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temperatures of the finite chain systems is severely hampered because of the molecular weight dependence of σ_e.

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Time–Cure Superposition during Cross-Linking†

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ABSTRACT: Using a dynamic scaling theory for the viscoelasticity of cross-linking polymers near the gel point, we predict the superposition of viscoelastic functions at differing extents of reactions. For example, to superpose the stress relaxation modulus, a vertical shift is needed to account for the increase in the equilibrium modulus with cure, $G_\infty \sim \epsilon^{8/3}$, and a horizontal shift for the divergence of the characteristic relaxation time, $\tau_z \sim \epsilon^{-4}$, where ϵ is the critical extent of reaction. Experiments on model epoxies show excellent superposition both below and above the gel point and give $G_\infty \sim \epsilon^{2.8\pm0.2}$ and $\tau_z \sim \epsilon^{-3.9\pm0.2}$. The critical regime where this superposition is valid is surprisingly wide, encompassing over half of the reaction.

Introduction

Although the critical dynamics that occur near a *thermodynamic* second-order phase transition are reasonably well understood, the critical dynamics of the gel point, a second-order transition in *connectivity*, have been investigated only recently.[1-5] At the sol–gel transition it is the divergent connectivity correlation length, not the spatial correlation length, that leads to complex dynamic behavior, so there are many interesting viscoelastic dynamical features that have no apparent analogue in thermodynamic transitions. The observed phenomenology is by now familiar: beneath the gel point, the viscosity η diverges continuously and above the gel point the equilibrium modulus G_∞ grows continuously. In addition, the longest relaxation time,[6] τ_z, that delineates the simple viscous or elastic regime from a complex viscoelastic fluid regime diverges as the gel point is approached from either

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above or below.

We have recently developed a dynamic scaling theory for viscoelasticity near the gel point[2,3] that not only predicts the critical divergences for η, G_∞, and τ_z but gives the functional forms of the viscoelastic functions. In its most elemental form, the theory reduces to a Rouse-type model for *branched* polymers of infinitely broad polydispersity.[5,7] Our previous experimental measurements[8] of the viscosity divergence and the viscoelastic behavior at the gel point agreed well with the theoretical predictions. In this paper, we show that viscoelastic functions at differing extents of reaction should superpose if the appropriate vertical and horizontal shifts are applied. These shift factors themselves describe critical divergences that cannot be measured directly by conventional techniques.

Theory

The dynamic scaling theory for the viscoelasticity of near-critical gels[2,3] predicts a spectrum of relaxation times of the form $H(\tau)\ \mathrm{d}\ln\tau \sim \tau^{-\Delta}f(\tau/\tau_z)\ \mathrm{d}\ln\tau$, where $^2/_3 \leq \Delta \leq 1$. Here, $f(x)$ is a function that rapidly truncates the algebraic decay of the spectrum for $x \gg 1$. Since viscoelastic properties may be expressed as transforms of $H(\tau)$, it is apparent that power-law expressions will be observed on time scales small compared to τ_z. For example, the shear relaxation modulus scales as $G(t) \sim t^{-\Delta}$ for $t \ll \tau_z$. Likewise, both the storage G' and loss G'' components of the complex shear modulus scale as ω^Δ for $\omega\tau_z \gg 1$. Therefore, the complex viscoelastic fluid regime is characterized by a single exponent that results from static and dynamic self-similarity.

The simple-fluid (or solid) regime can be characterized by the divergences of the viscosity and equilibrium modulus

$$\eta \sim \epsilon^{-k}, \qquad G_\infty \sim \epsilon^{z} \tag{1}$$

where, in terms of the bond probability p, $\epsilon = |p_c - p|/p_c$, with p_c the bond probability at the gel point. In three dimensions, the theory predicts $z \cong {}^8/_3$ for entropic elasticity and sets the bounds $0 \leq k \leq {}^4/_3$ on the viscosity exponent. The transition from a simple fluid (or solid) to a viscoelastic material is described by another critical exponent

$$\tau_z \sim \epsilon^{-y} \tag{2}$$

Fortunately, two relations temper the proliferation of exponents: $y = z + k$ and $\Delta = z/y$. In the limit of strongly screened hydrodynamic interactions (the Rouse limit), this gives $k = {}^4/_3$, $y = 4$, and $\Delta = {}^2/_3$.

The crossover from a complex to simple fluid is most easily understood in the time domain. After a gel is subjected to an abrupt shear strain, the stress will start to decay after some molecular time scale τ_0. For times much larger than τ_0 but smaller than τ_z, theoretical arguments indicate that the stress will then decay as the power law $G(t) - G_\infty \sim t^{-\Delta}$.[9,10] However, as the transition time τ_z is approached, the decay crosses over from a power law to the relatively rapid stretched exponential form,[3] $\ln [G(t) - G_\infty] \sim -(t/\tau_z)^b$, where $b = {}^2/_5$ beneath the gel point (the situation above p_c is especially complex). For times larger than τ_0, the full behavior may be usefully described by

$$G(t) \sim \frac{\eta}{\tau_z}\left(\frac{\tau_z}{t}\right)^{\Delta} e^{-(t/\tau_z)^b} \qquad p < p_c \tag{3a}$$

$$G(t) \sim G_\infty\left[1 + A\left(\frac{\tau_z}{t}\right)^{\Delta} e^{-(t/\tau_z)^{b'}}\right] \qquad p > p_c \tag{3b}$$

where A is a material constant that depends on the glassy modulus. Note that by using eqs 1 and 2 and standard exponent relations, the term η/τ_z can be shown to scale as ϵ^z, just as $G_\infty \sim \epsilon^z$. In fact, η/τ_z is just the energy stored in a creep experiment[11] (the steady-state compliance J_e^0), so it is not surprising that it diverges with the same exponent as the modulus albeit on the other side of the gel point.

Equations 3a and 3b describe master curves when the abscissa and ordinate are scaled by τ_z and G_∞ (i.e., ϵ^z), respectively. This constitutes a viscoelastic superposition principle, *time–cure superposition*, and is, of course, valid for any viscoelastic function. For example, the complex shear modulus can be expressed as the universal function $G^*(\omega\tau_z)/G_\infty$.

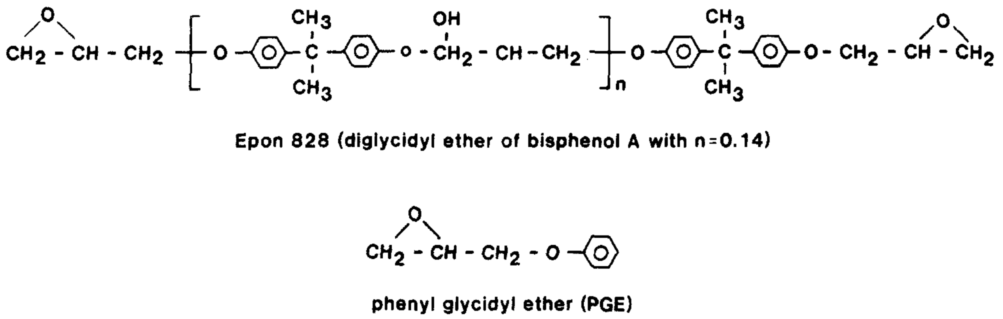
Time–cure superposition is similar to *time–temperature* superposition, a time-honored concept in polymeric viscoelasticity.[11] Simply stated, time–temperature superposition acknowledges that all normal modes feel the same temperature-dependent friction; thus the observed stress relaxation can be rendered temperature independent by an appropriate redefinition of time. This technique is commonly used to bring high- or low-frequency modes into the experimental frequency window by using temperature to change the friction.

Time–cure superposition is a more subtle effect resulting not from a change in friction, but from a change in connectivity. Since the near-critical gel is geometrically self-similar, a change in the extent of cure results in a mere change in scale: clusters become larger ($p < p_c$) or smaller ($p > p_c$) as p increases. This change in scale can then be absorbed by a suitable redefinition of time (larger clusters relax more slowly) and by accounting for the change in the shear contribution to the free energy density (G_∞^{-1} diverges at p_c). Time–cure superposition is useful in ameliorating certain experimental difficulties; for example, the divergence of τ_z has not been reported, since this time becomes so large near the gel point that the sample appreciably cures during the measurement. Time–cure superposition circumvents this problem by allowing the universal viscoelastic behavior of the system to be built from "snapshots" at discrete times during the course of the reaction.

Time–cure superposition has been examined previously for the *long-time* relaxations of *fully cured* networks.[12–14] However, the superposition principle presented above arises from different mechanisms and can be distinguished from prior versions by three points: first, the superposition applies for the sol as well as the gel; second, the entire relaxation modulus ($t > \tau_0$) superposes, not just the long-time portion; and third, our analysis is strictly valid in the critical regime near the gel point and not necessarily at reaction completion. Previous studies attempting to describe network dynamics at arbitrary cross-link densities examined fully cured networks and then reduced the cross-link density. In contrast, we have elucidated the dynamics at the gel point and worked toward higher extents of reaction.

Experimental Section

Our experimental system consists of 89 wt % diglycidyl ether of bisphenol A (Epon 828 epoxy) cured at 90 °C with 11 wt % diethanolamine (DEA), $HN(CH_2CH_2OH)_2$. These weight percents give a fully cured epoxy with a glass transition temperature, T_g, of 70 °C. The cure kinetics is discussed in detail elsewhere[15] but is outlined here. DEA endcaps approximately one-fifth of the epoxy groups in the first 5 min at 90 °C by reaction of the amine with the epoxy, producing a secondary hydroxyl. The cross-linking reaction then proceeds by the tertiary amine catalyzed reaction of epoxy and either primary or secondary hy-



Epon 828 (diglycidyl ether of bisphenol A with n=0.14)

phenyl glycidyl ether (PGE)

Figure 1. Structures of the difunctional (828) and monofunctional (PGE) epoxies.

droxyl with approximately equal probability. The gel point occurs at roughly 3 h at 90 °C, and the extent of reaction of epoxy groups, α, has been monitored independently by DSC, FTIR, and NMR. The extent of reaction at the gel point is ca. 0.65. The bond probability p for this system, which is needed to calculate ϵ, equals α^2, as described by Flory.[16]

We have investigated time–cure superposition in the frequency domain by measuring the storage G' and loss G'' components of the complex shear modulus G^*. The measurements were performed on a Rheometrics RDS-2 between 50-mm parallel plates at 0.2–2% strain that were kept at 90 °C. Dynamic scans from 2 to 200 rad/s were taken approximately every 4 min, with each scan lasting just over 1 min. The gel time of 188 min was not left as an adjustable parameter but was independently determined as the time at which $G'(\omega) \sim G''(\omega) \sim \omega^{\Delta}$ applies over the experimental frequency domain. For the extents of reaction measured here, friction changes due to increasing T_g with cure have been shown to be negligible.[8]

We have also *directly* measured the increase in the equilibrium modulus with extent of reaction. The samples were cured at 90 °C in rectangular geometry (2.5 in. × 0.5 in. × 0.25 in.) to differing extents past the gel point and placed in the RDS-2. The storage modulus G' was measured at 90 °C as a function of time at a fixed frequency of 1 rad/s, which is normally sufficiently low ($\omega \ll \tau_z^{-1}$) such that G' approximately equals G_∞. However, near the completion of reaction, $\alpha > 0.9$, where the ultimate T_g of 70 °C approaches the measurement temperature, G' will no longer equal G_∞ due to the increasingly long relaxation times associated with T_g, and $G' > G_\infty$.

Ideally, to measure the equilibrium modulus, we need samples of the DEA-cured epoxy that are chemically quenched at differing extents of reaction. We have effected a chemical quench by reacting mixtures of Epon 828 and phenyl glycidyl ether (PGE) in differing proportions with DEA. The chemical compositions of the difunctional 828 and the monofunctional PGE are shown in Figure 1. Since PGE is effectively half of 828, adding PGE to the 828/DEA mixture and then fully curing is comparable to taking molecular scissors and cutting bonds in a fully cured sample of just 828 and DEA. At a critical ratio of 828 to PGE (42 mol % 828 and 58 mol % PGE), the sample, when fully cured with DEA, is very close to the sol–gel transition. By increasing the amount of 828, we can then increase the effective extent of reaction and examine the equilibrium modulus.

The bond probability, $p = \alpha^2$, should be equal to the mole percent of 828 in the 828/PGE mixture. This relationship is seen to hold for the critical bond probability, p_c, at the gel point. We observed $p_c = (0.65)^2 = 0.42$ for the partially cured 828/DEA system and $p_c = 0.42$ as shown above for the fully cured 828/PGE/DEA system. We cured samples of 828/PGE/DEA at 90 °C for 2 days in rectangular geometry as above with 828/PGE mole ratios of 50/50, 60/40, 80/20, and 100/0 (pure 828). These ratios correspond respectively to ϵ = 0.19, 0.43, 0.91, and 1.38. The shear relaxation modulus, $G(t)$, was measured for 10 h at 90 °C and the equilibrium modulus was extracted.

These direct measurements of the equilibrium modulus indicate the width of the critical regime past the gel point, as determined by a single exponent describing the increase in modulus. We have also measured the viscosity divergence to discover the width of the critical regime prior to the gel point. Previous measurements of the viscosity using the RDS-2[8] have been supplemented with measurements on a Brookfield viscometer LVTDV-II with spindle 1 in a 10-cm-diameter beaker at 0.3–30 rpm at 90 °C. All reported viscosities are zero-shear-rate values.

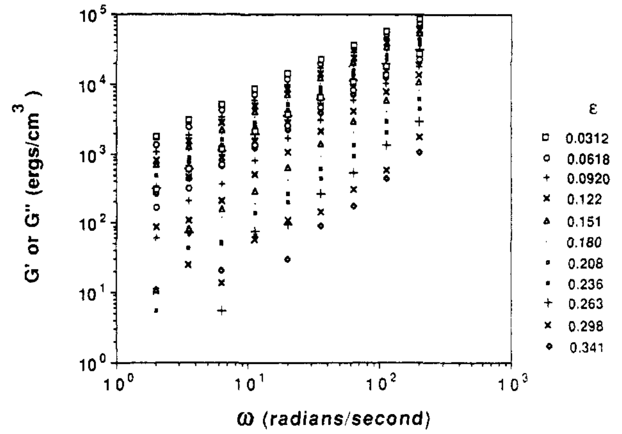


Figure 2. Pregel storage and loss components of the complex shear modulus as functions of frequency at various extents of reaction (ϵ).

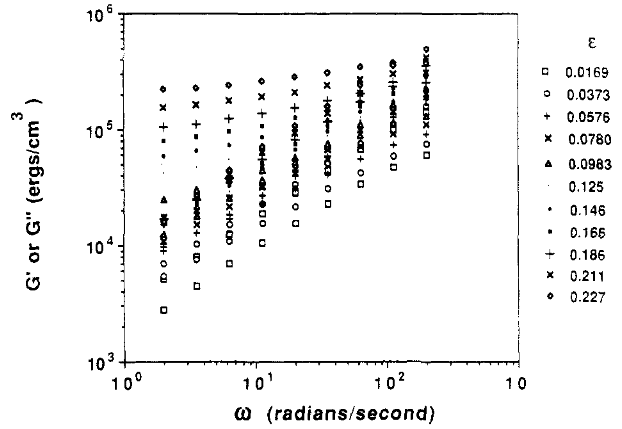


Figure 3. Postgel storage and loss components of the complex shear modulus as functions of frequency at various extents of reaction (ϵ).

Results and Discussion

The behavior of the complex shear modulus, G^*, is shown in Figure 2 (sol) and in Figure 3 (gel). Figures 4 and 5 show the master curves that result from time–cure superposition; the frequency and the energy density (G^*) for each value of ϵ were shifted by factors proportional to ϵ^{-y} and ϵ^{z}, respectively. The exponents z and y were chosen to give the best superposition of G' and G'' both before and after the gel point. Therefore, the exponents z and y have been extracted from four independent sets of data. Excellent superposition is achieved with z = 2.8 (±0.2) and y = 3.9 (±0.2), these agreeing very well with the predictions $z \cong 2.67$ and $y \cong 4$ of our dynamic scaling theory. From the scaling relationships, $k = y - z$ and $\Delta = z/y$, we then find

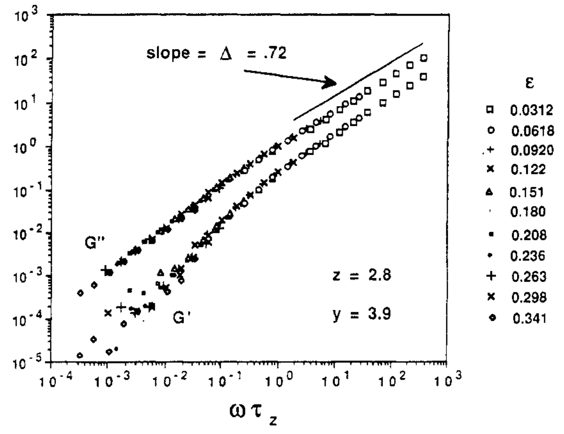


Figure 4. Results of superposition of the data in Figure 2, where frequency has been scaled by $\tau_z \sim \epsilon^{-y}$ and the complex modulus by $G_\infty \sim \epsilon^z$ with $y = 3.9$ and $z = 2.8$. The power-law regime in G^*, where $G' \sim G'' \sim \omega^\Delta$, obeys the scaling relationship, $\Delta = z/y = 0.72$.

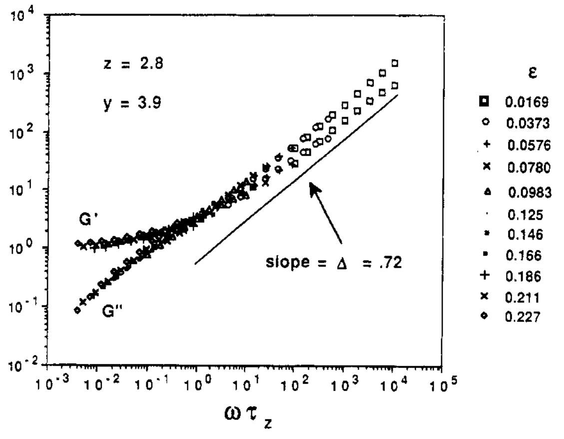


Figure 5. Results of superposition of the data in Figure 3, where frequency has been scaled by $\tau_z \sim \epsilon^{-y}$ and the complex modulus by $G_\infty \sim \epsilon^z$ with $y = 3.9$ and $z = 2.8$. The power-law regime in G^*, where $G' \sim G'' \sim \omega^\Delta$, obeys the scaling relationship, $\Delta = z/y = 0.72$.

$k = 1.1 \pm 0.4$ and $\Delta = 0.72 \pm 0.09$, which also compare well to the predictions[3] $k \cong 1.33$ and $\Delta \cong 0.67$, respectively. As in time–temperature superposition, the construction of the master curve is sensitive to the shift factors chosen, so the errors associated with the directly measured exponents are relatively small (±0.2).

In Figure 6, we have plotted the increase of the equilibrium modulus as determined by time–cure superposition, by direct measurement on partially cured 828/DEA, and by direct measurement on fully cured 828/PGE/DEA samples. The three independent measurements agree well with each other and are within experimental error of the theoretical predictions. The breadth of the critical regime where this theory applies is surprising. Within error, the divergence of the equilibrium modulus is described by a single exponent over the entire postgel regime. This broad critical regime is no doubt due in part to the extremely low molecular weight of the epoxy chains (MW = 380).[17]

The divergence of the viscosity is shown in Figure 7. Again, the width of the critical regime, as determined by the fit to a single power law, is fairly large, encompassing $\epsilon < 0.52$ or, in terms of extent of reaction, $0.45 < \alpha < \alpha_c$ (=0.65). Therefore, from measurements of the viscosity and modulus, we have shown that conservative bounds on the critical regime are given by $0.45 < \alpha < 1$, which is over half of the reaction.

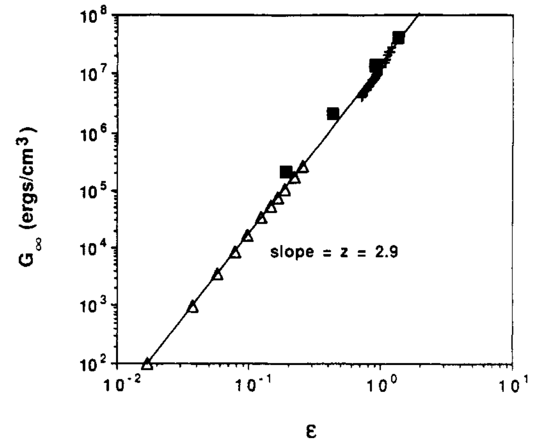


Figure 6. Increase of the equilibrium modulus where (Δ) are from time–cure superposition, (+) are from direct measurement, and (■) are from 828/PGE/DEA mixtures.

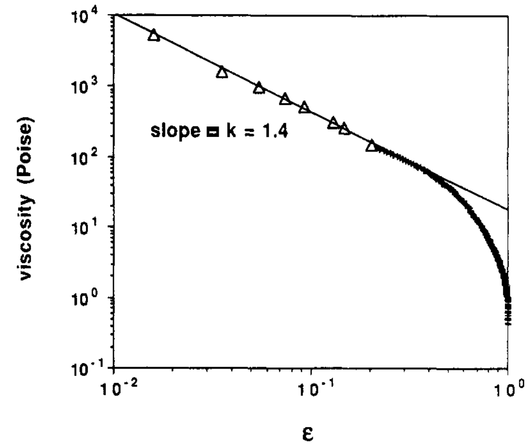


Figure 7. Divergence of the bulk viscosity where (Δ) are from RDS-2 measurements and (+) are from Brookfield measurements.

Although there have been no previous experimental determinations of the divergence of τ_z, there have been many attempts to determine the divergences of the bulk viscosity and equilibrium shear modulus. The bulk viscosity divergence has typically been measured by following the steady-state shear stress with time; however, the accuracy of this technique is severely limited since it is not possible to *independently* determine the gel point. Nonetheless, using this technique on epoxies,[8] we previously obtained $k = 1.4 \pm 0.2$, which is within experimental error of our present result. Other groups[18–21] have measured values of k ranging from 0.75 ± 0.04 to 1.5 ± 0.2, where the latter value was obtained from an interpretation of quasi-elastic light scattering data.

The growth of the equilibrium shear modulus has typically been determined at a frequency chosen to be sufficiently low (i.e., $\omega \ll 1/\tau_z$) to ensure that the measured modulus is actually the equilibrium value. Studies[18–22] have found values of z ranging from 2.1 ± 0.3 to 3.2 ± 0.6. In general, it is clear that there has been no consensus on the values of k or z in the critical regime. We believe time–cure superposition offers greater precision in these measurements.

The divergence of the equilibrium modulus has also been studied via computer experiments. Before the results of these simulations are presented, though, the prediction $G_\infty \sim \epsilon^{8/3}$ for the elastic modulus requires some discussion. This result is better expressed as the concentration of correlation "blobs", $G_\infty \sim kT/\xi^d$, where ξ is the connectivity correlation length. This purely entropic form of the elasticity has been conjectured previously[23] and bears analogy to semidilute linear polymer solutions, where the *osmotic* modulus is proportional to the density of concentration blobs.[24] The modulus can also be rewritten in the form $G_\infty \sim f/M_z$, where f is the gel fraction and M_z is the z-averaged molecular weight of the sol. Here we see a clear analogy to the original Flory theory of rubber elasticity,[16] where the modulus was found to be proportional to the density of elastically effective chains. In this interpretation, the gel fraction may be regarded as the elastically effective portion of the network, and the mass of a typical cluster is the size of an elastically effective unit.

Whereas in the dynamic scaling theory, the modulus is due to entropy alone, it is possible that there are energetic contributions to the modulus. These have been introduced in computer simulations via a bond-bending energy[25-28] and are intended to imitate the excluded volume forces that prevent network collapse. Simulations of percolation networks with bond-bending forces give $z \cong 3.96$[29] in two dimensions and $z \cong 3.7$ (estimated[30]) in three dimensions. Although it is difficult to judge the magnitude of the energetic contribution a priori, stress-temperature studies on elastomers show that the modulus increases in direct proportion to temperature, indicating that the elasticity is almost purely entropic.[31]

Summary

Our dynamic scaling theory has been shown to predict a new viscoelastic superposition principle: time-cure superposition. This states that viscoelastic functions at differing extents of reaction should superpose provided appropriate vertical and horizontal shifts are applied. The vertical shift required to superpose the complex shear moduli measured at various stages in the critical regime accounts for the increase in the equilibrium modulus with cure $G_\infty \sim \epsilon^{8/3}$, while the horizontal shift accounts for the change in the longest relaxation time $\tau_z \sim \epsilon^{-4}$. Experimental complex moduli for an epoxy system show excellent superposition both above and below the gel point, and the shift factors agree well with the theoretical predictions, $G_\infty \sim \epsilon^{8/3}$ and $\tau_z \sim \epsilon^{-4}$. The critical regime where this superposition is valid is shown to extend over at least half of the reaction.

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