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Effect of strongly favorable substrate interactions on the thermal properties of ultrathin polymer films

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The thermal behavior of ultrathin films of poly-(2)-vinylpyridine spin-cast on acid-cleaned silicon oxide substrates is considered. The interaction between the polymer and the substrate is polar in nature and very favorable. As a means of examining the thermal properties of the films, x-ray reflectivity is used to measure the temperature dependence of the film thickness. This experimentally measured thickness-temperature data is used to determine transition temperatures and thermal expansivities. Significantly increased transition temperatures (20–50 °C above the measured bulk glass transition temperature) are observed in ultrathin polymer films. The transition temperature increases with decreasing film thickness, while the degree of thermal expansion below the transition temperature decreases with decreasing film thickness. If one assumes that a region of reduced chain mobility exists near the solid substrate-polymer interface, an analysis of the measured thermal expansion behavior below the transition temperature indicates that the length scale of substrate interactions is on the order of the macromolecular size.

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Many high performance materials and devices contain polymer-inorganic interfaces. Despite their widespread technological importance, the properties of these polymer-inorganic interfaces are not well understood experimentally or theoretically [1,2]. This is unfortunate since the interfacial properties oftentimes determine the performance of these materials and devices. The properties of the macromolecules in the interfacial region near the solid substrate, or the interphase, are especially important and interesting. It is believed that the conformation and mobility of the macromolecules in the interphase will be strongly influenced by their specific interaction with the inorganic substrate, the properties of the macromolecules themselves and by external parameters like the temperature. These microscopic interphase properties are intimately related to the macroscopic phenomena of adhesion and debonding.

Although the behavior of polymeric molecules in the bulk is essentially known, as previously noted this is not the case for macromolecules near interfaces. The significant surface:volume ratios present in ultrathin polymer films make them highly interfacial in nature and excellent model systems for determining the properties of macromolecules within the interphase. That is, on average, each macromolecular constituent of such a system is in contact with an interface, either the solid substrate or the free surface. In the most extreme case, where the film thickness is much smaller than the unperturbed dimension of the chains themselves, each macromolecule is essentially confined between the solid interface and the free surface. Therefore, there are two factors by which macromolecules in ultrathin polymer films differ from those contained in the bulk: confinement and substrate interactions. One should note however, that regardless of the film thickness, there is an interphase region near the solid substrate where the physical properties are expected to be much different than those of the bulk material.

There is recent experimental evidence [3–11] that substrate interactions and confinement have a strong influence on the thermal properties of thin polymer films. It has been observed that ultrathin films of polystyrene (PS) on various silicon (Si) substrates display glass transition temperatures, T_g, which are greatly reduced from the value found for bulk polystyrene [3–6,8,9]. It should be noted that T_g was not directly measured in some cases, but was inferred from observations of enhanced chain mobility [3–6]. Recent studies [10,11] of ultrathin polymethylmethacrylate (PMMA) films on Si substrates bearing native oxide surfaces indicate that the T_g of PMMA increases slightly with decreasing film thickness (i.e., ~6 °C increase in T_g with a decrease in film thickness from 3000 to 150 Å) [11]. This is not very surprising since, due to the presence of polar forces, PMMA should display a more favorable interaction with these native oxide surface bearing Si substrates than PS [12]. The effect of this favorable substrate interaction also manifests itself in the thermal expansion behavior observed for these ultrathin films of PMMA. The thermal expansivities were found to be thickness dependent, with the thermal expansion coefficients decreasing with decreasing film thickness both below and above the glass transition temperature [10]. Therefore, it is reasonable that a polymer-substrate combination which is more favorable should display even more modified behavior. Due to its chemistry, one suspects that poly-(2)-vinylpyridine [P(2)VP] and acid-cleaned Si substrates are such a system and should exhibit interactions which are more favorable than those between PMMA and the same substrate.

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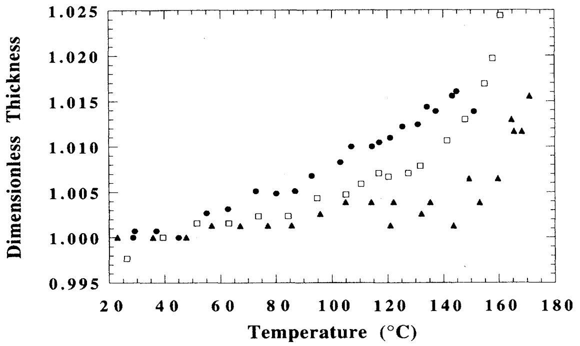

FIG. 1. The temperature dependence of the dimensionless thickness of spin-cast P(2)VP films on acid-cleaned silicon is shown for films which have been cooled back from ~160–175 °C. The film thicknesses displayed here are as follows: (▲) 77 Å, (□) 257 Å, and (●) 413 Å . The effect of diminishing film thickness on the observed thermal behavior is readily apparent.

P(2)VP (Aldrich Chemical Co.) with a weight-average molecular weight of 200 000 g/mol, a polydispersity index of 1.59, and a glass transition temperature of 98 °C (as measured by differential scanning calorimetry) was utilized in the study reported here. To the authors' knowledge the chain size-molecular weight relationship is not known for P(2)VP in the bulk. Assuming that the melt behavior of P(2)VP is similar to that found for PS, the radius of gyration of the P(2)VP used in the study described herein is estimated to be ~120 Å. The P(2)VP was spin-cast from *n*-butanol onto clean Si(111) wafers which had been pretreated with a sulfuric acid–NoChromix [13] solution for at least 12 h, followed by a thorough distilled water rinse. These investigators believe that the surface of these Si wafers is essentially the native oxide with a small fraction of hydroxyl groups. After drying with methanol and acetone, the wafer was rinsed with *n*-butanol several times prior to spin-casting the P(2)VP film at 2000 rpm. The polymer film thickness was controlled by varying the polymer concentration in solution (~1–25 mg/ml). The spin-cast P(2)VP films were then annealed at ~190 °C in a vacuum oven to remove any residual *n*-butanol which may still have been present after spin-casting. After this annealing procedure the ultrathin P(2)VP films were characterized in high vacuum by x-ray reflectometry [14] *in situ*. The films were maintained at the desired temperature for at least 45 min before any x-ray reflectometry measurements were performed. Modeling and fitting of the x-ray reflectivity data was performed by nonlinear least squares fitting of profiles generated using a recursive multilayer method [15]. Specular reflection of x rays allows one to measure the electron density profile perpendicular to a surface and, therefore, the film thickness [14,15]. In this manner the thickness versus temperature data were acquired for each film considered in the study described here.

In Fig. 1 dimensionless thickness-temperature curves are shown for three representative P(2)VP films which were measured as they were cooled from far above the bulk T_g (the results for forward heating are essentially the same with only films thinner than 100 Å exhibiting any hysteresis). The break in the thickness-temperature curve was used in the usual manner to determine the glass transition temperature of each P(2)VP film [7,9,11]. It is apparent that there is a large increase in the observed transition temperature, T^*_{obs}, with decreasing film thickness. The magnitude of the shifts in T^*_{obs} are much larger than those found for PMMA [8,9] and, to the authors' knowledge, are larger than those observed in any other system. The transition temperatures were determined by linear extrapolation from data points well within the glass and liquid states and are tabulated in Table I (they are also presented as a function of film thickness in the inset of Fig. 2). Since several theories of the glass transition propose that there is cooperative motion near the glass transition temperature [16–19], it seems likely that a strong surface interaction could affect the temperature at which this transition takes place. This would be especially true if strong substrate interactions influence chain mobility within the interphase to the extent that large length scale cooperative motions are precluded. These very favorable substrate interactions may lead to highly distorted chain conformations near the solid substrate due to strong adsorption of the P(2)VP onto the silicon oxide surface. Such strong chain distortions would have some influence on the chain mobility and expansion. In light of the fact that some of the observed transition temperatures are 20–50 °C greater than the measured bulk glass transition temperature, it is difficult to determine whether the break in the thickness-temperature curve is due to a glass transition or surface interaction phenomena.

From Fig. 1 it is also apparent that the degree of thermal expansion both above and below the glass transition temperature depends on the film thickness. Below the transition

TABLE I. Transition temperatures of ultrathin poly-(2)-vinylpyridine films.

Film thickness	Heating from glass	Cooling from melt	Heating after cooling
77 Å		152±3 °C	
146 Å		139±5 °C	139±6 °C
203 Å	118±5 °C		
211 Å		124±4 °C	
257 Å		126±5 °C	
272 Å		123±6 °C	
387 Å	116±6 °C		
413 Å		109±3 °C	113±4 °C
885 Å	109±3 °C		
Bulk polymer	98±3 °C		

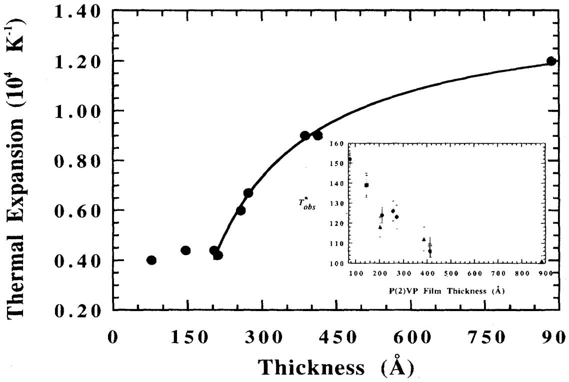

FIG. 2. The thickness dependence of the thermal expansion *below* the bulk glass transition temperature, $T_{g,\infty}=361.3$ K, is shown. The curve corresponds to Eq. (2b) with $A=207\pm3$ Å, $\beta_{h,\xi}=4.3\pm0.2\times10^{-5}$ K^{-1} (the average of the four thickness independent thermal expansivities for $h<200$ Å) and $\beta_{\infty,\text{glass}}=1.4\pm0.1\times10^{-4}$, which is a value one might expect for a thin film of P(2)VP. *Inset*: The thickness dependence of the transition temperatures of spin-cast P(2)VP films on acid-cleaned Si is shown. The very conservative reported errors in the measured values are due to the difficulty of precisely locating the transition temperature and are truly representative of their estimated values. The temperature cycling procedures for the films considered here were as follows: (▲) heating from the glassy state (~20–25 °C starting temperature), (●) cooling from the melt state (~160–175 °C starting temperature), and (□) heating from the glassy state after cooling from the melt state. The cooling and heating rates were essentially the same for all of the films considered in this report.

temperature the observed thermal expansion decreases with decreasing film thickness. This suggests that at these temperatures there is a region within the P(2)VP film in which thermal expansion is significantly retarded. Indeed, if one assumes that due to the presence of strongly favorable polymer-substrate interactions a polymer layer of retarded mobility exists at the polymer-solid interface and that the thickness, ξ, of this layer varies with temperature according to

$$\xi=Ae^{-(T/T^*)^n} \tag{1}$$

(where A is the cutoff length or maximum range of the surface interactions, the transition temperature T^* is defined as the temperature at which $\xi=A/e$ and the exponent n determines the sharpness of the transition), then it is possible to account for the unusual temperature-thickness behavior observed here. This transition temperature T^* is most likely indicative of an adsorptionlike transition and not the bulk glass transition temperature. This expression for ξ was chosen so the maximum extent of the surface interactions is of finite range (i.e., $0\leq\xi\leq A$). In order to recover the below thermal expansion observed here, the thickness of the reduced mobility layer must finite. Therefore, a divergent expression for the interphase thickness, such as $\xi=A[(T/T^*)-1]^{-\delta}$, has been avoided here. If the thickness of reduced mobility layer diverged as $T\rightarrow T^*$, then the entire layer would exhibit the reduced mobility thermal expansion. In this case the thermal expansion would not depend on the film thickness when $T<T^*$, which is contrary to what is observed here. If the above description (1) is such that the transition is very sharp, it is possible that a model of this type could also account for the thickness dependent thermal expansion behavior observed above the transition temperature, i.e., increasing thermal expansion with decreasing film thickness.

This hypothesized substrate interaction induced layer of reduced mobility can account for the thickness dependent thermal expansion observed below the bulk glass transition temperature, $T_{g,\infty}=361.3$ K, in the following manner. If one assumes that T^* and n are such that $\xi\cong A$ for $T<T_{g,\infty}$, the temperature dependence of the film thickness, h, can be described as follows:

$$\frac{1}{h}\frac{\partial h}{\partial T}=\begin{cases}\beta_\xi, \quad h<A,\ T<T_{g,\infty} & \text{(2a)}\\ \beta_\xi\dfrac{A}{h}+\beta_{\infty,\text{glass}}\left(1-\dfrac{A}{h}\right), \quad h>A,\ T<T_{g,\infty}. & \text{(2b)}\end{cases}$$

Here β_ξ is the thermal expansivity of the reduced mobility interphase layer and $\beta_{\infty,\text{glass}}$ is the thermal expansivity of the polymer beyond the interphase. For very thin films, $h<A$, the observed thermal expansion is essentially that of a reduced mobility layer. When the film thickness is greater than the extent of the reduced mobility layer, $h>A$, the thermal expansion behavior is that of a composite bilayer of two different thermal expansivities. It should be noted that this is a somewhat simple approximation as it does not allow for smooth, continuous variations of film properties.

Although crude, this approximate description of the thermal expansivity can account for the thickness dependent below T_g thermal expansion observed in Fig. 1. The measured film thickness dependence of the below T_g thermal expansivity is plotted in Fig. 2. When $h<200$ Å the observed thermal expansivity is essentially independent of thickness. This corresponds to the $h<A$ regime. Therefore, according to this crude model the break in the below T_g thermal expansion-thickness curve should provide an estimate of the length over which substrate-polymer interactions are important. As the films become thicker, the influence of the substrate-polymer interactions becomes less significant. The curve in Fig. 2 corresponds to Eq. (2b) (i.e., $h>A$) with $A=207\pm3$ Å, $\beta_\xi=4.3\pm0.2\times10^{-5}$ K^{-1} (the average of the four thickness independent thermal expansivities for $h<200$ Å) and $\beta_{\infty,\text{glass}}=1.4\pm0.1\times10^{-4}$ K^{-1}, which is a reasonable value for a laterally constrained film [20,21]. The value found for the extent of the reduced mobility interphase thickness, $A=207\pm3$ Å, suggests that the length scale of surface interactions is on the order of the macromolecular size.

When analyzed within a similar framework (in this case looking at the above T_g thermal expansion), a recent study of the thermal expansion behavior of ultrathin polystyrene films spin-cast on hydrogen-terminated silicon also indicates that the length scale of substrate interaction is on the order of several hundred angstroms [21]. The PS-H-terminated silicon system is nonpolar in nature and, therefore, should not display a strongly favorable substrate-polymer interaction. This indicates that the existence of an impenetrable boundary by itself influences the thermal expansion behavior of the interphase. Interestingly however, in contrast with previous work on this same system [9,11], these measurements of PS spin-cast on H-terminated silicon indicated an increase of glass transition temperature with decreasing film thickness.

The above observations demonstrate the importance of substrate interactions on the thermal properties of confined polymer systems. The strong deviations from the bulk material behavior observed here will be a critical issue for polymer systems which are highly interfacial in nature. Particularly relevant is the observation that the influence of the substrate-polymer interface persists over length scales on at least the order of the polymer size. Recent Monte Carlo simulations of chain molecules confined between two inert walls also indicate the existence of an interphase of macromolecular size [22]. These same simulations also indicate that the chain molecules within the interphase tend to align parallel to the wall and exhibit a concurrent density increase in this region. The thickness of the simulated interphase is observed to increase as the temperature approaches the glass transition temperature. These observations are in accord with this study's proposed interfacial region of reduced chain mobility (especially since the system considered here displays very favorable substrate-polymer interactions) and lend some credence to the simplistic interpretation of the observed thickness dependent thermal expansion below the transition temperature. The authors of the Monte Carlo study plan to consider the effect of strong substrate interactions in the near future, a system which is very similar to the one described herein.

The key question here is this: What is the mobility of a strongly adsorbed polymer? As noted earlier strong adsorption may lead to highly distorted chains in the interphase and should have some influence on the observed thermal properties. If thermal expansivity is determined by the accessibility of polymer conformations this would be particularly true. Strong adsorption would lead to decreased thermal expansion. Due to the strong polymer-substrate interactions present in the system it is most likely that confinement is not as important an issue as in the PS systems studied by these same investigators [6,21]. In fact, when confinement effects become dominant one can even envision *negative* thermal expansion as observed earlier in the PS–silicon oxide system [6]. This is undoubtedly an open argument and much remains to be done in both experiment and theory.

In conclusion, it has been demonstrated that strongly favorable polymer-substrate interactions lead to large changes in the observed transition temperature and thermal expansion behavior of ultrathin polymer films. Transition temperature elevation >50 °C above the measured bulk glass transition temperature has been observed. The transition temperatures and thermal expansivities are both found to depend on the ultrathin polymer film thickness, with the former increasing and the latter decreasing with decreasing film thickness. These observations can be interpreted within the framework of a macromolecular-sized interphase region of reduced chain mobility near the solid substrate. The estimated thickness of this interphase is in agreement with other recent experimental studies and Monte Carlo simulations.

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