Linear Viscoelastic Response in the Lateral Diffusion Model for Linear Chain Polymer Melts

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ABSTRACT: A model for stress relaxation of linear chain polymer melts in the linear viscoelastic regime is proposed. This model is developed in the context of the lateral diffusion model of polymer dynamics, which assumes that polymers diffuse in the melt by sliding laterally along the curvilinear contours of neighboring chains. It is assumed that in the post-plateau region of the time-dependent stress relaxation the stress is supported by the interchain contacts. At the time the strain is applied, each chain is in contact with a set of other chains, the centers of mass of which are distributed in a manner which reflects the strain. This network of connectivity is broken as the interchain contacts break. The unrelaxed stress is equated with the fraction of intitial contacts which are unbroken at a given later time. Calculations are performed for monodisperse and bidisperse melts, and these are compared with published experimental data. Very good agreement is found with experimental results.

I. Introduction

In the previous paper[1] we have proposed a model for polymer dynamics of linear chains in the melt. This model is based on the premise that the polymer chains slide laterally along the contours of the neighboring chains. While this motion is hindered by the presence of other chains, it is assumed in this model that the chains are able to diffuse past the time-dependent fluctuating barriers. In our model the curvilinear nature of the constraints imposed by the contours of neighboring chains results in a time-dependent friction coefficient, which is an increasing function of time.[1,2] We have shown that this model, which is based on quite a different assumption than the familiar reptation model,[3-6] leads to many of the same results as the reptation model. In particular, D_{cm} varies with chain length as N^{-2}. Also we find that t_f is proportional to N^3, where t_f is defined as the time at which the mean-squared center-of-mass displacement equals $2R_G^2$ and R_G is the radius of gyration. The model also predicts that D_{cm} for a probe chain is only weakly dependent on the length of the surrounding chains, if effects corresponding to constraint release are ignored. On the other hand, the predictions of the model for the time dependence of the bead mean-squared displacement $g(t)$ and the center-of-mass mean-squared displacement $g_{cm}(t)$ differ from those predicted by reptation theory.

In this paper we consider a simple model for stress relaxation within the context of our lateral diffusion model.[1,2] This model is appropriate for the linear viscoelastic regime. A brief preliminary account of this model has been presented previously.[7,8] The model provides an expression for the stress relaxation in the post-plateau regime, and the primitive form of the model presented here predicts a N^3 dependence of the terminal relaxation time and the viscosity for monodisperse samples. The general polydisperse case is also considered, and explicit calculations are performed for the viscoelastic response of bidisperse melts. These calculations are directly compared with the experimental results of Kornfield, Fuller, and Pearson[9] on bidisperse isoprene melts. The agreement between the calculated and experimental stress relaxation curves is very good. The shape of the experimental decay curve for the monodisperse samples is reproduced extremely well by this simple model. The results for the bidisperse samples are also in very good agreement, although some differences are apparent. These differences can be mainly attributed to the effects of orientational ordering.

The outline of this paper is as follows. In section II the model for the linear viscoelastic response of linear chain systems in the melt is described and the mathematical details are presented. The results of calculations are presented in section III, and these are compared with published experimental data. In section IV the results are summarized and discussed. Additional features, which are not included in this simple model, are also discussed.

II. Theory

Figure 1 outlines the basic mechanism of stress relaxation in our model. Immediately after a strain is applied to the polymer system, the density distribution of each chain is distorted from the equilibrium isotropic distribution. This distortion reflects the applied strain and gives rise to the stress in the system. There is a rapid relaxation as the chains slide along each other. This relieves much of the stress as the density distribution for each chain relaxes back toward the equilibrium distribution. However, each chain is entangled with a set of chains, the centers of mass of which are distributed in a fashion which reflects the strain applied to the system. For this reason the stress cannot completely relax until the contacts with the neighboring chains, that were presented at the time the strain was applied (defined as $t = 0$), are broken due to the relative motion of the chains.

This fast relaxation, combined with a slow relaxation of the stress due to the breaking of interchain contacts, gives rise to the plateau region in the relaxation modulus. In this work we focus entirely on the slow relaxation, and we do not attempt to describe the fast relaxation in detail or to calculate the value of the plateau modulus. We can model the stress in the system as pictured in Figure 2. The springs represent effective segments of the polymer chains, and the junction points represent the interchain contact points which support the stress. The contacts between the various chains form a network of connections which extends throughout the system. As the chains slide along each other, this anisotropic network of connections is not broken, and on average the stress supported by it does not relax until the interchain contacts break. As the interchain contacts are broken, this residual stress is removed.

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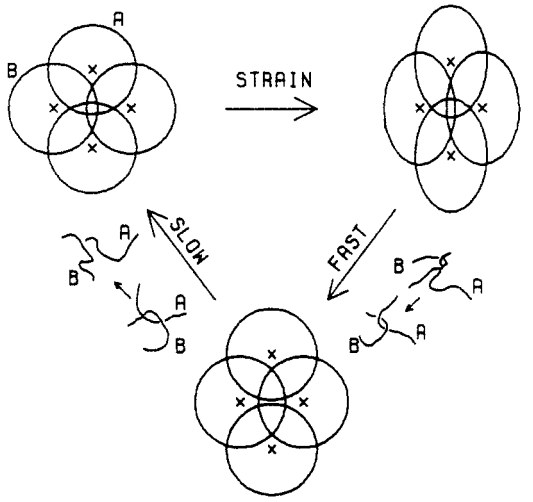

Figure 1. Schematic representation of the model for stress relaxation in a polymer melt. The circles indicate the density distributions for individual chains. The ×'s indicate the chain center of mass. Two chains are labeled A and B. The isotropic equilibrium system is shown at the upper left. Immediately after a strain is applied, the chain density distributions and the distribution of centers of mass in contact with any given chain reflect the applied strain. The stress is relieved by the relatively fast process, as the chains slide along each other, and the comparatively slow process, as the interchain contacts, which were present when the strain was applied, are broken.

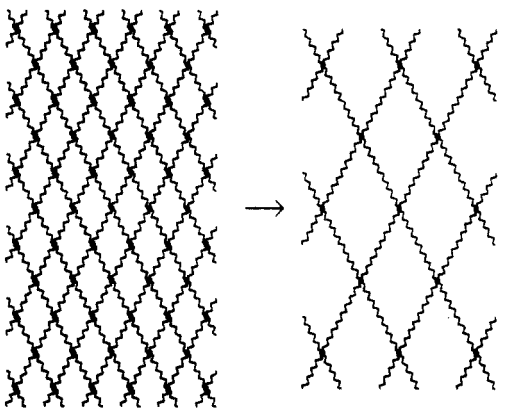

Figure 2. Representation of the stress relaxation. The springs represent chain segments between interchain contact points. As the interchain contacts, which were present when the strain was applied, break, the number of chain segments supporting the stress decreases.

As some of the contacts break, the network of remaining connections still extends throughout the entire system, and it still reflects the applied strain. The stress is proportional to the number of effective chain segments between the remaining unbroken contact points. Since this is just twice the number of contacts, the value of the relaxation modulus $G(t)$ is the plateau modulus times the fraction of original contacts that have not been broken at time t. Of course as some contacts are broken, new ones are formed. However, we assume for simplicity that these new contacts do not support the stress, and the chain segments connected to a newly formed contact have a random, equilibrium distribution of orientations. We comment on the effect of this simplifying assumption in section IV.

Recently des Cloizeaux has presented the double reptation model for viscoelastic response.[10,11] This model is similar to the one proposed here and previously[7,8] in that the stress is supported by the contacts between the chains and is equated with the fraction of surviving contacts in the terminal regime. des Cloizeaux's model, however, differs from current work by assuming that each chain moves by reptating along its primitive path.

The stress supported by a contact is lost when the contact between the chains is broken. This occurs when the contact point encounters the end of either of the chains involved in the contact. This motion of the chains along the backbones of each other and the resulting motion of the contact point are the main concerns of the model for polymer dynamics described in the previous paper.[1] The survival probability for a contact between two chains, chain A and chain B, is given by

$$F_{AB}(t) = P_A(t)\, P_B(t) \tag{1}$$

where $P_A(t)$ is the probability that the contact point has not encountered the end of chain A between time zero and time t. $P_B(t)$ is defined similarly for chain B. Equation 1 simply states that the probability of not encountering the end of chain A is uncorrelated with the probability of not encountering the end of chain B.

As in the previous paper we employ the expression

$$P_J(t) = \sum_{j=1,3,\ldots} \frac{8}{j^2\pi^2} \exp\left[-\frac{j^2\pi^2\langle L_J^2\rangle}{2L_{e,J}^2}\right], \quad J = A, B \tag{2}$$

for $P_A(t)$ and $P_B(t)$. In (2) $\langle L_J^2\rangle$ is the mean-squared contour displacement of the contact along the contour of chain J. It is a time-dependent quantity. $L_{e,J}$ is an effective total contour length for chain J. We typically choose $L_{e,J} = c_L N_J b_J$, where N_J is the number of segments in chain J and b_J is the segment length. The number of segments for chain J in our model is identified with the number of interchain contacts involving chain J. The parameter c_L would be unity if contacts could only be broken at the chain ends. However, we typically take c_L to be somewhat less than unity to allow for contact breakage at other than chain ends. This is discussed more completely in the previous paper.[1] The qualitative nature of the results are not strongly influenced by the choice of c_L over a reasonable range. The model for $P_J(t)$, (2), is exact for the case of a simple random walker on a one-dimensional contour of length $L_{e,J}$, given that the walker is distributed uniformly at $t = 0$. In this case $\langle L_J^2\rangle = 2Dt$, where D is the diffusion constant for the walker. It is only approximate for the case of a polymer chain moving along a neighboring chain. In this case $\langle L_J^2\rangle$ can be calculated from the knowledge of $g(t)$ for both chains involved in the contact.[1]

It is important to notice that the definition of contact breaking differs here from that in the previous paper.[1] In that paper we were concerned with the question of when a contact no longer has an influence on the effective friction per contact felt by a probe chain. Even if the contact point slides past the end of the neighboring chain involved in the contact, the curvilinear constraint on the dynamics of the probe chain would largely be carried on by other chains, and the contribution to the friction would remain. In the current context we are interested in the time at which a contact no longer supports part of the stress in the system. This happens when the contact point moves past the end of either chain involved in the contact. Even if another chain replaces the one whose end has just been encountered by the contact point in question, it is assumed that the location of the center of mass of this new chain is distributed according to an equilibrium distribution and that this new interchain contact supports no stress.

Equation 1 gives the probability that a specific contact between two chains has not been broken. In order to calculate the stress relaxation, we need to evaluate the

fraction of contacts in the system that have not been broken between time zero and time t. The simplest case is that of a monodisperse sample of identical chains. In that case there is only one type of chain and one type of contact, and $F_{AA}(t) = P_A(t)^2$ is the fraction of unbroken contacts. The relaxation modulus in the terminal regime is given by

$$G(t) = G_N P_A(t)^2 \tag{3}$$

where G_N is the plateau modulus, and $P_A(t)$ is given by (2) for the sole type of chain in the system.

For the monodisperse sample $\langle L_A^2 \rangle$ is proportional to $g_A(t)^2$ in the lateral diffusion model.[1] Since $g_A(t) \sim t^{1/3}$ in this model for t less than the time $t_f \sim N^3$, $G(t)$ takes the form

$$G(t) = G_N\left[\sum_{j=1,3,\ldots} \frac{8}{j^2\pi^2} \exp\left(\frac{-j^2 A t^{2/3}}{N^2}\right)\right]^2 \tag{4}$$

for $t < t_f$. A in (4) is just a constant to collect various other constants. The exponent in (4) can be rearranged to have the form $j^2 A_1 (t/\tau)^{2/3}$, where $\tau \sim N^3$. Thus, the terminal relaxation time varies as N^3. The shear viscosity, which is the integral of $G(t)$, is given by

$$\eta_s = \int_0^\infty G(t)\, dt = G_N \tau \int_0^\infty \left\{\sum_{j=1,3,\ldots} \frac{8}{j^2\pi^2} \exp[-j^2 A_1 (t/\tau)^{2/3}]\right\} d(t/\tau) \tag{5}$$

The integral over $X = t/\tau$ is a function only of the constant A_1 and does not depend on N. Therefore, η_s is proportional to τ and has an N^3 dependence. At times longer than t_f, $g(t)$ goes over to the simple diffusion form $g(t) \sim 6D_{cm}t$. In this region, $G(t)$ will decay more rapidly than indicated in (4). However, this will have a slight effect on (5).

Data from a number of polymer systems indicate that the dimensionless product of the equilibrium compliance J_e and the plateau modulus G_N is about 2.4[12] for monodisperse melts of linear polymers. On the other hand, recent work on polybutadiene indicates a somewhat lower value for this product, $J_e G_N = 1.8$.[13] This product can be evaluated from the related product of J_e and η_s, which equals the average relaxation time.[14]

$$J_e \eta_s = \int_0^\infty tG(t)\, dt / \int_0^\infty G(t)\, dt \tag{6}$$

Substituting for η_s from (5) gives

$$J_e G_N = G_N \int_0^\infty tG(t)\, dt / [\int_0^\infty G(t)\, dt]^2 \tag{7}$$

Inserting the expression for $G(t)$ from (4) yields

$$J_e G_N = \frac{\left(\frac{\pi^2}{8}\right)^2 \sum_{j,k=1,3,\ldots} \left[\frac{1}{j^2k^2(j^2+k^2)^3}\right] \int_0^\infty dx\, x e^{-x^{2/3}}}{\left[\sum_{j,k=1,3,\ldots} \frac{1}{j^2k^2(j^2+k^2)^{3/2}}\right]^2 [\int_0^\infty dx\, e^{-x^{2/3}}]^2} = \approx 2.5 \tag{8}$$

The variable x in (8) is equal to $[(j^2 + k^2)A/N^2]^{3/2}t$. The two integrals in (8) are easily evaluated using the change of variable $x = z^3$, and the sums can be evaluated numerically to obtain the final result. This result is in excellent agreement with the experimental value of 2.4[12] but somewhat higher than the estimate from the recent experiments.[13]

For the more general case involving polydisperse samples, the fraction of contacts in the system which remain unbroken from time zero to time t is obtained by averaging $F_{A,B}(t)$ from (1) over all possible types of A and B chains involved in specific contacts. For the case of a polydisperse sample

$$G(t) = G_N \int dN_A\, dN_B\, \rho(N_A)\, \rho(N_B)\, F_{A,B}(t) \tag{9}$$

where $\rho(N)$ is the probability density that a given monomer is in a chain of length N. If $f(N)$ is the probability density that a given chain has length N, then $\rho(N) = Nf(N)/Z$, where Z is a normalization constant. The factor of N accounts for the fact that there are more monomers in long chains. The calculation of (9) is feasible but somewhat tedious. The distribution $\rho(N)$ would have to be approximated by a discrete distribution, allowing only chains of lengths $N_1, N_2, \ldots, N_M$. The dynamics of the chains would require simultaneously evaluating the equations for each type of A–B contact pair and averaging the friction coefficient for each chain length over all contacts involving that chain in order to calculate $g(t)$ for that chain at each time. Since $\langle L_A^2 \rangle$ for a given A–B contact involves knowledge of $g_A(t)$ and $g_B(t)$, the $P_A(t)$ actually depends on the lengths of both chains involved in the contact. This quantity must also be averaged over all types of B chains in contact with a given A chain.

The situation is greatly simplified for the case of a bidisperse blend of two monodisperse samples of a given polymer. This is a case that has been studied experimentally.[9,14] In this case, (9) reduces to

$$G(t) = \phi_L^2 F_{L,L}(t) + \phi_S^2 F_{S,S}(t) + 2\phi_S\phi_L F_{S,L}(t) \tag{10}$$

where ϕ_L is the volume fraction of long chains, $\phi_S = 1 - \phi_L$

$$F_{L,L}(t) = P_{L,L}(t)^2 \tag{11}$$

$$F_{S,S}(t) = P_{S,S}(t)^2 \tag{12}$$

and

$$F_{S,L}(t) = P_{S,L}(t)\, P_{L,S}(t) \tag{13}$$

In these expressions $P_{A,B}(t)$ is the probability that a contact between an A chain and a B chain has not encountered the end of the A chain between time zero and time t. It is given by (2), where $\langle L_J^2 \rangle$ is $\langle L_A^2 \rangle$ for an A–B contact.

III. Calculations

In this section we present results for the stress relaxation in the terminal regime for a bidisperse melt. The calculations are characterized by the lengths of the long and short chains, N_L and N_S, respectively, and by the volume fraction of the long chains, ϕ_L. Since we consider $\phi_L = 0$ and 1 as well as intermediate cases, the results for the monodisperse samples are also obtained. The stress relaxation modulus for the terminal region is given by (2) and (10)–(13). Equation 2, which provides the probability that a given contact point has not encountered the end of chain J, depends on the mean-squared contour displacement in time t of the contact point along chain J, $\langle L_J^2 \rangle$. This quantity depends on the lengths of the two chains involved in the contact. It is evaluated from the expression for the time derivative of $\langle L_J^2 \rangle^{1/2}$ given in the previous paper.[1] Evaluation of this time derivative requires the knowledge of the time derivative of $g_J(t)$ for the two types of chains involved in the contact. In order to simplify the

calculations, we approximate $g_J(t)$ as

$$g_J(t) = \begin{cases} A_J t^{1/3}, & t < t_{f,J} \\ 6D_{cm,J}t, & t > t_{f,J} \end{cases} \quad (14)$$

This form for $g_J(t)$ is reasonable since we found in the previous paper[1] that $g_J(t)$ goes as $t^{1/3}$ for monodisperse melts within the lateral diffusion model for times short compared to $t_{f,J}$. At $t_{f,J}$ it crosses over to the simple diffusion form. We also found that the dynamics of a probe polymer, as measured by D_{cm}, is only weakly influenced by the length of the surrounding molecules. For this reason we use the form in (14) for $g_J(t)$ with the constants A_J, $D_{cm,J}$, and $t_{f,J}$ chosen to be independent of ϕ_L. We apply the conditions that g_J is continuous at $t_{f,J}$, that $D_{cm,J} \sim N_J^{-2}$, that $t_{f,J} \sim N^3$, and that $g_J = N_J/3$ at $t_{f,J}$, where the chain segment length has been defined to be unity. We also require that A_J is independent of chain length, since chain motion at short times should be largely independent of chain length for all sufficiently long chains. Therefore, there is only one independent parameter in (14), which can be taken to be $A_J = A$, which determines the time scale for the calculation. In this regard, this parameter A plays the same role as ζ_C in the previous paper (if the length scale and temperature are fixed). Once A is fixed, the proportionality constants for $t_{f,J}$ and $D_{cm,J}$ are determined.

The constant c_L in the definition of $L_{e,J}$ appearing in (2) is an additional parameter that needs to be specified. We have found that the calculations are not very sensitive to this parameter over a reasonable range of values. We set $c_L = (2\pi)^{-1/2}$, which is the value employed in most calculations in the previous paper.[1] Furthermore, since we require $D_{cm,J}$, $t_{f,J}$, and $g_J(t_{f,J})$ to scale exactly with an appropriate power of N_J, a change in A has the same effect as a change in N_J. Therefore, there are really only two independent parameters which determine the shear relaxation in this model. We take these to be A, which determines the overall time scale, and the ratio of the length of the long chains to the length of the short chains, N_L/N_S.

The calculations are performed by determining $g_L(t)$ and $g_S(t)$ for each time from (14). The subscripts L and S refer to long and short chains, respectively. Then for each time and each type of pair of chains (L–L, S–S, and L–S), the time derivatives of $\langle L_L^2\rangle^{1/2}$ and $\langle L_S^2\rangle^{1/2}$ are calculated from g_L, g_S, $\langle L_L^2\rangle^{1/2}$, and $\langle L_S^2\rangle^{1/2}$ at that time.[1] The values of $\langle L_L^2\rangle^{1/2}$ and $\langle L_S^2\rangle^{1/2}$ are then evaluated at time δt later from these time derivatives, and these are used to evaluate $G(t)$ from (2) and (10)–(13).

In Figure 3, the stress relaxation is shown for a bidisperse blend. The ratio of lengths of long chains to short chains is 8.5 in this calculation. This value of N_L/N_S is chosen so that the ratio of the terminal relaxation times for the long and short chains coincides with the value for the experimental system of Kornfield et al.[9] The value of N_L/N_S for the experimental system is 7. However, the terminal relaxation increases with chain length faster than N^3 in isoprene. To facilitate comparison with the experimental data, we opt to fit $t_{f,L}/t_{f,S}$ rather than N_L/N_S. The overall time scale in the calculations (i.e., the A parameter) is adjusted to obtain agreement with the experimental time scale for the short-chain relaxation. The level of agreement with the experimental data[9] is very good. In Figure 4, we directly compare the model calculations displayed in Figure 3 with the experimental data[9] for the pure long-chain case. The only parameter in the model that has been independently varied is N_L/N_S, so as to achieve agreement with experiment for the terminal

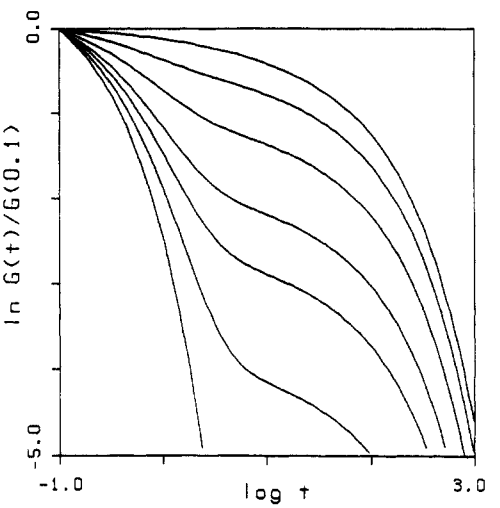

Figure 3. Relaxation modulus plotted for a bidisperse melt calculated using the lateral diffusion model. The ratio of the chain length of the long and short components is $N_L/N_S = 8.5$. The various curves are for different volume fractions of the long component. The curves correspond to $\phi_L = 1.0$, 7.5, 0.5, 0.3, 0.2, 0.1, and 0.0 from top to bottom.

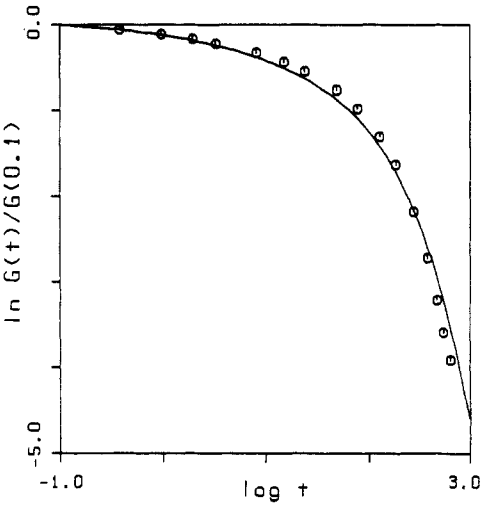

Figure 4. Relaxation modulus plotted for the monodisperse sample of long chains, $\phi_L = 1.0$. The dotted circles are the experimental data of Kornfield et al.[9]

relaxation time for the long chains. The shapes of the time-dependent stress relaxation evaluated in our model and the experimental results[9] are in excellent agreement over the entire range of the reported experimental results. Given the simplicity of the model, this level of agreement may be somewhat fortuitous. Nevertheless, it does indicate that the present model is capable of reproducing the experimentally observed stress relaxation in monodisperse samples.

The model calculations are directly compared with the experimental results for the cases $\phi_L = 0.5$ and $\phi_L = 0.1$ in Figure 5. Again the agreement is quite good, especially considering the simplicity of the model. Since the relaxation times for the long and short chains have been fixed by comparison with the experimental data[9] for the monodisperse samples $\phi_L = 1.0$ and $\phi_L = 0.0$, there are no additional parameters which are varied in obtaining the results shown in Figure 5. The $\phi_L = 0.5$ curve decays somewhat quicker in the experimental system than in the model calculations, and the dip in the $\phi_L = 0.1$ curve is somewhat deeper in the model calculations than in the experimental data. These presumably reflect the fact that we have used the simplest possible variant of our model. In the next section we discuss additional features which

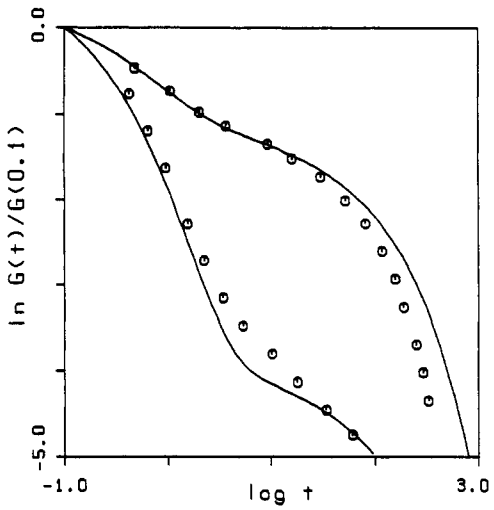

Figure 5. Relaxation modulus plotted for the cases $\phi_L = 0.5$ (upper curve) and $\phi_L = 0.1$ (lower curve). The dotted circles are the experimental data of Kornfield et al.[9]

might improve the agreement between the model and experiment. Even at this primitive level of the model the results are very good.

IV. Discussion

In this paper we have proposed a model for the linear viscoelastic response of linear polymer systems in the melt. The basic model, which is developed within the context of the lateral diffusion model,[1,2] assumes that, immediately after a strain is applied, there is a rapid relaxation of the induced anisotropy in the orientation distribution for the chain segments due to the sliding of chains along the contours of neighboring chains. However, each chain has contacts with a number of other chains, the centers of mass of which are distributed in a way which reflects the applied strain. This network of connections is not broken during this rapid relaxation stage of the dynamics. It can only be broken by the breaking of the interchain contacts which existed at the time at which the strain was applied. This contact breakage occurs on a longer time scale. This process, which accounts for the stress relaxation in the post-plateau regime, can be directly evaluated in the lateral diffusion model.

In developing the lateral diffusion model[1,2] a major simplifying assumption is that the effect of the interchain contacts on the motion of a given chain can be incorporated into an effective single-bead friction coefficient once the curvilinear nature of the constraining contours of the neighboring chains is accounted for. A Rouse model, employing this effective fraction coefficient, is then used for the chain dynamics. The use of an effective friction coefficient is a mean-field treatment of the constraints imposed by neighboring chains. It ignores the fact that each constraint restricts the chain motion in a specific direction. The model assumes that the chain has enough flexibility and freedom so that this does not have a significant effect on the bead mean-squared displacement. However, the model presented here for the stress relaxation takes the specific anisotropic nature of the constraints in the stressed system into account in that they support the stress through the network of connections extending throughout the system. If we were to ignore this aspect of the problem and merely use an isotropic Rouse model with a time-dependent friction coefficient to calculate the stress, then we would obtain a more rapidly decaying stress relaxation function with a weaker N dependence.[3]

We have shown that the simple model presented here for stress relaxation in the linear viscoelastic regime produces a terminal relaxation time and a shear viscosity which scale as N^3 for monodisperse samples. This is the same power law dependence as predicted by reptation.[3] It is a well-known fact that the observed experimental power law dependence of these quantities is somewhat stronger. It is usually taken to be roughly $N^{3.4}$. A number of explanations for the source of the discrepancy have been proposed in the context of the reptation model.[16-18] Most of these would apply to the current model as well. It is also possible that the model discussed in this paper may suggest still other possible explanations for this apparent disagreement.

We have also made a direct comparison of the time-dependent stress relaxation as predicted by our model with experimental data. We find that this model reproduces the shapes of the experimental stress relaxation curves very well for monodisperse and bidisperse samples.

In their experimental work, Kornfield et al.[9] are able to investigate the individual relaxation of the short chains and the long chains in the bidisperse samples. They find that the relaxation of the short chains slows significantly if the volume fraction of the long chains in the sample is increased. This has been interpreted in the context of reptation as a sign of orientational ordering[15,19,20] due to a neumatic interaction between the chain segment and nearby segments on other chains. An orientational ordering should also be included in the current model, although the rationale for it is slightly different. Since the chains move by sliding along neighboring chains, a chain segment should assume some orientational ordering as it performs a biased walk along the oriented contours of its neighbors. Furthermore, when contacts are broken and new ones are formed, the distribution of the chain center of mass for the new contacts is not random. Rather it reflects the remaining stress in the system at the time of contact formation. We neglect these effects when we assume that new contracts support no stress. We are currently considering how to correctly incorporate this into the model.

Kornfield et al.[9] also see a decrease in the relaxation time of the long chains if the volume fraction of short chains is increased. This is attributed to a combination of orientational ordering[15,19,20] and constraint-release effects in the context of reptation. The reptation model with the constraint-release[21-26] contribution to the stress relaxation results in a formula for the relaxation modulus which is similar to our model, (2) and (7)–(10), although the interpretation of the relaxation is quite different. Since we employ a primitive form of our model which does not include orientational ordering, we do not accurately reproduce these changes of the relaxation rates for the individual components. These changes in the relaxation of the components lead to the discrepancies that we find when we compare our model calculations for the bidisperse system with the experimental decay curves at intermediate values of ϕ_L.

Despite the neglect of this secondary effect in the current model, the calculations clearly show that the current model produces a relaxation curve for monodisperse samples in excellent agreement with experiment for the post-plateau region. Furthermore, the very good agreement found for bidisperse samples suggests that the model correctly weighs each type of interchain contact (i.e., long–long, short–short, and long–short) and provides an expression for the contribution of each type of contact which accurately

accounts for the experimental behavior. This level of agreement of the primitive model with the experimental relaxation for the total systems is very encouraging, and we are currently investigating the inclusion of secondary features such as orientational ordering into the calculations.

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References and Notes

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