Macromolecules 1983, 16, 968-973

A Pulsed Field Gradient NMR Study of Self-Diffusion in a Polydisperse Polymer System: Dextran in Water

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ABSTRACT: Self-diffusion coefficients have been obtained over a range of concentrations for dextran in deuterated water. The dextran samples were all derived from *Leuconostoc mesenteroides* strain B512 and were polydisperse, with M_w values of 10 500, 40 100, 75 800, 170 000, and 461 000 daltons. The implications of polydispersity for the pulsed field gradient experiment are considered. We predict the observation of a molar mass weighted self-diffusion coefficient, $\langle D \rangle_w$, under conditions of ensemble averaging and verify this using a mixture of well-characterized monodisperse polystyrene with differing molar masses in CCl_4 solution. The dextran data obey $D_s^{-1} = D_0^{-1}(1 + k_f c)$ except for the lowest molar mass, where anomalous behavior is observed. We find $D_0 \sim M^{-0.57(2)}$ and note consistency with D_0 values obtained by fluorescent labeling methods for two other molar masses. The k_f values for dextran/D_2O are molar mass independent, in contradiction with theory. In the semidilute regime of 170 000-dalton dextran/D_2O, a concentration-dependent scaling behavior is found with $D_s \sim c^{-1.92(5)}$, in accordance with the de Gennes reptation theory modified to allow for crossover effects. An upper limit to the dextran side-chain lengths of 10 monomer units is implied.

Introduction

Pulsed field gradient NMR (PFGNMR) has proven to be a valuable technique in investigating the self-diffusion of polymers in both dilute and semidilute solution.[1,2] Along with the forced Rayleigh scattering method[3] it has provided a test of theories concerning the dynamics of random coils, but to date only monodisperse linear polystyrene in organic solvents has been systematically examined by these two techniques. It is of considerable interest to test the models, which have been successful in explaining the polystyrene diffusion, against an entirely different polymer system and to investigate whether the dynamical behavior of synthetic and naturally occurring polymers is similar. Dextran is a water-soluble, biologically produced polysaccharide that is commonly used as a blood plasma substitute. A variety of dextran mass fractions is available commercially but most of these have a polydispersity characterized by M_w/M_n ratios greater than 2. Moreover, dextran is known to have some branching and this is expected to inhibit reptation, the mechanism for self-diffusion under conditions of polymer entanglement.

We have used the PFGNMR technique to obtain self-diffusion coefficients for dextran in water over a wide range of concentration and molar mass. The data provide a probe of the dependence of the dextran molecular dimensions on molar mass and the degree to which the reptation theory of de Gennes[4,5] applies to an entangled solution of random coil polysaccharide. The finite polydispersity of the dextran is an interesting feature of this study, and in order to determine the significance of a molar mass distribution, we have examined self-diffusion in a mixed solution of two widely separated molar masses of monodisperse linear polystyrene, each with well-characterized solution properties.

Polymer Self-Diffusion. The segments of an isolated flexible polymer in solution assume a conformation known as a self-avoiding random walk. A polymer dimension may be defined according to the measurement applicable to its determination. For example, the radius of gyration, R_G, may be expressed by

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

for N statistical segments labeled by subscripts i and j. The statistical segment is viewed as the smallest element of the random walk comprising the polymer conformation and will in practice be a few monomer units, the exact number depending on the intermonomer rotational flexibility.

The radius of gyration gives a useful static coil dimension, which can be measured by inelastic neutron scattering.[6] For polymer self-diffusion the relevant dimension is the coil hydrodynamic radius, and in the manner of the Kirkwood–Riseman theory[7] it may be shown that this quantity depends on the intersegment separation, r_{ij}, as

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

In the simple theory of the self-avoiding walk the r_{ij} scale as

$$r_{ij} = a|i-j|^{\nu} \tag{3}$$

with ν very close to $^3/_5$. Equations 1–3 imply that $R_D \sim R_G$. In fact, the relationship is more complex since excluded volume effects are masked when $|i - j|$ is small. Weill and des Cloizeaux[8] have defined a critical segment separation N_c such that

$$\begin{aligned} r_{ij} &= a|i-j|^{1/2} \qquad |i-j| < N_c \\ &= aN_c^{1/2}|(i-j)/N|^{\nu} \qquad |i-j| > N_c \end{aligned} \tag{4}$$

Equations 4 thus depict a *crossover* from Gaussian to excluded volume statistics in the random walk defining the coil conformation, and it is clear that $R_G \sim R_D$ no longer holds. Weill and des Cloizeaux define static and dynamic indices ν_G and ν_D such that

$$\begin{aligned} \nu_G &= \partial \ln R_G/\partial \ln N \\ \nu_D &= \partial \ln R_D/\partial \ln N \end{aligned} \tag{5a}$$

or

$$\begin{aligned} R_G &\sim N^{\nu_G} \\ R_D &\sim N^{\nu_D} \end{aligned} \tag{5b}$$

Both ν_G and $\nu_D = 0.5$ for $N < N_c$ and each index approaches 0.6, but at different rates for $N > N_c$.

In the infinite dilution limit the self-diffusion coefficient of a random coil polymer may be used to define the dynamic radius R_D in terms of the Stokes–Einstein expression

$$D_0 = k_BT/6\pi\eta_0 R_D \tag{6}$$

where η_0 is the solvent viscosity. In consequence it is expected that D_0 should scale as

$$D_0 \sim N^{-\nu_D} \tag{7}$$

Table I

dextran	M_w, daltons	M_w/M_n direct	M_w/M_n GPC	$10^{11}D_0$, $m^2\ s^{-1}$	k_f, $m^3\ kg^{-1}$
Pharmacia T10	10 500	2.1	3.1	8.3 (2)[a]	
				13.3 (9)[b]	0.026 (2)[b]
Pharmacia T40	40 100	1.22	1.35	5.4 (2)	0.032 (1)
Pharmacia T70	75 800	1.64	1.60	4.0 (4)	0.038 (3)
Sigma 170	170 000		1.25	2.4 (2)	0.042 (2)
Pharmacia T500	461 000	2.54	1.50	1.35 (8)	0.038 (2)
Pharmacia F104	19 100	1.10		8.3 (4)[c]	
Pharmacia F108	153 700	1.51		2.4 (2)[c]	

[a] Observed limit as $c \to 0$. [b] Extrapolated from higher c values. [c] Reference 20.

A dilute regime of finite concentration is said to exist when the polymer coils are on average separated. In such a regime polymer–polymer interactions occur both by occasional collision and, more importantly, via backflow effects in the solvent. In consequence the self-diffusion coefficient, D_s, is reduced below the infinite dilution limit and in its most simple form this reduction is expressed by expanding the friction coefficient as a power series in the polymer mass/volume concentration, c, so that

$$D_s^{-1} = D_0^{-1}(1 + k_f c ...) \tag{8}$$

We have previously observed[2] that the term linear in concentration appears to be sufficient to describe the friction coefficient concentration dependence almost up to c^*, the concentration above which entanglement occurs.

In the semidilute regime the predominant factor limiting the diffusion of a random coil polymer in solution is the presence of topological constraints such as entanglement. The lowest concentration of the semidilute regime, c^*, is given approximately by

$$c^* = M/N_A R^3 \tag{9}$$

where R is the polymer coil static dimension. Uncertainty arises in the definition of c^* because of different possible alternatives for R such as root-mean-square end-to-end length or radius of gyration. For our own part we prefer an empirical definition as that concentration where entanglement-dominated dynamic behavior begins. Equation 9 may then be used to scale c^* between different molar mass values of the same polymer system.

Where significant entanglement occurs, the only self-diffusion mechanism is reptation aided by tube reorganization[4,5] such that the polymer chains diffuse in a curvilinear path in a tube of diameter ξ formed by the topological constraints of neighboring chains, where ξ is the average distance between entanglements. de Gennes has shown that such a model leads to semidilute scaling law for self-diffusion of the form

$$D_s \sim M^{-2} c^{(2-\nu)/(1-3\nu)} \tag{10a}$$

or

$$D_s \sim M^{-2} c^{-1.75} \quad \text{if } \nu = 0.6 \tag{10b}$$

It can be shown[2] that if static and dynamic indices are separately accounted for, eq 10 can be rewritten

$$D_s \sim M^{-2} c^{(2-\nu_D)/(1-3\nu_G)} \tag{11}$$

If the polymer has side chains of length greater than ξ, the reptation of the polymer will be significantly inhibited and scaling laws such as eq 10 and 11 will not apply. In consequence the observation of semidilute scaling behavior with an index close to that predicted by a de Gennes-like law would give a good indication that polymer branching is negligible or that branch sections are so short that they do not significantly inhibit reptation.

Experimental Section

Dextrans were obtained from Pharmacia and Sigma and were all produced by the bacteria *Leuconostoc mesenteroides*, strain B512. Table I lists the dextrans used, their quoted M_w values obtained by light scattering, and their quoted M_w/M_n values. In addition, we carried out mass distribution measurements by gel permeation chromatography (Sepharose 2B) for all the dextrans used here. The column was calibrated with Blue dextran/dye and the known M_w values for the dextrans of Table I. Log-normal mass distributions were observed for each polysaccharide and equivalent M_w/M_n values calculated. These M_w/M_n values are also given in Table I.

Dextran/D_2O solutions for PFGNMR studies were thoroughly mixed in 1-mL volumetric flasks and allowed to equilibrate for several days before self-diffusion coefficients were obtained. The pulsed field gradient measurements on dextran were made at the University of British Columbia Physics Department, using a home-built apparatus interfaced to a Bruker SXP100 spectrometer. The technique used is the same as that of ref 9. The magnetic field gradients were calibrated to ±1% accuracy using the diffusion coefficient of water at 25.0 °C[10] and checked for consistency at slow diffusion using a sample of 2.9% 390 000 molar mass polystyrene/CCl_4 at 25.0 °C, for which the measured self-diffusion coefficient agreed within experimental error (±3%) with that obtained for the same polymer solution by the present authors on our New Zealand apparatus.[2] This latter apparatus was used for the experiments on mixed solutions of monodisperse polystyrene in carbon tetrachloride.

Dextran PFGNMR measurements were made at 25.0 °C on 9-mm-diameter samples using 90-MHz proton Hahn echoes. The water content of the dextran powder (~8% by weight) was determined by drying although the hydrous polysaccharide was used to prepare PFGNMR samples. All concentrations are quoted in units of dextran dry mass per solution volume. (Note that 1% (w/v) is equivalent to 10 kg m^{-3}). PFGNMR data were analyzed with the Stejskal–Tanner relationship[11] for a pair of gradient pulses of amplitude G, duration δ, and separation Δ

$$\ln\,[A(G)/A(0)] = -kD \tag{12a}$$

where

$$k = \gamma^2 G^2 \delta^2 (\Delta - \tfrac{1}{3}\delta) \tag{12b}$$

Echo attenuation plots of $\ln\,[A(G)/A(0)]$ vs. G^2 are used to obtain D by least-squares fitting, an example of these data being shown in Figure 1. In all experiments we observed a rapid initial decay due to protonated water present in solution. This water signal arises partly because of the H_2O initially adsorbed on the powdered polymer but also because of proton exchange between the dextran hydroxyl groups and the D_2O solvent. By deleting the low-k data, we obtained a good fit for the polymer self-diffusion coefficients.

Because of the different transverse relaxation rates of proton spin echoes arising from the protonated water and the various dextran hydrogen sites, it is difficult to ascribe a quantitative interpretation to the relative signal amplitudes in the fast and slow components evident in Figure 1. We may be sure, however, that hydroxyl proton exchange is complete in dextran.[12] The

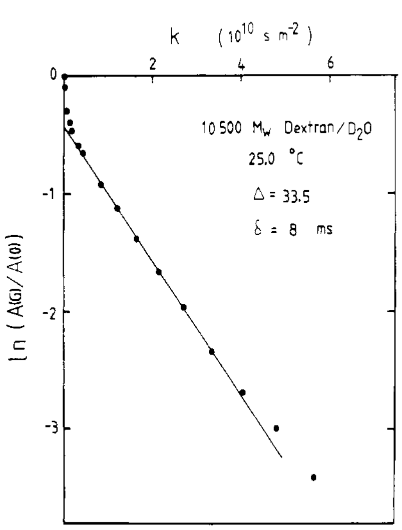

Figure 1. Echo attenuation plot for a 52 kg m^{-3} (5.2% (w/v)) solution of dextran (M_w = 10 500 daltons) in D_2O at 25.0 °C. The rapid decay at small magnetic field gradient is due to the signal from rapidly diffusing protonated water. Some deviation from linearity due to dextran polydispersity is apparent at very high attenuation.

exchange rate should be similar to that of alcohol hydroxyl, where, in excess water, an exchange time (τ_{ex}) of 10 ms is indicated.[13] While this time is shorter than the observation time Δ used in the PFGNMR experiments, it is of sufficiently similar order of magnitude for the influence of exchange on diffusion measurement to be seriously considered.

There are three exchangeable proton sites per dextran monomer. The fraction of available labile proton sites in the solution represented by the dextran hydroxyl groups is ≤4% for dextran concentrations of ≤20% as used here. In fact, the fraction of hydroxyl sites possessing ^1H rather than ^2H will be a little higher at ≤5.6% due to the protonated water introduced by the hydrous dextran.

The relevant time scale for the exchange rate is the diffusive observation time Δ. For $\tau_{ex} \ll \Delta$ fast exchange prevails and the hydroxyl influence is a modification of the fast-component diffusion coefficient such that $D_{fast} = (0.96D_{HDO} + 0.04D_{polymer})$ for c = 20% (w/v). For $\tau_{ex} \gg \Delta$ the exchange is termed slow and the ≤5.6% protonated hydroxyl sites contribute to the polymer signal in a manner indistinguishable from the remaining dextran protons. For intermediate exchange, where $\tau_{ex} \sim \Delta$, some difficulty can arise. The effect of a hydroxyl proton spending some time on a water molecule may distort the measured polymer self-diffusion coefficient. Such distortion will manifest itself in a self-diffusion coefficient dependent on the diffusive observation time Δ. In this work we found $D_{polymer}$ constant over a range of Δ spanning by a factor of 2 the value of 33.5 ms used in the results reported here and to this extent we may be sure that exchange effects have no significant influence. This exchange independence may be due in part to a prevailing condition of fast exchange and in part to the small fraction of the total proton signal arising from exchangeable hydroxyl sites.

There remains at least one other potentially troublesome aspect of the dextran system to be considered. It is a noteworthy feature of Figure 1 that a unique diffusion coefficient is found despite the finite polymer polydispersity. In fact, all echo attenuation plots in this study were approximately linear down to a spin-echo attenuation of $e^{-2.0}$, some deviation becoming apparent at $e^{-2.5}$. To preclude systematic error an upper limit attenuation of $e^{-2.0}$ was imposed on all data analyzed for self-diffusion coefficient.

Results and Discussion

Effects of Polydispersity. Three parameters of mass distribution may be defined for a polydisperse ensemble. These are the number-, mass-, and z-average molar mass as defined by eq 13–15, respectively, where p_i is the number of molecules of mass M_i.

$$M_n = \sum p_i M_i / \sum p_i \qquad (13)$$

$$M_w = \sum p_i M_i^2 / \sum p_i M_i \qquad (14)$$

$$M_z = \sum p_i M_i^3 / \sum p_i M_i^2 \qquad (15)$$

Note that in accordance with convention we preserve the subscript w (for molecular weight) for the mass-averaged molar mass, M_w.

In the summing of spin echoes arising from polymers of differing molar mass and, in consequence, differing self-diffusion coefficients, we must weight the echoes according to size or number of protons contained within the molecule.[14] We therefore expect a mass average of the type

$$\langle A(G)/A(0) \rangle = [\sum p_i M_i \exp(-kD_i)] / \sum p_i M_i \qquad (16)$$

Inherent in eq 16 is the assumption that there are no interactions between polymer coils of differing self-diffusion coefficient, so this analysis applies to extremely high dilution studies only. Equation 16 may be expanded as a power series and, keeping only the leading, linear, term, we find

$$\ln \langle A(G)/A(0) \rangle = -k[\sum p_i M_i D_i / \sum p_i M_i] = -k\langle D \rangle_w \qquad (17)$$

where $\langle D \rangle_w$ is the mass-averaged diffusion coefficient.

To the extent that eq 17 is valid we may say that the pulsed field gradient experiment gives a measure of the mass-averaged diffusion coefficient. An exact analysis shows, however, that curvature will result in spin-echo attenuation plots because of the presence of higher order terms, the leading quadratic term being $^1/_2 k^2[\langle D^2 \rangle_w - \langle D \rangle_w^2]$. We now examine the significance of this term in comparison with the first-order term $k\langle D \rangle_w$ used in the analysis of the PFGNMR experiment. We take first the case of an equal-mass mixture of two polymers with molar masses differing by a factor of 2. Here, the quadratic term is $0.021k^2\langle D \rangle_w^2$ so that the deviation from linearity is 2% for an attenuation of $e^{-1.0}$ (8% at $e^{-2.0}$). Next we consider the case of a log-normal mass distribution of characteristic M_w/M_n ratio. It is not difficult to show that the quadratic term is then $^1/_2 k^2 \langle D \rangle_w^2 [1 - (M_w/M_n)^{-4/5}]$. For M_w/M_n of 1.5 this corresponds to a deviation from linearity of 10% at $e^{-1.0}$ (40% at $e^{-2.0}$), with twice these deviations for M_w/M_n of 2.0. We note immediately that such deviations from linearity are not observed in this study for the dextran in water experiments despite the fact that M_w/M_n ratios of the order quoted are used. It is clear that at all finite polymer concentrations such as are used here, some mechanism exists to product a degree of *ensemble averaging* of diffusion coefficients. In other words the actual distribution of molecular diffusion coefficients over the time scale of the PFGNMR experiment is narrower than would be expected for an ensemble of isolated molecules with the known mass distribution. This implies that interaction between molecules tends to average the diffusion process. In semidilute solutions the coils are entangled and the reptation of one coil occurs through a pseudogel of other coils so that averaging of dynamic processes is to be expected. For dilute solutions collisions are an obvious mechanism for such averaging; however, it is likely that a more important influence is the long-range flow interaction via the solvent as depicted in the Kirkwood–Riseman model. This view is appealing in accounting for interaction averaging between molecules at high dilution such as the 0.5% (w/v) dextran solutions studied here. For these experiments the PFGNMR echo attenuation data are no less linear than for the higher concentrations.

The contention that PFGNMR measures a mass-averaged diffusion coefficient was tested as follows: Experiments were performed on solutions of 50/50 (w/w) admixtures of 110 000 and 233 000 molar mass polystyrene

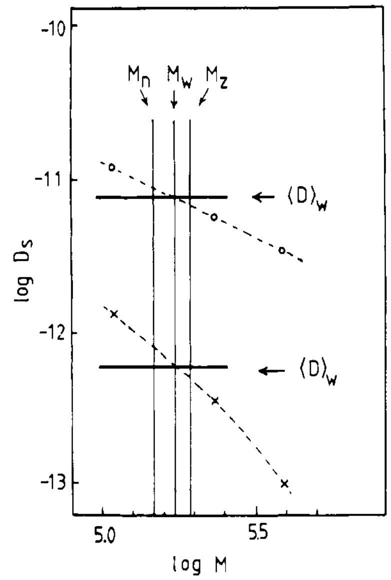

Figure 2. Comparison of the mean self-diffusion coefficient obtained by PFGNMR for equal-mass mixtures of 233 000 and 110 000 dalton polystyrene in CCl_4. The horizontal bars show the measured self-diffusion coefficient, the error being indicated by the thickness of the line. The upper and lower data refer to a 3.0% (w/v) (dilute) and 15% (w/v) (semidilute) solution, respectively. Excellent agreement is found with the respective molar mass averaged diffusion coefficients calculated using the known[2] self-diffusion coefficients for monodisperse 233 000- and 110 000-dalton polystyrene (circles, 3.0%; crosses, 15.0%). Interpolation of the data for monodisperse polystyrene shows that the measured mixture self-diffusion coefficients correspond with that of the mass-averaged molar mass, M_w.

in carbon tetrachloride at two (total) solute concentrations of 3.0% and 15.0% (w/v), which fall in the dilute and semidilute regimes, respectively. We note immediately that the echo attenuation data are linear within experimental error up to the attenuation used of e^{-2}. The self-diffusion data are shown in Figure 2 along with the D_s values for the monodisperse polymer solutions at the same concentration. The mass-averaged $\langle D \rangle_w$ values calculated in accordance with eq 17 are in excellent agreement with experiment in both the dilute and semidilute regimes. In fact, the self-diffusion coefficient agrees well with that predicted by linear interpolation on the log D_s vs. log M plot, choosing the mean mass-averaged molar mass M_w. For attenuations such that the ln $[A(G)/A(0)]$ vs. G^2 plot is linear we conclude that in both dilute and semidilute solution PFGNMR measures to a good approximation an ensemble-averaged diffusion coefficient, with a value corresponding to the mass-averaged molar mass, M_w.

Effect of Slight Branching of the Coils. It has been reported that the dextran molecules produced by the B512 strain of *Leuconostoc mesenteroides* are essentially linear, with only very few short side chains.[15] The dextran molecules from these bacteria have 95% α(1–6) linkages, the remaining 5% of monomers have α(1–3)-linked side chains, and fewer than 15% of these side chains are greater than 2 monomer units long.[16] Although this is indeed a slight degree of branching it is not insignificant. If we consider a chain of 1000 monomers [molar mass ~170 000 daltons], then the probability of the chain having no side chains greater than 2 monomer units long is approximately 5×10^{-5}. To that extent the dextrans examined here are branched coils. This branching is not expected to have a great effect on the dilute solution studies. However, if the side chains are longer than ξ, their presence would inhibit reptation[17] and hence strongly affect the semidilute studies. Indeed those coils with side chains significantly longer than ξ would have reptation times so long that they would be effectively locked in a permanent gel network and only those remaining polysaccharides with short side chains could reptate. The effect of this on the echo attenuation plot would be to render it severly curved.

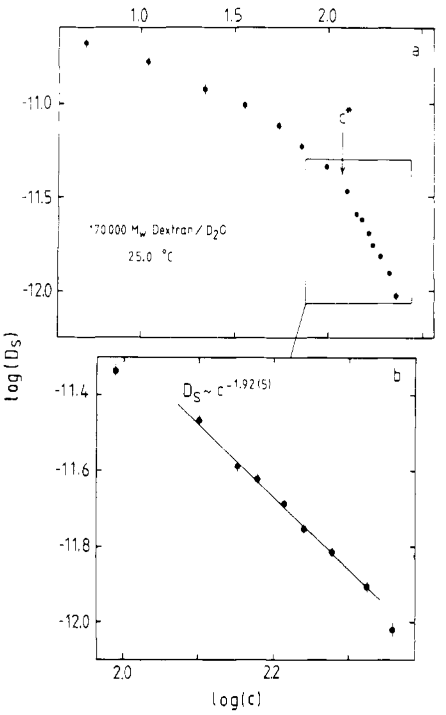

Figure 3. (a) log $[D_s\ (m^2\ s^{-1})]$ vs. log $[c\ (kg\ m^{-3})]$ for 170 000-dalton dextran in D_2O at 25.0 °C. A well-defined semidilute scaling region is apparent over a factor of 2 in concentration (an expanded plot is shown in (b)), indicating that the diffusion process is governed by reptation.

Self-Diffusion in the Semidilute Regime. An extensive range of concentration was used in the case of the 170 000 molar mass dextran solutions in order to test for reptational behavior and to find the boundary between dilute and semidilute behavior. We chose this particular molar mass for two reasons. First, it has a relatively narrow mass distribution. Second, the value of M_w is sufficiently high that we expect to find a wide semidilute regime $c^* < c <$ min (c_c, c^{**}), where c_c is the concentration above which crossover effects ensue and c^{**} is the upper concentration limit at which flexibility breakdown occurs.[2] A wide semidilute regime has been shown to be a prerequisite for the observation of reptation and in the case of polystyrene in organic solvents, a molar mass of 2×10^5 daltons has proven suitable for this purpose whereas 1×10^5 daltons exhibits only a narrow scaling regime. Brown et al.[18] have failed to observe a clearly defined reptation regime for 64 200-dalton ($M_w/M_n = 1.5$) dextran in water. The authors do not discuss the degree of branching in their dextran and the possibility that reptation is inhibited by side chains cannot be ruled out. However, we believe that the molar mass used in their experiment is inadequate and in view of the failure of other polymer solutions to exhibit semidilute scaling for molar masses less than 10^5 daltons, the data of Brown et al. cannot be taken as definitive evidence that reptation is inhibited.

The concentration dependence of self-diffusion for 170 000-dalton dextran in D_2O is shown in Figure 3a, with the semidilute regime expanded in Figure 3b. In the scaling region above c^* (12%) a least-squares fit to the slope of log D_s vs. log c yields $D_s \sim c^{-1.92(5)}$. This index agrees well with the de Gennes reptation model modified to allow for crossover effects. Overall Gaussian statistics

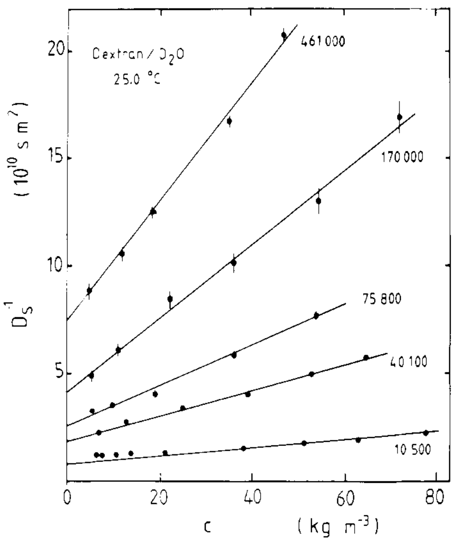

Figure 4. D_s^{-1} vs. c for dilute solutions of dextran in D$_2$O. A linear relation in accordance with eq 8 is found except in the case of M_w = 10 500 daltons.

prevail above the concentration c_c but below this an admixed set of critical indices applies, with $\nu_D \simeq 0.5$ and $\nu_G \simeq 0.6$. We have shown that these latter indices apply and hence $N > N_c$ for entangled solutions of polystyrene ($M_w \sim 10^5$ daltons) at the onset of entanglement.[2,19] For such circumstances eq 11 predicts $D_s \sim c^{-1.87}$, in good agreement with the behavior observed here. For dextran/D$_2$O the scaling ends at an upper concentration of 23%. If we assign this value to c_c, we find $c_c/c^* \simeq 2$ for 170 000-dalton dextran compared with $c_c/c^* \simeq 4$ for a similar molar mass polystyrene/CCl$_4$ solution. A lower value of c_c/c^* implies somewhat fewer statistical subunits for dextran than for polystyrene of the same molar mass, an effect which is not surprising given the differences in chemical structure and steric hindrance for monomer–monomer rotation.

The observation of a clearly defined reptational regime for dextran/D$_2$O solutions provides confirmation that the B512 strain of *Leuconostoc mesenteroides* produces essentially linear dextran with very few side chains, and these branches must, moreover, be short compared with ξ. The previous study by Larm et al.[16] gave no indication of the length of the very few side chains in excess of 2 monomers. Our reptation result can, however, be used to establish an upper limit since these branches must be less than ξ over the entire scaling regime. At the highest concentration ξ comprises of order 10 monomers so that we conclude that all B512 dextran side chains are smaller than 10 glucose units.

Self-Diffusion in the Dilute Regime. Following the observation that $c^* \simeq 12\%$ for 170 000 molar mass dextran in D$_2$O and the prediction $c^* \sim M^{1-3\nu_G}$, we expect to find dilute regime behavior below 5%, 22%, 38% and 120% respectively for 461 000, 75 800, 40 100, and 10 500 molar mass solutions. At low solute concentration we plot the self-diffusion data according to eq 8 as D_s^{-1} vs. c and extrapolate to $c = 0$ to find D_0, the self-diffusion coefficient at infinite dilution. Figure 4 shows the dilute regime plots for all the molar masses used here. Equation 8 works well for all except the lowest molar mass, where significant deviation is found at high dilution, as apparent in Figure 5, where the data are plotted in expanded form. The 10 500 molar mass data do, however, exhibit an approximately linear D_s vs. c region from 4% to 8% (w/v), the highest concentration used. This linear region may be extrapolated to obtain an apparent D_0 value in addition to that suggested by the lowest concentration data.

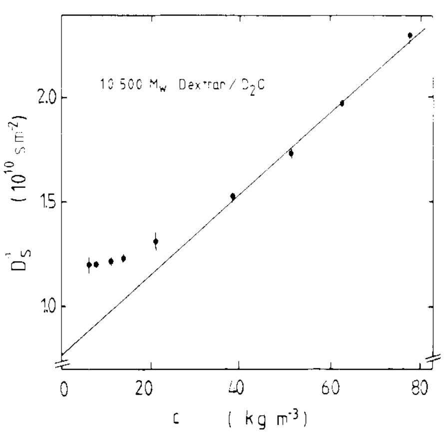

Figure 5. Expanded plot of D_s^{-1} vs. c for 10 500-dalton dextran in D$_2$O. The higher concentration data can be fitted to eq 8 but a significant deviation is found at higher dilution.

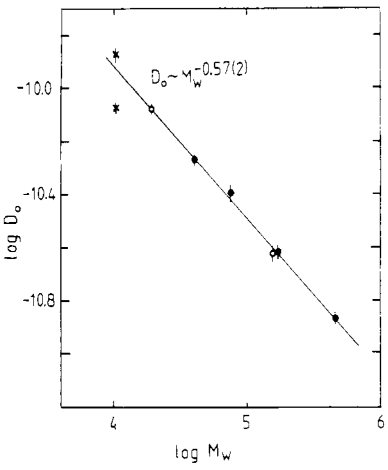

Figure 6. log [D_0 (m^2 s^{-1})] vs. log [M_w (daltons)] for dextran in D$_2$O at 25.0 °C. The open circles are the data of Laurent et al.[20] The data represented by asterisks refer to M_w = 10 500 daltons, where the lower point was obtained directly from high-dilution measurement and the upper point was obtained by linear extrapolation from higher concentration (see Figure 5). The scaling law line is obtained from the data with M_w > 10 500 daltons.

The D_0 and corresponding k_f values are given in Table I along with the D_0 data of Laurent et al.[20] for 19 100 and 153 700 molar mass dextran/water, for which an appropriate small temperature correction has been made for viscosity change so that it can be compared with our 25.0 °C data. A plot of log D_0 vs. log M_w is shown in Figure 6 and it is clear, with the exception of the 10 500 molar mass anomaly, that all the data are consistent and obey a scaling relationship of the form of eq 7. The D_0 values for M_w > 10 500 daltons yield $D_0 \sim M^{-0.57(2)}$ and although too much significance should not be attached to the exponent in view of the poorly defined mass distributions, the dextrans apparently exhibit the behavior of random coils with excluded volume interactions.

The anomalous behavior of the 10 500 molar mass dextran is difficult to understand. Two features are significant in this regard. First, this sample is the most polydisperse according to our chromatography measurements. Second, the much narrower 19 100-dalton fraction used by Laurent et al. gave a diffusion coefficient at infinite dilution in good agreement with that suggested by the scaling extrapolation of the higher molar mass dextrans. We therefore believe the large polydispersity with consequent ensemble averaging breakdown is the major cause of the 10 500-dalton dextran anomaly. The average coil separation at any given concentration increases for decreasing molar mass. The

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low molar mass and large dispersity of the 10 500-dalton dextran may thus combine to distort ensemble averaging of the diffusion coefficient for this polymer. However, at higher concentrations in the dilute regime the averaging process would be aided by greater polymer–polymer proximity, and the fact that the higher concentration data extrapolate to D_0 and k_f values consistent with those of the higher molar mass dextrans reinforces this view.

The apparent molar mass independence of the friction coefficient k_f values is surprising. Of the theories that account for the value of k_f,[21-23] all predict a significant mass dependence. The only molar mass independent term in the theoretical expressions for k_f is the polymer specific volume, and this is an order of magnitude smaller than the observed k_f plateau.

However, the dextran k_f values are unique only in that the mass independence persists up to $M_w \simeq 5 \times 10^5$ daltons. Both King et al.[24] and ourselves[2] have observed a plateau in k_f values for polystyrenes of low M. In our own study of polystyrene in CCl_4 we found that the Yamakawa theory[21] gave an excellent description of the data for $M > 20\,000$ daltons but below this molar mass, the k_f values were constant at $\simeq 10^{-2}$ m^3 kg^{-1}, in contradiction with theory.

Acknowledgment. We thank Dr. Alex Mackay and Professor Robert Molday for valuable advice. The dextran diffusion measurements were performed in the laboratory of Professor Myer Bloom and we are indebted to him for his interest and support.

Registry No. Dextran, 9004-54-0.

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Quasi-Elastic Light Scattering by Polyelectrolyte Solutions without Added Salt

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ABSTRACT: Quasi-elastic light scattering experiments as a function of macromolecular concentration have been performed on aqueous solutions of sodium poly(styrenesulfonates) in the semidilute regime. Two different molar masses were investigated ($M_w = 6.5 \times 10^5$ and 12×10^5 g mol^{-1}). An effective diffusion coefficient was obtained from the dependence on the scattering angle of the first cumulant of the scattered light intensity autocorrelation function. For both samples of NaPSS three concentration regions could be observed. At very low concentrations, close to the critical concentration, D_{eff} was found to be practically concentration independent but with a lower value for the higher molar mass. It probably corresponds to D of a freely diffusing macromolecule. At higher concentrations D_{eff} was still molar mass dependent but decreased with increasing concentrations to very small values. An interpretation based on a reptation model has been tentatively proposed for the diffusion mechanism in that concentration range. When a certain concentration is reached, roughly corresponding to conditions where the correlation length in the solution is of the same order of magnitude as the (electrostatic part of the) persistence length of the macromolecular chain, a fast diffusion mechanism appears at the same time as the slow diffusion mode becomes nearly undetectable. The former seems to be characterized by a molar mass independent D_{eff}, but it has not yet been possible to establish whether or not D_{eff} in this concentration region increases with concentration. The exact nature of this probably cooperative diffusion mechanism could not be established.

Introduction

Polyelectrolyte solutions without added low molar mass electrolyte are quoted to belong to the category of physical systems the behavior of which is most difficult to understand. It has been widely accepted that a highly charged polyelectrolyte chain in such a solution and at very high dilution will be nearly fully stretched due to the strong electrostatic repulsion of the like charges along the macromolecular chain, which are only weakly screened. Under these conditions the polyelectrolyte can be represented as a rigid uniformily charged rod as has been used by Katchalsky[1] in his cell-model theory for salt-free polyelectrolyte solutions. This theory can fairly well explain the thermodynamic and some transport properties observed with such solutions at low concentrations. It is not suitable, however, to describe the concentration dependence

0024-9297/83/2216-0973$01.50/0