Comparison of Various Measurements of Microscopic Friction in Polymer Solutions

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Received July 31, 1992; Revised Manuscript Received October 20, 1992

ABSTRACT: Six measurements of microscopic friction in polystyrene/tetrahydrofuran (THF) solutions are compared. Microscopic friction is inferred from the degree to which rigid probe molecules rotate or translate more slowly as the polymer concentration is increased. The fluorescence anisotropy decay method is used to measure rotational dynamics of anthracene and 9,10-bis(phenylethynyl)anthracene. NMR techniques (T_1 and PGSE) are employed to monitor rotational and translational diffusion of the solvent. These four measurements are supplemented by rotational diffusion data for 9,10-diphenylanthracene and translational diffusion coefficients of methyl red, available in the literature. All measurements span similar concentration (0–70% polymer) and temperature (5–45 °C) ranges. Dynamics of the four largest probes follow a common polymer concentration dependence. At each concentration they have a common temperature dependence, shared also by the temperature dependence of the viscosity of a closely related system. Dynamics of THF have weaker concentration and temperature dependences. In addition, THF rotational diffusion follows a different concentration dependence than THF translational diffusion. These trends are discussed in terms of probe size. Comparisons are made to dynamics in polystyrene solutions with other solvents.

Introduction

The concept of friction plays a fundamental role in the study of polymer dynamics. In the Rouse and Zimm theories of polymer motion, the dynamics of all modes of chain motion scale with the monomeric friction coefficient, ζ_0. This coefficient represents the effective friction experienced by one repeat unit in a particular environment. It can be calculated from mechanical measurements if a particular theory is known to be appropriate.[1]

In concentrated polymer solutions there is a well-known relationship[2] between the solution viscosity and the monomeric friction coefficient:

$$\eta(c,T,M) = \zeta_0(c,T)\, F(c,M) \qquad (1)$$

$F(c,M)$ is a structural factor determined by the topological structure of the polymer coils in solution. The terms in eq 1 are functions of the concentration, temperature, and molecular weight, as indicated. The local nature of ζ_0 is clear from the lack of any molecular weight dependence for this factor.[2] An equation analogous to eq 1 has been used for polymer self-diffusion in concentrated solutions.[3]

In the above examples the monomeric friction coefficient is a microscopic parameter which is used to interpret a macroscopic property of a polymer system. Naturally, there has been a great deal of interest in relating this friction *parameter* to microscopic *measurements* of friction.[4,5] Firm conclusions have remained elusive, however. In part this is because no single polymer/solvent pair has been well characterized by several types of microscopic friction measurements over comparable concentration and temperature ranges. Typically free volume theory has been used to interpret dynamics of binary and ternary systems.[6] The approach presented here is complementary to the free volume approach but attempts a more direct molecular interpretation.

The major goal of this paper is to compare six ways of measuring microscopic friction in a single system, polystyrene/tetrahydrofuran (PS/THF). In each case, the rotation or translation of a rigid probe molecule is monitored. Microscopic friction is inferred from the degree to which probe molecules rotate or translate more slowly as the polymer concentration is increased. We are particularly concerned with whether or not the six different measurements provide a consistent picture of microscopic friction.

The different probe molecules compared in this paper are shown in Figure 1, along with the polymer structure. We report here rotational reorientation times (τ) of anthracene and 9,10-bis(phenylethynyl)anthracene (BPEA) in PS/THF solutions. Rotational reorientation times and translational diffusion coefficients (D) of the solvent, THF, in these solutions are also reported. These new results are compared to two published sets of data. Landry et al. used forced Rayleigh scattering to measure translational diffusion coefficients for methyl red (MR) in PS/THF solutions.[7] Johnson et al. used time-resolved optical spectroscopy to measure rotational reorientation times of 9,10-diphenylanthracene (DPA) for these solutions.[4,8] Each probe's dynamics have been studied over similar concentration (0–70% PS) and temperature (5–45 °C) ranges.

The probes compared in this paper are nearly rigid, so each monitors dynamics on a particular length scale. By changing the probe identity, it is possible to change the length scale of the measurement. For this reason probes were chosen to span a range of sizes. In a sense, different probes allow investigations of local friction using rulers of different lengths. The experimental length scale is not an independent variable when only the polymer and solvent are studied; a ternary probe is required in order to have this capability. A complication in interpreting chain dynamics directly is that the length scale of local polymer motions may change with temperature and polymer concentration.[4,8,9]

Our premise is that probe molecules' dynamics reflect *local friction of the host solution.* We consider the probes essentially as passive participants. We assume that their presence does not greatly affect their environment. Very low probe concentrations support this assumption. These

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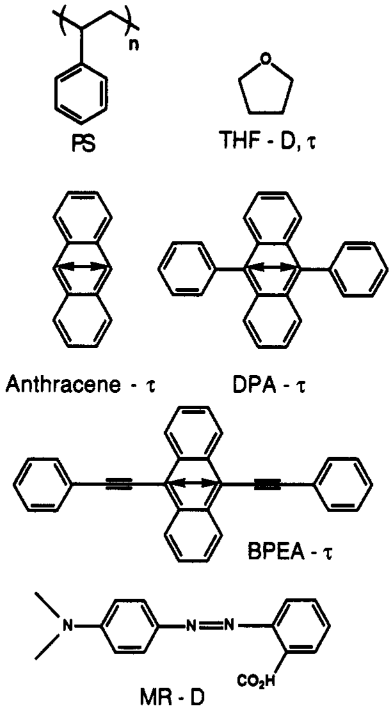

Figure 1. Structures of the matrix polymer (PS), solvent (THF), and the four ternary probes employed. Rotational correlation times (τ) and/or translational diffusion coefficients (*D*) of the solvent and probes were measured, as indicated. Double-headed arrows indicate the transition dipole moments of the electronic transitions observed in the time-resolved optical measurements. DPA and MR results are from refs 4 and 7.

concentrations are too low to affect any macroscopic solution properties. In addition, the nonpolarity of all species present diminishes the possibility of strong chemical interactions between probes and the matrix, which could perturb the host's dynamics. Other evidence will be presented below. From this point of view, the solvent is just another probe since rotational and translational diffusion coefficients of an ensemble of individual solvent molecules (as opposed to pairs or groups of molecules[10]) have been measured.

Our conclusions are as follows: (i) The rotation of the three largest probe molecules and the translation of a fourth all give a consistent picture of microscopic friction in polystyrene/tetrahydrofuran solutions. (ii) The microscopic friction of the largest probes has a temperature dependence consistent with that of the monomeric friction coefficient extracted from viscosity measurements. (iii) The rotation and translation of the smallest probe (the solvent) do not fit into this picture. Dynamics of THF have weaker concentration and temperature dependences than the larger probes. We suggest that the reason for point iii is that THF molecules are considerably smaller than the other probes. Apparently molecules must be larger than some certain size before their dynamics efficiently couple into the friction factor of eq 1. One implication is that the microscopic friction *measured* for a monomer-sized probe may be substantially different from the monomeric friction coefficient of the polymer in the same solution.

Table I
Rotational Correlation Times, τ_c (ps), of BPEA in PS/THF[a]

V_{PS}/V_{total}	4.5 °C	25.0 °C	45.5 °C
0.0	130	93	68
0.18	260	150	100
0.37	1100	550	320
0.51	7500	2600	1100
0.61	33000	16000	6300

[a] Uncertainty: ±10%.

Table II
Rotational Correlation Times, τ_c (ps), of Anthracene in PS/THF[a]

V_{PS}/V_{total}	4.5 °C	25.0 °C	45.5 °C
0.0	15	13	
0.18	58	39	32
0.40	210	110	78
0.53	1000	540	400
0.60	7000	2800	790
0.67	19000	7000	4400

[a] Uncertainty: ±25%.

Table III
PGSE-NMR Translational Diffusion Coefficients[a] of THF in PS/THF (T = 25 °C)

V_{PS}/V_{total}	log D (cm²/s)	V_{PS}/V_{total}	log D (cm²/s)
0.0	−4.61	0.57	−5.80
0.17	-4.84	0.67	−6.29[b]
0.32	−5.09		

[a] Uncertainty: ±0.02 log units. [b] Measured at T = 30.5 °C; M_{PS} = 10K.

Table IV
THF-d_8 ^{2}H NMR T_1 (s)[a] in PS/THF Solutions, δ = 3.6 ppm Measured at $\omega_0/2\pi$ = 55.3 MHz ($\omega_0/2\pi$ = 15.4 MHz)

V_{PS}/V_{total}	5 °C	25 °C	45 °C
0.0	2.43	3.03	3.46
0.093	2.22	2.74	3.30
0.24	1.66	2.26	2.81
	(1.66)		(2.83)
0.34	1.19	1.79	2.42
	(1.16)		(2.47)
0.37	0.972	1.59	2.07
0.43	0.672	1.22	1.88
	(0.629)		(1.87)
0.51	0.339	0.711	1.27
	(0.259)		(1.24)
0.59	0.202	0.386	0.742
	(0.111)		(0.657)
0.65	0.158	0.234	0.395
	(0.061)		(0.276)
0.68	0.146	0.199	0.310
	(0.048)		(0.181)

[a] Uncertainty: ±5%.

Table V
Rotational Correlation Times, τ_c (ps), of THF-d_8 in PS/THF[a]

V_{PS}/V_{total}	5 °C	25 °C	45 °C
0.0	0.87	0.70	0.61
0.093	0.95	0.77	0.64
0.24	1.28	0.94	0.75
0.34	1.80	1.18	0.87
0.37	2.18	1.33	1.02
0.43	≥3.4	1.74	1.13
0.51	≥8.2	≥3.0	1.69

[a] Uncertainty: ±5%.

Techniques and Results

Three experimental techniques were used to measure the dynamics of small molecules in PS/THF solutions. Time-resolved optical spectroscopy measures rotational dynamics of ternary probes, added in very small concentrations. Pulsed field gradient NMR measures self-diffusion coefficients of the solvent, and ^{2}H NMR spin-lattice relaxation times measure solvent rotational dynamics. These three techniques have been extensively described elsewhere. This section details our specific applications of them. All our results are presented in Tables I–V. Readers whose main interest is microscopic friction may wish to go directly to the Discussion section.

Materials and Sample Preparation. Atactic polystyrene (PS) was purchased from Polysciences and had a M_w = 50K and M_w/M_n = 1.05. This polymer was used except where indicated otherwise. Deuterated tetrahydrofuran (THF-d_8) was purchased from Aldrich and Cambridge Isotope Laboratories. 9,10-Bis(phenylethynyl)anthracene (BPEA) was a gift from 3M Corp. All other chemicals were purchased from Aldrich. Chemicals were used as received, except for 2,4,6-tri-*tert*-butylphenol, which was recrystallized three times from hexane. Chemical structures of the various probes are shown in Figure 1.

Samples were prepared in preweighed optical cuvettes or glass tubes. Solution concentrations were determined by weight and converted to volume fraction assuming volume additivity and densities of 1.04 (PS), 0.886 (THF), and 0.985 g/mL (THF-d_8). Optical samples were subjected to several freeze–pump–thaw cycles to remove O_2, increasing the fluorescence lifetime. PGSE-NMR and NMR T_1 samples were frozen once, evacuated, and sealed under N_2. After sealing, the tubes and cutoff tips were reweighed to ensure that no solvent was lost. Sample mixtures were allowed to diffuse until homogeneous. This sometimes required up to 1 month in a 50 °C oven. Samples were weighed repeatedly, including after making measurements, to check that concentrations did not change. We estimate the relative uncertainty in the reported volume fractions to be ±4% for the optical samples and smaller for the NMR samples. Anthracene and BPEA samples contained ~0.1% of 2,4,6-tri-*tert*-butylphenol scavenger to prevent degradation of the chromophores. ^{1}H and ^{2}H NMR spectra show that the NMR T_1 samples (solvent = THF-d_8) contain <0.02% water, except for the ϕ_{PS} = 0.37 sample, which has ~0.3% water. PGSE-NMR samples contained <1% H_2O, the sensitivity limit of ^{1}H NMR analysis for these samples. Sample temperatures were accurate within 1 °C for all experiments.

Time-resolved optical spectroscopy was used to study the rotational diffusion of anthracene and 9,10-bis(phenylethynyl)anthracene (BPEA) in PS/THF solutions. These ternary probes were present in only trace amounts (<50 ppm) and do not affect the solution viscosity or T_g. Time-resolved optical spectroscopy measures the decay of the second-order orientation autocorrelation function CF(t) of the electronic transition dipole (shown as arrows in Figure 1) of a chromophore. The integral of the correlation function is a model-independent characteristic time describing molecular reorientation:

$$\tau_c \equiv \int_0^\infty \mathrm{CF}(t)\,\mathrm{d}t \qquad (2)$$

Correlation times for BPEA and anthracene are reported in Tables I and II. Correlation times for 9,10-diphenylanthracene (DPA) in this same system have been published.[4]

The fluorescence anisotropy decay method employing time-correlated single-photon-counting detection was used. Basic experimental details are available in refs 4, 8, 11, and 12. BPEA was excited with 406-nm light. Fluorescence was observed at 476 nm, the first fluorescence peak. The fundamental anisotropy was large, typically $r(0) \approx 0.34$, although 406 nm is not the first absorption peak for BPEA. The excitation wavelength for anthracene was at the first absorption peak, 378 nm. Fluorescence was observed at 388, 402, and 414 nm. At all these wavelengths $r(0)$ was less than 0.25. We could not discern variations in the correlation times with the different observation wavelengths although the fundamental anisotropies varied by 0.1 units.[13] We estimate uncertainties of ±10% for τ_{BPEA} and ±25% for $\tau_{anthracene}$. The latter has a larger uncertainty due to the low $r(0)$ and the very short correlation times at low PS concentrations. The reported correlation times are averages of several different samples at each concentration.

PGSE-NMR Measurements. Pulsed field gradient spin-echo NMR was used to measure the self-diffusion coefficients of THF in PS/THF solutions. Further discussions and explanations of this technique have been published.[6,14] Results are listed in Table III. We estimate uncertainties of ±5% in D_{THF}.

The PS/THF sample with V_{PS}/V_{total} = 0.67 used an NBS reference polystyrene with molecular weight 10K and M_w/M_n < 1.2. Measurements on this sample were made at 30.5 °C. For reasons to be discussed, PGSE-NMR measurements were also made on PS/THF solutions which contained ~6% hexafluorobenzene. These solutions used a variety of polystyrene molecular weights (the 10K and 50K polymers already described and an NBS 179K reference with M_w/M_n = 1.07).

NMR T_1 Measurements. Solvent rotational correlation times have been determined by ^{2}H NMR T_1 measurements on PS/THF-d_8 solutions. NMR relaxation measurements were made on Bruker AM-360 and AC-100 spectrometers at ^{2}H Larmor frequencies of $\omega_0/2\pi$ = 55.3 and 15.4 MHz. A π–t–$\pi/2$–FID pulse sequence[15] was employed, with 15 delay times t, waiting >10 T_1 between acquisitions. All magnetization recovery curves were very well fit by a single exponential. T_1 values were reproducible within 5%. Our T_1 of neat THF-d_8 is in excellent agreement with the literature value.[16]

The electric quadrupole mechanism is the only important relaxation route for ^{2}H in our experiments. ^{2}H T_1 values and line shapes are independent of whether or not ^{1}H decoupling is used, even in the most concentrated PS solutions. A 2% solution of THF-d_8 in THF has the same T_1 as neat THF-d_8. These experiments demonstrate that ^{1}H–^{2}H dipole–dipole contributions do not affect ^{2}H T_1 values. They also suggest that deuteration of THF does not measurably affect its molecular dynamics. Although our PS/THF-d_8 solutions were not degassed, dissolved O_2 does not alter the ^{2}H T_1 values. A carefully degassed sample of THF-d_8 has the same T_1 as a neat THF-d_8 sample prepared in the manner described above for PS/THF-d_8 samples.

Deuterium spin–lattice relaxation times of THF-d_8 in solutions with polystyrene are listed in Table IV. Many measurements were made at two Larmor frequencies, as indicated. The data in Table IV are from the ^{2}H NMR peak at 3.6 ppm, which arises from the methylene groups adjacent to the ether linkage. Data from the other methylene groups (δ = 1.7 ppm, not shown) are very similar, always agreeing within 10%. Line widths for the two peaks were also very similar. In this paper we analyze the 3.6 ppm data only.

Rotational correlation times, τ_{THF}, of THF-d_8 can be calculated from data in Table IV. ^{2}H T_1 values are determined by the decay of the second-order orientation autocorrelation function for the ^{2}H–C bond vector. In the extreme narrowing regime τ_{THF} is inversely proportional to T_1;

$$\frac{1}{T_1} = \frac{3}{8}(2\pi\mathrm{QCC})^2\tau_{THF} \qquad (3)$$

It is important to note that this equation is valid for a correlation function of any shape as long as the extreme narrowing condition is appropriate. The τ value extracted is the integral of the correlation function for the ^{2}H–C bond vector. This is analogous to the calculation of τ_c for the optical experiments (eq 2).

The quadrupole coupling constant, QCC, is taken to be 178.5 ± 1.3 kHz. This value was determined by solid-state NMR of crystalline THF-d_8.[17] Other experiments find values of QCC in the range 173–200 kHz.[16,18,19] As we are concerned mainly with the temperature and concentration dependences of τ_{THF}, the precise value of QCC is not crucial. For the mixture of ^2H_2O in DMSO, the ^{2}H QCC has been found to vary appreciably with mixture composition.[20] This is attributed to changes in hydrogen bonding and is not expected to be a problem for our system. We are unaware of any similar changes in QCC for ^{2}H bonded to C in organic molecules.

We have also measured ^{1}H-decoupled ^{13}C NMR T_1s and NOEs of some PS/THF solutions (degassed, not deuterated). After accounting for spin rotation and the larger uncertainties in our ^{13}C measurements, reasonable agreement was found between the ^{13}C and ^{2}H T_1 measurements of τ_{THF}.[21-23]

Table V lists the rotational correlation times, τ_{THF}, calculated from eq 3 and data in Table IV. The extreme narrowing condition ($\tau_{THF} \ll \omega_0^{-1}$ and therefore T_1 is independent of ω_0) is met only for solutions with less than ~50% PS. ^{2}H spin–spin relaxation times, T_2, estimated from spectral line widths, similarly indicated that extreme narrowing conditions were not fulfilled in concentrated PS solutions. Interpretation of T_1 in terms of dynamics is much more complicated than eq 3 suggests when T_1 depends on ω_0.[15] For this reason, Table V does not include τ_{THF} for solutions with >51% PS.

The observed deviation from extreme narrowing conditions in concentrated PS solutions is surprising and informative. In these solutions the distribution of solvent reorientation times must be extremely broad. Alternatively stated, the time correlation function CF(t) is nonexponential, or its Fourier transform, the spectral density function $J(\omega)$, is not Lorentzian. If, as is commonly assumed for small-molecule dynamics, $J(\omega)$ were Lorentzian, then T_1 would differ by >10% at the two Larmor frequencies only when $T_1 < 0.0045$ s ($\tau_{\mathrm{THF}} > 530$ ps). In fact, we measure >10% differences when T_1 is as long as 0.7 s. In PS/THF solutions with >50% PS most of the solvent rotational dynamics are quite fast (picoseconds to tens of picoseconds) but significant parts of the dynamics require at least thousands of picoseconds ($\tau_{\mathrm{THF}} \geq \omega_0^{-1}$). One interpretation is that THF molecules move between dynamically different environments. If so, any given THF molecule must exchange between these environments on a time scale short compared to T_1.

Very recently naNagara et al. reported rotational (and translational) diffusion measurements of toluene in PS/toluene solutions.[24] They also observed deviations from extreme narrowing conditions. Earlier work by Rössler et al. at much lower temperatures in PS/toluene solutions indicated a very broad distribution of solvent rotation times.[25] Both of these results are qualitatively consistent with our observation in the PS/THF system.

Discussion

We define microscopic friction to be directly proportional to τ_c and inversely proportional to D. Microscopic friction is thus proportional to the time required for a probe molecule to rotate some characteristic angle or translate some characteristic length. Identical arguments were employed in the analysis of reorientational dynamics of DPA and anthracene-labeled PS in concentrated PS/THF solutions.[4] An equivalent approach frames rotational and translational diffusion data in terms of a local viscosity. In a previous publication studying concentrated polyisoprene/THF solutions we adopted this approach.[8] Hydrodynamic arguments (the Stokes–Einstein and Stokes–Einstein–Debye relations) quantitatively related molecular dynamics to the local viscosity. Approaches which emphasize the microscopically inhomogeneous character of polymer solutions have sometimes been used by other investigators.[24,26,27]

Molecular Weight Dependence. It is very well established that the rotation[28,29] and translation[7,14,30] of small probe molecules in concentrated polymer solutions are independent of polymer molecular weight. We have not systematically tested this here. In the course of our measurements we have verified this independence in a few select cases. Thus in the analysis below we may safely assume that all the measurements reported here are substantially independent of polymer molecular weight.

Concentration and Temperature Dependence. Figure 2 shows the polymer concentration dependence of small-molecule dynamics in PS/THF solutions. The different symbols correspond to determinations made with different molecular probes. D_{MR} data are from ref 7 and τ_{DPA} from ref 4. Each diffusion coefficient or correlation time (D or τ) has been scaled to the corresponding value (D_0 or τ_0) for that probe in THF, with no PS present. The ratios D/D_0 and τ_0/τ are inversely proportional to microscopic friction for a given probe as the concentration or temperature is varied. The axes in Figure 2 thus allow direct comparison of the concentration dependences of microscopic friction for the various probes. It is worth noting that the concentration dependence of the *macroscopic viscosity* is much stronger than any of the curves shown in Figure 2. In addition, the concentration dependence of the viscosity depends upon polymer molecular weight; the results in Figure 2 are independent of molecular weight.

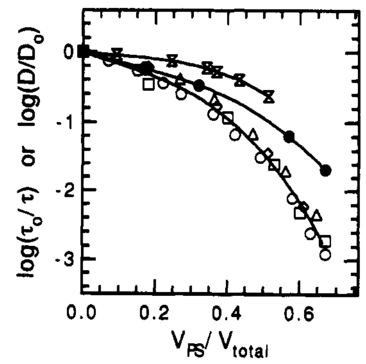

Figure 2. Local mobilities of various probes as a function of polymer concentration in PS/THF solutions. T = 25 °C. Mobilities are characterized by translational diffusion coefficients, D, or rotational correlation times, τ, scaled to their values in THF. Symbols are as follows: τ_{THF} (X); D_{THF} (●); D_{MR} (▲); $\tau_{\mathrm{anthracene}}$ (□); τ_{DPA} (○); τ_{BPEA} (◇). The mobilities of the four largest probes share a common concentration dependence. The concentration dependences of the D and τ of the smallest probe (THF) are weaker and different from each other.

Table VI
Polynomial Fit Parameters $Y = A + B\phi + C\phi^2 + D\phi^3$

Y	A	B	C	D
log (τ_0/τ), THF-d_8	0	−0.61	1.78	−5.83
log (D/D_0), THF	0	−1.53	1.62	−4.60
log (D/D_0), four probes	0	−1.84	2.00	−8.25
E_a, three probes (kJ/mol)	12.0	−0.99	65.2	55.0
E_a, THF-d_8 (kJ/mol)	6.4	16.2	−79.8	263.
log (D/D_0), four solvents	0	−1.67	1.97	−4.63

The curves in Figure 2 are third-order polynomial fits and are intended to guide the eye. Equations for these fits are in Table VI. The bottom curve is a simultaneous fit to the anthracene, DPA, BPEA, and MR data. It would also be possible to analyze the concentration dependences in terms of Fujita's free volume theory.[31] This has been done for D_{MR} and τ_{DPA}.[4,7]

The data in Figure 2 were collected at 25 °C. Most of these measurements were repeated at 5 and 45 °C (see Tables I–IV and refs 4 and 7). THF translational diffusion coefficients were not measured at 5 or 45 °C. Barring this omission, plots like Figure 2 have been made for 5 and 45 °C. All of the qualitative features are the same, but the concentration dependences are stronger at lower temperature and weaker at higher temperature. These temperature dependences can be characterized by apparent activation energies, E_a. E_a was calculated from the slope of an Arrhenius plot for each probe at each PS concentration. Although these plots were approximately linear, they probably would not be over a wide temperature range. We also note that each E_a was determined from a line through only three data points.

Figure 3 is a plot of E_a for several probes as a function of PS concentration. Two series of measurements are missing from Figure 3: D_{THF} and $\tau_{\mathrm{anthracene}}$. The temperature dependences of D_{THF} have not been determined. The temperature dependences of $\tau_{\mathrm{anthracene}}$ are included in Table I but omitted from Figure 3 because of large experimental uncertainties. These uncertainties do not greatly affect the concentration dependence of τ (i.e., Figure 2) but introduce large errors in calculations of E_a. The Arrhenius plot for τ_{BPEA} in the most concentrated solution is not linear; E_a for this solution is not shown. Estimated error bars are included for DPA and THF at the highest concentrations shown. At lower concentrations we estimate the values of E_a are ±10% (all probes). The lower curve is a polynomial fit to the THF-d_8 results. The

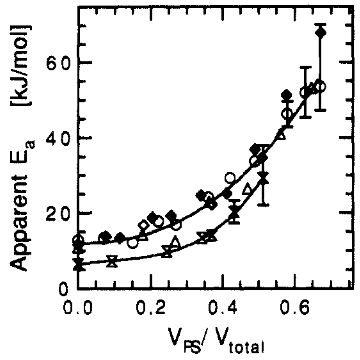

Figure 3. Apparent activation energies for τ_{THF} (⧖), D_{MR} (△), τ_{DPA} (○), and τ_{BPEA} (◇) as a function of PS concentration in PS/THF. These are compared to the temperature dependences of the viscosity of PS/diethylbenzene solutions (◆). The dynamics of the three largest probes have the same temperature dependence at each concentration. The temperature dependences of the solution viscosities are similar, but the temperature dependences of the smallest probe's mobility are weaker.

upper curve is a fit to the DPA, BPEA, and MR results. Equations are included in Table VI.

Figure 3 also shows the temperature dependences of the viscosity of PS/diethylbenzene solutions. These viscosity measurements were made by Bueche.[32] Over the temperature range 35–110 °C plots of log η vs T^{-1} are nearly linear, at least over the concentration range in Figure 3. Comparison of solution viscosity data to probe dynamics is motivated by eq 1; the temperature dependence of ζ_0 follows that of the macroscopic solution viscosity. We have used viscosity data for PS/diethylbenzene in Figure 3 because viscosity data for PS/THF solutions are not available. The viscosity behavior of these two systems is expected to be very similar. THF and diethylbenzene have similar densities and temperature dependences of their viscosities, although diethylbenzene is about twice as viscous.[33] The temperature dependences of the viscosities of PS/ethylbenzene, PS/isopropylbenzene, and PS/xylene solutions are similar to those of PS/diethylbenzene,[34-37] so it seems that the exact choice of solvent (within limits) is not crucial in this comparison. This feature of polymer solution viscosities was observed many years ago by Hirai.[37]

Comparison of Various Measurements of Microscopic Friction. The concentration dependence of D_{MR} is the same as the concentration dependences of $\tau_{anthracene}$, τ_{DPA}, and τ_{BPEA}. Furthermore, at each PS concentration these measurements of microscopic friction have approximately the same temperature dependence as each other and as $\eta_{PS/diethylbenzene}$. These results are consistent with the following working hypotheses for the four largest probes: (i) For any of these probes, the *concentration* dependences of rotational and translational diffusion are the same. (ii) For any of these probes, the *temperature* dependences of rotational and translational diffusion are the same. (iii) For each of these probes at any given concentration, the ratio of the probe's microscopic friction, ζ_{probe}, to the polymer's monomeric friction, ζ_0, is independent of temperature. (iv) For each of these probes at any fixed temperature, this same ratio is independent of polymer concentration. Schematically, for the four largest probes

$$D_{probe}^{-1} \propto \tau_{probe} \propto \zeta_{probe} \propto \zeta_0 \tag{4}$$

Each explicit term in this expression varies with polymer concentration and temperature; the implied proportionality constants do not.

We have not shown that all four statements in the previous paragraph are true. Although there is no direct evidence for the first two statements, the consistencies in the results shown in Figures 2 and 3 for the four largest probes would be an unlikely coincidence if statements i and ii were not true. The third statement is supported by the similar temperature dependences shown in Figure 3 for the four probes and $\eta_{PS/diethylbenzene}$. The fourth statement seems plausible since the microscopic frictions determined for the four largest probes all show the same concentration dependence. Experimental evidence of the kind which could directly test this last point[38] is not available for the PS/THF system.

Solvent dynamics do not fit into this picture. The concentration dependences of τ_{THF} and D_{THF} are weaker than for the other probes. E_a is smaller for τ_{THF} than for the other measurements. Two other features of τ_{THF} are also different from the other measurements: (i) The values of τ_{THF} are 1–2 orders of magnitude shorter than $\tau_{anthracene}$, τ_{DPA}, and τ_{BPEA} in solutions with no PS. (ii) In solutions with >50% PS, the distribution of time constants describing THF rotation broadens greatly (see the Techniques and Results section). This is not the case for the three optical probes we employ.[12]

Another difference between the behaviors of THF and the other probes can be found in the comparison of rotational and translational diffusion. Figure 2 shows that the concentration dependences of τ_{THF} and D_{THF} are not identical. This is inconsistent with the behavior which we have inferred for the larger probes. It is also inconsistent with the notion that a particular molecule should sense the same local viscosity in both translation and rotation.[8,39] Clearly for THF in PS/THF, the concentration dependences of the microscopic friction determined in rotation and translation are different.

Thus, it seems that on length scales as long or longer than an anthracene molecule, the microscopic frictions deduced from both rotational and translational diffusion measurements are proportional to $\zeta_0(c,T)$. Apparently THF is too small and is moving too rapidly to feel the same frictional environment as the larger probes. Modern theories of molecular dynamics in liquids suggest that when dynamics become very fast, the relevant microscopic friction decreases.[40-43] These approaches are not readily adaptable to probe diffusion in concentrated polymer solutions, but the general principles seem appropriate. These ideas do not address the difference in microscopic friction for THF rotation and translation. It is interesting to note that 30 years ago Fujita speculated that very small molecules (such as water) diffuse by a different mechanism in polymer solutions than do larger molecules.[44] He suggested that very small molecules diffuse by a solidlike interstitial mechanism while larger molecules diffuse by means of substitution.

Dynamics of very large probes should follow a much stronger concentration dependence than any of the probes described in this paper.[45] Consider a probe which is much larger than the solution entanglement spacing. Dynamics of such a probe are not expected to depend directly on a microscopic friction or local viscosity. Rather, they are expected to follow the macroscopic solution viscosity. Since the viscosity is molecular weight dependent, the minimum size of such a probe would also be molecular weight dependent.

It may be possible, therefore, to assign a molecular interpretation to ζ_0 in eq 1, but only over a limited range of length scales. The lower limit of this range is between the size of THF and anthracene; the upper limit is greater

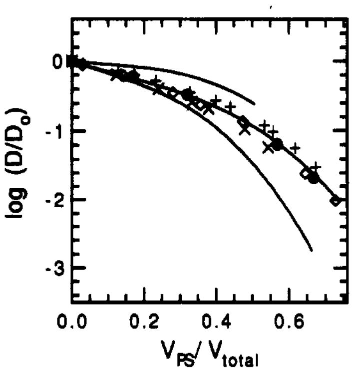

Figure 4. Concentration dependence of $D_{solvent}$ for PS solutions with four solvents at 25 °C. The four solvents are THF (●), toluene (+), benzene (◇), and cyclohexane (×). For these solvents, the concentration dependence of $D_{solvent}$ does not depend strongly on the solvent identity, as shown by the central curve. The other two curves are reproduced from Figure 2. They show the concentration dependences of THF rotation (top) and rotational and translational diffusion of four larger probes in PS/THF (bottom).

than or equal to the size of BPEA. Within this range, a consistent picture of microscopic friction is inferred from translational and rotational motion. On shorter length scales the situation is more complicated. It is likely that a monomer-sized probe molecule would be too small to provide an accurate measurement of the monomeric friction coefficient in this system.[46] This interpretation implies that size is the only important factor in determining microscopic friction and deemphasizes any role probe shape may play. It is possible that dynamics of nearly spherical molecules decouple from microscopic friction more so than nonspherical molecules.[47,48] We have not tested this hypothesis.

Comparison to Previous Work

Translational Diffusion of Other Solvents in Polystyrene Solutions. PGSE-NMR has previously been used to study $D_{solvent}$ in PS solutions with toluene, benzene, and cyclohexane.[24,27,49-51] These liquids have similar densities and viscosities to THF, with slightly larger molecular volumes and masses. THF, benzene, and toluene are thermodynamically good solvents for PS; cyclohexane is not (Θ = 35 °C).

Figure 4 shows the concentration dependence of log (D/D_0) at ~25 °C[52] for solvent molecules in PS solutions with different solvents. The D_{THF} data are reproduced from Figure 2 and Table III. The other data are from refs 27 and 49. The middle curve is a cubic fit through the data for all four solvents. The top curve represents the polymer concentration dependence of solvent rotation. The bottom curve represents rotation and translation of the four optical probes discussed earlier. These two curves are reproduced from Figure 2. Equations for all three curves are in Table VI.

The concentration dependences of $D_{solvent}$ for all four solvents are very similar over a wide concentration range (0–65% PS). The absolute values of $D_{solvent}$ generally agree within a factor of 3 at any PS concentration. The apparent activation energies of $D_{benzene}$, $D_{toluene}$, and $D_{cyclohexane}$ (not shown) are fairly similar to each other over this concentration range also and quite different from any of the curves in Figure 3, slowly increasing from ~13 kJ/mol in the pure liquids to ~20 kJ/mol at V_{PS}/V_{total} = 0.55. We expect that the apparent E_a of D_{THF} follows a similar concentration dependence.

It seems that solvent dynamics in PS solutions are fairly insensitive to the particular choice of solvent, for a range of solvents where the viscosity, density, and molecular volume do not change greatly. This is consistent with work by previous investigators.[53-57] By extension, we expect that the various other measurements of microscopic friction discussed in connection to Figures 2 and 3 might be rather insensitive to the solvent identity within this range. In fact, τ_{DPA} and D_{MR} follow the same PS concentration dependence in PS/toluene and PS/THF solutions.[4,7,58,59] Since the particular solvent choice does not greatly affect solvent or probe dynamics, specific chemical interactions between the solvent and polymer are not important factors in determining molecular dynamics in PS solutions. This supports our initial premise that ternary probes (present in very low concentrations) act essentially as passive reporters of local dynamics in PS/THF solutions.

Rotational Diffusion of Other Solvents in Polystyrene Solutions. Alms et al. used depolarized light scattering to study the reorientation of styrene in polystyrene/styrene solutions over a concentration range of 0–80% polymer at 90 °C.[60] They found that the reorientation time of the styrene increased by a factor of 1.5 over this concentration range. We cannot quantitatively compare our results with these results because of the different measurement temperatures. Nevertheless, the very weak dependence of styrene rotation on polymer concentration is qualitatively consistent with the weak concentration dependence on τ_{THF}.[48]

Probe Translational Diffusion in Extremely Concentrated Polystyrene Solutions. Frick et al. report forced Rayleigh scattering measurements of probe translational diffusion coefficients in very concentrated PS/toluene solutions.[61] Experiments were limited to the concentration range 79–90% PS and span the temperature range −15 to +60 °C. Two probes were employed, azobenzene and Aberchrome 540. They are slightly smaller and larger, respectively, than MR. Aberchrome is 25% larger by volume (40% by mass) than azobenzene. Frick et al. report that $D_{azobenzene}$ and $D_{Aberchrome}$ both vary more strongly with concentration and temperature than $D_{toluene}$. In spite of their fairly small size difference, diffusion of azobenzene shows substantially weaker concentration and temperature dependences than diffusion of Aberchrome. Similarly, the temperature dependence of D_{probe} in PS melts has been found to be stronger for larger probes.[62-64]

The variation with probe size in very concentrated PS/toluene solutions is unlike our results with four optical probes of different sizes, all of which share a common concentration and temperature dependence. As discussed above, it is unlikely that this difference is due to the different solvents employed (toluene instead of THF). It seems more likely that, as polymer concentration increases and temperature decreases to near the solution T_g, subtle effects of probe size and shape become drastically more important in determining molecular dynamics.

Previous Work on PS/THF. von Meerwall, Amis, and Ferry report self-diffusion coefficients of THF in polystyrene solutions.[14] They also report diffusion coefficients of the polymer and the third solution component, hexafluorobenzene (HFB). HFB makes up ~6% of the total weight of each solution. Those samples were prepared and diffusion measurements were made in 1983. The PS concentration dependences of D_{HFB} and D_{THF} are identical. (They are also independent of M_{PS}.) This is consistent with our interpretation of Figures 2 and 4, as HFB and THF have similar molecular volumes.

We have compared the 1983 D_{THF} results with those reported in Table III. Surprisingly, the 1983 samples have a significantly stronger dependence on polymer concentration. We reemphasize that the small difference in solvent (THF vs HFB/THF) is not likely to affect D_{THF} in PS solutions substantially, since the concentration dependences of $D_{solvent}$ are quite similar for THF, benzene, toluene, and cyclohexane solutions with PS. We have gone to considerable effort to sort out this discrepancy. We conclude that the polystyrene concentrations reported for the 1983 samples are systematically too low. The remainder of this section explains the basis for this conclusion.

We have remeasured D_{THF} of several of the 1983 samples to determine if an instrumental error was a factor. The samples include all six with M_{PS} = 37.4K, the three most concentrated samples with M_{PS} = 10K, and the two most dilute samples with M_{PS} = 1050K. They remain in excellent condition. In 1991 we repeated the PGSE measurements of D_{THF} for all but one of these samples. The concentration dependence of log (D/D_0) for THF is unchanged from the 1983 measurements. The fractions of the unattenuated spin echoes arising from THF were the same in the new and old measurements, indicating that the polymer/solvent mass ratios have remained constant in these samples. The new values of log D_{THF} for the 1983 samples are uniformly about 0.11 log units lower than in ref 14. This difference is thought to be due to an instrument recalibration between 1983 and 1991.

We have made PGSE measurements on a series of new PS/HFB/THF samples to determine if the presence of 6% HFB significantly changes D_{THF}. These samples span the concentration range V_{PS}/V_{total} = 0–0.70. As expected, D_{THF} is rather insensitive to the presence or absence of HFB over this range of PS concentrations.

In order to check for impurities, we have measured ^1H and ^{13}C NMR spectra of most of the old and new PGSE samples (T = 45 °C). As the samples were not prepared with high-resolution NMR in mind, accurate PS concentrations could not be determined from the NMR spectra. These spectra do confirm that no impurities are present in significant quantities in any of the samples. The spectral line widths are consistent with the conclusion that the 1983 samples are systematically more concentrated than the new samples.

The concentration difference between the 1983 and 1991 samples was quantified with Raman spectroscopy. These experiments did not allow absolute determinations of V_{PS}/V_{total}, however. Raman spectra were collected from the sealed PGSE sample tubes. All observed peaks are readily assigned to PS, THF, or HFB, confirming the absence of impurities. The intensity ratios I_{HFB}/I_{PS} and I_{HFB}/I_{THF} are similar for the old and new samples, so large differences in the HFB concentrations are not present. The ratio I_{PS}/I_{THF} is consistently and systematically larger for the 1983 samples than for the 1991 samples (both with and without HFB). This confirms that the 1983 samples are more concentrated than the new samples. It is possible to define a new concentration scale based only on the Raman intensity ratio I_{PS}/I_{THF}. This scale brings the concentration dependence of all the PGSE D_{THF} data (for 1983 and 1991 samples with HFB) into agreement.[65] Therefore, the Raman spectra confirm that the PS concentrations of the 1983 samples are systematically higher than the new samples *and* that this discrepancy is responsible for the differences in the diffusion data.

In the following we outline the evidence that the concentrations of the samples we prepared are correct. The agreement between D_{THF} (our samples) and $D_{benzene}$, $D_{toluene}$, and $D_{cyclohexane}$, shown in Figure 4, provides some indirect evidence for this conclusion. Repeated mass measurements of the new samples provide direct confirmation. Solutions were prepared by weight in glass tubes. After degassing and sealing, the tubes with contents and the detached glass tips were reweighed. The total mass changes were very small. They could be accounted for by the mass of air lost above the solution for those tubes which were sealed under vacuum. For our new samples, absolute V_{PS}/V_{total} uncertainties are always <0.015, and usually <0.005. Samples were reweighed repeatedly before PGSE measurements, and again many months later. The *solution* masses changed ≤0.7% since the samples were prepared. Similar detailed records of the 1983 sample weights are unavailable. Examination of the original laboratory notebooks from 1983 makes it clear that no calculation errors were involved in the preparation of those samples. It is possible that some solvent evaporated before the sample tubes were sealed. The results of an attempt to duplicate the preparation method used for the 1983 samples make this conclusion plausible.

Summary

We have compared the rotational and translational diffusion behavior of several rigid, small molecules in solutions of polystyrene/tetrahydrofuran. Several different experimental techniques were utilized to measure the dynamics of the probes over the same concentration (0–70% polystyrene) and temperature ranges (5–45 °C). The microscopic friction determined in these experiments was compared to the monomeric friction coefficient extracted from viscosity measurements.

The dynamics of the four largest probes follow a single concentration dependence. Three of these also show the same temperature dependence at each concentration. (Experimental uncertainties prevented including the fourth in this comparison.) These temperature dependences are approximately the same as those of the solution viscosity. These results are consistent with the conclusion that the four largest probes, whether rotating or translating, all sense a microscopic friction proportional to the monomeric friction coefficient.

The dynamics of the smallest probe, the solvent, do not fit into this picture. Rotation and translation of THF show different concentration dependences from the other probes and from each other. THF rotation shows different temperature dependences from the other probes. THF molecules seem to be too small to sense the frictional environment of the larger probes.

Acknowledgment. This research was supported by the National Science Foundation through the Division of Materials Research, Polymers Program (DMR-9123238 at Wisconsin and DMR-9014502 at Akron). Instrumentation for the fluorescence anisotropy decay measurements was purchased through a grant from the NSF Chemistry Division, Instrumentation Program (CHE-8804083), and matching funds from the Graduate School at the University of Wisconsin. Most NMR experiments were performed in the Instrument Center of the Department of Chemistry, University of Wisconsin. We thank the staff for assistance. D.J.G. is grateful for fellowship support from the U.S. Department of Education. M.D.E. thanks the Alfred P. Sloan Foundation for fellowship support. We thank D. B. Hess for technical assistance, Professor R. M. Corn for suggesting the Raman measurements and allowing us access to his spectrometer, and R. Naujuk for collecting the Raman spectra. We have been the beneficiaries of discussions with Professors J. D. Ferry, T. P. Lodge, T. W. Root, and G. C. Berry. We thank Professor E. J. Amis for his assistance in investigating the discrepancy between our results and those of ref 14.

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