Dye Diffusion in Isotropic and Liquid Crystalline Aqueous (Hydroxypropyl)cellulose

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ABSTRACT: Fluorescence photobleaching recovery has been used to measure the self-diffusion of fluorescein dye in dilute and concentrated aqueous (hydroxypropyl)cellulose (HPC). The mobility decreases with the concentration of the semistiff HPC almost exponentially, independently of polymer molecular weight. Arrhenius-type temperature dependence is observed, and there is no dramatic change in the activation energy for dye diffusion as the lyotropic liquid crystalline phase is crossed. The decline in dye mobility with polymer concentration is considerably steeper than in several other systems where small probes or solvents were measured. Measurements by pulsed-gradient spin-echo NMR of *N*,*N*-dimethylformamide diffusion in solutions of an even more rigid polymer, poly(γ-benzyl α,L-glutamate), demonstrate that backbone stiffness is not responsible. Interaction between the dye and (hydroxypropyl)cellulose is one possibility. However, at low concentations the microviscosity sensed by the dye is comparable to the viscosity of water, which is inconsistent with strong binding. Neither is there evidence from steady-state or time-resolved fluorescence spectroscopy for strong dye–HPC interactions. Bound water surrounding the somewhat hydrophobic polymer is clearly evident from differential scanning calorimetry. Immobile water should enhance the obstruction created by the polymer, but the measured amount of bound water is insufficient to explain completely the steep decrease of diffusion with added polymer. The possibility of binding too weak to observe by fluorescence spectroscopy is considered, and an effective binding constant between dye and the polymer–water complex is estimated by combining the differential scanning calorimetry and dye mobility data.

I. Introduction

The transport of small molecules is a central theme in macromolecular problems of longstanding importance, such as plasticization, swelling, film drying, and viscoelasticity. Most studies have involved linear random-coil polymers. Solutions containing "rodlike" polymers, defined here as macromolecules with a backbone stiff enough to demonstrate a lyotropic liquid crystalline phase, have been examined[1-6] but not in great detail. The diffusers in most of these studies have been colloidal, and large decreases in their mobilities accompanied the large increase in macroscopic viscosity prior to the lyotropic transition. Less is known concerning smaller probes.

(Hydroxypropyl)cellulose (HPC) forms cholesteric liquid crystals in water at appropriate concentrations.[7-10] Although the transition from isotropic fluid to liquid crystal is poorly defined compared to more rigid and less polydisperse rods,[11-13] HPC has the substantial advantage of water solubility without polyelectrolyte effects. In the present study, fluorescence photobleaching recovery, FPR,[14-20] is used to measure the mobility of fluorescein anion dispersed in HPC solutions. The very wide concentration range includes both isotropic and liquid crystalline solutions, thereby enabling a direct assessment of the effect of the lyotropic transition on the transport of the relatively small probe.

II. Methods

The three samples of HPC purchased from Scientific Polymer Products are named according to the manufacturer's reported molecular weight—e.g., HPC-60 000 for the sample with reported M = 60 000. The vendor claims a molar substitution, MS, of $\approx$3.5 propyl groups/anhydroglucose unit, but this does not agree with our own measurements (see below). Table I shows molecular characterization data from static light scattering measurements performed in our laboratory.[21] HPC-60 000 shows some signs of aggregation in water, so the measured molecular weight is in poor agreement with the manufacturer's value. The disodium salt of fluorescein was purchased from Aldrich and used as received. Partial specific volumes, $\bar{v}_2$, of HPC were determined at temperatures from 5 to 40 °C in 5 °C intervals, using a Mettler DMA/02D densitometer calibrated with dry air. For these measurements, HPC-60 000 was used at weight fractions $w_{HPC} \equiv w_2$ up to 0.03, without observing any concentration dependence in $\bar{v}_2$. Viscosity hampered attempts to measure $\bar{v}_2$ at higher concentrations and molecular weights, so the values obtained in the stated ranges were applied to compute volume fractions of HPC, ϕ_2, assuming volume additivity and molecular weight independence. Volume fractions calculated using the densities reported[22] for HPC in water were similar.

All samples for FPR measurements were prepared by weighing together HPC and aliquots of aqueous stock solutions of disodium fluorescein. The dye concentration in the final solutions was $\approx$1 mM. During steady-state fluorescence spectroscopy measurements, the final dye concentration was held at 3 μM, resulting in an absorbance of 0.1 in 1-cm-path-length cells at the absorption maximum, 470 nm. Bacterial degradation of the polymer was prevented by addition of NaN_3 in trace amounts. The HPC solutions were allowed to equilibrate (up to several months) prior to measurement; time-dependent behavior was not encountered. Most samples were loaded into rectangular glass cells (Vitro Dynamics) having a path length of 100 μm and flame sealed. Extremely viscous samples at high concentrations were placed on microscope slides with cover slips which were sealed around the perimeter with silicone grease. The temperature was maintained to $\pm$0.5 °C by a circulating water bath.

All the FPR experiments were of the pattern photobleaching type.[16-20,23] A striped pattern of period L was produced in the

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Table I
HPC Characteristics

sample code	$M_w \times 10^3$	R_g/nm	A_2/(mL mol g^{-2})
HPC-60 000	≈130	≈32	slightly negative
HPC-300 000	292 ● 30	63.0 ± 3	(4.0 ± 0.2) × 10^{-4}
HPC-1 000 000	855 ● 90	124 ± 34	poorly determined

sample by illuminating a Ronchi ruling (Edmund Scientific) held in the rear focal plane of a modified[21,23] Olympus BH-2 epifluorescence microscope. The source was a Lexel 3000 argon ion laser producing ≈1.5 W at 488 nm. Intensity shifting was accomplished with an acousto-optic modulator (Newport No. 35085-3) and matching modified digital controller with a diffraction efficiency of 86% and contrast of ≈2000 (optionally, >10 000). The fluorescent signal was detected by EMI9862 or RCA7265 photomultipliers, which were protected by an electronic shutter during the photobleaching pulse, and connected via a Pacific Precision Model 126 photometer to a 12-bit analog/digital converter residing in the IBM PC/AT computer used to synchronize the experiments. A variety of grating constants, $K = 2\pi/L$, were available by changing Ronchi rulings and microscope objectives. Modulation detection[19,20] was not used during these measurements but has since been added. Its advantages are not significant for rapid, single diffusers, and it requires slightly more work to vary the grating constants over a wide range. Additional details of the instrument are available.[21,23]

An important step to explore the presence or absence of dye–HPC interaction required dye-labeled (hydroxypropyl)cellulose (LHPC). HPC-60 000 and -300 000 were labeled with fluorescein isothiocyanate (FITC; Sigma). One dye molecule, at most, was attached to about every seventh HPC chain for labeling HPC-60 000. The dye–polymer chain ratio was ≈1:1 for HPC-300 000. Labeling simply involved dissolving HPC and FITC in acetone and allowing the reaction to run for 3 days, after which *n*-heptane (Mallinkrodt) was added to the bright greenish-yellow solution to precipitate the polymer. The supernatant was decanted. The precipitate was air-dried, followed by >24 h at 40 °C in a vacuum oven. The labeled polymer was then redissolved in water and dialyzed (using Spectrum membrane tubing, 12 000–14 000 MWCO) for about 5 days to remove free dye. The water in the stirred cell was changed periodically. Dialysis removed some, if not all, of the unattached dye and/or low molecular weight HPC as indicated by the yellow color of water outside the dialysis membrane. This implies that even fewer HPC chains were labeled than the stoichiometry predicts. The polymer was precipitated and dried as described above. Diffusion at concentrations <1% was 25–45 times slower than free dye at similar HPC concentrations, confirming that the polymers were fluorescently labeled.

Stiffness is a distinguishing characteristic of HPC, but there are certainly stiffer polymers. To gauge the effects of rigidity, solvent diffusion measurements were conducted in solutions of the very stiff polymer poly(γ-benzyl α,L-glutamate) (PBLG). This polymer was purchased from Sigma and used as received. As with HPC, the nomenclature specifies the manufacturer's claimed molecular weight. The solvent was anhydrous *N*,*N*-dimethylformamide (DMF) from Aldrich. Pulsed-gradient spin-echo (PGSE) NMR was used to monitor the diffusion coefficient of DMF. The equipment and procedure have been described elsewhere.[24] These measurements were limited to the isotropic phase and conducted at only one temperature, 40 °C.

Steady-state fluorescence measurements were made in an SLM 8000 photon-counting spectrofluorometer with single excitation (4-nm bandpass) and emission (8-nm bandpass) monochromators set at 470 and 520 nm, respectively. Anisotropic effects in intensity measurements were eliminated by using magic-angle polarizers, which were set to 55° on the excitation side and 0° on the emission side to avoid the Wood's anomaly of the emission grating. Fluorescence emission was measured in the ratio mode, and background fluorescence from an HPC solution without fluorescein was subtracted. Each data point was acquired for five 10-s time intervals, and the values were averaged. The temperature was controlled at 25 ± 0.05 °C by a water bath. Emission anisotropy r was calculated from $r = (F_{VV} - GF_{VH})/(F_{VV} + 2GF_{VH})$, where the first and second subscripts refer to the orientation of the excitation and emission polarizers, respectively (V = 0°; H = 90°), and $G = F_{VH}/F_{HH}$ is an instrumental correction factor.[25] Fluorescence decay measurements were made at 25 °C on a time-correlated single-photon-counting instrument described elsewhere.[26] Samples were excited at 296 nm using the frequency-doubled output of a synchronously pumped rhodamine 6G dye laser. Fluorescence emission was detected at 522 nm (8-nm bandpass). Polarized fluorescence decays were collected in 1024 channels of 4.4, 8.8, and 9.7 ps/channel to about 3×10^4 counts in the peak. A wedge-type depolarizer was placed between the emission polarizer and the monochromator so that $G = 1$. The polarized decays were analyzed by the Beechem global program,[27] adapted for reference deconvolution. The assumed decay functions were $F_{VV}(t) = (1/3)i(t)[1 + 2r(t)]$ and $F_{VH}(t) = (1/3)i(t)[1 - r(t)]$, where $i(t) = \sum_i \alpha_i \exp(-t/\tau_i)$ is the intensity decay, with α_i and τ_i representing amplitudes and lifetimes, respectively, while $r(t) = r(0)\exp(-t/\Phi)$ is the anisotropy decay with rotational correlation time, Φ. Fluorescein in water was used as a reference fluorophore. Its lifetime was fixed at a value of 3.9 ns determined in separate experiments with 30 ps/channel. Anisotropy data for fluorescein at pH 7–8 in the absence and presence of HPC were deconvolved simultaneously with the constraint that the lifetime and $r(0)$ values be the same for all the decay curves. Testing various decay laws for $i(t)$ and $r(t)$ produced no evidence for much more than one lifetime or rotational correlation time in any sample.

Solutions of varying polymer content were prepared for differential scanning calorimetry on a Seiko DSC 220C by dissolving HPC-300 000 in water with a trace of NaN_3 added as a preservative. Weight fractions >0.4 were achieved by evaporation. The equilibration time exceeded 6 months. Small aliquots, <25 μg, were loaded into hermetically sealable aluminum pans designed for liquid samples. Various reference samples were tried; the most successful was an empty, sealed pan. The pans were weighed before and after the experiment to check for leaks. When measuring the demixing transition that occurs slightly above 40 °C, the temperature was raised at 1 °C/min from 5 to 95 °C with a sampling time of 0.5 s. Repeat runs were performed on each sample. The samples were rapidly quenched to the starting temperature between runs. When measuring the heat of fusion of water, the temperature was ramped at 2.5 °C/min from −35 to +25 °C. Repeat runs were again performed, even though the precision associated with this high-enthalpy transition was much better than that for the demixing transition.

III. FPR Data Analysis

A typical FPR trace appears in Figure 1a. Figure 1b shows the recovery expressed as a decay of the intensity perturbation, using three different analyses described in detail elsewhere.[21,23] "Halfway" assumes the intensity will return from its initial depression halfway back to be prebleach level, as expected from the 50% duty cycle of the Ronchi ruling. In this case, the bleach depth must be determined accurately by polynomial fitting of the first few recovery points. In "last 10" analysis, the final intensity is assumed equal to the average of the last 10 measured points. "Slant" analysis allows for the spot recovery mode—i.e., the slow, nonexponential recovery that occurs if no Ronchi ruling is used at all.[14,15] The spot recovery mode is typically >50 times slower than the desired interfringe recovery mode, depending on the number of stripes illuminated. Its rate can be estimated from a linear fit to the last 10–30 data points. As shown in Figure 1b, the three analyses were usually fairly consistent. Slant analysis, highlighted in semilogarithmic form in Figure 1c, yielded slightly more stable results during repetitive measurements and was generally used.

Each diffusion coefficient is the result of 15–20 separate measurements spread among several K values. Figure 2 plots the recovery rate, Γ, vs K^2 for several concentrations of HPC-1 000 000 at 30 °C. The intercepts are all zero within the error of the experiment, and there is no difficulty identifying diffusion coefficients to a precision of 3–10% from the slopes.

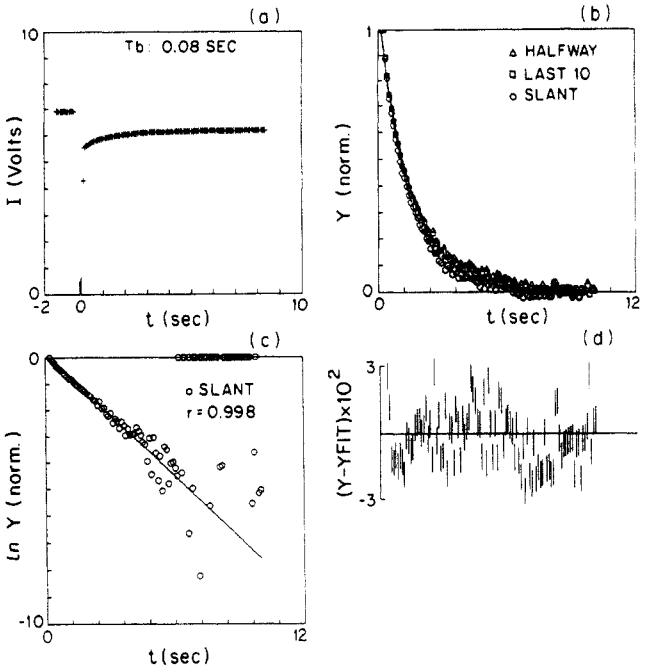

Figure 1. (a) Representative FPR raw data for a fluorescein anion in HPC. T_b is the duration of the photobleaching pulse. (b) Intensity recovery data from (a), normalized and rearranged to represent a decay in the perturbation caused by photobleaching. Three different curves can be drawn, depending on base line; see text. (c) Semilogarithmic plot, using the "slant" (see text) fitting method; r is the linear correlation coefficient of the fit. (d) Uncertainty of measurement for the slant fit; the abscissa is the same as in (b). Error bars are established empirically, the distance from the center of the bar to the horizontal line of zero error represents the closeness of fit.

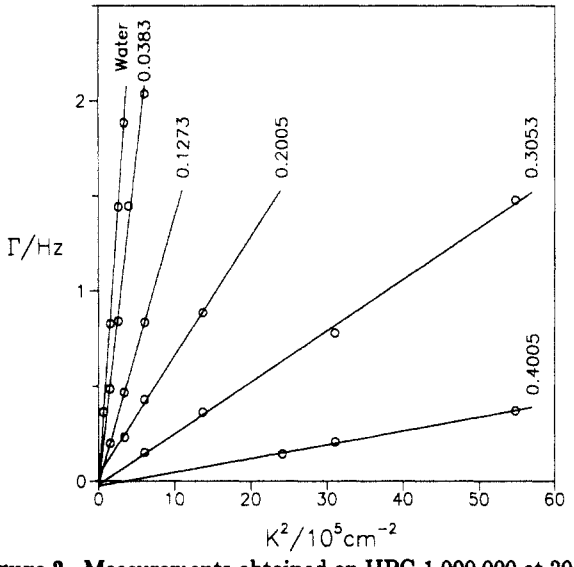

Figure 2. Measurements obtained on HPC-1 000 000 at 30 °C demonstrating the typical linear relationship between average recovery rate and K^2, from which all diffusion coefficients were obtained. The numbers refer to individual HPC concentrations; some concentrations are not shown to prevent crowding.

IV. Results and Discussion

IVa. Dye Diffusion in Water. The measured diffusion coefficient of dye in pure water, D_0, was $(5.5_4 \pm 0.2) \times 10^{-6}$ cm²/s at 30 °C. The rapid rotational diffusion of the dye (see below) ensures that it may be treated as an effective sphere with a Stokes' hydrodynamic radius, $R_h = 0.50_2 \pm 0.01_4$ nm. In a previous study at 25 °C, we reported $D_0 = (5.1 \pm 0.2) \times 10^{-6}$ cm²/s.[23] The corresponding hydrodynamic radius, 0.48 ± 0.02 nm, is within experimental uncertainty of the present value at 30 °C. Indeed, there is no systematic temperature variation of R_h with temperature.[21] Ware and co-workers have thrice reported diffusion coefficients of a fluorescein anion in water at 25 °C, obtaining $(6.3 \pm 0.5) \times 10^{-6}$,[28] 6.4×10^{-6},[29] and 5.2×10^{-6} cm²/s[30] (R_h = 0.39–0.47 nm).

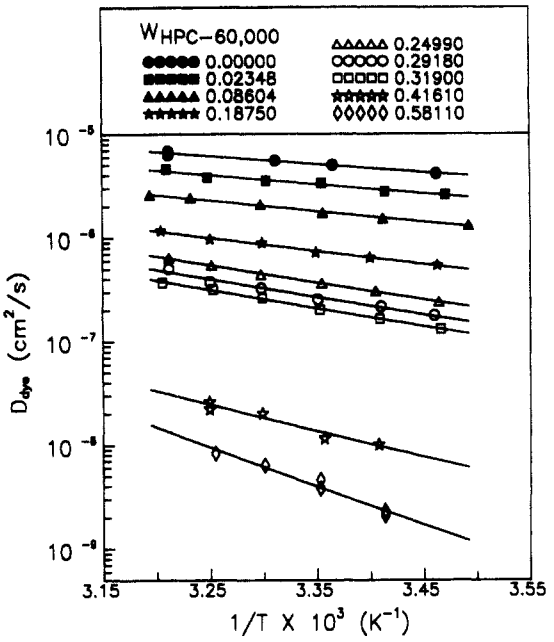

Figure 3. Arrhenius-style plot for fluorescein anion in HPC-60 000, at various weight fractions as shown in the legend. Also included is a portion of the data obtained on diffusion in pure water.

IVb. Activation Energy for Diffusion. The dye diffusion coefficient in pure water, D_0, was measured at temperatures, T, between 15 and 70 °C. As shown elsewhere,[21] the data approximately obey an Arrhenius relation, $D_{dye} = D'e^{-E_{dye}/RT}$, where R is the gas constant, D' is the apparent dye diffusion coefficient in the limit of infinite temperature (≈4×10^{-3} cm²/s), and E_{dye} is the apparent activation energy (4.0 ± 0.2 kcal/mol). The activation energy is comparable to the hydrogen bonding energy of water[31] and about 50% larger than the activation energy for toluene self-diffusion.[32] In HPC-60 000 solutions, dye diffusion was measured at ≈5 °C intervals from 15 to 40 °C at concentrations from 2 to 58% (w/w). The demixing transition to a gel or precipitated state, depending on concentration, occurs at ≈42 °C, accompanied by very high turbidity[7,33,34] that interferes with FPR measurements. (Note: FPR measurement in clear gels is possible.[23]) The results over the restricted temperature range are displayed as an Arrhenius plot in Figure 3, together with a subset of the data for dye in pure water for comparison. E_{dye} increases with w_{HPC}, as shown in Figure 4. The preexponential factor D' also increases monotonically with concentration.[21] There are no pronounced discontinuities in either quantity as the lyotropic liquid crystal boundary is crossed.

IVc. Comparison to Other Systems and the "Universal" Curve. There seems to be no other studies where a small probe's mobility is traced through a lyotropic polymer liquid crystal transition. However, it is illuminating to compare the present results to random-coil solutions. Dye diffusion coefficients normalized to D_0 are plotted against w_{HPC} in Figure 5 for all three HPC samples at 30 °C. The retardation of dye by HPC closely approximates an exponential form. The absence of a molecular weight effect is reasonable, notwithstanding the enormous difference in macroscopic solution viscosities, because of any of these polymers is relatively stationary

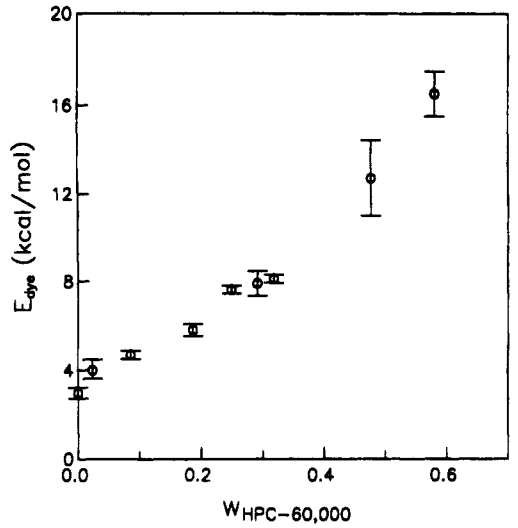

Figure 4. Apparent energy of activation for diffusion of fluorescein anion in HPC-60 000. The error bars represent the standard deviations in the linear fits used to obtain E_{dye} from Arrhenius plots similar to Figure 3.

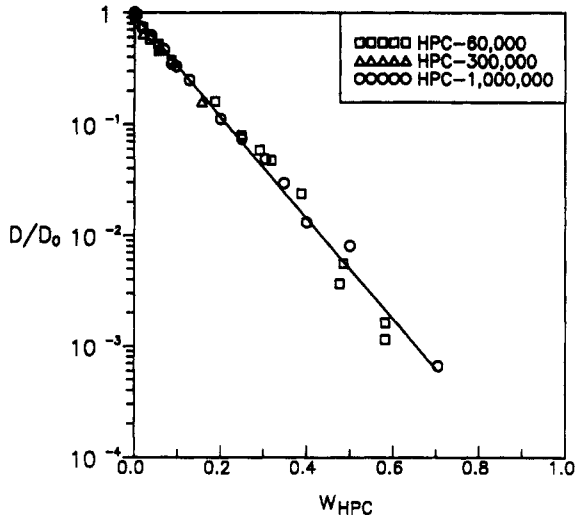

Figure 5. Diffusion coefficient of a fluorescein anion at 30 °C which decreases with w_{HPC} independently of molecular weight. See text.

compared to the dye probe. It suggests that the activation energy trend in Figure 4 for HPC-60 000 should be similar at other molecular weights.

The reduction of dye diffusion may arise from either physical or chemical effects. From a purely physical viewpoint, one might assert that molecular details of the probe, solvent, and polymer are unimportant for a diluted system where the polymers are effectively immobile on the time scale of diffusers, in the absence of specific probe–polymer interactions, and at temperatures exceeding that of the glass transition. The principal factor would then be the polymer volume fraction, ϕ_2. In this spirit, Figure 6 combines the present results with data on other systems. The nomenclature specifies, in order, probe/matrix/solvent. Diffusion of hexafluorobenzene in polystyrene/tetrahydrofuran (C_6F_6/PS/THF) was studied by von Meerwall et al.[35] using PGSE NMR. The solvent self-diffusivities for the toluene/polystyrene (Tol/PS/Tol) system of Pickup and Blum[32] were also measured by the same technique. Landry et al.[36] used forced Rayleigh scattering to measure the diffusivities of three different photochromic dyes through solutions of polystyrene and polyisoprene in tetrahydrofuran. Only their methyl red/polystyrene/tetrahydrofuran (MR/PS/THF) results are shown. The normalized diffusion coefficients of these

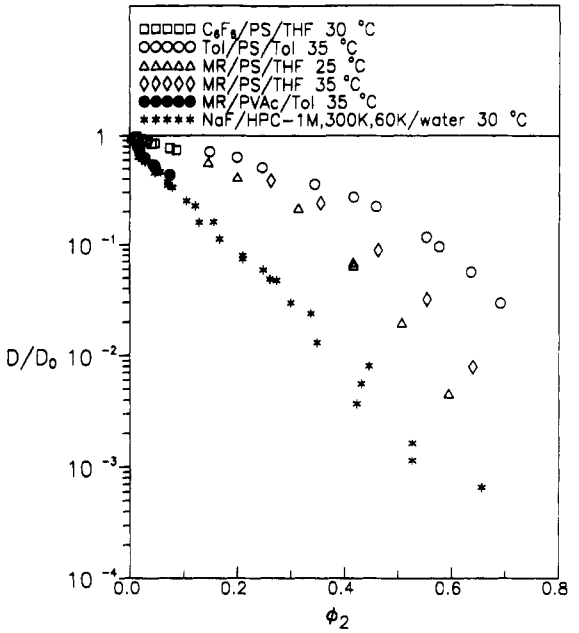

Figure 6. Diffusion coefficients normalized to values in the absence of polymer plotted against polymer volume fraction for several systems. See text. The code specifies probe/matrix polymer/solvent. NaF represents disodium fluorescein.

Table II
D/D_0 (±5–10%) for *N,N*-Dimethylformamide in Isotropic Poly(benzyl glutamate) Solutions at T = 40 °C

PBLG-28 000		PBLG-110 000		PBLG-210 000	
ϕ_{PBLG}	D/D_0[a]	ϕ_{PBLG}	D/D_0[a]	ϕ_{PBLG}	D/D_0[a]
0.0429	1	0.013 14	1.01	0.011 82	1.01
0.1390	0.76	0.034 63	1.00	0.027 64	0.97
		0.045 46	1.02	0.044 35	0.98
		0.080 43	0.92	0.093 66	0.82
		0.075 50	0.82	0.119 05	0.77
		0.109 75	0.81	0.139 52	0.68
		0.121 68	0.76		

[a] $D_0 = 2.2_7 \times 10^{-5}$ cm^2 s^{-1} (±5%).

several systems fall on nearly the same curve, especially at lower concentrations.

The physical viewpoint is indeed supported by the observation that several chemically different systems follow a "universal" D/D_0 curve. However, the present system clearly displays a more rapid decrease. Appearing in Table II are data for a system, DMF/PBLG/DMF, containing a very stiff polymer. These lie on (or perhaps even slightly above) the universal curve, with an apparent plateau at $D/D_0 \approx 1$ when $\phi_{PBLG} < 0.05$. This result, which is in agreement with an independent study on this same system,[37] indicates that rod stiffness itself will not account for the rapid decrease in diffusion observed in aqueous HPC. In fact, the fluorescein/HPC/water system resembles methyl red/poly(vinyl acetate)/toluene (MR/PVAc/Tol)[38] (Figure 6) for which specific hydrogen bonding between the MR dye and PVAc was postulated to explain the "nonuniversal" behavior. Therefore, a battery of fluorescence spectroscopic tests was applied to determine whether dye binding to HPC might be responsible for the steep decline in diffusivity.

The fluorescence lifetime of the dye is about 4 ns in the presence or absence of HPC; see Table III. The monoexponential intensity decay indicates a single emitting species. The fluorescence intensity fluctuates ±5%, with no significant trend, as $w_{HPC-1\,000\,000}$ is varied; see Figure 7. In the same figure, the anisotropy r measured at 470-nm excitation increases slightly with HPC concentration but remains <0.02, compared to a limiting value in the

Table III
Time-Resolved Fluorescence Data

	τ/ns[a]	Φ/ps[b]	r_0
dye/H_2O	4.2	35 ± 15	−0.20
dye /0.25% HPC/H_2O	4.2	60	−0.20
dye/0.5% HPC/H_2O	4.2	90	−0.20
LHPC/H_2O	3.9	2200	−0.07

[a] Error estimated at ±5%; τ was independent of pH from 7 to 11. [b] Error estimated at ±30%.

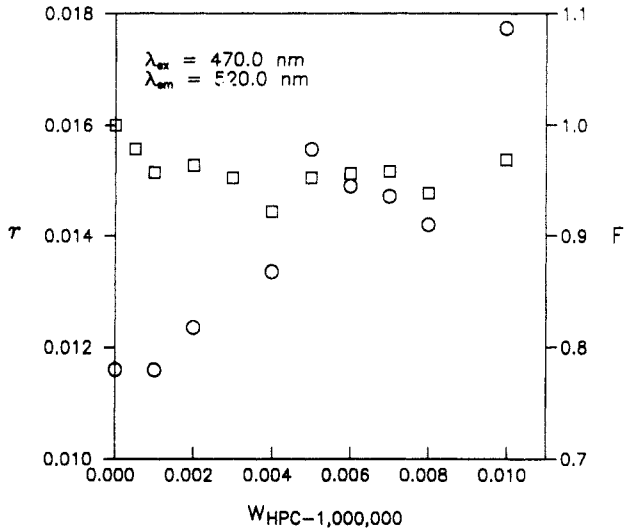

Figure 7. Fluorescence intensity divided by that in pure water (□). Steady-state fluorescence anisotropy of fluorescein anion in aqueous HPC-1 000 000 (○).

absence of rotation of 0.34.[39] Such low r values suggest that the dye is not seriously detained by any specific interaction with the polymer. The very short rotational correlation times (Table III) are near the temporal resolution of the instrument, and identical in the presence or absence of HPC, within the substantial uncertainty. Thus, the anisotropy decay $r(t)$ measured at 296-nm excitation shows that the rotational diffusion of the dye is not affected by polymer. The limiting anisotropy $r(0) = -0.20$ indicates that the absorption and emission dipoles are perpendicular at this excitation wavelength.

To explore the possibility that dye might be bound to HPC but still exhibit high mobility due to rapid chain motion, covalently attached dye was studied. The two labeled HPC's gave r values at 470-nm excitation of 0.084 ± 0.004. This is several times greater than the values observed for dye dispersed in HPC solutions but still far from the limiting anisotropy at 470-nm excitation. Thus, dye in solution is much less restricted than covalently attached dye. The covalently attached dye also has a single-exponential fluorescence decay. The lifetime is the same as Dye/H_2O or Dye/HPC/H_2O, but the rotational correlation time is increased ≈40-fold (Table III).

Limited information about dye–polymer interaction is available by varying the dye concentration in FPR experiments. Consider the reaction between free dye (F) and polymer repeat units (P), resulting in a bound complex (B): $fF + pP \rightleftharpoons bB$, where f, p, and b are stoichiometric coefficients. The appropriate equilibrium constant is K_{eq}. Let the fraction of free dye be x_F. The time scale of all FPR measurements is seconds or greater, so any weakly bound dye almost certainly exchanges with the solution during the course of measurement. Then only a single, average diffusion coefficient will be measured: $D = x_F D_F + (1 - x_F)D_B \approx x_F D_F$ where D_F and D_B represent the diffusion coefficients of free and polymer-bound dye, respectively. If $f = p = b = 1$, then $D \approx D_F(K_{eq}[P] + 1)^{-1}$, where [P] is the molar concentration of repeat units. Thus, experiments conducted at constant polymer concentration should be independent of molar dye concentration [F], indistinguishable from the case $K_{eq} = 0$. If $f > 1$, then D decreases with [F] at constant [P]. Experiments were conducted in 2.2% HPC-300 000, 1.1% HPC-60 000, and pure water, varying the dye concentration from 10^{-5} to 10^{-2} M in each case. In water and 1.1% HPC-60 000, there was no discernible trend, while in 2.2% HPC-300 000 D was constant within uncertainty up to $\approx 10^{-3}$ M dye, declining by about 25% at $\approx 10^{-2}$ M dye, where the color changed from the characteristic green-yellow to brown-green and photobleaching became difficult. Experiments at high dye content were less precise than at the intermediate dye concentrations used throughout the rest of the study. The 25% reduction seen for 2.2% HPC-300 000 is just a little beyond the population standard deviation based on repeat experiments—and perhaps within a more conservatively estimated uncertainty that includes systematic error. A really significant reduction would imply that K_{eq} is not strictly zero, but it would also demand that $f > 1$. In summary of these and the steady-state and time-resolved fluorescence experiments, there is no case for strong dye–polymer interactions. Before considering other chemical effects that could diminish diffusion, and in preparation for trying to handle them, we introduce some commonly used models based on purely physical assumptions.

IVd. Comparison to Physical Models. Theories devised to describe the diffusion of small molecules in gels[40,41] should be equally applicable for large, slowly moving polymer matrices. Obstruction, increased hydrodynamic drag, and alteration of solvent properties have all been considered. One of the most widely used obstruction theories is that of Fricke,[42] originally developed to treat electrical conductivity in a suspension of nonconducting objects. Translated to the present problem, the result is[40,43]

$$D/D_0 \approx 1/(1 + \phi_2/\chi) \quad (1)$$

where the form factor, χ, depends on the shape and orientation of the polymer. The expression represents an upper bound to the diffusion of small molecules impeded by spheres.[40,44] The χ values lie between 2 for spheres and 1.5 for rods perpendicular to the transport direction; for randomly oriented rods, $\chi \simeq 1.67$.[40,41] For subsequent analysis, $\chi = 1.5$ was used; this produces the maximum retardation effect.

The model of Mackie and Meares[45] considers the diffuser traveling through a cubic lattice, the sites of which are occupied by polymer segments. The blocked molecule must jump to a nearest-neighboring site for diffusion to take place. The size of the impenetrable barriers is assumed to be very small. The overall obstruction is evaluated in terms of the probability of the polymer segments occupying the sites, and the result is

$$D/D_0 = (1 - \phi_2)^2/(1 + \phi_2)^2 \quad (2)$$

A recent model by Phillips and Jansons[46] treats the case of randomly suspended, aggregated (or structured) rods. As HPC's side chains are much shorter than the side-chain-branched proteoglycans for which the model was designed, the most appropriate of several expressions given may be the one for simple cylinders:

$$D/D_0 = 1 - (5/3)\phi_2 \quad (3)$$

At small ϕ_2, the treatment of Lauffer[41] yields the same result. Figure 8 shows that all of these models predict

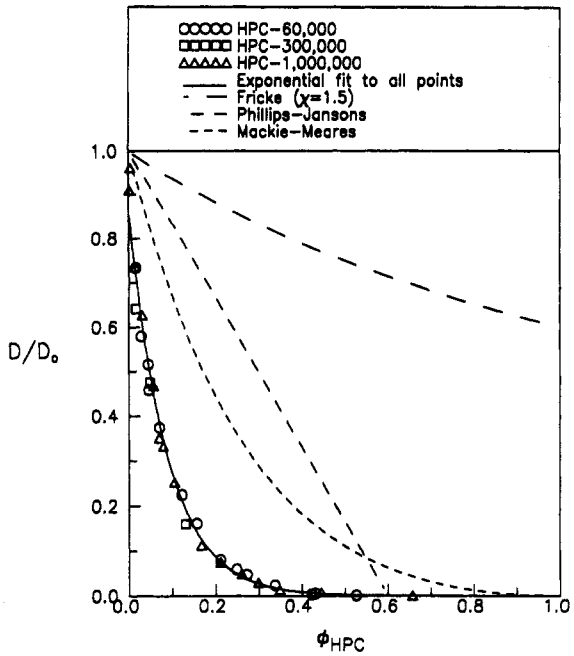

Figure 8. Present results at 30 °C compared to models by Fricke (for rods), Mackie and Meares, assuming a stationary matrix, and Phillips and Jansons.

more rapid diffusion than is found experimentally for dye/HPC/water.

IVe. Insights from Differential Scanning Calorimetry. It has been established that dye diffusion in aqueous HPC decreases more steeply with polymer concentration than in most random-coil solutions and also faster than the physical models suggest. There is no evidence for strong dye binding to the polymer. The DMF/PBLG/DMF results show that stiffness itself is not a factor, unless there is some difference in the ability of dye and solvent to avert the polymer segments. Preliminary measurements in this laboratory of an organophilic dye/helical poly(alkyl glutamate)/solvent system suggest that no such difference exists. In devising an explanation for the behavior of fluorescein anion in aqueous HPC, it is important to recall two characteristics of the polymer: (1) HPC is soluble in a truly amazing array of liquids, from water to moderately polar organic reagents; and (2) demixing occurs on heating aqueous HPC solutions.[7,33,34] These observations are consistent with a partially hydrophobic polymer, stabilized in aqueous environments by hydrogen bonding to a shell of "bound" water.[7,47] The disruption of this layer at high temperatures leads to demixing. The enhanced ability of HPC to retard dye diffusion might then be attributed to the inaccessibility of the dye not just to the polymer but also to its bound water layer. The measured dye diffusion coefficients can be made to agree with the Mackie and Meares model and, approximately, with the universal curve if the "obstruction" volume fraction of HPC, defined as the volume fraction unavailable to dye, is $\approx 3\phi_2$. If HPC can be modeled as a semiflexible cylinder, this corresponds to an effective diameter increase of about 70%. It remains to determine whether this much water is bound.

Using a very sensitive solution calorimeter, Robitaille et al.[47] showed that the transition enthalpy per unit mass HPC was a linearly decreasing function of polymer concentration, reaching zero at the weight fraction, w'_{HPC}, where a single phase liquid crystalline sample can no longer spawn a concentrated isotropic phase by a nearly athermal liquid–liquid phase separation.[47] Our results (Table IV) are similar. Extrapolated to $w_{HPC} = 0$, the demixing

Table IV
Calorimetry Results for HPC-300 000

w_{HPC}	temp/°C[a]	ΔH_{demix}/(cal/g_{HPC})	$\Delta H_{f,water}$/(kcal/g_{HPC})
0.046	42.0 ± 0.1	5.80 ± 0.30	1.608 ± 0.014
0.061	41.9 ± 0.2	6.12 ± 0.27	1.218 ± 0.014
0.094	42.3 ± 0.2	5.29 ± 0.10	0.672 ± 0.002
0.140	43.0 ± 0.0	4.81 ± 0.70	0.423 ± 0.000
0.180	42.6 ± 0.1	4.33 ± 0.17	0.313 ± 0.002
0.231	42.5 ± 0.1	4.26 ± 0.24	0.225 ± 0.003
0.314	41.8 ± 0.0	4.14 ± 0.05	0.126 ± 0.001
0.348	40.9 ± 0.0	3.80 ± 0.02	0.110 ± 0.001
0.398	41.0 ± 0.1	3.30 ± 0.10	0.075 ± 0.000
0.469	39.8 ± 0.1	2.22 ± 0.05	0.062 ± 0.000
0.550	40.5 ± 0.3	1.46 ± 0.02	0.056 ± 0.000

[a] Intersection of tangents drawn to "base line" and "peak" regions of DSC trace. The first deflection of the base line differs increasingly from this value as HPC content increases.

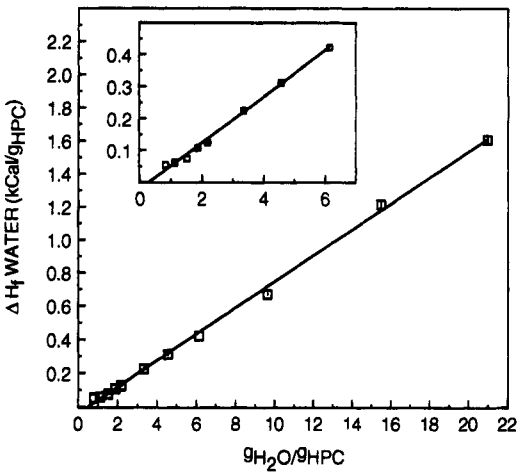

Figure 9. Enthalpy of fusion, per gram HPC, against water/HPC mass ratio. See text. These data are derived from heating cycles. Similar results were obtained from the cooling cycles.

transition enthalpy reached a maximum of ≈6.31 cal/g of HPC, to be compared to 6.55 cal/g in ref 47. It is noteworthy that one of the objectives of ref 47, use of calorimetry to determine MS, can be met with a standard calorimeter. On the basis of the transition temperature, ≈43 °C, the MS of our samples is ≈5.5 propyl groups per anhydroglucose unit[47]—considerably higher than the manufacturer's claim. This corresponds to a mass of about 480 g/mol of anhydroglucose unit, so the transition enthalpy is about 3.1 kcal/mol of anhydroglucose. Although this is the energy equivalent of 1–2 mol of water–water H-bonds,[31] the actual number of bound water molecules is greater because some of the energy input to displace water is recovered by formation of interpolymer H-bonds in the demixed state (presumably at $w'_{HPC} \approx 0.7$ if equilibrium is reached).

In order to estimate the amount of water bound to HPC, the heats of water fusion can be plotted[48] as shown in Figure 9, where g_{HPC} and g_{H_2O} respectively represent the mass of HPC and water. The slope, 78.4 cal/g, is in fair agreement with the known value for water fusion, 79.8 cal/g. The amount of water bound to HPC and therefore not available for freezing can be computed from the x-axis intercept. There are some uncertainties at the highest polymer concentrations, but a conservative estimate of all errors yields 0.4 g of water bound/g of HPC (±25%). At a mean substitution of 5.5, this corresponds to almost 11 water molecules bound per anhydroglucose unit, or about two per hydroxyl group. The increase in the effective volume can be approximated from solvent density and polymer specific volume. The volume of the polymer with bound water exceeds that of polymer alone by a factor H

≈ 1.5—far short of the 3-fold increase in the effective polymer volume fraction required to bring our results into compliance with the universal curve. The finite size of the dye may contribute some excluded volume also, although this appears not to be factor in dye/random-coil studies (Figure 6). In summary, there is certainly more evidence for bound water than for bound dye, but the amount is probably not large enough by itself to account for the strong retardation of dye diffusion with HPC.

IVf. Other Models and Dye Binding Revisited. Yam et al. have developed a model in which the polymer is surrounded by a region with high local viscosity.[49] With its short-chain branched structure, HPC seems a natural candidate for this type of interpretation even in the absence of the bound water—either due to steric hindrance or as a result of hydrodynamic interaction with the side chains. The previously mentioned model of Phillips and Jansons[46] also accommodates a diffuser that exhibits limited but finite mobility within the obstruction. This is a smooth cylinder model, and the volume fraction is specified geometrically. Therefore, if the probe exhibits partial mobility within the obstruction, the result is faster, not slower, diffusion. This model might be appropriate to smooth, semipermeable cylindrical obstructions whose diameter greatly exceeds that of the dye probe, but not to the present system. The model of Jonsson et al.[50] allows for penetration of the side chains by the diffuser. Olayo and Miller[37] presented simplified expressions for rods with extended side chains based on this model and had reasonable success modeling solvent diffusion in PBLG solutions. However, an arbitrary function had to be applied to the expressions to bring them into complete compliance with the data. The irregular side-chain character of HPC would further complicate the use of this model.

It is difficult to distinguish these models from very weak dye binding, driven by the high HPC concentrations and inaccessible to fluorescence spectroscopy. Perhaps such a weak interaction is the significance of the slight increases of Φ and r with HPC concentration in Table III and Figure 7, respectively. A realistic model for dye diffusion in aqueous HPC must include solvent–polymer binding, weak dye–polymer interaction, and/or other phenomena, as discussed in the preceding paragraph, that can be treated with an effective binding constant. In section IVc, we considered the equation $D \approx D_F(K_{eq}[P] + 1)^{-1}$ for the case of a one-to-one reaction between the free dye and polymer repeat unit, which we take as the substituted anhydroglucose unit. The molar concentration [P] may be converted to ϕ_2 using $\bar{v}_2$ (≈ 0.8 mL/g[21,22]) and the monomer molecular weight, M_0 (≈480; see above). Then ϕ_2 is increased in the obstruction terms for D_F by the factor H, representing the bound water. If the Mackie–Meares model is used for D_F, the resulting expression is

$$D/D_0 \approx \frac{(1 - H\phi_2)^2}{(1 + H\phi_2)^2}\left[1 + K_{eq}\left(\frac{1000\phi_2}{M_0\bar{v}_2}\right)\right]^{-1} \qquad (4)$$

In the absence of a bound water effect (i.e., if $H = 1$), then the data on dye/HPC can be fit with K_{eq} = 5–10 M^{-1}. If H = 1.5, as suggested by the DSC data, then K_{eq} = 3–5 M^{-1}. Given these low equilibrium constants, perhaps it is not surprising that time-resolved and steady-state fluorescence measurements were unable to detect a binding effect; at the concentrations used during the fluorescence measurements, bound dye would be less than 10% of the total. Within the limitations imposed by the Mackie–Meares model, or its extension to systems with bound solvent as represented in eq 4, FPR, which can operate well at high polymer concentrations, is a very sensitive probe for weak interactions.

IVg. Free Volume Considerations. Free volume theory is remarkably successful in accounting for diffusion of small probes or solvent molecules in random-coil solutions,[51–63] even fairly dilute ones. Its validity for rigid polymers is doubtful, but with flexible side chains and a persistence length of only ≈10 nm,[64,65] HPC is not truly rigid. Therefore, an interpretation following the simple Fujita approach, as recently exemplified by Landry et al.,[36] appears as supplemental material. Very briefly, it was found that the free volume parameters were sensitive to whether they were determined for low or high concentrations, with the boundary coinciding approximately with the liquid crystal transition. Depending upon which choices one makes in data anlaysis, the free volume theory can appear effective or ineffective in fitting the data. The question of its applicability to side-chain-substituted rodlike polymers remains open.

V. Summary and Conclusions

The diffusion coefficient of fluorescein anion decreases exponentially with HPC content, independently molecular weight. Neither diffusion nor apparent activation energy is altered markedly by the liquid crystalline transition. Identification of the biphasic regime, where isotropic and liquid crystalline phases usually coexist as a fine suspension, is more ambiguous in aqueous HPC than in polypeptide liquid crystals. Perhaps the broader transition obscured any sudden changes. It is probable that our measurements at high concentrations have averaged over biphasic states, and various orientations of liquid crystalline regions, because the domain sizes typically were smaller than the illuminated region. It is noteworthy that the error bars are larger at high concentrations than at small (see, for example, Figure 4). The poorer reproducibility in liquid crystalline and biphasic solutions may trace to either domain concentration or orientation effects.

The case for dye–polymer interaction is much less compelling than that for water–polymer binding, the only real evidence being failure of the dye diffusion to match the universal curve. Nevertheless, bound water cannot account for all the unusually steep retardation of dye diffusion. An adaptation, eq 4, of the Mackie–Meares model was suggested that includes both binding of solvent and dye. Within the context of this model, it was possible to combine DSC and FPR data to obtain an *effective* binding constant. However, the detailed factors that influence diffusion of a probe that is volumetrically many times larger than the solvent in a system where strong solvent–polymer interactions occur are not well understood. Preliminary PGSE measurements in the present system[66] show that water obeys the universal diffusion curve much more closely than dye. This argues in favor of dye binding, however weak. Yet the same PGSE experiments fail to show an obstruction due to the bound water, for unknown reasons. One may speculate that "bound" water is only loosely entrained and thereby capable of diffusing much more rapidly than polymer. For example, a water molecule may traverse along sites of the polymer, contributing to a kind of dynamic shield from hydrophobic interactions until it eventually exchanges back to the bulk water zone. In this type of model, the exclusion of an intermediately sized probe (e.g., dye) from the "bound" water zone rests on statistics; at least several entrained water molecules must vacate simultaneously in order for one of the volumetrically larger, slower probes to closely approach the polymer backbone. Once this

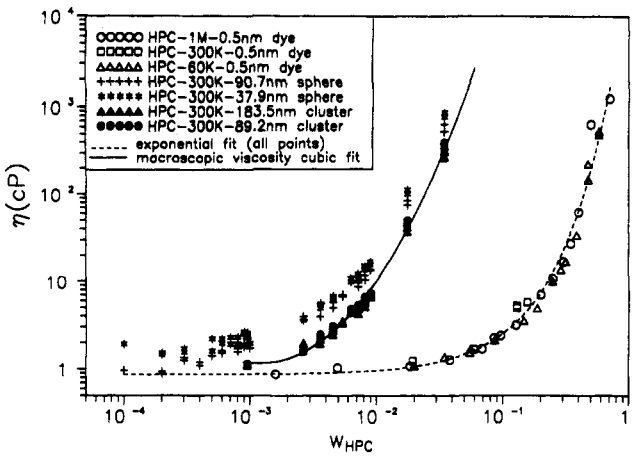

Figure 10. The solid curve represents a good cubic fit to the macroscopic viscosity obtained from a cone-and-plate viscometer.[3] Microviscosities are computed from the diffusion data[3,4] of two latex clusters in HPC-300 000 (stars and crosses) but using the bare latex sphere radii. They are recomputed (filled squares and triangles) using the cluster radii, whereupon good agreement with the macroscopic viscosity was obtained. Microviscosities obtained from the diffusion of a fluorescein anion in solutions of HPC-60 000 (open triangles), HPC-300 000 (open circles), and HPC-1 000 000 (open squares) are all well fitted by an exponential fit (dashed line) and lie well below the microviscosities computed from larger probes.

occurs, the probe may become attached to the polymer or feel an enhanced viscosity, either of which can be modeled with an effective equilibrium constant.

The present study is the third from this laboratory involving probe diffusion in the aqueous HPC system. The others[2,3] used dynamic light scattering to follow latex spheres much larger than a fluorescein anion. The three studies can be compared in terms of microviscosity,[67] defined via the Stokes–Einstein equation as $kT/(6\pi R_h D)$, where R_h is determined from measurements of the probe in pure solvent. Details of how the radii of the bare latex spheres and latex clusters were derived appear elsewhere.[3,4,21] It has been shown that latex probe particles and "limited" clusters of them sense a viscosity not very different from the macroscopic solution viscosity. There is one caveat: the nonexponentiality of the dynamic light scattering intensity autocorrelation functions[4] may contain some information about slightly enhanced diffusion over short distance scales, comparable to the inverse of the scattering vector magnitude. But the overall picture is that probes with a size of several hundred nanometers could almost be treated as macroscopic particles, insofar as the HPC solutions studied to date are concerned. Figure 10 emphasizes the very different behavior of fluorescein anion. At low concentrations, this small probe is essentially unhindered and reports a microviscosity virtually identical to the macroscopic shear viscosity of water. This forcefully argues (yet again) against strong dye–HPC interaction. Whereas dye diffusion is relatively insensitive to HPC molecular weight, the diffusion of latex particles is expected to have a strong molecular weight dependence if it follows the macroscopic viscosity. Dye/HPC/H_2O and latex/HPC/H_2O studies approach respectively the nanoscopic and macroscopic limits of probe diffusion. The behavior of intermediately-sized spherical probes in solutions of HPC at several percent could provide useful information about the transition away from Stokes–Einstein diffusion as probe size decreases.

Our closing remarks concern the intricacies and role of probe diffusion in real systems. In aqueous HPC, interesting and useful features for probe diffusion experiments—liquid crystallinity, high non-Newtonian viscosity at low polymer concentrations, compatibility with readily available probes over a very wide size range—carry the price of complexities such as polymer–solvent binding. Most other rodlike polymer systems have similar difficulties, but the present results reveal interesting behavior. For example, why is the energy of activation for diffusion of a small probe relatively insensitive to the liquid crystal transition? And, will free volume models play a role in side-chain-substituted rods? There is a need for better model rodlike polymers suited for fundamental transport studies spanning dilute, semidilute, and even bulk phases. At the same time, the characteristics of the HPC system are instructive because real solutions are often alarmingly complex. The combined DSC and FPR technique used here should be suitable for the characterization of weak probe–polymer interactions in the presence of solvent–polymer interactions. While the concentrations required are fairly high, both techniques use very small volumes, so that even precious biopolymers can be studied.

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Supplementary Material Available: Interpretation of the simplest free volume approach, that of Fujita, table of free volume parameters, and figures of the analysis of fluorescein anion diffusion in HPC by Fujita-type free volume theory and of a consistency check for free volume theory (7 pages). Ordering information is given on any current masthead page.

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