Dynamic Dilution, Constraint-Release, and Star−Linear Blends

S. T. Milner*

Exxon Research & Engineering, Route 22 East, Annandale, New Jersey 08801

T. C. B. McLeish

Department of Physics and Astronomy, University of Leeds, Leeds LS29JT, England

R. N. Young and A. Hakiki

Department of Chemistry, University of Sheffield, Sheffield S37HF, England

J. M. Johnson

Department of Physics, University of Sheffield, Sheffield S37HF, England

Received March 26, 1998; Revised Manuscript Received September 18, 1998

ABSTRACT: The dynamic dilution theory of stress relaxation, quantitative for star polymer melts, cannot be directly applied to star−linear blends. The linear chains on their reptation time scale τ_d release constraints on the star arms, resulting in constraint-release Rouse motion for the star arms not described by dynamic dilution. We present a microscopic theory without adjustable parameters for stress relaxation in such blends, which is in excellent agreement with dynamic rheology data for the full range of blend fractions.

Introduction

Star polymers are the simplest branched polymer, with three or more arms attached to a single branch point. Stress relaxation in melts of star polymers is described quantitatively by a microscopic theory[1] that contains three main ideas: (1) replacement of the entanglement constraints acting on a given chain segment by a tube, as in the reptation theory;[2] (2) stress relaxation by arm retraction,[3] i.e., by the fluctuation-driven motion of the arm free end down the tube toward the branch point and up again along a new tube segment; and (3) dynamic dilution,[4] the idea that on a time scale τ, the only dynamically relevant entanglements are those involving chain segments that themselves relax more slowly than τ.

The concepts developed for understanding stress relaxation in star polymer melts seem sufficiently general and robust, that they ought to work for more complex branched polymer systems. So what is the next most simple branched polymer system? We may increase the number of branch points, resulting in an H-polymer or more complex structures. Alternatively, we may consider mixtures of polymers with different branching structures. The simplest such mixture is a blend of star and linear polymers, which is the subject of this paper.

As for our previous work on star polymer melts,[1,6] we shall develop a theory for the dynamic modulus $G(\omega)$ of star−linear blends in which the only parameters are the entanglement molecular weight N_e and the monomeric friction factor ζ, in addition to those describing the polymer blend architecture (the star volume fraction ϕ_s, the star arm and linear chain molecular weights N_a and N_l). This should be possible in principle, since the tube diameter and hence N_e should be the same for a segment of a linear chain as for a branched polymer, and the local motions of a branched polymer are controlled by the same friction factor as the local motions of a linear chain. Note that for more than $f = 4$ star arms, the entire dynamic rheology of the star is independent of the number of arms (and, indeed, is very much the same to within 30% or so for $f = 3$),[3] so the number of arms f is not a parameter in our theory.

In principle, values for N_e and ζ can be determined from measurements on monodisperse linear chain melts, so that our theories for branched polymers may be called parameter-free. In practice, it is often difficult to get precise values for ζ, and the behavior of branched polymers depends so sensitively on N_e that we may use adjusted values of ζ and N_e for comparison to branch polymer data and then show that these parameter values are consistent with values obtained from measurements on linear chains (as we have shown in our previous work on star melts).

We shall find that for star−linear blends, the simultaneous relaxation by reptation of the finite volume fraction of linear chains renders the arm retraction/dynamic dilution theory invalid for an intermediate regime of the retraction. The reason is as follows. Dynamic dilution describes how more slowly relaxing star arm segments are able to retract in a dilated tube, because more quickly relaxing segments are able to get out of the way so much faster that entanglement with such segments is irrelevant. This is an important effect for branched polymers, because retraction in a tube is an activated process, with a barrier that is exponential in the number of entanglement segments along the tube to be retracted.

Dynamic dilution works when there is a broad, smooth distribution of relaxation time scales, so that the tube diameter dilates smoothly and continuously with increasing time scale, and there is an effective separation of time scales between segments relaxing more quickly than a given τ and those relaxing more slowly. A blend of monodisperse linear chains and stars is in effect designed to frustrate this requirement,

10.1021/ma980481v CCC: $15.00
Published on Web 12/04/1998

because under the dynamic dilution approximation, the tube diameter increases discontinuously at the reptation time τ_d of the linear chains.

In fact, it takes the star arms some considerable time to "explore" the newly dilated tube after τ_d, which must be accounted for. The mechanism for this exploration is Rouse motion of the star arm by constraint-release.[7] That is, on the time scale τ_d the star arms are able to make small transverse hops a distance of order the tube diameter, as linear chains reptate past and constraints are released.

This motion of the star arm looks like Rouse motion in that there are now no entanglement constraints except for those imposed by other star arms. Our picture is then that after τ_d, the star arms undergo constraint-release Rouse motion until they have explored the dilated tube defined by entanglements only with unrelaxed star arm segments. When this happens, a dynamic dilution picture resumes. One may regard the intermediate Rouse motion of the star-arm tube and the subsequent recovery of entangled arm fluctuations (with continuing dynamic dilution) as a coarse-grained replay of the transition from the Rouse to entangled dynamics at τ_e in pure star melts (where τ_e is the Rouse time of an entanglement segment in the melt).

For a dilute admixture of stars among linear chains, constraint-release Rouse motion describes the entire stress relaxation after τ_d (ignoring self-entanglement). As a result, contributions to the slowly relaxing stress (and thus the viscosity) from dilute admixtures of stars in a linear melt would be predicted to begin at order $O(\phi_s)$, in accord with the data and common sense. (In contrast, a strict dynamic dilution theory would imply that contributions to slowly relaxing stress in such a dilute admixture begin at $O(\phi_s^2)$, because a star needs another star with which to entangle.)

Our paper is arranged as follows: in section I, we review published dynamic rheology data on polybutadiene star−linear blends and present new data on polyisoprene star−linear blends, each for a wide range of values of ϕ_s; in section II, we discuss the breakdown of dynamic dilution and present a general criterion with examples for its validity; in section III, we describe constraint-release Rouse motion as the stress relaxation mechanism that follows the breakdown of dynamic dilution; in section IV the recovery of dynamic dilution after the dilated tube has been explored; in section V, we present the results of our calculation of the dynamic modulus $G(\omega)$ for star−linear blends and compare our results to published data; in section VI we summarize and discuss our results. Appendix A presents details of the synthesis and rheological measurement of polyisoprene star−linear blends reported here. Appendix B contains further discussion of some of our theoretical assumptions concerning constraint-release Rouse motion.

I. Star−Linear Data

Dynamic rheology data on star−linear blends as a function of star volume fraction ϕ_s such as those reported by Struglinski et al.[8] provide a stringent test of any theory for stress relaxation in such systems, because of the strong variation of the data with ϕ_s.

In ref 8, monodisperse polybutadiene (PBD) linear chains and three-arm stars had molecular weights of 105 000 and 127 000, respectively. With an entanglement molecular weight for PBD of 1815, this corresponds to linear chains and star arms of length $N_l/N_e = 58$ and $N_a/N_e = 23$, respectively.

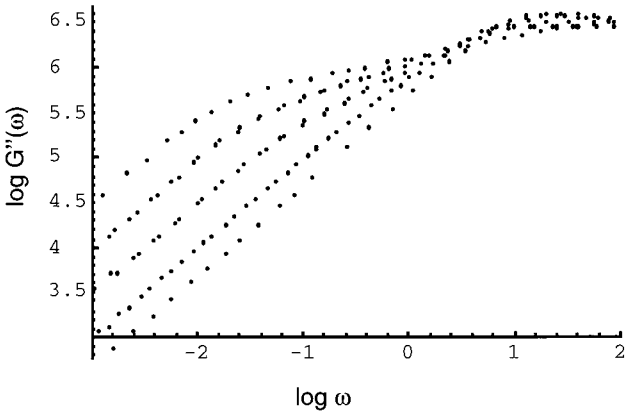

Figure 1. Dynamic rheology data of ref 8 on polybutadiene star−linear blends, for star volume fractions $\phi_s = 0$, 0.2, 0.5, 0.75, 1.

The data of ref 8 are suggestive of a subtle cooperative dynamics between the linear and star components but provide only one point on the space of the problem defined by the degree of entanglement of each species (N_l/N_e, N_s/N_e), and in one chemistry. To explore the entire parameter space (recalling that each point constitues experiments on a range of compositions over a wide sweep of frequencies) would require a very large experimental program.

However, since the interesting range for strong coupling of reptation and fluctuation always needs N_l/N_e not too different from N_s/N_e, a useful second set of experiments would retain this feature of the PBD data while reducing the degree of entanglement by a factor of 2. This is the motivation for the experiments we report here, in which 135 000 g/mol polyisoprene (PI) linear chains and 195 000 three-arm stars were used; with M_e for PI of about 5400,[9] this implies $N_l/N_e = 25$ and $N_a/N_e = 12$. (Synthesis and experimental details are given in Appendix A.)

In both cases the linear chains are about twice the "span length" of the stars, i.e., $N_L \approx 2N_a$. This situation is noteworthy because contour-length fluctuations of a linear chain are analogous to arm retraction in a star; a linear chain may be thought of on short time scales compared to its reptation time as a "two-arm star". For star−linear blends with $N_l = 2N_a$, at early times (before the reptation time $\tau_d(N_l)$ of the linear chains) the replacement of stars by linear chains has no effect, as the arm retraction events and the environment in which they occur are unchanged.

For the system of ref 8, the pure star melt is about 69 times more viscous than the pure linear melt. The dynamic rheology data (see Figure 1) extends to low frequencies well into the terminal region, and to high frequencies just above the main relaxation peak of the linear melt. For our PI star−linear blends, the star melt has a viscosity about 21 times that of the linear melt, and dynamic data are likewise available over a suitably wide frequency range (see Figure 2). Both sets of data are then ideal for examining the effect of blending star and linear polymers on the entire dynamic spectrum.

A striking feature of these data is that on a log−log plot of $G''(\omega)$, the terminal asymptotes at different star volume fractions ϕ_s are proportionally spaced; i.e., the viscosity $\eta_0(\phi_s)$ depends roughly exponentially on ϕ_s. In

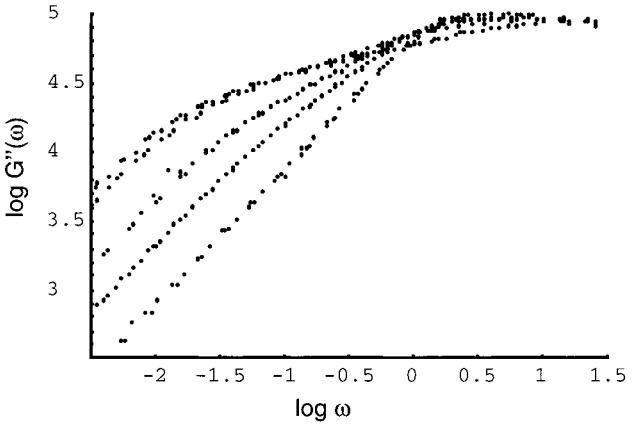

Figure 2. Dynamic rheology data of this work on polyisoprene star−linear blends, for star volume fractions $\phi_s = 0$, 0.4, 0.65, 0.9, 1.

particular, for small added amounts of stars the viscosity appears to increase smoothly from the linear-chain limit; the viscosity has about doubled at $\phi_s = 0.2$. (Samples with $\phi_s = 0$, 0.2, 0.3, 0.5, 0.75, 1 were studied in ref 8; we report rheology for $\phi_s = 0$, 0.4, 0.65, 0.9, 1.0.)

II. Dynamic Dilution, $t < \tau_D$

For times before the reptation time τ_d of the linear chains, the star arms and the two "arms" of the linear chains are both considered to be undergoing arm retraction.[10] The relaxation time $\tau_<(s)$ for an arm of length N as a function of fractional distance s down the arm is given by solving the Ball−McLeish equation in the dynamic dilution regime,

$$\frac{\mathrm{d}\log\tau}{\mathrm{d}s} = 2\nu s N/N_e(\tau) = 2\nu n s\Phi(s) \qquad (1)$$

where $\nu = 15/8$ is a constant arising from the tube model, $n = N/N_e$ is the length of the retracting arm in units of the entanglement length, and Φ is the unrelaxed volume fraction. Φ may be regarded either as a function of time or of s, since τ and s are related through eq 1.

As written, the Ball−McLeish equation contains the implicit assumption that the entanglement molecular weight dilutes as the inverse of the entangled fraction Φ. This corresponds to the physical assumption that entanglements are pairwise events between two chains, so that in a solution diluted by a factor Φ we must travel a distance N_e/Φ along a given chain before an entanglement is encountered. However, the data of Adam and Delsanti on concentration-dependent plateau moduli in Θ solutions,[11] and the scaling argument of Colby and Rubinstein,[12] suggest a $-4/3$ power rather than inverse dependence of N_e on Φ. From our previous work on star melts,[1] taking the naive scaling result is expected to work well, if we take a value for N_e that is about 20% larger than the experimental value.

To compute $\tau_<(s)$, note that eq 1 describes the retraction of star arms as well as the contour-length fluctuations of the linear chains, which may be thought of as "two-arm stars", but with an arm length of $n_l/2$. Note that the arc length variable $y = ns^2$ puts eq 1 in the form

$$\frac{\mathrm{d}\log\tau}{\mathrm{d}y} = \nu\Phi(y) \qquad (2)$$

that does not explicitly refer to the arm length and describes the retraction of arms regardless of length.

It remains to give an explicit expression for $\Phi(y)$. Before τ_d, the entangled volume fraction has contributions from both star arms and linear chains, each of the form $\phi_\alpha(1 - s_\alpha)$ where $\alpha = \{s, l\}$ refers to stars or linear chains, and s_α is the corresponding fractional distance variable. In terms of y, we have

$$\Phi(y) = \phi_s(1 - \sqrt{y/n_a}) + \phi_l(1 - \sqrt{2y/n_l}) \qquad (3)$$

where $\phi_l = 1 - \phi_s$ is the linear chain volume fraction.

We can then solve eq 2 (and convert back to the star-arm s as a variable) to obtain the effective potential $U_{s<}(s)$, where subscripts denote star (s) before τ_d (<), as

$$U_{s<}(s) = \nu n_a(s^2 - {}^2/_3(\phi_s + \phi_l\sqrt{2n_a/n_l})s^3) \qquad (4)$$

The relaxation time $\tau_{s<}(s)$ is proportional to the exponential of $U_{s<}(s)$,

$$\tau_{s<}(s) = p_{s<}(s)\exp[U_{s<}(s)] \qquad (5)$$

To complete the expression for $\tau_{s<}(s)$, we need the prefactor $p_{s<}(s)$ in eq 5, the "attempt frequency" in the expression for the relaxation time. We employ the same method as for star melts,[1] namely, to define $\tau_{s<}(s)$ precisely in terms of a first-passage time for the free end to diffuse to a given value of s.

Finally, we include the effects of fast relaxations for which the barrier height is less than k_BT and the rate is governed by the motion of the end of a semi-infinite Rouse chain in a tube.[1] Our final result constructs a crossover between this early-time (small s) result and the "activated" result, as

$$p_{s<}(s) = (1/\tau_{early}(s) + \exp[U_{s<}(s)]/\tau_{late}(s))^{-1} \qquad (6)$$

where the early- and late-time results are given in terms of the Rouse time of an entanglement segment $\tau_e = \tau_R(N_e/N)^2$ by

$$\tau_{early}(s) = (225\pi^3/256)\tau_e s^4(N/N_e)^4 \qquad (7)$$

$$\tau_{late}(s) \approx \frac{15\pi^2}{8}\left(\frac{N}{N_e}\right)^3\tau_e\frac{\exp[U_{s<}(s)]}{[U'_{s<}(s)^2 + 2s^2|U''_{s<}(1)|/\pi]^{1/2}}\left(\frac{\pi}{2U''_{s<}(0)}\right)^{1/2} \qquad (8)$$

(which is eq 21 of ref 1, with the tube contour length L and the curvilinear diffusion coefficient rewritten in terms of τ_e and N/N_e, and an extra factor of s^2 to prevent a spurious crossover for small s).

Since star arms and linear half-chain "arms" play a symmetrical role before τ_d, the relaxation time by retraction of the linear chain $\tau_l(s')$ [in terms of the fractional distance down the linear half-chain "arms" s'] is obtained from eqs 5 and 6 by exchanging ϕ_s and ϕ_l and n_a and $n_l/2$. The s variables for the star and linear chains are related through y by $n_a s^2 = y = (n_l/2)\,s'^2$. The constraint-release Rouse regime begins at $t = \tau_d$, the reptation time of the linear chains. At this time, the fractional length $s(\tau_d) = s_d$ of the star arms that has relaxed is given by the solution of

$$(15/4)n_l^3(1 - s_d\sqrt{2n_a/n_l})^2\tau_e = \tau_{s<}(s_d) \qquad (9)$$

Here the factor of $(1 - s_d\sqrt{2n_a/n_l})$ accounts for the reduction by contour-length fluctuations of the curvilinear distance the linear chain must reptate.[10]

Failure of Dynamic Dilution. Dynamic dilution and double reptation[13,14] are closely related ideas. In each, different fractions of an entangled melt are presumed to have widely differing disengagement times (reptation times for polydisperse linear chains, arm retraction times for stars). The time scales are assumed to be so widely separated that quickly relaxing portions of the system have no entanglement effect on slowly relaxing portions.

More precisely, in each case the time-dependent modulus after a step strain $G(t)$ is taken to depend only on the unrelaxed volume fraction $\Phi(t)$. The simple assumption that entanglements are pairwise events (which resulted in $N_e(\Phi) \sim \Phi^{-1}$) implies $G(t) = G_0\Phi(t)^2$; the Colby−Rubinstein scaling implies instead $G(t) = G_0\Phi(t)^{7/3}$.

As a consequence, a dilute admixture of star polymers to a linear matrix could only contribute to the stress relaxation at late times [beyond $\tau_d(N_L)$] at order $O(\phi_s^2)$ (or $O(\phi_s^{7/3})$, assuming the scaling of ref 12). This is because, according to dynamic dilution, the stars would only hold stress by entangling with each other, once the linear chains had reptated. As remarked in the previous two sections, the viscosity in the star−linear blends studied in ref 8 appears to grow linearly for small ϕ_s, contradicting dynamic dilution.

More microscopically, we expect that the effect of faster-relaxing components in a melt on slower relaxing components is to release entanglement constraints. Viovy, Colby, and Rubinstein[7] have argued that this constraint release may be thought of as enabling Rouse motion of the tube of a chain. In the particular case of a single slow-relaxing chain (such as a star arm) in a melt of linear chains, the hopping distance and time would be the tube diameter and the reptation time τ_d of the linear chains.

As we have argued in the context of both polydisperse linear chains[14] and star melts,[1] this constraint-release Rouse motion reduces approximately to double reptation or dynamic dilution, under certain conditions. This condition may be stated generally, as follows. Under the assumption of double reptation (or dynamic dilution), material is removed from the entangled volume fraction $\Phi(t)$ at some rate or other.

For a relaxing star melt, this rate is $d\Phi/dt = (d\Phi/ds)/(d\tau/ds) = -(15/4N_a/N_e s\Phi(s)\tau)^{-1}$, where we have used the Ball−McLeish equation for d log τ/ds, and s is the fractional distance down the star arm that relaxes on the time scale $\tau(s)$. For a polydisperse linear melt, we have instead $d\Phi/dt = (d\Phi/dn)/(d\tau/dn) = n\,\Phi'(n)/(3\,\tau)$, where $\Phi(n)$ is the volume fraction of material with molecular weight greater than n and $\tau(n) \sim n^3$ is the reptation time.

The assumed rate of decrease in $\Phi(t)$ is to be compared to the maximum possible rate at which the tube can dilate by constraint-release Rouse motion. The tube diameter $a(t)$ on a time scale t can be no larger than the radius of gyration of a segment able to relax by constraint-release Rouse motion on the time scale t. Since the Rouse time of a segment grows as chain mass squared, and the square radius of gyration goes as chain mass, we have $t \sim a^4(t)$.

The naive scaling $G(\Phi) \sim \Phi^2$ is equivalent to the entanglement length scaling as $N_e(\Phi) \sim 1/\Phi$, so the tube diameter scales as $a^2(\Phi) \sim 1/\Phi$. Here Φ is the "effective entanglement concentration", which corresponds via scaling to the diameter up to which the star arm's tube has been able to explore so far. Hence we have $\Phi(t) \sim t^{-1/2}$, which leads to $d\Phi(t)/dt = -\Phi/(2\tau)$ for the fastest rate of decrease of the entangled volume fraction by constraint-release Rouse motion.

Comparing these two estimates of $d\Phi/dt$ leads directly to the validity criteria previously derived for dynamic dilution of star arms and for double reptation of polydisperse linear polymers,

$$(15/8)(N_a/N_e)s\Phi(s)^2 > 1 \tag{10}$$

$$n\Phi'(n)/\Phi(n) > -3/2 \tag{11}$$

Evidently, dynamic dilution (or double reptation) will fail if the dilution is too abrupt, i.e., if too large a volume fraction of material relaxes at once. In such a case, constraint-release Rouse motion will not be able to keep up with the assumed dilution rate under dynamic dilution. In the extreme case, consider a single star in a linear matrix; at τ_d, according to dynamic dilution, the entanglement length jumps to infinity, the entangled fraction jumps to zero, and the barrier for star arm retraction vanishes. So the relaxation time of the remaining unrelaxed material (the star) is certainly shorter than the constraint-release Rouse time of the star arms, and dynamic dilution fails.

III. Constraint-Release Regime: $\tau_D < t < \tau_C$

Consider now the star−linear blend, for which dynamic dilution fails at the reptation time scale τ_d of the linear chains. When dynamic dilution fails, we adopt a complementary picture of stress relaxation. In this picture, the tubes of entangled chains undergo constraint-release Rouse motion, and stress is relaxed as the tubes are able to make progressively larger excursions. The regime ends when the tube has explored the "supertube"[7] defined by other remaining entangled segments.

Such a picture emerged naturally from experiments on star polybutadienes dilutely dispersed in a linear polybutadiene melt.[15] In those experiments the terminal zone was dominated by a frequency dependence of the dynamic modulus of $\omega^{1/4}$ up to a longest relaxation time. The spectra were consistent with a local hopping rate of entanglements on the star arms that were of the same order of magnitude as the reptation time of the linear chains. Some difference in these magnitudes were observed for the longest linear chains, the hopping rate consistent with a dependence on linear chain molecular weight M_l of $M_l^{2.4}$ rather than M_l^3. This has been attributed to nonindependent release of local entanglements.[16−18] In the following we take the local hopping rate for the Rouse tube to be τ_d, as departures due to cooperative constraint-release are expected to be small for the molecular weight of linear chains examined here.

In other words, we assume in this Rouse regime that the effective entangled volume fraction (corresponding to the tube diameter explored on a given time scale) is given by the scaling result of the previous section,

$$\Phi(t) = \Phi(\tau_d)(\tau_d/t)^{1/2} \tag{12}$$

where τ_d is the time at which dynamic dilution fails. (The entangled volume fraction $\Phi(\tau_d)$ consists of those

portions of the linear chains and star arms not relaxed by retraction before τ_d and will be computed in section VI.)

When dynamic dilution fails, the entangled volume fraction $\Phi(t)$ (which corresponds to the diameter the star arm has explored) is not the same as the unrelaxed volume fraction $\Psi(t)$ (the fraction of material not yet relaxed by reptation or retraction). In such a case, the time-dependent modulus $G(t)$ is given by

$$G(t) = G_0\Psi(t)\,\Phi(t)^{\alpha} \tag{13}$$

where $\alpha = 1$ corresponds to the naive scaling for dilution, and $\alpha = 4/3$ to the Colby−Rubinstein scaling.

The factor of $\Psi(t)$ represents the fraction of material still storing stress, and the factor $\Phi(t)^{\alpha}$ the effect of the constraint-release Rouse motion on the diameter explored by a star arm. If $\alpha = 1$ and $\Psi(t)$ remains roughly constant (no retraction during the Rouse regime, to be discussed below), the stress falls during this regime as $t^{-1/2}$, which is the simple Rouse scaling.

For a star−linear blend after τ_d, the unrelaxed volume fraction is $\Psi(t > \tau_d) = \phi_s(1 - s_d)$. The factor of $(1 - s_d)$ arises because only a portion $1 - s_d$ of the star arms are storing stress after τ_d (here s_d is such that $\tau(s_d) = \tau_d$). The time-dependent modulus $G(t)$ is then (for $\alpha = 1$)

$$G(t) = G_0\phi_s(1 - s_d)\Phi(t) \tag{14}$$

with $\Phi(t)$ given by eq 12.

The constraint-release Rouse regime ends when the entangled volume fraction $\Phi(t)$ becomes equal to the unrelaxed volume fraction $\phi_s(1 - s_d)$, at which point dynamic dilution is recovered. This occurs at a time τ_C given by

$$\tau_C = \tau_d\left(\frac{\Phi(\tau_d)}{\phi_s(1 - s_d)}\right)^2 \tag{15}$$

Possible Refinements. We have side stepped two thorny issues with this simple description, namely (1) the effect of the volume fraction of linear chains on the rate of constraint-release Rouse motion and (2) the possibility of arm retraction during the Rouse regime itself. We address those questions briefly now, and in more detail in the Appendix.

Mobile Fraction. Somehow, the rate of constraint-release Rouse motion must depend on the volume fraction of linear chains; smaller ϕ_l should mean slower exploration of the supertube by the star arms. The scaling law of eq 12 has no place for dependence on ϕ_l. Therefore, what seems likely is that a more refined expression for $\Phi(t)$ would cross over from $\Phi(\tau_d)$ to eq 12, with a slower crossover for smaller ϕ_l.

On the other hand, constraints can also be released by whatever portion of star arm is relaxed before the time scale τ_d, which can be a sizable volume fraction if τ_d falls in the middle of the range of the star relaxation spectrum. So even if ϕ_l is small, the "mobile fraction" releasing constraints is finite. And, of course, if ϕ_l is small, the duration of the Rouse regime is short, because the supertube to be explored is not much larger than the tube on time scale τ_d.

Therefore, the mobile fraction does not actually vary over much of a range, and so accounting for this effect is probably not very significant.

Retraction during Rouse Regime. We may ask, to what extent can arm retraction go on happening during the constraint-release Rouse regime? More specifically, what should be the tube diameter that pertains to such retractions? At a minimum, it seems plausible that the star arms should be able to go on retracting in a tube of diameter $a(\tau_d)$, which is to say with an apparent entanglement fraction of $\Phi(\tau_d)$. The unrelaxed volume fraction $\Psi(t)$ would decrease with time from its initial value $\Psi(\tau_d) = \phi_s(1 - s_d)$. The end of the Rouse regime would be delayed, since dynamic dilution would be recovered when $\Phi(t) = \Psi(t)$ rather than when $\Phi(t) = \Psi(\tau_d)$.

We might be tempted to say more, that the star arms ought to be able to retract within a tube of the diameter explored by the star arm on the time scale t, which is to say an effective entanglement fraction $\Phi(t)$. We could, in other words, go on solving the Ball−McLeish equation right through the constraint-release Rouse regime, with the entangled volume fraction given by eq 12. The unrelaxed volume fraction $\Psi(t)$ would decrease more strongly with time, because of the reduced barrier to retraction imposed by the dilating tube. Also, the end of the Rouse regime would be even more delayed, to the point that for sufficiently small $\phi_s < 0.4$, $\Phi(t)$ never catches up with $\Psi(t)$, and dynamic dilution is never recovered.

In fact, we have tried calculations of this sort, and they do not give good agreement with published data; the contributions of the stars to the stress are increasingly too little as ϕ_s is reduced, presumably because retraction in the widening tube is not in fact accessible to the star arm, despite our imagining such a process.

So why is the retracting star arm unable to take advantage of the widest available tube on time scales in the Rouse regime? We believe the answer lies in the separation of time scales and in the nature of the arm retraction process.

In general, the two questions "what is the largest tube diameter $a(\tau)$ explored by a chain on time scale τ?" and "what is the largest tube diameter in which the chain can create unentangled loops on time scale τ?" do not yield the same answer when the tube is dilating. For the first requires merely that the mean square transverse diffusion of a monomer on the chain $\langle r^2(\tau)\rangle$ be of order the tube diameter and so sets $a^2(\tau) = \langle r^2(\tau)\rangle$. The effective entanglement molecular weight for this transverse exploration can be defined on time scale τ by $a^2(\tau) = N_e(\tau)b^2$.

However, the creation of an unentangled loop with the same effective tube diameter is a much *rarer* occurrence—yet is precisely the defining dynamical process for primitive path length *fluctuation*. It requires the *correlated* motion of a small number n (we might conjecture $n \geq 3$) of effective entanglement segments on that time scale $N_e(\tau)$ (see Figure 3). The constraint-release Rouse time for such a correlated conformation is just $\tau_{loop} \approx n^2\tau$. Thus τ_{loop} is typically 1 order of magnitude longer than τ, even for the smallest possible unentangled loop that is effectively constrained by the tube diameter $a(\tau)$.

This argument explains why the motion during the constraint-release Rouse regime is not accompanied by path length fluctuations (arm retraction events) that radically increase the relaxation rate above that of a rescaled Rouse polymer. Of course it also explains a more familiar but unquestioned phenomenon—the un-

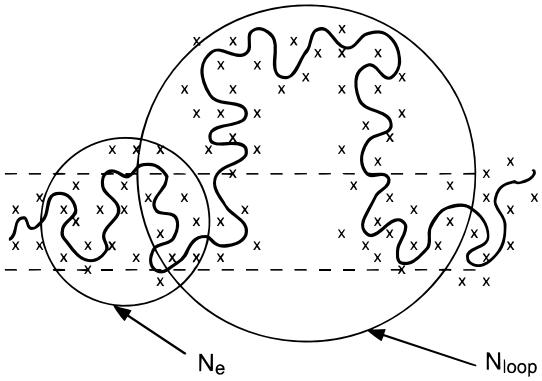

Figure 3. A small unentangled loop requires correlated motion of some small number n ($n \geq 3$, e.g.) entanglement segments. The dashed lines represent the tube on the current time scale τ, the x's other entangling chains that may release constraints.

importance of large path length fluctuations in a star arm before the Rouse time of an entanglement τ_e. The drama here is identical but acted out by the original chain in the smallest tube defined by the true plateau modulus. Typically, many attempts at expanding beyond the tube wall by a section of chain are required before the unlikely configurations called unentangled loops begin to occur.

Fortunately, this rather strong criterion for the physical validity of dynamic dilution does not upset our conclusion there: the correct tube diameter is indeed the one set by dilution of all unrelaxed material, when star-arm fluctuation is the only process active on time scale τ. In this case the constraint-release disentanglement events occur not just with a single rate (the inverse reptation time during the Rouse regime considered above) but with a continuous distribution of rates (coming from disentanglement by fluctuation of all portions of neighboring star arm faster than τ) most of which are exponentially faster than τ.

The tube expansion in this case is so slow that the increased number of attempts by a renormalized chain at traversing the tube wall required to form an unentangled loop (over and above the time taken just to reach it) does not alter the effective tube diameter for retraction. We can sharpen this conclusion by calculating the time taken to form an unentangled loop of n effective entanglement segments as above, but in the case when the constraint-release hops occur on exponentially spread time scales (this is generically true at some midrange time scale in the retraction phase of entangled arms).

At time scale τ, the correct distribution $p(\tau'; \tau)$ of relaxation times τ' to use is

$$p_{star}(\tau';\tau) = \frac{1}{\tau' \ln(\tau/\tau_0)} \qquad \tau_0 \leq \tau' \leq \tau \tag{16}$$

where τ_0 is the fastest constraint-release event. This distribution function contrasts with the single hopping time during the Rouse regime of $p_{lin}(\tau') = \delta(\tau - \tau')$. The time taken to form an unentangled loop from the tube defined by expansion on time scale τ is then

$$\tau_{loop} \simeq n^2 \int_{\tau_0}^{\tau} p(\tau')\tau' \, d\tau' = \frac{n^2}{\ln(\tau_1/\tau_0)} \tag{17}$$

Because the two time scales τ and τ_1 are typically exponentially separated, the logarithmic denominator will typically be as large as or larger than the factor n^2 (n being a small $O(1)$ integer) that made the crucial difference in the case where linear polymers reptating were responsible for the constraint release. So the star arm is always able to create unentangled loops on the same scale, as the tube is able to be explored by integer.

The consequence of these results for our star−linear blend is that during the Rouse intermediate relaxation regime, contour length fluctuations of the remaining unrelaxed portions of the star arm are permitted, but only within the tube diameter, as it was at the reptation time of the linear chains. The relaxation due to this continued retraction is completely masked by the renormalized Rouse relaxation (which follows a $t^{-1/2}$ form), so the calculations that follow have ignored it. We shall see in section V that this simple approach gives excellent agreement with the data.

IV. Recovery of Dynamic Dilution: $\tau_C < t$

The constraint-release Rouse regime begins when constraint release is unable to keep up with the tube dilation implied by the dynamic dilution ansatz. Likewise, dynamic dilution is recovered when constraint release is once again able to keep up.

After the constraint-release Rouse regime ends, the entangled volume fraction is given by

$$\Phi(s > s_d) = \phi_s(1 - s) \tag{18}$$

Solving the Ball−McLeish equation eq 1 then gives an effective potential $U_{s>}(s)$

$$U_{s>}(s) = \nu n_a \phi_s(s^2 - {}^2/_3 s^3) \tag{19}$$

Note the appearance of ϕ_s in this effective potential; this leads ultimately to an approximately exponential dependence of the terminal time and hence the zero-shear viscosity on ϕ_s, as seen in the data.

The same formal expression eq 6 for the prefactor in terms of the effective potential can be used with eq 19 to obtain the prefactor beyond the Rouse regime, $p_{s>}(s)$.

To maintain continuity of the relaxation time across the end of the Rouse regime, we write the relaxation time $\tau_{s>}(s)$ in terms of the crossover time τ_C as

$$\tau_{s>}(s) = \tau_C p_{s>}(s)/p_{s>}(s_d) \exp[U_{s>}(s) - U_{s>}(s_d)] \tag{20}$$

which is evidently proportional to $p_{s>}(s) \exp[U_{s>}(s)]$ and equal to τ_C at $s = s_d$.

In principle, at some still later time, star−linear blends with $\phi_s > \phi_s^*$ will exhibit a final crossover from dynamic dilution to Rouse dilution, when a criterion analogous to eq 10 is met. This final crossover occurs even for pure star melts, as discussed in ref 1. The dynamic dilution theory for stress relaxation in star melts is accurate because this crossover occurs for values of $1 - s$ of order $O(\sqrt{N_e/N_a})$, so that the remaining time-dependent modulus $G(t)$ not described by dynamic dilution is small. In fact, when this final crossover occurs, the remaining unrelaxed star arm segment is of order 1 diluted entanglement length,

which seems an appropriate place for the dynamic dilution story to come to rest.

V. Comparison to Data

To complete the theory of stress relaxation in star−linear blends, we require an expression for the stress relaxation function $G(t)$ in terms of the relaxation times we have computed. $G(t)$ (or equivalently $G(\omega) = i\omega F\mathcal{T}[G(t)]$, directly comparable to dynamic rheology data) is the sum of several contributions, from the star and linear polymers each before and after τ_d. The full expression for $G(\omega)$ is

$$G(\omega)/G_0 = 2\phi_s \int_0^{s_d} ds\ \Phi_<(s)\frac{i\omega\tau_{s<}(s)}{1 - i\omega\tau_{s<}(s)} + 2\phi_l \int_0^{s'_d} ds'\ \Phi_<(s')\frac{i\omega\tau_l(s')}{1 - i\omega\tau_l(s')} + \phi_s \int_{\tau_d}^{\tau_C} d\tau\ \Phi(\tau)/(2\tau)\frac{i\omega\tau}{1 - i\omega\tau} + 2\phi_s \int_{s_d}^{1} ds\ \Phi_>(s)\frac{i\omega\tau_{s>}(s)}{1 - i\omega\tau_{s>}(s)} + \Phi_d(\Phi_d - \phi_s(1 - s_d))\frac{i\omega\tau_d}{1 - i\omega\tau_d} \quad (21)$$

In the above, the entangled volume fraction $\Phi_<(s)$ and $\Phi_<(s')$ are obtained from eq 3 and $n_a s^2 = y = (n_l/2)s'^2$; $\Phi(t)$ comes from eq 12; and $\Phi_>(s)$ comes from eq 18.

The prefactors in each of the terms are obtained by considering the time-dependent modulus $G(t)$ to be written as

$$G(t) = \int_0^\infty d\tau\ \frac{dG(\Phi(\tau))}{d\tau}\exp[-t/\tau] = -2\int ds\ \Phi(\tau(s))\frac{d\Phi(s)}{ds}\exp[-t/\tau(s)] \quad (22)$$

The first two terms in eq 21 correspond to arm retraction of stars and contour-length fluctuations of linears before τ_d. The third term accounts for stress relaxed during the Rouse regime; the fourth term comes from star arm retraction after τ_C. The final term is the stress lost by reptation of the linear chains; the prefactor corresponds to an "instantaneous" drop at τ_d from $G(t) = G_0\Phi_d^2$ (end of dynamic dilution) to $G(t) = G_0\Phi_d\Psi(\tau_d)$ (beginning of Rouse regime), corresponding to the removal of the linear chains from the unrelaxed volume fraction. These prefactors do lead to a properly normalized time-dependent modulus, $G(t = 0)/G_0 = 1$.

The first test of the theoretical expressions for $G(\omega)$ is the terminal region; namely, for reasonable values of N_l and N_a, do we reproduce the approximately exponential dependence on ϕ_s of the zero-shear viscosity η_0? The explicit appearance of ϕ_s in eq 19, which determines the exponent for the terminal time, gives us reason to be optimistic. The results for $N_l/N_e = 58$ and $N_a/N_e = 18.6$ are shown in Figure 4. The computed values of the viscosity relative to the linear melt $\eta_0(\phi_s)/\eta_0(0)$ are within 10% at the experimental volume fractions $\phi_s = 0.2, 0.5, 0.75, 1$.

We may also compare the shape of the theoretical $G''(\omega)$ to the data, as shown in Figures 5 and 6. Of course, we know that the star melt is well described by the limit $\phi_s \rightarrow 1$ of this theory, with the proviso that we expect to

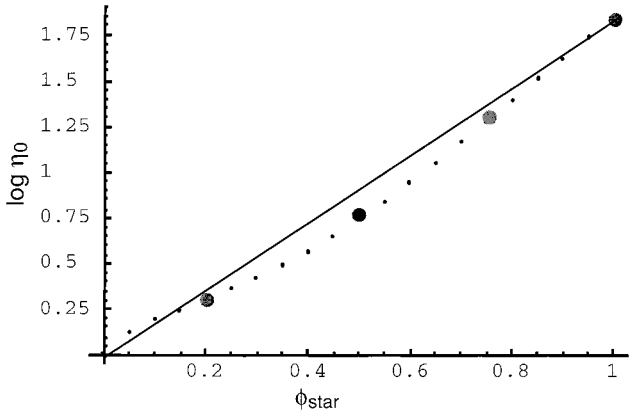

Figure 4. Semilog plot of zero-shear viscosity relative to the linear melt: experiments of ref 8 (large dots); exponential dependence (solid line); theory (small dots).

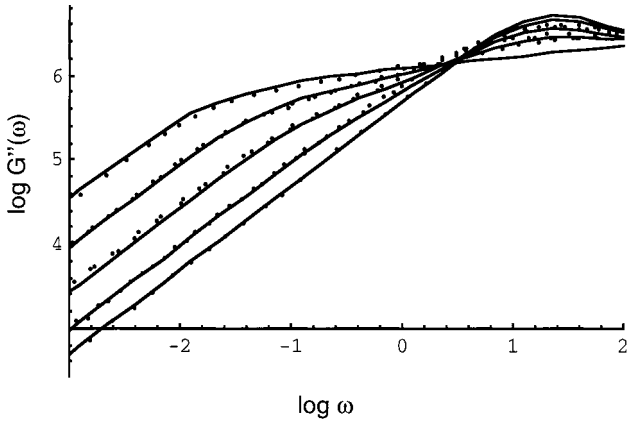

Figure 5. log−log plots of theoretical $G''(\omega)$ for $\phi_s = 0$, 0.2, 0.5, 0.75, 1, together with the Figure 1 data of ref 8.

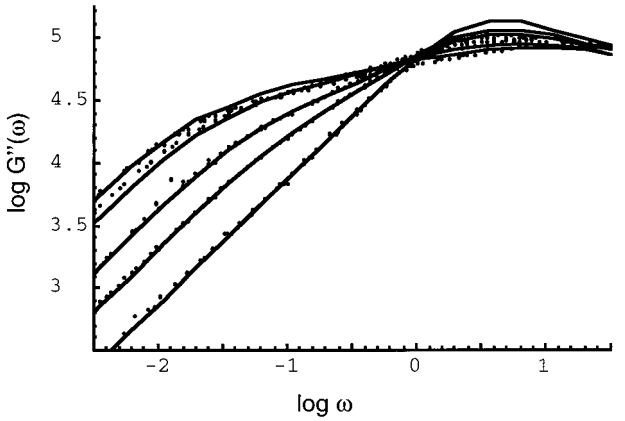

Figure 6. log−log plots of theoretical $G''(\omega)$ for $\phi_s = 0$, 0.4, 0.65, 0.9, 1, together with data of Figure 2.

take a slightly too small value of N_a/N_e to fit the width of the relaxation spectrum because of our use of $G(\Phi) \propto \Phi^2$ (rather than $\propto\Phi^{7/3}$). The values of N_l/N_e and N_a/N_e used here are $N_l/N_e = 58$ and $N_a/N_e = 18.6$ for the polybutadiene data; $N_l/N_e = 25$ and $N_a/N_e = 13.7$ for the polyisoprene data. The value of N_a/N_e for the polybutadiene data is smaller than the experimental value from GPC [$N_a/N_e = 23.1$, taking $N_e = 1815$] by about the expected amount from previous work.[1] (However, the value of N_a/N_e for the polyisoprene data is close to the experimental value [$N_a/N_e = 13$, taking $N_e = 5429$], which, paradoxically, is a slight cause for concern—or may possibly be the result of experimental error in determining N_a.)

Indeed, Figures 5 and 6 are in very good agreement with the data of refs 8 and our PI star−linear blend data for each star volume fraction, with our having adjusted only the modulus and time scales and taken a too small value of N_a/N_e as described above. In particular, the width and general shape of the spectrum are correct, and the loss peak associated with the linear chains appears in the right place and with the right magnitude. The dependence on the star volume fraction ϕ_s is within 10% of the data, as the viscosity increases from $\phi_s = 0$ (linear melt) to $\phi_s = 1$ (star melt) by a factor of about 70 for the data of ref 8 and by a factor of about 21 for our PI star−linear blends.

VI. Conclusions

The rheology of star polymer melts has been quantitatively understood in terms of the concepts of arm retraction and dynamic dilution, the latter being the idea that entanglements of a slow-relaxing segment with faster-relaxing segments are dynamically irrelevant. Dynamic dilution can be shown to be an approximation that works well when the time scales of the relaxing species in question are sufficiently separated, by appealing to a more precise description in terms of constraint-release Rouse motion.

In constraint-release Rouse motion, slowly-relaxing segments are permitted to move transverse to their confining tubes by the passage of an entangling chain end past an entanglement with the slowly-relaxing chain. Dynamic dilution works well as a description of star polymer melts, for two reasons. (1) There is a wide spectrum of time scales for relaxation of various portions of the star arm, because the arm retraction time is an exponential function of the fractional distance along the chain to be relaxed. (2) The spectrum of relaxation times is continuous, so that only a small fraction of material is relaxed on any given time scale. Thus, the remaining unrelaxed chain segments are able to explore their dilating tubes (dilated by the removal of faster-relaxing material) by constraint-release Rouse motion, more quickly than the tubes go on dilating.

Blends of monodisperse linear and symmetric star polymers turn out to invalidate the straightforward application of the ideas of arm retraction and dynamic dilution. This is because at the reptation time of the linear chains, a finite fraction of material would be regarded under dynamic dilution as suddenly unentangled, and the tube confining the remaining entangled segments (a portion of the star arms) would be suddenly dilated. In fact, the star arms can only explore the newly dilated tube as they are permitted to do so by constraint-release Rouse motion.

We have extended the theory of stress relaxation in star polymers to star−linear blends by taking explicit account of the constraint-release Rouse regime, which commences at the reptation time τ_d of the linear chains. During this regime, the entangled star arms relax stress essentially as Rouse chains (or their tubes may be regarded as undergoing Rouse motion), with a local hopping time of τ_d and a hopping distance of the dilated tube diameter on the time scale τ_d. In our simple picture, the dynamic dilution description is recovered when the star arms have explored via this Rouse motion their dilated tubes. In the limit of dilute stars, the entire stress relaxation after τ_d is described by this constraint-release Rouse motion.

Dynamical rheology data on star−linear blends as a function of star volume fraction constitutes a stringent test of our theory, which like our previous theory for star melts, contains only parameters directly accessible from experiment on linear chains (the entanglement length, the monomeric friction factor, the plateau modulus). Because the star−linear data contain pure stars and pure linears as end points, our parameters may be determined by comparison of the theory to these limits. The characteristic variation of the dynamic modulus $G(\omega)$ as the star volume fraction ϕ_s is varied is then predicted by the theory with no remaining parameters whatsoever. Even the variation of the zero-shear viscosity η_0 with ϕ_s is nontrivial, being far from a linear interpolation between the two limits; our theory reproduces not only this but also the entire shape of $G(\omega)$ for different ϕ_s, with fidelity to the data.

The concept of a constraint-release Rouse regime is general, in that such a regime must takeover whenever the dynamic dilution assumption implies that the tube diameter dilates faster than it possibly can by constraint-release Rouse motion. In fact, this unified notion leads directly to the criteria for validity of our previous theory of star melts, and of the double reptation theory; because, as has been shown previously, the double reptation theory for polydisperse linear chains depends on separation of time scales and removal of relaxed material from the entanglement network, just as dynamic dilution does.

Continuous polydispersity helps to preserve the conditions under which dynamic dilution or double reptation are valid. For example, consider a blend of monodisperse stars with commercially polydisperse linear chains. For such polydisperse linear chains, double reptation is typically a valid approximation; thus, no constraint-release Rouse regime need be invoked for the blend with stars, because the linear chains are removed from the entanglement network sufficiently smoothly that constraint-release can keep up with tube dilation. It would be of interest to test this idea experimentally, which we leave to future work.

Acknowledgment. We thank Bill Graessley, Dave Lohse, and Mike Rubinstein for many enjoyable discussions.

VII. Appendix A: Experimental Details

Benzene was distilled from sodium−potassium alloy onto solvent-free *n*-butyllithium and allowed to stand for several hours before distilling into the reactor. Methyltrichlorosilane was purified by distillation on the vacuum line and disolved in benzene. *sec*-Butyllithium was distilled under high vacuum onto a coldfinger in a short path length apparatus and dissolved in benzene. The concentrations of the solutions of $MeSiCl_3$ and *s*-BuLi were determined by hydrolysis and titration, and appropriate quantities were ampulized. Triethylamine was stored over sodium−potassium alloy. Isoprene was treated with dibutylmagnesium for at least 12 h then distilled on to *n*-BuLi and kept at −10 °C for 1 h before distilling into the reactor. Polymerization of the isoprene was initiated by benzene by *s*-BuLi and was allowed to proceed for 24 h to ensure complete reaction, and the chains were then capped by the addition of some 5 units of butadiene. Triethylamine (ca. 10 vol %) was added together with $MeSiCl_3$ in an amount such that there was a ratio of living polymer:$MeSiCl_3 = 3.1:1$, and reaction was allowed to continue for several days before methanol was added to terminate the small excess of

living polymer. The star polymers were purified by fractional precipitation from 1% solutions in toluene by the addition of methanol. In the case of the linear polymers no cross-linking, butadiene end-capping, or fractionation was necessary. Methanol termination was sufficient to provide a monodisperse sample. SEC was used to monitor the progress of the fractionation in the case of the star polymers and to determine the molecular weights in each case.

Rheological experiments were made on a Rheometrics RDAII rheometer in oscillatory mode. Frequency sweeps from 10^{-2} to 10^{2} rad·s^{-1} at temperatures from 25 to 120 °C were time−temperature superposed using WLF parameters for polyisoprene. Strains were everywhere within the regime of linear response.

VIII. Appendix B: Mobile Fraction Revisited

In the above, we have not considered the effect of the fraction of material able to release constraints on the rate of constraint-release. In the blend of monodisperse stars and linear chains, the "mobile fraction" of material able to release constraints on the time scale τ_d might be approximated by ϕ_l. More precisely, portions of star arms able to retract more quickly than a given time scale should somehow also contribute to the constraint-release tube motion; the mobile fraction ϕ_l might be better estimated as $\phi_l + s(\tau_d)\phi_s$.

We need some general way to include the contributions of species with different relaxation times to the constraint-release process. It is not obvious how to do this; for instance, consider a single very long chain in a polydisperse mixture of shorter but entangled chains. On time scales long compared to the short-chain reptation times (but short compared to the reptation time of the long chain), the long chain undergoes constraint-release Rouse motion. What is the appropriate friction coefficient for the entanglement segments of the long chain?

We might (1) average the hopping times of the shorter chains, so that a small population of sluggish entangling chains can slow the long chain or (2) average the hopping rates of the shorter chains, so that a small population of fast entangling chains can speed up the long chain. The first alternative might be called a "quenched" average, corresponding to a situation in which the segments of the long chain cannot move until the particular entangling chains around it have moved. The second alternative corresponds to an "annealed" average, since averaging the hopping rates amounts to saying that if a long-chain segment is entangled by a sluggish short chain, it will at some later time be entangled by a faster short chain.

There are other possible hypotheses. The problem of a chain exploring a dilated tube is more analogous to an colloidal particle in a high-density suspension "exploring its cage", than to the long-time diffusion coefficient of such a particle. A sensible ansatz intermediate between the "quenched" and "annealed" hypotheses might be that all species relaxing faster than t are able to relax constraints at time t, with a hopping distance $a(t)$ and a hopping time t. This limits the speeding-up effect of faster-relaxing species present in the annealed ansatz, for which a small population of chains with τ approaching zero would lead to a divergent hopping rate. On the other hand, the quenched ansatz leads to a vanishing hopping rate if some species have infinite relaxation times, which is likewise avoided in the intermediate ansatz.

For monodisperse star−linear blends, it turns out that ignoring this issue altogether as we have done gives an excellent representation of the rheological data. It would be interesting to study this situation theoretically and experimentally in blends of monodisperse stars and intentionally polydisperse linear chains.

References and Notes

(1) Milner, S. T.; McLeish, T. C. B. *Macromolecules* **1997**, *30*, 2159.
(2) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, U.K., 1986.
(3) Pearson, D. S.; Helfand, E. *Macromolecules* **1984**, *17*, 888.
(4) Ball, R. C.; McLeish, T. C. B. *Macromolecules* **1989**, *22*, 1911.
(5) McLeish, T. C. B. *Macromolecules* **1988**, *21*, 1062. McLeish, T. C. B. McLeish, *Europhys. Lett.* **1988**, *6*, 511. McLeish, T. C. B.; O'Connor, K. P. *Makromol. Chem. Macromol. Symp.* **1992**, *56*, 127.
(6) Milner, S. T.; McLeish, T. C. B. *Macromolecules* **1998**, *31*, 7479.
(7) Viovy, J. L.; Rubinstein, M.; Colby, R. H. *Macromolecules* **1991**, *24*, 3587.
(8) Struglinski, M. J.; Graessley, W. W.; Fetters, L. J. *Macromolecules* **1988**, *21*, 783.
(9) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, *27*, 4639.
(10) Milner, S. T.; McLeish, T. C. B. *Phys. Rev. Lett.* **1998**, *81*, 725.
(11) Adam, M.; Delsanti, M. *J. Phys. Fr.* **1984**, *45*, 1513.
(12) Colby, R. H.; Rubinstein, M. *Macromolecules* **1990**, *23*, 2753.
(13) Tuminello, W. H. *Polym. Eng. Sci.* **1986**, *26*, 1339. des Cloizeaux, J. *Europhys. Lett.* **1988**, *5*, 437. For a recent discussion see: Milner, S. T. *J. Rheol.* **1996**, *40*, 303.
(14) Milner, S. T. *J. Rheol.* **1996**, *40*, 303.
(15) Roovers, J. *Macromolecules* **1987**, *20*, 148.
(16) Montfort, J. R.; Marin, G.; Monge, P. *Macromolecules* **1986**, *19*, 1979.
(17) Klein, J. *Macromolecules* **1986**, *19*, 105.
(18) Rubinstein, M. In *Theoretical Challenges in the Dynamics of Complex Fluids*; McLeish, T. C. B., NATO ASI Series E, vol. 339; Ed.; Kluwer: Dordrecht, The Netherlands, 1997.

MA980481V