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Effective T_g of Confined Polymer−Polymer Mixtures. Influence of Molecular Size

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ABSTRACT: Polystyrene (PS) and poly(tetramethyl bisphenol polycarbonate) (TMPC) form thermodynamically compatible mixtures below a lower critical solution temperature. In this regime, the PS-component in thin PS−TMPC films, supported by SiO_x/Si substrates, preferentially enriches the free surface, forming a wetting layer, whereas the TMPC component enriches to the polymer−substrate interfacial region. We examined the dependence of the effective glass transition temperature, T_g, on film thickness, h, for 50/50 wt % mixtures on SiO_x/Si substrates. In these experiments, the molecular weight, M_{PS}, of the PS component was varied by over 2 orders of magnitude (4 kg/mol< M_{PS} <900 kg/mol) while the TMPC molecular weight remained fixed. The glass transition temperature of the M_{PS} = 4 kg/mol sample is approximately 25 °C lower than that of the other PS samples. We show that the effective glass transition temperature decreased with decreasing film thickness, $\Delta T_g < 0$, where $T_g(\infty)$ is the glass transition temperature at large h. Moreover, despite the variation in the glass transition temperatures associated with the PS components in the mixtures, $\Delta T_g(h)$ was, within experimental error, independent of M_{PS}. $T_g(\infty)$, on the other hand, was sensitive to the T_g of the PS component. The implications of these findings are discussed.

Introduction

Glass transition continues to be an active area of research, and interest has broadened in scope due to recent experiments which reveal evidence for a film thickness dependence of the effective glass transition temperature, T_g, of polymer films when the films are sufficiently thin.[1−26] In the polystyrene (PS)−SiO_x/Si system, the effective T_g decreases with decreasing film thickness when h is thinner than a threshold film thickness of $h_c \sim 50$ nm.[4,10,11,15] In freely standing PS films, the same trends are apparent, except that the effect is more significant, wherein the decrease is approximately twice as much as that of PS on SiO_x/Si.[10] The opposite trends, T_g increasing with decreasing h, have been observed in the poly vinylpyridine (PVP)−SiO_x/Si, poly(methyl methacrylate) (PMMA)−SiO_x/Si, and tetramethyl bisphenol polycarbonate (TMPC)/SiO_x/Si systems.[1,5,8,16] In these systems, unlike the PS−SiO_x/Si system, the polymer segments have particularly strong interactions with the substrate (hydrogen bonding). Therefore, in thin polymer films, the effective glass transition is influenced by the nature of the polymer segment−segment interactions in relation to the segment−“wall” (free surface or substrate) interactions. Sufficiently strong segment−“wall” interactions contribute to an increase in the glass transition temperature of the film, provided the film is sufficiently thin.

While to date there is no universally accepted explanation, a number of models have been proposed. Keddie et al. used an empirical equation to describe the decrease in T_g with decreasing film thickness for PS films on SiO_x/Si substrates[4]

$$T_g = T_g(\infty)\,[1 - (A/h)^{\delta}], \tag{1}$$

In the above equation $T_g(\infty)$ is the glass transition temperature at large h, δ indicates the degree to which T_g decreases with decreasing film thickness, and A is a length scale. They argue that the decrease in T_g is due to the presence of a high mobility (“liquidlike”) layer at the surface. The high mobility surface layer exerts an increasing influence on the effective T_g of the film as its thickness decreases, leading to the observed decrease in T_g. It suffices to mention that chain segments at the free surface exhibit higher segmental mobilities than those in the interior of the film.[28,29] This is consistent with the notion that the polymer segment−segment density is lower at the free surface and that these segments possess larger configurational freedom. It has further been suggested that the size of the high mobility surface region is related to the average size of the chains in the melt.[27]

Kim et al. proposed an alternate model for the decrease of T_g with decreasing h.[16] They suggest that a series of layers, each possessing a different T_g, comprise the film. The layer at the free surface has the lowest T_g whereas the layer adjacent to the substrate possesses the largest. Of course, the fact that chain segments at the free surface possess larger configurational freedom and lower packing density is not inconsistent with the possibility of a lower surface T_g.[27,31,32] An excess concentration of chain ends and associated larger free volume at the free surface are among other reasons that have been suggested to account for the possibility of a surface T_g.[29,30] Kim et al. predicted that the effective $T_g(h)$ of the film would be

$$T_g(h) = T(\infty)\frac{h}{\sigma + h} \tag{2}$$

Here, σ measures the extent to which T_g decreases with h, particularly at small h.

A percolation, free volume-based, model was proposed by Long and Lequeux.[3] In this model, they propose that domains of rapidly and of slowly relaxing clusters of particles comprise the sample (dynamic heterogeneity). Percolation of the slow domains denotes the onset of the

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glass transition temperature. Since the percolation threshold in three dimensions is lower than in two dimensions, the glass transition should in principle occur at a lower temperature in sufficiently thin films than in the bulk. The effect of the strong polymer−substrate interactions is to increase the effective number of slow domains in the sample; hence, the effective temperature at which percolation occurs is higher than that for bulk analogues.

Recently we used spectroscopic ellipsometry to examine the dependence of the effective T_g on film thickness in the miscible blend system of TMPC and PS.[1] While one might be initially inclined to argue that a study involving mixtures might complicate the issues further, there is a good reason to do this. Consider that in this miscible blend, the T_g of TMPC is much larger than that of PS, ∼220 °C compared to 100 °C. Second, TMPC interacts strongly with the SiO_x substrate whereas PS preferentially enriches the free surface (lower surface energy).[1,33−35] The friction coefficient, which controls the segmental mobilities, in TMPC is also much larger than PS. Hence this is a system in which a high-mobility, lower T_g, polymer−free surface region (layer) and a low mobility, and appreciably higher T_g, polymer−substrate ”layer” could be “tailored”.

In our previous study, we examined thin films (10 nm $< h <$ 200 nm) of TMPC and of PS−TMPC mixtures (the PS molecular weight was 49 kg/mol). We showed that the T_g of TMPC increased with decreasing h ($\Delta T_g(h) > 0$) for $h < h_c$, where $h_c \sim 50$ nm. On the other hand, the effective T_g of mixtures containing 30 and 50 wt % PS decreased with h for $h < 50$ nm ($\Delta T_g(h) < 0$). We also investigated the compositional dependence of mixtures of films with thicknesses $h > 50$ nm. While the compositional dependence of T_g for both bulk and thin films exhibited negative deviations from predictions based on a rule of mixtures, we learned that the deviation in the films was appreciably smaller. This difference was attributed to the fact that the increase in the specific volume that results from mixing PS and TMPC, leading to the negative deviation in the T_g vs composition dependence, is suppressed in thin films (confinement).

In this paper, we examine the effect of changing the molecular weight of the PS component by 2 orders of magnitude, from $M_{PS} = 4$ to 900 kg/mol, while keeping that of the TMPC molecular weight fixed. Decreasing the PS molecular weight from 900 to 4 kg/mol results in a decrease in the PS bulk T_g from 100 to 75 °C and a decrease in the radius of gyration of the PS chains by just over an order of magnitude. Since the PS component preferentially resides at the free surface, varying the PS molecular weight and associated T_g will enable an understanding of how the size of the chains and the T_g of the PS component influences $T_g(\infty)$ and $\Delta T_g(h)$.

Experimental Section

Variable angle spectroscopic ellipsometry was used to determine the glass transition temperatures of thin PS−TMPC films on SiO_x/Si substrates. Here, 50/50 wt % mixtures of polystyrenes of different molecular weights, 4, 49, 290, and 900 kg/mol (dispersity indexes of 1.06, 1.06, 1.06, and 1.10, respectively), with TMPC of molecular weight 37 900 (dispersity index 2.75) were dissolved in toluene and spin cast onto silicon substrates. The silicon substrate has a native SiO_x layer of thickness 2 nm. This thickness was determined by spectroscopic ellipsometry. By adjusting the spin rates and the solution concentrations, thin films ranging from ∼20 to ∼200 nm were prepared. All samples were then annealed above their bulk T_g for several hours before the spectroscopic ellipsometry measurements were performed.

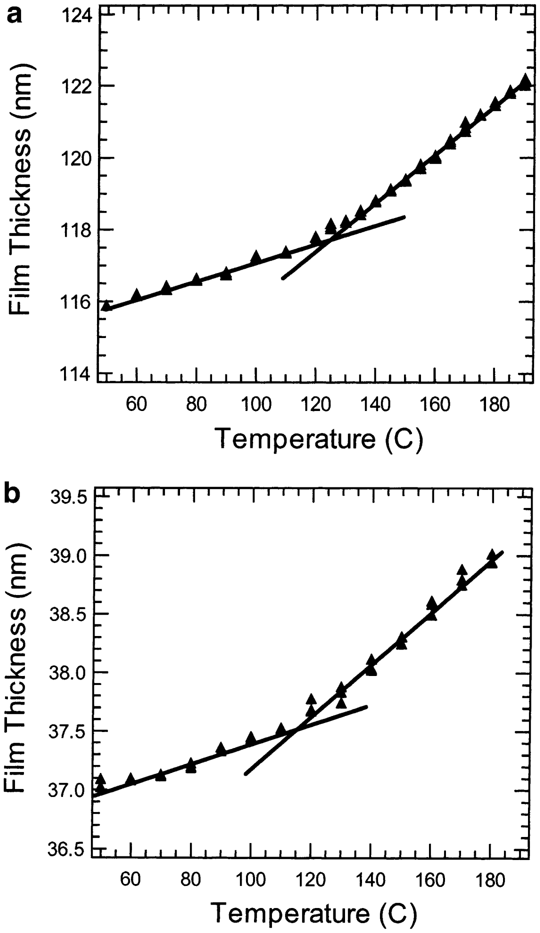

Figure 1. Typical temperature vs film thickness data for films of two different thicknesses for a 50/50 wt % blend of TMPC and PS are shown here. The glass transition is identified as the temperature at which the two lines drawn through the data intersect.

After the samples were annealed, thermal measurements were performed using the variable angle multiwavelength spectroscopic ellipsometer (J. A. Woollam Co.) equipped with a homemade heating stage. Ellipsometric angles, ψ and Δ, were measured with a constant heating rate of 1 °C /min. Increments of 10 and 5 °C were used for temperatures far away from and close to T_g, respectively. Each sample was held at a given temperature for approximately 2 min before increasing to the next temperature for subsequent measurements. Three data points were collected at each temperature. The temperatures were controlled with an accuracy of ±0.5 °C. Film thicknesses were measured by fitting the ellipsometric angles with a Cauchy model (using software provided by the manufacturer). Since the measurements and analysis are standard and will not repeated in this paper.[1,4,16] Parts a and b of Figure 1 show typical thermal scans of the samples. The data in each graph clearly exhibit distinct glassy and rubbery regions. T_g was determined by fitting straight lines through the data in the glassy and rubber regions. The temperature at which the lines intersect is identified as the average T_g of the film.

This is a well-characterized system, both in bulk and in thin films. It is well-known that in this mixture the free surface is enriched with PS and that TMPC resides at the substrate.[33−35] Since we are in the miscible regime, below the LCST, of the mixture, the layers of enrichment are essentially wetting layers and are therefore of order nanometers. We performed angle-resolved X-ray photoelectron spectroscopy (XPS) on samples that were annealed above the T_gs of the samples

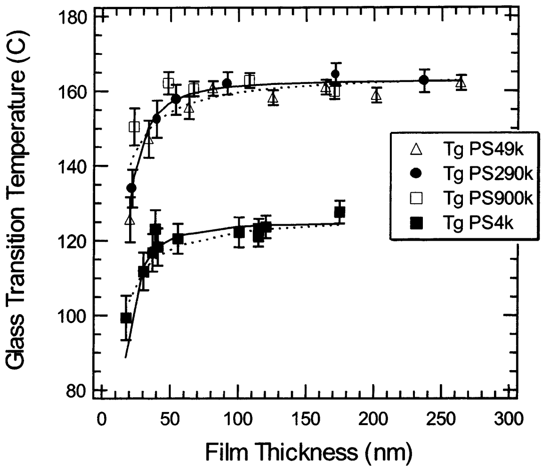

Figure 2. Glass transition temperatures plotted as a function of film thickness for 50/50 wt % mixtures of TMPC/PS4k, TMPC/PS49k, TMPC/PS290k, and TMPC/PS900k. The solid lines were computed using eq 1; the broken lines (- - -) were calculated using eq 2.

(typically at 150 °C) and the mass fraction of PS in these 50/50 mixtures ranged between 71 and 75%, regardless of the PS molecular weight. Note that in the miscible regime, the surface enrichment is, at best, weakly dependent on temperature and molecular weight. Note that in the temperature range above 240 °C, thin films of these samples undergo surface directed spinodal decomposition.[34−35] Here macroscopic layers of PS and TMPC develop at the appropriate boundaries and the interfacial segregation would be molecular weight dependent. Our experiments were conducted below this temperature in the miscible regime.

Result and Discussion

The thickness dependencies of the glass transition temperatures for different 50:50 wt % mixtures containing PS of varying molecular weight, M_{PS}, are plotted in Figure 2. The glass transition temperatures of the mixtures with the $M_{PS} = 4$ kg/mol PS component are approximately 40 °C lower than those which include PS molecular weights of $M_{PS} \geq 49$ kg/mol. We first comment on the latter data set involving PS samples of $M \geq 49$ kg/mol. T_g is constant (162 °C) for $h > h_c \sim 50$ nm, whereas it decreases for $h < h_c$. Equation 1 was used to fit these data, using $A = 5.4$ nm and 1.93 ± 0.3. These values of A and δ are, within experimental error, equal to those used by Kawana and Jones ($\delta = 1.1$, $A = 8.6$) to describe the PS/SiO$_x$/Si system.[15] Using eq 2, we found that $\sigma = 1.1 \pm 0.1$ nm, independent of M_{PS}.[16] Clearly, both predictions provide reasonable descriptions of our data.

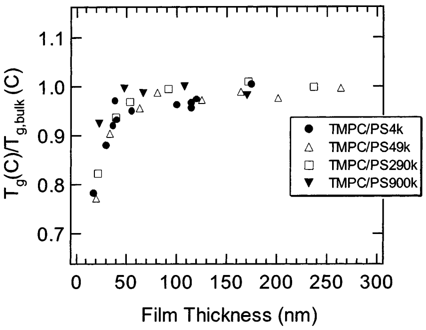

Figure 3. Glass transition temperatures, normalized by bulk glass transition temperature, $T_g(\infty)$, plotted as a function of h for different PS molecular weights.

The effective $T_g(\infty)$ of the mixture containing the $M_{PS} = 4$ kg/mol PS component is approximately 40 °C lower than that of the higher molecular weight PS−component mixtures. This is not surprising since it is well-known in miscible blends involving components with different T_gs, that the T_g of the mixture resides between the T_gs of the pure constituents. There are in fact two related reasons that low molecular weight polymers exhibit lower T_gs than their high molecular weight analogues. One explanation is that the lower T_g is due to the extra fractional free volume associated with the excess number of chain ends per unit volume in low molecular weight polymers compared to their high molecular weight analogues. This argument leads to the following prediction for the molecular weight dependence of the glass transition, $T_g(M_n) = T_g(M_n \rightarrow \infty) - \text{constant}/M_n$, where M_n is the number-average molecular weight.[36] DiMarzio and Gibbs, on the other hand, pointed out a long time ago that it is more useful to think about differences in configurational entropy of the chains.[37] Specifically, the low molecular weight species have lower T_g's than their high molecular weight analogues because of the larger configurational entropy associated with packing small chains compared to long chains. They predicted virtually the same dependence for T_g on M_n, avoiding ambiguities associated with specifying a reliable and consistent definition of free volume.

The depression in the effective glass transition, $\Delta T_g(h)$, of these 50:50 wt % samples is the same, regardless of M_{PS}. This is illustrated in Figure 3, which shows a plot of $T_g(h)/T_g(\infty)$ vs h. These data show that, regardless of the PS molecular weight, ΔT_g remains the same, within experimental error. We now proceed by recalling that this mixture is below the lower critical solution temperature, in the miscible regime, where the surface is enriched with a thin PS wetting layer with mass fraction ~72%. A wetting layer of TMPC resides at the substrate. The interior of the film is of course a mixture of both components. The data in Figures 2 and 3 indicate that changing M_{PS}, with the accompanying changes in T_g, mobility, chain size, and associated changes with fractional free volume, do not, at least to first order, affect $\Delta T_g(h)$. The primary effect of adding the 4 kg/mol PS-component to TMPC is to decrease $T_g(\infty)$, as anticipated. In addition, it is noteworthy that the depression in T_g is comparable to that observed in PS homopolymers.

While eqs 1 and 2 describe the trends in our data very well, there are obvious concerns. We begin by pointing out that variations in the composition of the film, from the free surface (enriched with the lower T_g PS component) and throughout the interior of the film, toward the substrate (enriched with the higher T_g TMPC-component) should, in principle, reflect local variations in T_g. It follows that if in fact a sample is composed of layers, with each layer possessing a different T_g, which increases from the free surface toward the substrate, then one would anticipate different values of ΔT_g between the high and low M_{PS} samples (recall that the T_g of the $M_{PS} = 4$ kg/mol sample is 25 °C smaller than the other). This was not observed. These observations therefore rule out the notion of such a heterogeneous layered structure. Our observations also rule out the existence of a "liquidlike" layer that would exert an increasing influence on the effective T_g of the film as the film thickness decreased. Had such been the case, then ΔT_g in PS(4 kg/mol)−TMPC sample should have been much larger than that observed in the others, and this too was not the case.

Studies of PS−poly(2,6-dimethyl-*p*-phenylene oxide (PPO) mixtures on SiO_x/Si substrates reveal that $\Delta T_g < 0$ over a range of compositions and that the magnitude of ΔT_g is comparable to that observed in the PS/SiOx/Si system.[39] Clearly the results of the PS−PPO/SiO_x/Si and PS−TMPC/SiO_x/Si systems suggest that ΔT_g is comparable for both the homopolymers and polymer−polymer mixtures.

We suggest that $\Delta T_g(h)$ is determined by the packing of chains over three basic length scales. The first is the distance from the free surface over which the polymer segment−segment packing (configurational entropy) are modified, the second length-scale is the distance from the substrate over which the polymer segment−segment packing is modified, and the third is the interior of the film which we assume is bulklike. There is, of course, ample precedence for such assignments.[13,31,32,38] The length scale of the packing density at the free surface is not believed to be determined by the size of the chains. Near the free surface, the chains will have a larger configurational freedom. Near a hard interface, the configurational freedom is reduced. Tentatively, it appears that $T_g(\infty)$ is determined largely by the "bulk" properties (packing), whereas ΔT_g is influenced by the packing of chains at the interfaces. This is more apparent below.

Curro and McCoy proposed the following model to describe the depression in the glass transition in thin homopolymer films.[38] They initially consider the packing of segments in a bulk material. They then imagine that segments in this material are confined within two impenetrable boundaries a distance H apart. The segment densities near the boundaries change in order to equalize the chemical potentials in the region. They suggest that the depression in the glass transition could be written as

$$\Delta T_g = \frac{1}{\kappa}\frac{\mathrm{d}T_g}{\mathrm{d}P}\frac{2\Gamma(H)}{H\rho_{\mathrm{bulk}}} \qquad (3)$$

where κ is the bulk modulus, $\Gamma(H) = {}^1/_2 \int_0^H[\rho(z) - \rho_{\mathrm{bulk}}]\,\mathrm{d}z$ and z is the direction normal to the sample surface. In this symmetrically confined system, $\Delta T_g < 0$ if there is a depletion of segments at the boundaries and $\Delta T_g > 0$ if the segment−"wall" interactions are strong in relation to the segment−segment interactions. Using equation-of-state information about some specific homopolymers polymers, they made reasonable estimates of ΔT_g. We argue, by extension, that if the system is asymmetric (bounded by a free surface and a substrate), then $\Delta T_g > 0$ if the monomer−"wall" interactions are sufficiently strong to dominate the depletion of chain segments near the free surface, otherwise $\Delta T_g < 0$. It would appear from the above equation that the bulk compressibility (κ^{-1}) largely determines the order of magnitude of the T_g depression.

While our sample is not a homopolymer, it is a miscible system in which the dissimilar chains pack intimately and define new free volume, or configurational entropy, characteristic of the system. The packing of chains in the interior plays an important role in determining the effective $T_g(\infty)$ of the mixture. The polymer chains at the boundaries and the nature of their interactions with the boundaries influence ΔT_g when the film becomes sufficiently thin.

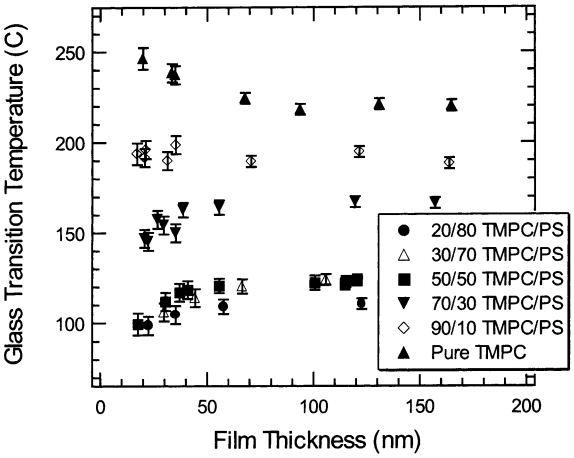

Figure 4. Film thickness dependencies of T_g for the TMPC−PS(4 kg/mol) mixtures plotted at different compositions, $\Delta T_g < 0$, for all mixtures containing more that 10 wt % PS.

Our results clearly indicate that the PS component has the opposite effect on the effective T_g compared to the TMPC component. Since $\Delta T_g > 0$ for TMPC, and $\Delta T_g < 0$ for PS, there must exist a PS composition at which $\Delta T_g \sim 0$. This composition is approximately 10 wt % PS, as shown in Figure 4, for the $M_{PS} = 4$ kg/mol PS component samples. For larger PS weight fractions, $T_g(\infty)$ decreases and ΔT_g increases slightly; the changes in $T_g(\infty)$ are larger than those of ΔT_g. When the PS composition increases beyond 50 wt %, ΔT_g becomes roughly independent of composition. These results confirm the fact that ΔT_g(PS−TMPC) ~ ΔT_g(PS) for PS weight fractions greater than 10%.

Conclusions

Effects associated with molecular weight and film thickness on the effective glass transition temperature of the TMPC/PS blend system on SiO_x/Si substrate were examined using spectroscopic ellipsometry. All experiments were conducted in the miscible range below the LCST, where the free surface is enriched with a PS layer and the substrate with a thin TMPC layer. The PS molecular weight varied by 2 orders of magnitude, with an accompanying change in the glass transition temperature of the polymer by 25 °C. For the studies conducted on the 50:50 wt % mixtures, T_g decreased with decreasing h and the depression in the glass transition, $\Delta T_g(h)$, remained relatively constant regardless of the glass transition temperature of the PS component. The primary influence of the low molecular weight PS component is to decrease $T_g(\infty)$, which is expected for miscible blends. The packing of the dissimilar, yet compatible, blend constituents in the interior of the film determine $T_g(\infty)$ whereas the comparative nature of the relevant monomer−"wall" interactions determines ΔT_g.

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