Concentration and Temperature Dependence of Local Motions in Polyisoprene/Tetrahydrofuran

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ABSTRACT: The fluorescence anisotropy decay method is used to measure the rotational diffusion of 9,10-diphenylanthracene and the segmental motion of anthracene-labeled polyisoprene in tetrahydrofuran solutions of polyisoprene. The concentration dependences of these two measures of local motion are reported from pure solvent to bulk 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. The translational and rotational diffusion measurements have the same concentration and temperature dependence. A somewhat weaker concentration and temperature dependence is observed for the labeled chain motions. The differences between the rigid probe and segmental motions are tentatively attributed to a decrease in the size of the motional unit for local chain dynamics at high concentrations and low temperatures. This explanation is consistent with recent dielectric relaxation results on a related system.

Introduction

Understanding polymer motions on the scale of the repeat unit has both practical and fundamental implications. Practically, these motions influence penetrant diffusion and sub-T_g toughness. Fundamentally, these motions provide important insight into structure–property relationships and material properties such as T_g. These motions may be studied directly by observing chain motions and indirectly by following the rotational or translational dynamics of a dilute molecular probe.[1-5]

The mobility of a dilute probe in a simple liquid is, to a good approximation, directly proportional to the solvent viscosity. For concentrated polymer solutions and melts, probe motion is not simply related to the solution or melt viscosity. For example, the mobility of a small probe in a polymer melt will be independent of the matrix molecular weight as long as the molecular weight is reasonably large. In contrast, the melt viscosity is a strong function of molecular weight.

The relationship between probe motion and the solution or melt viscosity has been handled in two related ways. One approach breaks the viscosity into two different contributions:[6,7]

$$\eta(C,T,M) = \zeta(C,T)\ F(C,M) \tag{1}$$

Here, $\zeta(C,T)$ represents a friction factor, and $F(C,M)$ is a factor determined by the topological structure of the chains in solution. These factors are functions of the concentration, temperature, and molecular weight as indicated. Equation 1 describes the viscosity of many concentrated polymer solutions to a good approximation. For some bulk polymers under certain conditions, there is good correspondence between the friction experienced by a probe and the friction factor inferred from viscoelastic measurements.[8,9]

Another method of relating probe motion and solution viscosity is with the concept of "local viscosity".[10] In order for this concept to be useful in a predictive sense, the local viscosity measured by various techniques should be comparable. One goal of the present work is to test whether this is the case for three different measures of local mobility in polyisoprene/tetrahydrofuran (PI/THF) solutions. For this system we have measured the rotational diffusion of 9,10-diphenylanthracene (DPA) and local segmental motions of anthracene-labeled polyisoprene (PI–A–PI). Using time-resolved optical spectroscopy, these measurements have been performed across the entire concentration range from dilute solution to the bulk at three different temperatures. We compare these results to probe translational diffusion studies of methyl red in PI/THF by Landry and co-workers.[11] Some comparisons are also made with dielectric relaxation results on a related system.

The findings of this paper are (1) the rotational and translational diffusion of the dilute probes in PI/THF have the same concentration dependence, (2) the segmental motions of the PI–A–PI chains have this same concentration dependence up to 60% polymer but a weaker concentration dependence at higher concentrations, (3) the segmental motions of PI in toluene as determined by dielectric relaxation show the same concentration dependence as the segmental motions of the labeled chains, and (4) the concentration dependence for each measurement is stronger at lower temperatures, as expected. We tentatively attribute the difference between the concentration dependences of free probe and local chain motions to the decreasing size of the motional unit for local chain dynamics at higher concentrations.

Experimental Section

Materials. Anthracene-labeled polyisoprene chains (PI–A–PI) were synthesized via anionic polymerization as described previously.[12] The resulting chains contain one anthracene label covalently bonded in the center of each chain, as shown in Figure 1. The labeled chains have a molecular weight of 104K (M_w/M_n <1.10); the microstructure is 54% cis-1,4, 36% trans-1,4, and 10% vinyl-3,4. 9,10-Diphenylanthracene (DPA, Aldrich, 99%) and tetrahydrofuran (THF, Aldrich 24,288-8) were used without further purification. The unlabeled matrix polyisoprene (PI) was purchased from Polysciences (16202, M_w = 34K, M_w/M_n = 1.04) and has a microstructure is 68% cis-1,4, 25% trans-1,4, and 7% vinyl-3,4.

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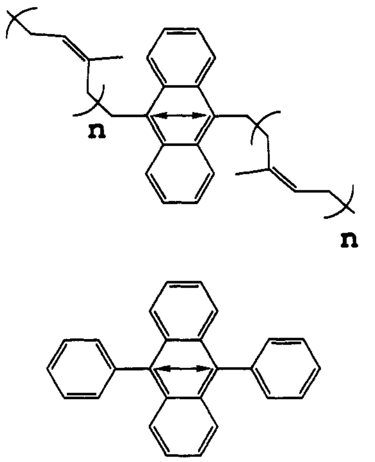

Figure 1. Probes used in these experiments. Anthracene-labeled polyisoprene (PI–A–PI) is shown at the top while 9,10-diphenylanthracene (DPA) is shown at the bottom. The double arrow denotes the transition dipole moment for the observed electronic transition.

Sample Preparation. These experiments require optically clear, homogeneous samples with a low optical absorbance. Dilute solutions of the unlabeled PI (<20 wt %) were prepared in THF, and either DPA or PI–A–PI was added. The resulting solution was subjected to freeze/pump/thaw cycles to remove molecular oxygen and increase the observed 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 (0.45-μm Teflon filter) into a specially adapted 3-mm path length quartz cuvette.

To obtain 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 and $\rho_{PI} = 0.913$ g/mL. Samples were allowed to diffuse until homogeneous (usually 1–2 days, sometimes at 45 °C). Just before data acquisition, we checked the UV–vis absorption and the concentration by weight. Bulk samples were prepared by removing THF under vacuum for 6–8 weeks at 70 °C. We estimate that the error in reported volume fraction is ±0.02 at low concentrations and ±0.04 for the higher concentration solutions. The bulk samples were analyzed by NMR and found to contain <0.5% solvent. The absorbance at the excitation wavelength was usually <0.4. We have determined that the results are independent of sample absorbance in this range. The maximum concentrations of DPA and PI–A–PI were less than 50 ppm and 1.5%, respectively.

Technique. The fluorescence anisotropy decay method was used to observe the dynamics of the DPA and PI–A–PI chains. In each case, the experiment monitors the reorientation of the transition dipole of the chromophore (shown as a double-headed arrow in Figure 1). For the labeled polymer, only motions which reorient the polymer backbone are detected.

The experimental apparatus, technique, and method of data acquisition have been described elsewhere.[13] Only a brief description will be given here. A 5-ps linearly polarized excitation pulse is used to photoselect an anisotropic distribution of excited-state chromophores. Since the chromophores emit light which is polarized along the transition dipole, the fluorescence from the sample is partially polarized until molecular motions randomize the orientation of the excited-state chromophores. Thus, the reorientation of the transition dipole can be observed 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 $r(t)$ of the excited state chromophores is given by

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \tag{2}$$

The anisotropy decays to zero when the molecular motions have randomized the orientations of the excited-state chromophores, i.e., when $I_{\parallel}(t)$ and $I_{\perp}(t)$ have equal intensities. The decay of the anisotropy is directly related the second-order orientation autocorrelation function CF(t)

$$r(t) = r(0)\ \mathrm{CF}(t) \tag{3}$$

where CF(t) is given by

$$\mathrm{CF}(t) = \langle P_2(\cos\theta(t))\rangle \tag{4}$$

Here, P_2 is the second Legendre polynomial, and $\theta(t)$ is the angle through which a transition dipole has rotated in time t since the excitation pulse. The angular brackets indicate an ensemble average. 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.

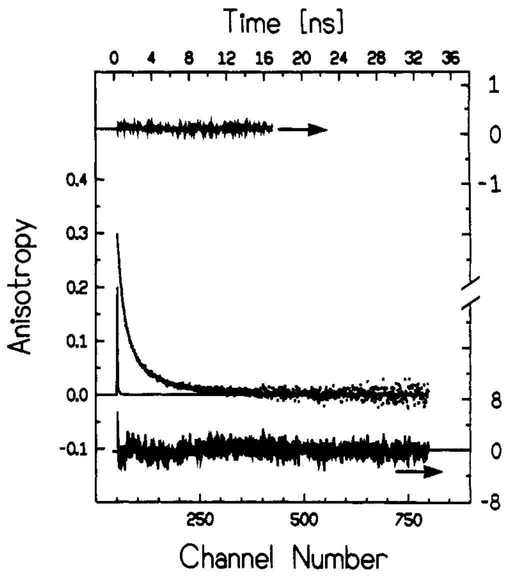

Figure 2. Anisotropy decay curve at 0.37 (v/v) for PI–A–PI in PI/THF (25.0 °C) fitted to a biexponential function. Fit parameters: $a_1 = 0.204$, $\tau_1 = 0.66$ ns, $a_2 = 0.105$, $\tau_2 = 3.48$ ns, $\chi_r^2 = 1.29$ (43.34 ps/channel). The weighted residuals are shown on the bottom, and the autocorrelations of the weighted residuals are in the upper left-hand corner. These two functions are plotted according to the right axes. The instrument response function is shown at $t = 0$.

The method of time-correlated single-photon counting was used to observe the time-dependent fluorescence decays.[14] The instrument response function for our apparatus has a fwhm of about 40 ps. Samples were excited at a 4-MHz repetition rate with the time to amplitude converter in reverse mode. Data were acquired at 20–30 kHz. For DPA and PI–A–PI, the excitation wavelengths were chosen to match the origin transitions at 394 and 406 nm, respectively. The fluorescence emission was observed at 414 nm.

Data Analysis. The anisotropy data for the PI–A–PI were initially fit to Hall–Helfand[15] and generalized diffusion loss[16] correlation functions. We observed that the shape of the correlation function changed systematically with concentration. At higher concentrations these functions did not provide adequate fits to the data. We found that a biexponential function could adequately reproduce the data throughout the concentration range:

$$r(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) \tag{5}$$

This function also provided adequate fits for the DPA anisotropy data; the shape of the correlation function also changed with concentration in these experiments. At any given concentration, the DPA anisotropy was typically more nearly exponential than the labeled chain anisotropy. The anisotropic rotational diffusion model[17] could be used to fit the DPA anisotropy data. We did not pursue this approach because we do not have confidence that the parameters extracted from fitting a single parallel transition would be meaningful.[18] The parameter values for all the fits are reported in ref 19. An example of a fitted data set is shown in Figure 2. All fitting was performed with a nonlinear Marquardt algorithm as described previously.

Ultimately, we would like to understand enough about dynamics in polymer solutions that the shapes of the correlation functions for DPA and labeled polyisoprene could be interpreted in detail. Since this is not possible at present, we take a broader approach to the data. In this paper we ask how dynamics slow as the concentration increases. The change in the shape of the correlation function with concentration makes it difficult to answer this question unambiguously, because this shape change implies a change in the shape of the distribution of relaxation times. Thus, different definitions of the average relaxation time could possibly lead to slightly different concentration dependences. We have chosen to use a model-independent measure of the average relaxation time, the correlation time τ_c. τ_c is defined as the integral of the correlation function:[20]

$$\tau_c \equiv \int_0^{\infty} \mathrm{CF}(t)\, \mathrm{d}t \tag{6}$$

Because the fluorescence lifetime is about 7 ns, at times longer than 40 ns it is difficult to accurately measure the anisotropy. For experiments in which the anisotropy decayed to <0.15 in 40 ns, we estimate the error in the reported correlation times to be <10%. For τ_c values >40 ns, we estimate an error of 15%.

We performed a test to determine how a different definition of the relaxation time would change the concentration and temperature dependence of the DPA and labeled chain motions. We used the initial slope of the anisotropy decay (calculated analytically from the biexponential fits) as an alternate measure of the relaxation time. This was chosen because it emphasizes the fast dynamics in the correlation function while the correlation time is more sensitive to slow components. The alternative approach yielded temperature dependences which were the same as those shown in Figure 6 within experimental error; the concentration dependences changed by more than the experimental error only at the highest concentrations. Even in this last case, the change was too small to modify any of the conclusions made in this paper. For example, the change was always less than 10% of the log $(\tau_{c,0}/\tau_c)$ values shown in Figure 4.

Results and Discussion

A major goal of this paper is to compare the "local viscosity" of polymer solutions as determined by various techniques. 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 labeled chain is the same as the overall solution composition. First, we define what we mean by local viscosity. For the case of DPA reorientation, we use the Stokes–Einstein–Debye equation for this purpose.[21,22] This equation relates the rotational diffusion constant of a sphere to the sphere volume V and the solvent viscosity η:

$$D_{\mathrm{rot}} = \frac{kT}{6\eta V} \tag{7}$$

While this equation describes molecular reorientation reasonably well for simple liquids, it cannot describe the reorientation of a probe in a polymer solution. As polymer concentration increases, the viscosity of the solution increases much more rapidly than D_{rot} decreases. Thus, we define the local viscosity η_L to be the viscosity which makes eq 7 correct. Since D_{rot} for a sphere equals $1/(6\tau_c)$, we can write

$$\eta_L = \frac{kT\tau_c}{V} \tag{8}$$

V is taken to be the volume which satisfies this equation for pure solvent with η_L equal to the solvent viscosity.

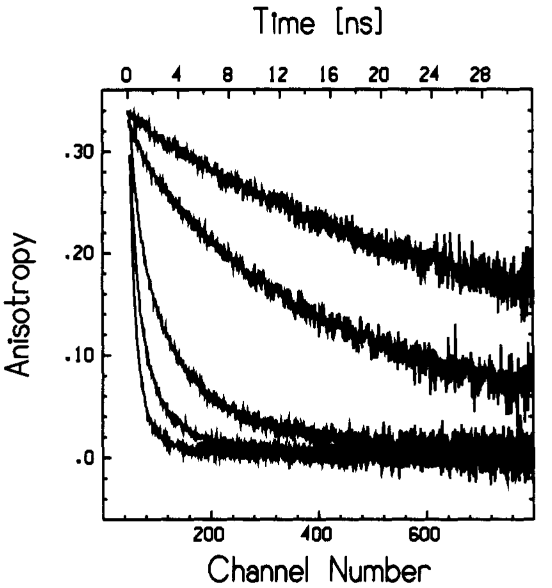

Figure 3. Anisotropy decays at 25.0 °C for PI–A–PI in PI/THF. From the bottom, the curves correspond to volume fractions of 0.13, 0.36, 0.61, 0.85, and 1.00.

For translational diffusion in a simple liquid, the Stokes–Einstein equation relates the diffusion coefficient of a sphere of radius r to the solvent viscosity:[23]

$$D_{\mathrm{trans}} = \frac{kT}{6\pi\eta r} \tag{9}$$

In a procedure analogous to that described above, we use this equation to define the local viscosity sensed by probe translational diffusion in polymer solutions; i.e., $D_{\mathrm{trans}} \propto 1/\eta_L$.

In order to relate the segmental motions of the anthracene-labeled chains to the local viscosity, we assume that the observed correlation times are proportional to η_L. This is consistent with the relations for rotational and translational diffusion. In each of those cases η_L is proportional to the time required to translate or rotate some characteristic length or angle.

Concentration Dependence. Polymer volume fraction has a strong effect on the motions of DPA and PI–A–PI in PI/THF. Figure 3 shows anisotropy decays for DPA in PI/THF at 25.0 °C. The concentration ranges from dilute solution to the bulk. The dynamics slow dramatically at higher concentrations. As discussed above, we can use τ_c to characterize the average decay time of the observed dynamics. τ_c values for PI–A–PI and DPA are reported in Table Ia,b. Each data point is a average of two to seven individual measurements performed on separate days and/or samples.

In Figure 4 we compare the concentration dependences of three different experiments which are sensitive to the local viscosity. Data at three different temperatures are shown. For the PI–A–PI measurements, the results at each temperature are scaled to the dilute solution result at that temperature. Data from the other two experiments were handled in an analogous manner. The y-axis of the plot is chosen such that it is inversely proportional to the local viscosity for all three types of measurements. While the rotational diffusion and labeled chain results are reported here for the first time, the translational diffusion results are from the work of Landry and co-workers.[11] They studied the translational diffusion of methyl red in the PI/THF system at the two highest temperatures shown in Figure 4.

Figure 4 indicates that the three different measurements have quite similar concentration dependences. This implies that the local viscosities sensed by the three

Table I
Correlation Times

(a) For PI–A–PI

	τ_c (ns)		
v/v	4.5 °C	25.0 °C	45.5 °C
0.00	0.66	0.46	0.34
0.13	0.97	0.64	0.42
0.20	1.25	0.82	0.52
0.36	2.74	1.59	1.01
0.40	2.95	1.66	0.94
0.61	8.32	4.09	2.27
0.85	47.3	18.8	8.84
0.95	96.7	36.9	16.4
bulk	114.	45.3	18.6

	τ_c (ns)		
	60.0 °C	65.5 °C	75.5 °C
bulk	11.5	9.22	7.36

(b) For DPA

	τ_c (ns)		
v/v	4.5 °C	25.0 °C	45.5 °C
0.00	0.073	0.050	0.036
0.10	0.090	0.063	0.045
0.20	0.13	0.084[a]	0.062
0.27	0.15	0.097	0.071
0.34	0.22	0.13	0.091
0.41	0.39	0.23	0.14
0.47	0.47	0.22	0.13
0.57	0.75	0.38	0.20
0.60	0.93	0.41	0.23
0.67	2.63	0.81	0.41
0.80	11.9	3.15	1.07
0.86	19.5	4.27	1.43
0.91	25.7	4.83	1.61
1.00	92.9	18.3	3.99

[a] T = 23.7 °C.

measurements are very similar throughout the concentration range. At the two temperatures for which the translational diffusion data are available, translational and rotational diffusion of probes have the same concentration dependence within experimental error from dilute solution to the bulk. At each temperature, the concentration dependence of the labeled chain motions is somewhat weaker than the probe diffusion data; this effect is stronger at lower temperatures. We will return to this difference.

We have fit the DPA and PI–A–PI results shown in Figure 4 in two different ways. Fits to Fujita's free volume theory[24] were performed as discussed in ref 11, with B = 1 and the bulk taken as the reference state. The fit parameters are reported in Table II. The fits adequately reproduced the data except at the lowest concentrations; this result is not unexpected.[11,25,26] The parameters for DPA at the two highest temperatures are in good agreement with those reported by Landry and co-workers for the translational diffusion of methyl red in PI/THF solutions.[11]

The parameters reported in Table II should be properties of the PI/THF system and hence should not differ for two different probe measurements. Free volume theory at this level fundamentally cannot account for the two different concentration dependences shown in Figure 4. This may not be surprising given that the theory was originally derived to describe free probe mobility.

We have used a polynomial in volume fraction to produce the fits shown in Figure 4. For the diffusion measurements

$$\log (D/D_0) = A\phi_2 + B(\phi_2)^2 + C(\phi_2)^3 \qquad (10)$$

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

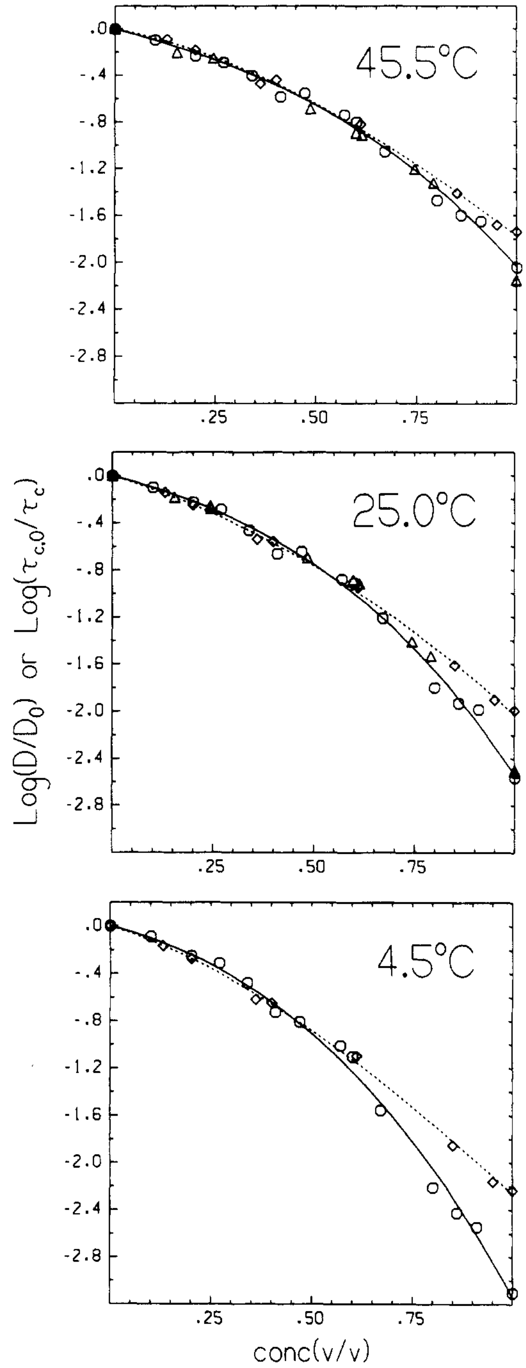

Figure 4. Concentration dependences of local mobility in PI/THF at 45.5, 25.0, and 4.5 °C: rotational diffusion of DPA (○), translational diffusion of methyl red (△), and segmental motions of PI–A–PI (◇). The lines are third-order polynomial fits (see Table III) to the data for DPA (solid line) and PI–A–PI (dashed line).

Table II
Fujita Free Volume Parameters

		4.5 °C	25.0 °C	45.5 °C
PI–A–PI	$f(0,T)$	0.06 ± 0.02	0.08 ± 0.03	0.09 ± 0.04
	$\beta(T)$	0.032 ± 0.001	0.048 ± 0.001	0.059 ± 0.002
DPA	$f(0,T)$	0.073 ± 0.007	0.098 ± 0.009	0.110 ± 0.015
	$\beta(T)$	0.09 ± 0.02	0.14 ± 0.04	0.12 ± 0.04

Temperature Dependence. Figure 5 presents an Arrhenius plot of the DPA rotational diffusion data at several different concentrations. As the concentration increases,

Table III
Polynomial Fit Parameters

	T (°C)	A	B	C
PI–A–PI	4.5	−1.073	−1.588	+0.3924
	25.0	−1.052	−0.9129	−0.0672
	45.5	−0.6536	−1.468	+0.3450
DPA	4.5	−0.8807	−1.489	−0.7730
	25.0	−0.9144	−0.7097	−0.9167
	45.5	−0.9362	−0.4384	−0.6631

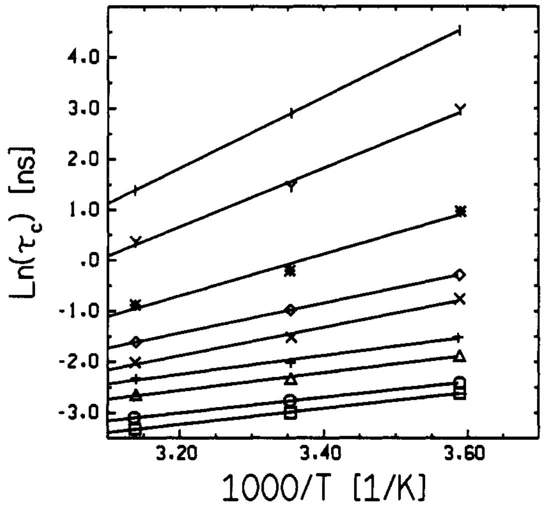

Figure 5. Arrhenius plot for the rotation of DPA in PI/THF at volume fractions: 0.0 (□), 0.10 (○), 0.27 (△), 0.34 (+), 0.47 (×), 0.57 (◊), 0.67 (*), 0.86 (Y), and 1.00 (|).

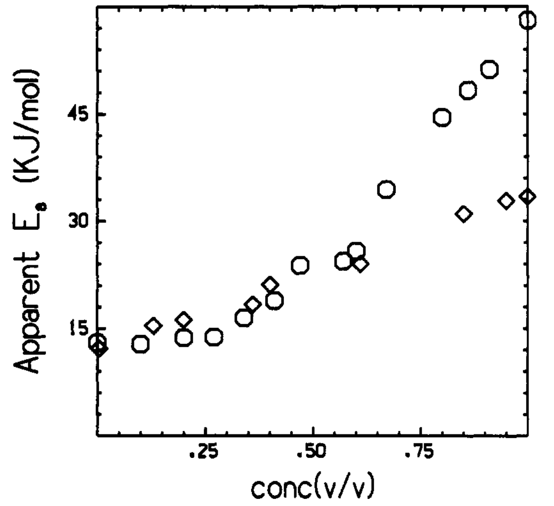

Figure 6. Apparent activation energies for reorientation of DPA (○) and the segmental dynamics of PI–A–PI (◊) in PI/THF.

the dynamics slow and become more temperature dependent. Although these plots would likely appear curved over a larger temperature range, over the observed range we can represent the data with an apparent activation energy E_a.[27]

In Figure 6 we compare the apparent E_a for rotational diffusion and labeled chain motion as a function of concentration. We estimate that the E_a extracted from Figure 5 and the analogous plot for the PI–A–PI data are accurate within about 10%. Up to a volume fraction of 0.60, the temperature dependences of the two measurements are quite similar. In more concentrated solutions, the DPA rotation shows a stronger temperature dependence. We have not shown the corresponding quantities for translational diffusion. These data are available only at two temperatures, and the error bars are rather large. However, the translational diffusion data show the same temperature dependence as the rotational diffusion data within error and do not match the temperature dependence of the labeled chain motions at higher concentrations.

The bulk DPA data have the same temperature dependence as the steady-shear viscosity of bulk polyisoprene.[7] Within experimental error, this result also matches the temperature dependence for translational diffusion of methyl yellow in PI,[28] rotational diffusion of anthracene[29] and 9,10-dimethylanthracene[29] in PI, and both normal-mode and segmental-mode motions of bulk PI as detected by dielectric relaxation experiments.[30] Adachi and co-workers performed dielectric studies on PI/toluene solutions (30.6% and 50.8% polymer) at lower temperatures than those used in this study.[31] Extrapolating their results to our temperature range, we find that their results for both the normal mode and the segmental mode are consistent with the results in Figure 6.

Comparison to Previous Results. Hyde and coworkers previously reported a study on the concentration and temperature dependence of the local dynamics of PI–A–PI in PI/3-iodotoluene solutions.[32] They utilized a transient holographic grating technique. The results reported in this paper (obtained with the time-correlated single-photon counting technique) are broadly consistent with this previous study but differ in one important respect. Reference 32 reports that the temperature dependence of PI–A–PI dynamics in bulk PI matches the temperature dependence of the bulk viscosity in the range from 25 to 80 °C. This is inconsistent with the results obtained here (see discussion of Figure 6). A comparison of the correlation times reported for the two studies indicates good agreement at high temperatures and disagreement by a factor of 2.2 near 25 °C, the lowest temperature reported in both studies. We believe that the present measurements are more reliable. The previous measurements effectively utilized a time window of 10 ns while the time window for the measurements reported here is about 40 ns. Thus, very long correlation times are more accurately estimated in the current work.

Veissier and co-workers have recently utilized time-correlated single-photon counting to study the local dynamics of PI–A–PI in bulk PI in the temperature range from 22 to 92 °C.[33] The temperature dependence of their results is in excellent agreement with the results reported here. Actual τ_c values in the current study differ from the results of ref 33 by about 60%. If our results are fitted to the same model of the correlation function used in their work, we observe similar correlation function shapes and the difference in absolute correlation times diminishes to about 20%.

Probe Rotation vs Labeled Chain Motions. In this section we address the differences in the concentration and temperature dependences of the DPA and PI–A–PI results (Figures 4 and 6). The labeled chain motions show a weaker concentration and temperature dependence than both probe rotation and probe translation. This can be explained by two general approaches: (1) The labeled chain motions always occur on a shorter length scale than the rigid probe motions. Shorter distance scale motions may have a weaker concentration and temperature dependence. The different temperature dependences of the α and β transitions would be an example of the latter effect. (2) The length scale of the labeled chain motion decreases as the temperature decreases or the concentration increases. If a smaller piece of chain needs to move at higher concentrations in order to reorient the transition dipole of the probe, the reorientation should occur more rapidly than would be expected based on the dilute solution result.

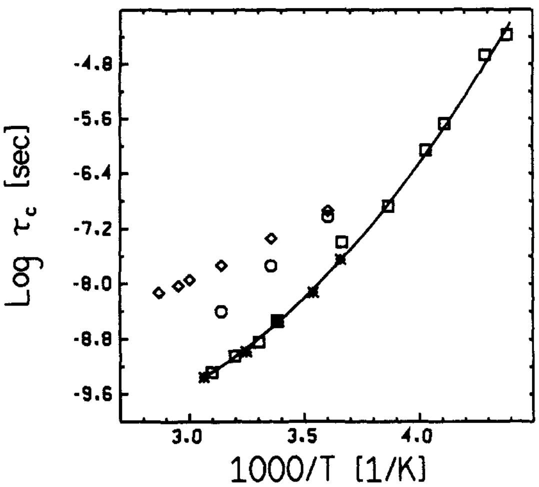

Figure 7. Correlation times for various dynamics measurements in bulk polyisoprene: PI–A–PI segmental motion (◇); reorientation of DPA (○), 9,10-dimethylanthracene (*), and anthracene (□). The last two measurements are from ref 22. The line is the bulk viscosity shifted vertically to coincide with the 9,10-dimethylanthracene data.

Thus, a weaker concentration dependence would be observed. A similar argument can be made about the temperature dependence. Changing the length scale of the motion is not an option for the rigid probes used in the translational and rotational diffusion measurements. For these experiments the length scale of interest is given by the size of the probe molecule.

Figure 7 can be used to distinguish between these two alternatives. This figure shows the temperature dependence of several dynamics experiments in bulk PI. In addition to the labeled chain motions, the rotational correlation times for anthracene,[29] 9,10-dimethylanthracene,[29] and DPA are shown. The line represents the temperature dependence of the bulk viscosity (arbitrarily shifted vertically). Throughout the 5–45 °C temperature range, the PI–A–PI chain motions occur more slowly than DPA rotation. Table I indicates that this is true at all concentrations. Thus, it seems unlikely that the first explanation above could be correct.

The second explanation invokes a concentration-dependent change in the size of the chain which must move to allow the chromophore to reorient. This explanation receives some support from recent dielectric relaxation results from Adachi and co-workers. They studied both the segmental-mode and normal-mode relaxations of PI in toluene solutions from 30% to the bulk. Their work supports the second explanation in two ways.

The concentration dependence of the segmental-mode motions (shifted from 273 to 278 K[34–36]) measured in the dielectric experiment is in excellent agreement with the labeled chain data shown in the top panel of Figure 4. The dielectric results clearly show a weaker concentration dependence than the rotational diffusion of DPA. We should be careful with this comparison as there are important differences in the measurements. The dielectric experiment measures a collective relaxation while the optical experiments measure single-particle P_2 relaxation. The two experiments measure the relaxation of vectors with different orientations relative to the chain backbone. Also, the dielectric experiments were performed in toluene rather than THF. Nevertheless, it is striking that the two experiments involving *chain* motions show the same concentration dependence while the experiments involving *rigid probe* motion show a different concentration dependence. Possibly the effective length scale associated with the dynamics is changing with concentration in the chain motion experiments.

A second argument in favor of the changing length scales explanation comes from ref 35. By comparing the normal-mode and the segmental-mode data with the Rouse theory, Adachi and co-workers have estimated the molecular weight of the dynamical chain unit as a function of concentration. They find that this unit monotonically decreases from about two repeat units at 30% polymer to one repeat unit in the bulk.

It is not difficult to rationalize the apparent changing length scales associated with local chain motions with a physical argument. Presumably, a distribution of different motions contributes to the reorientation of some vector attached in the molecular frame. This vector might be a permanent dipole (as in the dielectric experiment) or a transition dipole of a label (as in the optical experiment). As the concentration of a solution is increased, steric interference from neighboring chains increasingly interferes with motions which would otherwise cause the reorientation of the vector sensed by the experiment. This interference is strongest for those motions in the distribution which involve larger segments of the chain. This mechanism would suggest that the average length scale associated with reorientation of some local vector in the chain should decrease with concentration.

Summary

In this paper we have compared probe rotational and translational diffusion measurements to local chain dynamics in polymer solutions as a function of polymer concentration and temperature. We observe that all the measurements investigated show approximately the same concentration dependence. Thus, for these solutions and techniques, "local viscosity" is an approximately transferable quantity. The local viscosity inferred from measurements with one technique can approximately be used to predict the results for experiments with different technique.

In detail the concentration and temperature dependence of the labeled chain motions differ from those observed for the translational and rotational diffusion measurements. We have tentatively explained these results by postulating that the size of the chain involved in the observed motion of the anthracene label decreases with increasing concentration and decreasing temperature. In regard to the concentration dependence, this explanation is consistent with recent dielectric relaxation work on polyisoprene solutions.

More work will be required to test the generality of the features reported for the PI/THF system. We will soon publish a similar set of measurements for the polystyrene/THF system.[37] An important variable which needs to be explored is the size of rigid probes used for the translational and rotational diffusion measurements. There is some evidence that this can have a dramatic effect on the concentration dependence observed in translational diffusion.[38]

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