19]

$$\xi \sim c^{-D/3\Delta D} \qquad (5)$$

Using percolation exponents and the predicted swelling of $\Delta D=0.5$ gives $\xi \sim c^{-5/3}$. Light scattering measurements [19] on successively diluted silica clusters formed very close to the gel point give $\xi \sim c^{-2.0\pm0.3}$ for both acid- and base-catalyzed TMOS sols, in substantial agreement with eq. 5. It is important to note that the observed concentration dependence is strong and independent of the method of catalysis.

This observation conflicts with earlier studies [9] of silica that attempted to determine whether acid or base catalysis leads to *weakly branched* polymers with long linear chains between crosslink points or the *densely branched* polymers one would normally expect from a tetrafunctional monomer. In fact, these measurements are the basis of the well-known conjecture that acid catalysis leads to the formation of linear-like structures. In these SAXS studies, samples formed very close to the gel point were diluted and the change in the 'Guinier' radius was determined. However, because of the 200 Å resolution of the Kratky camera, it seemed that in the base-catalyzed samples the Guinier radius did not change upon dilution, whereas light scattering measurements, with a resolution of ~10,000 Å, demonstrate a large change in the spatial correlation length. Also, in this work it was argued that a Guinier radius that does not increase with concentration indicates branched polymers, since branched polymers do not overlap, whereas a Guinier radius that does increase with concentration indicates linear-like, weakly branched polymers. This led to the conjecture that acid-catalyzed gels are linear-like, or weakly branched, and base-catalyzed gels are densely branched. In fact, because of the effects of polydispersity and swelling (see eq. 5), the concentration dependence of the Guinier radius of densely branched polymers is actually much *stronger* than in linear-like polymers. For example, linear polymers in good solvents have a correlation length that diverges [4] as $\xi \sim c^{-3/4}$; thus for a 10-fold dilution the correlation length of branched polymers increases by ~100, whereas for linear polymers it increases by only ~5.

These observations are further supported by ^{29}Si NMR studies [20] that show that the Q-distributions observed under conditions of acid catalysis are consistent with the binomial distributions expected from percolation (the Statistical Reaction Model [21] is a percolative system). Percolation clusters are highly branched, having a *topological dimension* [22] of ~1.8 (versus 1 for linear structures and 2 for sheets) so the notion of linear-like chain formation in acid catalyzed gels is not supported by extant experimental evidence.

Viscoelasticity

Perhaps the most striking aspect of the sol-gel transition is the transformation of a viscous liquid into a rubbery solid. Prior to t_{gel} the viscosity of the sol diverges as $\eta \sim \varepsilon^{-k}$ and beyond t_{gel} the shear or tensile modulus grows as $E \sim \varepsilon^{z}$ [3,4]. The growth in the elastic modulus is related to the appearance of a *gel fraction* - the fractional mass belonging to the infinite network - which is given by yet another power law, $G \sim \varepsilon^{\beta}$.

A less obvious aspect of the fluid near the sol-gel transition is the appearance of dramatic viscoelastic properties [23,24]. An anomalous power law frequency dependence of the complex viscosity is observed near t_{gel}, which results in a slow, power law decay of stress with time. By taking advantage of the concept of self-similarity in the *time* domain, we have developed a dynamical scaling approach to the calculation of normal modes in branched polymers. By summing over these normal modes a complete description of the linear viscoelastic properties can be obtained [24]. For example, at the gel point the shear relaxation modulus decays algebraically in time according to

$$G(t) \sim t^{-3/(2+D)} \tag{6}$$

Using D=2.5 gives the percolation prediction $G(t) \sim t^{-2/3}$. Since the frequency-dependent complex shear modulus $G(\omega) = G'(\omega) + iG''(\omega)$ is a transform of G(t), the same gel point power law behavior is observed,

$$G'(\omega) \sim G''(\omega) \sim \omega^{3/(2+D)} \tag{7}$$

Here $G'(\omega)$ is the storage component and $G''(\omega)$ is the loss component of the modulus. Dividing by frequency then gives the percolation prediction for the complex viscosity $\eta'(\omega) \sim \eta''(\omega) \sim \omega^{-1/3}$. Experimental data taken for the TMOS system at the gel point, shown in figure 1, are in good agreement with this prediction, as are data for many organic gels [24,25].

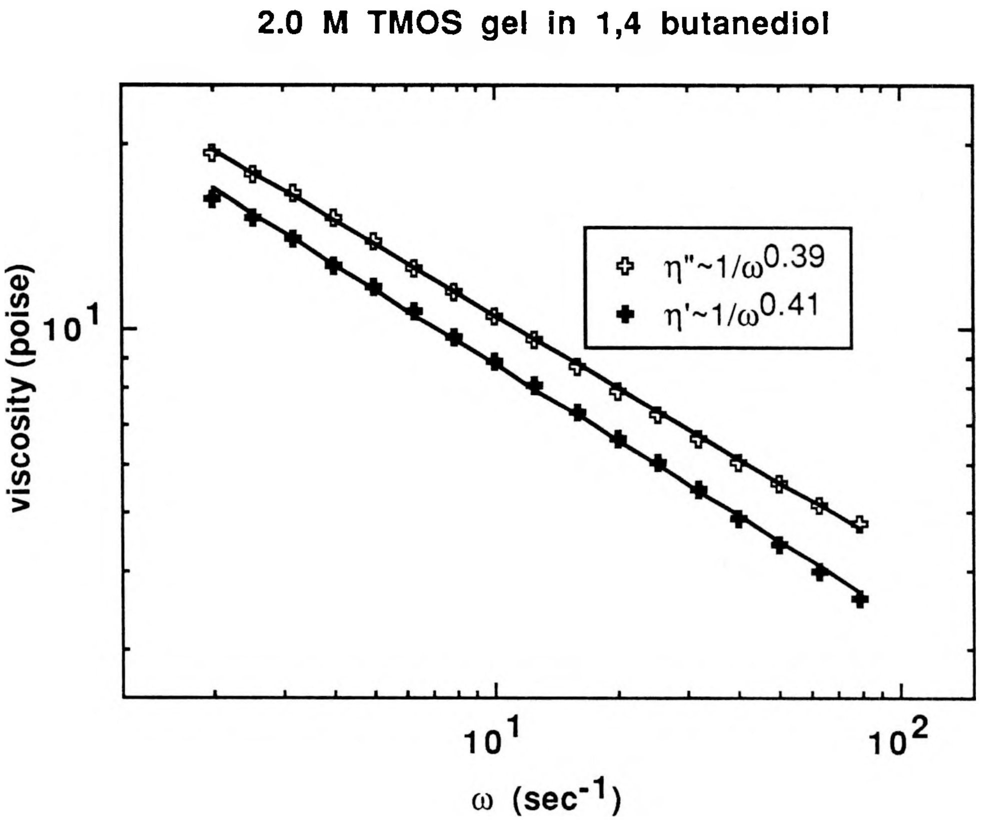

Fig. 1: The complex viscosity for a 2.0 M base cataylzed gel at the gel point shows a power law frequency dependence in accordance with the percolation prediction $\eta'(\omega) \sim \eta''(\omega) \sim \omega^{-1/3}$.

It turns out that these relations for the dynamical properties imply that beyond t_{gel} both the equilibrium shear and tensile moduli scale as [24]

$$E \sim kT/R_z^3 \qquad (8)$$

where R_z is the radius of a typical branched polymer in the reaction bath (above t_{gel} this is just the mesh size of the infinite network.) Thus the modulus, an energy density, is a statement of equipartition - in a unit shear deformation kT is stored per elastic cell of volume R_z^3. Since R_z decreases beyond the gel point, the modulus increases as $E \sim kT/\varepsilon^{8/3}$; this has been experimentally verified in organic resins [25], but not yet in silica gels.

Finally, the steady state shear viscosity diverges as

$$\eta \sim R_z^{2-d_c} \qquad (9)$$

where the *codimension* d_c=3-D. This leads to the percolation prediction $\eta \sim R_z^{3/2} \sim \varepsilon^{-1.4}$. From the light scattering measurements described below, we have determined $\eta \sim \varepsilon^{-1.5\pm0.1}$ for base catalyzed 1M TMOS gels. Direct viscosity measurements on organic resins are in excellent agreement with eq. 9.

Shear Modulus

The last topic we address is the dependence of the shear elastic modulus on the initial monomer concentration, this having more to do with aggregation than gelation. At the start of the reaction a dilute solution of silica monomers is activated by a catalyst. In order to react, these monomers must first diffuse together, colliding many times before reacting if the activation energy is large. This diffusion process is not described percolation, but may be thought of as an aggregation process in which clusters grow exponentially in time [5,26] until the entire volume of the solution is filled. The situation is then much like a huge container filled with tumbleweeds- the mass fraction is very small, but the bushes occupy the entire volume of the container. At this point the aggregates act as huge 'monomers' that then percolate to form a gel. The radius of these monomers is a second, nondivergent length scale that is sensitive to the reaction conditions. For example, the radius at cluster overlap is concentration dependent, becoming large at low monomer concentrations. If ϕ_o is the initial monomer volume fraction, cluster overlap will occur at an aggregate radius of

$$\xi_s \cong b\phi_o^{-1/(3-D)} \qquad (10)$$

where D is now the fractal dimension of the aggregates and b is the silica monomer radius.

Light scattering experiments [5] on TMOS gels grown under dilute conditions give D=2.3, so the radius $\xi_s \sim \phi_o^{-1.4}$. At this critical radius the system crosses over to gelation, passes through the sol-gel transition and cures into a more-or-less firm gel. However, being an inherently nonequilibrium structure, the final gel maintains the remnants of the early stage of growth, and *far beyond the gel point* the elastic modulus is dictated by the aggregation that occurred at the earliest times! If we accept the aforementioned equipartition of energy as a general rule, the shear modulus of the fully cured gel will be $E \sim kT/\xi_s^3 \sim kT\phi_o^{4.2}$. Thus the final gel shows a strong sensitivity to the reaction conditions. In fact, it is possible to maintain the initial monomer concentration and vary the spatial correlation by an order of magnitude by modifying the pH and ionic strength. This also has a large effect on the rigidity of the final gel.

Critical Dynamics

Reaction bath

It has long been known that when a laser beam is directed through a gel, a grainy pattern is discerned, indicating inhomogeneities in the gel. These structural inhomogeneities have been dignified with the term *microsyneresis* [4]. It is commonly believed that these irregularities arise from microphase separation and therefore would not occur in a perfectly compatible system. However, in quasielastic light scattering investigations [6,26] of the dynamics of the silica sol-gel transition, we have demonstrated that these inhomogeneities are a fundamental part of the physics of chemical gels, being a natural manifestation of the breaking of ergodicity at the gel point.

The scattering of light is due to spontaneous, thermally driven concentration fluctuations. These fluctuations typically have a very short lifetime ($1\text{-}10^4$ μsec) so the eye only sees a time-averaged, apparently homogeneous, emission from the sample. However, in a gel these fluctuations become very slow so that the human eye can easily resolve the motion. To quantify exactly how fluctuations slow down when a gel is formed, we used quasielastic light scattering (QELS) to measure the decay of a concentration fluctuation of wavevector q. We found that as the sol approaches the gel point, the relaxation time of a concentration fluctuation diverges to ∞ in a proper critical point fashion [6], as

$$<\tau>\sim\varepsilon^{-1.9\pm0.1} \qquad (11)$$

This *critical slowing down* of microscopic density fluctuations before t_{gel} forshadows the frozen inhomogeneities so commonly observed in gels.

More perplexing is the observed form of the relaxation of fluctuations. Most relaxation processes decay exponentially in time, or nearly so, but at the gel point, measurements of TMOS gels indicate that fluctuations relax via the ultra-slow power-law decay [6]

$$S(q,t)\sim t^{-0.27} \qquad (12)$$

where S(q,t) is the *homodyne*, or self-beating, dynamic structure factor, which is proportional to the relaxing part of the intensity autocorrelation function. This power law decay is novel, being found only in gelling systems at or beyond the gel point, and implies that the detected scattered photons break time into a fractal set of dimension $D=1-0.27=0.73$. This fractal time set may be thought of as a kind of random Cantor set [27].

To explain these dynamical phenomena we developed a theory that describes this system as a *heirarchically constrained dynamics* where the relaxation time of any mode is dependent only on the relaxation of faster modes, not on the relaxation of slower modes. Physically, this implies the existence of a length-scale-dependent viscosity: that is, at the gel point, where the bulk viscosity is ∞, a probe of radius R feels a finite viscosity that scales as $R^{\kappa/\nu}$. This theory of the dynamics of concentration fluctuations correctly predicts a homodyne power law decay of

$$S(q,t) \sim t^{-d_c/(3-d_c)} \qquad (13)$$

along with the critical point divergence of *two* distinct relaxation times. The net result is that QELS beneath the gel point allows determination of the viscosity exponent in $\eta \sim \varepsilon^{-k}$ and the gel fraction exponent in $G \sim \varepsilon^{\beta}$. Numerically, we find $k=1.5$, in good agreement with eq. 7, and $\beta=0.35$, in agreement with the percolation prediction of $\beta=0.39$.

Dilute solution

The relaxation of concentration fluctuations may also be studied in dilute solutions of the sol. In this case the observed relaxations are due to the translational and configurational diffusion of the polydisperse ensemble of branched polymers, and the observed dynamics [12,13,28] is analogous to critical slowing down at consolute points in binary fluids. In this case, *Kawasaki-Ferrel* dynamics is expected [7,28] wherein the relaxation time τ of a concentration fluctuation of wavevector q scales as $\tau \sim 1/q^3$. This result is consistent with self-similarity of the sol, and further justifies the critical point approach to the sol-gel transition. However, internal modes of monodisperse branched polymers can also give $\tau \sim 1/q^3$, so this result is not definitive.

Conclusions

The growth, structure, and dynamics of silica gels is well described by the critical point analogy, and reasonable agreement with percolation exponents is found. This implies that the chemistry is to a large degree an irrelevent aspect near the sol-gel transition. The notion of linear-like polymers in acid catalyzed gels conflicts with experimental evidence and proper theoretical analysis. The early time growth of silica is a nonuniversal aggregation process and accounts for many of the differences in the fully formed silica gels.

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