ISOTHERMAL RELAXATION OF RUBBED POLYSTYRENE THIN FILMS PROBED WITH OPTICAL BIREFRINGENCE MEASUREMENTS

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Optical birefringence measurements were used to observe the isothermal relaxation of rubbed polystyrene films on silica substrates below the glass transition temperature. The relaxation dynamics were described by the Kohlrausch–Williams–Watts relaxation function with Arrhenius temperature dependence on relaxation time. The isothermal results were in good agreement with results obtained using a 1 K min$^{-1}$ heating rate.

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1. Introduction

Rubbing polymer films lightly with a buffing cloth is known to induce the orientation of polymer chains.1–3 Understanding the orientation and relaxation of rubbed polymer thin films is not only technologically important in the manufacture of liquid crystal displays, but it is also fundamentally important in understanding relaxation of polymer chains at surfaces and in thin films.4 Recently, we have measured the relaxation of birefringence in rubbed polystyrene (PS) films as the films were heated at a constant rate of 1 K min$^{-1}$.5 The dynamics were assumed to follow a Kohlrausch–Williams–Watts (KWW) time dependence and an Arrhenius temperature dependence below the glass transition temperature as seen in Eqs. (1) and (2). In Eq. (1) $\Delta n(t)$ is the birefringence at time $t$, $\tau(T)$ is the relaxation time at temperature $T$, and $\beta$ is the stretch parameter and lies between 0 and 1. In Eq. (2), $\tau(T_0)$ is the relaxation time at a reference temperature $T_0$, $\Delta E$ is the activation energy, and $R$ is the Rydberg gas constant 8.315 J mol$^{-1}$ K$^{-1}$.

$$
\Delta n(t) = \Delta n(0) \exp \left[ -\left( \frac{t}{\tau(T)} \right)^\beta \right], \quad (1)
$$

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\[ \tau(T) = \tau(T_0) \exp \left[ -\frac{\Delta E}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right]. \] (2)

The relaxation parameters determined by fitting the relaxation curves in Ref. 5 were found to be \( \Delta E = -202 \pm 34 \text{ kJ mol}^{-1} \), and \( \beta = 0.38 \pm 0.05 \) which agree well with the literature values measured by isothermal relaxation of \( -188 > \Delta E > -209 \text{ kJ mol}^{-1} \) and \( 0.24 < \beta < 0.4 \).\(^{6-8}\)

More recently, Tsang et al. have performed isothermal and constant heating rate relaxation measurements on rubbed PS films using reflectance difference spectroscopy.\(^9\);\(^10\) They find that their relaxation data at a constant heating rate are similar to those reported in Ref. 5. However, they proposed a double-exponential relaxation equation to model their isothermal relaxation data (measured over a two hour period):

\[ \rho(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + C. \] (3)

In Eq. (3), \( C \) corresponds to the unrelaxed orientation \( \rho(t = \infty) \). From their studies all the parameters in Eq. (3) are a function of temperature. Based on the temperature dependence of \( \tau_1 \) and \( \tau_2 \), they determine activation energies that are almost a factor of ten lower than the values obtained using constant heating rate measurements in Ref. 5. The authors suggested that relaxation process in rubbed PS films correspond to a local relaxation mode that is not related with \( T_g \) of the polymer. It is difficult for us to reconcile the two different conclusions reached based on a constant heating rate\(^5\) of 1 K min\(^{-1}\) and isothermal measurements by Tsang et al.\(^9\);\(^10\)

To understand these differences, we have conducted isothermal birefringence relaxation measurements on rubbed PS films. We found that the isothermal relaxation data can be modeled using a KWW equation and Arhenius temperature dependence below \( T_g \). The parameters obtained from the fits are \( \Delta E = 230 \pm 20 \text{ kJ mol}^{-1} \) and \( \beta = 0.34 \pm 0.16 \) when all parameters are allowed to float or \( \Delta E = 185 \pm 30 \text{ kJ mol}^{-1} \) and \( \beta = 0.31 \pm 0.02 \) if a common \( \beta \) is used for all temperature measurements. This agrees well with our earlier measurements obtained using a 1 K min\(^{-1}\) heating rate.\(^5\)

2. Experimental Details

PS films were created by spin coating PS (\( M_n = 56,000 \text{ g mol}^{-1}, M_w/M_n = 1.06 \), Polymer Source Inc.) solutions 4 wt.% in toluene (Aldrich) onto silica substrates. The films were annealed in vacuum at 380 K for four hours and allowed to cool to room temperature under vacuum. The annealed films were mounted in a programmable hot stage (Mettler FP-82) at about 300 K and then rubbed repeatedly with a velour cloth until their initial retardation (see discussion for definition) saturated at approximately \( 6 \times 10^{-3} \) rad. The oven temperature was then increased to the experiment temperature, requiring at most 30 s to reach the final temperature. Once the experiment temperature was reached, the retardation was measured using
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a birefringence set-up very similar to that described in Ref. 11. Our data collection
scheme involved using two lock-in amplifiers (Princeton EG&G models 5209 and
5210) to determine the light intensity fluctuations at the photodiode (Hinds model
PEM 90) at 1× and 2× the PEM frequency (50.1 kHz). Each data point in Fig. 1
represents approximately 300 measurements of the retardation requiring ∼ 30 s of
time. After collecting data for approximately two hours, the samples were heated to
383 K to completely remove any orientation caused by rubbing. The value of the re-
tardation remaining at 383 K was subtracted and considered to be the background
birefringence caused by the PEM and the silica substrate.

Fig. 1. Normalized retardation relaxation curves at four different temperatures: 313 K (circles),
333 K (squares), 343 K (triangles), 363 K (diamonds). All samples were heated to 383 K after two
hours, as seen by the sharp drop in retardation. The solid lines are fits using a KWW equation
with parameters listed in Table 1.

The thicknesses of the films used in this study were determined from the visible
transmission spectra obtained using an HP 8435 UV-Vis spectrometer. The trans-
mission spectrum contains oscillations with an amplitude of roughly 3%, which can
be fit using the optical properties of PS\textsuperscript{12} and known optical reflectivity equations.\textsuperscript{13}
The thickness was found to be 200 ± 10 nm.

3. Results and Discussion

The birefringence experimental set-up measures the difference in phase between
light polarized parallel and perpendicular to the rubbing direction. This difference
Table 1. Relaxation parameters for floating $\beta$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta n(0) \times 10^{-3}$ rad</th>
<th>$\tau$ (s)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>313</td>
<td>6.11 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>333</td>
<td>5.78 ± 0.11</td>
<td>7.9 ± 26.8</td>
<td>0.40 ± 0.23</td>
</tr>
<tr>
<td>343</td>
<td>4.34 ± 0.55</td>
<td>9.91 ± 0.71</td>
<td>0.19 ± 0.09</td>
</tr>
<tr>
<td>353</td>
<td>5.62 ± 0.11</td>
<td>6.37 ± 0.43</td>
<td>0.34 ± 0.02</td>
</tr>
<tr>
<td>363</td>
<td>5.15 ± 0.69</td>
<td>3.68 ± 2.27</td>
<td>0.22 ± 0.04</td>
</tr>
<tr>
<td>368</td>
<td>4.89 ± 0.12</td>
<td>1.58 ± 0.07</td>
<td>0.62 ± 0.05</td>
</tr>
<tr>
<td>average $\beta$</td>
<td>0.34 ± 0.16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

in phase is called the retardation, $\delta$, and can be related to the film’s birefringence by the following equation:

$$\delta = \int_0^h \frac{2\pi \Delta n(z) dz}{\lambda},$$

where $\Delta n(z)$ is the magnitude of the film birefringence at a depth $z$, $\lambda$ is the wavelength of light used (632.8 nm), and $h$ is the thickness of the film. The birefringence in the film can be directly related to the measured retardation if we assume that the birefringence is uniform to a certain depth. This assumption is supported by the results discussed in Ref. 3. The time evolution of normalized retardation measured at four temperatures, 313, 333, 343 and 363 K can be seen in Fig. 1. The retardation values were baseline subtracted and then normalized to the initial retardation values, $\delta_0$, determined at the start of the experiment ($t = 0$). To determine the magnitude of the baseline subtraction, every sample was heated to 383 K after ~2 hours. This can be seen as the sharp drop in retardation in Fig. 1 after 7200 s. The average value of the retardation after this final heating process was considered the baseline value of retardation. This baseline is at most 1/7 of the total initial retardation and is due to imperfect polarizers and residual birefringence of the PEM and of the substrate. The baseline retardation was found to be invariant with temperature.

The relaxation curves taken at several temperatures were fit using two procedures very similar to the ones used in Ref. 5. In the first procedure, the variables $\tau, \beta$, and $\Delta n(0)$ were allowed to float freely (Table 1). In the second procedure, a common $\beta$ was used for the relaxations at all temperatures and $\tau$ and $\Delta n(0)$ were allowed to float freely (Table 2). $\Delta n(0)$ was used as a fitting parameter because the initial retardation value is never known exactly at high temperatures. We also tried to fit the data using a linearization procedure, plotting $\ln(-\ln(\delta/\delta_0))$ versus $\ln($time$)$ and determining $\beta$ and $\tau$ from the slope and intercept of a linear fit. Parameters obtained by fitting the data in this manner were identical to those obtained by fitting the data directly with Eqs. (1) and (2).

The relaxation data obtained at low temperatures ($T < 353$ K) yields relaxation times ($\tau \sim 10^6 \text{–} 10^7$ s) that are much greater than the time scale of the relaxation...
Table 2. Relaxation parameters with common $\beta$.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta n(0)$ ($10^{-3}$ rad)</th>
<th>$\tau$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>333</td>
<td>$5.83 \pm 0.50$</td>
<td>$(4.54 \pm 3.05) \times 10^7$</td>
</tr>
<tr>
<td>343</td>
<td>$3.89 \pm 0.07$</td>
<td>$(3.89 \pm 0.95) \times 10^5$</td>
</tr>
<tr>
<td>353</td>
<td>$5.73 \pm 0.11$</td>
<td>$(6.63 \pm 0.64) \times 10^4$</td>
</tr>
<tr>
<td>363</td>
<td>$4.17 \pm 0.15$</td>
<td>$(7.87 \pm 0.92) \times 10^3$</td>
</tr>
<tr>
<td>363</td>
<td>$7.39 \pm 0.21$</td>
<td>$(1.49 \pm 0.12) \times 10^4$</td>
</tr>
<tr>
<td>368</td>
<td>$4.25 \pm 0.17$</td>
<td>$(5.05 \pm 0.51) \times 10^3$</td>
</tr>
</tbody>
</table>

$\beta$ 0.31 $\pm$ 0.02

As a further comparison, we performed a constant heating rate experiment where the retardation was measured as a rubbed film was heated from 303 K to 383 K at a rate of 1 K min$^{-1}$. The baseline subtracted and normalized data is shown in Fig. 2. Also included in Fig. 2 is a cooling curve after the initial experiment where the sample was cooled from 383 K to 303 K at a rate of 1 K min$^{-1}$. The cooling curve demonstrates the permanent relaxation of birefringence in the sample as well as the temperature invariance of the baseline. The heating curve was fit using Eqs. (1) and (2). The parameters from the fit allowing all parameters to float were $\Delta E = 199$ kJ mol$^{-1}$, $\beta = 0.34$, and $T_g = 370$ K. If we fix $\beta$ at 0.31 (as in Table 2), we find that $\Delta E = 208$ kJ mol$^{-1}$ and $T_g = 368$ K. These values agree very well with those determined using the isothermal technique.

Finally, we would like to comment on the differences observed in activation energies using a KWW equation, Eq. (1), and Eq. (3) used by Tsang and co-workers.$^{9,10}$ The KWW equation models the relaxation using two parameters, $\tau$ and $\beta$. Also, the use of one KWW equation to model the relaxation data implies that the birefringence will eventually relax to zero with time. The time constant for complete relaxation may be seconds near $T_g$ to days or months at $T_g - 65$ K. This agrees with enthalpy,$^{14}$ mechanical, dielectric,$^{15}$ and optical probe$^{6,16-18}$ measurements in the glassy state. The Vogel–Tamman–Fulcher (VTF) or Williams–Landel–Ferry (WLF) equations are not valid below $T_g$ in a non-equilibrium glassy state, unless in special cases (5–10 K below $T_g$) where the system is cooled very slowly or allowed to relax toward equilibrium.$^{16-18}$ However, even 10 or 20 K below $T_g$, the time to
reach equilibrium could be days or even months. Therefore, the stress and volume relaxation time constants below $T_g$, for the non-equilibrium glassy states, are much lower than that predicted using VTF.\textsuperscript{18}

In comparison, Eq. (3) uses two exponential functions to model the fast relaxation dynamics along with an unrelaxed component, $C$. Based on the Fig. 1 in Ref. 10, we can deduce that at 313 K the unrelaxed term is roughly 75\% of the original anisotropy in comparison to almost 25\% near at 363 K. The use of a parameter $C$ that is a function of temperature and not time determined from a two-hour measurement is incorrect. This could lead to values of $C$ that are temperature dependent and also a function of the experimental time window. Therefore, it is expected that the activation energy obtained from the fast relaxation time constants may show lower activation energies than the relaxation modeled using the KWW equation.

4. Conclusions
The birefringence of rubbed PS films was measured at several temperatures. The relaxation dynamics were found to follow a KWW model with stretched exponential parameter, $\beta = 0.31$ and the relaxation times were found to follow an Arrhenius temperature dependence with an activation energy of $\Delta E = 184 \pm 29$ kJ mol$^{-1}$. In addition, we have demonstrated that useful relaxation parameters can be obtained from a single constant heating rate measurement rather than performing multiple lengthy isothermal measurements.
References
