Communications to the Editor

Quantitative Analysis of Rotational Dynamics in Doped Polymers above and below the Glass Transition Temperature: A Novel Application of Second-Order Nonlinear Optics

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Introduction. Segmental chain dynamics of amorphous polymers above and below the glass transition temperature, T_g, are characterized by a broad range of relaxation times. The reorientation of a chromophore either doped into or covalently bound to the polymer provides one means to characterize these dynamics. Time-resolved optical spectroscopy,[1] including fluorescence anisotropy decay (FAD)[2-4] and transient grating experiments,[5-7] has been employed in solutions and in rubbery polymers well above T_g to obtain the second-order orientation autocorrelation function, $CF(t)$; by comparing the experimental $CF(t)$ to those calculated from models,[8] conclusions may be drawn about the mechanism for local chain dynamics. Unfortunately, FAD provides information on nanosecond time scales, far shorter than the time scales for local polymer motions near T_g. This can be overcome, at least in part, by employing singlet and triplet transient grating[5-7] and photobleaching studies,[9] allowing a dynamic range of 14 decades in time, up to 10^4 s.

Here we report on the first measurements by second harmonic generation (SHG) of average rotational time constants and rotational diffusion coefficients of chromophores doped in rubbery and glassy polymers. With this second-order nonlinear optical (NLO) technique, the orientational contribution to the second-order macroscopic susceptibility $\chi_{zzz}^{(2)}$ (where z is the direction of the applied dc field and the direction of the polarization of the incident laser beam) is proportional to $\langle \cos^3 \theta \rangle$ (where θ is the angle between the applied dc field and the NLO chromophore dipole moment)[10] and hence is related to the third-order autocorrelation function. The temporal decay of $\chi_{zzz}^{(2)}$ (hence called $\chi^{(2)}$) after removal of the electric field has been shown[10-15] to be related qualitatively to glassy polymer relaxations. The present study represents a significant advance in that an alternative experimental protocol (based in part on ref 16) in which the laser pulse is triggered from 200 μs to 0.5 s after switching the dc poling field on (poling onset measurement) or off (temporal decay measurements) is used in conjunction with normal time-domain measurements, allowing dynamics to be monitored over time scales ranging up to 10 orders of magnitude from 10^{-4} s to as long as required (potentially 10^6 s). As the long-term temporal stability of second-order NLO polymers is key to the their utility, this represents an important development not only in accessing local chain dynamics in both rubbery and glassy domains but also in analyzing quantitatively the temporal decay of SHG in glassy NLO polymers.

Experimental Section. Poly(isobutyl methacrylate) (PIBMA; Scientific Polymer Products) and 3 wt % 4,4′-(dimethylamino)nitrostilbene (DANS; Kodak) were dissolved in chloroform and spin coated onto quartz substrates patterned with coplanar chrome electrodes. Films were dried under vacuum at 60 °C for 24–48 h. The final film thickness was 2–5 μm. The T_g of the doped system was 51 °C as measured by a DSC-7 at a heating rate of 10 °C/min. SHG was measured using a Q-switched Nd-YAG laser (pulse frequency of 10 Hz) with a 1.064-μm fundamental beam;[10] values were obtained relative to quartz. Each data point is an average of 100 pulses to obtain a high signal-to-noise ratio. The harmonic beam was incident with the polarization parallel to the applied poling field. Poling involved applying 2500 V across an 800-μm electrode gap.[17] The measurement from 200 μs to 0.5 s employed a variable time delay for the switching on or off of the poling field with respect to the laser pulse. Further experimental details will be provided elsewhere.[18]

Results and Discussion. Figures 1 and 2 show SHG results for poling (onset) and decay measurements, respectively, in a PIBMA + 3 wt % DANS system; $\chi_N^{(2)}$ is the susceptibility normalized with respect to its steady-state value (at the measurement temperature) with the electric field applied. The onset poling measurements involved heating at 82 °C for 10–15 min to erase thermal history followed by quenching to the measurement temperature. The delay-trigger measurements were done by using the time sequence shown in Figure 1, where t_d is varied from 200 μs to 0.5 s. The long time onset (poling) measurement was initiated by switching on the dc field permanently. The decay measurements involved poling at 82 °C until a steady value was reached followed by quenching the sample (with the dc field still applied) to the measurement temperature. The delay-trigger measurements were done by using the time sequence shown in Figure 2, where t_d is varied from 200 μs to 0.5 s. The long time decay measurement was initiated by removal of the dc field.[19]

On application of a dc field, E, the steady-state response of $\chi^{(2)}$ can be written as a sum of two terms:[20]

$$\chi^{(2)} \propto E\left(\gamma + \frac{\mu\beta}{5kT}\right) \tag{1}$$

where γ is the contribution of the electric-field-induced third harmonic generation term which may be considered instantaneous.[21] The second term in parentheses in eq 1 is due to orientation of the chromophores in response to the dc field where μ is the dipole moment, β is the microscopic susceptibility, k is the Boltzmann constant, and T is the absolute temperature. Best fits to the data in Figures 1 and 2 as well as more extensive studies of DANS in a variety of polymers[22] suggest that γ represents about 0.18 of the sum $\gamma + \mu\beta/5kT$ for the temperature

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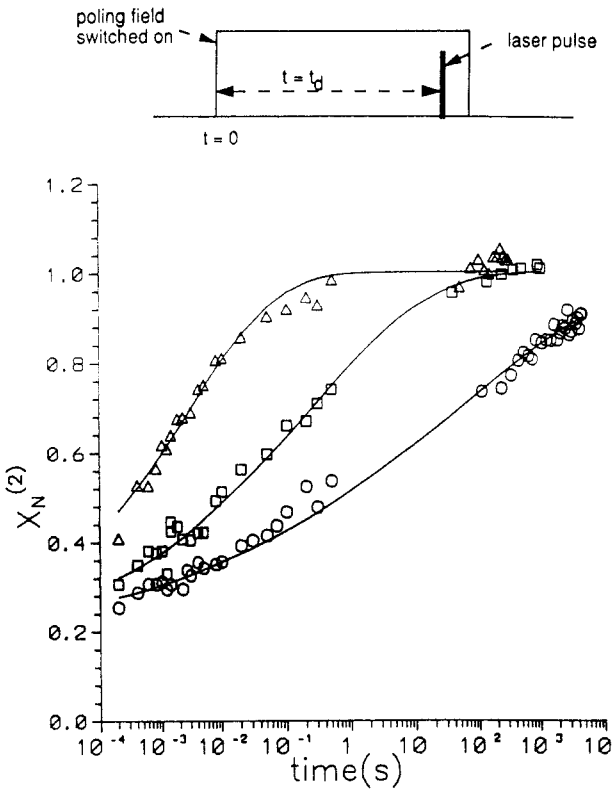

Figure 1. Poling data in a PIBMA + 3 wt % DANS system at 76 (△), 59 (□), and 41 °C (○) using the variable time delay technique (t_d is varied from 10^{-4} to 0.5 s) and the dc field measurement (20–10^4 s). $\chi_N^{(2)}$ is the normalized susceptibility with respect to the steady-state value (at the measurement temperature) with the electric field applied. The solid line is a fit to the Williams–Watts equation.

range tested. Thus by representing the transient rotational dynamics with a Williams–Watts[23] stretched exponential equation (WW) and appropriately subtracting out the electronic contribution to $\chi^{(2)}$, the orientational contribution to $\chi_N^{(2)}$, referred to as $\chi_{NO}^{(2)}$, may be represented by

$$\chi_{NO}^{(2)} = 0.82 \exp(-(t/\tau)^{\beta}) \text{ (decay)} \quad (2)$$

$$\chi_{NO}^{(2)} = 1 - 0.82 \exp(-(t/\tau)^{\beta}) \text{ (onset)} \quad (3)$$

where τ and β are the WW parameters. Table I provides values of τ and β as a function of temperature for the decay-mode measurements. The β values decrease with decreasing temperature, indicating a broader distribution of relaxation times in the glassy state. Over the 52 °C temperature range studied, τ varies by nearly 6 orders of magnitude.

To compare the dynamics as a function of temperature, an average rotational time constant, $\langle\tau\rangle$, can be defined[24] as

$$\langle\tau\rangle = \int_{t=0}^{\infty} \exp(-(t/\tau)^{\beta})\, dt = \frac{\tau\Gamma(1/\beta)}{\beta} \quad (4)$$

where Γ is the gamma function. The rotational diffusion equation has been solved by Wu[25] for $\chi_{NO}^{(2)}$; he predicts that the orientational onset and decay dynamics are predominantly single exponential with a time constant equal to $1/(2D)$ where D is the rotational diffusion constant. The solution of the rotational diffusion equation was based on the model proposed by Debye[26] of noninteracting dipoles floating in a viscous fluid. Dielectric relaxation studies in amorphous polymers show deviations from the

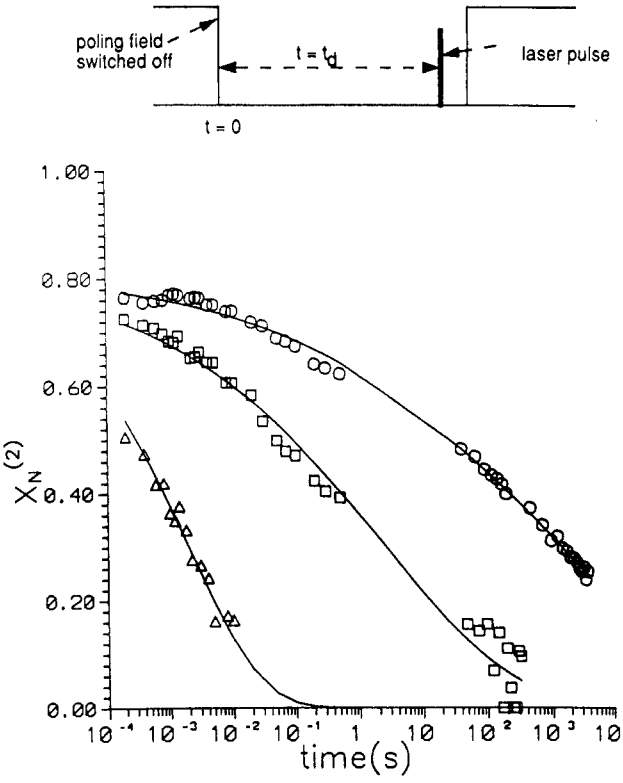

Figure 2. Decay-mode data in a PIBMA + 3 wt % DANS system at 76 (△), 53 (□), and 30 °C (○) using the variable time delay technique (t_d is varied from 10^{-4} to 0.5 s) and the dc field measurement (20–10^4 s). $\chi_N^{(2)}$ is the normalized susceptibility with respect to the value at $t = 0$ before switching off the dc poling field. The solid line is a fit to the Williams–Watts equation.

Table I
Williams–Watts Parameters, Average Rotational Time Constants ($\langle\tau\rangle$), and Average Rotational Diffusion Coefficients (D^*) as a Function of Temperature from the Decay-Mode Measurements

temp (°C)	τ (s)	β	$\langle\tau\rangle$ (s)	D^* (s^{-1})
30	1300	0.18_0	400000	1.3×10^{-6}
41	65	0.20_3	6000	8×10^{-5}
53	2.5	0.21_2	200	2.5×10^{-3}
59	0.5	0.25_3	10	0.05
64	0.04	0.28_2	0.5	1
70	0.022	0.30_4	0.2	2.5
76	0.002	0.37_9	0.008	63
82	0.0014	0.39_7	0.005	100

ideal response, and empirical models[27] (Cole–Davidson, Williams–Watts, Havriliak–Negami, etc.) have been proposed to account for this deviation. Based on $\langle\tau\rangle$, an average rotational diffusion constant, D^*, can be defined by analogy with Wu:[25]

$$D^* = \frac{1}{2\langle\tau\rangle} \quad (5)$$

Table I lists $\langle\tau\rangle$ and D^* values obtained in this study. Noteworthy is the dramatic temperature dependence of $\langle\tau\rangle$, changing from 5 ms at T_g + 31 °C to 200 s at T_g + 2 °C; at T_g − 21 °C, $\langle\tau\rangle$ increases to 4×10^5 s.

Figure 3 compares $\langle\tau\rangle$ values from both decay and onset measurements to a best fit of the WLF equation to data at $T \geq T_g$:[28]

$$\log \frac{\langle\tau\rangle}{\langle\tau\rangle_{T_g}} = \frac{-14(T - T_g)}{(51\ ^\circ\text{C} + T - T_g)} \quad (6)$$

The onset and decay data agree well over the temperature range studied. The data at $T > T_g$ agree well with a WLF fit but deviate significantly at $T < T_g$, being orders of

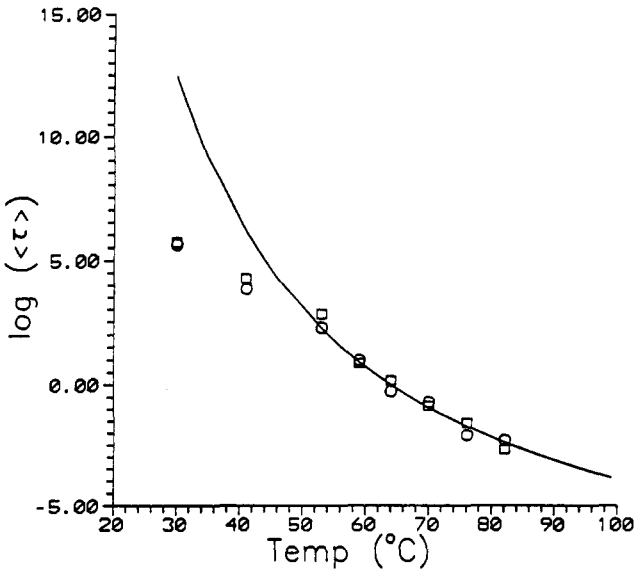

Figure 3. Temperature dependence of the average rotational time constant, $\langle\tau\rangle$ (units = seconds), above and below T_g in a PIBMA + 3 wt % DANS system from the onset (□) and decay-mode (○) measurements. The solid line is a fit to the WLF equation (eq 6). The WLF fit has been obtained from both SHG and dielectric relaxation measurements over a temperature range from 53 to 145 °C. (See ref 28 for details.)

magnitude below that predicted by an extension of the WLF equation into the glassy domain. This is to be expected, as a nonequilibrium glass has a specific volume greater than its value at equilibrium, resulting in an enhanced mobility and smaller $\langle\tau\rangle$ than at equilibrium. A similar departure from equilibrium below T_g has been seen in poly(vinyl acetate)[29] using dielectric relaxation measurements.

With the inclusion of the delay-trigger approach allowing one to access submillisecond time scales, SHG can be a powerful new tool in studying rotational dynamics in amorphous polymers above and below T_g. This will allow the quantitative investigation of not only very slow local polymer dynamics (using the NLO chromophore as a probe of polymer behavior) not easily accessed by other techniques but also the exact role of polymer dynamics in the temporal stability of NLO chromophore orientation and SHG. Comparison of SHG to dielectric relaxation measurements for a variety of NLO polymer systems and extension of SHG measurements to even shorter time scales allowing dynamics to be quantified far above T_g as well as deep in the glassy state are the subject of current work.

Acknowledgment. This work was supported by the Materials Research Center at Northwestern University which is funded by the National Science Foundation.

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