Macromolecules **2000,** *33,* 5273−5277

Diffusion with Contour Length Fluctuations in Linear Polymer Melts

Amalie L. Frischknecht* and Scott T. Milner

ExxonMobil Research and Engineering Company, Annandale, New Jersey 08801

Received December 20, 1999; Revised Manuscript Received May 1, 2000

ABSTRACT: We have calculated the self-diffusion constant in monodisperse linear polymer melts using a recent analytical theory of stress relaxation that incorporates contour-length fluctuations as well as reptation. We find over a broad range of chain lengths N that $D \sim N^{-2.25}$ before crossing over to the asymptotic reptation result of $D \sim N^{-2}$. This result is in agreement with recent experiments and single-chain simulations and resolves a long-standing discrepancy between the scaling of the zero-shear viscosity and the diffusion constant.

The reptation theory of the dynamics of entangled linear polymers introduced by de Gennes[1] and developed by Doi and Edwards[2] is remarkably successful at explaining many of the rheological and diffusive properties of linear chains. However, there are several long-standing discrepancies between the predictions of reptation theory and what is observed experimentally.

First, reptation theory predicts that the reptation time τ_d and therefore the zero-shear viscosity η scale with chain length N as N^3, whereas experimentally for a wide variety of polymers $\tau_d \sim \eta \sim N^{3.4}$. Second, for frequencies above τ_d^{-1} the Doi−Edwards theory predicts that the dynamic loss modulus $G''(\omega) \sim \omega^{-1/2}$, while most experimental results are that $G''(\omega) \sim \omega^{-\alpha}$ with α between 0 and $^1/_4$.[3]

Finally, from the scaling of the terminal time τ_d, reptation theory predicts that the chain self-diffusion constant scales as

$$D \sim \frac{R^2}{\tau_d} \sim N^{-2} \tag{1}$$

where R^2 is the mean-square end-to-end length of the chain. Previously, many experimental results for melts supported this scaling, but measurements of D in concentrated solutions found exponents stronger than −2, generally $D \sim N^{-2.5}$.[4] This apparently different behavior in solutions and melts was puzzling, since in an entanglement picture of the dynamics one would expect the scaling to be the same for both. Also, since the same physics should be involved in the scaling of the viscosity and the diffusion constant, one would expect them to display deviations of the same magnitude from the reptation scaling.[5] Very recently the experimental situation has changed. New experimental data[6,7] on concentrated solutions and melts of hydrogenated polybutadiene (hPB) have found that in both cases $D \sim M^{-2.4}$. Furthermore, Lodge found in a careful reanalysis of previous experimental results for seven different polymers that overall the melt self-diffusion constant $D \sim M^{-2.28\pm0.05}$.[4] Thus, it seems that experimentally the scaling of the melt self-diffusion constant does differ from the reptation prediction.

It has been generally understood that the physical origin of the 3.4 scaling in the viscosity is a result of processes that relax stress faster than in the reptation model. In pure reptation, the primitive chain is assumed to have a fixed contour length as it executes one-dimensional diffusion along a tube representing the entanglements with other chains. Doi first pointed out that fluctuations in the contour length will enhance stress relaxation, since as the chain contracts and expands in the tube, the orientations of the end segments of the tube are forgotten.[8] He argued that the fraction of the tube that is relaxed by these fluctuations scales as $N^{-1/2}$. As N gets larger, the effect of the contour length fluctuations becomes less important so that the viscosity increases faster than the asymptotic reptation result and meets it from below.

Recently, an analytical theory of stress relaxation in f-arm star polymer melts[9] was extended to treat in detail the spectrum of contour length fluctuation modes in *linear* melts by treating a linear chain as a two-armed star.[10] It was found that the viscosity does indeed scale with $N^{3.4}$ up to a crossover to N^3 which occurs for about 200 entanglements per chain. The power law for the loss modulus above τ_d^{-1} was also found to be in agreement with experiment, with no adjustable parameters. This work thus resolves the first two discrepancies discussed above. Since contour length fluctuations decrease the disengagement time τ_d relative to the asymptotic reptation result, one might anticipate from eq 1 that they would also enhance the self-diffusion constant.

In this paper, we calculate the effect of contour length fluctuations on the self-diffusion constant in linear melts, adapting the theory of ref 9 for star polymers. Star polymers in entangled melts cannot move by reptation since there is no single tube along which all the arms can slither. Instead, stars change their conformations and thus relax stress by individual arms retracting some distance down their tubes toward the center and then poking out in a new direction, thus “forgetting” the orientation of the end of the tube.[11] Since this is entropically unfavorable, arm retraction is an activated process, with retraction times which depend exponentially on arm length and on the fractional distance retracted.

We can apply these ideas to linear melts because contour length fluctuations at the end of a linear chain are very similar to the motion of arm retraction in stars, so we can treat the linear chains as 2-arm stars. On time scales less than the reptation time, the chain free ends can retract some distance down the tube and poke out in new directions into the entanglement network, randomizing portions of the chain conformation near the ends. These arm retractions are eventually cut off by

10.1021/ma992123d CCC: $19.00

reptation; any original tube segments not visited in a time τ_d by one of the retracting ends will subsequently be relaxed by reptation. Thus, the only retractions that are relevant to linear chains are the fast ones occurring near the chain ends, so that it is reasonable to model them with the center of the chain fixed.

The time $\tau(s)$ for a star arm to retract a fractional distance s ($0 \leq s \leq 1$, where $s = 1$ corresponds to the midpoint of the chain) from its free end was calculated in ref 9 as part of the theory for star melts. There are two different regimes. For small displacements s the entropic barrier to retraction is less than k_BT so the chain ends are free to move along the tube. Motion in this regime is well described by the Rouse modes of a semiinfinite chain in a tube. Initially, the chain is unaware that it is finite, so the mean-square displacement of the chain free end along the tube $z^2(t)$ must be independent of arm length $N_a = N/2$ (N_a is the length of the star arm, which for the case of a linear polymer modeled as a two-arm star is $N_a = N/2$). At the Rouse time τ_R of the arm, $z^2(t)$ must be of order the arm end-to-end radius $R_a{}^2 = N_a b^2$, where b is the Kuhn step length. The Rouse time can be written as $\tau_R = \tau_e(N_a/N_e)^2$, where τ_e is the Rouse time of an entanglement segment of length N_e. Thus, for $z^2(t)$ to be independent of arm length N_a for $t < \tau_R$, it must scale as $z^2(t) \sim R_a{}^2(t/\tau_R)^{1/2}$. The fractional distance down the tube is $s = z/L_a$ where $L_a = R_a{}^2/a$ is the equilibrium contour length of the tube. The tube diameter a is related to the entanglement length N_e by $a^2 = {}^4/_5 N_e b^2$. Inverting the scaling relation to obtain the time $\tau_{\text{early}}(s)$ required for the free end to retract a fractional distance s down the tube, we find

$$\tau_{\text{early}}(s) = (225\pi^3/256)\tau_e s^4 (N_a/N_e)^4 \tag{2}$$

where the prefactor is fixed by an explicit Rouse calculation.[9] This early time result is valid up to approximately $s = s_d$ of order $(N_e/N_a)^{1/2}$.

For larger displacements $s > s_d$ the entropic barrier is greater than k_BT, and the retraction is described by the uphill diffusion of the arm free end in an effective potential $U_{\text{eff}}(s)$. The time scale for retractions in this regime is[9]

$$\tau_a(s) \approx \frac{L_a{}^2}{D_{\text{eff}}}\left(\frac{\pi}{2U''_{\text{eff}}(0)}\right)^{1/2} \frac{\exp[U_{\text{eff}}(s)]}{[U'(s)^2 + 2s^2|U''(1)|/\pi]^{1/2}} \tag{3}$$

(this is eq 21 of ref 9, with an extra factor of s^2 to prevent a spurious crossover for small s; we are assuming a dynamic dilution exponent of $\alpha = 1$). Here D_{eff} is the effective one-dimensional diffusion constant for the retracting arms, $D_{\text{eff}} = D_R$ (with the Rouse diffusion constant $D_R = k_BT/N_a\zeta$ and the Rouse time $\tau_R = \zeta N_a{}^2 b^2/(3\pi^2 k_BT) = \tau_e(N_a/N_e)$).[12] The overall retraction time can be described by a crossover function:[13]

$$\tau(s) = \frac{\tau_{\text{early}}(s)\exp[U_{\text{eff}}(s)]}{1 + \exp[U_{\text{eff}}(s)]\tau_{\text{early}}(s)/\tau_a(s)} \tag{4}$$

Retraction becomes very slow beyond s_d, and motion by reptation dominates. We define s_d explicitly as the value of s for which reptation becomes faster than arm retraction:

$$\tau_d \equiv \tau(s_d) \tag{5}$$

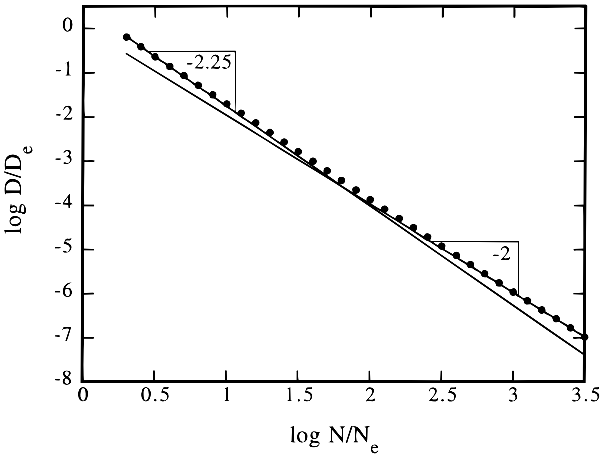

Figure 1. Predicted diffusion constant D/D_e as a function of chain length N/N_e (dots) has an effective exponent of about -2.25 below the crossover to the asymptotic reptation scaling.

Since tube segments within a distance s_d from the free ends relax by retraction faster than the reptation time scale, the distance any given chain segment has to diffuse reptatively along the tube to reach a relaxed part of the tube is shorter than the equilibrium contour length L by a factor of $1 - s_d$. This shortens the reptation time by a factor of $(1 - s_d)^2$, so that eq 5 becomes

$$\tau_d = (15/4)\tau_e(N/N_e)^3(1 - s_d)^2 \equiv \tau(s_d) \tag{6}$$

This then defines the reptation time τ_d including contour-length fluctuations and combined with eq 4 gives an implicit equation for s_d. (We use the full expression for $\tau(s)$ here, although the most important contribution for linear chains comes from $\tau_{\text{early}}(s)$.)

We can now calculate the self-diffusion constant in terms of s_d. In the reptation model, the diffusion constant is given by the mean-square distance the chain center of mass diffuses in a reptation time $\tau_{d,\text{rep}}$. Without contour length fluctuations this mean-square distance is simply the three-dimensional size of the chain, $R^2 = Nb^2 = La$. The contour-length fluctuations allow the ends of the chain to diffuse and be randomized before τ_d; during the now shorter reptation time τ_d the center of mass diffuses a mean-square distance of $La(1 - s_d) = R^2(1 - s_d)$. We therefore have

$$D_{\text{CLF}} \sim \frac{R^2(1 - s_d)}{\tau_d} = \frac{Nb^2}{(15/4)\tau_e(N/N_e)^3(1 - s_d)} \tag{7}$$

We define an "entanglement diffusion constant" $D_e = a^2/\tau_e$ and absorb all other numerical prefactors into D_e so that

$$D_{\text{CLF}} = D_e\left(\frac{N_e}{N}\right)^2 \frac{1}{1 - s_d} \tag{8}$$

Since $s_d \sim O(N_e/N)^{1/2}$, the corrections to the asymptotic reptation result give $D_{\text{CLF}} \sim N^{-2}[1 + O(N^{-1/2})]$, which increases the apparent power law of D. Note that the only parameters in the theory are N_e, τ_e, and the tube diameter a.

Figure 1 shows D_{CLF}/D_e from eq 8, plotted log−log vs N/N_e. We do not expect the theory to be valid below about $N/N_e \approx 2$, which gives a lower bound for all the theoretical curves in this paper. The effective exponent

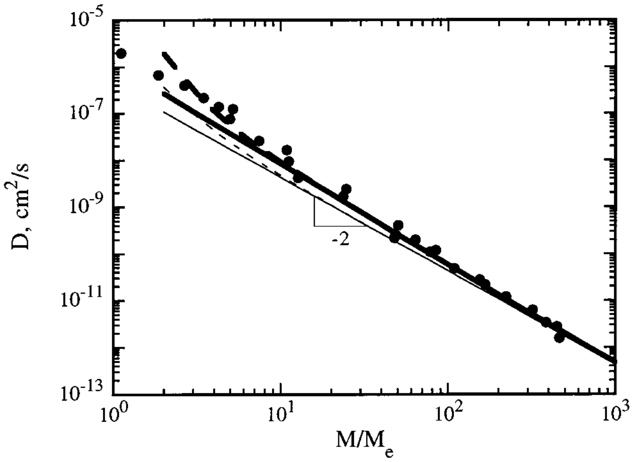

Figure 2. Predicted diffusion constant D_{CLF} (thick solid line) compared to self-diffusion data (dots) on hPB melts from ref 4. The long dashed line includes the contribution from constraint-release effects, $D_{CLF,CR}$, while the short dashed line is Graessley's result, D_G. The thin solid line has a slope of −2.

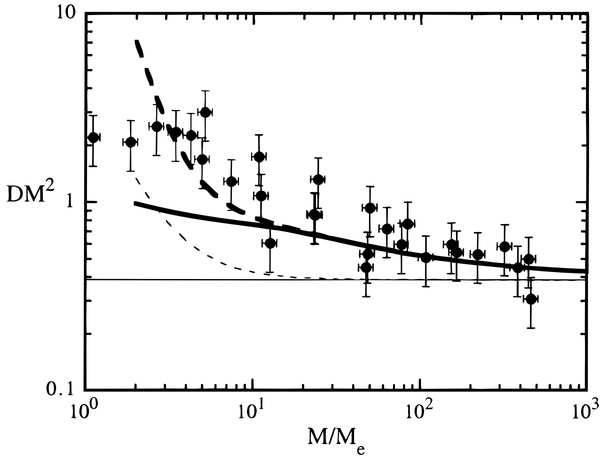

Figure 3. Diffusion data and theory from Figure 2, plotted as DM^2 versus M/M_e. The error bars on the data were estimated conservatively as 10% in M/M_e and 30% in D in ref 4. The horizontal line is the value for the reptation model, $k_D \equiv D_{rep}M^2$.

is clearly stronger than the reptation exponent of −2, to which D_{CLF} crosses over for large N/N_e. Our result gives $D_{CLF} \sim (N/N_e)^{-\alpha}$ with $2.2 < \alpha < 2.3$ without adjustable parameters. The exponent agrees with the recent experimental value of $\alpha = 2.28 \pm 0.05$ within the experimental uncertainty. From the figure, the crossover to a −2 slope occurs at about $N/N_e = 80$. This result for the crossover molecular weight may be somewhat low compared to experiment, although the data do not extend to high enough N/N_e to establish the crossover definitively. We note that we have not included any effects of polydispersity; however, a small amount of polydispersity, such as in anionically prepared samples, should not affect the exponent in the power law for D.[14]

We compare our results to a compilation of data on hPB melts at 175 °C from ref 4 in Figure 2. We assume an entanglement molecular weight of $M_e = 950$ g/mol for hPB. The constant D_e defined in eq 8 is related to the more usual prefactor in the reptation self-diffusion constant $D_{rep} = k_D/M^2$ by $D_{rep} = D_e(M_e/M)^2$, so that D_e is given by $D_e M_e^2 = k_D$. The constant k_D can in turn be written in terms of experimental observables using an expression developed by Graessley:[15]

$$k_D \equiv D_{rep}M^2 = \frac{2G_N R_g^{\,2}}{45M}(\rho RT/G_N)^2(M_c/\eta(M_c)) \qquad (9)$$

The value of k_D has an uncertainty of about 50%; we use a value for k_D which is 30% higher than that used in ref 4. The difference between these results and the reptation result can be more clearly seen in a plot of DM^2 versus M/M_e, as shown in Figure 3. We see that the theory is consistent with the data above about $M/M_e = 10$, and both seem to be approaching the reptation result somewhere above $M/M_e = 100$. It is not surprising that there are deviations for smaller M/M_e, especially since we are modeling the linear polymer as a two-arm star, so that the length of each star arm is only a few M_e when $M/M_e < 10$.

We might expect there to be further enhancements to the diffusion constant due to constraint-release effects, particularly at small N/N_e. In fact, tracer diffusion experiments[16] have demonstrated a significant constraint-release contribution to the self-diffusion constant for small N/N_e. In this case $s_d(N/N_e)$, the amount the ends retract before τ_d, can be a substantial fraction of the total tube length; e.g. $s_d(10) = 0.49$. Thus, for small N/N_e, contour-length fluctuations may be fairly effective at releasing entanglements, allowing tube segments to hop a distance of about a dilated tube diameter $a(\Phi)$, where $\Phi = 1 - s_d$ is the volume fraction of unrelaxed segments in the diluted entanglement network at τ_d.

We estimate the size of this effect on the self-diffusion constant, using an argument similar to one originally developed by Graessley.[17] We assume each tube segment of length $N_e(\Phi)$ can make a hop of size $a(\Phi)$ every τ_d. The jump frequency f for the entire tube of $N/N_e(\Phi)$ segments is then $f = (N/N_e(\Phi))/\tau_d$. The mean-square center-of-mass displacement due to the independent hops of each tube segment is $\Delta R^2 = a^2(\Phi)/(N/N_e(\Phi))^2$. The contribution of constraint release to the diffusion constant is the mean-square center-of-mass displacement times the jump frequency:

$$D_{CR} = pf\Delta R^2 = p\,\frac{a^2(\Phi)}{(N/N_e(\Phi))\tau_d} \qquad (10)$$

where the unknown constant p is related to the probability of a segment making a hop every τ_d. Using the Colby−Rubinstein scaling for the dilution of the entanglement network,[9,18] the dilated tube diameter and entanglement length at τ_d are $a^2(\Phi) = a^2/(1 - s_d)^{4/3}$ and $N_e(\Phi) = N_e/(1 - s_d)^{4/3}$, respectively. Including the expression for τ_d from eq 6 and writing the result in terms of $D_e = k_D/M_e^2$, we have

$$D_{CR} = \frac{4p}{5}D_e\left(\frac{N_e}{N}\right)^4\frac{1}{(1 - s_d)^{14/3}} \qquad (11)$$

Since diffusion by reptation and by constraint release are independent processes, we can add this result to D_{CLF} from eq 8 to obtain an expression for the diffusion constant including both effects:

$$D_{CLF,CR} = \frac{k_D}{M_e^{\,2}}\left[\left(\frac{M_e}{M}\right)^2\frac{1}{1 - s_d} + \frac{4p}{5}\left(\frac{M_e}{M}\right)^4\frac{1}{(1 - s_d)^{14/3}}\right] \qquad (12)$$

We can compare this result with the original calculation of Graessley from ref 17. That calculation did not include contour-length fluctuations, and so the diffusion constant is the sum of the reptative diffusion constant and the contribution from constraint release on a given chain by reptation of the surrounding chains. The constraint-release contribution is calculated quantitatively from a lattice-type model in which each tube segment of length N_e is surrounded by z constraints corresponding to the surrounding chains on the lattice. The result is[17]

$$D_G = \frac{k_D}{{M_e}^2}\left[\left(\frac{M_e}{M}\right)^2 + \alpha_{CR}\left(\frac{M_e}{M}\right)^4\right] \qquad (13)$$

where $\alpha_{CR} = (48/25)z(12/\pi^2)^{z-1}$. Both approaches lead to the same asymptotic scaling of D at large M/M_e, but the inclusion of the contour-length fluctuations in eq 12 significantly enhances both terms in the diffusion constant relative to Graessley's result.

The short dashed curves in Figures 2 and 3 correspond to D_G, with $\alpha_{CR} = 9.7$ corresponding to $z = 3.25$.[19] We see that constraint-release effects alone, without contour-length fluctuations, decay too rapidly to fit the data. The long dashed curves in the figures correspond to the full diffusion constant $D_{CLF,CR}$ with the parameter $p = 1$. The approach to $M/M_e = 1$ is not physical since throughout we have assumed $M/M_e \gg 1$. Constraint-release modes caused by contour-length fluctuations of surrounding chains do enhance D for small values of M/M_e, but these effects decrease rapidly with increasing M/M_e. Contour-length fluctuations are important over a much wider M/M_e range than the constraint-release effects considered here, and by themselves are sufficient to give a stronger exponent than -2 in D.

A remaining puzzle is that extensive tracer diffusion data[16,20-22] have been successfully described by the asymptotic reptation scaling of -2 for large M, combined with constraint-release effects as in eq 13. In large M matrices, constraint-release effects will be negligible, but one would still expect contour-length fluctuations of the diffusing chain to be significant. It is straightforward to calculate the diffusion constant for a diffusant in a matrix of infinitely long chains; the calculation proceeds as before, with the effective potential $U_{eff}(s)$ (which includes the dilution of the network as portions of chains relax) replaced with the Pearson−Helfand potential $U(s)$ for a chain in a fixed network.[9,11] The result is indistinguishable from the result for D_{CLF} as shown in Figure 2; this is because the relaxation time $\tau(s)$ is dominated by the early relaxation time $\tau_{early}(s)$, which is independent of the effective potential. Thus, the result D_{CLF} of eq 8 for self-diffusion should be equally valid for tracer diffusion in large M matrices. This predicts that tracer diffusion should also scale as $M^{-2.25}$, at variance with the available data.

Many numerical simulations have also investigated the scaling of the diffusion constant in linear polymers. The simulations can be classified into two broad categories: many-chain simulations and single-chain simulations. The many-chain simulations study polymer melts, and thus should include both constraint-release effects and contour-length fluctuations. Because of computational limits, the longest chains investigated in the many-chain simulations have been on the order of $8N_e$ or less. The self-diffusion constant for an entangled melt calculated in an extensive molecular dynamics study of a bead−spring model by Kremer and Grest[23] is consistent with $D \sim N^{-\alpha}$ with $2 < \alpha < 2.25$. Monte Carlo simulations of the bond-fluctuation model by Paul et al.[24] give similar results to those of ref 23, perhaps with a somewhat more shallow slope, whereas work on a similar model by Shaffer found $D \sim N^{-2.08}$.[25] Smith et al. report $D \sim N^{-2}$ for a molecular dynamics simulation of a tangent hard-sphere model.[26] We note that at the time of these simulations the experimental evidence was believed to give $D \sim N^{-2}$; there is almost no discussion in the literature of the best-fit power laws to the simulation data. A reanalysis of the many-chain simulation data may show that it is not inconsistent with the stronger power-law behavior found here. Further studies at somewhat longer chain lengths would also be interesting, in the light of the new experimental findings.

Recent simulations of single chains moving in a network of obstacles have found a stronger dependence of D on chain length. These simulations measure the tracer diffusion constant and thus should include the effects of contour-length fluctuations but not of constraint-release processes. Deutsch and Madden[27] found numerically that for a cage model $D \sim N^{-2.5}$. They also reanalyzed the results of Rubinstein's repton model[28] and found that the three-dimensional self-diffusion constant of the repton model scales as $D \sim N^{-2.3}$.[27] A Monte Carlo simulation of reptation dynamics by Reiter[29] found that $D \sim N^{-2.4}$. Barkema and Krenzlin[30] studied the same model as ref 27 and interpreted their results as giving $DN^2 = 0.173 + 1.9N^{-2/3}$. This is a stronger correction to the reptation scaling than that found in this paper. A best-fit power law to the diffusion results of ref 30 gives $D \sim N^{-2.3}$. These single-chain simulations are thus mostly consistent with the results of this paper.

It was originally thought that contour-length fluctuations would have only a small effect on the diffusion constant, and indeed they have little effect on the *one*-dimensional curvilinear diffusion of the chain in the tube, since on average they do not contribute to motion of the center of mass along the tube.[28,27] However, as we have seen above, length fluctuations reduce the time it takes the chain to escape from the tube, as well as the distance it must go to be uncorrelated with itself, and this does have a significant effect on the three-dimensional diffusion constant.

It therefore appears that experimental, analytical, and some numerical results all point to a stronger scaling of the self-diffusion constant with N than is predicted by pure reptation. Both our results and the single-chain numerical simulations give exponents within the experimental uncertainty. Thus, contour-length fluctuations do indeed lead to significant corrections to scaling in the diffusion constant. These may remove the need for different dynamics in melts and concentrated solutions of linear polymers, although the data seem to imply that a small difference in scaling remains, with exponents of -2.4 or -2.5 in solutions and -2.2 to -2.3 in melts.[4] Nevertheless, the inclusion of contour-length fluctuations largely resolves the discrepancy between the scaling exponents for the self-diffusion constant and the viscosity in linear entangled polymers.

Acknowledgment. We thank Tim Lodge for the data used in Figures 2 and 3 and Tim Lodge and Tom McLeish for helpful discussions.

References and Notes

(1) de Gennes, P.-G. *Scaling Concepts in Polymer Physics;* Cornell University Press: Ithaca, NY, 1979.
(2) Doi, M.; Edwards, S. *The Theory of Polymer Dynamics;* Clarendon Press: Oxford, 1986.
(3) An exception is a recent study on hydrogenated polybutadiene, which found $\alpha \approx 0.37$: Tao, H.; Huang, C.; Lodge, T. P. *Macromolecules* **1999**, *32*, 1212.
(4) Lodge, T. P. *Phys. Rev. Lett.* **1999**, *83*, 3218 and references therein.
(5) Rubinstein, M. In *Theoretical Challenges in Polymer Dynamics*; McLeish, T., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1997.
(6) Tao, H.; Lodge, T. P.; von Meerwall, E. D. *Macromolecules* **2000**, *33*, 1747.
(7) Tao, H. Ph.D. Thesis, University of Minnesota, 1998.
(8) Doi, M. J. *Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 667.
(9) Milner, S. T.; McLeish, T. C. B. *Macromolecules* **1997**, *30*, 2159.
(10) Milner, S. T.; McLeish, T. C. B. *Phys. Rev. Lett.* **1998**, *81*, 725.
(11) Pearson, D. S.; Helfand, E. *Macromolecules* **1984**, *17*, 888.
(12) In ref 9 it was argued that the effective diffusion constant should be twice the Rouse diffusion constant, $D_{\mathrm{eff}} = 2D_{\mathrm{R}}$. However, taking $D_{\mathrm{eff}} = 2D_{\mathrm{R}}$ leads to a viscosity scaling exponent for linear chains between 3.5 and 3.6, whereas using $D_{\mathrm{eff}} = D_{\mathrm{R}}$ leads to $\eta \sim N^{3.4}$, so we use $D_{\mathrm{eff}} = D_{\mathrm{R}}$ here. We find that we obtain similar scaling for D (eq 8) with $D_{\mathrm{eff}} = 2D_{\mathrm{R}}$ in eq 3, but with a somewhat higher crossover to reptation scaling, near $N/N_{\mathrm{e}} = 100$.
(13) Milner, S. T.; McLeish, T. C. B. *Macromolecules* **1998**, *31*, 7479.
(14) Bernard, D. A.; Noolandi, J. *Macromolecules* **1983**, *16*, 548.
(15) Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 27.
(16) See, e.g.: Green, P. F.; Kramer, E. J. *Macromolecules* **1986**, *19*, 1108. Green, P. F.; Mills, P. J.; Palmstrøm, C. J.; Mayer, J. W.; Kramer, E. J. *Phys. Rev. Lett.* **1984**, *53*, 2145. von Seggern, J.; Cantow, H.-J. *Macromolecules* **1991**, *24*, 3300.
(17) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 68.
(18) Colby, R. H.; Rubinstein, M. *Macromolecules* **1990**, *23*, 2753.
(19) von Seggern, et al. (see ref 16) found $\alpha = 9.7$ fit their data for self-diffusion of hPB. The curve for D_{G} in Figures 2 and 3 is not significantly different for $8.5 < \alpha_{\mathrm{CR}} < 21$, corresponding to the physically reasonable range of z, $3 < z < 5$.
(20) Klein, J.; Fletcher, D.; Fetters, L. J. *Nature* **1983**, *304*, 526.
(21) Green, P. F.; Palmstrøm, C. J.; Mayer, J. W.; Kramer, E. J. *Macromolecules* **1985**, *18*, 501.
(22) Antonietti, M.; Coutandin, J.; Sillescu, H. *Macromolecules* **1986**, *19*, 793.
(23) Kremer, K.; Grest, G. S. *J. Chem. Phys.* **1990**, *92*, 5057.
(24) Paul, W.; Binder, K.; Heermann, D. W.; Kremer, K. *J. Phys. II* **1991**, *1*, 37. See also: Binder, K.; Paul, W. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 1.
(25) Shaffer, J. S. *J. Chem. Phys.* **1994**, *101*, 4205.
(26) Smith, S. W.; Hall, C. K.; Freeman, B. D. *Phys. Rev. Lett.* **1995**, *75*, 1316. Smith, S. W.; Hall, C. K.; Freeman, B. D. *J. Chem. Phys.* **1996**, *104*, 5616.
(27) Deutsch, J. M.; Madden, T. L. *J. Chem. Phys.* **1989**, *91*, 3252.
(28) Rubinstein, M. *Phys. Rev. Lett.* **1987**, *59*, 1946.
(29) Reiter, J. *J. Chem. Phys.* **1991**, *94*, 3222.
(30) Barkema, G. T.; Krenzlin, H. M. *J. Chem. Phys.* **1998**, *109*, 6486.

MA992123D