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Ultraslow Relaxations in Networks: Evidence for Remnant Fractal Structures[†]

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ABSTRACT: An intriguing relationship has been found between the relaxation time spectra of a network at the gel point—the incipient gel—and in the fully cured state. Measurements of the dynamic shear moduli of several epoxy and siloxane networks, with equilibrium moduli varying by 4 orders of magnitude, show $G'' \sim \omega^{\Omega}$ at all extents of reaction past the gel point, where the viscoelastic exponent Ω remains at the incipient gel value of 0.5–0.8. This surprising correspondence suggests that chemical networks possess some remnant of the fractal structure of the incipient gel, so the implications of this are discussed. These viscoelastic results are compared to quasielastic light scattering studies on curing silica gels, where the power law decay $S(q,t) \sim t^{-\phi}$ of the dynamic structure factor has been observed at and beyond the gel point, with ϕ unaltered by the extent of reaction.

Introduction

The evolution of relaxation phenomena in chemically cross-linking networks has recently attracted widespread interest, due to the seductive simplicity of the universal scaling laws that describe the nascent gel. Theories of the *incipient* gel—the infinitely polydisperse ensemble of randomly branched polymers formed just at the gel point—have demonstrated that the geometrical self-similarity of the branched polymer ensemble leads to dynamically self-similar relaxation phenomena. For example, scaling theories[1] of the complex shear modulus $G(\omega) = G'(\omega) + iG''(\omega)$ of the incipient gel yield the power-law frequency dependence $G'(\omega) \sim G''(\omega) \sim \omega^{\Delta}$, with Δ expected to be in the range $0.66 \leq \Delta \leq 1$. Rheological measurements on incipient gels of silica,[2] siloxane,[3] polyurethane,[4] polyester,[5] and epoxy[6,7] have substantiated this power-law behavior, albeit without strong universality in the viscoelastic exponent Δ. However, a cross-linking network passes through the gel point rather quickly, so these simple observations on incipient gels have been viewed as a mere laboratory curiosity, with little relevance to fully cured networks, which are of indisputable utility. Given our current understanding of critical phenomena in general, it is reasonable to assume a narrow critical regime, but experiments show this is not the case. For example, the equilibrium modulus of epoxy resins shows the expected power-law critical point growth in the entire postgel point regime,[7] and we have found that the loss modulus of the fully cured network obeys the same power law $G''(\omega) \sim \omega^{\Delta}$, even in the frequency regime where the storage modulus $G'(\omega)$ is constant.

This similarity of the incipient gel dynamics to that of the fully cured network draws into question our understanding of the structural evolution of networks. By definition, the gel fraction of the incipient gel is vanishingly small, since this is the order parameter for the connectivity phase transition. Thus one would think that the dynamics of the heterogeneous, ill-connected incipient gel would bear little resemblance to that of a fully cross-linked network, which we normally envisage as a homogeneous, well-connected three-dimensional "tennis net". (The primitive bond percolation model is a paradigm of this elementary view of structural evolution in networks.) Insofar as the equilibrium modulus is concerned, there is little reason to object to the homogeneous network assumption, since the traditional theories of rubber elasticity, where each "effective" network chain contributes an energy kT to the elastic modulus, apparently support the well-connected network thesis, as evinced by the success of effective chain calculations[8] in predicting the modulus for networks of short interlinking chains. However, our current viscoelastic experiments and our previously reported[9] quasielastic light scattering experiments cast doubt upon this traditional view.

Our rheological studies consisted of complex shear modulus measurements on five fully cured networks—three epoxies and two siloxanes—with equilibrium moduli varying over 4 orders of magnitude. In each case we found that beyond the gel point the measured loss moduli of the network can be described by the power-law $G'' \sim \omega^{\Omega}$, where the exponent Ω is numerically equal to the viscoelastic exponent Δ for the incipient gel. Therefore, within our experimental frequency window, the relaxation spectrum for each cross-linked network has the same functional form as that of the critical gel, albeit the fully cross-linked network has a measurable density of infinitely long modes that give a finite equilibrium modulus.

Similarly, quasielastic light scattering (QELS) measurements of the relaxation of density fluctuations in tetramethoxysilicon gels[9] have shown that both at and beyond the gel point the homodyne correlation function is described by the same power-law decay $S_2(q,t) \sim t^{-\phi}$, where $\phi \cong 0.3$, although the amplitude of the decay (the ratio of the coherent to incoherent signal) diminishes beyond the gel point. That the fully cured network has a relaxation behavior similar to the incipient gel again suggests that some remnant of the structure of the incipient gel remains in the fully cured state.

Experimental Section

The epoxies we synthesized consisted of the diglycidyl ether of Bisphenol A (Shell Epon 828) combined with various curing agents. The first epoxy was cured at 90 °C with 11 wt % diethanolamine (DEA, Fisher). We have previously reported the evolution of structure and viscoelasticity in this system near the gel point[6,7] and found good agreement with percolation theory and dynamical scaling.[1] The second epoxy was cured at 110 °C with 20 wt % diethyltoluenediamine (DETDA, Ethyl Corp.) until

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past the gel point and then postcured at 190 °C. The third epoxy was cured at 90 °C with a 17 wt % mixture of aromatic amines (Shell curing agent Z) until past the gel point and then postcured at 190 °C. These three curing agents cross-link the epoxies by two different mechanisms;[10] the DEA produces cross-links by competing reactions—the tertiary amine catalyzed reaction of primary and secondary alcohols with the epoxy, and the tertiary amine catalyzed epoxy homopolymerization—whereas the aromatic amines, DETDA and Z, cross-link by an alcohol-catalyzed reaction with the amine.

The siloxane networks we prepared are similar to those studied extensively by Chambon and Winter,[11] consisting of α,ω-divinyl-terminated poly(dimethylsiloxane) (PDMS) cross-linked at ambient temperature with platinum-catalyzed tetrakis(dimethylsiloxy)silane (TKSS) (all Petrarch Chemicals). Proton NMR analysis indicates a number-average molecular weight of 8200 for the PDMS, which is approximately 20-fold that of the Epon 828. This relatively high PDMS molecular weight leads to a balanced stoichiometry of 98 wt % PDMS and 2.0 wt % TKSS; however, a maximum equilibrium shear modulus of 9.5×10^6 dyn/cm^2 was obtained with a higher than stoichiometric concentration of 2.5 wt % TKSS.

The complex shear moduli of the fully cured networks were measured at various temperatures on a Rheometrics RDS-2 dynamic mechanical spectrometer operating in the range of $0.1 \leq \omega \leq 30.0$ Hz, using torsion rectangular geometry for the epoxies and parallel plate geometry for the siloxanes. Time–temperature superposition was then used to construct master curves for each network. The complex shear moduli of the incipient epoxy networks were measured on the RDS-2, but a Carri-Med CS500 controlled-stress rheometer was used for the incipient siloxane networks, due to the greater sensitivity of this instrument. Rapid scans from 0.2 to 50.0 Hz were taken at frequent intervals on the materials curing within the parallel rheometer plates; the gel point data were taken as those which satisfied the relation $G' \sim G'' \sim \omega^{\Delta}$.

Results

Incipient Networks. The complex shear modulus measurements on the incipient epoxy resins agreed well with our previously reported results on the epoxy/DEA system,[6,7] wherein a viscoelastic exponent of $\Delta = 0.70 \pm 0.05$ was found. For example, in the present study the epoxy/DETDA incipient gel gave $\Delta = 0.65 \pm 0.05$, indicating that the chemical cross-linking mechanism may have a slight effect on the critical dynamics. The relaxation behavior of the incipient epoxy/Z networks could not be determined, due to sample vitrification and unduly rapid cure kinetics.

In the siloxane system we prepared three incipient gels that differed only in the stoichiometric ratio of silane to vinyl groups, r. The siloxane network prepared with the smallest stoichiometric ratio of 0.45 had just enough cross-linker to reach the gel point when fully cured. The viscoelastic exponent for this chemically stable incipient network was found to be $\Delta = 0.65 \pm 0.05$. However, when the cross-linker concentration was increased, the gel point viscoelastic exponent—now measured during cure—was found to decrease; for example, $r = 0.52$ gave $\Delta = 0.56 \pm 0.04$ and $r = 0.80$ gave $\Delta = 0.51 \pm 0.04$. The dependence of the viscoelastic exponent of siloxanes on stoichiometry, already well documented in studies by Chambon and Winter,[11] is not understood, and it is most vexing that the measured values of Δ differ from the theoretical scaling prediction of $^2/_3$ so consistently observed in epoxies. However, it is possible that the high molecular weight of the PDMS leads to a narrowing of the critical regime where percolation-based scaling theories apply.[12] In fact, our structural experiments on the molecular weight and radius divergence of siloxane sols are consistent with the Flory–Stockmayer, or classical, description of gelation even close to the gel point.

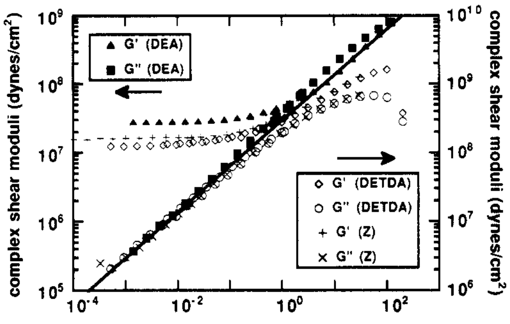

Figure 1. Complex shear moduli for three epoxy networks. The loss moduli, G'', exhibit the same power-law decay as observed for the critical gels. The solid line indicates a decay exponent of $^2/_3$, the dynamic scaling theory prediction that holds for the critical gels.

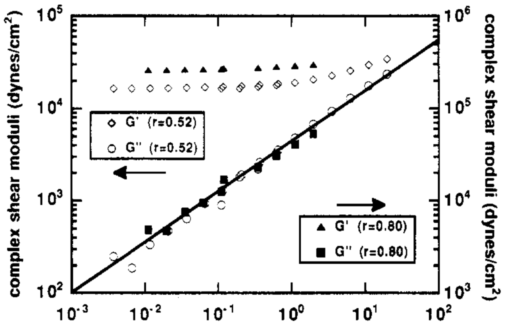

Figure 2. Complex shear moduli for two siloxane networks. The loss moduli, G'', exhibit the same power-law decay as observed for the critical gels. The solid line indicates a decay exponent of 0.55 that holds for the critical gels.

Fully Cured Networks. The complex shear moduli for the fully cured epoxy and siloxane networks are shown in Figures 1 and 2, respectively. For each system the loss component of the shear modulus can be described by the power-law $G'' \sim \omega^{\Omega}$ for $\omega < \omega_0$, where ω_0 is associated with the onset of the glassy transition and non-Rouse-like relaxation modes. While power-law decay for the long-time relaxations of *vulcanizates*, rather than these short-chain step-growth polymerized networks, has been documented,[13] it has been attributed to the "reptation" of tethered, or dangling, chains[14] rather than to a self-similar network structure.

The intriguing aspect of Figures 1 and 2, which these tethered chain theories cannot explain, is that the viscoelastic exponent Ω for each fully cured network is numerically equal to the viscoelastic exponent Δ for the incipient network; thus for the epoxy networks $\Omega = \Delta \cong {}^2/_3$, whereas for the two siloxane networks $\Omega = \Delta \cong 0.55$. This correspondence leads us to believe that some vestige of the incipient gel structure remains in the fully cured network. This clearly contradicts our traditional structural paradigm of a highly cross-linked network appearing as a roughly homogeneous "tennis net". Rather, we envision the network structure as an interwoven, interpenetrating entity with complex connectivity.

Discussion

Ergodicity Breaking: Divergent Characteristic Times beyond the Gel Point. The observations we have made indicate that the fully cured network is effectively a nonergodic medium with infinite relaxation times. The term nonergodic is justified, since an ensemble average in phase space is equivalent to averaging over many relaxation times of the system. This averaging is not possible in a system with an infinite characteristic time. The breaking of ergodicity occurs at the gel point, as we shall now discuss.

The power laws observed in the viscoelastic response of fully cured organic polymer networks are perhaps surprising, but they are consistent with the relaxation of spontaneous density fluctuations observed in QELS measurements on inorganic silica gels prepared from tetramethoxysilicon.[9] These time-domain measurements clearly demonstrate, at least over the observable five decades of time, a power-law decay of the homodyne intensity correlation function $S_2(q,t)$ at the gel point, with $S_2(q,t) \sim t^{-\phi}$ where q is the momentum transfer. Since the homodyne correlation function is just the time-domain photon–photon correlation function, this power-law decay indicates that the detected photons create a fractal time set, which has no characteristic time. A relaxation time divergence has been experimentally demonstrated by integrating $S_2(q,t)$ over time in the pregel regime to obtain the arithmetic average relaxation time $\langle\tau\rangle$ (which is physically analogous to the viscosity of the sol, since $\eta \sim \langle\tau\rangle$). Measurements[9] show that $\langle\tau\rangle$ tends to infinity as the gel point is approached ($\langle\tau\rangle \sim \epsilon^{-1.9}$, where $\epsilon = |p - p_c|$ is the time from the gel point and p_c is the bond probability at the gel point). The normal symmetry of critical point phenomena would lead one to expect that, beyond the gel point, $\langle\tau\rangle$ should decrease in the same fashion; however, experiments show that the decay remains a nonintegrable power law in the postgel regime, so that the arithmetic average relaxation time remains infinite in the postgel regime, or at least is much larger than can be resolved experimentally. Thus the gel permanently exists in a nonergodic state. This curious postgel point relaxation behavior is consistent with the frequency-domain data for the shear loss modulus, where no lower frequency cutoff was found for the power-law $G'' \sim \omega^{\Omega}$, again indicating an apparently infinite average relaxation time.

Ill-Connected Networks. We fell that the ultraslow relaxations observed in well-cured networks evince an ill-connected structure that in some way is related to the gel point structure. Indeed, use of network connectivity to rationalize the exceedingly long relaxation times observed in networks has been pursued by Eichinger's group,[15] who have long been aware that Rouse modes of a single interlinking chain are far too fast. In contrast, theories of the equilibrium elastic modulus are adequately developed in terms of single interlinking chains. This brings us to the issue of how a fully cured, spatially homogenous medium can be ill-connected. There are two distinct possibilities: (1) the network consists of collapsed fractal microdomains; (2) the network consists of interpenetrating fractal microdomains. When we refer to fractal domains, we mean a small number N of interlinking chains, each of volume v and consisting of $n = v/a^d$ monomers of radius a, that are connected to make a fractal cluster.

In general, the mass fractal dimension d_f is a product of a *geometrical* dimension and a *connectivity* dimension.[16] These dimensions describe the set of minimal paths on a fractal. If the fractal is composed of a set of discrete sites or monomers, then a minimal path is defined as a shortest sequence of monomers that connect two distal sites. The geometrical dimension d_g is just the fractal dimension of a minimal path; so if R is the root-mean-square end-to-end distance of the minimal path, and L is the number of monomers on the minimal path, then $R^{d_g} \sim L$. The connectivity dimension d_c describes the number of sites N that can be reached in L steps or less, via $N \sim L^{d_c}$. For a spatially homogeneous medium, the product $d_f = d_g d_c$ must be 3, the dimension of space, but that does not necessarily imply that the connectivity dimension itself is 3. For example, a ball has a connectivity dimension of 3, a crumpled piece of paper has a connectivity dimension of 2, and a ball of string has a connectivity dimension of 1; so although all of these objects have a mass fractal dimension of 3, their connectivity differs greatly.

(a) Collapsed Fractals. The crumpled sheet and string may be viewed as "collapsed" fractals since the connectivity dimension is less than the fractal dimension. In general, one can take a fractal of dimension d_f and crumple it so that $d_f \rightarrow d$. Since crumpling does not affect the connectivity dimension d_c, the geometrical dimension must increase to $d_g' = d_g(d/d_f)$. Thus, crumpling can produce compact structures with highly interesting connectivity. It may be appropriate to view a polymeric network as a collased fractal on intermediate length scales. For example, suppose we construct a network that in some convenient uncollapsed reference state has a correlation length ξ, below which it has a fractal dimension d_f. (Uncollapsed fractal networks can be synthesized by gelling low-molarity solutions of tetramethoxysilicon.[17] This gives a network of fractal aggregates with a fractal dimension of ~ 2 on length scales generally less than 1 μm.) The elastic modulus of this fractal network will scale as[1,18]

$$G_\infty \sim kT/\xi^d \tag{1}$$

since in a unit deformation there is $\sim kT$ of energy stored per correlation volume. This general result has been explicitly derived for the percolation network near the gel point by appeal to the scaling of the viscoelastic functions.[1] Since $\xi \sim \epsilon^{-\nu}$, where again $\epsilon = |p - p_c|$, this gives $G_\infty \sim \epsilon^{-d\nu} \sim \epsilon^{-2.7}$, which is in good agreement with experiments on a number of critical gels.[7] When the fractal network collapses to a bulk state of density ~ 1, the network density increases by ξ^d/Nv, where N is still the number of chains of volume v in ξ^d. The modulus increases by ξ^d/Nv to

$$G_\infty \sim kT/vN \tag{2}$$

Thus, a collapsed fractal network will have a modulus that is smaller by a factor N from that of a perfect network, which would have the classical modulus $G_\infty \sim kT/v$.

These results for the elastic modulus can be clarified by again appealing to the percolation model.[1] By use of the standard critical point exponent relation $d = d_f + \beta/\nu$, where $g \sim \epsilon^\beta$ is the gel fraction, eq 1 can be conveniently expressed as

$$G_\infty \sim kTg/vN \tag{3}$$

where $N \sim (\xi/v^{1/d})^{d_f}$ is the average number of units of volume v in a correlation volume. This relation has a simple interpretation; the gel fraction, $g \sim N/\xi^d$, is the only portion of the sol–gel that can contribute to the elasticity and vN is the average volume of a fractal domain. If the sol phase were extracted from the network, the density would increase by a factor $1/g$ and the modulus of the final, collapsed fractal network would be given by $G_\infty \sim kT/vN$. Thus eq 2 is not really new, but comes from reconsidering an old result.

Attempting to compute N for real networks leads to some surprising results. For PDMS networks of short chains[19] the junction affine modulus kT/v agrees within a factor of 2 with the measured modulus, indicating $N < 2$, and collapsed fractal structures do not exist. The softer phantom network modulus for an f-functional network, $(1 - 2/f)kT/v$, is actually smaller than the measured modulus! Thus the network softening predicted by small collapsed fractal domains is not justified by comparison of measured moduli to the affine or phantom theories.

However, we must remember that these microscopic theories drastically simplify the behavior of real polymer networks. Therefore, we cannot place too much physical significance on the magnitude of the *prefactors*. Rather, the scaling relationships derived from these theories are much more relevant and meaningful. In this perspective, eq 2 and both the phantom and affine theories agree fundamentally.

Let us suppose that N is of a significant size, as it is when the networks are not fully cured, or have an imbalanced stoichiometry, and consider the dynamics of such ill-connected networks. When an instantaneous deformation is applied to a network, the equipartition principle dictates that kT is stored in every degree of freedom, so the short-time modulus should be the entropic contribution kT/a^d to the glassy modulus, where a is roughly the monomer size and thus should not depend on connectivity. At long times, the stress in a well-connected network will decay until the initial entropic stress is reduced by a factor $1/v$, due to the fact that each interlinking chain of $n = v/a^d$ monomers only stores an energy kT at equilibrium. For an ill-connected, collapsed fractal network, however, there must be an *additional* stress decay, or softening, by a factor of N. These additional relaxations would occur within the fractal domains of the network. A dynamical scaling analysis of flexible fractals in the Rouse limit[1] gives a viscoelastic exponent of

$$\Delta = d_f/(2 + d_f)$$

For example, the θ chain, with $d_f = 2$ has $\Delta = 1/2$, and the good-solvent chain, with $d_f = 5/3$ gives $\Delta = 5/11$. Since a collapsed fractal has a dimension of 3, we take the limit $d_f \rightarrow 3$ to obtain $\Delta = 3/5$, in reasonable agreement with our experiments on fully cured networks. Thus, a collapsed fractal network should have a modulus that is much lower than the modulus $G \sim kT/v$ for the total density of chains and should exhibit the power-law dependence $G'' \sim \omega^{0.6}$ of the loss modulus on frequency.

(b) Interpenetrating Fractals. An interpenetrating fractal network can also be imagined. Consider the vulcanization of a melt of long, linear chains of fractal dimension 2. Each interlinking subchain of N units has a radius R, but the modulus is not kT/R^d as in eq 1 since linear chains do not screen other chains from their own domain of volume. Therefore, $1/R^d$ is not the number of chains per unit volume. We must divide kT/R^d by the density a^dN/R^d to obtain the classical modulus kT/a^dN, where $1/a^dN$ is the density of chains. In the more general case, where the chains themselves make overlapping fractal regimes, eq 2 should again apply, so the modulus does not distinguish between overlapping and collapsed fractal domains. However, the viscoelastic exponent $\Delta = d_f/(2 + d_f)$ should reflect the dimension of these overlapping domains.

Conclusions

Measurements of the complex loss modulus of both incipient and fully cured epoxy and siloxane networks show a power-law frequency dependence $G''(\omega) \sim \omega^{\Delta}$ that is independent of the extent of reaction once the gel point is reached. Quasielastic light scattering measurements of the relaxation of density fluctuations of inorganic silica gels show similar results, with the homodyne correlation function decaying as $S_2(q,t) \sim t^{-\phi}$ in the postgel regime. These power-law decays are observed at all experimental time scales, indicating that a network is a nonergodic medium with an infinite average relaxation time. Since these power-law decays are the signature of self-similar structures, we believe that the fractal branched polymers formed at the gel point persist as remnant-collapsed or interpenetrating fractal domains in the fully cured networks.

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