Concentration and temperature dependence of molecular motions in polystyrene/tetrahydrofuran solutions

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(*Received 15 August 1991; revised 15 October 1991; accepted 24 October 1991*)

The fluorescence anisotropy decay method is used to measure the rotational diffusion of 9,10-diphenylanthracene and the segmental motion of anthracene-labelled polystyrene in tetrahydrofuran solutions of polystyrene. The concentration dependences of these two measures of microscopic friction are reported from pure solvent to 70% polymer at 4.5, 25.0 and 45.5°C. These results are compared to previously reported measurements of the translational diffusion of methyl red in the same system, and to the temperature dependence of the solution viscosity of a closely related system. The three measures of microscopic friction show similar concentration dependences.

(Keywords: polystyrene; solution dynamics; diffusion; fluorescence; anisotropy; segmental dynamics; friction)

INTRODUCTION

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[1]. 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. In concentrated polymer solutions, there is a well known relationship between the solution viscosity and a local friction factor $\zeta(C,T)$[2]:

$$\eta(C,T,M)=\zeta(C,T)F(C,M) \qquad (1)$$

where $F(C,M)$ is a structural factor determined by the topological structure of the polymer coils in solution. These factors are functions of the concentration, temperature and molecular weight as indicated. The local nature of ζ is clear from the lack of any molecular weight dependence for this factor.

In both of the above examples, the friction term 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 these friction parameters to microscopic measurements of friction. Such measurements include the translational[3–7] and rotational[8–10] diffusion of small molecules, and the local segmental dynamics of polymer chains[8,11–14]. Free volume theory provides one theoretical framework for this comparison[4].

The conclusions of studies which compare microscopic friction measurements to the friction inferred from macroscopic measurements have been varied. For example, some studies have found that the translational diffusion of a small molecule in bulk polymer follows the temperature dependence of the friction parameters[3,5,7,15]. On the other hand, significant differences have also been noted[3,16]. The size of the probe and the glass transition temperature of the material may be important variables in attempting to reconcile the various studies[17]. Solution studies also report some similarities[18] and some differences[19] between microscopic friction measurements and deduced friction parameters.

The studies referred to in the previous paragraph differ in several important respects. A variety of techniques, polymer systems, probe molecules and temperature ranges were employed. Since these differences make it difficult to compare the various conclusions, we have elected to study two particular systems in greater detail using a variety of experimental techniques. This allows a comparison of the microscopic friction determined by different methods. (Alternatively, one could say that the local viscosities determined by different techniques can be compared.) We have recently reported results for the polyisoprene/tetrahydrofuran system[14]. In those experiments we were able to cover the entire concentration range from dilute solution to the bulk.

In the work reported here, we compare three different microscopic friction measurements for the polystyrene/tetrahydrofuran system (PS/THF). A polymer concentration range of 0–70% is covered at three temperatures between 5 and 45°C. We have observed the rotational diffusion of 9,10-diphenylanthracene (DPA) and the local segmental dynamics of anthracene-labelled polystyrene

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0032-3861/92/183916–09

(PS-A-PS) in these solutions using the fluorescence anisotropy decay method. These results are compared to translational diffusion measurements of methyl red in PS/THF reported by Landry *et al.*[20]. Finally, all these results are compared to $\zeta(C, T)$ extracted from viscosity measurements using equation (1). The viscosity measurements are from a closely related system, PS/ethyl benzene[21].

The use of fluorescence techniques to examine local friction in polymer solutions dates back at least to the work of Tanaka *et al.*[8]. They used steady-state fluorescence measurements to study the rotational mobility of free chromophores in solution and chromophores attached to the end of polyethylene oxide chains as a function of polymer concentration. The first time-resolved optical investigation of this problem was performed with PS-A-PS by Viovy and Monnerie[11]. The current paper extends the previous studies in several important ways.

The findings of this paper are:

(1) the segmental motions of PS-A-PS, the translational diffusion of methyl red, and the rotational diffusion of DPA all have similar concentration dependences;
(2) the rotational diffusion of DPA has a slightly stronger concentration dependence than the concentration dependences of the other two techniques;
(3) the temperature dependence of probe translation and rotation in PS/THF follows the temperature dependence of the solution viscosity of PS/ethyl benzene solutions at all concentrations up to 70% PS;
(4) the apparent activation energy for labelled chain motion has a different concentration dependence than the activation energies for the free probes or the solution viscosity.

EXPERIMENTAL

Materials

The unlabelled matrix PS was purchased from Polysciences (no. 16236, $M_w = 50\,000$, $M_w/M_n = 1.05$). Spectrophotometric-grade THF was purchased from Aldrich (no. 24 288-8). Either DPA (Aldrich) or PS-A-PS was added to solutions of the matrix PS in THF. PS-A-PS chains were synthesized via anionic polymerization as described previously[22]. The resulting chains contain one anthracene moiety covalently bonded into the polymer backbone as shown in *Figure 1*. The labelled chains are atactic with $M_n = 68\,000$ and $M_w/M_n = 1.01$. All of the commercial materials above were used without further purification. The PS-A-PS samples included a small amount of 2,4,6-tris-*tert*-butylphenol (Aldrich) as a free radical scavenger. This material was recrystallized three times from hexane before use.

Sample preparation

These experiments require optically clear, homogeneous samples. Dilute solutions of unlabelled PS in THF (<20 wt%) were prepared and the appropriate amount of either DPA or PS-A-PS was added. The final solution was subjected to several freeze–pump–thaw cycles to remove molecular oxygen, increasing the fluorescence lifetime. We have checked that the presence of O_2 does not change the shape of the correlation function or the correlation time. The solution was then filtered through a 0.45 μm Teflon filter into a specially adapted 3 mm quartz cuvette.

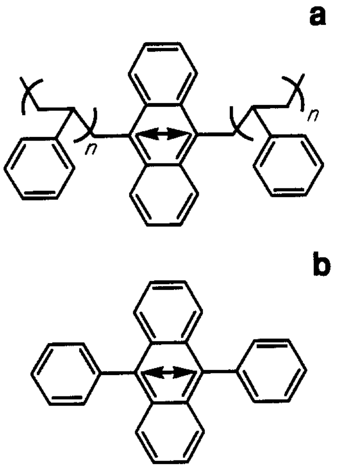

Figure 1 Probes used in these experiments: (a) anthracene labelled-polystyrene (PS-A-PS); (b) 9,10-diphenylanthracene (DPA). The double arrow indicates the transition dipole moment for the observed electronic transition

To prepare higher concentration samples, THF was removed under vacuum and the new concentration calculated by weight. Conversion to volume fraction was obtained assuming volume additivity using $\rho_{THF} = 0.886\,g\,ml^{-1}$ and $\rho_{PS} = 1.04\,g\,ml^{-1}$. Samples were allowed to diffuse until homogeneous (usually 1–2 days, at 50°C). Just before data acquisition, the concentration of the sample was checked by weight and the optical absorbance was measured. The absorbance at the excitation wavelength was usually 0.1–0.3. We did not notice any change in the results as long as the absorbance was below 0.4. We estimate the relative error in the reported volume fraction to be ±4%. The maximum concentrations of DPA and PS-A-PS were less than 50 ppm and 1.5%, respectively.

We noted a significant decrease in the optical absorption of solutions of PS-A-PS in THF over a 12 h period. The addition of 0.1% of a free radical scavenger (2,4,6-tri-*tert*-butylphenol) stabilized the samples. We believe that the small amount of added scavenger does not change the dynamics of the labelled chains in solution. We verified that the scavenger had no effect on the dynamics of DPA in PS/THF.

Technique

The fluorescence anisotropy decay method was used to observe the dynamics of DPA and PS-A-PS in PS/THF solutions. In each case, the experiment monitors the reorientation of an electronic transition moment for the chromophore (shown in *Figure 1*). For the labelled polymer, only motions which reorient the polymer backbone are detected.

The experimental apparatus, technique and method of data acquisition have been described elsewhere[14,22]. Only a brief description is given here. A 5 ps linearly polarized excitation pulse is used to photoselect an anisotropic distribution of excited-state chromophores. This anisotropy can be examined by monitoring the components of the fluorescence decay polarized parallel and perpendicular to the excitation polarization, $I_{\parallel}(t)$ and $I_{\perp}(t)$. The anisotropy decays to zero when the molecular motions have randomized the orientations of the excited-state chromophores. The decay of the anisotropy is directly proportional to the second-order orientation autocorrelation function[23]. Thus the observation of $I_{\parallel}(t)$ and $I_{\perp}(t)$ allows the direct evaluation of the orientation autocorrelation function without the assumption of any motional model.

The method of time-correlated single photon counting was used to observe the time-dependent polarized fluorescence decays[24]. The full width at half maximum (*FWHM*) of the instrument response function for our apparatus is about 40 ps. For DPA and PS-A-PS, the excitation wavelengths were chosen to match the origin transition at 394 nm and 406 nm, respectively. The fluorescence emission was observed at 414 nm.

Data analysis

The anisotropy data for the PS-A-PS was initially fitted to Hall–Helfand[25] and generalized diffusion and loss (GDL)[26] correlation functions. We observed that the shape of the correlation function changed systematically with concentration. At higher concentrations these functions do not provide adequate fits to the data. This effect is stronger at lower temperatures. We found that a biexponential function adequately reproduces the data throughout the concentration range:

$$r(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \qquad (2)$$

This function also provides adequate fits for the DPA anisotropy data; the shape of the correlation function also changes with concentration in these experiments. The individual parameter values for all the fits are reported elsewhere[27]. An example of a fitted data set is shown in *Figure 2*. All fitting is performed using a non-linear Marquardt algorithm. An iterative reconvolution procedure is used to account for the instrument response function.

In this paper we ask how much dynamics slow for a given concentration increase. As discussed previously[14], the change in the shape of the correlation function with concentration makes it difficult to answer this question unambiguously. Different definitions of the average relaxation time may lead to somewhat different concentration dependences (see below). We have chosen to use the correlation time τ_c as a model independent measure of the average relaxation time[28]:

$$\tau_c \equiv \int_0^\infty CF(t)\,dt = \frac{1}{r(0)} \int_0^\infty r(t)\,dt \qquad (3)$$

In concentrated solutions, τ_c is significantly longer than the fluorescence lifetimes of our probes (≈ 7 ns). Under these conditions we cannot observe the entire anisotropy decay and our determination of τ_c is less accurate. When τ_c is less than 40 ns, we estimate the uncertainty in the reported τ_c values to be about 10%. For τ_c values greater than 40 ns, we estimate a larger uncertainty of 15–20%. The very long correlation times reported in parentheses in *Tables 1* and *2* have even larger uncertainties.

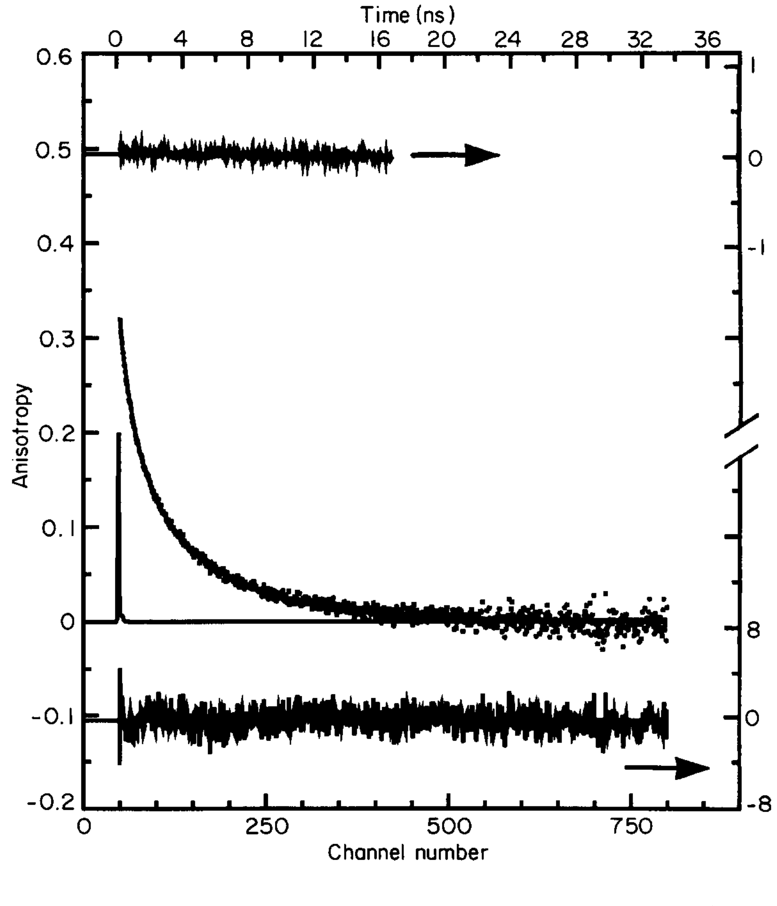

Figure 2 Anisotropy decay data set for PS-A-PS in 0.17 (v/v) PS/THF (25.0°C) fitted to a biexponential function. The fit parameters are: $a_1 = 0.162$, $\tau_1 = 1.03$ ns, $a_2 = 0.171$, $\tau_2 = 5.15$ ns, $\chi_r^2 = 1.06$. The weighted residuals are shown on the bottom and the autocorrelation of the residuals is displayed in the upper left hand corner. These two functions are plotted according to the right axes. The instrument response function is shown at $t = 0$

Table 1 Correlation times τ_c, for PS-A-PS

Concentration (v/v)	τ_c (ns)		
	4.5°C	25.0°C	45.5°C
0.004	2.56	2.01	1.10
0.11	4.3	2.66	1.70
0.17	5.6	3.21	1.96
0.26	9.0	4.8	2.76
0.35	16.6	8.3	4.6
0.42	41.0	17.3	8.2
0.51	88.0	39.8	16.6
0.58	(180.0)	75.0	32.3

Table 2 Correlation times, τ_c, for DPA

Concentration (v/v)	τ_c (ns)		
	4.5°C	25.0°C	45.5°C
0.00	0.073	0.050	0.036
0.07	0.096	0.067	0.046
0.15	0.13	0.092	0.066
0.22	0.21	0.14	0.078
0.27	0.26	0.20	0.10
0.36	0.73	0.38	0.19
0.42	1.63	0.64	0.32
0.49	4.1	1.61	0.63
0.58	25.2	6.4	1.92
0.63	82.0	20.5	4.5
0.67	(170.0)	41.0	8.4
0.71[a]	-	93.0	24.3

[a] Not used for the free volume analysis

RESULTS AND DISCUSSION

A major goal of this paper is to compare the microscopic friction in PS solutions determined by various probes. Implicit in this approach is the assumption that our solutions are homogeneous, i.e. the average composition of the solution in the immediate vicinity of a probe or labelled chain is the same as the overall solution composition. Qualitatively, the slower a probe molecule rotates or translates, the higher the friction. We assume that the microscopic friction is directly proportional to τ_c for the DPA and PS-A-PS measurements. Using Einstein's relation, we take the translational diffusion coefficient to be inversely proportional to the friction. In each of these cases the friction is proportional to the time required to translate or rotate some characteristic length or angle.

An equivalent way of considering these comparisons is in terms of a local viscosity. In a previous publication[14] we used hydrodynamic arguments[29] (the Stokes–Einstein and Stokes–Einstein–Debye relationships) to quantitatively relate the correlation times to the local viscosity.

Concentration dependence

Polymer volume fraction has a strong effect on the motions of DPA and PS-A-PS in PS/THF solutions. *Figure 3* shows anisotropy decays for PS-A-PS in PS/THF from dilute solution to a volume fraction of 0.58. Since the dynamics slow dramatically at higher concentrations we cannot observe all of the anisotropy decay. As discussed above, we use τ_c to characterize the average decay time of the observed dynamics. τ_c values for PS-A-PS and DPA are reported in *Tables 1* and *2*. Each data point is an average of two to seven individual measurements performed on separate days and/or samples. Experiments were not performed above a volume fraction of 0.71. At higher concentrations, essentially no reorientation of DPA or PS-A-PS would occur in our experimental time window of 40 ns. The 0.71 volume fraction solution has a T_g which is only about 30°C lower than our lowest measurement temperature[30].

In *Figure 4* we compare the concentration dependences of three different experiments which are sensitive to friction on the molecular level. Data at the three different temperatures are shown. In addition to our measurements of DPA and PS-A-PS dynamics, *Figure 4* shows translational diffusion results for methyl red in PS/THF solutions performed by Landry *et al.*[20]. For the labelled PS measurements, the results at each temperature are scaled to the correlation time for very dilute solution (volume fraction 0.004). The free probe data are scaled to the diffusion constant (or correlation time) with no polymer present. Thus the *y*-axis of the plot is chosen such that it is inversely proportional to the microscopic friction for all three types of measurements. Polynomial fits through the DPA (solid line) and PS–A–PS (dashed line) are shown.

Figure 4 indicates that the three different measurements have similar concentration dependences. This implies that the frictions sensed by the three measurements are similar throughout the concentration range. The concentration dependences of DPA rotation and the segmental motions of the PS-A-PS are somewhat different, with DPA showing a consistently stronger concentration dependence. The methyl red translational diffusion data have almost precisely the same concentration dependence as the labelled chain motions.

We have examined the DPA and PS-A-PS results shown in *Figure 4* in two different ways. Analysis

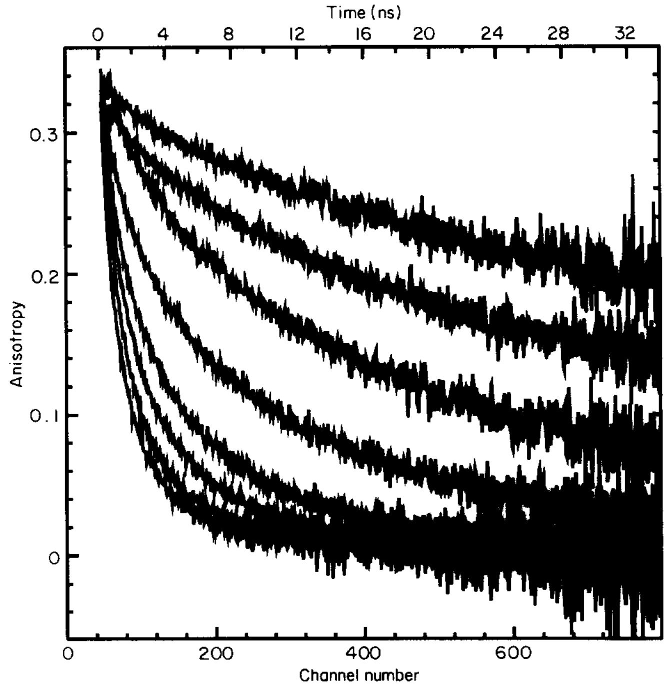

Figure 3 Observed anisotropy decays at 25.0°C for PS-A-PS in PS/THF. From the bottom, the curves correspond to volume fractions of 0.004, 0.11, 0.17, 0.26, 0.35, 0.42, 0.51 and 0.58

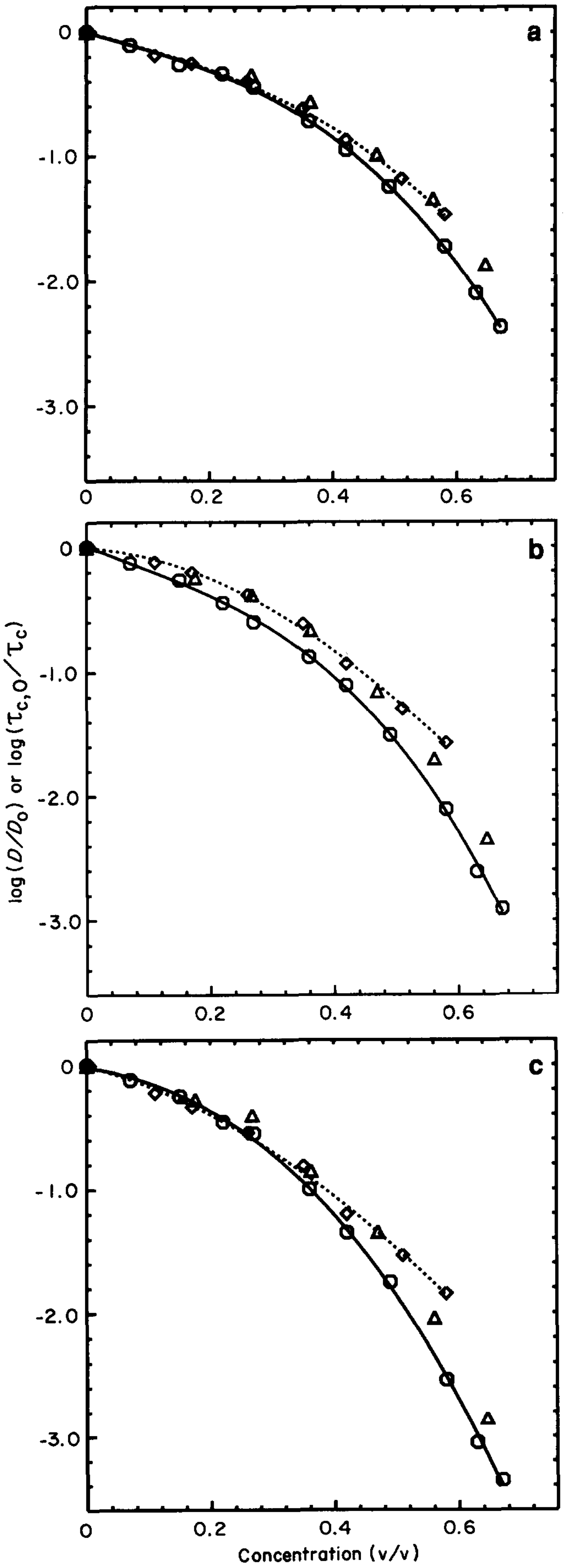

Figure 4 Concentration dependences of local mobility in PS/THF at (a) 45.5°C; (b) 25.0°C; (c) 4.5°C. Rotational diffusion of DPA (○), translational diffusion of methyl red (△) and segmental motion of PS-A-PS (◇). The lines are third-order polynomial fits (see *Table 4*) to the data for DPA (——) and PS-A-PS (····)

Table 3 Fujita free volume parameters

		4.5°C	25.0°C	45.5°C
DPA	$f(T, 0.33)$	0.075 ± 0.003	0.090 ± 0.004	0.109 ± 0.007
	$\beta(T)$	0.161 ± 0.014	0.211 ± 0.020	0.245 ± 0.030
DPA	$f(T, 0.42)$	0.086 ± 0.005	0.111 ± 0.006	0.131 ± 0.009
	$\beta(T)$	0.163 ± 0.015	0.227 ± 0.020	0.249 ± 0.030
PS-A-PS	$f(T, 0.42)$	0.097 ± 0.016	0.137 ± 0.020	0.145 ± 0.023
	$\beta(T)$	0.120 ± 0.031	0.244 ± 0.017	0.242 ± 0.065

Table 4 Polynomial fit parameters

	T(°C)	A	B	C
PS-A-PS	4.5	−1.254	−3.619	+0.487
	25.0	−0.290	−4.909	+1.228
	45.5	−1.294	−0.423	−2.967
DPA	4.5	−0.827	−4.041	−3.398
	25.0	−1.981	+1.412	−7.490
	45.5	−1.361	+0.070	−4.954

according to Fujita's free volume theory[31] was performed using[20]:

$$-\frac{1}{\ln a_c} = f_2(T, \phi_1^r) + \frac{f_2^2(T, \phi_1^r)}{\beta(T)} \cdot \frac{1}{(\phi_1 - \phi_1^r)} \tag{4}$$

where ϕ_1 is the solvent volume fraction. The smallest available value was used as the reference value of the solvent volume fraction ϕ_1^r, and dilute solution data were included in the fits. The 0.71 volume fraction data for DPA in PS/THF was not used in the free volume analysis. In addition we analysed the DPA data using the same ϕ_1^r as the PS-A-PS data ($\phi_2 = 0.58$). The fitted parameters are reported in *Table 3*. The free volume parameters derived from the DPA and PS-A-PS data roughly agree. These parameters also agree, within error bars, with those reported by Landry *et al.*[20] for the translational diffusion of methyl red in PS/THF solutions.

A third-order polynomial in polymer volume fraction is used to produce the curves shown in *Figure 4*. For the diffusion measurements:

$$\log(D/D_0) = A\phi_2 + B\phi_2^2 + C\phi_2^3 \tag{5}$$

This empirical function and its analogue for correlation times accurately reproduce the data throughout the concentration range. The parameters are presented in *Table 4*.

Temperature dependence

Figure 5 presents the Arrhenius plots of the DPA rotational diffusion data at several different concentrations. As the concentration increases, the dynamics slow and become more temperature dependent. Although these plots would probably appear curved over a larger temperature range, the data appear linear over the observed range. From the slope of each line we extract an apparent activation energy E_a. We estimate the uncertainty in E_a to be $\pm 10\%$, except for $c = 0.67$ where it is larger.

Figure 6 shows E_a for the rotation of DPA and the segmental motions of PS-A-PS as a function of concentration. For comparison, we show E_a for translational diffusion of methyl red[20]. The fourth set of data plotted is the temperature dependence of the solution viscosity

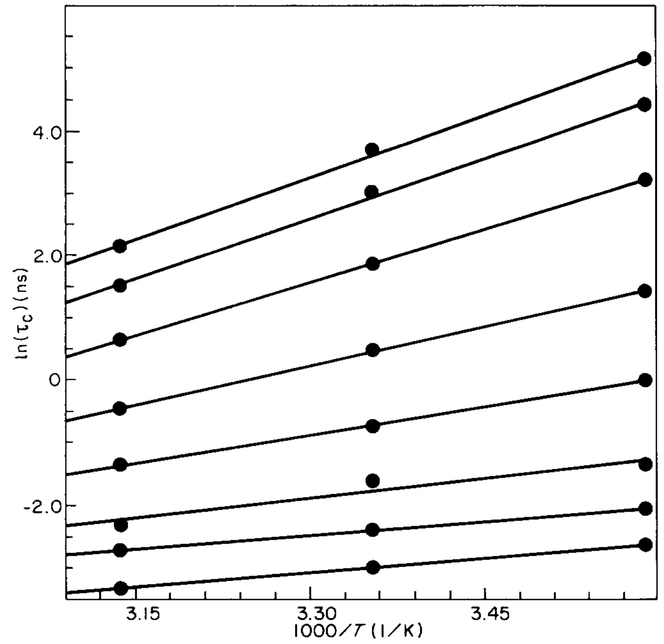

Figure 5 Arrhenius plot for the rotation of DPA in PS/THF. The volume fractions are, from the bottom: 0.00, 0.15, 0.27, 0.42, 0.49, 0.58, 0.63 and 0.67

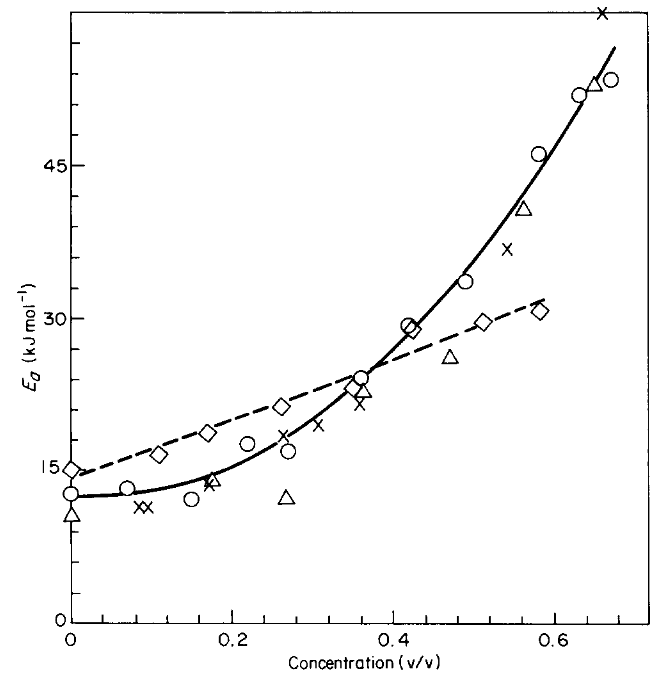

Figure 6 Apparent activation energies for the reorientation of DPA (○, ——) and the segmental dynamics of PS-A-PS (◇, ---) in PS/THF. These are compared to the apparent activation energies for translation of methyl red (△) and for the solution viscosity of PS/ethyl benzene (×)

of PS solutions with ethyl benzene[21]. Ethyl benzene is also a good solvent for PS, and both its viscosity and the temperature dependence of its viscosity are similar to those of THF. In addition, Biddle and Nordström[32] have shown, using steady-state optical experiments, that the dilute solution dynamics of labelled PS in THF and ethyl benzene are essentially identical. Thus the comparison of molecular mobility data from PS/THF solutions to viscosity data from PS/ethyl benzene solutions is reasonable*, as temperature-dependent viscosity data for PS/THF solutions are not available.

Figure 6 shows that the rotation of DPA, the translation of methyl red, and the solution viscosity all have the same temperature dependence at any given concentration. The comparison of the molecular mobility data to the solution viscosity is motivated by equation (1). That equation shows that all of the temperature dependence of the solution viscosity is contained in the local friction term. Thus *Figure 6* compares the temperature dependence of the friction parameter deduced from a macroscopic measurement tp the temperature dependence of our microscopic friction measurements. The fact that the same temperature dependence is seen for the solution viscosity and the free probe motion argues that the fundamental unit of motion responsible for the viscosity is fairly small (on the order of the size of the probe molecules). Note that the concentration dependence of the solution viscosity is much stronger than that of the rotation or translation of small probes. This is due to the second factor in equation (1).

Although equation (1) has been used for more than 25 years, direct comparisons between the temperature dependence of the solution viscosity and the temperature dependence of small probe mobility have not often been made. To our knowledge, this is the first direct comparison across such a wide concentration range. In an early paper, Tanaka *et al.* used steady-state fluorescence depolarization to study the rotational mobility of a chromophore bound to the end of polyethylene oxide chains[8]. The mobility of the free chromophore was also studied. For each measurement, concentrations from 0 to 60% polymer were investigated. They noted[8] that the temperature dependence of the viscosity was similar to the temperature dependence of probe motion. We reanalysed the results from Figures 3 and 5 of reference 8 and found that E_a for probe motion matched E_a for the solution viscosity throughout the concentration range. Several studies have shown that for bulk polymers the temperature dependence of small probe mobility matches the temperature dependence of the bulk viscosity[3,5,7,13,15,33]. Other studies have compared the concentration dependence of small probe motions and the monomeric friction coefficient extracted from mechanical measurements[34]. Possibly the expectation that free volume theory would only be valid for very concentrated solutions discouraged the comparison of these quantities in more dilute solutions. For concentrated solutions, free volume theory predicts that probe diffusion and solution viscosity should have the same temperature dependence if the 'B' parameter in the theory is the same for both measurements[4].

We will return later to the difference between the temperature dependence for the labelled chain motions and the other measurements shown in *Figure 6*. At this point we only note that similar behaviour has been observed in polyisoprene (PI)/THF[14].

Comparison to other results for PS solutions

To our knowledge, there is only one other set of molecular mobility measurements in PS/THF solutions. von Meerwall *et al.* used pulsed gradient spin echo n.m.r. to measure the translational diffusion of THF in PS solutions at 30°C[19]. Their solutions also contained 6% hexafluorobenzene. In reference 19, it is shown that the concentration dependence of THF translational diffusion is in good agreement with the concentration dependence of methyl red translational diffusion. Thus the reported

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*Results cited in reference 2, Section 2.51, support this comparison solvent diffusion results from reference 19 roughly agree with the concentration dependence shown in *Figure 4b*. The presence of a significant amount of hexafluorobenzene may make this comparison less straightforward than it appears. This point will be addressed in a future publication.

Three related sets of measurements have been performed in PS/toluene solutions. It is reasonable to compare these results to PS/THF results given that the two solvents have similar viscosities and are both good solvents for PS.

Viovy and Monnerie[11] studied the concentration dependence of PS-A-PS in toluene solutions at 50°C*. They also used the time-correlated single photon counting technique. They fit their results to the GDL correlation function. In order to compare our results to theirs, we have calculated correlation times from their fitted parameters using the equation given by Hyde *et al.*[13]. For the comparison, we shifted our 45°C data for PS-A-PS to 50°C using the apparent activation energies given in *Figure 6*†. The τ_c values which we obtain from this procedure are in excellent agreement (within 10%) with the results of Viovy and Monnerie[11]. Our fundamental anisotropies are somewhat higher than those reported in reference 11 (0.34 *versus* 0.26). This is due to our excitation and emission wavelengths being closer to the origin of the S_0–S_1 transition.

Kim *et al.*[36] have reported translational diffusion measurements of methyl red in PS/toluene solutions at 20°C. The concentration dependence of these results is in good agreement with the concentration dependence of methyl red diffusion in PS/THF solutions[20] at 25°C.

Adachi *et al.*[30] used dielectric relaxation to measure the concentration and temperature dependence of the segmental motions of PS in toluene. It is difficult to compare these results directly to ours because the shortest times addressed in their study are longer than the longest times addressed in our study. It is clear, however, that for solutions of about 60% PS, the dielectric relaxation times are 10–100 times longer than our results for PS-A-PS. (The temperature dependence of the dielectric measurements is also different. For a 60% solution the apparent activation energy is about twice as strong in reference 30 as in the present work.) For PI, dielectric measurements[37] of segmental relaxation times are more than a factor of 10 *shorter* than the relaxation times for anthracene-labelled polyisoprene (PI-A-PI)[13,14]. We should be careful with this comparison as there are important differences between the measurements. The optical technique measures a single-particle P_2 correlation function while the dielectric experiment is a collective P_1 measurement[29]. Nevertheless, the longer dielectric relaxation times in the PS solutions are striking, particularly when contrasted to the behaviour of concentrated solutions of PI and bulk PI.

Comparison of PS and PI in THF

We recently reported an investigation of molecular mobility in PI/THF solutions[14]. The rotation of DPA and the dynamics of PI-A-PI were measured from dilute solution to the bulk at 5, 25 and 45°C. As in this study, we compared our results with translational diffusion measurements of methyl red[20] in PI/THF and dielectric relaxation measurements of segmental dynamics[38] in PI/toluene. For the PI system we found that:

1. the translational diffusion of methyl red and the rotational diffusion of DPA have the same concentration dependence;
2. segmental motions of PI-A-PI have a slightly weaker concentration dependence;
3. E_a for the translational diffusion of methyl red was consistent with E_a for DPA rotation throughout the entire concentration range. The E_a for PI-A-PI motions was approximately linear in concentration, with an initial concentration dependence stronger than the initial dependence observed for DPA.

The first and second results for the PI/THF system are similar to the results reported here for the PS/THF system. For both PS and PI, similar concentration dependences are observed for DPA rotation, methyl red translation, and the segmental motions of the labelled chain. (Note that for each type of measurement the concentration dependence was steeper in PS solutions than in PI solutions.) Thus in each system, the microscopic friction measured by different techniques is approximately the same. For both systems, somewhat weaker concentration dependences are observed for labelled chain motions than for DPA rotation. One difference between the results for the two systems is that the concentration dependence of methyl red translation follows DPA rotation in PI/THF while it follows labelled chain motions more closely in PS/THF.

The third result for the PI/THF system is also in good agreement with the results reported here for the PS/THF system (*Figure 6*). In reference 14 we discussed a possible origin of the different temperature dependences observed for labelled chain motions and rigid probe translation or rotation. The length scale of the labelled chain motions may be decreasing as the temperature decreases. If a smaller piece of chain needs to move at lower temperatures in order to reorient the transition dipole of the probe, the reorientation should occur more rapidly than would be expected based on results at higher temperatures. Thus a weaker temperature dependence would be observed. Changing the length scale of the motion is not an option for the rigid probes used in the rotational and translational diffusion measurements. Presumably the length scale of interest in these experiments is given by the size of the probe molecule.

While the explanation of *Figure 6* in terms of changing length scales for labelled chain motions is speculative for the PS/THF system, there is additional evidence to support this position with respect to the PI/THF results (see Figure 7 of reference 14). Physically, it is not difficult to rationalize such a result. Presumably a distribution of different chain motions contributes to the reorientation of the transition dipole of the attached chromophore in PS-A-PS. As the temperature decreases, steric interference from neighbouring chains increasingly frustrates motions which would otherwise cause the chromophore to reorient. This interference will be strongest for those

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* There are several misprints[35] in Table 2 of reference 11. The correct τ_1 are (in ns): PS1300, $w_2=0.025$, $\tau_1=0.266$; PS420, $w_2=0.20$, $\tau_1=0.395$, $w_2=0.15$, $\tau_1=0.369$, $w_2=0.10$, $\tau_1=0.295$, $w_2=0.06$, $\tau_1=0.310$; PS23, $w_2=0.48$, $\tau_1=1.94$

† The shift from 45 to 50°C is determined using the measured apparent activation energy for PS-A-PS/THF in *Figure 6*. Log shift is determined by:

$$\log\frac{\tau(50°\mathrm{C})}{\tau(45°\mathrm{C})}=\left(\frac{1}{323}-\frac{1}{318}\right)\left(\frac{E_a(\mathrm{J\,mol^{-1}})}{2.3R}\right)$$

motions in the distribution which involve larger segments of the chain. This physical argument suggests that a decrease in the length scale for labelled chain motions with decreasing temperature is plausible. A decrease of length scale for labelled chain motion with increasing concentration could account for the different concentration dependences seen in *Figure 4*[14].

Concentration-dependent shapes of the correlation functions

As discussed in the Data Analysis section, the shapes of the correlation functions for DPA rotation and labelled chain motion change with polymer concentration. This change makes it difficult to represent the correlation function with a single parameter. We have chosen to use the integral of the correlation function in order to compare two correlation functions of different shapes (as in *Figure 4*). We believe that τ_c is the most fundamental model-independent measure of the average relaxation time. Nevertheless, it must be noted that other measures of the relaxation time may give significantly different concentration dependences.

We performed a test to determine how a different definition of the relaxation time (other than τ_c) would change the concentration and temperature dependence of the DPA and labelled chain motions. We used the initial slope of the anisotropy decay (calculated analytically from the biexponential fits) as an alternative measure of the relaxation time. The initial slope emphasizes the fast dynamics in the correlation function while τ_c is more sensitive to slow components. The alternative approach yields E_a values which are always less than those shown in *Figure 6*, in some cases by as much as 40%. E_a for the labelled chain motion is not a monotonically increasing function of concentration when the initial rate is used to characterize the correlation function. The concentration dependences do not change as dramatically. Plots analogous to those shown in *Figure 4* are always monotonically decreasing functions of concentration. The concentration dependence given by the initial rate method is weaker than that shown in *Figure 4* for both DPA and labelled chain motions. At each temperature, the concentration dependence of DPA rotation, as determined by the initial rate method, is similar to the concentration dependence of the labelled chain motions as determined from τ_c. The concentration dependence of labelled chain motion changes by a similar amount. Thus findings 2 and 3 (listed in the Introduction) are altered if the initial rate method is used to compare dynamics at different temperatures and concentrations.

Which method is more appropriate? While we believe that the correlation time is a better basis for comparison than the initial rate, there is no easy answer to this question. A great deal of information is contained in the time dependence of the correlation function; in general, it is not possible to unambiguously compress this information into a single parameter. Further advances in theory and simulation are required before the full time dependence of the correlation function can be understood[39]. Interestingly, in our previous study of PI/THF solutions there were no significant differences between the concentration and temperature dependences determined by the two methods. Thus the correlation function shapes change more substantially in PS solutions than in PI solutions. It may be that the close proximity of the glass transition for the PS system is responsible for this difference.

CONCLUDING REMARKS

In this paper we have compared the microscopic friction in PS/THF solutions as determined by three different techniques. Fairly good agreement was found among the results from the different techniques. The apparent activation energies for the translational and rotational diffusion of rigid probes in these solutions agreed with the activation energy of the local friction as determined by solution viscosity measurements throughout the concentration range. This argues that the fundamental unit of motion responsible for the solution viscosity occurs on a length scale less than or equal to the size of the probe molecules.

We have not explored the effect of changing the size of the probe molecules in this study or in our previous work on the PI/THF system. There is some evidence that smaller probes (such as toluene) show a substantially weaker concentration dependence in translational diffusion than do larger probes[40] (compare the concentration dependence of this paper to reference 41). Another study indicates that the rotation of small probes shows a weaker concentration dependence than that of large probes[10,42]. It is expected that still larger rigid probes (much larger than the entanglement spacing in a polymer solution) would show the same concentration dependence as the solution viscosity, i.e. a much stronger concentration dependence than that observed with the probes used in this study. We hope to systematically explore this effect in future studies in order to learn about the dynamics of polymer solutions on a variety of length scales.

ACKNOWLEDGEMENTS

This research was supported by the National Science Foundation through the Division of Materials Research, Polymers Program (DMR-8822076) and the Chemistry Division, Instrumentation Program (CHE-8804083). We thank the Graduate School at the University of Wisconsin for matching funds used in the purchase of instrumentation. M.D.E. thanks the Alfred P. Sloan Foundation for Fellowship Support. Professors J. D. Ferry, L. Monnerie, K. Adachi, J. L. Viovy and E. von Meerwall are acknowledged for helpful discussions.

NOTE ADDED IN PROOF

Very recently it was brought to our attention that four points describing the viscosity of PS/ethyl benzene solutions in *Figure 6* are the result of calculations and not direct experimental results ($c=0.11$, 0.31, 0.54 and 0.66). This does not modify our conclusions, as data from other PS/solvent systems[21] follow the DPA data shown in *Figure 6*. In particular, this is the case for PS/diethylbenzene[43] where data is available throughout the concentration range shown. This point wll be addressed further in a future publication.

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