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Parameter-Free Theory for Stress Relaxation in Star Polymer Melts

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ABSTRACT: We present a theory of stress relaxation in star polymer melts with no adjustable parameters beyond those measurable in linear melts. We incorporate the effect of higher Rouse modes on star arm retraction and the Colby−Rubinstein scaling of entanglement length within "dynamic dilution". Our results for $G''(\omega)$ compare well with experimental data, with excellent agreement in shape and within a factor of 2 in time and modulus scales.

Following the success of the Doi−Edwards reptation theory in describing the detailed rheology of monodisperse linear polymer melts, attention has turned to the rheology of branched polymers. Logically, the first branched architecture to receive intensive study has been the star polymer, with a single branch point.

Just as for linear chains, the entanglement network prevents motion except along the confining "tube"; but in this case, the branch point prevents reptation. Stress in star polymers relaxes instead by arm retraction, in which star arms explore new configurations by retreating along their tubes and poking out again in a new direction. Retraction is entropically unlikely, so arm retraction is thermally "activated", and stress relaxation in star polymer melts is exponentially slow as the star arms become long.

Because the same confining entanglement network and the same conformational entropy are relevant to the dynamics of star polymers as for linear polymers, it should be possible to give a theory for stress relaxation in star melts that contains no additional free parameters beyond those present in the Doi−Edwards theory. Our goal in this paper is to provide such a theory.

This paper builds on the work of Pearson and Helfand,[1] who considered the stress relaxation of a star polymer in a fixed network, and Ball and McLeish,[2] who extended the work of ref 1 to include the effect of mutually disentangling star arms on speeding up stress relaxation.

In particular, we add three elements to the results of ref 2: (1) the contribution of higher Rouse modes to the retraction of star arms a short distance along their tubes; (2) a detailed calculation of the "first-passage time" of a star arm a given distance down the tube; and (3) a stronger effect of mutual disentanglement, in terms of how the entanglement length $N_e(\phi)$ depends on the volume fraction ϕ of unrelaxed material, implied by results of Colby and Rubinstein[3] on the concentration dependence of the plateau modulus in semidilute Θ solutions of linear chains.

The result is a theory of the dynamic modulus $G(\omega)$ for star melts which is in excellent agreement with experimental data in the shape of $G(\omega)$ and within a factor of 2 in the overall modulus and time scales, without adjustable parameters. The good agreement is strong evidence that the model of ref 2, of stress relaxation in star melts by arm retraction with "dynamic dilution", is substantially correct. Our results also give encouragement to more recent theories of stress relaxation in multiply branched polymers,[4] which also rely on the tube model of entanglements, arm retraction, and dynamic dilution.

This paper is organized as follows: in sections I and II, we review the results of refs 1 and 2, respectively; in section III, we present our extension of their work; section IV compares our results to experiment; section V contains concluding remarks.

I. Star in a Fixed Network

Pearson and Helfand[1] considered the problem of stress relaxation for a single star polymer in a fixed network of entanglements, as provided by a loosely cross-linked rubber or a melt of extremely long linear chains. We now briefly recount their results.

Suppose a star polymer in such a fixed network were subjected at $t = 0$ to a small affine step strain. Unlike a linear chain, a star molecule cannot reptate to recover an equilibrium set of conformations after such a strain. Instead, the arms of the star must undergo "arm retraction". That is, the free ends of the star arms must retract some distance back along the primitive path of the arm (i.e., back along the tube confining the arm) and then poke out again along a new section of tube. In this way, a portion of the old tube, and the stress associated with it, is forgotten. To relax all the stress held by the strained conformations of the arm, the free end must retract all the way back to within an entanglement length of the junction point of the star.

If the star arm length N_a is many times the entanglement length N_e, arm retraction is very unlikely. An entropically generated "thermal tension" T_{th} exists in the arm, which pulls the free end of the arm outward to explore new conformations.[5] The thermal tension opposes arm retraction.

More precisely, the magnitude of the thermal tension is found[5] by requiring that an arm in equilibrium have a primitive path length L corresponding to the proper square end-to-end distance $R^2 = N_a b^2$; namely, L such that

$$(L/a)a^2 = R^2 \qquad (1)$$

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The chain in the tube can be represented as a Gaussian spring with an applied thermal tension, with stretching free energy ($k_BT = 1$)

$$F(L) = \frac{3L^2}{2R^2} - LT_{\rm th} \tag{2}$$

Choosing $T_{\rm th}$ such that the minimum of $F(L)$ satisfies eq 1 implies $T_{\rm th} = 3/a$ (of order k_BT per entanglement length).

The arm free end, as it makes excursions a fractional distance s ($0 < s < 1$) back along the primitive path, can be thought of as moving in a potential $U(s)$. The potential $U(s)$ is derived from eq 2, using eq 1 and the relation[6]

$$a^2 = (4/5)N_{\rm e}b^2 \tag{3}$$

between tube diameter and entanglement length, to obtain

$$U(s) = \frac{15Ns^2}{8N_{\rm e}} \tag{4}$$

When $N/N_{\rm e}$ is large, the activation barrier for arm retraction a finite fraction s of the way back along the primitive path is many k_BT. Thus the time $\tau(s)$ for this retraction to take place is exponentially long,

$$\tau(s) = \tau_0 \exp[U(s)] \tag{5}$$

where τ_0 is an "attempt frequency".

Naively, one might take τ_0 to be the Rouse time $\tau_{\rm R} = \tau_{\rm e}(N/N_{\rm e})^2$ (where $\tau_{\rm e}$ is the Rouse time of an entanglement segment, which for us is a convenient microscopic time). On the time scale $\tau_{\rm R}$, the arm explores values of s within k_BT of the bottom of the potential, or $s \sim (N_{\rm e}/N)^{1/2}$. Other authors have assumed τ_0 to be the reptation time;[7] below, we shall see that neither guess is quite correct, when we compute τ_0 with more detailed analysis.

Because the terminal time for stress relaxation is so long for large $N/N_{\rm e}$, melts of star polymers are extremely viscous; a simple scaling argument that $\eta \sim G_0\tau(1)$ implies that the zero-shear viscosity of star polymer melts is exponential in the arm molecular weight and independent of the number of arms. Both of these results have been observed experimentally,[1] a striking confirmation of the Pearson–Helfand theory.

II. Dynamic Dilution

But the Pearson-Helfand theory is not correct in detail when applied to star polymer melts, as it predicts far too strong an exponential dependence on $N/N_{\rm e}$ when compared to experiment.[1] For example, consider the dynamic rheology data of ref 8 (see Figure 1), log $G'(\omega)$ and log $G''(\omega)$ versus log ω for a 12-arm star of 1,4-polybutadiene, with anionically synthesized arms of molecular weight 30 820. The entanglement weight for 1,4-PBD is reported as $M_{\rm e} = 1815$,[9] so that $N/N_{\rm e} = 17$.

If we use eq 5 to estimate the terminal time and hence the width of the relaxation spectrum $G''(\omega)$ for the system of Figure 1, we find $\log(\tau(1)/\tau_0) = 13.8$, so that the spectrum is predicted to be nearly 14 decades wide when it is in fact only 5 decades wide. This would correspond to an error in the zero-shear viscosity of a factor of 10^9. (Alternatively, the coefficient in $U(s)$, or the value of $1/N_{\rm e}$, could be artificially adjusted by a factor of 1/3.)

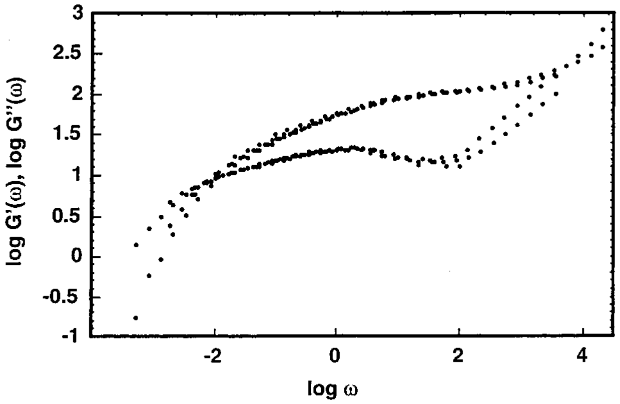

Figure 1. Log–log plot of $G'(\omega)$ and $G''(\omega)$, for a melt of 12-arm stars of 1,4-polybutadiene, with arm molecular weight M = 30 280 (data of ref 8).

The remedy to this shortcoming was given by Ball and McLeish,[2] who recognized that relaxation of a star polymer in a melt of other star polymers was different in an important respect from relaxation in a fixed entanglement network. We now summarize their arguments and results.

Consider the retraction of a star arm in a star polymer melt. Because the spectrum of relaxation time scales is so broad, on the time scale $\tau(s)$ at which a portion of the arm a fraction s from the free end is relaxing, chain segments with $s' < s$ have long since relaxed, and indeed may be thought of as completely mobile. In other words, entanglements of arm segments at s with segments at $s' < s$ are not effective on the time scale $\tau(s)$ in restricting the motion of the arm segments at s.

As a consequence, the relaxing segments at s see a *diluted* entanglement network. The concentration of entangling chains is reduced by a factor $1 - s$. The conformations of these entangling chains are uncorrelated random walks (as are all chains in a melt), so the diluted entangling network looks like a semidilute solution under Θ conditions.

McLeish and Ball assumed that in such a diluted network with a volume fraction ϕ of chains, the entanglement length $N_{\rm e}(\phi)$ is given by

$$N_{\rm e}(\phi) = N_{\rm e}/\phi, \qquad N_{\rm e}(s) = N_{\rm e}/(1 - s) \tag{6}$$

This follows from the assumption that entanglements are "binary events" involving two chains and that the conformations in the diluted network are unchanged; thus, along the arc length of a given chain, only a fraction ϕ of the original entanglements (in the undiluted network) are present.

To compute the relaxation time $\tau(s)$ in the presence of this "dynamic dilution", ref 2 considers the process of arm retraction to be hierarchical: to retract from $s + \Delta s$, the attempt frequency is $\tau(s)$, and the additional barrier is $U(s{+}\Delta s;N_{\rm e}(s)) - U(s;N_{\rm e}(s))$, so that $\tau(s{+}\Delta s) = \tau(s) \exp[U(s{+}\Delta s;N_{\rm e}(s)) - U(s;N_{\rm e}(s))]$. [We write $U(s;N_{\rm e}(s))$ to denote the dependence of $U(s)$ on s through the diluted $N_{\rm e}(s)$.] Taking Δs small leads to

$$\frac{\rm d}{{\rm d}s} \ln \tau(s) = \frac{\partial U}{\partial s}(s;N_{\rm e}(s)) = \frac{{\rm d}U_{\rm eff}}{{\rm d}s}(s) \tag{7}$$

Here we have defined a new potential $U_{\rm eff}(s)$ by

$$U_{\rm eff}(s) = \frac{15N}{8N_{\rm e}}(s^2 - 2s^3/3) \tag{8}$$

in terms of which we evidently have $\tau(s) = \tau_0 \exp[U_{\rm eff}(s)]$.

The modified potential $U_{\rm eff}(s)$ is shown in Figure 2. From eq 8 it is evident that $U_{\rm eff}(1)$ is reduced by a factor of 3, which gives a much more reasonable range of time scales for the system of Figure 1.

To go further in comparing to dynamic rheology data, ref 2 wrote an expression for the stress relaxation function $G(t)$ in terms of $\tau(s)$, as

$$G(t) = 2G_0\int_0^1 {\rm d}s\,(1 - s)\exp[-t/\tau(s)] \tag{9}$$

The stress relaxation is summed over different arm segments s; the factor $(1 - s)$ arises from dynamic dilution, because the modulus goes as $1/N_{\rm e}(\phi(s))$; and the stress in a given arm segment is assumed to relax exponentially on the time scale $\tau(s)$.

For times t between τ_0 and $\tau(1)$, $G(t)$ relaxes approximately as $G(t) \approx G_0(1 - s(t))^2$, because the factor $\exp[-t/\tau(s)]$ behaves roughly as a step-function, cutting off the integration over s when $\tau(s) = t$ [which defines $s(t)$]. This behavior is related to the "double reptation" approximation for polydisperse linear melts.[10]

Dynamic rheology data is of course taken in the frequency domain; the correspondence with $G(t)$ is made by noting that an arbitrary strain history $\gamma(t)$ can be thought of as a sequence of small step strains $\dot\gamma(t)\,{\rm d}t$, so that

$$\sigma(t) = \int_{-\infty}^{t} {\rm d}t'\, G(t - t')\dot\gamma(t') \tag{10}$$

Transforming to the frequency domain and defining $\sigma(\omega) = G^*(\omega)\gamma(\omega)$ shows that $G^*(\omega)$ so defined is related to the Fourier transform of $G(t)$; thus we have

$$G^*(\omega) = 2G_0\int_0^1 {\rm d}s\,(1 - s)\left[\frac{-i\omega\tau(s)}{1 - i\omega\tau(s)}\right] \tag{11}$$

Using eq 11 for $G^*(\omega)$ and $\tau(s)$ given by eq 5 with $U(s)$ replaced by $U_{\rm eff}(s)$ of eq 8, we can compare to the data of Figure 1. Taking G_0, τ_0, and $N_{\rm e}$ as adjustable parameters, a fit such as shown in Figure 3 can be obtained; however, the value of $N_{\rm e} = 2570$ is noticeably larger than published values.[9] Also, the shape of the relaxation spectrum $G''(\omega)$, while reasonable at low frequencies, is too sharply peaked at higher frequencies around τ_0^{-1}.

III. A More Refined Theory

In the present paper, we refine the approach of ref 2, to include the following:

(1) As mentioned briefly above, arm retraction for small s such that $U_{\rm eff}(s) < k_{\rm B}T$ is not "activated", and not well described by the motion of a single breathing mode in the potential $U_{\rm eff}(s)$. Rather, the motion of the free end for such small s and hence short times is that of the end of a long Rouse chain, which moves faster than diffusively. This early fast relaxation will smooth out the too-sharp peak in $G''(\omega)$ at high frequencies (near $\omega\tau_{\rm e} = 1$).

(2) Given an effective potential $U_{\rm eff}(s)$, it is possible to compute exactly the "first-passage" time for a diffusing free end to first retract to a segment position s. This will reproduce the behavior of eq 5, but will also give the prefactor. This will enable us not only to determine $\tau(s)$ more precisely but to set the time scale by comparison to published data on monomeric friction coefficients for linear chains, eliminating the formerly adjustable parameter τ_0.

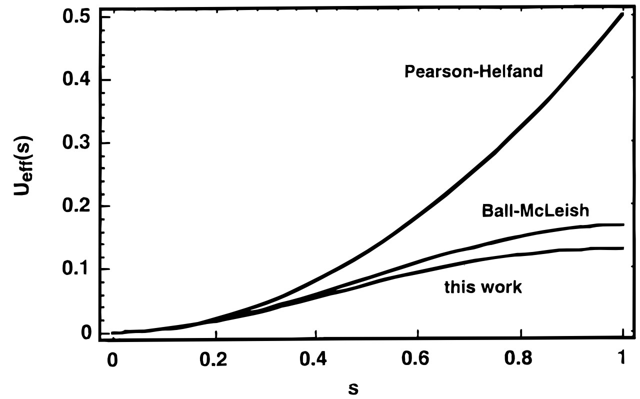

Figure 2. Comparison of the arm free end effective potentials of Pearson and Helfand,[1] Ball and McLeish,[2] and modified to account for the dilution result eq 23.

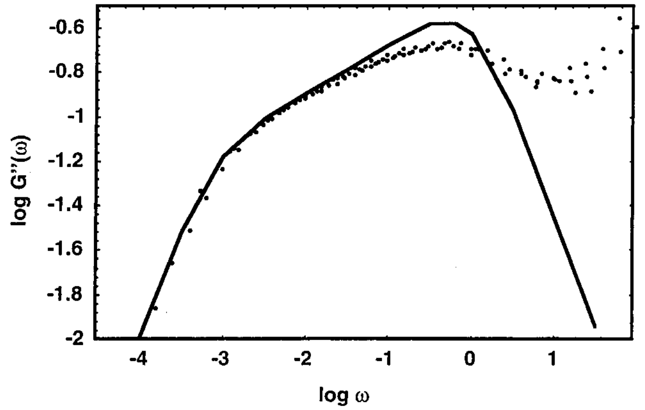

Figure 3. Fit to data of Figure 1 using the result eq 11, with time scale τ_0, modulus scale G_0, and $N_{\rm e}$ adjusted.

(3) As pointed out by Colby and Rubinstein,[3] the scaling $N_{\rm e}(\phi) = N_{\rm e}/\phi$ is not supported by rheological data on semidilute Θ solutions. They present in ref 3 an alternative scaling argument that leads to $N_{\rm e}(\phi) = N_{\rm e}/\phi^{4/3}$, which is supported by Θ solution data. This stronger dependence of diluted entanglement length on $\phi = 1 - s$ will further "soften" the potential $U_{\rm eff}(s)$, leading to a narrower spectrum $G''(\omega)$ for a given value of $N/N_{\rm e}$, and ultimately to a more reasonable value of $N_{\rm e}$ to fit the data of Figure 1.

A. Early Fast Diffusion. For displacements of the arm free end a small fractional distance s toward the junction point such as $U_{\rm eff}(s) \ll k_{\rm B}T$, which implies $s \ll s^* = (N_{\rm e}/N)^{1/2}$, the potential $U_{\rm eff}(s)$ is irrelevant, and the arm end diffuses freely. The corresponding time scale $\tau(s^*)$ scales as the Rouse time $\tau_{\rm R}$.

A simple scaling argument reveals the expected behavior of $\tau(s)$ for $s \ll s^*$. We expect that at early times $t \ll \tau(s^*)$, the arm free end moves under the action of many Rouse modes, with no influence of the junction point. Thus, its mean-square displacement along the tube $\langle l^2(t)\rangle$ must be independent of $N_{\rm a}$; and at $t = \tau_{\rm R}$, $\langle l^2(t)\rangle$ must scale as R^2. Because $\tau_{\rm R} \sim \tau_{\rm e}(N_{\rm a}/N_{\rm e})^2$, we must have

$$\langle l^2(t)\rangle = \frac{4R^2}{3\pi^{3/2}}\left(\frac{t}{\tau_{\rm R}}\right)^{1/2} \tag{12}$$

for $t \ll \tau_R$. The prefactor has been computed from a detailed one-dimensional Rouse model.[11]

Making the correspondence $l/L = s$ and solving for the characteristic time $\tau(s)$, we find

$$\tau(s) = \frac{225\pi^3}{256}\left(\frac{N}{N_e}\right)^2 \tau_R s^4 \qquad (13)$$

B. First-Passage Time. For larger values of s or longer times, arm retraction is activated. We compute the time $\tau(s)$ with prefactor (improving on eq 5) by solving a first-passage time problem. Consider the arm free end as a random walker with diffusion coefficient D_{eff} in the potential U_{eff}; the probability distribution $P(s)$ evolves according to

$$0 = \frac{\partial P}{\partial t} + D_{eff}\frac{\partial}{\partial z}\left(\frac{\partial P}{\partial z} + P\frac{\partial U}{\partial z}\right) \qquad (14)$$

where the curvilinear displacement along the tube z is related to the fractional distance s by $z/L = s$. We take the effective diffusion coefficient to be twice the Rouse diffusion coefficient, $D_{eff} = 2D_R$, because the average curvilinear velocity in a uniformly retracting star arm is half of the velocity of the free end (hence the sum of the monomeric drag is halved, and the mobility is doubled).

Now impose an absorbing boundary condition at $z = z_0$ and take an initial condition $P(z) = \delta(z)$ of a walker at the origin (an unretracted arm). The mean first-passage time is the time-weighted average of the flux absorbed at z_0,

$$\bar{\tau}(z_0) = \int_0^\infty dt\, t D_{eff}\left.\frac{\partial P}{\partial z}\right|_{z=z_0} \qquad (15)$$

It is easy to show (using eq 14) that this definition is equivalent to a simpler steady-state problem: continuously supply walkers at $z = 0$ at a rate J_{in}, thus establishing a steady-state profile $P(z)$, and then

$$\bar{\tau}(z_0) = J_{in}^{-1}\int dz\, P(z) \qquad (16)$$

In words, the mean lifetime is the number of walkers divided by the rate at which they are added to the system.

To use eq 16, we need the solution to the steady-state equation (eq 14 with $\partial P/\partial t = 0$; the input current J_{in} corresponds to a break in slope at the origin, $J_{in} = D_{eff}(P'(0-) - P'(0+))$. To the left of $z = 0$, there is no absorbing boundary and hence no current, so $P(z< 0)$ is the equilibrium distribution, $P(z< 0) = P(0) \exp[-U_{eff}(z)]$. To the right of $z = 0$, there flows the constant current J_{in}, and so

$$D_{eff}\left(\frac{\partial P}{\partial z} + P\frac{\partial U}{\partial z}\right) = -J_{in} \qquad (17)$$

Equation 17 is easily integrated; putting the answer in eq 16 gives an explicit expression for the first-passage time,

$$\tau(s) = (L^2/D_{eff})\int_0^s ds' \exp[U_{eff}(s')]\int_{-\infty}^{s'} ds'' \times \exp[-U_{eff}(s'')] \qquad (18)$$

For large N/N_e and finite s, the outer exponential factor becomes very large and the integral over s' is dominated by the region near s. The inner integral, approximately extended to all s'', is dominated by the region near $s'' = 0$ and can be approximated by $[\pi/(2U''_{eff}(0))]^{1/2}$. For s away from $s = 1$, the potential $U_{eff}(s)$ has finite slope, and we can approximate

$$\tau(s) \approx \frac{L^2}{D_{eff}}\frac{\exp[U_{eff}(s')]}{U_{eff}'(s)}\left(\frac{\pi}{2U''_{eff}(0)}\right)^{1/2} \qquad (19)$$

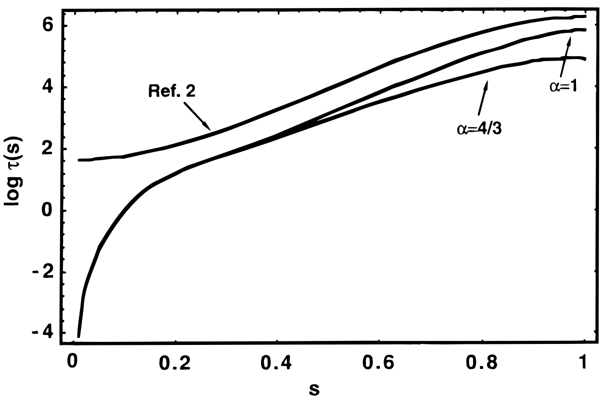

Figure 4. Comparison of the relaxation time $\tau(s)$ as given by eqs 5 and 8 (results of ref 2), eq 21 including effects of early-time diffusion, and eq 22 including both early-time diffusion and the modified dilution exponent of eq 23.

This result makes evident the scaling of the prefactor in $\tau(s)$. The integral $\int ds'' \exp[-U_{eff}(s'')]$ has a width of order $s^* = (N_e/N)^{1/2}$, and $U'_{eff}(s)$ scales as N/N_e, so $\tau(s) \sim \tau_e(N/N_e)^{3/2} \exp[U_{eff}(s)]$: the prefactor depends more weakly on N/N_e than the Rouse time τ_R.

For s near $s = 1$, the potential $U_{eff}(s)$ becomes flat, and we approximate the outer integral in eq 18 as a Gaussian, with the result

$$\tau(s) \approx \frac{L^2}{D_{eff}}\frac{\pi \exp[U_{eff}(s')]}{2[|U''_{eff}(s)|U''_{eff}(0)]^{1/2}} \qquad (20)$$

Comparing the approximations eqs 19 and 20, we see that they cross over for $1 - s$ of order $(N_e/N)^{1/2}$. We can assemble a simple crossover function that incorporates these results by replacing $U'_{eff}(s)$ in eq 19 by $[(U'_{eff}(s))^2 + 2U''_{eff}(1)/\pi]^{1/2}$; the resulting approximation for $\tau(s)$,

$$\tau(s) \approx \frac{L^2}{D_{eff}}\frac{\exp[U_{eff}(s')]}{[(U'_{eff}(s))^2 + 2U''_{eff}(1)/\pi]^{1/2}}\left(\frac{\pi}{2U''_{eff}(0)}\right)^{1/2} \qquad (21)$$

compares favorably to the exact integration of eq 18.

Finally, we construct a second crossover from the early-time result eq 13 to the activated result eq 21, simply taking

$$\tau(s) \approx \frac{\tau_e(s)}{1 + \tau_e(s)/\tau_a(s)} \qquad (22)$$

where $\tau_e(s)$ (e for "early") and $\tau_a(s)$ (a for "activated") are given by eqs 13 and 21, respectively. (See Figure 4.)

C. Dilution Exponent. Some time ago, Colby and Rubinstein examined the treacherous question of the concentration dependence of the entanglement length (and hence the tube diameter and plateau modulus) in semidilute Θ solutions.[3] This question bears directly on our dynamic dilution calculations, as well as on double reptation calculations of stress relaxation in polydisperse linear polymer melts.[10] We summarize and comment on their results here.

We begin by presenting three candidate arguments to determine the form of $N_e(\phi)$: (1) The canonical scaling argument is that "there is only one length in the problem", because microscopic length scales ought to be irrelevant to the scaling of physical properties of self-similar structures such as polymeric random walks.[12] We may take the correlation length for concentration fluctuations $\xi(\phi)$ as the characteristic length scale; according to the scaling assumption, the tube diameter $a(\phi)$ should scale with ϕ in the same way as $\xi(\phi)$.

Since the correlation length must equal the chain radius R at the overlap concentration $\phi^* \sim N/R^3$, and must become independent of chain length N for concentrations well above ϕ^*, we thus have $\xi(\phi) \sim R(\phi^*/\phi)$, or $\xi(\phi) = b/\phi$ for Θ solutions. Since the tube diameter is related to N_e by $a^2 \sim N_e b^2$, this implies $N_e(\phi) = N_e/\phi^{1/2}$. This scaling result does indeed describe the static correlation length; however, this scaling for $a(\phi)$ is at variance with the data.[3]

(2) As in ref 2 and section II above, the assumption that entanglements are "binary events" involving two chains, and chain conformations are ideal in Θ solutions, implies $N_e(\phi) = N_e/\phi$. Using the relation $a(\phi)^2 \sim N_e(\phi)b^2$, this implies $a(\phi) \sim a_0\phi^{-1/2}$. The corresponding result for the plateau modulus is $G(\phi) \sim k_BT\phi/(N_e(\phi)b^3)$ (i.e., the modulus is k_BT times the number of entanglement strands per unit volume), which can also be written as $G(\phi) \sim k_BT\phi/(a(\phi)^2b)$. This implies $G(\phi) \sim G_0\phi^2$, where $G_0 \sim k_BT/(N_eb^3)$ is the plateau modulus of the undiluted melt. This too does not agree with the Θ solution data.

Also, it has an unfortunate theoretical consequence; since the density of entanglements scales as ϕ^2 (they are binary events), the average distance between entanglements $l(\phi)$ scales differently from $a(\phi)$, as $(a_0{}^2b)^{1/3}\phi^{-2/3}$. We must have $a(\phi) > l(\phi)$, else an entanglement strand does not reach between near-neighbor entanglements. This would only hold for $\phi > 1/N_e$ (using $a^2 = N_eb^2$). But even this does not make sense, because then an entanglement strand would bypass a nearest-neighbor entanglement point and connect up with some more distant entanglement point—trapping new entanglements in the process.

(3) Perhaps in response to this paradox, Colby and Rubinstein in ref 3 makes the following argument. They assume that entanglements are binary events between chains with a concentration $\phi^2/(a_0{}^2b)$, where a_0 is the tube diameter in the melt. (This expression scales as ϕ^2, and goes to the melt result as $\phi \to 1$.) And, they require that the tube diameter $a(\phi)$ scale as the near-neighbor distance between entanglements $l(\phi)$ above, as $a(\phi) = a_0\phi^{-2/3}$. Because the entanglement strands are Gaussian random walks (i.e., $a^2 \sim N_eb^2$), this implies

$$N_e(\phi) = N_e\phi^{-\alpha}, \qquad \alpha = 4/3 \tag{23}$$

The corresponding result for the modulus (as in the first argument) is $G(\phi) \sim k_BT\phi/(N_e(\phi)b^3)$, which now implies $G(\phi) \sim G_0\phi^{7/3}$.

This argument is in good agreement with the Θ solution data,[3] but also has an unusual consequence worth noting. By assumption, the density of entanglement points scales as $\phi^2/(a_0{}^2b)$, whereas the density of entanglement strands scales as $\phi/(N_e(\phi)b^3)$. Thus the number of entanglement strands per entanglement point is ϕ-dependent, scaling as $\phi^{1/3}$ and becoming increasingly small for small ϕ, which would seem to contradict the idea that entanglements are binary events. At the very least, this scaling law can be regarded as a phenomenological description of data on semidilute Θ solutions.

Reference 3 points out that their scaling law cannot persist to arbitrarily small volume fractions, because eventually $a(\phi) = a_0\phi^{-2/3}$ would become smaller than $\xi(\phi) = b/\phi$, which does not make sense. They speculate that for volume fractions less than $\phi^* = N_e{}^{-3/2}$, the naive scaling argument applies—but because N_e is typically so large, this limit is not easily reached.

The change in the dilution exponent affects the results eq 8 for $U_{\text{eff}}(s)$, eqs 10 and 11 for the stress relaxation function $G(t)$ and its Fourier transform $G(\omega)$ [because of the factors of $(1 - s)$ that arose from dilution], and eqs (18–20) for the first-passage time $\tau(s)$ with prefactor. Fortunately, the same procedures used above and in ref 2 can be used to derive explicit results with the altered dilution exponents, which we now present.

Solving the differential equation eq 7 with $N_e(\phi = 1 - s)$ given now by eq 23, we obtain

$$U_{\text{eff}}(s) = \frac{15N}{4N_e}\,\frac{1 - (1 - s)^{1+\alpha}[1 + (1 + \alpha)s]}{(1 + \alpha)(2 + \alpha)} \tag{24}$$

We may choose $\alpha = 4/3$ to recover the Colby–Rubinstein dilution exponent; with $\alpha = 1$, eq 24 reduces to eq 8, the simple binary-contact assumption.

The stress relaxation equation also incorporates the dilution exponent, and eq 9 becomes

$$G(t) = (\alpha + 1)G_0\int_0^1 \mathrm{d}s\,(1 - s)^\alpha \exp[-t/\tau(s)] \tag{25}$$

or in frequency space

$$G(\omega) = (\alpha + 1)G_0\int_0^1 \mathrm{d}s\,(1 - s)^\alpha\left[\frac{-i\omega\tau(s)}{1 - i\omega\tau(s)}\right] \tag{26}$$

We use the same result eq 13 for the early-time behavior of $\tau(s)$, and the same simple crossover expression eq 22 to join up the early and activated results for $\tau(s)$. The expression eq 20 for $\tau_a(s)$ changes, because $U_{\text{eff}}(s)$ no longer has a quadratic maximum at $s = 1$. Instead, near $s = 1$ we have $U_{\text{eff}}(s) \approx U_{\text{eff}}(1) - (15/4)(N/N_e)(1 - s)^{1+\alpha}/(1 + \alpha)$, which leads to

$$\tau(s) \approx \frac{L^2}{D_{\text{eff}}}\exp[U_{\text{eff}}(s)]\left(\frac{\pi}{2U''_{\text{eff}}(0)}\right)^{1/2}\left(\frac{15N}{4N_e}\right)^{\alpha/(\alpha+1)} \times (1 + \alpha)^{-(2\alpha+1)/(\alpha+1)}\Gamma\left(\frac{1}{\alpha + 1}\right) \tag{27}$$

Thus in place of eq 21 we have a new crossover expression for $\tau_a(s)$,

$$\tau(s) \approx \frac{L^2}{D_{\text{eff}}}\left(\frac{\pi}{2U''_{\text{eff}}(0)}\right)^{1/2} \times \frac{\exp[U_{\text{eff}}(s)]}{\left[(U'_{\text{eff}}(s))^2 + \left[\left(\frac{15N}{4N_e}\right)^{\alpha/(\alpha+1)}(1 + \alpha)^{-(2\alpha+1)/(\alpha+1)}\Gamma\left(\frac{1}{\alpha + 1}\right)\right]^{-2}\right]^{1/2}} \tag{28}$$

For reference, we give the result of substituting eq 24 into eq 21, with $D_{\text{eff}} = 2D_R$ [and $D_R = k_BT/(N\zeta)$, $\tau_R = \zeta N^2b^2/(3\pi^2k_BT)$]:

$$\tau(s) \approx \tau_e \left(\frac{N}{N_e}\right)^{3/2} \left(\frac{2\pi^5}{15}\right)^{1/2} \times \frac{\exp[U_{\rm eff}(s)]}{s\left[(1-s)^{2\alpha} + \left(\left(\frac{4N_e}{15N}\right)(1+\alpha)\right)^{2\alpha/(\alpha+1)} \Gamma\left(\frac{1}{\alpha+1}\right)^{-2}\right]^{1/2}} \tag{29}$$

(recall that τ_e is the Rouse time of an entanglement segment). Note that we have taken a factor of s [from $U'_{\rm eff}(s)$] outside the square root to avoid a spurious crossover at small s (where for large N/N_e the second term in the square root is negligible).

IV. Parameter-Free Comparison to Data

Using the result for the characteristic time $\tau(s)$ with prefactor, we are able to compute the stress relaxation function $G(t)$ or $G(\omega)$ with no adjustable parameters. The only parameters in the theory, which are the plateau modulus G_0, the entanglement molecular weight N_e, and the Rouse time of an entanglement segment τ_e, can be obtained from rheological data on linear chains.

From ref 9, for 1,4-polybutadiene at 413 K, the chain end-to-end radius squared per chain mass $\langle R^2 \rangle / M$ equals 0.876 Å/(g/mol), and the density is $\rho = 0.826$ g/cm^3. With a monomer molecular weight $M_0 = 54$, this implies a value of $b = (M_0 \langle R^2 \rangle / M)^{1/2} = 6.9$ Å.

The entanglement molecular weight from ref 9 is $M_e = 1815$; from Ferry,[13] the monomeric friction constant ζ at 298 K is $\log_{10} \zeta = -6.75$ in cgs units. So the Rouse time of an entanglement segment is $\tau_e = \zeta N_e^2 b^2 / (3\pi^2 k_B T) = 7.8 \times 10^{-6}$ s. Finally, the plateau modulus from ref 9 is $G_0 = 1.25$ MPa (consistent with the value of M_e used above).

We compute $G(\omega)$ using eq 26, with $\tau(s)$ given by eq 22 with $\tau_e(s)$ from eq 13 and $\tau_a(s)$ from eq 29 with the Colby−Rubinstein value of $\alpha = 4/3$, performing the integral over s numerically for each value of ω.

The results are compared in Figure 5 to the data of Figure 1. Several comments are in order:

(1) The shape of the relaxation spectrum $G''(\omega)$ is in excellent agreement with the data over five decades in frequency, from the terminal region up to the start of the high-frequency Rouse regime [the minimum in $G''(\omega)$]. The effect of the early-time fast diffusion is to spread out the peak in $G''(\omega)$ (compare Figures 3 and 5).

(2) The width of $G''(\omega)$ is very sensitive to the value of N/N_e and sensitive also to the value of the dilution exponent α. If we has chosen the "double reptation" value of $\alpha = 1$, a too-large value of $M_e = 2400$ or so would be required to fit the data.

(3) Without making any horizontal or vertical shifts on the log−log plot and using the published data for the modulus G_0 (ref 9) and τ_e via the monomeric friction constant ζ (ref 13), the theory comes within a factor of $10^{0.3} = 2$ on the time scale and $10^{0.2} = 1.6$ on the modulus scale of superimposing on the data.

Naturally it is of interest to check the assumptions of this theory with star polymers of different N/N_e, and if possible of different chemistry. Fortunately a number of data sets for polybutadiene, polystyrene, and polyisoprene (monomers readily polymerized anionically) are available in the literature. In Figure 6 we present data[15] for $G''(\omega)$ for a three-arm polyisoprene star with an arm molecular weight of 95 000 compared with our theory, taking a value of 4000 for M_e and adjusting the plateau modulus G_0 and friction coefficient ζ to bring the curve into coincidence with the data.

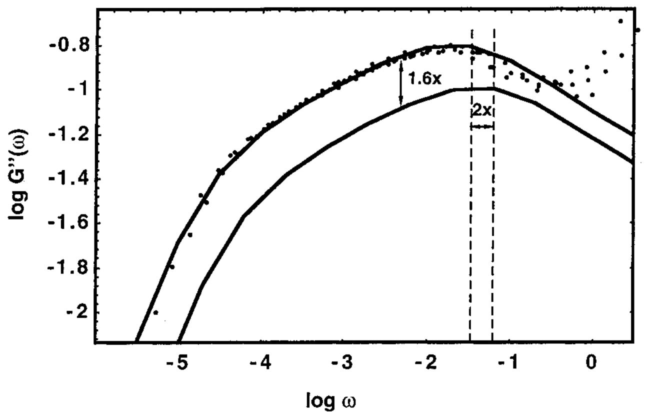

Figure 5. Comparison of the experimental $G'(\omega)$ and $G''(\omega)$ of ref 8 to the theoretical dynamical modulus, with literature values of G_0, N_e, and ζ.

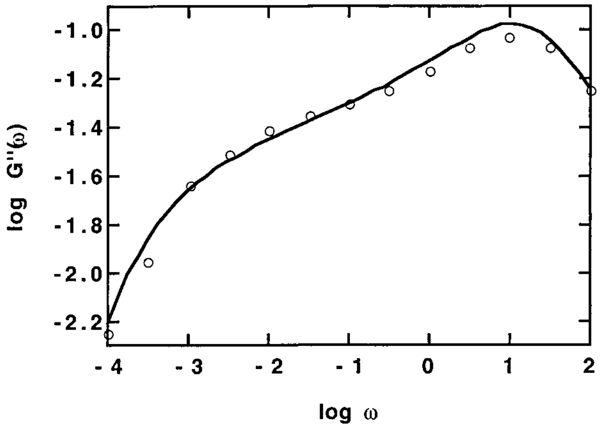

Figure 6. Comparison of data from ref 15 (circles) to theory (line). The values of G_0 and ζ have been adjusted by factors of 1.1 and 3 to superimpose theory and experiment.

Again we notice that both the width of the spectrum and the peak shape are accurately predicted by the theory at this greater value of N/N_e (24 in this case). Compared to literature values, the value of G_0 we require is larger by a factor of 1.1, and ζ by a factor 3. These compare with the ratios of 1.6 and 2 found above in the case of polybutadiene, and indicate that the remaining small discrepancies may be systematic. The evidence for universality of our theory is strong.

We close this section with a theoretical argument as to why the dynamic dilution approximation works so well in describing the stress relaxation of star polymer melts.

The validity of the dynamic dilution ansatz depends on a separation of time scales, between the time required for entanglement constraints on a portion of star arm from faster-relaxing chain segments to be fully released and the time for the stress in that portion of star arm to be relaxed by arm retraction. More simply, a portion of star arm must explore the larger tube (made larger by dilution) before it relaxes by arm retraction. This is analogous to the condition for the validity of the "double reptation" ansatz for stress relaxation in polydisperse linear melts, which depends on a separation of time scales between the time required for a long chain to explore its diluted tube via constraint release and the reptation time of the long chain.[10]

Entanglement constraints from segments a fractional distance s along a star arm are released by "constraint-release Rouse motion", with a hopping time $\tau(s)$, a hopping distance of the diluted tube diameter $a(s)$ on the time scale s, and an effective "monomer size" of the entanglement length $N_e(\phi(s))$ on the time scale s. In other words, the tube constraining a star arm itself undergoes Rouse motion as constraints are released. The Rouse time by constraint release for a chain segment of length n is then $\tau(s)[n/N_e(\phi(s))]^2$.

The chain segment length of interest is an entanglement strand of the network diluted by the removal of the material between s and $s' = s + ds$ with time scale $\tau(s)$. Recalling the scaling of entanglement length with unrelaxed volume fraction $N_e(\phi) = N_e/\phi^\alpha$ (with $\alpha = 1$ naively and $\alpha = 4/3$ from the Colby–Rubinstein argument), we see that the segment of interest, the ratio $n/N_e(\phi(s))$ is given $[\phi(s)/\phi(s')]^\alpha$. The separation of time scales we require for dynamic dilution to be valid is then

$$\tau(s)(\phi(s')/\phi(s))^{2\alpha} < \tau(s') \tag{30}$$

Taking $s' = s + ds$ and expanding, using the differential equation eq 7 for the time scale $\tau(s)$ and eq 24 for the effective potential, and recalling $\phi(s) = 1 - s$, we obtain

$$\frac{15}{8\alpha}\frac{N_a}{N_e}s(1 - s)(1 + \alpha) > 1 \tag{31}$$

We see that this inequality fails both for small s of order $O(N_e/N_a)$ (when the star arm is relaxing quickly because the retraction barrier is less than k_BT) and for small $1 - s$ of order $O(N_e/N_\alpha)^{1/(1+\alpha)}$ (when the entanglement network is so dilute that the time to explore the diluted tube becomes long). But for reasonably large values of N_a/N_e, dynamic dilution is a good approximation for almost all of the star arm.

V. Conclusions

Pearson and Helfand[1] described the stress relaxation of a star polymer in a fixed network, capturing two of the main features of stress relaxation in melts of star polymers: exponential dependence of stress relaxation time (and hence zero-shear viscosity η_0) on arm molecular weight N_a, and no dependence on the number of arms. However, the dependence on N_a in this theory is too strong, leading to overprediction of η_0 by 9 orders of magnitude for arm length $N_a = 15N_e$ or so.

Ball and McLeish[2] extended the theory to include "dynamic dilution", the enabling effect of the relatively more mobile outer portions of star arms on the stress relaxation of the inner portions of the arms. Their approach weakens the exponential dependence of $G(\omega)$ on N/N_e enough that predictions for η_0 are within an order of magnitude of experiment; the remaining discrepancy can be masked by taking a slightly too-large value of N_e. This amended theory still has adjustable modulus and time scale factors, and the theoretical shape of $G''(\omega)$ does not agree with data at higher frequencies.

In principle, the only parameters needed to describe stress relaxation in star polymer melts should be the entanglement length N_e and the monomeric friction constant ζ, both measurable from melts of linear chains: in the present paper, we have extended the approach of ref 2 to reach this goal.

To that end, we have computed the stress relaxation time for star arm segments a fractional distance s down the arm $\tau(s)$ complete with prefactors in terms of ζ and N_e, to fix the time scale. To improve the theory at high frequencies, we have included the effect of higher Rouse modes in the diffusive motion of the star arm end over short distances. Finally, we have incorporated the scaling law of Colby and Rubinstein for the volume fraction dependence of the diluted entanglement length, $N_e(\phi) = N_e/\phi^{4/3}$. This stronger concentration dependence than that assumed in ref 2 leads to a width of the theoretical $G''(\omega)$ in good agreement with experiment without having to adjust N_e.

The resulting theoretical $G(\omega)$ is in excellent agreement with the shape of rheological data on star polymer melts and within factors of 1.6 and 2 in the modulus and time scales, respectively, without adjustable parameters. This is strong evidence that the theory of stress relaxation in star polymers, with "dynamic dilution", is substantially correct.

These results also have implications for stress relaxation in polydisperse linear melts, where the "double reptation" ansatz has been applied.[10] In the double reptation model, stress is regarded as held in entanglements between two chains, which disappear as the free end chain reptates past the entanglement. This leads directly to an expression for the stress relaxation function

$$G(t) = 2G_0\int_0^\infty dN\ \phi(N)\left[\int_N^\infty dN'\ \phi(N')\right] \exp[-t/\tau(N)] \tag{32}$$

where $\phi(N)$ is the mass fraction of chains with length N. Comparing to eq 9, chain length N corresponds to s, $\phi(N)\ dN$ to ds, and the factor $\int_N^\infty dN'\ \phi(N')$ plays the role of $1 - s$, the fraction of unentangled material. Double reptation and dynamic dilution are analogous.

But eq 9 assumed the dilution law $N_e(\phi) = N_e/\phi$, instead of $N_e(\phi) = N_e/\phi^{4/3}$ which ref 3 argues holds for Θ solutions and our results suggest holds for star melts. Thus "double reptation" perhaps should be replaced by "7/3 reptation" [$G(\phi) \sim \phi^{7/3}$], and thus eq 32 replaced by

$$G(t) = (7/3)G_0\int_0^\infty dN\ \phi(N)\left[\int_N^\infty dN'\ \phi(N')\right]^{4/3} \exp[-t/\tau(N)] \tag{33}$$

by analogy to eq 25. Sufficiently polydisperse linear melts should distinguish between this relation and "double reptation".

As ref 2 corrected errant factors of 10^9 in ref 1, and the present paper dealt with factor-of-10 discrepancies in the results of ref 2, the question remains: is there physics still lurking in the factors of 1.6 and 2? With regard to the time scale, the difficulty in extracting the monomeric friction constant from high-frequency Rouse model data, with time–temperature shifts and other uncertainties, the factor of 2 is perhaps not yet worrisome.

On the other hand, the downward vertical shift by factor of 1.6 with respect to the data may be significant, as the plateau modulus G_0 is somewhat easier to determine experimentally from linear melts than is ζ. A possible explanation for this is that the removal of entanglements by "dynamic dilution" is not perfect, because the separation in relaxation time scales between different arm segments is not infinite. The theory would thus somewhat overestimate the amount of stress relaxed, which is at least in the right direction. Whether this effect is important, or explains the factor of 1.6, is a subject for future work.

One final important remark concerns the experimental validity of the statement that stress relaxation in star polymer melts only depends on knowing the arm molecular weight, and the plateau modulus and monomeric friction constant from measurements on linear chains. This is not true for every polymer; in particular, polyethylene shows a different temperature dependence for the viscosity of star and linear melts. As Graessley has suggested,[14] this is evidence that different microscopic motions are involved in arm retraction and reptation for polyethylene. In such a case, we would be obliged to determine ζ directly from data on stars.

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