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Effects of Chain Ends and Chain Entanglement on the Glass Transition Temperature of Polymer Thin Films

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ABSTRACT: Monodispersed polystyrene with different molecular weights, M_w, from below the entanglement molecular weight, M_e (∼20K Da), to well above was studied for effects of chain ends and chain entanglement on the glass transition temperature, T_g, of polymer thin films. The relative importance between these two effects is expected to reverse as M_w crosses over M_e. We found that the T_g generally decreases with decreasing film thickness, t, consistent with previous findings. The difference between results from the $M_w = 13.7$K and the 550K samples was negligible, suggesting that entanglement has little significance on the thickness dependence of the T_g of polymer under confinement in thin films. On the other hand, the M_w dependence of T_g was markedly weakened compared to that of the bulk when t was reduced to 15 nm. According to Fox and Flory's theory, our result reveals that some of the chain ends in the film have been segregated to the surface, but they have little effect on the T_g of the film. Our findings undermine a surface mobile layer where the surface chain ends localize being the cause for the reduction of T_g observed.

Introduction

When the physical dimension of a sample becomes comparable to the length scale characteristic of the motion of the constituting molecules, the dynamical properties may display deviations from the bulk. This confinement effect on the glass transition dynamics has been observed in a large number of confined polymer systems recently.[1] However, the physical mechanism remains unknown thus far. In an elaborate experiment by Jones and co-workers,[2] the glass transition temperature, T_g, of polystyrene (PS) thin films deposited on silicon covered with native oxide was found to be depressed with respect to the bulk T_g (∼100 °C) when the film thickness, t, was less than ∼40 nm, and the reduction in T_g grew with decreasing t, becoming ∼20 °C when t reached ∼20 nm. In a later experiment, Forrest et al. found that the reduction in T_g could be drastically exacerbated if the PS films were free-standing[3] where a ∼70 °C reduction in T_g was found in a 30 nm thick film. On the other hand, polymer thin film systems where the T_g increased with decreasing t were also found.[4] In supported polymer films that are stable against dewetting from the underlying substrate, the interaction between the polymer and the substrate surface has to be attractive.[5] From this point of view, stable supported polymer thin film systems wherein the T_g decreases with decreasing film thickness necessitate existence of a mechanism that opposes the attractive polymer−substrate interactions.

Jones and co-workers[2] suggested that a high-mobility surface layer exists well below the bulk T_g, which expands as the temperature, T, is increased. The T_g is reached when the high-mobility surface layer covers the entire film. By assuming that the thickness of the high-mobility surface layer, $\xi(T)$, expands according to $\xi(0)(1 - T/T_g^\infty)^{-1/\nu}$, where T_g^∞ is the bulk T_g and ν is a positive constant, a model for the thickness dependence of T_g was obtained:

$$T_g(t) = T_g^\infty[1 - (\xi(0)/t)^\nu] \qquad (1)$$

Good quantitative agreement has been found between this simple model and the observed thickness dependence of T_g.[2] This idea of a high-mobility surface layer being the basis for the mechanism governing the reduction of T_g in polymer ultrathin films is by far the most accepted and consistent with experiments.[1]

A number of factors may render the free surface of a polymer with added mobility. Incorporating the Sanchez−Lacomb lattice fluid model[6] to the Cahn−Hilliard theory of inhomogeneous fluid surface,[7] Poser and Sanchez showed that the surface of a polymer has a density gradient that tapers asymptotically to zero toward the vacuum side.[8] In the molecular dynamics simulations by Mansfield and Theodorou of the glassy atactic polypropylene,[9] the center-of-mass motion of the chains located within 2−3 times the unperturbed macromolecule radius of gyration from the free surface was found to be enhanced, which the authors attributed to the reduced mass density of the polymer near the surface. However, two other origins are likely also at work.

One is segregation of chain ends to the surface, which may come from an entropic penalty suffered by polymer segments located at an interfacial boundary, or enthalpic favoritism for chain ends with lower surface energy to be segregated to the surface.[11] This interesting effect has been seen in the Monte Carlo simulation study of Cifra et al.[10] and a dynamic secondary ion mass spectroscopy (SIMS) study of Kajiyama et al. on low number-averaged molecular weight, M_n (≤30K Da) PS that are end-labeled with deuteration.[12] (In the present experiment, all samples have $M_w/M_n \leq 1.1$. Hence, we do not distinguish between M_w and M_n in our discussion.) Since chain ends are known to act as plasticizer to the T_g of a polymer,[13] an increase in the number fraction of chain ends at the free surface should render the surface molecules higher mobility. The other

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possible origin for an enhanced surface molecular motion is a reduction in the polymer entanglement expected to take place near an interface:[14] Spatial limitations imposed by the boundary wall cause the neighboring polymer coils to be compressed along the direction normal to the interface. On the other hand, the in-plane dimensions remain intact because the segmental random walk along orthogonal directions are independent. The volume pervaded by chains neighbor to an interface should thus be reduced. The resultant densification in packing within the polymer coil will give rise to a diminished amount of overlap between neighboring chains as the mass density of a polymer is usually not perturbed (because of the insurmountably large compressibility typical of polymers), leading to an enhanced mobility locally.

In this paper, we study the M_w dependence of the T_g of polymer thin films over a wide M_w range to decide whether either or both of these two effects are at work. For the effect on chain ends, results of Kaijiyma et al.[12] suggest that effects of segregated surface chain ends diminish as M_n increases. In particular, these authors found that enhancement in the surface mobility of a PS sample could no longer be detectable when M_n became bigger than 30K Da. On the other hand, effects associated with reduced entanglement at an interface should demise if M_n is smaller than the entanglement molecular weight, M_n (~20K Da). In the following, we will compare the thickness dependence of T_g of monodispersed PS thin films with M_w = 13.7 K (< M_e) and M_w = 550K Da ($\gg M_e$) (polydispersity $\leq$ 1.05 for both) to inspect for any difference in the data due to a crossover of the two effects. We will also investigate for any variation in the M_w dependence of T_g for PS films with different thicknesses, which, on the basis of Fox and Flory's theory,[13] may shed light on the effects of chain ends on the T_g of polymers under confinement. Previous studies on the effect of molecular weight on the thickness dependence of T_g of polymer thin films[2] was limited to M_w ($\leq$120K Da) much larger than the M_e, in which no dependence on M_w was discernible. In the present study, we extend the minimum M_w to 13.7K Da, below the M_e, to resolve the issues explicated.

Experimental Section

Measurements were carried out in a VASE system by J.A. Woollam Co. (Lincoln, NE) of the rotating analyzer type with wavelengths variable from 300 to 1700 nm and incident angle of the probe beam from 0° to 90°. The procedure involves monitoring the ellipsometric angles, δ and ψ, which are directly related to the film thickness and sample refractive index, as a function of temperature, T, at a heating rate of 2 °C/min, whereby no detectable change in the measured T_g could be found upon further reduction in the heating rate. The T_g was determined as the temperature at which slope of δ or ψ vs T plot changed discontinuously. For samples with low M_w and thickness $\leq$ 15 nm where dewetting instability may be a concern, measurements were repeated at least twice on the same sample to ensure reproducibility. Monodispersed PS were purchased from Scientific Polymer Products, Inc. (Ontario, NY). PS thin films were prepared by spin-coating solutions of the polymer in toluene (0.3−2 wt %) onto Si substrates covered with a native oxide layer (~12 Å). Before measurement, samples were annealed in a vacuum oven (~10^{-2} Torr) at 125 °C for 5 h and allowed to cool under vacuum at ~0.8 °C/min to room temperature. With this sample preparation protocol, no change in the measured T_g was noticeable by increasing the annealing temperature or annealing time had dewetting not occurred. Film thickness was determined by model fitting the VASE spectroscopic data to multiple Fresnel reflectivity of a polymer/SiO_2/Si three-layer using the analysis software built into the VASE.

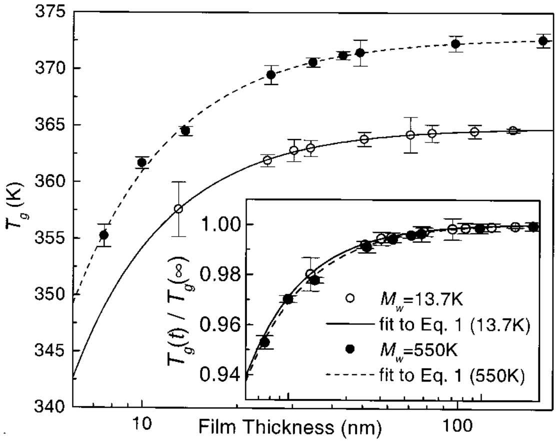

Figure 1. (main panel) T_g vs t for samples with M_w = 13.7K (open circles) and 550K Da (solid circles). (inset) Same data but normalized by the corresponding T_g^∞, which is determined by fitting data of the main panel to eq 2. Solid and dashed lines are the fits.

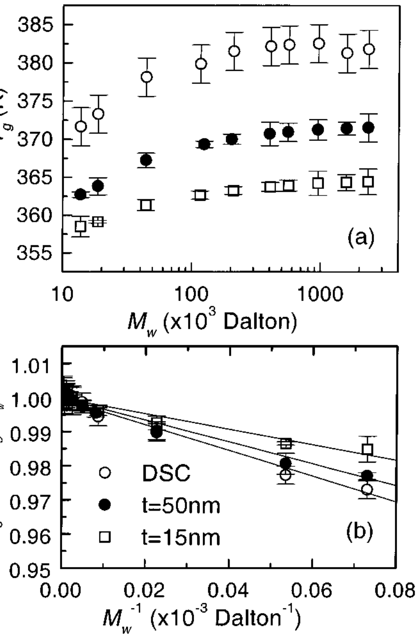

Figure 2. (a) M_w dependence of the T_g of PS thin films with t = 15 nm (open squares) and 50 nm (solid circles). Open circles are T_g data of the bulk. (b) Same data as in (a) but normalized by the corresponding T_g of the M_w = 2.3M Da thin film and plotted against $1/M_w$. Solid lines are linear fits to the data.

Results and Discussion

The main panel of Figure 1 shows the thickness dependence of T_g of the M_w = 13.7K and the M_w = 550K Da PS films. The two sets of data are far apart because of the strong M_w dependence of T_g of the bulk samples (see Figure 2a). Fits to the model by Jones and coworkers (eq 1) were shown in the figure by the smooth lines drawn through the respective data. The fitted parameters together with results of ref 2 are tabulated in Table 1. For a better comparison, we normalize the data shown in the main panel of Figure 1 by the corresponding fitted value of T_g^∞ using eq 1. Results were shown in the inset. As seen, the difference between the two sets of data is negligibly small, which is also manifested in the closeness of the fitted $\xi(0)$ and ν

Table 1. Comparison between Fitted Parameters for Data in Figure 1 Using Eq 1 and Those Obtained in Ref 2

fitted data	$\xi(0)$ (nm)	ν
$M_w = 13.7$K Da	0.87 ± 0.06	1.44 ± 0.04
$M_w = 550$K Da	0.78 ± 0.13	1.35 ± 0.11
ref 2	3.2 ± 0.6	1.8 ± 0.2

parameters found for the two sets of data (Table 1). We note that there is apparent discrepancy between our data and those of ref 2 (Table 1). The reason is unclear at the present time. To make sure that it did not come from erroneous measurements of t, which is plausible if estimation of the thickness of the native SiO_2 layer were inaccurate, we rechecked the measurements of t by X-ray reflectivity. Excellent agreement ($\leq \pm 5\%$) between results obtained by the two different techniques confirms accuracy of our measurements. Notwithstanding the noted difference between our data and results of ref 2, the close agreement between data of the 13.7K and 550K samples found indicates that neither the chain end effect nor the entanglement effect elucidated above are essential factors for the reduction of T_g observed in PS thin films supported on native SiO_2.

To investigate whether there is at all any change in the influence of chain ends on the T_g of polymer thin films, especially there is likelihood due to segregation of chain ends to the surface, we studied the M_w dependence (13.7K to 2.3M Da) of T_g of PS films at two different thicknesses (t = 15 and 50 nm). Shown in Figure 2a are the data plotted as T_g vs M_w. Data of the bulk samples obtained by DSC are also shown. The three sets of data are distinctive attributable to the strong t dependence of T_g (see Figure 1). According to Fox and Flory (FF),[13]

$$T_g(M_w) = T_g|_{M_w=\infty}(1 - m_0/M_w) \qquad (2)$$

where m_0 is a constant signifying the difference in mass density between a chain segment, ρ_s, and a chain end, ρ_e, i.e., $m_0 \sim \rho_s - \rho_e$. For PS, it has been found that $T_g|_{M_w=\infty} = 373$ K and $m_0 = 455.8$.[13] We normalize the data of Figure 2a by the corresponding T_g of the M_w = 2.3M Da sample and plot them vs M_w^{-1} in Figure 2b. As seen, the data fall into straight lines for $M_w \leq \sim 10^5$ Da, in accordance with the FF relation (eq 2). Small deviations, however, are notable in the large M_w region. Similar upturn in the data has also been observed by Rudin et al. in a comparable study.[15] The authors showed that the apparent disagreement with FF's came from the different M_w–viscosity relation used by FF to derive the M_w from the viscosity data of the polymer solutions, which in fact deviates from the more general relation Altares et al. found.[16] The M_w values of our samples had been determined by the manufacturer by gel permeation chromatography and reconfirmed by light scattering to ~1.5% agreement and hence cannot be the cause for the observed deviation from the FF relation (eq 2). Nevertheless, FF's interpretation provides by far the most fitting physical picture for the M_w dependence of T_g, and in light of the smallness of the deviations found, we will use the picture of FF as the basis for our interpretation of the data.

As seen in Figure 2b, the slope of the best linear fits to the data (solid lines) based on eq 2 decreases in magnitude as the sample dimension is decreased. In particular, the fitted value of m_0 for data of the 15 nm thick films is 40% less than that from data of the bulk samples. We recall from the above that $m_0 \sim \rho_s - \rho_e$. Therefore, a reduction in m_0 may be due to either an increase in ρ_e or a decrease in ρ_s. We eliminate the observed reduction in m_0 comes from a reduction in ρ_s. As seen in Figure 1, the T_g of 15 nm thick PS films reduces by only ~2% from T_g^∞. Even if we attributed the entire amount of reduction to a decrease in ρ_s of the polymer under confinement, the amount of change in ρ_s is still too small to account for the 40% reduction in $\rho_s - \rho_e$ deduced above. Most probably, the apparent reduction in m_0 is due to an increase in ρ_e as the film thickness is reduced. A tempting explanation for this observation is an enhanced segregation of chain ends to the surface as the polymer film gets thinner, which then leads to a reduction in the number of chain ends remaining in the film body that ultimately determines the T_g. A simple argument will immediately show that this scenario is unlikely. A reduction in the film thickness can only result in a trim down in the entropy of the film body, which will narrow the entropy disparity between the film body and the surface. On the basis that surface segregation of chain ends is driven by entropic favoritism of chain ends to be located at the film surface, the degree of surface segregation of chain ends in thin films should in fact lessen. We think that the apparent increase in ρ_e revealed in the data is due to an increase in the number fraction of the surface chain ends as the film thickness is decreased:

$$\rho_{e,apparent} = \rho_e N_{e,t}/(N_{e,t} - N_{e,s}) \qquad (3)$$

where $\rho_{e,apparent}$ is the apparent mass density of chain ends in the body of the film excluding the surface region, ρ_e is the actual mass density of chain ends in the polymer film, $N_{e,t}$ is the total number of chain ends in the film, and $N_{e,s}$ is the number of chain ends in the surface region only. Equation 3 describes how the percentage difference, $\Delta m_0/m_0 \sim (\rho_{e,apparent} - \rho_e)/\rho_e$, varies with the number fraction of the surface chain ends, $N_{e,s}/N_{e,t}$. In a bulk sample, the ratio $N_{e,s}/N_{e,t}$ approaches zero, so the apparent mass density of chain ends, $\rho_{e,apparent}$, is the same as ρ_e. In a 15 nm thin film, however, the ratio may deviate substantially from zero, depending on the thickness of the surface region and the amount of enhancement (or diminishment) in the segregation of chain ends to the surface. To account for the observed 40% increase in $\Delta m_0/m_0$ in the 15 nm thick films, the present model predicts that 28.6% of the total chain ends belong to the surface region. This corresponds to an effective surface layer thickness of 4.3 nm, which is in excellent agreement with previous experiments.[12]

To further confirm that the surface chain ends does indeed cause the change in T_g vs M_w observed, we studied the thickness dependence of T_g for a binary blend of 13.7K and 550K PS (in 1:1 wt ratio). For a binary blend of polymers with different molecular weights, Hariharan et al.[17] showed that entropic effects will drive the low-M_w component to the boundary wall, producing a local enrichment of this component at the sample surface. In our blend films, we also expect the 13.7K constituent to segregate to the surface. If the chain ends indeed affected the T_g of a polymer blend in thin films and in the bulk alike, the T_g of the blend films should follow the model of FF (i.e., $T_g = 1/[1/T_g|_{M_w=13.7K} + 1/T_g|_{M_w=550K}]$),[13] which is displayed in Figure 3 by the dashed line. Shown in the same figure are the measured T_g's of the blend films (solid squares). As seen, the data

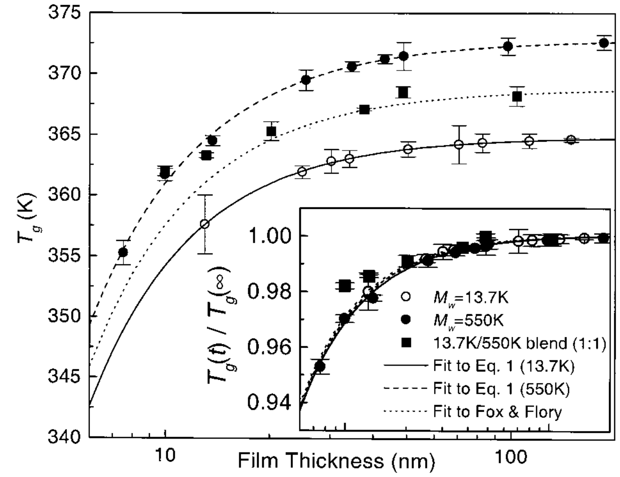

Figure 3. (main panel) Comparison between T_g of the 13.7K/550K blend films (solid squares) and data of the pure constituents reproduced from Figure 1. The dashed line shows the model by Fox and Flory (see text). (inset) Same data but normalized by the corresponding T_g^∞.

agree quite well with FF's model for films that are thicker than ~30 nm but approaches that of the 550K sample for films that are thinner. We have checked by SIMS that the composition of a similarly prepared set of binary blend films (except that one component was deuterated for labeling and the films dried under vacuum at room temperature to avoid phase separation between the two components) is independent of the film thickness for $t = 10-200$ nm. This excludes the possibility that the anomalous behavior of the T_g of the blend films noted in the $t \leq \sim 30$ nm region of Figure 3 is due to changes in the mixture composition because of variations in the spin-coating conditions employed in preparing the thinner films, such as diluter polymer solutions and higher spinning speeds. Our result therefore suggests strongly that those chain ends that are segregated to the surface do not contribute to the T_g of the film, but instead only those that remain in the film body do. We remark that we do not notice any sign of two T_g's from our data of the blend films. However, it is possible that the feature associated with the chain end enriched region is too small to produce features detectable in the ellipsometric data. Kajiyama and co-workers[12] found that the surface T_g of PS containing molecular weight components with $M_n \leq \sim 30$K Da is less than the bulk T_g attributable to the promoted population of chain ends at the free surface. Our findings reveal that this dynamically more active surface layer is not directly related to the T_g of polymer ultrathin films. On the basis of the above discussions, it seems that a mechanism that accounts for a more global enhancement in the molecular mobility than one that is local to within a surface layer of a few nanometers thick, where localization of surface chain ends was found,[12] is at work in causing the T_g reduction in polymer thin films observed in this study and by others recently.

Conclusions

In conclusion, we have studied the M_w dependence of the T_g of monodispersed PS ultrathin films supported on Si covered with native oxide over $M_w = 13.7$K to 2.3M Da. Consistent with previous results, we found that the T_g of the thin films decreased as the film thickness was reduced. Close agreement between the thickness dependence of T_g found for the $M_w = 13.7$K and the $M_w = 550$K Da sample (Figure 1) suggests that perturbations in chain entanglement and chain end distributions in thin films cannot play a significant role in the observed variations in the T_g of polymer ultrathin films. On the other hand, the Fox and Flory relation governing the T_g vs M_w of the polymer films was found to deviate progressively from that of the bulk as the film thickness was decreased (Figure 2). In particular, the m_0 parameter in Fox and Flory's model that signifies the difference between the mass density of a chain segment and that of a chain end diminished substantially by ~40% as the film thickness was reduced to 15 nm. We interpret this observation as a revelation that chain ends that are segregated to the surface do not contribute to the measured T_g of the film, which is supported by results from the study on 1:1 (wt ratio) binary blend films of 13.7K and 550K PS (Figure 3). If the proposed independence between surface chain ends and thin film T_g were correct, the observed reduction in the T_g of the polymer films cannot be due to a surface rubbery layer originated from the segregated chain ends.

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