Reorientational motion of a cross-link junction in a poly(dimethylsiloxane) network measured by time-resolved fluorescence depolarization

Alan D. Stein
Department of Chemistry, Stanford University, Stanford, California 94305

D. A. Hoffman
Department of Materials Science and Engineering, Stanford University, Stanford, California 94305

C. W. Frank
Department of Chemical Engineering, Stanford University, Stanford, California 94305

M. D. Fayer
Department of Chemistry, Stanford University, Stanford, California 94305

(Received 15 October 1991; accepted 13 November 1991)

The reorientational dynamics of a cross-link junction in poly(dimethylsiloxane) networks, measured by the fluorescence anisotropy decay of a chromophore tagged to the cross-link, have been investigated over a range of temperatures from $T_g + 75$ to $T_g + 150$. The probe chromophore, 1-dimethylamino-5-sulfonylnaphthalene amide (dansyl amide), is pendant to a trifunctional silane that acts as a cross-linking molecule. In cyclohexanol, the fluorescence anisotropy decay is in agreement with Debye–Stokes–Einstein hydrodynamic theory (rotational diffusion) demonstrating that the cross-linker can be used as a probe of orientational relaxation. The fluorescence anisotropy decays at a rapid rate in an end-linked poly(dimethyl siloxane) network reflecting fast reorientational motion of the cross-link junction. This reorientation appears diffusive and has a temperature dependence in accord with the Williams–Landel–Ferry equation. A model is proposed that suggests that reorientation and translational motion of the cross-link occur simultaneously and are both coupled to fluctuations of the polymer chain ends.

I. INTRODUCTION

The technological importance and unique properties of polymer networks have motivated extensive studies of the microscopic and molecular nature of cross-linked systems.[1] Theories which explain the viscoelastic properties of elastomeric networks in terms of models of cross-link dynamics have been developed.[2] In recent years magnetic resonance,[3–8] neutron-scattering experiments,[3,9,10] and fluorescence techniques[11–15] have been used to directly measure molecular properties of polymer networks. Experimental advances such as these contribute to a refined understanding of the molecular structure and dynamics of networks and can better define how macroscopic properties are related to molecular properties.

Luminescence measurements have been widely used to characterize electronic, structural, and dynamical properties of polymers.[16–18] Light emitted from electronically excited chromophores, which are either intrinsic or extrinsic probe molecules, contains information about the interactions between the polymer host environment and the electronically excited chromophores. Recent advances in pulsed optical techniques have been applied to studying dynamics of bulk polymers above the glass transition temperature.[19–26] These measurements provide details of dynamics of segments and individual chains 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 decay from probe molecules, have also been used to evaluate theories of small-scale chain motions in polymer solutions and polymer melts.[21–23,26]

It is generally found that the segmental dynamics of an unstrained cross-linked polymer network above T_g are identical to the segmental dynamics in a melt of chains with similar degree of polymerization.[6,13,27,28] On a molecular scale, the environment in a network is unperturbed by the presence of cross-links. However, there are dramatic differences between elastomeric properties of polymer networks and polymer melts.[29] These differences in the bulk properties result from the connectivity of the polymer chains by cross-links. The molecular-scale properties of the cross-link sites influence the physics of polymer networks.[2] In particular, the mobility or spatial fluctuations of cross-links are believed to play a role in determining the elastic properties of networks.

Placing probe molecules at the cross-link junctions in a polymer network provides a method for directly investigating the environment and dynamics of these points. A series of experiments to increase our understanding of the molecular dynamics and properties of poly(dimethyl siloxane) (PDMS) melts and networks have been performed. PDMS has vast technological applications owing to the unique flexibility and stability of this polymer.[30,31] PDMS has also been widely used in investigating the physics and structure of networks.[32,33] The experiments presented here focus on studying PDMS through the use of a probe chromophore that is attached to a cross-linking molecule. This molecule, dansyl triethoxysilane (DTES), contains a trifunctional silyl group

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with dansyl amide attached by a three-carbon linkage. Dansyl amide has been used extensively as a probe of biochemical and physical chemical systems.[11,12,34] These fluorescent probe molecules are shown in Fig. 1.

A study of the reorientation of the DTES probe dispersed in uncross-linked PDMS above the glass transition temperature, by measurements of time-dependent fluorescence anisotropy, has revealed properties of the highly local, segmental motions that occur in this polymer.[26] The dependence of the probe reorientation on the molecular weight of the host polymer shows the highly localized nature of the dynamics to which this experiment is sensitive. We have also found that the activation energy for local segmental dynamics, given by the temperature dependence of the rate of reorientation of the probe, is larger than for the polymer dynamics responsible for viscous flow.

In the experiments reported here the reorientational dynamics of a cross-link junction in a PDMS network are studied. Hydroxy terminated poly(dimethyl siloxane) molecules (PDMS) undergo condensation reactions with the triethoxy silane group of DTES, leading to the formation of a PDMS network, which is an elastomer at room temperature. In light of its fluorescent properties, the dansyl amide species acts as a spectroscopic probe of the environment and dynamics of the cross-link junctions.

Before using DTES to probe dynamics in polymeric systems it was necessary to characterize its behavior in a simpler, small molecule solvent. In particular, the photophysics of the dansyl amide molecule are complicated by two closely spaced excited states with varying amounts of charge-transfer character.[35,36] It was important to determine whether these photophysics contribute to the fluorescence anisotropy decay. In Ref. 26 the fluorescence anisotropy decay of dansyl amide and DTES in cyclohexanol is analyzed in detail. It is found that the anisotropy decay is due to reorientation of these molecules in agreement with predictions of hydrodynamic theory. These results are reviewed here.

Having established that the fluorescence anisotropy decay reveals the orientational relaxation dynamics of the DTES molecule, we investigate the anisotropy decay from dansyl tagged cross-links in PDMS networks. The results reveal that reorientational motion of the cross-link junction occurs on a subnanosecond time scale at room temperature. This is consistent with recent measurements of translational motion of cross-links in PDMS networks that were made by neutron scattering.[28] A model that attributes both translational and reorientational motion of cross-links to diffusive motion of polymer chain ends is discussed. The temperature dependence of the cross-link reorientation time suggests that the polymer dynamics that affect cross-link motion are the same as those responsible for the viscoelastic response of the system.

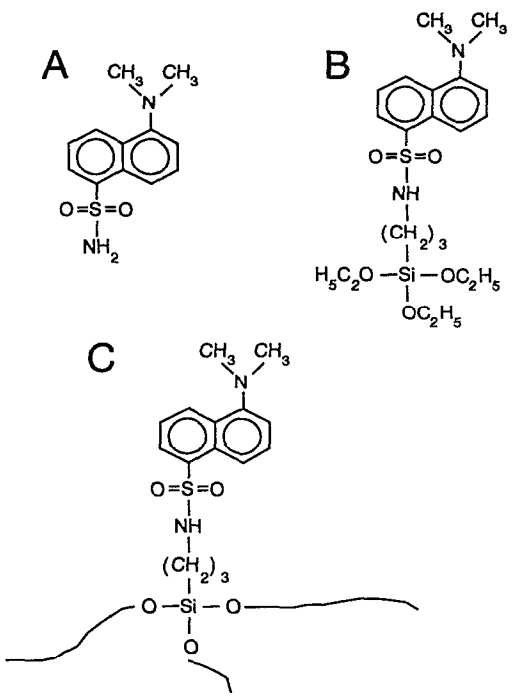

FIG. 1. Probe molecules used in this study. (A) dansyl amide, (B) *N*-(triethoxysilylpropyl)dansyl amide (DTES), a silane cross-linking molecule. (C) DTES molecules couple the ends of PDMS polymers, creating a network structure. The dansyl chromophore probes the environment and dynamics of the cross-link.

II. EXPERIMENTAL PROCEDURES

1-dimethylamino-5-sulfonylnaphthalene amide (dansyl amide, 99%, Aldrich) and *N*-(triethoxysilylpropyl)dansyl amide (DTES) (Huls-Petrarch) were used without further purification. Solutions of 10^{-3}M and 10^{-5}M dansyl amide and DTES in cyclohexanol (Baker) were studied by time-dependent fluorescence depolarization to investigate the excited-state dynamics of these probe molecules in a small molecule solvent.

Cross-linked PDMS networks were prepared by condensing a stoichiometric excess of trifunctional silane cross-linking molecules with hydroxy terminated PDMS chains ($M_w = 24\,000$, $M_w/M_n \sim 1.6$) (Huls-Petrarch). The ratio of ethoxy groups (on cross-linkers) to hydroxy groups (chain ends) was 1.67/1. 0.1% of the cross-linking molecules were DTES, the remaining cross-linkers (99.9%) were methyl triethoxysilane (MTES), the trifunctional cross-linking molecule with the dansyl probe replaced by a methyl group. The concentration of DTES molecules in PDMS was 8×10^{-5}M. The PDMS and cross-linking molecules were mixed with a catalyst, tin octoate, and cured in a nitrogen atmosphere for two days.

The cured, solid networks were subsequently swollen in THF for three days and toluene for three days to remove unreacted species, and then dried. Steady-state fluorescence measurements on the extractable material reveal that 99% of the DTES had reacted. The weight percentage of extractable polymer (chains that have not been incorporated into the network) was 3.5%. The network preparation and measurements of extractable material are described in more detail in another publication.[37]

Fluorescence decays were measured for the PDMS network over a range of temperatures from 298 to 225 K, and for the cyclohexanol solutions from room temperature

to 343 K. Measurements at subambient temperatures were made by placing the network in contact with the coldfinger of a closed-cycle He refrigerator. Temperatures were read from a resistance thermometer in thermal contact with the sample. The accuracy in the temperature readings are ± 2 K. The PDMS appeared to crystallize when cooled below 215 K. For this reason, anisotropy measurements were not made below 225 K. Above room temperature a heated, temperature-controlled sample block was used. All temperatures for these measurements were within ± 0.5 K.

Time-resolved fluorescence depolarization measurements were made by time-correlated single-photon counting. The apparatus[38] and technique[39] were 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 was detected from the front face of the sample by a Hamamatsu microchannel plate detector. Detection was made using a filter that cut scattered UV laser light but passed a broad band of visible fluorescence. Typical instrument response functions for this apparatus have a full width at half maximum of 50 ps.

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, to average out laser intensity fluctuations. 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,

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

Time-dependent fluorescence anisotropy has been widely used to study the dynamics of intermolecular electronic excitation transport[17,18,40] and reorientational dynamics[21,22,41-42] 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 ($\cos \Omega$) of an excited chromophore,

$$r(t) = \tfrac{2}{5} P_2(\cos \psi_{ae}) \langle P_2(\cos \Omega, t), P_2(\cos \Omega, 0) \rangle, \quad (2)$$

where ψ_{ae} is the angle between the absorption and emission dipole directions. This decay is independent of the rate of decay of the 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. 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.

The fluorescence anisotropy data were fit with theoretical expressions convolved with experimentally determined instrument response functions, using a 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 $I_{\perp}$.[42,43] Qualities of fits were judged both by the reduced χ^2, and by visual examination of differences between the data and fit.

III. RESULTS AND ANALYSIS

A. Cyclohexanol

Cyclohexanol is a relatively viscous liquid at room temperature ($\eta = 54$ cP). Hydrodynamic theory[44] predicts that the time for reorientation of a molecule is proportional to the solution viscosity divided by the temperature. Thus, the reorientation of dansyl amide and DTES should occur on a few nanosecond time scale in this solvent at ambient temperatures. This time scale is appropriate for detection by fluorescence anisotropy decay because it is similar to the excited-state lifetime of the dansyl fluorophore in this solvent (~ 15 ns) and it is much longer than the time resolution of the single-photon counting apparatus. By analyzing and comparing the results for solutions of dansyl amide and the dansyl amide tagged cross-linking molecule, DTES, in cyclohexanol we can determine if 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 dansyl amide in cyclohexanol and a solution of DTES in cyclohexanol at room temperature. The decay for dansyl amide is faster than that for DTES on all time scales. This reflects the fact that dansyl amide is a somewhat smaller molecule than DTES and indicates that both

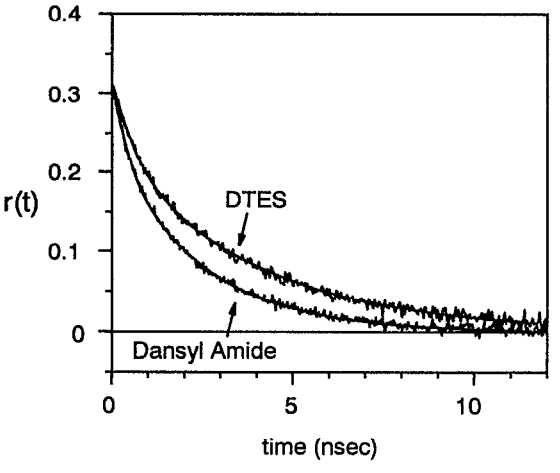

FIG. 2. Time-dependent fluorescence anisotropy decay, $r(t)$, for solutions of dansyl amide and DTES in cyclohexanol (10^{-3}M) at room temperature. $r(t)$ decays due to reorientation of the electronically excited probe molecule. Dansyl amide reorients more quickly than DTES due to its smaller volume, in agreement with hydrodynamic theory. Solid lines through the data are best fits to biexponential decay functions.

the short-time and long-time relaxations depend on the size of the chromophore. The lines running through the data are the best fits to biexponential decay functions.

Identical fluorescent lifetimes and anisotropy decays were obtained for both 10^{-3}M and 10^{-5}M solutions in cyclohexanol, demonstrating that concentration effects and intermolecular excitation transfer were not contributing to the anisotropy decay. Due to the large Stokes shift for 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.[45] Thus, it is reasonable that there is no electronic energy transfer observed at these concentrations. All of the measurements reported in this work were obtained using the 10^{-3}M solutions.

The orientation relaxation (rotational diffusion) of aromatic molecules in small molecule organic solvents has been studied extensively in recent years.[41,42,46-56] The anisotropic rotational diffusion model,[57-61] in which the molecule is described as an asymmetric rotating body diffusing in a continuum solvent, and the Debye–Stokes–Einstein (DSE) equation,[44,62] which relates the rotational diffusion constants of spheroidal molecules to the viscosity and temperature of a small molecule solvent, have provided an accurate context for understanding the experimental results. The fluorescence anisotropy decays of dansyl amide and DTES in cyclohexanol have been analyzed using these models.

The Debye–Stokes–Einstein hydrodynamic equation, modified for ellipsoid-shaped molecules by Perrin,[63] relates τ, the time associated with a rotational diffusion coefficient D ($\tau = 1/6D$) to 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.[62] The factor 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.[64]

If the molecule is modeled as an ellipsoid there are only two unique diffusion constants, $D_{\|}$ for rotation about the symmetry axis, and $D_{\perp}$ for rotation about an axis perpendicular to the symmetry axis. Within the anisotropic rotational diffusion model it is reasonable to obtain a biexponential decay.[26,41,42,54,60,61] Both components of the decay are related to two rotational diffusion constants and therefore should have activation energies equal to that of the viscosity.

In Fig. 3, both the long and short relaxation times from the biexponential fits to the anisotropy decays are plotted vs the viscosity divided by temperature for the solutions of dansyl amide and DTES in cyclohexanol. These plots are linear

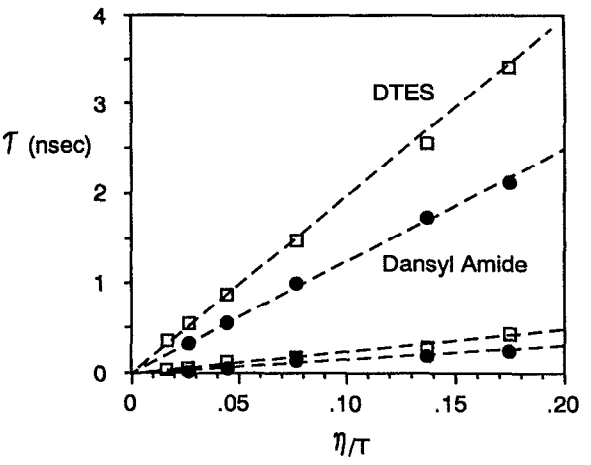

FIG. 3. The fast (lower) and slow (upper) decay times from biexponential fits to the anisotropy decays for dansyl amide (●) and DTES (□) in cyclohexanol plotted vs the viscosity divided by temperature. The Debye–Stokes–Einstein equation predicts a linear relation, with the slope proportional to the hydrodynamic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

as predicted by the DSE equation. Both the fast and slow decay times have a weaker dependence on η/T for dansyl amide than for DTES, reflecting the larger size of the dansyl tagged cross-linker.

If the probe molecules are modeled as ellipsoids, the long decay component (τ_2) is a function only of the slowest diffusion coefficient ($\tau_2 = 1/6D_{\perp}$). From the slopes of the long anisotropy decay times vs η/T (Fig. 3), we obtain hydrodynamic volumes (Vf/S) from the DSE equation [Eq. (3)].[26] Molecular volumes have been obtained from measurements of space-filling models and from van der Waals increments.[65] For both DTES and dansyl amide the hydrodynamic volume is smaller than the molecular volume, suggesting that slip boundary conditions are appropriate.[26,47,48,53,58]

Figure 4 shows a plot of the natural logarithm of the fast and slow components of the anisotropy decay for dansyl amide 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 described by the Arrhenius equation,

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

From the slopes of these curves, we obtain activation energies for reorientation. $E_a = 46 \pm 3$ kJ/mol for dansyl amide, and $E_a = 44 \pm 3$ kJ/mol for DTES. 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 molecule are the same within experimental error as the activation energy for the viscosity.

The purpose for this study of the dansyl chromophore in cyclohexanol was to determine if the photophysics of this molecule affect the fluorescence anisotropy measurements. The results from the measurements in cyclohexanol demon-

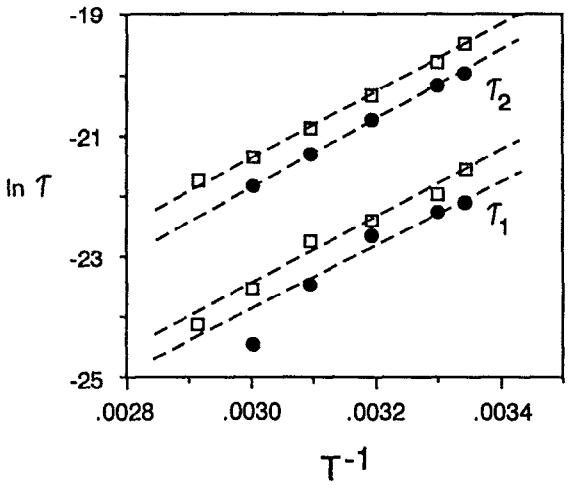

FIG. 4. Arrhenius plot of the fast (lower) and slow (upper) decay times from biexponential fits to the anisotropy decays for dansyl amide (●) and DTES (□) in cyclohexanol. The activation energy (E_a) for orientational relaxation is obtained from the slopes of lines through the data [Eq. (4)]. $E_a \sim 45$ kJ/mol for both the fast and slow decay components for dansyl amide and DTES. The activation energy for the bulk viscosity of cyclohexanol is 43 ± 1 kJ/mol. Both decay components are due to molecular reorientation, which requires movement of solvent molecules, in agreement with hydrodynamic theory.

strate that DTES and dansyl amide behave similarly to aromatic molecules in small molecule solvents. The fluorescence anisotropy decays are due to the molecules undergoing reorientational diffusion in a conventional liquid. The biexponential decays can be rationalized from the anisotropic rotational diffusion model. The measured viscosity dependence of the decay components are in agreement with hydrodynamic theory. Both the fast and slow decay components depend on the size of the molecule. If a component of the anisotropy decay was due to a property of the electronic states of the probe, that component should be identical for both dansyl amide and DTES. Finally, both components of reorientational motion are exponentially activated, with activation energies equal to that for viscous flow in cyclohexanol. In addition, the results taken together show that rotation around the propyl linkage does not contribute to the observed anisotropy decay of DTES. Space-filling models suggest that this is sterically hindered. As a consequence of the above DTES can be used as a probe of orientational relaxation.

B. Cross-linked PDMS network

The reorientational dynamics of a probe molecule attached to a trifunctional cross-link site can be more complicated than when the probe is dispersed freely in a small molecule liquid or polymer melt. If the cross-link density is not too high (large distance between cross-links), the dynamics of the polymer chains surrounding the probe molecule are expected to be similar to those that occur in the uncross-linked polymer melt.[6,13,27-28] However, the probe is covalently bound to a junction of chain ends, and therefore is not free to reorient completely unless there is motion of the cross-link junction itself. This restriction could retard the rate of reorientation of the dansyl molecule, as if it had a larger hydrodynamic volume. Alternatively, there could be a bifurcation in relaxation times,[66] with a fast partial decay of anisotropy reflecting rapid, restricted motion, and a slow component leading to complete depolarization that is due to slower motion of the junction of three chain ends.

Fluorescence anisotropy decays for the end-linked PDMS network, in which 0.1% of the cross-linking molecules are DTES (tagged with the dansyl probe), were measured at temperatures between room temperature and $T = 225$ K. Figure 5 shows the fluorescence anisotropy decay for the dansyl probe in the network at room temperature. For comparison, the anisotropy decay obtained for DTES dissolved in uncross-linked PDMS ($M_w = 28\,000$) at room temperature is also shown.[26] This molecular weight is similar to the molecular weight between cross-links in the end-linked network. Identical anisotropy decays are obtained for the 0.1% tagged network and for networks made with 1% DTES (99% MTES), indicating that at these low tagging percentages the presence of additional probe molecules does not perturb the experimental observable.[37]

Comparing the two decays in Fig. 5, we observe that reorientation of the probe molecule at room temperature is influenced by covalent bonding to a cross-linking site. The rate of reorientation of dansyl attached to the cross-link junction, given by the decay of the polarization of fluorescence, is 50% slower than in the polymer melt. However, it is remarkable that there is not a greater reduction in the time scale for reorientation of the dansyl probe when it is attached to the junction of three chain ends. Furthermore, there is no indication from the shape of the anisotropy decay of hindered, partial reorientational motion, which would cause a nonzero or slowly decaying long-time anisotropy.

The anisotropy data for the 0.1% tagged network were fit with a biexponential decay function, which is found to be appropriate for diffusive reorientation of DTES in a small molecule liquid and in uncross-linked PDMS above T_g.[26]

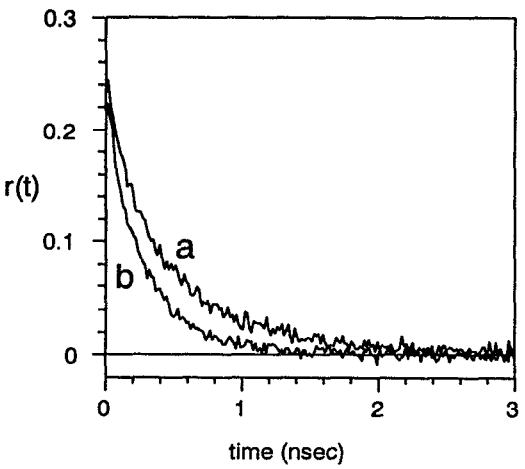

FIG. 5. $r(t)$ measured at room temperature (298 K) for (a) dansyl amide tagged to cross-links in a PDMS network and (b) DTES dispersed in uncross-linked $M_w = 28\,000$ PDMS (Ref. 26). The probe reorientation is 50% slower at room temperature when it is covalently bonded to the cross-link.

The anisotropy initially decays on a time scale that is faster than the 50 ps instrument response can resolve. Therefore, the fit was constrained to have a value of $r_0 = 0.315$, the initial anisotropy obtained at low temperatures in the PDMS network and in a variety of viscous solvents at room temperature.[26] Figures 6(a) and 6(b) show a comparison of the data and biexponential fit at two temperatures, 298 and 250 K. At room temperature the fit is very good. The reorientational motion of the cross-link junction is well described by a diffusive model. As was observed in uncross-linked PDMS,[26] as the temperature is lowered the quality of the fit is not as good, though it continues to model the essential features of the decay.

Figure 7 shows a plot of the natural logarithm of the two biexponential decay components vs $1/T$. This plot appears linear, demonstrating that the temperature dependence is described by the Arrhenius expression, Eq. (4). The activation energy for probe reorientation is obtained from the slope of the Arrhenius plot. Within experimental error, identical activation energies are obtained for the two decay components. This is analogous to the results in cyclohexanol. The activation energy for reorientation of the dansyl tagged cross-link in a PDMS network is 19 ± 2 kJ/mol. This is slightly larger than the activation energy for the viscosity of PDMS, 16 ± 1 kJ/mol.[26,67] The reorientational motion of the dansyl tagged cross-link junction can be described using the orientational diffusion model; the anisotropy decay has the shape of a biexponential function and the two decay components have the same activation energy.

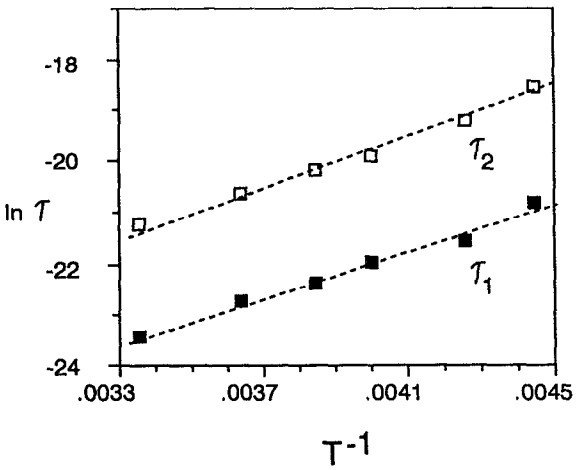

FIG. 7. Arrhenius plot of fast (■) and slow (□) decay times from the biexponential fits to the anisotropy data for dansyl tagged cross-links in a PDMS network. Linear fits to the data (---) are very good, indicating that the probe reorientation is thermally activated. Activation energies for reorientation are obtained from the slopes of the lines: E_a(fast) $= 19 \pm 2$ kJ/mol, E_a(slow) $= 20 \pm 2$ kJ/mol. These activation energies are slightly higher than the activation energy for the bulk viscosity of PDMS, 16 ± 1 kJ/mol.

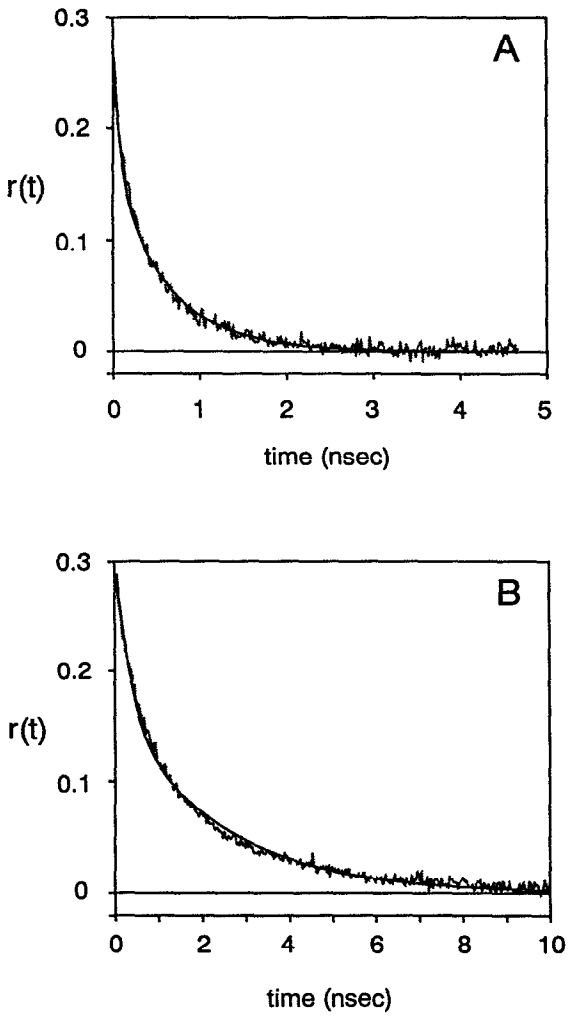

FIG. 6. (A) $r(t)$ for the PDMS network made with 0.1% DTES cross-linking molecules at room temperature ($T = 298$ K) and best fit to a biexponential decay function. (B) $r(t)$ and best-fit biexponential decay at $T = 250$ K. The fit is not as good at 250 K as it is at room temperature, but still satisfactorily reproduces the shape of the anisotropy decay.

It has been shown using a statistical model for cross-linking reactions that for the concentration of cross-link functionality and chain-end functionality that were used in preparing this network, the network should form with 20% extractable polymer.[68] The small weight percentage of extractable polymer that has been obtained[37] (3.5%) indicates that self-condensation between cross-linking molecules occurs during cure. This point is discussed in detail elsewhere.[37] Reactions between cross-linking molecules lowers the total concentration of cross-link functionality in the mixture. It also causes larger, higher functionality cross-link junctions. The possibility of self-condensation between cross-links has been discussed previously, and is believed to occur during network formation.[30,69]

Both MTES and DTES self-condense,[37] they react with like molecules and with each other. The cross-link junctions are on average composed of 2–3 cross-linking molecules, with either one or no dansyl groups incorporated into the junction. The cross-link is a complex, multifunctional intersection point of several PDMS chain ends. The junctions that are monitored in this fluorescence experiment are those that contain a covalently bonded dansyl amide molecule. Thus, we model the cross-link as an object containing a fluorophore with a number of emanating chain ends. [Fig. 8(a)].

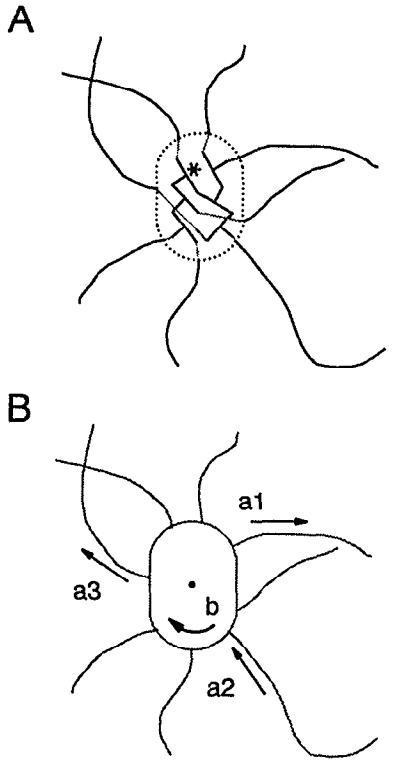

FIG. 8. (A) Illustration of a self-condensed cross-link with a dansyl amide molecule (*). During cure cross-linking molecules react together creating high functionality, super-cross-links which condense with polymer chain ends. (B) Fluctuations in the positions of polymer chain ends impart forces on the self-condensed cross-link (a1, a2, a3). These forces cause both translational motion and reorientational dynamics. A force with a component directed tangential to the cross-link causes a translational step in that direction in addition to reorientation about the center of mass (b).

Due to the thermal energy in the system the polymer chains and cross-link junctions are constantly fluctuating in space. The spatial fluctuations of cross-links are believed to be related to the elastic properties of networks.[2] The fluorescence anisotropy measurement is sensitive to reorientational motion of dansyl amide labeled cross-link junctions.

Recent neutron-scattering measurements from PDMS networks made at temperatures above room temperature have measured translational motion of cross-link junctions.[28] These measurements have demonstrated that the cross-link positions fluctuate over an extensive distance scale on a several nanosecond time scale.

The neutron-scattering experiment is performed on PDMS networks prepared with deuterated polymer chains and protonated tetrafunctional cross-links. The protons on the cross-links scatter neutrons, causing the measurement to be sensitive specifically to properties of the cross-link. Through a Fourier-transform relationship, the neutron-scattering experiment measures the decay in time of the self-correlation function for the position of the cross-link. The self-correlation function decay results from translational motion of the scatterer. Measurements made at a number of scattering angles (wave vectors) give both the time dependence and extent of translation of the junction of chain ends.

The results of the scattering experiment demonstrate that there are large fluctuations in the cross-link position, similar in magnitude to the radius of gyration of the network chains. However, due to the fact that it is attached to several chain ends, translation of the junction is confined to a region in space; it cannot explore the entire sample as a chain end would in an uncross-linked system. For chains of $M_w = 5500$ the standard deviation of fluctuations in the cross-link position is 25 Å. This translational motion occurs on a several nanosecond time scale. This result is in agreement with the phantom network model of cross-link dynamics.[2(b)]

We propose that translational and orientational fluctuations of the cross-link junction are coupled and occur simultaneously. Since the cross-link is actually attached to several chain ends, it is simultaneously pulled in various directions to different extents by the emanating polymer chains [$a1$, $a2$, $a3$ in Fig. 8(b)]. These tugs cause translational diffusion. The tugs that cause translational steps can also lead to orientational diffusion. Forces directed tangentially to the cross-link junction (not through the center of mass) will cause a torque. Successive pulls will lead to orientational fluctuations [b in Fig. 8(b)]. Thus, the cross-link undergoes translational and orientational diffusion simultaneously due to the thermal fluctuations of the chain positions in the network.

The results of neutron-scattering measurements of cross-link translational diffusion support the coupled orientational/translational diffusion model. The fluorescence anisotropy measurements are not sensitive to translational dynamics. However, consider the cross-link site moving in a sphere 50 Å in diameter. It does this on a ~ 10 ns time scale.[28] The displacement is essentially diffusive and requires an extremely large number of individual "steps." It is extremely improbable that the site orientation, as defined by the chromophore transition dipole direction, can be maintained as the site diffuses over this very large volume. Almost all steps in the random walk will involve tangential components of force resulting in orientation relaxation. Since the translational diffusion occurs randomly in three-dimensional space, there are no angular correlations in the directions of the tugs. This suggests that there will be rapid loss of orientational correlation. The fluorescence anisotropy data show that the orientational diffusion (~ 1 ns) is faster than the translational diffusion.[28] Thus, orientational correlation is lost on a time scale corresponding very roughly to the time required to undergo translational diffusion of 1/3 of a standard deviation. This is a distance approximately the size of the self-condensed cross-link site.

The Williams–Landel–Ferry (WLF) equation,[29,70] has been quite successful in predicting the temperature dependence of viscoelastic relaxation times in polymeric systems. The WLF equation relates the logarithm of the time (or frequency) associated with a specific relaxation measured at one temperature, T_0, with the relaxation time at a temperature T, through a shift factor, $\ln a_T$,

$$\ln(a_T/a_{T_0}) = -2.303c_1(T-T_0)/(c_2+T-T_0). \quad (5)$$

c_1 and c_2 are constants that are determined empirically for a specific polymer. The values for PDMS,[29] with T_g as the

reference temperature, are $c_1 = 6.1$ and $c_2 = 69$. Relaxation times of processes that are described by the WLF model will have a temperature dependence with a functional form given by Eq. (5).

In Fig. 9 the biexponential decay times for reorientation of a dansyl tagged cross-link are compared to the WLF equation over the temperature range investigated here. Since the relaxation time at the reference temperature T_0 is unknown, it is standard practice to shift the WLF curve along the vertical axis to obtain the best agreement with the data. Figure 9 demonstrates that over the range of $T_g + 75$ to $T_g + 150$ the data and the functional form of the WLF equation for PDMS are in good agreement. This suggests that the same chain dynamics that contribute to the viscoelastic response of PDMS are also responsible for the reorientational motion of the cross-link.

Plotted as $\ln(a_T)$ vs $1/T$, the WLF equation predicts a nearly linear temperature dependence over this range of temperatures (far above T_g). The slope gives an activation energy that is the same as the activation energy of the bulk viscoelastic response. We have also shown that the anisotropy decay times are well fit by a linear expression (Fig. 7). The fact that the temperature dependence of cross-link reorientational dynamics can simultaneously be fit by both models results from the fact that the measurements were made at temperatures far above T_g. It is significant that the slope of the WLF equation and the Arrhenius plot are similar.

The agreement between the measurements of the cross-link reorientational motion and the WLF equation is consistent with the coupled orientation/translation model of cross-link dynamics. The reorientational motion of the cross-link arises from the simultaneous fluctuations of many chain ends. The dynamics of these chain ends results from cooperative motion of many segments of the polymer chains, some far removed from the cross-link. Thus, the temperature dependence of cross-link motion should to be similar to that of correlated chain motion. Cooperative, long-range fluctuations of polymer chains are the dynamics that are responsible for viscous flow and other low-frequency viscoelastic responses of the system; these are the dynamics that also cause motion of the cross-link junction.

This result can be contrasted with a comparison of our measurements of reorientation of DTES randomly dispersed in uncross-linked PDMS above T_g with the WLF equation.[26] In those measurements we find that the temperature dependence of probe orientation relaxation has a steeper slope than the WLF equation predicts. The activation energy for the dynamics leading to probe reorientation ($E_a \sim 27$ kJ/mol) is considerably larger than the activation energy for viscous flow ($E_a \sim 16$ kJ/mol). The difference between the results in cross-linked and uncross-linked PDMS reflect the differences in the nature of polymer dynamics that cause the probe reorientational motion. While the coupled model states that fluctuations in chain-end positions determine motions of the tagged cross-link in a network, the reorientation of DTES freely dissolved in PDMS requires smaller distance scale, segmental motions of the polymer chains.[26]

Polymer networks often swell to several times their initial volume in solvents that are chemically compatible with the polymer. The extent of swelling reflects the elasticity of the network, and varies with the cross-link density, functionality, and molecular weight of polymer chains between cross-links.[71] An extensive study of the swelling properties of PDMS networks made under a variety of preparation conditions, and with varying ratios of DTES/MTES cross-linkers, are reported in another publication.[37]

In Fig. 10 we compare the fluorescence anisotropy decays measured at room temperature for a dry PDMS network, made with 0.1% DTES cross-linkers, to an identical network that has been swollen in THF. The network

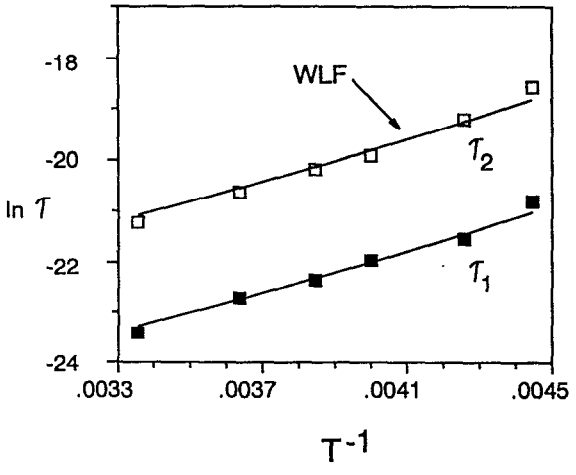

FIG. 9. Comparison of the temperature dependence of the decay times from biexponential fits to the anisotropy decay for the 0.1% DTES tagged PDMS network to the prediction of the WLF equation. This agreement with the WLF equation supports the model for diffusional motion of cross-links: reorientation of the cross-link is governed by the motion of polymer chain ends. Motion of chains are usually associated with the viscoelastic response of a polymer (such as the viscosity), which typically has the same temperature dependence as the WLF equation.

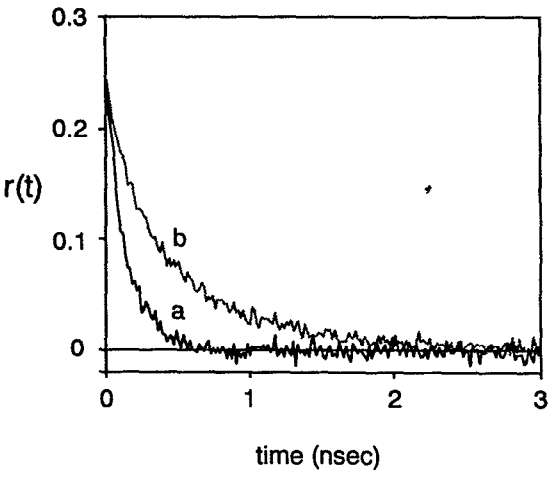

FIG. 10. Fluorescence anisotropy decays measured at room temperature for PDMS networks (0.1% of the cross-links are DTES molecules). (a) The network is swollen in THF. The volume of the network increases by a factor of ~4. The anisotropy decay, which reflects dynamics of the cross-link junction, becomes faster by a factor of ~3. (b) Dry PDMS network.

volume has increased to ~4 times its dry volume. It can be seen that the reorientation time of the cross-link decreases by roughly a factor of 3 in the swollen network. This is consistent with the coupled model for cross-link reorientation. In the swollen system the polymer chain motion occurs at a faster rate.[7,8] The faster motion reflects that fact that the polymer chains are spaced further apart and feel less friction from other PDMS chains. Since it is these chain dynamics that lead to reorientation of the cross-link junction, faster reorientation dynamics are observed in the swollen system.

IV. CONCLUDING REMARKS

Reorientational dynamics of a dansyl amide tagged cross-link have been studied in a poly(dimethyl siloxane) network by time-resolved fluorescence anisotropy measurements. The fluorescence anisotropy decay reflects the orientational relaxation of the probe molecules attached to the cross-link junction. Rapid fluorescence depolarization measured in PDMS networks reflects fast fluctuations in the cross-link angular orientation. These results are consistent with recent neutron-scattering measurements that detect translational motion of cross-link junctions. High-frequency relaxations of polymer chain ends lead to reorientation of the tagged cross-link that appears diffusive in nature.

The activation energies for cross-link reorientation in a PDMS network are similar to the activation energy for the bulk viscosity of PDMS. The temperature dependence of reorientational motion also coincides with the prediction of the WLF equation, consistent with the polymer chains being responsible for the fluctuations that lead to cross-link orientational dynamics.

Further experiments that study properties of cross-links have been made on PDMS networks prepared under varying conditions by fluorescence anisotropy measurements of the DTES probe.[37] In networks made with a higher proportion of tagged cross-link sites (10%–100%), the reorientational motion of the cross-link junctions is affected by the additional dansyl molecules. We attribute this to larger, more highly constrained cross-links arising from the increased likelihood of having more than one dansyl species in a condensed, high-functionality cross-link junction. However, we have measured no correlation between the bulk elasticity of polymer networks, measured by solvent swelling, and the molecular scale dynamics that are measured by fluorescence anisotropy decay. Using a constant fraction of tagged cross-links, varying curing conditions has no effect on the cross-link dynamics as measured by probe reorientation, whereas the macroscopic property, the degree of solvent swelling, is strongly influenced.

ACKNOWLEDGMENTS

A. D. S. and M. D. F. would like to acknowledge the Department of Energy, Office of Basic Energy Sciences (Grant No. DE-FGO3-84ER13251) for support of this research. D. A. H. and C. W. F. would like to acknowledge the Ford Motor Company for support of this research. Additional equipment support was provided by the National Science Foundation, Division of Materials Research (Grant No. DMR90-22675). In addition, an NSF departmental instrumentation grant (No. CHE88-21737), which provided computer equipment used in the calculations, is acknowledged. All of the authors would like to thank the Stanford Center for Materials Research Polymer Thrust Program for support of this research and for the use of the CMR picosecond fluorescence instrument.

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