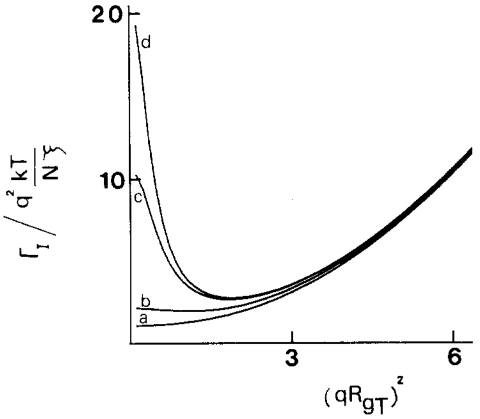

Figure 1. Variation of $\Gamma_I/(q^2(kT/N\xi))$ as a function of $(qR_{gT})^2$; $v\phi_T N = 1$; and $\chi/v = 5 \times 10^{-2}$ for different values of the weight fraction of copolymer y: (a) $y = 0\%$; (b) $y = 50\%$; (c) $y = 90\%$; (d) $y = 95\%$.

with respect to the other. For reasons of simplicity, we assume that our system is made of identical homopolymers except for the contrast factors and the interaction parameter χ between monomer species. The copolymer is merely a junction of two different homopolymers. All quantities used here have their standard meanings and were clearly defined earlier.[1-3] Therefore, these definitions are not reproduced here.

To proceed further, we note the two limits. (i) Mixture of homopolymers in solution with a composition $x = {}^1/_2$ is the first. In this case, Γ_I was found as

$$\Gamma_I = q^2 \frac{kT}{\xi N P(q)} \left[1 - \frac{\chi \phi_T N}{2} P(q) \right] \qquad (1)$$

N is the number of monomers per chain, $P(q)$ is the form factor, and ϕ_T is the total polymer concentration. (ii) Diblock copolymers in solution is the second case. Here the following result was obtained:

$$\Gamma_I = q^2 \frac{kT}{2N\xi(P - P_T)(q)} [1 - \chi\phi_T(P - P_T)(q)] \qquad (2)$$

where N and P are the number of monomers and the form factor of each block and P_T is the form factor of the chain of $2N$ monomers.

The two relaxation frequencies show an entirely different behavior as a function of q. While Γ_I for a mixture of homopolymers behaves as an ordinary interdiffusion mode and goes to zero as $q \to 0$, for copolymers it is more subtle and goes to a constant limit when $q \to 0$. Furthermore, eq 1 shows that Γ_I at $q = 0$ vanishes for $\chi\phi_T N/2 = 1$, whereas in the copolymer case, Γ_I as given by eq 2 cannot be zero at $q = 0$,

$$\Gamma_I = \frac{3kT}{2N\xi R_{gT}}$$

and is independent of χ, where R_{gT} is the radius of gyration of the whole copolymer chain. However, this frequency can vanish at a finite value of the wave vector q_m such that

$$\chi\phi_T N[P(q_m) - P_T(q_m)] = 1 \qquad (3)$$

Therefore, since the behavior of Γ_I for two systems was so different in the small q region, it was interesting to see what happens when a fraction y of copolymers is present in the system containing a mixture of homopolymers. The calculation of Γ_I in this case is straightforward and is based on the general formulas given in ref 1 and 2. The result can be verified easily as

$$\Gamma_I = q^2 \frac{kT}{N\xi} \frac{1}{P + y(P - 2P_T)} \left[1 - \frac{\chi\phi_T N}{2} [P + y(P - 2P_T)] \right] \qquad (4)$$

One observes that for $y = 0$ (no copolymers) eq 1 is obtained and for $y = 1$ (no homopolymers) eq 2 is recovered correctly. In the figure below, we have plotted the variation of $\Gamma_I/(q^2kT/N\xi)$ as a function of $(qR_{gT})^2$ for various values of the copolymer composition y. It shows that the effect of adding copolymers to the mixture of homopolymers is really significant only for relatively high values of y (i.e., $y > 50\%$). This does not seem to be the case for static properties where a small fraction of copolymers is found to induce a significant compatibilizing effect in mixtures of incompatible homopolymers.[5]

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Polymer Melt Dynamics Model with a Relaxation Time Exponent of 10/3

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Introduction

Reptation provides a clear and useful limiting model of polymer chain motion in dense, entangled fluids[1] and is the basis of current molecular theories of viscoelasticity.[2] In its simplest form, it replaces the three-dimensional Brownian motion of segment beads (c.f., Rouse–Zimm solution theories) by one-dimensional diffusion along a chain contour "tube" created by excluded-volume interactions with neighbor chain molecules. Since chain segments move in directions both parallel and perpendicular to their backbones and since neighbor chains are not stationary, refinements of the simple picture have appeared, improving and extending the fit to experiment, as well as removing unphysical features.[3,4] For the most part though, the important scaling predictions of reptation are not altered, namely, a center-of-mass diffusion constant D

$$D \sim M^{-2} \qquad (1)$$

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and a terminal relaxation time, τ_r (i.e., reptation time),

$$\tau_r \sim M^3 \tag{2}$$

where M is the polymer chain length. Equation 1 has been confirmed by IR microdensitometry of deuteriated diffusant chains, forced Rayleigh scattering of photochromatic labeled chains, and pulsed field gradient NMR.[5-7] On the other hand, eq 2 is in conflict with viscoelastic data[8] as well as some recent Monte Carlo simulations which indicate an exponent[9] of 3.4 ± 0.1, rather than 3.0. Theoretical explanations of the discrepancy include (a) a cross-over (finite-size) effect[10,11] with the actual high-molecular weight limit being 3.0, (b) an activation energy for chain-end migration leading to a higher power[12] of M, and (c) a waiting-time distribution for segment hops that modifies de Gennes's Brownian motion result.[13]

Recently, Scher and Shlesinger[14] (vide infra) proposed that stress relaxation in the terminal region might be a many-chain effect and that relaxation is related to the time required for $M^{1/2}$ chains mutually entangled at time zero to escape their sphere of correlation. They argued that $M^{3.5}$ is an upper bound to this many-chain escape time.

The Scher–Shlesinger idea can be understood in terms of older "transient-network" models of entangled liquids.[9,15,16] In these theories, the elastic free energy is assumed to reside in a three-dimensional rubberlike network of segments and junctions. The plateau modulus measures the number density of network junctions under the applied load. The rate of stress relaxation is determined by the rate of junction loss, and in the reptation theories[1,2,4] this is identified with the rate of tube renewal. In contrast, the Scher–Shlesinger model equates the rate of network segment loss to the rate of emptying a sphere of radius equal to the entanglement distance of all chains initially correlated. The criteria for all correlated chains to vacate the junction produces a higher power of molecular weight than that predicted by de Gennes's reptation model.

In this paper we present a more precise calculation for the time it takes a group of chains to empty a sphere for the first time. In view of the Scher–Shlesinger hypothesis, this is related to the rate of junction loss and, hence, stress relaxation in the terminal zone. A constitutive model based on this idea is planned.

Scher–Shlesinger Framework[14]

Let λ be the average size of a link in the polymer chain. An individual chain with M links will be assumed to have ideal statistics[11] with an average end-to-end distance proportional to $M^{1/2}$. It is further assumed that a chain, at any time, possesses a number of kinks proportional to the chain length M and that these kinks, each independently, move by Brownian motion. This implies that the average time for each of these kinks to reach one or the other end of the chain is proportional to M^2. When a kink reaches an end it initiates a chain motion that changes the chain center of mass. It was shown[4] that a chain's center-of-mass mean-square displacement at time $t \sim M^2$ varies as

$$\langle R^2(t \sim M^2) \rangle \sim \lambda^2 \tag{3}$$

and thus the diffusion constant D behaves as

$$D = \frac{\langle R^2(t \sim M^2) \rangle}{M^2} \sim \frac{1}{M^2} \tag{4}$$

as in eq 1.

Essentially, the chain center-of-mass performs a random walk with each jump (of characteristic length λ) needing a time $\tau \sim M^2$ to be completed. In a time $t \sim M^3$, a chain center of mass will have moved M random steps (each of average length λ) and a new chain configuration will be reached independent of the initial configuration. The time $t \sim M^3$ was called τ_{rep}, the reptation time.[1] This is a characteristic time associated with a single chain, but it does not correspond to the experimental relaxation time in a melt (see eq 1).

The time $t \sim M^3$ can be interpreted in another manner. The chain will be initially enclosed in a sphere of radius proportional to $M^{1/2}$. A random walker, representing the chain center of mass, will take an average number of steps proportional to M to leave this sphere, and each step takes a time which scales to M^2. Thus, the random walker will leave this sphere and the chain will not overlap its inital position in a time $t \sim M^3$. However, the chain may still be entangled with other chains with which it was entangled at $t = 0$. The sphere in question has volume $M^{3/2}$ and a single chain occupies a volume M. Thus, $M^{1/2}$ entangled chains can be placed in this sphere. We replace these other chains by $M^{1/2}$ random walkers, representing other chain center-of-mass points. Let the origin of the sphere represent the center of mass of a reference chain. We will measure the motion of the remaining chains relative to this fixed origin. When all of the other $M^{1/2}$ chains leave the sphere, they will no longer be entangled with the reference chain. Scher and Shlesinger[14] considered the average time for this sphere of radius $M^{1/2}$ to be emptied of $M^{1/2}$ random walkers to be the statistical quantity related to the mass dependence of the viscosity of a polymer melt. The basic dynamics is still described by de Gennes's reptation concept of kink movements initiating chain displacements, except that now a question is asked about $M^{1/2}$ chains, rather than a single chain. Note that some random walkers may leave the sphere and then reenter before other random walkers have left. This means that a chain may break some of its initial entanglements with other chains and then get reentangled with them before some of the remaining initial entanglements are broken. In the next section, we suggest that these reentangling possibilities will lead to a time scale of $M^{10/3}$, as opposed to the M^3 result obtained from the original de Gennes theory.

Diffusion of N Particles out of a Sphere

We idealize this situation by supposing that the kinks can be modeled in terms of independent particles undergoing Brownian motion that are initially randomly distributed in a sphere of radius R. The quantity of interest in the present physical problem is the average time for the system to reach a state in which all of the particles have left the sphere for the first time. The mean first passage time for all N random walkers to leave the sphere for the first time will be denoted by $\langle t_N \rangle$. In some recent work, Professor Harry Kesten[17] has shown that the rigorous asymptotic dependence of $\langle t_N \rangle$ on N goes like

$$\langle t_N \rangle \sim (N/\ln N)^{2/3} \tag{5}$$

in three dimensions, aside from constants. The proof is mathematically quite sophisticated, but it is simple and instructive to show that $\langle t_N \rangle \leq N^{2/3}$ in three dimensions, which contradicts the estimate by Scher and Shlesinger that $\langle t_N \rangle = \mathcal{O}(N)$.

For this purpose, let us therefore consider a quantity $\langle \tau_N \rangle$, which is the average time during which the sphere is occupied by at least one particle. It is clear that $\langle \tau_N \rangle > \langle t_N \rangle$ since the process of original interest terminates at time t_N, while τ_N has contributions from the sphere being refilled after it is emptied. If $S(t)$ denotes the probability that a particle initially in the sphere is found in the sphere at time t, then $\langle \tau_N \rangle$ can be expressed as

$$\langle \tau_N \rangle = \int_0^\infty [1 - [1 - S(t)]^N]\, dt \qquad (6)$$

To calculate $S(t)$, we note that in spherical coordinates, the probability density for a Brownian particle to go from $\mathbf{r}_0$ to $\mathbf{r}$ at time t is

$$p(\mathbf{r},t|\mathbf{r}_0,0) = 4\pi\left(\frac{3}{4\pi D_s t}\right)^{3/2} \exp\left[-\frac{3(\mathbf{r}-\mathbf{r}_0)^2}{4D_s t}\right] \qquad (7)$$

where D_s is the diffusion constant for a single chain. Hence, the probability that the Brownian particle is within the sphere at time t is

$$S(t) = 4\pi\left(\frac{3}{4\pi D_s t}\right)^{3/2} \int \ldots \int \exp\left[-\frac{3(\mathbf{r}-\mathbf{r}_0)^2}{4D_s t}\right] d\mathbf{r}\, d\mathbf{r}_0 \qquad (8)$$

where $\mathbf{r}_0$ and $\mathbf{r}$ take all values inside the sphere. When t is sufficiently large that $D_s t \gg R^2$, the exponential tends to the limit 1 and the integral tends toward V^2, where V is the volume of the sphere. Hence, we find

$$S(t) \sim (2\pi)^{1/2}(R^2/D_s t)^{3/2} \qquad (9)$$

When the number of Brownian particles, N, is large, we may rewrite eq 6 as

$$\langle \tau_N \rangle \sim \int_0^\infty (1 - e^{-NS(t)})\, dt \qquad (10)$$

From this form it is evident that the integrand is very close to 1 as long as $NS(t) \gg 1$ and only goes to zero when $S(t) \sim 1/N$, which is in the region in which the asymptotic representation in eq 8 is valid. Hence, we may write

$$\langle \tau_N \rangle \sim \int_0^\infty (1 - e^{-N(T_0/t)^{3/2}})\, dt = T_0 N^{2/3} \int_0^\infty (1 - e^{-x^{-3/2}})\, dx \qquad (11)$$

in which

$$T_0 = AR^2/D_s \qquad (12)$$

where A is a dimensionless constant of no importance to the argument.

In order to translate Kesten's result into the language of the reptation problem, we note that the radius of the sphere scales as $M^{1/2}$, N also scales as $M^{1/2}$, and D_s scales as M^{-2}. Thus

$$\tau_r \sim \frac{M^{1+1/3+2}}{(\ln M)^{2/3}} = \frac{M^{10/3}}{(\ln M)^{2/3}} \qquad (13)$$

The dominant factor in this last equation is $M^{10/3}$ while the logarithmic term would only be detectable when measurements are made over many orders of magnitude of the mass.

Conclusions

Within de Gennes's original reptation model of kink-generated motion, we follow Scher–Shlesinger to treat the measured polymer melt diffusion constant as a single chain quantity and the reptation time as a multichain quantity to reconcile for the first time the experimentally observed and theoretical compatible results $D \sim M^2$ and $\tau_r \sim M^{10/3}/(\ln M)^{2/3}$ in which the logarithmic term would not ordinarily be detectable.

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Communications to the Editor

Synchrotron Small-Angle X-ray Scattering of Sulfonated Polystyrene Ionomers

The field of ion-containing polymers, with its many industrial applications, has undergone explosive growth in recent years.[1] Nevertheless, a fundamental understanding of the spatial arrangement of the ionic groups in ionomers has remained elusive. Initial theoretical developments by Eisenberg,[2] MacKnight et al.,[3] Yarusso and Cooper,[4] and Fujimura et al.[5] have led to the concepts of ion pair, multiplet, and cluster formation as well as inter- and intraparticle interactions among the ion pairs, multiplets, or clusters. The models of the structure of ionomers are based mainly on results from small-angle X-ray scattering (SAXS) and electron microscopy. While transmission electron micrographs may suggest the presence of ion aggregates or domains, the details of ion distribution can best be achieved by using SAXS. Earlier SAXS profiles[4-7] of metal salts of sulfonated polystyrene (S–PS) show only one ionic peak occurring at the scattering vector $q \sim 1.7$ nm^{-1} where $q = (4\pi/\lambda) \sin(\theta/2)$ with λ and θ being the X-ray wavelength and the scattering angle, respectively. The absence of "fine" structure in the scattering profile means that the experimental data with finite q range and precision can be interpreted by using a variety of models.[3-5] Unfortunately, the details of the spatial arrangement of the ionic groups cannot be retrieved from scattering data on the ionic peak alone.

The radial distribution function (RDF) approach which is essentially model independent and is applicable to the structural determination of amorphous materials in general has been used to analyze the SAXS profile.[3,8] In the absence of reliable scattering data in the asymptotic small-

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