Ultrafast Side Group Motions of Polymers

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The local dynamics of poly(2-vinylnaphthalene) (P2VN) have been investigated using femtosecond transient grating optical Kerr effect measurements. In solid P2VN, a single exponential 140-fs decay is observed. This decay is attributed to librational relaxation of the naphthyl side groups. In P2VN/CCl₄ solution, besides the librational decay, there exist two slower orientational relaxation components. These decays are temperature independent in the range −3 to +55 °C, although the bulk sheer viscosity of the solution and the viscosity of pure CCl₄ change considerably. This is in contrast to the orientational relaxation of 2-ethylnaphthalene in CCl₄ solution which displays a conventional (hydrodynamic) temperature dependence. The measurements on P2VN solid and solutions are discussed in terms of the local environments of the naphthyl side groups.

I. Introduction

Here we report the investigation of the femtosecond and picosecond orientational dynamics of the naphthyl side groups of the polymer poly(2-vinylnaphthalene) (P2VN), both as an amorphous solid (glass) and in CCl₄ solution. Local dynamics of a polymer in the amorphous glassy state or in solution depend on the extent of motional freedom that exists at the monomeric level. While local dynamics can result in fast orientational relaxations in polymeric systems, global relaxations, involving large scale backbone reorientation, occur on much longer time scales.[1] Unlike a small molecule isotropic liquid, in polymeric systems connectivity of the bonds, restricted bond angles, and steric interactions of pendant groups give rise to cooperativity through the coupling of local and global modes.[2-4] Although large scale motions are slow, observation of local dynamics, as demonstrated below, can require measurements on picosecond and femtosecond time scales.

The transient grating optical Kerr effect (TG-OKE) technique has proven to be very useful for the study of femtosecond and picosecond orientational relaxation dynamics in liquids and liquid crystals.[5-23] Here we report the first application of this method to the study of polymeric systems and, to our knowledge, the first direct ultrafast measurements on polymeric systems. The TG-OKE is a nonresonant four wave mixing experiment that probes the third-order nonlinear susceptibility, $\chi^{(3)}$. The technique directly measures the time correlation function of the orientational motions.[21] In principle, dynamic light scattering (DLS) and TG-OKE experiments contain the same information.[24] However, TG-OKE has proven to be substantially better for the investigation

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of dynamics on picosecond and femtosecond time scales.[21]

In the TG-OKE experiments presented below, we compare the naphthyl orientational dynamics of solid P2VN (glass) with that of P2VN in CCl_4 solution. The polymer dynamics are contrasted to those of 2-ethylnaphthalene (2EN) in CCl_4. Solid P2VN undergoes a single 140-fs exponential decay. This is attributed to librational damping. In solution, P2VN exhibits a picosecond time scale biexponential orientational decay in addition to the ultrafast librational damping. A particularly interesting observation is that the orientational relaxation of P2VN in CCl_4 does not show a temperature dependence between −3 and +55 °C, even though the viscosity of CCl_4 and the shear viscosity of the bulk polymer solution changes considerably over this temperature range. This is in contrast to 2-ethylnaphthalene in CCl_4 which displays a normal (hydrodynamic) temperature dependence.

Nuclear spin–lattice relaxation, the nuclear Overhauser effect, DLS, the optical Kerr effect, dielectric relaxation, fluorescence spectroscopy, and depolarized Rayleigh scattering have been used extensively to study the reorientation of polymers in solids and in solutions.[1,25-33] A modification of dielectric relaxation, time domain reflectometry (TDR), has been used to observe fast dielectric relaxation of local dipoles on the side groups of a macromolecule.[34] Pecora et al. applied depolarized Rayleigh spectroscopy to measure the orientational relaxation time of polystyrene phenyl groups in solution.[1] However, none of these experiments observed picosecond or subpicosecond dynamics in polymeric systems, and in some, slower relaxations were assigned to the dynamics of side groups.[1,29,30,34] A discussion of the distinction between the TG-OKE technique and other methods is presented following the presentation of the TG-OKE data.

Besides the contribution to transient birefringence that is measured in a TG-OKE experiment, the motions of side groups have bearing on the high frequency viscoelastic behavior of polymer solutions[2,35] and the physicomechanical behavior of polymeric solids.[36] The high frequency (>MHz) limiting behavior of the complex viscosity[2,35] ($[\eta]_\infty$) has drawn the attention of polymer researchers. To explain the experimental behavior of $[\eta]_\infty$, several theoretical models have been put forward. All of them indicate that the mobility of the side groups can play an important role.[3,37-40] In addition, mechanical and dielectric relaxations have been observed in amorphous polymeric glasses, and the origin of the β-relaxation has been postulated to involve side group rotations.[25-27] For example, the motion of the nitroxide spin label (di-*tert*-butyl nitroxide) in a solid polymer, investigated using electron–electron double resonance,[41] suggests that conformational restrictions in the packing of the polymeric glass results in free volume about the side group which permits its motion.

The results presented below on P2VN solid and P2VN in solution provide direct information on the time scales and nature of side group dynamics. In the solid, the observation of a single 140-fs decay with no residual long lived anisotropy suggests that the conformations of the naphthyl side groups are rigidly defined and little or no conformational freedom exists. The lack of temperature dependence for the longer lived decays in solution demonstrates that the dynamics are dominated by local structural environments rather than bulk properties of the solution.

II. Experimental Procedures

Detailed descriptions of the subpicosecond dye laser system[42] and the TG-OKE experimental setup[21] employed in these experiments are available elsewhere. The DCM dye laser was turned to 665 nm to avoid two photon absorption by the naphthyl groups. The laser provided 300-fs, 10-μJ pulses at a repetition rate of 1.75 kHz.

We have used the technique pioneered by Etchepare et al.[6] and later extended by Deeg et al.[43] to selectively probe the different dynamic processes contributing to the formation and relaxation of a phase grating. Following the notation of Deeg et al., we define the configuration of the grating experiment as (0°/α/90°/β) where the four quantities within the parentheses stand for the angle of polarization of the two excitation beams, the probe beam, and the detected signal beam, respectively. All the angles were in

reference to the polarization of the excitation beam nearest the probe beam. Near zero delay of the probe beam ($t < 1.5$ ps), we used the (0°/45°/90°/135°) configuration which detects only nuclear $\chi_n^{(3)}$ processes by suppressing the overwhelmingly large electronic contribution. Before and after each of these nuclear scans, an electronic scan with the configuration (0°/45°/90°/56°) was taken. Since the electronic response is instantaneous, this configuration gives the instrument response. Any change in the pulse width during the nuclear OKE measurement can be detected. In addition, this instrument response is a three pulse correlation which provides a very accurate method for determining the pulse duration and shape.[42] Since the instrument response is taken with all components of the experiment identical to the actual measurement (in contrast to using an autocorrelator) and it provides pulse shape information as well as information on the pulse duration, it makes possible very accurate deconvolutions for obtaining quantitative informations for times shorter than the pulse duration. At longer times ($t > 1.5$ ps), when the electronic OKE no longer contributes to the signal, we employed the polarization grating configuration (0°/90°/90°/0°). The S/N ratio is truly outstanding in this configuration as the polarizer in the signal beam eliminates all the (nondepolarized) scattered light from the nearby excitation beam. It also ensures no formation of acoustic and thermal gratings that can contaminate the signal at longer times.[43,44] Typical excitation and probe pulse energies were 100 nJ to 2 μJ and 50 nJ to 0.2 μJ, respectively. The polarization of all beams was preserved upon passing through the sample cell.

Poly(2-vinylnaphthalene) (Scientific Polymer Products, Inc.), CCl_4 (Baker, for UV spectrophotometry), and 2-ethylnaphthalene (Aldrich) were used without further purification. The P2VN supplied by Scientific Polymer Products was not synthesized with a particular tacticity. We, therefore, assume it is atactic. Two different methods were used to prepare the optical quality solid P2VN samples. A P2VN pellet (1-mm thickness) was made by using a die press. P2VN was heated to 160 °C ($T_g = 151$ °C) under vacuum, held for 20 min, and then pressed with 0.8 metric tons for 1 min. The sample was held at 160 °C for another 15 min. The last two steps were repeated, and then the sample was cooled slowly to room temperature. In the second procedure, P2VN was solvent cast. A P2VN film was made by slow evaporation of a solution of P2VN in CCl_4 to constant weight. The concentration of the P2VN/CCl_4 solution was 1.5 M with respect to naphthyl groups at 25 °C. The concentration of the 2EN/CCl_4 solution was 1 M with respect to 2EN at 25 °C. Both solutions were filtered through Gelman 0.2-μm Acrodisk CR filters to remove dust particles.

The solid sample was held carefully to prevent stress induced birefringence. The liquid samples were sealed in a 1-mm spectrophotometric cuvette. For temperatures above room temperature, the cuvette was mounted inside an aluminum block heated by resistive heating wire. The temperature was regulated and held constant to ±0.1 °C. Below room temperature, the cell was mounted in a thermoelectrically cooled metal block held constant to ±0.3 °C. The viscosity of the 2EN solution was measured using a Cannon–Ubbelohde semimicrotype viscometer. The sheer viscosity of the P2VN/CCl_4 solution was measured using a Brookfield Digital viscometer (Model DV II).

III. Results

The TG-OKE data are divided into two time scales: dynamics that are much faster than 1 ps and dynamics that are on a 1 ps and longer time scale. The ultrafast dynamics (<1 ps) involve an initial interaction of the radiation field with the molecules which excites local vibrational modes that are generally referred to as librations.[14,17,21,24,43] Because the pulses are very short, an ultrafast rise of the signal as well as a decay is observed. The rise occurs as the displacement of the impulsively excited librators generates an orientational anisotropy in the sample. The damping (dephasing) of the anisotropy in the distribution of excited librators causes an immediate decay of the signal.[11,14,16,17,24,45] Following the damping, a residual anisotropy may exist.[17] This residual anisotropy decays on the solvent time scale (≥1 ps). In a simple
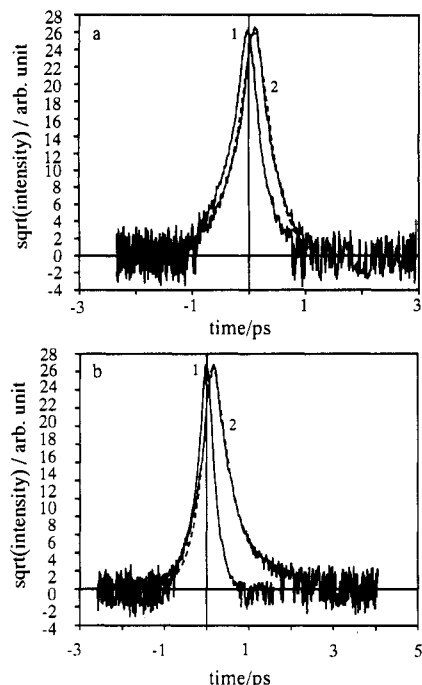
Figure 1. Optical Kerr effect transient grating signal of poly(2-vinyl-naphthalene). Traces 1 and 2 are the square root of the signal. The signal was obtained using electronic only (0°/45°/90°/56°) and nuclear only (0°/45°/90°/135°) transient grating configurations, respectively. a and b show the fast time scale behavior in P2VN glass and 1.5 M (with respect to naphthyl groups) P2VN/CCl₄ solution, respectively, at 25 °C. The dashed lines are the fit calculated through the evaluation of the convolution integral in eq 1. The fit through trace 1 (electronic Kerr or instrument response) was calculated with a δ(t) sample response function. The response function in eq 2 gives the fit through trace 2 in a (nuclear Kerr signal of P2VN glass), and the response function in eq 3 gives the fit through trace 2 in b (nuclear Kerr signal of the P2VN/CCl₄ solution).

liquid, the residual anisotropy decays by orientational diffusion[7,8,12,21,46] and follows the Debye–Stokes–Einstein equation.[47]

The Bragg scattered intensity, $S(t)$, of a probe pulse delayed by time t with respect to the excitation pulses is given by

$$S(t) = \int_{-\infty}^{+\infty} dt'' \, I_p(t'' - t) \left[\int_{-\infty}^{t''} G^{ee}(t'' - t') \, I_e(t') \, dt' \right]^2 \quad (1)$$

where $I_e(t)$ and $I_p(t)$ are the intensity profiles of the excitation and probe pulses, respectively. The sample response function, $G^{ee}(t)$, depends on the particular dynamic process probed.[6,43,48–50] As discussed in section II, $I(t)$ is obtained by observing the electronic OKE. $I(t)$ is found to be well described by a double sided exponential[42] with typical $1/e$ widths of 82 and 187 fs. The curves labeled 1 in Figure 1a,b show the electronic responses from the P2VN pellet and the P2VN/CCl₄ solution, respectively.

Once $I(t)$ is obtained, it is numerically convolved with an analytic response function, $G_n^{ee}(t)$, according to eq 1 to fit the nuclear OKE data. Traces labeled 2 in Figure 1a,b show fits to the short time scale nuclear OKE data. The response functions, $G_n^{ee}(t)$, that give the best fit to the data are the following:[21]

for P2VN solid

$$G_n^{ee}(t) = C_l[\exp(-t/\tau_b) - \exp(-t/\tau_a)] \quad (2)$$

for the P2VN/CCl₄ solution

$$G_n^{ee}(t) = C_l[\exp(-t/\tau_b) - \exp(-t/\tau_a)] + C_r[1 - \exp(-t/\tau_b)] \exp(-t/\tau_1) \quad (3)$$

The C_l term describes the ultrafast excitation and damping of the librations.[21] τ_a and τ_b are the rise and decay time constants, respectively. The C_r term describes the fast reorientational relaxation. The prefactor $[1 - \exp(-t/\tau_b)]$ accounts for the delayed onset of the anisotropy that decays by orientational relaxation following the librational damping.[21]
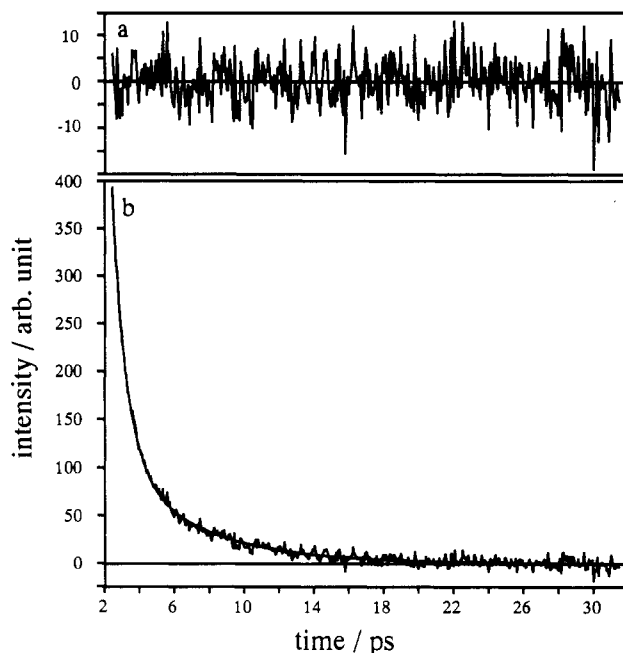

Figure 2. Slow time scale behavior of the 1.5 M (with respect to naphthyl groups) P2VN/CCl₄ solution: TG-OKE signal at $t > 2$ ps obtained using a polarization grating configuration (0°/90°/90°/0°). The solid line through the data is a fit using a biexponential decay response function (5). The residuals of the fit are shown on the top.

The TG-OKE data at $t > 1.5$ ps were analyzed in a straight forward manner without the necessity of considering the convolution effects of the instrument response. At these longer times, the TG-OKE signal is proportional to the square of the sample response function

$$S(t) \propto |G^{ee}(t)|^2 \quad (4)$$

For the P2VN/CCl₄ solution, we found a sum of two exponentials to be an accurate expression for $G^{ee}(t)$

$$G^{ee}(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (5)$$

τ_1 in eq 5 is the same as in eq 3. Figure 2 shows that the square of eq 5 fits the data extremely well.

Using eqs 1–5 and fits to the data such as those shown in Figures 1 and 2, the time constants associated with the dynamics of the different systems can be determined accurately. The P2VN pellet and the solvent cast P2VN film showed no difference in their nuclear response. The librational damping constant $\tau_b = 140$ fs. The librational damping of the P2VN/CCl₄ solution is very similar to the solids with $\tau_b = 190$ fs. τ_a, the rise of the librational signal, is not infinitely fast.[7,14,17,24] The estimated error in the τ's is ±20 fs. However, because of the duration of the pulses used here, only an estimate of $\tau_a = 20$ fs can be made. In contrast to P2VN solid, P2VN in solution shows a residual anisotropy following the ultrafast librational decay. As shown in Figure 2, the residual anisotropy decays as a biexponential. The two time constants are significantly different, so it is not difficult to obtain their values unambiguously. The values obtained for these slower decay constants are $\tau_1 = 0.95 \pm 0.1$ ps and $\tau_2 = 9.0 \pm 0.5$ ps.

There was one other consideration in the analysis of the ultrafast dynamics in the P2VN/CCl₄ solution. Neat CCl₄ gives a relatively weak but nonnegligible signal (approximately one-tenth of the signal from the P2VN/CCl₄ solution) due to collision induced processes.[51–54] Therefore, we subtracted the normalized nuclear OKE data of pure CCl₄ from that of the P2VN/CCl₄ solution before analysis. However, because the decay of the neat CCl₄ signal is extremely fast, it does not influence the τ_1 and τ_2 values and at most introduces a small error in the value of τ_b for the solution.

Figure 3 shows that the two orientational relaxation components of the dynamics of P2VN in CCl₄ are independent of temperature
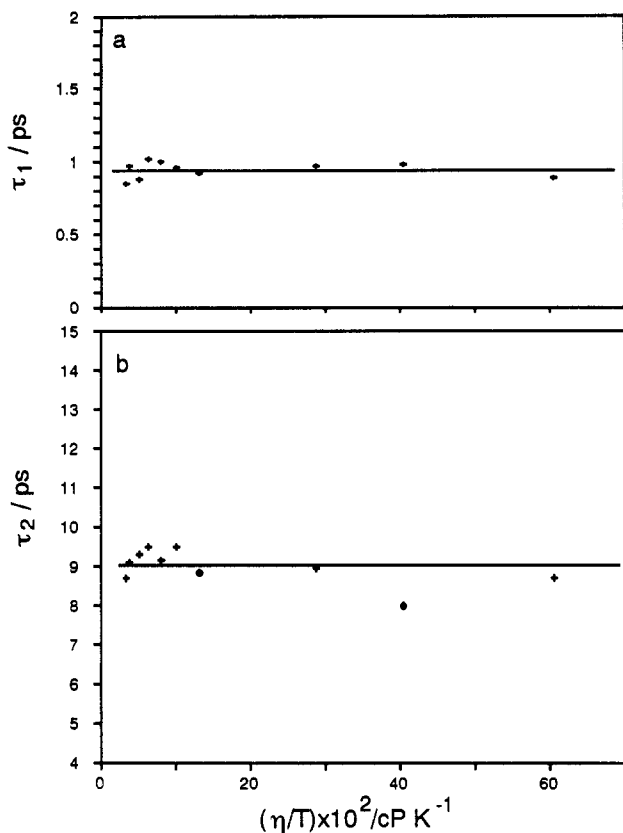
Figure 3. Nonhydrodynamic behavior of the reorientational decay in 1.5 M (with respect to naphthyl groups) P2VN/CCl$_4$ solution from -3 to $+55$ °C. (a) Fast component: τ_1 does not show any viscosity/temperature (η/T) dependence. (b) Slow component: τ_2 does not show any η/T dependence either.

Figure 4. Hydrodynamic behavior of the rotational diffusion components in the 1 M 2-ethylnaphthalene/CCl$_4$ solution. (a) Fast component: τ_f from -30 to $+25$ °C. The straight line fit through the τ_f vs η/T shows the hydrodynamic behavior. (b) Slow component: τ_s from -30 to $+25$ °C. A straight line also fits the τ_s vs η/T data and establishes the hydrodynamic behavior.

over the range studied, -3 to $+55$ °C. The bulk sheer viscosity of the P2VN/CCl$_4$ solution changes by a factor of 20 and the viscosity of pure CCl$_4$ changes by a factor of 2.5 over this range of temperature. The orientational dynamics is not affected by this change in viscosity. Thus the observed orientational relaxation does not arise from rotational diffusion; i.e., it is nonhydrodynamic in nature. To make sure that the lack of temperature and viscosity dependence is not due to some anamolous behavior of either the naphthyl moiety or the CCl$_4$ solvent, we studied the orientational relaxation of 2-ethylnaphthalene in CCl$_4$. Following the ultrafast librational dynamics, 2EN in CCl$_4$ also display biexponential dynamics. Figure 4 shows the behavior of both the fast and the slow orientational relaxation components of the biexponential decay. Both decays change considerably as the viscosity/temperature (η/T) of the solution is varied. They display changes of greater than a factor of 2 when η/T changes by a factor of 3. The behavior of 2EN shown in Figure 4 is hydrodynamic in that the Debye–Stokes–Einstein equation is obeyed. In contrast, the data in Figure 3 display no change although η/T of the P2VN/CCl$_4$ solution varies by a factor of 20.

IV. Discussion

The polarizability anisotropy of the naphthyl group is much greater than that of the polymer backbone. At the pulse energies used in these experiments, neat liquids of long chain hydrocarbons gave measureable but extremely weak signals.[55] Thus, the strong signals detected in these experiments come from the naphthyl pendant group. Both in the glassy solid and in the CCl$_4$ solution, P2VN displays ultrafast librational decays which are 140 and 190 fs, respectively. The small difference in the decay time reflects a small change in the librational damping in the two environments.

More important than the small difference in the decay times is the fact that solid P2VN displays a single decay while the P2VN/CCl$_4$ solution shows two additional decays of 0.95 and 9 ps. These decays in solution are associated with the loss of residual anisotropy that remained after the librational decay. The exci-
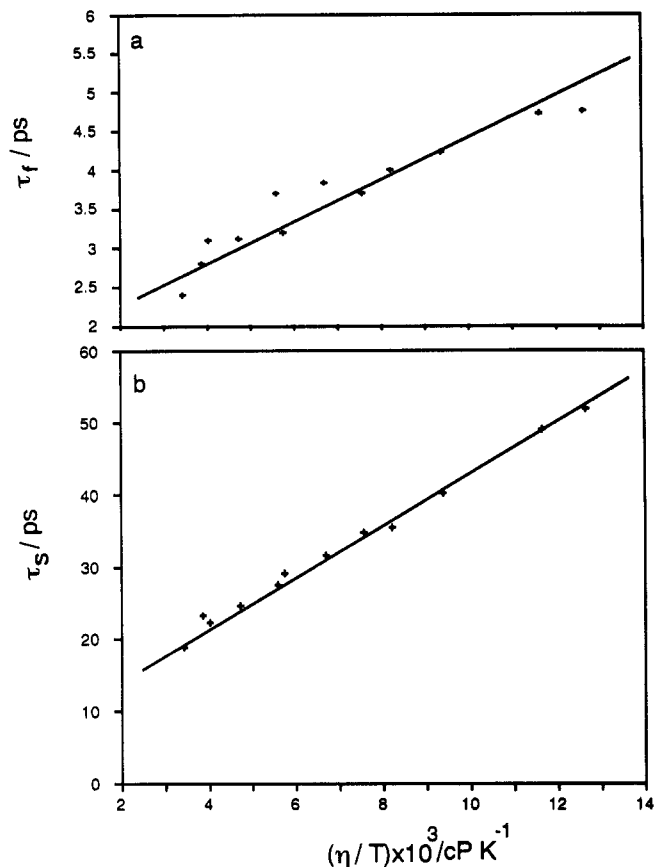
tation of the librations can be viewed as rotational Raman scattering. In a crystal, this type of excitation will excite optical phonons (coupled librations). When the librations damp, no residual anisotropy remains because the molecules are left in their initial precisely determined lattice positions. The amorphous glass of P2VN behaves exactly like a crystal. Following the librational damping, the naphthyl side groups return to their original configurations.

Considering the structural constraints on the packing of a polymer glass, one might expect that the local potential surface that determines the orientational configurations would involve multiple nearly isoenergetic minima (see Figure 5a). In such a situation, after the ultrafast decay of libration is over, the naphthyl groups could return to any of a variety of local minima. This would result in a residual anisotropy. Slower orientational decays would be observed in the data in a manner analogous to the situation observed in the P2VN/CCl$_4$ solution. The ultrafast single exponential decay seen in P2VN glass demonstrates that a single well constitutes the local potential energy surface with relatively high barriers separating the minimum from other orientational local minima. The picture in Figure 5a does not apply to the solid; the packing around the naphthyl side groups permits the naphthyl groups to have strictly a single orientation, with even very small angular variations forbidden.

The P2VN/CCl$_4$ solution displays a residual anisotropy following the damping of the anisotropically distributed librations generated by the excitation field. The addition of solvent has loosened the packing to the point where damping of the libration can leave the naphthyl groups with a distribution of orientations. This is the same as the behavior of small molecules in dilute solution and of many neat liquids. However, in such systems the residual anisotropy decays because of orientational diffusion. These systems display hydrodynamic behavior, i.e., steep depen-
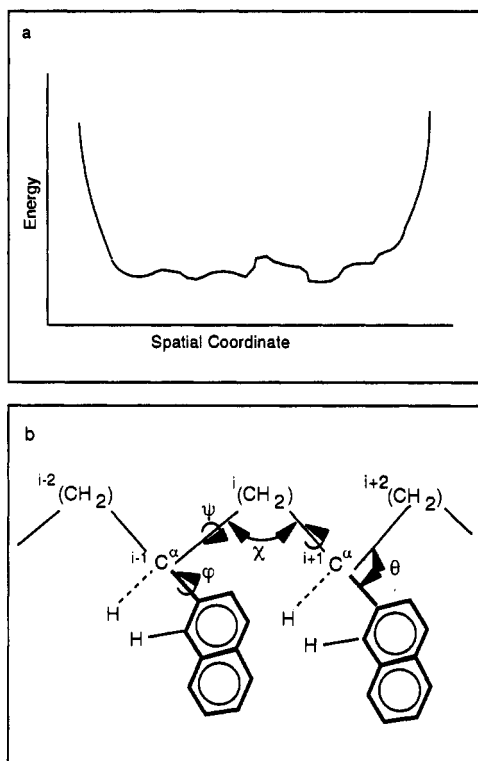
Figure 5. (a) Schematic diagram of an arbitrary section of a hypothetical local potential energy surface for the orientational fluctuation of a naphthyl group in P2VN glass. This might allow a redistribution of naphthyl group orientations after the ultrafast librational decay. A residual anisotropy would be observed since the naphthyl groups would not return to their original positions. (b) Schematic diagram of the isotactic portion of an atactic P2VN chain. It shows the different degrees of freedom that might be important for reorientational relaxational of the residual anisotropy left after librational decay in the P2VN/CCl₄ solution.

dences of the decays on η/T, obeying the Debye–Stokes–Einstein (DSE) equation. An example of this is the behavior of 2EN, as shown in Figure 4. Even orientational relaxation of internal degrees of freedom of moderate size molecules, e.g., the phenyl rings in biphenyl[21] or *trans*-stilbene,[56] is diffusive.

In contrast to small molecules in solution, the naphthyl side groups do not obey the DSE equation. Figure 3 shows that over a very substantial range of η/T, the relaxation of the residual anisotropy is independent of η/T. In two other distinctly different types of systems, η/T independent orientational relaxation has been observed. These are the fast relaxations (1 ps to 1 ns) of the liquid crystal, pentylcyanobiphenyl (5CB) in the isotropic phase[23] and the fast relaxation (3.5 ps) in neat 2-ethylnaphthalene liquid.[22] In both of these systems, the lack of η/T dependence has been attributed to the existance of well-defined local structures[23,57] that exist for a time much longer than the time scale of the observed relaxations. On a short time scale, the system's structure is at the minimum of a free energy surface. The TG-OKE excitation changes the relative orientations, moving the system away from the surface minimum. The measured orientational relaxation is relaxation on the surface back to a minimum. On the short time scale on which the local minimum exists, the η/T dependence of the DSE equation is not obeyed. Rotational diffusion, governed by the DSE equation, occurs on a longer time scale.

To gain insight into the relaxation of the naphthyl side groups of P2VN in CCl₄ solution, it is useful to examine the relative geometries and the nonbonded interactions of the naphthyl groups. The naphthyl group is rather bulky which results in significant van der Waals interaction with the neighboring side groups as well as with the methine H and the methylene H. For a given configuration, the steric energy of the naphthyl group arises mainly from the difference between the nonbonded interaction energy and the bending energy associated with the bond angles. The

details of these interactions depend on the tacticity of the chain. Figure 5b shows the isotactic portion of an atactic P2VN molecule. The C^α–H bond and the C^α–C^2(naphthyl) bond define a plane. In the o-conformation, the naphthyl plane is perpendicular to the H–C^α–C^2 plane, and in the π-conformation the naphthyl plane is parallel to the H–C^α–C^2 plane. De Schryver et al.[58] pointed out that the results of excimer formation experiments on P2VN solutions suggest the presence of oo and $\pi\pi$ conformations for adjacent naphthyl groups when the naphthyl groups are in their ground state. Molecular force field calculations[59] for P2VN show that $oo\pi$ conformations for isotactic and $\pi\pi o$ conformations for heterotactic sequences are the most stable. Frank et al.[31] concluded that the preferred backbone conformations for isotactic chains are trans–gauch or gauch–trans and for syndiotactic chain it is trans–trans. Thus the perferred conformations do not have trans naphthyl groups. The isotactic portion of P2VN chain may also form a 3_1 helix with the naphthyl groups stacked parallel to each other.[60]

The above informations indicate that in all the preferred conformations, independent of the tacticity (which is unspecified for the sample studied), significant rotation of the naphthyl group about the C^α–C^2(naphthyl) bond will be highly hindered because of steric interactions. The data on the solid sample demonstrate that these steric interactions define a single minimum on the potential energy surface for the naphthyl group orientation. The librational states are determined by this surface. Excitation and damping of the libration returns the system to the initial minimum.

In the solution, there is more freedom for small changes in the backbone conformation. The librational motion is coupled through steric interactions to the backbone conformation. The experimental results suggest that librational excitation results in small conformational changes in the local geometry. When the libration damps, the local geometry is different from the initial one. Once the perturbation of the backbone caused by the excited libration is gone, the deformed local structure relaxes back to its initial geometry. The deformed local structure is responsible for the residual anisotropy observed on the picosecond time scale. Relaxation back to the initial structure causes the observed decays.

Following the librational damping, P2VN in solution displays two picosecond time scale orientational decays, 0.95 ps and 9 ps. While it is not possible from these measurements to determine the nature of the motions involved, the following is a possible scenerio. The experimental results do prove that in solution there is relatively more freedom than in the solid for orientational change. The calculations of Seki et al.[60] show that the minimum energy of the trans–trans state for the meso configuration appeared over a range of θ (114°–120°). Due to connectivity of the –CH₂–CH₂–naphthyl groups in P2VN, the libration could cause elastic deformation of the angles θ and χ. After the libration damps, the χ, φ, and θ angles could be left with altered values, no longer corresponding to the minimum energy configuration. Relaxation of the angles θ and χ does not involve the solvent structure significantly and, therefore, could be temperature independent. Because of the inertial nature of this relaxation, it may be associated with the 0.95-ps decay. Following the relaxation of the angles θ and χ, the angle φ could relax by interrupted rotation of the naphthyl group about the C^α–C^2(naphthyl) bond. The distance between the two naphthyl rings in meso dyad for $\psi_i \psi_{i+1} = 0°, 0°$ is 2.60–2.77 Å.[60] Due to the proximal alignment of the naphthyl groups, the intrapolymer interactions probably contribute more significantly to the local potential energy than interactions with the solvent, leading to temperature independent relaxations on a potential energy surface that is fixed on the time scale of the observed dynamics.

V. Comparison to Other Methods

Femtosecond TG-OKE experiments have aspects that are fundamentally different from other methods that examine orientational dynamics of polymers or small molecules. To describe these aspects, it is necessary to briefly discuss the femtosecond TG-OKE experiment as it contrasts to slower OKE experiments and other techniques.

First consider a solute molecule (not a polymer) in a liquid solution. The orientational degrees of freedom of the solute, which would give rise to true rotations in the gas phase, are restricted by intermolecular interactions with the solvent. These interactions give rise to a local, short lived, potential surface that restricts the rotational degrees of freedom. The shortest time scale orientational motions of the solute molecule, which is constrained by the potential, are librational modes, i.e., approximately harmonic oscillations that have a set of quantized energy levels. The transition energies for the librational modes will be in the range of a few tens of cm^{-1}. Since the thermal energy, kT, is large compared to the mode energy, the librational modes are constantly being thermally excited and are constantly relaxing.

In a femtosecond TG-OKE experiment, the radiation field couples to the orientational degrees of freedom of a molecule via stimulated rotational (librational) Raman scattering. The transform limited bandwidth of the laser pulses used in the experiments is approximately 100 cm^{-1}. This bandwidth is greater than the frequency of the librational modes. Therefore, there are many combinations of frequencies within the pulse bandwidth that have a difference equal to the librational mode frequency. An incoming photon can be annihilated in conjunction with the necessary lower frequency photons to stimulate the creation of another lower frequency photon and the excitation of a libration. Thus, in addition to the thermally populated librations, additional excitations are generated by stimulated Raman scattering. For molecules such as naphthalene, the Raman matrix element is anisotropic. The excitation pulses are polarized. Therefore, an orientationally anisotropic distribution of librations is excited. The net result is that an orientationally anisotropic distribution of librations is added to the isotropic, thermally excited librations. This ensemble of initially excited librations is responsible for the rise and fall of the very short time (first few hundred femtoseconds) signal in the experiments. Damping of the optically excited libration of a molecule in a liquid will leave a molecule in a different orientation than it had prior to excitation. Thus when the ensemble of optically excited librating molecules damps, a residual anisotropy remains in the solution. In a simple liquid, the anisotropy is relaxed by orientational diffusion, and the relaxation will display a hydrodynamic temperature dependence.

Now consider the situation for the standard Kerr effect in which a static electric field is applied. Molecules in solution are constantly undergoing rotational diffusion, i.e., an orientational random walk. With a static electric field, which couples to the molecules either through their permanent dipole moment or an induced dipole moment if there is no permanent moment, the molecules execute a biased random walk. Orientational steps in all directions are not equally probable but rather have a greater probability in directions that align the molecular dipoles with the field. The extent of the alignment will depend on the strength of the field–dipole interaction relative to kT and the duration of the application of the electric field. When the field is turned off, the induced orientational anisotropy will relax at the rate of rotational diffusion. The OKE with long laser pulses (10 ns) is very similar to this. The coupling of the optical field to the molecule is through an induced dipole moment. Since the transform limited bandwidth of the optical field is much smaller than the librational frequencies, stimulated Raman scattering does not occur. Instead, as with the case of a static field, the molecules execute a biased walk, and an anisotropy is generated in the sample. When the optical field is removed, the anisotropy will relax by rotational diffusion.

In all three types of Kerr effect experiments (femtosecond OKE, long pulse OKE, or static field KE), an orientational anisotropy is induced in the sample. However, only the femtosecond OKE experiment actually excites librations. In translational diffusion, collisions excite a ballistic translation that is rapidly damped. This ballistic translation is the fundamental step in translational diffusion. Librational excitation and damping are the fundamental events in the orientational random walk that lead to rotational diffusion in liquids. In slow OKE experiments and in KE experiments, thermal excitation of librations, and therefore rotational

diffusion, is an inherent part of generating the orientational anisotropy. In femtosecond OKE experiments, the pulses are sufficiently short to excite librations, and the generation of orientational anisotropy is not directly dependent on rotational diffusion.

Experiments such as time resolved fluorescence anisotropy (or equivalent pump–probe and excited-state transient grating experiments) or magnetic resonance line shape experiments do not induce an actual mechanical orientational anisotropy in a sample. For fluorescence depolarization measurements, an orientationally anisotropic distribution of molecules is created by electronically exciting them with polarized light. The anisotropy in the distribution of excited molecules relaxes by rotational diffusion causing depolarization of the fluorescence. Magnetic resonance experiments examine a line shape (T_2) or population relaxation (T_1). T_1 and T_2 experiments are indirectly related to rotational diffusion through a model that relates orientational motions to spin dynamics. Like slow OKE and KE experiments, fluorescence depolarization and magnetic resonance experiments do not excite librations.

Orientational relaxation measurements on polymers involve a vast range of time scales from the ultrafast librational motions of side groups to very slow motions involving large scale backbone reorientation. What will be observed depends on the time scale and the nature of the measurement. An OKE experiment using long optical pulses or a KE experiment in which the static field is applied for a relatively long time will result in anisotropy developing due to the slow polymer degrees of freedom undergoing a biased random walk. If the application of the field lasts for a time scale that is on the same order as the time scale for diffusion of the slow degrees of freedom, substantial anisotropy will be generated. Observations following the application of the field (optical or static) will reveal the diffusive relaxation of the slow degrees of freedom. In contrast, a femtosecond OKE experiment will excite librations. The librations damp, leaving a residual anisotropy as observed in the polymer in solution experiments discussed above. However, on the ultrafast time scale, there is essentially no diffusive motion of the slow degrees of freedom, and, therefore, there is no buildup of anisotropy in the slow degrees of freedom. For example, if the characteristic time for some backbone motion is a microsecond, then the number of such events that occur during a several hundred femtosecond pulse will be vanishingly small. In principle, there will be a very small anisotropy. The TG-OKE signal should not decay to zero until many microseconds have passed. However, not only would the anisotropy be vanishingly small, but the TG-OKE signal depends on the square of the anisotropy. Therefore, no slow decay will be observed. TG-OKE experiments using long pulses will observe slow polymer dynamics.

From the discussion given above, it is clear why the experiments presented here directly observe ultrafast dynamics in polymers while previous experiments have observed much slower time scale motions although some magnetic resonance experiments have indicated the existence of fast dynamics. Fluorescence depolarization experiments observed nanosecond time scale decays in polystyrene[61,62] and poly(methyl methacrylate) (PMMA)[63] labeled with anthracene in the middle of the chain. The decays showed solvent viscosity and temperature dependence. Excited-state transient grating experiments using 35-ps pulses on polyisoprene,[64,65] similarly labeled with anthracene, detected backbone reorientation occurring from several hundreds of picoseconds to a few nanoseconds. Temperature and solvent viscosity dependences of an average nanosecond correlation time were studied in these experiments.

NMR studies of side group motions were performed on polystyrene,[66–68] PMMA,[69] poly(p-fluorostyrene),[70] and other polymers.[71] Correlation times for internal motions of side groups are obtained using theoretical models[69,72–74] that relate T1 and T2 measurements to orientational relaxation. In some instances the interpretations of the experiments change dramatically with the model that is applied.[67,75] There are reports of very fast dynamics. Polyisoprene experiments were interpreted as yielding a 100–300-fs orientational relaxation of the methyl group, and the results were

found to be independent of temperature.[76] This could be a methyl libration. In contrast, rotational correlation times of methyl and phenyl groups in polycarbonate are reported to have the same value, 10 ps, and a large activation energy.[77]

Very slow relaxations, slower than 10^{-7} s, have been observed in dielectric relaxation and transient birefringence measurements. These involve large displacements of backbone segments comprising many monomeric units. In a transient birefringence measurement, Pecora and co-workers[78] used electric field pulses with durations ranging from microsecond to millisecond. They observed an enhancement of the amplitude of slower modes with longer pulses. This is consistent with the discussion given above that stated the time scale of the application of the electric field must be on the order of the time scale of the diffusional relaxation of a degree of freedom for significant anisotropy to develop in that degree of freedom.

The femtosecond TG-OKE experiments reported here provide direct measurements of the ultrafast dynamics of polymer side groups. Of the other techniques that have been applied, only magnetic resonance experiments have yielded any indications of the ultrafast motions that can occur in polymeric systems. The reason for this is the time scale of the experiments. The slower time scale measurements, such as nanosecond fluorescence depolarization, do not have the time resolution required to observe the femtosecond and picosecond dynamics. However, femtosecond TG-OKE experiments will not observe slow relaxation because, on the time scale of the optical pulse, virtually no anisotropy is developed in the slowly evolving degrees of freedom. TG-OKE experiments using 100 ps, nanosecond, or longer pulses will be able to observe long time scale relaxations. It may be possible to probe the dynamics reported here using femtosecond fluorescence depolarization experiments. This can be done using fluorescence mixing.[79-81] However, complications could arise from relaxation of the local structure around the excited state, electronic excitation transport, and excimer formation. These effects will complicate the interpretation of the results in a manner that does not occur in the nonresonant TG-OKE experiments.

VI. Concluding Remarks

In the experiments presented here, we investigated the local dynamics of the naphthyl side groups of P2VN both in the glassy solid and in CCl_4 solution over the temperature range from −3 to +55 °C. The most striking observations are the single ultrafast (140-fs) decay in the solid and the temperature independence of the additional picosecond time scale decays in the solution. The single decay in the solid is associated with librational damping (dephasing) of the naphthyl groups. The fact that no long lived residual anisotropy is observed following librational damping demonstrates that packing constraints force the naphthyl side groups to have a precisely determined local geometry. The naphthyl groups have virtually no orientational freedom. This does not imply that all naphthyl groups have identical geometries but rather that the geometry of each naphthyl side group, determined by local constraints, is very well defined.

In solution, the two slower reorientational components are not hydrodynamic in nature. This is in contrast to 2EN in CCl_4, which displays hydrodynamic behavior. Even though the bulk sheer viscosity of P2VN solution and the viscosity of CCl_4 change considerably over the temperature range of the investigation, there is no effect on the orientational relaxation of the naphthyl side groups. This demonstrates that the dynamics of the naphthyl groups are controlled by the local intramolecular constraints. The orientational anisotropy induced by the femtosecond TG-OKE experiment does not decay by diffusive randomization of the orientations but rather by relaxation back to the initial local geometry.

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