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# Effect of Interfacial Interactions on the Glass Transition of Polymer Thin Films

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**ABSTRACT:** Previous studies had demonstrated that the  $T_g$  of polymer thin films is strongly dependent on the interactions,  $\gamma_s$ , between the polymer and the underlying substrate. We present a study of the glass transition temperature,  $T_g$ , in thin films of polystyrene, PS, as a function of film thickness and as a function of  $\gamma_s$  by measuring the change in the thermal expansion using X-ray reflectivity. The  $T_g$  for PS on native silicon oxide was found to decrease with decreasing film thickness, consistent with results by others. Using random copolymers of styrene and methyl methacrylate anchored to the substrate,  $\gamma_s$  could be varied by changing the styrene fraction,  $f$ . With a constant PS film thickness of 330 Å, the  $T_g$  was depressed by  $\sim 20$  °C as  $f$  was decreased from 1 to 0.75. An analysis analogous to the Gibbs–Thompson model indicated that the surface energy was not a suitable parameter to use to describe the effects of interfacial interactions on the  $T_g$  of polymer thin films. An associated local fractional change in the segment density at the substrate interface is instead proposed to describe the changes in  $T_g$  observed with different  $\gamma_s$ . Only a small change ( $< 1.4\%$ ) in the density at the interface is required to produce a 20 °C depression in  $T_g$  found in this experiment.

## Introduction

The glass transition, in its most widely accepted terms, is the kinetic arrest of a liquid upon cooling. While commonplace, there is no generally accepted theory for the glass transition. The concept of a cooperative length scale that diverges with decreasing temperature is widely used in many models.<sup>1,2</sup> Recent studies on simple glass-forming liquids suggested that these cooperative regions were a few nanometers in size at the experimental glass transition temperature.<sup>3,4</sup> Existence of a characteristic length suggests that a perturbation to the  $T_g$  will occur when the dimension of the system approaches this length scale. By confining organic liquids in nanoporous glass, a depression was noted in the calorimetric  $T_g$ .<sup>4–6</sup> Similar observations were subsequently found in polymer solutions.<sup>5</sup> Most recently, a substantial thickness dependence was also observed in the  $T_g$  of thin films of polymer melts.<sup>7–12,20</sup>

The confinement of polymers in films with thicknesses comparable to or less than a molecular diameter may alter the configuration of a polymer chain<sup>13</sup> and the extent of entanglements<sup>14</sup> in comparison to the bulk. In addition, interfacial effects and packing constraints at both the air and substrate interfaces become increasingly important in thin films. Keddie et al.<sup>7</sup> observed a progressive depression in the  $T_g$  with film thickness ( $< 100$  nm) for PS films on native silicon oxide, with a drop of over 25 °C when the thickness was 100 Å. Similar behavior was also observed for poly(methyl methacrylate) (PMMA) films supported on gold.<sup>8</sup> To explain such a depression in  $T_g$ , the existence of a low-density, highly mobile layer at the air interface was

suggested which diverges as the temperature is increased from below the bulk  $T_g$ . The concept of a highly mobile surface layer has found evidence in the atomic force microscopy measurements of Kajiyama and co-workers.<sup>15,16</sup> These were attributed to the enrichment of chain-end groups at the surface, which was supported by computer simulation studies of Cifra et al.,<sup>17</sup> entropy arguments of Mayes,<sup>18</sup> and dynamic secondary ion mass spectroscopy studies of end-labeled PS by Kajiyama and co-workers.<sup>15</sup> Surface relaxation studies by Russell and co-workers,<sup>19</sup> on the other hand, found no evidence of a distinct, highly mobile layer at the polymer–air interface. Forrest et al. studied the  $T_g$  of supported PS films capped with a thin layer of evaporated SiO<sub>2</sub> and found no noticeable difference from the results of uncapped samples.<sup>20</sup> Recent atomic force microscopic adhesion studies by Tsui et al.<sup>21</sup> found that the dynamical behavior at the surface of poly(*tert*-butyl acrylate) is identical to the bulk. These studies argue against a well-defined, highly mobile surface layer. On the other hand, a reduction of more than 70 °C in  $T_g$  for a 300 Å thick, free-standing PS film was found by Forrest et al.<sup>9</sup> This, together with the previous study by Wu and co-workers<sup>10</sup> using PS supported on hydrogen-terminated silicon and the substrate surface dependent result obtained by Jones and co-workers<sup>8</sup> using PMMA supported on native silicon oxide and gold, indicates that interfacial interactions are important.

In this experiment, the  $T_g$  of PS films was studied on surfaces with *tunable* interfacial surface energies, which was achieved by adjusting the styrene fraction,  $f$ , of a random copolymer of styrene and MMA anchored onto silicon substrates. It was found that only a small change in the interfacial energy markedly influenced the  $T_g$  of the thin film. A reduction in the interfacial energy ( $\gamma_s$ ) of 0.43 erg cm<sup>-2</sup>, which is orders of magnitude smaller

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than the activation energy required of molecular motions at the glass transition, was sufficient to cause a  $\sim 20$  °C reduction in the  $T_g$ . This shows that effects of the interfacial energy on the  $T_g$  of polymer thin films must be mediated by mechanisms that are highly effective in changing  $T_g$ . A mechanism involving a local change in the segment density at the homopolymer film/brush interface is proposed.

## Experimental Section

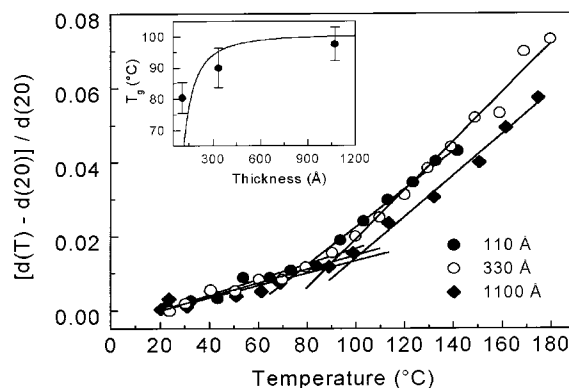
**Samples.** The  $T_g$  of PS films on silicon substrates with a native oxide layer was studied as a function of film thickness,  $d$ . In addition, the  $T_g$  of 330 Å thick PS films ( $M_w = 96\,000$ ,  $M_w/M_n = 1.04$ ) spin-coated onto (P(S-*r*-MMA)) brushes ( $M_w \sim 10\,000$ ,  $M_w/M_n \sim 1.1-1.8$ ) was studied as a function of  $f$ , the fraction of styrene segments in the brush. Contact angle measurements of Mansky et al.<sup>22</sup> on brush-coated silicon substrates showed that the interfacial energy of PS with the brush,  $\gamma_{sf}$ , is given by  $\gamma_{sf} = 0.77 - 1.08f$  (in ergs cm<sup>-2</sup>) for  $f < 0.65$ . When  $f$  is larger, PS wets the surfaces and  $\gamma_{sf}$  could not be determined. Since the interfacial width between PS and the brush varies continuously with  $f$  for  $0 < f < 1$ <sup>23</sup> and since the contact angle of water on the brush changes gradually with  $f$  over the entire composition range of the brush,<sup>22</sup> a linear dependence of  $\gamma_{sf}$  on  $f$  for  $f > 0.65$  was assumed here.

End-functionalized random copolymers of styrene and methyl methacrylate, denoted P(S-*r*-MMA), were synthesized by a nitroxide-mediated polymerization.<sup>24</sup> The copolymers were end-grafted onto clean Si(111) surfaces by annealing the copolymer-coated substrates at 170 °C for 2 days, which allows the terminal OH group of the copolymer to diffuse and react with the native oxide layer on the silicon. The unattached copolymer was removed by repeated rinsing with toluene. The typical thickness of a brush so obtained is  $\sim 3$  nm. The PS homopolymer was purchased from Polymer Laboratories and used without further purification. Films were prepared by spin-coating solutions of PS in toluene onto either a bare silicon substrate or a substrate coated with the anchored P(S-*r*-MMA). The concentration of the solution or the spinning speed was varied to control the film thickness.

**Technique.** X-ray reflectivity was used to measure the thickness of the PS film as a function of temperature.  $T_g$  was identified as the temperature at which the slope in a plot of thickness vs temperature changed. X-ray reflectivity measurements were performed with an 18 kW rotating anode generator equipped with a channel-cut silicon monochromator that delivered the 1.54 Å Cu K $\alpha$  radiation onto the sample ( $\Delta\lambda/\lambda \sim 1.5 \times 10^{-4}$ , where  $\lambda$  denotes the wavelength). Specular X-ray reflectivity profiles were obtained in the  $\theta-2\theta$  geometry as a function of the wave vector  $k_{z0}$  ( $= (2\pi/\lambda) \sin \theta$ ) up to  $0.1 \text{ \AA}^{-1}$  where  $\theta$  is the grazing angle of incidence. Reflectivity data were fit using the Parrat formalism assuming a three-layer model (PS or PS and P(S-*r*-MMA)/SiO<sub>2</sub>/Si) as described elsewhere.<sup>25</sup> X-ray reflectivity gives excellent accuracy in determining the film thickness independent of the density of the film. A variation of 0.1 nm in the fitted value of  $d$  ( $\sim 33$  nm here) will increase the  $\langle \chi^2 \rangle$  value by 10%. Measurements were performed from 150–180 to 30 °C (cooling only) in 10 °C decrements with 45 min being allowed for the sample to thermally equilibrate. The sample was kept under vacuum ( $\sim 10^{-2}$  Torr) with a temperature control of better than  $\pm 0.5$  °C. Unless otherwise stated, the samples were annealed in the vacuum at the starting temperature for 2–5 h prior to each measurement to remove the residue solvent and erase any thermal history.

## Results

Figure 1 shows the fractional increase in  $d$ , referenced to  $T = 20$  °C, as a function of temperature for PS thin films on native SiO<sub>2</sub> with three different film thicknesses. Since the polymer is in contact with the silicon substrate, the in-plane linear expansion is restricted



**Figure 1.** Fractional increase in film thickness referenced to the data at 20 °C as a function of temperature for three PS films with the specified thicknesses spin-coated onto a silicon substrate. The inset shows the  $T_g$  as a function of film thickness determined in this study (solid points) and the data of Keddie et al.<sup>7</sup>

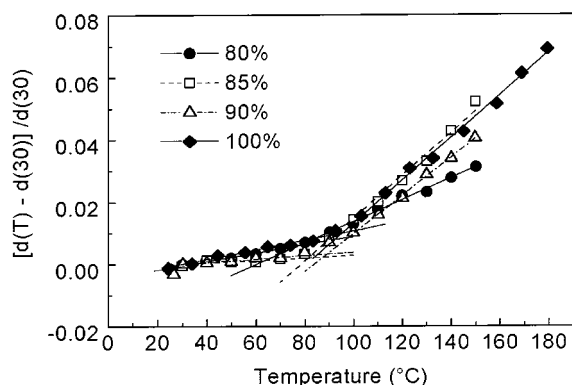
**Table 1.** Average Normal Thermal Expansion Coefficient of PS Thin Films on Native SiO<sub>2</sub> Determined from Slopes of the Curves in the Main Panel of Figure 1<sup>a</sup>

thickness (Å)	$\alpha_G^N$ (°C <sup>-1</sup> )	$\alpha_L^N$ (°C <sup>-1</sup> )
110	$(2 \pm 0.6) \times 10^{-4}$	$(5.1 \pm 0.4) \times 10^{-4}$
330	$(2.1 \pm 0.6) \times 10^{-4}$	$(6.8 \pm 0.4) \times 10^{-4}$
1100	$(1.4 \pm 0.6) \times 10^{-4}$	$(5.4 \pm 0.4) \times 10^{-4}$

<sup>a</sup> The quoted errors are the average of the errors in fitting the slopes for  $\alpha_G^N$  and  $\alpha_L^N$  separately.

laterally and may assume the same value as that of silicon, which is negligibly small ( $\sim 2.49 \times 10^{-6}$  °C<sup>-1</sup>). Therefore, the linear thermal expansion coefficient normal to the film surface (designated with a superscript N), which equals the slope of the lines in Figure 1, will be enhanced by a factor  $(1 + \nu)/(1 - \nu)$  that depends on the Poisson ratio  $\nu$  of the polymer.<sup>10</sup> In the glassy state, the linear expansion coefficient of a PS film is expected<sup>10</sup> to be  $\alpha_G^N = 1.1 \times 10^{-4}$  °C<sup>-1</sup>, whereas in the liquid state, it should be  $\alpha_L^N = 5.1 \times 10^{-4}$  °C<sup>-1</sup>. The average linear expansion coefficient of our films in the liquid state was found to be  $(5.8 \pm 0.6) \times 10^{-4}$  °C<sup>-1</sup>, which is in excellent agreement with the bulk value. The quoted error is the greater of either the average error of the linear expansion coefficients determined from fits to the data of Figure 1 or the standard deviation of the data used to compute the average linear expansion coefficient. In the glassy state, the average linear expansion coefficient was found to be  $(1.9 \pm 0.4) \times 10^{-4}$  °C<sup>-1</sup>, in reasonable agreement with the bulk value. From the values of  $\alpha^N$  in the glassy and liquid state, summarized in Table 1, no systematic dependence on the film thickness was observed.

As seen in Figure 1, the change in the thermal expansion of the sample from the glassy to liquid state occurred over a relatively narrow temperature range. The intersection of linear extrapolations from the liquid and glassy states was used to determine  $T_g$ . The error in the evaluation of  $T_g$  is less than  $\pm 5$  °C. In the inset of Figure 1,  $T_g$  is shown as a function of the film thickness along with the data of Keddie et al. (solid line).<sup>7</sup> As seen, the two results qualitatively agree with each other. For  $d > 1000$  Å, the bulk  $T_g$  is observed. As the film gets thinner,  $T_g$  decreases. It is noted, however, that the reduction in  $T_g$  observed here for the 110 Å thick film is somewhat less than that observed by others.



**Figure 2.**  $[d(T) - d(30)]/d(30)$  as a function of temperature for four PS films spun-cast on brushes with different styrene content as labeled. The straight lines are best fits to the data.

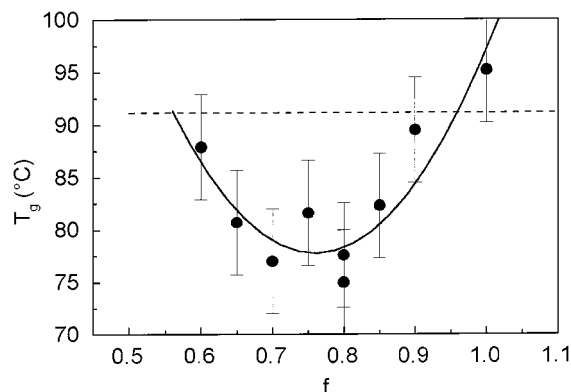
**Table 2. Average Normal Thermal Expansion Coefficient of PS Homopolymer Films on Random Copolymer Brushes of Styrene and MMA with Different Styrene Content<sup>a</sup>**

styrene content of the brush (%)	$\alpha_G^N$ ( $^{\circ}\text{C}^{-1}$ )	$\alpha_L^N$ ( $^{\circ}\text{C}^{-1}$ )
80	$(1.4 \pm 0.6) \times 10^{-4}$	$(3.5 \pm 0.4) \times 10^{-4}$
85	$(5.8 \pm 0.6) \times 10^{-5}$	$(7.5 \pm 0.4) \times 10^{-4}$
90	$(9.7 \pm 0.6) \times 10^{-5}$	$(5.8 \pm 0.4) \times 10^{-4}$
100	$(1.5 \pm 0.6) \times 10^{-4}$	$(6.8 \pm 0.4) \times 10^{-4}$

<sup>a</sup> The quoted errors are the average of the errors in fitting the slopes for  $\alpha_G^N$  and  $\alpha_L^N$  separately.

Similar experiments were performed on 330 Å thick PS films spin-coated onto surfaces to which P(S-*r*-MMA) brushes were anchored. The fraction of styrene segments,  $f$ , in the P(S-*r*-MMA) brush was varied from  $0.6 < f < 1$ . Typical results are shown in Figure 2 for four different brush compositions. Values of  $\alpha_L^N$  and  $\alpha_G^N$  obtained from the slopes are summarized in Table 2. No systematic variation of  $\alpha_G^N$  or  $\alpha_L^N$  with  $f$  is evident. The average value of  $\alpha_G^N$  was  $(1.1 \pm 0.6) \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$  while that of  $\alpha_L^N$  was  $(5.9 \pm 1.6) \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$ . These agree quite well with the expected values. The measured  $T_g$ 's as a function of  $f$ , obtained by extrapolating the data in the liquid and glassy states, are shown as the solid symbols in Figure 3. For PS (330 Å thick) on a PS brush,  $T_g$  is 95 °C, slightly higher than that obtained for a 330 Å PS film on SiO<sub>2</sub> (shown as the horizontal dashed line). As  $f$  decreases, the  $T_g$  was found to decrease to ~78 °C at  $f \sim 0.75$ . With a further reduction in  $f$ , however,  $T_g$  was found to increase again, reaching a value of ~88 °C at  $f = 0.6$ .

The changes observed in  $T_g$  are substantial but, due to the nonmonotonic dependence on  $f$ , cannot be explained simply by changes in interfacial interactions given by the average brush composition. The interpenetration of the homopolymer into the brush must be considered. For  $f = 1$ , neutron reflectivity studies have shown that the PS penetrates completely into the brush which effectively increases the thickness of the pure PS film by 30 Å. This would account for the higher value of  $T_g$  in this  $f = 1$  case. While neutron reflectivity measurements show a decrease in the interpenetration with decreasing  $f$ ,<sup>23</sup> the changes are not large enough to explain the observed magnitude of decrease in  $T_g$  with decreasing  $f$  and cannot explain the increase in  $T_g$  for  $f < 0.75$ . Furthermore, as the concentration of MMA segments in the brush increases with decreasing  $f$ , the configuration of the anchored chain should also be



**Figure 3.**  $T_g$  for 330 Å thick PS films spin-coated onto random copolymer brushes as a function of the styrene content in the copolymer. The solid symbols represent results of the samples. The dashed horizontal line is the  $T_g$  for a 330 Å thick PS film on a bare Si substrate for reference. The solid line is only a guide to the eye.

considered. MMA contacts with the substrate surface are more favorable than S contacts. In addition, the PS homopolymer interacts more favorably with the S segments in the brush. If the anchored chains on the surface assume a configuration that maximizes MMA/substrate contacts and minimizes MMA/S contacts between the brush and the homopolymer, then the interfacial energy can effectively decrease with decreasing  $f$ . To fully understand the results in Figure 3, a mechanism involving interplay between all three factors—interactions at the interface, amount of polymer/brush interpenetration, and reconfiguration in the anchored chain—must be invoked.

When the styrene content,  $f$ , is not far removed from 1, the driving force for reconfiguration in the anchored chain is small, and extensive interpenetration between the homopolymer and the brush occurs, maximizing segmental contacts between the homopolymer and anchored copolymer. Under these circumstances, interfacial interactions dominate. Results in Figure 3 for  $f > 0.75$  showing a monotonic decrease in the  $T_g$  of the film with decreasing  $f$  can be understood simply by the increasingly nonfavorable interactions with the (copolymer modified) substrate. As  $f$  is decreased further, both the reduction in the polymer/brush interpenetration and the diminished MMA segments at the interface due to a reconfiguration of the chains anchored to the surface are likely the causes for the increase in the  $T_g$  seen with decreasing  $f$  for  $f < 0.75$ . Although an interesting subject in its own right, no attempt will be made to quantify the behavior of  $T_g$  in this regime of  $f$  since the purpose of the present work is to elicit effects due to interfacial interactions on the  $T_g$  of polymer thin film.

Focusing on the data with  $f > 0.75$  in Figure 3, where the  $T_g$  of the thin film can be accounted for simply by effects due to interactions with the substrate, the data show that the  $T_g$  of the film decreases by ~20 °C as  $f$  is decreased from 1 to 0.75 or, correspondingly, as  $\gamma_{sf}$  decreases by ~0.43 erg cm<sup>2</sup>. Previously, Jackson and McKenna<sup>26</sup> studied the  $T_g$  and melting temperature,  $T_M$ , of *o*-terphenyl and benzyl alcohol confined in controlled porous glass. The observed depression in  $T_M$  of the organic liquids with decreasing pore size was explained using the Gibbs–Thompson equation, which states simply that the change in interfacial energy of the crystallite at melting (significant when the crystal size is small) will modify  $T_M$ . The reduction in  $T_g$  of the same



confined liquid, however, was found to be much smaller than the depression observed in  $T_M$ . In general, it should not be expected that the heat of fusion is the appropriate energy to use to describe the effect of interfacial energy on  $T_g$ . In the model of Adam and Gibbs, the transition of a liquid into a glass is the kinetic slowing down of cooperative molecular rearrangements in order to allow any molecular movement. If  $N_\xi$  is the number of molecules contained in a cooperativity region and  $\epsilon_a$  the activation energy one molecule needs to make some movement, the glass transition temperature is dictated by the energy,  $N_\xi \epsilon_a$ , required to enable all molecules within a cooperativity region to rearrange simultaneously for the move. Using published data for PS with a molecular weight similar to that used here,<sup>27</sup>  $\epsilon_a \sim 125 \text{ J g}^{-1}$  or  $130 \text{ J cm}^{-3}$  (assuming a mass density of  $1.04 \text{ g cm}^{-3}$ ). For a cooperativity region of size  $d$ , to first order, the interfacial energy,  $\gamma_{sf}$ , will, on average, produce a change in the glass transition temperature,  $\Delta T_g \sim \gamma_{sf} T_g / \epsilon_a d$ . To obtain the observed change of  $20^\circ \text{C}$  in  $T_g$  with a change of  $0.43 \text{ erg cm}^{-2}$  in the interfacial energy (as  $f$  decreases from 1 to 0.75),  $d$  would have to be  $0.6 \text{ \AA}$ , which is unphysical. This suggests that  $\gamma_{sf}$  alone is not sufficient to describe the observed changes. It should, also, be noted that the  $T_g$  of a  $330 \text{ \AA}$  thick PS film does not recover the bulk value until the brush composition is 100% styrene.

At the interface between the homopolymer and the brush, the specific interactions between monomers and packing constraints will produce perturbations to the chain conformations. Consider  $(\delta T_g / \delta \rho)$ , the reduction in  $T_g$  due to a decrease in the mass density,  $\rho$ .  $(\delta T_g / \delta \rho) = (\delta T_g / \delta P)(\delta P / \delta \rho) = (\delta T_g / \delta P)(1/\rho\kappa)$ , where, for PS, the pressure coefficient of  $T_g$  is  $3.09 \times 10^{-7} \text{ }^\circ\text{C Pa}^{-1}$ ,<sup>28</sup> the isothermal compressibility  $\kappa = 2.2 \times 10^{-10} \text{ Pa}^{-1}$ ,<sup>29</sup> and  $\rho = 1.04 \text{ g cm}^{-3}$ , yielding  $(\delta T_g / \delta \rho) = 1.35 \times 10^3 \text{ }^\circ\text{C}/(\text{g cm}^{-3})$ . To produce a  $20^\circ \text{C}$  drop in the  $T_g$  for a  $100 \text{ \AA}$  thick film requires density decrease of  $\sim 1.4\%$ .<sup>30</sup> Such a large change in the average density of a thin film polymer has not been observed in either the twin neutron reflectivity measurements of Wallace et al.<sup>32</sup> or the Brillouin light scattering studies of Forrest et al.<sup>33</sup> where, to within  $\sim 0.5\%$ , the densities of thin PS films were found to be equal to that of the bulk. Thus, a reduced average film density cannot be used to explain the observations here. A mechanism focusing on changes at the interface between the polymer and the substrate is more likely to be operative.

Using dynamic Monte Carlo simulations, Baschnagel and Binder<sup>35</sup> investigated the effect of a neutral, nonpenetrable wall on the configuration of polymer chains at the interface. They showed that, immediate to such a wall, the average segment density is significantly higher than that in the bulk. This was attributed to the reduced number of chain configurations at the solid boundary, resulting in a local densification of chain segments. Their calculations indicate that this density perturbation decays within a radius of gyration of the polymer from the interface. For an attractive interface, Bitsanis and Hadziioannou found that the magnitude of the perturbation would be even larger.<sup>35</sup> Near an interface that is sufficiently repulsive, one would expect the segment density to be lower than that of the bulk and, hence, the mobility enhanced. Jones and co-workers<sup>7,8</sup> proposed that a surface rubbery layer existed whose thickness,  $\xi(T)$ , diverged with temperature,  $T$ , according to  $\xi(T) \sim (1 - T/T_g^{\text{bulk}})^{-1/2}$  (where  $T < T_g^{\text{bulk}}$ ),

and  $T_g$  of the film is reached when the rubbery layer covers the entire thickness of the film. This model (solid line in the inset of Figure 1) suitably accounts for the thickness dependence of  $T_g$  but does not include effects due to the substrate. Furthermore, theoretical models of the glass transition based on mobile regions with diverging length scale is still lacking. Using a bilayer model, van Zanten et al.<sup>11</sup> found that their thermal expansivity data could be explained by a layer of reduced chain mobility near the solid substrate. Using the same model, DeMaggio et al.<sup>36</sup> also obtained good fits to their results. A trilayer model that included an additional surface mobile layer was also employed by the same authors who found that it gave equally good fits to the data as the bilayer model did. However, little attempt was made to use these models to explain the observed thickness dependence of  $T_g$ .

To use only the essence of these models, namely, the existence of a nonuniform density and, hence, mobility, we limit our discussions to a bilayer model, which should suffice for the present study since focus is being put in the changes in  $T_g$  due to changes in the polymer/substrate interactions. Consider a film of thickness  $d$ , where, at the substrate, the density of the polymer is  $\rho_i$  over a distance  $\zeta$  from the interface, with the remaining film,  $(d - \zeta)$  thick, having the bulk density  $\rho$ , then the film thickness would be a sum of the thickness of the two layers. The  $T_g$  of the film as whole, in turn, would be given by  $T_g = T_g^{\text{bulk}} + (\delta T_g / \delta \rho)(\zeta/d)(\Delta\rho)$ , where  $\Delta\rho = \rho_i - \rho$ . For a  $100 \text{ \AA}$  thick film, a  $20^\circ \text{C}$  reduction in  $T_g$  would be found when  $\zeta\Delta\rho \sim 1.48 \times 10^{-8} \text{ g/cm}^2$ . If we take  $\zeta = 30 \text{ \AA}$  (several Kuhn lengths), then  $\Delta\rho = -0.05$ ; a 5% density decrease at the interface is required. It should be noted that  $\Delta\rho\zeta/d$  gives the fractional density change due to the interfacial layer, and it is not possible to determine  $\zeta$  and  $\Delta\rho$  separately using this simple model. As the film thickness increases, the interfacial effect on the suppression of  $T_g$  will decrease accordingly to  $\Delta\rho\zeta/d$ . This, together with the empirical finding by Jones and co-workers<sup>7</sup> that the change in  $T_g$  should be  $\sim 1/d^{1.8}$ , would mean that the perturbation in the mass density of the film due to the polymer/substrate interaction, being  $= \zeta\Delta\rho$ , varies according to  $1/d^{0.8}$ .

Confinement effects may also strongly perturb the conformations of the polymer chain and, hence, the density of the film.<sup>37</sup> However, recent experimental results indicate that the chain conformation is not perturbed until the film thickness is less than  $2R_G$ .<sup>38</sup> Since the films investigated here are greater than  $2R_G$ , confinement effects would be expected to be minimal.

Most measurements of  $T_g$  (including those reported here) in thin films are based on an average characteristic of the film, for example the film thickness, and are not able to distinguish between effects at either surface. The bilayer model discussed above essentially describes the combined effects of the air and the substrate interfaces, parametrized by the product  $(\Delta\rho\zeta)$ , which provides a quantitative measure for the perturbations on the overall segment density. The foregoing discussion has focused on a reduction in  $T_g$  with decreasing film thickness, resulting in an increase in favorable interactions that makes  $\Delta\rho$  positive. The present model will also describe an increase in  $T_g$  with decreasing film thickness. When  $\Delta\rho = 0$ , the  $T_g$  of a film will remain the same as the bulk. This is expected to occur when the interface produces no perturbation to the chain density, which is likely to be realized by a substrate

coated with a brush of the same composition as the polymer itself. Indeed, no change in  $T_g$  is found with the  $f = 1$  brush.

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## References and Notes

- (1) Adam, G.; Gibbs, J. J. *Chem. Phys.* **1965**, *43*, 139.
- (2) See also, for example: Nagai, K. L., Wright, G. B., Eds.; *Proceedings for the International Discussion Meeting on Relaxation in Complex Systems* [*J. Non-Cryst. Solids* **1994**, *131–133*; **1994**, *174*].
- (3) Fischer, E. W.; Donth, E.; Steffen, W. *Phys. Rev. Lett.* **1992**, *68*, 2344.
- (4) Jackson, C. L.; McKenna, G. B. *J. Chem. Phys.* **1990**, *93*, 9002; *Rubber Chem. Technol.* **1991**, *64*, 760; *J. Non-Cryst. Solids* **1991**, *131–132*, 221.
- (5) Park, J.-Y.; McKenna, G. B. *Phys. Rev. B* **2000**, *61*, 6667.
- (6) Arndt, M.; Stannarius, R.; Groothues, H.; Hempel, E.; Kremer, F. *Phys. Rev. Lett.* **1997**, *79*, 2077.
- (7) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Europhys. Lett.* **1994**, *27*, 59. The silicon substrate used in this work has been reportedly hydrogen passivated. However, it is later believed to be oxidized during the course of measurement which was carried out in air.
- (8) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Faraday Discuss.* **1994**, *98*, 219.
- (9) Forrest, J. A.; Dalnoki-Veress, K.; Stevens, J. R.; Dutcher, J. R. *Phys. Rev. Lett.* **1996**, *77*, 2002.
- (10) Wallace, W. E.; van Zanten, J. H.; Wu, W. L. *Phys. Rev. E* **1995**, *52*, 3329.
- (11) van Zanten, J. H.; Wallace, W. E.; Wu, W.-l. *Phys. Rev. E* **1996**, *53*, 2053.
- (12) Xie, L.; DeMaggio, G. B.; Frieze, W. E.; DeVries, J.; Gidley, D. W.; Hristov, H. A.; Yee, A. F. *Phys. Rev. Lett.* **1996**, *74*, 4947.
- (13) Jones, R. A.; Kumar, S. K.; Ho, D.; Briber, R.; Russell, T. P. *Nature* **1999**, *400*, 146.
- (14) Brown, H. R.; Russell, T. P. *Macromolecules* **1996**, *29*, 798.
- (15) Tanaka, K.; Takahara, A.; Kaijiyama, T. *Macromolecules* **1997**, *30*, 6626.
- (16) Tanaka, K.; Taura, A.; Ge, S.-R.; Takahara, A.; Kaijiyama, T. *Macromolecules* **1996**, *29*, 3040.
- (17) Cifra, P.; Nies, E.; Karasz, F. E. *Macromolecules* **1994**, *27*, 1166.
- (18) Mayes, A. M. *Macromolecules* **1994**, *27*, 3114.
- (19) Liu, Y.; Russell, T. P.; Samant, M. G.; Stohr, J.; Brown, H. R.; Cossy-Favre, A.; Diaz, J. *Macromolecules* **1997**, *30*, 7768.
- (20) Forrest, J. A.; Kalnoki-Veress, K.; Dutcher, J. R. *Phys. Rev. E* **1997**, *56*, 5705.
- (21) Tsui, O. K. C.; Wang, X. P.; Ho, Jacob, Y. L.; Ng, T. K.; Xiao, X. *Macromolecules* **2000**, *33*, 4198.
- (22) Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. *Science* **1997**, *275*, 1458.
- (23) Huang, E.; Hawker, C. J.; Russell, T. P., unpublished work.
- (24) Hawker, C. J.; Elce, E.; Dao, J.; Volksen, W.; Russell, T. P.; Barclay, G. G. *Macromolecules* **1996**, *29*, 2686.
- (25) Russell, T. P. *Mater. Sci. Rep.* **1990**, *5*, 171.
- (26) Jackson, C. L.; McKenna, G. B. *Chem. Mater.* **1996**, *8*, 2128.
- (27) Santangelo, P. G.; Roland, C. M. *Macromolecules* **1998**, *31*, 4581.
- (28) Eisenberg, A. *J. Phys. Chem.* **1963**, *67*, 1333.
- (29) Brandrup, J., Immergut, E. H., Eds.; *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989.
- (30) An alternative approach is to assume that glass transition is an iso-free volume transition so that the depression in  $\Delta T_g$  can be attributed to an increase in the fractional free volume,  $\delta f_0 \sim (\alpha_L - \alpha_G)\Delta T_g$ , giving  $\delta f_0 \sim 0.8\%$ . This estimate is slightly smaller than what we obtained in the text based on changes in  $T_g$  due to density change with pressure, consistent with what Ferry observed.<sup>31</sup> It should be emphasized that the present exercise should be treated as an order of magnitude estimate only.
- (31) Ferry, J. D. *Viscoelastic Properties of Polymers*, John Wiley & Sons: New York, 1980.
- (32) Wallace, W. E.; Beck-Tan, N. C.; Wu, W. L. *J. Chem. Phys.* **1998**, *108*, 3798.
- (33) Forrest, J. A.; Kalnoki, K.; Dutcher, J. R. *Phys. Rev. E* **1998**, *58*, 6109.
- (34) Baschnagel, J.; Binder, K. *Macromolecules* **1995**, *28*, 6808.
- (35) Bitsanis, I.; Hadziioannou, G. *J. Chem. Phys.* **1990**, *92*, 3827.
- (36) DeMaggio, G. B.; Frieze, W. E.; Gidley, D. W.; Zhu, M.; Hristov, H. A.; Yee, A. F. *Phys. Rev. Lett.* **1997**, *78*, 1524.
- (37) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*, Cornell University Press: Ithaca, NY, 1996.
- (38) Blum, F. D.; Xu, G.; Liang, M.; Wade, C. *Macromolecules* **1996**, *29*, 874.

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