# Thermal Characterization of Adsorbed Polystyrene Using Modulated Differential Scanning Calorimetry

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ABSTRACT: The glass transition behavior of dried polystyrene (PS) samples adsorbed on silica, originally cast from carbon tetrachloride, has been studied using modulated differential scanning calorimetry (MDSC). The adsorbed amounts of the polymers on silica were very small, ranging from about 2 to 0.4 mg polymer/$m^2$ silica. The glass transitions for the surface-adsorbed polymers were higher and broader than those for the bulk polymer. As the amount of adsorbed polymer decreased, the middle ($T_g$) and maximum ($T_+$) of the transition increased significantly, while the minimum temperature ($T_-$) decreased only slightly. The increased width and shift of the thermal transitions were not as large as those previously observed for adsorbed poly(methyl methacrylate) on silica; however, they were similar in that the breadth increased with decreased adsorbed amounts. The influence of the surface became less pronounced, and the behavior became more bulklike, as the amount of adsorbed PS increased.

## Introduction

There have been many studies of the physical properties of thin polymer films. Potential applications of these films in areas such as electronics, biomedical devices, and coatings make the understanding of them critical. As the trend to make devices smaller continues, the influence of the thin-film geometry on a material's overall properties becomes more prominent. It has also been shown that thin polymer films have characteristics different from those of bulk polymers.[1] For a polymer adsorbed on a solid substrate in air, there are two interfaces to be considered: the polymer−substrate and polymer−air interfaces. These two different interfaces can both influence the properties of the films and may even have opposite effects.

Polystyrene (PS) is perhaps the most studied polymer thin-film system. Nevertheless, the behavior of polystyrene in films is far from clear. The interface with air can be effectively probed in free-standing films, though the minimum thickness (about 20 nm) of these films is limited by their ability to remain free-standing. The effect of the interface with air was apparent in the thermal expansion measured from Brillouin scattering[2] or transmission ellipsometry.[3] For films thicker than 20 nm, decreases in glass transition temperatures ($T_g$) were found, with higher molecular weight polymers showing effects at larger thicknesses. The range of the effect is apparently 40−80 nm. It was proposed that the film is motionally heterogeneous, with more highly mobile material at the air interface and bulklike material in the middle. The sharpness of the glass transition suggested that some type of averaging of the different segments occurred over the time scale of the experiment.[3]

For supported films, the additional interface leads to additional complexity. In general, the magnitude of the decreases in the measured $T_g$'s of supported films is less than those measured in unsupported ones. Some of the complexities were recognized in conjunction with the dewetting of PS on glass, as evidenced through microscopy[4] or X-ray reflectometry.[5] The rate of structural changes in PS thin films suggested that both the $T_g$ and densities of the surface polymers were lower in thinner films.[5] Consistent with this notion, ellipsometry has also indicated a lowering of the PS $T_g$ for films at a hydrogen-passivated silicon interface,[6] though more recent experiments have shown that the transition is not a simple one, and the temperature range over which it occurs broadens with decreasing film thickness.[7] Jones et al.[6,7] proposed a liquidlike layer of about 10 nm at the air interface. Brillouin scattering has also been used to probe silicon oxide-supported PS films.[8] For thicknesses of 30−180 nm, only a slight lowering of $T_g$, compared to bulk, was found with little difference found between "capped" (supported on one side) and "uncapped" (supported on both sides). In contrast, X-ray reflectivity[9] and near-edge absorption fine structure[10] studies find little evidence of enhanced mobility at the free surface.

Other probes, such as positron annihilation spectroscopy, measure local free volume. A decreased $T_g$ was found for PS films on passivated silicon[11] or copper.[12] Interestingly, the depth resolution obtained on relatively thicker films by Jean et al.,[12] at the vacuum−polymer interface, was not as pronounced as that in unsupported films via Brillouin scattering.[2] In addition, the estimated expansion coefficients from positronium lifetimes were less than the corresponding bulk values.[11] A three-state model, with a rigid layer (at the polymer−air interface, referred to as "dead"), surface layer (at the vacuum−polymer interface, we would prefer to call this the mobile layer), and a bulklike layer (in between), could adequately fit the data of DeMaggio et al.[11] The thickness of their rigid layer was estimated to be about 5 nm. A review of some of the models has been made[13] with an emphasis on PS studies.

Translational or segmental dynamics of the PS molecules themselves have also been used to study the behavior around the glass transition. Dielectric spectroscopy of PS sandwiched between Al plates suggested lowered $T_g$'s for at least part of the thin films as well as a frequency dependence.[14] Again, a three-component

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model was used to explain the data. Optical studies of probe molecules in thin PS films on quartz suggested either decreased[15,16] or increased[17] diffusion coefficients. It was suggested that the apparently different results might be accounted for on the basis of different behavior in different regions of the film and preferential partitioning of the labeled polymer in either region. There is also the sensitivity of different experiments parallel or perpendicular to the surface of the substrate. Secondary ion spectroscopy[18] has also found decreased diffusion coefficients of deuterated PS near a silicon interface. Diffuse X-ray scattering[19] also indicates a reduced surface diffusion coefficient.

DSC has previously been used to characterize small molecules[20] and polymer solutions[21] in controlled-pore glass. For silanized glass, *o*-terphenyl and *o*-terphenyl/polystyrene solutions had $T_g$'s that decreased with decreasing pore size, although the polymer solution showed a second, higher-temperature transition. The apparent specificity and the complexities introduced by the solvent systems have also been noted.[22] More direct thermal measurements have been made on polymer thin films with local thermal probes.[23,24] These studies agree with recent simulations from the same group,[25] suggesting the interaction with the substrate can play a major role in determining the direction of the shift in glass transition. The thermal probe method provides an excellent way to estimate the properties of the films around the probe tip but cannot make representative measurements of the entire sample.

Modulated differential scanning calorimetry (MDSC) has made it easier to analyze the thermal behavior of polymers in very low adsorbed amounts. The technique uses a sinusoidal modulated heating ramp that yields a profile in which the instantaneous heating rate is increased. This results in an increase in sensitivity and allows us to determine the thermal behavior of very thin polymer films. We have recently applied this technique to adsorbed poly(methyl methacrylate) (PMMA) on silica[26] where a strong positive interaction between the polymer and substrate (H-bonding) is expected. We found that the $T_g$ of the interfacial polymer (as measured by the center of the transition) on silica was increased considerably compared to bulk, with a similar increase in breadth. The results were in excellent agreement with our previous NMR experiments on poly(vinyl acetate)-$d_3$ (PVAc-$d_3$)[27] and poly(methyl acrylate)-$d_3$ (PMA-$d_3$)[28,29] on silica. These demonstrated the presence of a segmental−motional gradient perpendicular to the substrate surface in the adsorbed polymers with the least mobile segments being next to the silica.

In the present work, we apply the MDSC technique to PS on silica. The amount of adsorbed polymer in this study is very low, and we are probing a range of adsorbed amounts that the studies mentioned above have not. It is also interesting to compare the behavior of PS with PMMA on silica because of the difference in the strengths of the interactions between the polymer and the surface. In doing so, we hope to shed some additional light on a complicated, even contradictory, problem, especially in the regime of very thin polymer materials.

## Experimental Section

**Adsorption.** Polystyrene was purchased from Aldrich Chemical, Milwaukee, WI. The $M_w$ was 300 kg/mol with a polydispersity of 1.4, as measured in our laboratory using gel permeation chromatography in tetrahydrofuran (THF) with a Dawn EOS (Wyatt Technology Corp., Santa Barbara, CA) light scattering and Optilab RI (Wyatt) detectors. PS was adsorbed from a carbon tetrachloride solution onto heat-treated amorphous fumed silica, M5 (Cabot Corp., Tuscola, IL), with a surface area of 200 $m^2/g$. From the gravimetric determination of the initial and steady-state (after adsorption) polymer concentrations, the adsorbed amounts were calculated. A detailed description of the adsorption procedure has been documented in our previous study.[26] After adsorption, some of the dispersion-containing coated samples were rinsed with solvent to remove any excess polymer (beyond a monolayer in the presence of solvent) that may have been present. Other adsorbed samples were not rinsed to obtain higher adsorbed amounts. All samples were dried under vacuum at 70 °C for 12 h and then stored in a desiccator until analyzed.

**Thermal Analysis.** The thermal behavior of the treated silica samples was examined using a TA Instruments 2920 MDSC (New Castle, DE). The heat flow signal of the adsorbed polymer was emphasized by attempting to mask the effect of silica which had an increasing heat capacity with temperature (not shown). This was achieved by placing approximately the same amount of silica in the reference pan as was in the sample. This procedure was generally successful, but it is not known whether the entire silica signal was canceled, leading to $C_p$ and $\Delta C_p$ uncertainties. The thermal behavior was followed from 25 to 240 °C (heating and cooling) at a rate of 2.5 °C/min and a modulation amplitude of ±1 °C with a period of 60 s.[30,31] The results of the second heating scan are reported. Nitrogen, with a flow rate of 50 mL/min, was used as a purge gas during the scans.

We have chosen to characterize the glass transition with three parameters, $T_-$, $T_g$, and $T_+$, representative of the minimum, middle, and maximum of the transition, respectively. $T_-$ and $T_+$ were determined by the intersection of the line segments tangent to the heat flow curves below and above the transition with a line segment drawn along the curve in the middle of the transition. The $T_g$ value was calculated to be the temperature corresponding to the half-height of the transition step as commonly used for determining $T_g$.[32] The line segments used in the determinations are shown in the thermograms. Estimation of these values was made from at least two separate runs with variation of less than 2 °C found between runs. It is recognized that tails occurred in the observed transitions, which are not necessarily accounted for in the measurement of the three temperatures reported. The values reported were the averages from three runs, and the individual temperatures were reproducible to less than 2 K.

We were not able to accurately determine values for $\Delta C_p$ for the surface polymers as a function of the adsorbed amount although our $C_p$ and $\Delta C_p$ values for the bulk polymer were close to those found by others.[33] We believe this reproducibility problem was due to either incomplete balancing of the silica or differences in thermal gradients in the sample pan. Ideally, a thin uniform layer on the bottom of the sample pan would minimize thermal gradients. To maximize the signal, we placed a large amount of the sample in the sample pan (typically about 10 mg). Given this decreased thermal contact and the inherent inhomogeneous nature of the substrate (i.e., aggregate structure of the Cab-O-Sil), there may have been an uneven distribution of mass in the sample pan that could have affected the breadths of the observed transitions. To test this, we ran samples with bulk polymer sandwiched in between a lower and an upper layer of silica, so that the polymer had minimum thermal contact with the pan. We found that there was no appreciable difference in the $T_g$ behavior between the "sandwich" and bulk polymer behavior (not shown). We therefore believe that the nature of the sample did not cause a significant instrument broadening, though this cannot be completely ruled out.

## Results

**Effect of Adsorbed Amount.** The adsorption isotherm for PS adsorbed onto silica from carbon tetrachloride is shown in Figure 1. Saturation coverage of

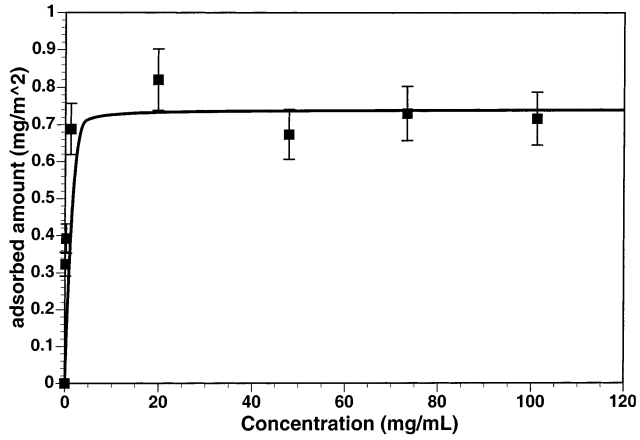


**Figure 1.** Adsorption isotherm for PS ($M_w$ = 300 000 g/mol, PD = 1.4) adsorbed on silica from $CCl_4$.

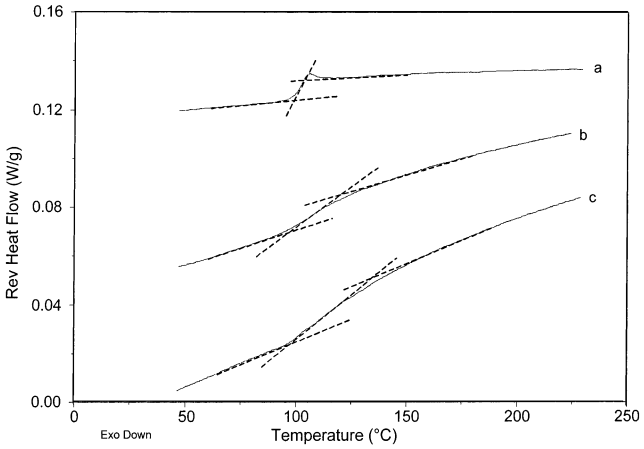


**Figure 2.** MDSC thermograms for (a) bulk PS, (b) 1.0 $A_m$, and (c) 0.5 $A_m$. 1.0 $A_m$ corresponds to 0.75 mg/m$^2$ on silica. The position on the vertical axis is shifted to distinguish between the different curves. The dashed lines are those used to estimate the $T_-$, $T_g$, and $T_+$.

the polymer in this solvent, found from the flat part of the isotherm, defined as 1.0 $A_m$, was found to be about 0.75 mg/m$^2$. Other adsorbed amounts are referred to as relative to this amount. Since this adsorbed amount is low, it is unlikely that the polymer forms a continuous, hole-free film when dried. A rough estimation of thickness can be made assuming a continuous film. With a density of 1 g/cm$^3$, the film would be approximately 0.8 nm thick. We are therefore dealing with a very small amount of adsorbed polymer.

The thermograms for the bulk polymer, 1.0 $A_m$, and 0.5 $A_m$ polymer samples on silica are shown in Figure 2. Thermal analyses of samples with adsorbed amounts lower than 0.5 $A_m$ were attempted but were not successful. For the bulk polymer, a $T_g$ of 100 °C with a breadth of 5 K was found. A small exotherm due to enthalpy relaxation was also found. [34] Because of the narrow width of the transition for the bulk sample, the number of oscillations in the MDSC is smaller than the five or so required for accurate characterization of the transition.[31] For this and similar samples, a similar transition width is found for bulk PS in normal DSC mode. This should not be a problem for the broader transitions for the adsorbed samples. For the 1.0 $A_m$ sample, the $T_-$ decreased slightly, as compared to bulk, but the $T_+$ was 14 K higher than that for the bulk polymer resulting in the $T_g$ value estimated at 106 °C.

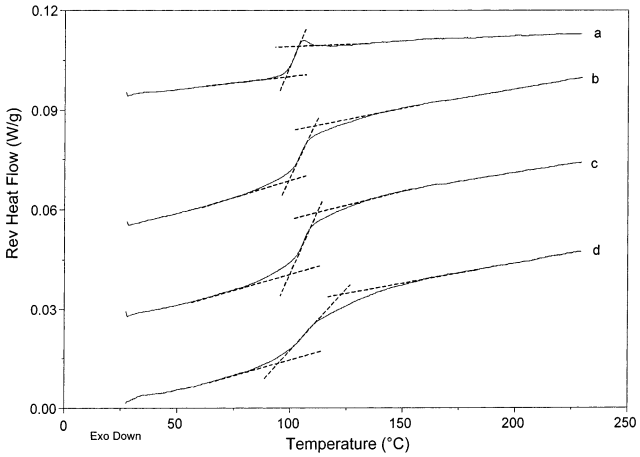


**Figure 3.** MDSC thermograms for (a) bulk PS, (b) 2.7 $A_m$, (c) 1.7 $A_m$, and (d) 1.2 $A_m$. 1.0 $A_m$ corresponds to 0.75 mg/m$^2$ on silica. The position on the vertical axis is shifted to distinguish between the different curves. The dashed lines are those used to estimate the $T_-$, $T_g$, and $T_+$.

**Table 1. Glass Transition Data for Bulk and Surface-Adsorbed Polystyrene**

| sample | $T_g$ (±2 K) | $T_-$ (±2 K) | $T_+$ (±2 K) | breadth (±2 K) |
|---|---|---|---|---|
| bulk | 100 | 98 | 103 | 5 |
| 2.7 $A_m$ | 104 | 99 | 108 | 9 |
| 1.7 $A_m$ | 106 | 100 | 111 | 11 |
| 1.2 $A_m$ | 106 | 96 | 115 | 19 |
| 1.0 $A_m$ | 106 | 95 | 117 | 22 |
| 0.5 $A_m$ (2nd heat scan) | 116 | 96 | 136 | 40 |
| 0.5 $A_m$ (cooling scan) | 120 | 96 | 145 | 49 |
| 0.5 $A_m$ (4th heat scan) | 119 | 95 | 144 | 49 |

An increase in the span of the transition was also observed: from 5 K for the bulk polymer to 22 K for the 1.0 $A_m$ sample. At half of this adsorbed amount, 0.5 $A_m$, the minimum temperature was again only slightly lower than bulk; however, the maximum temperature increased to about 33 K higher. The midpoint, $T_g$ value, increased to about 116 °C. For all surface samples, the apparent increase in the half-height $T_g$ value resulted from more significant increases in the maximum temperature. A summary of these temperatures is given in Table 1.

The behavior of samples with additional adsorbed polymer has also been studied. Samples that were not rinsed were prepared to have adsorbed amounts of 1.2, 1.7, and 2.6 $A_m$ (all ±0.1 $A_m$). As the adsorbed amount increased, the thermal behavior of the films became more bulklike, as seen in Figure 3. The $T_g$ values for the 1.2, 1.7, and 2.6 $A_m$ samples were 106, 106, and 104 °C, respectively, compared to the bulk value of 100 °C. Clearly, the thermal behavior of the higher adsorbed amount samples approached that of the bulk samples, but at these adsorbed amounts, the presence of the solid substrate still plays a significant role. In this case, its main effect is to increase the breadth of the transition, especially the $T_+$.

One additional complexity found in the adsorbed samples is the tails, which either precede or follow the "main" transition. While they are difficult for us to quantify, we can make some general observations. First, they appear to be relatively larger for the adsorbed samples with smaller adsorbed amounts. Second, the amounts in the higher temperature regions are generally larger than those in the lower temperature regions.

**Low-Coverage Polystyrene.** Generally, the second heating curves and cooling curves were very similar for all samples except the 0.5 $A_m$ one. This suggested that the systems reached a more or less steady-state condition. For the 0.5 $A_m$ sample, the width of the heating curve in the transition region was initially narrower than that of the cooling curve. After repeated scans with a maximum temperature of 240 °C (well above $T_g$), the difference between heating and cooling decreased and became the same within experimental error, as shown in Table 1. It took about four scans for this sample to reach steady state.

## Discussion

At first glance, our current measurements are inconsistent with the previous measurements of thin PS films on either silicon oxide or silicon. Basically, our data show primarily an increase in the measured $T_g$, while most other studies suggest a decrease. There is some apparent disagreement, so we must take a closer look at the differences between this and previous studies. Perhaps the most important difference is in the adsorbed amount. Our highest adsorbed-amount sample corresponds to a film thickness of about 2 nm, thinner than most other previously reported data. The very low adsorbed amounts mean that some of our samples are probably not continuous hole-free films, especially at our lower adsorbed amounts. Nevertheless, the polymers must exist on the surface in very thin regions, and their behavior may be dominated by the interaction of the polymer with the solid substrate. Consequently, we would expect the effects due to the substrate to be prominent in these results.

Sample preparation could be a factor in the observed results. In most previous studies on supported films, spin-coating was used to deposit the polymer. We used solvent deposition with rinsing for some of the samples. Samples dried from solvents may be difficult to anneal.[22] It has been suggested that solvent-cast thin films may contain polymers with different conformations than spin-cast films.[35,36] When a film is spin-cast, centripetal forces act upon the polymer film and result in polymer chain extension. Annealing the film above $T_g$ for several hours can relieve most of the stresses that exist due to the extension. However, Kosbar et al.[36] found that spin-cast films subjected to long annealing times still had more stress than solvent-cast films. Since the conformations of polymer chains vary with the mode of adsorption and the thermal history, it could be part of the discrepancy. Yet, somehow, these reasons seem insufficient to explain all of the differences. This is particularly true as our samples with larger adsorbed amounts showed little, almost no, dependence on repeated runs, save that of the 0.5 $A_m$ samples (see below).

The type of probe used to analyze the samples may also play a role in the type of observation made. Experiments such as ellipsometry, neutron scattering, and X-ray refraction are sensitive to certain changes in film properties such as density. It is generally recognized that since there are two different interfaces in the films, one might expect differences in behavior across the film thickness. In many cases, the $T_g$ is estimated from the intersection of two portions of an experimental curve. Recently, careful examinations of ellipsometry data[7] showed that the transitions observed broadened with decreasing film thickness. While these experiments have been used to estimate the thicknesses of various layers within the film, it seems possible that they are most sensitive to the *onset* of the thermal transition. Our data show "tails" of thermal activity that are small and difficult for us to evaluate. It is tempting to ascribe this behavior to more mobile parts of the surface polymer in contact with air to which ellipsometry may be very sensitive and MDSC may not. For example, a small amount of mobile material may be difficult to observe in the MDSC experiment, especially if those segments have a lower heat capacity associated with them.

A few previous studies have implied the existence of a layered model to explain their experimental data. For example, DiMaggio et al.[11] suggested that the thickness of their rigid layer near the substrate was on the order of 5 nm, based on measurements for 7−300 nm thick samples. For our samples, which are well below the 5 nm thickness, we expect that the proximity of most segments to the silica surface will result in primarily lower mobility segments. If we were to characterize our samples in a single generalization, we would say that the surface effect was to increase the $T_g$ of the adsorbed samples. However, upon more careful inspection, it becomes apparent that this effect is primarily due to increases in $T_+$. A significant amount of the material in our roughly 2 nm layers had thermal behavior which might be classified as bulklike as evidenced by the $T_-$ values being very near the bulk $T_g$.

It has been speculated that the region near the polymer/air interface has increased free volume compared to that near the polymer/substrate interface.[12,37,38] As a result of the increased free volume, those segments should have a lower temperature for the onset of large-scale segmental motion compared to bulk, i.e., a lower $T_g$. A slightly lower minimum temperature for the lower adsorbed amount samples was found; however, the effect was not large. It is difficult to definitively characterize the small decrease in the minimum temperature since the inherent sensitivity (i.e., heat capacities) of MDSC for different regions of thin films is unknown, and our attempts to determine this information were unsuccessful. It seems as though the polymer's interaction with the substrate dominates the free-volume effect at the polymer/air interface; however, the dependence on adsorbed amounts suggests that the free surface does play a role, consistent with the suggestion of other authors.[6,8,12,15,27−29,39] Both PVAc-$d_3$[27] and PMA-$d_3$[28,29] on silica showed small numbers of segments with enhanced mobility believed to be at the polymer−air interface. For PMA-$d_3$ on silica, subsequent studies have shown that a polymer overlayer reduces the mobility of the polymer previously at the air interface.[40] It might be that these segments correlate with the "tails" at lower temperatures than the main transition in the thermograms of the surface species. Similarly, adsorbed PVAc-$d_3$ and PMA-$d_3$ showed the presence of rigid groups at temperatures well above the main transition. These slowly convert to mobile segments with temperature, similar to what one might expect to correlate with the high-temperature "tails".

It is instructive to compare the behavior for PS with that for PMMA on silica in previous studies.[26] The attraction between the PS and silica is much less than those for PMMA and silica, with the latter polymer being capable of hydrogen bonding to the silica surface hydroxyls. For the PMMA−silica thermal transitions, widths of nearly double that in the present study are

found for similar adsorbed amounts. There were also significant increases in the measured $T_g$ for PMMA−silica due to both the $T_-$'s and $T_+$'s significantly increasing. We believe that this is due primarily to the stronger interaction of PMMA with the silica, but there may also be a contribution to differences in the polymer segments at the air interface where the PS may also be more mobile.

The effects of thermal cycling observed for the 0.5 $A_m$ sample should be considered further. During the drying process, the volume of the polymer film decreases as the polymer collapses from its solvated dimensions. As evaporation of the solvent continues, the system eventually becomes glassy. The polymer may be kinetically stuck in rather unfavorable configurations that may relax as the polymer film is heated near its $T_g$. This phenomenon was only observed to be significant for the lowest adsorbed amount sample.

Finally, as in the case of PMMA adsorbed in silica,[26] we propose that the PS films are structured in terms of mobility on the surface, the more mobile segments being near the air interface and the less mobile segments being near the silica surface. That the less mobile segments are located at the polymer−substrate interface is likely due to the interaction between the polymer and the substrate (Cab-O-Sil silica). Recent studies have confirmed that the dynamics can be altered one way or the other on the basis of the interfacial energy between the substrate and polymer.[41]

## Conclusions

We have shown that the temperature at which segmental mobility occurs in PS films is probably better described as an extended temperature range rather than the narrower range found for the bulk polymer. The increased breadth of glass transition behavior is consistent with a distribution of segmental mobilities for the PS−silica systems as it was for the PMMA−silica system. The differences between this study and previous studies are undoubtedly due to a combination of effects, including the thinness of the adsorbed polymers studied and the interaction between the polymer and the substrate.

From the standpoint of thermal analysis, the interactions between PS and silica were more dominant than those at the polymer/air interface. The thermal behavior of the polymer films became more like the bulk polymer as the adsorbed amount increased. The $T_g$ was observed to increase primarily due to increases in $T_+$, with $T_-$ remaining relatively constant. These results are similar to those for the PMMA−silica system; however, in that system the increases were much greater due to the stronger interaction of the polymer and the substrate.

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