b between 0.49 and 0.60 ($b' = 0.062$–0.076). Last, in the very low range of N/N_τ, i.e., $N/N_\tau < 0.4$, our data are well described by the Stockmayer–Albrecht linear relationship, $\alpha_H = 1 + 0.609z$. We have simply confirmed here a well-established result.

We are presently trying to extend our measurements toward larger N/N_τ values by working on systems with relatively low Θ temperatures and by using even higher molecular weight fractions. We thus hope to better approach the stringent validity conditions of the thermal blob theory for hydrodynamic variables.

Acknowledgment. One of us (P.V.) wants to thank the C.I.E.S. and the Joliot Curie Foundation for the attribution of two scholarships during his doctoral stay at the Collège de France. We acknowledge helpful discussions with P.-G. de Gennes, M. Adam and M. Delsanti.

Registry No. Polystyrene, 9003-53-6.

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(36) Note that the eq 20 in ref 17 is incorrect. Using the same notations, it should be written as

$$\alpha_H^{-1} = \frac{3}{2Z}\left\{\left(\frac{5}{4}\alpha_R^4 - \frac{3}{2}\alpha_R^2 + \frac{1}{4}\right) - \frac{1}{Z^2}\left(\frac{5}{14}\alpha_R^{14} - \frac{13}{12}\alpha_R^{12} + \frac{11}{10}\alpha_R^{10} - \frac{3}{8}\alpha_R^8 + \frac{1}{840}\right)\right\}$$

where $Z = (N/N_\tau)^{1/2}$. For large Z, $\alpha_H \rightarrow 0.747Z^{1/5}$. For small Z, $\alpha_H \rightarrow 1 + {}^1/_4Z$. On the other hand, the plot of α_H for the modified blob theory (Figure 3 of the same paper) seems to be correct.
(37) We thank one of the referees for bringing this point to our attention.

Concentration Dependence of Polymer Self-Diffusion Coefficients

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ABSTRACT: An approach is presented for analyzing the concentration dependence of polymer self-diffusion coefficients for concentrated polymer solutions. The random motion of expanded polymer chains is treated by using the free-volume theory of transport. The effect of polymer molecular weight on the concentration dependence of the polymer self-diffusion coefficient is studied. In addition, the effect of the free-volume characteristics of the polymer and solvent on the concentration behavior of both polymer and solvent self-diffusion coefficients is investigated. Calculations are carried out on two model polymer–solvent systems, and the computed concentration trends are compared with experimental data.

Useful information about molecular mobility can be obtained from diffusion studies in the absence of any concentration gradients. Both polymer and solvent self-diffusion coefficients in polymer–solvent mixtures have been measured by using radioactive tracer[1,2] and NMR techniques.[3,4] For the solvent self-diffusion coefficient, D_1, experiments[2,3] reveal the following type of concentration dependence:

$$\partial \ln D_1/\partial \omega_1 > 0 \qquad (1)$$

$$\partial^2 \ln D_1/\partial \omega_1^2 < 0 \qquad (2)$$

where ω_1 is the solvent mass fraction. Here, and in the remainder of this paper, we suppose that the concentration dependence of the solution density is sufficiently small so that, for example, $\partial^2 \ln D_1/\partial \omega_1^2$ has the same sign as ∂^2 ln

$D_1/\partial\rho_1^2$ and $\partial^2 \ln D_1/\partial\phi_1^2$, where ρ_1 and ϕ_1 are solvent mass density and volume fraction, respectively. The kind of concentration behavior described by eq 1 and 2 can be explained by considering free-volume changes in the polymer–solvent system. Since solvents typically contain more free volume than polymers at the same temperature, the addition of solvent leads to a loosening of the polymeric solution and hence to an enhancement of molecular transport ($\partial \ln D_1/\partial\omega_1 > 0$). However, once the polymeric structure has been loosened somewhat, the rate at which solvent addition facilitates molecular motion diminishes ($\partial^2 \ln D_1/\partial\omega_1^2 < 0$).

The experimental data of Tanner et al.[4] show that the polymer self-diffusion coefficient in a polymer–penetrant mixture, D_2, exhibits a significantly different concentration dependence that apparently cannot be explained solely in terms of free-volume concepts. At the lowest polymer molecular weight studied by these investigators for poly(dimethylsiloxane) (PDS)–solvent systems, the concentration dependence of D_2 was identical with that for D_1 for a typical solvent, as given by eq 1 and 2. However, at three higher polymer molecular weights, the observed concentration behavior was of the following type:

$$\partial \ln D_2/\partial\omega_1 > 0 \tag{3}$$

$$\partial^2 \ln D_2/\partial\omega_1^2 > 0 \tag{4}$$

As noted above, free-volume considerations alone cannot explain this experimentally observed concentration dependence of D_2. The purpose of this paper is to propose a possible explanation for this experimental concentration behavior by considering the effect of concentration on both the free volume and the entanglement density in the polymer–solvent mixture.

Theory

For sufficiently concentrated polymer solutions, it is reasonable to expect that the movement of both solvent molecules and small portions of a polymer chain is governed by a jumping process into adjacent voids. Hence, this random thermal jumping should be adequately represented by a free-volume theory of transport. In the case of diffusion of a polymer molecule, the molecule can be entangled with the polymer matrix, and it is thus necessary to consider how such entanglements affect the molecular motion. Bueche[5] has proposed that the self-diffusion of a chain with N freely orienting segments is equivalent to the random motion of a larger chain with N^* effective segments when entanglements influence molecular movement. The expanded chain size serves to correct for the dragging action of the entangled chains. Bueche estimated N^*/N by considering the enhanced friction of the entangled network. Although Bueche's theory of entanglement friction has some deficiencies,[6] we believe that it is adequate for the present purpose since we are interested in establishing trends rather than in precise predictions of self-diffusion coefficients. The equations presented below should be reasonable representations of both polymer and solvent self-diffusion processes in the concentrated region, which can be defined as the region where chain dimensions are independent of concentration.[7] For a typical polymer–good solvent system, this region extends from 10% to 100% polymer.[7] The free-volume results complement the predictions of theories for the dilute and semidilute regions.[8]

From a new version of the free-volume theory of diffusion,[9-14] the following equations have been derived for the self-diffusion coefficients of the solvent and polymer:

$$D_1 = D_{01} \exp\left[-\frac{\omega_1 \hat{V}_1{}^* + \omega_2 \xi \hat{V}_2{}^*}{\hat{V}_{\mathrm{FH}}/\gamma}\right] \tag{5}$$

$$D_2 = \frac{A}{(N^*/N)M_2} \exp\left[-\frac{\omega_1 \hat{V}_1{}^* + \omega_2 \xi \hat{V}_2{}^*}{\xi \hat{V}_{\mathrm{FH}}/\gamma}\right] \tag{6}$$

$$\frac{\hat{V}_{\mathrm{FH}}}{\gamma} = \omega_1 \frac{\hat{V}_{\mathrm{FH}}(1)}{\gamma} + \omega_2 \frac{\hat{V}_{\mathrm{FH}}(0)}{\gamma} \tag{7}$$

$$\frac{\hat{V}_{\mathrm{FH}}(0)}{\gamma} = \frac{K_{12}}{\gamma}(K_{22} + T - T_{\mathrm{g}2}) \tag{8}$$

$$\frac{\hat{V}_{\mathrm{FH}}(1)}{\gamma} = \frac{K_{11}}{\gamma}(K_{21} + T - T_{\mathrm{g}1}) \tag{9}$$

In these equations, the subscripts 1 and 2 refer to solvent and polymer, respectively. Also, $\hat{V}_{\mathrm{FH}}$ is the average hole free volume per gram of mixture, $\hat{V}_{\mathrm{FH}}(0)$ is the specific hole free volume of the pure polymer at temperature T, and $\hat{V}_{\mathrm{FH}}(1)$ is the specific hole free volume of the pure solvent at T. Also, $\hat{V}_I{}^*$ is the specific critical hole free volume of component I required for a jump, ω_I is the mass fraction of component I, $T_{\mathrm{g}I}$ is the glass transition temperature of component I, and γ is an overlap factor for free volume. In addition, M_2 is the molecular weight of the polymer, K_{11} and K_{21} are free-volume parameters for the solvent, K_{12} and K_{22} are free-volume parameters for the polymer, and D_{01} and A are preexponential factors, which can in general be dependent on temperature. The definitions of the free-volume parameters K_{11}/γ, K_{21}, K_{12}/γ, and K_{22}, which are given elsewhere,[10,12] are not repeated here since they are not needed in the present context. Finally, ξ is the ratio of the critical molar volume of the solvent jumping unit to the critical molar volume of the polymer jumping unit. This quantity can be expressed as

$$\xi = \hat{V}_1{}^* M_{\mathrm{j}1} / \hat{V}_2{}^* M_{\mathrm{j}2} \tag{10}$$

where $M_{\mathrm{j}I}$ is the molecular weight of the jumping unit of component I.

An expression for the ratio of the effective number of segments in each polymer chain to the number of freely orienting segments in the polymer molecule, N^*/N, has been derived by Bueche:[5]

$$\frac{N^*}{N} = \left(1 + \frac{M_2}{8M_\mathrm{e}}\right) \times \left\{1 + \hat{K}\left(\frac{M_2}{2M_\mathrm{e}}\right)^{3/2} \sum_{n=1}^{\infty} s^n (2n-1)^{3/2}[1 - \exp(-B_n)]\right\} \tag{11}$$

$$\frac{1}{B_n} = \hat{K}\left(\frac{M_2}{2M_\mathrm{e}}\right)^{3/2-n} (2n-1)^{3/2} \tag{12}$$

$$\hat{K} = \frac{\rho_2 N_\mathrm{A}}{3}\left(\frac{\langle R^2 \rangle}{M_2}\right)^{3/2} (2M_\mathrm{e})^{1/2} \tag{13}$$

Here, M_e is the average molecular weight between entanglement points along a polymer molecule and s is a slippage factor that is the ratio of the velocity of a secondary molecule (which is entangled to the primary molecule) to the velocity of the primary molecule. Also, N_A is Avogadro's number, $\langle R^2 \rangle$ is the mean-square end-to-end distance of the polymer chain, and ρ_2 is the mass density of the polymer in the polymer–solvent mixture. The dependence of N^*/N on polymer concentration is portrayed explicitly in the above equations through ρ_2 and implicitly through the concentration dependence of M_e. The variation of M_e

with ρ_2 can be computed from the relation[5,15]

$$M_e \rho_2 = E \tag{14}$$

where E is a constant that can be calculated from a known value of M_e at a given set of conditions.

The above set of equations for D_1 and D_2 represent simplified forms of more general free-volume results. These simplified equations have been derived by introducing the following assumptions:

(1) All thermal expansion coefficients needed to calculate the various volumes required for the theory are approximated by average values in the temperature range under consideration.

(2) The partial specific volumes of polymer and solvent are assumed to be independent of concentration so that the influence of volume change on mixing on the free volume of the system is considered negligible.

(3) The molecular weight dependence of the polymer specific volume is considered to be negligible.

The second assumption leads to the following relationship between polymer mass density and polymer mass fraction:

$$\rho_2 = \frac{\omega_2}{\omega_1 \hat{V}_1{}^\circ + \omega_2 \hat{V}_2{}^\circ} \tag{15}$$

where $\hat{V}_I{}^\circ$ is the specific volume of pure component I.

The mass fraction, temperature, and polymer molecular weight dependences of D_1 and D_2 can be determined for a particular polymer–solvent system from eq 5–9 and 11–15 if the following parameters are known: D_{01}, A, ξ, $\hat{V}_1{}^*$, $\hat{V}_2{}^*$, K_{11}/γ, K_{12}/γ, $K_{21} - T_{g1}$, $K_{22} - T_{g2}$, $\hat{V}_1{}^\circ$, $\hat{V}_2{}^\circ$, $\langle R^2 \rangle / M_2$, E, and s. Although the number of parameters is rather large, they do have exact physical meaning, and they can be determined from experimental data. Since $\hat{V}_1{}^*$ and $\hat{V}_2{}^*$ can be estimated by equating them to equilibrium liquid volumes at 0 K, density data for pure polymer and pure solvent used with density correlations[16] can be used to determine $\hat{V}_1{}^*$, $\hat{V}_2{}^*$, $\hat{V}_1{}^\circ$, and $\hat{V}_2{}^\circ$. Solvent and polymer viscosity data can be used to evaluate K_{11}/γ, K_{12}/γ, $K_{21} - T_{g1}$, and $K_{22} - T_{g2}$. The parameters K_{11}/γ, K_{21}, K_{12}/γ, and K_{22} are directly related to the WLF constants[10,13,15] of the solvent and polymer. The preexponential factor A can be determined from polymer viscosity data.[10] A value of $\langle R^2 \rangle / M_2$ can be determined for a particular polymer from light-scattering or intrinsic viscosity measurements of unperturbed chain dimensions.[17] The constant E can be evaluated by using rheological data to compute M_e for the pure polymer.[15] The slippage factor s can be estimated from the viscosity–molecular weight curve for the polymer.[5,18] Finally, data on the temperature dependence of the mutual diffusion coefficient in the limit of zero solvent mass fraction can be used to determine D_{01} and ξ.[10,19,20] The mutual diffusion coefficient at $\omega_1 = 0$ is of course equal to the solvent self-diffusion coefficient at $\omega_1 = 0$. It is clear that all of the parameters can be evaluated by using only self-diffusion data at the two extremes of the concentration range. More details of the parameter evaluation are presented elsewhere.[19,20]

In this paper, we shall be interested in two aspects of the concentration dependences of D_1 and D_2. We shall use the above equations to assess the effect of polymer molecular weight on the concentration behavior of D_2. This will be done by constructing D_2 vs. ω_1 curves for two model polymer–solvent systems at a single temperature each for various values of M_2. In addition, we shall be interested in determining what effect the free-volume characteristics of the polymer and solvent have on the concentration behavior of D_1 and D_2. This will be done by studying two model polymer–solvent systems with widely different free-volume characteristics. The first model polymer–penetrant mixture will approximate the free-volume behavior of the polystyrene–toluene system. For this case, the glass transition temperatures for polymer and solvent are very different, 373 K for polystyrene and an estimated 114 K for toluene.[21] Hence, at a given temperature, the specific hole free volume of the solvent is significantly greater than that of the polymer, and free-volume effects will be very important in the concentration dependences of both D_1 and D_2. The second model polymer–penetrant system will approximate the free-volume behavior of the PDS–toluene system. In this case, the glass transition temperatures of polymer and solvent are relatively close (150 vs. 114 K) so that the difference between $\hat{V}_{FH}(0)$ and $\hat{V}_{FH}(1)$ should be relatively small. Thus, free-volume effects will be less important in the concentration behavior of D_1 and D_2, and the influence of concentration on the entanglement density will play a more important role.

It should be emphasized that the self-diffusion calculations presented below for the two model polymer–solvent systems are not necessarily quantitative predictions for D_1 and D_2. The purpose of these computations is simply to establish concentration trends for self-diffusion coefficients for concentrated polymer–solvent systems. It has been shown elsewhere[19,20] that the concentration and temperature variations of D_1 can be accurately predicted by the above theory over wide ranges of temperature and concentration. Hence, it is reasonable to expect that the free-volume part of the expression for D_2 (the exponential term in eq 6) will adequately represent the concentration variations in D_2 due to solvent effects on the mixture free volume. However, the N^*/N expression of Bueche[5] may be open to question, and quantitative predictions for D_2 vs. ω_1 cannot be expected at this time.

Results and Discussion

The concentration dependences of D_1 and D_2 were determined for the model polystyrene–toluene system at 533 K and for the model PDS–toluene system at 310 K. In both cases, the system temperature is 160 K above the glass transition temperature of the pure polymer. This corresponds approximately to the experimental temperature conditions used by Tanner et al.[4] for PDS. In addition to the presentation of the self-diffusion calculations, we shall introduce some derived free-volume expressions that can be used to anticipate and interpret the computed results.

From eq 5 and 7–9, it can be shown that

$$\frac{\partial \ln D_1}{\partial \omega_1} = \frac{\hat{V}_1{}^* \gamma \left[\dfrac{M_{j1}}{M_{j2}} \dfrac{\hat{V}_{FH}(1)}{\hat{V}_{FH}(0)} - 1 \right] \hat{V}_{FH}(0)}{\hat{V}_{FH}{}^2} \tag{16}$$

$$\frac{\partial^2 \ln D_1}{\partial \omega_1{}^2} = - \frac{2 \hat{V}_1{}^* \gamma \hat{V}_{FH}(0) \left[\dfrac{M_{j1}}{M_{j2}} \dfrac{\hat{V}_{FH}(1)}{\hat{V}_{FH}(0)} - 1 \right] [\hat{V}_{FH}(1) - \hat{V}_{FH}(0)]}{\hat{V}_{FH}{}^3} \tag{17}$$

The ratio M_{j1}/M_{j2} is generally not too different from 1 except for the diffusion of very small solvents, like water, in amorphous polymers.[11] Hence, since $\hat{V}_{FH}(1) > \hat{V}_{FH}(0)$ for typical polymer–solvent systems, it is evident from eq 16 and 17 that $\partial \ln D_1 / \partial \omega_1 > 0$ and $\partial^2 \ln D_1 / \partial \omega_1{}^2 < 0$, as has been observed in experimental studies.[2,3] This type

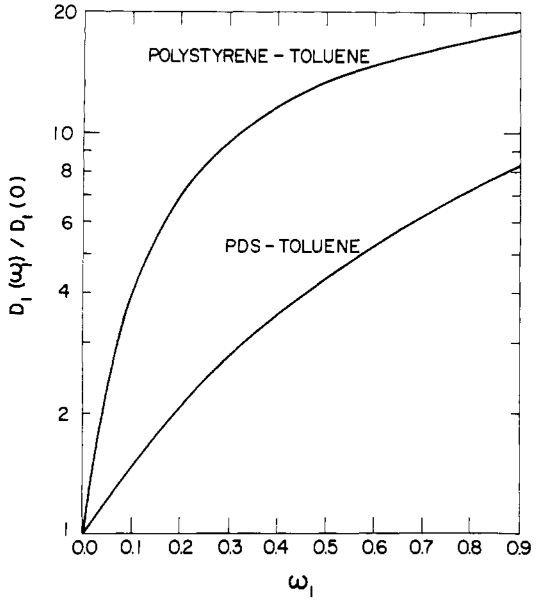

Figure 1. Concentration dependence of toluene self-diffusion coefficient for polystyrene–toluene system at 533 K and for PDS–toluene system at 310 K.

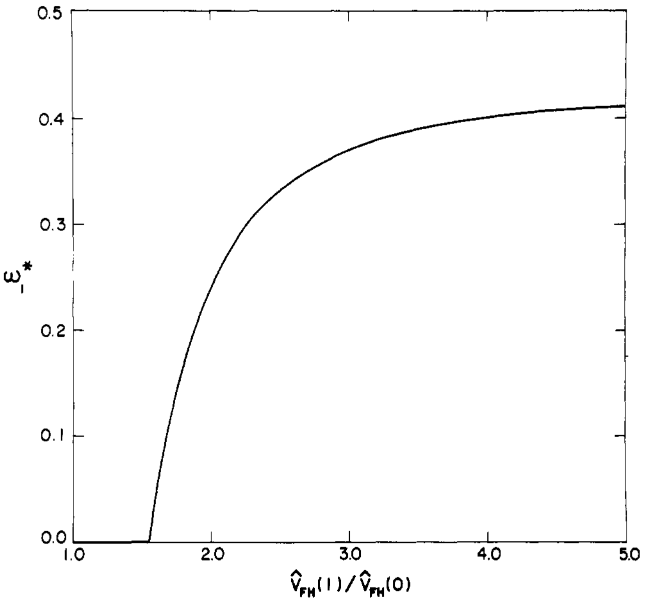

Figure 2. Dependence of ω_1^*, the solvent mass fraction above which $\partial^2 \ln D_2/\partial\omega_1^2 > 0$, on $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$. The curve is based on the predictions of eq 23 with $M_{j1}/M_{j2} = 1$, $\xi = 1$, and $2\hat{V}_1{}^*\gamma/\hat{V}_{FH}(0) = 10$.

of concentration dependence is also depicted in Figure 1 for the two model systems considered here. Note that D_1 is of course independent of polymer molecular weight since the molecular weight dependence of the polymer specific volume has been ignored. Also, from eq 16, it is evident that

$$\left(\frac{\partial \ln D_1}{\partial \omega_1}\right)_{\omega_1=0} = \frac{\gamma \hat{V}_1{}^*}{[\hat{V}_{FH}(0)]}\left[\frac{M_{j1}}{M_{j2}}\frac{\hat{V}_{FH}(1)}{\hat{V}_{FH}(0)} - 1\right] \tag{18}$$

This limiting concentration derivative is significantly larger for the polystyrene–toluene system than for the PDS–toluene system, partially because toluene at 533 K has substantially more free volume than toluene at 310 K. Hence, as is evident from Figure 1, the solvent self-diffusion coefficient for the polystyrene–toluene system undergoes a more rapid variation with concentration near the pure polymer limit than the solvent self-diffusivity for the PDS–toluene system.

The dependence of the concentration behavior of D_2 on polymer molecular weight can conveniently be ascertained by utilizing limiting forms of eq 11 for low and high polymer molecular weights. For low molecular weights ($M_2 \ll 2M_e$), we have

$$\frac{\partial \ln D_2}{\partial \omega_1} = \frac{1}{\xi}\frac{\partial \ln D_1}{\partial \omega_1} > 0 \tag{19}$$

$$\frac{\partial^2 \ln D_2}{\partial \omega_1{}^2} = \frac{1}{\xi}\frac{\partial^2 \ln D_1}{\partial \omega_1{}^2} < 0 \tag{20}$$

If the concentration variation of the solution density is ignored, similarly, for high molecular weights ($M_2 \gg 2M_e$), it can be shown that

$$\frac{\partial \ln D_2}{\partial \omega_1} = \frac{3}{\omega_2} + \frac{1}{\xi}\frac{\partial \ln D_1}{\partial \omega_1} > 0 \tag{21}$$

$$\frac{\partial^2 \ln D_2}{\partial \omega_1{}^2} = \frac{3}{\omega_2{}^2} + \frac{1}{\xi}\frac{\partial^2 \ln D_1}{\partial \omega_1{}^2} \tag{22}$$

From eq 19 and 20, it is clear that the concentration derivatives for D_2 have the same sign as those for D_1 in the low molecular weight limit. This prediction is consistent with the low molecular weight concentration behavior reported by Tanner et al.[4] In addition, eq 19 and 21 suggest that $\partial \ln D_2/\partial\omega_1 > 0$ for all molecular weights, a result that again corresponds to the experimental data of Tanner et al. Finally, since the first term on the right-hand side of eq 22 is positive and the second term is negative, both positive and negative values of $\partial^2 \ln D_2/\partial\omega_1^2$ are possible in the limit of high molecular weights. To examine this possibility further, we consider the following expression for the second concentration derivative of D_2:

$$\frac{\partial^2 \ln D_2}{\partial \omega_1{}^2} = \frac{3}{\omega_2{}^2} - \frac{\dfrac{2\hat{V}_1{}^*\gamma}{\hat{V}_{FH}(0)}\left[\dfrac{M_{j1}}{M_{j2}}\dfrac{\hat{V}_{FH}(1)}{\hat{V}_{FH}(0)} - 1\right]\left[\dfrac{\hat{V}_{FH}(1)}{\hat{V}_{FH}(0)} - 1\right]}{\xi\left[\omega_1\dfrac{\hat{V}_{FH}(1)}{\hat{V}_{FH}(0)} + \omega_2\right]^3} \tag{23}$$

The first term on the right-hand side of eq 23 represents concentration effects on the entanglement density of the system, and the second term depicts the influence of concentration on the system free volume. It is clear that free-volume effects will be very important when $\hat{V}_{FH}(1)/\hat{V}_{FH}(0) \gg 1$ for low ω_1. For this condition, the free-volume term will dominate the entanglement term ($\partial^2 \ln D_2/\partial\omega_1^2 < 0$) for at least part of the concentration range. However, regardless of the value of $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$, $\partial^2 \ln D_2/\partial\omega_1^2$ will become positive at sufficiently high solvent concentration because the first term dominates the second as ω_2 becomes small. For $\hat{V}_{FH}(1)/\hat{V}_{FH}(0) \approx 1$, the free-volume term has a much smaller effect, and it is possible that the first term dominates the free-volume term ($\partial^2 \ln D_2/\partial\omega_1^2 > 0$) for most or all of the concentration range.

Figure 2 shows how ω_1^*, the solvent mass fraction above which $\partial^2 \ln D_2/\partial\omega_1^2 > 0$, depends on the free-volume characteristics of the polymer and solvent, as represented by the ratio $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$. This figure is based on eq 23 with $M_{j1}/M_{j2} = 1$, $\xi = 1$, and $2\hat{V}_1{}^*\gamma/\hat{V}_{FH}(0) = 10$. The second derivative is positive over the complete concentration range when $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$ is less than about 1.6.

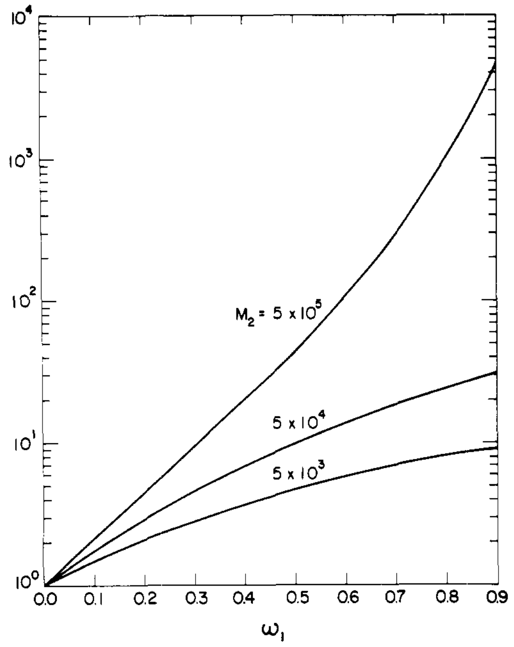

Figure 3. Concentration and molecular weight dependence of PDS self-diffusion coefficient for PDS–toluene system at 310 K.

Hence, for a system like PDS–toluene, which has $\hat{V}_{FH}(1)/\hat{V}_{FH}(0) < 2$ at 310 K, we would expect that $\partial^2 \ln D_2/\partial\omega_1^2 > 0$ over most of the concentration range for sufficiently high polymer molecular weight. This suggested behavior for a typical PDS–solvent system agrees with that observed by Tanner et al.[4] for their high molecular weight samples. The change of the concentration behavior with increasing molecular weight, from $\partial^2 \ln D_2/\partial\omega_1^2 < 0$ at low M_2 to $\partial^2 \ln D_2/\partial\omega_1^2 > 0$ at high M_2, is depicted in Figure 3 for the PDS–toluene system.

It is further evident from Figure 2 that ω_1^* increases rapidly with increasing $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$. Consequently, for a system like the polystyrene–toluene mixture, which has $\hat{V}_{FH}(1)/\hat{V}_{FH}(0) > 5$ at 533 K, $\partial^2 \ln D_2/\partial\omega_1^2$ will be negative over a substantial part of the concentration range even at the high molecular weight limit. This type of behavior is illustrated in Figure 4 for the polystyrene–toluene system. At the highest molecular weight for which calculations were performed, $\partial^2 \ln D_2/\partial\omega_1^2 < 0$ over nearly half of the concentration range. Consequently, it is evident that the shape of the D_2 vs. ω_1 curve is strongly dependent on the free-volume characteristics of the polymer–solvent system. For polymers like PDS with low glass temperatures, $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$ should be relatively close to 1, and the D_2 vs. ω_1 behavior should be of the type illustrated in Figure 3. As noted above, Tanner et al.[4] have presented data that appear generally to confirm the validity of this prediction. On the other hand, for polymers like polystyrene with high glass transition temperatures, $\hat{V}_{FH}(1)/\hat{V}_{FH}(0)$ will be substantially greater than 1, and the D_2 vs. ω_1 curves should be of the types presented in Figure 4. Even at the highest polymer molecular weights, a substantial concentration range for which $\partial^2 \ln D_2/\partial\omega_1^2 < 0$ should be evident. We know of no data that can be used to test this prediction.

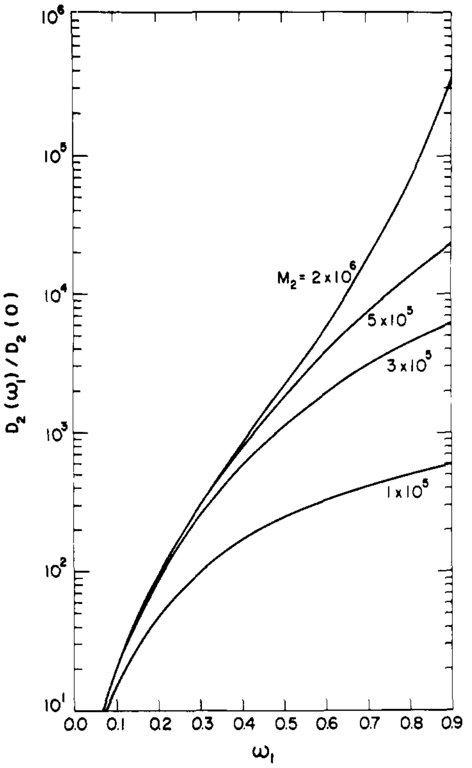

Figure 4. Concentration and molecular weight dependence of polystyrene self-diffusion coefficient for polystyrene–toluene system at 533 K.

In summary, an approach has been presented for analyzing the polymer self-diffusion process for concentrated polymer solutions. The random motion of expanded polymer chains is treated by using the free-volume theory of transport. From the success[19,20] of free-volume theory in describing the solvent self-diffusion process in polymer–solvent system, it is reasonable to expect that the movement of small parts of polymer chains can also be adequately represented by a free-volume analysis. (The success of free-volume theory[19,20] has actually been tested on the mutual diffusion process, which for polymer–solvent systems is equivalent to the self-diffusion process,[2] aside from a thermodynamic factor.) The size of the expanded chain is computed by using an approximate theory for entanglement friction. Finally, we note that the free-volume analysis predicts that $\partial \ln D_2/\partial\omega_1 > 0$ and $\partial^2 \ln D_2/\partial\omega_1^2 > 0$ for sufficiently high solvent concentrations in the limit of high M_2. Furthermore, reptation-scaling theory predicts the following concentration dependence for the semidilute region:[8,22]

$$D_2 \sim \rho_2^{-7/4} \tag{24}$$

so that $\partial \ln D_2/\partial\omega_1 > 0$ and $\partial^2 \ln D_2/\partial\omega_1^2 > 0$ for this theory also. Hence, the concentration behavior predicted by free-volume theory at the high solvent end of the concentrated region is at least qualitatively consistent with the concentration dependence suggested by reptation-scaling theory for the semidilute region. We note that, at this time, reptation-scaling theory is not capable of predicting the concentration dependence of polymer self-diffusion coefficients in the concentrated region.

The principal objective of this paper is to illustrate how the concentration and molecular weight dependencies of D_1 and D_2 can be predicted by considering the variations of the free volume and entanglement density with concentration and molecular weight. In addition, we have illustrated how the variations of D_1 and D_2 are strongly dependent on the free-volume properties of the polymer–solvent system. Although the equations used to establish the concentration and molecular weight trends are based on what must be regarded as an approximate model, the theory predicts all the trends observed in the laboratory. Furthermore, the equations lead to some additional predictions that await experimental testing.

Acknowledgment. This work was supported by National Science Foundation Grant ENG 78-26275.

Registry No. Polystyrene, 9003-53-6.

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Damped Orientational Diffusion Model of Polymer Local Main-Chain Motion. 3. Inclusion of Chain–Chain Interactions

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Received February 19, 1982

ABSTRACT: The damped orientational model of polymer local main-chain motion is generalized to include chain–chain interactions using multiple scattering theory in the mean field approximation and an optical potential. The resulting dynamical equation, which is in the form of a complex damped diffusion equation, still permits analytic solutions for the bond orientational correlation function and the spectral density. Thus by incorporating chain–chain interactions into an orientational diffusion model, the theory should be capable of describing local motions for concentrations outside the dilute solution regime. The resulting three-parameter analytic expression for the spectral density is fit to the low-temperature-phase ^{1}H NMR relaxation times of poly(vinyl acetate) (PVA) in toluene. In this phase PVA is a compact random coil. Both the real and complex dampled diffusion models are found to fit the data equally well. The real damped diffusion model parameters fit to the low-temperature phase are considerably different in magnitude from those for the high-temperature phase. Therefore the low-temperature parameters presumably are effective parameters and reflect the role of intrachain interactions. The complex and real damped diffusion models also are capable of fitting the high-temperature proton relaxation data equally well. Thus, based on goodness of fit and given the uncertainty of some of the NMR relaxation data, the real and complex damped diffusion models cannot be distinguished at this time.

I. Introduction

In a recent pair of papers (papers 1 and 2 of this series) we developed a damped diffusion model of polymer local main-chain motion and applied this model to calculate both ^{1}H NMR relaxation times and dielectric relaxations of poly(vinyl acetate) (PVA) in toluene solution.[1,2] The damped diffusion model is a natural extension of the cutoff diffusion model of Bendler and Yaris[3,4] in that the long-wavelength cutoff introduced by them to "mock up" the damping has been replaced by an explicit damping term in the diffusion equation. The resulting model is analytically solvable for the dipole correlation function and its Fourier transform, the spectral density function.

When the two-parameter expression for the spectral density function is fit to the measured PVA proton relaxation times,[5] a very good fit is obtained (the results for the cutoff diffusion model and the damped diffusion model are indistinguishable) except at the lowest temperature, −45 °C. At −45 °C, the two parameters required to give a good fit to the PVA proton relaxation times are substantially different from those for the high-temperature phase. A search for parameters of the same order of magnitude as for the high-temperature phase required that the short-wavelength cutoff, representing the smallest motional unit, be larger than the damping length.[2] The reason for this is that there is a phase transition at −20 °C (observed by dielectric relaxation[6]). Above the phase transition temperature, PVA is in a loose random coil configuration with little chain–chain interaction. Below the phase transition temperature, the polymer is in a compact random coil configuration with presumably considerable chain–chain interaction. Thus it is not at all surprising that the two parameters fit to the real damped diffusion model are substantially different in the low-temperature fit from those in the high-temperature fit. The damping parameter in the context of real damped diffusion model is an effective parameter that implicitly incorporates chain–chain interactions.

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0024-9297/83/2216-0266$01.50/0