Relaxation dynamics of rubbed polystyrene thin films

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Abstract. – Optical retardation measurements were used to probe the chain relaxation dynamics in rubbed polystyrene films of varying thicknesses on glass substrates. A model based on Kohlrausch-Williams-Watts relaxation was developed and used to determine the glass transition temperature (T_g) of the films. Results showed reductions of 15–20 K in T_g for thin films of thicknesses comparable to the radius of gyration as well as for cast films rubbed with different strengths. These results provide evidence of a faster relaxation dynamics relative to the polymer-substrate interface for thinner films and enhanced chain mobility at the polymer-air interface.

The surface dynamics of ultra-thin polymer films has been extensively studied in the recent years due to its importance in device applications as well as in fundamental research [1, 2]. The large surface-area–to–volume ratio in the thin film geometry allows one to explore interfacial interactions, confinement effects, and other properties which are different from the bulk polymer. Among these properties, the dependence of the glass transition temperature T_g on the confining dimension is the least understood. It is believed that below T_g, the polymer is hard and glassy and above T_g, it is soft and rubber-like. T_g is intrinsically related to structural relaxation and thus in polymers to the segmental mobility.

In a number of studies, T_g has been measured for polymer films deposited on substrates [3–6] as well as for freely standing films [4]. The results revealed a reduction of T_g for decreasing film thickness in the absence of strong polymer-substrate interactions [3]. For example, experiments using ellipsometry [3] and dielectric measurements [6] of polystyrene (PS) films supported on substrates showed a slight reduction ($< 10\,\mathrm{K}$) of T_g from its bulk value, whereas Brillouin light scattering measurements [4] of free-standing films revealed a large reduction ($70\,\mathrm{K}$) of T_g with decreasing film thickness. Chain mobility measurements performed using scanning force microscopy [7] revealed rubber-like properties at the PS surfaces. Monte Carlo simulations [8] showed a higher mobility at the polymer-air interface due to a reduction in polymer segment density near the surface. These results provide evidence that the reduction of T_g values is caused by the presence of a liquid-like layer at the polymer-air interface and

that chain mobility is therefore higher at the polymer-air interface relative to the bulk. However, near-edge X-ray absorption fine structure results showed negligible differences in surface polymer dynamics to within 10 Å and the first 100 Å indicating the small influence of the surface on the dynamics of the system [9]. On the other hand, X-ray reflectivity measurements of PS films show an increase in the films' T_g as the film thickness decreases [10]. To elucidate these contrasting effects, a systematic study of the relaxation dynamics of polymer thin films is performed.

In this paper, we present a simple method to probe the relaxation dynamics of polystyrene (PS) films on glass substrates using optical retardation measurements. The films were rubbed to orient the chains inducing birefringence (Δn) related to the measured optical phase retardation, $\delta = (2\pi/\lambda)d\Delta n$, where d is the thickness of the film and λ is the wavelength of a monochromatic light. The δ was monitored as the temperature of the film was subsequently raised at a predetermined rate. This allowed us to determine the temperature dependence of the chain mobility at the polymer-air interface. Additionally, we developed a model based on Kohlrausch-Williams-Watts (KWW) relaxation equation [11] to determine the T_g for the PS films using the optical retardation data.

Polymer thin films of PS with $M_w = 48.5 \times 10^3$ and a polydispersity index of 1.03 dissolved in toluene were spin-coated on glass substrates. Film thicknesses were controlled by varying the spin-coating speed and the PS concentration. Prior to spin-coating, glass substrates were cleaned in sulfuric-acid–Nochromix solution, rinsed in deionized water then dried with N_2 gas. The films were allowed to dry under vacuum for 24 hours for complete removal of the solvent. To remove residual birefringence created by the spin-coating process and to remove thermal history, the films were annealed at 105 °C for 5 minutes. Cast films were prepared using an effective zero spin speed followed by drying at 110 °C for 1-2 hours. PS thin films were rubbed gently with a velvet cloth until no further increase in birefringence was observed, whereas the cast films were rubbed in varying strengths.

The thickness of the PS films was determined by X-ray reflectivity (XRR) measurements. XRR was also used to ensure that no dewetting occurred upon annealing and that the rubbing process did not significantly change the film thickness.

Optical retardation measurements were done using an optical set-up [12] with a He-Ne laser, photoelastic modulator (PEM90, Hinds Instruments) and the sample placed between crossed polarizers. Its optic axis was kept at 45° to the axes of the polarizers. The rubbed samples were mounted on a heating stage (Mettler) for programmed heating (1 K/min) and placed between the PEM and analyzer such that the incident laser is normal to the substrate and rubbing direction perpendicular to the optic axes of PEM. The signal from the photodetector placed after the analyzer was fed to a lock-in amplifier (EG & G Princeton Applied Research, model 5210) tuned to 50 kHz signal from PEM.

The relaxation dynamics of glass-forming materials is described by KWW stretched exponential function [11]. Based on this model, the time dependence of birefringence Δn at temperature T of an oriented polymer film can be written as

$$\Delta n(t) = \Delta n_0 \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right], \tag{1}$$

where τ is the average relaxation time, and β is the relaxation exponent which is related to the distribution of relaxation times in the polymer: $\beta = 1$ for a distribution with a single relaxation time and $\beta < 1$ for a distribution with a long tail of short relaxation times.

In a more general form, eq. (1) can be expressed in the form of an integral,

$$\Delta n(t) = \Delta n_0 \exp\left[-\int_0^t \frac{\beta t'^{(\beta-1)}}{\tau^\beta} \mathrm{d}t'\right].$$ (2)

For a variation of Δn relaxation with temperature, which is the case in our study, Δn becomes temperature dependent. The temperature is related to time by $T' = T_0 + \alpha t'$, where T_0 is the initial temperature and α is the heating rate. The temperature-dependent Δn can then be written as an integral from the starting temperature T_0 to the temperature T at which Δn is measured:

$$\Delta n(T) = \Delta n_0 \exp\left[\int_{T_0}^T \frac{\beta(T' - T_0)^{\beta-1}}{(\tau(T')\alpha)^\beta} \mathrm{d}T'\right].$$ (3)

Assuming a simple Arrhenius-type temperature dependence below T_g and a Williams-Landell-Ferry [13] temperature dependence above T_g, the relaxation time is written as

$$\tau(T) = \tau_{T_\mathrm{g}} \exp\left[-\frac{\Delta E}{R}\left(\frac{1}{T} - \frac{1}{T_\mathrm{g}}\right)\right], \qquad T < T_\mathrm{g},$$

$$\tau(T) = \tau_{T_\mathrm{g}} \cdot 10^{\frac{-13.7(T - T_\mathrm{g})}{50 + T - T_\mathrm{g}}}, \qquad T \geq T_\mathrm{g},$$ (4)

where ΔE is the activation energy, R is the Rydberg gas constant and τ_{T_g} represents the relaxation time at T_g. Typically, τ_{T_g} at the α-relaxation can range between 0.5–20 s [14]. In this study, $\tau_{T_\mathrm{g}} = 5\,\mathrm{s}$ was arbitrarily chosen which yields T_g's for cast films ($\sim 370\,\mathrm{K}$) comparable to bulk T_g (370–378 K) of PS determined from DSC.

The T_g's of the films are determined from the fits of eq. (3) and (4) to the relaxation data where the ΔE and β are also set as adjustable parameters. For relaxations of amorphous hydrocarbon polymers below T_g, ΔE and β are typically in the range -190 to $-210\,\mathrm{kJ/mol}$ [13] and 0.24 to 0.40 [13, 15], respectively. This study yields $\Delta E = -207 \pm 34\,\mathrm{kJ/mol}$ and $\beta = 0.38 \pm 0.02$ which lie within the range, affirming the validity of this model.

Films with thickness 58, 125, 150, 280, 480, 540 and 1150 Å were studied. However, for the purpose of clarity, only representative samples are shown. The Δn relaxation curves of the rubbed cast PS film ($10\,\mu\mathrm{m}$) and the thin films with thicknesses $h = 58$ and 480 Å are shown in fig. 1. Fits to eq. (3) and (4) are represented by the three curves. The initial retardation is progressively higher for thicker films because more chains align upon rubbing. On heating, the retardation of the film decreases monotonically to zero at temperatures above T_g. The decrease in the retardation is associated with the (randomization) reorientation of the PS chains. This is demonstrated by the cooling curve for the 480 Å film represented by the filled squares where the retardation remains unchanged (zero) indicating a permanent randomization of the PS chains after complete relaxation. The difference in the relaxation dynamics of different films is manifested in the temperature at which the films are completely relaxed, $T = 360\,\mathrm{K}$ and $T = 385\,\mathrm{K}$ for the 58 Å and the cast film, respectively. This relaxation behaviour is indicative of enhanced chain mobility in thinner films which results in a reduction of T_g. The film thickness limit up to which the optical retardation technique is valid is $h \cong 58$ Å which is about the size of the radius of gyration, R_g of the polymer used in this study ($R_\mathrm{g} = 56$ Å). For $h < 58$ Å, dewetting occurred during the heating cycle.

From the fits to the model discussed above, T_g's of the thin films are determined and are shown in the inset of fig. 1 as a function of thickness. The T_g of the cast and the 300 Å films are close to the $T_\mathrm{g}^{\mathrm{bulk}}$ and it drops by 15–20 K as the film thickness approaches 58 Å. The two points at 300 Å are two different samples rubbed to different extent with the lower
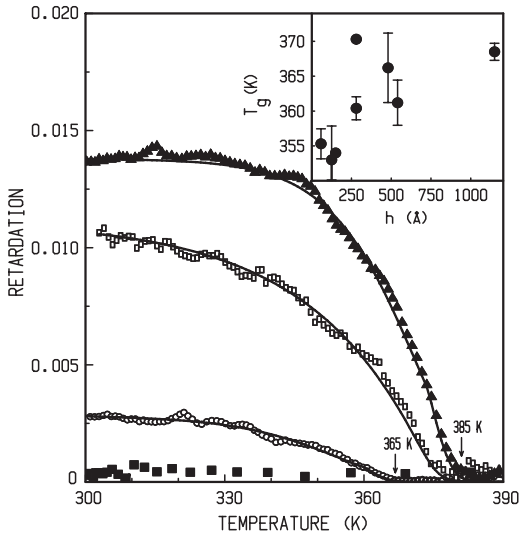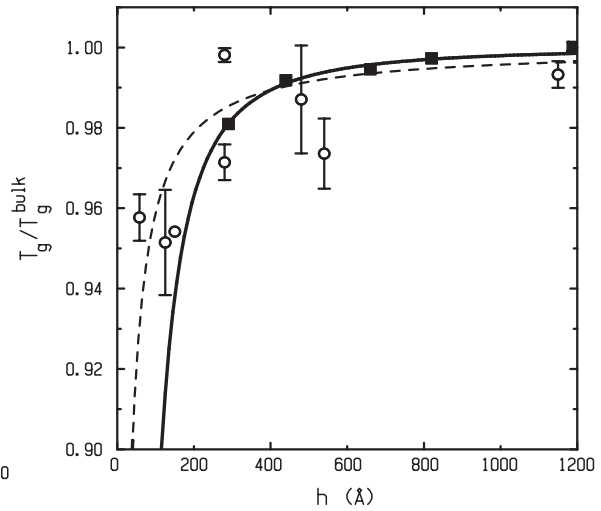
Fig. 1

Fig. 2

Fig. 1 – Optical retardation curves as a function of temperature for ▲ cast, □ 480 Å, ○ 58 Å and ■ cooling curve of the 480 Å film. Experimental data of other films used in the study are omitted for clarity. Fits to eq. (3) are shown for all data sets. The inset shows the T_g as a function of thickness, h. The size of the symbol exceeds the error bars for some data points.

Fig. 2 – Comparison of T_g/T_g^{bulk} as a function of film thickness, h with previous studies on similar systems: ○ this study, ■ Forrest *et al.* [4], — Keddie *et al.* [3], and - - - Fukao *et al.* [6]. Symbol size exceeds the error bars for some data points.

point representing the lightly rubbed one. This indicates a strong influence of the rubbing process on the relaxation dynamics due to the penetration depth of rubbing. A comparison of our results with previous studies [3, 4, 6] is illustrated in fig. 2. The values agree well for $h > 250$ Å below which, significant deviations begin to occur. These results suggest that T_g of polymer films is not significantly affected (to within $< 2\%$) until the film thickness falls below ~ 200–300 Å.

The relaxation data of the cast film rubbed with different rubbing strengths as well as the fits to the curves are shown in fig. 3. It is evident that the initial retardation becomes progressively higher with rubbing strength, which is expected since stronger rubbing causes more PS chains to align. Also, the rate of relaxation is found to be faster for the lightly rubbed films from the results of fits and is more evident if the data were normalized and then plotted. This is an indication that the molecules at the polymer-air interface are more mobile than the interior molecules. Although it can be argued that by increasing the rubbing strength, the molecules become highly extended with nonlinear relaxation times resulting in a faster relaxation, quantitative analysis of the relaxation curves in our study proves otherwise. T_g's of the cast film rubbed to different degrees were determined from the fits to the relaxation curves and shown in the inset of fig. 3. On the horizontal axis is the initial retardation related to the effective rubbing depth (Δnd_{eff}) which is proportional to the rubbing strength [16]. Results show that T_g increases with rubbing depth. This essentially means that molecules closer to the PS-air interface relax faster than the molecules farther from the PS-air interface. The similarity of the T_g drop between the effects of film thickness and effects of d_{eff} suggests that
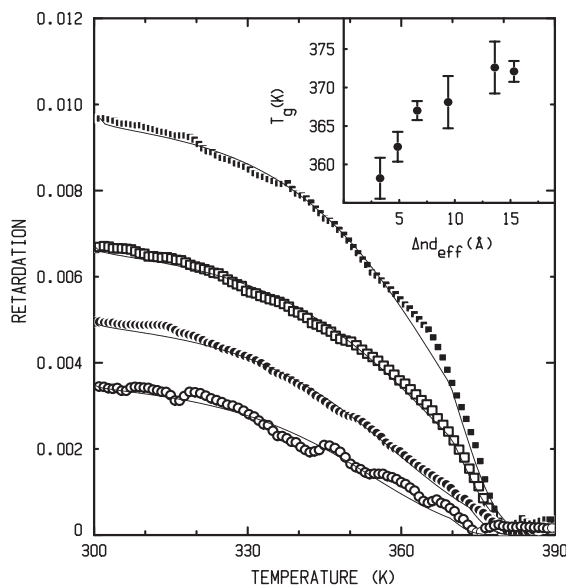
Fig. 3 – Relaxation curves as a function of temperature of the cast film rubbed in varying degrees: ○3×, ●6×, □9× and ■12×. Fits to eq. (3) are shown for all data sets. The inset shows T_g as a function of rubbing depth, $\Delta nd_{\rm eff}$.

the mobility at the polymer-air interface influences the dynamics more than the PS-substrate interface.

We have introduced a simple technique to probe polymer relaxation in ultra-thin films. The relaxation of the rubbed PS films in different thickness films supported on glass substrates has provided significant evidence for faster relaxations in thinner films. Also, we have measured the glass transition temperature T_g of polystyrene (PS) films as a function of thickness as well as of the rubbing (strengths) depth using the relaxation model based on KWW. T_g reductions of 15–20 K for films of thickness less than 250 Å correlate very well with previous results on similar systems [3, 4, 6]. The dependence of T_g on rubbing depth provides the evidence that chain mobility is enhanced at the polymer-air interface relative to the polymer-substrate interface and is undoubtedly responsible for the reductions in T_g of thin films.

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