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Experimental Observation of the Molecular Weight Dependence of the Critical Exponents for the Rheology Near the Gel Point

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ABSTRACT

Linear viscoelasticity experiments are shown to follow a regular pattern near the gel point of chemical and physical gels. Experimental observations are reviewed for the three critical exponents of rheology: the relaxation exponent (n) *for the material directly at the gel point, the critical exponent* (α) *of the divergence of the longest relaxation time in the approach of the gel point, and the exponent* (κ) *for the rate of change of the spectrum at the transition. The molecular weight of the precursor is an important parameter which has been studied recently. Other parameters are addition of diluent (solvent), off-balancing of stoichiometry, and bulkiness of crosslinking points.*

INTRODUCTION

Network forming systems undergo a liquid–solid transition when the largest molecular or super-molecular cluster diverges to infinity in size. The instant of transition, called the gel point, is defined by the divergence of the largest molecular cluster. Linear viscoelastic properties near the gel point depend on three critical exponents: the relaxation exponent (n) for the material directly at the liquid–solid transition (gel point), the critical exponent (α) of the divergence of the longest relaxation time in the approach of the gel point, and the exponent (κ) for the rate of change of the relaxation time spectrum at the transition. These exponents do *not* necessarily have universal values contrary to what one might have expected for properties at a critical point. The molecular weight of the precursor materials from which the gels have been made has a large effect on the rheology in general and on the critical

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exponents in particular. Especially for the relaxation exponent, a wide range of values have been observed experimentally in many different laboratories.

In addition to the three rheological exponents, two additional exponents should be considered, one for the diverging size of the largest cluster and one for the size distribution. Elaboration of these so-called static exponents would exceed the narrow scope of this study which has the objective to find common trends in the rheological behavior near the gel point.

THE RELAXATION EXPONENT

The critical gel is the material directly at the transition point from liquid to solid. It could be considered as the distinctive material state which every material has to go through during a connectivity transition. The rheology of the critical gel fits into the same formalism which one normally uses for liquids or solids: the relaxation time spectrum, $H(\lambda)$, or its Laplace transform, the relaxation modulus $G(t)$, e.g. Ferry (1980)[1]

$$G(t) = G_e + \int_0^{\lambda_{max}} H(\lambda) e^{-t/\lambda} \frac{d\lambda}{\lambda} \tag{1}$$

The critical gel has the longest relaxation time which is infinitely long and an equilibrium modulus G_e which is zero (like in liquids). The distribution of relaxation times simplifies into a self-similar spectrum:[2–4]

$$H(\lambda) = \lambda^{-n} S/\Gamma(n) \qquad \text{for } \lambda_0 < \lambda < \infty \tag{2}$$

and a relaxation modulus

$$G(t) = St^{-n}, \qquad \text{for } \lambda_0 < t < \infty \tag{3}$$

where $\Gamma_{(n)}$ is the gamma function. The self-similar spectrum is only valid at long times, $\lambda > \lambda_0$, where the details of chemical structure are less important. The relaxation exponent (n) is the first of the three critical exponents. It defines the rheology of the critical gel which serves as a reference for analyzing the transition behavior near the gel point.

DIVERGING PROPERTIES

The other two exponents concern the rate of change during the transition. The independent variable of the transition process, clearly defined (and measurable) for chemical gelation processes, is defined by the extent of the crosslinking reaction (p) which is zero for the precursor before crosslinking and approaches unity when driving the reaction to completion. The threshold p_c defines the gel point at which the largest cluster diverges to infinity.

The longest relaxation time diverges when approaching the gel point from either side

$$\lambda_{max} \sim \begin{cases} (p_c - p)^{-\alpha_-} & \text{for sol, } p < p_c \\ (p - p_c)^{-\alpha_+} & \text{for gel, } p > p_c \end{cases} \tag{4}$$

$p - p_c$ is the distance from the gel point. α_- and α_+ are the critical exponents for the sol and the gel. The largest cluster of the sol reaches infinite size at the gel point and the corresponding λ_{max} becomes infinitely large. Beyond the gel point, the relaxable components (for chemical gelation this would be the sol fraction, unattached chain ends, long loops, etc.) gradually incorporate into the permanent network and λ_{max} decays again. The analysis simplifies considerably when assuming symmetry of the diverging λ_{max} on both sides of the gel point:[5]

$$\alpha = \alpha_- = \alpha_+ \tag{5}$$

Further experiments are needed to evaluate this hypothesis.

Critical exponents of other diverging properties only depend on the values of α and n. No new exponents have to be introduced provided that the symmetry hypothesis is valid[5–8] and that n does not change in the vicinity of the gel point. The most commonly discussed diverging properties are the zero shear viscosity η_0, the first normal stress coefficient ψ_1 at vanishing shear rate, the equilibrium compliance J_e^0, and the equilibrium modulus G_e:

$$\eta_0(p) \sim (p_c - p)^{-\alpha(1-n)}, \quad \text{for sol, } p < p_c \tag{6}$$

$$\psi_1(p) \sim (p_c - p)^{-\alpha(2-n)}, \quad \text{for sol, } p < p_c \tag{7}$$

$$J_e^0(p) \sim (p_c - p)^{-\alpha n}, \quad \text{for sol, } p < p_c \tag{8}$$

$$G_e(p) \sim (p - p_c)^{\alpha n}, \quad \text{for gel, } p > p_c \tag{9}$$

Sample dependent values of n directly affect the critical exponents of these properties which shows that the exponents can not be universal.

MONOTONOUSLY CHANGING PROPERTIES

The dynamic moduli do not diverge at the gel point but adopt finite values which depend on frequency. The finite moduli values for $p \to p_c$ are

$$G'(\omega) = \int_0^{\lambda_{max}} \frac{H(\lambda)\omega^2\lambda^2}{1+\omega^2\lambda^2}\frac{d\lambda}{\lambda}$$

$$= \int_0^{\infty} \frac{S\lambda^{-n}\omega^2\lambda^2}{\Gamma(n)(1+\omega^2\lambda^2)}\frac{d\lambda}{\lambda} = S\Gamma(1-n)\cos\left(\frac{n\pi}{2}\right)^n \tag{10}$$

$$G''(\omega) = \int_0^{\lambda_{max}} \frac{H(\lambda)\omega\lambda}{1+\omega^2\lambda^2}\frac{d\lambda}{\lambda}$$

$$= \int_0^{\infty} \frac{S\lambda^{-n}\omega\lambda}{\Gamma(n)(1+\omega^2\lambda^2)}\frac{d\lambda}{\lambda} = S\Gamma(1-n)\sin\left(\frac{n\pi}{2}\right)^n \tag{11}$$

The spectroscopic character of the dynamic mechanical experiment probes the gel at time scales near $\lambda = 1/\omega$ without recognizing the divergence of the longest time. Only at very low frequencies, $\omega \to 0$, would one recognize the divergence.

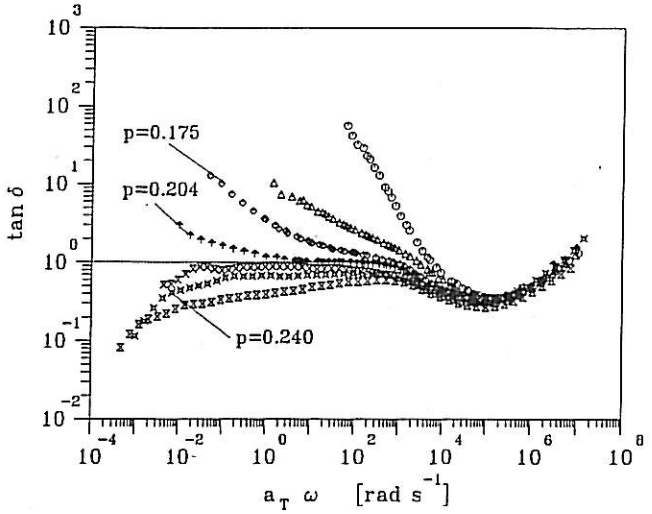

Fig. 1. Evolution of tan δ master curves for vulcanizing polybutadine ($M_w = 20700$, $M_w/M_n = 1{\cdot}04$) at $T_{ref} = 28°C$. The reaction was stopped at discrete extents of reaction, p. For three of the samples, p was measured by FT Raman spectroscopy (see labels).

Figure 1 gives an example of the gradually evolving dynamic mechanical properties during gelation. The loss tangent, $\tan\delta = G''/G'$, shows three regions: the low frequency region which most strongly expresses the changing molecular mobility due to the liquid–solid transition, the entanglement region at intermediate frequencies, and the high frequency glass transition. For the liquid states, tan δ in the low frequency region slopes downward and for the solid states, tan δ is sloped upward. The transition occurs gradually. The gel point is marked by a zero slope, i.e. tan δ is independent of frequency (for low ω).

A general observation with all network forming systems has been that the dynamic moduli (at some reasonably accessible frequency) grow steadily during the transition through the gel point. The storage modulus grows about twice as fast as the loss modulus. We have observed this on a wide range of samples. A more detailed study of this phenomenon is in progress.

The rate of change of the dynamic moduli decreases with frequency. The frequency dependence is the same for both, G' and G'',[9] and it follows a power law

$$\left(\frac{\partial G'}{G'\,\partial p}\right)_\omega \sim \left(\frac{\partial G''}{G''\,\partial p}\right)_\omega \sim \omega^{-\kappa} \quad \text{for } p \text{ near } p_c \tag{12}$$

This brings us to the third critical exponent, κ, which has a value of about 0·2 for the systems reported so far.[9,10] Its value seems to be insensitive to molecular detail. The frequency range of the above observations has to be explored further.

Of the three critical exponents for the rheology near the gel point, the relaxation exponent n can be measured most accurately. Its value will be discussed in the following. Hardest to measure is the critical exponent for the

divergence of the longest relaxation time (or of any of the other diverging properties). Its reported values vary significantly from laboratory to laboratory.

SOFT VERSUS STIFF CRITICAL GELS

Critical gels are generally very soft and fragile. This softness expresses itself in the parameters of the relaxation modulus, eqn (3). The gel is especially soft when the front factor S is small and the relaxation exponent is large, $n \to 1$. Such parameter values guarantee that the stress is low during deformation of the critical gel and the relaxation rate is high. Vice versa, somewhat stiffer gels can be produced by making them with a large S and a small n value, $n \to 0$. For many systems, there seems to be a regular pattern between the front factor S and the relaxation exponent[11–13]

$$S = g_0 \lambda_0^n \tag{13}$$

where g_0 represents the plateau modulus of the fully crosslinked material ($p \to 1$) and λ_0 the longest relaxation time of the precursor molecule (building block of the gel). The above relation also suggests that we can make soft gels with polymers of small λ_0 and somewhat stiffer gels with high molecular weight precursors which have a large relaxation time λ_0.

The relaxation exponent strongly depends on molecular and structural details which affect the development of long range connectivity. These are the molecular weight of the precursor, stoichiometric ratio, amount of inert diluent in the material, and bulkiness of the crosslinks (filler effect).

For describing the observed molecular weight effects in chemical gels from linear flexible precursor molecules, we propose to distinguish three regions of increasing molecular weight:

(1) low molecular weight M:	$M < M_p$:	$n \simeq 0{\cdot}7$–$0{\cdot}8$
(2) intermediate molecular weight:	$M_p < M < M_e$	$n \simeq 0{\cdot}4$–$0{\cdot}7$
(3) high molecular weight:	$M_e < M$:	$n \simeq 0{\cdot}4$–$0{\cdot}5$

The low molecular weight precursors are too short to adopt Gaussian conformation. We therefore propose that the limiting molecular weight, M_p, is associated with the transition from non-Gaussian to Gaussian behavior. Very short chains, $M < M_p$, associate into molecular clusters with non-Gaussian building blocks and the resulting critical gel is relatively soft. Many data have been reported in the literature on these systems.[7,10,14]

The next molecular size up is associated with the formation of entanglements and is called the entanglement molecular weight M_e. Intermediate molecular weight precursors, $M_p < M < M_e$, already give much lower relaxation exponents.[2,3,5,11,15–17] The lowering of the relaxation exponent has been attributed to screening.[18]

Little is known about highly entangled precursors, $M_e < M$, and the resulting critical gels. Experiments of De Rosa *et al.*[13] with vulcanizing polybutadienes show a relaxation exponent of about 0·5 or somewhat below 0·5. The front factor, S, increased with about the 1·7th power of molecular weight. The

polybutadiene molecules were of (nearly) uniform molecular weight which was chosen to be 10–100 times the entanglement molecular weight.

Off-balancing of stoichiometry was found to increase the relaxation exponent value.[3,19] The gel becomes more 'lossy' and stress relaxation is accelerated. Adding an inert solvent also increases the relaxation exponent,[11] even in physical gels.[20]

On the other hand, 'bulky' crosslinks as developed during the crystallization of polymer melts (no solvent) lower the relaxation exponent. The lowest values of n, which we have been able to generate so far, occurred with physical gels in which the crosslinks consisted of large crystalline regions.[21,22]

CONCLUSIONS

The relaxation exponent, n, and the gel strength, S, vary with molecular weight in a regular pattern. Such a pattern has been recognized for liquid–solid transitions in a wide range of chemically and physically gelling systems. The molecular or structural origin of these variations is not yet known to the extent where quantitative predictions could be derived from first principles. The relaxation exponent obviously is not universal, but it seems to have an upper limiting value of about 0·7 for gels from short flexible precursor molecules and a lower value of about 4·5 for long precursor molecules. Additional influences, such as dilution or off-balancing of stoichiometry, extend this range even further.

Little is known about universality, symmetry, or even value of the critical exponent α of the diverging longest relaxation time. While α might be universal, the exponents for the diverging viscosity, $\alpha(1-n)$, and the growth of the equilibrium modulus, αn, are most definitely not universal. The third exponent, κ, seems to be insensitive to molecular or super-molecular detail, having a value of about 0·2. Its origin is the least known of the three exponents.

The above analysis shows that there are systematic patterns in the wide range of gel properties. These should be explored further and they should be utilized technically.

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