

Limits of Reptation in Polymer Melts

Peter F. Green, Peter J. Mills, Christopher J. Palmstrøm, James W. Mayer, and Edward J. Kramer

*Department of Materials Science and Engineering and the Materials Science Center,
Cornell University, Ithaca, New York 14853*

(Received 15 August 1984)

Tracer diffusion coefficients D^* of deuterated polystyrene of molecular weight M diffusing into polystyrene of molecular weight P are measured by means of an ion-beam analysis method. While for $P > 200\,000$, these D^* values are independent of P , consistent with a reptation mechanism ($D^* = D_R$) for the diffusion of M chains, D^* increases rapidly as P is decreased, in quantitative agreement with $D^* = D_R + D_{CR}$, where D_{CR} is the diffusion coefficient of the M chain by constraint release.

PACS numbers: 66.10.Cb, 61.40.Km, 82.35.+t

Diffusion of high polymer chains in an entangled melt has been successfully described by reptation, a process by which a given chain crawls along a primitive path defined by topological constraints due to the other chains in the melt. These constraints are assumed to remain fixed for the time it takes the chain to diffuse its length along the primitive path.^{1,2} A reptating chain of molecular weight M (M chain) should have a center-of-mass diffusion coefficient D^* at infinite dilution given by³

$$D^* = D_R = D_0 M^{-2}, \quad (1)$$

where D_0 depends on the Rouse mobility of the chain and M_e , a critical molecular weight for entanglement. The magnitude of D_0 can be estimated from viscoelastic parameters of the polymer.⁴ Note that because the topological constraints are assumed to be fixed, the reptation diffusion coefficient D_R is independent of the molecular weight P of the polymer into which the M chains are diffusing. Recent experiments⁵⁻¹³ have confirmed the M^{-2} dependence over a wide range of M 's under conditions where $M_e < M < P$. For example, polystyrene (PS) M chains ($50\,000 < M < 800\,000$) diffusing into P chains of $P = 2 \times 10^7$ obey Eq. (1) with $D_0 = 0.008$ cm²/sec,¹¹ which agrees well with the theoretical⁴ $D_0 = 0.004$ cm²/sec at 170 °C, the diffusion temperature. Klein⁷ has also demonstrated that D^* is only weakly dependent on P , the molecular weight of the matrix chains, for polyethylene chains with M not much greater than M_e .

For long enough M chains and short enough P ones, processes in addition to reptation must contribute to diffusion. Under these conditions the topological constraints due to P chains surrounding the M chains are no longer fixed on the time scale of reptation. One possibility is that the primitive path of the M chain diffuses by reptation of the P chains defining it.¹⁴⁻¹⁷ Such motion results in a diffusion coefficient D_{CR} given by¹⁴⁻¹⁷

$$D_{CR} = \alpha_{CR} D_0 M_e^2 M^{-1} P^{-3}, \quad (2)$$

where the constant $\alpha_{CR} = (48/25)z(12/\pi^2)^{z-1}$, where z is defined as the "number of suitably situated constraints" per M_e .¹⁷ This mechanism is usually called tube renewal or constraint release.

In this Letter we show conclusively that the reptative diffusion of chains of molecular weight M becomes only a minor contribution to their D^* in a matrix of P chains when $M_e < P \ll M$, an observation that can be best rationalized by the constraint release mechanism. In the experiments we monitor the concentration profile of a thin layer (< 30 nm) of monodisperse¹⁸ deuterated polystyrene (d -PS) of molecular weight M diffusing into a thick film (≈ 4 μ m) of monodisperse undeuterated polystyrene (h -PS) of molecular weight P . The thick film of h -PS was cast by pulling a silicon wafer at a constant rate from a solution of the polymer. The top d -PS film was produced by spinning a dilute solution of d -PS onto a glass slide. This film was floated off the slide onto the surface of a water bath from where it was picked up on the PS coated wafer. The bilayer films were allowed to interdiffuse for various times at 170 °C.

The concentration profile of d -PS diffusing in the P chain, h -PS, is determined after the sample has cooled to room temperature by use of forward recoil spectrometry, an ion-beam analysis method originally developed by Doyle and Peercy¹⁹ for depth profiling of hydrogen and deuterium in metals. In this method a $^4\text{He}^{++}$ beam with energy $E_0 = 3$ MeV strikes the film at a glancing angle of 15°. Nuclei from the film, including hydrogen (^1H) and deuterium (^2H), recoil from the surface and near surface as a result of elastic collisions with the incoming He^{++} ions. A large number of these ions are also scattered in the forward direction at an angle of 30°, but are stopped, along with any heavier nuclei, from entering the energy-sensitive detector by a 10- μ m-thick Mylar stopper foil. The hydrogen and deuterium nuclei pass through the foil with some energy loss and their energies are

recorded by the detector and displayed on a multichannel analyzer. Since ^2H nuclei recoiling from the surface receive a much higher fraction ($\sim \frac{2}{3}$) of E_0 than do ^1H nuclei ($\sim \frac{1}{2}$), surface peaks due to ^2H and ^1H are well separated. ^2H and ^1H nuclei recoiling from depths below the surface are shifted to lower energies as a result of inelastic particle collisions with electrons in the polymer. The particle yield versus particle energy curve thus obtained is called the forward recoil spectrum. This spectrum may be analyzed in a straightforward manner to obtain the concentration of d -PS as a function of depth. Details of this analysis and the experimental apparatus are available elsewhere.^{11, 19, 20}

Figure 1(a) shows two forward recoil spectra from bilayer films that were both heated for the same time to 170°C . The M of the d -PS was the

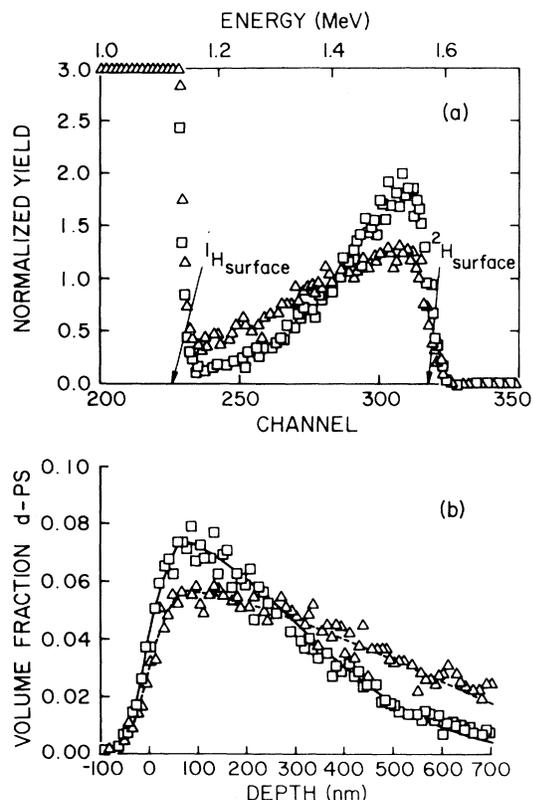


FIG. 1. (a) Forward recoil spectra from d -PS(M chains)-PS(P chains) bilayer films diffused 200 sec at 170°C . (b) Volume fraction of d -PS vs depth x from the spectra shown in (a). Triangles, $M = 110\,000$, $P = 36\,000$; squares, $M = 110\,000$, $P = 54\,000$. The dashed and solid lines in (b) represent solutions to the diffusion equation, that have been convoluted with the Gaussian instrumental resolution function, for $D^* = 5.3 \times 10^{-12}$ cm^2/sec and $D^* = 2.1 \times 10^{-12}$ cm^2/sec , respectively.

same, 110 000, but the P chains were 36 000 in one case and 54 000 in the other. The volume fraction of d -PS versus depth curves have been computed from each of these spectra and are displayed in Fig. 1(b). The solution to the diffusion equation for a thin film of initial thickness h on the surface of a semi-infinite slab is²¹

$$\phi(x) = 0.5 \{ \text{erf}[(h-x)/d] + \text{erf}[(h+x)/d] \}, \quad (3)$$

where $\phi(x)$ is the volume fraction of d -PS as a function of depth x [under the initial conditions of our experiment, $\phi(x) = 1$ for $x < h$ and $= 0$ for $x > h$] and $d = (4D^*t)^{0.5}$, with D^* the infinite dilution diffusion coefficient²² of the d -PS, and t the diffusion time. The experimental depth profile is integrated to find h and then the function defined by Eq. (3) is convoluted with the instrumental resolution function, a Gaussian with a full width at half maximum (FWHM) of 80 nm, to compare it with the experimental profile. Fits to the data are obtained by adjusting D^* ; the best fits, shown as the solid and dashed lines in Fig. 1(b), correspond to $D^* = 2.1 \times 10^{-12}$ cm^2/sec for $P = 54\,000$ and $D^* = 5.3 \times 10^{-12}$ cm^2/sec for $P = 36\,000$. These values of D^* are significantly above the $D^* = 5.8 \times 10^{-13}$ cm^2/sec measured previously for $M = 110\,000$ chains diffusing into a $P = 2 \times 10^7$ matrix.¹¹

The values of D^* extracted from forward recoil

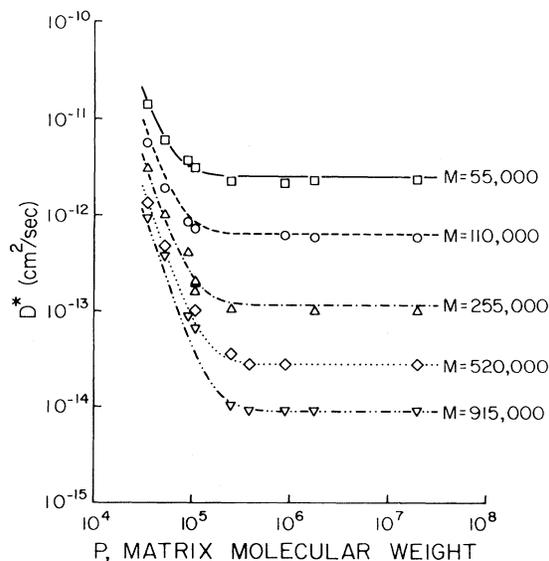


FIG. 2. Tracer diffusion coefficient D^* of d -PS of molecular weight M diffusing in PS of molecular weight P vs P . The lines represent the sum of the theoretical reptation and constraint-release contributions, $D_R + D_{CR}$, for given values of M .

spectra of the various bilayer films²³ are shown in Fig. 2. At high P , the D^* 's decrease as M^{-2} and are independent of P , as expected for reptation. As P is decreased below a certain value P^* for a given M , D^* begins to increase rapidly. P^* , which corresponds to the knee in the $\log D^*$ vs $\log P$ plot, increases roughly as $M^{1/3}$. This behavior is qualitatively that expected for the onset of constraint release. Since the diffusion mechanisms discussed above are independent, the actual D^* should be the sum of the D 's of the mechanisms,¹⁷ i.e.,

$$D^* = D_R + D_{CR}. \quad (4)$$

The theoretical prediction, based on Eqs. (1), (2), and (4), is shown as the lines on Fig. 2. The values $M_e = 18\,000$ and $\alpha_{CR} = 13.3$ corresponding to $z = 3.5$ are used. The theory fits the data well, perhaps fortuitously well, since the exact value to be used for z is uncertain. However, Graessley and Struglinski²⁴ have found that a value of $z \approx 3$ also is required to fit viscoelastic data on mixtures of polybutadienes. Moreover, the P^{-3} dependence of D^* predicted at low P is obeyed by the data as is the M^{-1} dependence in the same regime.²⁵ There seems little doubt that the effects of constraint release have been observed. These results are qualitatively consistent with previous experiments²⁶⁻²⁸ which indicated an effect of P on the D^* of M chains but only at $P < M$. For large enough M 's self-diffusion, $M = P$, is in the regime where reptation dominates and D^* is independent of P . At small values of M , however, e.g., 55 000, D_{self} is significantly above D_R .

Thus we have demonstrated that while reptation is the dominant diffusion mechanism when P is greater than a certain P^* which increases as $M^{1/3}$, constraint release dominates at P 's well below P^* . The measured magnitude of the constraint release is in agreement with values calculated using the theory of Graessley.¹⁷ While reptation dominates for large P 's for linear M chains, constraint release is expected to be an important mechanism even here for branched and ring M molecules^{8,16} that cannot diffuse easily by reptation.

We acknowledge the support of this research by the National Science Foundation, Division of Materials Research, Polymers Program and the use of the facilities of the Cornell Materials Science Center which is funded by the National Science Foundation, Division of Materials Research, Materials Research Laboratories Program. One of us (P.G.) received a Public Health Service Pre-doctoral Fellowship and one of us (P.M.) is a Post-doctoral Fellow of the Cornell University Materials

Science Center. We thank W. W. Graessley, J. Klein, O. Meyer, B. Doyle, and S. S. Lau for helpful discussions.

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²²While for concentrated polymer mixtures the correct D is the interdiffusion coefficient \bar{D} , it is nonetheless true that $\bar{D} \rightarrow D^*$ of the dilute species when $\phi < 0.1$. This condition holds after very short diffusion times in our experiments.

²³Because it required unrealistically short diffusion times, < 100 sec, to measure the D^* of $M = 55\,000$ d -PS diffusing into low- P PS matrices, measurements on $M = 55\,000$ d -PS were made at 140°C and were scaled by the ratio of the D^* 's of $M = 55\,000$ d -PS diffusing into $P = 2 \times 10^7$ PS at 170 and 140°C , respectively. Such scal-

ing with temperature should be independent of P and M .

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in theta solvents, however, we predict that $D_{SE} > D_{CR}$ only at $M > 2 \times 10^7$, which is greater than the M 's we have.

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