

Dynamics of near-critical polymer gels

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We report the viscosity and the modulus of near-critical polyester gels. Previous work has shown that these gels lie in the middle of the static crossover between mean-field and critical percolation. Above the gel point, the modulus data are well described by the scaling law attributing kT of stored elastic energy per unentangled network strand. Below the gel point, the viscosity data disagree with both the de Gennes conductivity analogy and the Rouse model, possibly due to a subtle effect of chain entanglement.

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INTRODUCTION

Polymerization involving monomers with functionality larger than 2 leads to the formation of branched polymers and ultimately gels. The problem of polymer gelation has been recognized as a phase transition in connectivity, and percolation ideas have been used to interpret both static [1,2] and dynamic [2] data. While the static properties of branched polymers and gels near the gel point are apparently well understood in terms of critical percolation and the crossover to the mean field [3,4], our understanding of dynamics lags far behind. Here we present a complete set of data for the dynamics of near-critical polymer gels that have been extensively characterized in terms of static properties [4]. The crucial advantages of this study over previous ones are that (i) the reaction is stopped and samples are fully characterized in terms of molecular weight distribution both above and below the gel point (and gel fraction beyond the gel point), (ii) the gelation reaction proceeds at elevated temperature by an interchange reaction that maintains ergodicity in the gels [4], and (iii) there is a range of temperatures between the glass transition ($T_g \cong 60^\circ\text{C}$) and the temperature below which the reaction is effectively stopped ($\sim 130^\circ\text{C}$) that allows for viscoelastic measurements to be made.

BACKGROUND THEORY

A random step-growth branching process initially creates small randomly branched polymers. As the reac-

tion proceeds, the viscosity of the liquid builds as the polymers link together to form larger randomly branched polymers. At the gel point, the viscosity diverges and an incipient macroscopic gel is formed. The presence of the gel makes the sample a solid, with a steady-state modulus that grows as the reaction continues.

Both the mean-field and critical percolation theories predict similar power-law forms for the divergence and growth of various measurable quantities near the gel point. The main distinction between the two theories is in the values of the scaling exponents, summarized in Table I and defined below. The static quantities [1] we are concerned with are all connected to the distribution of molecular weights, defined as $n(M)$, the number density of molecules with mass M . This distribution is a power law (with Fisher exponent τ) near the gel point, truncated by a cutoff function f at the characteristic largest molecular weight M_{char} :

$$n(M) = M^{-\tau} f(M/M_{\text{char}}). \tag{1}$$

The characteristic largest molecular weight diverges with exponent $1/\sigma$, as the gel point is approached from either side:

$$M_{\text{char}} \sim |p - p_c|^{-1/\sigma}. \tag{2}$$

The extent of reaction p ranges from zero initially to unity for complete reaction, and p_c is the critical extent of reaction (the gel point).

The measurable static quantities of interest are defined as moments of the molecular weight distribution. The

TABLE I. Static-exponent predictions [1].

Theory	τ	σ	β	γ	ν	D	$(\tau-1)/\sigma$	$2\nu-\beta$
Critical	2.2	0.46	0.43	1.7 ₄	0.88	2.5	2.6	1.3
Mean field	$\frac{5}{2}$	$\frac{1}{2}$	1	1	$\frac{1}{2}$	4	3	0

k th moment of the distribution is defined as an M^k -weighted sum:

$$m_k = \sum_K M^k n(M) \sim |p - p_c|^{(\tau - k - 1)/\sigma}. \quad (3)$$

The order parameter for the phase transition is the gel fraction P_{gel} , which is related to the first moment m_1 (P_{gel} is zero below the gel point, and grows beyond the gel point with exponent β):

$$P_{\text{gel}} \sim (p - p_c)^\beta, \quad p > p_c. \quad (4)$$

The weight-average molecular weight M_w is the ratio of the first and second moments of the distribution, and diverges with exponent γ as the gel point is approached from either side:

$$M_w \sim |p - p_c|^{-\gamma}. \quad (5)$$

Scaling relations among the static exponents [1] can be obtained from the $k = 1$ and 2 cases of Eq. (3):

$$\beta = (\tau - 2)/\sigma, \quad (6)$$

$$\gamma = (3 - \tau)/\sigma. \quad (7)$$

The size of the largest branched polymer is the correlation length [1], which diverges with exponent ν as the gel point is approached from either side:

$$\xi \sim |p - p_c|^{-\nu}. \quad (8)$$

The fractal dimension D is defined in the usual way, i.e., $M_{\text{char}} \sim \xi^D$, resulting in another useful scaling relation:

$$D = 1/(\sigma\nu). \quad (9)$$

Dynamic critical exponents are defined as follows [2]. The viscosity η diverges below the gel point with exponent s :

$$\eta \sim (p_c - p)^{-s} \sim M_w^{s/\gamma} \sim M_{\text{char}}^{s\sigma}, \quad p < p_c. \quad (10)$$

The equilibrium modulus G grows beyond the gel point with exponent t :

$$G \sim (p - p_c)^t \sim M_w^{-t/\gamma} \sim M_{\text{char}}^{-t\sigma} \sim P_{\text{gel}}^{t/\beta}, \quad p > p_c. \quad (11)$$

At the critical point, the frequency dependence of viscoelastic response obeys a power law [5]:

$$G^*(\omega) \sim (i\omega)^u, \quad p = p_c. \quad (12)$$

From a simple self-consistency argument [6], based on earlier work on dielectric properties of percolation clusters [7], it has been suggested that there are only two independent dynamic exponents:

$$u = t/(s + t). \quad (13)$$

One idea [8,9] for the equilibrium modulus of percolation networks is that it is proportional to kT per correlation volume ξ^d , leading to

$$t = d\nu, \quad (14)$$

where $d = 3$ (space dimension). For the vulcanization

case [3] (mean-field) and the crossover between mean-field and critical behaviors, network strands overlap. Rubber elasticity [10] predicts the modulus of gels to be kT per elastically active network strand. If network strands are not entangled with each other, one expects

$$G \cong nkT\xi^{-d}, \quad (15)$$

where n is the number of overlapping network strands in the volume ξ^d . In general, n is determined [11] as the ratio of the gel fraction and the density of a single network strand inside the volume ξ^d , hence

$$\begin{aligned} n &\sim P_{\text{gel}}\xi^{d-D} \sim (p - p_c)^{\beta - \nu(d-D)} \\ &\sim (p - p_c)^{(\tau-1)/\sigma - d\nu}. \end{aligned} \quad (16)$$

For the critical percolation, hyperscaling [1] requires $(\tau - 1)/\sigma = d\nu$, so n is a constant of order unity independent of the extent of the reaction, leading to (14), while in the mean field, $n \geq 1$ and increases with $|p - p_c|$. Combining Eqs. (15) and (16) we get

$$t = (\tau - 1)/\sigma, \quad (17)$$

obtained previously for the critical percolation [12] but valid for the mean field as well, if entanglements are not important. In the critical percolation limit, hyperscaling [1] equates (14) and (17). Using the general result (17), a simple relation between modulus and experimentally measured quantities emerges for unentangled gels:

$$\begin{aligned} G &\sim (p - p_c)^{(\tau-1)/\sigma} \sim (p - p_c)^{\gamma + 2\beta} \\ &\sim P_{\text{gel}}^2 / M_w, \quad p > p_c. \end{aligned} \quad (18)$$

Much earlier, de Gennes [13] suggested a different idea for the modulus, based on an analogy with the conductivity of a percolating system of resistors, predicting $t \cong 1.9$.

The Rouse model [14] describes polymer dynamics when hydrodynamic interactions are negligible and chains are unentangled. For critical percolation, hyperscaling dictates that branched polymers of a given size only overlap with smaller ones [15], so entanglement effects are not expected to be important in the critical regime. In fact, above the gel point we have shown [16] that permanent entanglements do not become important until far into the mean-field regime, so it is relevant to discuss unentangled dynamics for the mean-field regime as well.

As discussed previously [12], since Rouse dynamics predicts a friction coefficient ξ proportional to mass m , the diffusion coefficient $D = kT/\xi \sim m^{-1}$. The relaxation time T of a branched polymer is the time it takes to diffuse a distance equal to its size r , so $T \cong r^2/D \sim mr^2$. For the longest relaxation time \mathcal{T} we apply this reasoning to the largest branched polymer:

$$\mathcal{T} \sim M_{\text{char}}\xi^2 \sim (p_c - p)^{-(1/\sigma + 2\nu)}, \quad p < p_c. \quad (19)$$

The viscosity is determined as the product of the longest relaxation time and the modulus at that time [14]. Since the Rouse model effectively assigns kT per mode, this modulus scales in the same way as the modulus above the

gel point, Eq. (18):

$$\eta \cong G \mathcal{T} \sim (p_c - p)^{(\tau-2)/\sigma-2\nu} \sim (p_c - p)^{\beta-2\nu}, \quad p < p_c. \quad (20)$$

Martin, Adolf, and Wilcoxon [9] arrived at a Rouse prediction for the exponent $s = (D - d + 2)\nu$, where D is the fractal dimension. This prediction is related to Eq. (20) by using hyperscaling, which is only valid in the percolation limit [1]. Thus we believe Eq. (20), originally derived by de Gennes [17], to be the general result for the Rouse model, in that it is valid for both the critical percolation and the mean field as long as entanglements and hydrodynamic interactions are negligible.

The Rouse model predicts the power-law viscoelastic response of Eq. (12) with [12]

$$u = D(\tau - 1)/(2 + D). \quad (21)$$

An alternate idea about the viscosity exponent s was suggested by de Gennes [18] through an analogy with the divergence of conductance in a percolating system of superconductors and resistors. This superconductivity exponent has been suggested to be [19]

$$s = \nu - \beta/2 = [(D - d)/2 + 1]\nu, \quad (22)$$

exactly half the Rouse value.

EXPERIMENT

The preparation and molecular characterization of all samples have been discussed previously [20,4]. The five samples below the gel point were 91B-F of Ref. [20] (also discussed elsewhere [12]). The 12 samples above the gel point were C and E-O of Ref. [4]. Experimentally [4] the Fisher exponent $\tau = 2.35 \pm 0.03$ (95%), and hence the samples are roughly in the middle of the crossover between the critical percolation ($\tau = 2.2$) and the mean field ($\tau = 2.5$).

Viscosity was measured for samples below the gel point at a temperature 41 K above the glass transition [12] by two methods. The viscosity of samples far below the gel point was determined from the low-frequency response in a Rheometrics System Four rheometer using oscillatory shear between parallel circular plates. Closer to the gel point torsional creep in a magnetic elevation creep apparatus (Time-Temperature Instruments) was used due to the long relaxation times involved (also in parallel plate geometry). Agreement between the two techniques was excellent.

Beyond the gel point, serrated parallel plates were used, due to problems experienced with sample slippage at the sample/plate interface in the smooth parallel plate geometry. This slip is presumably caused by a small layer of sol being squeezed out of the gel to wet the plates. For the linear viscoelastic response studied here, the only effect of the serrations is a constant apparent shift in the modulus scale of 1.49 due to the irregular geometry, as evidenced by identical frequency dependences of the ratio G'/G'' for different serration depths. The shift was calibrated with linear polymers, whose viscoelastic response

could be measured in all geometries. The equilibrium modulus was taken as the limiting value of G' at low frequencies. For the sample closest to the gel point, G' had not quite leveled off at the lowest frequency, and the reported modulus is based on an extrapolation that is certainly accurate to within a factor of 1.5.

RESULTS

As discussed in Ref. [4], we were not able to determine the extent of the reaction p with adequate precision to evaluate critical exponents. We therefore plot quantities determined with better precision against one another and evaluate ratios of critical exponents. In Fig. 1, we plot the modulus above the gel point against the weight-average molecular weight and the characteristic largest molecular weight of the sol fraction. The apparent power law for G vs M_w determines

$$t/\gamma = 2.16 \pm 0.55 \quad (95\%).$$

The power law for G vs M_{char} yields

$$t\sigma = 1.44 \pm 0.27 \quad (95\%).$$

The conductivity analogy grossly underpredicts both t/γ ($=1.06$) and $t\sigma$ ($=0.87$). However, the experimental values for both t/γ and $t\sigma$ are between the predictions of the critical percolation ($t/\gamma = 1.48$ and $t\sigma = 1.23$) and the mean field ($t/\gamma = 3$ and $t\sigma = 3/2$) based on Eq. (17). Our system is known from static measurements [4,20] to be roughly in the middle of the crossover between the two limits. Since $0.46 \leq \sigma \leq 0.50$, we conclude

$$t = 3.0 \pm 0.7 \quad (95\%),$$

inconsistent with the conductivity analog [13] ($t = 1.9$) and strongly supporting the prediction of Eq. (18) ($t = 2.6$) for the critical percolation and $t = 3$ for the mean field).

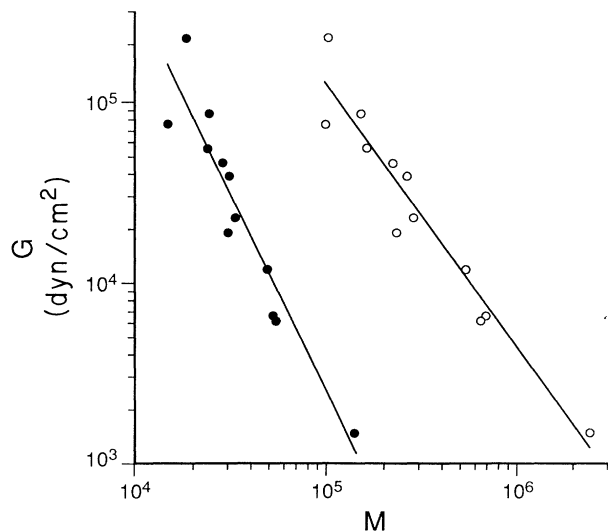


FIG. 1. Modulus as functions of M_w (filled symbols) and M_{char} (open symbols). Lines are linear regression.

A plot of modulus vs gel fraction (not shown) yields a slope

$$t/\beta = 4.02 \pm 0.82 \quad (95\%),$$

which agrees with the conductivity analogy ($t/\beta = 4.4$). However, this apparent agreement is actually fortuitous based on the serious underpredictions of the conductivity model for t/γ and $t\sigma$ noted above. Using the scaling relation [1] $\beta = (\tau - 2)/\sigma$, Eq. (17) predicts $t/\beta = (\tau - 1)/(\tau - 2)$, so the experimental value of t/β is between the mean field ($t/\beta = 3$) and critical ($t/\beta = 6.2$) limits of Eq. (17), once again consistent with the crossover. The apparent $\tau = 2.35$ leads to the prediction $t/\beta = 3.9$, in good agreement with experiment.

The physics embodied in Eqs. (15) and (18) should be valid for unentangled gels, irrespective of the static universality class. We test Eq. (18) in Fig. 2, where we plot the modulus as a function of the square of the gel fraction divided by the weight-average molecular weight of the sol. Clearly, Fig. 2 has the expected slope of unity within experimental error [the slope is 1.06 ± 0.21 (95%)]. We conclude from Fig. 2 that Eqs. (15) and (18) describe the modulus of our gels.

In Fig. 3 we plot viscosity data below the gel point against weight-average molecular weight and characteristic largest molecular weight. From the power law of η vs M_w , we conclude

$$s/\gamma = 1.02 \pm 0.17 \quad (95\%).$$

The power law of η vs M_{char} determines

$$s\sigma = 0.72 \pm 0.10 \quad (95\%).$$

We previously reported [12] the exponent $u = 0.69 \pm 0.02$ for our polyester system. Since we have measured s/γ , t/γ , and u for the same system, we can test Eq. (13), and

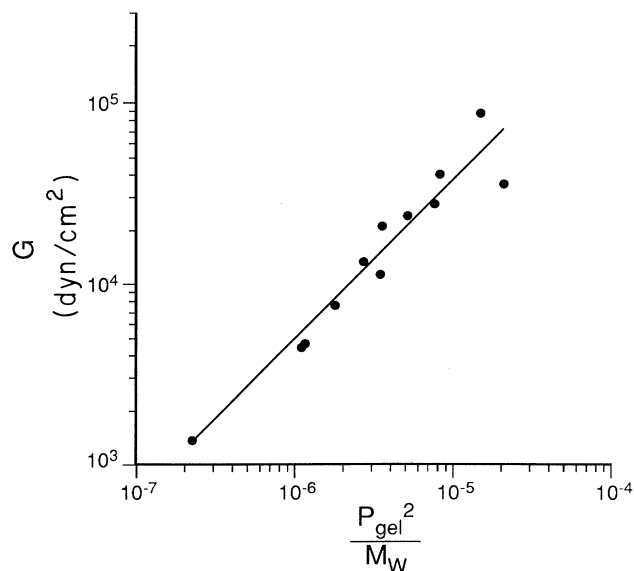


FIG. 2. Modulus as a function of gel fraction squared divided by weight-average molecular weight of the sol. Line is linear regression.

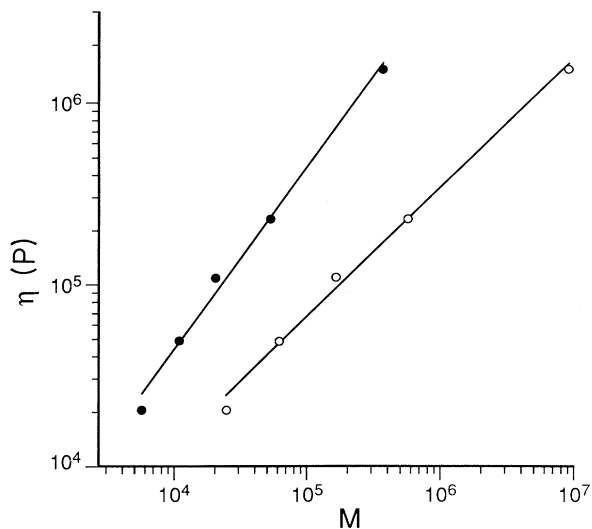


FIG. 3. Viscosity as functions of M_w (filled symbols) and M_{char} (open symbols). Lines are linear regression.

we find that it works perfectly. Therefore, there are only two independent dynamic exponents.

DISCUSSION

Both s/γ and $s\sigma$ are clearly higher than any of the available theoretical predictions. The superconductivity analogy [18,19] predicts $s/\gamma = 0.37$ and $s\sigma = 0.31$. The Rouse model [9,12] in the mean-field limit predicts $s = s/\gamma = s\sigma = 0$ (logarithmic divergence of viscosity). For critical percolation, the Rouse model predicts $s/\gamma = 0.74$ and $s\sigma = 0.61$. In the crossover we expect values of s/γ and $s\sigma$ between zero and the critical percolation values. We conclude that neither the Rouse model nor the superconductivity analogy describes the viscosity of our branched polyesters. We know that far into the mean-field regime dynamics will be strongly influenced by temporary interchain entanglement constraints [21]. Both modulus and swelling data [4] indicate that entanglement effects are unimportant in our polymers above the gel point, so it is surprising that the Rouse model does not describe the viscosity of our pregel branched polymers. However, only permanent (trapped) entanglements affect modulus and swelling beyond the gel point [16], whereas temporary entanglements may play a role in viscosity below the gel point [21].

The result for s/γ being roughly unity agrees well with some literature data [22], while other data yield even higher values [23]. This nonuniversal behavior might be explained by the samples corresponding to different areas of the static crossover between the mean field and the critical percolation, as we suspect that all three systems lie in the crossover. Of the three, the one that should be closest to the critical percolation limit, a polyester system starting with difunctional and trifunctional monomers [22], has the lowest exponent value, $s/\gamma = 1.0$. The other two systems were made by end-linking polydimethylsilox-

anes [23] of molecular weight $M_w=26\,000$. Using a tetrafunctional crosslinker led to an exponent $s/\gamma=1.5$, while a trifunctional crosslinker gave an exponent $s/\gamma=2.6$. The reaction rate of a crosslinker's last bond is typically slower than the others [9]. Therefore, the trifunctional crosslinker should make for a longer average chain length between crosslinks at the gel point than the tetrafunctional one. The chain length between crosslinks is the control parameter for the crossover [3,4]—the longer the chain length the closer to the mean-field limit one gets. Thus all literature data for s/γ seem to be consistent with the idea of s/γ increasing as chain length between crosslinks increases (and the mean field is approached). Clearly, a systematic study of the crossover is warranted, and such a study is currently being made in our research group.

CONCLUSIONS

The modulus of our gels beyond the gel point is well understood in terms of a simple model assigning kT of stored energy per network strand. This suggests that entanglements are not trapped in our gels, as expected for gels close enough to the gel point [16]. The exponent describing the modulus growth just beyond the gel point is completely determined by static exponents [see Eq. (17)]. Thus the exponent t is really static in nature, and *there is only one dynamic exponent*.

Below the gel point, viscosity is the product of modulus and relaxation time [see Eq. (20)]. Thus, in anal-

ogy with other phase transitions [24] we define the sole dynamic exponent in terms of the correlation length ξ and its relaxation time $T=\eta/G$:

$$T \sim \xi^z \sim |p - p_c|^{-\nu z}. \quad (23)$$

We expect both modulus and relaxation time to be characterized by the same scaling exponents above and below the gel point. We can then write the conventionally defined [2] dynamic exponents for polymer gelation in terms of this single dynamic exponent and static exponents [with t given by Eq. (17)]:

$$s = \nu z - t = \nu z - (\tau - 1)/\sigma, \quad (24)$$

$$u = t / (\nu z) = D(\tau - 1)/z. \quad (25)$$

Since the measured viscosity exponent is not consistent with currently available theories, neither is the relaxation-time exponent. Our best estimate of νz for our polyester gels comes from Eqs. (9) and (25), since τ and u are measured with high precision and σ is nearly the same for critical and mean-field percolation:

$$\nu z = (\tau - 1)/(u\sigma) = 4.1 \pm 0.4 \quad (95\%).$$

Another estimate [25] indicates that $\nu z \cong 4.8 \pm 0.5$ for end-linking polydimethylsiloxanes of various chain lengths.

In summary, static exponents (including t) are consistent with percolation ideas, but more theoretical work is needed to understand the dynamic exponent.

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