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neously performing Brownian ("jittering") motion. Non-Newtonian systems often show nonlinear hydrodynamics. If the motion of a body has two velocity components, the total drag on that body in a non-Newtonian fluid may not be the sum of the drags experienced if the body performed each of the component motions separately. The sedimentation of a Brownian particle need not be the same as the sedimentation of an elsewise similar particle whose Brownian motion has been suppressed. Einstein's arguments refer to the drag coefficient of a particle which simultaneously sediments and diffuses, not to a body which sediments without undergoing Brownian motion.

In conclusion, we have observed probe diffusion in a polyelectrolyte solution, noting the dependence of D on the major experimental variables: polymer concentration, polymer neutralization, ionic strength, probe radius, and solution viscosity. Relatively simple relations connect these variables. The available theoretical models for D are not entirely satisfactory, in that they predict incorrectly the dependence of D/D_0 on R and do not predict accurately the dependence of D on I or c. Identification of the relationship between D and viscosity requires a more extensive study of the rheological properties of the polyelectrolyte solutions used for the probe diffusion measurements.

Registry No. Polystyrene, 9003-53-6; poly(acrylic acid) sodium salt, 9003-04-7.

Supplementary Material Available: Tables of D values for polystyrene spheres at various electrolyte concentrations as a function of polymer concentration and at various pHs and polymer concentrations as a function of the concentration of added NaCl and tables of results at various pHs on polystyrene spheres in different poly(acrylic acid) and NaCl concentrations (13 pages). Ordering information is given on any current masthead page.

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Reptation of Living Polymers: Dynamics of Entangled Polymers in the Presence of Reversible Chain-Scission Reactions

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ABSTRACT: A theoretical study is made of the dynamics of stress relaxation in a dense system of "living" polymers. These are linear chain polymers that can break and recombine on experimental time scales. A simple model for the reaction kinetics is assumed, in which (i) a chain can break with equal probability per unit time per unit length at all points in the chemical sequence and (ii) two chains can combine with a rate proportional to the product of their concentrations. The chain length distribution is then exponential with mean $\bar{L}$; $\bar{L}$ is taken to be large enough that $\alpha = L_e/\bar{L} \ll 1$, where L_e is the entanglement length. It is further assumed that stress relaxation proceeds by the reptation mechanism—a process that may, however, be abetted by the constant breaking and reforming of the chains (thus enhancing the rate at which portions of unrelaxed tube become first occupied by a chain end, causing them to relax). Two relevant time scales are τ_{rep}, the reptation time of a polymer of length $\bar{L}$, and $\tau_{\text{break}} \equiv \tau_{\text{rep}}\zeta$ (say) the mean time for such a chain to break into two pieces. For $\zeta \gtrsim 1$, the dominant stress-relaxation mechanism is simple reptation (with characteristic time τ_{rep}). For $\alpha \lesssim \zeta \lesssim 1$, it is predicted that stress relaxation is characterized by a new *intermediate* time scale, $\tau = \tau_{\text{rep}}\zeta^{1/2} = (\tau_{\text{rep}}\tau_{\text{break}})^{1/2}$, associated with a process whereby the chain breaks at a point close enough to a given segment of tube for reptative relaxation of that segment to occur before the new chain end is lost by recombination. Crossovers are ascribed to similar relaxation mechanisms involving the breathing modes of the chain and local Rouse-like motion, which dominate respectively when $\alpha^3 \lesssim \zeta \lesssim \alpha$ and $\zeta \lesssim \alpha^3$.

1. Reptation Model

The dynamical theory of polymer melts has advanced remarkably in recent years. It was first suggested by de Gennes[1a] that the chief relaxation mechanism, for long linear polymers in the melt, is that of reptation. This process consists in the gradual disengagement of any given chain, by curvilinear diffusion along its own contour, from a tubelike environment. The tube is made up of neighboring chains; these present a set of topological obstacles to diffusion normal to the chain contour (Figure 1). For chains of length L, the fundamental relaxation time of the system is then

$$\tau = \tau_{\text{rep}} = L^3/D_0 \tag{1}$$

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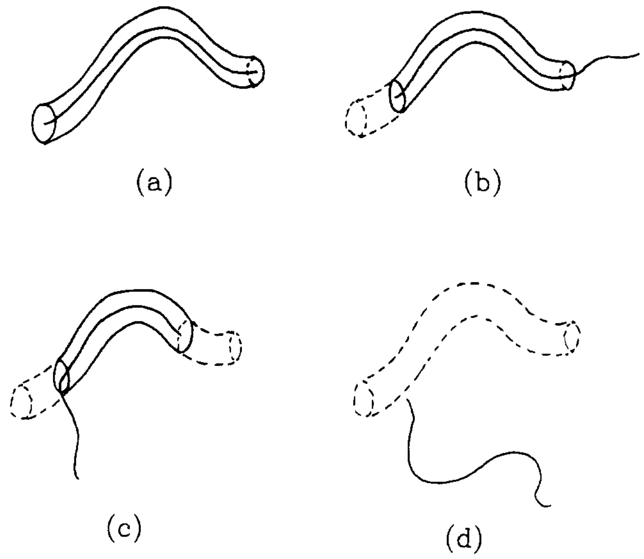

Figure 1. Reptation of a chain in its tube. The tube is defined at time $t = 0$ (a). Curvilinear diffusion causes parts of the tube to be lost (b,c); the new tube that is formed (not drawn) is in equilibrium and does not support stress. At $t \gtrsim \tau_{\text{rep}}$, none of the original tube remains (d).

Here D_0 is a mobility constant, independent of L; the curvilinear diffusion constant of a chain along its own contour is

$$D_c = D_0/L$$

Since each chain has to diffuse a curvilinear distance L to disengage from its tube, we have

$$L^2 \cong D_c\tau$$

which gives the result (1). Since successive acts of disengagement are uncorrelated and each results in a displacement of the center of mass of the chain by a distance of order its gyration radius $R \sim (Ll)^{1/2}$ (with l the Kuhn length), the diffusion constant of the chain in real space is

$$D \cong R^2/\tau_{\text{rep}} \cong D_0 l L^{-2} \tag{2}$$

The result (2) is well confirmed experimentally,[2] for chains longer than a critical length L_e, the entanglement length. For shorter chains, the topological obstruction of one chain by another is much less important; the dominant relaxation mechanism is not reptation, but a Rouse-like motion.[3]

It follows[1] from eq 1 that the zero-shear viscosity, η, should obey

$$\eta \cong G_0\tau_{\text{rep}} \sim L^3 \tag{3}$$

for a homologous series of melts of different chain lengths $L \gtrsim L_e$. Here G_0 is the instantaneous shear modulus, which is proportional to the density of degrees of freedom that couple to the reptative relaxation mechanism (i.e., the number density of "entanglements") and is independent of L for $L \gtrsim L_e$. Notice that by demanding continuity (at $L \cong L_e$) of eq 2 and 3 with the corresponding results from the Rouse model[3] ($D \sim 1/L$; $\eta \sim L$; $G_0 \sim 1/L$), one obtains the following dependence on L_e of the parameters in the reptation model:[1b]

$$D_0 \sim L_e; \qquad G_0 \sim 1/L_e$$

The result (3) is somewhat less satisfactory than (2), since the experimental data is traditionally described[2] by the law $\eta \sim L^{3.4}$. However, various explanations for this discrepancy have been proposed within the framework of the tube model.[4] (In particular, it is possible that the observed behavior is simply a misleading crossover from the Rouse-like regime at $L \lesssim L_e$.)

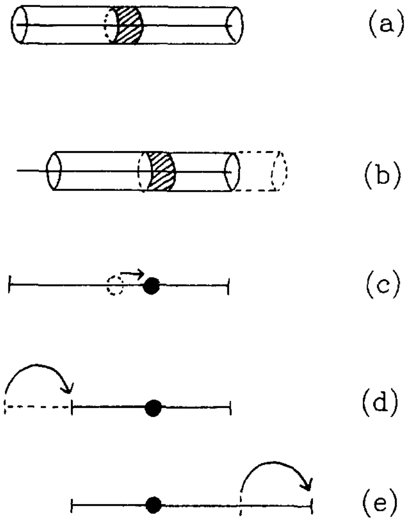

Figure 2. (a,b) History of a given portion of tube (shaded) can be traced by imagining the tube to diffuse relative to the chain (for clarity this is drawn fully extended). As soon as the shaded portion passes either end of the chain (of length L), the stress associated with it is lost. The probability $\mu(t)$ that this has not happened by time t is therefore the survival probability of a particle diffusing on the line segment $[0,L]$ with absorbing boundary conditions at each end (c). Averaging over all tube segments present at time zero is equivalent to averaging over all starting positions of the particle. In the presence of breakage and recombination, the process is modified (eq 10) so that the absorbing walls can make discrete jumps toward or away from the particle (corresponding to breakage (d) and recombination (e), respectively). The instantaneous diffusion constant of the particle varies inversely with the total length of the chain and so fluctuates in time.

Doi and Edwards[5] examined in detail the consequences of the reptation hypothesis, and constructed a constitutive equation that describes the linear and nonlinear viscoelastic response of polymer melts under a variety of deformation conditions.[2] In the Doi–Edwards theory, a central object is the stress relaxation function $\mu(t)$, which describes the fraction of imposed stress remaining at time t after an infinitesimal stress is imposed at time 0. This is simply the average fraction of tube (existing at time zero) that has not been lost by disengagement by time t:

$$\mu(t) = (8/\pi^2) \sum_{p=\text{odd}} p^{-2} \exp(-tp^2/T_d) \tag{4}$$

where $T_d = L^2/D_c\pi^2 \cong \tau_{\text{rep}}$. This result is found by observing that the parts of the original tube remaining at time t are those through which neither end has passed. By imagining the chain to be at rest in a moving tube (Figure 2a–c), it is easy to see that $\mu(t)$ is the survival probability a particle of diffusion constant D_c, launched at $t = 0$ with uniform probability on the line segment $[0, L]$ with absorbing boundary conditions at either end. The result (4) is easily found by Fourier decomposition. The zero-shear viscosity η is then given by

$$\eta = G_0 \int_0^\infty \mu(t)\, dt \tag{5}$$

In deriving $\mu(t)$, an important assumption is that the tube constraint imposed on any given chain by its neighbors remains intact on the time scale τ_{rep} of the disengagement. Since these neighbors are themselves disengaging from their own tubes on the same time scale, this assumption is not obviously self-consistent. Nonetheless, the Doi–Edwards theory is remarkably successful at describing the experimental results for high polymers of narrow molecular weight distribution.[2] For polydisperse systems, however, a simple superposition of the Doi-Edwards $\mu(t)$ for different chain lengths proves to be inadequate,[6] and explicit account must be taken of the "tube renewal" effects[7] that result from rearrangement of neighboring chains. Nonetheless, unless the system contains (in significant numbers) chains of two or more *completely dissimilar* lengths, the characteristic relaxation time τ that enters the viscosity, $\eta \cong G_0\tau$, should remain comparable to the reptation time $\tau_{\text{rep}}(\bar{L})$ of a chain of some average length, $\bar{L}$.

2. Living Polymers

In the present paper, we discuss the modifications that must be made to the reptation picture in order to describe the dynamics of long linear chains ($L \gg L_e$) that can break and re-form on experimental time scales ("living polymers"). Our principal motivation comes from three types of experiment:

(i) Recent studies of surfactant organization in micellar systems and microemulsions[8] have demonstrated that, under special conditions, the equilibrium structure consists of a concentrated solution of tubular micelles that are very much longer than an appropriately defined Kuhn length; they can therefore be treated theoretically as polymers.[10] Preliminary experimental data on shear behavior,[9] which indicates a strong dependence of viscosity on the volume fraction of surfactant, appears to be qualitatively compatible with the results from a reptation theory.[11] However, theoretical work on micellization[10,12] suggests that, under appropriate conditions, there may be no upper limit to the length of the micelles in equilibrium. Presumably therefore, there exists a regime of parameters in which the reptation time of the micelles is so long that it exceeds the time scale characterizing the dynamic equilibrium of their breakage and reformation; in anticipation of experiments in this regime, we ask here what can be said theoretically about the resulting dynamics.

(ii) Systems of end-functionalized linear polymers are of increasing experimental interest,[13] especially insofar as they provide well-characterized examples of a much larger class of "associating polymers". These are polymers that can form transient reversible linkages with one another; they are of considerable technological significance as flow-modifying additives.[14] If both ends of each polymer are capped with a functional group that tends to form dimers (such as carboxylic acid groups in a nonpolar environment), then at high density the polymers will themselves be predominantly polymerized into longer linear chains. The reptation time can then become very great, and one certainly expects the kinetics of chain breakage and recombination to be relevant in determining the time scale of stress relaxation in the melt and concentrated solutions.

(iii) Third, one may be interested in the dynamics of chemically homogeneous equilibrium polymers, as seen in systems such as liquid sulfur.[15,16] In fact it is found that the present model (as extended in section 4 to cover the case of very small τ_{break}) gives an excellent account of the experimentally observed viscosity of sulfur over a wide temperature range above the polymerization point. Details of the relevant calculation will be presented elsewhere.[17]

2.1 Kinetics of Breaking and Recombination. We start from the simplest possible model for the kinetics of chain breakage and recombination. In this model it is assumed that a chain can break with a fixed probability per unit time per unit length anywhere along its length, L. (Thus L is treated as a continuous variable and can take any positive value.) It is further assumed that the reverse reaction proceeds at a rate proportional to the product of the concentrations of the two reacting subchains and, moreover, that the rate constant involved is independent of the molecular weights of these two subchains. This latter assumption is based on the idea that, at high enough concentration, the rate-limiting step is not the diffusion of the reacting chains over a large distance[18] but some local kinetic process. We also assume successive breakage and recombination events for a given chain to be uncorrelated—there is no higher probability for a chain end to link up with the chain from which it was recently detached than with any other chain end in the vicinity. The conditions under which these assumptions are self-consistent will be discussed in section 3.2. Finally we note that since only the *linear* viscoelastic response will be considered, it is unnecessary to consider whether or not these reaction kinetics are significantly altered by the application of a strain field.

With these assumptions, the equation governing the time development of the number density $N(L)\,\mathrm{d}L$ of chains of length $L \pm {}^1/_2\,\mathrm{d}L$ may be written as

$$\dot{N}(L) = -c_1 L N(L) - c_2 N(L) \int_0^\infty \mathrm{d}L'\, N(L') + 2c_1 \int_L^\infty \mathrm{d}L'\, N(L') + c_2 \int_0^\infty \int_0^\infty \mathrm{d}L'\, \mathrm{d}L''\, N(L')N(L'')\delta(L' + L'' - L) \quad (6)$$

Here the first term represents the decrease in $N(L)$ by breakage, the second is the decrease by reaction of chains of length L with others to form longer chains, the third is the rate of creation of chains of length L by breakage of longer chains, and the final term is the rate of creation by reaction of two shorter chains to produce one of length L. The parameters c_1 and c_2 are (appropriately dimensioned) rate constants for the breakage and recombination processes, respectively.

This equation has the steady-state ($\dot{N}(L) = 0$) solution

$$N(L) = (2c_1/c_2) \exp(-L/\bar{L}) \quad (7)$$

where $\bar{L}$ depends as follows on the rate constants and the overall arc concentration of polymer, $\rho = \int_0^\infty LN(L)\,\mathrm{d}L$:

$$2\bar{L}^2 = \rho c_2/c_1 \quad (8)$$

It is convenient to define the characteristic time

$$\tau_{\text{break}} = (c_1\bar{L})^{-1} \quad (9)$$

which is the expected survival time of a chain of the mean length $\bar{L}$ before it breaks into two pieces. Note that the survival time of a typical chain end, before it is lost by recombination, is of the same order as τ_{break}; the equivalence of these two time scales is a direct consequence of the principle of detailed balance.

2.2 Dynamics of Stress Relaxation. We imagine a system of chains in a steady state of dynamic equilibrium as described by eq 6–9. In a small time interval δt, a chain of length $L(t)$ can break in any small interval δl along its length, with probability $c_1\delta l\delta t$, or either of its ends can join with another chain of length $L' \pm \delta L$, in each case with probability $c_1 \exp(-L'/\bar{L})\delta L\delta t/2$.

It is simple enough in principle to couple this stochastic process with that describing the curvilinear diffusion of a chain in its tube, as described after eq 4. We recall that, in that case, it was convenient to consider a section of the original tube as a particle of diffusion constant D_c launched with uniform probability on the line segment $[0,L]$ with absorbing walls at either end (Figure 2); $\mu(t)$ is then the survival probability at time t after launch. In the present case we must allow the absorbing walls themselves to make jumps according to the stochastic process described in the previous paragraph (Figure 2d,e). Let us denote the length of the line segment to the left of the particle by $L_{\mathrm{left}}(t)$, and that to the right by $L_{\mathrm{right}}(t)$; the sum of these is $L(t)$. Without loss of generality, we can set in eq 7 $\bar{L} = 1$ (by choosing it as the unit of length), in which case $\langle L_{\mathrm{left}} \rangle = \langle L_{\mathrm{right}} \rangle = 1$. (Note that *each half* of the chain has average length $\bar{L}$, not $\bar{L}/2$. This is because we are averaging over all points on all chains, which is a weight average.)

This gives the following transition probabilities in a small time interval δt:

$$p = 1/2: \qquad L_{\mathrm{left}} \rightarrow L_{\mathrm{left}} + \Delta; \quad L_{\mathrm{right}} \rightarrow L_{\mathrm{right}} - \Delta \tag{10a}$$

$$p = 1/2: \qquad L_{\mathrm{left}} \rightarrow L_{\mathrm{left}} - \Delta; \quad L_{\mathrm{right}} \rightarrow L_{\mathrm{right}} + \Delta \tag{10b}$$

$$p = 2c_1\delta L\delta t: \qquad L_{\mathrm{left}} \rightarrow L'_{\mathrm{left}} \pm \delta L \quad (L'_{\mathrm{left}} < L_{\mathrm{left}}) \tag{10c}$$

$$p = 2c_1\delta L\delta t: \qquad L_{\mathrm{right}} \rightarrow L'_{\mathrm{right}} \pm \delta L \quad (L'_{\mathrm{right}} < L_{\mathrm{right}}) \tag{10d}$$

$$p = c_1 \exp(-L')\delta L\delta t: \qquad L_{\mathrm{left}} \rightarrow L_{\mathrm{left}} + L' \pm \delta L \tag{10e}$$

$$p = c_1 \exp(-L')\delta L\delta t: \qquad L_{\mathrm{right}} \rightarrow L_{\mathrm{right}} + L' \pm \delta L \tag{10f}$$

In these equations, $\pm\delta L$ represents symbolically an infinitesimal length interval. Equations 10a and 10b represent the Doi–Edwards diffusion process, in which a small portion of the chain to the left of the particle is transferred to the right, (10a), or vice versa, (10b); for simplicity we have defined the transition probability as $^1/_2$, independent of the time step δt, and accordingly taken a diffusive step length

$$\Delta = (2D_c\delta t)^{1/2} = [2(D_0/L(t))\delta t]^{1/2}$$

Note that Δ depends on the instantaneous curvilinear mobility, $D_c = D_0/L(t)$, and so changes stochastically with time. Equations 10c and 10d describe the kinetics of the breaking process, and eq 10e and 10f that of recombination; each of these occurs independently for the left and right half of the chain. To complete the specification of the system, we state that at time $t = 0$, L_{left} and L_{right} are chosen independently from an exponential distribution with mean $\bar{L} = 1$; moreover, if in any time interval δt either L_{left} or L_{right} becomes negative, the particle dies. With these definitions, the stress relaxation function $\mu(t)$ is simply the survival probability of the particle to time t, just as in the simpler case of ordinary reptation.

Since the jumps in L_{left} and L_{right} corresponding to breakage and recombination are not infinitesimal (as $\delta t \rightarrow 0$), the stochastic process described by eq 10 is no longer purely diffusive, and we do not expect an analytic solution to the problem. Nonetheless, various things can be said.

First, if $\tau_{\mathrm{break}} \rightarrow \infty$, we are left with the Doi–Edwards stress-relaxation calculation for a system of chains with exponential polydispersity, as given by eq 7. Thus eq 10a and 10b will give

$$\mu(t) = \bar{L}^{-1}\int_0^\infty L \exp(-L/\bar{L})\mu(L,t)\, \mathrm{d}L \tag{11}$$

where $\mu(L,t)$ is given by eq 4. A steepest descents analysis then suggests that to a good approximation (11) can be replaced by

$$\mu(t) \sim \exp[-(t/\tau_{\mathrm{rep}})^{1/4}] \tag{12}$$

where τ_{rep} stands for $\tau_{\mathrm{rep}}(\bar{L}) = D_0/\bar{L}^3$. This is a rather disperse relaxation function, which in practice one would expect to be significantly modified by tube renewal effects, as discussed in section 1. Nonetheless, one does not expect the power law dependence on $\bar{L}$ of the viscosity,

$$\eta \sim \int_0^\infty \mu(t)\, \mathrm{d}t \sim \tau_{\mathrm{rep}}(\bar{L}) \sim \bar{L}^3 \tag{13}$$

to be affected by tube renewal, since this occurs on a comparable time scale to reptation itself. Generalizing to the case when $\tau_{\mathrm{rep}} \lesssim \tau_{\mathrm{break}} \neq \infty$, we expect the relaxation function in (12) to be reduced at long times ($t \gtrsim \tau_{\mathrm{break}}$), by which time it is, however, already small. Thus the viscosity η is still given by (13).

The interesting new regime occurs when $\tau_{\mathrm{break}} \lesssim \tau_{\mathrm{rep}}$. In this regime, chain breakage and reformation will both occur often, for a typical chain, before it has disengaged from its tube by ordinary reptation. We propose that the dominant relaxation mechanism for the relaxation of a typical tube segment x, initially not close to the end of a chain, is then as follows: (i) The chain breaks within a certain distance λ of x along the chemical sequence. (ii) Curvilinear diffusion brings the new chain end past x before this chain end is lost by recombination (Figure 3).

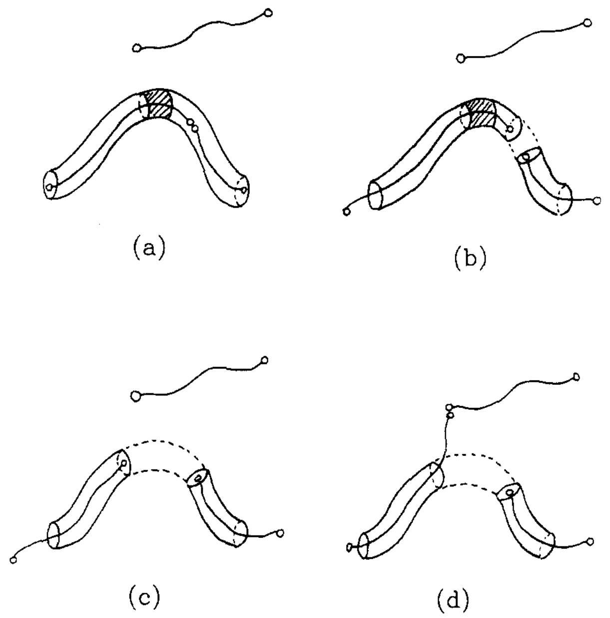

Figure 3. *Relaxation mechanism proposed in the text.* The relaxation of the shaded segment proceeds when a break occurs within a distance λ in the chemical sequence (a). The break must be close enough that the new end can pass through the shaded segment (b,c) before it recombines with that of a neighboring chain (d).

Since the recombination time is comparable to τ_{break} (by detailed balance; see section 2.1), we find that λ, the largest distance at which a break can usefully occur for relaxation by this mechanism, obeys

$$\lambda^2 \cong D_c(L)\tau_{\mathrm{break}}$$

where L is the length of the newly broken chain. Presuming this to be of order the mean, $\bar{L}$, we obtain

$$\lambda^2 \cong D_0\, \bar{L}^{-2}/c_1 = \bar{L}^2\zeta \qquad (\zeta \ll 1) \tag{14}$$

where we have introduced

$$\zeta \equiv \tau_{\mathrm{break}}/\tau_{\mathrm{rep}} \tag{15}$$

We claim that the rate-limiting step in the relaxation process for a typical tube segment involves waiting for a break to appear within a distance λ given by eq 14. Since the probability of a break per unit length per unit time is c_1, the corresponding waiting time is of order

$$\tau \cong (c_1\lambda)^{-1} \cong D_0^{-1/2}c_1^{-1/2}\bar{L} = \tau_{\mathrm{rep}}\zeta^{1/2} \tag{16a}$$

This may be rewritten as

$$\tau \cong (\tau_{\text{rep}}\tau_{\text{break}})^{1/2} \qquad (\zeta \lesssim 1) \qquad (16b)$$

which emphasizes that the dominant relaxation process involves a cooperation between the breaking and reptation mechanisms. Notice that the result expressed in this form has no explicit dependence on the overall chain concentration, the Kuhn length, and other parameters; these only enter through τ_{break} and τ_{rep}. Thus we expect the result to apply whenever the reptation model is appropriate for the description of chain dynamics on scales of order λ. (This condition is quantified in section 4 below.)

One might imagine that a tube segment on a very long chain could relax faster than this by waiting for *two* breaks to occur nearby (one on either side). This would leave the segment on a chain of length $L \ll \bar{L}$, with a corresponding gain in curvilinear mobility. However, a straightforward extension of the above analysis shows that this would lead to a fundamental relaxation time (for $\zeta \lesssim 1$)

$$\tau \cong \tau_{\text{rep}}^{2/3}\tau_{\text{break}}^{1/3} = \tau_{\text{rep}}\zeta^{1/3}$$

which is longer than that given by eq 16 when ζ is small. Consequently this alternative relaxation mechanism can be neglected in the asymptotic limit of small ζ.

In summary, for $\zeta \lesssim 1$, we expect $\tau \cong (\tau_{\text{rep}}\tau_{\text{break}})^{1/2}$, as given by eq 16a and 16b, to be the fundamental time scale for stress relaxation in the system. Also, since the breaking process occurs randomly everywhere along a chain, we expect the relaxation function $\mu(t)$ to be much closer to a pure exponential decay than, say, eq 12. For the viscosity η, we obtain from (16)

$$\eta \cong G_0\tau \cong G_0D_0^{-1/2}c_1^{-1/2}\bar{L}$$

Thus, at fixed c_1 and D_0, η varies linearly with $\bar{L}$ rather than with $\bar{L}^3$, which was the result for reptation without breakage. (Note that for experimental purposes, it may be simplest to vary $\bar{L}$ by controlling ρ, the overall polymer density (cf. eq 8). In this case the fact that D_0 and G_0 also depend on ρ must, of course, also be taken into account.)

Since the individual chains have only transient identity, it is meaningless to discuss their center-of-mass diffusion. However, one can ask what is the spatial diffusion constant D_{mon} of a labeled monomer as it moves through the system. To calculate this, we introduce a characteristic arc length, $\hat{L}$, and a time, $\hat{\tau}$, as follows:

$$D_c\hat{\tau} \cong \hat{L}^2 \qquad (17a)$$

$$\hat{\tau} \cong (c_1\hat{L})^{-1} \qquad (17b)$$

which may be solved to give

$$\hat{L} \cong \bar{L}\zeta^{1/3} \qquad \hat{\tau} \cong \tau_{\text{rep}}\zeta^{2/3}$$

Equations 17 define the time $\hat{\tau}$ that a chain can typically diffuse along a given tube before a breakage/recombination event occurs within the length $\hat{L}$ of tube that the chain has traversed in this time. When such an event occurs, the monomer we are following will be diverted off along another portion of tube, originally belonging to a different chain, and hence uncorrelated with the first. Thus the motion of the chain at long times consists of random steps of mean-square spatial extent $\hat{L}l$ on the time scale $\hat{\tau}$. The corresponding diffusion constant D_{mon} obeys

$$D_{\text{mon}} \cong \hat{L}l/\hat{\tau} \cong l\bar{L}^{-2/3}D_0^{2/3}c_1^{1/3} \cong D_{\text{rep}}\zeta^{-1/3} \qquad (18)$$

where D_{rep} is the long-time diffusion constant for a monomer (or chain), in the ordinary reptation model (eq 2). It is notable that $\hat{\tau}$, the time for a monomer to transfer out of its original tube, is much less than τ (given by eq 16), the decay time for the relaxation of the tube itself. This is possible because a given tube segment remains unrelaxed so long as it remains continuously occupied by a chain (i.e., without an end having passed through) even if the material constituting the chain itself has, in this period, been replaced many times over.

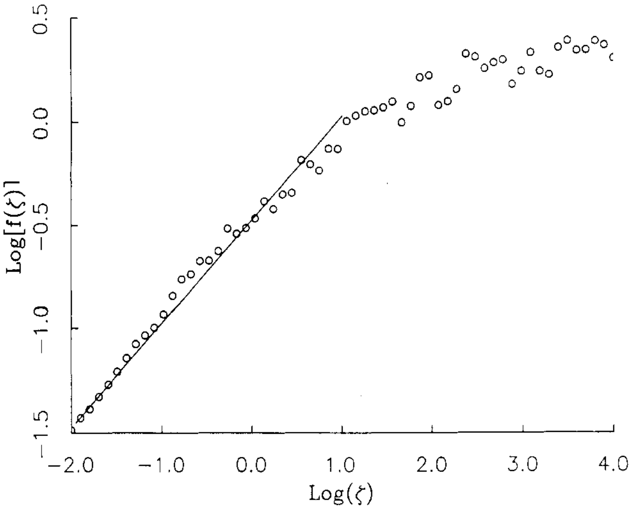

Figure 4. log–log plot of the dimensionless viscosity $f(\zeta)$ against $\zeta \equiv \tau_{\text{break}}/\tau_{\text{rep}}$. The circles denote data points; the statistical error is of order the scatter. The solid line has slope $^1/_2$ as predicted by eq 16 for the regime $\zeta \ll 1$. For $\zeta \gtrsim 1$, log f tends to a constant ($\simeq$0.3), as expected.

2.3 Numerical Study of the Coupled Equations. In order to test the argument leading to (16), a direct implementation of the stochastic equations (eq 10) was performed numerically. Rewriting the equations in terms of the variables

$$\tau_{\text{rep}} \equiv \tau_{\text{rep}}(\bar{L}) = \bar{L}^3/D_0 \qquad \zeta \equiv \tau_{\text{break}}/\tau_{\text{rep}}$$

(introduced above) one finds that the viscosity η may be written in the form

$$\eta = G_0\tau_{\text{rep}}f(\zeta)$$

Here the function $f(\zeta)$ is dimensionless and should tend to a constant at large argument (by eq 13). The result (16) then amounts to predicting that $f(\zeta) \rightarrow \zeta^{1/2}$ for $\zeta \ll 1$. Figure 4 shows the numerical results for $f(\zeta)$ on a log–log plot; the theoretical slope for small ζ is indicated. These results were computed by taking averages over 400 runs for each of 60 values of ζ; for each ζ the scaled time increment was chosen short enough that the average diffusive step length, $\Delta(\bar{L})$, and the probability per timestep of breaking or joining, $c_1\bar{L}\delta t$, remained small. It was checked explicitly that the stationary probability distributions for L_{left} and L_{right} were conserved by the dynamics (to the expected statistical accuracy) and that the results for $f(\zeta)$ were insensitive to small changes in δt. As might be expected from eq 13, a small fraction of the runs for $\tau_{\text{break}} \gg \tau_{\text{rep}}$ persisted for a very long lifetime; a cutoff was introduced at $t = 100\ \tau_{\text{rep}}$ by which time $\mu(t)$ was at most of order 10^{-2}. To check that this cutoff was not important, a separate algorithm for the case of $\tau_{\text{break}} = \infty$ was run for a much longer time; the asymptotic value of $\log_{10}[f(\infty)] \cong 0.29$ found in this way was not significantly different from that approached at large ζ, as shown in Figure 4.

As seen from the figure, the numerical results are quite consistent with the predicted result (16) for the asymptotic behavior of $f(\zeta)$ at small ζ: $f \sim \zeta^{1/2}$. As expected, there is a smooth crossover to purely reptative behavior ($f \rightarrow$ constant) at $\zeta \gg 1$. Figure 5 shows a selection of plots of the relaxation function $\mu(t)$ for different ζ. As predicted

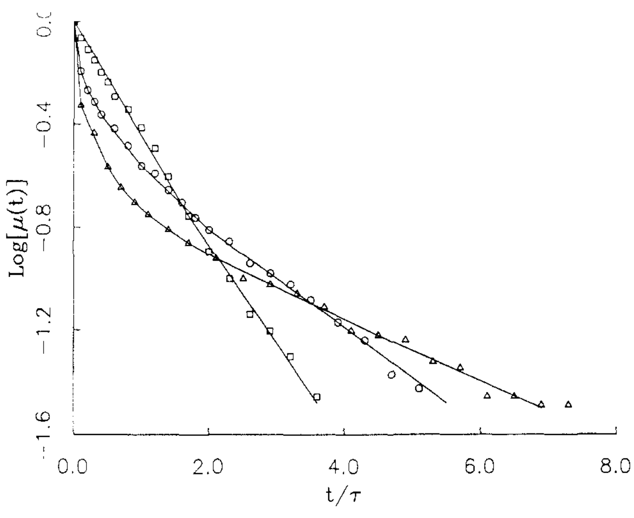

Figure 5. log–linear plots of the stress-relaxation function $\mu(t)$ against time for $\zeta = 0.01$ (squares), $\zeta = 2.75$ (circles), and $\zeta = 3100$ (triangles). These curves were computed numerically from eq 10, as described in the text. In each case the time axis is scaled by the corresponding relaxation time, $\tau = \eta/G_0 = f(\zeta)\ \tau_{\rm rep}$. The solid curves are to guide the eye. Note that for ζ small the decay is almost purely exponential (linear on this plot), whereas for large ζ it is much more disperse.

in section 2.2, those for small ζ are close to pure exponential in form, whereas for ζ large the decay profile is much more disperse—as would apply in the limiting case of no breakage, eq 12.

3. Discussion

3.1. Fixed-Tube Assumption. An obvious question arising from the above analysis is that of to what extent the assumption of a fixed tube, inherent in the reptation picture, continues to be applicable when all the chains can break and reform. As discussed in section 1, for the reptation model itself, one can expect the rearrangement of neighboring chains to occur on the same basic time scale as the disengagement of a given chain; hence it should have some effect on the form of the relaxation function $\mu(t)$, without altering the scaling with chain length of the fundamental relaxation time, $\tau = \eta/G_0 \sim \bar{L}^3$ (eq 13). It seems likely that similar remarks will apply in the present case; that is, we expect the tube to survive at least a time of order τ as given by (16), beyond which time the stress has, in any case, substantially relaxed. With this in mind, we should perhaps not attach much weight to the particular forms of $\mu(t)$ indicated in Figure 5 but instead draw attention again to the more general result describing the dependence of fundamental relaxation time, τ, on $\tau_{\rm break}$ and $\tau_{\rm rep}$:

$$\tau \cong (\tau_{\rm break}\tau_{\rm rep})^{1/2} \tag{16}$$

Of course, even this result can only be trusted insofar as one believes the reptation prediction, eq 3, to be asymptotically correct for ordinary linear chains of sufficient length—a conclusion which itself remains unclear experimentally, as was discussed in section 1.

3.2. Self-Consistency of the Kinetic Equations. It was assumed in section 2.1 that (a) the reaction rate for the amalgamation of two chains was proportional to the product of their concentrations, with a proportionality constant independent of the chain lengths and (b) successive breakage and recombination events were uncorrelated. Both of these conditions are likely to hold so long as the volume $V_{\rm e}$ that is explored by a chain end before it recombines is large enough to contain the ends of many other chains. If this is true, the recombination process involving that end will make an unbiased sampling of the ensemble of other chains, in proportion to their number density and with no particular preference for the chain end that was involved in the preceding dissociation event. Since exploration by a reptating chain end is compact,[18] the volume $V_{\rm e}$ is of order $(\lambda l)^{3/2}$; in a melt, the condition for consistency is then

$$(\lambda l)^{3/2}/(\bar{L}l^2) \gg 1$$

The factor $1/(\bar{L}l^2)$ in this expression is just the density of chain ends. Since $\lambda \cong \bar{L}\zeta^{1/2}$ this may be rewritten as

$$\zeta \gg (\bar{L}/l)^{-2/3}$$

This, for long chains, is a rather weak restriction on $\zeta = \tau_{\rm break}/\tau_{\rm rep}$; only for very small values will the effects of chain diffusion on reaction rates be noticeable. Of course, for partially diluted systems, they may become much more important.

In any case it should be noted that the fundamental scaling result for the relaxation time, eq 16, does not depend in detail on our assumptions for the recombination kinetics. The only requirements are that a chain can break with roughly equal probability per unit time anywhere along its length and that the recombination kernel depends sufficiently smoothly on chain lengths that, by detailed balance, the lifetime of a broken end before recombination is comparable to the lifetime of the original chain before breaking. Thus, for example, the argument leading to eq 16 would not necessarily be invalidated even if recombination were to often involve the same end as took part in the preceding breakage event.

4. Crossover to Regimes Involving "Breathing" and Rouse-Like Motion

It is important to discuss under what range of parameters the combined reptation/breakage mechanism proposed above will dominate over those involving (i) the "breathing modes" of a chain in its tube (leading to fluctuations in the tube-length) and (ii) the Rouse-like motion of stretches of chain shorter than the entanglement length, $L_{\rm e}$.

One might guess that the criterion for the present mechanism to dominate is that λ, defined in eq 14, should greatly exceed $L_{\rm e}$:

$$\lambda = \bar{L}\zeta^{1/2} \gg L_{\rm e}$$

However, though necessary, this is not sufficient. In fact we require

$$\lambda \gtrsim (L_{\rm e}\bar{L})^{1/2} = \bar{L}\alpha^{1/2} \tag{19}$$

where we have introduced the parameter

$$\alpha = L_{\rm e}/\bar{L} \lesssim 1$$

The condition (19) arises because an entangled chain undergoes a constrained Rouse-like motion within its tube, which results in fluctuations in the tube length of order $\Delta L \cong \bar{L}\alpha^{1/2}$, on a time scale[1b,18,19]

$$\tau_{\rm breathe} \cong \alpha\tau_{\rm rep} \tag{20}$$

When $\lambda \lesssim \Delta L$, the newly created chain end need not reptate to the position occupied by our chosen tube segment but typically gets there more quickly by means of a "breathing" fluctuation in which the chain contracts down its tube. It is known that the mean curvilinear distance ξ traveled by a chain end (or any other monomer) as a function of time under such a fluctuation scales as[1b,18,19]

$$\xi \cong D_0^{1/2}t^{1/4}$$

Hence we define a characteristic arc distance λ' by

$$\lambda' \cong D_0^{1/2}\tau_{\mathrm{break}}^{1/4} \cong \bar{L}\alpha^{1/4}\zeta^{1/4} \qquad (21)$$

which is the maximum distance away along the chemical sequence that a break can typically occur for a breathing fluctuation to carry it through our chosen tube segment before recombination. The rate-limiting step for stress relaxation is then waiting for a break within the distance λ', with a corresponding fundamental relaxation time

$$\tau \cong (c_1\lambda')^{-1} \cong \tau_{\mathrm{rep}}\zeta^{3/4}\alpha^{-1/4} \qquad (22)$$

The crossover between the regime described by eq 16 and that of eq 22 is when $\lambda \simeq \lambda'$, that is, when $\zeta \simeq \alpha$.

This breathing picture is itself only applicable at arc-length scales larger than the entanglement length, L_e. Hence eq 22 breaks down when τ_{break} is so small that $\lambda' \lesssim L_e$, that is, when

$$\zeta \lesssim \alpha^3$$

In this case, the relaxation time τ should be the waiting time for a break to appear within an arc length such that a purely Rouse-like motion (characterizing the behavior of the chain at distances smaller than the entanglement length) can relax the tube segment before recombination occurs. If one imagines the entanglements to be localized at intervals L_e along the chain, then for a given entanglement to be relaxed, a break must occur within distance

$$\lambda'' \cong (D_0/L_e)^{1/2}\tau_{\mathrm{break}}^{1/2} \qquad (23)$$

The expression on the right arises because the mean-square spatial displacement r^2 of the end of a chain undergoing Rouse-like motion at scales less than L_e varies as[1b]

$$r^2 \cong (D_0/L_e)^{1/2}t^{1/2}l$$

Requiring $r^2 \cong \lambda'' l$ at $t \cong \tau_{\mathrm{break}}$ then gives (23). The resulting waiting time is

$$\tau \cong (c_1\lambda'')^{-1} \cong \tau_{\mathrm{rep}}\zeta^{1/2}\alpha^{1/2} \qquad (24)$$

Of course, this result might appear to depend on a rather literal picture of the entanglements as spaced out at intervals along the chain. However, one can also consider the opposite point of view,[17] namely, that topological constraints which on a time-averaged basis make up the tube (which has a rather large effective diameter $(L_e l)^{1/2}$) are, at a microscopic level, distributed uniformly along the chain contour, although fluctuating in time due to the short-scale Rouse motion of the neighboring chains. It is clear that this alternative picture leads to exactly the same result. (It should be emphasized that neither interpretation of the tube is uniquely implied by the reptation model, which does not concern itself with tube dynamics on these short time scales.) Since both viewpoints give eq 24, we can be reasonably confident that that equation is correct. This claim is supported by the remarkable accuracy with which eq 24 can account for the experimentally observed temperature dependence of the viscosity of polymeric liquid sulfur.[17]

To summarize our predictions for the relaxation time τ $(\cong\eta/G_0)$ in the various different regimes, recalling our notation $\zeta = \tau_{\mathrm{break}}/\tau_{\mathrm{rep}}$, $\alpha = L_e/\bar{L}$, we have

$$\zeta \gtrsim 1: \qquad \tau \cong \tau_{\mathrm{rep}} \qquad (13)$$

$$\alpha \lesssim \zeta \lesssim 1: \qquad \tau \cong \tau_{\mathrm{rep}}\zeta^{1/2} \qquad (16)$$

$$\alpha^3 \lesssim \zeta \lesssim \alpha \lesssim 1: \qquad \tau \cong \tau_{\mathrm{rep}}\zeta^{3/4}\alpha^{-1/4} \qquad (22)$$

$$\zeta \lesssim \alpha^3 \lesssim 1: \qquad \tau = \tau_{\mathrm{rep}}\zeta^{1/2}\alpha^{1/2} \qquad (24)$$

As has been made clear above, the essential ingredient of all the results for $\zeta \lesssim 1$ is as follows: The time scale for stress relaxation is the waiting time, $\tau \cong 1/(c_1\tilde{\lambda})$, for a break in the chain to appear within some characteristic arc distance, $\tilde{\lambda}(\tau_{\mathrm{break}})$, of a given tube segment, defined such that the new chain end is likely to pass through that segment within time τ_{break}, which is the lifetime of the free end before it recombines with another chain. The characteristic arc distance ($\tilde{\lambda} \simeq \lambda$, λ', or λ'') is computed by using whatever dynamics (reptation, breathing, or Rouse) is appropriate to describe the motion of the chain on the time scale τ_{break}.

Note that, for all time regimes, the quantity $l\tilde{\lambda}(t)$ is comparable to the mean-square spatial displacement $r^2(t)$ of a monomer on an (unbreakable) chain of length $\bar{L}$ in time t. The three regimes described by eq 24, 22, and 16 correspond respectively to the successive Rouse-like [$r^2(t) \sim L_e^{-1/2}(D_0t)^{1/2}$], breathing [$r^2(t) \sim L_e^{1/4}(D_0t)^{1/4}$], and reptative [$r^2(t) \sim L^{-1/2}(D_0t)^{1/2}$] regimes[1b] for this correlation function. Thus, the predicted behavior of the relaxation time τ when $\tau_{\mathrm{break}} \lesssim \tau_{\mathrm{rep}}$ can all be put succinctly in the form

$$\tau \cong \tau_{\mathrm{break}}\bar{L}l/r^2(\tau_{\mathrm{break}}) \qquad (25)$$

which embodies the main result of this paper.

5. Closing Remarks

We have seen that the interplay between the dynamics of polymer diffusion and the kinetics of breakage and recombination can lead to new characteristic time scales for stress relaxation in concentrated systems of living polymers. As described elsewhere,[17] the theory has already proved remarkably successful in accounting for the viscosity of polymeric liquid sulfur. In addition, it is hoped that the several new predictions given above will stimulate further studies of stress relaxation in various other experimental systems, such as concentrated end-linking polymers[20] and flexible tubular micelles, that may also be described by the idealized models investigated in this paper. Since in these equilibrium systems the degree of polymerization can in principle become arbitrarily great—without the tendency to degradation and/or unmanageably high viscosity that hampers studies of ordinary linear polymers of high molecular weight—we expect studies on them to provide new information about the dynamics of entangled polymers, which may lead to new and possibly demanding tests of the reptation model.

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(20) An additional condition for these systems to be described by the theory of section 2 is that the approximation by which we treat L as a continuous variable be applicable. During the process of waiting for a nearby break, a total arc length of order $L^* \cong (D_c\tau)^{1/2} \cong \bar{L}\zeta^{1/4}$ passes through any tube segment. Hence, for self-consistency, we require only that the individual functionalized polymers that make up the longer chains have length $L_0 \ll L^*$. If this is not the case, one expects instead a longer relaxation time, $\tau \cong D_0^{-1}\bar{L}L_0^2$, corresponding to a rate-limiting step that involves a given tube segment waiting for one of the junction points—at which breakage is comparatively frequent—to reptate past.

Holographic Grating Relaxation Measurements of Dye Diffusion in Linear Poly(methyl methacrylate) and Cross-Linked Poly(methyl methacrylate) Hosts

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ABSTRACT: Laser-induced holographic grating relaxation studies of camphorquinone (CQ) diffusing in linear poly(methyl methacrylate) (PMMA) and cross-linked PMMA are carried out. Diffusion coefficients of CQ in the polymer hosts are derived from the decay constant of the intensity diffracted from the laser-induced holographic grating. The diffusion coefficient (D) of the photoproduct of CQ in cross-linked PMMA is found to decrease about 2 orders of magnitude as the concentration of the cross-linking agent increases to 50%. The relationship between the concentration of the cross-linking agent and polymer-free volume is discussed. The diffusion coefficients in linear and cross-linked PMMA are also measured as functions of temperature (T). The temperature dependence of D can be described by the Williams–Landel–Ferry (WLF) equation. The C_2 constant obtained from the D vs. T fit for the linear PMMA sample agrees with that from the viscosity measurement.

Introduction

In our previous work,[1] we have reported the study of the diffusion process of camphorquinone (CQ) in linear and cross-linked polystyrene (PS) using the holographic grating relaxation technique. In this paper, we report results of the study of the diffusion process of CQ in linear and cross-linked poly(methyl methacrylate) (PMMA) by using the same technique.

The laser-induced holographic grating relaxation (LIHGR) technique has been shown to be capable of measuring a very slow diffusion coefficient of photochromophores dissolved in transparent polymer hosts in the vicinity of their glass transition temperatures. This technique involves splitting of a single-frequency radiation from an Ar$^+$ laser radiation into two equal-intensity beams. Interference of two beams induces a holographic phase grating by photobleaching the dye molecules. In the present study, the distance between bright and dark fringes ($d/2$) is varied between 0.84 and 11.62 μm by changing the crossing angle of the two beams. Diffusion of the dye molecules over a length less than $d/2$ is detected immediately as it reduces the diffracted intensity. Since $t = d^2/(4\pi^2 D)$ (t being the time of diffusion and D the diffusion coefficient), and since the diffusion distance d involved in the LIHGR technique is on the order of the wavelength of the writing beam, the LIHGR technique can be employed to obtain the diffusion coefficient several (up to 8) orders of magnitudes smaller than the slowest D that the conventional tracer technique can provide. Applying this technique, it is possible to measure the mass diffusion coefficients as low as 10^{-15} cm^2/s in a period of several hours.

Recent LIHGR works reported from our laboratory differ from the LIHGR studies carried out elsewhere in that chromophore molecules are not chemically attached to the polymer chains. In our work, foreign dye molecules are introduced in the polymer matrices without modifying the polymer chains. The dye molecules (or penetrants) are introduced only in a trace amount (on the order of 1% or less by weight). The frictional resistance that the penetrants encounter during diffusion serves to monitor that experienced by the polymer segments themselves in

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