Crossover from scalar to vectorial percolation in silica gelation

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We present a rheological study of the gel transition in silica gels resulting from the hydrolysis-condensation of a silicon alkoxide. The complex shear modulus is measured in a large frequency range (10^{-2}–10^2 rad/s). The exponents for the viscosity $s = 0.7\pm0.1$, for the elasticity $t = 2.0\pm0.1$, for the dynamic crossover frequency $z = 2.9\pm0.2$, and for the scaling-frequency power law $\Delta = 0.72\pm0.03$ are in agreement with the scalar percolation model in a restricted region around the gelation time (3%). Beyond, there is a crossover to a vectorial percolation regime characterized by a much higher elasticity exponent $t' = 3.6\pm0.1$.

INTRODUCTION

When allowed to cross-link, polymers can go through gelation: a transition from liquid to solid during which the polymeric systems suffer dramatic modifications, especially on their macroscopic viscoelastic behavior. Fifteen years ago, it was conjectured by de Gennes [1] and Stauffer [2] that gelation could be described as a percolation transition. In particular, this should imply universal critical behavior, on which system details are irrelevant. Although the experimental evidence is not completely convincing, it is generally accepted that percolation provides a good description for the static properties of the gelling systems (polymer mass distribution, divergence of the connectivity correlation length, growing of the gel fraction) [3]. The situation is quite different for the dynamical properties. According to the original de Gennes' proposal, the critical exponents of the viscosity [4] and the elasticity [1] are expected to be, respectively, the same as those of the dielectric constant and the conductivity of a random network of insulating and conducting bonds. Later, different models were worked out and led to different exponents. Some of them consider the hydrodynamical interactions in the gelling solution [5–9], others take into account the tensorial nature of the elasticity [10–12]. The experimental situation remains confusing, each polymeric system seeming to have its own exponents.

However, the electric analogy has been fully verified in a recent investigation on the viscoelastic properties of the physical gels of pectin biopolymers [13]. In that study, it has been shown that a definite conclusion can be obtained by careful dynamic measurements below and above the gelation point. It is the aim of the present paper to check whether it holds for a completely different system, namely, the inorganic covalent silica gels resulting from the hydrolysis-condensation of a silicon alkoxyde. This work is partially motivated by a previous study by Gauthier-Manuel *et al.* [14], who actually found exponent values higher than those predicted by the electrical analogy, but observed deviations towards lower values in the close vicinity of the gelation point. Such deviations have also been observed by Adam, Delsanti, and Durand [15] during the polycondensation reaction leading to polyurethane gels. In order to be able to quantify this deviation, we have performed continuous dynamic measurements during the gelation process in the large frequency range (from 10^{-2} to 10^2 rad/s) and we have improved the time resolution by using systems with long gelation times (8 and 16 days). This allows one (i) to have a better definition of the gel time t_g, (ii) to be sure that the measured viscosity and elasticity are really the static ones, and (iii) to measure the dynamic exponents z and Δ (to be defined below).

THEORETICAL BACKGROUND

The complex shear modulus $G^*(\omega)$ measured in linear dynamic viscoelastic experiments is the stress response to a harmonic strain excitation [16]. In polymeric systems, this response reflects the distribution of the relaxation times. Near a gelation point, the behavior of $G^*(\omega)$ is controlled by the ratio of the measurement frequency ω to a characteristic frequency ω_0 equal to the inverse of the longest relaxation time τ_z. For $\omega\tau_z \ll 1$, one observes the static behavior for a viscous liquid before the gelation point and for an elastic solid after the gelation point. For $\omega\tau_z \gg 1$, the broad distribution of relaxation times gives rise to a power-law frequency variation of the complex modulus. This can be schematized as follows [13,17]:

$$G''(\omega) = \omega\eta_0 \quad \text{for } t < t_g \text{ and } \omega \ll \omega_0 \, ,$$

$$G'(\omega) = G_0 \quad \text{for } t > t_g \text{ and } \omega \ll \omega_0 \, , \tag{1}$$

$$G^*(\omega) \sim (i\omega/\omega_0)^\Delta$$

for any t close to t_g and for $\omega \gg \omega_0 \, ,$

where η_0 and G_0 are, respectively, the static limits ($\omega=0$) of the viscosity and elastic modulus. At $t=t_g$, the crossover frequency ω_0 goes to 0, giving rise to a power-law behavior in the whole frequency range (this frequency range is, however, limited at high frequencies by a crossover to the regime which characterizes the internal viscoelastic behavior of the gelling units). The singular behavior near the gelation point is described by a set of critical exponents defined by $\omega_0 \sim \epsilon^z$, $\eta_0 \sim \epsilon^{-s}$ and $G_0 \sim \epsilon^t$, where ϵ is the relative distance from the gelation point. In the case of an irreversible chemical reaction, one can take $\epsilon = |(t-t_g)/t_g|$ if one assumes that the control parameter of the reaction is proportional to time (this point will be discussed below in relation to our NMR study of the silica gelation kinetics [18]). From the analyticity of the complex function $G^*(\omega)$, which reflects the unity of the physical phenomenon governing the viscoelastic properties below and above the gelation point, one deduces two relations between the exponents, namely, $z=s+t$ and $\Delta=t/z$, which allow only two independent exponents. This scaling behavior has been demonstrated for random electrical networks [19] as well as in the case of the different models which have been proposed to describe the dynamical properties of branched polymers [8,9].

Then the question of the values of these dynamic exponents is raised. Table I displays the predictions of different models. Some of them introduce relations with the static exponents d_f and v and with the spectral dimension d_s. The fractal dimension d_f characterizes the geometrical structure of the gelling polymeric units and v is the exponent of the diverging correlation length (the typical radius of the largest finite clusters): $\xi \sim \epsilon^{-v}$ [20]. The spectral dimension d_s describes the density of the vibrational modes on the fractal clusters (fractons) or correlatively the diffusion of a random walker on such a structure [21–23].

The classical theory (Flory-Stockmayer) relies on mean-field approximations. For example, it expects, at the most, a logarithmic divergence for the viscosity, whatever the interactions between the polymers. Proposed by de Gennes [1], the electrical analogy associates the critical mechanical behavior of gelling systems with the conductivity properties of a random network of conductors. The values in the table correspond to the numerical estimations for the tridimensional case [24,25]. The next two lines give the results of the hydrodynamical

models [5–9]. These models generalize the results of the Rouse and Zimm dynamics for linear polymers to branched polymers [16]. They assume a scaling law for the relaxation times, the longest relaxation time being fixed either by the diffusion on the polymer (Rouse dynamics) or by the hydrodynamic interactions through the solvent (Zimm dynamics). After t_g, they imply a mean-field equirepartition of energy on the typical volume unit $V=\xi^d$, which leads to $G_0 \sim kT/\xi^d$ and thus gives $t=vd$ [26]. Instead, the model proposed by Daoud (last two lines) [27] retains for t the conductivity expression involving d_s which takes into account the anomalous diffusion on the fractal percolating cluster. This is completed by postulating a value of the exponent z according to the type of hydrodynamic interactions. It can be seen that the Daoud-Zimm gelation model is the one whose results are the closest to the numerical estimates for the electrical network. Moreover, it appears to be consistent with both the Straley ($z=vd$) [28] and the Kertesz ($s=v-\beta/2$) [29] conjectures.

It should be noticed that in all of these models elastic interactions are considered as scalar or isotropic. This was justified by Alexander [30] who claims that the liquidlike hydrostatic stresses should be dominant for the very tenuous structure formed by gels near the gelation point. However, it has been stated by others [10–12] that the elasticity is mainly due to bending forces which are vectorial by nature and that this should lead to different universality classes for conductivity and gelation transitions. Two conjectures have been proposed for the elasticity exponent t' in vectorial models: $t'=1+vd$ [10] and $t'=t+vd$ [11,12], leading to higher exponent values than in scalar percolation, $t'=3.64$ and 4.58, respectively, for $d=3$.

EXPERIMENT

The systems under investigation result from the hydrolysis-condensation of a silicon alkoxide, the tetraethoxysilane or TEOS. The molar composition of the polymerization solutions was TEOS: water:ethanol$=1$:10:6, corresponding to a Si concentration of 1.3 mol/l. Two solutions were studied under different catalysis conditions: acidic (water pH$=4$) and basic (water pH$=9$). The gel times of these solutions were, respectively, 8 and 3 days at room temperature (21 °C). In order to slow down the kinetics, the rheologi-

TABLE I. Predictions of different scalar models. The dynamic exponents t, z, s, and Δ are related by $z=s+t=t/\Delta$. The numerical results are obtained assuming the standard values for $d=3$ percolation: $v=0.88$, $d_f=2.5$, and $d_s=\frac{4}{3}$. The exponents β and θ are defined as usual as $\beta=v(d-d_f)$ and $\theta=2(d_f/d_s-1)$.

Model	t	z	s	Δ
Classical theory	3	3	0	1
Electrical analogy	1.94	2.69	0.75	0.72
Rouse dynamics	$vd=2.64$	$v(d_f+2)=3.96$	$2v-\beta=1.32$	$d/(d_f+2)=0.67$
Zimm dynamics	$vd=2.64$	$vd=2.64$	0	1
Daoud-Rouse	$\beta+v\theta=1.96$	$2vd_f/d_s=3.75$	$2v-\beta=1.32$	0.53
Daoud-Zimm	$\beta+v\theta=1.96$	$vd=2.64$	$v(d-\theta)-\beta=0.66$	0.75

cal experiments were performed at 16 °C for the acid catalyzed reaction ($t_g = 16$ days) and at 14 °C for the base catalyzed reaction ($t_g = 8$ days).

These two systems display quite different kinetics during the aggregation phase prior to gelation. In the acidic solution, the hydrolysis of the alkoxide is fast and complete and it is followed by a slow condensation phase [31], while, in the basic solution, the hydrolysis is the limiting step of the polymerization reaction. This is reflected in the ^{29}Si NMR spectra recorded near the gelation time (Fig. 1). For the acidic solution, there is no more Q^0 or Q^1 species (here Q^n denotes a silicon linked to n other silicon atoms through oxygen bridges) and the degree of condensation is $c = 0.81$ at $t = t_g$. For the basic solution, there is still a large amount of unreacted monomers at the gelation time (21%) and the degree of condensation is only $c = 0.63$. This is of some consequence on the structure of the gels, as evidenced by small angle scattering experiments: in the aggregation growing range (typically 1 to 10 nm), one usually observes a larger fractal domain for the acidic catalyzed gels than for the basic ones [32]. This can be explained by assuming that, in basic gels, the progressive releasing of the reactive partially hydrolyzed monomers leads to the formation of dense units (poisoned Eden process) which connect each other by colloidal aggregation. On the contrary, in acidic gels, where the starting units are small oligomers [31], the formation of a much more interconnected polymeric network is obtained. Thus it seems very promising to compare the gelation behavior of these two systems which exhibit the same chemical composition, but which present so different structures: according to the universality principle, one expects these structural details to be irrelevant as concerns the properties at the gel transition.

Small-amplitude oscillatory shear measurements were performed with a Rheometrics, model RFS2, mechanical rheometer using a cone-plate geometry (diameter 5 cm, angle 2.29°). The polymerizing solution was put in the rheometer measuring cell long before the gelation time and maintained at a constant temperature. Paraffin oil was layered onto the plunger cone and sample to prevent solvent evaporation. It was checked that this protection
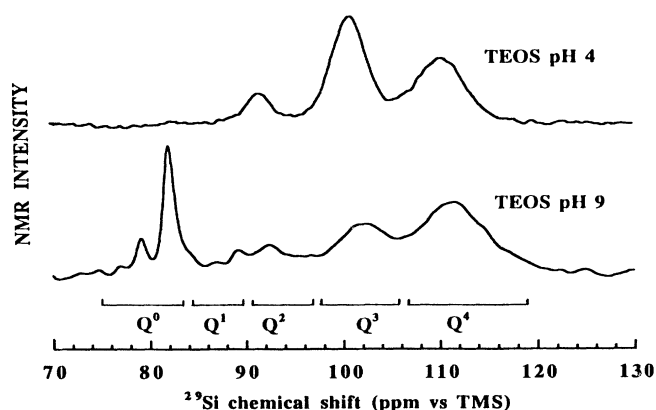
was not disturbing for the stress measurement. A periodic strain was applied to the bottom plate while the top cone was mounted on a torque transducer for force measurements. The amplitude of oscillation of the bottom plate was selected to keep the strains imposed on the sample during measurements within its linear viscoelastic response range. The real and imaginary parts of the complex shear modulus $G^*(\omega)$ were recorded as a function of the oscillation frequency between 10^{-2} and 10^2 rad/s. The frequency scanning was cycled continuously. A frequency scan lasts about half an hour, which corresponds to $\delta t / t_g$ equal to 1.3×10^{-3} and 2.6×10^{-3} for the acidic and basic gels, respectively. The rheometer sensitivity set a modulus value of 10^{-2} Pa as a lower limit for reliable measurements of $G'(\omega)$ and $G''(\omega)$.

RESULTS

Figure 2 displays the frequency variation of $G'(\omega)$ and $G''(\omega)$ at different times around the gelation point. The gelation time is determined as the time for which $G'(\omega)$ and $G''(\omega)$ are parallel in log-log plot over the whole frequency range. It appears that this condition is fulfilled only for one or two frequency scans, leading to an incertitude of about one hour on the determination of t_g. Thus the relative uncertainty on t_g is $\pm 10^{-3}$ for the acidic system and $\pm 2 \times 10^{-3}$ for the basic system. The frequency dependence of $G(\omega)$ at $t = t_g$ is fitted as a power law as

$$G'(\omega) = 0.16 \times \omega^{0.74}, \quad G''(\omega) = 0.34 \times \omega^{0.72}$$

(acidic system)

$$G'(\omega) = 0.07 \times \omega^{0.72}, \quad G''(\omega) = 0.15 \times \omega^{0.71}$$

(basic system) .

Then, the value of the frequency power-law exponent Δ appears to be in full agreement with the prediction of the electrical network analogy. Moreover the ratio $\tan\delta = G''(\omega)/G'(\omega)$ is equal to 2.1 for both systems. This is consistent with Eq. (1), which predicts $\tan\delta = \tan(\pi\Delta/2)$ and thus gives $\tan\delta = 2.13$ when one
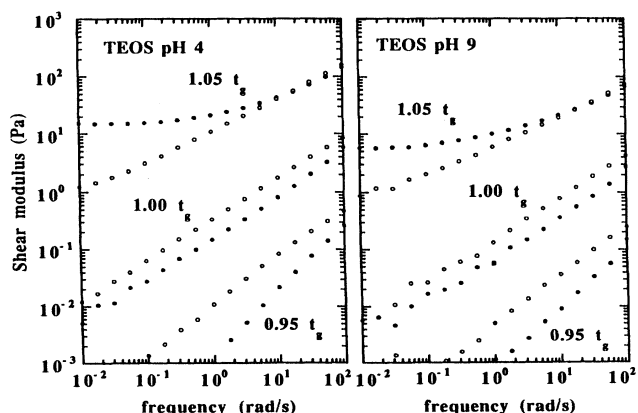

FIG. 1. ^{29}Si NMR spectra for $t = t_g$ for the acidic and basic TEOS gels. The reference for chemical shift is TMS (tetramethylsilane).

FIG. 2. $G'(\omega)$ and $G''(\omega)$ for $t < t_g$, $t = t_g$, and $t > t_g$ for the acidic and basic TEOS gels. The data at $t = 0.95 t_g$ and $t = 1.05 t_g$ are shifted by a factor 10 downwards and upwards, respectively.
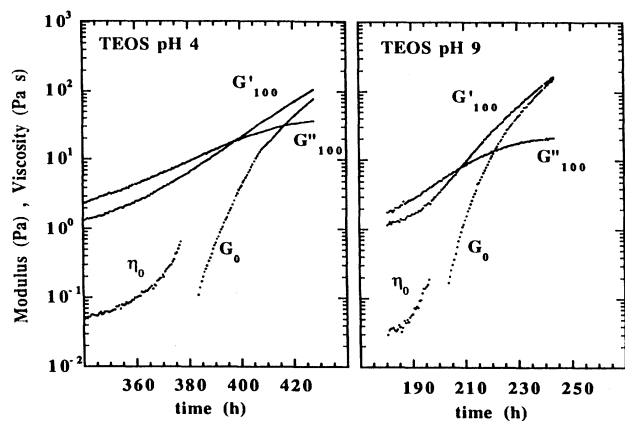
FIG. 3. Time variation of η_0, G_0, $G'(\omega = 100$ rad/s), and $G''(\omega = 100$ rad/s) for the acidic and basic TEOS gels.

FIG. 4. Log-log plot of η_0, G_0, and ω_0 vs $\epsilon = |(t - t_g)/t_g|$ for the acidic and basic TEOS gels.

takes $\Delta = 0.72$.

Below t_g, one expects a change in the frequency variation of $G'(\omega)$ and $G''(\omega)$ with the low-frequency part becoming $G'(\omega) \sim \omega^2$ and $G''(\omega) \sim \omega$ below the crossover frequency ω_0. This behavior is apparent on the frequency scans at $0.95t_g$ in Fig. 2. However the ω^2 law becomes rapidly difficult to observe because $G'(\omega)$ drops below the rheometer sensitivity at low frequency, especially for the basic system. From the linear variation of $G''(\omega)$, one obtains the static viscosity η_0. Above t_g, one observes the coming out of the finite static elasticity G_0 as a plateau on the low-frequency side of $G'(\omega)$. Moreover, one can consider the frequency for which $G'(\omega) = G''(\omega)$ as a measurement of the crossover frequency ω_0. [As a matter of fact, ω_0 could also be determined below t_g from the changes in the slopes of $G'(\omega)$ and $G''(\omega)$, but this determination would be quite subjective in practice.]

Figure 3 displays the time variation of the static viscosity and elasticity η_0 and G_0, as well as the values of $G'(\omega)$ and $G''(\omega)$ at the finite frequency $\omega = 100$ rad/s for the acidic and basic gels. A primary observation shows two important differences between these two systems: first, the kinetics is two times faster for the basic system, second, the values of the moduli are two to three times smaller in the basic system at a given stage of evolution. These lower values can be understood as resulting from the less interconnected nature of this gel with respect to the acidic one which forms a more rigid network. Both effects make the study of the gelation in the basic system less favorable as the time resolution is poorer and the measurements of small moduli are limited by the sensitivity of our rheometer.
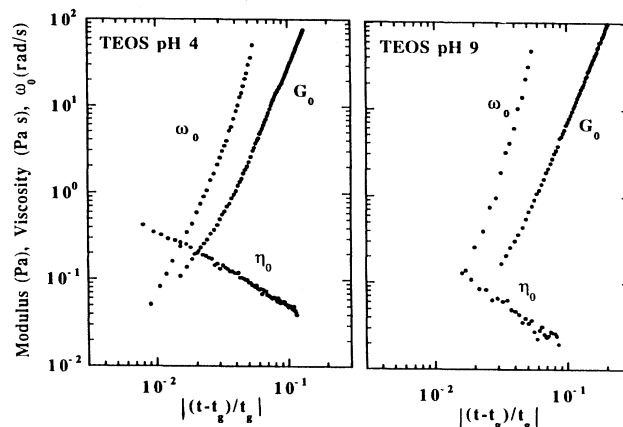
Figure 4 displays a log-log plot of η_0, G_0, and ω_0 versus

$\epsilon = |(t - t_g)/t_g|$ for both systems. There are clear deviations from the linear behavior expected for power laws. We have fitted the linear parts of the experimental data in Fig. 4 by power laws. For the acidic gel, this gives two sets of exponents "near t_g" and "far from t_g." For the basic gel, there are not enough points to obtain the exponents "near t_g," although a deviation towards smaller exponents is clearly apparent. The results are given in Table II. The uncertainties mentioned in this table give the range of values which are obtained by slightly changing t_g and by choosing different fitting ranges.

It turns out that the values of the exponents for the acidic gels near t_g are in very good agreement with the numerical results for the electrical network (second line in Table I). As the experimental values are somewhat dependent on the choice of t_g and on the chosen fitting range, it is interesting to test directly this model by an alternative procedure which permits us to get rid of any uncertainty in t_g determination. This is done in Fig. 5 where one has plotted $\eta_0^{-1/s}$, $G_0^{1/t}$, and $\omega_0^{1/z}$ as a function of time by taking for the exponents the values predicted for the electrical percolation network (namely, $s = 0.75$, $t = 1.94$, and $z = 2.69$). It can be seen that the three curves display linear behaviors which converge to the same time t_g on the abscissa axis. Besides, this value of t_g is the same as the value determined from the parallelism between $\ln[G'(\omega)]$ and $\ln[G''(\omega)]$. These results strongly support the electrical analogy.

Another method which is often used to determine the exponents is to rescale the frequency variations of $G'(\omega)$ and $G''(\omega)$ on the same master curves [13,33]. The time dependence of the frequency and modulus scaling factors

TABLE II. Experimental values of the critical exponents for the acidic and basic TEOS gels.

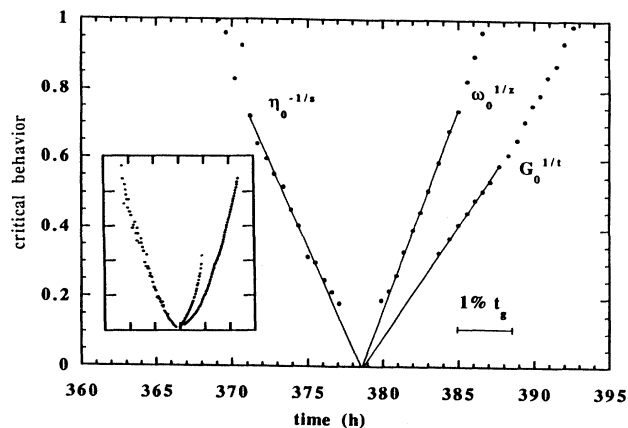|	Experiment	t	z	s	Δ
pH$=4$	near t_g	2.0 ± 0.1	2.9 ± 0.2	0.7 ± 0.1	0.73 ± 0.02
	far from t_g	3.6 ± 0.1		1.1 ± 0.1	
pH$=9$	near t_g				0.72 ± 0.03
	far from t_g	3.6 ± 0.1		1.0 ± 0.1	

FIG. 5. Test of the electrical network exponents for the acidic TEOS gel: $\eta_0^{-1/s}$, $G_0^{1/t}$, and $\omega_0^{1/z}$ are plotted vs time in the vicinity of the gel time with $s = 0.75$, $t = 1.94$, and $z = 2.69$. The inset shows the whole variation which evidences the deviation from the model far from t_g.

gives the exponents z and t, respectively. This procedure is inadequate in the present case, because of the existence of two different scaling regimes.

DISCUSSION

Before comparing our results with those of previous studies, we would like to mention that our conclusions, namely, the values of the exponents s, t, and z as well as the existence of two successive regimes of elasticity, are dependent on the implicit assumption that the degree of reaction (the probability p of the percolation theory) is actually proportional to time. This assumption is very difficult to ascertain. However, in the absence of any pertinent information, it is generally considered as valid, at least in a limited range around t_g. In the present case, the experimental range for ϵ is restricted to $1-10\%$ (see Fig. 4). Besides, we have some experimental indications in favor of the validity of the proportionality hypothesis in silica. In a recent NMR study of the gelation kinetics [18], we have shown that the degree of condensation, which is the mean number of Si—O—Si bonds per silicon, increases proportionally to time in the range $\epsilon = \pm 50\%$ around t_g. Of course, this is not a definite proof that p is proportional to t, because some of these new bonds may be related to intracluster reactions rather than gel-forming intercluster reactions. However, a deviation from the proportionality would require an increasing (or decreasing) proportion of intracluster bondings. There is, at present, no evidence for or against such a deviation.

Our results for η_0 and G_0 are in full agreement with those of Gauthier-Manuel et al. which were performed at low and fixed frequency ($\omega = 0.6 \times 10^{-2}$ rad/s). As we benefit from a better time resolution, we have been able to measure s and t near the gel transition in the acidic gel. Moreover, we have obtained independently the exponents z and Δ using the frequency dependence of $G^*(\omega)$. The fact that all these four exponents obey, within the experimental accuracy, the expected scaling relations $z = s + t$

and $\Delta = t/z$ gives further confidence in the results. Dynamic viscoelastic studies of the silica gel transition have also been performed at higher frequencies and in more restricted frequency ranges by Hodgson and Amis ($6 \times 10^2 - 7 \times 10^4$ rad/s) [33], by Martin, Adolf, and Odinek ($2-10^2$ rad/s) [34], and by Soskey et al. ($0.6-10^2$ rad/s) [35]. Our results are consistent with those of Hodgson and Amis as concerns s and Δ, but disagree for the value of t. Instead of two successive values $t = 2$ and 3.6, they find an intermediate result $t = 2.4$. It is probable that this is due to the use of a unique master curve for the analysis of the data. Moreover, it is clear that the lower the measurement frequency, the closer the approach of t_g. This is especially important in the present case, where the critical regime is restricted to a very small region around t_g.

When one compares the experimental results in Table II and the theoretical predictions for the scalar percolation in Table I, it is clear that the only models which account for the scaling near t_g are the electrical network analogy and the Daoud-Zimm model. In particular the hydrodynamic model which predict $t = vd = 2.67$ should be discarded. On the other hand, none of them appears as relevant far from t_g where the exponent for the elasticity $t = 3.6$ is consistent with the conjecture of Webman and Kantor for the vectorial percolation.

Thus, in agreement with de Gennes's proposal [1] and Alexander's arguments [30], this gelation transition appears to belong to the same universality class as the percolation of a random conductor network. However, this critical regime is restricted in the present case to a very narrow region around t_g (about 3%), beyond which the tensorial nature of elasticity becomes dominant. This is in contrast with different systems in which the scalar elasticity regime can be observed in a large range away from the percolation threshold: gelatin [36], hydrolyzed polyacrylamide in presence of chromium salts [37], and pectin biopolymers cross-linked by Ca^{2+} ions [6]. This difference may be accounted for by the nature of the cross-links and the rigidity of the polymeric structure between reticulation points. The later cases of gelation are quasiequilibrium situations, in the sense that the weak hydrogen or ionic bonds between chains are not expected to be permanent. This makes a thermodynamic description more appropriate than for the silica gelation for which the formation of irreversible covalent bonds, with a well-defined orientation between silicon tetrahedra, enhances the vectorial elasticity response due to the bending terms in the energy. Moreover, the fractal aggregates, which should be considered as the basic units for the gelation transition in silica, are expected to be much more rigid than the linear chains in the organic systems. In this respect, an important parameter for the crossover from scalar to vectorial elasticity is probably the ratio from the polymer persistence length to the distance between reticulation points. This view is supported by the results on polyurethane gels, where deviations from vectorial behavior become apparent when the mean molecular weight between two successive junctions is raised [15].

Some qualitative predictions can be made on the

dependence of this crossover upon silica concentration. On the one hand, the scalar term due to the osmotic pressure should provide an elastic modulus contribution proportional to the concentration. On the other hand, due to the structure resulting from the aggregation, the modulus raising from the response of the network itself does not behave so simply. Experiments on alcogels and aerogels give a power-law dependence on concentration, with an exponent of 3.7 ± 0.2 [38,39]. Even though these systems are far from the gel point, one can expect a rather similar behavior for the gel fraction after the threshold. Hence one gets $G_{\text{scal}}\sim c\epsilon^{t}$ and $G_{\text{vect}}\sim c^{k}\epsilon^{t'}$, with $t\approx2$, $t'\approx3.6$, and $k\approx3.6$. The crossover from the scalar to the vectorial regime is then expected to scale with the concentration as a power law: $\epsilon_{\text{co}}\sim c^{-(k-1)/(t'-t)}$. It would be interesting to check experimentally this concentration dependence.

In conclusion, we expect that the scalar percolation is actually the relevant model to describe the dynamic properties of the gelation transition. However, this behavior is difficult to observe in silica and in other covalent strong gels, because it can be restricted to a narrow region around the gel point.

ACKNOWLEDGMENTS

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