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(23) The D_{tr}^{∞} data have been reanalyzed by using a value of D_{tr}^{∞} at $M = 0.2M_e$ for reduction. Better superposition has been obtained in comparison with that in Figure 3. $D_{tr}^{\infty}(0.2M_e)$-$0.2M_e$ is found to be proportional to $c^{-0.55\pm0.05}$.

Polymer Diffusion in Melt Blends of Low and High Molecular Weight

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ABSTRACT: Forward recoil spectrometry (FRES) was used to measure the tracer diffusion coefficient D^* of deuterated polystyrene (d-PS), of molecular weight 255 000 daltons, into a matrix blend of high and low molecular weight polystyrene (PS), as a function of the volume fraction φ of the high molecular weight polymer. The low molecular weight PS, 10 000, was too short to entangle, whereas the three different PS's of high molecular weight P = 20 000 000, 250 000, and 93 000 blended with the low molecular weight sample were well above the entanglement molecular weight M_e of the melt at $\varphi = 1$. For the highest P, $D^*(\varphi) \propto \varphi^{-1}$ for $\varphi \geq 0.1$ when appropriate corrections for the change in the glass transition temperature of the blend with φ are made. These results are in good agreement with the prediction of the reptation model, which predicts $D^* \propto M_e$, since experimentally $M_e \approx M_e(\varphi{=}1)/\varphi$. For lower values of P, the constraint release mechanism must also be included to predict values of D^* in agreement with the data. However, below a critical value of $\varphi = \varphi_c = P_c/P$ where P_c is the critical molecular weight for entanglement, the PS blend matrix becomes unentangled and D^* approaches its value for the pure low molecular weight PS.

Introduction

Diffusion of polymer chains in entangled melts and solutions has recently received considerable experimental and theoretical attention.[1-12] In melts consisting only of long entangled chains, the reptation model of de Gennes[2,3] and Doi and Edwards,[4] as extended by Graessley,[5,6] has served well to describe diffusion. The reptation diffusion coefficient for a tracer chain of molecular weight M moving through a matrix of fixed constraints is given by

$$D_R = D_t/3N_M \tag{1}$$

Here the M chain is modeled as a random walk of N_M steps of length a, the mesh size imposed by the topological constraints of the matrix chains; one can loosely think of N_M as the number of entanglements along the M chain. The one-dimensional diffusion coefficient D_t for the movement of the chain within the virtual tube defined by the constraints is taken to be that for a Rouse chain, i.e.,

$$D_t = k_B T M_0/\zeta_0 M$$

where ζ_0 is the friction coefficient of a monomer of molecular weight M_0.

The extension of the model to systems in which the matrix chains are not fixed constraints but mobile chains of molecular weight P yields an additional contribution to the diffusion coefficient of the M chain due to the release of its constraints as the P chains move.[13,14] This diffusion may be characterized by the constraint release diffusion coefficient[5,6]

$$D_{CR} = z\left(\frac{12}{\pi^2}\right)^{z-1}\frac{D_t}{N_P^{\,3}}$$

where z is the number of "suitably situated constraints" defining the tube at any cross section, and N_P is the number of steps of length a along a P chain in the matrix. Since the mean-square displacement of the M chain due to reptation is independent of that due to its motion by constraint release, the tracer diffusion coefficient is the sum of the reptation and constraint release contributions, or

$$D^* = D_R + D_{CR} = D_t\left[\frac{1}{3N_M} + \frac{z}{N_P^{\,3}}\left(\frac{12}{\pi^2}\right)^{z-1}\right] \tag{2}$$

An important issue for diffusion of long polymer chains in solutions[7-12] is the dependence of D^* on the concentration of polymer in the solution. While most results on such diffusion in small molecule solvents have been analyzed in terms of the scaling law approach[2] in the semidilute regime, it has been difficult to test such laws over a sufficiently wide range of concentration to be convincing. A somewhat simpler approach has been recognized recently.[15] By preparing a polymer–polymer "solution" consisting of a volume of a fraction ϕ of long polymer chains in chains of the same polymer that are too short to be entangled, D^* can be measured in the concentrated regime where the theory outlined above should hold. Our experiments will adopt this approach.

The concentration dependence of D^* predicted by eq 2 arises from both the concentration dependence of the factor D_t and the concentration dependence of the number of entanglements N_M and N_P. The change of D_t with φ is due entirely to the effect of φ on ζ_0, caused by the decrease in glass transition temperature $T_g(\varphi)$ of the matrix as the long chains are diluted with shorter ones. This dependence can be accounted for by the factor

$$a_c(\varphi) = \zeta_0(\varphi)/\zeta_0$$

thus

$$D_t(\varphi) = D_t/a_c(\varphi)$$

The correction factor $a_c(\varphi)$ can be written in terms of the WLF shift factor[16] a_T since the monomeric friction coef-

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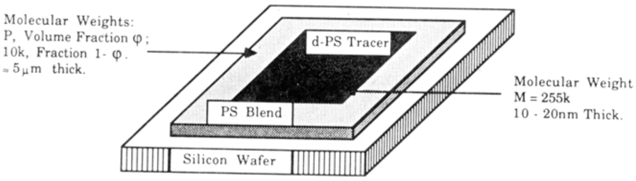

Figure 1. Schematic representation of a typical sample. The overall area is a few square centimeters.

ficient ζ_0 should be proportional to the zero-shear viscosity η_0, which is affected by free volume changes via

$$\eta_0 \sim a_T(T - T_g)$$

Thus

$$a_c(\varphi) = \frac{a_T(T - T_g(\phi))}{a_T(T - T_g)} \tag{3}$$

The glass transition temperatures of the pure components were measured by differential scanning calorimetry; $T_g(\varphi)$ was interpolated by using the approximate inverse proportionality between the glass transition temperature and the number-averaged molecular weight.[17]

The concentration dependence of the number of entanglements can be determined by using the relationship between the entanglement molecular weight M_e and the plateau modulus, as follows. Letting c be the chain concentration, Graessley's result,[6]

$$G_N{}^0 = {}^4\!/_5 cNk_BT$$

combined with the defining relation for M_e,

$$G_N{}^0 = c\frac{M}{M_e}k_BT$$

gives

$$N_M = \frac{5}{4}\frac{M}{M_e} \quad \text{and} \quad N_P = \frac{5}{4}\frac{P}{M_e}$$

Since $M_e(\varphi)$ has been found experimentally to be inversely proportional to φ,[18] both N_M and N_P should be proportional to φ. After applying these relations to eq 2, we have

$$D^*(\phi) = \frac{D_t}{a_c(\varphi)}\left(\frac{4}{5}\frac{M_e}{M\varphi} + \frac{64}{125}z\left(\frac{12}{\pi^2}\right)^{z-1}\frac{M_e{}^3}{P^3\varphi^3}\right)$$

where M_e is the entanglement molecular weight of the undiluted matrix. Using eq 1, we find

$$D^*(\varphi) = \frac{D_R}{a_c(\varphi)}\left(\frac{1}{\varphi} + \alpha_{CR}\frac{MM_e{}^2}{P^3\varphi^3}\right) \tag{4}$$

where

$$\alpha_{CR} = \frac{48}{25}z\left(\frac{12}{\pi^2}\right)^{z-1}$$

The M and P dependences of this relation have been observed experimentally in undiluted melts.[19-21] Our experiments are designed to test the predicted concentration dependence. The WLF free volume corrections represented by a_c have been used successfully by previous workers.[22] Thus we will focus on the φ^{-1} and φ^{-3} terms, whose origin is the prediction that the number of constraints along a diffusing chain is proportional to the concentration of matrix chains.

Experimental Procedure

Figure 1 is a schematic diagram of a typical sample, which consists of two layers of polystyrene supported on a silicon substrate. The bottom PS layer is a blend of long solute chains of molecular weight P, diluted by solvent chains (molecular weight $P_D = 10\,000$) which are too short to entangle. This 2–4 μm thick layer is formed by mixing the solute and solvent chains in toluene, then spreading the solution over a silicon wafer, and allowing it to dry. A solution of deuteriated polystyrene (molecular weight $M = 255\,000$) in toluene is spun onto a glass slide, creating a film of 10–20-nm thickness. This thin tracer film is then floated off the slide onto the surface of a water bath and subsequently picked up on the coated wafer, completing the top layer of the bilayer diffusion couple. The couple is then annealed at a diffusion temperature of either 150 or 178 °C for a time sufficient for the tracer chains to diffuse to a depth of about 400 nm into the matrix. The tracer chains are diluted rapidly as diffusion proceeds; the d-PS tracer concentration during most of the diffusion period is less than 0.05 volume fraction.

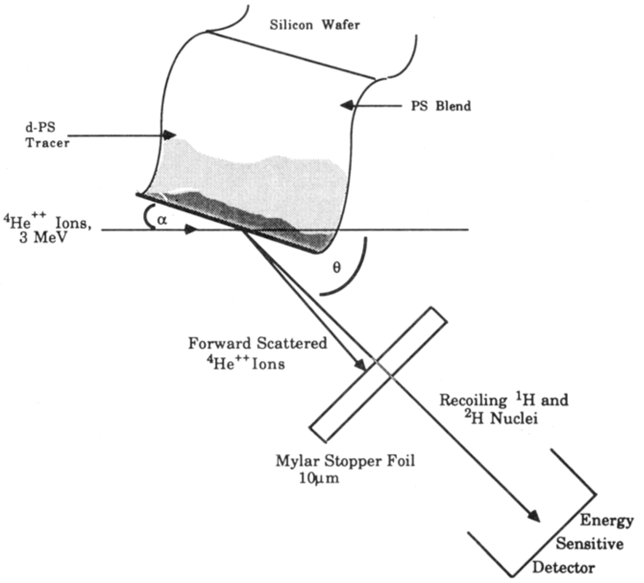

Figure 2. Schematic diagram of the geometry of the FRES technique.

The tracer diffusion coefficient D^* of the deuteriated chains in the melt is obtained by forward recoil spectrometry (FRES),[20,21] the geometry of which is displayed in Figure 2. A $^4\mathrm{He}^{2+}$ beam of energy $E_0 = 3$ MeV impinges on the sample at a glancing angle $\alpha = 15°$. Scattered $^4\mathrm{He}^{2+}$ ions are stopped in the Mylar stopper foil; deuterons (^{2}H) and protons (^{1}H) recoiling from the sample are gathered in an energy-sensitive detector (silicon surface barrier) at the scattering angle $\theta = 30°$. The output pulses from this detector, the height of which are proportional to the energy of the detected particle, are analyzed by a multichannel analyzer to obtain a yield versus energy spectrum, an example of which may be seen in Figure 3a.

The recoil of ^{1}H or ^{2}H nuclei from the sample results from an elastic collision between an incident $^4\mathrm{He}^{2+}$ ion and the nucleus. If the energy of the $^4\mathrm{He}^{2+}$ ion of mass m_{He} just below the collision is E_{He}, the energy of the recoiling target nucleus of mass m_t just after the collision is

$$E_{\mathrm{target}} = E_{\mathrm{He}}\frac{4m_{\mathrm{He}}m_t}{(m_{\mathrm{He}} + m_t)^2}\cos^2(\theta) \tag{5}$$

Deuterons recoil with about 1.4 times the energy of the protons, allowing separate ^{1}H and ^{2}H peaks to be resolved. The diffused d-PS tracer molecules are the source of the recoiling deuterium particles; therefore our interest is the ^{2}H spectrum.

The observed volume fraction versus depth profile for the tracer, an example of which is shown in Figure 3b, is obtained from the yield versus energy spectrum as follows.[20] First one notes that the yield of ^{2}H particles recoiling from a given depth in the sample must be proportional to the local deuterium density. Thus dividing the observed spectrum by a standard spectrum obtained from a thick film of the deuteriated polymer converts the yield scale to the volume fraction of the tracer.

The energy scale is related to the depth from the surface, since the $^4\mathrm{He}^{2+}$ ion loses energy by inelastic collisions with electrons

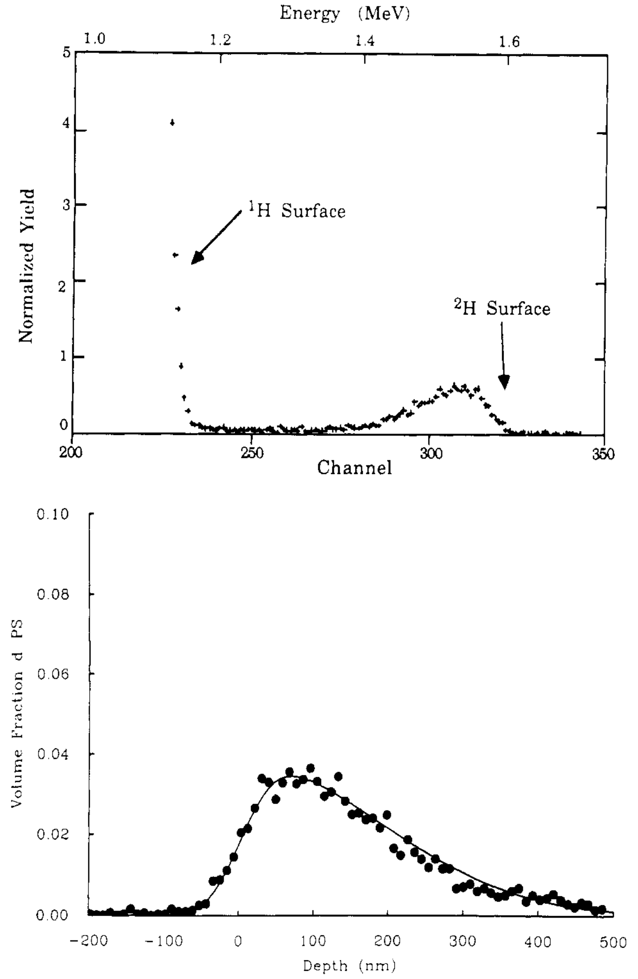

Figure 3. (a) FRES spectrum from a bilayer sample composed of a 255 000 molecular weight d-PS tracer on a 255 000, 10 000 PS blend, $\varphi = 0.5$ volume fraction of the 255 000 component. The sample had been annealed for 11 460 s at 178 °C. (b) Volume fraction of the PS-*d* tracer versus depth profile obtained from the spectrum in (a). The solid line represents the convolution of the Gaussian system resolution function with the Fickian solution to the diffusion equation for a tracer thickness 9 nm (equal to the integral of the experimental data) and $D^* = 5.4 \times 10^{-13}$ cm^2/s.

en route to the target d-PS tracer chain, and the recoiling ^{2}H particle suffers energy loss by the same process along its journey to the surface. The depth from the sample surface which corresponds to a given ^{2}H energy is calculated from the energy loss rates for the incident and target particles in the sample which are obtained from a table of stopping cross sections.[23]

The tracer diffusion coefficient D^* is determined by assuming Fickian diffusion for a thin film on a semiinfinite body. The volume fraction ϕ_{tracer} versus depth x of the tracer chain is then given by[24]

$$\phi_{\text{tracer}} = 0.5\left[\operatorname{erf}\left(\frac{h-x}{w}\right) + \operatorname{erf}\left(\frac{h+x}{w}\right)\right] \qquad (6)$$

where h is the tracer film thickness (found by integrating the experimental data), $w = 2(D^*t)^{1/2}$ is the diffusion depth,[25] and t is the duration of the diffusion anneal. The tracer diffusion coefficient D^* is found by fitting the solution above (after convolution with the Gaussian system resolution function) to the ϕ_{tracer} versus x data with w as the adjustable parameter. One such fit which corresponds to a D^* of 5.4×10^{-13} cm^{-}/s is shown by the solid line in Figure 3b. Repeated measurements on different specimens give results that are the same to within 20%.

Results and Discussion

Figure 4 shows the diffusion coefficient D^* as a function of φ, the volume fraction of the long-chain PS in the matrix blend. The molecular weight of d-PS tracer was 255 000 whereas the molecular weight P of the long chains in the matrix was 20×10^6 and the molecular weight P_D of the diluent was 10 000. The diffusion anneal was at performed at 178 °C. As expected, dilution of the matrix enhances the diffusion process: D^* increases monotonically with decreasing φ until a limiting value corresponds to the diffusion of the tracer in the unentangled 10 000 molecular weight diluent polymer is reached at $\varphi = 0$.

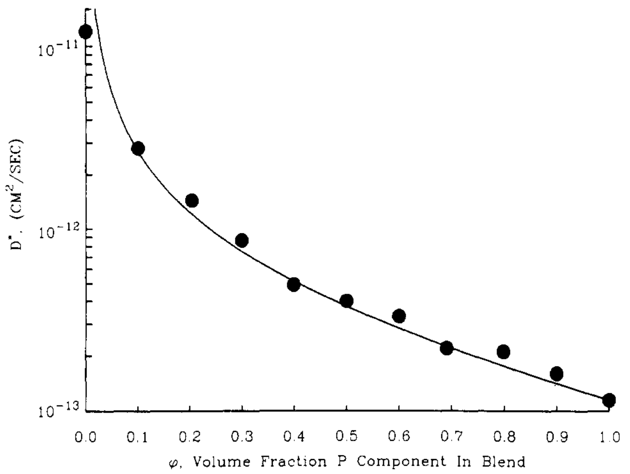

Figure 4. Plot of the tracer diffusion coefficient D^* of d-PS, molecular weight $M = 255\,000$ versus the volume fraction of high molecular weight PS in the matrix. Matrix is PS, molecular weight $P = 20 \times 10^6$, diluted with 10 000 molecular weight PS. Line represents the theoretical prediction of eq 4.

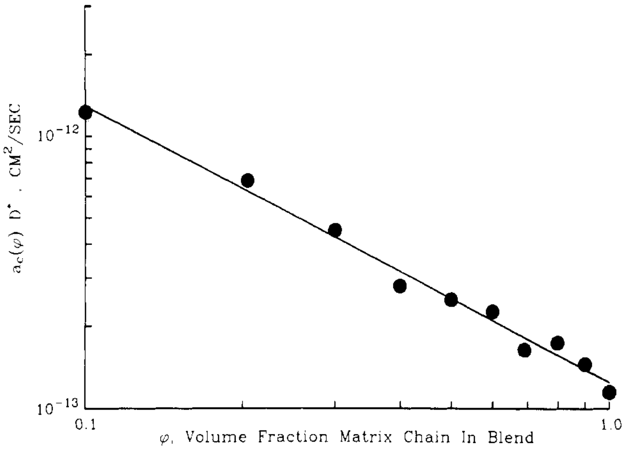

Figure 5. Data of Figure 4, after adjustment to remove change in free volume with dilution. Line is a least-squares fit with a slope of −0.99 ± 0.04.

In the range of concentration from $\varphi = 1$, corresponding to the undiluted melt, down to $\varphi = 0.1$ the tracer is predicted to diffuse by reptation only, since the constraint release contribution (the second term in eq 4) due to the motion of the 20×10^6 solute chains in the matrix is negligible. Thus the diffusion coefficient of the tracer chain is expected to scale as φ^{-1} if the correction for the change in ζ_0 with concentration is made. In Figure 5, the experimental diffusion coefficients have been multiplied by the shift factor $a_c(\varphi)$ of eq 3 and plotted versus φ on a log–log scale. The line of best fit gives $a_c(\varphi)D^* \propto \varphi^{-0.99\pm0.04}$ consistent with the prediction of eq 4 and the empirical law $M_e \propto \varphi$. Equation 4 itself produces an excellent fit of the original data as shown by the solid line on Figure 4.

These results are in excellent agreement with those of a recent experimental study of the viscoelastic relaxation times of high/low molecular weight polystyrene blends.[26] However, our result $a_c(\varphi)D^* \propto \varphi^{-1}$ is in strong disagreement

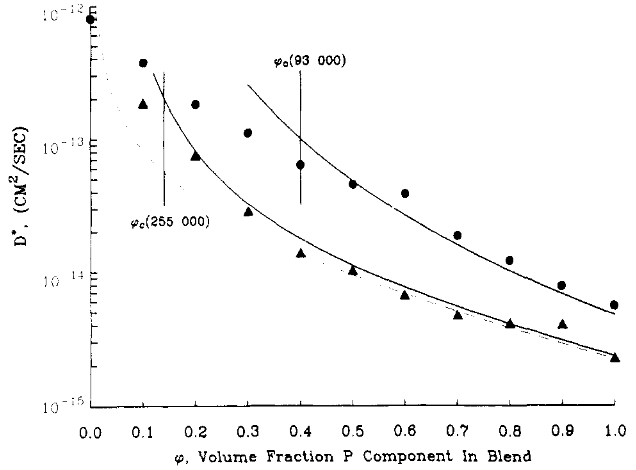

Figure 6. Tracer diffusion coefficient D^* versus the volume fraction of high molecular weight PS in the matrix for molecular weight $M = 255\,000$ d-PS tracer in matrices with molecular weight $P = 255\,000$ (triangles) and $P = 93\,000$ (circles), at 150 °C. Solid lines represent the prediction of eq 4. The dotted line shows the contribution expected solely from reptation. Critical concentrations for entanglement from eq 7 are also displayed.

with recent diffusion measurements of Smith et al.[15] on polypropylene oxide matrix blends of high and low molecular weights. In the limit $\varphi > 0.3$ they found $a_c(\varphi)D^* \propto \varphi^{-2.2}$ and suggested that perhaps their measured D^*s were increased by a constraint release contribution. To see if indeed constraint release could affect the exponent of φ if the molecular weight P of the longer chain in the matrix was low enough, we measured D^* versus φ for matrix blends in which $P = 255\,000$ and $P = 93\,000$.

Figure 6 displays the D^* versus φ results for these two blends; the tracer and diluent molecular weights remained 255 000 and 10 000, respectively. In this case the diffusion temperature was chosen to be 150 °C so that the diffusion times were not too short. The two systems display a qualitatively similar increase of D^* with dilution for concentrations near that of the pure melt; the higher molecular weight blend shows a steeper rise for lower concentrations. The diffusion coefficients converge to the value of D^* corresponding to diffusion of the tracer in the pure diluent chains.

In these blends the molecular weight M of the tracer is no longer much less than P, thus we anticipate a contribution to D^* from the constraint release mechanism. The net tracer diffusion coefficient is expected to be given by eq 4; the prediction for each of the two values of P is shown as a solid line in Figure 6. The value for M_e, the entanglement molecular weight for undiluted polystyrene, was taken to be 18 100;[16] the parameter α_{CR} was computed by using $z = 3.5$, which provides a good fit of the data for undiluted matrices.[21] The diffusion coefficient for pure reptation, corresponding to the first term in eq 4, is shown as a dotted line for comparison. One sees that for the $P = 255\,000$ matrix, constraint release is predicted to make a significant contribution for $\varphi < 0.3$. Below $\varphi = 0.15$, however, the anticipated value of D^* exceeds the observed value. For matrices with molecular weight $P = 93\,000$, the constraint release contribution plays an important role at all concentrations and provides a reasonably good prediction for D^* at concentrations greater than about 0.45. Once again the diffusion coefficient is overestimated at lower concentrations. The agreement of the data with the reptation plus constraint release model at high concentrations lends further support to the prediction that N_M, the effective number of constraints per tracer chain, is proportional to the matrix concentration. The failure of eq 4 to hold for low matrix concentrations can be anticipated, as we shall now show.

The failure of the reptation plus constraint release model for low concentrations as noted above can be interpreted in terms of a critical concentration for entanglement, φ_c, i.e., the minimum concentration for entanglement in the blend. Since the models of reptation and constraint release depend on the existence of a highly entangled matrix, φ_c should place a lower limit on the concentration range over which these models are applicable. The entanglement concentration can be estimated for a polymer melt in the following way:[18] if P_c is the critical molecular weight for entanglement in the undiluted melt (approximately 36 000 for polystyrene[16]), then for the blend we can expect

$$P_c(\varphi) = P_c/\varphi$$

This equation can be rewritten to yield a critical concentration for entanglement,

$$\varphi_c = P_c/P \tag{7}$$

Employing this relation for blends with $P = 20 \times 10^6$, 255 000, and 93 000, one obtains for the entanglement concentration values φ_c of 0.002, 0.14, and 0.39, respectively, as indicated on Figure 6. The latter two concentrations are indeed near the concentration at which the reptation plus constraint release model deviates from our data. Again, these results are in good agreement with the viscoelastic measurements of Montfort et al.[26]

Finally, it is interesting to note that over no range of concentration was D^* seen to follow the scaling law[2] for semidilute solutions. This law predicts that $a_c(\varphi)D^* \propto \varphi^{-3}$ since the long chains are not expected to be significantly swollen by the diluent for our matrix blends. A similar failure of the scaling law was noted in Smith et al.'s study of diffusion in polypropylene oxide melts.[15] While one might argue that the volume fraction range from $\varphi = 0.1$ to $\varphi = 1$ should be well above the semidilute regime, it seems clear that the difference between the D^* of the tracer into the pure diluent melt and the D^* of the tracer into the pure long chain melt is too small for there to be any appreciable region of φ over which D^* could follow a φ^{-3} dependence.

Conclusions

1. The tracer diffusion coefficient D^* of long d-PS chains was measured in a matrix blend of an extremely high molecular weight PS (20×10^6), volume fraction φ, diluted with PS of too low molecular weight (10 000) to entangle. Following correction to constant matrix T_g, D^* decreases as φ^{-1}, in excellent agreement with the prediction of the reptation model for concentrated solutions.

2. When the molecular weight P of the long chain component of the matrix is decreased, the constraint release mechanism makes an increasing contribution to the φ dependence of D^* at high φ. As P is decreased, however, the range of φ over which the effects of constraint release can be followed decreases. The departure of the data from the model is anticipated, since the matrix becomes unentangled below a critical value of $\varphi = \varphi_c = P_c/P$, where P_c is the critical molecular weight for entanglement of the pure high molecular weight polymer.

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Viscoelastic Properties of Polybutadiene Rings[†]

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ABSTRACT: The linear viscoelastic properties of a series of linear and three ring polybutadienes have been studied. It is observed that melt viscosity of a pure ring is about 10 times smaller than that of the linear polymer with the same molecular weight. The plateau modulus is similarly 5 times smaller. Rings contaminated with 20–25% linear polymer have the same melt viscosity as linear polymers, although their plateau modulus is only about one-half times that of the linear polymer. Synthetic mixtures of ring and linear polymers were used to complete a study of the effect of linear impurities on the melt properties of rings. The data are compared with data obtained previously on polystyrene ring samples.

Introduction

Ever since the introduction of the reptation model[1] for the relaxation and diffusion of long linear polymers in the melt and in concentrated solutions, a wide search has gone on to determine the range of validity of this powerful concept. Research has proceeded in two directions. In one approach the application of the reptation model to linear polymers has been finetuned by the introduction of tube renewal[2] and contour-length fluctuation[3] effects. Experiments have been performed to evaluate the former by studying relaxation of linear polymers in networks,[4] by studying binary mixtures of linear polymers,[5–7] and by measuring the diffusion rates of linear polymers in various linear matrices.[8] Contour-length fluctuations are shown to be very important in the relaxation of low molecular weight polymers in the range $M = 2$–$5M_e$,[9] where M_e is the molecular weight between entanglements, and to disappear gradually for $M > 200M_e$.[10] The other approach taken consists of modifying the polymers with long branches and making ring polymers. For example, the central branch point of star polymers prevents reptation,[11] and arm retraction, an extended countor-length fluctuation, becomes the prominent relaxation mechanism,[11–14] for which substantial experimental evidence has been gathered.[15–18] The role of tube renewal in stars is also being documented.[19,20] It has been shown that in long-chain comb polymers the longest relaxation times are associated with the tube renewal relaxation of backbone segments between branches.[21]

In entangling ring polymers neither reptation nor arm retraction are expected to operate and since tube renewal is a second relaxation process driven by a primary relaxation process such as reptation or arm retraction it is not clear how rings in rings can relax and diffuse. A number of theoretical papers have recently appeared on the general subject of relaxation and diffusion of rings. Klein has introduced the distinction between pinned (with entanglements on the inside of the ring) and unpinned rings and estimated their concentrations.[22] Diffusion and relaxation would occur mainly by the unpinned fraction. Others explore the statistics and dynamics of rings in networks and touch upon the more difficult problem of rings in rings and rings in linear polymers.[23,24] A study of diffusion of rings in linear polymers found rings to diffuse slower than linear polymers, almost with the rate expected for a tube renewal mechanism.[25]

With respect to viscoelastic measurements two sets of data have been published recently on the molecular weight dependence of the melt viscosity, η_0, of ring poly-

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