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Eliminating the Enhanced Mobility at the Free Surface of Polystyrene: Fluorescence Studies of the Glass Transition Temperature in Thin Bilayer Films of Immiscible Polymers

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ABSTRACT: By selective placement of fluorescent dyes, we have measured the glass transition temperature (T_g) of individual layers within supported bilayer films of different polymers to determine the extent to which strong free-surface effects and substrate interactions are mediated by a narrow interface between immiscible polymers. We have discovered that the impact a free surface has on T_g within an ultrathin PS layer is extremely sensitive to the polymer species used in the underlayer. The large T_g reduction of ~ 32 K relative to bulk T_g observed for a 14 nm thick surface layer of polystyrene (PS) supported on bulk PS is virtually eliminated when a 14 nm thick surface layer of PS is placed on an underlayer of poly(methyl methacrylate) or poly(2-vinylpyridine) (P2VP), even of bulk thickness. Thus, the cooperative segmental mobility associated with the T_g of the PS free-surface layer is greatly hindered by the narrow, several-nanometer-wide interfacial region formed with the dissimilar polymer underlayer. This indicates that the dynamics of nanoscale layers can be strongly modified by adjacent layers or domains of unlike polymers via propagation of effects across an interfacial layer of cooperatively rearranging regions containing segments of the two immiscible polymers, which has important implications for multilayer films and nanostructured blends. Conversely, the T_g of an ultrathin P2VP film is unaffected by the presence of a PS capping layer, indicating that strong attractive interactions of P2VP with hydroxyl groups on the surface of the silica substrate dominate over a much weaker free-surface effect in P2VP.

Introduction

Free surfaces and substrate interactions can significantly perturb the physical properties and dynamics of polymers and small-molecule glass formers that are confined at or near the nanoscale. One of the most heavily characterized confinement effects is that associated with the glass transition temperature (T_g); free surfaces, substrate interfaces, and confinement have led to deviations from bulk T_g ranging from the barely measurable to many tens of degrees kelvin.^{1–30} Rates of physical aging in the glassy state have also exhibited an array of effects associated with surfaces, interfaces, and confinement, ranging from enhancement to a nearly total arresting of aging.^{27–31} (For recent reviews of the effects of confinement on glassy material behavior, see refs 13 and 14.) Modification of the physical properties of polymer that is located tens of nanometers from a surface or interface impacts applications ranging from membranes for gas separation^{31,32} and photoresists in microelectronics³³ to nanocomposites.^{30,34,35}

Despite significant research, it remains unclear exactly how perturbations to the mobility of chain segments at an interface affect the cooperative segmental dynamics deep within a film. It is believed that the presence of a free surface typically results in enhanced mobility of chain segments residing at the free surface due to a reduction in the requirement for cooperativity

in the segmental mobility associated with T_g . This leads to a decrease of T_g in a layer adjacent to the free surface, and as shown in the case of polystyrene (PS), the bulk value of T_g (T_g^{bulk}) is only recovered several tens of nanometers into the film.⁵ The strength of this “free-surface effect” is dependent on the polymer repeat unit structure. Studies with free-standing films indicate that the T_g reductions associated with the free surface are roughly a factor of 3 larger for PS than for poly(methyl methacrylate) (PMMA).^{7,8}

The presence of attractive substrate interactions can reduce the mobility of chain segments, and the strength of this effect also depends on the polymer repeat unit structure. Increases in T_g with decreasing film thickness are observed for polymers that undergo secondary bonding with the substrate surface, such as PMMA² and poly(2-vinylpyridine) (P2VP)³ supported on silica which can hydrogen bond with hydroxyl groups naturally occurring on the silica surface. In contrast, PMMA films supported on gold show a decrease in T_g with decreasing thickness since there are no hydroxyl groups on the gold surface and hence no attractive polymer–substrate interactions to compete against the free-surface effect.² Several studies have shown that the extent of free-surface-induced T_g reductions can be controlled by fine-tuning the interactions at the substrate.^{15–18} In addition, grafting of chain ends^{19,20} or side groups¹⁹ to the substrate has yielded increases in T_g with confinement for PS supported on silica.

A major outstanding issue pertaining to the T_g –confinement effect is the large length scale over which perturbed cooperative dynamics originating at the free surface or substrate interface propagate into the film. For PS films supported on silica, deviations in T_g from T_g^{bulk} are observed for films less than

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~60 nm in thickness.^{1,5,6} The fact that there is no molecular weight (MW) dependence of the T_g -confinement effect in supported PS films for MWs from 2000 to 3 000 000 g/mol^{6,21} indicates that the effect is not related to the radius of gyration of the polymer. In contrast to the null MW effect, changes to the repeat unit structure of PS result in large changes to the T_g -confinement effect. For example, films of poly(4-*tert*-butylstyrene), with a large, rigid side group attached to the carbon-carbon single-bond backbone, show deviations in T_g from T_g^{bulk} at thicknesses of 300–400 nm.⁶ Ellison and Torkelson suggested that the length scale over which perturbations to T_g originating at a surface propagate into a film may be linked not to that of an individual cooperatively rearranging region (CRR), which is only a few nanometers near T_g ,⁶ but to the “length scale encompassing the full breadth of the distribution of cooperative relaxation dynamics in bulk glass formers”,⁵ which is expected to be many tens of nanometers^{36,37} and a function of repeat unit structure. An assumption made by Adam and Gibbs,³⁸ who defined CRRs in their study of the glass transition, is that the cooperative mobility in an individual CRR is independent of neighboring CRRs. This can be used to justify models^{39,40} that indicate that perturbations to T_g caused by surfaces are limited to length scales similar to those of CRRs. However, the results of the multilayer film studies by Ellison and Torkelson⁵ indicate that when the average cooperative dynamics in a layer of CRRs are perturbed substantially relative to bulk by the presence of a free surface, then the average dynamics of neighboring layers of CRRs are also perturbed but to a lesser extent.

Given the large length scales over which perturbed T_g dynamics originating at a surface or substrate propagate into a film, an interesting system for investigation is that involving bilayer films, with one layer being PS, which exhibits a strong free-surface effect on T_g , and the second layer being a polymer that is immiscible with PS and exhibits attractive interactions with a silica substrate. Examples of such a polymer are P2VP³ and PMMA.² No study of the T_g -confinement effect in an immiscible bilayer film system has been previously reported. However, recent studies^{41,42} have indicated that a low-viscosity interfacial region is present in the liquid state of PS/poly(4-bromostyrene) bilayer films and that a wrinkling instability in the PS capping layers of PS/poly(ethylene oxide) (PEO) bilayer films is caused by strain induced by changes in the PEO/PS interfacial area during melting of PEO.

While many techniques can measure the T_g in single-layer ultrathin films,¹³ the use of fluorescent dyes as local probes of T_g provides unique advantages in multilayer films. By placing a dye within a single layer of a multilayer film, T_g can be probed as a function of distance from an interface or surface.⁵ Using this approach with pyrene-labeled polymer, Ellison and Torkelson⁵ discovered that a layer of PS adjacent to a free surface has a significantly reduced T_g and that this effect persists for several tens of nanometers into a PS film. Attempts at using doped or labeled pyrene^{5,6,10,27,43} have proven unsuccessful in yielding precise T_g determinations in ultrathin films of P2VP.⁴⁴ Thus, here we use the fluorescence of a wavelength-shifting, charge-resonance dye, 7-(dimethylamino)-1-methylquinolinium tetrafluoroborate (QB),^{45–47} to measure T_g in thin and ultrathin P2VP films. Recent studies in bulk films have shown that this dye is sensitive to T_g via the temperature dependence of the position of the intensity maximum of the fluorescence emission spectrum.^{46,47} This sensitivity to T_g by a shift in the energy (wavelengths) associated with the fluorescence emission spectrum is fundamentally different from that of pyrene, which

exhibits a change in the temperature dependence of the fluorescence emission intensity at T_g . Identifying T_g by a shift in the emission spectrum has the advantage that the measurement is insensitive to changes in intensity due to dye sublimation or photobleaching. Other wavelength-shifting dyes, such as charge-transfer probes, are also sensitive to T_g .⁴⁸

Here we show that fluorescence of the QB dye yields T_g values of P2VP films that are in excellent agreement with previous measurements on ultrathin P2VP films by X-ray reflectivity³ and ellipsometry.¹⁵ We exploit the advantage of fluorescence by selectively placing dyes (QB dopants or pyrene labeled to polymer at trace levels) to measure the T_g s of individual layers within bilayer films. We find that the strong substrate interactions dominate the dynamics of the P2VP underlayer films while the T_g values of the ultrathin PS surface layers are highly sensitive to the underlying material. In particular, the substantial reduction observed in T_g at or near the free surface of PS films can be nearly eliminated when an ultrathin layer of PS is placed atop a PMMA or P2VP layer.

Experimental Section

The T_g s of P2VP films were measured using a charge-resonance dye, 7-(dimethylamino)-1-methylquinolinium tetrafluoroborate (QB).^{45–47} The content of the QB dye in the P2VP films was <0.2 wt % of dry polymer content. Poly(2-vinylpyridine) from Scientific Polymer Products (reported value of $M_v = 200\,000$ g/mol) was used after drying the as-received material in a vacuum oven at ~383 K to remove residual monomer. Thin films of P2VP with the QB dye were spin-coated⁴⁹ from dilute solutions using 1,1,2-trichloroethane to produce smooth films with uniform thickness while maintaining the strong fluorescence activity of the QB dye.⁵⁰ The silica substrates were initially cleaned with base (10 wt % sodium hydroxide, 20 wt % water, 70 wt % ethyl alcohol) and acid (1 M HCl) solutions, rinsed thoroughly, and then subsequently solvent-cleaned between experiments. The T_g measurements by fluorescence of thick films agreed well, to within experimental error, with the onset T_g value of 374 K from differential scanning calorimetry (DSC) (Mettler-Toledo DSC822, second heating at 10 K/min).

The steady-state fluorescence of the QB dye was measured using a Photon Technology International fluorimeter. The excitation wavelength was 430 nm, and emission spectra were collected from 460 to 675 nm. The angle of incidence of the beam normal to the sample was maintained at 34° to eliminate backscattering of the excitation light. Slit widths were adjusted in order to obtain sufficient fluorescence intensity at the detector: 1.5 mm excitation and 3 mm emission slits (band-pass = 6 nm) were used for films with thicknesses (h) > 300 nm, 2 mm excitation and 4 mm emission slits (band-pass = 8 nm) for films with $h = 100$ –300 nm, and 3 mm excitation and 6 mm emission slits (band-pass = 12 nm) for films with $h < 100$ nm. A neutral density filter with 50% transmission was generally used to reduce the intensity of the excitation beam in order to limit photobleaching of the QB dye; use of the filter was not absolutely necessary as the method employed for determining T_g via intensity ratio (discussed in Results section) is insensitive to overall changes in intensity. A quartz cover slide was placed on top of each film to reduce the potential for probe sublimation during measurement; however, the film adhered only to the glass substrate on which it was spin-coated.

Sample temperature was controlled to within ± 0.2 K using a microprocessor-controlled (Minco Products) Kapton ribbon heater with a resistance temperature detector. Samples were heated to a temperature at least 25 K above the expected T_g of the film and equilibrated for 15 min before T_g measurements were made upon cooling in 5 K increments, waiting 5 min after each temperature jump before taking a fluorescence spectrum. Data were collected well below (~40 K) the measured film T_g to ensure sufficient data for an accurate determination of T_g .

Bilayer films with top layers of PS (neat or pyrene-labeled) were spin-coated from toluene directly onto the P2VP films, since toluene

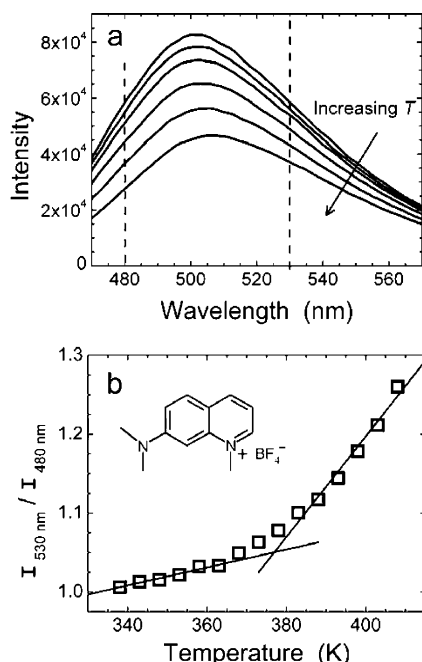


Figure 1. Fluorescence emission spectra of the QB dye doped at 0.2 wt % in a 2.0 μm thick P2VP film taken upon cooling from 413 to 333 K; spectra every 15 K are shown in (a). The vertical dashed lines to the left and right of the peak indicate the wavelengths used to calculate the intensity ratio $I_{530\text{ nm}}/I_{480\text{ nm}}$, shown in (b) as a function of temperature, which highlights the small shift in peak emission wavelength as a function of temperature used to identify $T_g = 377$ K for this film. The chemical structure of the QB dye is shown in the inset.

is a nonsolvent for P2VP.⁵¹ However, bilayer films with underlayers of PMMA (Pressure Chemical, $M_w = 255\,000$ g/mol, $M_w/M_n \leq 1.15$, T_g by DSC (onset) = 393 K) were made by spin-coating the PS layer onto mica substrates and subsequently floating them onto the PMMA films using a water transfer process.²⁵ Pyrene-labeled PS was synthesized by copolymerizing 1-pyrenylbutyl methacrylate with styrene, resulting in a polymer in which 1 in 338 repeat units is a pyrene-labeled methacrylate, with $M_n = 464\,000$ g/mol and $M_w/M_n = 1.57$, as determined by gel permeation chromatography (GPC) (Waters) relative to PS standards. Details of the synthesis are reported in ref 5.

Steady-state fluorescence of multilayer films containing the labeled pyrene dye was measured using a SPEX Fluorolog II fluorimeter. The pyrene dye was excited at 324 nm with emission collected from 360 to 460 nm using a front-face geometry with 5 mm slits (band-pass = 9 nm). The T_g was identified by a break in the linear increase in fluorescence intensity with decreasing temperature as described in ref 5. For bulk pyrene-labeled PS, $T_g^{\text{bulk}} = 377$ K by DSC (onset) and 375 K by fluorescence. Film thicknesses were measured using a Tencor P10 profilometer or a Woollam M-2000D spectroscopic ellipsometer.

Results and Discussion

We have used the wavelength-shifting QB dye^{45–47} (see Figure 1) to measure the T_g s of thin and ultrathin P2VP films. The fluorescence spectrum of the QB dye red shifts slightly with increasing temperature and is sensitive to T_g when lightly doped in P2VP. Figure 1a shows emission spectra of the QB dye doped at 0.2 wt % in a 2 μm thick P2VP film taken upon cooling from 413 to 333 K (only spectra every 15 K are shown for clarity). Given that the emission peak of the QB dye is very broad and the shift in the wavelength of maximum intensity is relatively small (7 nm or less over the temperature range shown in Figure 1a), we have chosen not to use the temperature dependence of the wavelength of maximum emission intensity

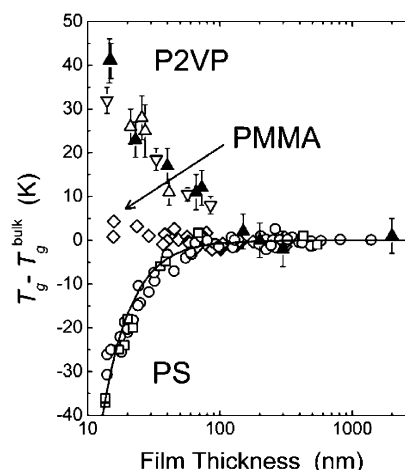


Figure 2. $T_g - T_g^{\text{bulk}}$ as a function of film thickness for P2VP films measured by fluorescence (solid triangles, QB doped P2VP), X-ray reflectivity (hollow up triangles) from ref 3, and ellipsometry (hollow down triangles) from ref 15; for PMMA films measured by ellipsometry (hollow diamonds) from ref 2; and for PS films measured by fluorescence (hollow circles, pyrene doped PS and hollow squares, pyrene-labeled PS) from refs 5 and 6.

to identify T_g , which was previously used for T_g determination in bulk films in refs 46 and 47. Instead, we employed a ratio of intensities at fixed wavelengths above and below the peak maximum to characterize the shift in the position of the broad spectrum. (The use of intensity ratios to characterize the shift in the emission spectra of wavelength-shifting chromophores was described previously in refs 52 and 53, where the applications were related to in-situ, nondestructive monitoring of various phenomena in polymeric media ranging from sorption and mixing to fractional conversion during curing/polymerization.) The wavelength values used to calculate the intensity ratios ($\lambda_1 = 530$ nm and $\lambda_2 = 480$ nm) are indicated by vertical, dashed lines in Figure 1a. In order to obtain the most precise results, linear fits to the intensities were performed over small regions, 20 nm in breadth for $\lambda_1 = 530$ nm and 12 nm in breadth for $\lambda_2 = 480$ nm, of each spectrum in the neighborhood of the chosen wavelengths. The values of λ_1 and λ_2 were chosen to be in the middle of the nearly linear regions adjacent to the peak.

Figure 1b shows that the temperature dependence of the intensity ratio $I_{530\text{ nm}}/I_{480\text{ nm}}$ undergoes a characteristic change near T_g . The T_g is identified by the intersection of two linear best-fit lines determined using data far above and below the transition. For a 2.0 μm thick P2VP film, $T_g = 377 \pm 4$ K via fluorescence,⁵⁴ which is within experimental error of $T_g = 374$ K obtained by DSC (onset) for bulk P2VP.

Similar analysis was done of the temperature dependence of the QB dye fluorescence spectra obtained for all P2VP films ranging in thickness from 15 nm to 2.0 μm. However, a different set of λ_1 and λ_2 values were used for the thinner films because the peak position of the QB emission spectrum was substantially red-shifted by ~8 nm in the thinner films.⁵⁵ As a result, $\lambda_1 = 540$ nm and $\lambda_2 = 490$ nm were chosen for determining intensity ratios for film thicknesses ≤ 150 nm. The reasons for the observed spectral shift of QB and other wavelength-shifting dyes in ultrathin films are the subject of current study.⁵⁵

Figure 2 shows $T_g - T_g^{\text{bulk}}$ values as a function of film thickness for three different polymers supported on silica substrates. The data obtained for single-layer films of P2VP via fluorescence of the QB dye are in excellent agreement with the limited T_g values previously measured by X-ray reflectivity³ and ellipsometry¹⁵ for P2VP films supported on silica (shown as hollow triangles in Figure 2). The data in Figure 2 indicate

that P2VP exhibits a very strong increase in T_g with decreasing film thickness below 150 nm. This behavior has been explained as originating from the hindered dynamics at the substrate interface caused by the strong interaction of the nitrogen atom in the P2VP repeat unit with the hydroxyl groups at the substrate interface.³ For comparison, we have included thickness-dependent $T_g - T_g^{\text{bulk}}$ data in Figure 2 for ultrathin PS films (from refs 5 and 6 obtained using fluorescence) and for ultrathin PMMA films (from ref 2 obtained using ellipsometry). Ultrathin PS films supported on silica display a strong decrease in T_g with decreasing thickness since there is no mechanism by which preferential bonding or attractive interactions with the substrate can occur and thereby compete with the strong, well-characterized “free-surface” effect in these systems.^{3,56} In contrast, PMMA, which has a repeat unit structure that can hydrogen bond with the hydroxyl groups on the silica substrate, displays a slight increase in T_g with decreasing film thickness. Measurements on free-standing PS and PMMA films have shown that T_g reductions observed with decreasing thickness due to the presence of the free surface are ~ 3 times larger for PS than for PMMA.^{7,8} This indicates that the attractive substrate interactions present in the PMMA films supported on silica have a greater impact in modifying the T_g behavior across the films than does the relatively weak “free-surface effect” present in PMMA films.

The fact that supported, ultrathin P2VP films show an increase in $T_g - T_g^{\text{bulk}}$ that is much greater at a given thickness than that for supported, ultrathin PMMA films (>35 K difference in 15 nm thick films) suggests two possibilities regarding the origins of the T_g -confinement effect in P2VP. The first is that the free-surface effect leading to a T_g reduction at a P2VP free surface may be weak in comparison to that exhibited by PMMA and nearly negligible in comparison to that exhibited by PS. (To date, no measurement of T_g has been performed on free-standing films of P2VP.) In addition, the attractive substrate effect may be substantially greater for P2VP on silica substrates than for PMMA, which may arise from two separate considerations. The interaction between the repeat unit and the substrate may be more favorable for P2VP, and/or the hindered mobility due to this favorable interaction with the substrate may restrict chain conformations and cooperative segmental mobility more readily in P2VP than in PMMA.

To investigate the impact of the free-surface effect on P2VP, we measured the T_g s of 40 nm thick P2VP layers supported on silica substrates in various multilayer geometries, as outlined in Figure 3. This was accomplished without difficulty using the QB dye doped freely in the P2VP layers since the dye is insoluble in PS and, therefore, does not migrate into the PS layer during measurement.⁵⁷ Capping a 40 nm thick P2VP film with either a 78 nm thick layer or a 10 nm thick layer of PS, both of which effectively eliminate the free surface of the P2VP layer, does not appreciably affect the T_g of the underlying P2VP layer. For all cases depicted in Figure 3, the T_g s of the P2VP films/layers are identical within experimental error and significantly increased relative to T_g^{bulk} . This indicates that the cooperative segmental dynamics of the 40 nm thick P2VP layers supported on silica are dominated by the strong attractive substrate interactions, irrespective of the P2VP surface being uncapped or capped by a thin or ultrathin PS layer.⁵⁸

Using pyrene-labeled PS, we measured the T_g of PS free-surface layers supported on P2VP or PMMA underlayers. Earlier studies of PS multilayer films by Ellison and Torkelson⁵ using pyrene-labeled PS revealed that free-surface layers of PS exhibit significantly reduced T_g values relative to bulk. Figure 4a–c shows schematically three multilayer geometries studied by

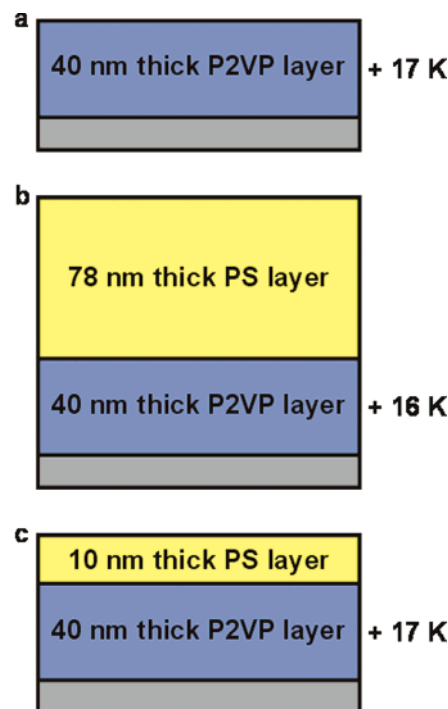


Figure 3. $\Delta T_g = T_g - T_g^{\text{bulk}}$ values for 40 nm thick P2VP films doped with the QB dye supported on silica substrates that are uncapped (a), capped with a 78 nm thick layer of PS (b), or capped with a 10 nm thick layer of PS (c). (The experimental error associated with each ΔT_g value is ± 4 K.)

Ellison and Torkelson, indicating the large negative values of $\Delta T_g = T_g - T_g^{\text{bulk}}$ measured for 12 and 14 nm thick PS surface layers supported on 12, 46, or 500 nm thick underlayer films of PS. (We have repeated these measurements and obtained similar, large negative ΔT_g values.) For cases in which the underlayer PS films are at least 46 nm thick, the 14 nm thick PS surface layers exhibit a common ΔT_g value of ~ -32 K, which indicates that the cooperative segmental dynamics associated with T_g in the free-surface layer are unaffected by the presence of the substrate. However, when the overall bilayer film thickness is 24–60 nm, Ellison and Torkelson⁵ found that the T_g of the free-surface layer increases with decreasing thickness, which they interpreted as being related to a limitation in the gradient in cooperative dynamics from the free surface to the substrate interface that could be supported over several tens of nanometers. Here, in order to investigate the impact of the underlying material on the T_g of the PS surface layer, we have performed related measurements in which we have placed 12 and 14 nm thick layers of PS on top of 12, 46, or 500 nm thick layers of PMMA (Figure 4d–f) or P2VP (Figure 4g–i).

Figure 4h is analogous to the case of Figure 3c; thus, we know that the T_g of the underlying P2VP layer in Figure 4h is unaffected by the presence of the PS surface layer and that the ΔT_g value of the P2VP layer is expected to be ~ 15 K. Figure 4h shows that the T_g value of the 14 nm thick PS surface layer is nearly unchanged relative to T_g^{bulk} , in strong contrast to the case shown in Figure 4b where the T_g value of a 14 nm thick PS surface layer sitting atop a 46 nm thick PS layer exhibits a ~ 32 K reduction relative to T_g^{bulk} . This indicates that the T_g of the PS surface layer in Figure 4h is greatly affected by the underlying P2VP layer. Nearly identical outcomes are observed via comparisons of Figure 4e with Figure 4b and Figure 4f,i with Figure 4c. In all cases, the T_g value of a 14 nm thick PS surface layer sitting atop a 46 nm thick or 500 nm thick PMMA or P2VP layer is within several degrees of T_g^{bulk} and vastly

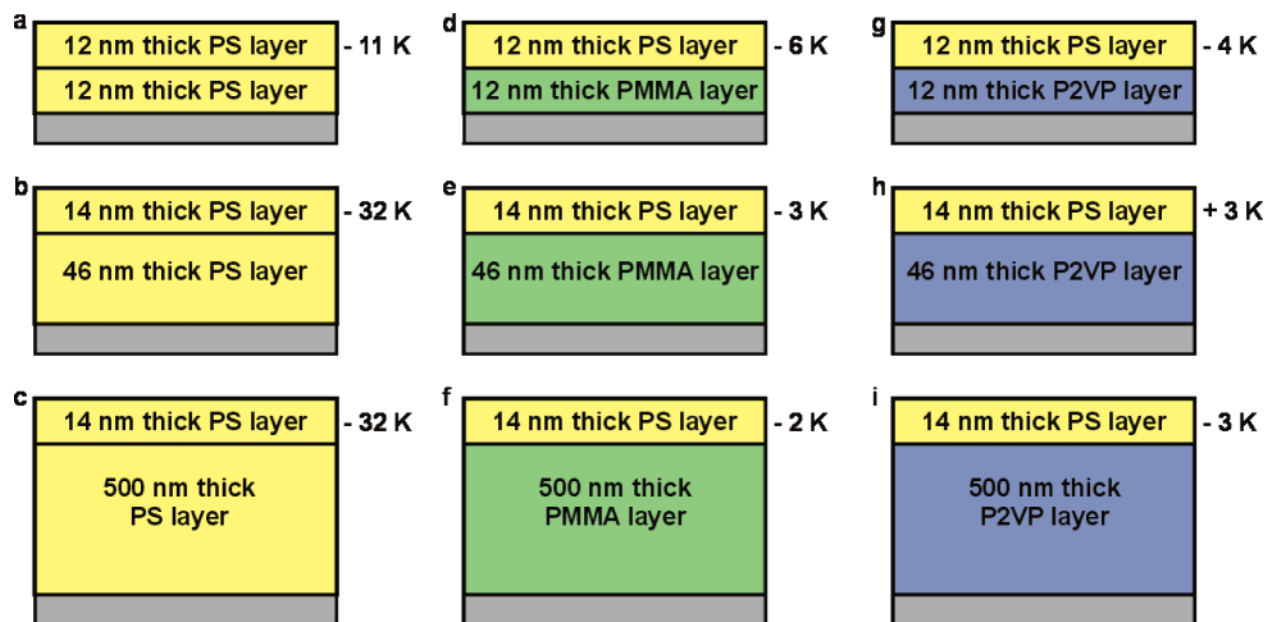


Figure 4. $\Delta T_g = T_g - T_g^{\text{bulk}}$ values for 12 and 14 nm thick pyrene-labeled PS free surface layers supported on top of 12, 46, or 500 nm thick films of PS (a–c), PMMA (d–f), and P2VP (g–i). Silica substrates are the underlying support in all cases. (The error bars associated with the ΔT_g values are ± 2 K in (a–c) and ± 2 –3 K in (d–i).)

different from the large 32 K reduction in T_g relative to T_g^{bulk} observed in analogous bilayer PS films. These results demonstrate that strong reductions in T_g relative to T_g^{bulk} at the free surface of certain types of films can be virtually eliminated by producing bilayer films with the underlayer polymer species carefully selected to modify and control the properties of the free surface.

The situation is more complex when comparing the ΔT_g values of the 12 nm thick PS surface layers in Figure 4d ($\Delta T_g = -6$ K) and Figure 4g ($\Delta T_g = -4$ K) with Figure 4a ($\Delta T_g = -11$ K). Given the fact that nanoscale confinement is limiting the magnitude of the T_g reduction in the 12 nm thick PS surface layer sitting atop a 12 nm thick PS underlayer (Figure 4a),⁵⁹ it may also be anticipated that the nanoscale confinement in the 24 nm thick PS/PMMA and PS/P2VP bilayer films (Figure 4, d and g, respectively) would alter the T_g behavior of the PS free-surface layer. The fact that the values of ΔT_g for the 12 nm thick PS surface layers are less negative in the 24 nm thick bilayer films containing PMMA and P2VP underlayers than in the bilayer film containing only PS may be a reflection of two possible effects. First, the attractive substrate interactions at the PMMA–substrate and P2VP–substrate interfaces which slow cooperative segmental dynamics many tens of nanometers within PMMA and P2VP single-layer films may also be able to propagate across the PS/PMMA and PS/P2VP interfaces, thereby making the ΔT_g values less negative in the PMMA/PS and P2VP/PS bilayer films. Second, the PS surface layer may also be sensitive to the increased T_g of the underlying 12 nm thick layers of PMMA or P2VP (relative to that of the underlying 12 nm thick PS layer in Figure 4a).

In any case, Figure 4 clearly establishes that an ultrathin PS surface layer is extremely sensitive to the polymer species used in the underlayer. These results have important implications for developing a fundamental understanding of the roles of surfaces, interfaces, and confinement in altering properties in polymers, including T_g . From a scientific standpoint, these results may be considered remarkable because, even though only a few nanometers of the 14 nm thick PS surface layer are incorporated into the interface with the underlying polymer, the remaining ~ 10 nm of PS in the free-surface layer is also greatly affected.

Several studies have previously indicated that 10–14 nm thick single-layer PS films supported on silica exhibit ΔT_g values of at least -35 K.^{1,5,20} Thus, in our PS/PMMA and PS/P2VP bilayer films shown in Figure 4, the cooperative segmental mobility of the PS surface layer is greatly hindered by its narrow interfacial region with the underlying PMMA or P2VP layer.⁶⁰ (The equilibrium interfacial width between PS and PMMA has been reported to be 5.0 nm,⁶¹ which is larger than the value of 3.4 nm reported for PS and P2VP.⁶²) The narrow interface creates interpolymer CRRs in which both PS and PMMA or PS and P2VP segments must move together for cooperative motions to occur. Surprisingly, both bulk PMMA and P2VP produce approximately the same impact on the T_g of the PS surface layer despite differing interfacial widths. A larger interfacial width may be expected to allow for increased dynamical coupling between the layers. However, it is worth noting that T_g^{bulk} of PMMA is ~ 20 K higher (393 K by DSC) than that of P2VP (374 K by DSC), resulting in a possibly stiffer underlayer in PS/PMMA bilayer films when the top PS layer passes through its T_g . Further study is warranted using underlayer polymers with T_g^{bulk} values vastly different from that of PS and for which there is greater tunability of the interfacial layer thickness.

The discovery that the strong free-surface effect leading to a sharp reduction in the T_g at the free surface of certain polymer films can not only be mediated but virtually eliminated also has important implications for technological applications of films and coatings in which control of the T_g of the surface layer is vital. In addition, these results indicate that multilayer films with layer thicknesses at or near the nanoscale^{63–65} and nanostructured or quasi-nanostructured polymer blends with substantial interfacial area^{66–68} have the potential for properties that are strongly modified from those expected on the basis of the behavior of bulk, neat polymer or thin films of individual polymers. Bilayer and multilayer experiments employing fluorescence dyes in one layer provide a particularly sensitive method for characterizing novel behavior associated with nanostructured multilayer films and nanostructured blends, and further studies are underway.

Summary

We have employed a wavelength-shifting dye, 7-(dimethylamino)-1-methylquinolinium tetrafluoroborate (QB), to measure the T_g of ultrathin films of P2VP, which demonstrate a large increase in T_g with decreasing film thickness due to strong, attractive interactions with the silica substrates. We find that the large T_g increase exhibited in ultrathin P2VP films is unperturbed by the presence of a PS capping layer, indicating that the strong substrate interactions dominate and that the impact of the free surface on P2VP may be negligible in dictating the T_g behavior of supported, ultrathin P2VP films. In contrast, the T_g of a PS surface layer in a bilayer film is extremely sensitive to the polymer species used in the underlayer. Exploiting the advantages of the fluorescence technique, we explored the competing strong free-surface effects and substrate interactions acting across PS/P2VP and PS/PMMA bilayer films by measuring the T_g of PS surface layers using a covalently labeled pyrenyl dye. The large T_g reductions observed in 14 nm thick PS surface layers supported on bulk PS are nearly completely eliminated when the 14 nm thick PS surface layers are placed on bulk P2VP or bulk PMMA. These findings indicate that the dynamics of nanoscale layers can be greatly influenced by adjacent domains even when the two polymers form a narrow interface. This has important implications for understanding the roles of surfaces, interfaces, and confinement in modifying glass transition behavior in amorphous polymers, multilayer films, and nanostructured blends of immiscible polymers.

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- (51) Similar results were obtained when bilayer films consisting of a P2VP underlayer and a PS capping layer were made by floating the PS layer on water and picking up the PS layer with the P2VP film supported on silica. However, the approach of directly spin-coating PS onto the P2VP film eliminates any concerns about water sorption by the P2VP film when it is used to pick up the floating PS capping layer.
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- (58) We note related measurements by Lin and Blum [Lin, W.-Y.; Blum, F. D. *J. Am. Chem. Soc.* **2001**, *123*, 2032–2037], who observed a disappearance of the slightly enhanced dynamics at the free surface of an adsorbed poly(methyl acrylate) film upon capping with a PS overlayer.
- (59) This behavior was explained in ref 5 as resulting from the requirement for PS films supported on silica to be at least ~ 60 nm thick in order to support a gradient in dynamics with a 14 nm thick surface layer exhibiting $T_g = T_g^{\text{bulk}} - 32$ K and $T_g = T_g^{\text{bulk}}$ somewhere in the interior of the PS film.
- (60) For the high MW value of PS used in this study, we do not anticipate any dewetting of the ultrathin PS surface layers during the time scale of the experiment. In addition, it has been well documented with block copolymer films of poly(styrene-*block*-methyl methacrylate) [Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. *Phys. Rev. Lett.* **1989**, *62*, 1852–1855] and poly(styrene-*block*-vinylpyridine) [Sohn, B.-H.; Seo, B.-W.; Yoo, S. I.; Zin, W.-C. *Langmuir* **2002**, *18*, 10505–10508] that the favorable interfacial interactions are maximized when PS is at the free surface and PMMA or P2VP is at the substrate interface. Even for miscible blend systems, there is nearly complete surface enrichment of the lower surface energy component [Jones, R. A. L.; Kramer, E. J. *Polymer* **1993**, *34*, 115–118], meaning that for the PS/PMMA and PS/P2VP bilayer films (an immiscible blend system) we do not expect any PMMA or P2VP segments to be present at the free surface.
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