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Dynamics in Poly(dimethylsiloxane) Melts: Fluorescence Depolarization Measurements of Probe Chromophore Orientational Relaxation

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Dynamics in poly(dimethylsiloxane) (PDMS) melts from $T_g + 75$ to $T_g + 175$ K have been measured by the fluorescence anisotropy decay of a probe chromophore. The reorientational dynamics of the probe chromophore, 5-(dimethylamino)-1-naphthalenesulfonamide (dansylamide), attached to a trifunctional silane, are characterized in a small molecule solvent, cyclohexanol, and compared to its reorientation in the polymer system. In cyclohexanol, the orientational dynamics obey the Debye–Stokes–Einstein equation with a thermal activation energy equal to that of the cyclohexanol viscosity. In contrast, the rate of reorientation of the probe dispersed in PDMS polymer melts does not reflect the bulk properties of the samples. The local dynamics are exponentially activated, with activation energies that are higher than that of the viscosity of the bulk material. This result is different than conclusions of analogous studies made on carbon-based polymers. Two possible explanations are given based on the unique characteristics of the silicon–oxygen bonds in PDMS.

I. Introduction

Luminescence measurements can be used to characterize electronic, structural, and dynamic properties of polymers on a molecular scale.[1-3] Fluorescence from chromophores that are either intrinsic or extrinsic probe molecules reflects the effect of the local environment on the electronically excited chromophore. With pulsed optical techniques, the time evolution of an ensemble of excited chromophores can be followed. Recent advances in these time-resolved spectroscopic techniques have been applied to studying dynamics of bulk polymers above the glass transition temperature.[4-10] These measurements provide information on small distance scale relaxations in polymer melts and can be contrasted with high-frequency viscoelastic and dielectric measurements. Direct measurements of molecular dynamics, such as from the fluorescence anisotropy of probe molecules, have also been used to evaluate theories of small scale chain motions in polymer solutions and polymer melts.[6-8]

In this report, the time-dependent fluorescence anisotropy of a probe molecule is studied in melts of poly(dimethylsiloxane) (PDMS) above the glass transition temperature. The probe molecule, dansyltriethoxysilane (DTES), contains a trifunctional silyl group with a dansylamide chromophore attached by a three-carbon linkage. Dansylamide has been used extensively as a probe of biochemical and physical chemical systems.[11-13] When it is attached to a trifunctional silane, the chromophore can also probe the properties of cross-links in PDMS networks. Dansylamide and DTES are shown in Figure 1. Dynamics of the DTES molecule have not been previously investigated.

Before using DTES as a fluorescent probe of polymer dynamics, it was necessary to characterize its excited-state dynamics in a simpler, small molecule solvent. The photophysics of the dansylamide molecule are complicated by two closely spaced excited states with varying amounts of charge-transfer character.[14,15] It is necessary to determine whether the photophysics affect the fluorescence anisotropy decay. To be a useful tool for studying solvent motion, the anisotropy decay must be dominated by probe

reorientation. In cyclohexanol the reorientational dynamics of dansylamide and DTES are in agreement with the predictions of hydrodynamic theory. The orientational relaxation times are proportional to the solvent viscosity divided by the temperature. The activation energy for reorientational motion is the same as that of the motions responsible for the viscosity.

Having established that its fluorescence anisotropy decay can be used to measure reorientational dynamics in a small molecule liquid, DTES has been used to probe local dynamics in PDMS melts of a number of molecular weights at several temperatures. The rate of reorientation of the probe is much faster than would be predicted from the melt viscosity, in agreement with previous analogous studies.[1,4,10] A "microviscosity" can be used to characterize the environment about the probe molecule.

Over the range of temperatures that have been investigated, the change in rate of probe reorientation does not agree with the predicted behavior of the Williams–Landel–Ferry (WLF) equation,[16] a free volume based expression, which typically describes the temperature dependence of relaxation measurements in amorphous materials. An Arrhenius (exponentially activated) temperature dependence accurately describes the orientational relaxation. Unlike all previous systems that have been investigated, the activation energies for the orientational relaxations (microviscosity) in PDMS are higher than for the viscosity of the bulk material. This indicates that the dynamics leading to probe orientational relaxation are different than the dynamics responsible for the bulk properties. This finding is quite different than results obtained from measurements of probe reorientation in melts of polybutadiene, polyisoprene, and poly(propylene oxide). Ediger has recently reviewed this work.[4] In all of these studies, the probe motion was found to follow the same temperature dependence as the bulk viscosity.

DTES is a unique fluorescent probe since it can also act as a cross-linking molecule. Hydroxy-terminated poly(dimethylsiloxane) molecules (PDMS) can undergo condensation reactions with the triethoxysilane group of DTES, leading to the formation of a PDMS network, which is an elastomer at room temperature. In networks such as this, the DTES molecule acts as a spectroscopic probe of the environment and dynamics of the cross-link junctions. Further studies employ fluorescence anisotropy to investigate some aspects of molecular scale dynamics in PDMS networks.[17,18] The dynamics of the cross-linking molecule dispersed

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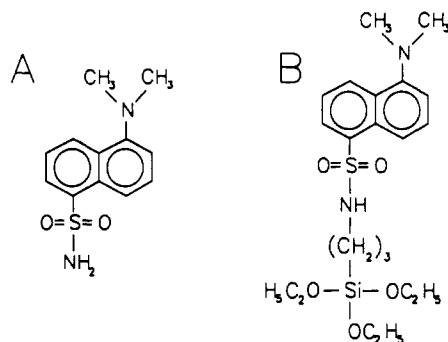[⊥] Rohm & Haas Co., Bristol, PA.
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Figure 1. Probe molecules used in this study: (A) dansylamide, (B) *N*-(triethoxysilylpropyl)dansylamide (DTES), a silane cross-linking molecule.

TABLE I: Properties of Poly(dimethylsiloxane) Melts Used in This Study

$M_w{}^a$	ν (cSt)^{a,b}	ρ (g/cm^3)^a	T_g (K)^c
1250	10	0.935	146
2000	20	0.950	150
3780	50	0.960	151
5970	100	0.966	152
28000	1000	0.971	153

^{a} Huls–Petrarch specifications, room temperature. ^{b} The kinematic viscosity, ν, is related to the absolute viscosity, η, and the density, ρ: $\eta = \nu\rho$. ^{c} Measured in this work.

in the uncross-linked polymer that are reported here are contrasted with results from networks prepared with dansyl-tagged cross-links to isolate dynamics that are specific to a cross-link junction.[17] The effect of variations in network composition and cure procedures on the elasticity of the networks and fluorescence anisotropy of probe molecules are also described.[18]

II. Experimental Procedures

5-(Dimethylamino)-1-naphthalenesulfonamide (dansylamide, 99%, Aldrich) and *N*-(triethoxysilylpropyl)dansylamide (DTES) (Huls-Petrarch) were used without further purification. DTES in poly(dimethylsiloxane) (PDMS) (Huls-Petrarch) melts of a number of different molecular weights were investigated with time-dependent fluorescence depolarization. Concentrations of 10^{-3} and 10^{-5} M DTES in polymer were used. Table I gives characteristics of the different molecular weight polymers used in this study. Solutions of dansylamide and DTES in cyclohexanol (Baker) with concentrations 10^{-3} and 10^{-5} M were also studied by time-dependent fluorescence depolarization. These experiments were done to investigate the excited-state dynamics of the DTES molecule and the fluorescent portion of the probe in a small molecule solvent.

Fluorescence decays were measured for the PDMS samples at a series of temperatures from 225 to 325 K and for the cyclohexanol solutions from room temperature to 343 K. Above room temperature a heated, temperature-controlled sample block was used. All temperatures for these measurements were within ±0.5 K. Optical measurements at subambient temperatures were made using a closed-cycle He refrigerator. Temperatures were read from a resistance thermometer in thermal contact with the sample. The accuracy in the temperature readings is ±2 K. For all but the lowest molecular weight polymer it was found that upon cooling below 225 K the PDMS crystallized. This occurred below 200 K for the M_w = 1250 PDMS sample. For this reason, anisotropy measurements were not made below 225 K.

The viscosity of cyclohexanol was measured at a number of temperatures above room temperature, using an Ubbelhode viscometer, and plotted as the natural logarithm of viscosity vs $1/T$ (K). This plot was linear and was used to determine the viscosity at the same temperatures as the anisotropy data. The shear viscosity of M_w = 28000 PDMS liquid was measured in the range 260–335 K using a Brookfield cone and plate viscometer. This temperature dependence also showed a linear relation when plotted as ln (η) vs $1/T$ (K).

The glass transition temperatures (T_g) were determined for the actual PDMS solutions used in this study by differential scanning calorimetry at a cooling rate of −10 °C/min.

Time-resolved fluorescence depolarization measurements were made using time-correlated single photon counting. The apparatus[19] and technique[20] have been described previously. The excitation light pulses were provided by a frequency-doubled, synchronously pumped and cavity dumped dye laser. The laser pulse repetition rate was 823 kHz; the pulses were 10 ps in duration and were tuned to 345 nm for all experiments reported here. Fluorescence ($\lambda \geq 360$ nm) was detected from the front face of the sample by a Hamamatsu microchannel plate detector. The instrument response function measured for this apparatus is typically 50 ps full width at half-maximum.

Fluorescence from the dansyl chromophore has a Stokes shift of 100–200 nm, depending on the polarity of the solvent. Detection was made using a filter that cut the scattered UV laser light but passed a broad band of visible fluorescence.

Time-dependent fluorescence decays polarized parallel ($I_{\parallel}$) and perpendicular ($I_{\perp}$) to the polarized excitation beam were collected in an alternating fashion under computer control for identical amounts of time. The detection polarizer was held fixed, while a Pockels cell was used to rotate the polarization of the excitation beam. With this procedure no correction for a possible bias in the detection system for parallel or perpendicular fluorescence intensity is necessary. The time-dependent fluorescence anisotropy, $r(t)$, was calculated from these decays by point-by-point addition and subtraction of data sets

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

Typically, data were collected until 10–20000 counts were accumulated in the peak channel of the parallel fluorescence decay. Several data sets were collected for each sample at each temperature to assess the reproducibility of the results, and these could be averaged together to improve the signal-to-noise ratio.

Time-dependent fluorescence anisotropy has been widely used to study the dynamics of intermolecular electronic excitation transport[2,3,21] and reorientational dynamics[6b,7,22,23] of probe molecules. Fluorescence anisotropy measures the rate of decay of the ensemble-averaged correlation function for the second Legendre polynomial of the cosine of the direction of the emission transition dipole (cos Ω) of an excited chromophore. This decay is independent of the rate of decay of excited-state population. The theoretical limits for $r(t=0)$ (r_0), before the anisotropy is reduced due to excited-state dynamics, are 0.4 for parallel absorption and emission dipole directions and −0.2 for perpendicular transition dipoles.

$$r(t) = \tfrac{2}{5}P_2(\cos \psi_{ae}) \; P_2(\cos \Omega,t) \; P_2(\cos \Omega,0) \tag{2}$$

where ψ_{ae} is the angle between the absorption and emission dipole directions. In practice, r_0 values at the theoretical limits are rarely obtained because of dynamics which occur on time scales much faster than the instrument response and because it is uncommon for absorption and emission dipoles to be perfectly parallel or perpendicular.

Identical fluorescent lifetimes and anisotropy decays were obtained for both 10^{-3} and 10^{-5} M solutions in cyclohexanol and PDMS, demonstrating that concentration effects and intermolecular excitation transfer were not contributing to the anisotropy decay. As a result of the large Stokes shift in the fluorescence from the dansyl chromophore, there is very little spectral overlap between the absorption and emission spectra. The strength of the interaction leading to excitation transfer is proportional to this quantity.[24] Thus, it is reasonable that there is no electronic energy transfer observed at these concentrations. All of the measurements reported for this study were obtained using the 10^{-3} M solutions.

The fluorescence anisotropy decays were fit with theoretical expressions, convolved with experimentally determined instrument response functions, using an iterative least-squares algorithm. The sum of the squared differences between the theoretical expression and measured $r(t)$ were weighted by propagating uncertainties in $I_{\parallel}$ and $I_{\perp}$.[34,36] Qualities of fits were judged both by the reduced
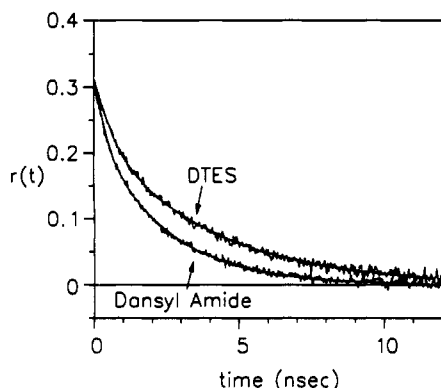
Figure 2. Time-dependent fluorescence anisotropy decay, $r(t)$, for solutions of dansylamide and DTES in cyclohexanol (10^{-3} M) at room temperature. $r(t)$ decays due to orientational relaxation of the probe molecule while electronically excited. Dansylamide reorients more quickly than DTES due to its smaller size. Solid lines through the data are best fits to biexponential decay functions.

χ^2 and by visual examination of differences between the data and fit. The several data sets obtained for each sample, at each temperature, were fit independently. The average of the fitting parameters was used in generating the results reported here.

III. Results and Analysis

A. Cyclohexanol. Cyclohexanol is relatively viscous at room temperature ($\eta = 54$ cP). Hydrodynamic theory[26] predicts that the time for reorientation of a molecule is proportional to the solution viscosity divided by the temperature. The reorientation of dansylamide and DTES should occur on a few nanosecond time scale in this solvent at ambient temperatures. This time scale is such that complete reorientation should be observed during the excited-state lifetime of the dansyl fluorophore in this solvent (15 ns) but significantly longer than the time resolution of the single photon counting apparatus. By analyzing and comparing the results for these two molecules, we can determine whether internal excited-state dynamics contribute to the fluorescence polarization decay. To be a useful probe of polymer dynamics, the fluorescence depolarization must be dominated by orientation relaxation rather than electronic excited-state relaxation.

Figure 2 shows fluorescence anisotropy decays measured for a solution of dansylamide in cyclohexanol and a solution of DTES in cyclohexanol at room temperature. The decay for dansylamide is faster than that for DTES on all time scales. This reflects the fact that dansylamide is somewhat smaller than DTES and indicates that both the short time and long time relaxations depend on the size of the molecule. The lines running through the data are best fits to biexponential decay functions.

The orientational relaxation (rotational diffusion) of aromatic molecules in small molecule organic solvents has been studied extensively in recent years.[22,23,27-37] The anisotropic rotational diffusion model[38-42] and the Debye–Stokes–Einstein (DSE) equation[26,43] provide an accurate description of the experimental results. In the anisotropic rotational diffusion model, the fluorescence anisotropy decay is described as the rotational diffusion constants of an asymmetric rotating body, while the DSE equation relates the rotational diffusion constants to properties of the solvent and probe molecule. We have analyzed the fluorescence anisotropy decays of dansylamide and DTES in cyclohexanol using these models.

From the Debye–Stokes–Einstein hydrodynamic equation, modified for ellipsoid-shaped molecules by Perrin,[44] τ, the time associated with a rotational diffusion coefficient D ($\tau = \frac{1}{6}D$), is expressed in terms of the volume of the rotating body (V), the viscosity of the medium (η), Boltzmann's constant multiplied by the temperature (kT), and S, a shape factor for nonspherical molecules:

$$\tau = V\eta f/kTS + \tau_0 \tag{3}$$

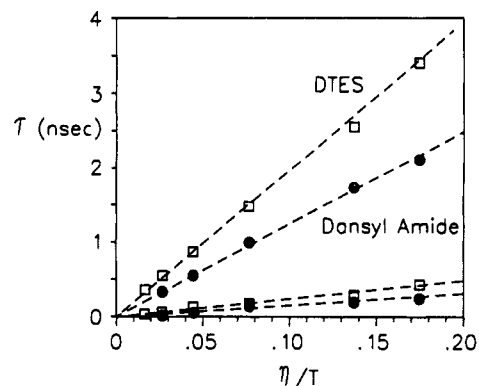τ_0 is the value of τ extrapolated to zero viscosity.[43] The factor

Figure 3. Fast (lower) and slow (upper) decay times from biexponential fits to the anisotropy decays for dansylamide (●) and DTES (□) in cyclohexanol plotted against the viscosity divided by temperature. The Debye–Stokes–Einstein equation predicts a linear relation, with the slope proportional to the hydrodynamic volume. The reorientation dynamics of dansylamide and DTES in a small molecule liquid are in agreement with hydrodynamic theory.
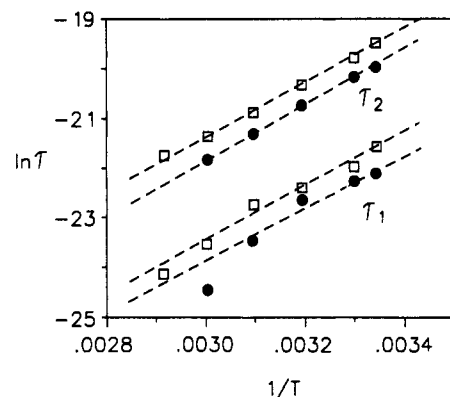

Figure 4. Arrhenius plot of the fast (lower) and slow (upper) decay times from the biexponential fits for dansylamide (●) and DTES (□) in cyclohexanol. The activation energy (E_a) for orientational relaxation is obtained from the slopes of lines through the data (eq 4). $E_a \sim 45$ kJ/mol for both the fast and slow decay components for dansylamide and DTES. The activation energy for the bulk viscosity of cyclohexanol is ~ 43 kJ/mol. Both the fast and slow decay components are due to molecular reorientation, which requires movement of solvent molecules.

f is a friction coefficient which depends on both the shape of the rotating spheroid and how it interacts with the first layer of solvent at its surface. For stick boundary conditions, in which a layer of solvent rotates with the solute (the tangential velocity of the spheroid relative to solvent vanishes at its surface), $f = 1$ for all shapes of spheroids. For the extreme of slip boundary conditions, where the solute rotates independent of the solvent, $f < 1$. Values of f for slip conditions have been tabulated for ellipsoids of varying major and minor axes.[45]

In Figure 3, both the long and short relaxation times obtained from the biexponential fits to the anisotropy decays are plotted vs the viscosity divided by temperature for the solutions of dansylamide and DTES in cyclohexanol. These plots are linear as predicted by the DSE equation. The shorter relaxation times have a much weaker dependence on η/T than the longer decay times. We find that for both dansylamide and DTES the short component of the decay is roughly 8 times faster than the long component. Both the fast and slow decay times have a weaker dependence on η/T for dansylamide than for DTES, reflecting the larger size of DTES.

Figure 4 is a plot of the natural logarithm of the fast and slow components of the anisotropy decays for dansylamide and DTES in cyclohexanol vs $1/T$. The data vary linearly with the inverse of the temperature, indicating that both the fast and slow relaxation times are exponentially activated processes which can be described by the Arrhenius equation

$$\tau = A \exp(E_a/RT) \tag{4}$$

TABLE II: Measured Hydrodynamic Volumes and Calculated Molecular Volumes for Dansylamide and DTES in Cyclohexanol

	hydrodynamic volumes experimental ($\text{Å}^3 \pm 10$)	molecular volumes calculated ($\text{Å}^3 \pm 20$)
dansylamide	168	240
DTES	263	430

From the slopes of these curves, we obtain activation energies (E_a) for reorientation. R is the gas constant, and T is the absolute temperature. $E_a = 46 \pm 3$ kJ/mol for dansylamide and $E_a = 44 \pm 3$ kJ/mol for DTES, from the slower relaxation times. Within the experimental uncertainty, the same activation energy (43 ± 1 kJ/mol) was obtained from the variation of the natural logarithm of viscosity of cyclohexanol with the inverse temperature. The activation energies for reorientation for each probe molecule are, within experimental error, the same as the activation energy for the viscosity.

The anisotropic rotational diffusion model[38-42] expresses the anisotropy decay, in general, as a sum of five exponential decays. If the molecule is modeled as an ellipsoid, there are only two unique diffusion constants, $D_{\parallel}$ for rotation about the symmetry axis and $D_{\perp}$ for rotation about an axis perpendicular to the symmetry axis. In this case, the anisotropy decay simplifies to, at most, a sum of three exponentials. The decay constants are functions of these two rotational diffusion constants. In many cases two of these three decay times may be indistinguishable, or one of the preexponential factors may be negligibly small.[41] This further simplifies the expression for the anisotropy decay, and only two decay components would be extracted. The directions of the transition dipoles relative to the symmetry axis can further limit the anisotropy decay to a single or biexponential decay.[22,23,35,42] Therefore, within the anisotropic rotational diffusion model, it is reasonable to obtain a biexponential decay with activation energies for each decay component equal to that of the viscosity. In several cases we also fit the experimental anisotropy decay with a triexponential decay function. We found that typically two of the three decay times were nearly identical or that one of the preexponential factors was close to zero. This result is in accordance with the anisotropic rotational diffusion model.

If the probe molecules are modeled as ellipsoids, the long decay component (τ_2) is a function only of the slowest diffusion coefficient ($\tau_2 = 1/_6 D_{\perp}$). From the slopes of the long anisotropy decay times vs η/T (Figure 3), we obtain hydrodynamic volumes (Vf/S) from the DSE equation (eq 3). These values are reported in Table II. Molecular volumes obtained from measurements of space-filling models and from van der Waals increments[46] are also included in Table II. For both DTES and dansylamide the hydrodynamic volume is smaller than the molecular volume, indicating that slip boundary conditions are appropriate. Stick boundary conditions commonly describe cases in which the solute is much larger than the solvent molecules (continuum limit).[34] As the solute size is reduced to that of the solvent, it has often been found that slip boundary conditions must be used to explain the observed results.[44] Slip conditions have also been proposed previously for reorientation in solvents which form hydrogen-bonding networks.[28,29] The large (factor of 8) difference between the faster and slower relaxation times that we observe also suggests that slip conditions apply. Anisotropy decay times for spheroids of this shape rotating with stick boundary conditions would only differ by a factor of 2.[39]

Dansylamide has been used in numerous photophysical studies because the Stokes shift of the emission spectrum strongly depends on the solvent polarity. This effect is due to solvent relaxation about a highly polar excited state that has charge-transfer character.[14,15] The major purpose of this detailed study of the dansyl chromophore in cyclohexanol was to determine whether relaxation between the closely spaced excited electronic states could contribute to the fluorescence anisotropy decay. The results from the measurements in cyclohexanol demonstrate that DTES and dansylamide behave similarly to aromatic molecules in small molecule solvents. The fluorescence anisotropy decays arise from the molecules undergoing reorientational motion in a conventional
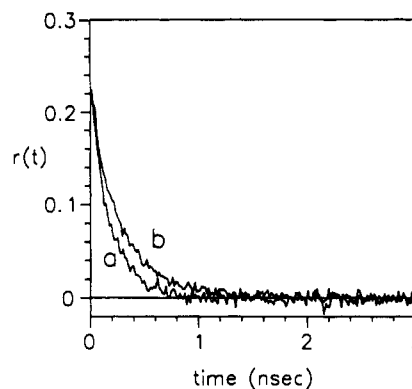

Figure 5. $r(t)$ for DTES dissolved in PDMS at room temperature: (a) $M_w = 1250$ PDMS, (b) $M_w = 28\,000$ PDMS. The anisotropy decay is faster in the lower molecular weight polymer, but in both cases $r(t)$ decays more quickly than expected based on the bulk viscosities of the melts.

liquid. The biexponential decays are consistent with the anisotropic rotational diffusion model. The measured viscosity dependence of the decay components is in agreement with hydrodynamic theory. Both the fast and slow decay components depend on the size of the molecule. If a relaxation time was due to a property of the electronic states of the probe, that component would be identical for both dansylamide and DTES. Finally, both components of reorientational motion are exponentially activated, with activation energies equal to that for viscous flow in cyclohexanol.

Fluorescence anisotropy decays were measured for dansylamide and DTES in other viscous solvents of varying polarity—mineral oil, propylene glycol, and glycerol—at room temperature. In both mineral oil and glycerol the anisotropy decays were clearly biexponential. In propylene glycol, the two exponential fit was indistinguishable from a single-exponential fit. In all solvents, including cyclohexanol, initial anisotropy values were between $r_0 = 0.31$ and $r_0 = 0.32$. This value is less than the maximum possible value of 0.4, which would be observed for parallel transition dipoles. If the reduction in r_0 is not caused by rapid dynamics that are too fast to be resolved by the single photon counting experiment, then the initial anisotropy value gives the angle between the absorption and emission dipole directions. From eq 2, $\psi_{ae} = 22°$. The fact that this angle is similar in polar and nonpolar solvents further indicates that any solvent dependence to the emitting state does not affect the direction of the emission dipole relative to the absorption dipole.

B. PDMS. Fluorescence anisotropy decays from DTES dissolved in two different molecular weight PDMS melts at 10^{-3} M concentration are shown in Figure 5. The measurements were made at room temperature. One decay is from DTES in $M_w = 1250$ PDMS, kinematic viscosity 10 cSt (see Table I) at room temperature, and the other is for DTES in $M_w = 28\,000$ PDMS, viscosity 1000 cSt. In this figure, r_0 appears less than the value in cyclohexanol and other small molecule solvents. It can be inferred from low-temperature decays that this apparent reduction in r_0 at room temperature is caused by a very fast decay of anisotropy that cannot be resolved by the 50-ps instrument response time. Identical decays are obtained for concentrations of 10^{-3} and 10^{-5} M, demonstrating that intermolecular electronic excitation transfer is not the cause of the fast (~ 1 ns) decays. As demonstrated in section III.A, intramolecular electronic state relaxation is not responsible for anisotropy decay of DTES. As in cyclohexanol, orientational relaxation of the DTES molecule causes the anisotropy decay. These decays are faster than would be predicted by the DSE equation from the viscosity of the bulk material. While the bulk viscosities of these melts differ by 2 orders of magnitude, the rates of anisotropy decay differ by only a factor of 2.

Figure 6 shows the anisotropy decays measured at 250 K for DTES randomly distributed in the five different molecular weight PDMS samples. All of the anisotropies decay more slowly than the room temperature results (Figure 5). The decays fall into
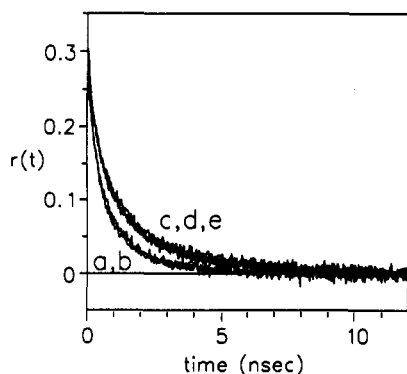
Figure 6. $r(t)$ at T = 250 K for DTES dissolved in five different molecular weights of PDMS: (a) M_w = 1250, (b) M_w = 2000, (c) M_w = 3780, (d) M_w = 5970, (e) M_w = 28 000. The anisotropy decays fall into two groups, indicating that for a molecular weight between (b) and (c) the time scale of dynamics in the polymer that lead to probe reorientation changes abruptly.

two groups: in the two lower molecular weight samples (M_w = 1250 and M_w = 2000) the probe exhibits faster reorientation than in the three higher molecular weight polymers. The dynamics of PDMS measured by this experiment are insensitive to crossing M_e, the molecular weight for which entanglement effects are first evident in viscoelastic measurements. M_e is 8100 for PDMS, measured by the plateau modulus.[47] This molecular weight is between two of the samples studied here that give the same anisotropy decay, M_w = 5000 PDMS and M_w = 28 000 PDMS. The reorientation of the probe molecule (8 Å in length) is governed by motions that occur on a distance scale much smaller than that defined by M_e, in agreement with several previous studies on a variety of polymers.[4-10] Experiments that measure low-frequency relaxations of polymers, such as viscosity, are highly sensitive to molecular weight, particularly above the molecular weight where topological constraints become important.[48]

Differences in density, high-frequency viscoelastic measurements, and the glass transition temperature for low molecular weight polymers are commonly explained by the concept of free volume.[47] It is believed that the free volume associated with the ends of polymer chains is larger than for internal segments due to a difference in packing about chain ends.[49] Thus, the fractional free volume, defined as the ratio of unoccupied volume to the total (occupied plus unoccupied) volume of the polymer, is inversely proportional to the number-average molecular weight, M_n.

Free volume theory[50] for molecular motion is based on the condition that a certain amount of free volume be available for segmental jumps to occur. The probability that there will be a sufficiently large void for a certain size segment to move depends on the total amount of free volume in the sample. It is believed that bulk polymers contain a constant fraction of free volume at the glass transition. Thus, T_g would be expected to be depressed for polymers with larger fractions of free volume. Glass transition temperatures measured for the different M_w PDMS samples used in our study are listed in Table I. T_g increases gradually with increasing M_w, in agreement with the above argument. The density of PDMS follows a similar trend, increasing with increasing M_w at low molecular weight (Table I).

The reorientational dynamics of DTES in PDMS are in qualitative agreement with the free volume prediction; faster motion is measured in the lower molecular weight hosts. However, there is an abrupt decrease in the rate of anisotropy decay in increasing M_w from 2000 to 3780 (Figure 6). Compared with the more gradual changes observed in T_g and in the anisotropy decays both above and below this M_w, this effect does not appear to be explained by the free volume theory. Recent measurements of intermolecular excimer formation in linear PDMS have observed a similar abrupt change in dynamics in this range of molecular weights.[51] PDMS has a tendency to adopt a helical structure due to differences in bond angles at the silicon and oxygen atoms.[52-54] A change in polymer structure or conformation with molecular weight could be the cause of the dramatic change

in local dynamics observed here, as was suggested in the excimer work.[51] Alternatively, in analogy to M_e for bulk measurements, this break point could suggest a degree of polymerization (M_w) above which the dynamics of polymer chains that contribute to the probe reorientational motion change abruptly.

The time-dependent fluorescence anisotropy decays of DTES dispersed in PDMS melts were analyzed with three different decay functions: the biexponential decay, derived from the hydrodynamic model which was shown to be valid for DTES in small molecule solvents, a correlation function for polymer chain dynamics developed by Hall and Helfand,[55] and a stretched exponential decay function. Previous work by Ediger and co-workers[7,8] and by Monnerie and co-workers[6] has focused on using functions such as these to analyze anisotropy decays of probe molecules randomly distributed in carbon-based polymer melts above T_g and for chromophores fixed into the backbone of a carbon-based polymer chain dissolved in similar untagged polymers. The fluorescence anisotropy decay contains detailed information on the dynamics of the polymer chains as sensed by the probe. These studies investigated which correlation functions best describe the shape of anisotropy decays.

Focusing on the studies of probes dispersed randomly in polymer melts, Monnerie et al.[6b] found that the fluorescence anisotropy decays were best fit with a modification of the Hall and Helfand diffusion and loss model for polymer segmental motion, a three-parameter fit. Hyde and Ediger[7] recently applied the anisotropic rotational diffusion model to the analysis of anisotropy measurements for probe chromophores dissolved in bulk polyisoprene and concluded that in general this model inadequately fit their data.

There is an important difference between molecular scale dynamics that occur in a polymeric liquid and a small molecule liquid. In a small molecule liquid, motion of the solvent molecules is generally diffusive and uncorrelated. In the polymer, segmental motion can be restricted due to the connectivity of many individual units in the polymer chain. However, a polymer may be quite flexible; the motions of the segments and substituents of the chain surrounding a probe chromophore can occur almost independent of long-range motions involving a large number of segments. In this case, motion of the probe molecule would be insensitive to the connectivity of the segments, and a diffusive model could successfully describe probe orientational relaxation. On the other hand, if the chain backbone is stiff, correlated motions of a large number of segments could be the rate-limiting step in probe reorientation. In this second case, these correlated motions would make the diffusive model inappropriate. A jump diffusion model or one that accounts for correlated motion of a number of segments would be more appropriate.

In light of this, it is apparent that an important parameter determining the functional form of the fluorescence anisotropy decay is the distance scale of the polymer motions that affect the reorientation of the probe molecule. Collective motions involving many segments of the polymer chain over long distances may occur on a time scale much longer than the fluorescence lifetime of the probe (12 ns in PDMS). Very little anisotropy decay would be observed if the probe reorientation was governed by these correlated relaxations. In addition, there would be a strong molecular weight dependence; for low molecular weights the chain length would strongly affect the rate of probe reorientation. However, if dynamics of individual or a few relaxing segments permit reorientation of the probe, the observed depolarization would occur on a much faster time scale and the experiment would be insensitive to the slower collective motions.

PDMS is known for its extremely low glass transition temperature (T_g = 150 K) and extraordinary flexibility of the chain backbone which are due to the long Si–O bond lengths, partial ionic character of the silicon–oxygen bond, and small methyl substituents.[53,54,56,57] X-ray scattering measurements[53,54,58] indicate that rotation about the Si–O bond is essentially barrier free. Neutron scattering results also indicate that the Rouse segment, the smallest relaxing unit in Rouse theory of chain dynamics,[59] is only a few monomers or less in PDMS.[60] Bulk viscoelastic
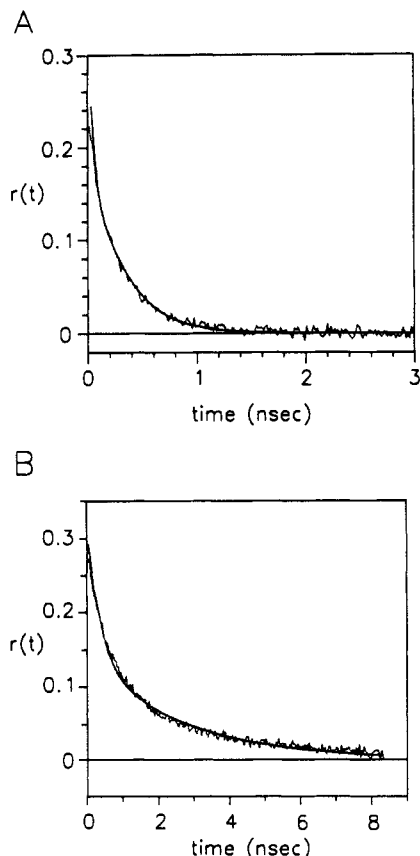
A

B

Figure 7. (A) $r(t)$ for a 10^{-3} M solution of DTES in $M_w = 28\,000$ PDMS at room temperature ($T = 298$ K) and best fit to a biexponential decay. (B) $r(t)$ and best fit biexponential decay at $T = 250$ K. The fit is not as good at 250 K as it is at room temperature but still satisfactorily reproduces the shape of the anisotropy decay.

measurements suggest that in many instances PDMS behaves more like a small molecule liquid than do other polymers.[61]

These observations and our analysis of the reorientation of the DTES probe in cyclohexanol lend support for using the biexponential function in the data analysis. Fits were made with a biexponential constrained to have $r_0 = 0.315$, the value obtained at low temperatures in PDMS and in a variety of viscous solvents of different polarity. The fits are quite good for the various M_w polymer melts at higher temperatures ($T > T_g + 100$ K). Figure 7A demonstrates this for the $M_w = 28\,000$ PDMS melt at room temperature, $T_g + 150$ K. It appears that for sample temperatures above $T_g + 100$ K probe reorientation can be modeled with a biexponential decay obtained from the hydrodynamic model. As the sample temperature is cooled to 250 K ($T_g + 100$ K) and below, the fits are not quite as good, predominantly due to a slow component in the decay to zero anisotropy (Figure 7B), but are certainly adequate. This result is generally true for all of the molecular weights of PDMS investigated here.

The longer decay time (τ_2) from the fluorescence anisotropy decay can be used to obtain the apparent viscosity sensed by the DTES probe with eq 3. Using the hydrodynamic volume determined from the cyclohexanol measurements, the anisotropy decay results for the probe dispersed in bulk polymer solution indicate that this microviscosity is 5 cP in the $M_w = 28\,000$ PDMS and 3 cP in $M_w = 1250$ PDMS at room temperature. The microviscosity is only slightly sensitive to the polymer chain length and is significantly smaller than the bulk viscosity, particularly for the higher molecular weights. These values of microviscosity are consistent with a recent study of translational diffusion of a fluorescent probe in PDMS, which arrived at an estimate of 10 cP for the microviscosity.[51]

Figure 8 is a plot of the natural logarithm of the fast and slow decay times from the biexponential fit to the anisotropy decays vs the inverse temperature for the solution of DTES in $M_w = 28\,000$ PDMS polymer. The temperature dependences of the two
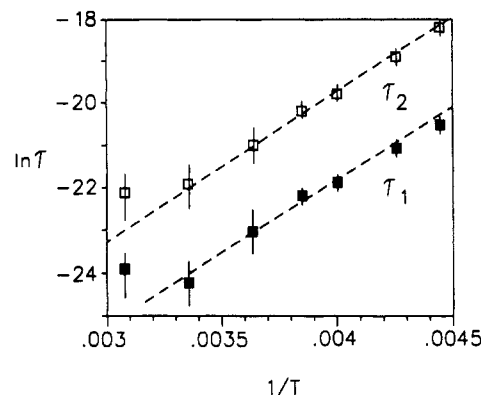

Figure 8. Arrhenius plot of fast (■) and slow (□) decay times from the biexponential fits to the anisotropy data for DTES in a melt of $M_w = 28\,000$ PDMS. Typical error bars are shown in the figure. Linear fits to the data are very good, indicating that the probe reorientation is thermally activated. Activation energies for reorientation are obtained from the slopes of the lines: E_a(fast) = 27.5 kJ/mol and E_a(slow) = 28 kJ/mol. These activation energies are much higher than the activation energy for the bulk viscosity of PDMS, 16 kJ/mol.

TABLE III: Activation Energies E_a for Reorientational Relaxation in PDMS from ln τ vs $1/T$ Using Different Anisotropy Decay Models

M_w of PDMS sample	E_a (kJ/mol)		
	biexponential (τ_1, τ_2)	Hall–Helfand (τ_1)[a]	stretched exponential (τ)
1250	28[b]	20	22
2000	25[b]	17.5	20
3780	27, 28	20.5	24.5
5970	29, 26	22	23.5
28000	27.5, 28	22	24

[a] From fits to the Hall and Helfand model, ln τ_2 vs $1/T$ is not linear. [b] From biexponential fits, ln τ_2 vs $1/T$ is not linear.

decay components are linear. The activation energy for each molecular weight PDMS host, obtained from the slopes of lines through these data, is reported in Table III. The average value is ~27 kJ/mol for both components of the decay for the probe dispersed in PDMS. Viscosity measurements of $M_w = 28\,000$ PDMS over the range 260–335 K also can be described by an exponentially activated process (linear plot of ln (η) vs $1/T$). The activation energy for viscous flow obtained from these measurements is 16 ± 1 kJ/mol, in agreement with previously published measurements.[62] In contrast to the results in cyclohexanol, the activation energy for probe reorientation does not correspond to that of viscous flow in any of the molecular weights of PDMS investigated here, and the difference is large. To our knowledge, PDMS is the first polymer for which the activation energy of local dynamics, as measured by probe molecule reorientation, is larger than the activation energy for the bulk viscosity.

Given the biexponential results for cyclohexanol, which are in agreement with the DSE equation, a biexponential description of the orientational relaxation in PDMS is very reasonable. Its physical validity is strongly supported by the observation of a well-defined activation energy that is the same for the two exponential components.

However, the fluorescence anisotropy decay data have also been analyzed with two other model functions. The Hall and Helfand model incorporates the connectivity of the segments of a polymer chain in calculating a correlation function for the segmental dynamics associated with motion of a single chain. Identifying the Hall and Helfand correlation function for segmental motion with the anisotropy decay function

$$r(t) = A \exp(-t/\tau_1) \exp(-t/\tau_2) I_0(t/\tau_1) \qquad (5)$$

where $I_0(x)$ is a zeroth-order modified Bessel function. τ_1 is the time constant for migratory or pair bond rotations (what we refer to as local dynamics) while τ_2 is the time constant for single-bond rotations which require movement of a large number of distant segments.[63] The activation energies for probe rotation are obtained

from the slopes of plots of ln (τ_1) vs $1/T^{64}$ for various M_w of PDMS (Table III). While the activation energies are lower than the values obtained from fits with the biexponential decay, they are nonetheless significantly greater than the activation energy for the viscosity of the bulk material.

A variety of relaxation measurements of bulk polymers have been analyzed using stretched exponential decay functions[65]

$$r(t) = A \exp(-t/\tau)^\beta \qquad (6)$$

Physical interpretations of the stretched exponential form for dynamical relaxations have been made from a random walk of relaxations[66] and from the coupling of polymer chain motion with primitive segmental relaxation times.[65] Decay times, τ, and β parameters have been obtained from fits to the anisotropy data. β decreases with decreasing temperature, reflecting the observed change in shape of the anisotropy decays. Activation energies (Table III) are obtained from linear fits to Arrhenius plots of the decay times.

All three models for the fluorescence anisotropy decay are equally successful in describing the shapes of the experimental curves at temperatures above T_g + 100 K (250 K). At 250 K and below, none of the models perfectly reproduce the shape of the anisotropy decay. Perhaps a better model for reorientation of a small probe in PDMS would include diffusive motion at short times, leading to partial depolarization, followed by slower correlated motion causing complete reorientation of the probe and zero anisotropy.[67]

The logarithm of the time (or frequency) associated with a specific relaxation measured at one temperature, T_0, can often be related to the logarithm of the relaxation time at a different temperature, T, by a shift factor log a_T. This is the well-known time–temperature superposition principle.[47] The WLF equation,[16] which has been related to free volume theory, in many cases successfully predicts how relaxation times change with temperature. The WLF equation, written in terms of the natural logarithm, is

$$\ln (a_T/a_{T_0}) = -2.303 c_1 (T - T_0)/(c_2 + T - T_0) \qquad (7)$$

where c_1 and c_2 are constants determined empirically for a specific polymer. The values for PDMS,[47] with T_g as the reference temperature (T_0), are c_1 = 6.1 and c_2 = 69. Being related to free volume theory, the WLF equation will be expected to apply when the rate-determining step in a relaxation mechanism is the presence of sufficient free volume for segmental motion to occur. The segmental motion itself does not contribute to the activation energy.

If the temperature dependence of the orientational relaxation of the probe chromophore is governed by the amount of free volume available in the polymer, then the temperature dependence of the anisotropy decays is expected to follow the prediction of the WLF equation. The typical region over which this free volume theory applies to viscoelastic properties is T_g to T_g + 100 K, though in some cases it has been shown to be successful over a more limited range.[68] For temperatures above this range, segmental relaxation times have been found to be exponentially activated according to the Arrhenius equation (eq 4). This relation is believed to be appropriate if the segmental mobility is the rate-limiting step; i.e., sufficient free volume for the segmental motion is always present. Relaxations in small molecule liquids are often exponentially activated, as we observed in cyclohexanol.

Figure 9A shows ln (τ_1) and ln (τ_2) vs $1/T$ for the biexponential fits to the fluorescence anisotropy decays in M_w = 28 000 PDMS compared to the predictions of the WLF equation, calculated using the parameters for PDMS. The WLF curves have been shifted along the vertical axis to give the best agreement. The temperature dependence of the WLF equation is close to linear in this temperature region, but it has a more gradual slope than the data. However, we have found that the WLF equation does characterize the change in viscosity with temperature. An exponentially activated process (Figure 8) better describes the temperature dependence of the anisotropy data than does free volume theory. As was discussed earlier, and can be seen again in this figure, the
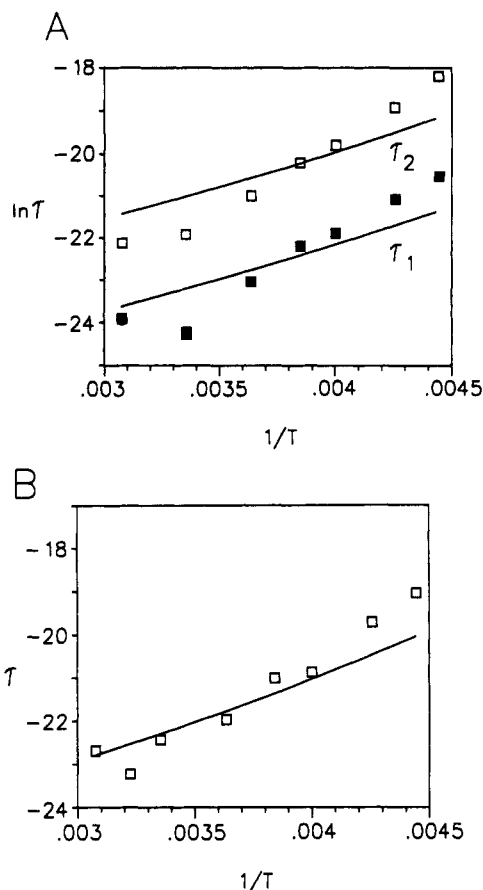

Figure 9. (A) Comparison of the temperature dependence of decay times from biexponential fits to the anisotropy decays of DTES in M_w = 28 000 PDMS to the prediction of the WLF equation. The WLF curves have been arbitrarily shifted on the ln τ axis. The WLF equation, which describes the temperature dependence of the viscosity of PDMS, is nearly linear when plotted in this fashion over this temperature interval. However, the activation energy (proportional to the slope) is smaller than for probe reorientation. (B) Comparison of the average correlation time of the fluorescence anisotropy decays (eq 8) for the M_w = 28 000 PDMS to the WLF equation. The result is similar to that of the biexponential decays. This figure demonstrates that the different temperature dependences of the reorientational correlation time and the WLF equation are independent of the model used to analyze the anisotropy decays.

temperature dependence for probe reorientation (activation energy) is significantly higher than for the bulk property.

Finally, Figure 9B compares the temperature dependence of an average correlation time for the anisotropy decays to the temperature dependence of the WLF equation. The average correlation time[43] has been used to show the temperature dependence in previous studies[7] because it is independent of the model chosen to analyze the anisotropy decays. The correlation time is given by

$$\tau_c = \frac{1}{r_0} \int_0^\infty r(t) \, dt \qquad (8)$$

τ_c has been calculated from the anisotropy decays for the M_w = 28 000 solution measured at various temperatures. The average correlation time appears exponentially activated, and the temperature dependence is more steeply sloped than the WLF equation predicts (Figure 9B). This is the same result as we obtained for the biexponential decay components and also the parameters from the fits with the Hall and Helfand model and the stretched exponential decay. Thus, the lack of agreement with the WLF equation and the large activation energy for probe reorientation are not a result of the model chosen to analyze the anisotropy decays. The inability of the WLF expression to describe the data is also independent of polymer molecular weight. Measurements of probe molecule dynamics in carbon and carbon/oxygen-based polymers, such as polybutadiene, polyisoprene, and poly(propylene

oxide), exhibit the same temperature dependence as bulk properties. This demonstrates that the bulk properties, such as the glass transition and viscosity, are dependent on the local structure and dynamics. The results presented here indicate that in PDMS the motions responsible for dynamics of the probe and the viscosity of the polymer are not the same. We propose two possible explanations for this result.

As discussed earlier, silicone polymers possess unique flexibility owing to the nature of the silicon–oxygen bonds in the backbone. This causes silicones to exhibit substantial differences from many other polymers in a variety of physical properties.[54] Thus, when comparing local chain motions to larger scale dynamics, PDMS may in fact behave quite differently than other polymers. The small probe used in this study may be sensitive to dynamics that do not correlate with the large distance scale motions that are responsible for viscoelastic properties. If this were the case, it would be reasonable that the local dynamics and bulk properties would exhibit different temperature dependences.

In support of this explanation are recent results of measurements of reorientation of dansyl probe molecules fixed to cross-link sites in PDMS networks.[17] We have found that the temperature dependence of probe motion, when the probe is bonded to the junction of chain ends, is similar to that of the bulk viscosity. We rationalize this by hypothesizing that motions of polymer chain ends, which could involve correlated motions of many chain segments, are necessary for the probe to reorient. Thus, the reorientational dynamics result from correlated polymer chain dynamics. In the results presented here for the free probe, long-range motions of polymer chains do not appear to affect the reorientation, and the temperature dependence for probe reorientation is different than for bulk properties.

An alternative explanation for these results is that, because of the polar nature of silicon–oxygen bonds and their unique flexibility, the DTES probe is not a passive observer of local polymer dynamics. DTES is a polar molecule with an excited state that has charge-transfer character. The polar probe may cause the partially ionic silicon–oxygen bonds to reconfigure around it. In this way, DTES would perturb the local polymer environment. Measurements of probe reorientation in PDMS would then reflect not only polymer dynamics but also properties of the interaction between DTES and PDMS. If this were the case, it would be reasonable that the temperature dependence for PDMS dynamics would be quite different than the temperature dependence for reorientation of the PDMS/probe interactive complex. The activation energy that we have measured would then reflect both polymer dynamics and some energetics of the interaction between PDMS and a polar impurity.

A previous study of intramolecular excimer formation in PDMS[69] may be used to support either of these two analyses. The authors measure a temperature dependence of excimer formation for two different probe molecules that is more steeply sloped than the temperature dependence of the viscosity of PDMS. These investigators attribute this result to a high-energy barrier to formation of the excimer state. However, it should be pointed out that the two probe molecules that they used were both quite polar. Measurements of intermolecular excimer formation in PDMS,[51] which observed the same activation energy for excimer formation and bulk viscosity, were made with a less polar probe molecule. The latter measurement is significantly different than our measurements of probe reorientation and the intramolecular excimer experiment in that they measure translation of probe molecules over a distance of the order of 100 Å, whereas our measurement is sensitive to shorter distance scale dynamics.

IV. Concluding Remarks

Rapid orientational relaxations of probe molecules have been measured in PDMS melts of a number of different molecular weights. In agreement with analogous studies made on carbon-based polymers, the results indicate that dynamics of the probe are sensitive to local, segmental motions in the polymer that take place on the distance scale of the size of the probe (8 Å). Low-frequency, correlated motions of a large number of chain segments

are responsible for the viscoelastic properties of the polymer.

The temperature dependence of local polymer dynamics in PDMS is exponentially activated. This is likely due to the unique flexibility of PDMS chains and temperatures far above T_g. The success of a biexponential decay function, from the hydrodynamic theory for probe reorientation, in describing the fluorescence anisotropy decay further suggests that segmental dynamics in PDMS behave similarly to simple liquids at these temperatures.

While previous measurements of probe dynamics in other polymers have observed the same activation energy for local motion and for the viscosity, the activation energy of probe reorientation in PDMS is higher than the activation energy for the bulk viscosity. This result can be explained by considering the unique characteristics of the silicon–oxygen backbone. This could result in local motion that is quite distinct from large distance scale chain dynamics. Alternatively, the probe dynamics may reflect a perturbation of the local polymer structure by an interaction between the polar probe and the polar silicone polymer.

Further studies of molecular dynamics occurring in PDMS systems are reported elsewhere.[17,18] DTES molecules have been employed as fluorescent cross-links in PDMS networks. Dynamics specific to the cross-link junctions can be characterized by measuring fluorescence anisotropy decays from the probe bound to the cross-link site. The results demonstrate that the cross-link site undergoes very rapid orientational relaxation, and a model of coupled rotational/translational diffusion is proposed.

Registry No. DTES, 70880-05-6; dansylamide, 1431-39-6; cyclohexanol, 108-93-0.

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