Macromolecules 1981, *14*, 1334–1340

Self-Diffusion of Random-Coil Polystyrene Determined by Pulsed Field Gradient Nuclear Magnetic Resonance: Dependence on Concentration and Molar Mass

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ABSTRACT: Self-diffusion coefficients (D_s) have been obtained over a range of concentrations for polystyrene random coils in carbon tetrachloride, the polymer molar masses being 2000, 4000, 17 500, 37 000, 110 000, 233 000, and 360 000 daltons. Using $D_s^{-1} = D_0^{-1}(1 + k_f c)$ in the dilute regime, we obtain D_0 and k_f values and find consistency with results obtained by classical methods. We observe $D_0 \sim M^{-0.51(2)}$ and note that k_f varies with M according to Yamakawa for $M > 2 \times 10^4$ but is anomalous for low M. In the semidilute regime a de Gennes concentration dependent scaling behavior is observed with a scaling index of −1.83 (4), close to the predicted value. In contrast, D_s^+ values obtained indirectly from mutual diffusion and sedimentation (Roots et al., 110 000 molar mass in toluene) do not scale with the required self-diffusion exponent and we conclude that the D_s^+ calculations are invalid under conditions of polymer entanglement. Both the experimental scaling indices obtained in this work from diffusion measurements can be explained in terms of the model of Weill and des Cloizeaux, in which separate static and dynamic exponents characterize a chain of finite length.

Introduction

Self-Diffusion. The self-diffusion coefficient of a macromolecule in solution gives a direct indication of its laboratory-frame thermally driven translational motion. According to the theory of the Brownian random walk the mean-square displacement of the molecular center of mass in a time interval t is

$$\langle r^2 \rangle = 6D_s t \tag{1}$$

where D_s, the self-diffusion coefficient, is a parameter of fundamental importance in describing macromolecular solution dynamics and a knowledge of D_s enables important tests of theoretical models concerning such systems. This is particularly so for random-coil macromolecules which adopt the so-called random flight configuration when in solution.

Until recently the self-diffusion coefficients of random-coil macromolecules have been susceptible to measurement only through radioactive tracer techniques and then with great difficulty since $(\langle r^2 \rangle)^{1/2}$ is typically a few millimeters over a period of days. Because of the problems associated with direct measurement, self-diffusion coefficients have often been determined indirectly. One such method depends on a knowledge of the more accessible mutual diffusion coefficient, D_m, of the macromolecular solute and solvent along with the appropriate thermodynamic parameters. Another indirect determination employs the sedimentation coefficient s, derived from ultracentrifugation studies. We use the symbol D_s^+ to represent the self-diffusion coefficient obtained by these indirect methods. Roots et al.[1] have demonstrated that D_s^+ values obtained from D_m and s measurements are consistent for monodisperse 110 000 molar mass (M) random-coil polystyrene in toluene.

Recently two techniques have been developed which enable direct and accurate measurement of self-diffusion coefficients of random-coil macromolecules. Pulsed field gradient nuclear magnetic resonance (PFG NMR) employs the noninvasive molecular "label" provided by the characteristic Larmor frequencies of the macromolecular proton nuclei. This label is given a spatial dependence arising from an applied magnetic field gradient imposed in the form of two successive pulses, the molecular displacement being detected over the intervening period.[2] We have shown[3,4] that accurate self-diffusion coefficients can be obtained for polystyrene molecules down to solute concentrations of 5 kg m^{-3} (0.5% w/v). A minor restriction to this technique is that the solvents must not yield a proton NMR signal. This limits the application of the technique to either non-hydrogen-containing solvents such as carbon tetrachloride or to deuterated solvents. We have limited our work in this paper to carbon tetrachloride solutions to avoid the complications with the interpretation of results obtained from deuterated solutions.

The other technique enabling direct measurement of D_s is that reported by Hervet, Urbach, and Rondelez,[5] who call their approach force Raleigh scattering (FRS). Labeling is achieved by exciting, with spatial periodicity, a photochromic dye attached to the macromolecules. The relaxation of this periodic excitation is subsequently observed. Hervet et al.[6] have reported polystyrene self-diffusion coefficients down to a similar lower concentration limit to that of PFG NMR.

In a recent paper[7] we demonstrated that the self-diffusion coefficients of entangled 110 000 molar mass polystyrene random-coil macromolecules in carbon tetrachloride displayed a scaling law region consistent with the theory of de Gennes.[8,9] We now extend this work with the same solvent to obtain polystyrene self-diffusion coefficients over a wide range of solute molar masses and concentrations. We have improved the sensitivity of our apparatus and can now present accurate results for high dilution. These agree with those obtained from mutual diffusion studies where available and our data show consistency with the predictions of theory of both the dilute and semidilute regimes.

Dilute Regime: Random Coils. A solution of random-coil polymer molecules is termed dilute if the average intermolecular separation is sufficient to preclude overlapping. In solution an isolated random-coil polymer molecule can be considered as a ball of mean size equivalent to the radius of gyration,[10] R_G, where for a simple random flight model

$$R_G = (1/6^{1/2}) l N^{1/2} \tag{2}$$

N is the number of statistical segments of length l and is proportional to M, the polymer molar mass. For a real polymer solution where excluded volume effects are taken into account

$$R_G = aN^{\nu} \tag{3}$$

where a is a constant and ν, the Flory index, exceeds 0.5.

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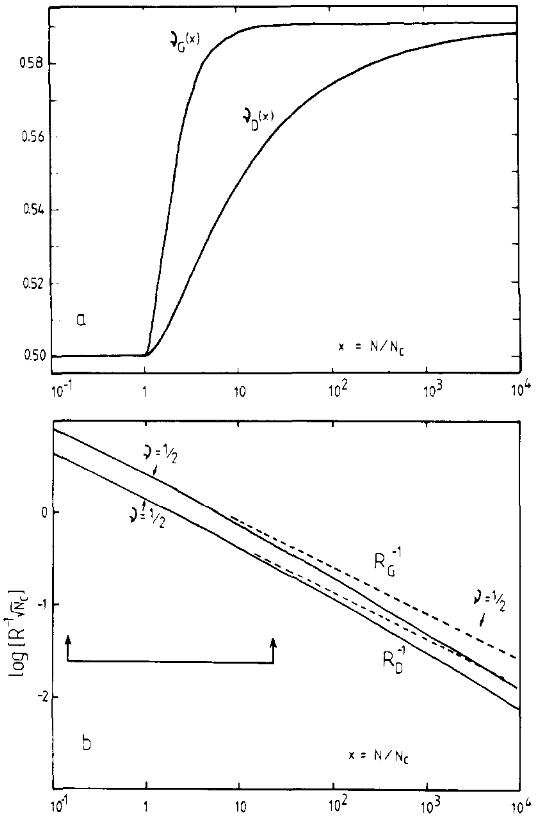

Figure 1. (a) Static and dynamic scaling indices taken from the model of Weill and des Cloizeaux.[12] These indices approach the asymptotic limit, 0.588, at different rates as the polymerization index, N, increases. N_c corresponds to a molar masss of about 2×10^4 daltons for polystyrene in benzene but will vary slightly with solvent. (b) Dependence of R_G and R_D on N, after Weill and des Cloizeaux. The relationship is plotted as $\log R^{-1}N_c^{1/2}$ vs. $\log N$ and is directly akin to the experimental $\log D_0$ vs. $\log M$ graphs since $D_0 \propto R^{-1}$ and $M \propto N$. The experimental region used in this work ($2000 \leq M \leq 390000$) is shown.

The value of ν, originally suggested by Flory to be 0.60, has recently been recalculated by renormalization theory to be 0.588.[11]

Weill and des Cloizeaux[12] have suggested, however, that a unique index applies only in the asymptotic limit, $N \to \infty$. These authors point out that excluded volume effects become more significant the longer the polymer coil and define, as an approximation, a critical segment separation, N_c, for which the index of eq 3 changes from 0.500 to 0.588. They clearly distinguish static and dynamic radii defined, respectively, by

$$R_G^2 = \frac{1}{2N^2}\sum\langle r_{ij}^2\rangle \tag{4a}$$

$$R_D^{-1} = \frac{1}{2N^2}\sum\langle 1/r_{ij}\rangle \tag{4b}$$

for N segments labeled by subscripts i and j and describe the behavior of these radii by

$$\nu_G = \partial \ln R_G/\partial \ln N \qquad \nu_D = \partial \ln R_D/\partial \ln N$$
$$R_G \sim N^{\nu_G} \qquad R_D \sim N^{\nu_D} \tag{5}$$

Figure 1 indicates the dependence of the indices ν_G and ν_D and the radii R_G and R_D on the number of statistical segments, N. N_c represents a critical molar mass of about 2×10^4 daltons for polystyrene.[12]

In our work at high dilution the dynamic experimental parameter, the self-diffusion coefficient, is sensitive to a hydrodynamic radius, R_H. Particle self-diffusion coefficients are given by the Einstein relation

$$D_s = k_BT/f \tag{6}$$

where f is the particle friction coefficient. In the infinite-dilution limit, f takes the simple Stokes law form for an equivalent sphere

$$f_0 = 6\pi\eta_0R_H \tag{7}$$

η_0 is the solvent viscosity and eq 7 serves as a definition of the hydrodynamic radius. In this dilute limit, the macromolecular self-diffusion coefficient is indistinguishable from the solution mutual diffusion coefficient and both are ascribed the symbol D_0. An examination of the scaling of D_0 with molar mass provides a probe of the dynamical index appropriate to the hydrodynamic radius. Weill and des Cloizeaux have shown that R_H scales with the dynamical index, ν_D. An examination of the variation of D_0 with molar mass should yield a value of ν_D for polystyrene in carbon tetrachloride and reproduce the graph of Figure 1b.

At finite concentrations in the dilute regime the macromolecules occasionally interact and in consequence raise the frictional coefficient from the solvent-dominated limit. It is customary to express f in terms of a power series in the mass/volume concentration, c:

$$f = f_0(1 + k_fc + ...) \tag{8}$$

where k_f and similar higher order coefficients are independent of c. It follows that D_s and D_0 are related by

$$D_s^{-1} = D_0^{-1}(1 + k_fc + ...) \tag{9}$$

We present here an investigation of this regime, using self-diffusion measurement, and find k_f values which, for high molar masses, are in good agreement with the theoretical predictions of Yamakawa.[13]

Because diffusion has been classically studied via the mutual diffusion process, it is pertinent to indicate the relationship between D_s and D_m. While D_m is sensitive to frictional terms in common with D_s, some additional parameters enter.[14] These are the solute partial specific volume, $\bar{v}$, and the virial coefficients, A_n, obtained from osmotic pressure measurements.

$$D_m^{-1} = D_0^{-1}(1 + k_fc + ...) \times (1 - \bar{v}c)^{-1}(1 + 2A_2Mc + 3A_3Mc^2 + ...)^{-1} \tag{10}$$

Equation 10 reduces to the first-order expression[14,15]

$$D_m = D_0(1 + k_Dc)$$

where

$$k_D = 2A_2M - k_f - \bar{v} \tag{11}$$

In a similar fashion the sedimentation coefficient s is given by the Svedberg relation[16]

$$s^{-1} = \frac{N_{Av}f}{M(1 - \bar{v}\rho)} \tag{12}$$

where ρ is the solution density and N_{Av} is Avogadro's number. Again the expression reduces in first order to one involving the infinite-dilution sedimentation coefficient, s_0:

$$s^{-1} = s_0^{-1}(1 + k_sc) \tag{13}$$

where $k_s = k_f + \bar{v}$. Typically $\bar{v} \ll k_f$, so k_s and k_f may be taken as equivalent.[15] Comparison of eq 6, 9, 10, and 12 shows that an indirect self-diffusion coefficient, D_s^+, may be calculated from a knowledge of the mutual diffusion coefficient or the sedimentation coefficient according to

$$D_s^+ = D_m(1 - \bar{v}c)^{-1}(1 + 2A_2Mc + ...)^{-1} \tag{14}$$

or

$$D_s^+ = sN_{Av}M^{-1}k_BT(1 - \bar{v}\rho)^{-1} \tag{15}$$

These relationships apply to any solution involving a polymer and a low molar mass solvent. In particular Roots et al.[1] have demonstrated the internal consistency of eq 14 and 15 over a wide concentration range for random-coil polystyrene of molar mass 110 000 daltons dissolved in toluene. However, it should be noted that D_s^+ is a derived quantity and is not necessarily identical with the measured self-diffusion coefficient, D_s, of the polymer molecule under conditions of entanglement. We demonstrate here that D_s^+ fails to exhibit the scaling law behavior expected for the self-diffusion coefficient in the entangled regime.

Semidilute Regime: Entangled Coils. Under conditions of concentration sufficient for overlap of the polymer coils, the solution is termed semidilute. The boundary concentration between the dilute and semidilute regimes is accorded the symbol c^* and may be defined by equating the characteristic coil radius to the average macromolecular separation so that

$$c^* = M/N_{Av}R^3 \tag{16}$$

Convention dictates the use of R_G for R although recent experiments suggest that the much larger root-mean-square end-to-end distance $\langle R^2 \rangle$ gives a more accurate measure. Indeed Roots and Nyström[18] define c^* from the experimental results as the lowest concentration at which scaling law behavior is observed. We retain the use of R_G here while noting that its use probably overestimates c^*. The calculated values of c^* are not crucial to the present work.

de Gennes[8,9] has shown that the self-diffusion of entangled polymer coils in semidilute solutions may be treated in terms of the motion of individual chains through a transient network formed by the overlapping coils. Each chain "reptates" in a tube of the diameter ξ, which may be regarded as the average distance between entanglement points. The time taken for the chain to diffuse end-to-end along its curvilinear path, T_r, is called the reptation time or the relaxation or renewal time since it provides a measure of the time taken for entanglement renewal. In the de Gennes model the overall self-diffusion coefficient of the chains is expressed in terms of the mean-square end-to-end distance of the tube, $R^2(c)$, so that

$$D_s = R^2(c)/6T_r \tag{17}$$

Both $R(c)$ and T_r are estimated by considering the chain inside the tube to consist of N/g blobs of size ξ, where g is the number of statistical units per blob and may be written, according to eq 3

$$\xi \sim g^\nu \tag{18}$$

It is straightforward to show that

$$T_r = 6\pi\eta_0(N/g)^3\xi^3/2k_BT \tag{19}$$

and, if the tube is considered to follow a random flight path

$$R^2(c) = (N/g)\xi^2 \tag{20}$$

Thus[19]

$$D_s = k_BT/18\pi\eta_0(N/g)^2\xi \tag{21}$$

In the entangled regime, ξ depends on concentration as

$$c = (g/N)MN_{Av}^{-1}\xi^{-3} \tag{22}$$

so that

$$\xi \sim c^{\nu/(1-3\nu)} \tag{23}$$

Equation 21 can now be rewritten

$$D_s \sim N^{-2}c^{(2-\nu)/(1-3\nu)} \tag{24a}$$

$$\sim N^{-2}c^{-1.75} \text{ for } \nu = 0.6 \tag{24b}$$

Inherent in the above derivation is the assumption that the blobs are comprised of several statistical units. Equation 23 reveals that as c increases, this assumption will not hold indefinitely. In fact a random-coil polystyrene concentration of $\simeq$200 kg m^{-3} would result in a blob segment length of order 2 Kuhn statistical units. Whatever flexibility criterion is used it is clear that a maximum concentration, c^{**}, will occur beyond which the scaling law will fail. For very low molar mass polymer this breakdown may occur at any concentration sufficient to product entanglement so that no true semidilute regime is encountered. It is necessary that the molar mass be sufficient that $c^* \ll c^{**}$ if a wide semidilute regime, sufficient to investigate eq 24, is to be observed. However, an upper limit to M is often encountered due to other experimental constraints. To observe reptation it is necessary that the experimental time scale greatly exceed T_r. In PFG NMR the characteristic time scale is of the order of a few tens of milliseconds, which dictates that the polymer mass be less than 0.5×10^6 daltons.

There are also scaling laws governing the sedimentation of random-coil macromolecules in semidilute solutins.[20] Sedimentation is assumed to occur by solvent flowing through a permanent network of interpenetrating random coils, the so-called "porous plug" model. Notice no account is taken of any reptational motion. A permeability coefficient k can be defined which is simply related to the sedimentation coefficient. For sedimentation in good solvents, the de Gennes scaling laws predict

$$s \sim c^{-0.5} \tag{25a}$$

and

$$k \sim c^{-1.5} \tag{25b}$$

Roots and Nyström have reported that semidilute solutions of random-coil polystyrene molecules of 110 000 molar mass dissolved in toluene obey de Gennes-like scaling laws for sedimentation over the concentration range 13–125 kg m^{-3}. They report

$$s \sim c^{-0.8} \tag{26a}$$

$$k \sim c^{-1.7} \tag{26b}$$

We now use eq 5 to obtain a de Gennes scaling law for D_s^+ in good solvents. Allowing that $1 - \bar{v}\rho$ varies with concentration much more slowly than does the sedimentation coefficient, s

$$D_s^+ \sim s$$

i.e.

$$D_s^+ \sim c^{-0.5} \tag{27}$$

The sharp distinction between eq 24b and 27 should be noted.

Experimental Measurements

Monodisperse polystyrene was obtained from Pressure Chemical Co. Table I lists the molecular weights and M_n/M_w ratios quoted for these samples. Spectroscopic grade carbon tetrachloride was used and solutions were thoroughly mixed before transfer to 4.5-mm NMR sample tubes. Self-diffusion measurements were made with our home-built pulsed field gradient system interfaced to a JEOL FX60 spectrometer. Further details are given in ref 3 and 4. The solute proton nuclei were observed at 60 MHz. Spin echoes were accumulated in the PAPS mode[3]

Table I
Polystyrenes Used in This Work[a]

M, daltons	2000	4000	17 500	37 000	110 000	233 000	390 000
batch	61222	11b	41220	7b	4b	50124	3b
M_n/M_w	<1.06	<1.10	<1.06	<1.06	<1.06	<1.06	<1.10
c^*, kg m^{-3}			270	160	60	35	22
D_0, m^2 s^{-1}	2.8 (3) × 10^{-10}	1.9 (1) × 10^{-10}	7.8 (4) × 10^{-11}	5.2 (6) × 10^{-11}	3.6 (3) × 10^{-11}	2.3 (2) × 10^{-11}	1.85 (6) × 10^{-11}
k_f, m^3 kg^{-1}	1.1 (2) × 10^{-2}	1.0 (2) × 10^{-2}	9.1 (8) × 10^{-3}	1.5 (3) × 10^{-2}	5.7 (8) × 10^{-2}	1.1 (2) × 10^{-1}	1.4 (1) × 10^{-1}

[a] D_0 and k_f values are for carbon tetrachloride solutions at 28.0 °C. Note that $c^{**} \simeq 200$ kg m^{-3}.

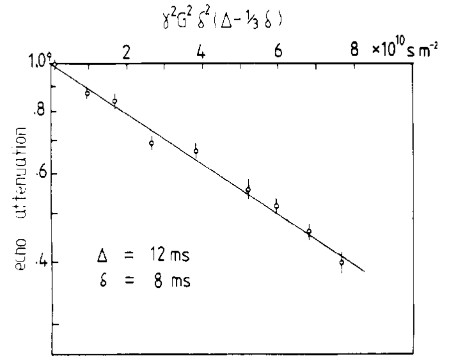

Figure 2. Spin-echo attenuation plot for a solution of 10 kg m^{-3} (1.0% w/v) 233000 molar mass polystyrene in carbon tetrachloride at 28.0 °C.

to inhibit coherent signal distortion and up to 600 echoes were summed before Fourier transformation and peak area measurement.

All spin-echo data obeyed the Stejskal-Tanner relationship[2] for the attenuation of the echo signal under the influence of magnetic field gradient pulses of magnitude G

$$\ln [A(G)/A(0)] = -D_s\gamma^2G^2\delta^2(\Delta - \delta/3) \qquad (28)$$

where δ and Δ are the pulse width and separation, respectively, and γ is the nuclear gyromagnetic ratio. Self-diffusion coefficients reported here were found to be independent of the effective experimental time scale, $\Delta - \delta/3$, over the available range of a few tens of milliseconds. It should be noted that the size of displacements necessary for detection by PFG NMR precludes any influence from intramolecular modes.

Our PFG NMR system has been calibrated to a precision of 1% using water[3] and accurately reproduces literature values for the self-diffusion coefficients of benzene and glycerol.[4] In order to check the consistency of our polystyrene self-diffusion results with those obtained by the FRS method we have compared the FRS D_s value for 123000 molar mass polystyrene in benzene with the PFG NMR result for the closest system available to us, that of 110000 molar mass polystyrene in hexadeuteriobenzene. We obtain, at 25.0 °C, $D_s = 3.2$ (1) × 10^{-11} m^2 s^{-1} for a solute concentration of 20 kg m^{-3} while Hervet et al. obtain $D_s = 3.5$ (4) × 10^{-11} m^2 s^{-1} at 14 kg m^{-3} and $D_s = 2.9$ (2) × 10^{-11} m^2 s^{-1} at 21 kg m^{-3}. The agreement would seem to be quite good.

Figure 2 shows an echo attenuation plot for 10 kg m^{-3} 233 000 molar mass polystyrene in carbon tetrachloride at 28.0 °C. All the data given here are for the same temperature.

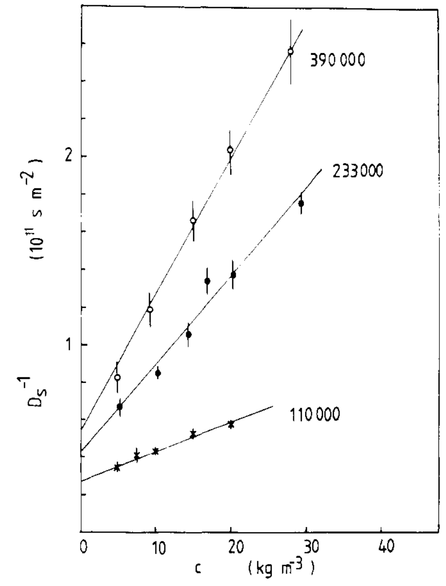

Figure 3. D_s^{-1} vs. c for dilute CCl$_4$ solutions of the higher molar mass polymers used in this work. Similar linearity was found with the low molar mass polystyrene solutions.

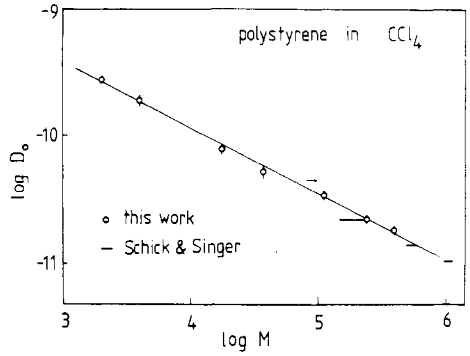

Figure 4. log [D_0 (m^2 s^{-1})] vs. log [M (daltons)] for polystyrene in CCl$_4$ at 28 °C. We find $D_0 = 1.26$ (12) × $10^{-8}M^{-0.51(2)}$ m^2 s^{-1}. Bar data are those of Schick and Singer, who used mutual diffusion methods.

Results and Discussion

Self-Diffusion in the Dilute Regime ($c < c^*$). In order to find D_0 and k_f values using eq 6 we have measured D_s for all the molar masses listed in Table I over a range of low concentrations ($c < c^*$) down to our low-concentration limit of 5 kg m^{-3}. The maximum concentration used in the analysis was restricted to 60 kg m^{-3} for 2000 molar mass, lowering to 30 kg m^{-3} for 390000 molar mass, the largest polymer used. Despite the fact that the higher polymer maximum concentrations were close to c^*, the plots of D_s^{-1} against c were distinctly linear for all molecular weights, in accord with eq 6. This linearity is apparent in the higher molar mass examples plotted in Figure 3. Roots et al have used ultracentrifugation to measure the frictional coefficient of 110000 molar mass random-coil polystyrene in toluene over a large concentration range. These authors also report that the linear relationship between frictional coefficient and concentration persists up to the surprisingly large concentration, 125 kg m^{-3}, in their system.

D_0 and k_f values obtained by linear regression are given in Table I. In Figure 4 we plot log D_0 vs. log M and it is clear that D_0 closely follows a scaling law. We obtain, using our data

$$D_0 = 1.26\ (12) \times 10^{-8}M^{-0.51(2)}\ \text{m}^2\ \text{s}^{-1} \qquad (29)$$

Also shown in Figure 4 are the data of Schick and Singer[21]

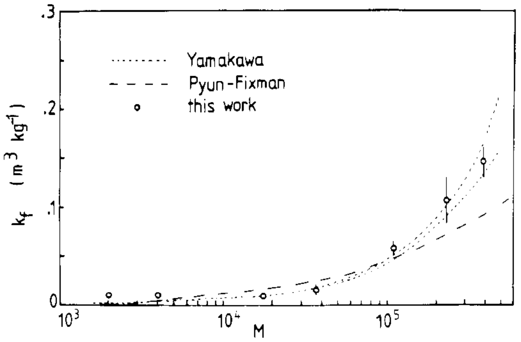

Figure 5. k_f vs. log M. k_f values (Table I) are obtained from the D_s^{-1} vs. c data using eq 6. The theoretical curves of Yamakawa ($A_2 = 3.2 \times 10^{-7}$, 2.6×10^{-7}) and Pyun and Fixman are shown. The Yamakawa model works well except at low molar masses.

obtained from classical mutual diffusion measurements. The agreement is excellent, allowing for some uncertainty in their molar masses.

Using mutual diffusion data obtained from quasi-elastic light scattering experiments, King et al.[15] have reported

$$D_0 = 5.5\ (2) \times 10^{-8} M^{-0.561(5)}\ \mathrm{m^2\ s^{-1}} \qquad (30)$$

for polystyrene in 2-butanone and Adam and Delsanti[22] have reported

$$D_0 = 2.18\ (32) \times 10^{-8} M^{-0.55(2)}\ \mathrm{m^2\ s^{-1}} \qquad (31)$$

for polystyrene in benzene. The difference between our scaling index for carbon tetrachloride and those for benzene and 2-butanone almost certainly reflects the difference in the molar mass regimes used and to a smaller extent in the goodness of the respective solvents. It should be noted that the average value of $\partial \ln D_0 / \partial \ln M$ obtained in these experiments represents an average of ν_D in the Weill and des Cloizeaux model for N values between $N < N_c$ and $N > N_c$. Significantly, both King et al. and Adam and Delsanti worked in the range $10^4 < M < 10^7$ daltons whereas our data fall in the range $10^3 < M < 10^6$ daltons. The scaling index of 0.51 (2) found here in fact agrees very well with the average slope over the same mass range apparent in Figure 1b. The higher indices obtained by King et al. and Adam and Delsanti can be explained by shifting the range to the higher molar masses appropriate to their work. It is not surprising that all three sets of data find average ν_D values less than the asymptotic limit of 0.588 with the lowest index found for our data.

In examining our k_f values given in Table I, we have compared them with the theories of Yamakawa[13] and Pyun and Fixman.[23] We closely follow the approach of King et al. in applying these models. In the case of the Yamakawa theory, which depends on the second virial coefficient, we have used $A_2 = 2.6 \times 10^{-7}$ m^3 kg^{-1} dalton^{-1} [24] and $A_2 = 3.2 \times 10^{-7}$ m^3 kg^{-1} dalton^{-1} [25] for polystyrene in carbon tetrachloride. Figure 5 shows our data plotted as k_f vs. log M along with the values calculated from the Yamakawa and Pyun–Fixman equations. While the Yamakawa model agrees well for either A_2 value at high molar masses, it fails for $M < 2 \times 10^4$ daltons. It is instructive to plot log k_f vs. log M as in Figure 6, where the discrepancy at low molar masses is more apparent; however, it is also clear that our k_f values are consistent with those obtained at high M by Tsvetkov and Klenin,[25] who used eq 10 to yield k_f values from classical mutual diffusion data.

The Yamakawa and Pyun–Fixman theories are clearly differentiated in their ability to predict the data we have shown in Figures 5 and 6, with the Yamakawa model working well at high M. The failure of either theory to give high k_f values at low molar masses has been pointed out by King et al.,[17] who noticed anomalous k_D values for $M < 10^5$ daltons for polystyrene in 2-butanone. Our data show the same trend; indeed it would seem that k_f is very nearly independent of M for $M < 2 \times 10^4$ daltons.

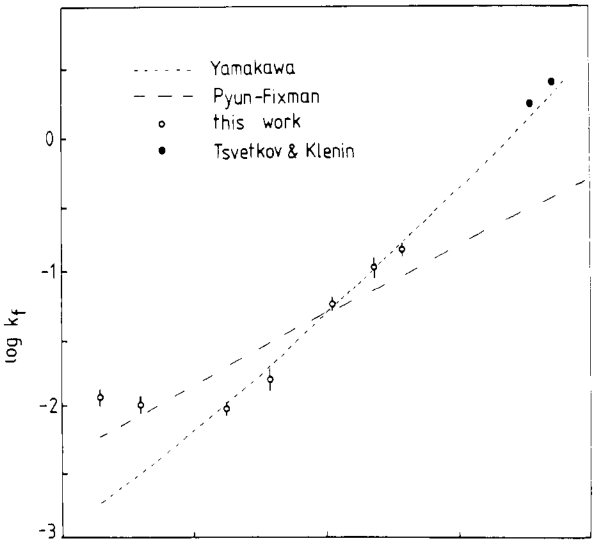

Figure 6. log [k_f (m^3 kg^{-1})] vs. log [M (daltons)]. The Yamakawa ($A_2 = 3.2 \times 10^{-7}$) and Pyun–Fixman curves are shown. The breakdown of the Yamakawa model at low M is more apparent. Tsvetkov and Klenin's data were obtained by mutual diffusion methods and are consistent with the present work.

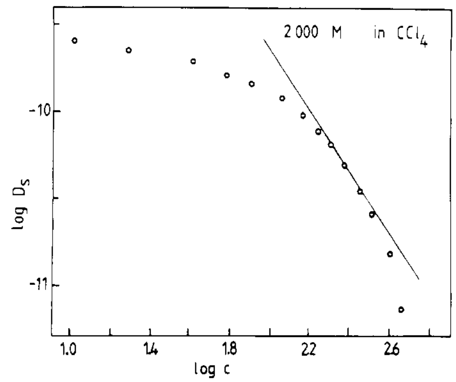

Figure 7. log [D_s (m^2 s^{-1})] vs. log [c (kg m^{-3})] for 2000 molar mass polystyrene in CCl$_4$ at 28 °C. No obvious scaling region is apparent. The tangent with slope −1.75 meets the graph at a concentration of 250 kg m^{-3}. This exceeds c^{**}, the concentration at which scaling breaks down.

Self-Diffusion in the Semidilute Regime ($c > c^*$). In order to distinguish the dependence of self-diffusion on concentration in the dilute and semidilute regimes, we have obtained D_s values over the widest possible range of experimentally available concentrations for our lowest polymer and for the highest polymer consistent with the requirement $\Delta - \delta/3 \ll T_r$ for all concentrations. The low polymer (M = 2000 daltons) has $c < c^*$ for all possible concentrations and in consequence has no semidilute regime. The plot of log D_s vs. log c for this polymer, shown in Figure 7, nowhere exhibits a well-defined scaling law region although a tangent of the appropriate slope can be drawn to the data. Polystyrene of molar mass 2000 in carbon tetrachloride is an example of a system for which the "flexibility assumption" breaks down before a semidilute regime is encountered.

In marked contrast, Figure 8 shows the log D_s vs. log c plot for 233 000 molar mass polystyrene, for which a scaling law region, as predicted by de Gennes, is clearly apparent.

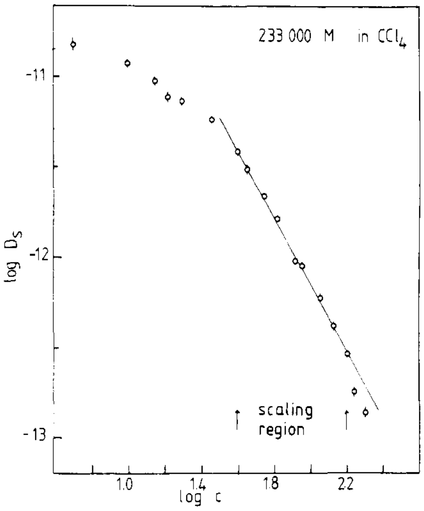

Figure 8. log [D_s (m^2 s^{-1})] vs. log [c (kg m^{-3})] for 233 000 molar mass polystyrene in CCl$_4$ at 28 °C. A well-defined scaling region is present with an empirical exponent of −1.83 (4).

We obtain by linear regression in the scaling region ($40 < c < 160$ kg m^{-3}) an index of −1.83 (4).

The manifest linear region in the log D_s vs. log c data for 233 000 molar mass polystyrene in carbon tetrachloride arises because c^* is much less than the upper concentration limit, c^{**}, where scaling breaks down. As expected, this linear region is observed to be narrower for the higher c^* 110 000 molar mass polystyrene, where a similar scaling index was found[7] consistent with the de Gennes model. A molar mass of 110 000 daltons is practically the lowest molar mass for which semidilute scaling behavior can be observed. The collapse of scaling at high concentrations cannot be attributed entirely to the reduction of ξ to a value comparable with the statistical element length, l. ξ is approximately independent of M, so scaling breakdown should occur at identical concentrations for 233 000 and 110 000 molar mass polystyrene whereas we observe this phenomenon at 180 and 220 kg m^{-3}, respectively. The explanation for breakdown of scaling is probably more complex and involves more than one mechanism.

In explaining the dependence of D_0 on M in the dilute regime, we used the molar mass dependent dynamical scaling index, ν_D, to determine the hydrodynamic radius and hence the diffusion coefficient. Using the Weill and des Cloizeaux values shown in Figure 1, we found a good agreement. de Gennes' scaling equation for the semidilute regime (eq 24a) can be used to obtain ν with some precision. Assuming that the index ν is the dynamic index ν_D, we obtain $\nu_D = 0.590$ (5) if D_s scales as $c^{-1.83(4)}$, as observed. This value of ν_D compares well with asymptotic value 0.588. Yet recourse to the Weill and des Cloizeaux model shows that $\nu_D \simeq 0.55$ for 233 000 molar mass polystyrene (N/N_c) $\simeq 10$ in Figure 1a), so such agreement is rather unexpected! It is remarkable both in our work on 233 000 molar mass polystyrene in carbon tetrachloride and in that of Hervet et al. for 245 000 molar mass polystyrene in benzene that we should find a scaling behavior consistent with ν close to the asymptotic limit. In a simplistic manner we could of course argue that for entangled polymer coils excluded volume effects are so important that ν_D is more extremal than the value suggested by Figure 1 for an isolated coil. In fact a closer examination of the derivation of eq 24a suggests that this view is only partially true and that in any case a unique index ν_D may not be appropriate.

Weill and des Cloizeaux give a practical rule which dictates that in deriving scaling law expressions for any experimental parameter, all distances are governed by the static radius of gyration, R_G, and all relaxation times, τ, by the product $R_G{}^2R_D$. On inspecting the de Gennes model, we find that the fundamental relaxation time occurs in the diffusive behavior of a segmental "blob" and the only dynamical radius is the blob hydrodynamic radius. Labeling this distance ξ_D, we allow, in accordance with eq 5, that

$$\xi_D \sim g^{\nu_D} \qquad (32)$$

whereas for all other dimensions the static scaling index, ν_G, is appropriate. In consequence the Weill and des Cloizeaux model would predict

$$D_s \sim N^{-2}c^{(2-\nu_D)/(1-3\nu_G)} \qquad (33)$$

A similar approach has been used by Pouyet et al.[26] in examining sedimentation scaling behavior in the semidilute regime. These authors find a similar admixture of static and dynamic scaling indices in the exponent. It is sensible to give ν_D and ν_G their extreme values for $N < N_c$ and $N > N_c$, respectively. In the semidilute regime the solution is sufficiently concentrated that static dimensions measured over distances larger than ξ will suffer excluded volume effects and be described by ν_G values close to 0.6. In the spaces between entanglements, where the short blob segments have a hydrodynamic radius determined by ν_D, such excluded volume arguments will not apply and the relevant indices will be those of the low N segments, namely, ν_D close to 0.5. Using these limits, we find

$$D_s \sim c^{-1.87}$$

which is entirely consistent with the observed behavior

$$D_s \sim c^{-1.83(4)}$$

In the absence of a more rigorous description in the semidilute regime the simple approach offered here gives an adequate representation of the observed scaling behavior while taking some account of the suggestion that more than one critical index may be required to describe a random polymer of finite length.

Given the consistency of the PFG NMR and FRS self-diffusion coefficients with the scaling law behavior of de Gennes in the semidilute region, it is interesting to examine whether or not $D_s{}^+$ values calculated according to eq 14 and 15 from mutual diffusion (or equivalently from sedimentation) show a similar scaling law behavior. We have taken $D_s{}^+$ values from the published data of Roots et al. for 100 000 molar mass polystyrene in toluene and have plotted them as log $D_s{}^+$ vs. log c in Figure 9. The data show scaling at the higher concentrations, where the ex-

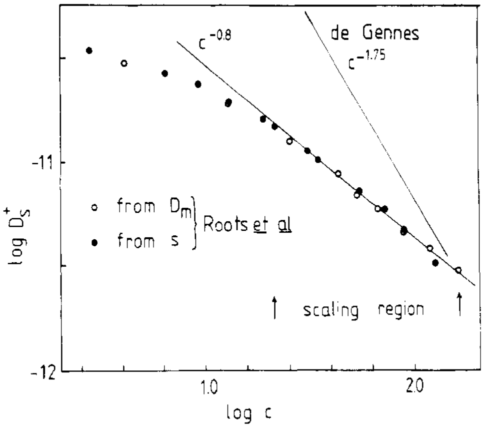

Figure 9. log [$D_s{}^+$ (m^2 s^{-1})] vs. log [c (kg m^{-3})] obtained from that data of Roots et al.[1] The semidilute region exhibits the wrong scaling exponent for self-diffusion.

ponent is approximately −0.8, and not −1.75 as required by the de Gennes law. Notice this is the same scaling index as that found by Roots et al. for the sedimentation coefficient of the same system over the same concentration range, which again illustrates that eq 14, 15, and 27 are self-consistent. The fact that D_s and D_s^+ can be shown experimentally to obey different scaling laws in the semidilute regime gives a clear indication that these two quantitites are physically distinct. An additional contrast is provided by the difference in the concentration range of the scaling region. In Figure 9 the onset of scaling occurs at 20 kg m^{-3} whereas we have previously observed the onset of D_s scaling at 60 kg m^{-3}, a discrepancy unlikely to be explained by the solvent difference in the two cases. The quantity D_s^+ can be derived from either the measured mutual diffusion coefficient or the sedimentation coefficient; however, this quantity cannot be identified with the self-diffusion coefficient D_s in the semidilute regime. This dissimilarity is consistent with the proposition that while the mechanisms governing mutual diffusion and sedimentation of random-coil polymer solutions are similar in the semidilute regime, they are quite different from the mechanism governing self-diffusion. As previously noted, sedimentation for entangled random-coil polymer may be viewed as governed by the motion of solvent through an essentially fixed network of interlocked coils akin to motion through a porous plug. Such assumptions are implicit in the derivation of the scaling index for sedimentation in the de Gennes model. In contrast, self-diffusion concerns the relative motion of coils in a network regarded inherently as transient. The physical nature of self-diffusion and sedimentation for random-coil polymers in the semidilute regime is such as to render invalid the inherent assumption in the D_s^+ equation.

Conclusions

We have shown that our values for the infinite-dilution diffusion coefficients of random-coil polystyrenes in carbon tetrachloride are in good agreement with the previous estimates of D_0 obtained by Schick and Singer from mutual diffusion measurements and that our D_0 values scale with molar mass in an appropriate manner. In studying the behavior of the frictional coefficient with polymer concentration and with polymer size, we find that our results are in good agreement with the earlier measurements of Tsvetkov and Klenin and also with the theoretical predictions of Yamakawa although these predictions are found defective at low molar mass.

In the semidilute regime we observe a well-defined scaling law region for 233 000 molar mass polystyrene in carbon tetrachloride, with an exponent close to that predicted by de Gennes. Our measurements of self-diffusion coefficients have enabled us to test the concept of separate dynamic and static Flory indices, which depend differently on the polymerization index. The variation of D_0 with polymer molar mass indicates $\nu_D = 0.51$ (2), this value being an average over masses in the range 2000–390 000 daltons. By contrast, the concentration scaling law governing the variation of the self-diffusion coefficient of 233 000 molar mass polystyrene in the semidilute regime implies the high value of 0.590 (5) if a unique dynamic Flory index is calculated using the de Gennes scaling law. This value exceeds the ν_D value for 233 000 molar mass polystyrene predicted by Weill and des Cloizeaux but we suggest that a unique critical index is inappropriate in this case and that a model which allows both static and dynamic terms is preferable.

While it can be agreed that mutual diffusion or sedimentation coefficients can be used with good effect to calculate reliable self-diffusion coefficients for random-coil macromolecules at high dilution, it is apparent that this is not the case in the semidilute regime, a result which is none too surprising in view of the entirely different dominant mechanisms governing these parameters under conditions of polymer entanglement. Self-diffusion coefficients must be obtained by a technique which measures, from first principles, the mean-square displacements of molecules in thermally driven random motion under conditions of thermodynamic equilibrium.

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