instead τ should be determined from dynamical measurements on the appropriate diblock melt in the disordered phase far from the critical point.
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Dynamics of Polymers in Polydisperse Melts

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ABSTRACT: The dynamical behavior of a mixture of two narrow molecular weight distribution homopolymers is analyzed on the basis of the concepts of reptation and constraint release. We propose that constraint release causes not only tube renewal (the relaxation of the tube) but also tube dilation (the enlargement of the effective tube diameter). A general scheme of accounting for these effects is given. As an example, the rheological properties of the mixture are analyzed in the entire parameter space, which consists of the molecular weights of each component and the mixing ratio. It is shown that even though the molecular weight dependence of the longest relaxation time is reptation-like the shape of the relaxation modulus can be Rouse-like.

1. Introduction

In a melt of polymers of high molecular weight, it is now well established that molecular motion is dominated by reptation, the slithering motion of a polymer through a tubelike region formed by surrounding polymers.[2,3] For polymer melts of narrow molecular weight distribution, the diameter of the tube is an intrinsic property of the polymer and is characterized by the entanglement molecular weight M_e. In this case, the tube can be assumed, in the first approximation, to be fixed during the characteristic time of reptation.

The fixed-tube assumption becomes invalid if the system has a broad molecular weight distribution. Consider for example a system having a bimodal distribution of molecular weight, i.e., a mixture of short (S) and long (L) polymers. If the molecular weight of the short polymers M_S is close to that of the long polymers, M_L, the fixed-tube assumption will be valid. However, as M_S decreases, the constraints imposed by the short polymers must become weaker, and in the extreme case of M_S being comparable to that of monomers, the constraints that are due to the short polymers become effectively null. A natural question is how such weakening of the tube takes place when the molecular weight M_S and the volume fraction ϕ_S of the short polymers are varied. The purpose of this paper is to give a qualitative answer to that question.

In the limiting case of a dilute blend ($\phi_L = 1 - \phi_S \to 0$), theories for the problem have been presented in the context of the diffusion of a polymer in a matrix,[4,5] and the results have been confirmed by experiments using forward recoil spectroscopy.[6,7] On the other hand, the case of finite concentration, which is particularly important for rheological properties, has not been investigated in detail.

Experimentally, considerable work has been done to find "blending laws" for rheological properties.[8-10] Although success has been achieved in some individual studies, the blending laws are empirical and do not seem to have general validity. This is not surprising considering that many parameters are involved in the problem: even in the simplest case of a bimodal distribution there are already three independent parameters M_L, M_S, and ϕ_L, which leads to a rather complex analysis. In general polydisperse melts, there is no guarantee that the system can be characterized by a few kinds of average molecular weight. In this paper, we do not attempt to give a general blending law. Rather we offer some theoretical guidelines for this complex problem by examining the bimodal distribution case in detail.

According to the pure reptation model, the relaxation modulus $G(t)$ of a blend of two monodisperse samples obeys the linear additivity law[11]

$$G(t) = \phi_L G_L(t) + \phi_S G_S(t) \tag{1.1}$$

where $G_L(t)$ and $G_S(t)$ are the relaxation moduli of the pure components. This simple relation, however, is inconsistent with many experiments.[9,10,12-15] Amendment of the theory has been made,[16-19] but so far the understanding has been limited to the special cases in the parameter space spanned by (M_L, M_S, ϕ_L).

In this paper we shall discuss the behavior of a polymer blend in the entire parameter space. We shall divide the space into regimes and discuss their characteristic features. Such a delineation will be useful to interpret experimental data and to plan further experiments.

The basic proposal of this paper is that the tube diameter of long chains can change when short chains are added. We shall call this effect tube dilation. (Tube dilation should not be confused with the concept proposed recently by Marrucci[20] and Viovy,[21] who argued that even in monodisperse systems the tube diameter increases as the stress relaxes. We do not take this view. In our theory, tube dilation takes place only for polymer blends, not in monodisperse systems.)

The idea that the tube in blends may dilate has been suggested by several authors.[12,19,22] However, no systematic theory has been given to estimate the effect. In this paper we shall propose a general method of estimating tube dilation and its effect on diffusion and rheological properties. Although the method can be applied to a general polydisperse system, we shall focus our attention to a

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binary mixture of monodisperse polymers.

Since our purpose is to predict the qualitative features, we disregard additional complications, such as the contour length fluctuation,[23] the excluded volume effect,[5] and the correlated release of constraints during tube renewal.[24] We shall consider the constraint release process as the only mechanism for tube weakening. Even with this simplification, the results are somewhat unexpected and worthy of an experimental check.

2. Reptation and Constraint Release

First we briefly review the conventional reptation theory. The theory assumes that each polymer in a melt is forced to move through a tubelike region due to constraints imposed by surrounding polymers. The diameter of the tube, a, is a basic constant of the polymer and is related to the entanglement molecular weight M_e

$$a \propto M_e^{1/2} \tag{2.1}$$

The length of the tube L is proportional to the molecular weight of the polymer, and the ratio $N \equiv L/a$ corresponds to the number of entanglement points per chain

$$N = M/M_e \tag{2.2}$$

N is also related to the mean-square end-to-end distance of the polymer R^2 by

$$N = R^2/a^2 \tag{2.3}$$

In the conventional model, it is assumed that the tube is fixed in the material and that the conformational change of the polymer can take place only by reptation, i.e., one-dimensional diffusion of a polymer along the tube. This assumption leads to the following conclusion for the diffusion constant D_G and the longest relaxation time $\tau_{\max}$ of the polymer:

$$D_G \simeq \frac{1}{N} D_c \tag{2.4}$$

$$\tau_{\max} \simeq \frac{N^2 a^2}{D_c} \tag{2.5}$$

where D_c is the curvilinear diffusion constant, which is proportional to M^{-1}

$$D_c \propto M^{-1} \tag{2.6}$$

From eq 2.3–2.6, it follows

$$D_G \simeq \frac{a^2}{R^2} D_c \propto \frac{M_e}{M^2} \tag{2.7}$$

$$\tau_{\max} \simeq \frac{R^4}{D_c a^2} \propto \frac{M^3}{M_e} \tag{2.8}$$

These results have been confirmed experimentally for monodisperse polymers of large molecular weight.[3]

In real systems, the assumption that the tube is fixed in the material is not strictly true. Indeed the tube may diffuse through the material due to the motion of surrounding polymers. A mechanism for such "tube diffusion" is constraint release[25] shown in Figure 1: a surrounding polymer (dashed line) which has been imposing a topological constraint on the test polymer (thick line) diffuses away and releases the constraint. In the schematic representation of topological constraints, constraint release corresponds to the disappearance of an obstacle (Figure 2, parts a and b). Obviously, the same motion of surrounding polymers can create new obstacles, and at any instance, the average distance between obstacles is constant, which is denoted by a.

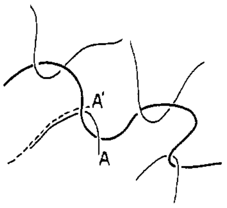

Figure 1. Constraint release. The polymer segment at A moves to A′ and releases the topological constraint imposed on the test polymer (thick line).

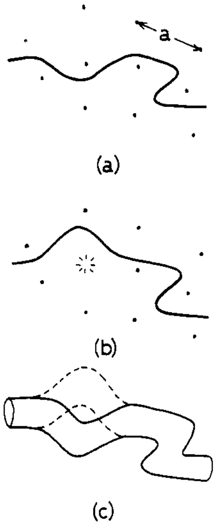

Figure 2. (a) Two-dimensional representation of the topological constraints imposed on the test polymer. The constraints are represented by dots across which the test polymer cannot move. (b) Constraint release corresponds to the disappearance of a dot. (c) This process corresponds to the local conformational change of the tube.

For a monodisperse system, constraint release has been shown to have only a minor effect,[4,5,16] but it can be quite important in polydisperse system. In the following sections we shall study the effects of constraint release in polydisperse systems using the model that obstacles are created and destroyed randomly. An important parameter in this model is the lifetime of obstacles. In real systems this parameter is not known and must be determined theoretically. We shall do this in section 5, but first we shall study the problem by assuming that the lifetimes of the obstacles are given.

3. Motion of a Polymer in a Monodisperse Matrix

Let us consider the system shown in Figure 2: a polymer moving in a matrix of obstacles which have lifetime τ_{obst}, i.e., being created and destroyed with probability $1/\tau_{\text{obst}}$ per unit time. The random displacement of obstacles causes two effects, tube renewal and tube dilation.

Tube Renewal. When an obstacle next to the test polymer is destroyed and recreated in another place, the tube changes its conformation as shown in Figure 2c. We shall call this process tube renewal. It can be modeled by allowing a local jump of each tube segment with jump rate $1/\tau_{\text{obst}}$.[4,16] It is known that such local jump motion creates Rouse-like motion[26] and gives the following diffusion constant and longest relaxation time for the tube:

$$D_{\text{ren}} \simeq \frac{a^2}{N\tau_{\text{obst}}} \tag{3.1}$$

$$\tau_{\text{ren}} \simeq N^2 \tau_{\text{obst}} \tag{3.2}$$

While the tube is moving around by tube renewal, the polymer is simultaneously reptating through it. If the

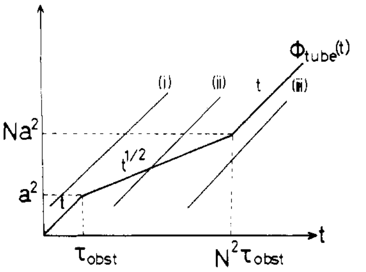

Figure 3. log–log plot comparing the mean-square displacement of a tube segment $\Phi_{tube}(t)$ with the mean-square displacement of a polymer segment $\Phi_{polymer}(t)$. The three lines (i), (ii), and (iii) represent $\Phi_{polymer}(t)$ with different values of D_c.

coupling between their motion is neglected,[27] the diffusion constant D_G and the longest relaxation time (or the rotational relaxation time) τ_{max} of the polymer are given by

$$D_G \simeq D_{ren} + D_{rep} \tag{3.3}$$

$$1/\tau_{max} \simeq 1/\tau_{ren} + 1/\tau_{rep} \tag{3.4}$$

where D_{rep} and τ_{rep} represents the contribution of reptation.

In the previous theories, it has been assumed that reptation is not affected by constraint release.[4,5] This assumption is not correct. Consider for example the case of $\tau_{obst} \to 0$. In this case, even if the polymer is hindered by an obstacle at a certain moment, the obstacle will be gone at the next moment, so that dynamically the obstacles have no effect; i.e., there will be no tube constraint, or the tube diameter will be infinite. Thus in the general case, the constraint release causes the following effect also.

Tube Dilation. The effective diameter a' of the tube through which the polymer reptates becomes larger than a if the obstacles have finite lifetimes.

The effective diameter a' may be estimated as follows. Let us focus our attention on a certain polymer segment and compare the distance that the *polymer* travels by diffusion in free space with the distance that the *tube* moves by tube renewal. The mean-square distance of the segment due to the self-diffusion of the polymer is given by

$$\Phi_{polymer}(t) \simeq D_c t \tag{3.5}$$

On the other hand, the mean-square displacement of the tube can be calculated by the Rouse model and is given by[3,28]

$$\begin{aligned} \Phi_{tube}(t) &\simeq a^2\frac{t}{\tau_{obst}} \quad t < \tau_{obst} \\ &\simeq a^2\left(\frac{t}{\tau_{obst}}\right)^{1/2} \quad \tau_{obst} < t < N^2\tau_{obst} \\ &\simeq a^2\frac{t}{\tau_{obst}N} \quad N^2\tau_{obst} < t \end{aligned} \tag{3.6}$$

$\Phi_{polymer}(t)$ and $\Phi_{tube}(t)$ are compared in Figure 3. (Notice that in this and subsequent figures all plots are log–log.) Depending on the value of τ_{obst}, there are three situations.

(i) $a^2 < \Phi_{polymer}(\tau_{obst})$; i.e., $a^2/D_c < \tau_{obst}$. In this case, the motion of the tube is always slower than that of the polymer, so that the tube diameter will be a, the original diameter.

(ii) $a^2 > \Phi_{polymer}(\tau_{obst})$ and $Na^2 < \Phi_{polymer}(N^2\tau_{obst})$, i.e. $a^2/ND_c < \tau_{obst} < a^2/D_c$. In this case $\Phi_{tube}(t)$ and $\Phi_{polymer}(t)$ cross at t', where

$$t' \simeq \frac{1}{\tau_{obst}}\left(\frac{a^2}{D_c}\right)^2 \tag{3.7}$$

The polymer will not feel the tube constraint for $t < t'$ but will feel the constraint for $t > t'$. Thus the effective tube diameter may be estimated by

$$a'^2 \simeq D_c t' \simeq \frac{a^4}{D_c\tau_{obst}} \tag{3.8}$$

(iii) $Na^2 > \Phi_{polymer}(N^2\tau_{obst})$, i.e., $\tau_{obst} < a^2/ND_c$. In this case, the tube is not effective at all and the motion of the polymer is the same as in free space.

The tube dilates in regime (ii), where D_{rep} and τ_{rep} are obtained from eq 2.7, 2.8, and 3.8

$$D_{rep} \simeq \frac{a'^2}{R^2}D_c \simeq \frac{a^4}{R^2\tau_{obst}} \simeq \frac{a^2}{N\tau_{obst}} \tag{3.9}$$

$$\tau_{rep} \simeq \frac{R^4}{D_c a'^2} \simeq \frac{R^4}{a^4}\tau_{obst} \simeq N^2\tau_{obst} \tag{3.10}$$

These expressions are precisely the same as eq 3.1 and 3.2 for D_{ren} and τ_{ren}, so that

$$D_G \simeq \frac{a^2}{N\tau_{obst}} \tag{3.11}$$

$$\tau_{max} \simeq N^2\tau_{obst} \tag{3.12}$$

for $a^2/ND_c < \tau_{obst} < a^2/D_c$. Thus the conclusions of the previous theories,[4,5] which account for the tube renewal only, are essentially unaltered when tube dilation is taken into account.

It is important to emphasize that although D_{rep} and τ_{rep} agree with D_{ren} and τ_{ren}, reptation is a valid picture in regime (ii). This is shown by the following argument. Support that some of the obstacles shown in Figure 2a are permanently fixed (their lifetimes being set to infinity). This situation is illustrated in Figure 4, where large and small circles represent permanently fixed obstacles and those with lifetime τ_{obst}. In such a system, reptation is valid for any values of τ_{obst}: when τ_{obst} is infinite, the polymer reptates through a tube of diameter a, and when $\tau_{obst} = 0$, it reptates through an enlarged tube of diameter a_p, the mean separation between the permanent obstacles. Thus there must be a crossover of the effective tube diameter from a to a_p, which we propose to be given by eq 3.8. If a' given by eq 3.8 is less than a_p (i.e., if $a^4/a_p^2D_L < \tau_{obst} < a^2/D_c$), the polymer will reptate through a tube of diameter a' without noticing the permanent obstacles. Thus in regime (ii), reptation is an entirely valid model.

In the present example, reptation and tube renewal coincidentally make comparable contributions to the dynamics. In general, however, there contributions are different, and tube dilation represents an effect that cannot be represented by tube renewal. This will be shown in subsequent sections.

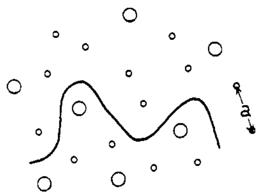

Figure 4. Polymer chain in a mixture of obstacles with long lifetimes (large circles) and short lifetimes (small circles).

4. Motion of a Polymer in a Polydisperse Matrix

Let us now consider the case that there are two kinds of obstacles (Figures 4): the fraction ϕ_L of the obstacles has the long lifetime τ_L and the remaining fraction $\phi_S = 1 - \phi_L$ has a short lifetime τ_S. We shall call the obstacles with long (or short) lifetimes simply long (or short) obstacles.

Table I
Diffusion Constant D_G and Relaxation Time τ_{max} of a Polymer Moving in a Matrix of Obstacles Having Two Different Lifetimes τ_L and τ_S

condition		D_G	τ_{max}
$\tau_S/\phi_L{}^2 < \tau_L$ and $N\phi_L > 1$	$a^2/D_c < \tau_S$	D_c/N	N^2a^2/D_c
	$\tau_S < a^2/D_c < \tau_S/\phi_L$	$a^2/N\tau_S$	τ_SN^2
	$\tau_S/\phi_L < a^2/D_c < \tau_L\phi_L$	$D_c/N\phi_L$	$a^2N^2\phi_L/D_c$
	$\tau_L\phi_L < a^2/D_c < N\phi_L{}^2\tau_L$	$a^2/N\phi_L{}^2\tau_L$	$(N\phi_L)^2\tau_L$
	$N\phi_L{}^2\tau_L < a^2/D_c$	D_c	Na^2/D_c
$\tau_S/\phi_L{}^2 > \tau_L$ or $N\phi_L < 1$	$a^2/D_c < \tau_S$	D_c/N	N^2a^2/D_c
	$\tau_S < a^2/D_c < N^2\tau_S$	$a^2/N\tau_S$	τ_SN^2
	$N^2\tau_S < a^2/D_c$	D_c	Na^2/D_c

Our purpose is to calculate D_G and τ_{max} of a polymer chain moving in such a matrix as a function of τ_L, τ_S, and ϕ_L. To do this, we have to know $\Phi_{tube}(t)$, the mean-square displacement of a tube segment due to tube renewal. Precise calculation of $\Phi_{tube}(t)$ is not easy, but the qualitative features are clear.

On a short time scale, tube renewal is dominated by the short chains, so that $\Phi_{tube}(t)$ is given by $a^2(t/\tau_S)$ (for $t < \tau_S$) or $a^2(t/\tau_S)^{1/2}$ (for $t > \tau_S$). When $\Phi_{tube}(t)$ becomes comparable to a^2/ϕ_L, the mean-square distance between the long obstacles,[28] tube renewal is stopped. This happens when $a^2(t/\tau_S)^{1/2} \simeq a^2/\phi_L$, i.e., $t \simeq \tau_S/\phi_L{}^2$. For $\tau_S/\phi_L{}^2 < t < \tau_L$, $\Phi_{tube}(t)$ remains essentially constant since long obstacles stay at their position until τ_L. For $t > \tau_L$, long obstacles start to jump, and $\Phi_{tube}(t)$ is given by the local jump model with the jump frequency $1/\tau_L$ and the mean-square jump distance a^2/ϕ_L. Thus

$$\begin{aligned} \Phi_{tube}(t) &\simeq a^2\frac{t}{\tau_S} && t < \tau_S \\ &\simeq a^2\left(\frac{t}{\tau_S}\right)^{1/2} && \tau_S < t < \tau_S/\phi_L{}^2 \\ &\simeq a^2/\phi_L && \tau_S/\phi_L{}^2 < t < \tau_L \\ &\simeq \frac{a^2}{\phi_L}\left(\frac{t}{\tau_L}\right)^{1/2} && \tau_L < t < \tau_L(N\phi_L)^2 \\ &\simeq \frac{a^2}{N\phi_L{}^2\tau_L}t && \tau_L(N\phi_L)^2 < t \end{aligned} \tag{4.1}$$

Here we have assumed that the following condition is satisfied:

$$\tau_S/\phi_L{}^2 < \tau_L \quad \text{and} \quad N\phi_L > 1 \tag{4.2}$$

Equation 4.1 is plotted in Figure 5. The effective tube diameter is obtained from the intersect between $\Phi_{tube}(t)$ and D_ct. Depending on the value of D_c, there are five situations shown in the figure, each of which gives the following tube diameter:

$$\begin{aligned} a'^2 &\simeq a^2 && \text{for } \tau_2 > a^2/D_c \\ &\simeq a^4/D_c\tau_S && \text{for } \tau_S/\phi_L > a^2/D_c > \tau_S \\ &\simeq a^2/\phi_L && \text{for } \tau_L\phi_L > a^2/D_c > \tau_S/\phi_L \\ &\simeq a^4/\phi_L{}^2D_c\tau_L && \text{for } N\phi_L{}^2\tau_L > a^2/D_c > \tau_L\phi_L \\ &\simeq \infty \text{ (no tube)} && \text{for } a^2/D_c > N\phi_L{}^2\tau_L \end{aligned} \tag{4.3}$$

Given a'^2, D_{rep} and τ_{rep} are easily calculated as in eq 3.9 and 3.10. On the other hand, when eq 4.2 is satisfied, D_{ren} and τ_{ren} are given by

$$D_{ren} \simeq \frac{a^2}{N\phi_L{}^2\tau_L} \tag{4.4}$$

$$\tau_{ren} \simeq N^2\phi_L{}^2\tau_L \tag{4.5}$$

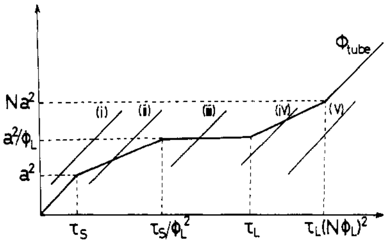

Figure 5. Diagram of $\Phi_{tube}(t)$ and $\Phi_{polymer}(t)$ for the case of $\tau_L > \tau_S/\phi_L{}^2$ and $Na^2 > a^2/\phi_L$.

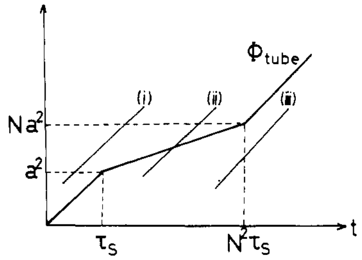

Figure 6. Diagram of $\Phi_{tube}(t)$ and $\Phi_{polymer}(t)$ for the case of $\tau_L < \tau_S/\phi_L{}^2$ or $Na^2 < a^2/\phi_L$.

For all cases in eq 4.3 it can be shown that $D_{ren} < D_{rep}$ and $\tau_{ren} > \tau_{rep}$, so that D_G and τ_{max} are given by D_{rep} and τ_{rep}.

If the condition of eq 4.2 is not satisfied, tube renewal is always dominated by short obstacles, so that the diagram of $\Phi_{tube}(t) - \Phi_{polymer}(t)$ becomes as shown in Figure 6. In this case a'^2 is given by

$$\begin{aligned} a'^2 &\simeq a^2 && \text{for } \tau_S > a^2/D_c \\ &\simeq a^4/D_c\tau_S && \text{for } N^2\tau_S > a^2/D_c > \tau_S \\ &\simeq \infty && \text{for } a^2/D_c > N^2\tau_S \end{aligned} \tag{4.6}$$

and D_{ren} and τ_{ren} are

$$D_{ren} \simeq \frac{a^2}{N\tau_S} \tag{4.7}$$

$$\tau_{ren} \simeq N^2\tau_S \tag{4.8}$$

In this case also, one can check that $D_{ren} < D_{rep}$ and $\tau_{ren} > \tau_{rep}$. Thus in all cases examined here

$$D_G \simeq D_{rep} \qquad \tau_{max} \simeq \tau_{rep} \tag{4.9}$$

The results for D_G and τ_{max} are summarized in Table I.

5. Motion of Long Polymers in a Binary Blend

So far we have been considering the case when the lifetimes of the obstacles are given. Let us now consider real polymer melts consisting of two homopolymers of molecular weight M_L and M_S. We assume that both molecular weights are larger than the entanglement molecular weight M_e.

$$M_L > M_S > M_e \tag{5.1}$$

The volume fraction of each polymers is denoted by ϕ_L and

ϕ_S, respectively ($\phi_L + \phi_S = 1$).

When eq 5.1 is satisfied, tube dilation does not occur for the short polymers. Thus we shall consider tube dilation for the long polymers only. Let D_L be the curvilinear diffusion constant of the long polymers. In pure melts, the reptation times of the two types of polymers are given by

$$\tau_L \simeq \frac{a^2}{D_L}\left(\frac{M_L}{M_e}\right)^2 \propto M_L{}^3 \tag{5.2}$$

$$\tau_S \simeq \tau_L\left(\frac{M_S}{M_L}\right)^3 \tag{5.3}$$

In the blend, the reptation time of the short polymers is unchanged, while that of the long polymers may change due to tube dilation and is denoted by τ_L'.

The reptation time τ_L' can be obtained by reasoning similar to that in section 4. However, there is an important distinction. In the present problem, the lifetimes of the obstacles are not known a priori.

Since the constraint release is caused by the reptation of the surrounding polymers, the lifetimes of each obstacle may be assumed to be equal to their reptation time (apart from a numerical constant). Thus the lifetime of a short obstacle is τ_S and that of a long obstacle is τ_L'. The latter is not known and must be determined self-consistently. Therefore the general procedure for determining τ_L' will be as follows:

(i) Assume a value for τ_L' and substitute it for τ_L in the calculation of $\Phi_{\text{tube}}(t)$.

(ii) Obtain the tube diameter a' from the intersection of $\Phi_{\text{polymer}}(t)$ and $\Phi_{\text{tube}}(t)$

$$a'^2 \simeq D_L t' \simeq \Phi_{\text{tube}}(t') \tag{5.4}$$

(iii) Calculate the reptation time by

$$\tau_L' \simeq R_L{}^4/D_L a'^2 \tag{5.5}$$

where $R_L{}^2$ is the mean-square end-to-end distance of the long polymer

$$R_L{}^2 \simeq \frac{M_L}{M_e}a^2 \tag{5.6}$$

(iv) Repeat the procedure until the calculated value of τ_L' agrees with the assumed one.

As in the previous section, $\Phi_{\text{tube}}(t)$ can have one of the two shapes shown as case A and case B in Figure 7. Case A is realized when $\tau_L' > \tau_S/\phi_L{}^2$ and $M_L\phi_L/M_e > 1$, and case B is realized otherwise. Case A is further divided into three cases, Ai, Aii, and Aiii, depending on the position of the intersection between $\Phi_{\text{tube}}(t)$ and $\Phi_{\text{polymer}}(t)$ (see Figure 7). Case Aiv shown by the dashed line cannot take place since $D_L\tau_L' \simeq R_L{}^4/a'^2$ is always larger than $R_L{}^2 \simeq a^2(M_L/M_e)$. Similarly, case is divided into cases Bi, and Bii. In each case, one can calculate τ_L' and check the self-consistency of the solution.

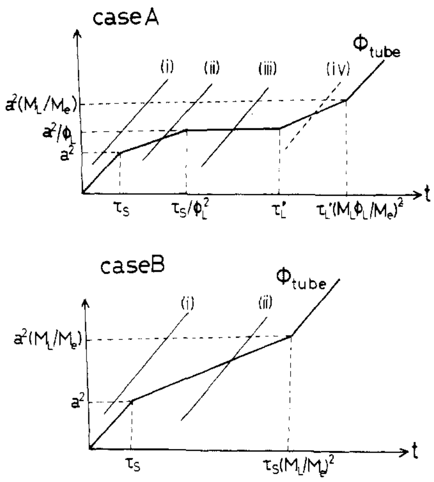

Figure 7. Diagram of $\Phi_{\text{tube}}(t)$ and $\Phi_{\text{polymer}}(t)$ for a blend. Case (A) is realized when both $\tau_L' > \tau_S\phi_L{}^2$ and $M_L\phi_L/M_e > 1$ are satisfied, otherwise case (B) is realized.

For example, let us consider case Aiii. This is realized when the following conditions are simultaneously satisfied:

$$\tau_L' > \tau_S/\phi_L{}^2 \tag{5.7}$$

$$M_L\phi_L/M_e > 1 \tag{5.8}$$

and

$$D_L\tau_S/\phi_L{}^2 < a^2/\phi_L < D_L\tau_L' \tag{5.9}$$

The first two conditions are for case A to happen, and the last one is for the third case to take place. If these conditions are satisfied, a'^2 is found to be equal to a^2/ϕ_L, whence $\tau_L' \simeq \phi_L\tau_L$. From this and eq 5.2–5.5, the above conditions are written as

$$M_L\phi_L/M_S > 1 \tag{5.10}$$

$$M_L\phi_L/M_e > 1 \tag{5.11}$$

$$M_L\phi_L M_e{}^2/M_S{}^3 > 1 \tag{5.12}$$

Equations 5.10 and 5.11 can be absorbed into a stronger condition 5.12 due to eq 5.1. We may thus conclude that $\tau_L' \simeq \phi_L\tau_L$ when $M_L\phi_L M_e{}^2/M_S{}^3 > 1$.

Similar considerations for other cases lead to the following conclusions:

(i) When $M_S{}^3/M_e{}^2M_L > 1$ (which happens in cases Ai and Bi)

$$a'^2 \simeq a^2 \qquad \tau_L' \simeq \tau_L \propto M_S{}^0 M_L{}^3 \phi_L{}^0 \tag{5.13}$$

(ii) When $1 > M_S{}^3/M_e{}^2M_L > \phi_L$ (which happens in cases Aii and Bii)

$$a'^2 \simeq \frac{a^4}{\tau_S D_L} \qquad \tau_L' \simeq \tau_S\left(\frac{M_L}{M_e}\right)^2 \propto M_S{}^3 M_L{}^2 \phi_L{}^0 \tag{5.14}$$

(iii) When $\phi_L > M_S{}^3/M_e{}^2M_L$

$$a'^2 \simeq a^2/\phi_L \qquad \tau_L' \simeq \phi_L\tau_L \propto M_S{}^0 M_L{}^3 \phi_L \tag{5.15}$$

Tube dilation does not take place in case (i) but does take place in cases (ii) and (iii). In case (ii), the long polymers impose no restriction on tube dilation: the tube diameter is determined by the short polymers only. In case (iii), the tube dilation is restricted by the long polymers. Thus we shall refer to cases (i), (ii), and (iii) as no dilation (ND), free dilation (FD), and restricted dilation (RD), respectively.

As in section 4, it can be shown that $D_{\text{ren}} < D_{\text{rep}}$ and $\tau_{\text{ren}} > \tau_L'$, so that D_G and τ_{max} are given by D_{rep} and τ_L', respectively. For completeness, explicit expressions for D_G are given below:

(i) The case of no dilation ($M_S{}^3/M_e{}^2M_L > 1$)

$$D_G \simeq \frac{M_e}{M_L}D_L \propto M_L{}^{-2}M_S{}^0\phi_L{}^0 \tag{5.16}$$

(ii) The case of free dilation ($1 > M_S{}^3/M_e{}^2M_L > \phi_L$)

$$D_G \simeq \frac{M_e}{M_L}\frac{a^2}{\tau_S} \propto M_L{}^{-1}M_S{}^{-3}\phi_L{}^0 \tag{5.17}$$

(iii) The case of restricted dilation ($\phi_L > M_S{}^3/M_e{}^2M_L$)

$$D_G \simeq \frac{M_e}{\phi_L M_L}D_L \propto M_L{}^{-2}M_S{}^0\phi_L{}^{-1} \tag{5.18}$$

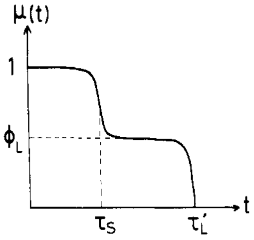

Figure 8. The probability $\mu(t)$ that an arbitrarily chosen polymer segment is in the deformed tube is plotted against t.

It must be noted that the terms ND, FD, and RD are concerned with only the molecular weight dependence of D_G and τ_{max} and do not completely classify the molecular motion. Depending on the phenomena under consideration, the properties of the blends can vary qualitatively within each regime. Thus further classification may be needed in each regime. Such an example will be given in the next section.

6. Rheological Properties of the Binary Blend

We now consider the rheological properties of the binary blends. This is conveniently characterized by the shear relaxation modulus $G(t)$, which is the shear stress divided by the shear strain when a step shear strain is applied.

According to the reptation theory, the macroscopic stress is related to the orientation of the chain in the deformed tube.[3,11] Thus the stress relaxation can take place by two mechanisms, i.e., reptation by which the chain disengages from the deformed tube and tube renewal by which the deformed tube itself relaxes. Assuming their mutual independence, we can write the shear relaxation modulus as

$$G(t) = G_N{}^0\mu(t)\phi(t) \tag{6.1}$$

where $G_N{}^0$ is the plateau relaxation modulus which is independent of the molecular weight. The function $\mu(t)$ represents the probability that an arbitrarily chosen polymer segment is confined in the deformed tube. For a monodisperse system, $\mu(t)$ has been calculated as[11]

$$\mu(t) = \frac{8}{\pi^2}\sum_{p=1,3,...}\frac{1}{p^2}\exp(-p^2t/\tau_{rep}) \equiv m(t/\tau_{rep}) \tag{6.2}$$

For the binary blend, $\mu(t)$ is given by

$$\mu(t) = \phi_L m(t/\tau_L') + \phi_S m(t/\tau_S) \tag{6.3}$$

The schematic behavior of $\mu(t)$ is shown in Figure 8.

The function $\phi(t)$ represents the effect of the tube renewal and may be calculated from the Rouse model which has a random distribution of jump frequencies. Corresponding to cases A and B in Figure 7, $\phi(t)$ can have two shapes (see Figure 9):

In case A

$$\begin{aligned}\phi(t) &\simeq 1 & t &< \tau_S \\ &\simeq (\tau_S/t)^{1/2} & \tau_S &< t < \tau_S/\phi_L{}^2 \\ &\simeq \phi_L & \tau_S/\phi_L{}^2 &< t < \tau_{ren}\end{aligned} \tag{6.4}$$

In case B

$$\begin{aligned}\phi(t) &\simeq 1 & t &< \tau_S \\ &\simeq (\tau_S/t)^{1/2} & \tau_S &< t < \tau_{ren}\end{aligned} \tag{6.5}$$

Since $\tau_{ren} > \tau_L'$, the product $\mu(t)\phi(t)$ has one of two typical shapes (Figure 10): (A) If $\tau_L' > \tau_S/\phi_L{}^2$, $G(t)$ has two plateaus, intercepted by a wedge type relaxation ($G(t) \propto t^{-1/2}$) (Figure 10, top). (B) If $\tau_L' < \tau_S/\phi_l{}^2$, $G(t)$ has a single plateau, followed by a wedge type terminal region (Figure 10, bottom). We shall refer to them as box type and wedge type, respectively.

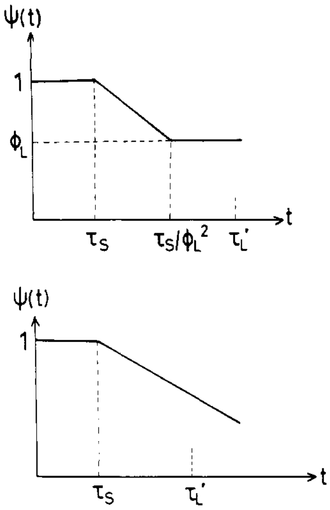

Figure 9. The orientational relaxation function of the tube due to tube renewal is plotted against t.

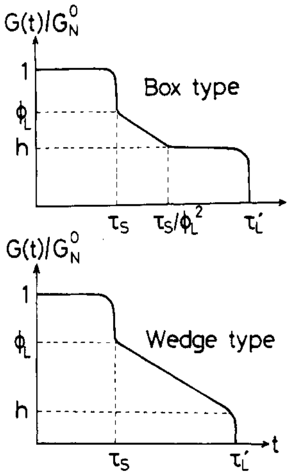

Figure 10. The two types of shape for the relaxation modulus $G(t)$; (A) box type, (B) wedge type. The value of $h = G_{term}/G_N{}^0$ is given in Table II.

The crossover concentration $\phi_L{}^*$ between the wedge and the box type is given by $\tau_L' \simeq \tau_S/\phi_L{}^{*2}$. Using eq 5.13–5.15, we have

$$\begin{aligned}\phi^* &\simeq \left(\frac{M_S}{M_L}\right)^{3/2} && \text{if } M_S{}^3/M_LM_e{}^2 > 1 \\ &\simeq \frac{M_e}{M_L} && \text{if } \phi_L < M_S{}^3/M_LM_e{}^2 < 1\end{aligned} \tag{6.6}$$

In the case of restricted dilation ($M_S{}^3/M_LM_e{}^2 < \phi_L$), τ_L' is always larger than $\tau_S/\phi_L{}^2$, so that the relaxation is always the box type.

In both the wedge and the box types, the relaxation behavior at short times is the same, independent of M_L and ϕ_L: $G(t)$ starts from a plateau region, terminated at $t = \tau_S$, and then followed by the wedge region $G(t) \propto t^{-1/2}$. The long-time behavior is characterized by the maximum relaxation time $\tau_{max} = \tau_L'$ and its strength G_{term}

$$G_{term} \equiv G(\tau_{max}) \tag{6.7}$$

The maximum relaxation time has the three types of the molecular weight dependence given by eq 5.13–5.15. This and the criterion for box–wedge type roughly divide the entire parameter space spanned by (M_L,M_S,ϕ_L) into 3 × 2 = 6 regions. Actually, since there is no combiantion of

Table II
Characteristic Parameters of the Relaxation Modulus Shown in Figure 10 for a Mixture of Polymers with Molecular Weight M_L and M_S

region	condition	$\tau_{max} = \tau_L'$	$G_{term}/G_N^0 = h$
ND box	$M_S^3/M_LM_e^2 > 1$	$\tau_L \propto M_L^3$	ϕ_L^2
	$\phi_L > (M_S/M_L)^{3/2}$	$\tau_L \propto M_L^3$	ϕ_L^2
ND wedge	$M_S^3/M_LM_e^2 > 1$	$\tau_L \propto M_L^3$	$\phi_L(M_S/M_L)^{3/2}$
	$\phi_L < (M_S/M_L)^{3/2}$	$\tau_L \propto M_L^3$	$\phi_L(M_S/M_L)^{3/2}$
RD box	$\phi_L > M_S^3/M_LM_e^2$	$\phi_L\tau_L \propto \phi_LM_L^3$	ϕ_L^2
FD box	$M_S^3/M_LM_e^2 < 1$	$\tau_S(M_L/M_e)^2 \propto M_L^2M_S^3$	ϕ_L^2
	$M_e/M_L < \phi_L < M_S^3/M_LM_e^2$	$\tau_S(M_L/M_e)^2 \propto M_L^2M_S^3$	ϕ_L^2
FD wedge	$M_S^3/M_LM_e^2 < 1$	$\tau_S(M_L/M_e)^2 \propto M_L^2M_S^3$	ϕ_LM_e/M_L
	$\phi_L < M_e/M_L$	$\tau_S(M_L/M_e)^2 \propto M_L^2M_S^3$	ϕ_LM_e/M_L

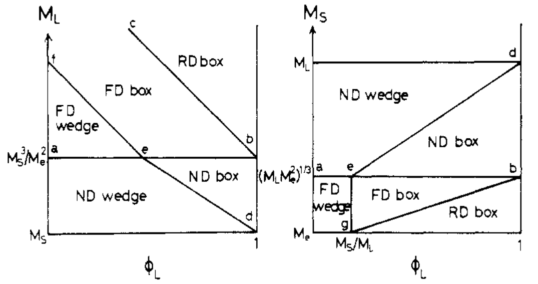

Figure 11. Various regimes in the parameter space. Left: (ϕ_L,M_L) plane (M_S being constant). Right: (ϕ_L,M_S) plane (M_L being constant). The abbreviations ND (no dilation), FD (free dilation), and RD (restricted dilation) indicate the maximum relaxation time, and box and wedge indicate the shape of the relaxation modulus shown in Figure 10. The curves in the figures are (ab) $M_S^3/M_LM_e^2 = 1$, tube dilation threshold; (bc, bg) $\phi_L = M_S^3/M_LM_e^2 = 1$, crossover between RD and FD; (ed) $\phi_L = (M_S/M_L)^{3/2}$, crossover between wedge and box; (ef, eg) $\phi_L = M_S/M_L$, crossover between wedge and box.

wedge and restricted dilation, there are five regions. These regions are illustrated in Figure 11. The expressions for τ_{max} and G_{term} in each region are summarized in Table II.

The schematic behavior of the relaxation moduli shown in Figure 10 has already been proposed.[13] However, the criterion for such a behavior to be observed and the expressions for τ_{max} and G_{term} have not been given explicitly. It is important to emphasize that the wedge shape of $G(t)$ in the terminal region is not always associated with the Rouse-like molecular weight dependence of τ_{max}. Indeed in the ND wedge region, the terminal relaxation time is the same as that in the pure melt of long polymers despite the wedge shape of $G(t)$ in the terminal region. Likewise, the FD box regime indicates that the Rouse-like molecular weight dependence $\tau_{max} \propto M_L^2$ can be consistent with box-type behavior in the terminal region.

7. Conclusion

As was noted by Struglinski and Graessley,[13] the experimental work for binary blends can be broadly classified into two categories, dilation and no dilation depending on the value of M_S^3/M_LM_e. The nondilation case has been studied by Struglinski and Graessley, who showed that the longest relaxation time is independent of ϕ_L if $M_S^3/M_LM_e^2 > 1$. On the other hand, earlier works[9,12,14,15] are for the dilation case, where the longest relaxation time changes with ϕ_L. It will be thus interesting to check the theory in the entire parameter space.

In this paper, we considered only linear viscoelasticity. In the nonlinear regime, complications arise since other time constants related to the relaxation of the contour length come into play.[30] This problem has recently been studied by Takahashi and Masuda.[19]

The purpose of this paper is to establish a framework by which experimental data may be examined. No great accuracy can be expected in the quantitative aspects: to do quantitative comparison, one has to account for various side effects such as contour length fluctuation, the excluded volume effect, and cooperativity during the constraint release. However, we hope that the qualitative aspects that emerged from the present theory are useful in organizing various experimental results.

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(27) This assumption, often employed in previous theories, is a crude approximation. In general there is a coupling between tube renewal and tube dilation. M.D. thanks Dr. Watanabe for pointing out this fact.
(28) Strictly speaking, eq 3.6 holds when the inequalities are strong (much less than or much greater than), but for simplicity we disregard the crossover regime and use < and > instead of ≪ and ≫.
(29) Here we used the conventional assumption that in polymer solutions the spatial distance between entanglement scales as $a \propto \phi^{-1/2}$. The validity of this relation may be challenged, but in the present crude argument we used the simplest assumption.
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