Dynamics in Polydimethylsiloxane: The Effect of Solute Polarity

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Abstract: The temperature dependent dynamics of polydimethylsiloxane (PDMS) melts are investigated by measuring orientational relaxation of a dissolved probe molecule, 2-naphthyltriethoxysilane (NTES) using time resolved fluorescence depolarization. The temperature dependent viscosity of PDMS is also reported for two molecular weights. The measurements of nonpolar NTES probe dynamics are compared to previous measurements on the polar probe, *N*-(triethoxysilylpropyl)dansylamide. The activation energies for the orientational relaxation of the two probes are very different. This is discussed in terms of the influence of the polarity of the solutes on the local structure in the melts. The results have implications for possible modifications of the physical properties of PDMS materials by using solutes or side groups of varying polarity. The synthesis of the NTES probe, which can also be used as a cross-linking reagent for PDMS, is also described.

I. Introduction

Silicone polymers are specialty materials used in a wide variety of commercial products including lubricants, cosmetics, construction sealants, oxygen-permeable membranes, drug delivery systems, and biomedical implants.[1-3] Much of this multibillion dollar industry is based on polydimethylsiloxane (PDMS) and its copolymers, either as melts or cross-linked rubbers. The increasing demands for siloxane polymers are fueled by the desirable properties of their inorganic backbone. Siloxane oils enjoy high thermal stability, a low melting point, a weak viscosity dependence on temperature, high hydrophobicity, and relatively good biocompatibility. Most of these properties are macroscopically observable, yet they are ultimately derived from the characteristics of the silicon–oxygen bond, and the interactions between siloxane chain segments.

This study concentrates on the relationship between local siloxane chain dynamics, over a distance scale of a few monomer lengths, and the long range interactions measurable by viscometry. The main experimental technique employed is the measurement of time resolved fluorescence polarization anisotropy of a chromophore attached to a probe molecule that is dissolved in the bulk polymer. The specific systems studied are melts of polydimethylsiloxane above the polymer glass transition temperature ($T_g \approx 152$ K) that contain a low concentration of the fluorescent probe 2-naphthyltriethoxysilane (NTES).

For fluid systems, time resolved fluorescence polarization anisotropy of a low concentration probe chromophore is determined by the rate of orientational relaxation, *i.e.*, the decay of the orientational correlation function of the probe. Since probe-chromophore motions depend on the dynamics of surrounding polymer segments, the anisotropy decay becomes a sensitive measurement of local chain dynamics. However, it is also necessary to consider other interactions between the probe molecule and the polymer segments. Because the probe's size is small compared to that of a polymer molecule, the probe dynamics reflect the local motions of a few polymer chain segments, and any probe–polymer interactions will occur primarily over this distance scale. Determination of the temperature dependence of the fluorescence anisotropy decay rate yields information about the thermal activation of the polymer segmental dynamics. Comparison of the thermal activation energies of time resolved fluorescence anisotropy data acquired from systems containing either a polar or a nonpolar probe can establish the presence or absence of polar probe–polymer interactions.

In a previous study, the temperature dependent dynamics of PDMS were initially investigated by dissolving a probe of *N*-((triethoxysilyl)propyl)-5-(dimethylamino)-1-naphthalenesulfonamide (dansyltriethoxysilane, or DTES) in the polymer melt.[4] The resulting analysis, using several models, indicated that the activation energy of the local reorientation of the probe was much larger than that for the bulk viscosity of the polymer. Two possible explanations were presented based on distance scale and polarity arguments. One speculation was that the activation energy differences were due to different distance scales. Fluorescence depolarization measures motions on a microscopic scale, while viscosity is a macroscopic property. The possibility was suggested that the short distance scale polymer dynamics responsible for probe reorientation were not the microscopic motions that lead to the macroscopic viscosity. A second prospect concerned the nature of the probe–polymer interactions. In PDMS, the possibility of polar interactions between a probe and the silicon–oxygen bond must be considered. There is a large net dipole moment along a Si–O bond in PDMS, so the opportunity exists for a polar probe molecule to interact with one or more bonds in the PDMS backbone, altering the local structure and dynamics of the system. Since the dansyl moiety causes the DTES to be very polar, there could exist significant perturbations of the silicon–oxygen bonds, with subsequent rearrangements of the polymer chain near the probe. Hence, the local dynamics around the probe molecule, as determined by the fluorescence anisotropy decay, would not necessarily reflect the motions of the unperturbed bulk polymer.

The purpose of this investigation is to explore the nature of polar interactions of the PDMS backbone with a dissolved probe molecule and to definitively resolve the previously measured difference between microscopic and macroscopic activation energies. To undertake this study it was necessary to choose an appropriate nonpolar probe molecule with a size comparable to DTES. Since the photophysics of the naphthyl chromophore have been previously explored and employed in recent investi-

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gations of polymer systems,[5-13] it is a useful chromophore for this type of study. It was necessary to synthetically attach the naphthyl chromophore to a silane molecule. Details of the synthesis of 2-naphthyltriethoxysilane are presented in the Experimental Section.

Since NTES is essentially nonpolar, observation of a large reorientation activation energy result similar to the previous study of DTES would indicate that the distance scale argument is correct. However, it will be shown below that the data support the argument that probe polarity is the important factor. This implies that the local structure and dynamics of PDMS may be significantly perturbed by the inclusion of chemical groups of high polarity.

II. Experimental Procedures

A. Synthesis. Ether solvents were distilled under nitrogen over sodium/benzophenone prior to use. The 2-bromonaphthalene was purchased from Aldrich Chemical, Mg shavings from Fluka, tetraethylorthosilicate from Hüls-America, and the linear trimethyl-end-tagged host PDMS from Hüls-Petrarch.

All operations involving air-sensitive materials were performed in an inert atmosphere using Schlenk-line techniques. The product 2-naphthyltriethoxysilane was obtained by nucleophilic substitution reaction of tetraethylorthosilicate (TEOS) with the Grignard reagent produced from 2-bromonaphthalene. The procedure involves three steps: formation of the aryl Grignard reagent, reaction of the Grignard with TEOS, and separation of the NTES from side products. One important precaution was taken during synthesis: since the formation of the Grignard reagent is slow, the reaction must be carefully monitored to insure that the exothermic reaction does not run out of control.

Preparation of the Grignard Reagent. A 250-mL, round-bottom flask equipped with a reflux condenser and pressure equalizing addition funnel was charged with Mg shavings (2.9 g, 0.119 mol). The 2-bromonaphthalene (10.0 g, 0.108 mol) was placed in the addition funnel and diluted with 100 mL of diethyl ether (Et_2O). Formation of the Grignard reagent was initiated by addition of 5–10 mL of the bromide solution to the Mg-containing flask. Since the reaction is extremely slow, a sonicator was employed to aid the Grignard formation process during the dropwise addition of the bromide solution. The color of the solution gradually darkened during the course of the reaction, resulting in a brown/black solution upon completion. After addition of the bromide, the solution was stirred for 7 h.

Reaction of the Grignard with $Si(OEt)_4$. A second 250-mL, round-bottom flask was fitted with a reflux condenser and pressure equalizing addition funnel. Then, 50 mL of Et_2O and 40 mL of TEOS (0.4 mol) were added to this flask. The Grignard reagent was transferred via cannula to the addition funnel and added dropwise to the flask over 30 min. The addition funnel was replaced with a glass stopper, and a heating mantel was employed to raise the solution temperature to its boiling point (~35 °C). The mixture was stirred under gentle reflux for 7 days.

Recovery and Characterization of the Substitution Product. After the reaction mixture was cooled and filtered to remove the salt byproducts, most of the Et_2O solvent was removed by rotoevaporation. The remaining yellow oil was partitioned by fractional vacuum distillation at 30 mmHg at 50 °C. About 5.9 g (~20% overall yield) of the monosubstitution product was obtained and characterized. The boiling point was 270–273 °C. The ^1H NMR spectra were recorded on a Gemini 200 MHz instrument in deuterated chloroform with tetramethylsilane as an internal reference: δ 8.21 ppm (s, 1H, ArH), 7.91–7.42 ppm (m, 6H, ArH), 3.91 ppm (q, 6H, CH), 1.37 ppm (t, 9H, CH). Gas chromatography analyses were obtained on a Hewlett-Packard 5890 equipped with an SE 54 column (5% phenylmethylsilicone, 95% methylsilicone, 0.33 μ × 0.2 mm × 25 m) in conjunction with a flame ionization or thermocouple detector. Product purity was estimated to be above 99%.

Table 1. Characterization of Polydimethylsiloxane Solutions

M_w	ν at 298 K, cSt	[NTES], M
5970	100	10^{-3}
28000	1000	10^{-3}

B. Physical Measurements. The concentration of NTES in PDMS was low enough that no electronic excitation transport between naphthyl chromophores occurred (reduced concentration of the chromophore in the melt $<10^{-2}$). By eliminating energy transport as a mechanism of fluorescence depolarization, the only source of time-dependent depolarization is chromophore reorientation. The two polymer systems, distinguished by their kinematic viscosities, ν, are characterized in Table 1.

Viscosity measurements on both types of host PDMS were acquired with the appropriate size Cannon–Übbelohde viscometer over a temperature range from 220 to 340 K. Temperature stability of ±1 K was ensured by a large water or dry ice–acetone bath and was monitored with a resistance thermometer.

The apparatus[8,11] and procedure[14] for measuring the time-resolved fluorescence anisotropy have been previously described. Time-correlated single photon counting was used to acquire the fluorescence depolarization data. Excitation pulses of ~10 ps (FWHM) duration at 320 nm were provided by the frequency doubled output of a cavity dumped dye laser that was synchronously pumped by a mode locked and frequency doubled Nd:YAG laser.

The excitation beam photoselectively excites an ensemble of chromophores having absorption dipoles aligned ($\cos^2$ distribution) with the polarization of the laser pulse. The fluorescence decay of such an excited state can be described by

$$I_{\parallel}(t) = e^{-t/\tau}(1 + 2r(r)) \quad (1)$$

$$I_{\perp}(t) = e^{-t/\tau}(1 - r(t)) \quad (2)$$

where τ is the excited state fluorescence lifetime, $I_{\parallel}$ and $I_{\perp}$ are the fluorescence intensities with polarizations parallel and perpendicular to the initial excitation beam, and $r(t)$ is the time-dependent fluorescence polarization anisotropy.

The maximum $t = 0$ value that $r(t)$ can have is 0.4. However, this will only occur if the absorption and emission transitions are perfectly polarized and the emission transition dipole moment is parallel to the absorption transition dipole moment. In the experiments, $r(t)$ is observed to have a maximum value of ~0.2. This is the value that has also been observed in all other studies using naphthyl as a fluorescence anisotropy probe.[5-13] These studies include experiments in which the naphthyl is attached to a polymer backbone in a solid polymeric sample at low temperature. Thus it is unlikely that the observed maximum value of $r(t)$ arises from a very fast unresolved motion of the chromophore. The likely explanation is that very broad band fluorescence was detected. The fluorescence includes emission to more than one vibrational level. This can result in a reduction of the polarization of the transition.

Front face fluorescence from the sample passed through a dispersive subtractive monochrometer and was detected by a photomultiplier tube (Hamamatsu R 1527). A fixed polarizer before the monochrometer ensured that no polarization bias was inherent in the photon detection system. Fluorescence was detected over a wavelength range of approximately 325 to 370 nm.

A Pockels cell was used to periodically rotate the polarization of the excitation beam relative to the fixed polarizer. The polarized fluorescence intensities parallel and perpendicular to the excitation pulse were collected in alternate 20-s intervals to eliminate the effects of any long term drifts in laser intensity. The parallel and perpendicular decays were each stored in arrays having 2048 time points (8 ps per point). To construct the fluorescence anisotropy decay, $r(t)$ was calculated from $I_{\parallel}$ and $I_{\perp}$ using

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$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \quad (3)$$

For a single data set, the maximum number of counts, occurring in the time zero channel, was usually between 10 000 and 20 000. Three or four data sets were averaged to improve the decay curve's signal-to-noise ratio at longer times. The instrument response function, measured by the time-resolved scattering intensity profile at 320 nm from a nonfluorescent scatterer, was a near-Gaussian curve with a full width at half maximum of ~56 ps.

To minimize fluorescence reabsorption, the samples were placed in either a 1.0- or 4.0-mm path length quartz cuvette such that the optical density of the solution was always less than 0.2 at the peak of the absorption. Sample cuvettes were mounted on a copper substrate in thermal contact with the cold finger of a closed-cycle He refrigerator. Feedback from a sensor mounted directly on the sample cuvette provided accurate temperature measurement to ±0.2 K.

Each experimental $r(t)$ data set was fit to both a biexponential and a stretched exponential decay function. First, initial parameters were determined to generate an approximate $r(t)_{\text{exponential}}$, which was used to calculate $I_{\parallel}(t)$ and $I_{\perp}(t)$ from eqs 1 and 2. Then, the measured instrument response function was numerically convolved with each of the calculated polarized intensity decays in order to calculate $r(t)_{\text{convolved}}$ from eq 3. The calculated $r(t)$ was compared to the experimental $r(t)$ using a least-squares algorithm. Final fitting parameters from either three or four individual data sets were averaged at each temperature.

III. Results and Discussion

For many liquids and solutions, the dependence of viscosity (η) on temperature (T) can be described by an Arrhenius–Frenkel–Eyring equation[15,16]

$$\eta = A\exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

where E_a is the activation energy, R is the ideal gas constant, and A is the Arrhenius preexponential factor. For both the low (100 cSt) and the high (1000 cSt) molecular weight PDMS, a slightly nonlinear dependence of ln (η) on $1/T$ is shown in Figure 1. Such deviations over a wide temperature range are expected for a polymer such as PDMS. Observations of this type of curvature are abundant in the literature.[17,18] Alternatively, it is possible to treat the data with a Vogel–Fulcher equation.[17,19,20] Previous measurements of the viscosity of PDMS have been reported in terms of an activation energy.[4,18] Here, the data will also be analyzed with eq 4. This will allow comparison of the curvature of thermal activation plots for the viscosity (macroscopic) and orientational relaxation (microscopic) measurements.

Fitting the best straight lines through the data in Figure 1 using a linear least-squares algorithm yields bulk viscosity activation energies of 16.6 and 16.2 kJ/mol for the 100 cSt PDMS and the 1000 cSt PDMS, respectively. Since the plots show curvature, this should not be considered a quantitatively accurate activation energy, but its value enables comparison with data relevant to local dynamics. The form of viscosity activation is essentially identical for both molecular weights (see below). These viscosity activation results are consistent with previous investigations.[4,18] Note that least-squares fits constrained to either the high- or low-temperature points will yield activation energies marginally lower or higher than the values given above.

Fluorescence anisotropy decays for NTES in the lower viscosity (100 cSt) PDMS are displayed in Figure 2 (dotted lines) for three temperatures, 225, 250, and 298 K. As the temperature is lowered the decays become slower, corresponding to the reduced rate of reorientation of the probe molecule. The temperature-dependent behavior of the fluorescence anisotropy in the high viscosity (1000 cSt) PDMS (solid lines in Figure 2) follows the same trend for the same three temperatures. At each temperature the anisotropy decay is slower for the probe dissolved in the higher molecular weight PDMS. This is in contrast to the earlier results for DTES, where the fluorescence anisotropy in the 100 and 1000 cSt hosts had identical decays at 250 K.

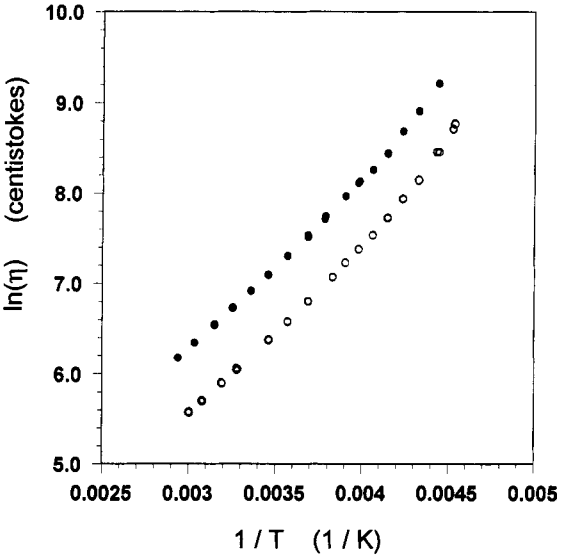

Figure 1. Ln (viscosity) for 100 cSt (open circles) and 1000 cSt (filled circles) polydimethylsiloxane plotted against $1/T$. The plots exhibit a slight positive curvature at higher viscosities. Using a linear fit yields activation energies of 16.6 and 16.2 kJ/mole for the 100 cSt and 1000 cSt melts, respectively.

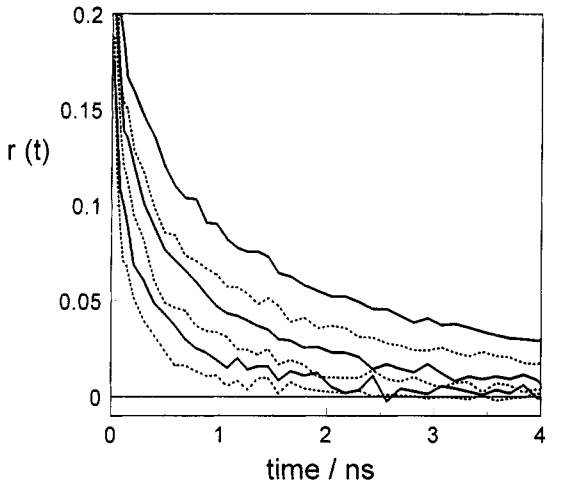

Figure 2. Fluorescence anisotropy decay, $r(t)$, for 2-naphthyltriethoxysilane dissolved in 100 cSt polydimethylsiloxane (dotted curves) and in 1000 cSt polydimethylsiloxane (solid curves) at 225 (highest), 250, and 298 K (lowest). As the temperature is lowered, the orientational dynamics slow. The trend in the temperature dependent orientational dynamics of the probe is the same in the two melts, but the data show that the dynamics depend on the molecular weight of the PDMS.

To quantitatively characterize the temperature dependence of chain dynamics, individual fluorescence anisotropy decays were analyzed by fitting with both biexponential (eq 5) and stretched exponential (eq 6) decay functions.

$$r(t) = A\exp(-t/\tau_1) + B\exp(-t/\tau_2) \quad (5)$$

$$r(t) = A\exp(-t/\tau)^B \quad (6)$$

All fits were acceptable, both in appearance and in the near-unity values of the χ^2 parameter.

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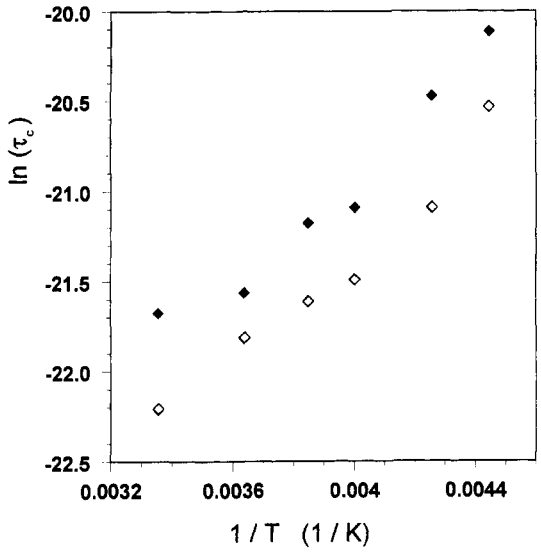

Figure 3. The natural log of the correlation time (ln (τ_c)) obtained from the fluorescence anisotropy decays for NTES dissolved in 100 cSt (open diamonds) and 1000 cSt (filled diamonds) PDMS plotted against $1/T$. The trend in the orientational dynamics with temperature is the same for the two melts, but the dynamics depend on the PDMS molecular weight. A linear fit to the data for each molecular weight yields an activation energy of ~12 kJ/mol.

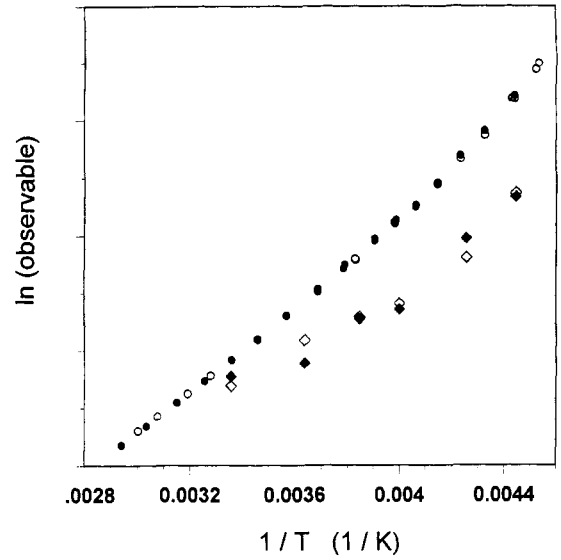

Figure 4. The natural log of the viscosities (circles) and of the correlation times (diamonds) for both the 100 cSt (open symbols) and 1000 cSt (filled symbols) PDMS melts. The data have been shifted along the vertical axis to bring them into coincidence. The viscosity data for the two molecular weight PDMS melts clearly have the same functional form. While the data for the correlation times (orientational dynamics) have more scatter, they also display the same functional form for the two molecular weights. The figure also shows that the temperature dependence of the viscosity and the correlation time are not the same. This is consistent with the linear fits that gave activation energies of ~16 and ~12 kJ/mol for the viscosity and correlation time, respectively.

Probes that experience simple hydrodynamic rotational diffusion have dynamics that are described by the Debye–Stokes–Einstein (DSE) equation

$$\tau = \frac{V_{\text{eff}}\eta(T)}{kT} \tag{7}$$

where V_{eff} is the effective hydrodynamic volume. If the probe were undergoing diffusion by a DSE mechanism, then individual decay components would correspond to different components of the rotational diffusion tensor. According to this model, the two components of the decay would have the same temperature dependence. However, the individual decay components of the biexponential fit to the NTES data do not exhibit the same temperature dependence. Therefore, it is not possible to assign the two biexponential decay components to separate reorientation processes.

For a model-independent analysis of the reorientational dynamics, the correlation time τ_c was calculated for each data set[21]

$$\tau_c = \frac{1}{r_0}\int_0^\infty r(t)\mathrm{d}t \tag{8}$$

where $r_0 = r(t = 0)$. Since the correlation time is a scaled integration over the anisotropy decay curve, it contains overall dynamical information about all depolarizing processes occurring on the relevant time scale. Equation 5 is used in eq 8; τ_c was calculated using the parameters from the biexponential fit. This method of analysis combines the convenience and accuracy of the biexponential fit without the assignment of either decay component to a specific type of relaxation process.

An Arrhenius plot of ln (τ_c) vs $1/T$ for both host polymers is shown in Figure 3. As expected, ln (τ_c) monotonically increases with increasing $1/T$, as the chromophore reorientation slows at lower temperature. Because of the scatter in the data it is unclear if ln (τ_c) has a linear dependence on $1/T$ or if there is some curvature. Previous studies of carbon backbone polymers have shown both linear[22,23] and nonlinear[24,25] dependencies of τ_c on $1/T$. For the PDMS data presented here, linear least-squares fits yield activation energies of 12.4 and 11.9 kJ/mol for NTES dissolved in the 1000 and 100 cSt hosts, respectively. Within the experimental uncertainty, these two activation energies are indistinguishable.

Here we are interpreting the anisotropy decay to arise from the rotational diffusion of the entire NTES molecule and the activation energies for NTES and DTES (studied previously[4]) to be the activation energies for the reorientational motion of these molecules. The possibility that all or part of the biexponential decays arise from rotation of the naphthyl group around the linkage to the rest of the molecule was ruled out in the detailed study of the rotational dynamics of DTES.[4] DTES has a longer, more flexible linkage than does NTES. The orientational relaxation of DTES was studied in a small molecule organic solvent as a function of temperature. As with NTES, a biexponential decay was observed. Both components of the biexponential had identical activation energies that corresponded exactly to the activation energy of the solvent viscosity. This is as expected for simple hydrodynamic rotational diffusion (see eq 7). Rotation of the dansyl chromophore about the linkage to the rest of the molecule would yield a distinct activation energy. In NTES, rotation about the linkage is sterically hindered to a much greater degree than in DTES. Thus it is safe to conclude that in both systems, the observed decay of the fluorescence anisotropy arises from the rotational diffusion of the entire probe molecule.

A comparison of the activation of both viscosity and local dynamics with $1/T$ is shown in Figure 4. The ln (η) for 100 cSt PDMS and the ln (τ_c) curves have been arbitrarily shifted on the logarithmic y-axis to allow comparison of curvatures. The viscosity data for the two molecular weights have identical functional form. The temperature-dependent correlation times for 1000 and 100 cSt PDMS have much greater scatter than the viscosity data, but nevertheless the two sets of correlation time

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data display the same functional form. It is clear from the figure that the viscosity and τ_c data do not have the same functional form. This is consistent with their 16.4 and 12.2 kJ/mol average activation energies.

In a previous study, the activation energy of a polar probe, DTES, was measured in the identical PDMS liquids.[4] In contrast to the activation energy obtained for the nonpolar NTES probe, the value of E_a obtained from the reorientation of the polar DTES probe (~27 kJ/mol) was much larger than that of the bulk viscosity.[4] It was proposed that the differences between the probe activation energies and that of the bulk viscosity could be understood in terms of chain dynamics that occur on a local length scale rather than a global one. According to the Rouse model, the segmental motions that occur in a polymer melt can be described as a superposition of dynamical modes.[26] The relaxation time associated with each mode depends on the number of segments involved; the high-frequency modes are due to the concerted motion of just a few segments, while the low-frequency modes involve the cooperative motion of many segments. In the context of the Rouse model, the lowest frequency motions are those which give rise to the activation energy associated with the bulk viscosity. It was suggested that the local motions (associated with the probe reorientation measurement) might exhibit a different temperature dependence than the global motions because of the differences in the associated distance scales.

The size argument, however, is inconsistent with the results of this study. Since NTES and DTES are virtually the same size, the argument predicts that they would have the same activation energy, although it would be different from the bulk viscosity activation energy. The vast difference between the two probe activations demonstrates that domain size is not the most important aspect of the local chain dynamics that give rise to the rotational motion of the probes. Furthermore, it has been observed in carbon backbone polymers that the activation energy for probe reorientational dynamics is the same as that of the bulk viscosity.[22,24,25] This suggests, for the present study, that chemical interactions between the probe molecules and the polar substituents of the polysiloxane backbone are a more important influence on the local chain dynamics.

A second mechanism proposed in ref 4 stated that the interactions of the highly polar DTES with the local polar bonds of PDMS could cause a perturbation of the local structure of the polymer. Then, the activation energy for the reorientation is the activation energy associated with the perturbed structure, not the bulk polymer. In connection with this mechanism, it was suggested that substituting a nonpolar probe of a similar size would have a dramatic effect on the activation energy. This was the motivation for the synthesis of NTES and the reorientation measurements of it in PDMS. The decrease in the activation energy by greater than a factor of 2 upon changing the probe from DTES to NTES strongly supports this mechanism.

The mechanism applies the concepts of solvation in simple liquids to a PDMS melt. If a molecule with a very large permanent dipole moment is placed in a polar solvent, the solvent dipoles will attempt to align to accommodate the local electric field generated by the solute dipole. This results in the dynamic local liquid structure around the solute being distinct from the dynamic structure found in the unperturbed bulk liquid. A nonpolar solute placed in a polar solvent will also have an effect on the local structure. The volume excluded to dipoles by the presence of the nonpolar solute will cause the local solvent structure to be different from the bulk. The Si–O bond has ~40% ionic character[27] and a dipole moment of ~0.6–0.9 D.[28–30] DTES has a very large dipole moment estimated to be ~6 D, based on measurements on chemically similar molecules.[31] The PDMS backbone is very flexible with virtually free rotation about the Si–O bond.[32–34] This is responsible for the locally low viscosity and almost liquid-like behavior even of cross-linked PDMS networks.[35,36] When DTES is dissolved in PDMS, the local structure reorganizes to solvate the DTES dipole, resulting in local chain configurations and dynamics that are different from the ensemble average bulk structure and dynamics which are associated with the 16.4 kJ/mol activation energy of the bulk viscosity. The PDMS must reorient in an environment that is organized around the DTES dipole pointing in a certain direction. Since thermally activated solvent fluctuations give rise to solute orientational relaxation, changing the local solvent structure can result in an activation energy other than the bulk value. Furthermore, it is possible that the solvation of the DTES dipole will tend to lock the structure based on the instantaneous DTES dipole direction. This would give rise to a higher activation energy for DTES reorientation than for the bulk viscosity.

NTES has a reorientation activation energy (12.2 kJ/mol) that is relatively close to, but lower than, the activation energy of the bulk viscosity. With NTES as the solute, the lack of a dipole moment yields another dynamic local structure in which dipolar interactions are reduced. From the experimental activation energy, this apparently yields a local structure that is less dynamically constrained than the bulk structure. The net result of the observations on NTES and DTES is that the polarity of the solute can significantly modify the activation energy of the "microviscosity" over the distance scale that influences solute orientational dynamics.

In the present study using NTES, changing the polymer molecular weight leads to differences in both the macroscopic viscosity and the microscopic probe dynamics. However, in the study using DTES, the probe orientational dynamics were found to be independent of the PDMS molecular weight. The entanglement molecular weight (M_e) (average polymer mass between chain loops) of PDMS ($M_e \approx 8100$) lies between the two molecular weights used in this study.[37] Thus, there is a qualitative difference in the chain topologies of the two melts. The change in NTES reorientation dynamics with chain molecular weight suggests that the perturbation of the environment by the probe is small enough that the local structure and dynamics are still influenced by the bulk chain topology. However, the larger perturbation of local structure caused by the very polar DTES may overwhelm influences of chain topology, yielding the observed lack of dependence of DTES orientational dynamics on molecular weight.

IV. Concluding Remarks

The enormous difference between the activation energies for DTES and NTES orientational dynamics indicates that the microscopic properties of PDMS melts are highly sensitive to local polarity. This suggests a route for synthetically modifying the properties of polysiloxane materials. In the NTES and DTES studies, the probes were in such low concentration that the bulk properties of the melts should be unaffected. However, it should

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be possible to synthetically prepare copolymers having controlled concentrations of side groups with polarities substantially different from the PDMS backbone. These could also be cross-linked to form networks. It is possible that by controlling the polarity and the concentration of the side groups, the macroscopic properties of the networks could be altered.

NTES is also useful as a probe of polysiloxane network structure and dynamics. NTES is a trifunctional cross-linking reagent. Any 2-naphthyltriethoxysilane probe molecule that reacts to form a cross-linked junction results in a naphthyl chromophore tethered to the junction. The naphthyl presence allows the investigation of junction dynamics by time resolved fluorescence anisotropy. Experiments using DTES as a cross-linking reagent suggest that there is self-condensation, yielding cross-linked sites with a functionality greater than 3.[35,38] Unlike DTES, which cannot undergo Förster excitation transport, NTES can be used as a structural probe by observing the fluorescence depolarization caused by excitation transport among chromophores bound to self-condensed cross-linked sites. Investigations of the structure and dynamics of naphthyl-tagged network junctions are currently in progress.

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