Tube Dilation and Reptation in Binary Blends of Monodisperse Linear Polymers

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ABSTRACT: We extend the Milner−McLeish theory for monodisperse linear polymers to binary blends, where the reptation time of the long chain is set to either the reptation time in the undilated tube or the reptation time in the dilated tube depending on the value of the "Graessley parameter" $Gr \equiv M_2M_e^2/M_1^3$, where M_1 is the short chain molecular weight, M_2 is the long chain molecular weight, and M_e is the entanglement molecular weight. We find experimentally that, in blends in which Gr is much smaller than the critical value $Gr_c \approx 0.064$ established by an observed crossover in diffusivity measurements [Green et al. *Phys. Rev. Lett*. **1984**, *26*, 2145], the long-chain motion in the binary blend is well predicted by the Milner−McLeish model using reptation in the undilated tube. However, for Gr larger than Gr_c, reptation must to be assumed to occur in a dilated tube to obtain agreement with the experimental data. These results confirm that the crossover behavior observed in diffusivity also occurs in rheology and show that existing tube models can accurately predict linear rheology in both regimes where reptation occurs in a dilated or an undilated tube.

Introduction

While polymer reptation along a tube created by the sea of surrounding polymers is known to be the dominant mechanism for diffusion and relaxation of linear entangled polymers, it has long been known that mechanisms other than pure reptation must also be accounted for to obtain a complete quantitative description.[1−3] The most important of these are "contour-length fluctuations" and "constraint release". Contour-length fluctuations shorten the portion of the tube that remains occupied and thereby decrease the reptation time relative to pure reptation.[4,5] In addition, because of motion of the surrounding chains, the reptating chain can move laterally out of the original tube; this is called constraint release. To describe constraint release, several models have been suggested, including "double reptation",[6−8] "constraint release Rouse motion",[9] and "dynamic tube dilation".[10] The double reptation theory can be thought of as a simplified version of the theory of constraint release developed by Viovy et al.[9] because the stress carried by an entanglement point is considered as completely relaxed after multiple constraint-release processes in the latter and immediately after a single constraint-release process in the former.[11] Milner[11] has given a more complete argument that defines the requirements that the molecular weight distribution must meet for double reptation to be a reasonable approximation. On the other hand, if the volume fraction of the long chain is very small, the prediction of the double reptation theory for bidisperse polymers is not as successful because in that case it implies that the test chain can relax completely after the constraints from short chains have relaxed only once. In reality, once constraints are released, the test chain can only move a short distance before it encounters new entanglement constraints. These new constraints must again be released before the test chain can continue its relaxation. Therefore, stress relaxation resulting from constraint release occurs by repeated cycles of constraint release and localized test-chain motion. One way to describe this process is by assuming that the tube itself moves in response to local constraint-release events in a manner analogous to Rouse motion; hence, this process is called "constraint-release Rouse motion".[9] As a simpler way to describe gradual constraint-release-induced motion of a chain beyond the boundaries of the original tube, Marrucci[10] introduced the concept of "tube dilation" or "dynamic dilution", in which the relaxed portions of surrounding polymers are thought of as a solvent for the unrelaxed reptating chain. The effective concentration of solvent therefore gradually increases as relaxation progresses, and this increases the effective tube diameter. The "dynamic dilution" concept has been successfully applied to star polymers,[12] and Milner[11] showed that double reptation and dynamic dilution are essentially the same approximation, applied to smooth and broad molecular weight distributions of linear polymers.

Binary blends of linear polymers are useful systems for investigating constraint-release effects, including the possible role of dynamic dilution, since they allow control of the constraint-release time scale through the molecular weight of the shorter molecule in the blend. There have been many experimental data and theoretical models for binary blends of monodisperse polymers.[13−17] However, an important regime has not yet been adequately addressed in these rheological studies, namely the regime where both polymers in the binary blend are well entangled, yet the low-molecular-weight component is of low enough molecular weight to be effectively a solvent on the time scale that controls the reptation of the high-molecular-weight component, i.e., the time it takes the long chain to reptate of order one tube diameter. This regime is accessed at high values of the "Graessley parameter" $Gr \equiv M_2M_e^2/M_1^3$, where M_2 is the molecular weight of the long chain, M_1 is the molecular weight of the short chain, and M_e is the entanglement molecular weight.[13,14] If we neglect contour-length fluctuations, the Graessley parameter represents

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the ratio of the reptation time of the long chain in an undiluted tube to the constraint-release Rouse time, that is, $Gr = [3\tau_e(M_2/M_e)^3]/[3\tau_e(M_1/M_e)^3(M_2/M_e)^2] = M_2M_e^2/M_1^3$.

In the case of $Gr < 1$, both Doi et al.[18] and Viovy et al.[9] predicted that the long chain reptates in an undilated tube, and the reptation time of the long chain is not dependent on the length or concentration of the short chain. In the case of $Gr > 1$, Viovy et al. argued that if $M_1 > M_e$, then the long chain always reptates in an undilated tube and the undilated tube itself reptates in a "supertube", which is the dilated tube formed by constraints imposed by other long chains only, but Doi et al. argued that the long chain itself rather than the undilated tube reptates in the dilated tube. Tracer diffusion data for long linear polymers in a matrix of short linear polymers showed that even if $M_1 > M_e$, the diffusivity of the long chain begins to be affected by the short chains when Gr exceeds 0.1 or so but cannot establish which, if either, of the two models for long-chain motion is correct.[14,19,20]

In this work we show how the relaxation time of the long chain in a binary blend of well-entangled long and short polymers is changed as a function of the Graessley parameter for linear 1,4-polybutadienes and extend the theory developed by Milner and McLeish[5] for a monodisperse linear polymer to the binary blend. Likhtman and McLeish[21] recently developed a more rigorous description of the combination of reptation, contour length fluctuations, constraint release, and longitudinal stress relaxation along the tube than was achieved by Milner and McLeish,[5] but the Likhtman and McLeish theory was developed for monodisperse linear polymers only. Since we obtain predictions similar to those of Likhtman and McLeish from the simpler Milner−McLeish theory by merely adjusting the equilibration time τ_e for the terminal relaxation, we limit ourselves here to the simpler Milner−McLeish theory.

Theory

Milner and McLeish[5] analyze the early-time relaxation of a linear polymer by considering it to be a "two-arm star" polymer; i.e., the contour-length fluctuations of a linear polymer are treated using the theory for arm retraction of a star polymer. The portion of the stress relaxing by arm retraction is given by

$$G_{\text{retract}}(t) = -\int_0^{\xi_d} d\xi \frac{dG[\Phi(\xi)]}{d\xi} \exp[-t/\tau(\xi)] \quad (1)$$

where ξ stands for a fractional arm coordinate that runs from zero to unity as one moves along the contour of the "arm" from the free end to the middle of the linear polymer, i.e., to the joint of the "two-arm star", and ξ_d is the value of ξ at which reptation becomes faster than arm retraction. $G(\Phi)$ is the concentration-dependent modulus, and Φ is the unrelaxed volume fraction, which is given by $\Phi(\xi) = 1 - \xi$. The modulus depends on Φ as $G(\Phi) = G_N^0\Phi^{1+\alpha}$, where G_N^0 is the plateau modulus and α is the dilution exponent, which is typically set to either $\alpha = 1$ or $\alpha = {}^4/_3$. The precise value of dilution exponent is important for star polymers, but for monodisperse linear polymers its effect is not large.[5] However, in the case of binary blend of linear polymers, especially for the case where the long chain reptates in the dilated tube, the effect of the dilution exponent is important. In this work we compare theoretical predictions using both $\alpha = 1$ and ${}^4/_3$ with experimental data.

Equation 1 can be rewritten by using the concentration dependence of the relaxation modulus as

$$G_{\text{retract}}(t) = -\int_0^{\xi_d} d\xi \frac{dG}{d\Phi}\frac{d\Phi}{d\xi} \exp[-t/\tau(\xi)]$$

$$= -(1+\alpha)G_N^0\int_0^{\xi_d} d\xi\, [\Phi(\xi)]^\alpha \frac{d\Phi}{d\xi} \exp[-t/\tau(\xi)]$$

$$= (1+\alpha)G_N^0\int_0^{\xi_d} d\xi\, (1-\xi)^\alpha \exp[-t/\tau(\xi)] \quad (2)$$

$\tau(\xi)$ is given by the early-time relaxation time for a star:[22]

$$\tau(\xi, S) = \tau_{\text{early}}(\xi) = \frac{9}{16}\pi^3\tau_e\left(\frac{S}{2}\right)^4\xi^4 \quad (3)$$

where $S \equiv M/M_e$, with M the molecular weight of the linear polymer and τ_e the equilibration time, i.e., the Rouse time of a single entanglement length of polymer. Equation 3 is valid for relaxation up to ξ_d, after which the remaining portion of the chain relaxes by reptation. Because the contour-length fluctuations shorten the tube length occupied by the chain by a factor of $(1 - \xi)$, the reptation time is reduced according to

$$\tau_d = 3\tau_e S^3(1-\xi_d)^2 = \tau_{\text{early}}(\xi_d) \quad (4)$$

ξ_d is set by the time when reptation takes over; i.e., ξ_d is given by equating the reptation time τ_d in eq 4 with τ_{early} in eq 3. The reptation contribution to the stress is given by

$$G_{\text{reptate}}(t) = G_N^0(1-\xi_d)^{1+\alpha}\sum_{p\ \text{odd}} (8/\pi^2)p^{-2} \exp[-p^2t/\tau_d] \quad (5)$$

In this work we neglect the high-frequency Rouse relaxation processes, which have no effect at the low and modest frequencies of interest here. The total stress relaxation function is then given by the addition of the contributions of retraction and reptation.

$$G(t) = G_{\text{retract}}(t) + G_{\text{reptate}}(t) \quad (6)$$

By using the relaxation spectrum obtained for a monodisperse linear polymer, we can calculate the relaxation modulus for a binary blend of linear polymers. The unrelaxed volume fraction of chains Φ before the reptation time of a short chain in the binary blend is given by

$$\Phi = \phi_1(1-\xi_1) + \phi_2(1-\xi_2) \quad (7)$$

where ϕ_1 is the volume fraction of the short chain, ϕ_2 is the volume fraction of the long chain, and ξ_1, ξ_2 are the fractional arm coordinates of along the short and long chains, respectively. Because the chain lengths are different in the short and long chains, the two different chains relax a different fraction ξ_1 or ξ_2, respectively, of their fractional distance at a given relaxation time. Therefore, we need to know the value of ξ_1 for a given value of ξ_2 and vice versa. Frischknect and Milner[17] implicitly defined two functions by equating relaxation times:

$$\tau[\xi_1^*(\xi_2),S_1] = \tau(\xi_2,S_2)$$
$$\tau[\xi_2^*(\xi_1),S_2] = \tau(\xi_1,S_1) \quad (8)$$

Using these equations, we can obtain $\xi_1^*(\xi_2)$ [or $\xi_2^*(\xi_1)$], which is the value of ξ_1 (or ξ_2) for the short (or long) chain, given a distance ξ_2 (or ξ_1) along the long (or short) chain. Thus, before the reptation time of the short chain the relaxation modulus is

$$G(t) = (1+\alpha)G_N^0\phi_1\int_0^{\xi_{d1}} d\xi_1\,[\phi_1(1-\xi_1)+\phi_2(1-\xi_2^*)]^\alpha \exp[-t/\tau(\xi_1)] + (1+\alpha)G_N^0\phi_2\int_0^{\xi_{d2}^*} d\xi_2\,[\phi_1(1-\xi_1^*)+\phi_2(1-\xi_2)]^\alpha \exp[-t/\tau(\xi_2)] \quad (9)$$

where $\xi_{d2}^* = \xi_2^*(\xi_{d1})$ is the arm coordinate of the long chain at the reptation time of the short chain.

After the reptation time of the short chain, the tube in which the long chains reside experiences constraint-release Rouse motion. The relaxation modulus during the constraint-release Rouse motion is given by[23]

$$G(t) = G_N^0\phi_2(1-\xi_{d2}^*)\Phi_{ST}(t)^\alpha \quad (10)$$

where Φ_{ST} is the fraction of constraints defining the portion of the supertube explored by constraint-release Rouse motion at time t, which is given by $\Phi_{ST}(t) = \Phi(\tau_{d1})(\tau_{d1}/t)^{1/2\alpha}$, where $\Phi(\tau_{d1})$ is the unrelaxed volume fraction at the reptation time of the short chain, which is $\phi_1(1-\xi_{d1}) + \phi_2(1-\xi_{d2}^*)$, and τ_{d1} is the reptation time of the short chain. The constraint-release Rouse motion ends when Φ_{ST} becomes equal to the unrelaxed volume fraction $\phi_2(1-\xi_{d2}^*)$. This occurs at a time τ_C, which is obtained from equating the unrelaxed volume fraction $\phi_2(1-\xi_{d2}^*)$ with the fraction of constraints Φ_{ST}:

$$\tau_C = \tau_{d1}\left(\frac{\phi_1(1-\xi_{d1})+\phi_2(1-\xi_{d2}^*)}{\phi_2(1-\xi_{d2}^*)}\right)^{2\alpha} \quad (11)$$

After the time τ_C the long chain relaxes again by arm retraction until the reptation time of the long chain is reached.

In the model of Doi et al.[18] for a binary blend of linear polymers, in which the long chain is self-entangled, there are three regimes for the terminal relaxation time τ_t. In the first regime, $Gr < 1$, the long chain reptates in the undilated tube of diameter a, and τ_t is given by

$$\tau_t = \tau_{d2} = 3\tau_e S_2^{\,3}(1-\xi_{d2})^2 \text{ (for } Gr < 1\text{; chain reptation in the undilated tube)} \quad (12)$$

In the second regime, which is the case of free dilation, $Gr > 1$ and $\phi_2 Gr < 1$, the long chain reptates in a tube of diameter a', which has a value between the undilated tube diameter a and the diameter $a/\phi_2^{\alpha/2}$ of the dilated tube (or "supertube"), which is the tube defined by entanglements involving only the long chains and τ_t is given by

$$\tau_t = \tau_{d1}S_2^{\,2} \text{ (for } \phi_2 Gr < 1\text{; free dilation)} \quad (13)$$

The tube diameter a' is given by $a^2/\sqrt{\tau_{d1}D_2}$, where D_2 is the curvilinear diffusion constant of the long chain. While in the case of the free dilation the terminal time is the same as the constraint-release Rouse time of the long chain, Doi et al. argued that reptation of the long chain occurs in a tube diameter a'.

In the third regime, the tube diameter grows to the diameter of the supertube, and the long chain then reptates in a tube of diameter $a/\phi_2^{\alpha/2}$, i.e., tube dilation is restricted by entanglements with the long chains, which leads to the case of restricted dilation, and τ_t is given by

$$\tau_t = \tau_{d2} = 3\tau_e S_2^{\,3}(1-\xi_{d2})^2\phi_2^{\,\alpha} \text{ (for } Gr > 1 \text{ and } \phi_2 Gr > 1\text{; restricted dilation)} \quad (14)$$

Equation 14 can be rewritten as follows:

$$\tau_{d2} = 3\tau_e S_2^{\,3}(1-\xi_{d2})^2\phi_2^{\,\alpha} = 3\tau_e[M_e/(M_e\phi_2^{\,\alpha})]^2(S_2\phi_2^{\,\alpha})^3(1-\xi_{d2})^2 \quad (15)$$

Thus, chain reptation time in the dilated tube amounts to replacing M_e by M_e/ϕ_2^{α} and replacing τ_e by the Rouse time of a diluted entanglement segment $\tau_e[M_e/(M_e\phi_2^{\alpha})]^2$ in the equation for the reptation time in the undilated tube.

In the theory of Viovy et al.[9] the terminal relaxation time τ_t is given as follows:

$$\tau_t = \tau_{d2} = 3\tau_e S_2^{\,3}(1-\xi_{d2})^2 \text{ (for } Gr < \phi_2 S_2\text{; chain reptation in the undilated tube)} \quad (16)$$

$$\tau_t = \tau_{d1}S_2^{\,3}(1-\xi_{d2})^2\phi_2^{\,\alpha} \text{ (for } Gr > \phi_2 S_2\text{; tube reptation in the dilated tube)} \quad (17)$$

While the theory of Doi et al. predicts that the tube diameter for the long chain can be any value between a and $a/\phi_2^{\alpha/2}$, Viovy et al. argued that the tube diameter is only allowed to take on two discrete values, i.e., a or $a/\phi_2^{\alpha/2}$. In the theory of Viovy et al. the tube reptation time in the dilated tube can be rewritten as follows:

$$\tau_t = \tau_{d1}S_2^{\,3}(1-\xi_{d2})^2\phi_2^{\,\alpha} = \tau_{d1}[M_e/(M_e\phi_2^{\,\alpha})]^2(S_2\phi_2^{\,\alpha})^3(1-\xi_{d2})^2 \quad (18)$$

Thus, the tube reptation time in the dilated tube amounts to replacing τ_e by the constraint-release time scale for a dilated tube entanglement strand $\tau_{d1}[M_e/(M_e\phi_2^{\alpha})]^2$ and replacing M_e by M_e/ϕ_2^{α}.[24] Therefore, the ratio of the chain reptation time in the dilated tube of Doi et al. to the tube reptation time in the supertube (or dilated tube) of Viovy et al. is $1/[S_1^{\,3}(1-\xi_{d1})^2]$. This ratio is very small if the molecular weight of the short chain is not very small. Thus, we expect that chain reptation in the dilated tube will be much faster than tube reptation in the dilated tube, and so eq 17, from the theory of Viovy et al., will rarely be applicable.

Once the value of τ_{d2} is established, the full expression for $G(t)$ is

$$G(t)/G_N^0 = (1+\alpha)\phi_1\int_0^{\xi_{d1}} d\xi_1 [\phi_1(1-\xi_1) + \phi_2(1-\xi_2^*)]^\alpha \exp[-t/\tau(\xi_1)] + (1+\alpha)\phi_2\int_0^{\xi_{d2}^*} d\xi_2 [\phi_1(1-\xi_1^*) + \phi_2(1-\xi_2)]^\alpha \exp[-t/\tau(\xi_2)] + \phi_2(1-\xi_{d2}^*)\int_{\tau_{d1}}^{\tau_c} d\tau \times [\Phi_{ST}(\tau)^\alpha/(2\tau)] \exp[-t/\tau] + (1+\alpha)\phi_2\int_{\xi_{d2}^*}^{\xi_{d2}} d\xi_2 [\phi_2(1-\xi_2)] \exp[-t/\tau^*(\xi_2)] + [\phi_1(1-\xi_{d1}) + \phi_2(1-\xi_{d2}^*)]^\alpha [\phi_1(1-\xi_{d1})] \sum_{p\ \mathrm{odd}} (8/\pi^2)p^{-2} \exp[-p^2 t/\tau_{d1}] + [\phi_2(1-\xi_{d2})]^{1+\alpha} \sum_{p\ \mathrm{odd}} (8/\pi^2)p^{-2} \exp[-p^2 t/\tau_{d2}] \quad (19)$$

The first two terms on the right side correspond to the contour-length fluctuations of the short and the long chains, respectively, before the reptation time of the short chain. The third term accounts for stress relaxation during the constraint-release Rouse process. The fourth term accounts for contour-length fluctuations of the long chain before the reptation time of the long chain, where $\tau^*(\xi_2)$ is the shifted early-time relaxation time given by $\tau^*(\xi_2) = \tau_{early}(\xi_2) + \tau_c - \tau_{early}(\xi_{d2}^*)$. The shift is used because arm retraction is not allowed during the constraint-release Rouse process, as discussed by Milner et al.[23] The final two terms describe the stress relaxation by reptation of the short and the long chains, respectively. The complex modulus $G^*(\omega)$ is given by the Fourier transform of $G(t)$, $G^*(\omega) = i\omega\int_0^\infty dt \exp(-i\omega t)G(t)$.

Experimental Section

Two monodisperse linear 1,4-polybutadienes were purchased from Polymer Source, Inc. The molecular weights were measured by laser light scattering (ALV-5000, $\lambda = 488$ nm, $dn/dc = 0.117$ mL/g). Linear ($M_1 = 20\,000$)/linear ($M_2 = 550\,000$) blends were prepared by dissolving weighed amounts of the two components in excess dichloromethane. The dichloromethane was removed under vacuum at room temperature. Rheological measurements were carried out using the Rheometrics Advanced Rheometric Expansion System (ARES) in an oscillatory shear mode, with 25 mm diameter parallel plates. All measurements were performed at $T = 25$ °C, except for the monodisperse long chain for which we cannot obtain the terminal region at $T = 25$ °C because of its excessively long relaxation time. The storage and loss modulus of the long chain, which were measured at $T = 70$ °C, were shifted to $T = 25$ °C by using the WLF equation without any vertical shift along the modulus axis.[3]

Results and Discussion

The parameters needed for the model calculations are the plateau modulus G_N^0, the entanglement spacing M_e, and the equilibration time τ_e. We have used the G_N^0 value for 1,4-polybutadiene reported by Fetters et al.,[25] which is 1.15×10^6 Pa at $T = 25$ °C. The value of M_e can be calculated from $M_e = (4/5)\rho RT/G_N^0$,[21,26,27] which gives $M_e = 1543$, where ρ is the density of polymer melt, R is the gas constant, and T is the absolute temperature. The value of τ_e is related to the monomeric friction coefficient ζ and the tube diameter a by $\tau_e = \zeta a^2 M_e/3\pi^2 M_0 k_B T$. Therefore, in principle, we could obtain the τ_e value from the literature values of the tube diameter and the monomeric friction coefficient.[3] That leads to a value of $\tau_e = 5.6 \times 10^{-7}$ s. [In our previous paper,[28] the τ_e value inferred from the monomeric friction coefficient was erroneously reported as 8.8×10^{-7} s.] We note, however, that the value of ζ is based on data from the transition region and might not be accurate for calculation of slow relaxation processes. Thus, in this work we choose the τ_e value from a best fit of the zero-shear viscosities of monodisperse linear polymers using the Milner−McLeish theory.[5] Figure 1 shows the zero-shear viscosities η_0 of linear polymer melts available in the literature.[14,15,29−31] The values of η_0 at temperatures slightly different from 25 °C are shifted to 25 °C using time−temperature superposition via the WLF equation with $c_1^0 = 3.64$, $c_2^0 = 186.5$ K, and reference temperature $T_0 = 25$ °C.[3] The solid line in Figure 1 is the theoretical prediction calculated with $\tau_e = 2.5 \times 10^{-7}$ s using the Milner−McLeish theory for $\alpha = 1$, and the dotted line is the theoretical prediction calculated with $\tau_e = 2.8 \times 10^{-7}$ s for $\alpha = 4/3$. As shown, the Milner−McLeish theory explains well the molecular weight dependence of the viscosity of linear polymers, and for the monodisperse linear polymers the predictions using both $\alpha = 1$ and $\alpha = 4/3$ are almost the same except for the small difference in the fitted τ_e value. This is because the dynamic dilution effect is not important for monodisperse linear polymers. In what follows, we use $\tau_e = 2.5 \times 10^{-7}$ for $\alpha = 1$ and $\tau_e = 2.8 \times 10^{-7}$ for $\alpha = 4/3$.

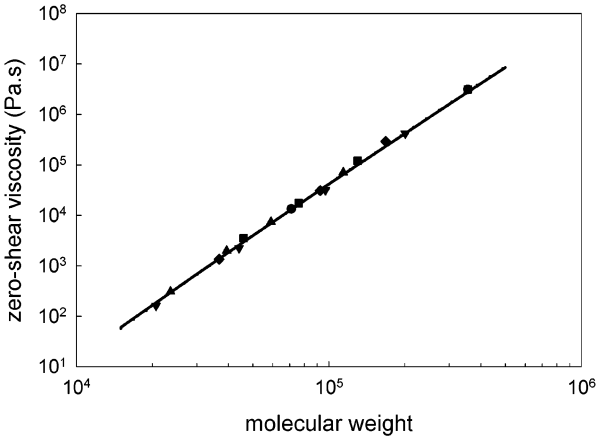

Figure 1. Zero-shear viscosity vs molecular weight of linear polybutadienes at $T = 25$ °C: ◆, Struglinski and Graessley;[14] ■, Colby et al.;[29] ▲, Roovers;[30] ●, Rubinstein and Colby;[15] ▼, Baumgaertel et al.[31] The solid line is the prediction of the Milner−McLeish theory using $\alpha = 1$, and the dotted line is the prediction using $\alpha = 4/3$.[5]

While we can find many experimental data for binary blends of linear polybutadienes in the literature, the value of Gr is less than 0.1 for all available literature data, except for some very recent data of Wang et al.[32] Thus, with this exception, for the available polybutadiene data the relaxation time of the long chain in the blend is not expected to be dependent on the volume fraction of the long chain. For polystyrene solutions, there are data available for which $Gr > 0.1$, but in these solutions the low molecular weight component was only slightly entangled ($M/M_e \leq 3$), and so the data are not appropriate for testing tube models.[13] We note that the critical value $Gr_c = 0.1$ from tracer diffusion studies is based on the definition $M_e = \rho RT/G_N^0$, which differs from the definition used here by a factor of 4/5. Thus, if the factor of 4/5 is accounted for, the critical Gr_c is 0.064. For our experiments, the low-molecular-weight chain has $M/M_e \approx 13$ entanglements and so is well enough entangled for the tube theory to apply. Recently, Wang et al.[32] carried out systematic experiments to determine the dependency of the long-chain reptation time on the

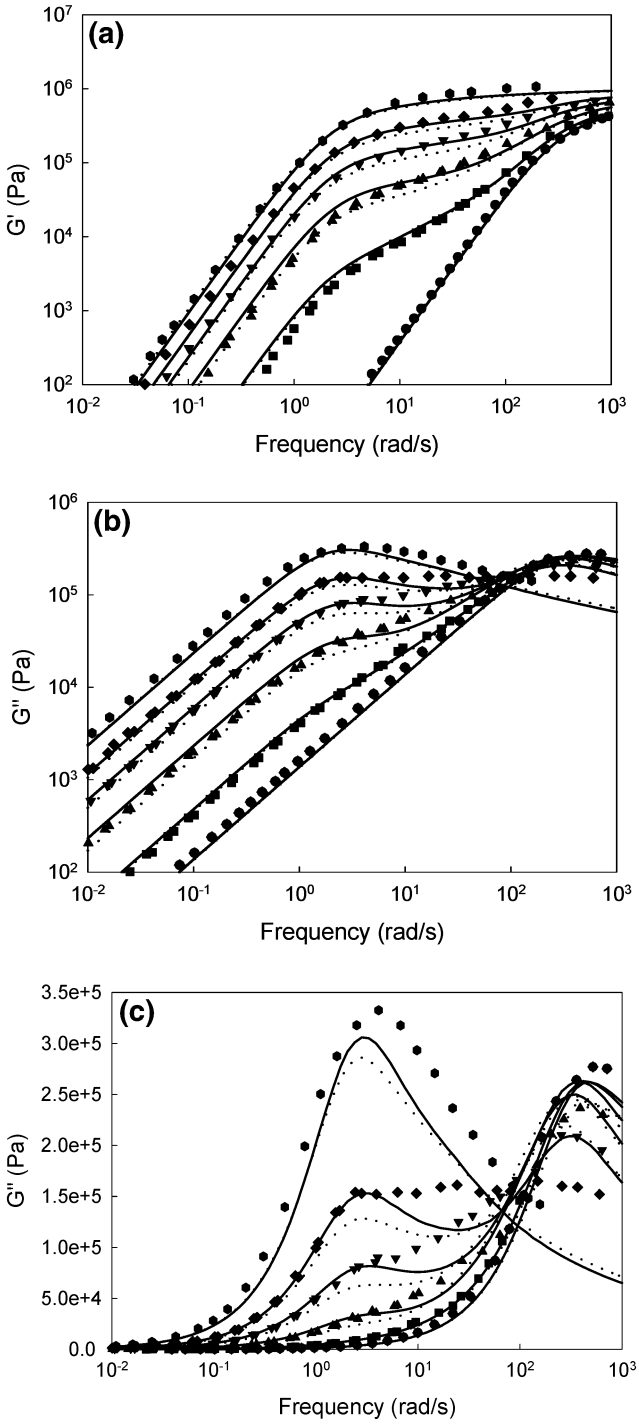

Figure 2. Comparison of model predictions with measurements for bidisperse polybutadiene linear melts containing molecular weights 36 800 and 168 000 at long-chain volume fractions, from right to left, of 0.0, 0.1, 0.3, 0.5, 0.7, and 1.0 at $T = 25$ °C. The symbols are experimental data from Struglinski and Graessley,[14] the solid lines are the model predictions with the long-chain reptation time for reptation in the undiluted tube using $\alpha = 1$, and the dotted lines are the model predictions using $\alpha = {}^4/_3$: (a) G' (log−log scale), (b) G'' (log−log scale), (c) G'' (linear−log scale).

short-chain length in binary blends of 1,4-polybutadiene, where the values of Gr range from 1.0×10^{-3} to 1.4, and we will compare these results with ours and with theoretical predictions in what follows.

Experimental data from Struglinski and Graessley[14] for the storage and loss moduli shown in Figure 2 for linear ($M_1 = 36\,800$)/linear ($M_2 = 168\,000$) blends with

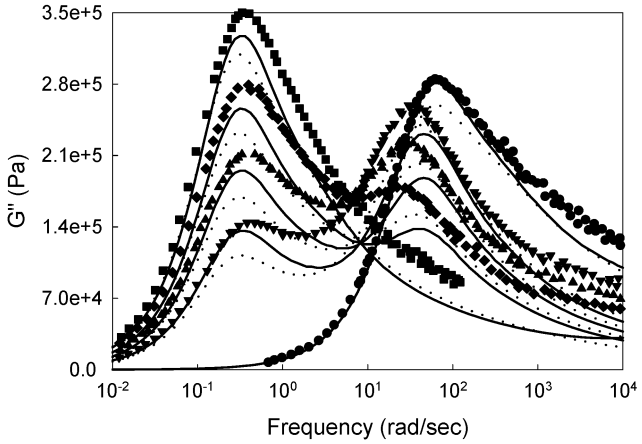

Figure 3. Comparison of model predictions with measurements for bidisperse polybutadiene linear melts containing molecular weights 70 900 and 355 000 at long-chain volume fractions, from right to left, of 0.0, 0.638, 0.768, 0.882, and 1.0 at $T = 30$ °C. The symbols are experimental data from Rubinstein and Colby,[15] the solid lines are the model predictions with the long-chain reptation time for reptation in the undiluted tube using $\alpha = 1$, and the dotted lines are the model predictions using $\alpha = {}^4/_3$.

long-chain volume fractions (ϕ_2) of 0.0, 0.1, 0.3, 0.5, 0.7, and 1.0 and are compared with the model predictions using both $\alpha = 1$ and $\alpha = {}^4/_3$. In these blends the value of Gr is 0.008, which is smaller than $Gr_c = 0.064$. Thus, for the long chain we have taken the relaxation time of the long chain as the reptation time in the undilated tube. The solid lines are the predictions using $\alpha = 1$, and the dotted lines are the predictions using $\alpha = {}^4/_3$. As shown, the model predictions using either $\alpha = 1$ or $\alpha = {}^4/_3$ are in good agreement with the experimental data.

Figure 3 compares the loss moduli of linear ($M_1 = 70\,900$)/linear ($M_2 = 355\,000$) blends with long-chain volume fractions (ϕ_2) of 0.0, 0.638, 0.768, 0.882, and 1.0 at $T = 30$ °C from Rubinstein and Colby[15] with the model predictions using both $\alpha = 1$ and $\alpha = {}^4/_3$. For the model prediction at $T = 30$ °C, the τ_e values at $T = 25$ °C are shifted to 1.98×10^{-7} s for $\alpha = 1$ and 2.21×10^{-7} s for $\alpha = {}^4/_3$ using the WLF equation. In these blends the value of Gr is 0.0024. While the model predictions do not perfectly match the experimental data, the shapes are very similar to those of the self-consistent theory of Rubinstein and Colby.[15] In addition, considering that the parameters used in the model predictions of this work are determined a priori, the model predictions seem to be reasonable.

In the case of $Gr \ll 1$, because the long chain reptates in the undilated tube, the difference of the terminal time between for $\alpha = 1$ and for $\alpha = {}^4/_3$ is not large. The predictions of this work for the blends shown in Figures 2 and 3 are very similar to those of Pattamaprom et al.[16] and Frischknecht and Milner.[17] However, the dual-constraint model presented in Pattamaprom et al. needs to solve a more complex partial differential equation to obtain solutions, and the theory of Frischknecht and Milner assumes a reptation time scaling as 3.4 power of molecular weight and needs two additional parameters, which determine the crossover from the early-time fluctuations to reptation. On the other hand, the model presented here does not need additional parameters and can be extended to a more general algorithm for polydisperse branched polymer.[33]

Figures 4 and 5 respectively compare the experimental data for a binary blend (M_1 = 20 000 and M_2 = 550 000) with the model predictions using $\alpha = 1$ and $\alpha = 4/3$ for ϕ_2 = 0.0, 0.01, 0.05, 0.1, 0.2, and 1.0. In this blend system, the value of Gr is 0.16, which is greater than the critical value $Gr_c = 0.064$. In the case of $Gr > Gr_c$, the theory of Doi et al. predicts two regimes depending on the concentration of the long chain, which are free dilation for $\phi_2 < 1/Gr$ and restricted dilation for $\phi_2 > 1/Gr$. Thus, chain reptation in the dilated tube is only valid for the case of high volume fraction of the long chain. However, since the value of Gr_c used in this work is 0.064, the terminal time predicted for free dilation is longer than the long-chain reptation time in the undilated tube. Therefore, the free dilation regime is not relevant in what we report here. Similarly, the theory of Viovy et al. also predicts two regimes, which are tube reptation in the dilated tube for $Gr > \phi_2 S_2$ and chain reptation in the undilated tube for $Gr < \phi_2 S_2$. That is, the tube reptates in the dilated tube for $\phi_2 < (M_e/M_1)^3$, and above this concentration, the long chain reptates in the undilated tube. Therefore, the concentration range where tube reptation applies is very small for the binary blend with well-entangled short chains, that is, $\phi_2 < (M_e/M_1)^3$, and we need not consider this case. Thus, in the binary blend of M_1 = 20 000 and M_2 = 550 000 we take for the terminal time either the chain reptation time in the undilated tube of Doi et al. or Viovy et al., given equivalently by eq 12 or 16, or the reptation time in the dilated tube, given in the theory of Doi et al. by eq 14.

In Figures 4 and 5, the dotted lines are the model calculations using the reptation time of the long chain in the undilated tube and the solid lines use the reptation time of the long chain in the dilated tube. As shown, for $\alpha = 1$ the model predictions using reptation in the dilated tube agrees with the experimental data, while the predictions using the reptation time in the undilated tube predict very poorly the relaxation in the low-frequency region dominated by reptation of the long chain. Because the tube reptation time is much larger than the chain reptation time in the undilated tube, choosing the tube reptation time as the terminal time would certainly not improve the model predictions. In this blend, because $M_1/M_e \approx 13$, the short chain is well entangled. In addition, because $\phi_2 M_2$ is greater than M_e for even the lowest concentration of the long chain, the long chain is always self-entangled. In this blend the relaxation behavior of the long chain at low frequency is similar to that in entangled, but low-concentration, polymer solutions of long chain only.

In the case of $\alpha = 4/3$, predictions using both the reptation time in the dilated tube and the reptation time in the undilated tube are not in agreement with experimental data. In our previous paper[28] we showed that $\alpha = 4/3$ gives good agreement with experimental data of monodisperse linear, star, and star−linear blends using the literature value for the plateau modulus ($G_N^0 = 1.15 \times 10^6$ Pa) and a slightly adjusted entanglement spacing (M_e = 1650), which is close to the value (M_e = 1543) calculated from the plateau modulus. However, in the case of $\alpha = 1$, while we could also predict the rheology of linear, star, and star−linear blends with an adjusted entanglement spacing (M_e = 2200), the required value of M_e was 40% higher than the one calculated from the plateau modulus. Therefore, the results of the earlier work suggesting $\alpha = 4/3$ is the better choice than $\alpha = 1$ seem to be contradicted by the findings reported here. In the previous paper the value of M_e was adjusted to fit the experimental data of linear and star polymers simultaneously. If we only consider linear polymers, however, we can use the value of M_e obtained from the plateau modulus without adjustment. Thus, while $\alpha = 1$ gives good agreement with experimental data for bidisperse linear polymers without needing to adjust M_e, for star polymers good agreement with data requires choosing $\alpha = 4/3$ or making a large adjustment in M_e for the case of $\alpha = 1$. Dynamic dilution theory[22] predicts that the terminal relaxation time (τ_a) of a star polymer is proportional to $\exp(2\nu(M_a/M_e)/[(\alpha + 1)(\alpha + 2)])$, where M_a is the arm molecular weight of the star polymer and $\nu = 3/2$, that is, $\tau_a \sim \exp[0.5(M_a/M_e)]$ for $\alpha = 1$ and $\tau_a \sim \exp[0.386(M_a/M_e)]$ for $\alpha = 4/3$. However, we note the slip-link simulations of Shanbhag et al.[34] found that the terminal time of the star polymer was proportional to $\exp[0.38(M_a/M_e)]$ even though $\alpha = 1$ was used in their simulation. Dilution effects predicted by the dynamic dilution theory seem to be weaker than those predicted by the slip-link simulations. Discussion of the dynamic dilution theory for the star polymer is beyond the scope of this work, but the large adjustment of M_e for the case of $\alpha = 1$ might be related to this finding of the slip-link simulations.

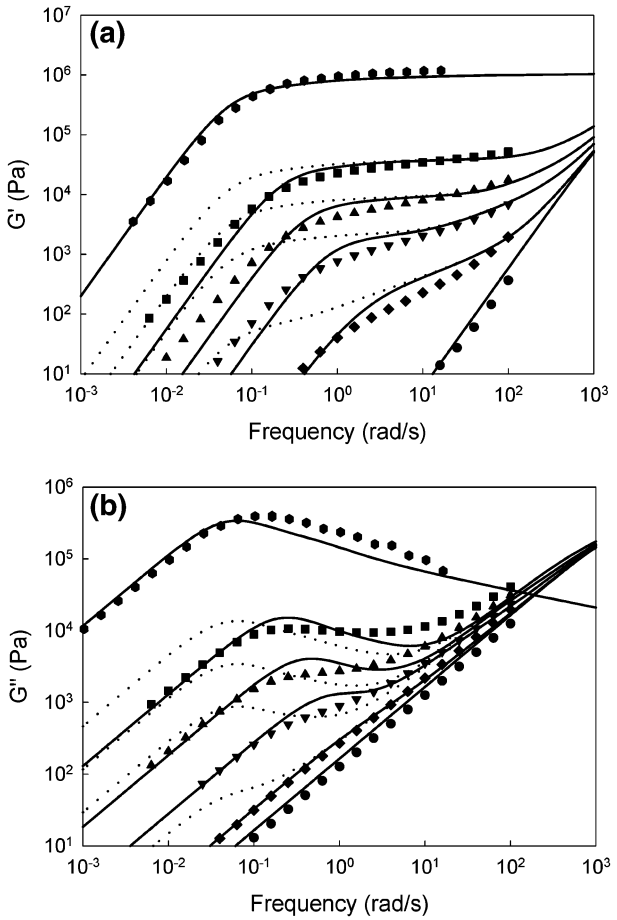

Figure 4. Comparison of model predictions for $\alpha = 1$ with measurements of (a) G' and (b) G'' for bidisperse polybutadiene linear melts containing molecular weights 20 000 and 550 000 at long-chain volume fractions, from right to left, of 0.0, 0.01, 0.05, 0.1, 0.2, and 1.0 at T = 25 °C. The dotted lines are the model predictions with the long-chain reptation taken to be in the undiluted tube (eq 12 or 16), and the solid lines are the model predictions with the long-chain reptation taken to be in the diluted tube (eq 14).

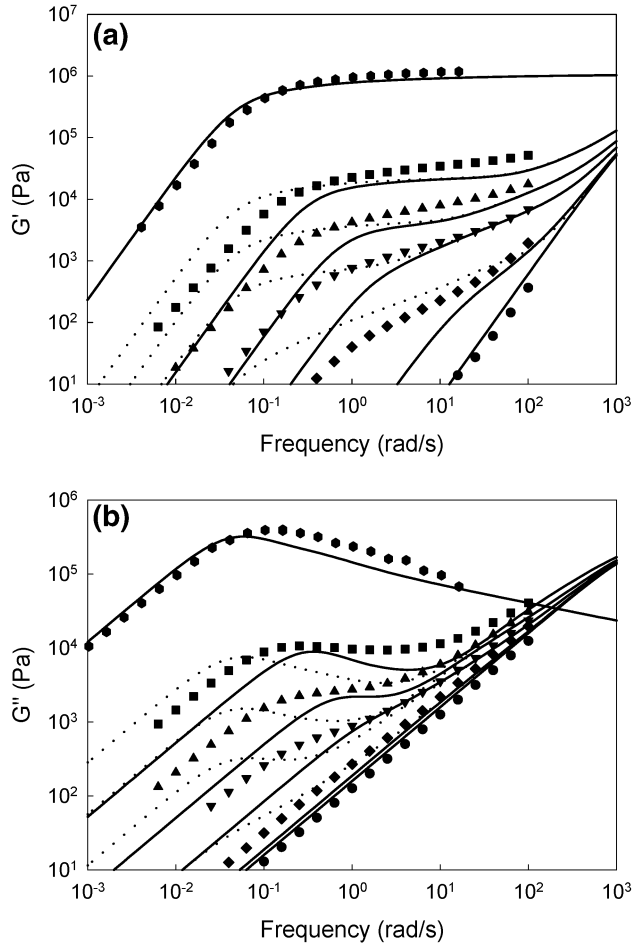

Figure 5. The same as Figure 4 except for $\alpha = {}^4/_3$.

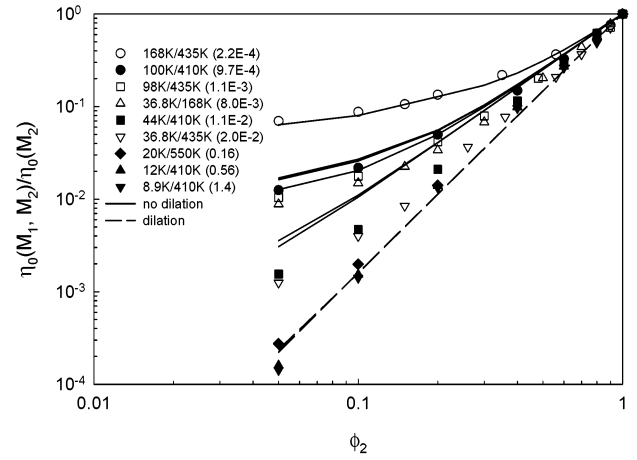

Figure 6. Normalized viscosity of binary blends of 1,4-polybutadienes. The filled symbols are experimental data from Wang et al.[32] at $T = 40$ °C (except for ◆), the open symbols are from Struglinski and Graessley[14] at $T = 25$ °C, and the filled diamonds (◆) are from this work at $T = 25$ °C. The solid lines are for model calculations using the reptation of the long chain in the undilated tube, which are carried out for all blends for which $Gr < Gr_c = 0.064$ (the six solid lines correspond to the six symbols), and the dashed lines are for the reptation of the long chain in the dilated tube, which are carried out for $Gr > Gr_c$, for which include 20K/550K (◆), 12K/410K (▲), and 8.9K/410K (▼). There are therefore three dashed lines, which almost superimpose in this figure. The predictions are calculated using $\alpha = 1$.

In Figure 6 we plot the normalized viscosity ($\eta_0(M_1,M_2)/\eta_0(M_2)$) of 1,4-polybutadienes, which is defined as the ratio of the zero-shear viscosity of the binary blend $\eta_0(M_2)$, to see the effect of constraint release. In Figure 6, we can see the clear dependency of the long-chain relaxation behavior, which dominates η_0, on the Graessley parameter, which spans from 2.2×10^{-4} to 1.4. Note the relatively large difference in the normalized viscosity that occurs between closely spaced value of Gr, $Gr = 8.0 \times 10^{-3}$ (△) and $Gr = 1.1 \times 10^{-2}$ (■). The solid lines are the model calculations using the reptation of the long chain in the undilated tube, and the dashed lines are obtained using the reptation of the long chain in the dilated tube. In these calculations $\alpha = 1$ is used. The theory predicts the results quite well with no adjustable parameters except in the region near $Gr \approx Gr_c$, which includes the data sets (■ and ▽) for which $Gr = 1.1 \times 10^{-2}$ and $Gr = 2.0 \times 10^{-2}$.

While Viovy et al.[9] ruled out reptation motion of the long chain in the dilated tube if $M_1 > M_e$, the experimental data agree well with the theoretical predictions (dashed lines) using the long chain reptation in the dilated tube if $Gr \gg Gr_c$. The concept of tube reptation of Viovy et al. predicts a dependency of the terminal relaxation time on the long chain volume fraction, i.e., $\tau \sim \phi_2(M_1/M_e)^3\tau_{d2}$. That leads to $\eta_0(M_1,M_2)/\eta_0(M_2) = \phi_2{}^3(M_1/M_e)^3$. Thus, the theory of Viovy et al. predicts a strong dependency of $\eta_0(M_1,M_2)/\eta_0(M_2)$ on the short-chain length. However, the experimental data show that the dependency of $\eta_0(M_1,M_2)/\eta_0(M_2)$ on the short-chain length is very small. Note that there are actually three dashed lines in Figure 6, which nearly superimpose and agree fairly well with the data sets for $Gr \gg Gr_c$, which are the bottom three data sets (◆, ▲, and ▼) in Figure 6. This supports the theory of Doi et al., which predicts no dependency of $\eta_0(M_1,M_2)/\eta_0(M_2)$ on M_1, rather than that of Viovy et al., in the region of $Gr \gg Gr_c$. We have therefore provided evidence here that reptation of the long chain takes place in the dilated tube, in agreement with the theory of Doi et al., when $Gr \gg Gr_c$, with Gr_c in the vicinity of 0.064, the value established by diffusion measurements.

Conclusions

The linear viscoelastic properties of binary blends of monodisperse linear 1,4-polybutadienes spanning a range of values of the "Graessley parameter" $Gr \equiv M_2M_e{}^2/M_1{}^3$ were compared to the predictions of the Milner−McLeish theory, which we extended to bidisperse linear polymers, allowing for reptation of the long chain in either a dilated or undilated tube. We find reasonable agreement between experimental data and the Milner−McLeish theory if we let the long chain reptate in the dilated tube for $Gr \gg Gr_c$, and in the undilated tube if $Gr \ll Gr_c$, with $Gr_c \approx 0.064$, as established by diffusion measurements and if we take the dilution exponent α to be unity. However, in the case of $\alpha = {}^4/_3$, while the predictions for the case of $Gr \ll Gr_c$ are similar to those of $\alpha = 1$, the predictions for the case of $Gr \gg Gr_c$ do not match experimental data. In the crossover region near $Gr \approx Gr_c$, neither reptation in the dilated tube nor in the undilated tube give accurate predictions.

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