Residual Stress Relaxation and Stiffness in Spin-Coated Polymer Films: Characterization by Ellipsometry and Fluorescence

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Abstract: Ellipsometry and fluorescence are used via measurements of film thickness and pyrenyl dye emission spectral shape, respectively, to characterize residual stress relaxation in polystyrene (PS) films. In particular, fluorescence of pyrene-labeled PS (MPy-PS) films, with ~1 mol% pyrene label, provide sensitivity to film stress relaxation and stiffness by the dependence of the ratio of the first to third vibronic peak intensities (I_1/I_3) of the pyrenyl dye to nanosecond-time-scale molecular caging. Both techniques show that residual stress relaxation occurs over a period of hours despite the PS films being 15 – 40 °C above the film glass transition temperature (T_g). Both techniques also show that film T_g is unaffected by stress relaxation, even when stress relaxation is accompanied by measurable changes in thickness. Fluorescence shows that stress relaxation time follows an Arrhenius temperature dependence with an activation energy of ~110 kJ/mol, which is consistent with stress relaxation occurring by β -relaxation. Using a bilayer/fluorescence technique with bulk bilayer films, it was observed by I_1/I_3 measurements that a 30-nm-thick MPy-PS layer located at a glass substrate interface is stiffer than a 30-nm-thick MPy-PS layer located at a free surface. Over a 20 to 400 nm thickness range, fluorescence of MPy-PS films show a significant effect of substrate on molecular caging and hence stiffness, with stiffness increasing in the following order: free-standing films (no substrate) < films supported on a PDMS (soft) substrate < films supported on a glass (hard) substrate.

1. Introduction

Residual stresses in polymer films are a function of processing method, e.g., spin-coating resulting in non-equilibrium local chain conformations, and of thermal history, e.g., heating or cooling which leads to stresses arising from different thermal expansion coefficients of the film and its substrate.¹⁻¹² Residual stresses remain in the films until sufficient thermal annealing is done to relax the stresses. Unrelaxed residual stresses in thin polymer films have been observed to induce crack formation,¹³ delamination from substrates,¹³ and dewetting,^{14,15} all of which are critical considerations for the fabrication of nanoconfined polymeric devices.

Approaches to characterize residual stresses include the curvature method,^{16,17} cylindrical punch,¹⁸ blister method,¹⁹ surface wrinkling,¹¹ cantilever bending method,²⁰ dewetting,²¹⁻²⁵ and intrinsic excimer fluorescence.¹⁰ With curvature measurements, sensitivity to residual stresses decreases for ultrathin films since it is difficult to resolve small changes in curvature.^{11,26} Contact methods that perturb polymer chains such as cylindrical punch, blister, and cantilever bending techniques involve imparting external stresses on polymer samples which may convolute stress relaxation measurements.¹¹ Optical methods may be used to avoid such issues arising from contact methods. Nearly ten years ago, we demonstrated that intrinsic excimer fluorescence of styrene-containing polymer systems could be used to sense stress relaxation via small changes in local chain conformation that lead to changes in the ratio of excimer to monomer fluorescence.¹⁰ However, this approach is limited to polymers and copolymers that contain sufficient levels of styrene-styrene dyads along a chain to exhibit substantial excimer fluorescence.

Here, we demonstrate that non-contact, non-destructive optical methods involving ellipsometry and a self-referencing fluorescence method, which exhibits sensitivity of the shape of the pyrenyl dye fluorescence emission spectrum to local molecular caging (see Section 2 below), can be used to monitor and characterize residual stress relaxation in polymer films. Ellipsometry provides sensitivity to residual stress relaxation via time- and temperature-dependent changes in thickness of films that have been spin-coated onto Si/SiO_x substrates and subjected to a variety of thermal history conditions. As shown below, depending on thermal

history and measurement temperature, stress relaxation in polystyrene (PS) films may be accompanied by small but measurable decreases or increases in thickness, with residual stress relaxation characterized by ellipsometry occurring over periods of hours in the rubbery state. With fluorescence, we monitor the time- and temperature-dependent changes in an intensity ratio associated the emission spectrum of pyrenyl dyes covalently attached at trace levels to the polymer. Previous studies have used the temperature dependence of such an intensity ratio to characterize the glass transition temperature (T_g) of homopolymers, as supported and free-standing thin and ultrathin films, and polymer blends.²⁷⁻³² With the present study, we extend this approach to characterize stress relaxation and to provide sensitivity to stiffness in thin films. In agreement with ellipsometry measurements, fluorescence shows that residual stress relaxation occurs over periods of hours in the rubbery state and that stress relaxation has no effect on film T_g . Fluorescence characterization also provides evidence that the mechanism underlying stress relaxation is β -relaxation and that ultrathin, free surface layers of bulk films are less stiff than ultrathin substrate layers. With 20- to 400-nm-thick PS films, fluorescence characterization at 60 °C indicates that film stiffness is a significant function of the substrate character, with stiffness increasing as follows: free-standing (no substrate) films < films supported on a very soft polymer substrate < films supported on a rigid glass substrate.

2. Rationale for Using the Spectral Shape of Pyrene Emission Fluorescence to Characterize Polymer Stress Relaxation and Stiffness

Stiffness or modulus can be related to short time scale (~nanosecond) vibrations or mobility in materials.³⁷ Experimental connections have been drawn between dynamics associated with the boson peak and mean-squared displacement (MSD), $\langle u^2 \rangle$, and polymer modulus. The boson peak is associated with collective vibrational modes with frequencies in excess of what is predicted by the Debye model of acoustic modes.³⁸ Soles et al.³⁸ used Brillouin light scattering to demonstrate that the boson peak energy correlates with the velocity of acoustic waves traveling through polymer. In turn, the velocity of acoustic waves is proportional to the square root of bulk

modulus.³⁷ In addition to the boson peak, vibrational dynamics associated with the MSD have been correlated with polymer modulus via incoherent neutron scattering (INS).³⁸⁻⁴⁰ At sufficiently low temperature, the MSD is inversely proportional to the harmonic force constant^{38,39} or spring constant⁴⁰. Inoue et al. state that the force constant in PS films corresponds to “those for torsion of the C-C bond in the main chain and/or the force constant for the interaction potential between nonbonded atoms.”⁴⁰ The force or spring constants scale roughly with polymer modulus, and INS experiments find that supported polymer films stiffen upon confinement.³⁸⁻⁴⁰ Similar conclusions have recently been reached using atomistically informed coarse-grained molecular dynamics simulation.^{42,43}

Mean-squared displacement effects can be rationalized via a “caging” mechanism. Decreases in MSD (increases in harmonic force constant) correspond to environments in which atoms are “caged” and trapped in deep potential energy minima.³⁹ In a stiff or caged environment, vibrations associated with MSD are suppressed. Similarly, in stressed environments, atoms are trapped in potential energy minima. Stress relaxation decreases the force constant as atoms are less trapped in potential energy minima, or less caged.

The caging mechanism underlies the sensitivity of the spectral shape of pyrenyl dye fluorescence to stress relaxation and stiffness. The time scale associated with fluorescence, from absorption to emission, is some nanoseconds,⁴⁴ similar to the time scale associated with MSD measurements. Furthermore, the ability to use fluorescence to characterize the Debye-Waller factor (related to MSD) as a surrogate to INS experiments, as done by Cicerone et al.,⁴⁵ suggests that the caging mechanism is common to both INS and selective fluorescence studies. We exploit the sensitivity of pyrene fluorescence spectral shape to caging to characterize stress relaxation and stiffness in pyrene dye-labeled PS films. We find that as stresses relax, or as stiffness decreases, reduced caging results in corresponding changes in the pyrene fluorescence emission spectrum. Specifically, the ratio the fluorescence intensity of the first and third vibronic band peaks, I_1/I_3 , decreases as caging decreases and thus as stress is relaxed in the polymer sample.

Experimental support for the caging mechanism comes from the sensitivity of pyrene

fluorescence spectral shape to local solvent polarity. Originally reported by Kalyanasundaram and Thomas,⁴⁶ the sensitivity was attributed to an induced dipole-dipole coupling mechanism between pyrene and surrounding solvent molecules. In the ground state, pyrene electrons are symmetrically distributed. However, upon excitation by UV light, the electrons become asymmetric in distribution, which induces a dipole moment in pyrene. Depending on solvent polarity, solvent molecules re-orient and cage the excited-state pyrene molecules. In a high-polarity solvent, this caging is stronger and suppresses non-radiative forms of energy decay and enhancements of high-energy transitions of electrons from the excited state to the ground state. With pyrene fluorescence, the intensity of the first vibronic band peak, I_1 , is associated with high-energy transitions to the ground state and the intensity of the third vibronic band peak, I_3 , is associated with low-energy transitions. The ratio I_1/I_3 increases with increasing solvent polarity due to greater caging that suppresses non-radiative pathways of energy decay.^{46,47} The changes in I_1/I_3 with stress relaxation or stiffness are qualitatively consistent with the I_1/I_3 dependence on solvent polarity,^{46,47} which indicates that caging is the underlying mechanism for the sensitivity of fluorescence emission spectral shape of pyrene to its local environment.

3. Experimental Section

3.1 Materials

Polystyrene (Pressure Chemical, made by anionic polymerization) with number-average molecular weight (M_n) of 160 kg/mol and dispersity = 1.06 was used as received. Using azobisisobutyronitrile (Aldrich, under the name 2,2'-azobis(2-methylproprionitrile)) as initiator, 1-pyrenylmethyl methacrylate (MPy) (Toronto Research Chemicals) was copolymerized at very low levels with styrene (SigmaAldrich) at 70 °C via bulk free radical polymerization to yield two MPy-labeled polystyrene (MPy-PS) samples. The MPy-PS samples were washed by dissolving in toluene and precipitating in methanol seven times to remove any residual MPy or styrene monomer and were placed in a vacuum oven at 105 °C for 3 days prior to use. As determined by gel permeation chromatography (Waters 2410, calibrated with PS standards in tetrahydrofuran,

refractive index detector), the two washed MPy-PS samples had M_n values of 200 and 800 kg/mol, each with a dispersity of 1.3. As determined by UV-Vis absorbance spectroscopy (Perkin Elmer Lambda 35) following the approach of Gebert and Torkelson,⁴⁸ the 200 and 800 kg/mol MPy-PS samples contained 1.2 and 1.1 mol% MPy as fluorescence label. Bulk T_g s were determined by differential scanning calorimetry (Mettler Toledo DSC822e, second-heat T_g onset method at 10 °C/min heating rate): T_g s were 100 °C for 160 kg/mol PS, 101 °C for 200 kg/mol MPy-PS, and 103 °C for 800 kg/mol MPy-PS.

3.2 Spin-Coated Films

Films of PS or MPy-PS were spin-coated onto glass slides from toluene (SigmaAldrich) solutions containing 0.5 to 7.0 wt% polymer with spin speeds ranging from 1500 to 3000 rpm. Glass slides were thoroughly cleaned by etching in 1.0 M hydrochloric acid, rinsed with water, and dried prior to submerging in base solution (10 wt% sodium hydroxide/20 wt% water/70 wt% ethanol). Substrates were then rinsed with water and dried prior to use. With multilayer films, samples were spun onto freshly cleaved mica and annealed under vacuum at $T_{g,bulk} + 20$ °C for 2 h. (As shown in detail in ref. 49, no residual solvent remains in PS films made by spin coating from toluene solution.) After annealing, mica-supported films were transferred at room temperature onto glass-substrate supported films by a water transfer technique.³⁶ Residual water evaporated overnight under ambient conditions prior to annealing the multilayer film in the vacuum oven at 120 °C for 3 h before fluorescence measurement. These annealing conditions were chosen to ensure that the multiple layers welded into a consolidated film but did not allow for substantial interdiffusion between layers.^{29,34} Polydimethylsiloxane (PDMS) substrates were prepared from Dow Corning Sylgaard 184 at a base to catalyst ratio of 10:1 and cured at ambient conditions overnight prior to heating in an oven at 100 °C. Thin MPy-PS layers were floated off mica and placed onto PDMS substrates prior to measurement. For free-standing films, MPy-PS films were floated onto nylon washers^{27,29} after 120 °C annealing for 2 h before floating.

3.3 Ellipsometry

Spectroscopic ellipsometry (J. A. Woollam Co. M-2000D over a range of wavelengths

from 400 to 1000 nm) was used to measure ellipsometric angles (ψ and Δ) of incident light reflected off silica-supported PS or MPy-PS films. Using a Cauchy layer model, ellipsometric angles were fitted to determine film thickness. The Cauchy layer model included a PS layer atop a silicon substrate containing a 2-nm-thick silicon oxide surface layer. Thickness values were determined by fitting ψ and Δ to the PS layer in the model. To determine thickness of films or layers used in fluorescence studies, PS and MPy-PS films were spin-coated at the same time from the same solutions with the same spin speeds onto silicon slides with a native silicon oxide surface layer and measured via ellipsometry. Thicknesses were determined at room temperature.

To investigate the relaxation of residual stresses in bulk-like PS films by ellipsometry, the thickness of two 800-nm-thick PS films was monitored during 300 min of isothermal annealing at $T_{g,bulk} + 40$ °C. Prior to annealing at $T_{g,bulk} + 40$ °C, one film was placed in a vacuum oven overnight at 60 °C and the other at 110 °C. Following that, the films were placed on a pre-heated Instec heating element at $T_{g,bulk} + 40$ °C (sample transfer time of ~30 s) for time-resolved thickness measurements. To reduce the noise associated with measuring thickness, reported thickness values are the averages of seven data points taken over a period of 2 min.

Ellipsometry was also used to measure T_g before and after annealing at $T_{g,bulk} + 40$ °C. Once spin-coated, a bulk-like PS film was annealed overnight in a vacuum oven at 60 °C. The film was then placed on a heater pre-heated to 140 °C for 5 min prior to monitoring thickness during cooling from 140 to 60 °C at a rate of 1 °C /min. After the first cooling cycle, the sample was re-heated to 140 °C to monitor the change in isothermal thickness over 1 h as residual stresses relaxed. The thickness response to cooling at a rate of 1 °C /min was then monitored during a second cooling cycle using the same film. The T_g was determined by the intersection of lines fitted to the temperature-dependent rubbery and glassy thickness responses.³³

3.4 Fluorescence Spectroscopy

Fluorescence was used to measure T_g and characterize residual stress relaxation of MPy-PS films. After spin-coating and annealing films overnight at 60 °C under vacuum, emission spectra were collected (Photon Technology International fluorimeter in front-face geometry) at

wavelengths from 370 to 405 nm (0.5 nm increment, 1 s integration), with excitation at 324 nm. Excitation and emission slit widths were 0.5 nm (1 nm bandpass). Spectra were used to determine the ratio of the first vibronic band peak intensity to the third vibronic band peak intensity (I_1/I_3) of the pyrene-labeled polymer. Peak intensities were calculated from an average of five data points spanning a 2 nm window: I_1 was an average of five points between 376 to 378 nm and I_3 an average of five data points between 387 to 389 nm.⁵⁰

Fluorescence was also used to characterize the effect of spin speed on I_1/I_3 . MPy-PS films were spin coated from toluene solution containing 4 to 6 wt% polymer and spin speeds of 1500 to 3000 rpm. The four 680-nm-thick films were annealed overnight in a vacuum oven at 60 °C and then placed on a heater to collect emission spectra at 25, 60, and 120 °C.

To characterize residual stress relaxation, bulk MPy-PS films (annealed under vacuum at 60 °C overnight) were placed on a heater pre-heated to anneal temperatures ranging from 110 to 140 °C (sample transfer time of ~1 min). Samples were held isothermally at the respective annealing temperatures for 12 h with spectra collected every 1 h.⁵⁰

To determine T_g via fluorescence, a 650-nm-thick single-layer PS film (annealed at 60 °C for 12 h under vacuum) was placed on an Instec heater pre-heated to 140 °C and held for 10 min. Emission spectra were collected upon cooling from 140 to 60 °C in 5 °C decrements. Before spectral measurement, the sample was held for 5 min to ensure equilibration to the temperature of the heating element. After the first cooling cycle, the sample was re-heated to 140 °C and held for 1 h to relax residual stresses. The cooling cycle was then repeated to collect emission spectra a second time. The T_g was determined by the intersection of lines fit to the temperature-dependent rubbery and glassy responses of I_1/I_3 .^{27,29}

An investigation of T_g and stiffness on bilayer films and a single 30-nm-thick MPy-PS film supported on glass was conducted in a different manner. Prior to fluorescence measurements, films were annealed under vacuum at 120 °C for 3 h to weld the layers while avoiding significant interdiffusion of polymer between layers.^{29,34} After annealing, films were placed on the Instec heater pre-heated to 140 °C for 10 min prior to cooling from 140 to 60 °C in

5 °C decrements and were cooled through one or two cooling cycles. Fluorescence measurements needed to address the effects of confinement on T_g and I_1/I_3 values in MPy-PS films supported on glass or on cross-linked PDMS or as free-standing films were done in a manner similar to that for the 30-nm-thick MPy-PS film but using only a single cooling cycle.

4. Results and Discussion

This section is divided into three parts. The first describes ellipsometry measurements of thickness to characterize residual stress relaxation in bulk PS films under various thermal history conditions and a study on whether stress relaxation affects the film T_g . The second describes a fluorescence study that characterizes stress relaxation in bulk, dye-labeled PS films under similar thermal history conditions as those in the ellipsometry study and a proof-of-concept experiment demonstrating the sensitivity of fluorescence to stiffness in PS films. The third involves using fluorescence to compare T_g - and stiffness-confinement effects in MPy-PS as films supported on glass and cross-linked PDMS substrates and as free-standing films.

4.1 Ellipsometry Characterization of Residual Stress Relaxation in Supported PS Films

Spectroscopic ellipsometry was used to determine the effect, if any, of residual stress relaxation on thickness in rubbery-state bulk PS films ($M_n = 160$ kg/mol). Prior to measurement, two 800-nm-thick PS films were annealed under vacuum at 60 or 110 °C for 12 h. After annealing, each film was placed on a heater pre-heated to 140 °C ($T_g + 40$ °C) and held isothermally for 300 min as thickness was characterized via ellipsometry. Figure 1 shows that the thicknesses for the two PS films decrease by slightly less or slightly more than 2 parts per 10000 over the 300 min of heating isothermally at 140 °C. Since residual toluene is not present in spin-cast PS films made from toluene solutions,⁴⁹ the decrease in thickness is not related to solvent loss upon exposure to elevated temperature (T) but instead is related to residual stress relaxation. The thickness of the film annealed overnight at 60 °C prior to ellipsometry measurements decreased more than that of the film annealed overnight at 110 °C.

This difference in the thickness decrease during isothermal heating at 140 °C can be

Figure 1: Normalized thickness of two 800-nm-thick PS films as a function of anneal time at 140 °C. Prior to annealing at 140 °C, one film was annealed at 110 °C for 12 h under vacuum (closed circles) and the other at 60 °C (open squares). Thickness was monitored isothermally at 140 °C for 300 min for both films. Each data point represents the average of seven thickness measurements collected over a period of 2 min to smooth the data.

attributed to two factors. First, prior to ellipsometry measurement, the film annealed for 12 h at 110 °C underwent greater stress relaxation than the film annealed for 12 h at 60 °C. Second, the film annealed at 60 °C prior to thickness measurements at 140 °C was subjected to a greater step change in T (+ 80 °C) compared to the film annealed at 110 °C (+ 30 °C). The larger step change in T associated with the film annealed at 60 °C likely imparted greater thermal stresses on that film (the film is supported on silica, which has a much smaller thermal expansion coefficient than rubbery-state polymer). The relaxation of the additional stresses is manifested as larger thickness changes during the subsequent isothermal heating of the film at 140 °C. Figure 1 shows that bulk PS films with these thermal histories are not in equilibrium as determined via thickness (or, equivalently, specific volume) measurements even though they are at $T_g + 40$ °C and that residual stress relaxation at $T_g + 40$ °C occurs over a period of hours.

Ellipsometry was also used to investigate whether the presence of residual stresses perturbs T_g in bulk, spin-coated PS ($M_n = 160$ kg/mol) films. Thermal expansivity is greater above T_g than below T_g , and T_g can be determined by the intersection of lines fitted through the

rubbery and glassy T -dependences of thickness. Figure 2 shows the thickness of a PS film (annealed 12 h under vacuum at 60 °C prior to ellipsometry) upon cooling from 140 to 60 °C at a rate of 1 °C/min (closed squares); these data yield $T_g = 101$ °C.

Figure 2: Thickness measurements as a function of temperature of a bulk PS film on cooling from 140 °C to 60 °C at a rate of 1 °C/min. Prior to ellipsometry measurements, the film was spin-coated and annealed under vacuum at 60 °C for 12 h and placed on a heater pre-heated to 140 °C. Closed squares show the thickness during the first cooling cycle. After completion, the sample was re-heated to 140 °C and annealed for 1 h. Open squares show the thickness measurements during the second cooling cycle. Inset shows data over a 4 °C temperature range to demonstrate thickness increase after isothermal annealing at 140 °C. A T_g of 101 °C was determined by the intersection of the lines fitted through the rubbery and glassy responses of thickness to temperature.

After the first cooling cycle, the film was heated rapidly from 60 to 140 °C and held for 1 h annealing time at 140 °C prior to measuring T_g during a second cooling cycle (open squares). As shown in Fig. 3, the thickness increased by ~ 0.15 nm during the annealing for 1 h (data from 10 to 60 min) at 140 °C during which time some stress relaxation occurs. Thus, relaxation of residual stress in bulk, supported PS films can result in either a thickness decrease (Fig. 1) or a thickness increase (Fig. 3) depending on thermal history. (The complex thermal history for the film in Fig. 3 likely introduced additional thermal stresses from thermal expansivity mismatches between the film and substrate.⁵¹) In spite of the slightly greater thickness of the film during the second cooling cycle as compared to the first cooling cycle, as shown in Fig. 2 the film T_g measured from the second cooling was 101 °C, identical to that from the first cycle. This result is

Figure 3: Ellipsometry measurements of thickness as a function of anneal time (1 h) at 140 °C for the same film used in Figure 2. Upon completion of the first cooling cycle (from 140 °C to 60 °C at 1 °C/min), the sample was re-heated to 140 °C, and thickness was monitored as a function of isothermal annealing at 140 °C. Each black square represents the average of seven thickness measurements collected over a period of 2 min. A best-fit line demonstrates that the thickness increases with increasing anneal time at 140 °C.

consistent with neutron reflectivity studies of film thickness by Kanaya et al.,⁵² who concluded that the T_g of a polymer film measured upon cooling from the rubbery state is independent of thermal history. Since T_g was the same before and after annealing for 1 h at 140 °C, which relaxes residual stresses, residual stress relaxation does not alter the T_g of spin-coated polymer films even though the specific volume of the films may be affected by the relaxation.

4.2 Novel Fluorescence Characterization of Residual Stress Relaxation in Supported PS Films

Fluorescence measurements were done using PS ($M_n = 200$ kg/mol) containing 1.2 mol% MPy as comonomer in order to characterize residual stress relaxation for PS films supported on glass. The fluorescence technique involves interpreting changes in the shape of the pyrenyl dye fluorescence emission spectrum in response to local changes in molecular caging, which is related to polymer stiffness (see Section 2).

Figure 4 compares emission spectra for a 680-nm-thick film of PS ($M_n = 160$ kg/mol) doped with 0.2 wt% pyrene as free dye (Fig. 4A) and a 650-nm-thick film of MPy-PS ($M_n = 200$

Figure 4: A: Fluorescence spectrum of a 680-nm-thick PS film doped with 0.2 wt. % pyrene at 60 °C. After spin coating, fluorescence emission spectra were collected after 2 h anneal time in a vacuum oven at 60 °C. Arrows indicate locations of the first through fifth vibronic band peak intensities ($I_1 \rightarrow I_5$). B: Typical fluorescence spectrum of a 650-nm-thick MPy-PS film at 60 °C. Arrows indicate locations of the first and third vibronic band peak intensities in B. (Note: The abscissas are different in the two figures. Background noise was subtracted.)

kg/mol) (Fig. 4B) at 60 °C. In Fig. 4A, arrows point to peaks corresponding to the first through fifth vibronic band intensities for the pyrene emission spectrum. Figure 4B shows that upon covalent attachment of pyrenyl dye to PS in MPy-PS, the emission spectrum changes such that only the first and third vibronic band peak intensities I_1 and I_3 are distinguishable, whereas the second vibronic band is nearly invisible and the fourth and fifth bands merge. Covalent attachment of pyrenyl dye to PS also shifts peak wavelengths by a few nanometers.⁵³ Changes in the intensity ratio of the first vibronic band peak to the third vibronic band peak, I_1/I_3 , were used to characterize the stress state of films as described in Section 2 above. I_1/I_3 is expected to increase in a more caged environment, such as one in which stress or stiffness is elevated.

As shown in Fig. 5, the spin speed used in preparing spin-coated PS films was varied to study its effect on I_1/I_3 . 680-nm-thick MPy-PS films were spin-coated from 4 to 6 wt% solutions in toluene onto glass slides at spin speeds from 1500 to 3000 rpm. (This range of spin speeds

Figure 5: Intensity ratio as a function of spin speed for 680-nm-thick MPy-PS films prepared by spin-coating 4-6 wt% solutions of PS in toluene. Prior to fluorescence measurements, films were annealed at 60 °C for 12 h. Intensity ratios were acquired at 25 °C (triangles), 60 °C (circles), and 120 °C (squares). (Background noise was subtracted.)

matched that used to make all films in this study.) After spin-coating, films were annealed for 12 h at 60 °C under vacuum and were then placed on a heater pre-heated to 25, 60, or 120 °C to collect emission spectra. Within experimental error, the results from Fig. 5 indicate that the spin speed in the range of 1500 to 3000 rpm does not affect I_1/I_3 values for bulk MPy-PS films over a wide range of T above and below T_g . This result implies that, as measured by fluorescence, the stress state of the films is independent of spin speed over the range studied.

The effect of isothermal heating on stress relaxation of bulk MPy-PS films was also studied by fluorescence. Figure 6 shows the evolution of I_1/I_3 over 12 h of isothermal heating over a T range of 110 to 140 °C. Prior to high- T heating, the 680-nm-thick films were annealed at 60 °C for 12 h in a vacuum oven and then transferred to a heater pre-heated to the respective heating T . The thermal histories of samples in Fig. 6 are similar to those of samples in Fig. 1 (open squares). For annealing at 110 °C, I_1/I_3 remained constant, indicating a lack of stress relaxation at $T_g + \sim 10$ °C as measured by fluorescence. For annealing T s ranging from 115 to 140 °C, I_1/I_3 decreased with annealing time and then reached apparent steady-state values, consistent

Figure 6: Intensity ratios for 680-nm-thick MPy-PS films monitored over 12 h of annealing time at 110 °C (stars), 115 °C (triangles pointing right), 120 °C (X's), 130 °C (circles), and 140 °C (triangles pointing up). Lines were drawn to indicate the change in the direction of I_1/I_3 values as a function of anneal time. Prior to fluorescence measurements at the respective anneal temperatures, samples were spin-coated and then annealed under vacuum at 60 °C for 12 h. (The thermal histories of these films are similar to the thermal histories of the films in Figure 1 (open squares). Background noise was subtracted.)

with stress relaxation. Relaxation times were obtained from the intersection of lines corresponding to the decreasing and steady regimes (see dashed drop lines in Fig. 6). At 115 °C, relaxation occurred over ~8 h, whereas at 140 °C relaxation occurred over ~1 h.⁵⁴ (Similar results to those in Fig. 6 were obtained for films that were made and processed like those in Fig. 6 with the exception that they were not annealed under vacuum at 60 °C for 12 h after spin-coating and prior to fluorescence measurements.)

After 12 h annealing, samples were placed at 120 °C for 10 min to compare I_1/I_3 values at a common T . For films annealed for 12 h at 115 to 140 °C, I_1/I_3 at 120 °C was 1.11 ± 0.02 , indicating that the films reached a common final stress state. For the film annealed at 110 °C, the I_1/I_3 value after 10 min at 120 °C was 1.16. This difference is consistent with the conclusion that isothermal annealing for 12 h at 110 °C ($T_g + \sim 10$ °C) was insufficient to relax residual stresses in bulk PS films.

A 1960 viscoelastic shear stress relaxation study by Tobolsky and Murakami⁵⁵ provides

further support that data in Fig. 6 are associated with stress relaxation. They found that the shear stress relaxation time for PS ($M_w = 200$ kg/mol) at 115 °C is 8.4 h. Although the method in the present study differs from that in ref. 55, the time required for stress relaxation as measured by fluorescence (~ 8 h at 115 °C) agrees well with that measured by shear stress relaxation.

Residual stress relaxation times determined from I_1/I_3 values in Fig. 6 exhibit significant T dependence. Although the apparent relaxation responses in the present study are not exponential decay functions which are often associated with stress relaxation,⁵⁵ we note that the relaxation times obtained at 115 to 140 °C from the data in Fig. 6 exhibit Arrhenius behavior; see Fig. 7. (Fig. 7 includes a relaxation time at 135 °C from data not shown in Fig. 6.) Using the slope of the best-fit line in Fig. 7, an activation energy (E_a) of ~ 110 kJ/mol was obtained for residual stress relaxation over the T range from $T_g + \sim 15$ °C to $T_g + \sim 40$ °C.

Figure 7: Natural logarithm of residual stress relaxation times obtained from Fig. 6 plotted against $1/T$. Error bars represent the plausible range of times based on the fit lines in Fig. 6.

The Arrhenius T -dependence associated with the stress relaxation times above T_g is consistent with β -relaxation processes and inconsistent with α -relaxation, the latter of which follows the Williams-Landel-Ferry (WLF) equation or Vogel-Fulcher-Tammann (VFT) equation. Although the WLF equation does not follow an Arrhenius T -dependence, it is possible to calculate apparent activation energies using WLF fit parameters at a particular T .⁵⁶ Depending

on WLF fit parameters for bulk PS,⁵⁷⁻⁶¹ apparent activation energies vary from 430 to 550 kJ/mol at 115 °C and 260 to 320 kJ/mol at 140 °C. The E_a value of 110 kJ/mol determined in this study via pyrenyl dye fluorescence over the same T range is much lower than the apparent E_a values associated with α -relaxation. In contrast, the E_a value of 110 kJ/mol is in reasonable accordance with E_a values of 120 to 140 kJ/mol reported for β -relaxation in bulk PS.^{47,62} Thus, in agreement with other reports,⁶³⁻⁶⁵ our fluorescence results are consistent with β -relaxation being the underlying mechanism of residual stress relaxation in polymers.

The effects of stress relaxation on overall intensity and T_g were also studied. Figure 8 shows emission spectra for a 650-nm-thick MPy-PS film subjected to thermal history conditions similar to those for the film characterized by ellipsometry in Fig. 2. After spin-coating and annealing under vacuum at 60 °C for 12 h, the film was placed on a heater pre-heated to 140 °C, and spectra were collected upon cooling from 140 to 60 °C in 5 °C decrements after waiting 5 min at each T to allow for thermal equilibration between measurements (red upper curves). After

Figure 8: Fluorescence emission spectra of a single 650-nm-thick MPy-PS film cooled from 140 °C to 60 °C in 5 °C decrements. Red upper curves are spectra collected during the first cooling cycle. After the first cooling cycle, the sample was re-heated to 140 °C and annealed for 1 h to relax residual stresses. Fluorescence emission spectra were then collected during a second cooling cycle (black lower curves). Prior to the first set of fluorescence measurements, the film was annealed under vacuum at 60 °C for 12 h. The arrow indicates that the intensities of fluorescence emission spectra increase during cooling. (Background noise was subtracted.)

the first cooling cycle, the film was re-heated to 140 °C and annealed for 1 h prior to a second cooling cycle (black lower curves). The intensity increased with decreasing T for both data sets.

Part of the reason for the T dependence of intensity is that at elevated T , greater thermal energy in the environment enhances pathways (increased vibrations and librations, etc.) for non-radiative decay of excited-state pyrenyl dyes. Another part of the T dependence of intensity is related to molecular caging. Upon cooling, the increasingly rigid environment surrounding the dyes suppresses pathways for non-radiative decay via caging and increases the intensity of the emitted light with greater increases in I_1 relative to I_3 . The results also show that after annealing for 1 h at 140 °C, fluorescence intensities decreased at all T s (second cooling cycle compared to first cycle). The decrease in intensities after annealing at 140 °C is consistent with enhancements in pathways for non-radiative decay of the excited-state pyrenyl dye after stress relaxation during the 1 h annealing at 140 °C (indicative of reduced caging).

Figure 9 shows the determination of T_g from the T dependence of I_1/I_3 from data in Fig. 8. Previous research^{27-29,31,66,67} has shown that self-referencing intensity ratios can be used to characterize T_g of a film via the intersection of lines fitted through the rubbery and glassy T dependences. (Several fluorescence studies used the ratio I_3/I_1 to measure T_g in MPy-labeled polymers,^{27-29,31} whereas here we use the inverse, I_1/I_3 .) The red circles in Fig. 9 correspond to I_1/I_3 values (from the red upper curves in Fig. 8) during a cooling cycle from 140 to 60 °C. The sample was then re-heated to 140 °C and annealed for 1 h. The black triangles in Fig. 9 correspond to I_1/I_3 values (from the black lower curves in Fig. 8) during the second cooling cycle. Although the I_1/I_3 values are lower during the second cooling cycle than in the first (due to stress relaxation), the T_g of the film, 101 °C (± 2 °C), was invariant within error, consistent with ellipsometry results in Fig. 2. Thus, both ellipsometry and fluorescence sense residual stress relaxation of unrelaxed PS films during high- T annealing and indicate that T_g is independent of stress relaxation.

Figure 9: Fluorescence intensity ratio values (I_1/I_3) for the same 650-nm-thick MPy-PS film in Fig. 8 as a function of temperature upon cooling from 140 °C to 60 °C in 5 °C decrements. Red circles represent I_1/I_3 values during the first cooling cycle calculated from the red upper curves in Fig. 5. Black triangles represent I_1/I_3 values measured during a second cooling cycle calculated from the black lower curves in Fig. 8. The T_g value of 101 °C, measured from the intersection of the rubbery- and glassy-state T dependence of I_1/I_3 , is identical for the two cooling cycles. (The thermal history of this film closely matches the thermal history of the film used for Figure 2. Background noise was subtracted.)

Besides providing quantitative characterization of T_g , the data in Fig. 9 also indicate the relaxation of residual stresses in bulk MPy-PS films. Because of stress relaxation during the 140 °C annealing step for 1 h between the first and second cooling cycles, I_1/I_3 values at a given T decrease by 0.03 to 0.05 between the first and second cycles. This result is consistent in two ways with a reduction in caging around excited-state pyrenyl dyes and thus a decrease in stiffness of the polymer films. First, the intensity ratios are lower when the polymer is in the rubbery state, and higher when the polymer is cooled to the rigid, glassy state, which is consistent with I_1/I_3 values being reduced in less caged or less stiff environments. Second, upon exposure to high T , the chains have enough thermal energy to relax towards a less stressed or caged state, thereby decreasing the stiffness in the second cycle relative to the first cycle.

Figure 10 shows results from a proof-of-concept experiment in which selective placement of the MPy-labeled PS layer in bilayer and single-layer films was used to study the influence of

Figure 10: I_1/I_3 values as a function of temperature upon cooling in 5 °C decrements for single and bilayer films. Data are shown for a 30-nm-thick MPy-PS layer capped with a 620-nm-thick unlabeled PS layer (squares), a single 30-nm-thick MPy-PS film (circles), and a 30-nm-thick MPy-PS layer atop a 610-nm-thick supported unlabeled PS layer (stars). (Background noise was subtracted.)

the polymer-substrate and polymer-air interfaces on film stiffness. Shown are data for three films supported on glass substrates. The first data set is for a bilayer film consisting of a 30-nm-thick MPy-PS substrate layer capped by a 620-nm-thick PS layer. Within 30 nm of the substrate interface $T_g = 100$ °C, within error equal to bulk T_g , and the I_1/I_3 values are the highest of the three cases. The latter point indicates that the 30-nm layer nearest the substrate is the stiffest, which is consistent with results from a coarse-grained molecular dynamics simulation study.⁴²

In contrast, Fig. 10 also shows that when a 30-nm-thick MPy-PS layer is placed atop a 610-nm-thick PS layer, the I_1/I_3 values are the lowest, which indicates that the layer nearest the free surface is the least stiff. This conclusion is also consistent with results from a coarse-grained molecular dynamics simulation study.⁴³ In agreement with previous experimental results,³⁴ the T_g for a 30-nm-thick free-surface layer on bulk PS is 90 °C, reduced by ~10 °C from bulk PS T_g .

The final data set in Fig. 10 is that of a single-layer 30-nm-thick MPy-PS film. Both the free surface and substrate interface influence the film stiffness, and the I_1/I_3 values are intermediate to those of the free surface and substrate layers in the two bulk bilayer films. Additionally, the T_g is reduced from bulk T_g to 90 °C due to free surface effects.³⁴ This proof-of-

concept study demonstrates that it is possible to employ a fluorescence/multilayer approach to interrogate the influence of the polymer-air and polymer-substrate interfaces on the stiffness of confined polymer films as long as the fluorescence measurable is sensitive to stiffness. Future work will include studies to characterize the gradient in caging and hence stiffness as a function of distance from a free surface or substrate interface in polymer films.

4.3 Fluorescence Approach to Investigate Effects of Confinement on T_g and Stiffness of Free-Standing and Supported PS Films on Soft (PDMS) and Hard (Glass) Substrates

As shown above, an advantage of the self-referencing pyrene fluorescence technique using I_1/I_3 values lies in its ability to obtain T_g and provide sensitivity to stiffness from the same experiment. Using a protocol similar to that for the 30-nm-thick MPy-PS film in Fig. 10, T_g s were determined for MPy-PS ($M_n = 800$ kg/mol) as free-standing films as well as films supported on PDMS and glass substrates. (A very high molecular weight PS sample was used in this section because of challenges in preparing free-standing PS films of lower molecular weight that would not develop holes during the fluorescence measurements taken upon cooling from well above T_g .)

Figure 11 shows that all films with thickness exceeding 100 nm have $T_g = 100$ °C or slightly higher and that T_g -confinement effects are evident for nanoconfined films. In agreement with previous studies,^{27,29,68} free-standing PS films exhibit a much greater T_g -confinement effect than the substrate-supported films. (The three data points in Fig. 11 showing T_g -confinement effects in free-standing PS films are in good agreement with data summarized in Fig. 2 of ref. 29 that compare T_g s as a function of molecular weight in nanoconfined, free-standing PS films.⁶⁹) Figure 11 also shows that PS exhibits substantially similar T_g reductions with confinement when supported on glass or on PDMS. This latter result is in disagreement with past fluorescence studies showing that nanoconfined free-surface layers of PS atop bulk layers of other polymers may exhibit significant perturbations to T_g based on the polymer species making up the underlying layer.³⁵ We hypothesize that the substantial lack of effect observed with a PDMS substrate is related to the extraordinarily large difference in the dynamics exhibited by PS and

Figure 11: Effect of substrate on the T_g -confinement for MPy-PS films: supported on PDMS (squares), supported on glass (triangles), free-standing MPy-PS films (circles).

PDMS at 60 °C, which implies that no significant T_g perturbation occurs when the neighboring polymer layers have essentially totally uncoupled dynamics.

For the same films used in Fig. 11, Fig. 12 shows I_1/I_3 values⁷⁰ of MPy-PS films at 60 °C (results are from the data sets obtained upon cooling to measure T_g) which make evident that the stiffness-confinement response is qualitatively and quantitatively different from the T_g -confinement response. In particular, PS films supported on glass or cross-linked PDMS exhibit increases in I_1/I_3 values upon confinement at ~400 nm thickness, which is much larger than the onset thickness for T_g -confinement effects. Furthermore, whereas T_g decreases with confinement, caging, as measured by I_1/I_3 values, and thus stiffness increase with confinement in substrate-supported PS films. A stiffening effect with confinement has been previously reported for polymer films on a hard substrate (like glass or Si) via coarse-grained dynamics simulations⁴² as well as nanoindentation experiments,^{71,72} INS characterization of MSD,^{39,40} and surface capillary wave studies by X-ray photon correlation spectroscopy⁷³ (the length scales at which stiffness-confinement effects are observed are smaller in several of those studies.) Different results indicating a reduction in modulus with confinement have been obtained via wrinkling experiments of glassy polymer on cross-linked PDMS.^{74,75}

Figure 12: Intensity ratio as a function of thickness at 60 °C for MPy-PS films supported on PDMS (squares), and on glass (triangles), and for free-standing MPy-PS films (circles). Horizontal line corresponds to bulk intensity ratio value for MPy-PS. (Background noise was not subtracted.)

Upon decreasing thickness from ~400 nm down to ~20 nm, the MPy-PS films supported on the harder, glass substrate exhibit somewhat higher I_1/I_3 values and thus greater caging and stiffness compared to films supported on the softer, PDMS substrate. Related effects of PS film stiffness have been reported for Si and cross-linked PDMS substrates via surface capillary wave studies.⁷³ Furthermore, the free-standing films in this thickness range exhibit substantially lower I_1/I_3 values than the substrate-supported films, which indicates that the free-standing films are the least stiff. These results show the importance of substrate and substrate hardness in affecting the stiffness of confined PS films and are qualitatively consistent with predictions from coarse-grained dynamics simulation studies.⁴³ Further investigation into the effects of substrate on polymer film stiffness is underway.

With free-standing MPy-PS films, Figure 12 shows a major reduction in I_1/I_3 values with decreasing thickness from ~400 nm to ~200 nm corresponding to a reduction in caging and stiffness. Below a thickness of ~200 nm, the free-standing films exhibit a major increase in I_1/I_3 values with decreasing thickness, consistent with an increase in stiffness. The stiffening effect with decreasing thickness below 200 nm in the free-standing films is unanticipated based on the

fact that both fluorescence results associated with bilayer films in section 4.2 above and coarse-grained dynamics simulations^{42,43} indicate that PS free surface layers exhibit a substantial reduction in caging and thus stiffness relative to bulk PS. However, the free-standing film results below a thickness of ~ 200 nm are consistent with results of a microbubble inflation study that showed stiffening of glassy-state, free-standing PS films with decreasing thickness and below 112 nm.⁷⁶ In the ultrathin regime at ~ 20 nm thickness, all three supported and free-standing PS film systems exhibit the same I_1/I_3 value, consistent with similar caging and stiffness in the various supported and free-standing films. While unusual, the stiffness-confinement behavior exhibited by free-standing PS films is no more unusual than the molecular-weight dependent T_g -confinement effect behavior in PS films reported in the literature.^{27,29,68}

5. Conclusions

Ellipsometry and fluorescence are used in novel ways to characterize and investigate residual stress relaxation in bulk PS films. With ellipsometry, stress relaxation is characterized by the film thickness response to several thermal history conditions. Depending on thermal history, stress relaxation can manifest as either small thickness increases or decreases in bulk PS films, with the evolution in thickness occurring over periods of hours at $T_g + 40$ °C. Nevertheless, as measured by ellipsometry, stress relaxation has no effect on the T_g of PS films.

A self-referencing fluorescence method based on the I_1/I_3 intensity ratio of the pyrene dye emission spectrum (and its sensitivity to molecular caging, which is related to stiffness or modulus) is also used for the first time to study stress relaxation. In agreement with ellipsometry results, residual stress relaxation as measured by fluorescence occurs in the rubbery state over periods of hours. The rubbery-state stress relaxation times obtained via fluorescence exhibit an Arrhenius T dependence with an activation energy of ~ 110 kJ/mol which is consistent with β -relaxation. Also in agreement with ellipsometry results, fluorescence measurements show that the T_g of bulk PS films is unaffected by residual stress relaxation.

The special ability of fluorescence to investigate behavior within one layer of a

multilayer film was exploited to compare the effects of confinement on stiffness near a free surface and a substrate interface. Bilayer bulk film studies reveal that 30-nm-thick free-surface layers are less stiff and 30-nm-thick substrate layers are more stiff than bulk PS films and 30-nm-thick PS films supported on glass. The effect of confinement on the stiffness of films was further studied as a function of relative stiffness of the substrate (glass vs. cross-linked PDMS) and in free-standing films lacking a substrate. The studies revealed that the effects of confinement on T_g and stiffness are qualitatively and quantitatively different and that in confined films between 20 and 400 nm in thickness, the PS films exhibited increasing I_1/I_3 values and hence stiffness in the following order: free-standing films < PDMS-supported films < glass-supported films.

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69. With our fluorescence method, we do not observe the presence of two apparent T_g s in nanoconfined free-standing PS films as has been reported from ellipsometry studies by Pye and Roth (Pye JC and Roth CB. Phys. Rev. Lett. 2011;107;235701). We note that the fluorescence measurements used to determine T_g values of free-standing PS films in the current study as well as in refs. 27 and 29 occurred over a sufficiently broad range of temperature range that it would have been possible to characterize a second T_g close to the values reported by Pye and Roth if such a T_g were accompanied by a change in the temperature dependence of I_1/I_3 .
70. Background counts (due to thermal noise associated with the photomultiplier tube) were subtracted from MPy-PS emission spectra prior to determination of I_1/I_3 values reported for all films in Figs. 5, 6, 9 and 10. This background subtraction was almost totally negligible for bulk films as it did not significantly alter the intensity ratio values for bulk films nor did it affect the reported T_g values. For ultrathin film or layer study in Fig. 10, the background spectrum was collected by spin-coating a 30-nm-thick unlabeled PS film onto glass and measuring the emission. Such background subtraction has a larger effect on the I_1/I_3 values for an ultrathin MPy-PS film than for a bulk MPy-PS film. Background emission counts were subtracted from all fluorescence data except Figs. 11 & 12. We also note that the T_g results (Fig. 11) will be unaffected by the lack of background subtraction. Although background subtraction would affect the particular I_1/I_3 values in Fig. 12, the trends indicated by the data are still valid— I_1/I_3 values for thin films deviate from their bulk values.

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