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Diffusion in Branched Polymer Melts†

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ABSTRACT: Recent theories of viscoelasticity and density fluctuations in gelling systems rely on the concept on Stokes-Einstein diffusion of a branched polymer in a medium with a length scale dependent viscosity. We propose some interdiffusion experiments which would demonstrate that the diffusion of labeled branched polymers is described by anomalous power laws in both time and space. These anomalies provide a direct measure of the scaling of the diffusion constant with the radius.

Introduction

It has recently been observed that branched polymers formed near the sol-gel transition exhibit remarkably slow relaxation phenomena. On *microscopic* length scales (25-400 nm), a slow, power law time decay of thermally induced concentration fluctuations has been observed in quasielastic light-scattering experiments.[1] On *macroscopic* length scales the power law relaxation of stress after a shear strain (or its Fourier transform) has been observed in several viscoelastic experiments.[2-6] Theories of the quasielastic light scattering[1] and of the viscoelasticity[7-9] depend critically on the diffusion of the extremely polydisperse ensemble of branched polymers. Each individual branched polymer relaxes on a time scale that depends on its diffusion constant, so the dependence $\theta \sim R^{-\mu}$ of the diffusion constant θ on the branched polymer radius dominates these theories. For example, near the sol-gel transition both the storage and loss components of the complex shear modulus have the frequency dependence[7-9] $\omega^{d/(2+\mu)}$, where d is the spatial dimension. The situation is quite analogous to linear polymer systems, where theories of viscoelasticity[10] are derived from the reptation diffusion mechanism of a single chain.

In the following, we consider the diffusion of deuterium-labeled branched polymers into a compatible hydrogenated host of the same molecular weight. The results we obtain depend on the dimension of the source, d_s, as well as on the dimension of the space, d, through the codimension in the diffusion problem, $\Delta d = d - d_s$. Several source dimensions are possible—a small labeled sphere ($d_s = 0$), a cylinder ($d_s = 1$), a sheet ($d_s = 2$), and a semi-infinite slab ($d_s = 3$). It is likely, however, that practical experiments will use the labeled sheet geometry. Branched polymers are formed near a connectivity critical point—the sol-gel transition—so it is not surprising that the divergent polydispersity in these systems gives rise to some novel effects. First, after an initial growth in concentration of the labeled species, there is an anomalous time and space decay $c(r,t) \sim 1/(t^{1/2\mu} r^{\Delta d - 1/\mu})$ in the concentration, independent of any length scale. Thus the interdiffusion experiment provides a direct method of determining the exponent μ. This is in contrast to the usual Gaussian concentration field[11] $c(r,t) \sim (\theta t)^{-\Delta d/2} \exp(-r^2/b\theta t)$, with the associated length scale $(b\theta t)^{1/2}$. Second, it is observed that the fractionation that naturally accompanies diffusion in a disperse system gives rise to unique scaling relations for the dispersity in layers of varying distance from the source.

Although several source geometries show anomalous effects, casting a labeled sheet onto a compatible host is the canonical experimental approach and has been widely used in studies of linear polymer systems. In the linear polymer studies[12,13] a deuterated polymer film of thickness ~10 nm is cast onto a normal host, and the deuterium concentration profile, $c(r,t)$, is studied by a technique variously known as elastic recoil detection (ERD) or forward recoil spectrometry (FRS). In the linear polymer studies there are no anomalies in $c(r,t)$ on length scales larger than a single-chain radius, so to study the molecular weight dependence of the diffusion coefficient many samples of varying molecular weight must be prepared. In branched polymer systems all molecular weights are present simultaneously, so the molecular weight dependence of the diffusion coefficient can be determined from a single sample.

Theory

Percolation. To describe the ensemble of branched polymers, we use the bond percolation model.[14-16] In bond percolation monomers (sites) on a d-dimensional lattice are randomly bonded with probability p, often loosely referred to as the extent of reaction. In the initial stages of the reaction only small clusters form, but as p increases, very large "branched polymers" appear, until at the gel point p_c an infinite cluster appears and certain average cluster sizes diverge. Beyond p_c the very largest clusters attach to the infinite cluster to form a network, within which are embedded finite clusters: the average size of these clusters decreases as p approaches 1. Near the gel point, the percolation model exhibits self-similarity in two distinct ways. First, clusters smaller than the *typical* cluster radius or correlation length $\xi \sim \epsilon^{-\nu}$ have a mass fractal dimension D, so $R^D \sim M$. Second, the cluster size distribution is self-similar on length scales smaller than ξ, so that clusters of radii $R \pm d \ln R$ are separated by an average distance $\sim R$. Thus at the gel point the number of clusters of radius R is $N(R) d \ln R \sim R^{-d} d \ln R$. Expressed in terms of the equivalent mass distribution $N(m) dm \sim m^{-1-d/D} dm$, this is the so-called *hyperscaling* relation. Slightly beneath the gel point this self-similarity is exponentially truncated at the correlation length: in this regime $N(R) d \ln R \sim R^{-d} \exp[-(R/\xi)^D]\, d \ln R$. These two forms of self-similarity express themselves in an important way: the fractal dimension[18] $D \cong (d + 2)/2$ of a single cluster is significantly different from the fractal dimension of the polydisperse ensemble,[19] $2D - d \cong 2$.

In a branched polymer melt it has been postulated[1,17] that the diffusion of a cluster of radius R is Stokes-Einstein, $\theta(R) = kT/(6\pi\eta(R)R^{d-2})$, but in a medium with a *size-dependent* viscosity $\eta(R)$. If we assume that clusters larger than the correlation length feel the bulk viscosity, $\eta_b \sim \epsilon^{-k} \sim \xi^{k/\nu}$, and that smaller clusters feel a finite viscosity (*independent* of η_b since this diverges), we obtain the scaling relation $\eta(R) \sim \eta_b f(R/\xi)$. For $R \gg \xi$, the function $f(R/\xi) = 1$, but for $R \ll \xi$, $f(R/\xi)$ must be $(R/\xi)^{k/\nu}$ in order to satisfy $\eta(R \ll \xi) \sim \eta_b{}^0$. Thus the diffusion coefficient is

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$$\theta(R) \sim k_B T/[\eta_0 (R/a)^{k/\nu} R^{d-2}] \qquad R \ll \xi \tag{1}$$

where η_0 is the viscosity felt by a monomer. The length scale dependent viscosity may be viewed as a *hydrodynamic screening* effect. If hydrodynamic interactions between monomers on a cluster are completely screened by smaller clusters, as in a *Rouse* melt, then the diffusion coefficient should be $\theta \sim kT/\xi_0 m \sim R^{-D}$. On the other hand, if there is no hydrodynamic screening, then the *Zimm* result $\theta \sim kT/\eta_0 R^{d-2}$ should be obtained. In general, the reaction bath should be between the Rouse and Zimm limits,[7] so the diffusion exponent μ should have the limits $d - 2 \leq \mu \leq (d + 2)/2$, where we have used the Flory-type estimate[18] $D \cong (d + 2)/2$ for the fractal dimension of a percolation cluster.

Labeled Diffusion. To solve the interdiffusion problem, we first consider the diffusion of a labeled polymer of radius R and then sum over all R to find the bulk concentration. The solution of the diffusion equation is $c_R(r,t) = L^{-\Delta d} \exp[-(r/L)^2]$, where $L = (\theta t)^{1/2}$ is the diffusion length for a cluster of radius R (the semi-infinite slab is a special case). Summing over the *weight* distribution $R^D N(R)$ gives the labeled monomer concentration

$$c(r,t) = \int_a^\infty \frac{\mathrm{d}R}{R} \frac{e^{-(R/\xi)^D}}{R^{d-D}} \frac{e^{-(r/L)^2}}{L^{\Delta d}} \tag{2}$$

where a is the monomer radius. Since we are interested in the scaling behavior of this system, it will suffice to simply truncate the cluster size distribution at the typical cluster radius ξ. Then the concentration of labeled monomer can be written

$$c(r,t) \sim \frac{1}{t^{\Delta D/2}} \int_{L_\xi}^{L_a} \frac{\mathrm{d}L}{L} \frac{e^{-(r/L)^2}}{L^{d-\Delta D}} \tag{3}$$

Here L_a is the diffusion length for a monomer, L_ξ is the diffusion length for a typical cluster and $\Delta D = 2(d - D)/\mu$ is an exponent that in some sense acts like a fractal codimension for the diffusion problem. Using the Flory-type estimate $D \cong (d + 2)/2$ for the fractal dimension of a percolation cluster gives $\Delta D \cong (d - 2)/\mu$, so for three-dimensional branched polymers we obtain the simple result $\Delta D \cong 1/\mu$.

On length scales small compared to the monomer diffusion length L_a, the solution of eq 3 can be summarized as

$$c(r,t) = \frac{1}{\xi^{d-D} {L_\xi}^{\Delta d}} f(r/L_\xi) \tag{4}$$

where $f(x) = \exp(-x^2)$ for $x \ll 1$ and $f(x) \sim 1/x^{\Delta d - \Delta D}$ for $x \gg 1$. In the *intermediate* length scale regime $L_\xi \ll r \ll L_a$, we can thus write

$$c(r,t) \sim \frac{1}{t^{\Delta D/2} r^{\Delta d - \Delta D}} \qquad L_\xi \ll r \ll L_a \tag{5}$$

In this regime, the diffusion field is independent of any length scale and so has both anomalous time and space dependencies. Equation 5 applies as long as the codimension Δd is greater than the diffusion dimension ΔD. The semi-infinite slab ($\Delta d = 0$) is a special case and does not exhibit any power law scaling regime. For this reason, the semi-infinite slab does not seem a fruitful experimental approach to the determination of μ.

As a specific example, consider a thin sheet of deuterated branched polymer on a hydrogenated, compatible branched polymer host of the same molecular weight. Taking the Rouse limit $\mu = D = 2.5$ for the diffusion coefficient gives $c(r,t) \sim t^{-1/5} r^{-3/5}$. Thus if we were to monitor the label concentration at some distance r as a function of time, we would find the behavior illustrated in Figure 1. There are two time scales in this problem: the time it takes a monomer to diffuse a distance r, $\tau_a = r^2/\theta(a)$, and the time it takes a cluster the size of the correlation length to diffuse this distance, $\tau_\xi = r^2/\theta(\xi)$. The ratio of these times, $\tau_\xi/\tau_a = (\xi/a)^\mu$, is large even for low degrees of polymerization. For example, branched polymers of $\xi = 100$ nm and a monomer size of ~0.5 nm give $\tau_\xi/\tau_a \cong 10^6$. The overall behavior is as follows: On times small compared to τ_a, the label concentration grows as $t^{-1/2} \exp[-(\tau_a/t)^2]$. On intermediate time scales, defined by $\tau_a \ll t \ll \tau_\xi$, the concentration undergoes the slow power law decay $c(r,t) \sim t^{-1/5}$; Finally, for times larger than τ_ξ, the concentration decays as $c(r,t) \sim t^{-1/2} \exp[-(\tau_\xi/t)^2]$.

The concentration profile at fixed time is given in Figure 2. On lengths small compared to L_ξ the label concen-

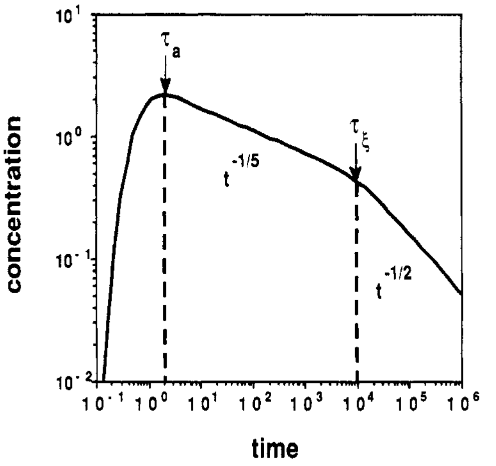

Figure 1. Time dependence of the labeled chain concentration $c(r,t)$ for a thin labeled sheet on a normal host. At early times, the concentration of labeled chains increases until time τ_a, which is the average time it takes a monomer to diffuse a distance r. At this time, the concentration starts to decrease with the anomalous time dependence $c(r,t) \sim t^{-1/5}$ as the self-similar distribution of clusters parades by. Finally, when clusters the size of the correlation length start to appear in force, $t \sim \tau_\xi$, the self-similar parade is terminated by the usual $t^{-1/2}$ tail.

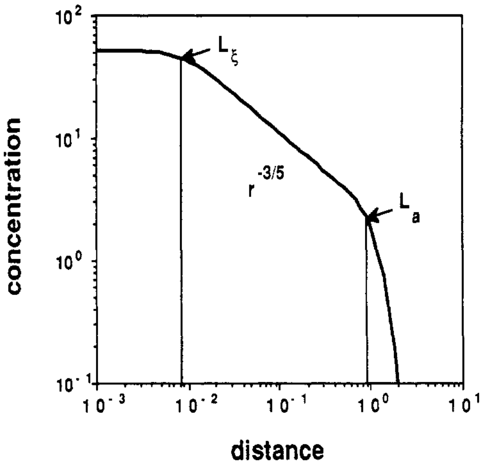

Figure 2. Spatial dependence of the labeled chain concentration $c(r,t)$ for a thin labeled sheet on a normal host. Very close to the source, the decay is given by the Gaussian result for clusters the size of the correlation length. On intermediate length scales, between the diffusion length for typical clusters, L_ξ, and for monomers, L_a, the concentration follows the anomalous spatial dependence $c(r,t) \sim r^{-3/5}$. In this regime, clusters are fractionated into more weakly disperse fractions that obey the scaling relations given in eq 6 and 7. Finally, this scaling regime is terminated by a Gaussian tail, representing the diffusion of monomers.

tration is given by $\exp[-(r/L_\xi)^2]$, on intermediate length scales $c(r,t) \sim r^{-3/5}$, and on large length scales $c(r,t) \sim r^2 \exp[-(r/L_a)^2]$. Once again, the intermediate length scale regime $L_a/L_\xi \sim (\xi/a)^{\mu/2}$ is very large, giving a wide power law domain. This power law concentration profile should be relatively easy to measure since a power law gives a large amplitude nearly everywhere.

Fractionation. An interesting aspect of branched polymers is the chromatography, or fractionation, that occurs during diffusion. As the labeled branched polymers diffuse away from the source, the molecular weight distribution in successive layers changes in a significant way. Layers close to the source become relatively depleted of small clusters, and layers far from the source become relatively depleted of large clusters. This chromatographic separation leads to a new scaling relation for the size distribution and gives rise to a series of fractions that are essentially monodisperse, in the sense that the fractal dimension of the ensemble and the fractal dimension of a single cluster are equal.

Let $N(R,r^2/t)d \ln R$ denote the (unnormalized) number distribution in a thin layer or shell a distance r from the source at time t. The weight distribution is just the concentration of R-mers, eq 2, so $N(R,r^2/t) = c_R(r,t)/R^D$ gives the modified distribution

$$N(R,r^2/t)d \ln R = R^{\mu d_c/2} e^{-R^\mu/\xi^\mu (L_\xi/r)^2} N(R) d \ln R \quad (6)$$

The power law term decreases the relative number of small clusters in the distribution, whereas the exponential term decreases the number of large clusters at large distances. Recalling that the number distribution is $N(R) = R^{-d} \exp[-(R/\xi)^D]$ allows us to rewrite $N(R,r^2/t)$ in a familiar form. The result is particularly clear if we specialize to the Rouse case, where $\mu = D$. In this case

$$N(R,r^2/t)d \ln R = R^{-\varphi} e^{-(R/\xi_r)^D} d \ln R \quad (7)$$

Although the form of the distribution is unaltered, there are two noteworthy changes: the power law decay of the distribution is now much weaker, with $\varphi = d - D\Delta d/2$, and a new *r-dependent* correlation length, ξ_r, serves to truncate the distribution. This new correlation length is given by $\xi_r^{-D} = \xi^{-D}[1 + (r/L_\xi)^2]$. In the regime $r \ll L_\xi$, the correlation length is unaltered, so $\xi_r = \xi$, but for $r \gg L_\xi$, the correlation length decays rapidly with r, $\xi_r = a(L_a/r)^{2/D}$, and becomes completely independent of ξ. In other words, the size distributions obtained in a layer are independent of the molecular weight of the original starting material. Note that in the limit $r = L_a$ the correlation length is the monomer size a, as it must be.

The reduction in the exponent of the power law decay is most easily discussed in terms of the equivalent mass distribution. The initial mass distribution is given by $N(m)dm \sim m^{-\tau} e^{-m/M_z} dm$ where $\tau = 2 + (d - D)/D \geq 2$. As we have alluded to, because τ is greater than 2 there are two divergent mass scales associated with the distribution, the weight-average molecular weight $M_W \sim \xi^{D(3-\tau)}$ and the z-average molecular weight $M_z \sim \xi^D$. The exponent $D \cong (d + 2)/2$ is just the fractal dimension of a single cluster, but $D(3 - \tau) \cong 2$ is the fractal dimension of the polydisperse ensemble.[19,20] These dimensions are quite different, and it is the ensemble dimension $D(3 - \tau)$ that is determined in an intermediate scattering experiment. However, in the fractionated mass distribution the power law decay is $N(m) \sim m^{-\tau+\Delta d/2}$: since the exponent $\tau - \Delta d/2$ is now less than 2, there is only one divergent mass and therefore one fractal dimension,[21] so $M_W \sim M_z \sim \xi^D$. Thus the fractal dimension of the ensemble is the fractal dimension of a single cluster, D. A neutron-scattering experiment on a single layer, say taken near the source, would enable the determination of the melt fractal dimension of a single labeled chain. The melt fractal dimension has not yet been determined by any method.

Conclusions

We have shown that a labeled diffusion experiment on branched polymers gives rise to a concentration profile that is a power law in both time and space. These power laws provide a direct measure of the radius dependence of the diffusion coefficient of a branched polymer, a property that has direct application to theories of viscoelasticity[7-9] of branched polymer melts near the sol-gel transition. Finally, diffusion of the disperse labeled chains results in fractionation, since smaller polymers penetrate further than large ones. The fractions obey a new scaling relation for the molecular weight distribution, and unlike the unfractionated ensemble, these fractions can be described by a single fractal dimension. The average molecular weight of a fraction decreases with the penetration depth.

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