Stiffness of Thin, Supported Polystyrene Films: Free-Surface, Substrate, and Confinement Effects Characterized via Self-Referencing Fluorescence

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Abstract: Stiffness-confinement effects are characterized via a non-contact, self-referencing fluorescence approach in polystyrene (PS) films labeled with trace levels of 1-pyrenylmethyl methacrylate. The pyrene fluorescence measurable I_1/I_3 is sensitive to molecular caging, which increases with stiffness. At 140 °C, molecular caging and hence stiffness in single-layer PS films supported on silica is independent of thickness down to 240 nm and increases with decreasing thickness at 165 nm and below. In contrast, near T_g at 100 °C and in the glassy state at 60 °C, molecular caging and hence stiffness in single-layer films is independent of thickness down to 63 nm and increases with decreasing thickness at 36 nm and below. In bulk bilayer films, perturbations originating at the substrate interface (free-surface interface) cause major increases (decreases) in caging and hence stiffness in 20-nm-thick substrate-adjacent (free-surface-adjacent) layers. In contrast, in 40-nm-thick bilayer films, the 20-nm-thick substrate-adjacent and free-surface-adjacent layers exhibit little difference in caging and stiffness. Thus, the gradient in stiffness from a film interface depends significantly on confinement, which we hypothesize begins to occur when thickness becomes comparable to the combined length scales over which free-surface and substrate perturbations propagate inside the film. Bulk bilayer films were used to investigate the length scales associated with interfacial perturbations. At 100 °C and 60 °C, stiffness-gradient length scales extend ~45 – 85 nm from the substrate and ~35 – 85 nm from the free surface. At 140 °C, the stiffness-gradient length scales extend ~85 – 200 nm from the substrate and $\lesssim$ 20 nm from the free surface.

Keywords: Stiffness-confinement effects; polymer thin films; interfacial effects

1. Introduction

The vast majority of studies investigating confinement effects on glass transition temperature (T_g)¹⁻²⁵ of linear polymers show qualitative and often quantitative agreement for particular polymer-substrate pairs or free-standing polymer films. In contrast, general trends observed regarding stiffness- or modulus-confinement effects²⁶⁻⁶⁰ are less clear. However, reasonable agreement is apparent regarding stiffness-confinement effects in polystyrene (PS) films supported on rigid substrates.

Using Brillouin light scattering (BLS), Gomopoulos *et al.*⁴³ and Cheng *et al.*⁴⁴ measured the modulus of supported PS films as a function of thickness at room temperature. Polystyrene films exhibited invariance in modulus down to thicknesses of 40 nm. Neither BLS study investigated films with thicknesses below 40 nm. Lee *et al.*³⁷ used picosecond acoustics to measure changes in longitudinal wave velocity (the square of which is proportional to through-film elastic modulus³⁷) in supported poly(methyl methacrylate) (PMMA) films as a function of overall thickness. They reported invariance in the wave velocity with thickness down to 40 nm in PMMA single-layer films supported on aluminum. Enhancements in the wave velocity and thus stiffness were reported in films with decreasing thickness below 40 nm. Although data were not explicitly given, Lee *et al.*³⁷ stated that similar enhancements in wave velocity and thus stiffness were observed for ultrathin PS films. Inoue *et al.*²⁸ used incoherent neutron scattering to measure changes in mean-squared displacement, $\langle u^2 \rangle$, (which is related to the Debye-Waller factor) in supported PS films with thicknesses of 100,000, 100, and 40 nm at 40 °C and 135 °C. (The relationship between $\langle u^2 \rangle$ and stiffness has been described recently in several reports,^{26,27,29,58,61-64} with several references^{58,61-64} indicating that local stiffness $\sim 1/\langle u^2 \rangle$.) Relative to bulk response in glassy-state PS films at 40 °C, $\langle u^2 \rangle$ decreased slightly in 100-nm-thick films and more significantly in 40-nm-thick films. Larger percentage reductions from bulk response were observed in the rubbery state at 135 °C in these nanoconfined films.

When a rigid substrate is replaced by a soft substrate or a free surface, experimental studies have most commonly reported a reduction in stiffness with confinement. Studies using a

film wrinkling technique on PDMS-supported polymer films reported reductions in modulus with decreasing thickness.³⁹⁻⁴¹ Stafford *et al.*⁴⁰ reported that PDMS-supported PS films exhibit reductions in room-temperature modulus with decreasing thickness at ~40 nm and below. Using ultrathin film tensile testing, Liu *et al.*⁴⁸ investigated stiffness-confinement effects in room-temperature, free-standing PS films via the stress-strain response of stretched films floating on water. They reported that the modulus decreased precipitously below thicknesses of ~25 nm.⁴⁸ Other studies^{52,53} that have utilized beam-bending in nanopatterned PMMA structures at room temperature observed structural collapse as beam width was reduced below 100 nm⁵² and 50 nm.⁵³ It can be rationalized that with decreasing width, free-surface effects dominate and cause nanobeam collapse. In contrast, nanobubble inflation studies of free-standing polymer films exhibit differences compared to ultrathin film tensile testing and beam-bending studies; in a 10 – 15 °C temperature range above and below T_g , these studies have reported stiffening with decreasing thickness below ~200 nm.⁴⁹⁻⁵¹

Several simulation studies have focused on characterizing the impacts of confinement on supported polymer films with no free surfaces,^{55,56} supported polymer films with one free surface,⁵⁸ and free-standing polymer films.^{57,59} Simulations are in general qualitative agreement with many experimental reports that the presence of a rigid substrate increases stiffness,^{55,56,58} the presence of a free surface reduces stiffness,⁵⁷⁻⁵⁹ and free-standing polymer films exhibit reduced stiffness with reduced thickness.^{57,59} Specifically, Xia and Keten⁵⁸ simulated stiffness behavior of 5-, 10-, and 19-nm-thick supported PMMA films. They reported that $\langle u^2 \rangle$ decreases and stiffness increases within ~2 nm of the substrate interface and that stiffness decreases within a comparable length scale of the free surface. Xia and Keten⁵⁸ did not comment on the impact of overall film thickness on the length scales associated with stiffness perturbations near the substrate and free-surface interfaces, *i.e.*, whether the length scales are limited to ~2 nm because of the extreme confinement of film thickness.

There is only one experimental report³⁶ on stiffness gradients in supported, bulk polymer films. Cheng *et al.*³⁶ used nanoindentation to determine the extent to which a silica or an alumina

substrate impacts the room-temperature modulus of PMMA films as a function of distance from the PMMA-substrate interface.³⁶ This was achieved by indenting the polymer parallel to the substrate. Cheng *et al.*³⁶ reported that PMMA films exhibited greater stiffness near a silica substrate, with gradients extending up to ~100 nm or ~170 nm towards the interior of films supported on silica or alumina substrates, respectively. These length scales were determined by the distance from the substrate at which the normalized modulus exhibited a very small (~2%) enhancement relative to bulk response. There is no published experimental report of stiffness gradients as a function of distance from a free-surface interface.

Here, we use a non-contact, self-referencing fluorescence technique that is sensitive to local molecular caging to investigate effects of confinement on average stiffness across a film as well as stiffness gradients near the substrate and free-surface interfaces. Average stiffness-confinement effects are investigated by characterizing silica-supported, single-layer PS films as a function of overall thickness. The effects of confinement on interfacial perturbations are investigated using ultrathin bilayer films, and the length scales associated with interfacial perturbations are investigated using bulk bilayer films. The bulk bilayer film results represent the first experimental characterization of caging or stiffness gradients near a free surface in polymer films. This work also provides a comparison of the length scales associated with stiffness perturbations near the substrate and free-surface interfaces.

Stiffness gradients in bilayer polymer films are characterized via the sensitivity of pyrenyl dye-label fluorescence to its local environment. As described in Ref. 60, fluorescence of vibronic coupling dyes (such as some pyrenyl dyes) is sensitive to polymer stiffness via a caging mechanism. After absorption of UV-light, excited-state electrons may return to the ground state (with an excited-state lifetime of ~200 ns⁶⁵) by either non-radiative means (bond vibrations, etc.) or by radiative means (fluorescence).⁶⁶ In a caged environment, *e.g.*, one that is stiff or highly stressed, the excited-state pyrenyl labels have fewer pathways for non-radiative energy decay because vibrational mobility is restricted. In pyrenyl dyes, suppression of non-radiative forms of energy decay causes enhancements in the highest-energy (lowest-wavelength) fluorescence

emission at the expense of lower-energy (higher-wavelength) fluorescence emission.^{67,68}

Specifically, this leads to increases in the ratio of the first vibronic band peak intensity to the third vibronic band peak intensity, I_1/I_3 . (I_1 corresponds to the highest-energy fluorescence emission peak intensity, and I_3 is a lower-energy fluorescence emission peak intensity. The use of a ratio of emission intensities means that the value is self-referencing, *i.e.*, independent of excitation intensity,⁶⁹ sample geometry,⁶⁹ etc.) Thus, I_1/I_3 increases in a more caged environment, *i.e.*, one that is stiffer or highly stressed. Analogous molecular caging arguments are used to explain the relationship between $\langle u^2 \rangle$ and stiffness.^{26,27,29,58,61-64}

There are several key advantages associated with this fluorescence technique. For instance, by incorporating dye-labeled layers in bilayer films, gradients may be characterized near free-surface and substrate interfaces. Other advantages include the ability to characterize polymer stiffness several tens of degrees above T_g and many tens of degrees below T_g , as well as the non-contact nature of the technique, which eliminates issues inherent to contact-based approaches that may perturb polymers during measurement. (Given the ~200 ns excited-state lifetime of the pyrenyl dye,⁶⁵ yielding a response that is akin to a high frequency measurement, we interpret that the stiffness being probed by the fluorescence method is related to a glassy, high frequency modulus even at temperatures several tens of degrees above T_g .) Similar self-referencing fluorescence approaches have been used in a range of studies including those measuring T_g ,^{10,23,70,71} residual stress relaxation,^{7,60} aggregate and micelle formation,^{67,72,73} and polarity in heterogeneous polymeric systems^{74,75} and solvents.^{67,76}

2. Experimental Methods

2.1 Materials

Polystyrene (Pressure Chemical, synthesized by anionic polymerization) with nominal molecular weight of 400 kg/mol and dispersity = 1.06 was used as received. Using azobisisobutyronitrile (Aldrich, under the name 2,2'-azobis(2-methylpropionitrile)) 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 MPy-labeled polystyrene (MPy-PS). The MPy-PS product was dissolved in toluene and precipitated in methanol seven times to remove any residual MPy or styrene monomer. The washed polymer was 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 washed MPy-PS sample had $M_n = 370$ kg/mol, with dispersity = 1.7. As determined by UV-vis absorbance spectroscopy (Perkin Elmer Lambda 35), MPy-PS contains 0.6 mol% pyrene label. Bulk T_g was determined via differential scanning calorimetry (Mettler Toledo DSC822e, second-heat T_g onset method at 10 °C/min heating rate): T_g s were 102 °C for 400 kg/mol PS and 101 °C for 370 kg/mol MPy-PS.

2.2 Film Preparation

Films were spin-coated onto green glass slides from toluene (SigmaAldrich) solutions containing 0.5 to 7.0 wt% PS or MPy-PS with spin speeds ranging from 1500 to 3000 rpm. Glass slides were thoroughly cleaned by etching in 1.0 M hydrochloric acid, rinsing with water, and drying 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 bilayer films, samples were spun onto freshly cleaved mica and annealed under vacuum at $T_{g,bulk} + 20$ °C for 2 h. After annealing, mica-supported films were transferred at room temperature onto glass-substrate supported films by a water transfer technique.³ Residual water was evaporated overnight under ambient conditions prior to annealing the bilayer film in a vacuum oven at 120 °C for 3 h before fluorescence measurement. These annealing conditions ensured that the bilayers healed into a consolidated film without substantial interlayer diffusion.^{6,10,77}

2.3 Ellipsometry

To measure film thickness, PS and MPy-PS were first spin-coated onto silicon slides with a native silicon oxide layer from the same solutions with the same spin speeds at the same time as the films spin-coated onto the glass slides. Measurements were performed at room temperature using spectroscopic ellipsometry (J. A. Woollam Co. M-2000D over a range of

wavelengths from 400 to 1000 nm). The ellipsometric angles (ψ and Δ) of incident light reflected off silica-supported PS or MPy-PS films were measured and fitted to a Cauchy layer model to determine thickness. The Cauchy layer model included a PS layer atop a silicon substrate containing a 2-nm-thick silicon oxide surface layer. Film thickness was determined by fitting ψ and Δ to the PS layer in the Cauchy model.

2.4 Fluorescence Measurements

Fluorescence was used to characterize I_1/I_3 values, which reflect molecular caging and hence are related to stiffness, of MPy-PS films or layers as a function of temperature; these measurements also yield characterization of T_g .^{10,23,24,60} After spin-coating and annealing films (see Section 2.2), 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 mm (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 points between 376 and 378 nm and I_3 an average of points between 387 and 389 nm.

Fluorescence spectra were collected from 140 °C to 60 °C in 5 °C decrements. Before collecting an emission spectrum, films were held for 5 min at each temperature to enable temperature equilibration. Once spectra were collected, background noise was measured by acquiring the spectra of unlabeled PS films of thickness similar to the MPy-PS films. Values of I_1/I_3 at particular temperatures were used to gather stiffness information for each film in the rubbery and glassy states and near T_g . After plotting I_1/I_3 as a function of temperature, lines were fit to the rubbery and glassy temperature dependences to determine T_g .^{10,23,24,60}

3. Results and Discussion

3.1 Average Stiffness-Confinement Effects in Supported Single-Layer PS films

Figure 1A shows typical fluorescence emission spectra for a 935-nm-thick 1-

pyrenylmethyl methacrylate-labeled PS film supported on silica at 140 °C, 100 °C, and 60 °C (bottom to top). Fluorescence intensity increases substantially with decreasing temperature but non-uniformly as a function of emission wavelength. Upon cooling, non-radiative pathways of energy decay for excited-state pyrenyl electrons are suppressed and fluorescence is enhanced. Figure 1A also shows the locations of the first and third vibronic band peaks. The intensities of these peaks were used to determine the I_1/I_3 ratio. (We note that the second vibronic band peak is almost invisible; covalently attaching pyrene to PS chains slightly alters the spectral shape compared to doped pyrene.^{23,60}) With decreasing sample temperature, I_1 increases more significantly than I_3 . With vibronic coupling dyes, such as pyrene and phenanthrene appropriately labeled to polymer,⁷⁸ the highest-energy fluorescence emission peak is enhanced relative to lower-energy emission peaks with decreasing temperature.^{67,68} This trend is consistent with the sensitivity of I_1/I_3 to molecular caging and hence stiffness.⁶⁰ As excited-state pyrenyl dye labels experience greater molecular caging from the surrounding local environment upon cooling, I_1/I_3 values increase.

Figure 1B shows I_1/I_3 values as a function of temperature for two silica-supported single-

Figure 1: A: Normalized fluorescence emission intensity spectra for a 935-nm-thick 1-pyrenylmethyl-labeled PS film. Spectra are shown for 140 °C, 100 °C, and 60 °C (from bottom to top). Arrows indicate emission peak intensity values (I_1 and I_3). B: Intensity ratio (I_1/I_3) values as a function of temperature for 935- and 36-nm-thick films. Both films are supported on silica. (Background noise was subtracted from all spectra in this work.)

layer MPy-PS films. Data are shown for a 935-nm-thick, bulk, single-layer film (black squares) and a 36-nm-thick single-layer film (open squares). While not the focus of this study, T_g values may be determined using the intensity ratio method by the intersection of lines fitted to the rubbery and glassy temperature dependences of I_1/I_3 .^{10,23,24,60,79} The single-layer bulk PS film exhibits $T_g = 100 \pm 1$ °C, in reasonable agreement with DSC measurements. Relative to bulk T_g , there is a reduction in T_g to 92 ± 2 °C for the 36-nm-thick film; this reduction is due to the free surface perturbing T_g from its bulk value, with perturbations propagating into the film interior.^{6,8-11,80} Importantly, despite the fact that the 36-nm-thick supported PS film exhibits a significant reduction in T_g relative to bulk, as evidenced by higher I_1/I_3 values the confined film exhibits enhanced molecular caging and thus stiffness relative to bulk response at all temperatures.

Figure 2 shows I_1/I_3 values of single-layer MPy-PS films as a function of logarithmic film thickness at 60 °C, 100 °C, and 140 °C. The dotted lines in the plots correspond to I_1/I_3 values determined for the bulk, 935-nm-thick, single-layer MPy-PS film. For single-layer films at 60 °C and 100 °C, I_1/I_3 remains invariant (within error) with decreasing thickness down to 63 nm and

Figure 2: Intensity ratio (I_1/I_3) values as a function of film thickness for single-layer films supported on silica at 60 °C (blue triangles), 100 °C (black squares), and 140 °C (red circles). The dotted lines represent the I_1/I_3 values for a 935-nm-thick film at the various temperatures. Error bars and dashed lines indicate the variation in I_1/I_3 associated with slight position changes in the film.

exhibits increasing values (outside error) at 36 nm and below.⁸¹ In 16-nm-thick films, I_1/I_3 values increase relative to bulk response by ~ 0.04 at 60 °C and ~ 0.05 at 100 °C. For single-layer films at 140 °C, I_1/I_3 remains invariant (within error) with decreasing thickness down to 240 nm and exhibits increasing values (outside error) at 165 nm and below. In 16-nm-thick films, I_1/I_3 increases relative to bulk response by ~ 0.04 at 140 °C. The increases in I_1/I_3 values indicate an enhancement in caging and thus average stiffness across sufficiently thin films.

The results on glassy-state (60 °C) and near T_g (100 °C) single-layer, supported PS films shown in Fig. 2 are in major agreement with results from BLS studies of single-layer, supported PS films that reported invariance in stiffness with decreasing thickness for PS films down to 40 nm.^{43,44} (Related BLS studies that do not allow for direct comparison with results in Fig. 2 have revealed invariance in stiffness with decreasing thickness down to the smallest measured thickness: down to 100 nm in supported polyimide films⁴² and with decreasing ridge width in PS nanostructures with widths as small as 88 nm⁴⁶ and 80 nm.⁴⁵) As mentioned in the Introduction, a picosecond acoustic study³⁷ that measured longitudinal wave velocity in aluminum-supported, single-layer PMMA films reported an invariance with thickness down to 40 nm. Below 40 nm, wave velocity and hence modulus increased with decreasing thickness. Although results were not explicitly given, similar enhancements were reportedly obtained for PS films.³⁷ Thus, our fluorescence results for glassy-state, single-layer PS films also agree with results in Ref. 37.

The results on glassy-state (60 °C) and rubbery-state (140 °C), single-layer, supported PS films shown in Fig. 2 may be compared with mean-squared displacement results. As stated by Ye *et al.*, based on a simple Maxwell model a “reduction in $\langle u^2 \rangle$ is expected...to reflect an enhancement in the local elastic properties of a glass”,²⁹ and hence stiffness. This is because reductions in $\langle u^2 \rangle$ correspond to increases in a harmonic spring constant, which is “expected to scale roughly with the high frequency shear modulus.”²⁹ Several references have also indicated that stiffness $\sim 1/\langle u^2 \rangle$.^{58,61-64} Using incoherent neutron scattering, Inoue *et al.*²⁸ measured $\langle u^2 \rangle$ for 40-, 100-, and 100,000-nm-thick supported PS films at temperatures ranging from -193 °C to 135 °C. Relative to bulk PS response, at 40 °C, $\langle u^2 \rangle$ decreased substantially ($\sim 37\%$) in a 40-nm-

thick film but relatively little ($\sim 11\%$) in a 100-nm-thick film. The relative reductions in $\langle u^2 \rangle$ with confinement increased in the rubbery state at 135 °C, with $\langle u^2 \rangle$ decreasing by $\sim 42\%$ and $\sim 18\%$ in 40- and 100-nm-thick films, respectively. While not providing exact quantitative correspondence with our fluorescence measurements in Fig. 2, they agree in indicating that the confinement length scale at which substantial stiffening relative to bulk is observed is greater in the rubbery state than in the glassy state.

Thus, the novel fluorescence technique yields results that are in substantial agreement with BLS,^{43,44} picosecond acoustic,³⁷ and incoherent neutron scattering²⁸ studies that have characterized properties or behavior related to stiffness in single-layer, supported PS films. A particular advantage of our fluorescence technique is the ability to place dye-labeled polymer layers within bilayer films to investigate the impact of both the substrate and free-surface interfaces in perturbing behavior relative to bulk response. Such studies have been reported previously for T_g -confinement effects^{6,8-10} and physical aging-confinement effects.⁸² Below, we describe the first study to characterize the roles of free surfaces and substrates in perturbing molecular caging and thus stiffness of polymer films and to provide insight into how temperature relative to T_g can impact the length scales over which such free-surface and substrate perturbations can propagate into films.

3.2 Roles of Substrate and Free-Surface Interfaces in Stiffness-Confinement Effects: Bilayer Film Studies

Figure 3 shows I_1/I_3 values for MPy-PS layers within single-layer and bilayer films at 140 °C, 100 °C, and 60 °C (data for 120 °C and 80 °C are shown in Fig. S1 of Supplemental Information). MPy-PS layers are depicted in green rectangles, which also contain a number corresponding to the I_1/I_3 value of that layer. Unlabeled PS layers are depicted in open rectangles. The thicknesses of the single-layer and bilayer films are shown via double-headed arrows. For films at 140 °C, the numbers in Figs. 3A and 3D represent the I_1/I_3 values for 935- and 36-nm-thick single-layer MPy-PS films, respectively. In Figs. 3B, 3C, 3E, and 3F, the number within each green layer represents the I_1/I_3 value for a 20-nm-thick MPy-PS layer within

Figure 3: Intensity ratio (I_1/I_3) values of single-layer and bilayer films at 140 °C (top row), 100 °C (middle row) and 60 °C (bottom row). The numbers in A & D represent I_1/I_3 values for 935- and 36-nm-thick single-layer films at 140 °C. The numbers in the green layers of B & C and E & F represent I_1/I_3 values at 140 °C for 20-nm-thick MPy-PS layers within bilayer films that are either 1500-nm-thick (B & C) or 40-nm-thick (D & E) overall. G-L and M-R represent the I_1/I_3 values at 100 °C and 60 °C for the same films described in A-F.

bilayer films with overall thicknesses of either 1520 nm (B & C) or 40 nm (E & F).

Figures 3A-3C show that, in the rubbery state at 140 °C, 20-nm-thick substrate and free-surface layers in bulk PS bilayer films exhibit substantial differences in I_1/I_3 values relative to average I_1/I_3 values across a bulk film. The value of $I_1/I_3 = 1.25$ in the substrate layer indicates significant enhancement in molecular caging and thus stiffness relative to the average across a bulk film with $I_1/I_3 = 1.12$. As well, the value of $I_1/I_3 = 1.08$ in the free-surface layer indicates a reduction in caging and thus stiffness relative to the bulk average response. Notably, the magnitude of the change in I_1/I_3 relative to bulk response is substantially greater in the substrate layer than in the free-surface layer. This indicates that the perturbation to caging and stiffness caused by an interface is greater for the polymer-substrate interface than for the polymer-air interface. Similar conclusions can be drawn for the bulk single-layer and bilayer films that were characterized near T_g at 100 °C and in the glassy state at 60 °C in Figs. 3G-3I and Figs. 3M-3O, respectively.

These results and associated conclusions are opposite to what has been observed and concluded regarding T_g -confinement effects in PS films supported on silica.⁶ Using a related fluorescence method in bilayer PS films with overall thickness yielding bulk T_g ($T_{g,bulk}$) response, Ellison and Torkelson⁶ reported that $T_g = T_{g,bulk}$ in a 12-nm-thick dye-labeled layer adjacent to the substrate but $T_g - T_{g,bulk} = -32$ °C in a 14-nm-thick dye-labeled free-surface layer. In other words, the T_g -confinement effect in supported PS films lacking significant attractive polymer-substrate interactions originates at the free surface (and not at the polymer-substrate interface) and, in sufficiently thick films, propagates some tens of nanometers into the film interior.

A comparison of Figs. 3D-3F with Figs. 3A-3C reveals that, in the rubbery state at 140 °C, the perturbations to caging and stiffness caused by interfaces depend strongly on confinement. The difference in I_1/I_3 values between 20-nm-thick substrate and free-surface layers decreases from 0.17 in 1520-nm-thick bilayer films to 0.03 in 40-nm-thick bilayer films. Thus with sufficient confinement, as in the 40-nm-thick bilayer films, the substrate and free-surface layers exhibit much more similar molecular caging and stiffness characteristics, which are also

very close to that of a single-layer film of a comparable overall thickness (36 nm). Similar conclusions can be drawn for confined single-layer and bilayer films characterized near T_g at 100 °C and in the glassy state at 60 °C.

The effect of confinement in causing free-surface and substrate layers to exhibit more similar responses has also been observed with T_g -confinement effects in PS films supported on silica.⁶ Using a fluorescence method and bilayer films that varied in overall thickness from several hundred to 24 nm, Ellison and Torkelson⁶ reported that when overall bilayer thickness exceeds 60 nm, a 14-nm-thick surface layer exhibits $T_g - T_{g,bulk} = -32$ °C independent of overall thickness. However, as overall thickness decreases below 60 nm, there is a sharp rise in the surface-layer T_g until overall thickness reaches 25 nm, below which the surface layer simply reports the same T_g as a single-layer film of the overall thickness. Experiments with multilayer films revealed that, unlike films with overall thicknesses exceeding ~60 nm, in 24-nm-thick bilayer films both the 12-nm-thick free-surface and 12-nm-thick substrate layers exhibit the same T_g depression relative to bulk ($T_g - T_{g,bulk} = -11$ °C) as that reported by a single-layer 24-nm-thick film. In other words, with a sufficiently nanoconfined, supported PS film, the length scale is insufficient to support a substantial, smooth T_g gradient from the free surface to substrate.⁶

Ellison and Torkelson⁶ concluded that if the total film thickness is below a certain value (~60 nm), then the system adjusts “to satisfy the constraint that the gradient in (T_g) from surface to substrate is not too sharp and abrupt.”⁶ We hypothesize that a related constraint in caging or stiffness gradient also holds in the current study. In particular, the caging or stiffness represented by $I_1/I_3 = 1.53$ and 1.27 in 20-nm-thick substrate and free-surface layers, respectively, in 1520-nm-thick bulk films would result in too sharp of a gradient in caging or stiffness if the substrate and free-surface layers were adjacent to each other as in a 40-nm-thick bilayer film.

The major narrowing of the distribution of caging or stiffness response from free surface to substrate with sufficient confinement may also be rationalized as follows. Perturbations to T_g caused by interfaces have been observed to propagate inside a film interior by several tens of nanometers or even greater length scales.^{6,8-11} We hypothesize that perturbations to caging and

hence stiffness caused by interfaces also propagate some substantial distance into a film interior. When the length scale over which an interfacial perturbation propagates inside the film becomes comparable to or greater than one-half of the film thickness, then the behaviors near both interfaces begin to exhibit less difference with sufficient reduction in film thickness. The behaviors very near the free-surface and substrate interfaces should be similar due to the combined propagation of interfacial perturbations across the whole film.

If the free-surface and substrate layers exhibit more similar caging and stiffness effects with increasing overall film confinement, then why is an increase in caging and stiffness evident in sufficiently thin single-layer films at 60 °C, 100 °C, and 140 °C? The apparent stiffening with sufficient confinement results from the fact that at all temperatures studied, the perturbation to caging and stiffness is greater at the substrate interface than at the free surface. Thus, unlike T_g -confinement effects in PS films supported on silica where the T_g reduction originates at the free surface with little or no effect of the substrate interface,⁶ the effect of the rigid substrate layer on stiffness is greater in magnitude than and thus dominates over the effect of the free-surface layer in sufficiently thin films. In this respect, stiffness-confinement effects in supported PS films are more similar to T_g -confinement effects in supported polymer films that have attractive interactions with the substrate, which result in T_g enhancements with confinement.⁸

The length scales associated with free-surface and substrate perturbations are explored further in Fig. 4. Figure 4 shows I_1/I_3 values for MPy-PS layers within bulk bilayer films as a function of MPy-PS layer thickness, h , at 140 °C, 100 °C, and 60 °C; total bilayer film thickness exceeds 1500 nm. (Data for 120 °C and 80 °C are shown in Fig. S2 in Supplemental Information). Single-layer film data are reproduced from Fig. 2.

To investigate the length scales associated with stiffness perturbations near the free surface, the thicknesses of free-surface MPy-PS layers within bulk bilayer films were varied. At 140 °C (Fig. 4A), I_1/I_3 values decrease from ~1.12 in a 490-nm-thick free-surface layer to ~1.08 in a 20-nm-thick free-surface layer. The plot shows that the 20-nm-thick free-surface layer exhibits reduced I_1/I_3 values relative to bulk response (outside error). However, extending the

surface layer thickness to 36 nm yields bulk response within error. These results indicate that while the gradient in caging and hence stiffness extends far enough to perturb the overall response of a 20-nm-thick surface layer, the gradient does not extend far enough to perturb the overall response of a 36-nm-thick surface layer. Thus, the stiffness-gradient length scale propagating from the free surface can be estimated to extend $\lesssim 20$ nm at 140 °C.

Comparisons may be made to the results from the free surface at 100 °C and 60 °C in Figs. 4B and 4C, respectively. In contrast to results at 140 °C, in both cases the 36- and 86-nm-thick surface layers exhibit I_1/I_3 values that are reduced relative to bulk response (outside error). Bulk response averaged across the free-surface layer is ultimately achieved when its thickness is 200 nm. These results indicate that the gradient in caging and hence stiffness extends far enough to perturb the overall responses of 36- and 86-nm-thick surface layers but does not extend far enough to perturb the overall response of a 200-nm-thick surface layer. The stiffness gradient propagating from the free surface can be reasonably estimated to extend $\sim 35 - 85$ nm at 100 °C and 60 °C. Thus, the length scale over which free-surface perturbations to molecular caging and hence stiffness propagate inside the film at 140 °C is significantly less than those at 100 °C and 60 °C. This result may be explained by the fact that in the rubbery state at 140 °C, bulk PS has a lower modulus (as conventionally measured by ~ 3 orders of magnitude⁸³) than glassy-state PS and is thus much less susceptible to perturbations from the free surface relative to PS near T_g at 100 °C or in the glassy state at 60 °C.

To investigate the length scales associated with stiffness perturbations near the substrate, the thicknesses of substrate MPy-PS layers within bulk bilayer films were varied. At 140 °C (Fig. 4A), I_1/I_3 values increase from ~ 1.14 in a 490-nm-thick substrate layer to ~ 1.25 in a 20-nm-thick substrate layer. The 86- and 200-nm-thick substrate layers exhibit enhanced I_1/I_3 values relative to bulk response (outside error). Bulk response is ultimately achieved when the substrate layer thickness is 490 nm. These results indicate that the caging- and hence stiffness-gradient length scales extend far enough from the substrate to perturb the overall responses of 86- and 200-nm-thick substrate layers but is insufficient to perturb the overall response of a 490-nm-

Figure 4: I_1/I_3 values as a function of thickness at 140 °C (A), 100 °C (B) and 60 °C (C) for single-layer and bilayer films. I_1/I_3 values are shown for substrate-adjacent MPy-PS layers within bilayer films (red circles), single-layer MPy-PS films (black squares), and free-surface-adjacent MPy-PS layers within bilayer films (blue triangles). Single-layer film data are reproduced from Fig. 2. The dotted line represents the I_1/I_3 value for a 935-nm-thick single-layer MPy-PS film. Error bars and dashed lines indicate the variation in I_1/I_3 associated with slight position changes in the film.

thick substrate layer. Thus, the stiffness-gradient length scale propagating from the substrate can be reasonably estimated to extend $\sim 85 - 200$ nm at 140 °C.

A comparison may be made to the results from the substrate at 100 °C and 60 °C in Figs. 4B and 4C, respectively. At 100 °C and 60 °C, the 45- and 86-nm-thick substrate layers yield I_1/I_3 values that are elevated relative to bulk (outside error). Bulk response is very nearly

achieved by extending the substrate layer thickness to 200 nm. Thus, the stiffness-gradient length scale can be estimated to extend $\sim 45 - 85$ nm at 100 °C and 60 °C. These results indicate that the caging- and hence stiffness-gradient length scale associated with the polymer-substrate interface is larger at 140 °C relative to those at 100 °C and 60 °C. Thus, in the rubbery state at 140 °C, the much lower-modulus PS is more susceptible to perturbations from the rigid substrate relative to the higher-modulus PS near T_g at 100 °C or in the glassy state at 60 °C.

It is evident from Fig. 4A at 140 °C that the perturbations from the substrate, both in terms of I_1/I_3 values and gradient length scales, are substantially greater than those from the free surface. As the thickness approaches the length scales associated with stiffness gradients from the interfaces, stiffening is observed for single-layer films with thicknesses of 165 nm and below since substrate effects dominate at 140 °C. However at 100 °C and 60 °C, the length scales associated with substrate and free-surface perturbations are more similar. Therefore, stiffening is only observed for single-layer films with thicknesses of 36 nm and below. These results support the hypothesis that the effects of the propagation of stiffness perturbations from the substrate and free-surface interfaces are exhibited in the overall response of sufficiently confined PS films.

While bilayer experiments yield information about the approximate length scales associated with stiffness gradients, more definitive determinations of stiffness-gradient length scales may be obtained in trilayer experiments, which involve placing ultrathin dye-labeled layers at particular distances away from the free-surface and substrate interfaces. In this manner, the I_1/I_3 values associated with stiffness perturbations could be determined at specific locations. Similar approaches have been used to characterize T_g and physical aging gradients.^{6,10,82} Such fluorescence trilayer investigations of stiffness-gradient length scales are warranted.

The length scales associated with stiffness gradients near the substrate investigated in this study may be compared to the only published experimental study³⁶ on stiffness gradients, which via nanoindentation reported stiffness enhancements near the substrate interface for bulk, room-temperature supported PMMA films. In Ref. 36, stiffness gradients were reported to extend as much as ~ 100 nm or ~ 170 nm in PMMA films supported on silica or alumina, respectively.

These length scales were equated to the distance at which the normalized modulus exhibited a greater than a very small ($\sim 2\%$) increase relative to bulk response. Substantial changes in modulus ($\geq 10\%$) were reported at distances extending $\sim 50 - 70$ nm from a PMMA-silica interface or $\sim 50 - 105$ nm from a PMMA-alumina interface. Our fluorescence results indicate that there is stiffening near the PS-silica interface and that stiffness gradients extend $\sim 45 - 85$ nm from the substrate. Although PS and PMMA films differ regarding the absence or presence of attractive interactions with the substrates, it is interesting to note that our results regarding length scales over which substrate interfaces perturb stiffness in bulk PS films agree reasonably well with the length scales over which substantial ($\geq 10\%$) enhancements in normalized modulus are reported via nanoindentation studies of PMMA films.³⁶

Comparisons may also be made with a recent simulation study by Xia and Keten,⁵⁸ who studied supported PMMA films with thicknesses of 5 to 19 nm. They reported that stiffness was reduced near the free surface and enhanced near the substrate with perturbation length scales extending ~ 2 nm. Based on the results in Fig. 3 of this study, as film thickness is reduced to length scales comparable to or less than those associated with interfacial perturbations, the behavior near each interface becomes more similar. In particular, the stiffness-gradient length scales near each interface must decrease to adjust to the constraint that the change in stiffness is not too sharp or abrupt. Taken alone, the stiffness-gradient length scales characterized in bulk bilayer films in this study (tens of nanometers) may appear to be inconsistent with those characterized in ultrathin films (~ 2 nm) in the simulation study.⁵⁸ However, the gradient length scales may be consistent when comparing films that are much more highly confined, *e.g.*, the 40-nm-thick bilayer films in which 20-nm-thick substrate and free-surface layers exhibited little difference within error in I_1/I_3 values and hence stiffness. These results indicate that care must be taken when comparing stiffness-gradient length scales from various studies that consider films of very different thicknesses, *i.e.*, the overall film thickness must be considered because stiffness-gradient length scales are a function of confinement.

We also note that recent theoretical work by Mirigian and Schweizer^{84,85} concerned with

activated glassy relaxation and mobility gradients in free-standing films is particularly relevant to the results of our study. The key, basic idea associated with their work is that “vapor interfaces speed up barrier hopping in two distinct but coupled ways by reducing *both* near-surface local caging constraints and spatially long range collective elastic distortion.”⁸⁵ In other words, the energy barrier that impedes relaxation in glasses is governed by units or particles having to break out of local cages as well as a contribution resulting from the long-range, high-frequency elastic properties of the glassy matrix that must dilate to accommodate a unit or particle breaking out of its cage. In their study, they determined that there are “two *generic dynamical* mechanisms of how a free surface modifies the spatially nonlocal activated event: (i) a ‘direct surface’ effect close to the interface mainly associated with the loss of nearest neighbors and its effect on the local cage barrier and (ii) a longer range ‘confinement’ effect mainly associated with the cutoff of the strain field at the vapor interface which reduces the collective elastic barrier. These two film effects are fundamentally coupled in a spatially heterogeneous manner via gradients of *all* physical properties of the dynamic free energy.”⁸⁵ Our experimental results related to gradients from the free surface are in qualitative accord with the theoretical picture developed by Mirigian and Schweizer and may be useful in informing the local modulus used by them as well as the incorporation of long-range effects on elasticity. Related, future theoretical development to address films on solid supports, such as our supported PS films, may also be able to take advantage of our experimental results on gradients from the substrate.

Finally, a comparison between T_g - and stiffness-confinement effects of silica-supported PS films reveals that the two are distinct. This conclusion is evident based on the following reasons. In a report by Ellison and Torkelson,⁶ T_g gradients were reported to extend tens of nanometers into supported PS films from the free surface and were non-existent within error near the substrate. Fluorescence results indicate that stiffness gradients propagate from both the free surface and the substrate. Even in the absence of T_g -confinement effects near the PS-substrate interface, stiffness gradients extend between $\sim 85 - 200$ nm above T_g and between $\sim 45 - 85$ nm below and near T_g (Fig. 4) in bulk bilayer films. Additionally, Fig. 4 shows that single-layer

films exhibit stiffening in sufficiently thin films due to substrate perturbations that dominate over free-surface perturbations. The opposite is true for T_g -confinement effects in silica-supported PS films in which T_g reductions are observed in sufficiently thin PS films due to free-surface perturbations.⁶ These reasons demonstrate that stiffness-confinement effects and T_g -confinement effects are distinct, in agreement with other reports in literature.^{29,86}

4. Conclusions

We employed a self-referencing fluorescence technique to characterize molecular caging in supported MPy-PS films via the fluorescence measurable I_1/I_3 . The I_1/I_3 value is sensitive to local molecular caging which increases with stiffness. Single-layer films were used to investigate average stiffness-confinement effects. In the glassy state and near T_g , single-layer, supported PS films exhibit an invariance of caging and hence stiffness down to thicknesses of 63 nm and enhancements for films with thicknesses of 36 nm and below. In the rubbery state, single-layer supported PS films exhibit an invariance of caging and hence stiffness down to thicknesses of 240 nm and enhancements for films with thicknesses of 165 nm and below. The results on single-layer, supported PS films are in good agreement with other experimental reports of single-layer, supported PS films probing properties related to stiffness using BLS,^{43,44} picosecond acoustics,³⁷ and incoherent neutron scattering.²⁸

Bilayer film experiments were conducted to investigate the role that the substrate and free-surface interfaces play in perturbing stiffness-confinement behavior. In 20-nm-thick substrate or free-surface layers within bulk bilayer films, caging and hence stiffness is substantially enhanced near the substrate and reduced near the free surface with perturbations near the substrate being significantly stronger. However, when the bilayer film thickness is reduced to 40 nm overall, the 20-nm-thick substrate and free-surface layers exhibit more similar responses indicating that the stiffness gradients from interfaces depend on confinement. Bulk bilayer films were used to characterize length scales associated with stiffness gradients near the substrate and free-surface interfaces. In the glassy state and near T_g , stiffness-gradient length

scales in bulk PS films are reasonably estimated to extend $\sim 45 - 85$ nm from the substrate and $\sim 35 - 85$ nm from the free surface. In the rubbery state, the length scales associated with stiffness gradients in bulk PS films are reasonably estimated to extend $\sim 85 - 200$ nm from the substrate and $\lesssim 20$ nm from the free surface. Thus, because confinement modifies stiffness gradients originating from interfaces, bulk polymer films can exhibit stiffness gradients from interfaces over length scales that equal or substantially exceed the overall thickness at which average stiffness-confinement effects become evident in nanoconfined films.

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79. The Torkelson research group has used several analysis methods to obtain T_g values from temperature-dependent fluorescence responses. Integrated fluorescence intensity (over a broad range of wavelengths) as a function temperature with pyrenyl dye dopants or labels (with 1-pyrenylbutyl methacrylate) is the generally preferred method, yielding highly-reproducible data subject to little intrinsic error or noise. However, in studies associated with free-standing films the generally preferred method does not provide data of sufficient quality to yield accurate and precise T_g values; this has been explained (see Refs. 10 and 23) by presumed film rippling on cooling, which leads to changes in the film surface area being exposed to the fluorescence excitation light. Hence, in our free-standing film studies, we employed a self-referencing method involving an intensity ratio

(in Refs. 10 and 23 it was the inverse of the I_1/I_3 ratio employed in this manuscript, with 1-pyrenylmethyl methacrylate being the dye label incorporated in at trace levels in the polymer) which eliminated any issues associated with fluctuations in the surface area being exposed to excitation light. However, because the I_1/I_3 data result from a ratio of intensities with each intensity averaged over only 2 nm of emission, there is more error inherent in the use of I_1/I_3 data than in integrated fluorescence data. The quality of the I_1/I_3 data is sufficient to yield good determinations of T_g but insufficient to comment with confidence on issues such as glass transition breadth, which can be quantified with confidence using temperature-dependent integrated fluorescence intensity data. .

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