Self-Diffusion with Dynamic Dilution in Star Polymer Melts

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ABSTRACT: We use a recent theory of arm retraction in star polymer melts to calculate the self-diffusion constant of symmetric stars. Star polymers can only take a diffusive step when an arm fully retracts to the center. Because of the wide separation of relaxation times along the star arms, star polymers obey dynamic dilution, in which the effective entanglement network dilutes as portions of the star arms relax. This implies a picture of self-diffusion in which the junction point hops a distance of order the dilated tube diameter a_d associated with the diluted network, rather than a distance of order the original "skinny" tube diameter a_0 defined by the entanglement molecular weight. The difference is substantial, since a_d scales with arm length N as $a_0N^{2/7}$. However, comparing our results to self-diffusion data of Bartels et al.,[1] we find that the data are more consistent with diffusive hops of a length scale a_0 rather than a_d.

Introduction

The dynamics of entangled polymers have been very successfully described by tube models. Every chain is constrained to move in a tube of diameter a_0, formed by entanglements with the surrounding chains. Many of the diffusive and linear viscoelastic properties of linear polymer melts are well described by the reptation theory introduced by de Gennes[2] and developed by Doi and Edwards,[3] in which chains move by curvilinear diffusion along their tubes. However, for quantitative agreement with experiment, additional mechanisms beyond pure reptation must be considered. These include contour-length fluctuations of the chain in its tube and constraint-release effects, in which the motion of surrounding chains allows transverse motion of the tube.

These mechanisms are crucial for the dynamics of star polymer melts. Entangled star polymers cannot move by reptation due to their nonlinear architecture; there is no single tube along which all the arms can slither. The junction point can only take a diffusive step when an arm fully retracts down its tube to the center, adopting an unentangled configuration. The arm can then poke out in a new direction in the entanglement network, allowing the center point to take a diffusive hop. This mechanism for star diffusion was first proposed by de Gennes,[4] who considered the motion of a symmetric f-arm star in a fixed network. The probability for an arm of length N to retract fully to the junction point is exponentially unlikely, so that the longest relaxation time is exponential in the arm length. Subsequent theories calculated the terminal relaxation time as

$$\tau_t \propto N^{\beta} e^{\gamma' N} \tag{1}$$

with various values of β in the power law in the prefactor.[5−8] Each time an arm retracts fully, the junction point can hop some distance ξ, so the diffusion constant is

$$D \sim \frac{\xi^2}{\tau_t} \sim c(N) e^{-\gamma' N}$$

where in general the prefactor c has a power law dependence on N. The hopping distance ξ has generally been assumed to be of order the tube diameter a_0. Tracer diffusion data on stars in a high molecular weight matrix[9−11] and computer simulations of stars in fixed networks[12,13] have confirmed the exponential dependence of the diffusion constant on N. Further confirmation comes from measurements of the zero-shear viscosity, which also depends exponentially on N as one would expect from eq 1 since in general $\eta_0 \propto \tau_t$.

Early theories also predicted that D would decrease exponentially with the number of star arms f, since they assumed that a diffusive step of the junction point required all but two of the arms to retract simultaneously. However, experiments found a much weaker dependence on f,[14] consistent with the prediction that a star can diffuse by retracting one arm at a time.[15,16] An additional mechanism for the diffusion of stars first proposed by Klein[8] is that the junction point can diffuse down the tube of one of the arms, dragging the remaining arms behind it. This leads to $D \sim \exp[-\gamma'' N(f-2)]$ and so is expected to be a negligible effect for $f > 3$. This contribution to the diffusion constant should increase D somewhat for three-arm stars, and in fact measurements show that the viscosity of three-arm stars is lower than that of four-arm stars with the same arm length by about 20%, though the viscosity is independent of arm functionality for $f > 3$.[17] Diffusion of the star due to the center diffusing down one arm scales in the same way with N as the arm retraction mechanism, so we will neglect it in this paper.

In a melt of star polymers, constraint-release effects due to the motion of all the arms lead to significantly faster self-diffusion compared to tracer diffusion.[1,9,10] These effects are well described in star polymers by dynamic dilution.[18] The exponential dependence of the arm retraction time on N means that there is a wide separation of relaxation time scales along the star arm. The arm will retract short distances down the tube on a fast time scale but will only rarely retract a large fraction of the way toward the junction point. Consider a tube segment located a fractional distance s ($0 < s < 1$) from the free end of the arm. By the time $\tau(s)$ that the arm free end reaches this tube segment by arm retraction, segments located closer to the free end at $s' < s$ have long since relaxed; on this time scale the fractions of the star arms with $s' < s$ have all diffused out of their original tubes, releasing any constraints

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they were imposing on other arms. Therefore, these segments are no longer effective at entangling with the remaining unrelaxed fraction of the arm, which sees an entanglement network which is diluted by the removal of faster-moving, relaxed tube segments. The fraction of the remaining unrelaxed segments at time $\tau(s)$ is simply $\phi = 1 - s$. Thus, the distance between effective entanglements increases as the network dilutes, increasing the effective tube diameter a_d. This implies that once an arm has fully retracted, the junction point should hop a distance of order the dilated tube diameter a_d associated with the diluted network, rather than a distance of order the original "skinny" tube diameter a_0 defined by the entanglement molecular weight. As we will see below, a_d scales with arm length N as $a_0 N^{2/7}$, so that the difference between the two cases is significant. Previous theories of star self-diffusion with constraint-release effects assumed that the junction point hops in a skinny tube.[1,6] Investigations (which included dynamic dilution) of "pom-pom" polymers have assumed that the two branch points make diffusive hops in skinny tubes,[19] whereas a recent study of H-polymers assumed that the branch points hop in dilated tubes.[20]

In this paper, we use a recent theory of arm retraction in star polymers,[21] which successfully describes their distinctive rheology, to calculate the self-diffusion constant of symmetric star polymer melts. We explore the question of whether the junction point hops in a dilated or skinny tube and compare with self-diffusion data of Bartels et al.[1]

The Diffusion Constant

The self-diffusion constant due to arm retraction is simply given by the mean-square distance the junction point hops in an arm retraction time τ_{arm}:

$$D = \frac{(pa)^2}{6\tau_{arm}} \tag{2}$$

where a is either a dilated or skinny tube diameter. The mean hopping distance during the time τ_{arm} could be some fraction of a tube diameter, so in eq 2 the junction point is assumed to hop a distance pa, where p is a dimensionless constant of order unity. As discussed above, we will neglect any explicit dependence on the number of star arms. Thus, to calculate D, we need to know (1) the effective tube diameter when an arm has retracted to the center and (2) the arm retraction time in the diluting network. In the dynamic dilution picture one assumes that the entanglement network dilutes smoothly as arms retract, so that the entanglement length $N_e(\phi)$ depends on the volume fraction $\phi = 1 - s$ of unrelaxed chain segments as

$$N_e(\phi) = N_e/\phi^\alpha, \quad N_e(s) = N_e/(1-s)^\alpha \tag{3}$$

In this paper we use the Colby−Rubinstein value of $\alpha = 4/3$ for the concentration dependence of the entanglement network,[22] since the diluted network looks like a semidilute Θ solution (all the entangling chains are still uncorrelated random walks). The tube diameter ($a^2 \sim N_e b^2$) then scales as

$$a_d(\phi) = a_0/(1-s)^{\alpha/2} = a_0/(1-s)^{2/3} \tag{4}$$

where the tube diameter in the absence of dilution is defined by $a_0^2 = (4/5)N_e b^2$.

Clearly, as $s \to 1$ the tube diameter diverges, since the entanglement network is diluting to zero volume fraction. This divergence is due to a breakdown of the dynamic dilution ansatz. Dynamic dilution depends on a separation of time scales; in order for the tube diameter to smoothly dilate, a portion of the star arm at s must be able to fully explore the tube made larger by dilution before it relaxes by arm retraction at $\tau(s)$. This requirement on separation of time scales leads to a condition for the validity of dynamic dilution:[21]

$$\frac{15}{8\alpha}\frac{N}{N_e}s(1-s)^{1+\alpha} > 1 \tag{5}$$

Thus, dynamic dilution fails at small s, $s \sim O(N_e/N)$ when the arm retraction barrier is still less than $k_B T$, and also at small $1 - s \sim O(N_e/N)^{1/(1+\alpha)}$ when the tube diameter has diluted so much that the star arm takes a long time to explore it. As a retracting arm approaches the junction point, eventually dynamic dilution will fail, since by the time the arm free end is within an entanglement length N_e of the junction point the tube diameter will have diverged. Therefore, the junction point can hop no further than the size of the effective tube diameter at the point when dynamic dilution fails. The dilated tube diameter at this point is $a_d = a_0/(1 - s^*)^{\alpha/2}$, where s^* satisfies

$$\frac{15}{8\alpha}\frac{N}{N_e}s^*(1-s^*)^{\alpha+1} = 1 \tag{6}$$

The time scale $\tau(s)$ for a star arm to retract a fractional distance s from the arm free end was calculated in ref 21. There are two regimes in the arm retraction. For sufficiently large displacements s down the tube, the retraction is entropically unfavorable and can be described by an uphill diffusion of the arm free end in a potential. Pearson and Helfand calculated the free energy cost of these retractions for a star arm in a fixed network to be $U(s) = \nu(N/N_e)s^2$ (in units of $k_B T$), where the constant $\nu = 15/8$.[7] For large N/N_e the barrier is many times $k_B T$, so the arm retraction is activated and $\tau(s) \sim \exp[U(s)]$. In a melt, dynamic dilution leads to a renormalized effective potential for arm retraction through the Ball−McLeish equation[18]

$$\frac{\mathrm{d}}{\mathrm{d}s}\ln\tau(s) = \frac{\partial U}{\partial s}(s; N_e(s)) \equiv \frac{\mathrm{d}U_{eff}}{\mathrm{d}s}(s) \tag{7}$$

which with eq 3 gives

$$U_{eff}(s) = \frac{2\nu N}{N_e}\frac{1-(1-s)^{1+\alpha}[1+(1+\alpha)s]}{(1+\alpha)(2+\alpha)} \tag{8}$$

Solving a first-passage time problem to calculate the prefactor in $\tau(s) \sim \exp[U_{eff}(s)]$, the arm retraction time in the effective potential is[21]

$$\tau_a(s) = \tau_e\left(\frac{N}{N_e}\right)^{3/2}\left(\frac{\pi^5}{30}\right)^{1/2} \times \frac{\exp[U_{eff}(s)]}{s\left[(1-s)^{2\alpha} + \left(\left(\frac{N_e}{2\nu N}\right)(1+\alpha)\right)^{2\alpha/(\alpha+1)}\Gamma\left(\frac{1}{\alpha+1}\right)^{-2}\right]^{1/2}} \tag{9}$$

where τ_e is the Rouse time of an entanglement segment of length N_e. For small s the entropic barrier to retrac-

tion is less than k_BT, so the potential is unimportant and the arm free end diffuses freely by Rouse motion in the tube. The relaxation time $\tau_{early}(s)$ in the small s or early time regime is

$$\tau_{early}(s) = (225\pi^3/256)\tau_e s^4 (N/N_e)^4 \tag{10}$$

These two regimes can be combined into a single crossover function for $\tau(s)$ as[23]

$$\tau(s) = \frac{\tau_{early}(s)\,\exp[U_{eff}(s)]}{1 + \exp[U_{eff}(s)]\tau_{early}(s)/\tau_a(s)} \tag{11}$$

The relevant time for diffusion of the star is the time for an arm to retract fully to $s = 1$, which is given by the activated result of eq 9. The application of eq 11 (with the expression for the relaxation function $G(t)$; see eq 21) to stress relaxation in stars leads to excellent quantitative agreement with dynamic rheology data on star melts.[21,23]

We can now calculate the self-diffusion constant. If the junction point hops in a dilated tube, the self-diffusion constant is

$$D_d = \frac{p^2 a_d^{\,2}(s^*)}{6\tau_a(s{=}1)} = \frac{p^2 a_0^{\,2}}{6}\frac{1}{(1-s^*)^\alpha \tau_{arm}} \tag{12}$$

where $\tau_{arm} \equiv \tau_a(s{=}1)$. Alternatively, if the junction point makes a hop of order the skinny tube size a_0, we simply have

$$D_0 = \frac{p^2 a_0^{\,2}}{6}\frac{1}{\tau_{arm}} \tag{13}$$

Both these results are inversely proportional to τ_{arm} so they have the same exponential dependence on N/N_e, but the prefactors scale differently with N/N_e. From eq 9, the arm relaxation time scales as

$$\tau_{arm} \sim \left(\frac{N}{N_e}\right)^{3/2+\alpha/(1+\alpha)} \exp\left[\frac{2\nu}{(1+\alpha)(2+\alpha)}\frac{N}{N_e}\right] \tag{14}$$

Asymptotically for large N/N_e, dynamic dilution fails at

$$1 - s^* \sim \left(\frac{\alpha}{\nu}\frac{N}{N_e}\right)^{1/1+\alpha} \tag{15}$$

The dilated tube diameter at the failure of dynamic dilution then scales as

$$a_d \sim a_0\left(\frac{N}{N_e}\right)^{\alpha/(2(1+\alpha))} \sim a_0\left(\frac{N}{N_e}\right)^{2/7} \tag{16}$$

for $\alpha = {}^4/_3$. Thus, from eq 12 the self-diffusion constant for hopping in dilated tubes scales asymptotically as

$$D_d \sim \left(\frac{N}{N_e}\right)^{-3/2} \exp\left[-\frac{2\nu}{(1+\alpha)(2+\alpha)}\frac{N}{N_e}\right] \sim \left(\frac{N}{N_e}\right)^{-3/2} e^{-(27/56)N/N_e} \tag{17}$$

whereas from eq 13, the diffusion constant for hopping in skinny tubes scales asymptotically as

$$D_0 \sim \left(\frac{N}{N_e}\right)^{-3/2-\alpha/(1+\alpha)} \exp\left[-\frac{2\nu}{(1+\alpha)(2+\alpha)}\frac{N}{N_e}\right] \tag{18}$$

$$\sim \left(\frac{N}{N_e}\right)^{-29/14} e^{-(27/56)N/N_e} \tag{19}$$

where we have taken $\alpha = {}^4/_3$ in the second expressions. This difference in scaling in the prefactors is quite significant. We note that the value of the constant in the exponential factor $\exp(-\gamma N/N_e)$, $\gamma = 27/56 = 0.48$, also includes the effect of dynamic dilution through the arm retraction time, and thus is different than that predicted for stars in fixed networks.

The diffusion constant depends on three parameters: the entanglement length N_e, the "skinny" tube diameter given by $a_0^2 = (4/5)N_e b^2$, and the Rouse time for an entanglement segment $\tau_e = \zeta N_e^2 b^2/(3\pi^2 k_B T)$, which depends on the monomeric friction factor ζ. All of these parameters can in principle be calculated from the properties of linear chains; thus, the theory of star dynamics is parameter free. The entanglement length and the tube diameter have been well determined for many polymeric systems. The monomeric friction constants are known less precisely. A convenient way to remove the dependence on ζ and also the dominant exponential dependence on N is to consider the product of the diffusion constant with the zero-shear viscosity, $D\eta_0$. The zero-shear viscosity scales approximately as $\eta_0 \sim G_0\tau_{arm}$ where G_0 is the plateau modulus. The product $D\eta_0$ is independent of τ_e and hence of the monomeric friction factor ζ. Furthermore, the dominant exponential behavior in τ_{arm} cancels so that $D\eta_0$ is sensitive to the remaining power law behavior.

We can obtain the zero-shear viscosity more precisely from the theory for stress relaxation in stars. The viscosity is simply the integral over the stress relaxation function:

$$\eta_0 = \int_0^\infty G(t)\,dt \tag{20}$$

The stress relaxation is summed over the different arm segments s, which are assumed to relax exponentially on the time scale $\tau(s)$:[21]

$$G(t) = (1+\alpha)G_0\int_0^1 ds\,(1-s)^\alpha \exp[-t/\tau(s)] \tag{21}$$

The factor of $(1-s)^\alpha$ comes from dynamic dilution, since the modulus scales as $1/N_e(\phi(s))$. The viscosity η_0 is then given by

$$\eta_0 = (1+\alpha)G_0\int_0^1 ds\,(1-s)^\alpha \tau(s) \tag{22}$$

From this expression we see that η_0 will have the same exponential dependence on N as τ_{arm}, but the integral over s will introduce additional power law behavior in the prefactor. Since $\tau(s)$ depends exponentially on N and s, the major contribution to η_0 will come from late times and for s near one. Substituting the activated relaxation time τ_a from eq 9 into eq 22, we find

$$\eta_0 \sim \left(\frac{N}{N_e}\right)^{3/2}\int_0^1 ds \times \frac{[U_{eff}(s) + \alpha\ln(1-s)]}{s\left[(1-s)^{2\alpha} + \left(\left(\frac{N_e}{2\nu N}\right)(1+\alpha)\right)^{2\alpha/(\alpha+1)}\Gamma\left(\frac{1}{\alpha+1}\right)^{-2}\right]^{1/2}} \tag{23}$$

For large N/N_e, the factor in the exponential has a maximum at $s \approx 1 - \sqrt{\alpha N_e/2\nu N}$. Expanding to second order about the maximum and performing the resulting Gaussian integral in s, we find to leading order in N/N_e that

$$\eta_0 \sim \frac{N}{N_e} \exp\left[\frac{2\nu}{(1+\alpha)(2+\alpha)} \frac{N}{N_e}\right] \sim \frac{N}{N_e} e^{-(27/56)N/N_e} \tag{24}$$

This immediately leads us to the expected asymptotic scaling for the product $D\eta_0$ for the two cases:

$$D_d\eta_0 \sim \left(\frac{N}{N_e}\right)^{-1/2}, \quad \text{dilated tubes} \tag{25}$$

$$D_0\eta_0 \sim \left(\frac{N}{N_e}\right)^{-15/14}, \quad \text{skinny tubes} \tag{26}$$

for $\alpha = 4/3$. Note that from eqs 12, 13, and 22, $D\eta_0 = a_0^2 G_0 f(N/N_e)$ where f is a function of N/N_e only.

We compare our predictions for $D\eta_0$ with self-diffusion and viscosity data of Bartels et al.[1] for melts of hydrogenated polybutadiene (hPB) three-arm stars at 165 °C. To our knowledge, this is the only data set in the literature on *self*-diffusion (as opposed to tracer diffusion) of star polymers. The data range over relatively small values of M/M_e. The entanglement molecular weight for linear hPB is $M_e = 976$.[24] However, a recent extension of the star theory to materials that display thermorheological complexity, such as hPB, found from a comparison of the predicted relaxation spectra and data on hPB that the apparent entanglement molecular weight of hPB stars is larger than that corresponding to linear polymers.[25] This discrepancy between the effective entanglement molecular weights of hPB stars and linear chains is unresolved, although it does not occur in materials which obey time−temperature superposition (where the theory is a good fit to star rheology data using M_e values from measurements on linear chains). The discrepancy does occur for the data of ref 1; comparing the M dependence of the theoretical result for the viscosity (from eq 22) to the data, we find that the data are only consistent with an entanglement molecular weight larger than the value for linear hPB, with the best fit in the range $1300 < M_e < 1450$. In the rest of the paper we take the effective entanglement molecular weight, as defined by the fit to the viscosity, to be $M_e = 1375$, so that the data ranges from $M/M_e = 5.6$ to $M/M_e = 24$ as shown in Figure 1. The fit in Figure 1 is quite good, but the uncertainty about the appropriate value of M_e precludes quantitative comparison of our predictions for D_d and D_0 with the data and in particular of the value of the constant γ in the exponential.

We can make a quantitative comparison with the product $D\eta_0$ since the exponents in eqs 25 and 26 are independent of M_e. Figure 2 shows the exact results for the products $D_d\eta_0$ and $D_0\eta_0$ with $p = 1$, plotted log−log as a function of M/M_e (again with $M_e = 1375$). The viscosity is calculated by numerically integrating eq 22, using the full expression for the relaxation time $\tau(s)$ from eq 11. The dilated tube diameter a_d is found by numerically solving eq 6 for s*. Dynamic dilution fails entirely for $M/M_e \leq 6$, which is therefore the lower bound in Figure 2 for $D_d\eta_0$, although it has been found that the star theory for stress relaxation with dynamic dilution works well at least down to $M/M_e \approx 3$,[23] which we have taken as the lower bound for the calculation of $D_0\eta_0$. The thin dotted lines have slopes of −1/2 for $D_d\eta_0$ and −15/14 for $D_0\eta_0$. We see that there are deviations from the asymptotic scaling at small M/M_e, particularly in the case of the skinny tube expression. This is due mostly to a decrease in η_0 for small M/M_e which is more rapid than the asymptotic scaling.

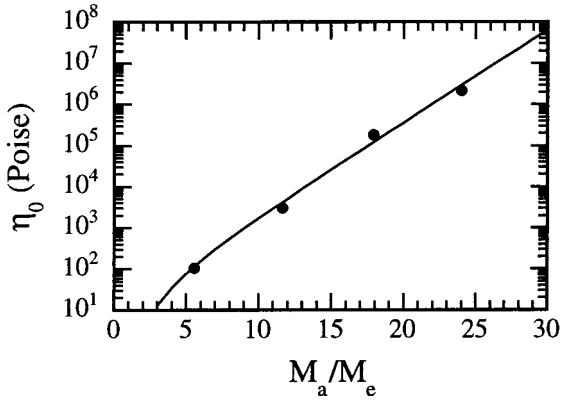

Figure 1. Viscosity data from Bartels et al. for 3-arm stars (circles) compared with the predicted viscosity (solid curve), with the magnitude adjusted to fit the data. We have taken $M_e = 1375$.

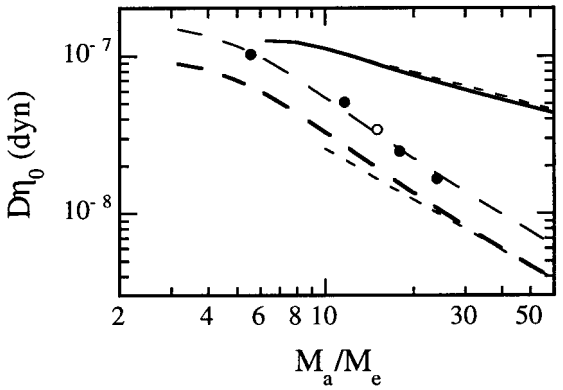

Figure 2. Data from Bartels et al. for 3-arm stars (circles) compared with the predicted results $D_d\eta_0$ for hopping in a dilated tube (thick solid curve) and $D_0\eta_0$ for hopping in a skinny tube (thick dashed curve). The corresponding dotted lines have slopes of −1/2 and −15/14, respectively. The open circle is from an unfractionated sample as explained in ref 1. The thin dashed curve corresponds to $D_0\eta_0$ with $p = 1.3$.

The magnitude of $D\eta_0$ is set by $a_0^2 G_0$. The plateau modulus for hPB is $G_0 = 2.21 \times 10^7$ dyn/cm^2, and the tube diameter has been measured by neutron spin echo to be $a_0 = 38.5$ Å, both at 140 °C.[24] The thick curves in Figure 2 show the predictions for $D_d\eta_0$ and $D_0\eta_0$ using these values. The slope of the data is clearly more consistent with the skinny tube M dependence of $D_0\eta_0 \sim M^{-15/14}$ than it is with the dilated tube M dependence of $D_0\eta_0 \sim M^{-1/2}$. The calculated magnitude of $D\eta_0$ is remarkably close to the data for both cases, especially considering that there are many uncertainties, including the value of p, the appropriate M_e for the stars, and the experimental uncertainty. Increasing the value of the unknown factor p in the hopping distance to $p = 1.3$ results in the thin dashed curve for $D_0\eta_0$ shown in Figure 2. This is a fairly modest change in the hopping distance of the junction point. Also, as discussed above, three-arm stars should be able to diffuse by the junction point moving down one tube, as well as by arm retraction, which we have not taken into account here. We anticipate that this extra mechanism

would increase D, although it should also decrease η_0 and should not change the N dependence of either, so it may not have much effect in Figure 2. In any case, the difference in M dependence between the two results clearly favors hops in skinny tubes as given by eq 13.

Conclusions

We have calculated the self-diffusion constant for symmetric stars, including the effects of dynamic dilution. These effects are critical for a quantitative understanding of the rheological properties of stars. Arm retraction occurs in a continuously diluting entanglement network, and so we would expect the junction point to make diffusive hops in this diluted network. Even in the absence of the retraction of its own arms, the junction point of a star should be able to make diffusive hops in a tube dilated due to the motion of the other star arms in the melt.

However, the slope of $D\eta_0$ for the available data is clearly inconsistent with hops in a dilated tube. Instead, the data seem consistent with the predictions for hops in skinny tubes. This seems to imply that our physical picture of dynamic dilution, while describing the relaxation of star melts, does not hold for the diffusive motion of the junction point. The experimental magnitude of the product $D\eta_0$ is consistent with what we expect from the simple scaling $D\eta_0 \sim a_0^2 G_0$, and the theory overlays the data if the hopping distance is increased to about $1^1/_2$ times the skinny tube diameter a_0. It would be worthwhile to do further self-diffusion measurements in another chemical system to compare with the theory. This would be particularly useful in a system that does not display thermorheological complexity for star polymers, such as polybutadiene or polyisoprene, to remove the uncertainty about the appropriate value of the entanglement molecular weight. Such a study would allow comparison with both the product $D\eta_0$ and with the self-diffusion constant itself, which we predict scales as $D_0 \sim (N/N_e)^{-29/14} \exp[-(27/56)N/N_e]$ for hops in skinny tubes.

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