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Concentration Dependence of Self-Diffusion Coefficient by Forced Rayleigh Scattering: Polystyrene in Tetrahydrofuran

In a previous report from this laboratory[2] we have examined the temperature dependence of the self-diffusion coefficient D_s of a polyisoprene sample in the bulk state by forced Rayleigh scattering (FRS). We have proposed that D_s may be described by an expression analogous to the one for the steady-shear viscosity η_0:

$$\eta_0 = K_1\zeta_0(c,T)g_1(c,M) \tag{1}$$

$$D_s = K_2\zeta_0^{-1}(c,T)g_2(c,M) \tag{2}$$

Here K_i ($i = 1, 2$) is a constant, ζ_0 is the monomeric friction coefficient whose T dependence is well accounted for by the free volume theory,[3,4] and g_i ($i = 1, 2$) is the structural factor whose molecular weight dependence is determined by the long-range global chain dynamics. In the bulk state, eq 1 and 2 represent a separation of two variables, T and M, whereby the T dependence is imbedded in ζ_0 and the M dependence is contained in g_i. Contrasting M dependences of g_1 and g_2 across the entanglement threshold have been reported; while g_2 is proportional to M^{-2} irrespective of entanglement coupling,[5–7] g_1 exhibits a pronounced effect at entanglement onset by changing the power law dependence on M from 1 to 3.4 at the critical molecular weight $M_{c,0}$.[8] The proposal put forth here is not original with us. Factorization of D_s into ζ_0 and g_2 has been earlier indicated by Schaefer.[9]

In order to extend the above factoring of D_s for bulk polymers to polymer solutions, we note at the outset that both ζ_0 and g_2 depend on concentration[10] as stated explicitly in eq 2. We now postulate that the structural factor $g_2(c,M)$ is the term which expresses the concentration dependence of long-range chain dynamics while $\zeta_0(c,T)$ exhibits the corresponding dependence of short-range viscous drag through the fractional free volume. Thus, the conclusion of Léger et al.[11] that the c and M dependences of D_s for polystyrene in benzene agree with the scaling predictions of de Gennes[12] in the semidilute regime in a good solvent is inconsistent[13] in this context. In fact, we have recently shown[14] that there is no unique power law between the observed D_s and concentration for PS in tetrahydrofuran (THF) which is also a good solvent. On the other hand, D_s is shown to depend on c and steady-shear viscosity η_0 according to

$$D_s/c \propto 1/\eta_0 \tag{3}$$

and on M according to

$$D_s \propto 1/M^2 \tag{3'}$$

at all concentrations above c^*. Equation 3 is characteristic of a Rouse chain and is incompatible with eq 3′ which is at least a necessary condition for a reptating chain. We thus come to the point of our postulate. These seemingly disparate results appear to arise because D_s has been examined in toto as opposed to factoring it into ζ_0 and g_2 terms and scrutinizing the g_2 term for the c and M dependencies attributable to the long-chain dynamics. Our ultimate goal is to specify unequivocally the c and M dependencies of g_2 and to provide a consistent molecular picture for those dependences of g_1 and g_2.

In this communication, we reanalyze the D_s data of PS in THF by Wesson et al.[14] according to eq 2. In order to obtain the concentration dependence of $\zeta_0(c,T)$, we take advantage of the fact that a tracer or permeant with the friction coefficient ζ_1 probes the c dependence of monomeric friction coefficient ζ_0 in the limit of permeant size comparable to that of the monomeric unit.[15] As the permeant we chose methyl red, a photochromic acid–base indicator dye, and measured at 25 °C its diffusion coefficient D_{tr} by FRS in the same PS–THF system at different polymer concentrations. $\zeta_1(c)$ at a given c is then obtained by

$$\zeta_1(c) = kT/D_{tr}(c) \tag{4}$$

In assessing the validity of equating ζ_0 with ζ_1 of methyl red, we estimate the concentration shift factor a_c of ζ_0 according to the free volume theory[16] as follows:

$$\log a_c = \frac{B}{2.303}\left(\frac{1}{f_\phi} - \frac{1}{f_r}\right) \tag{5}$$

Here, B is an empirical constant, f_ϕ is the fractional free volume of a solution with polymer volume fraction ϕ and f_r is the value at a reference volume fraction ϕ_r. As the reference volume fraction, we choose 0.562 at which D_{tr} of methyl red has been determined. For simplicity, B is put equal to unity, and additivity of the fractional free volume is assumed

$$f_\phi = \phi f_p + (1 - \phi)f_s \tag{6}$$

where f_p and f_s are the fractional free volume of the polymer and solvent, respectively; f_s is in turn defined as

$$f_s = f_{g,s} + \alpha_{f,s}(T - T_{g,s}) \tag{7}$$

where $f_{g,s}$ is the fractional free volume of solvent at its glass transition temperature $T_{g,s}$, and $\alpha_{f,s}$ is the corresponding thermal expansion coefficient. By appropriate choices of the parameters, we arrive at $f_\phi = 0.025\phi + 0.250(1 - \phi)$; f_p of PS at 25 °C is taken as 0.025 which is the fractional free volume at its T_g, and f_s of THF is estimated from $f_{g,s} = 0.025$, $T_{g,s} = 100$ K,[17] and $\alpha_{f,s} = 1.136 \times 10^{-3}$ K^{-1} which is the liquid-state thermal expansion coefficient. With 0.562 for ϕ_r, we obtain $\log a_c$ according to eq 5 and this is drawn in Figure 1 as the solid curve that is in turn compared with the observed ratio of the permeant friction coefficient, $\zeta_1(\phi)/\zeta_1(\phi_r)$. Despite several crude approximations and assumptions invoked in the above, we obtain a_c which simulates the observed relative concentration dependence of $\zeta_1(\phi)$ over the entire range of ϕ; of course the agreement for low concentration region, $\phi < 0.2$, is fortuitous since the free volume concept is less applicable in such a dilute region. Nevertheless, the largest deviation of a_c from the observed $\zeta_1(\phi)/\zeta_1(\phi_r)$ amounts to only about 35% which is small indeed compared to the overall range of magnitude of 2 orders. Hence, the indicated agreement between a_c and $\zeta_1(\phi)/\zeta_1(\phi_r)$ exhibited in Figure 1 lends support to our initial assumption that

$$a_c \equiv \zeta_0(\phi)/\zeta_0(\phi_r) = \zeta_1(\phi)/\zeta_1(\phi_r) \tag{8}$$

We should emphasize here the eq 8 is still an assumption which ignores hydrodynamic scaling[18] and hence must be taken with caution.

Having found the concentration dependence of ζ_0, we can now proceed to focus on $g_2(c,M)$. Since the molecular weight dependence of D_s was shown[14] as eq 3′, it is possible that the concentration dependence of g_2 can be separated from the M dependence. This amounts to examining how $D_s a_c(M/M_r)$ depends on concentration, where M_r is a reference molecular weight to which all other molecular weight data are normalized. Upon choosing $M_r = 130\,000$ which is entirely arbitrary, the results shown in Figure 2 are obtained, where error bars indicate the experimental uncertainty of 95% confidence interval of D_s determina-

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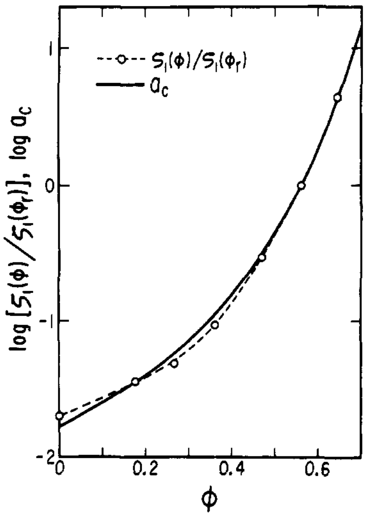

Figure 1. Comparison of a_c (the solid curve) calculated by eq 5 with the friction coefficient ratio $\zeta_1(\phi)/\zeta_1(\phi_r)$ of a tracer (methyl red) in PS–THF solutions. The abscissa denotes polymer volume fraction ϕ. The dashed curve is an empirical one obtained by smooth interpolation of $\zeta_1(\phi)/\zeta_1(\phi_r)$.

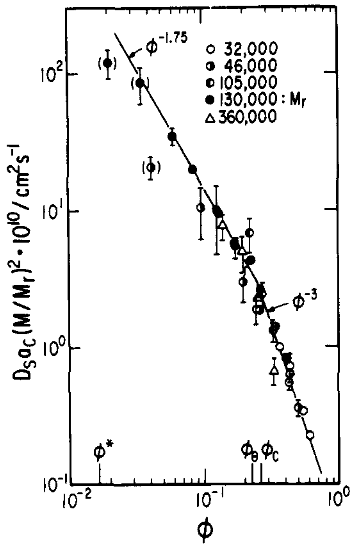

Figure 2. Concentration dependence of the structure factor of the self-diffusion coefficient of PS in THF. The dashed curve in Figure 1 is used as a_c. ϕ^*, ϕ_Θ, and ϕ_c are indicated on the abscissa. See text for the explanation of data points in parentheses.

tions. The concentration dependence of $D_s a_c(M/M_r)^2$ appears to be represented by two intersecting straight lines with slopes of -1.75 ± 0.15 and -3.0 ± 0.3. These values are identical with those predicted by de Gennes as the exponents for the concentration dependence of the chain self-diffusion coefficient via the reptation mechanism in good solvent and Θ solvent, respectively, in the semidilute regime. It is important to note that these exponents are extracted only after the concentration dependence of ζ_0 through the free volume correction is effected.

Turning to the three specific concentration marks indicated in Figure 2, the first is the critical overlap concentration[12] denoted by ϕ^*. The second arises from the observation[19] that excluded-volume effect must eventually be screened out as polymer concentration is increased, designated as ϕ_Θ, since at larger concentrations the chain dimension asymptotes out to that of the Θ-condition. The third one, ϕ_c, is the characteristic concentration of entanglement coupling at a given molecular weight.[20] These concentrations are calculated according to

$$\phi^* = 3M\bar{v}_2/4\pi R_g^3(0)N_0 \tag{9}$$

$$\phi_\Theta = \phi^*[R_{g,\Theta}/R_g(0)]^{-8} \tag{10}$$

$$\phi_c = \bar{v}_2\rho M_{c,0}/M \tag{11}$$

where $\bar{v}_2$ is the polymer partial specific volume in the solvent under study, $R_g(0)$ and $R_{g,\Theta}$ are, respectively, the radii of gyration in a good solvent at infinite dilution and in Θ-condition, N_0 Avogadro's number, ρ the density of polymer in the bulk state, and $M_{c,0}$ the critical entanglement molecular weight determined from the $\eta_0 - M$ relationship.[8] For polystyrene with $M = 130\,000$ in THF, ϕ^* and ϕ_Θ are calculated with $\bar{v}_2 = 0.96$ cm^3/g, and with use of the $R_g(0)$ value interpolated from the data of Miyaki et al.[21] for PS in benzene and the $R_{g,\Theta}$ value similarly obtained from the data of Fukuda et al.[22] for PS in *trans*-decalin. For ϕ_c we use $\bar{v}_2\rho = 1$ and 35 000 for $M_{c,0}$ for PS. We note that ϕ_Θ is independent of molecular weight[19,23,24] which is unique to ϕ_Θ as contrasted to ϕ^* and ϕ_c. As shown in the figure, ϕ_Θ and ϕ_c are very close to each other which is entirely accidental due to the choice of $M_r = 130\,000$. Since the definition of ϕ^* is not exact, we must not take the numerical values of ϕ^* and ϕ_Θ calculated according to eq 9 and 10 seriously. For this reason, we have shown in Figure 2 those data points close to ϕ^* as obtained from eq 9 distinguished by parentheses from the rest that are well above ϕ^*.

It is most striking that we appear to have shown in Figure 2 consistency with the following behaviors of $g_2(\phi,M)$:

$$D_s = K_2\zeta_0^{-1}(\phi,T)g_2(\phi,M) \tag{2'}$$

and

$$g_2(\phi,M) = \phi^{-1.75}M^{-2} \qquad (\phi^* < \phi < \phi_\Theta) \tag{12}$$

$$= \phi^{-3}M^{-2} \qquad (\phi_\Theta < \phi) \tag{13}$$

We claim that the concentration exponent of g_2 crosses over from -1.75 to -3 at around ϕ_Θ and not around ϕ_c; this is easily shown by examining the molecular weight dependence of the crossover point. If a molecular weight other than 130 000 is chosen for M_r, all the data points in Figure 2 shift uniformly either upward or downward by a given amount depending on the new M_r without affecting the crossover point where the exponent changes. This is precisely the unique property of ϕ_Θ, namely molecular weight independence. The accidental coincidence of ϕ_Θ and ϕ_c at $M = 130\,000$ therefore does not confuse the assignment of the exponent change to ϕ_Θ, and not to ϕ_c. At the risk of repetition, we emphasize that our findings in Figure 2 are consistent with eq 12 and 13, but the precision and range of the data are such that we cannot claim to have established the behavior.

We finally propose that the concentration dependence of g_2 displayed in Figure 2 is the behavior of a semidilute solution by polystyrene in a good solvent crossing over into the Θ behavior when the excluded-volume effect is screened out at $\phi > \phi_\Theta$. In so proposing, we have raised many questions such as: Would entanglement coupling ever be exhibited in D_s as it is in η_0?; In Θ-condition, should we observe only -3 exponent for $\phi > \phi^*$? These and others will be examined in the future. For the moment, however, our immediate task is to focus on the resolution of the discrepancy in eq 3 and 3′ which is not centrally addressed here; the factorization of D_s into ζ_0 and g_2 terms does not resolve the discrepancy of eq 3 and 3′. Our analysis here seems to indicate that there are different long-range dynamical mechanisms controlling η_0 and D_s through g_1 and g_2, respectively. For this reason, we should examine first D_s and in entangled solutions with very high molecular weight chains where the free volume effect could be neglected. This will be the subject of our forthcoming full paper.

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References and Notes

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CORRECTIONS

William H. Starnes, Jr.,* Irene M. Plitz, Frederic C. Schilling, Gilberto M. Villacorta, Geoffrey S. Park,* and Abdul H. Saremi: Poly(vinyl chloride) Structural Segments Derived from Azobis(isobutyronitrile). Volume 17, Number 12, December 1984, p 2507.

The following corrections are needed in order to rectify significant typesetting errors that were introduced after author's proof had been read.

In the first paragraph of the Discussion section on p 2509, the last sentence should read as follows: Also, it might be argued that when the monomer concentration is diminished, decreased initiator efficiencies tending to decrease the "CN" concentration are accompanied by increasing amounts of primary radical coupling, which would tend to cause the "CN" content to rise.

The first sentence after eq 16 should read as follows: When k_d is 2.2 × 10^{-3} h^{-1}, the predicted concentrations are 30–130% too high, but if k_d is only 7.75 × 10^{-4} h^{-1}, the predicted values are too low by some 20–50%.

Reference 1a should read as follows: Ayrey, G.; Evans, K. L.; Wong, D. J. D. *Eur. Polym. J.* **1973**, *9*, 1347 and references cited therein.