Rotational reorientation dynamics of disperse red 1 in polystyrene: 
alpha-relaxation dynamics probed by second harmonic generation and 
dielectric relaxation

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(Received 27 July 1993; accepted 7 January 1994)

Using a novel experimental protocol involving second harmonic generation (SHG), the rotational, reorientation dynamics of disperse red 1 (DR1) chromophores doped at 2 wt. % in polystyrene (PS) have been monitored over 11 decades in time, from $10^{-6}$ s onwards. This nonlinear optical (NLO) technique allows quantification of the average rotational, reorientation time constant $\langle \tau \rangle$ over a broad range of temperatures, 28 to 138 °C, above and below the glass transition temperature $T_g$. Good agreement was obtained between $\langle \tau \rangle$'s determined from SHG and dielectric relaxation measurements. This is expected since both SHG and dielectric relaxation measurements of PS+2 wt. % DR1 monitor the rotational reorientation of DR1 chromophores. Values of $\langle \tau \rangle$ fit well to a Williams–Landel–Ferry equation above $T_g$, indicating that the rotational reorientation of DR1 is coupled to the $\alpha$ relaxation of PS; below $T_g$ the values of $\langle \tau \rangle$ show an apparent Arrhenius temperature dependence with an activation energy of 45–50 kcal/mol. Above $T_g$, the SHG data are in agreement with the literature values of the temperature dependence of the $\alpha$-relaxation dynamics for homopolymer PS obtained using NMR, viscosity, compliance, and photon correlation spectroscopy measurements; at $T_g$ the absolute values of $\langle \tau \rangle$ obtained by SHG are also in good agreement with the literature values obtained for relaxation times in PS using NMR, photon correlation spectroscopy, and enthalpy relaxation. Upon scaling the data using a reduced parameter, $T_g/T$, where $T_g$ is close to the calorimetrically determined $T_g$, an excellent overlap of SHG results for the rotational reorientation dynamics of DR1 and thereby the $\alpha$ transition in PS, poly(ethyl methacrylate), and poly(isobutyl methacrylate) is observed below $T_g$; however, above $T_g$, the PS data show a much stronger temperature dependence, suggesting that PS may be a more “fragile” glass-former than the methacrylate-based polymers. Physical aging greatly shifts the relaxation to longer times, resulting in a significant increase in the temporal stability of SHG properties in these NLO polymers.

I. INTRODUCTION

Significant interest has been generated over the last decade for using polymers doped or labeled with nonlinear optical (NLO) chromophores for second harmonic generation (SHG),1–22 the conversion of light from frequency $\omega$ to $2\omega$. Most of this interest is due to the fact that polymeric materials may provide significant cost and processing advantages in comparison to inorganic crystals for use in an array of technological applications, including laser, optical data storage, and electro optic devices,4–6 where frequency doubling and associated second-order NLO phenomena may be employed. However, it has also been recently demonstrated14,15 that SHG may be employed as a novel tool to investigate quantitatively basic scientific issues related to polymer dynamics, especially under circumstances near or below the glass transition temperature $T_g$, where many of the more conventional approaches are difficult or impossible to employ.

In order to obtain SHG properties in an amorphous polymer doped or labeled with NLO chromophores, it is necessary to make the system noncentrosymmetric.1 This involves applying a dc poling field $E_z$ near or above the glass transition temperature $T_g$, resulting in net alignment of the NLO chromophores. For a steady-state situation the SHG intensity $I(2\omega)$ is given as7

$$[I(2\omega)]^{0.5} \propto N\chi^{(2)}_{zzz} [\gamma^\top \frac{\mu \beta_{333}}{5kT}],$$

where $\chi^{(2)}_{zzz}$ is the second-order macroscopic susceptibility (for simplicity $\chi^{(2)}_{zzz}$ will be abbreviated as $\chi^{(2)}$), $\gamma$ is the direction of the incident polarization of the fundamental beam and also the direction of the dc field, and $N$ is the number density of the chromophores. $\gamma$ is a contribution due to an electric-field-induced third-order effect which for all practical purposes appears and disappears instantaneously upon application and removal of the dc field.5 The term $N\chi^{(2)}_{zzz}\gamma^\top \frac{\mu \beta_{333}}{5kT}$, where $\mu$ is the dipole moment, $\beta$ is the microscopic susceptibility, $k$ is the Boltzmann constant, and $T$ is absolute temperature, is due to the orientation of the chromophores which balances in response to the dc field and thermal randomization.

Once a second-order NLO polymer system is poled to achieve steady state, orientation of the chromophores is maintained by cooling the system to temperatures below $T_g$ with the dc field applied. However, even below $T_g$, upon

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[IJCPC_100_8_6046]
removal of the poling field randomization of NLO chromophore orientation occurs over time, resulting in a decrease in $\chi^{(2)}$. This loss of orientation with time is a major stumbling block in the technological application of polymers for SHG devices. The underlying basis for the randomization of chromophore orientation has been the subject of significant inquiry. Several studies have indicated that the decay of $\chi^{(2)}$ is associated with the glass transition temperature $T_g$ of the polymer. Recently, by using a novel experimental protocol which allowed us to monitor rotational dynamics from $10^{-4}$ s onwards, we have quantitatively shown that the rotational reorientation dynamics of disperse red 1 (DR1) dopants in poly(isobutyl methacrylate) (PIBMA) and poly(ethyl methacrylate) (PEMA) are directly coupled to the $\alpha$-relaxation dynamics in those polymers. (The $\alpha$-relaxation is associated locally with segmental mobility permitting cooperative conformational rearrangement of a number of repeat units along polymer chain backbones and macroscopically with $T_g$.) This conclusion was reached on the basis of a direct comparison between SHG, which monitors the rotation of the DR1 chromophore, and dielectric relaxation, which measures the rotation of the polar side groups in PIBMA and PEMA. In the case of PIBMA, where dielectric relaxation shows only the $\alpha$-relaxation, the rotational reorientation of DR1 monitored using SHG agrees with the dielectric relaxation measurement. For the PEMA system, where dielectric relaxation shows only the $\beta$-relaxation dynamics at temperatures $T < 1.1 - 1.2 T_g$ and the merging of the $\beta$ with the $\alpha$-relaxation at higher temperatures, the rotational reorientation of DR1 monitored using SHG agrees with the dielectric relaxation results associated with the $\alpha$-relaxation.

In this study we report SHG and dielectric relaxation measurements on polystyrene (PS) doped with 2 wt. % DR1 chromophores. PS was chosen for several reasons. First, a nonpolar polymer such as PS is dielectrically inactive in comparison to DR1; thus, both SHG and dielectric relaxation measurements will directly monitor the rotational reorientation of DR1 chromophores. Monitoring rotational reorientation of polar chromophores in nonpolar polymers by dielectric relaxation was used before by Davies and Edwards, and Hains and Williams. We have shown previously that the transient dynamics monitored by $\chi^{(2)}$ are predominantly sensitive to $\langle \cos \theta \rangle$, where $\theta$ is the angle between the chromophore dipole moment and the applied dc field. As dielectric relaxation directly monitors $\langle \cos \theta \rangle$ relaxation, SHG and dielectric relaxation results in the PS+DR1 system should be similar. Second, choosing a polymer with a $T_g$ near 100 °C allows rotational dynamics to be monitored easily over a broad range of temperature below $T_g$. We will demonstrate that for technological application the necessity of using a polymer with a $T_g$ high in comparison to used temperature may be explained in terms of the temperature dependence of the average rotational, reorientation relaxation time $\langle \tau \rangle$ in the glassy state. More importantly, from a basic scientific standpoint we will demonstrate how SHG can be employed as a powerful new technique to monitor chromophore and polymer dynamics above and below $T_g$ over a dynamic range of at least 11 decades in time. By using PS for our studies, we are able to reinforce this conclusion by demonstrating agreement between values of $\langle \tau \rangle$ obtained from SHG with literature values for the relaxation times obtained above $T_g$ in PS using a variety of other approaches including photon correlation spectroscopy, dielectric relaxation, viscosity, compliance, and NMR measurements.

II. EXPERIMENT

Polystyrene (PS; $M_w = 430,000, M_n = 119,600$) was obtained from Scientific Polymer Products and used as received. Disperse red 1 (DR1; Aldrich) was recrystallized using toluene. For SHG studies, polymer+2 wt. % DR1 was dissolved in spectroscopic grade chloroform and spin coated onto a quartz substrate which was patterned with planar chrome electrodes using standard photolithographic techniques. The gap between the two chrome electrodes was 800 μm. The films were dried below $T_g$ for 24 h and above $T_g$ for 12 h under vacuum. The final film thicknesses were 5–10 μm. The $T_g$ of the PS+2 wt. % DR1 films was 94 °C, measured as the onset temperature of the heat capacity change with a Perkin-Elmer DSC-7 at a heating rate of 10 °C/min.

SHG measurements employed a Q-switched Nd-YAG laser (10 Hz frequency) with a 1.064 μm fundamental beam. The measurement of rotational dynamics from 20 s onwards was done by monitoring the SHG intensity after switching on or off the dc poling fields. Rotational dynamics from 5 μs to 2 s was monitored by using a variable time delay for the switching on or off the poling field with respect to the laser pulse. Further experimental details regarding the variable time delay measurements are provided elsewhere. Several modifications have been introduced to the scheme followed in Refs. 14 and 15. First, we have extended the range of accessible time to 5 μs by using a power supply which has rise time of <2 μs from 0 to 1500 V. Second, for the scheme followed in Refs. 14 and 15, the data were collected from 200 μs to 0.5 s by delaying the laser pulse before switching on or off the dc poling field. This approach of monitoring one point at a time is convenient for fast times, but becomes very time consuming for monitoring data from 25 ms onwards. In particular, the time required between the two sequences to ensure that $\chi^{(2)}$ returns to its steady-state value is very time consuming. In order to optimize the data acquisition we have made the following improvements. The data from 25 ms to 2 s were monitored by turning off or on the dc field only once during that time. While the dc field is off or on, SHG intensity is recorded for all the laser pulses, which occurs after every 100 ms interval, and the results are stored as an array keeping track of the time delay between the laser pulse scanning the sample and the switching on or off the dc field. This event is repeated after every 12–15 s. After 100 such events an average of 100 points is taken to give simultaneous values of $\chi^{(2)}$ for the various times between 25 ms and 2 s.

SHG was measured both in the onset mode and the decay mode. For the onset mode studies, done over a temperature range of 95 to 115 °C, the samples were heated to 130–140 °C to erase the thermal history followed by cooling the system to the measurement temperature. The rotational dynamics from 200 μs to 0.5 s were monitored using the delay-trigger approach while the dynamics after 20 s were measured.
sured by switching on the dc field permanently. The decay mode measurements at temperatures from 28 to 100 °C involved heating the sample to 130–140 °C to erase thermal history followed by cooling the system to 105 °C. A dc field of 1200–1300 V (=15–16 kV/cm) was applied for less than 30 s followed by cooling the sample to the measurement temperature with the dc field on. The dynamics from 5 μs to 2 s were measured using the delay-trigger approach while the dynamics after 20 s were measured by switching off the dc field permanently. For the decay mode data at temperatures of 105–138 °C the thermal history of the samples was erased at 130–140 °C followed by cooling to 115 °C where the samples were poled until a final stable value of \( \chi^{(2)} \) was achieved, followed by cooling or heating the samples to measurement temperature with the dc field on. It should be noted that in the samples poled at 115 °C a first plateau in \( \chi^{(2)} \) was observed after less than 0.1 s which corresponds to the orientation of the chromophores associated with the \( \alpha \) relaxation. However, an additional increase in the value of \( \chi^{(2)} \), of 10% to 20%, was observed when the samples were poled for longer times at 115 °C. Although an increase in \( \chi^{(2)} \) can only result due to orientation of the chromophores, we believe that this additional increase in \( \chi^{(2)} \) is due to charge diffusion in the system and not to polymer dynamics. (The timing of the additional, small increase in \( \chi^{(2)} \) is sensitive to whether the electrode used is chrome or aluminium while the dynamics associated with the first plateau in \( \chi^{(2)} \) are not.) The decay mode data at temperatures of 105 to 138 °C are corrected for the presence of this additional drop off in \( \chi^{(2)} \) at longer times.

Samples for dielectric relaxation were prepared by spin coating PS+DR1 solution onto a glass substrate sputtered with a gold layer. The films were dried below \( T_g \) for 24 h and above \( T_g \) for 12 h under vacuum. After drying, another gold layer was sputtered on top of the polymer film. The dielectric relaxation was measured from 5 to \( 10^6 \) Hz using a Hewlett-Packard 4192A impedance analyzer.

III. RESULTS AND DISCUSSION

Figure 1 shows the SHG decay mode measurements for the PS+2 wt. % DR1 system deep in the glassy state at 78 °C. The decay mode data are represented as \( \chi^{(2)} \), which is \( \chi^{(2)} \) normalized to its value just before switching off the dc field. Within 5 μs of the removal of the dc field, \( \chi^{(2)} \) has decreased to a value of 0.83, signifying a 17% decrease in \( \chi^{(2)} \) as compared to that before removal of the dc field. This decrease is associated with the electric-field-induced third-order effect. In a previous study we have demonstrated that for DR1 the relative contribution of this effect to the overall \( \chi^{(2)} \) with the electric field applied is 12±2%, in PEMA, PIBMA, and poly(methyl methacrylate) (PMMA). However, the relative contribution of \( \gamma \) to the overall value of \( \chi^{(2)} \) for the PS+2 wt. % DR1 system was found to be slightly greater. The small differences in these values in PS and the methacrylate-based polymers may be due to the polarity differences in these polymers. In any case, it is important that these effects be accounted for by measurement in the polymer systems used for study.

Figure 2 shows the decay mode dynamics associated with the orientation component of \( \chi^{(2)} \), here designated \( \chi^{(2)}_{NO} \), for selected temperatures ranging from 47 to 128 °C. \( \chi^{(2)}_{NO} \) has been calculated at each temperature by dividing \( \chi^{(2)} \) by the fraction which is due solely to orientation (or equivalently one minus the fraction due to the electric-field-induced third-order effect). Noteworthy is the dramatic difference in the dynamics associated with the NLO chromophore rotational reorientation above and below \( T_g \). At 128 °C (\( T_g+34 \) °C), virtually all of the chromophore orientation has relaxed away within 1 ms. However, at 47 °C (\( T_g-47 \) °C), approximately complete retention of orientation is present at 1 ms. At \( 10^5 \) s approximately the same \( \chi^{(2)}_{NO} \) is achieved at 47 °C and after only \( 10^{-3} \) s at 128 °C.

The solid curves in Fig. 2 correspond to fits using the Kohlrausch–Williams–Watts (KWW) equation.
TABLE I. Average rotational time constant $\langle \tau \rangle$ as a function of temperature from the decay mode measurements for the PS+DRl system.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\langle \tau \rangle$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>138</td>
<td>$8 \times 10^{-6}$</td>
</tr>
<tr>
<td>128</td>
<td>$4 \times 10^{-3}$</td>
</tr>
<tr>
<td>119</td>
<td>$3 \times 10^{-4}$</td>
</tr>
<tr>
<td>115</td>
<td>$8 \times 10^{-4}$</td>
</tr>
<tr>
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</tr>
<tr>
<td>28</td>
<td>$6 \times 10^{9}$</td>
</tr>
</tbody>
</table>

TABLE II. Average rotational time constants $\langle \tau \rangle$ as a function of temperature from the poling onset mode measurements for the PS+DRl system.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$\langle \tau \rangle$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>110</td>
<td>$8 \times 10^{-3}$</td>
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<tr>
<td>105</td>
<td>$1 \times 10^{-1}$</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>95</td>
<td>100</td>
</tr>
</tbody>
</table>

$\chi^{(2)}_{\text{NO}} = \exp \left[ -\left( \frac{t}{\tau} \right)^{\beta_w} \right], \tag{2}$

where $\tau$ and $\beta_w$ are the KWW parameters. Over the range of temperatures considered in this study (28 to 138 °C), $\tau$ was found to decrease monotonically with increasing temperature from values of approximately $4 \times 10^6$ s at 28 °C to $4 \times 10^{-6}$ s at 138 °C. Values of $\beta_w$ exhibited relatively little temperature dependence below $T_g$; a typical $\beta_w$ value is 0.21 at 47 °C. However, above $T_g$, $\beta_w$ increases dramatically with temperature from a value of about 0.24 at 95 °C to 0.51 at 128 °C. The increase in $\beta_w$ with increasing temperature above $T_g$ is indicative of a narrowing of the distribution of relaxation times and demonstrates that the system is not thermorheologically simple, i.e., that time-temperature superposition does not hold strictly over this range in temperature. Similar trends in $\tau$ and $\beta_w$ have been observed previously in PIBMA and PEMA systems doped with 2 wt. % DR115 or 3 wt. % 4-4' dimethylaminonitrostilbene (DANS).14 It is important to note that data of the type shown in Fig. 2, including transient dynamics ranging over as much as 11 decades in time from the $\mu$s time scale onwards, cannot be modeled accurately by a single, bi-, or even triexponential equation, as has often been done in the SHG literature9,19-22 for data taken over a more limited dynamic range in the absence of short-time data. It is also important to note that the electric-field-induced third-order effect to $\chi^{(2)}$ has been accounted for in calculating $\chi^{(2)}_{\text{NO}} [\chi^{(2)}_{\text{NO}} = (\chi^{(2)} - 0.17)/0.83]$. The solid curves are best fits to the KWW equation. The resulting values of $\langle \tau \rangle$ determined using Eq. (3) are shown in Table II. The values of $\langle \tau \rangle$ are in good agreement with those obtained from the decay mode measurements given in Table I. The correspondence in decay and onset mode data is in agreement with the theoretical prediction of Wu37 and experimental results obtained earlier in longer relaxation times.) The values of $\langle \tau \rangle$ vary from $8 \times 10^{-6}$ s at 138 °C to $6 \times 10^9$ s at 28 °C. The 15 order of magnitude change in $\langle \tau \rangle$ over a temperature range of 110 °C is characteristic of the dynamics coupled with the $\alpha$ transition. $\langle \tau \rangle$ is a strongly decreasing function of temperature in the rubbery state, decreasing by 6.7 decades in magnitude in going from $T_g +1$ °C to $T_g +44$ °C. The temperature dependence of $\langle \tau \rangle$ is reduced but nevertheless substantial in the glassy state with $\langle \tau \rangle$ decreasing by more than 6.2 decades in magnitude in going from $T_g -66$ °C to $T_g -3$ °C.

Very similar conclusions about NLO chromophore rotational dynamics can be achieved from poling onset mode measurements. Figure 3 shows the poling onset mode results for the PS+2 wt. % DR1 system for selected temperatures from 95 to 115 °C. Here $\chi^{(2)}_{\text{NO}}$ is the orientation component of $\chi^{(2)}$ normalized to the steady-state value with the field applied; the contribution of the electric-field-induced third-order effect to $\chi^{(2)}$ has been accounted for in calculating $\chi^{(2)}_{\text{NO}} [\chi^{(2)}_{\text{NO}} = (\chi^{(2)} - 0.17)/0.83]$. The solid curves are best fits to the KWW equation. The resulting values of $\langle \tau \rangle$ determined using Eq. (3) are shown in Table II. The values of $\langle \tau \rangle$ are in good agreement with those obtained from the decay mode measurements given in Table I. The correspondence in decay and onset mode data is in agreement with the theoretical prediction of Wu37 and experimental results obtained earlier in
Dielectric relaxation measurements have also been done in the rubbery state for the PS+2 wt. % DR1 system. As PS is dielectrically inactive in comparison with DR1, the dielectric relaxation measurements sense the rotational motion of the chromophore DR1. Since the transient dynamics monitored using SHG and dielectric relaxation are sensitive to \( \langle \cos \theta \rangle \), it is expected that the values of \( \langle \tau \rangle \) obtained from SHG and dielectric relaxation measurements should be similar. Figure 4 shows the dielectric relaxation spectroscopy data taken at 119, 128, and 138 °C plotted as a function of \( f/f_m \), where \( f_m \) is the frequency at which there is a peak in the value of \( \varepsilon'' \), the dielectric loss component. A good overlap of the data in Fig. 4 at those temperatures indicates that the value of \( \beta_w \) is essentially constant over that limited temperature range. The complex permittivity \( \varepsilon^* \) can be expressed as a one-sided Fourier transform or a pure imaginary Laplace transform of the time derivative of the normalized response function \( \varphi(t) \):}

\[
\varepsilon^*(\omega) = \frac{\varepsilon''(\omega) - \varepsilon''(\omega)}{\varepsilon_0 - \varepsilon_m} = \int_0^\infty \left( -\frac{d\varphi(t)}{dt} \right) e^{-i\omega t} \, dt, \tag{4}
\]

where \( \varepsilon''(\omega) = \varepsilon''(\omega) - \varepsilon''(\omega) \), \( \varepsilon_0 \) and \( \varepsilon_m \) are the limiting low- and high-frequency permittivities, respectively, and the response function \( \varphi(t) \) is taken to be the KWW function. The solid curve in Fig. 4 corresponds to a fit using Eq. (4) with \( \beta_w = 0.5 \). This value of \( \beta_w \) is in reasonable agreement with those obtained in the same temperature range by SHG, e.g., \( \beta_w = 0.51 \) at 128 °C from SHG decay data. In order to determine the KWW parameter \( \tau \) for each temperature, it is necessary to know the product \( (2\pi f_m)\tau \). In the case of a single exponential response function, this product is unity; however, for a response function modeled by the KWW equation, it will be a function of \( \beta_w \). In the case of \( \beta_w = 0.5 \), \( (2\pi f_m)\tau = 0.74 \). Given that \( f_m \) is a function of temperature, it is possible to determine \( \tau \) and, using Eq. (3), \( \langle \tau \rangle \).

Figure 5 illustrates the temperature dependence of \( \langle \tau \rangle \) obtained from SHG and dielectric relaxation techniques. Several important points must be noted from these results. First, good agreement is observed between \( \langle \tau \rangle \) values obtained by SHG and dielectric relaxation. This is expected since both techniques are sensitive to the rotational, reorientation dynamics (and \( \langle \cos \theta \rangle \)) of DR1 chromophores. Second, while \( \langle \tau \rangle \) exhibits an apparent Arrhenius temperature dependence below \( T_g \), above \( T_g \) the dynamics are described by a WLF equation (solid curve in Fig. 5):

\[
\log \left( \frac{\langle \tau \rangle}{\langle \tau \rangle_{T_g}} \right) = \frac{-C_1(T - T_g)}{C_2 + T - T_g}, \tag{5}
\]

with \( C_1 = 15 \), \( C_2 = 40 \), and \( \langle \tau \rangle_{T_g} = 200 - 300 \) s. While the WLF equation fits the SHG and dielectric relaxation data very well above \( T_g \), there is significant deviation below \( T_g \), where the experimental values of \( \langle \tau \rangle \) are far below those predicted by the WLF equation. This deviation below \( T_g \) is expected as the WLF equation is valid only for the equilibrium rubbery state; the quenched nonequilibrium glass has a higher free volume and thus relaxation times smaller than those of the theoretical equilibrium state below \( T_g \). Such effects below \( T_g \) have been observed earlier in polymers such as PIBMA and PEMA using SHG, and by others in a variety of polymers using thermally stimulated discharge and dielectric relaxation measurements. The fit to the data above \( T_g \) by the WLF equation implies that the rotational dynamics of the DR1 chromophores are strongly

![FIG. 4. Dielectric relaxation data in PS+2 wt. % DR1. \( \varepsilon''/\varepsilon_m \) is the dielectric loss normalized by the maximum value at the peak. \( f/f_m \) is the frequency normalized by the frequency at which there is a maximum in \( \varepsilon'' \). Solid curves correspond to fits using the KWW equation with \( \beta_w = 0.5 \).](image)

![FIG. 5. Temperature dependence of the average rotational time constant \( \langle \tau \rangle \) above and below \( T_g \) in PS+2 wt. % DR1 from poling onset (O) and decay (D) data, and dielectric relaxation measurements (Δ). Data without error bars have errors equal to or smaller than symbol size. Solid curve corresponds to a fit using the WLF equation.](image)
These results are consistent with what has been previously observed in stress relaxation measurements where physical aging shifts the stress relaxation spectrum to longer times. Coupled to the α transition associated with $T_g$, this is in agreement with what has been observed previously for DR1 chromophores in the PIBMA and PEMA systems.

The temperature dependence of $\langle \tau \rangle$ below $T_g$ can be modeled using an Arrhenius temperature dependence with an activation energy of around 45–50 kcal/mol. The value of the activation energy below $T_g$ has important technological implications in the design of temporally stable, doped second-order NLO polymers. For example, if technological application mandates no more than a 5%–8% loss in $\chi^{(2)}$ over a four-year period, then a device could require $\langle \tau \rangle$ greater than $10^{13}$ s. (This calculation assumes an average value of $\beta_w$ in the glassy region of 0.21, as is typical for the PS samples studied here.) Using an activation energy of 45 kcal/mol, one predicts that this condition will be achieved at $T=--20$ °C or $T_g-114$ °C. If it is required that a second-order NLO device should be temporally stable at around 80 °C, this will mandate use of a polymer with $T_g \approx 200$ °C, assuming similar values of $\beta_w$ and activation energy in the glassy state.

Another way to improve the stability for device application is to physically age the system below $T_g$. When an amorphous polymer is cooled below $T_g$, excess thermodynamic quantities are “frozen” into the system because relaxation times in the glassy state are much longer than in the liquid or rubbery state. Excess quantities such as specific volume or enthalpy will attempt to relax towards equilibrium upon isothermal annealing in a process called physical aging. The loss of specific volume with time results in a decrease in mobility in the system. Figure 6 shows the effect of physically aging the polymer for 0 and 70 h at 81 °C, with the dc field on, before measuring the decay dynamics. Physically aging the system for 70 h at 81 °C results in a shift of the decay dynamics to longer times by 2 decades. These results are consistent with what has been previously observed in stress relaxation measurements where physical aging shifts the stress relaxation spectrum to longer times.

Further details of the effects of physical aging on temporal stability of SHG and rotational reorientation dynamics of NLO chromophores are provided in Ref. 46.

The general conclusions regarding the temperature dependence of $\langle \tau \rangle$ reached in this study for PS+DR1 and for the PIBMA and PEMA systems reported previously in conflict with those reported by Goodson and Wang and Stahelin et al., who studied a poly(methyl methacrylate)+3 wt. % DANS system ($T_g-85$ °C), reported that the temperature dependence of $\tau$ below $T_g$ is in better agreement with data reported by Singer and King who studied PMMA doped with 10 wt. % DR1. In contrast, our apparent Arrhenius temperature dependence below $T_g$ is as evident in our present study (Fig. 2). There may be several reasons for this difference. Most importantly, they did not access any $\chi^{(2)}$ decay data on time scales less than 100–200 s; this would significantly skew the determination of relaxation times as Figs. 1 and 2 clearly illustrate that not far above $T_g$ ($T_g+11$ °C or higher) all or nearly all of the relaxation in DR1 orientation occurs on time scales of 1 s or less while Goodson and Wang report $\tau=27$ s at $T_g+20$ °C.

Stahelin et al., who studied a variety of polymer systems doped or labeled with NLO chromophores, reportedly did not observe an apparent Arrhenius temperature dependence below $T_g$ as is evident in our present study (Fig. 5). There may be several reasons for this difference. Most importantly, they did not access any $\chi^{(2)}$ decay data on time scales less than 100–200 s; this would significantly skew the determination of relaxation times as Figs. 1 and 2 clearly demonstrate that substantial NLO chromophore reorientation can occur on those time scales even at $T_g-66$ °C. Also, they plotted the relaxation time constant $\tau$, obtained from a KWW fit to data obtained over only a several decade time range, instead of $\langle \tau \rangle$ obtained from a KWW fit over up to an 11 to 12 decade time range as done in our experiments. While our data indicate that there is not a substantial temperature dependence of $\beta_w$ in the glassy state of $T_g+2$ wt. % DR1, any dependence in $\beta_w$ which may be present for their systems will result in somewhat different dependencies for $\tau$ and $\langle \tau \rangle$. Finally, they had much higher NLO chromophore content than used in our experiments. Preliminary studies by us on the effects of chromophore content (ranging up to 5 wt. % dopant) and chromophore labeling (done at present to comparably low chromophore content) indicate very similar results to those reported here, once the effects of plasticization or labeling on $T_g$ are taken into account.

In contrast, our apparent Arrhenius dependence below $T_g$ is in better agreement with data reported by Singer and King who studied PMMA doped with 10 wt. % DR1. While isothermal decay mode data were obtained by Singer and King over only a 30 °C temperature range well below $T_g$, which they admitted could make a definitive determination questionable, their results were consistent with Arrhenius behavior. Furthermore, their calculation of the activation energy below $T_g$ can be modeled using an Arrhenius temperature dependence with an activation energy of around 45–50 kcal/mol.
energy from a fit of temperature-ramped electric-field-induced second harmonic generation data was found to be in agreement with that from their isothermal decay data. In the past, dynamics associated with the \( \alpha \) relaxation in PS have been probed at and above \( T_g \) by a variety of techniques such as NMR,\(^{26}\) photon correlation spectroscopy,\(^{26}\) dielectric relaxation,\(^{27,28}\) and viscosity and compliance (mechanical relaxation).\(^{29}\) The main conclusion drawn from these studies is that the relaxation is a strong function of temperature and can be modeled using the WLF equation. A second important conclusion is that the similarity in the relaxation times obtained by these techniques indicates that the relaxation probed by them is associated with the monomeric relaxation time at \( T_g \) of 100 s obtained by NMR measurement.\(^{30}\)

The most recently reported relaxation data, by Pschorn\(^{30}\) et al. using NMR, also found a temperature dependence of \( \beta_\omega \) above \( T_g \), in agreement with our present studies. Pschorn\(^{30}\) et al.\(^{30}\) calculated mean rotational correlation times in neat PS over a temperature \( T/T_g = 0.84 \) to 1.00 which allows excellent comparison with our monomer static \( \langle \tau \rangle \) values ranging from \( T/T_g = 0.89 \) to 1.00. (For the purpose of comparison, the \( T_g \) value for neat PS in Fig. 7 was taken to be 100 °C while a \( T_g \) of 94 °C was used for PS+2 wt. % DR1.) Our \( \langle \tau \rangle / \langle \tau \rangle_{T_g} \) data are in excellent agreement with the ratio of mean correlation time to that at \( T_g \) obtained from NMR.\(^{30}\)

Classic data taken decades earlier on neat PS by mechanical (viscosity and compliance)\(^{29}\) and dielectric measurements\(^{27,28}\) assume that the polymer is thermoreologically simple over the experimental temperature range, i.e., that \( \beta_\omega \) is constant and that time-temperature superposition is strictly valid. In this case, the best comparison between our relaxation results (both SHG and dielectric) and the other data may be made by plotting our values of \( \tau \) rather than \( \langle \tau \rangle \), the latter of which explicitly accounts for a temperature dependence in \( \beta_\omega \). When plotted in Fig. 7, our \( \tau \) values exhibit a somewhat smaller temperature dependence than \( \langle \tau \rangle / \langle \tau \rangle_{T_g} \) and are in very good agreement with the data obtained earlier by others on neat PS by viscosity and compliance measurements (plotted in Ref. 29 as \( a_\tau \) where \( a_\tau \) is the shift factor\(^{34}\) and dielectric relaxation measurements (plotted in Ref. 27 as \( 1/f_m/(1/f_m)_{T_g} \), where \( f_m \) is the frequency where there is a maximum in the dielectric loss factor, \( \varepsilon^\prime \)). It must be noted that \( a_\tau \) as determined in Ref. 29 is equivalent to \( \tau / \tau_{T_g} \), as is \( 1/f_m/(1/f_m)_{T_g} \) from Ref. 27 presuming \( \beta_\omega \) is constant.

\( \langle \tau \rangle / \langle \tau \rangle_{T_g} \) data for neat PS obtained by photon correlation spectroscopy\(^{26}\) are also plotted in Fig. 7. These data appear to be in somewhat better agreement with our \( \tau / \tau_{T_g} \) data (and equivalent data taken by dielectric relaxation, viscosity, and compliance measurements) than with our \( \langle \tau \rangle / \langle \tau \rangle_{T_g} \) data (and equivalent data taken by NMR). As the data in Fig. 7 are very sensitive to the exact value chosen as \( T_g \) and how it is measured, some of the smaller temperature dependence observed in the photon correlation data as compared to our SHG and dielectric relaxation data and the NMR data of Pschorn et al.\(^{30}\) may be due to this effect. For example, according to the WLF equation, the \( \alpha \) relaxation has a relaxation time at \( T_g + 1 \) °C which is approximately one-half that at \( T_g \). Given this strong temperature dependence of \( \tau \) and \( \langle \tau \rangle \) near \( T_g \), our \( \langle \tau \rangle / \langle \tau \rangle_{T_g} \) measured from SHG, 200–300 s, is in excellent agreement with the mean correlation time at \( T_g \) of 100 s obtained by NMR measurement.\(^{30}\) These values are also in agreement with values of the relaxation time at \( T_g \) in polymers obtained for PS by photon correlation spectroscopy\(^{26}\) for a variety of glass-formers by enthalpy relaxation measurements.\(^{48}\)

Various values of WLF parameters are reported in the literature for homopolymer PS based on the data in Fig. 7. The solid and dashed curves in Fig. 7 correspond to fits of the WLF equation using the \( C_1 \) and \( C_2 \) values reported in Ref. 29 for viscosity data, Ref. 30 for NMR data, and those obtained for PS+DR1 in this study. The results using \( C_1 \) and \( C_2 \) values from the SHG measurements compare very well with those from the NMR measurements. An exact determination concerning whether \( C_2 \) is 40 °C (as obtained from SHG data) or 49 °C (from the NMR data) would require dynamics to be monitored over a much wider temperature range as well as a much higher signal-to-noise ratio in the SHG data. The fit to the viscosity data seems to predict higher values of \( a_\tau \) as compared to the NMR or SHG data. As discussed earlier, these differences may be due to the

![FIG. 7. Values of \( \log((\tau)/(\tau)_{T_g}) \) (O) and \( \log(\langle \tau \rangle_{T_g}) \) (*) from both SHG and dielectric relaxation measurements obtained in this study for PS+2 wt. % DR1, scaled using the reduced variable \( T_g/T \). Also included for comparison are data for neat, homopolymer PS: \( \log((\tau)/(\tau)_{T_g}) \) from photon correlation spectroscopy (Ref. 26) (±); \( \log(\langle \tau \rangle_{T_g}) \) from NMR (Ref. 30) (○); \( \log(\langle \tau \rangle) \) from viscosity (Ref. 29) (Δ) and compliance (Ref. 29) (Δ) measurements; and \( \log[(1/f_m)/(1/f_m)_{T_g}] \) from dielectric relaxation (Ref. 27) (×). (See the text for further explanation.) The solid and dashed curves correspond to WLF equations with a fit from the present study: \( C_1=15.6, C_2=40.9 °C \), and \( T_g=100 °C \) (solid curve); fit from Ref. 26: \( C_1=12.7, C_2=47.9 °C \), and \( T_g=100 °C \) (—); fit from Ref. 30: \( C_1=15.9, C_2=49 °C \), and \( T_g=100 °C \) (—–).]
temperature dependence of the distribution of relaxation times (or $\beta$), obtained in SHG and NMR data as compared to the constant distribution obtained from mechanical relaxation data.

Finally, it is important to compare the SHG data from this study to our previous results obtained for 2 wt. % DR1 doped into PIBMA and PEMA.\textsuperscript{15} In our previous study, it was observed that a single master curve describing the temperature dependence of $\langle \tau \rangle$, above and below $T_g$, in both PIBMA and PEMA resulted from scaling the data using the reduced variable $T/T_g$. Such scaling has been used recently by Angell\textsuperscript{16} to compare macroscopic viscosity for glass-forming systems and by Roland and Ngai\textsuperscript{17} to compare $\alpha$-transition dynamics for various molecular weights of PS. Rosslers\textsuperscript{18} has also used a similar scaling approach employing $T/T_g$ where $T_g$ is correlated with $T_g$. We have chosen to draw a comparison using the reduced variable $T_r/T$, where $T_r$ represents the point at which there is a deviation in $\langle \tau \rangle$ from the WLF equation below $T_g$. Figure 8 shows the plot of $\langle \tau \rangle/T_r$ for 2 wt. % DR1 doped into PS, PEMA, and PIBMA. For the PS+DR1 system, $T_r=92^\circ$C, 2 $^\circ$C lower than the $T_g$ measured calorimetrically by differential scanning calorimetry. (This slight deviation between our calorimetrically determined $T_g$ and the temperature at which $\langle \tau \rangle$ is measured is in good agreement with $T_g$ measured by DSC at a heating rate of 10 $^\circ$C/min, meaning that $T_g$ is measured on response times of less than a minute period. Such differences have also been seen in small-molecule translational diffusion measurements\textsuperscript{19} in a variety of polymers, where the translational diffusion coefficients begin to deviate from the WLF equation at temperatures a few degrees below $T_g$.) For PIBMA and PEMA, $T_g$ is, within experimental error, observed to be the calorimetrically determined $T_g$. Figure 8 indicates that there is a good overlap of data obtained from SHG measurements for PS, PIBMA, and PEMA systems below $T_g$. However, while PEMA and PIBMA exhibit the same dynamics above $T_g$, the PS+DR1 system has a much stronger temperature dependence in the rubbery state near $T_g$, suggesting that PS may be a more "fragile" glass former\textsuperscript{20} than the methacrylate based polymers. As a result of the nearly 12 decade time range that can be accessed by this SHG technique, we have demonstrated that the $\alpha$-transition dynamics for diverse polymers may exhibit a very similar temperature dependence below $T_g$ and a very different dependence above $T_g$. Such a demonstration may not be possible with other techniques which access a more limited dynamic time range. The substantial similarities in dynamics below $T_g$ in these diverse polymers may be of technological importance. If the substantial similarity below $T_g$ is general, then it may be useful in predicting which polymer-dye system will be suitable for device application without requiring a significant number of tests.

**IV. SUMMARY**

A new tool for quantitatively investigating polymer dynamics associated with the $\alpha$ relaxation both above and below $T_g$ has been developed involving SHG. By modifying the technique, which monitors rotational reorientation dynamics of NLO chromophores dispersed in the polymer matrix, to allow measurement over up to 11 to 12 decades in time, from $\mu$s to days, it is possible to determine average chromophore rotational, reorientation relaxation times, $\langle \tau \rangle$. By choosing a nonpolar polymer matrix such as PS, similar $\langle \tau \rangle$'s may also be measured by dielectric relaxation. (The transient dynamics measured by both SHG and dielectric relaxation are sensitive to $\langle \cos \theta \rangle$.)

For the PS+2 wt. % DR1 system studied here, ample proof of the coupling of the DR1 rotational reorientation dynamics to the $\alpha$ relaxation in PS is provided by several results. First, above $T_g$, the temperature dependence of $\langle \tau \rangle$ fits well to a WLF equation. Second, excellent correspondence was obtained between the rubbery-state temperature dependence of $\langle \tau \rangle$ (or $\langle \tau \rangle$ determined by SHG and data obtained for $\alpha$-relaxation dynamics in neat PS by NMR,\textsuperscript{21} viscosity, \textsuperscript{22} compliance,\textsuperscript{23} dielectric relaxation,\textsuperscript{24} and photon correlation spectroscopy measurements. Finally, the value of $\langle \tau \rangle$ at $T_g$, about 3 to 5 min, is in good agreement with $\alpha$-relaxation times obtained in neat PS by NMR\textsuperscript{25} and photon correlation spectroscopy\textsuperscript{26} and by enthalpy relaxation\textsuperscript{27} in a variety of glass-formers. In contrast to the WLF dependence of $\langle \tau \rangle$ above $T_g$, below $T_g$ $\langle \tau \rangle$ follows an apparent Arrhenius temperature dependence with an activation energy of about 45-50 kcal/mol. This Arrhenius dependence is important in predicting the conditions for long-term stability of $\chi^{(2)}$, necessary for NLO device application. Physical aging for several days prior to removal of the dc poling field shifts the relaxation to longer times by several decades, enhancing the temporal stability of $\chi^{(2)}$. Scaling the average rotational relaxation time (as $\langle \tau \rangle$) with the reduced variable $T/T_g$ revealed a substantial similarity between the $\alpha$-relaxation dynamics of PS, PIBMA, and PEMA below $T_g$. However, while PEMA and PIBMA also exhibit similar $\alpha$-relaxation...
dynamics above $T_g$, the PS+DR1 system has a stronger temperature dependence. Extensions of these studies to the effects of NLO chromophore size and concentration and covalent attachment of the chromophore to the polymer are underway.

ACKNOWLEDGMENTS

We gratefully acknowledge the Materials Research Center at Northwestern University funded by the National Science Foundation and the receipt of a Terminal Year Cabell Fellowship (A. D.) and a NSF-PYI award (J. M. T.) for supporting this work. We also thank Professor T. O. Mason (Materials Science and Engineering, Northwestern University) for use of the dielectric spectrometer, Mr. Bruce Christensen for helpful discussions and instructions regarding its use, and Mr. Bob Lloyd and Mr. Peter Weiss (Chemistry Electronics Shop, Northwestern University) for their help in building the electronics for our delay-trigger method.


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