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Modulus, Confinement, and Temperature Effects on Surface Capillary Wave Dynamics in Bilayer Polymer Films near the Glass Transition

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Abstract. We report relaxation times (τ) for surface capillary waves on 27-127 nm polystyrene (PS) top layers in bilayer films using x-ray photon correlation spectroscopy. At ~ 10 °C above the PS glass transition temperature (T_g), τ tracks with underlayer modulus, being significantly smaller on softer substrates at low in-plane scattering wavevector. Relative to capillary wave theory, we also report stiffening behavior upon nanoconfinement of the PS layers. At PS $T_g + 40$ °C, both effects become negligible. We demonstrate how neighboring polymer domains impact dynamics over substantial length scales.

With some exceptions,¹ studies of confined polymers have revealed large deviations in properties, e.g., glass transition temperature (T_g), compared with bulk behavior.²⁻¹⁹ Supported films of linear polymers without attractive polymer-substrate interaction report a reduced T_g relative to bulk T_g ($T_{g,bulk}$) upon confinement.^{2-5,7-14} For example, the seminal 1994 study by Keddie et al.² revealed that $T_g - T_{g,bulk} = \sim -24$ °C for a 17-nm-thick polystyrene (PS) film on silica. The T_g reduction in ultrathin films was attributed to a layer of enhanced mobility at the air/polymer interface with lower requirements for cooperative motions associated with T_g .² The enhanced surface mobility propagates into the film several tens of nanometers,^{3,4} and in the absence of attractive polymer-substrate interactions, the propagation of the free-surface effect causes a reduction of average film T_g with decreasing thickness.^{3,4} Studies have probed the film surface and interfacial regions, and the local T_g s differ from the average T_g across the film.³⁻⁵ For example, in bulk PS films in which a 14-nm-thick free-surface layer has been labeled with a fluorescent dye, $T_g - T_{g,bulk} = \sim -32$ °C in the surface layer.^{3,4} Herminghaus⁶ developed a model in which dynamics at a film surface, which are assumed to be faster than bulk dynamics, couple to dynamics in the film interior through capillary waves. The enhanced surface dynamics propagate into the film over distances on the order of the wavelength of the capillary modes involved, resulting in a mobility gradient. For PS on silicon, a fit of the model⁶ using elastic modulus as a fit parameter agreed quantitatively with T_g s of nanoconfined films.⁷

Although less studied, modulus-confinement effects in polymers have been investigated nearly as long as T_g -confinement effects.²⁰⁻³⁷ Some studies indicate that modulus increases with confinement. For example, two nanoindentation studies^{20,21} reported that modulus increases by up to a factor of 2 over bulk values within the top ~ 10 nm of supported PMMA, PS, and polycarbonate films. A third nanoindentation study²² reported an increase in modulus with decreasing thickness in supported PMMA films but found that modulus increases with nanoindentation depth. As described in a recent review,²³ nanofiber studies have indicated that elastic modulus increases with decreasing fiber diameter. All of these studies involved glassy-state polymers. O'Connell and McKenna²⁴⁻²⁶ applied a bubble inflation method to suspended

polymer films (considered free-standing) and extracted creep compliance values, which indicate stiffening in the rubbery and glassy regimes with confinement. Other studies of glassy films report invariant or decreasing modulus with confinement. Brillouin light scattering has indicated that modulus is thickness-independent in free-standing PS films as thin as 29 nm,²⁷ supported polyimide films as thin as 97 nm,²⁸ and supported PS or PMMA films as thin as 40 nm.²⁹ Picosecond acoustic studies³⁰ have reported that modulus is invariant down to a PMMA film thickness of 40 nm but increases below 40 nm. In contrast, elastic wrinkling studies found that modulus decreases with confinement in PS and poly(alkyl methacrylate) layers supported on cross-linked poly(dimethyl siloxane) (PDMS).³¹⁻³⁶ A nanopatterned PMMA beam study, in which a liquid was placed in the interbeam channels and capillary forces deformed the beams, has also reported decreasing modulus with decreasing beam size.³⁷ These limited, conflicting results reveal that there is an opportunity to employ new methods for studying effects of confinement on stiffness-related behavior in polymers.

X-ray photon correlation spectroscopy (XPCS) is an emerging technique for studying film dynamics at surfaces and interfaces.³⁸⁻⁴⁵ Thermally induced capillary waves at a surface are probed by coherent x-rays, and fluctuations in surface heights are monitored over a range of in-plane scattering wavevector (q) and correlated in time. For a fixed q , a surface wave relaxation time is extracted from the decay of the intensity autocorrelation function (g_2). Due to the experimental geometry, the x-ray electric field decays evanescently into the film and probes the top ~ 10 nm.³⁸ Hu *et al.*^{41,42} applied XPCS to bilayer films of PS atop polybromostyrene at a temperature very far above the PS T_g ($T_g + \sim 95$ °C). Here, we study thin PS layers supported on silicon wafers and various polymer substrates and probe surface wave relaxations over a large q range near the PS T_g ($T_{g,bulk} + 9$ °C). We demonstrate for the first time that substrate modulus strongly influences capillary wave relaxations at the PS surface even when the PS layer thickness exceeds 100 nm. These effects are more pronounced at low q (longer wavelengths) and within 10 °C of the PS T_g . The effect of substrate modulus is vastly reduced at high q and at $T_{g,bulk} + 40$ °C. These results highlight the importance of both the length scale of the waves being probed and

temperature in confinement effects.

Films of PS ($M_w = 108$ kg/mol; $T_{g,bulk} = 101$ °C by differential scanning calorimetry (DSC); synthesized by anionic polymerization), poly(isobutyl methacrylate) (PiBMA) ($M_w = 431$ kg/mol; $T_{g,bulk} = 65$ °C; synthesized by free radical polymerization), and poly(4-vinyl pyridine) (P4VP) ($M_w = 160$ kg/mol; $T_{g,bulk} = 150$ °C; Sigma-Aldrich) were made by dissolving 1-4 wt% polymer in toluene or acetic acid and spin coating onto silicon wafers or cleaved mica (PS films). Cross-linked PDMS was prepared from Dow Corning Sylgard 184 at a 10:1 base to catalyzing agent ratio by spin coating onto silicon and curing at 100 °C overnight. The underlayer (500-700 nm thickness) was annealed overnight in vacuum at the underlayer $T_g + 40$ °C (except for cross-linked PDMS which was annealed at 100 °C) before a top PS layer (annealed overnight at 120 °C) was floated off mica onto the underlayer. A second annealing was done at 140 °C for 2 hr to consolidate the bilayer, except for PS on PiBMA which was annealed at 120 °C to prevent dewetting of PS.

Measurements were done at Sector 8-ID of the Advanced Photon Source at Argonne National Laboratory using a previously described geometry and analysis procedure.^{38,40-43} Coherent x-rays (7.35 keV) probe the film surface below the angle of total external reflection; intensity is recorded by a 2D CCD camera. Fluctuations in off-specular scattering are analyzed, yielding the intensity autocorrelation function.

Bulk polymer tensile storage modulus (E') was determined by dynamic mechanical analysis (DMA; TA Instruments 2980) at 110 °C and 1 Hz frequency in strain-controlled tension. Samples were hot pressed and cut by razor blade into 3 x 20 x 0.5 mm strips. Thermal analysis was by DSC (Mettler-Toledo DSC 822e). Samples were heated to at least 30 °C above T_g to erase thermal history and then cooled below T_g at 40 °C/min and reheated at 10 °C/min. Reported $T_{g,bulk}$ values are second-heat T_g onset values.

Figures 1 shows decays of the normalized intensity autocorrelation function (normalized

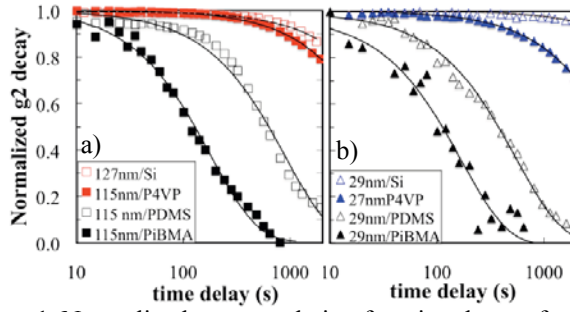


Figure 1. Normalized autocorrelation function decays for a) thin PS layers on various substrates ($q \sim 0.006 \text{ nm}^{-1}$) at 110°C and b) ultrathin PS layers on the same substrates ($q \sim 0.014 \text{ nm}^{-1}$) at 110°C . Curves are single exponential decay fits.

g_2) at 110°C for PS supported on the four substrates. The normalized g_2 decays were fit to single exponential decays ($e^{(-2t/\tau)}$, where the factor 2 comes from the fact that the correlation function is sensitive to the normalized intermediate scattering function squared,⁴¹ $f(q,t)^2 = (e^{(-t/\tau)})^2$) to determine the characteristic relaxation time for equilibrium surface height fluctuations (τ). Pronounced differences in τ are observed with substrate near the PS T_g , with relaxation times tracking qualitatively with the magnitude of underlayer modulus. Such effects are absent at 140°C . (Data not shown.) As measured by DMA at 110°C , moduli of 1800, 5.4 and 1.3 MPa were obtained for P4VP, crosslinked PDMS, and PiBMA, respectively; silicon wafers have reported modulus values of 125-180 GPa.⁴⁶ Relaxation times at the surface of 27-29 nm PS top layers are longest for PS on silicon ($\sim 85000 \text{ s}$)⁴⁷ followed by glassy P4VP (11500 s), cross-linked, rubbery PDMS (340 s) and rubbery PiBMA (110 s). (At the longest XPCS measurement time (2000 s), XPCS yields $\sim 10\%$ or less of the autocorrelation function decay for $\tau > \sim 40000 \text{ s}$; thus, τ values exceeding 40000 s have substantial quantitative uncertainty.⁴⁷ Nevertheless, τ values for PS on silicon are qualitatively much larger than for the same PS thickness on P4VP.) The role of substrate modulus is similarly evident in 115-nm-thick PS layers at 110°C , indicating the long-range effect of the substrate in perturbing the PS layer free-surface relaxations. (Relaxation times do not track with substrate T_g because cross-linked PDMS has an estimated T_g of -128°C ,⁴⁸ the lowest T_g of the three polymers.)

Figure 2a shows τ values of PS layers determined for a range of q values at 140°C . Far above T_g , the surface relaxations depend on film thickness but not appreciably on substrate. A

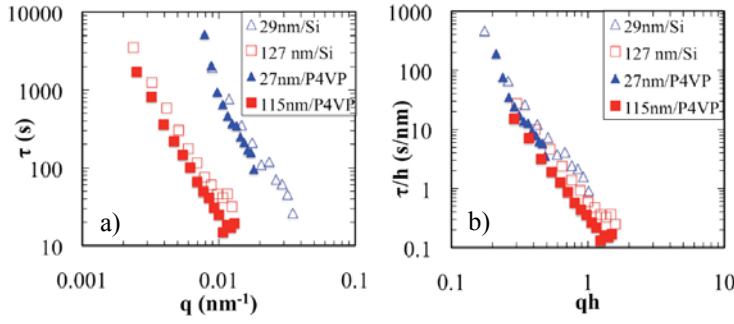


Figure 2. a) Capillary wave relaxation times at 140 °C for PS on silicon and P4VP. b) Relaxation times normalized by film thickness result in data overlap at 140 °C ($T_g + 40$ °C).

film thickness dependence of surface relaxations is well known and anticipated by simple capillary wave theory.³⁸ This theory predicts that the data in Figure 2a should overlap when τ/h is plotted as a function of qh , where h is the PS layer thickness. The excellent overlap of normalized surface relaxation time data in Fig. 2b indicates that simple capillary wave theory is valid at $T_{g,bulk} + 40$ °C for PS on silicon and P4VP. (Supported PS on PDMS and PiBMA dewetted during measurement at 140 °C, and thus no data is presented for these cases.) Therefore, at $T_{g,bulk} + 40$ °C there is no appreciable effect of confinement or substrate modulus.

Figure 3a depicts τ values extracted from the g_2 decays as a function of q for 115-127 nm PS layers atop the four substrates at 110 °C. Emphasizing the distance over which the substrate influences surface dynamics, a decrease in τ with decreasing substrate modulus is most pronounced at low q ($< \sim 0.01$ nm⁻¹), corresponding to larger length scale regions on the surface. The same qualitative behavior is observed in 27-29 nm PS layers at 110 °C (Fig. 3b). In both Figures 3a and 3b, we observe a transition to a weaker q -dependence of τ at lower q , most noticeably for the P4VP and PiBMA supported films. The transition to a weaker q -dependence for lower q may correspond to a transition from a viscosity dominated regime (high q) to a modulus dominated regime (low q). The underlayer is not anticipated to perturb the viscosity and modulus of the top PS layer in an identical manner, which is why the crossover occurs at different q for different substrates; however, further experiments would be required to confirm this hypothesis. We note that the lateral length scale being probed on the surface (which exceeds 1 μ m at low q) is unrelated to the PS layer thicknesses that exhibit substrate effects (as evidenced

by Fig. 2 data at 140 °C where substrate effects are absent in 27-127 nm layers even at low q). Fluorescence studies of bilayer films have revealed a strong dependence of the T_g of a thin top PS layer on the bulk underlayer T_g .^{15,16} For instance, when placed atop a 500-nm-thick PS underlayer, a 14-nm-thick dye-labeled PS top layer reports $T_g = T_{g,\text{bulk}} - \sim 32$ °C.^{3,4} In contrast, when placed on a 500-nm-thick PMMA layer, an identical PS top layer reports $T_g = T_{g,\text{bulk}} - \sim 2$ °C which was interpreted by the T_g dynamics of the top layer being slaved to those of the underlayer.¹⁶ Thus, neighboring immiscible domains may induce large changes in the T_g of an ultrathin layer. The present work reinforces the importance of neighboring layers as it shows that the dynamics associated with substrate modulus can exert a large influence on the surface wave relaxations of a thin top layer, even over thicknesses exceeding 100 nm.

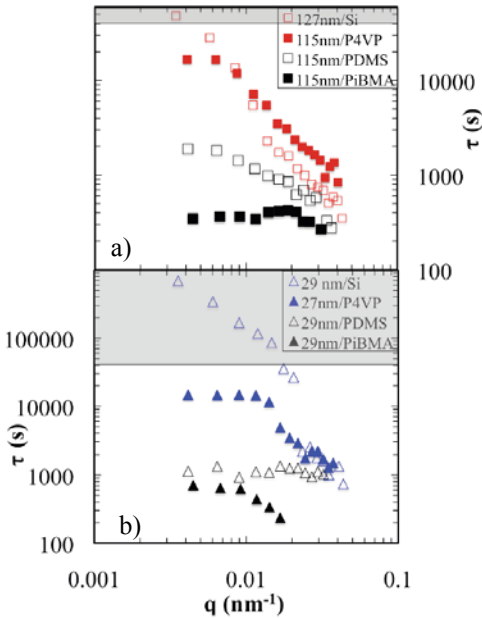


Figure 3. Capillary wave relaxation times for a) thin PS layers and b) ultrathin PS layers on silicon, P4VP, crosslinked PDMS, and PiBMA substrates measured at 110 °C.⁴⁹ Substrate moduli measured by DMA at 110 °C were 1800, 5.4, and 1.3 MPa for P4VP, PDMS, and PiBMA, respectively. Gray areas correspond to surface relaxation times exceeding 40000 s.⁴⁷

The extent to which substrate modulus influences capillary wave relaxation dynamics depends on temperature and the length scale probed by XPCS. The lack of substrate or confinement effects at high temperature or high q is potentially related to studies of T_g -confinement effects measured as a function of cooling rate. Using ellipsometry, Fakhraai and

Forrest⁹ showed that the T_g depression in thin supported PS films relative to $T_{g,bulk}$ is reduced with increasing cooling rate. A possible explanation concerns the temperature-dependent correlation length for glass transition dynamics; it is well accepted that the size-scale of cooperativity or the number of polymer segments involved in cooperative segmental mobility associated with the glass transition increases dramatically with cooling toward T_g .^{8,50,51} The measured T_g increases with increasing cooling rate because the material is unable to maintain equilibrium to the same temperature as at a lower cooling rate. Thus, the observation by Fakhraai and Forrest⁹ may be explained by the ideas that at higher cooling rates the T_g s reflect smaller cooperativity length scales and that the extent to which nanoscale confinement affects T_g tracks with the size scale of cooperativity at the measured T_g .¹⁰

The present results indicate that the effect of substrate modulus on PS surface capillary wave dynamics is most evident at q values and temperatures related to larger length-scale dynamics. Based on the explanation of the Fakhraai/Forrest results,⁹ measurements at higher temperatures, where cooperativity length scales are reduced, are expected to show a smaller (or even no) effect of substrate on PS surface relaxations. Measurements of supported PS layers at 140 °C support this idea as the substrate exerts negligible influence on PS surface dynamics (Fig. 2b). The fact that differences in surface relaxations are more pronounced at low q (at 110 °C) may also be influenced by the role of a slip/no-slip boundary condition. Simple capillary wave theory equations have been modified to include slip at a polymer/substrate interface.³⁹ Slip was predicted to reduce the lower q relaxation times, leaving higher q relaxation times unperturbed.

Figure 4 compares data for ultrathin (27-29 nm) and thin (115-127 nm) PS layers on the various substrates at 110 °C by plotting τ/h as a function of qh . While this format results in data overlap for the two thicknesses at 140 °C (Fig. 2b) in the absence of confinement or substrate effects, Fig. 4 shows stiffening behavior with confinement for $qh < \sim 0.7$ with a 29 nm PS layer reporting larger τ/h values than a 127 nm PS layer supported on silicon. (The data for 115 nm PS on P4VP do not extend to low enough qh to reveal appreciable confinement effects in the 27 nm PS on P4VP sample.) Stiffening behavior upon confinement was also observed for PS on

PiBMA and PDMS with a thinner PS layer reporting higher τ/h values than a thicker film on the same substrate. For example, τ/h increases by a factor of ~ 3 at $qh = 0.51$ for PS on PiBMA when the PS thickness is decreased from 115 to 29 nm. These results emphasize the role of length scale of the capillary waves on confinement effects. When probing higher q or measuring at higher temperatures (or shorter time scales, as in the Fakhraai/Forrest work⁹), confinement effects are less pronounced. Future work should bear this fact in mind, specifically when comparing data from techniques that are sensitive to different time and length scales.

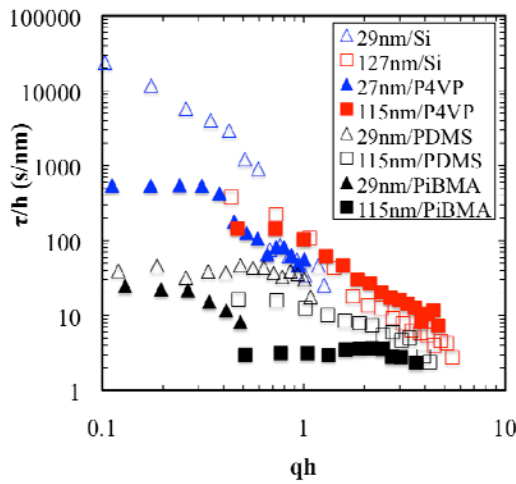


Figure 4. Capillary wave relaxation times normalized by PS layer thickness for thin (115 nm) and ultra thin (29 nm) PS layers on various substrates measured at 110 °C. In the absence of confinement or substrate modulus effects, the τ/h values should overlap for thin and ultrathin films.

The results from our bilayer studies indicate that there are two principal factors governing PS capillary wave relaxation near T_g . First, substrate modulus perturbs the PS top layer dynamics, with softer substrates leading to faster PS layer relaxations. Second, decreasing PS layer thickness increases the surface capillary wave relaxation times, specifically at low qh values. These factors compete to govern capillary wave relaxations and can be used to tune the dynamics of thin polymer layers.

For the first time, thin polymer layers supported on substrates with varying modulus were characterized by XPCS. At the PS $T_{g,bulk} + 9$ °C, the PS surface wave relaxation times track with substrate modulus, with lower modulus leading to faster PS surface relaxations even when the PS

top layers exceed 100 nm in thickness. These results show that an immiscible polymer domain may significantly influence the dynamics of a second, neighboring immiscible polymer at a temperature near the T_g of the second polymer and over length scales that greatly exceed those of both cooperative segmental mobility near T_g ($\sim 1-4$ nm)^{10,50} and the polymer radius of gyration. This work also illustrates the effect of confinement on surface wave relaxations in polymer films near T_g and at low qh (< 1), with τ/h values increasing with decreasing PS layer thickness when measured on a given substrate at 110 °C. In contrast, both substrate and confinement effects are negligible when measurements are taken far above T_g ($T_{g,bulk} + 40$ °C).

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