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Local Segmental Dynamics of Polyisoprene in Concentrated Solutions and in the Bulk

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ABSTRACT: Time-resolved optical spectroscopy has been utilized to study the local segmental dynamics of anthracene-labeled polyisoprene in concentrated solutions of polyisoprene and in the bulk. In bulk polyisoprene, we observe a temperature dependence in the local dynamics that matches the temperature dependence of the steady shear viscosity within experimental error. The concentration dependence of the local segmental dynamics is reasonably well described by a free volume approach. The relative change in correlation times for local dynamics between dilute solutions and the bulk matches the change in translational diffusion coefficients for a small probe molecule under comparable conditions. The optical results are compared to NMR and dielectric studies.

I. Introduction

A major goal of polymer physics has been to understand the link between the bulk properties of polymeric materials and the chemical structure of their repeat units. Important data for the construction of structure/property relationships come from the study of local segmental dynamics. It is expected that dynamics occurring on the length scale of a few monomer units are intimately related to the larger scale motions which contribute to the mechanical and viscoelastic properties of these materials. Experiments which probe local dynamics include dielectric relaxation,[1] NMR,[2] dynamic light scattering,[3] ESR,[4] and time-resolved optical spectroscopy.[5-11]

In this paper we report measurements of the local segmental dynamics of anthracene-labeled polyisoprene in concentrated solutions and the bulk. We utilize time-resolved optical spectroscopy to measure chain motions by observing the reorientation of an anthracene chromophore which is covalently attached to the chain. The transition dipole of the anthracene chromophore is in the chain backbone so that only chain motions are observed. The major strength of this type of experiment is that the entire time dependence of the orientation autocorrelation function of a backbone bond can be observed in a model-independent way. This allows the unambiguous comparison of chain motions in polymer solutions as the temperature and concentration are changed. A major part of this paper is a comparison of our results for the temperature and concentration dependence of local segmental dynamics with steady shear viscosity measurements, probe translational diffusion experiments, and local dynamics measurements by ^{13}C NMR and dielectric spectroscopies.

Our major conclusions are as follows: (1) The temperature dependence of the local segmental dynamics measured by the optical technique substantially follows the temperature dependence of the steady shear viscosity over the temperature range studied. (2) The concentration dependence of the local dynamics of anthracene-labeled polyisoprene chains in polyisoprene/3-iodotoluene solutions is reasonably well described by the free volume theory for two-component systems derived by Fujita. (3) For polyisoprene, NMR experiments are sensitive to shorter range motions than those observed by the optical technique. This leads to different concentration dependences being observed in the optical and NMR experiments. (4) The relative change in correlation times for local dynamics between dilute solution and the bulk matches the change in translational diffusion constants for a small probe molecule under comparable conditions.

II. Experimental Section

Materials. Anthracene-labeled polyisoprene chains were prepared anionically.[5] The resulting polymer chains contain one anthracene label covalently bonded in the center of each chain. The structure of the labeled chains is shown in Figure 1. The labeled chains had M_n = 104 000 (vapor-phase osmometry) and M_w/M_n = 1.09 (GPC). The chain microstructure is 54% cis-1,4, 36% trans-1,4, and 10% vinyl-3,4.

The polyisoprene matrix polymer (Polysciences) had an M_w = 34 000 and M_w/M_n = 1.04 with a microstructure of 68% cis-1,4, 25% trans-1,4, and 7% vinyl-3,4. The matrix polymer contained <0.5% BHT as an antioxidant. The glass transition temperature of the matrix polymer with antioxidant was determined to be −69 ± 2 °C by DSC at a scan rate of 5 °C/min.

The solvents utilized in preparing the concentrated polyisoprene solutions and bulk samples were 3-iodotoluene (Aldrich, 99%) and benzene (Aldrich Gold Label). These solvents were used without further purification.

Sample Preparation. These experiments require polymer samples which are deoxygenated, are homogeneous over several squared centimeters, and are of high optical quality. Bulk polyisoprene samples were prepared by starting with a ~5% solution of the labeled chains and matrix polymer in benzene. After filtering through a 0.45-μm filter, the solution was subjected to several freeze–pump–thaw cycles to remove oxygen. Under a nitrogen atmosphere, a few drops of the polymer solution were dripped into a 0.5-mm-thick Teflon ring (diameter ~2 cm) resting on a fused silica optical flat. The benzene was then removed under vacuum. This process was repeated until a ~0.5-mm-thick benzene-free polyisoprene film was produced. A second fused silica flat was then used to seal the sample. The residual benzene concentration in the film was determined to ≤0.5 wt % by NMR. Due to the large surface area of the film subjected to the vacuum, this method of sample preparation produced bulk polyisoprene samples after only 48 h under a vacuum of ~10^{-3} Torr.

The concentrated polymer solutions were prepared by dripping degassed 3-iodotoluene onto a bulk polymer film prepared as described above. After dissolution the 3-iodotoluene was removed by vacuum until the desired concentration was obtained as determined by NMR. We believe the solvent concentration to be correct to ±0.5 wt %. As a check of the NMR determination, the composition of a known mixture of 3-iodotoluene and the matrix polymer was measured by NMR. The measured weight fraction agreed to within 0.5% of the known value. The samples utilized in these experiments have polymer weight fractions of 1.00, 0.67, and 0.40. In all of the samples, the labeled chains accounted for 5–10% of the polymer mass. The chromophore concentration for all samples was on the order of 5×10^{-4} M. The

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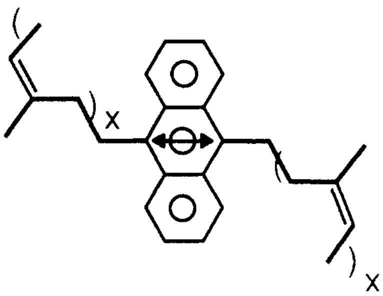

Figure 1. Structure of anthracene-labeled polyisoprene chains. The orientation of the transition dipole for both the excitation and probe transitions is indicated by the double-headed arrow. Because the transition moment is directed along the chain backbone, its motion directly reflects local conformational dynamics.

optical density for the $S_0 \rightarrow S_1$ transition at 405 nm for these samples ranged from 0.18 to 0.22.

Experimental Technique. The picosecond holographic grating technique has been previously utilized to investigate subnanosecond local segmental dynamics in dilute polyisoprene solutions.[5-7] Here we briefly describe the technique. The experimental observable is the orientation autocorrelation function of the transition moment of an anthracene chromophore which is covalently bonded in the center of the polyisoprene chain. The structure of the labeled chain is shown in Figure 1. Since the transition moment of the chromophore is oriented along the chain backbone, the reorientation of the transition dipole directly reflects the local conformational dynamics of the polymer chain.

In this experiment two vertically polarized laser pulses having a FWHM ~30 ps are temporally and spatially crossed on an absorbing sample. The resulting optical interference pattern creates a periodic spatial distribution of excited states. This excited-state grating acts to diffract a third probe pulse which is optically delayed in time with respect to the two excitation pulses. We observe the time-dependent intensity of the diffracted probe pulse polarized parallel ($T_{\parallel}(t)$) and perpendicular ($T_{\perp}(t)$) to the polarization of the excitation pulses. The time-dependent anisotropy function, $r(t)$, is constructed from the transient grating signals in the following manner:

$$r(t) = \frac{(T_{\parallel}(t))^{1/2} - (T_{\perp}(t))^{1/2}}{(T_{\parallel}(t))^{1/2} + 2(T_{\perp}(t))^{1/2}} \tag{1}$$

The correlation function, CF(t), is obtained from $r(t)$ by

$$\mathrm{CF}(t) = r(t)/r(0) \tag{2}$$

where $r(0)$ is an experimentally determined constant related to the relative orientation of the transition moments for the excitation and probe transitions of the anthracene chromophore. In this manner, the correlation function is sampled independent of any assumed model for the dynamics.

Data Analysis. The time-dependent anisotropy function, $r(t)$, was measured as a function of temperature for the two concentrated polyisoprene solutions and the bulk polyisoprene sample. In each case the anisotropy curves were fit with theoretical models for CF(t) proposed by Hall and Helfand,[12] Viovy et al.,[8] and Bendler and Yaris.[13] The generalized diffusion and loss model (GDL) of Viovy et al. proved to be the best fit for the 67 wt % polyisoprene solution, while all three models fit the 40 wt % polymer solution about equally well. For these two concentrations, the observed anisotropy decayed to zero within the experimentally accessible time range. The anisotropy decays for the bulk sample were slow enough that a significant part of the correlation function could not be observed. At the highest temperatures where most of the correlation function was sampled, the GDL model fit the data much better than either other model. Overall the GDL model provided the best description of the experimental data under the range of conditions examined and will be used in the rest of this paper to further analyze the results.[14] The GDL model is given by

$$\mathrm{CF}(t) = \exp(-t/\tau_1)\exp(-t/\tau_2)[I_0(t/\tau_1) + I_1(t/\tau_1)] \tag{3}$$

where I_0 and I_1 represent modified Bessel functions. τ_1 and τ_2 represent time constants for correlated and uncorrelated conformational transitions, respectively.[8,12] An iterative reconvolution procedure utilizing a nonlinear least-squares algorithm based on the Marquardt technique was employed to extract $r(0)$, τ_1, and τ_2 from the experimental anisotropies.[15,16]

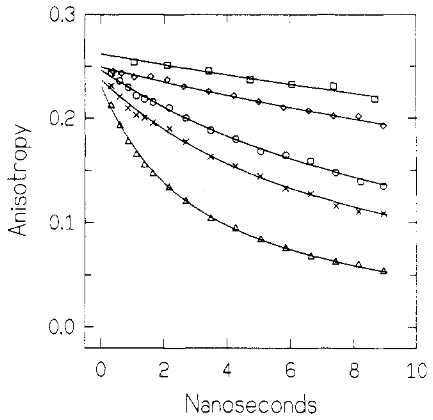

Figure 2. Temperature dependence of the anisotropy function for anthracene-labeled polyisoprene in a bulk polyisoprene matrix. The symbols represent the experimental anisotropies, and the lines are fits to the GDL correlation function with the constraint that $\tau_2/\tau_1 = 11$. The symbols indicate independent measurements of the anisotropy function for the following temperatures: 24 °C (□), 35 °C (◇), 50 °C (○), 60 °C (×), and 82 °C (△).

The shape of CF(t) is characterized by the ratio τ_2/τ_1. This ratio was found to be at most a weak function of both temperature and polyisoprene concentration (from 40 wt % to the bulk) and was equal to 11 ± 2 under all conditions investigated. In previous work on dilute solutions of polyisoprene, we found that the Hall–Helfand model provided a better fit to the data than the GDL model.[5] Even so, the fits to the GDL model yielded values of τ_2/τ_1 close to those found in this study. Experiments by Viovy et al. on anthracene-labeled polybutadiene in a bulk polybutadiene matrix (using the fluorescence anisotropy decay technique) found that the GDL model provided the best fit to their data, although with a τ_2/τ_1 ratio of ~35.[9] The different shapes of the correlation functions observed for the two different polymers presumably reflect true differences in the dynamics due to the different molecular structures.

Because of the observation that the correlation function has an approximately constant shape over a wide range of concentrations and temperatures, we utilized a constrained fitting procedure to extract decay parameters from the anisotropy decays measured for the bulk polyisoprene sample from 24 to 83 °C. The bulk sample decays were fit to the GDL expression with the constraint that $\tau_2/\tau_1 = 11$ so that the parameters $r(0)$ and τ_1 could be recovered. (The parameters obtained in this manner are not very sensitive to the precise value of τ_2/τ_1 chosen. Changing τ_2/τ_1 by ±2 results in $r(0)$ and τ_1 changing by less than 1% and 6%, respectively.)

In order to obtain a characteristic decay time for all of the correlation functions measured in these experiments, the correlation time, given by

$$\tau_c = \int_0^{\infty} \mathrm{CF}(t)\, \mathrm{d}t \tag{4}$$

was calculated. For the GDL function, this integral yields

$$\tau_c = \left(\frac{2}{\tau_1\tau_2} + \frac{1}{\tau_2^2}\right)^{-1/2}\left(\frac{1}{\tau_1}\left(\frac{1}{\tau_1} + \frac{1}{\tau_2} + \left[\frac{2}{\tau_1\tau_2} + \frac{1}{\tau_2^2}\right]^{1/2}\right)^{-1} + 1\right) \tag{5}$$

III. Results and Discussion

Temperature Dependence of Local Dynamics in Bulk Polyisoprene. Figure 2 shows the time-dependent anisotropy for anthracene-labeled polyisoprene in a bulk polyisoprene matrix at temperatures between 25 and 82

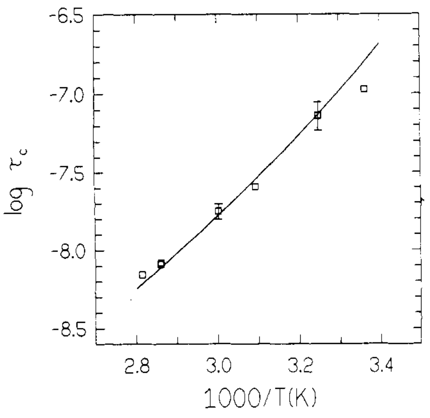

Figure 3. Temperature dependence of the correlation time for anthracene-labeled polyisoprene in a bulk polyisoprene matrix plotted in an Arrhenius format. The symbols are correlation times (in seconds) obtained from the anisotropy functions in Figure 2. Typical experimental uncertainties in the correlation time are indicated for two points. The line represents the temperature dependence of the steady shear viscosity for a bulk polyisoprene sample having a similar microstructure. The steady shear viscosity curve has been vertically shifted to coincide with the correlation time at ~70 °C.

°C. As the temperature falls below ~25 °C, the decay of $r(t)$ becomes longer than the accessible time scale afforded by the fluorescence lifetime of the anthracene chromophore (~10 ns). The lines drawn through the data represent the best fits to the data using the GDL expression with the constraint that $\tau_2/\tau_1 = 11$.

In order to examine the temperature dependence of the correlation function, the correlation time was determined for each of the anisotropy decays in Figure 2. An Arrhenius plot was constructed from these values for τ_c and is shown in Figure 3. The solid curve in this figure shows the temperature dependence of the steady shear viscosity for a bulk polyisoprene sample having a molecular weight of 48000 and a microstructure similar to the matrix polymer used in these experiments (61% cis-1,4, 32% trans-1,4, and 7% vinyl-3,4). The steady shear viscosities were measured from −0.3 to 78.3 °C by Nemoto et al. and were fit to a WLF equation of the form[17]

$$\log a_T = \frac{-4.98(T - 25\ °\mathrm{C})}{147.5 + (T - 25\ °\mathrm{C})} \tag{6}$$

The absolute value of log a_T has been vertically shifted to coincide with log τ_c at ~70 °C. A linear least-squares fit to the data in Figure 3 yields an apparent activation energy of 43 ± 3 kJ/mol. An apparent activation energy of 49 kJ/mol is obtained from eq 6 at 50 °C, the center of the range of the optical experiments. Viscosity data of Gotro and Graessley[18] on polyisoprene chains with a similar microstructure (77% cis-1,4, 15% trans-1,4, and 8% vinyl-3,4) yield an apparent activation energy of 46 kJ/mol at 50 °C. We consider the apparent activation energies from the local dynamics experiment and the viscosity experiments to be in substantial agreement. Previous work by Viovy et al. on anthracene-labeled polybutadiene in bulk polybutadiene gave similar agreement between the viscosity data and the local dynamics measurements.[9] These results indicate that the friction felt by the largest distance scale polymer motions has the same temperature dependence as the friction that opposes the local conformational dynamics measured in the optical experiments. It could be that the local dynamics probed in these experiments are the driving force for the larger distance scale motions sensed by the steady shear viscosity measurements.

It is interesting to compare the temperature dependence of the microscopic dynamics reported in this paper to other measurements of local dynamics performed in bulk polyisoprene with NMR and dielectric spectroscopies. Howarth conducted ^{13}C NMR experiments at two frequencies on the methine carbon in natural rubber.[19] The spin–lattice relaxation time, T_1, was measured from 15 to 90 °C. To fit the data, Howarth employed a motional model referred to as the "three-τ" theory. This theory incorporates rapid and slow librational motions coupled with an underlying isotropic motion. It was found that the rapid librational motion and the isotropic motion have essentially no temperature dependence. The apparent activation energy of 45 kJ/mol recovered for the slow librational process is consistent with the optical and mechanical measurements discussed above. The choice of a motional model is necessary when dynamics are measured by NMR. It is often difficult to assess the uniqueness of such a motional model, and important results such as the temperature dependence of a particular motion will depend upon the model chosen. One of the strengths of the time-resolved optical measurements presented in this paper is that the complete temporal evolution of the correlation function can be sampled independent of any assumed model for the dynamics. We have fully exploited this capability for the concentrated solutions examined in this paper but have not been able to fully sample the correlation function in the bulk sample. We are currently developing experimental techniques which will access a wider time range and allow local conformational dynamics to be characterized at temperatures near T_g.

In another local dynamics study, Adachi and Kotaka performed dielectric measurements on the segmental mode relaxation process in an undiluted polyisoprene sample with $M_w = 41900$ and a microstructure of 84% cis-1,4, 12% trans-1,4, and 4% vinyl-3,4.[1] The temperature dependence of the frequency of the loss maximum was fit to a WLF-type equation. At 50 °C an apparent activation energy of 41 kJ/mol was obtained. This is in good agreement with the optical results discussed above. In the same study, Adachi and Kotaka examined the dielectric relaxation of the normal mode process in polyisoprene. They found an apparent activation energy of 46 kJ/mol at 50 °C. It is interesting to note that the activation energy for the normal mode process is about 10% higher than for the segmental mode process. Although it might be possible that experimental errors account for this difference, the same trend is noted in the comparison between our optical measurements of the local dynamics and the viscosity data (which is primarily influenced by large-scale chain motions such as the normal mode process). We will not speculate further on the possible significance of this observation except to note that investigations of local motions in polypropylene and polybutadiene utilizing photon correlation spectroscopy have observed a different temperature dependence than that observed in viscosity measurements on the same materials.[20] However, in contrast to the results discussed above, in these cases the local motions showed the stronger temperature dependence.

Bulk Dynamics Compared to Dynamics in Dilute Solution. Measurements of segmental dynamics in the two extremes of concentration (i.e., bulk samples and dilute solutions) permit a means to evaluate the effect of the local environment on the motions being probed by different experimental techniques. In this section, we compare the time scales for dynamics occurring in the bulk state relative to dilute solution for three different techniques: the optical experiments reported here, ^{13}C NMR measurements, and probe translational diffusion studies.

Transient grating experiments have been performed in which the correlation time is measured as a function of temperature for anthracene-labeled polyisoprene in bulk polyisoprene (this study) and in dilute solutions of several solvents.[7] The dilute solution work has shown that the local dynamics measured by this technique scale with solvent viscosity for solvents with the same thermodynamic quality. Hence, we can use previous data for dilute solutions of polyisoprene in toluene to estimate the dynamics of the polymer in dilute solutions of 3-iodotoluene. The two solvents have the same viscosity (within 4%) over the range from 25 to 75 °C and are both good solvents for polyisoprene.

We choose to compare the ratio of τ_c(bulk)/τ_c(dilute solution) at temperatures of 25 and 45 °C. The three techniques we wish to compare utilized different solvents for the dilute solution measurements. For ease of comparison, we scale the results of the various techniques by solvent viscosity to approximate the results which would have been obtained in each case had the solvent been tetrahydrofuran (THF). This no doubt introduces some error into the comparison but should not affect the qualitative conclusion, as the scaling of local dynamics with solvent viscosity has been observed to be roughly correct by several different techniques.[7,21] After taking into account the above considerations, the ratios of τ_c(bulk)/τ_c(dilute solution) for our optical measurements are 300 ± 45 at 25 °C and 140 ± 15 at 45 °C.

^{13}C NMR T_1 measurements of the methine carbon in natural rubber have been performed in the bulk[19] over a range of temperatures and in dilute solutions of chloroform at 27 °C.[22] A motional model must be assumed to compare the correlation times for these two measurements. For convenience, we choose the isotropic rotor model, understanding that this will not be quantitatively correct. Extrapolated values from correlation times calculated from ^{13}C T_1 values in the extreme narrowing limit were utilized to obtain a correlation time in the bulk at 27 °C. (This is required because the T_1 value at 27 °C in the bulk is close to the T_1 minimum.) The dilute solution correlation time was scaled to the viscosity of THF at 27 °C. Utilizing these assumptions, we can calculate the value of τ_c(bulk)/τ_c(dilute solution) to be 20 ± 4 at 27 °C. This ratio is much smaller than the same quantity determined by the optical measurement. While the calculated value will be in error to some extent because of the model chosen for the motion, we note that any model for which the shape of the correlation function is not concentration dependent would yield essentially the same result.

Finally, we compare the optical and NMR results to probe translational diffusion measurements made by the forced Rayleigh scattering technique. In measurements by Landry et al., the translational diffusion coefficient of methyl red was determined as a function of temperature and concentration in polyisoprene/THF solutions ranging from dilute solution to the bulk.[23] The ratios of the translational diffusion coefficients for dilute solution and bulk polyisoprene are 330 ± 25 at 25 °C and 140 ± 15 at 45 °C. These ratios are in excellent agreement with the ratios of correlation times determined by the optical technique. This implies that the increase in friction upon increasing the concentration is the same for the local conformational dynamics measured with the optical technique and the translational diffusion of a small probe molecule. This is not altogether surprising since it has been suggested that the friction experienced by a probe molecule during translational diffusion should be related to the monomeric friction coefficient.[24] Indeed, it might be argued that measurements of local segmental dynamics such as the work reported here would be a better method of determining the monomeric friction coefficient since the motions of chain segments are being directly observed. In future work, we will examine the entire concentration dependence of local conformational dynamics in polyisoprene/THF solutions in order to allow a detailed comparison with probe translational diffusion data.

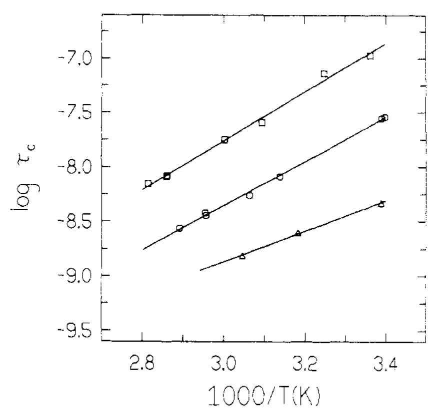

Figure 4. Temperature dependence of the correlation time for anthracene-labeled polyisoprene in concentrated solutions of polyisoprene/3-iodotoluene and in the bulk. The symbols represent correlation times obtained from independent measurements of the anisotropy for bulk (□), 67 wt % (○), and 40 wt % (△) polyisoprene samples. The lines are least-squares fits.

We speculate that the NMR results show a smaller concentration dependence than the other two techniques because at least some of the motions being sensed are too small to feel the full friction introduced by increasing the polymer concentration. As an extreme example of this, it is well-known that the rotation of a methyl group is relatively insensitive to its environment.[25] It may be that a more sophisticated motional model (which allows the correlation function to change shape with concentration) might show that part of the motion has the same concentration dependence as the other two measurements. Unfortunately such a model could not easily be tested because T_1 for dilute polymer solutions is usually on the extreme narrowing side of the T_1 minimum. Under such conditions, T_1 becomes independent of Larmor frequency and the shape of the correlation function cannot be determined.

Free Volume Analysis of the Concentration Dependence of Local Dynamics. In Figure 4 we show the temperature dependence of the correlation time for the two polyisoprene/3-iodotoluene solutions and the bulk polyisoprene sample. The lines drawn through the data represent linear least-squares fits. As can be observed from Figure 4, a decrease in the polymer concentration results in a corresponding decrease in the correlation time and in the apparent activation energy. In a preliminary attempt to describe these data, we will apply the free volume theory adapted by Fujita for two-component systems.[26] It is assumed that the volumes of the two components (solvent and polymer) are additive and that the volume change of the system upon mixing is zero. We choose the bulk state as the reference state. Fujita's theory finds that the concentration shift factor, a_c, is given by

$$\log a_c = \log \frac{\tau_c(\phi_1)}{\tau_c(\text{bulk})} = \frac{-B\phi_1}{2.303 f_2(T)[f_2(T)/\beta(T) + \phi_1]} \tag{7}$$

Here ϕ_1 is the volume fraction of the solvent and B is a constant of order unity.[24] The function $\beta(T)$ is the dif-

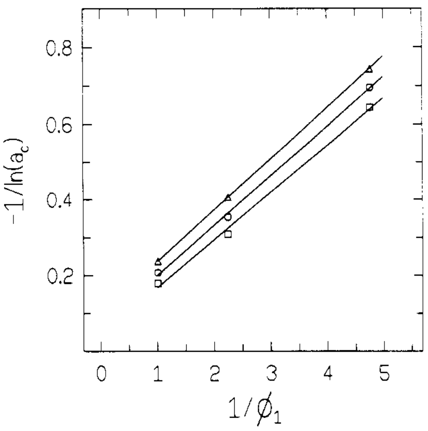

Figure 5. Application of the Fujita free volume theory (eq 9) to the polyisoprene/3-iodotoluene system. Data for three different temperatures are shown: 65 °C (△), 45 °C (○), and 25 °C (□). The bulk state was used as the reference concentration.

Table I
Fujita Free Volume Theory Parameters[a]

T, °C	$f_1(T)$	$f_2(T)$	$\beta(T)$	f_2(calcd)[b]
25	0.07 (±0.02)	0.051 (±0.011)	0.022 (±0.010)	0.071
45	0.12 (±0.02)	0.074 (±0.007)	0.043 (±0.009)	0.081
65	0.18 (±0.01)	0.102 (±0.005)	0.077 (±0.004)	0.090

[a] Confidence intervals for parameters obtained from eq 8–10. [b] Calculated from eq 11.

ference between the fractional free volume of the solvent, $f_1(T)$, and that of the polymer, $f_2(T)$:

$$\beta(T) = f_1(T) - f_2(T) \tag{8}$$

Assuming that $B = 1$, Fujita pointed out that eq 7 can be rearranged into two linear equations of the form

$$-\frac{1}{\ln a_c} = f_2(T) + \frac{[f_2(T)]^2}{\phi_1\beta(T)} \tag{9}$$

$$-\frac{\phi_1}{\ln a_c} = \frac{[f_2(T)]^2}{\beta(T)} + \phi_1 f_2(T) \tag{10}$$

where the slopes and intercepts can be used both to check the applicability of the theory and to determine the constants $f_2(T)$ and $f_1(T)$. Figure 5 is a fit of eq 9 to the data in Figure 4. Values for τ_c at temperatures of 25, 45, and 65 °C for each polyisoprene concentration were obtained from the least-squares fits in Figure 4. The dilute solution data points shown in Figure 5 were taken from measurements of CF(t) for anthracene-labeled polyisoprene in toluene over the same temperature range studied in this paper.[7] As discussed above, previous work has shown optical measurements of local dynamics scale with the solvent viscosity for good solvents. Figure 5 shows that the concentration dependence of the local dynamics is successfully described by the free volume theory. Table I contains the parameters obtained from the application of eq 9 and 10 to the data in Figure 4. The final column in the table contains values for $f_2(T)$ which have been calculated from

$$f_2(T) = f_2(T_g) + \alpha_f(T - T_g) \tag{11}$$

where $T_g = 204$ K, $f_2(T_g) = 0.026$,[24] and $\alpha_f = 4.8 \times 10^{-4}$/K.[24] In Figure 6 we show our data at 25, 45, and 65 °C plotted against the free volume theory using the parameters from Table I (columns 3 and 4). Several observations can be made about the quality of the fit and values of the parameters: (1) The free volume theory appears to more readily fit the higher temperature data. At lower temperatures, the low concentration data seem to systematically deviate from the theory. This is consistent with previous experimental observations by von Meerwall and co-workers.[27,28] (2) The measured values of $f_2(T)$ are in qualitative agreement with those calculated from eq 11. However, it is clear that the temperature dependence of the fitted values is stronger than that suggested by eq 11. (3) The values for the fractional free volume of 3-iodotoluene seem qualitatively reasonable in comparison with the fractional free volume of THF in the same polymer system. In studying probe translational diffusion, Landry et al.[23] determined the fractional free volume of THF in polyisoprene. The fractional free volume of THF was significantly greater than the values reported here for 3-iodotoluene. This is reasonable given that THF has a much lower melting point [mp(THF) = −104 °C and mp(3-iodotoluene) = −27 °C] and presumably a much lower T_g.

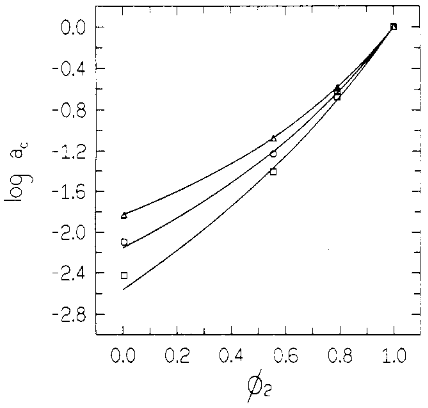

Figure 6. Dependence of the concentration shift factor, a_c, on the volume fraction of polyisoprene in solutions of 3-iodotoluene. The solid lines are generated from the free volume parameters tabulated in Table I utilizing eq 7. The symbols are the same as in Figure 5.

Overall, the free volume theory provides a reasonable fit to the concentration dependence of the local segmental dynamics of polyisoprene in 3-iodotoluene. More detailed work will be done with a different solvent in the future. We have not attempted to fit the temperature dependence of the data with the free volume theory of Fujita. This theory was developed to describe the translational diffusion of a free probe molecule in polymer solutions. In the dilute solution limit, the translational diffusion coefficient scales as T/η. In contrast, it is well-known that the temperature dependence of local polymer motions in dilute solution includes an activation energy term.[7,29] Thus, any comparison of the temperature dependence of local dynamics in polymer solutions with Fujita's theory will fail as the polymer concentration goes to zero.

Absolute Time Scales for Local Dynamics in the Bulk. In this section, we compare the absolute time scales for local dynamics in bulk polyisoprene as determined by three different experimental techniques: dielectric relaxation, ^{13}C NMR, and transient grating experiments described in this paper. At 35 °C, our measurements show a correlation time for local dynamics in anthracene-labeled polyisoprene of 62 ns. Schaeffer made ^{13}C T_1 NMR measurements on the methine carbon in bulk polyisoprene and used a model with a distribution of correlation times to fit the data.[30] At 35 °C, he obtained an average correlation time of 0.5 ns. As discussed earlier, Howarth[19] utilized a three-τ theory to fit his polyisoprene data, which gave a correlation time of 2.0 ns at 35 °C for the motion with the same temperature dependence as the optical and dielectric measurements. Adachi and Kotaka have measured the dielectric relaxation of the segmental mode process in bulk polyisoprene.[1] At 35 °C, they report a relaxation time of 1.9 ns.

In comparing these three techniques, we note that the dielectric experiment measures a first-order correlation function, while the NMR and optical techniques probe second-order correlation functions. For isotropic, small-step diffusion, the second-order correlation function decays 3 times faster than the first-order function. In order to put all the measurements on the same basis, we can approximately correct for the difference in the order of the correlation functions by dividing the dielectric relaxation time by three. This gives relaxation times of ~1 ns for both the NMR and dielectric relaxation measurements and 62 ns for the optical experiment. Slight differences in T_g for the samples used in the different experiments due to different microstructures cannot explain these differences. A further consideration in the comparison of these three experiments is the orientation of the relaxing vector with respect to the chain backbone. The NMR and dielectric experiments involve vectors essentially orthogonal to the chain backbone, while the vector of the optical experiment is in the chain backbone. Computer simulations on polyethylene-like chains performed by Weber and Helfand found that the correlation function associated with a vector oriented perpendicular to the backbone decays 4 times faster than the correlation function for a vector in the chain backbone.[31] We do not know what the corresponding factor would be for polyisoprene, but it seems reasonable to presume that some fraction of the difference between the time scales of the optical experiments and those of the other two measurements can be accounted for by this factor.

It seems likely from the above comparisons that the optical experiments measure motions occurring on a larger length scale than the NMR or dielectric measurements. As noted above, the optical and dielectric experiment show the same temperature dependence and match the temperature dependence of the bulk viscosity. The NMR measurements show this same temperature dependence only when the model used to analyze the T_1 data also includes motions with a weaker temperature dependence. These latter motions presumably are more local in character than any of the motions detected by the other two techniques. This interpretation is consistent with the weaker concentration dependence observed in the NMR experiment relative to the optical experiment. It is interesting that the dielectric measurement is not sensitive to these more local motions, even though the motions responsible for the NMR and dielectric responses have about the same relaxation times.

IV. Summary

In this paper we have used time-resolved optical spectroscopy on the picosecond and nanosecond time scales to characterize the local segmental dynamics of anthracene-labeled polyisoprene chains in concentrated solutions and the bulk. The temperature and concentration dependence of the dynamics observed with this technique were compared to the steady shear viscosity and measurements of local dynamics using dielectric and NMR spectroscopies. The observed temperature dependence in the bulk is approximately in accord with the temperature dependence of steady shear viscosity measurements over the range from T_g + 100 °C to T_g + 150 °C. This implies that local segmental dynamics observed in bulk polyisoprene by the optical technique are resisted by the same temperature-dependent frictional forces as large distance scale polymer motions. We are currently developing experimental techniques that will allow the correlation function for local motions to be measured at temperatures closer to T_g.

We have also demonstrated in a preliminary manner that the concentration dependence of the local segmental dynamics in polyisoprene/3-iodotoluene can be successfully described using Fujita's free volume theory for two-component systems. The change in correlation times observed in going from dilute solution to the bulk matches the change in translational diffusion constants for a small probe molecule under comparable conditions. This important observation provides direct experimental evidence for the common assumption that the friction coefficient of a small probe molecule in a polymer solution should be proportional to a "monomeric friction coefficient". We have also shown that a straightforward interpretation of ^{13}C NMR T_1 data for polyisoprene leads to a much smaller concentration dependence than that observed in the optical measurements of local dynamics or the probe translational diffusion experiments. This is presumably due to a contribution to the correlation time in the NMR experiment from motions which are more localized than the motions which affect the other techniques. It should be emphasized that the ability of time-resolved optical experiments to measure the entire correlation function allows an unambiguous comparison of local dynamics as concentration and temperature are varied. Future optical experiments with the polyisoprene/THF system will permit a more detailed comparison with probe translational diffusion experiments and a more critical evaluation of the applicability of free volume theory to the concentration dependence of local segmental dynamics.

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Registry No. Anthracene, 120-12-7; polyisoprene, 9003-31-0.

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Molecular Dynamics Simulation of Polymer Liquid and Glass.
3. Chain Conformation

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ABSTRACT: Molecular dynamics simulation has been performed with dense systems of alkane-like chain molecules subject to potentials restricting bond lengths, bond angles, and trans–gauche torsional angles and interacting with neighboring chains according to a truncated Lennard-Jones potential. The distributions of bond lengths, bond angles, and torsional angles have been evaluated for a range of density varying by a factor of 2. The overall population of trans conformer was found to be independent of density, in contrast to experimental results suggesting an enhancement of gauche conformer on densification of short-chain alkanes. A closer examination showed, however, that gauche enhancement occurred mainly among bonds at the chain ends and only at the high end of the density range studied. The nonbonded interaction energy was found to go through a minimum as the density was increased, and at densities higher than that corresponding to the potential energy minimum, the molecular shape was somewhat modified through reductions in the bond lengths and bond angles as well as the trans conformer populations. The conformer population over a temperature range sufficiently above the T_g is well reproduced by the rotational isomeric state model, provided an "effective" trans–gauche energy difference, rather than the true value of the parameter used for the simulation, is used for the prediction.

1. Introduction

In recent work[1,2] we have performed molecular dynamics simulations of short polymethylene chains in the bulk state and have found that, on cooling at constant pressure, the simulated systems undergo changes with features in common with glass-forming materials studied in the laboratory. In particular, one observes that over a fairly narrow temperature range, the temperature coefficients of density and internal energy undergo characteristic changes. This occurrence is preceded at slightly higher temperature by cessation of conformational changes and followed at lower temperature by a cessation of translational diffusion.[1] A subsequent study of short-range order in these supercooled liquid and glassy systems[2] showed that, on cooling, a local alignment of short sections of chains begins to develop and that the volume of the associated correlated regions appears to diverge at a temperature above the previously determined glass temperature. Annealing just below this temperature was found to produce a highly ordered, but noncrystalline, structure.

In the present work, in which we continue our program of evaluating detailed properties of the simulated system, we focus our attention on the conformational properties of the chain molecules in the bulk liquid state with respect to distribution of bond lengths, bond angles, and trans–gauche conformers. We investigate, in particular, the effect of densification on the chain conformation above the glass transition temperature.

Experimental evidence indicating that pressure densification enhances the population of gauche conformers was first reported by Schoen et al.[3a] from their Raman scattering studies on *n*-heptane subjected to pressures up to 14.7 kbar. In a later, more detailed study,[3b] these workers found the same trend in *n*-hexane and *n*-octane as well as, to a lesser degree, in *n*-hexadecane. The analysis of the *n*-heptane data also suggested that the populations of those conformers with only a single gauche bond decreased with increasing pressure, while those with 2–4 gauche bonds increased. These findings were contradicted by Schwickert et al.,[4] who reported their Raman measurements showing that, with the *n*-alkanes C_6, C_8 C_9, and C_{12} at pressures up to 6 kbar, various bands of interest narrowed but no change in integral intensities was observable. The subsequent Raman measurements by Wong et al.,[5] however, confirmed the earlier conclusions of Schoen et al.,[3] showing a decrease in the overall trans population with increasing pressure, although in this case the population of both the single and double gauche forms exhibited the same pressure dependence.

A pressure densification effect on conformer population was found also in the Monte Carlo simulation of *n*-butane by Jorgensen.[6] The simulation, run at pressures of 1, 5000,

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