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Comparison of the Sedimentation Data with the Hess Theory and with Self-Diffusion Coefficient Data of Polystyrene in the Semidilute Regime and in Melts[†]

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ABSTRACT: The topological function ψ, obtained from analysis of sedimentation coefficient data of poly(methyl methacrylate) (PMMA) in semidilute solutions of high molecular weight (MW) polystyrene (PS) in part 4 of this series, has been compared with a theory for self-diffusion of flexible polymers in the semidilute regime developed by Hess and also with ψ evaluated from tracer diffusion coefficient (D_{tr}^{∞}) data in the semidilute regime and from self-diffusion coefficient (D_s) data in melts. It has been found that the Hess theory can reasonably well explain the observed dependence of ψ^{-1} on the ratio of MW of PMMA to MW between entanglements of PS, $M_{e,PS}$. ψ from D_{tr}^{∞} data of a tracer PS in semidilute solutions of high MW PS has shown poor agreement with ψ from the s data. On the other hand, ψ from the s data has been found to asymptotically approach ψ from D_s data in melts in the highly entangled region.

Introduction

In part 4 of this series "Dynamics of Polymer–Polymer–Solvent Ternary Systems", we have studied the molecular weight dependence of the sedimentation coefficient s of a tracer poly(methyl methacrylate) (PMMA) in semidilute solutions of high molecular weight polystyrene (PS) over a wide range of PS concentration c_{PS}.[1] We have shown that s versus M curves for respective c_{PS} can be superposed on one another to form a single composite curve from reduction of variables s and M with $s(0.1M_{e,PS})$ and $M_{e,PS}$, respectively. Here $M_{e,PS}$ is the molecular weight between entanglements of a matrix component PS, and $s(0.1M_{e,PS})$ is a value of s at $M = 0.1M_{e,PS}$ for each c_{PS}. In the reduction, we have assumed that $s(0.1M_{e,PS})$ represents the screening effect of the hydrodynamic interaction and is reciprocally proportional to the effective friction coefficient $\zeta(c_{PS})$, provided that a test PMMA chain is substituted for the free-draining Rouse chain of n segments with $\zeta(c_{PS})$. It has been also assumed that the quantity $M_{e,PS}$ characterizes the PS entanglement network which is spatially fixed during the characteristic time for self-diffusion of the test polymer, and $M/M_{e,PS}$ represents the strength of topological restrictions on the mobility of the polymer. From success of the superposition, we have concluded that the master curve, hereafter called as the topological function ψ, uniquely represents the effect of the topological interaction on the friction coefficient f of a PMMA chain over a wide range of both M and c_{PS} in the semidilute regime. Then remaining tasks may be, first, interpretation of the function ψ from a microscopic level on the basis of a well-defined molecular model and, second, examination of whether our reduction scheme is applicable for data of self-diffusion coefficient D_s in the semidilute regime as well as in melts. This has been done and is described in this report.

Results and Discussion

1. Determination of the Topological Function ψ. The reduced plot of $s/s(0.1M_{e,PS})$ versus $M/M_{e,PS}$ in Figure 8 in part 4 is reproduced in Figure 1 with additional reduced data (filled circles) whose s values are given in Table III of part 2.[2] Here reduction for additional data has been made exactly in the same way as described in part 4. It is seen that newly added data are located on the master curve. This indicates the validity of our reduction scheme with two parameters of the effective segment friction coefficient ζ and molecular weight between entanglements M_e. The topological function ψ thus determined is going to be compared with theory and D_s data in literature.

2. Comparison of ψ with Hess Theory. First of all, it should be mentioned that the scaling theory with the reptatiton model[3] is insufficient for comparison with ψ which has been determined over a range of $M/M_{e,PS}$ from 0.1 to 5, because the theory is valid in the highly entangled region only, that is, at large values of $M/M_{e,PS}$. Quite recently, Hess has presented a theory which predicts in a microscopic and self-consistent way the existence of a reptation transition in self-diffusion of a flexible polymer in semidilute solutions of homogeneous polymers.[4] His theory may be briefly summarized as follows. The model used is the free-draining Rouse chain consisting of n segments with concentration-dependent effective friction coefficient $\zeta(c)$, into which the effect of the screened hydrodynamic interaction is absorbed. By starting from a Fokker–Planck equation for the phase-space distribution function of segments of N Rouse chains and using the projection operator method, a general formula for D_s has been rigorously obtained by use of the dynamic friction function $\Delta\zeta(0,t)$.

The long-time result of $\Delta\zeta(0,t)$ in the semidilute regime was then calculated by considering center-of-mass diffusion as coupled motion of curvilinear and lateral modes. Here the curvilinear motion denotes large-scale motion along the polymer chain axis and the lateral one perpendicular to the chain axis. The former motion corresponds to the motion of a one-dimensional Rouse chain. The lateral motion is more and more impeded with increasing c due to repulsive interactions from other chain segments. Above a critical strength of interaction, the lateral motion becomes completely blocked and only curvilinear motion, i.e., reptation, becomes possible. The final formula for D_s reads as

$$\begin{aligned} D_s/D_0 &= 1 - \tfrac{2}{3}\phi(c,n) \qquad 0 \le \phi \le 1 \\ &= \frac{1}{1 + 2\phi(c,n)} \qquad 1 \le \phi \end{aligned} \tag{1}$$

Here D_0 ($\equiv k_BT/n\zeta(c)$) is the self-diffusion coefficient of the model Rouse chain without topological constraints and $\phi(c,n)$, called the entanglement parameter, is given as

$$\phi(c,n) = n\Delta F/2ck_BT \equiv n/n_c \tag{2}$$

where ΔF is the mean free energy density from interactions among different chains and c is the segment number

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[†] Part 5 of the series "Dynamics of Polymer–Polymer–Solvent Ternary Systems".

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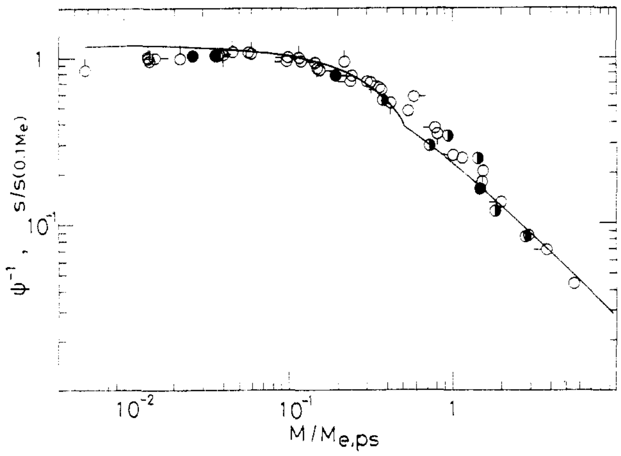

Figure 1. Comparison of reduced sedimentation data with the Hess theory. Symbols are (○) and (◑) data reproduced from Figure 8 in ref 1 and (●) reduced data from s of $P - 1$ (M_W = 260 000) given in Table III of ref 2. The solid curve is the theoretical prediction from eq 3 with $\phi(c,n) = M/M_{e,PS}$.

concentration. Equation 1 indicates that, at a critical chain length of n_c ($\equiv 2ck_BT/\Delta F$), a reptation transition takes place. In a case of tracer diffusion such that a test chain diffuses through an immobile entanglement network, the expression for D_s should be modified a little and is given by eq 3.[5] Equations 2 and 3 contain one adjustable parameter $\phi(c,n)$.

$$\begin{aligned} D_s/D_0 &= 1 - {}^4\!/_3\phi(c,n) \qquad 0 \le \phi \le {}^1\!/_2 \\ &= \frac{1}{1 + 4\phi(c,n)} \qquad {}^1\!/_2 \le \phi \end{aligned} \tag{3}$$

In order to compare the topological function ψ with the theory, $\phi(c,n)$ was set equal to $M/M_{e,PS}$ ($\equiv n/n_{e,PS}$) and ψ^{-1} ($\equiv D_s(n)D_0(0.1n_{e,PS})/D_0(n)D_s(0.1n_{e,PS})$) was calculated from eq 3. Results are shown as a solid curve in Figure 1. The theory seems to be successful in prediction of the initial decrease in ψ^{-1} at low values of $M/M_{e,PS} \simeq 0.1$ as well as the strong M dependence of ψ^{-1} at higher $M/M_{e,PS}$. At intermediate values of $M/M_{e,PS}$ from 0.5 to 1, however, agreement is not good compared with that observed at other $M/M_{e,PS}$, and a reptation transition is not as sharp as predicted by the theory. Hess has already remarked in his paper[4] that the sharpness of the transition might be an artifact originated from neglect of coupling between center-of-mass motion and internal fluctuation in the segment distribution of the chains. From an experimental point of view, polydispersity of PMMA samples used might be supposed as another source which would broaden the transition, even though we have used fairly narrow distribution polymers. Reasonable agreement between theory and experiment seems to suggest that an almost correct answer is given for the molecular mechanism of large-scale motion of a polymer in the semidilute regime under the screened hydrodynamic interaction and topological restrictions, leading to pure reptation in the highly entangled state.

In the above fitting procedure $\phi(c,n)$, or n_c, was treated as an adjustable parameter. In principle, however, molecular weight M_{cr} corresponding to n_c can be calculated from the definition $M_{cr} \equiv M_s n_c \equiv 2c_M RT/\Delta F$ (M_s is the molecular weight of a segment and c_M mass concentration in units of g/cm^3) by making use of a fact that ΔF can be estimated from integration of the osmotic pressure versus c curve in the semidilute regime. Comparison of calculated M_{cr} with $M_{e,PS}$ evaluated from viscoelastic data then makes it possible to examine the basic assumption of the theory that the mechanism which causes the reptational motion is the excluded-volume interaction. We have utilized the osmotic pressure versus c relation of PS in toluene in the limit of long chains for this purpose[6] and obtained

$$M_{cr}c_M^{1.27} = 1.27 \times 10^3 \tag{4}$$

Equation 4 indicates that M_{cr} has a little weaker concentration dependence than $M_{e,PS}$, and the former takes a one-tenth smaller value than the latter at the same c. In a previous report[7] it has been shown that the hydrodynamic screening length ξ_H of PS in benzene obtained from dynamic light scattering measurements on semidilute PS solutions has the same c dependence as the correlation length ξ_e corresponding to $M_{e,PS}$ ($\xi_e^2 \propto M_{e,PS}$) and is about one-fifth of ξ_e; i.e., the ratio $M_{\xi_H}/M_{e,PS}$ amounts to about $^1/_{25}$. M_{cr} given by eq 4 is, therefore, in the middle of M_{ξ_H} and $M_{e,PS}$, or relatively closer to M_{ξ_H}. The basic assumption of the Hess theory or de Gennes's argument[8] that entanglement coupling in good solvents is related to the number of contact points among chains may be correct. However, such a small M_{cr} value given by eq 4 suggests that modification of the theory may be more or less necessary. In this connection, it may be pointed out that light scattering measures concentration fluctuation of segments under osmotic force, being one of the volume forces that hardly gives rise to any entanglement phenomena in contrast to the shear force. A typical example is seen for the bulk and the shear modulus in viscoelasticity of polymer melts.[9] Thus it seems to be inadequate to express the effect of topological constraints on slow motion of a polymer by use of the hydrodynamic screening length as a fundamental parameter or as a mesh size of the entanglement network. This is one of reasons why we have preferred to use M_e obtained from viscoelastic measurements in the reduction of the data as is shown in Figure 1.

3. Comparison of ψ with D_{tr}^{∞} Data in the Semidilute Regime. Kim et al.[10] have measured the tracer diffusion coefficient D_{tr} of PS in semidilute solutions of PS with higher molecular weights and obtained an asymptotic limiting value D_{tr}^{∞}, independent of a matrix polymer molecular weight. In order to apply our reduction scheme to their D_{tr}^{∞} data, D_{tr}^{∞} was first multiplied by the respective molecular weight M.

$$D_{tr}^{\infty}M = K_2/\zeta(c)\psi(M/M_{e,PS}) \tag{5}$$

Here K_2 is a constant. A logarithmic plot of $D_{tr}^{\infty}M$ against M is shown in Figure 2. Next, $M_{e,PS}$ was calculated for each c from eq 13 in part 4, and then $D_{tr}^{\infty}(0.1M_{e,PS})$, a value at $M = 0.1M_{e,PS}$, was read from the curve for each c, as is shown by an arrow in Figure 2. Finally all data in Figure 2 were reduced by using $D_{tr}^{\infty}(0.1M_{e,PS})0.1M_{e,PS}$ to derive the topological function. ψ^{-1} is plotted against $M/M_{e,PS}$ in Figure 3 where ψ^{-1} from the s data is also shown for comparison. In Figure 4, $D_{tr}^{\infty}(0.1M_{e,PS})0.1M_{e,PS}$, which is reciprocally proportional to $\zeta(c)$, is plotted against c with $s(0.1M_{e,PS})$ obtained in the previous study.[1] Figure 3 shows that superposition for D_{tr}^{∞} could not be achieved so well compared with that for the sedimentation data. A scrutiny of the data tells us that data scattering mainly comes from D_{tr}^{∞} data at the highest concentration of c = 20 wt % (shown as ȯ in Figure 3). In Figure 4, $D_{tr}(0.1M_{e,PS})0.1M_{e,PS}$ at c = 20 wt % deviates downward by a factor of about 2 from the straight line which resprsents the concentration dependence of $\zeta(c)$ at lower c fairly accurately. The deviation has been attributed to an increase of local friction by the authors. If we would use, for reduction, a value at c = 20 wt %, which may be obtained from extrapolation of the straight line, superposition would be greatly improved.[23]

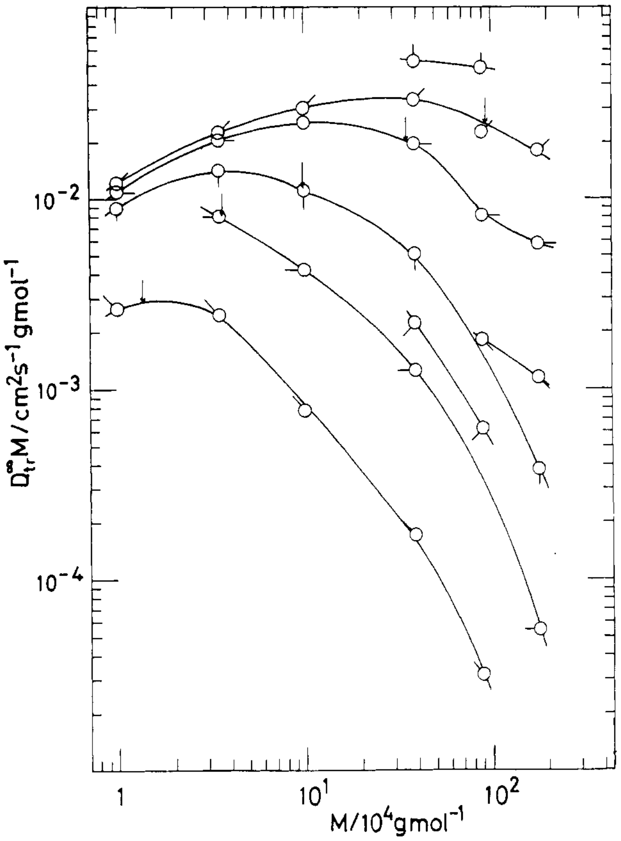

Figure 2. Products of asymptotic tracer diffusion coefficient D_{tr}^{∞} of PS in PS matrices given in Table II of ref 10 and their respective molecular weight M are plotted against M for illustration of our reduction scheme. Polymer concentration is, from the top, (ȯ) 0.5; (ó) 1.0; (O-) 2.0; (Q) 4.0; (ϙ) 5.0; (ρ) 7.0; (-O) 10; (ò) 20 wt %, respectively. A value of $D_{tr}^{\infty}(0.1M_e)0.1M_e$ at each c is marked with an arrow.

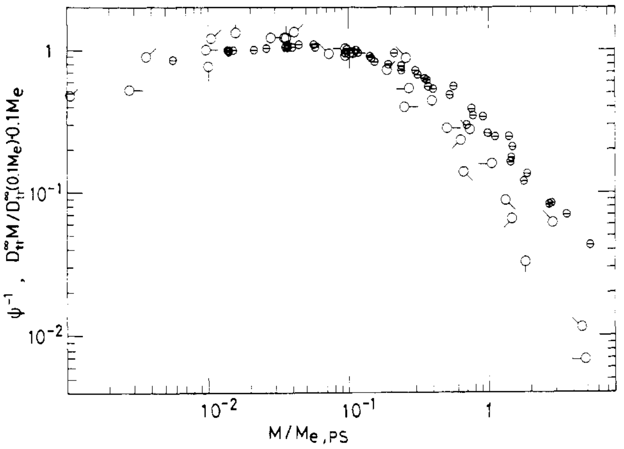

Figure 3. Superposition of $D_{tr}^{\infty}M$ has been made from reduction of $D_{tr}^{\infty}M$ and M with $D_{tr}^{\infty}(0.1M_e)0.1M_e$ and M_e, respectively. Symbols are same as in Figure 2. Reduced s data (⊖) in Figure 1, termed as ψ^{-1}, are reproduced for comparison.

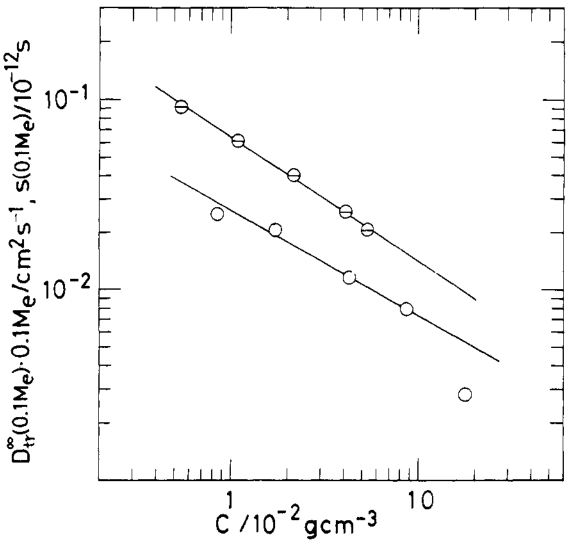

Figure 4. $D_{tr}^{\infty}(0.1M_e)0.1M_e$ and $s(0.1M_e)$ are plotted against c to show concentration dependence of the effective friction coefficient $\zeta(c)$. (⊖) s of PMMA in PS matrices. The slope of the straight line is −0.68 ± 0.02. (○) D_{tr}^{∞} of PS in PS matrices. The slope of the straight line is −0.56 ± 0.05.

As Figure 3 indicates, ψ^{-1} for D_{tr}^{∞} appears to be different from ψ^{-1} for s. The former decreases more rapidly with increasing $M/M_{e,PS}$ in the range of $M/M_{e,PS}$ from 0.1 to 1 and exhibits stronger molecular weight dependence at larger $M/M_{e,PS}$ like $\psi \propto (M/M_{e,PS})$,^{2} which agrees with a conclusion of Kim et al. that $D_{tr}^{\infty} \propto M^{-3}$ is a better representation than $D_{tr}^{\infty} \propto M^{-2}$ in entangled semidilute solutions. The effective friction coefficient $\zeta(c)$ also seems to have a different concentration dependence. The slope of 0.56 ± 0.05 obtained from the straight line in Figure 4 is quite close to the theoretical value of 0.5 in good solvents,[11] whereas the slope is 0.68 for $\zeta(c)$ of the s data. These differences might reflect the difference in polymer–polymer interaction between PS–PS–toluene and PMMA–PS–thiophenol ternary systems investigated. Both studies used a matrix polymer solution composed of the same PS and a good solvent to PS, though toluene may be slightly better than thiophenol. In the sedimentation study, PMMA used as a test chain is incompatible with PS, while the tracer diffusion study of PS in PS solutions is free from the problem of incompatibility. PS chains may be more expanded in PS solutions than PMMA chains with the same molecular weight.[12] Thus the effect of topological restrictions on self-diffusion of polymers may be seen at lower $M/M_{e,PS}$ for the PS–PS–toluene system compared with the PMMA–PS–thiophenol system. This conjecture qualitatively explains the difference of ψ^{-1} in the range of $M/M_{e,PS}$ from 0.1 to 1. However, it seems quite difficult to reconcile molecular weight dependence of the two ψ in the entangled region to each other with the same idea. The relation $D_s \propto M^{-2}$, i.e., $\psi \propto M$, has been already confirmed experimentally for melts of high molecular weight polymers.

By referring to results of Kim et al., we see that the exponent appearing in the molecular weight dependence of the self-diffusion coefficient takes a maximum with increase in c from dilute solution to melt. Or, if reptation motion becomes the only possible motion for self-diffusion in the highly entangled state as the Hess theory predicts, $D_{tr}^{\infty} \propto M^{-3}$ observed in the semidilute regime is only transient and D_{tr}^{∞} must diminish its molecular weight dependence with further increase in M. From a purely experimental point of view, we should investigate the molecular weight dependence of D_{tr}^{∞} in concentrated solutions whose $M/M_{e,PS}$ exceeds 10. Such a study is in progress in our laboratory.

4. Comparison of ψ with D_s Data in Melts. In previous sections, we discussed ψ obtained from s data in the semidilute regime in relation to the Hess theory for reptation transition and also to D_{tr}^{∞} data in the semidilute regime. We have pointed out that M_e which has been determined from viscoelastic measurements is quite a useful quantity for representation of the effect of topological constraints on slow large-scale motion such as self-diffusion. From extensive studies on self-diffusion in

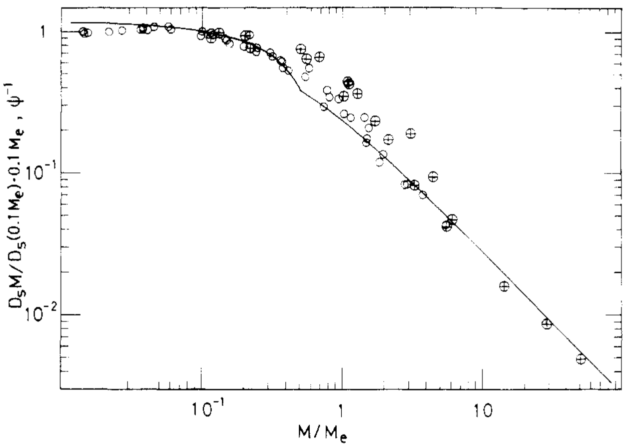

Figure 5. Comparison of ψ^{-1} from s data in solutions with $D_sM/D_s(0.1M_e)0.1M_e$ from D_s data in melts; (○) from s of PMMA in PS matrices; (⊕) from D_s of PS in melts. The solid curve is the theoretical prediction from eq 3 with $\phi = M/M_e$.

polymer melts, on the other hand, it has turned out that for $M \leq M_e$, D_s does not show the Rouse chain behavior of $D_s \propto M^{-1}$, but decreases more rapidly with increasing M, and also that for $M \gg M_e$, D_s conforms to the prediction of the reptation theory.[13-17] This is in contrast to the zero-shear melt viscosity which is proportional to M until M exceeds the critical molecular weight M_c, being about twice as large as M_e, and then becomes proportional to M^α with $\alpha \geq 3.4$.[9] The proportionality of η to M at low M may be the greatest evidence which has lead to the belief that polymer chains behave as the free-draining Rouse chain in melts if their molecular weights are smaller than M_c. The observed D_s behavior casts suspicion on such a view. Nevertheless, as long as we treat with slow molecular motion over the length scale with which the detailed chemical structure of polymer chains can be smeared out, the effect of the topological interaction among polymer molecules on D_s in melts may be characterized by M_e. Thus it is interesting to calculate ψ from D_s data in melts for comparison with ψ obtained in the semidilute regime. For this purpose, we can use, fortunately, D_s data recently reported by Watanabe.[18] He has collected D_s data of PS in homogeneous PS melts measured at various temperatures[15,17,19-21] and estimated values at the iso-free volume state ($T_r = T_g + 125$ deg) by use of the shift factor given by Allen and Fox.[22] The reduced quantity $D_sM/D_s(0.1M_e)0.1M_e$ ($\equiv\psi^{-1}$) is plotted against M/M_e in Figure 5 with ψ^{-1} from the s data. Here M_e has been taken as 18000. The reduced D_s starts to decrease, as ψ^{-1} from solution data does, from unity at a value of M/M_e as low as 0.2, i.e., at a molecular weight of 3600. This indicates that free Rouse chain behavior is hardly observable in PS melts as far as we judge in terms of self-diffusion data. In the transition zone of $M/M_e \simeq 1$, the two ψ^{-1} decrease with increasing M almost parallel to each other with a horizontal shift of about 0.2 in the logarithmic scale to the right for D_s data. Although the Hess theory is, in a strict sense, inapplicable for self-diffusion in melts, it is noteworthy that the theory predicts a horizontal shift of ψ^{-1}, shown as the solid curve in the figure, to the right by about 0.3 when spatially fixed matrix chains are allowed to relax with diffusion motion of the test chain (see eq 1 and 3). The reduced D_s data finally follow the prediction of the reptation theory above $M/M_e \geq 5$, where D_s becomes independent of matrix polymer molecular weight.[17] ψ^{-1} obtained from the s data in the semidilute regime looks to smoothly merge to ψ^{-1} from D_s in melts in the highly entangled region. Thus we tentatively propose a hypothesis that the effect of topological constraints on transport of a polymer molecule is approximately expressed for any c and M by one universal function ψ which depends only on M/M_e, i.e., number of entanglements per chain. This is another reason why M_e has been used for the reduction of molecular weight in the preceding paper.[1] For example, the friction coefficient f of a PS molecule with $M = 100\,000$ in PS melts with the same M at $T_r = T_g + 125$ deg is easily calculated to be about 60 times larger than f of a PMMA molecule with $M = 4\,000\,000$ in a 5% solution of PS with $M = 8\,420\,000$ at $T = 25$ °C, while ψ^{-1} should take the same value of 0.044 for both polymers. It is desired that the hypothesis is examined by a self-diffusion study on concentrated polymer solutions.

Finally we should make a comment concerning the free volume correction made for D_s of low molecular weight PS in melts. It has been based on assumption that free volume is associated with the local segment motion, i.e., it affects only the mobility of segments.[9] However, extra free volume f_e for low molecular weight polymers actually comes from two chain ends and it is ambiguous how f_e is distributed on middle chain segments. It is well-known that chain ends play a special role in the tube model because of its extra degree of freedom. We do not have any clear-cut answer about the role of chain ends on slow chain dynamics before the reptation transition takes place. Thus there remains a possibility that our data analysis on D_s in melts in terms of the topological function diminishes its validity. The problem is, however, obviously beyond our ability.

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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 deuteriated 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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