Constraint Release in Polymer Melts: Tube Reorganization versus Tube Dilation

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ABSTRACT: We consider the concepts of reptation and constraint release to model the dynamics of polydisperse linear polymers. The mechanisms of constraint release at work in concentrated polymer solutions can be divided into two categories. Tube dilation occurs when constraint release causes a widening of the effective tube confining the chain. Tube reorganization refers to relaxation of the tube due to motion of the surrounding chains without changing the effective tube diameter. By comparing the motion of the chain with the motion of the tube, we determine the effective tube diameter and conclude that the tube only dilates when some of the constraints are below the entanglement molecular weight. In binary mixtures of long and short chains that have entanglements between the long chains, Rouse motions of the tube are only allowed up to the length scale of entanglements between the long chains, a_L. We suggest that tube reorganization beyond those length scales occurs by reptation of the tube in the supertube of diameter a_L. Experimental tests are suggested to distinguish between the predictions of the newly proposed process of tube reptation and the older idea of tube dilation.

1. Introduction

The dynamic properties of monodisperse high molecular weight (entangled) polymers are qualitatively well described by the reptation model.[1,2] Each chain is supposed to perform a curvilinear 1-dimensional diffusion along a tube[1,3] representing the topological constraints exerted by the surrounding chains. The simplification of the many-chain problem to a single chain moving in a tube of permanent obstacles enabled a solution to be reached, but this picture was rapidly shown to be oversimplified.

In actual polymer melts (or entangled solutions), the lifetime of obstacles is finite, leading to some *constraint release*[4-8] not accounted for in the original theory. This process was originally termed *tube reorganization* by de Gennes.[4,5] Constraint release has also been referred to as "*tube renewal*", but this has led to some confusion because reptation also leads to a "renewal" of the tube. We use the term tube reorganization here to describe relaxation processes of the chain due to constraint release, whenever the effective diameter of the tube is unchanged.

The first models proposed to account for constraint release[6,7] treated the tube itself as a Rouse chain, with elementary segments of the size of the tube diameter, and a jump time proportional to the lifetime of the obstacles. In this approach, the relaxation of a chain results from *two independent and concurrent processes*, reptation inside the tube and tube reorganization, the latter depending on the environment. For a homopolymer melt, tube reorganization was shown to be slower than reptation and have little effect on diffusion properties.[6,7] Later on, Graessley[8] showed that tube reorganization could, nevertheless, significantly affect viscoelastic properties, because of the very different mode spectra of Rouse and reptation dynamics.

Another consequence of constraint release, called *tube dilation*, was later proposed. If the time taken by a chain to explore the volume between obstacles is longer than the lifetime of these obstacles, they become irrelevant to the dynamics of the chain. The chain feels a tube "dilated" up to the scale at which its dynamics eventually becomes comparable with the lifetime of the "walls" of the tube. This idea, first proposed as an alternate treatment of tube reorganization,[9,10] was then recognized as an independent process and has recently been applied to polydisperse melts of linear chains,[11,12] melts of stars,[13] and branched polymers of more complex topology.[14-16]

In spite of this significant amount of work, we believe that the problem of constraint release is still not well understood. Our view of both tube reorganization and tube dilation[17] leads to some predictions that are qualitatively different from those of ref 11. The purpose of this paper is to describe these predictions.

We start by reviewing Rouse and reptation dynamics in section 2, followed by a review of the solved problem of a chain surrounded by mobile obstacles with a single lifetime in section 3. We next consider the problem of a chain surrounded by mobile and immobile obstacles in section 4, where the new concept of reptation of the tube is introduced. This leads us to the case of mixtures of long chains (polymerization index N_L) and short ones (polymerization index N_S) of the same species, in section 5. Finally, we compare our predictions with those of Doi, Graessley, Helfand, and Pearson[11] in section 6 and suggest experiments to distinguish the two ideas.

Throughout the paper, we make the following assumptions:

(1) We restrict ourselves to screened excluded-volume interactions, i.e., cases in which the longer chains are not swollen by the smaller ones[18] (this would occur for $N_L > N_S^2$, roughly). The mean-square end-to-end distance of a chain is therefore always $R^2 = Nb^2$, where b is the Kuhn length and N is the number of (Kuhn) monomers.

(2) Hydrodynamic interactions are also assumed to be screened. This assumption is certainly a reasonable one for melts.

(3) In order to focus on constraint release, we ignore crossover effects due to the finite size of real chains such as tube length fluctuations[19,20] and the divergence of the tube diameter[21] as N approaches N_e. We therefore always consider unentangled modes of relaxation to be Rouse-

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like and entangled modes of a single chain to be purely reptative.

(4) We neglect all numerical prefactors of order unity to focus on physical concepts.

2. Rouse and Reptation Dynamics

The Rouse model was originally developed to describe the dynamics of a chain in free space (or dilute solution). Each of the N monomers (of Kuhn length b) is represented by a bead, and the beads are connected by springs. There is a fundamental time τ associated with the motion of a monomer. The longest relaxation time of the free Rouse chain is

$$T_{Rouse}^{chain} \equiv T_{Rouse}(\tau,N) \cong \tau N^2 \qquad (1)$$

The mean-square displacement of a monomer in the free Rouse chain is[1]

$$\Phi_{Rouse}^{chain} \equiv \Phi_{Rouse}(t;\tau,N,b) \cong$$

$$\begin{cases} b^2(t/\tau)^{1/2} & \tau < t < T_{Rouse}(\tau,N) \\ b^2 N t/T_{Rouse}(\tau,N) & t > T_{Rouse}(\tau,N) \end{cases} \qquad (2)$$

In the reptation model for dynamics of entangled polymer melts and solutions, the Rouse motions of the chain are confined to a tube made up of surrounding chains. The *tube diameter*, a, has a phenomenological status, although some rather general connections with molecular parameters have been recently exhibited.[21,22] The number of monomers in an entanglement strand, N_e, is determined from random-walk statistics

$$N_e = a^2/b^2 \qquad (3)$$

The longest relaxation time of the reptation model is

$$T_{rep}^{chain} \equiv T_{rep}(\tau,N,N_e) \cong T_{Rouse}(\tau,N) \, N/N_e \cong \tau N^3/N_e \qquad (4)$$

The mean-square displacement of a monomer in the reptation model is[1]

$$\Phi_{rep}^{chain} \equiv \Phi_{rep}(t;\tau,N,N_e,b) \cong$$

$$\begin{cases} b^2(t/\tau)^{1/2} & \tau < t < T_{Rouse}(\tau,N_e) \\ b^2 N_e(t/T_{Rouse}(\tau,N_e))^{1/4} & T_{Rouse}(\tau,N_e) < t < T_{Rouse}(\tau,N) \\ b^2 N(t/T_{rep}(\tau,N,N_e))^{1/2} & T_{Rouse}(\tau,N) < t < T_{rep}(\tau,N,N_e) \\ b^2 N t/T_{rep}(\tau,N,N_e) & t > T_{rep}(\tau,N,N_e) \end{cases} \qquad (5)$$

Throughout the paper we use the symbols T and Φ to denote relaxation time and mean-square displacement, respectively. Moreover, the functions defined in eqs 1, 2, 4, and 5 will be utilized to describe other Rouse and reptative motions, with different parameters entering into the functions (for example, the Rouse time of an entanglement strand, $T_{Rouse}(\tau,N_e) = \tau N_e^2$, has already been used).

The mean-square monomer displacements of the Rouse and reptation models (eqs 2 and 5) are compared in Figure 1. For times shorter than the Rouse time of an entanglement strand, the predictions are identical (the chain in the reptation model has not yet "discovered" that it is confined to the tube). Beyond that time scale, the mean-square displacement in the reptation model is slower due to the presence of the tube. The long-time behavior from both models is Fickian diffusion, with the diffusion coefficient of the reptation model being smaller by a factor of N/N_e.

3. Terminal Time of a Chain Surrounded by Mobile Obstacles

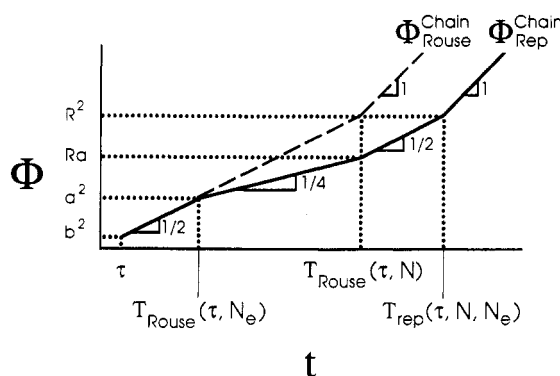The reptation predictions of the previous section are for a chain embedded in a fixed tube. The problem of a

Figure 1. Time dependence of the mean-square displacement of a monomer for the Rouse model (dashed line) and the reptation model (solid line). Logarithmic scales.
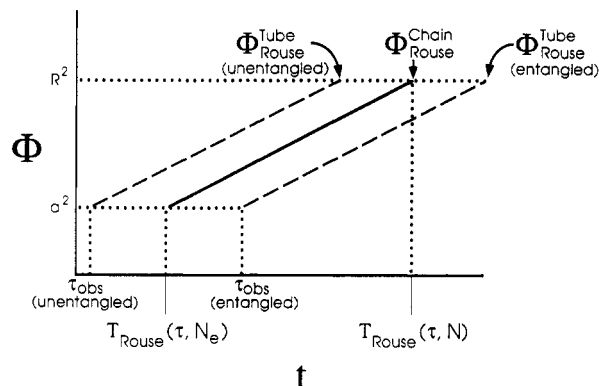

Figure 2. Time dependence of the mean-square displacement of the chain (solid line) and the tube (dashed lines) due to Rouse motion. Two possibilities exist: If the tube moves faster than the chain, the chain is unentangled. If the tube moves slower than the chain, the chain is entangled. Logarithmic scales.

chain trapped in a tube of mobile obstacles (with a single lifetime) has been solved,[8,23] but we review those results here (cast in our notation) as they are useful for understanding subsequent sections.

In the original "Rouse tube" reorganization models,[6-8,23-25] the tube relaxes in precisely the same way as a Rouse chain. The Rouse time for the tube (or longest tube reorganization time) is

$$T_{Rouse}^{tube} \equiv T_{Rouse}(\tau_{obs},N/N_e) \qquad (6)$$

where τ_{obs} is the obstacle lifetime. The mean-square displacement of a tube segment by Rouse motion is

$$\Phi_{Rouse}^{tube} \equiv \Phi_{Rouse}(t;\tau_{obs},N/N_e,a) \qquad (7)$$

In order to determine whether the chain "feels" the constraints imposed by the obstacles (and thus is termed entangled), we need to compare the Rouse motion of the tube with the Rouse motion of the chain. Such a comparison is made in Figure 2 for lengths between the tube diameter a and the coil size R. There are two possibilities: If the motion of the tube is faster than that of the chain (when $\tau_{obs} < T_{Rouse}(\tau,N_e)$), the chain does not feel the presence of the obstacles and is *unentangled* (and free to relax by simple Rouse relaxation; eqs 1 and 2). If, on the other hand, the motion of the tube is slower than the motion of the chain, the chain is confined in the tube. There are then two relaxation mechanisms available to the chain: reptation of the chain in the tube and Rouse relaxation of the tube. Because of the assumed independence of the reptation and tube reorganization processes,
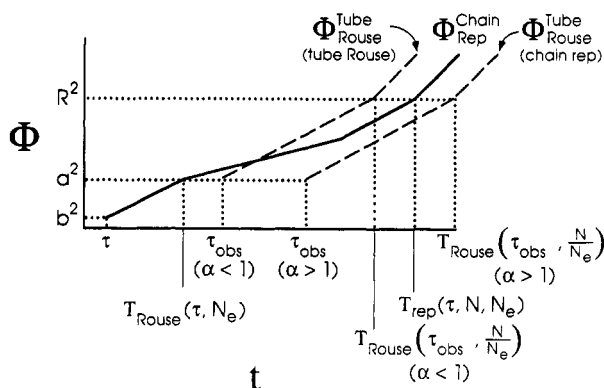
Figure 3. Time dependence of the mean-square displacement of the chain due to chain reptation (solid line) and due to Rouse tube rearrangement (dashed lines). There are two possibilities: If $\alpha < 1$, the terminal relaxation is dominated by Rouse tube rearrangement. If $\alpha > 1$, the terminal relaxation is dominated by chain reptation. Logarithmic scales.
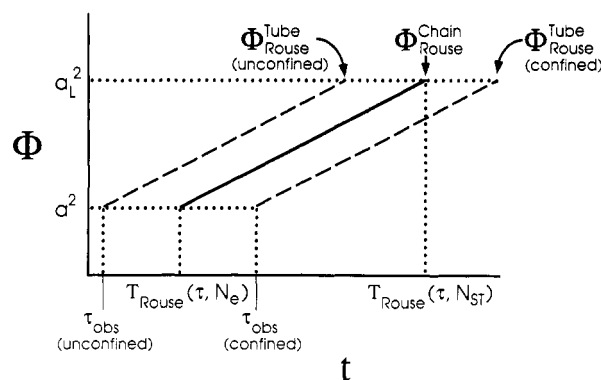

Figure 4. Time dependence of the mean-square displacement of the chain (solid line) and the tube (dashed lines) due to Rouse motion. Two possibilities exist: If the tube moves slower than the chain, the chain is confined to the tube made up by the mobile obstacles. If the tube moves faster than the chain, the chain does not feel the mobile obstacles and is only confined to the supertube of permanent obstacles. Logarithmic scales.

the net mean-square displacement of the chain is

$$\Phi(t) \cong \Phi_{rep}(t;\tau,N,N_e,b) + \Phi_{Rouse}(t;\tau_{obs},N/N_e,a) \quad (8)$$

and the terminal relaxation time, T, of the chain is given by

$$1/T \cong 1/T_{rep}(\tau,N,N_e) + 1/T_{Rouse}(\tau_{obs},N/N_e) \quad (9)$$

The fastest process dominates the relaxation. We introduce the dimensionless parameter

$$\alpha \equiv T_{Rouse}(\tau_{obs},N/N_e)/T_{rep}(\tau,N,N_e)$$
$$= (N_e/N)(\tau_{obs}/T_{Rouse}(\tau,N_e)) \quad (10)$$

The terminal relaxation is dominated[7] by reptation for $\alpha > 1$ and by tube reorganization for $\alpha < 1$. We can see this schematically in Figure 3, where mean-square displacements from reptation of the chain and Rouse motion of the tube are compared. When $\alpha < 1$ (labeled *tube Rouse* in Figure 3), tube reorganization controls the terminal relaxation time. When $\alpha > 1$, reptation controls the terminal time (labeled *chain reptation* in Figure 3).

There are, therefore, three possibilities for the case of a chain surrounded by obstacles with a single lifetime. If the obstacles are faster than the chain (when $\tau_{obs} < T_{Rouse}(\tau,N_e)$), the chain is unentangled and relaxes completely by Rouse motions of the chain. If the obstacles are slower than the chain, either $\alpha < 1$ and relaxation of the chain is dominated by Rouse motion of the tube or $\alpha > 1$ and relaxation is dominated by reptation of the chain in its tube.

In the particular case of a mixture of dilute long chains (of N_L monomers) entangled with shorter chains (of N_S monomers) with the same chemical structure, $\tau_{obs} \cong T_{rep}(\tau,N_S,N_e)$ and α becomes

$$\alpha = (N_e/N_L)(N_S/N_e)^3 = N_S^3/(N_L N_e^2) \quad (11)$$

The criterion for the unentangled regime in this case becomes $N_S < N_e$, which means that the long chains only relax by Rouse chain motion if the short chains are below the entanglement threshold. The above predictions are in reasonable qualitative agreement with experiments performed on long chains embedded in a "sea" of shorter chains,[26-30] although the experimental exponent for the dependence of τ_{obs} on N_S seems closer to 2.5 than to the theoretical value of 3 corresponding to reptation. Some explanations for this discrepancy have been proposed,[27,31] but it may as well be a crossover effect, and the issue remains unsettled. We ignore this point in what follows

and assume that the obstacle lifetime is equal to the reptation time of the surrounding chains.

4. Terminal Time of a Chain among Mobile and Immobile Obstacles

As an introduction to bimodal melts, we treat the simpler model of a single chain in a uniform mixture of mobile and permanent obstacles. If these permanent obstacles are dense enough, they may form around the test chain a permanent tube of diameter a_L, the average distance between permanent obstacles. To avoid confusion with the transient tube associated with the mobile obstacles, we call this permanent tube the *supertube*. The average number of permanent obstacles along the supertube is

$$\beta \equiv (R/a_L)^2 \quad (12)$$

and the average number of monomers in the chain between permanent obstacles is

$$N_{ST} = N/\beta \quad (13)$$

The parameter β plays an essential role in the theory: If $\beta < 1$ ($a_L > R$), a typical long chain does not "see" more than one permanent obstacle at a time, and the description of section 3 remains valid. In the opposite case, we have to reconsider the possible mechanisms of constraint release.

In order to determine the mechanism of constraint release at work when $\beta > 1$, we must first determine whether the chain "feels" the constraints from the mobile obstacles (with obstacle lifetime τ_{obs}). In this case, the length range to look for confinement of the chain is between the bare tube diameter, a, and the supertube diameter, a_L. We therefore compare Rouse motion of the tube with Rouse motion of the chain in Figure 4 for length scales between a and a_L. Even for the other modes of motion of the tube discussed below, tube motion is Rouse-like for length scales smaller than a_L. As in section 3, there are only two possibilities: If the motion of the tube is faster than that of the chain (when $\tau_{obs} < T_{Rouse}(\tau,N_e)$), the chain is not confined by the mobile obstacles at all. We refer to this as the *tube dilation* regime (after ref 11). *The tube is fully dilated*, and the fastest mode of relaxation of the chain is reptation of the chain in the large tube of diameter a_L. If, on the other hand, the motion of the tube is slower than the motion of the chain, the chain is confined by the mobile obstacles. The effective tube diameter for the chain is then a. In this case we predict that there are two modes of motion available to the chain, exactly analogous to
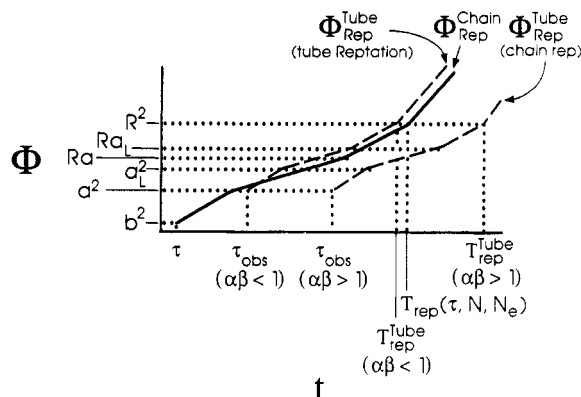
Figure 5. Time dependence of the mean-square displacement of the chain due to chain reptation (solid line) and due to reptative tube rearrangement (dashed lines). There are two possibilities: If $\alpha\beta < 1$, the terminal relaxation is dominated by reptative tube rearrangement. If $\alpha\beta > 1$, the terminal relaxation is dominated by chain reptation. Logarithmic scales.

section 3: reptation of the chain in the tube of diameter a and tube reorganization.

Earlier treatments of tube reorganization in the presence of obstacles with different lifetimes introduced a distribution of jump times in the rescaled Rouse equation.[24,25] For a nonvanishing fraction of permanent obstacles, this idea would lead to an infinite terminal time for tube reorganization. We believe that this prediction is wrong—permanent obstacles along the tube slow down the tube reorganization process, but they do not stop tube reorganization. The original tube reorganization hypothesis amounts to say that the tube does exactly what a Gaussian chain would do, apart from a renormalized jump time. In the presence of permanent obstacles with average distance a_L, we know that the dynamics of a chain with N/N_e steps of length a and jump time τ_{obs} would be well described by reptation in a "supertube" of diameter a_L. We believe that this is the correct model for the tube, as well. *The tube of diameter a reptates in a larger permanent tube of diameter a_L*, called the supertube. The mean-square displacement of a monomer moving by reptation of the tube in the supertube is

$$\Phi_{rep}^{tube} \equiv \Phi_{rep}(t;\tau_{obs},N/N_e,N_{ST}/N_e,a) \quad (14)$$

The terminal time for reptation of the tube in the supertube is

$$T_{rep}^{tube} \equiv T_{rep}(\tau_{obs},N/N_e,N_{ST}/N_e)$$
$$= \beta T_{Rouse}^{tube} = \alpha\beta T_{rep}(\tau,N_L,N_e) \quad (15)$$

The presence of permanent obstacles slows down tube reorganization, as expected, but it does not stop it because the tube can reptate. Note also, that T_{Rouse}^{tube} (eq 6) and T_{rep}^{tube} (eq 15) smoothly crossover at $R = a_L$ ($\beta = 1$).

We assume that the processes of chain reptation and tube reorganization are independent (as was done in section 3). The net mean-square displacement of the chain (with $\beta > 1$ and $\tau_{obs} > T_{Rouse}(\tau,N_e)$) can be approximated by a simple sum

$$\Phi(t) \simeq \Phi_{rep}(t;\tau,N,N_e,b) + \Phi_{rep}(t;\tau_{obs},N/N_e,N_{ST}/N_e,a) \quad (16)$$

in analogy with eq 8. The terminal relaxation time, T, is given by

$$1/T \simeq 1/T_{rep}(\tau,N,N_e) + 1/T_{rep}(\tau_{obs},N/N_e,N_{ST}/N_e) \quad (17)$$

In Figure 5 we compare mean-square displacements of

a monomer due to reptation of the chain in its tube with those due to reptation of the tube in the supertube. Reptation of the tube in the supertube dominates the terminal relaxation when $\alpha\beta < 1$ (we refer to this as *tube reptation* in Figure 5), and reptation of the chain in its tube (of diameter a) dominates for $\alpha\beta > 1$ (*chain reptation*).

In summary, three possibilities exist for the case of a long chain surrounded by mobile and immobile obstacles. If the mobile obstacles are faster than the chain, the chain feels a tube that is fully dilated to diameter a_L. If the mobile obstacles are slower than the chain, either $\alpha\beta < 1$ and relaxation of the chain is dominated by reptative motion of the tube or $\alpha\beta > 1$ and relaxation occurs predominantly by ordinary chain reptation in the bare tube of diameter a.

Note also that the border between tube dilation and tube reptation corresponds to $\tau_{obs} = T_{Rouse}(\tau,N_e)$. For the special case of a binary blend of nondilute long chains (with N_L monomers) and short chains (with N_S monomers) of the same chemical species, this occurs when $N_S = N_e$. Thus in a homopolymer blend, one only encounters a fully dilated tube when the short chains are unentangled and act as solvent! Once the short chains consist of more than N_e monomers, the long chain is confined in the tube of short chains. Tube dilation ideas can be important for miscible blend of two different polymers, however. Consider a miscible blend of short chains of species A and long chains of species B, where the elementary time for monomer motion of the short chains τ_A is faster than that of the long chains τ_B. In that instance the regime of tube dilation is extended to include some short chain lengths above the critical molecular weight for entanglement of the A chains in the blend. Tube dilation has also been shown to be important for dynamics of branched polymers.[13-16]

5. Linear Viscoelasticity of a Bimodal Homopolymer Melt

We now consider a blend of long chains (of N_L monomers) and short chains (of N_S monomers) with the same chemical structure. The volume fraction of long chains is ϕ (the volume fraction of short chains is $1 - \phi$). We ignore the case $N_S < N_e$, which can be treated as a solution of long chains in a Θ solvent (with screened hydrodynamic interactions) and does not require a constraint release approach. Indeed, in this domain our model crosses over to Rouse behavior for $\beta < 1$ and to reptation in a tube of size a_L for $\beta > 1$, each with a fundamental time τ for monomer motion that may depend on N_S through the dependence of a local friction coefficient on N_S (which also changes the glass transition temperature of the sample). These predictions are identical with those of the Rouse and reptation models in solution.

Terminal Relaxation Time. To transpose from a model of point obstacles (with $\tau_{obs} > T_{Rouse}(\tau,N_e)$) to bimodal melts, we need an expression for the obstacle lifetime τ_{obs}. According to the original ideas about tube rearrangement,[6-8] the relevant lifetime for short-lived obstacles is the terminal time of the short chains, which we identify with their reptation time

$$\tau_{obs} \simeq T_{rep}(\tau,N_S,N_e) \simeq \tau N_S^3/N_e \quad (18)$$

Equivalently, the lifetime of the long-lived obstacles is the terminal time of the long chains, i.e., the longest relaxation time in the system. In a qualitative approach, the lifetime of these obstacles can be taken as infinite because constraint release processes due to motion of the long chains would just be starting when the system reaches
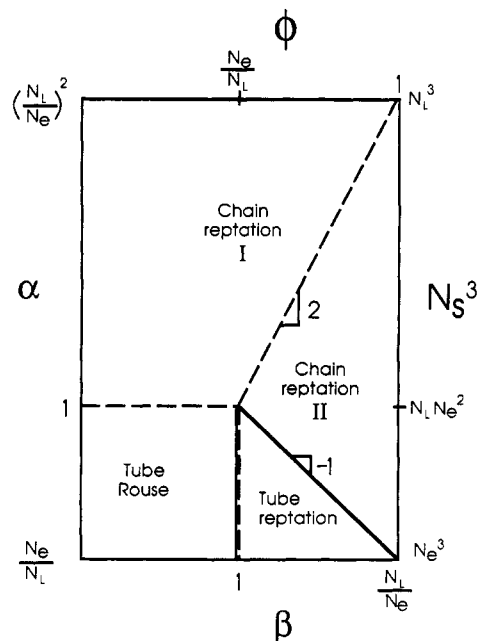
Figure 6. Four regimes of terminal relaxation for bimodal homopolymer melts shown in the α,β parameter space. Solid lines represent borders between different predictions for terminal time. Dashed lines represent borders between different predictions for terminal modulus. Logarithmic scales.
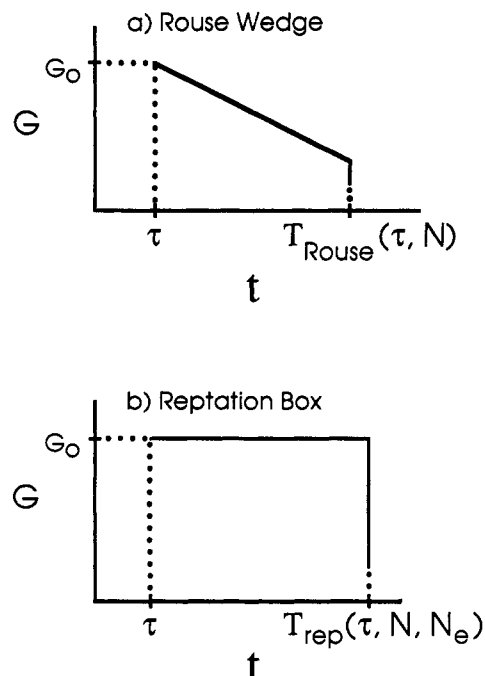

Figure 7. Schematic representations of the two types of relaxation moduli: (a) Rouse relaxation modulus (a wedge) and (b) reptation relaxation modulus (a box). Logarithmic scales.

its longest relaxation time. Therefore, the results of section 4 are applicable here, and three possibilities exist for the terminal relaxation time of binary blends of linear chains. These possibilities are shown in the α,β parameter space in Figure 6. For $\alpha < 1$ and $\beta < 1$ the relaxation is dominated by *Rouse tube* rearrangement

$$T \simeq T_{\text{Rouse}}(\tau N_S^3/N_e, N_L/N_e) \simeq \tau N_S^3 N_L^2/N_e^3$$
$$\beta < 1 \text{ and } \alpha < 1 \quad (19)$$

For $\beta > 1$ and $\alpha\beta < 1$ the relaxation is dominated by *tube reptation*

$$T \simeq T_{\text{rep}}(\tau N_S^3/N_e, N_L/N_e, N_L/(\beta N_e))$$
$$\simeq \beta\tau N_S^3 N_L^2/N_e^3 \quad \beta > 1 \text{ and } \alpha\beta < 1 \quad (20)$$

For the remainder of the α,β parameter space, terminal relaxation is controlled by *chain reptation* (in a tube of size a)

$$T \simeq T_{\text{rep}}(\tau, N, N_e) \simeq \tau N_L^3/N_e \quad (21)$$

$$(\beta < 1 \text{ and } \alpha > 1) \text{ or } (\beta > 1 \text{ and } \alpha\beta > 1)$$

Concentration Dependence of the Tube Diameter. To remain general, we have deliberately postponed discussion of the dependence of a_L (or equivalently, β) upon ϕ. This is an important issue, however, since the new process of tube reptation depends on the size of the supertube (i.e., through β in eq 20). The problem is that the concentration dependence of the tube diameter in the absence of excluded volume is still a controversial subject. We shall not attempt to settle this point, which has been discussed extensively in the literature (see refs 21, 22, 32, 33, and references therein). Following earlier work,[3,32] in semidilute Θ solution, a_L should scale as $\phi^{-1/2}$, so that

$$\beta \equiv (R/a_L)^2 = \phi/\phi_c = \phi N_L/N_e \quad (22)$$

where ϕ_c is the critical concentration for entanglement of long chains in a Θ solvent (different from the overlap concentration ϕ^*). This scaling is presently the most

widely used (it is, for instance, the scaling adopted in ref 11). Therefore, for the sake of simplicity and comparison, we also use this scaling in the following derivations of viscoelastic functions (alternate treatments using the scaling laws proposed in ref 21 ($\beta \simeq (N_L/N_e)\phi^2$) or ref 33 ($\beta \simeq (N_L/N_e)\phi^{4/3}$) would proceed in the same way).

Relaxation Modulus. In order to clarify the role of various constraint release processes and to estimate the viscosity of binary blends, we now derive the relaxation modulus in the terminal region $G(t)$, assuming only chain reptation and tube rearrangement relaxation processes. The relaxation modulus of a free Rouse chain[1] is

$$G(t)/G_0 = (1/N) \sum_{p=1}^{N} \exp[-p^2 t/T_{\text{Rouse}}(\tau, N)] \quad (23)$$

Since this Rouse relaxation spectrum has an equally weighted mode distribution, an approximate graphical representation of the spectrum is a *wedge* (on a logarithmic scale) shown in Figure 7a (after refs 11 and 28).

The relaxation modulus of the reptation model[1,2] (for a Rouse chain in a tube) is identified with $\mu(t)$, the fraction of the tube still occupied after time t

$$G(t)/G_0 = \mu(t) \simeq \sum_{p=\text{odd}} (1/p^2) \exp[-p^2 t/T_{\text{rep}}(\tau, N, N_e)] \quad (24)$$

The reptation relaxation spectrum has an unequally weighted distribution of modes, with the majority of the stress being relaxed in the vicinity of $T_{\text{rep}}(\tau, N, N_e)$. We therefore represent it schematically in Figure 7b as a *box*. Following earlier work,[8,11,23-25] we assume independence of reptation and constraint release, and the blending law:[23]

$$G(t)/G_0 = \phi\mu_L(t) R_L(t) + (1 - \phi)\mu_S(t) R_S(t) \quad (25)$$

The functions $\mu_L(t)$ and $\mu_S(t)$ represent relaxation of the long and short chains in their respective tubes (here only due to reptation), given by eq 24. The functions $R_L(t)$ and $R_S(t)$ represent the relaxation of stress by tube rearrangement relaxation processes for the long and short chains,

respectively. The function $R_S(t)$ remains of order unity during the reptation of the short chains.[34] Thus, it only remains to derive expressions for $R_L(t)$, the relaxation of the long chains by tube rearrangement, for which there are two possibilities.

(i) For $\beta < 1$, constraint release occurs by Rouse tube rearrangement (see section 3). $R_L(t)$ is given by the Rouse relaxation function (eq 23) applied to the tube (the reptation time of the short chains play the role of τ, and N is replaced by N_L/N_e, the number of tube segments):

$$R_L(t) =$$

$$(N_e/N_L) \sum_{p=1}^{N_L/N_e} \exp[-p^2 t / T_{Rouse}(\tau N_S^3/N_e, N_L/N_e)]$$

$$\beta < 1 \quad (26)$$

This corresponds to a wedge-shaped spectrum, with a terminal value (defined as the value of $R_L(t)$ at the terminal relaxation time)

$$R_{term} \cong$$

$$R_L(T_{Rouse}(\tau N_S^3/N_e, N_L/N_e)) \cong N_e/N_L \quad \beta < 1 \quad (27)$$

(ii) For $\beta > 1$, $R_L(t)$ corresponds to Rouse motion of the tube up to the Rouse time of an entanglement strand of the supertube $T_{Rouse}(\tau N_S^3/N_e, N_L/(\beta N_e))$, followed by reptation of the tube in the supertube. $R_L(t)$ is given by the product of two relaxation functions: (1) the Rouse relaxation function of the supertube entanglement strand (eq 23, with $N_L/(\beta N_e)$ the number of monomers in that strand) and (2) the reptation relaxation function (eq 24) applied to the tube (again, the reptation time of the short chains plays the role of τ, N is replaced by N_L/N_e, the number of tube segments, and the number of tube segments between long entanglements, $N_L/(\beta N_e)$, is the effective N_e). The result is, for $\beta > 1$

$$R_L(t) = \beta(N_e/N_L) \times$$

$$\sum_{p=1}^{N_L/(\beta N_e)} \exp[-p^2 t / T_{Rouse}(\tau N_S^3/N_e, N_L/N_e)] \times$$

$$\sum_{p=odd} (1/p^2) \exp[-p^2 t / T_{rep}(\tau N_S^3/N_e, N_L/N_e, N_L/(\beta N_e))]$$

$$(28)$$

The terminal part of tube reptation has a box-shaped spectrum with a terminal value

$$R_{term} \cong R_L(T_{rep}(\tau N_S^3/N_e, N_L/N_e, N_L/(\beta N_e))) \cong$$

$$\beta(N_e/N_L) \cong \phi \quad (29)$$

We are now in a position to estimate the shape of the relaxation modulus, $G(t)$, for the different regimes shown in Figure 6. There are five cases (a–e below), which we need to consider for the relaxation modulus of binary blends of homopolymers, and the results are in Figure 8a–e. Cases a and b are for $\beta < 1$ and thus correspond to the treatment in section 3. Cases c–e are for $\beta > 1$, treated in section 4.

(a) The case of nonentangled long chains ($\beta < 1$) with terminal relaxation due to chain reptation ($\alpha > 1$) appears in Figure 8a. The contribution of the short chains to the relaxation is the filled box. Due to the boxlike approximation of reptation, the relaxation of the long chains (full line) follows the fastest of the chain reptation (dash-dotted box) and Rouse tube rearrangement (dashed wedge) processes. The value of the modulus at the terminal time

$$G_{term} \cong G_0 \phi(N_S/N_L)^{3/2} \quad \beta < 1 \text{ and } \alpha > 1$$

$$\text{(chain reptation I)} \quad (30)$$
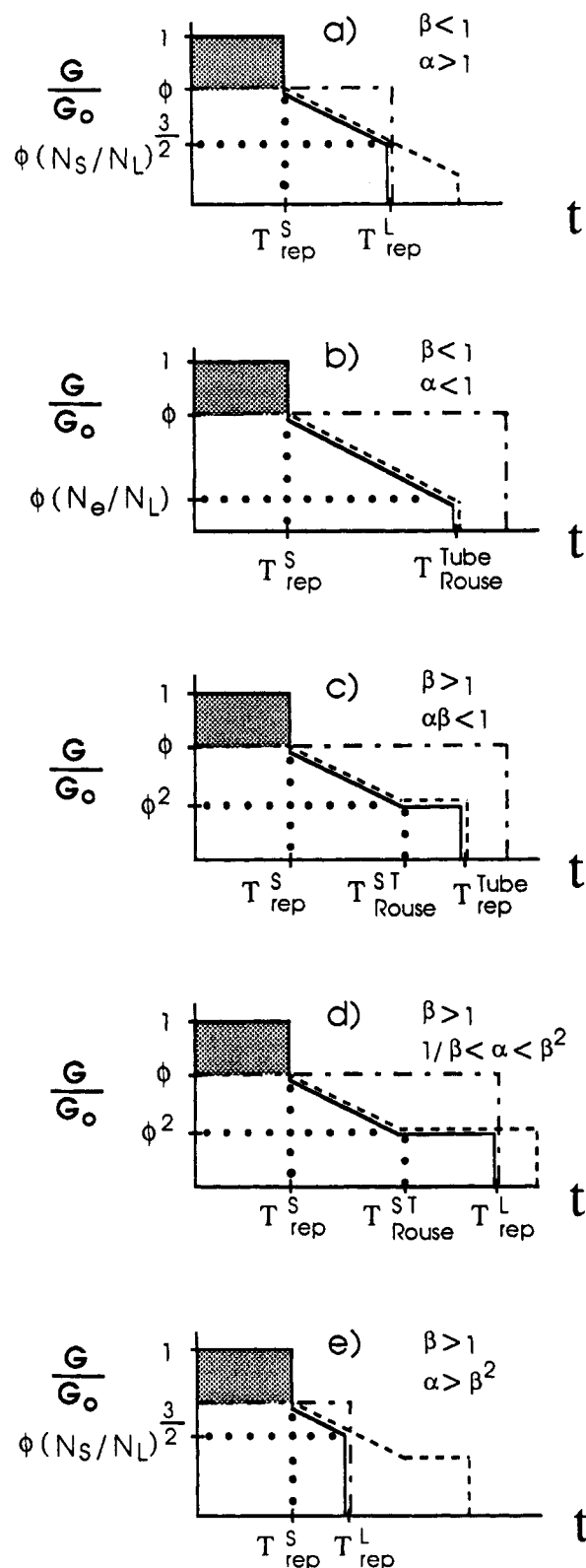

Figure 8. Schematic representations of the five possibilities for the relaxation modulus of bimodal homopolymer melts: (a) $\beta < 1$ and $\alpha > 1$ (chain reptation I), (b) $\beta < 1$ and $\alpha < 1$ (Rouse tube rearrangement), (c) $\beta > 1$ and $\alpha\beta < 1$ (reptative tube rearrangement), (d) $\beta > 1$ and $1/\beta < \alpha < \beta^2$ (chain reptation II), and (e) $\beta > 1$ and $\alpha > \beta^2$ (chain reptation I). Full lines are the relaxation moduli, which are the faster of two relaxation mechanisms: tube rearrangement (dashed lines) and chain reptation (dash-dotted lines). Indicated times are $T_{rep}^S = T_{rep}(\tau, N_S, N_e)$; $T_{rep}^L = T_{rep}(\tau, N_L, N_e)$; $T_{Rouse}^{tube} = T_{Rouse}(\tau N_S^3/N_e, N_L/N_e)$; $T_{Rouse}^{ST} = T_{Rouse}(\tau N_S^3/N_e, N_L/(\beta N_e))$; $T_{rep}^{tube} = 0$ $T_{rep}(\tau N_S^3/N_e, N_L/N_e, N_L/(\beta N_e))$. Logarithmic scales.

Table I
Summary of Predictions for the Terminal Viscoelastic Response of Bimodal Homopolymer Blends

regime	criteria	terminal time	terminal modulus	viscosity
tube Rouse	$\alpha < 1$ $\beta < 1$	$\tau N_S^3 N_L^2/N_e^3$	$G_0\phi(N_e/N_L)$	$G_0\phi\tau N_S^3 N_L/N_e^2$
chain reptation I	$\alpha > 1$ $\alpha/\beta^2 > 1$	$\tau N_L^3/N_e$	$G_0\phi(N_S/N_L)^{3/2}$	$G_0\phi\tau(N_L N_S)^{3/2}/N_e$
chain reptation II	$1/\beta < \alpha < \beta^2$	$\tau N_L^3/N_e$	$G_0\phi^2$	$G_0\phi^2\tau N_L^3/N_e$
tube reptation	$1 < \beta < 1/\alpha$	$\phi\tau N_S^3 N_L^3/N_e^4$	$G_0\phi^2$	$G_0\phi^3\tau N_S^3 N_L^3/N_e^4$

·is given by the intercept between the chain reptation and Rouse tube rearrangement curves. Physically, it represents the fraction of the stress not relaxed by Rouse modes of the tube faster than $T_{rep}(\tau,N_L,N_e)$.

(b) The case of nonentangled long chains ($\beta < 1$) with terminal relaxation due to Rouse tube rearrangement ($\alpha < 1$) is shown in Figure 8b. In this case, relaxation of the long chains occurs entirely by Rouse tube rearrangement, and the value of the modulus at the terminal time is

$$G_{term} \simeq G_0\phi(N_e/N_L) \qquad \beta < 1 \text{ and } \alpha < 1$$

$$\text{(tube Rouse) (31)}$$

(c) The case of self-entangled long chains ($\beta > 1$) with terminal relaxation due to tube reptation ($\alpha\beta < 1$) is shown in Figure 8c. Here relaxation of the long chains occurs entirely by reptative tube rearrangement, and the value of the modulus at the terminal time is

$$G_{term} \simeq G_0\phi\beta(N_e/N_L) \simeq \phi^2 \qquad \beta > 1 \text{ and } \alpha\beta < 1$$

$$\text{(tube reptation) (32)}$$

Note that eqs 31 and 32 smoothly crossover at $\beta = \phi N_L/N_e = 1$.

Only the case of self-entangled long chains ($\beta > 1$), which relax by chain reptation ($\alpha\beta > 1$), merits special attention. The terminal time in this case is always $T_{rep}(\tau,N_L,N_e)$, but the value of the terminal modulus may take two different values depending on the relative position of $T_{Rouse}(\tau N_S^3/N_e,N_L/(\beta N_e))$, the Rouse time of an entanglement strand of the supertube, and $T_{rep}(\tau,N_L,N_e)$.

(d) If $T_{rep}(\tau,N_L,N_e) > T_{Rouse}(\tau N_S^3/N_e,N_L/(\beta N_e))$, the tube is in the terminal phase of its reptation process at $T_{rep}(\tau,N_L,N_e)$, and the G_{term} is given by eq 32 (chain reptation II in Figure 6). The time criteria is equivalent to requiring $\alpha/\beta^2 < 1$. This case is shown schematically in Figure 8d.

(e) In the opposite case, where the tube rearrangement is still occurring by Rouse motions of the tube when the terminal time of the chain is reached ($\alpha/\beta^2 > 1$), the G_{term} is given by eq 30 (chain reptation I in Figure 6). The relaxation function for this case appears in Figure 8e.

In short, this leaves us with three different values for the G_{term}, separated by the dashed lines in the α, β parameter space of Figure 6. We have a total of four regimes in Figure 6; the criteria for, and results in, those four regimes are summarized in Table I, along with the predictions for the terminal viscosity

$$\eta \simeq G_{term}T \tag{33}$$

The four regimes and the predictions in them are compared with those in earlier work in the next section.

6. Discussion

In this paper, we have explored the mechanisms of constraint release at work in polymer dynamics and applied those ideas to the relaxation of bimodal blends of linear homopolymers. The scope of our results and the general framework of the paper bear a close resemblance to that of Doi, Graessley, Helfand, and Pearson.[11] There is one major conceptual difference between this work and ref 11; that is, the question of how to determine confinement of a chain in a tube. Doi et al.[11] introduced the useful concept of comparing motion of a free chain with motion of the tube to determine confinement. They compared Rouse motion of a tube segment with *terminal diffusion of a free chain* (motion of the center of mass of the chain) on length scales between a and R. This effectively ignores the Rouse-like fluctuations of the chain (see Figure 2), which lead to a mean-square monomer displacement scaling as $t^{1/2}$ on length scales less than R. *Segments of a free chain only exhibit terminal diffusion* (with $\Phi \sim t$) *for length scales larger than R.* Instead of comparing parallel lines (as in Figure 2), Doi et al.[11] have the possibility that the lines can cross, since they have $\Phi_{chain} \sim t$ and $\Phi_{tube} \sim t^{1/2}$.

Since they neglect these fluctuations, Doi et al.[11] predict that the effective tube diameter for the long chains can adopt any value within a certain range (between a and R for dilute long chains and between a and a_L for nondilute long chains), as the point where Φ_{chain} and Φ_{tube} cross determines the effective tube diameter. In contrast, we contend that the segmental motions of a free chain (i.e., Rouse fluctuations) are important for determining confinement and predict that the tube diameter is only allowed to take on two discrete values. For the case of dilute long chains, either the chains are entangled (in a tube of diameter a) or they are unentangled (with an infinite effective tube diameter). Similarly, long chains are either confined to a tube of diameter a or a tube of diameter a_L for the case of nondilute long chains. The fact that the tube diameter "jumps" is, at first glance, conceptually alarming. However, in each case this jump occurs when $N_S = N_e$, which is the critical molecular weight where entanglements become important for the short chains. Thus, it is not so surprising that the tube diameter is discontinuous, as *the jump in the tube diameter corresponds to the onset of entanglement between the short chains* and is really the same phenomenon that occurs in monodisperse melts when $N = N_e$. One should note that this abrupt change in tube diameter does not lead to any related discontinuities in measurable quantities such as terminal relaxation time or viscosity. The terminal time for reptation of the chain in the fully dilated tube of diameter a_L is

$$T_{rep}(\tau,N_L,N_e a_L^2/a^2) \simeq (\tau N_L^3/N_e)(a/a_L)^2 \simeq \tau\beta N_L^2 \tag{34}$$

and this smoothly crosses over with the reptation time of the tube in the supertube (eq 20) when $N_S = N_e$.

The fact that for $N_S > N_e$ a long chain is always confined in a tube of diameter a leads us quite naturally to propose a new mechanism of relaxation—*tube reptation*. This relaxation mechanism can become important for nondilute long chains (see section 4), as free Rouse motions of the tube are forbidden beyond the length scale a_L (just as ordinary chain reptation results from free Rouse motions of the chain being forbidden beyond the length scale a).
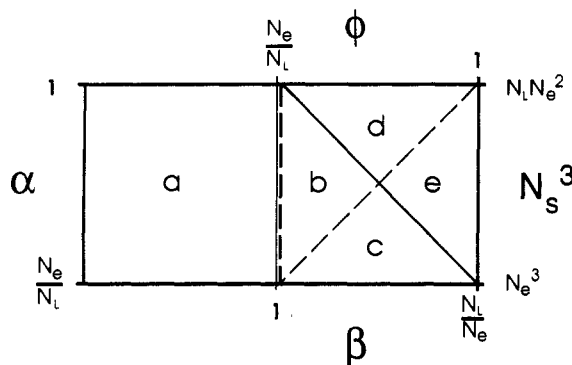
Figure 9. Comparison of regimes of predictions for this work and ref 11 in the α,β parameter space. For this work: (a) Rouse tube rearrangement, (b and c) reptative tube rearrangement, (d and e) chain reptation II. For ref 11: (a) free dilation wedge, (b and d) free dilation box, (c and e) restricted dilation box. Logarithmic scales.

We can compare our predicted regimes with those of ref 11 via our Figure 6 and Figure 11 of ref 11. The predictions for $\alpha > 1$ are qualitatively identical,[35] as both theories crossover to chain reptation for $\alpha > 1$. Similarly, for $N_S < N_e$ (or $\alpha < N_e/N_L$) the predictions are identical (this case is not shown in either our Figure 6 or Figure 11 of ref 11 because it corresponds to behavior of a polymer dissolved in a low molecular weight solvent, instead of blends of two entangled polymers). We therefore focus on comparison in the region $N_e/N_L < \alpha < 1$ of the α,β parameter space in Figure 9. Indeed, this region can be thought of as the crossover between the behavior of solutions of polymers in low molecular weight Θ solvents (neglecting hydrodynamic interactions) and blends with N_S large enough that ordinary chain reptation dominates the relaxation of the long chains. The two theories simply provide different ideas about the nature of this crossover. Doi et al.[11] predict tube dilation to be the crucial concept for understanding relaxation in this crossover region, whereas we predict that *tube dilation only occurs for $N_S < N_e$!*

For $\beta < 1$ in Figure 9, predictions of the two theories disagree in concept but not in qualitative results. We view relaxation as occurring by Rouse motion of the tube in this regime, and while this is conceptually different from the idea of free tube dilation in ref 11, the predictions for terminal time and viscosity are identical.[35] Doi et al.[11] expect tube dilation to a size a' in this regime, where a' is controlled by reptation of the short chains. However, the renormalized reptation time associated with a tube of diameter a', as predicted in ref 11, is the same as the Rouse tube rearrangement time discussed here and in earlier models of constraint release.[8,22-25]

For $\beta > 1$ in Figure 9, predictions for the terminal modulus are the same in the two theories, but the predictions for the terminal time are different. Both theories predict two regimes. We predict that tube reptation dominates the terminal relaxation for $\alpha\beta < 1$ and simple chain reptation dominates for $\alpha\beta > 1$. Doi et al.[11] predict free dilation for $\alpha < \phi$ and restricted dilation for $\alpha > \phi$. The terminal times predicted by the two theories for the $\beta > 1$ region of Figure 9 are listed in Table II.

A good way to exemplify the differences between the two ideas is to consider moving along a horizontal line in Figure 9 ($N_e/N_L < \alpha < 1$) and see how the terminal time changes as we increase the concentration of long chains. For $\phi < N_e/N_L$ (or $\beta < 1$) the terminal time predicted by both models is $\tau N_S^3 N_L^2/N_e^3$ (eq 19), which is independent of ϕ, so it remains constant along the horizontal line. At

Table II
Terminal Time Predictions for $N_e/N_L < \alpha < 1$ and
$1 < \beta < N_L/N_e$

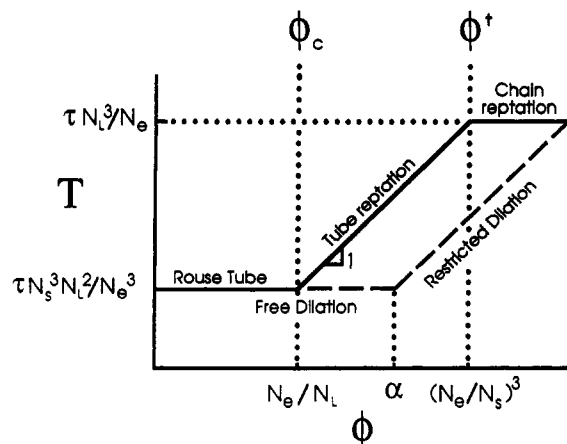| source	criteria	regime	terminal time
ref 11	$N_e/N_L < \alpha < \phi$	restricted dilation	$\phi\tau N_L^3/N_e$
ref 11	$\phi < \alpha < 1$	free dilation	$\tau N_S^3 N_L^2/N_e^3$
this work	$\beta > 1$ and $\alpha\beta < 1$	tube reptation	$\phi\tau N_S^3 N_L^3/N_e^4$
this work	$\beta > 1$ and $\alpha\beta > 1$	chain reptation	$\tau N_L^3/N_e$

Figure 10. Comparison of predicted dependencies of terminal relaxation time on the concentration of long chains in a bimodal homopolymer melt with $N_e/N_L < \alpha < 1$: this work (solid line) and ref 11 (dashed line). Logarithmic scales.

the onset of entanglements between long chains ($\phi = \phi_c \cong N_e/N_L$ or $\beta \cong 1$), we predict that the terminal time will start increasing with ϕ (see Table II). Indeed, we expect that the terminal time will depend on the three parameters ϕ, N_S, and N_L in this regime of tube reptation. As ϕ is increased further, we eventually enter the chain reptation regime (when $\phi = \phi^\dagger \cong (N_e/N_S)^3$ or $\alpha\beta \cong 1$) and the terminal time again becomes independent of ϕ.

In sharp contrast, ref 11 predicts that the terminal time should not change on the onset of entanglements between long chains (i.e., it remains equal to the Rouse time of the tube that is independent of ϕ). The terminal time starts to increase with concentration only when the restricted dilation regime is reached ($\phi \cong \alpha$; see Table II). In fact, according to ref 11, the terminal time does not reach the reptation time of the long chains in a tube of diameter a until $\phi = 1$.

These different predictions, schematically represented in Figure 10, should provide clear-cut criteria for experiments. Probably, the most demonstrative one is the ϕ dependence of the terminal time near $\phi = 1$. Although significant amounts of stress will be relaxed by constraint release, we predict the terminal time to be controlled by chain reptation and be independent of ϕ, while ref 11 predicts a linear dependence on ϕ. The presence of a regime in which the terminal time depends on N_S, N_L, and ϕ is also a unique feature of our model (see Table II), but this criterion may be rendered rather inconclusive by crossover effects, which tend to "mix up" regimes.

Predictions for the ϕ dependence of the terminal time at the onset of entanglements between long chains ($\beta = 1$) are also very different, but an experimental check here is more delicate, because one has to know the actual position of this onset. The scaling we use for the sake of simplicity leads to a well-defined concentration $\phi_c \cong N_e/N_L$, but this scaling is far from being quantitatively reliable (see, e.g., ref 33). Until this issue is resolved, the onset of entanglement between the long chains will need to be independently determined from measurements of viscosity as a function of concentration in a Θ solvent.

A further complication may also arise from partial swelling of the long chains by the short ones,[7,18] which was neglected here. Experiments must be planned to avoid this complication by requiring $N_L < N_S{}^2$. We can suggest an experiment that meets all of these criteria, using binary blends of monodisperse polystyrene. For this polymer, the molecular weight of a Kuhn segment[36] is $M_K = 520$ and the entanglement molecular weight[37] is $M_e = 18\,000$ ($N_e = 35$). Blends with $N_S = 140$ ($M_S = 73\,000$) and $N_L = 8500$ ($M_L = 4\,400\,000$) could be prepared with different concentrations. We predict that the terminal time of such blends should start to increase in the vicinity of $\phi_c = N_e/N_L \cong 0.004$ and level off at the terminal time of the pure long chains at $\phi^\dagger = (N_e/N_S)^3 \cong 0.016$. In contrast, Doi et al.[11] predict the terminal time to be constant for $\phi < \alpha = 0.25$ and to increase beyond $\phi = 0.25$ (see Figure 10). The longest relaxation time of the pure long chains will be roughly 6000 s at the highest stable temperature for polystyrene, 180 °C. This imposes two conditions on the proper experiments. First, the blends must be held at 180 °C for many times this longest relaxation time to ensure that an equilibrium structure is reached (roughly 1 week). Second, the terminal time of the blends is probably outside the convenient range for oscillatory measurements, but creep and recovery experiments should be able to measure these terminal times quite accurately (terminal time is determined from the product of viscosity and recoverable compliance in this experiment[37]).

Watanabe and Kotaka[28] have studied blends of polystyrene with $M_S = 70\,000$ and $M_L = 2\,600\,000$, and these should certainly fall in the proper range for Figure 10 as $\alpha \cong 0.4$. However, this was done as part of a large (and very impressive) survey of possible behaviors of binary blends, so they only measured terminal time for four concentrations for this pair. The terminal time indeed seems to be roughly constant for $\phi = 0.005$ and $\phi = 0.01$, slightly larger for $\phi = 0.02$, and significantly larger at $\phi = 0.05$. We predict the terminal time should start to increase near $\phi_c \cong 0.007$, whereas Doi et al.[11] predict the increase to start at much higher concentrations, $\phi \cong 0.4$. In any case, the data are too few to be conclusive, and further experiments (such as those outlined above, particularly for large ϕ) are needed.

The differences between our theory and that of ref 11 are not terribly important for industrial polydisperse melts of linear polymers, as both theories are relevant to very special (and difficult to achieve) polydispersities. In most cases, theories such as those proposed in refs 23–25 are sufficient. It is important to recall, however, that the underlying conceptual problem is the proper criterion for tube dilation. A better understanding of this criterion is necessary for branched polymers in which the tube dilation process is expected to be qualitatively important, even for the simplest branched polymers, monodisperse stars.[13]

Interestingly, the two theories predict identical terminal moduli over the entire α,β parameter space, even though the terminal relaxation time predictions are different in some cases. In both theories, the terminal modulus is only sensitive to terminal relaxation time for the chain reptation I regime (Figure 8a,e), where Rouse tube rearrangement is terminated by chain reptation. The other cases (Figure 8b–d) all have terminal moduli that are insensitive to the terminal relaxation time and hence the type of terminal relaxation process. Since the differences in the two theories arise from processes where the terminal modulus is insensitive to terminal time (Figure 8c,d), it is not so surprising that the predictions for the terminal modulus are identical in the two theories.

7. Conclusions

There is a range of molecular weights of the components of a binary blend of linear homopolymers in which relaxation is dominated by constraint release. As suggested by Doi et al.,[11] this range falls between the limits where ordinary chain reptation dominates on one hand (N_S large) and the short chains become unentangled on the other ($N_S < N_e$). We picture constraint release as being a means for a chain to find new configurations via motion of its surrounding tube. There are two processes by which constraint release can occur. The first is by Rouse motion of the tube[6-8] in which the tube moves like a free Rouse chain with a fundamental jump time given by the relaxation time of the surrounding chains. The second is the new concept of reptation of the tube, which occurs when there are effectively permanent obstacles that prevent full relaxation of the tube by Rouse motion.

In contrast, ref 11 proposed a different mechanism of constraint release—tube dilation. This concept, originally due to Marrucci,[9] envisions the tube widening due to relaxation of the surrounding chains. This widening then accelerates the reptation relaxation of the chain in the tube. Reptation of the tube and tube dilation actually play similar roles in the two theories, when the long chains are entangled with each other, but lead to different predictions (full comparison of the two theories is in section 6). Both processes relax the part of the stress carried by the entanglements between long chains. However, for binary blends of homopolymers, we show that tube dilation only occurs when $N_S < N_e$.

In order to focus on constraint release, we used the simplest single-chain relaxation function for a chain in a tube—reptation. Thus our predictions are only qualitative, as we have ignored all other single-chain relaxation mechanisms, such as tube length fluctuations, that are known to be necessary for quantitative prediction of both terminal modulus and terminal time.

The final predictions of our constraint release model for binary blends of linear homopolymers are qualitatively different from those of ref 11 only in a limited range of component molecular weights. We recommend possible experiments to elucidate these qualitative differences in section 6. The detailed mode spectra of constraint release predicted by tube reorganization and tube dilation are also quite different, but these differences will be difficult to detect experimentally due to complications such as tube length fluctuations.

However, constraint release is a far more important process for branched polymers. Tube dilation ideas have already had some success in explaining relaxation dynamics of these complex polymers.[13-16] It is our hope that the constraint release concepts discussed in this paper will be of use for understanding dynamics of polymers with complex (nonlinear) architectures. However, we have only just begun to consider tube reorganization for dynamics of nonlinear polymers, and detailed discussion of this problem will have to await a future publication.

References and Notes

(1) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1986.

(2) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(3) Edwards, S. F. *Proc. Phys. Soc.* **1967**, *92*, 9.
(4) de Gennes, P.-G. *J. Phys. (Les Ulis, Fr.)* **1975**, *36*, 1199.
(5) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 587.
(6) Klein, J. *Macromolecules* **1978**, *11*, 852.
(7) Daoud, M.; de Gennes, P.-G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1971.
(8) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*, 67.
(9) Marrucci, G. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 159.
(10) Viovy, J. L. *J. Phys. (Les Ulis, Fr.)* **1985**, *46*, 847.
(11) Doi, M.; Graessley, W. W.; Helfand, E.; Pearson, D. S. *Macromolecules* **1987**, *20*, 1900.
(12) Lin, Y.-H. *Macromolecules* **1989**, *22*, 3075.
(13) Ball, R. C.; McLeish, T. C. B. *Macromolecules* **1989**, *22*, 1911.
(14) McLeish, T. C. B. *Macromolecules* **1988**, *21*, 1062.
(15) McLeish, T. C. B. *Europhys. Lett.* **1988**, *6*, 511.
(16) Rubinstein, M.; Zurek, S.; McLeish, T. C. B.; Ball, R. C. *J. Phys. (Les Ulis, Fr.)* **1990**, *51*, 757.
(17) Viovy, J. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30* (1), 41.
(18) de Gennes, P.-G. *Scaling Concepts of Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(19) Doi, M. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 265.
(20) Doi, M. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 667.
(21) Kavassalis, T. A.; Noolandi, J. *Macromolecules* **1989**, *22*, 2709.
(22) Graessley, W. W.; Edwards, S. F. *Polymer* **1981**, *22*, 1329.
(23) Graessley, W. W.; Struglinski, M. J. *Macromolecules* **1986**, *19*, 1754.
(24) Rubinstein, M.; Helfand, E.; Pearson, D. S. *Macromolecules* **1987**, *20*, 822.
(25) Rubinstein, M.; Colby, R. H. *J. Chem. Phys.* **1988**, *89*, 5291.
(26) Green, P. F.; Kramer, E. J. *Macromolecules* **1986**, *19*, 1108.
(27) Montfort, J.-P.; Marin, G.; Monge, P. *Macromolecules* **1984**, *17*, 1551.
(28) Watanabe, H.; Kotaka, T. *Macromolecules* **1984**, *17*, 2316.
(29) Watanabe, H.; Sakamoto, T.; Kotaka, T. *Macromolecules* **1985**, *18*, 1436.
(30) Watanabe, H.; Kotaka, T. *Macromolecules* **1987**, *20*, 530.
(31) Klein, J. *Macromolecules* **1986**, *19*, 105.
(32) de Gennes, P.-G. *J. Phys. Lett. (Les Ulis, Fr.)* **1974**, *35*, L-133. Brochard, F.; de Gennes, P.-G. *Macromolecules* **1977**, *10*, 1157.
(33) Colby, R. H.; Rubinstein, M. *Macromolecules* **1990**, *23*, 2753.
(34) To focus on qualitative aspects, we ignore the small amount of relaxation due to constraint release from motion of surrounding chains of the same size (see refs 8 and 25).
(35) The predictions for terminal modulus and time are identical, but the details of the mode spectrum are different for the two models.
(36) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Hanser Publishers: New York, 1989.
(37) Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley: New York, 1980.