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# Effects of Nanoscale Confinement and Interfaces on the Glass Transition Temperatures of a Series of Poly(n-methacrylate) Films

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We use fluorescence from dye-labelled polymer to measure the glass transition temperatures ( $T_g$ s) across single-layer films and near surfaces and silica interfaces in bilayer films for a series of poly(n-methacrylate)s. With nanoscale confinement, the average  $T_g$  across a film supported on silica increases for poly(methyl methacrylate) (PMMA), decreases for poly(ethyl methacrylate) (PEMA) and poly(propyl methacrylate), and is nearly invariant for poly(*iso*-butyl methacrylate) (PIBMA). These trends are consistent with the relative strengths of local perturbations to  $T_g$  caused by surfaces and substrates as measured in bilayer films. The substrate effect, which increases  $T_g$  via hydrogen-bonding interactions between the polymer and hydroxyl groups on the silica surface, is stronger than the free-surface effect in PMMA. The free-surface effect, which reduces  $T_g$  via a reduction in the required cooperativity of the glass transition dynamics, is stronger than the substrate effect in PEMA. The substrate and free-surface effects have similar strengths in perturbing the local  $T_g$  in PIBMA, resulting in a net cancellation of effects when measurements are made across single-layer films.

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## Introduction

As the confining dimension is decreased below a certain critical value in thin polymer films (with thickness as the confining dimension) and polymer nanocomposites (with internanoparticle distance as the confining dimension), an increasingly large fraction of polymeric material is directly in contact with interfaces or surfaces. Properties can be strongly perturbed by the interfacial interactions and surfaces in such confined polymers, and these perturbations to average properties or the distributions of properties within such systems are commonly referred to as the confinement effect. The study of the effect of nanoscale confinement on the glass transition temperature  $(T_g)$  of amorphous polymers began more than a dozen years ago.<sup>[1,2]</sup> In 1994, Keddie et al. showed that ultrathin polystyrene (PS) films exhibit a reduction in  $T_g$  with decreasing thickness.<sup>[1]</sup> In the same year, they also found that ultrathin poly(methyl methacrylate) (PMMA) films exhibit a  $T_{\rm g}$ -confinement effect that depends on the substrate supporting the films, with  $T_g$  decreasing with confinement when PMMA is supported on gold and increasing with confinement when PMMA is supported on silica.<sup>[2]</sup> Since then, many studies have demonstrated that nanoscale confinement of amorphous polymers can lead to changes in  $T_g$  and related dynamics from their bulk values, whether in supported polymer films,<sup>[1-30]</sup> freely standing polymer films,<sup>[31-34]</sup> or polymer nanocomposites.<sup>[19,20]</sup> This behaviour has implications for applications ranging from photoresists to asymmetric membranes.

In systems exhibiting a decrease in  $T_g$  with confinement, [1,2,4-14,18,21,22,24-28] it is now reasonably well accepted that the effect originates at the free surface or polymer-air interface.<sup>[4,11,15]</sup> Taking advantage of the fact that fluorescence has proved to be very useful in studies of dynamics and thermodynamics associated with polymer-based materials,<sup>[35–46]</sup> our group developed a novel multilayer fluorescence technique that demonstrated that  $T_g$  reductions originating at the free surface can propagate some tens of nanometres into the film interior.<sup>[11,15,16,17,24]</sup> This behaviour can be understood qualitatively by recognizing that the glass transition in polymers is associated with cooperative segmental mobility of tens to hundreds of repeat units and that the presence of the free surface locally reduces the requirement for cooperativity, thereby reducing  $T_{g}$ .<sup>[11]</sup> In contrast, the presence of attractive polymer– substrate or polymer-nanoparticle interactions, e.g. hydrogen bonds, increases the requirement for cooperativity in the dynamics associated with the glass transition.[3,5,12,13,15,17-20] This leads to an increase in  $T_g$  with confinement<sup>[2,3,5,8,12,13,15,17–20]</sup> when the effects of attractive interactions are strong and dominate the free-surface effects. Although most research in this area has been experimental, simulations  $^{[47-50]}$  have reached similar conclusions regarding the roles of free surfaces and attractive

Table 1.	Molecular characterization and bulk T <sub>g</sub> s of polymer	rs used in the present study
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DSC, differential scanning calorimetry; PMMA, poly(methyl methacrylate); PEMA, poly(ethyl methacrylate); PPMA, poly(propyl methacrylate); PIBMA, poly(*iso*-butyl methacrylate)

Material	$M_{\rm n}  [{\rm g}  {\rm mol}^{-1}]$	$M_{\rm w}/M_{\rm n}$	Bulk T <sub>g</sub> [K] (onset, DSC)	Bulk T <sub>g</sub> [K] (fluorescence)	Label content [mol-%]
PMMA	355 000 <sup>A</sup>	1.54 <sup>A</sup>	394	_	_
PEMA	460 000 <sup>B</sup>	1.70 <sup>B</sup>	348	_	_
PIBMA	300 000 <sup>B</sup>	2.00 <sup>B</sup>	337	_	_
TC1-labelled PMMA	509 000 <sup>A</sup>	1.67 <sup>A</sup>	394	395	1.4
Pyrene-labelled PEMA	202 000 <sup>B</sup>	1.80 <sup>B</sup>	348	347	0.6
Pyrene-labelled PPMA	188 000 <sup>B</sup>	1.78 <sup>B</sup>	320	320	0.3
TC1-labelled PIBMA	$181000^{B}$	1.96 <sup>B</sup>	337	339	0.6

<sup>A</sup>Determined via gel permeation chromatography using the universal calibration method and appropriate Mark–Houwink parameters.

<sup>B</sup>Determined via gel permeation chromatography relative to polystyrene standards using tetrahydrofuran as eluent.

polymer–substrate interactions in defining the  $T_{g}$ -confinement effect. Recent reviews summarize the results, progress, and challenges in this field.<sup>[51–53]</sup>

Recently, our group<sup>[10]</sup> investigated the impact of slight modifications to the repeat unit structure of PS on the  $T_{g}$ -confinement effect observed in films supported on silica. In addition to PS, we studied two other systems, including poly(4-methylstyrene) (P4MS) and poly(tert-butylstyrene) (PTBS), none of which exhibits any significant attractive interaction with hydroxyl groups on the surface of the silica substrate; this means that all  $T_{\rm g}$ -confinement effects originate at the free surfaces of PS, P4MS, and PTBS films. We observed that the  $T_g$  reductions in the ultrathin films increased dramatically with the presence of large, rigid side groups on the phenyl ring. In the case of 25nm-thick films supported on silica, we obtained the following reductions in  $T_g$  relative to bulk  $T_g$ : ~12 K for PS, ~18 K for P4MS, and  $\sim 47$  K for PTBS.<sup>[10]</sup> In addition, the onset thickness for the  $T_g$  reduction in PTBS was 300–400 nm, much larger than in PS or P4MS, where the onset thickness for the  $T_{g}$  reductions is  $\sim 60 \text{ nm}$ .<sup>[10]</sup> These results indicate that small changes to the repeat unit structure of the polymer, presumably leading to changes in the packing efficiency of the polymer repeat units and thereby the effective chain stiffness, can lead to substantial tunability in the  $T_{g}$ -confinement effect.

Here, we continue this line of investigation by studying how the  $T_g$ -confinement effect is impacted by slight variations to the side groups of poly(n-methacrylate) films supported on silica, which exhibit both free-surface effects and attractive polymer–substrate interactions. We use a fluorescence method to determine  $T_g$  values in single-layer films and in bilayer films in which only one layer has polymer labelled with a fluorescence dye. The latter experiments allow us to measure directly the local  $T_g$ s in ultrathin free-surface layers and substrate layers. The polymers used in the present study include PMMA, poly(ethyl methacrylate) (PEMA), poly(propyl methacrylate) (PPMA), and poly(*iso*-butyl methacrylate) (PIBMA).

## Experimental

Three unlabelled polymers, PMMA, PEMA, and PIBMA, were synthesized at 70°C by bulk free radical polymerization using benzoyl peroxide (Aldrich) as initiator. Following a procedure originally described by McCusick and coworkers,<sup>[54]</sup> the dye 4-tricyanovinyl-(*N*-(2-hydroxyethyl)-*N*-ethyl)aniline (TC1) was

synthesized by reaction with tetracyanoethylene (TCI America) and 2-(*N*-ethylaniline)ethanol (TCI America) dissolved in dimethyl formamide (Fisher) at 55°C for 15 min and then recrystallized from glacial acetic acid. The 1-pyrenyl butanol-labelled (Aldrich) and TC1-labelled methacrylate monomers were synthesized through an esterification of 1-pyrenyl butanol or TC1, respectively, with methacryloyl chloride (Aldrich) in the presence of triethylamine (Aldrich) and dichloromethane (Aldrich) at 0°C for 2 h.<sup>[55]</sup>

Dye-labelled versions of PMMA, PEMA, PPMA, and PIBMA were synthesized by bulk free radical polymerization of methyl methacrylate (Aldrich), ethyl methacrylate (Aldrich), propyl methacrylate (Aldrich), and *iso*-butyl methacrylate (Aldrich), respectively, in the presence of trace amounts of pyrene-labelled or TC1-labelled methacrylate monomer. All dye-labelled polymers were washed by dissolving in toluene (Fisher) and precipitating in methanol (Fisher) at least five times to remove residual unreacted dye-labelled monomer, and then dried in a vacuum oven at  $T_g + 15$  K for 24 h. Table 1 lists the number-average molecular weight ( $M_n$ ) values, polydispersity indexes, bulk  $T_gs$ , and label content of the poly(n-methacrylate) samples, and Fig. 1 shows the repeat unit structures.

# Differential Scanning Calorimetry

The bulk  $T_g$  of each polymer was determined using a Mettler-Toledo 822 differential scanning calorimeter. Sample masses of 5–10 mg were placed in sealed aluminium pans with a pinhole in the top to allow measurements to be conducted in a nitrogen environment. The  $T_g$ s were determined on heating at 10 K min<sup>-1</sup> after annealing the samples at 423 K to erase the previous thermal history. The reported  $T_g$ s are onset values.

## Gel Permeation Chromatography

The  $M_n$  value and polydispersity index of each polymer were determined using a Waters Breeze gel permeation chromatograph equipped with refractive index and fluorescence detectors. Molecular weight values were determined relative to PS standards or universal calibration using the appropriate Mark– Houwink constants. Tetrahydrofuran was used as the eluent at  $30^{\circ}$ C.

#### Determination of Label Content

The label content of each dye-labelled polymer was determined using a Perkin-Elmer Lambda 35 UV-Vis absorbance



Fig. 1. Structures of polymers used in the present study.

spectrophotometer. Dye-labelled polymer was dissolved in chloroform at a known concentration, and the absorbance spectrum of the solution was measured. Using wavelengths at which only the dye contributes to the absorbance spectrum, the concentration of the dye in the solution, and thereby the label content in the dye-labelled polymer, can be determined using the Beer-Lambert law with measured extinction coefficients for the TC1-labelled monomer and pyrene-labelled monomer. (The technique assumes that the dye attached to the polymer has the same extinction coefficient at its absorbance maximum as the dye-labelled monomer even though the absorbance spectrum of the dye attached to the polymer is shifted by a few nanometres compared with the dye-labelled monomer. The extinction coefficient for each dye-labelled monomer was determined from absorbance measurements taken from solutions containing varying amounts of dye-labelled monomer. The extinction coefficient is the slope of a plot of absorbance versus concentration). The label contents were as follows: 1.4 and 0.6 mol-% TC1labelled monomer in PMMA and PIBMA, respectively, and 0.6 and 0.3 mol-% pyrene-labelled monomer in PEMA and PPMA, respectively.

# Film Preparation

Single-layer films were prepared by spin casting<sup>[56]</sup> polymer/ toluene solutions onto silica slides using solution concentrations ranging from 0.5 to 4.0 wt-% and spin speeds ranging from 1000 to 4000 rpm. The films were allowed to dry in vacuum at  $T_g + 5$  K for 8 h. Bilayer films were prepared by spin coating polymer/toluene solutions onto either a silica slide or an NaCl salt disc. Films spun-cast onto NaCl salt disks were placed in water, allowing the salt to dissolve, and leaving the polymer film floating on the water surface. Films spun-cast on silica were then submersed in the water and used to pick up the films floating on the water surface, resulting in bilayer films. These bilayer films were dried in vacuum at room temperature for 12 h and then annealed at  $T_{\rm g}$  + 25 K for 10 min to ensure completely consolidated films. Film thicknesses were measured with a Tencor P10 profilmeter using an average of at least ten measurements.

All polymers were of sufficiently high molecular weight to ensure that interlayer diffusion occurred over at most several nanometres during the experimental measurement time, which includes the time to create a consolidated film. Estimation of interlayer diffusion of similar bilayer films has been described elsewhere.<sup>[15,24]</sup>

# Fluorescence Measurements

Steady-state fluorescence emission spectra were measured as a function of temperature (on cooling) using a Photon Technology International fluorimeter or an SPEX Fluorog-2 DM1B fluorimeter with 5-nm bandpass excitation and emission slits used for pyrene-labelled polymer and 12-nm bandpass excitation and emission slits used for TC1-labelled polymer. Excitation wavelengths of 254 and 480 nm were used for pyrene-labelled and TC1-labelled polymer, respectively, where there were maxima in absorbance. The emission spectra of pyrene-labelled and TC1-labelled polymer were measured at 360–460 nm and 540–690 nm, respectively. The  $T_{\rm g}$ s of films were determined by fitting the temperature dependence of the integrated fluorescence intensity to linear correlations in both the rubbery and glassy states. In fitting the data to linear correlations, only data well away from  $T_{\rm g}$  were used in the fitting procedure.

In all cases,  $T_g$  data were obtained from fluorescence measurement obtained on cooling from the equilibrium rubbery or liquid state. Polymer films were heated to the maximum measurement temperature and held for a minimum of 10 min before measuring the fluorescence emission spectrum. Then the temperature was decreased by 5 K where the sample was held for 5 min to ensure thermal equilibrium before again measuring the fluorescence emission spectrum. This 'cooling, holding, measuring' protocol was repeated well into the glassy state of each film



Fig. 2. Temperature dependence of the fluorescence emission spectrum of a 500-nm-thick pyrene-labelled poly(ethyl methacrylate) (PEMA) film supported on silica: 383 K (solid curve), 348 K (dashed curve), and 308 K (dotted curve). Data have been normalized to one at the maximum peak value at 383 K.

being measured and has previously been shown to yield  $T_g$  measurements in bulk films that are in good agreement with onset  $T_g$ s measured by differential scanning calorimetry (DSC) using a 10 K min<sup>-1</sup> heating rate.<sup>[10,22]</sup> (The good agreement is likely due to the temperature ramping by DSC being within an order of magnitude of the effective average cooling rate of 5 K/5 min (or 1 K min<sup>-1</sup>) used in our fluorescence measurements of  $T_g$ ). Additional information on the use of fluorescence to monitor  $T_g$  is found in refs [10–13] and [15].

## **Results and Discussion**

Fig. 2 shows the fluorescence emission spectrum of a pyrenelabelled PEMA film supported on silica as a function of temperature, which consists solely of fluorescence from isolated excited-state pyrenyl units, which is called monomer fluorescence. (When two pyrenyl dyes are separated from each other by a several Angstrom distance, it is possible to observe excimer fluorescence or fluorescence from an excited-state dimer, which is a broad, structureless emission centred with a maximum intensity at 480-490 nm.<sup>[57]</sup> Such fluorescence is absent in the film measurements done in the current study, indicating that, within error, all pyrenyl dye fluorescence is from single pyrene dyes isolated in the polymer matrix). A decrease in temperature yields an increase in fluorescence intensity. The increase in intensity results because a reduction in temperature leads to reduced thermal energy and densification of the nanoscale medium surrounding the dye, both of which reduce the rate of non-radiative decay from the excited state of the pyrene dye. We also observed increases in intensity with decreasing temperature in the other pyrene-labelled and TC1-labelled polymers used in the present study.

Fig. 3 shows the temperature dependence of the normalized integrated fluorescence intensity of thin and ultrathin, singlelayer pyrene-labelled PEMA and TC1-labelled PIBMA films. We have previously shown that such data originating from appropriately chosen dyes can be used to determine  $T_g$  in bulk and nanoconfined polymers<sup>[10–13,15–22]</sup> and have provided a rationale for why the temperature dependence of dye fluorescence, which is sensitive to the temperature dependence of polymer density, can yield a precise and accurate determination of polymer  $T_{g}$ .<sup>[11]</sup> (Here we employ both pyrene-labelled and TC1-labelled polymers because we already had in our possession several of the polymers, some labelled with pyrene and others labelled with TC1, needed for the current study). The intersection of linear correlations fitted to data points deep in the rubbery state and glassy state provides a measure of  $T_{g}$ . There is an interesting difference in fluorescence of pyrene-labelled and TC1-labelled polymers, with pyrene fluorescence yielding a greater temperature dependence in the rubbery state above  $T_g$  and TC1 fluorescence yielding a greater temperature dependence in the glassy state below  $T_{\rm g}$ . This difference is related to the different mechanisms by which each dye undergoes non-radiative decay from its excited state and is explained in more detail in refs [11], [13], and [19]. Nevertheless, both dyes report  $T_{gs}$  for bulk polymers that are in good agreement with  $T_{g}$  values obtained by classic techniques such as DSC.

Fig. 3a illustrates that nanoscale confinement leads to a decrease in the  $T_g$  of PEMA. The  $T_g$  values of the 500- and 20-nm-thick pyrene-labelled PEMA films are 347 and 336 K, respectively. In contrast, Fig. 3b shows that nanoscale confinement leads to no change within experimental error ( $\pm 1$  K) in the  $T_g$  of PIBMA. The  $T_g$  values of the 500- and 20-nm-thick TC1-labelled PIBMA films are 339 and 341 K, respectively. Related measurements of  $T_g$  were also obtained in thin and ultrathin PMMA and PPMA films.

Fig. 4 shows the thickness dependence of the deviation of  $T_{\rm g}$ from bulk T<sub>g</sub> for single-layer films of PMMA, PIBMA, PEMA, and PPMA supported on silica. This figure reveals that slight modifications to the repeat unit structure of a series of poly(nmethacrylate)s can have a profound impact on how confinement to thicknesses less than 100 nm affects  $T_g$ . (Little change, in the case of PPMA, or no change, in the case of PMMA, PIBMA, and PEMA, in  $T_{g}$  is observed as a function of thickness for films with thickness exceeding 100 nm. This is because the perturbations to  $T_{g}$  response caused by the polymer-air and polymer-substrate interfaces are too small to modify the average  $T_{g}$  response across films that are thicker than 100 nm). For TC1-labelled PMMA, the increase in  $T_g$  with confinement is consistent with previous studies of single-layer PMMA films supported on silica.<sup>[2,5,19]</sup> The increase in  $T_g$  with confinement has been related to attractive hydrogen-bonding interactions between the ester side groups of PMMA and the hydroxyl groups on silica that reduce segmental mobility at the substrate interface.<sup>[2,5,15]</sup> Changing the side unit off the ester group of PMMA from a methyl unit to an ethyl (PEMA) or propyl (PPMA) unit leads to an opposite effect of confinement on  $T_g$ , with  $T_g$  decreasing from its bulk value by 11 K in a 20-nm-thick PEMA film and by 17 K in a 30-nm-thick PPMA film. Changing the methyl unit off the ester group of PMMA to an *iso*-butyl unit (PIBMA) leads to a  $T_g$  that is, within error, independent of confinement down to a film thickness of 14 nm.

Why do these small modifications to the repeat unit structure have such an enormous impact on how confinement affects  $T_g$  in this series of poly(n-methacrylates)? From our previous studies on the distributions of  $T_g$ s and physical aging rates in PS, PMMA, and other films, we know that the free surface and substrate interface affect  $T_g$  and glassy-state dynamics differently in different polymers.<sup>[11,15–17,58]</sup> Here we use a bilayer fluorescence method to investigate directly the local  $T_g$ s in the free-surface and substrate-interface layers of the series of poly(nmethacrylate)s and show that the modifications to the repeat



**Fig. 3.** (a) Temperature dependence of integrated fluorescence intensity of 500-nm-thick ( $\Box$ ) and 20-nm-thick ( $\bigcirc$ ) pyrenelabelled poly(ethyl methacrylate) (PEMA) films. Data have been normalized to  $T_g$  and arbitrarily shifted vertically for clarity. Inset shows the structure of pyrene. (b) Temperature dependence of integrated fluorescence intensity of 500-nm-thick ( $\Box$ ) and 20-nm-thick ( $\bigcirc$ ) TC1-labelled poly(*iso*-butyl methacrylate) (PIBMA) films. Data have been normalized to  $T_g$  and arbitrarily shifted vertically for clarity. Inset shows the structure of TC1.



**Fig. 4.** Deviation of  $T_g$  from bulk  $T_g$  as a function of film thickness for TC1-labelled poly(methyl methacrylate) (PMMA) ( $\triangle$ ), TC1-labelled poly(*iso*-butyl methacrylate) (PIBMA) ( $\Box$ ), pyrene-labelled poly(ethyl methacrylate) (PEMA) ( $\bigcirc$ ), and pyrene-labelled poly(propyl methacrylate) (PPMA) ( $\diamondsuit$ ) films.

unit structure affect how the free surface and substrate interface affect the local  $T_{gs}$  and thereby the average  $T_{gs}$  measured across ultrathin single-layer films.

Our bilayer films consist of a dye-labelled poly(n-methacrylate) layer and an unlabelled poly(n-methacrylate) layer. We construct bilayer films in such a manner that an ultrathin labelled layer can be placed at either the free surface or substrate interface. Heating the bilayer films for a short time above  $T_g$  produces a consolidated film with only the labelled layer contributing to the fluorescence signal.

Fig. 5 shows the results of the bilayer film measurements for PMMA, PEMA, and PIBMA where the films are sufficiently thick to yield bulk  $T_g$  values if measured as single-layer films. In all cases, there is a reduction in  $T_g$  at the 12- or 14-nm-thick free-surface layers, qualitatively consistent with previous studies<sup>[1,4,6,10,11,13,19,21,22,25,31,33]</sup> of how the presence of a free surface perturbs the local  $T_g$ . In all cases, there is an increase in  $T_g$  at the polymer–substrate interface, consistent with expectations

for polymers that can undergo hydrogen bonding with hydroxyl groups naturally on the surface of the silica substrates. However, the magnitude of the deviations in  $T_g$  at the interfaces depends strongly on chemical structure. For PMMA, the 12-nm-thick substrate layer has a  $T_g$  enhanced by 10 K compared with the bulk  $T_g$ , whereas for PEMA and PIBMA, the 14-nm-thick substrate layers have  $T_g$ s enhanced by only 5 K compared with the bulk  $T_g$ s. The 14-nm-thick free-surface layer of PEMA has a  $T_g$  reduced by 14 K compared with its bulk  $T_g$ . In contrast, the  $T_g$  reductions are only 7 and 6 K in 12-nm-thick PMMA and 14-nm-thick PIBMA free-surface layers, respectively.

A comparison of Fig. 4 and Fig. 5 reveals a correlation between the observed deviations in  $T_g$  with confinement for the single-layer films (Fig. 4) and the relative strength of the deviations in  $T_g$  in the free-surface and substrate-interface layers (Fig. 5) of the poly(n-methacrylate) films. When substrate effects are stronger than free-surface effects (as quantified by a greater  $T_g$  deviation in the substrate layer than in the free-surface layer), the  $T_g$ s of single-layer films. When free-surface effects are stronger than substrate effects, as in the case for PEMA, the  $T_g$ s of single-layer films decrease with confinement. When freesurface and substrate effects are of nearly equal strength, as in the case of PIBMA, the  $T_g$ s of single-layer films are invariant with confinement.

Regarding the effects of the substrate and free surface on the  $T_{gs}$  of the poly(n-methacrylate) layers shown in Fig. 5, the increase in  $T_g$  in the layer next to the silica substrate is understood qualitatively to arise from hydrogen-bonding interactions between the ester groups of the poly(n-methacrylate)s and the hydroxyl groups on the silica surface, whereas the reduction in  $T_{g}$ in the free-surface layer is related to how the free surface reduces the requirement for cooperative segmental mobility. Poly(methyl methacrylate), which has the smallest alkyl side group of the series of poly(n-methacrylate)s studied, exhibits the greatest substrate effect. This is likely because the small methyl units off the ester side groups in PMMA are relatively ineffective relative to the larger ethyl and iso-butyl units of PEMA and PIBMA, respectively, in impeding hydrogen bonding between the oxygen atoms on the ester side groups and hydroxyl units on the surface of the silica. The detailed cause of the substantially larger effect in the



**Fig. 5.** Deviation of  $T_g$  from bulk  $T_g$  in ultrathin free-surface and substrate layers in bilayer films. (a) 12-nm-thick TC1-labelled poly(methyl methacrylate) (PMMA) layer placed at the free surface and substrate interface of PMMA bilayer films. Film thicknesses of bulk overlayer and bulk underlayer are 240 nm. (b) 14-nm-thick pyrene-labelled poly(ethyl methacrylate) (PEMA) layer placed at the free surface and substrate interface of PEMA bilayer films. Film thicknesses of bulk overlayer and bulk underlayer are 500 nm. (c) 14-nm-thick TC1-labelled poly(*iso*-butyl methacrylate) (PIBMA) layer placed at the free surface and substrate interface of PIBMA bilayer films. Film thicknesses of bulk overlayer and bulk underlayer are 500 nm.

free-surface layer of PEMA relative to the effects observed in PMMA and PIBMA is not yet known. However, it likely relates to how the chemical structure of PEMA better supports a strong free-surface effect, with its perturbation of  $T_g$  dynamics via a reduction of the requirement for cooperativity at the polymer–air interface. Further experimental, theoretical, and simulation studies are warranted to provide an understanding regarding why the perturbations to  $T_g$  at free surfaces are strongly dependent on chemical structure.

## Conclusion

Fluorescence spectroscopy has been used to determine the effects of confinement and interfaces on the  $T_{os}$  and their distributions in PMMA, PEMA, PPMA, and PIBMA films supported on silica. The average  $T_{\rm g}$  across thin and ultrathin films of PIBMA is invariant with confinement, whereas that of PMMA increases with confinement and those of PEMA and PPMA decrease with confinement. The relative roles of perturbations to the  $T_g$  by free surfaces and polymer-substrate interfaces in the presence of hydrogen-bonding interactions were determined by a series of bilayer fluorescence experiments. In all cases, reductions in  $T_g$  relative to bulk  $T_g$  were observed in ultrathin free-surface layers, whereas increases in  $T_g$  relative to bulk  $T_g$ were observed in ultrathin substrate-interface layers. The effects of confinement of the average  $T_{\rm g}$  across single-layer films are fully consistent with observed relative strengths of the perturbations caused by free surfaces and polymer-substrate interfaces. When the free-surface effect is greater, as in the case of PEMA, the average  $T_{\rm g}$  across a film decreases with nanoscale confinement. When the substrate effect is greater, as in the case of PMMA, the average  $T_g$  across a film increases with nanoscale confinement. When the effects of the substrate and free surface in perturbing  $T_g$  are nearly equal, as in the case of PIBMA, within error the average  $T_g$  across a film is independent of nanoscale confinement.

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