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# Modulated Differential Scanning Calorimetry of Ultrathin Adsorbed PS-*r*-PMMA Copolymers on Silica

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ABSTRACT: A series of polystyrene-*random*-poly(methyl methacrylate) (PS-*r*-PMMA) copolymers with different compositions, adsorbed from toluene onto silica, were studied with modulated differential scanning calorimetry (MDSC). The equilibrium adsorbed amount increased monotonically with an increase in the methyl methacrylate (MMA) content in the copolymers. From the derivative MDSC curves, $dC_p/dT$ vs $T$, the thermal transitions of the adsorbed chains were found to be dependent on the composition of the copolymers and representative of films with chain segments which were spatially heterogeneous. The intensities of the thermal transitions associated with more-mobile fractions in the polymer films decreased, and those associated with the more-rigid fractions increased when the MMA content in the copolymers increased. These changes were attributed to the strong interaction between MMA units and silanol groups on the silica surface. In addition, for the polymers studied, the relative intensities of the transitions associated with the more-mobile segments increased with increases in the adsorbed amounts.

## Introduction

Composite materials are used in many applications. The interaction of polymers with surfaces plays a crucial role in determining the properties of these materials. Through an understanding of their surface behavior and adsorption mechanisms, better systems can be designed. The behavior of polymer molecules at interfaces has been the topic of many studies in recent years. However, because of the complexity and small length scale of the interfaces, it is very difficult to characterize the interfacial species. Although many techniques have been used to determine the surface properties of polymer chains, and a rough picture of these chains at interfaces has been obtained, the topic is still far from well understood.

To understand the behavior of interfacial polymers, different polymer−substrate pairs have been used, including those with strong interactions between the polymers and solid substrates, such as poly(methyl methacrylate) (PMMA) on silica,[1] and those with weak interactions, like polystyrene (PS) on silica[2] or PMMA on gold.[1] For PMMA films deposited onto the native oxide coating of Si wafers, the measured glass transition ($T_g$) values increased with decreasing film thickness ($15 < h < 120$ nm), whereas the $T_g$'s for PMMA films, deposited on Au-coated Si wafers, decreased as the thickness ($30 < h < 130$ nm) decreased. These results indicated that a strong attraction between the polymer film and substrate (H bonding between PMMA and the Si native oxide) was responsible for the increases in $T_g$ with decreasing film thickness. The weaker interaction between PMMA and gold resulted in a decrease in $T_g$ with decreasing film thickness. This effect was further verified by $T_g$ measurements of polystyrene films on hydrogen-passivated silicon substrates.

The different environments on either side of a supported polymer film (solid−polymer and air−polymer interfaces) also cause heterogeneity at different distances from the surface.[2−4] The mobility of polymer segments at an air interface would be expected to be greater than those in the bulk polymer,[3−5] while those at a solid interface would be expected to be lower than those in bulk. Both behaviors decay as a function of the distance from the interfaces with certain length scales. One expects changes in many properties normal to a solid surface, including segment mobility,[5−7] density,[5,8] thermal expansion coefficient,[9] and so on.

The length scale has been estimated to be 8−13 nm for a air−polymer interface.[4,5,9] For the substrate effect, the length scale may vary from several segments to tens of nanometers as a function of the interaction between the substrate surface and polymer chains.[2,4] The stronger the interaction, the greater the length scale. On the other hand, the solid surface can also affect chain entanglements[10] and configuration.[8,11,12] The properties at a certain location in the chains are determined by a balance of all of these effects, and the overall properties are results of the averages over the range. Different methods are sometimes sensitive to the different averages.

One method of control of the interface between polymers and substrates is through the use of copolymers. Combinations of monomers like styrene (S) and methyl methacrylate (MMA) may be varied in composition to fine-tune the surface interactions. It has been shown that the bulk $T_g$[13,14] and the adsorbed amounts from solutions[15,16] of PS-*r*-PMMA copolymer depend on monomer composition. A variation in the monomer composition allowed Tsui et al.[17] to control the surface energy of PS−PMMA copolymer films. However, how the combination of these different monomers in the copolymer affects the glass transition behavior of adsorbed PS-*r*-PMMA copolymer is not known.

In our laboratory, we have been concerned with the behavior of adsorbed polymers, at much smaller adsorbed amounts, than in the aforementioned studies. Solid-state NMR has been a useful tool for studying the behavior of the polymer at or near the $T_g$ in adsorbed polymers at the solid−polymer−air and solid−polymer−polymer interfaces.[18−21] We found that a motional

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gradient existed in the polymer for both poly(vinyl acetate)[21] and poly(methyl acrylate)[18,19] on silica at the solid−polymer−air interface. The more mobile segments (with a lower $T_g$) were believed to be at the air interface and the less mobile segments (with a higher $T_g$) near the silica surface. We are interested in finding other ways of verifying this behavior.

Temperature-modulated differential scanning calorimetry (MDSC) can be useful in measuring the thermal behavior of low adsorbed amounts of polymers on high surface area substrates.[22,23] The modulated heating ramp produces an instantaneous heating rate which is higher than that without it, resulting in increased sensitivity. For PMMA adsorbed on silica,[22] the $T_g$ of the adsorbed polymer was found to increase (based on the center of the transition) by about 20 °C, and the width of the transition increased from about 10 °C for bulk to about 60 °C for the adsorbed polymer. The temperature of the thermal transition also increased with decreased adsorbed amounts. These results were consistent with previous NMR studies, in terms of an interfacial polymer film with graded mobility, and were also consistent with the nature of the effect of a system with a strong attraction between the polymer and the substrate. For PS on silica,[23] the increase was not as large (on the order of 10 °C) as that for PMMA, but it still resulted in a higher $T_g$ with a broader width. This suggested that, at the low adsorbed amounts (on the order of 0.5−3 mg/m$^2$) studied, the effects of the interaction of the polymer with the solid surface dominated the interaction of the polymer with the air.

In the present paper, we present the results of MDSC studies of low adsorbed amounts of PS-*r*-PMMA on silica as a function of the adsorbed amount and copolymer composition. The derivative heat capacity signals, $dC_p/dT$, from MDSC curves were used to elucidate the fractions of different mobilities. Song et al.[24] have shown how the MDSC curves can be used to quantify the interfacial fractions in polymer blends. Thus, these curves can be used to observe the changes in the fractions related to segments of different mobilities from the DSC curves. We found that the structure and relative intensities of the different regions varied systematically with the copolymer composition and adsorbed amounts.

## Experimental Section

Azobis(isobutyronitrile) (AIBN), purified by recrystallization from ethanol, was used as the initiator. Methyl methacrylate (MMA) and styrene were obtained from Aldrich Chemical (Milwaukee, WI) and purified by washing with a NaOH solution, followed by vacuum distillation. All of the polymer samples used in this work were synthesized by free radical solution polymerization in toluene at 60 °C with 33% monomer concentration. The reactions were run for 1−2 days to conversions of 25−30%. The compositions of the copolymers, determined by $^1$H NMR,[13] were controlled by following the kinetics and adding appropriate amounts of the more quickly consumed monomer during the polymerization. With this method, the feeds, with respect to composition, were uniform to within 2% (absolute) or better. The polymers were precipitated from the reaction mixtures by adding methanol, purified by reprecipitation from toluene several times, and drying overnight in a vacuum oven at 100 °C.

Molecular mass was measured using gel permeation chromatography (GPC) in tetrahydrofuran (THF), with an Optilab DSP differential refractometer (Wyatt Technology, Santa Barbara, CA) and a DAWN EOS light scattering detector (Wyatt Technology) at 690 nm. The d*n*/d*c* values were measured with the Optilab DSP from solutions of less than 1.2 mg/mL. The uncertainty in the d*n*/d*c* values was less than 5%, and although the results are in good agreement, they were 3−4% higher than those previously reported as values extrapolated to 690 nm.[25] The characterization results for the samples used in the MDSC runs are shown in Table 1. We note that the molecular masses of the copolymers are nearly the same, in the 60−78 kg/mol range, except for PS-MA-70, which has a lower molecular mass.

**Table 1. Characterization of Bulk Polymer and Copolymer Samples**

| sample name | composition[a] | $T_g$ (°C) | $M_w$ (g/mol) | polydispersity | d*n*/d*c*[b] (mL/g) |
|---|---|---|---|---|---|
| PS | 0 | 105 | 52 400 | 1.27 | 0.186 |
| PS-MA11 | 11.6 | 104 | 64 100 | 1.21 | 0.172 |
| PS-MA14 | 14.9 | 104 | 65 500 | 1.28 | 0.182 |
| PS-MA30 | 30.6 | 102 | 60 400 | 1.19 | 0.163 |
| PS-MA50 | 50.4 | 104 | 67 900 | 1.10 | 0.137 |
| PS-MA70 | 70.7 | 112 | 22 000 | 1.27 | 0.118 |
| PMMA | 100 | 126 | 136 200 | 1.39 | 0.091 |

[a] Mole % of MMA units. [b] Specific refractive index increment at 690 nm in THF.

**Table 2. Composition of Some Surface-Adsorbed Samples**

| designation | polymer adsorbed | adsorbed amount (mg/m$^2$) |
|---|---|---|
| Si-PS-1 | PS | 1.23 |
| Si-PS-MA11-1 | PS-MA11 | 1.23 |
| Si-PS-MA14-1 | PS-MA14 | 0.92 |
| Si-PS-MA14-2 | PS-MA14 | 1.97 |
| Si-PS-MA14-3 | PS-MA14 | 4.26 |
| Si-PS-MA30-1 | PS-MA30 | 1.01 |
| Si-PS-MA50-1 | PS-MA50 | 1.16 |
| Si-PS-MA70-1 | PS-MA70 | 1.13 |
| Si-PMMA-1 | PMMA | 1.30 |

Adsorption experiments were conducted by first preparing polymer solutions in toluene. These solutions were allowed to equilibrate in centrifuge tubes with known quantities of Cab-O-Sil M5 fumed silica (Cabot Corp, Tuscola, IL), with a surface area of 200 m$^2$/g, in a mechanical shaker for 48 h at 23 °C. The tubes were centrifuged, and the coated silica was washed several times with toluene to remove polymers adsorbed beyond monolayer coverage. The polymer-coated silica was dried at ambient temperature, slowly at first, and then put under vacuum at 70 °C overnight. We suspected that some dewetting of the polymer occurred under these conditions.[8,26] The amounts of polymer adsorbed were measured by thermogravimetric analysis (TGA) (TA Instruments, New Castle, DE), and the results were used to plot the adsorption isotherms. Samples with adsorbed amounts greater than the maxima adsorbed from the above procedure, and adsorbed PS samples, were prepared without washing. For PS, rinsing was not used because the procedure was found to wash off significant amounts of polymer, including that directly adsorbed on to the silica. The isotherm for PS was obtained by measuring the differences between the initial solution and supernatant solution concentrations. The compositions of the adsorbed samples are listed in Table 2.

The thermal behavior in the $T_g$ region was measured with a TA Instruments model 2920 MDSC (New Castle, DE). For the coated silica samples, the reference pan was loaded with approximately the equivalent amount of silica used in the sample pan to emphasize the thermal behavior of the adsorbed polymer. Two heating scans and one cooling scan were taken from 25 to 280 °C, at a rate of 2.5 K/min, modulation amplitude of ±1 K, and a period of 60 s. The total run time per sample was around 5 h. For the bulk samples, the DSC was run in the standard mode at a rate of 10 K/min, from 25 to 200 °C. Our experience with PMMA is that the reversing signal from the modulated experiment has a $T_g$ which is about 2−5 °C higher that from the regular DSC signal. These differences are small compared to the size of effects due to the surfaces

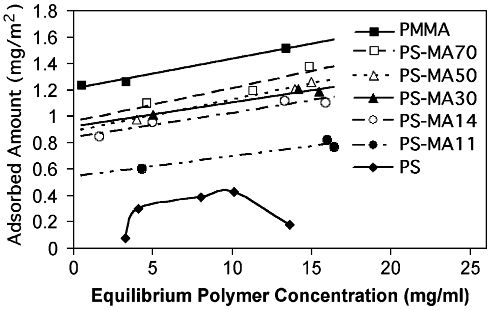

**Figure 1.** Partial adsorption isotherms for all homo- and copolymers absorbed onto silica from toluene. The lines (curves) are drawn to aid the eye.

which we are reporting in this work. The mass of the samples used was approximately 8−12 mg, and the cell was purged with nitrogen gas at 50 mL/min during the scans. The second heating scans are reported so that all of the samples have a similar thermal history. The second and subsequent scans were found to be consistent with each other but generally different from the first scan. Normal and adsorbed *syn*-PMMA do not exhibit any obvious degradation behavior below 350 °C.[27] The results are shown as differential reversing heat flow ($dC_p/dT$) vs temperature ($T$). The $T_g$ values of all bulk samples were reported as the temperatures of the peaks (inflection points of the heat flow curves). The inflection points are generally about 2 °C higher than middle of transition from a typical DSC curve for a polymer. The thermograms shown in the figures were purposely shifted vertically on the differential heat flow axis to aid in comparing the transitions of the different samples.

## Results

The partial adsorption isotherms for all of the surface polymers adsorbed from toluene are shown in Figure 1. In the concentration range studied, the adsorbed amounts increased slightly as the concentration increased. The adsorbed amounts for the different polymers decreased as the MMA fraction in copolymers decreased. The shape of the isotherm for PS is irregular, probably because the interaction between PS segments and the silica surface is weak, thereby allowing PS chains to be washed off the silica surface with toluene. The samples for thermal analysis with adsorbed amounts just greater that about 1 mg/m$^2$ were prepared from solutions of approximately 5 mg/mL.

The $T_g$ of the bulk polymers was estimated as the maximum in the derivative DSC curves and is listed in Table 1. Each has a sharp peak in the glass transition region, all with widths of about 10 K. When the fraction of MMA units increased from 0 to 100% in the copolymers, the $T_g$ went down a little at first and then went up to 125 °C for homo-PMMA. This behavior is similar to that previously reported.[13,14] Generally, the $T_g$ of PMMA is in the range 105−128 °C, depending on the tacticity. Free radical propagation typically gives predominantly syndiotactic segments,[28] and the $T_g$ of syndiotactic PMMA is about 130 °C.[29] We also note that the peak of the derivative curve is at a little higher temperature than that estimated from the midpoint of the transition.

The DSC results for PS and PMMA homopolymers in bulk and on silica are shown in Figures 2 and 3, respectively. Both bulk polymers show relatively narrow transitions (ca. 10 °C)×e2 with small tails due to enthalpy relaxation.[30,31] For the adsorbed samples, the thermal behavior is fairly complex as is easily seen in the derivative mode thermograms. These and other surface samples show “humps” in the regions around 160, 130, and 100 °C, which we have labeled (from highest to lowest temperature) as *a*, *b*, and *c*, respectively. It has been suggested that each hump in the derivative curve represents a different transition.[24] For PS, the majority of the thermal activity of the surface-bound polymer (1.23 mg/m$^2$) is found at temperatures similar to those for the bulk polymer (transition *c*), though broader. For PMMA, the most intense thermal transition of the adsorbed polymer (1.30 mg/m$^2$) is found at a temperature of about 60 °C higher (transition *a*) than the relatively sharp transition for the corresponding bulk polymer. The observations for both polymers were consistent with our previous studies on the homopolymers[22,23] and are included here for comparison with the copolymers.

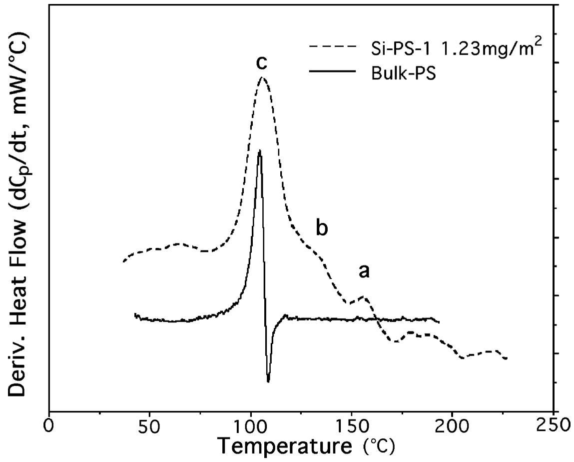

**Figure 2.** Derivative heat flow curves for bulk (DSC) and adsorbed (MDSC, 1.23 mg/m$^2$) PS.

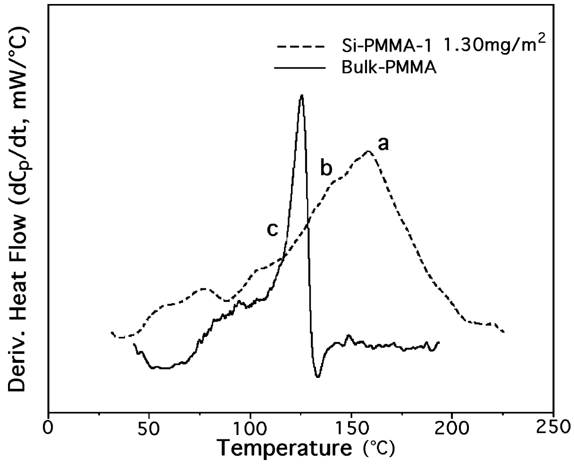

**Figure 3.** Derivative heat flow curves for bulk (DSC) and adsorbed (MDSC, 1.30 mg/m$^2$) PMMA.

Comparisons of the thermal behavior of bulk and surface-adsorbed copolymers are made in Figures 4 and 5 for PS-MMA11 and PS-MMA30, respectively. Again, the simplicity and narrowness of the thermograms for the bulk samples contrast with the complexity and breadth of the adsorbed samples. A comparison of the thermograms for the adsorbed PS-MMA11 (1.23 mg/m$^2$) and PS-MMA30 (1.01 mg/m$^2$) shows the shifting of intensities from domination of transition *a* (PS-MMA11) to about equal amounts of *a* and *c* (PS-MMA30). We can generalize that all of the copolymers contrast similarly between the bulk and adsorbed samples, with the adsorbed copolymer intensities shifting for the accordance with the composition.

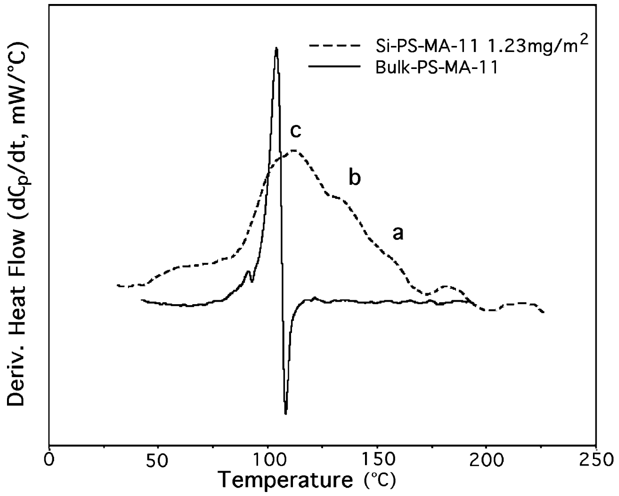

**Figure 4.** Derivative heat flow curves for bulk (DSC) and adsorbed (MDSC, 1.23 mg/m$^2$) PS-MA11.

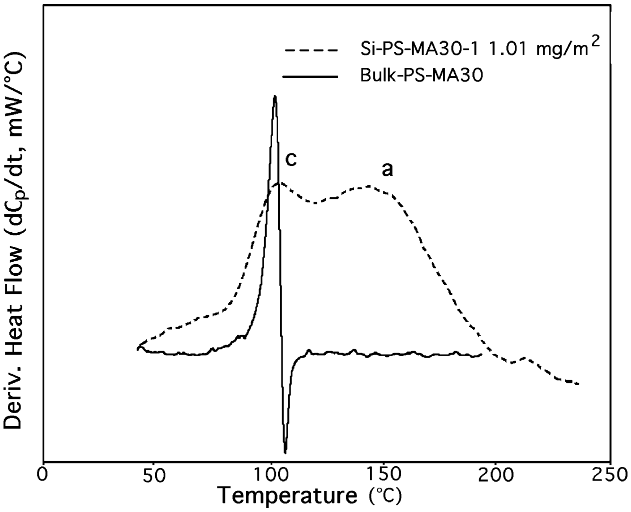

**Figure 5.** Derivative heat flow curves for bulk (DSC) and adsorbed (MDSC, 1.01 mg/m$^2$) PS-MA30.

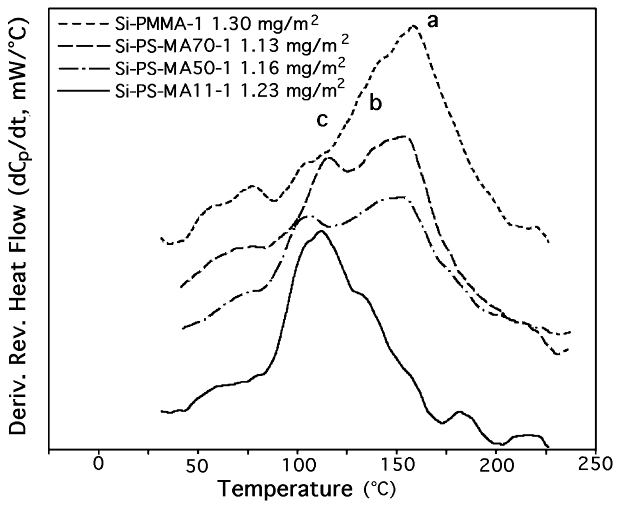

**Figure 6.** MDSC traces for four adsorbed polymers (with different MMA unit percentages) with similar adsorbed amounts.

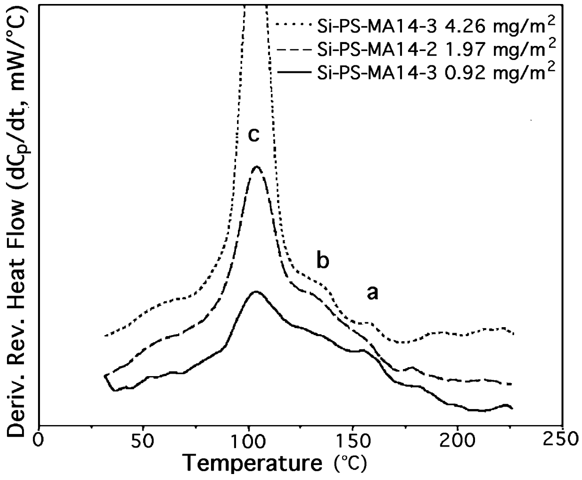

**Figure 7.** MDSC results for adsorbed copolymer PS-MA14 (14.9% MMA unit) with different adsorbed amounts.

Comparisons of the DSC curves of four adsorbed samples with similar adsorbed amounts, but with different polymer compositions, are displayed in Figure 6. In the glass transition region, the relative intensities of transitions *a* and *c* changed regularly as a function of MMA content. In other words, the intensity of *c* decreased, and that of *a* increased as the MMA content in the polymer increased. The intensity of transition *b* stayed relatively the same.

The DSC results for the adsorbed copolymer PS-MA14, with different adsorbed amounts (0.95, 1.35, and 5.00 mg/m$^2$), are shown in Figure 7. The curves, obtained at similar sensitivities, indicated that transitions *a* and *b* had about the same intensities, but *c* increased dramatically as the adsorbed amount increased. For the sample with the largest adsorbed amount, transition *c* became very narrow, consistent with a much more homogeneous grouping of segments. It is also tempting to ascribe the small hump (around 65 °C) to the kind of effect seen by other researchers as the reduced $T_g$ material, but uncertainties in the baseline prevent us from doing this with confidence.

## Discussion

The adsorption of PS-*r*-PMMA copolymers from different solvents has been previously investigated.[15,16,32] From the results of copolymer adsorption studies, it can be concluded that the adsorption behavior of a copolymer at the liquid−solid interface, in general, is chiefly governed by two effects:[15] (i) the solubilities/interactions of the components of the copolymer in the solvent and (ii) the strength of the interaction between components of the copolymer and the surface. These interactions may vary for the two different components of the copolymer.

Studies of the adsorption of PS-*r*-PMMA on to silica from trichloroethylene have yielded different dependencies for the adsorbed amounts on the copolymer compositions. Clearly, the MMA units have a much stronger interaction (vide infra) with the surface (silanol groups) than do the styrene units[32,33] due to H bonding. Despite this, Herd et al.[16] found the plateau adsorbed amount to be constant over a wide range of compositions. Yamagiwa et al.[15] found that the adsorbed amount went up a little and then dropped to a lower value as the relative number of styrene units in the copolymers increased to a maximum adsorbed amount of 75% styrene. Yamagiwa et al.[15] attributed the differences to the high polydispersity of the samples used by Herd et al.[16] Since the interactions between either styrene or methyl methacrylate with trichloroethylene are expected to be similar (Flory−Huggins parameters:[15] $\chi =$

0.44 for PS and 0.45 for PMMA), the adsorbed amounts for copolymers were determined mainly by the surface interaction rather than by solution effects.[15] In contrast with the results for trichloroethylene, toluene is a much better solvent for PS than PMMA (Flory–Huggins parameters: $\chi = 0.33$ for PS and 0.41 for PMMA).[34] In our case, we believe that the increases in the adsorbed amounts are likely due to decreases in coil size with increases in MMA content. A smaller coil size for the same mass polymer would lead to a smaller footprint on the surface.

It has been suggested[24] that the different regions of thermal activity in the MDSC curves are related to different segment mobilities, and a three-layer model was required to account for the behavior observed through positron-annihilation lifetime spectroscopy.[35] Interestingly, Figures 2–6 show distinct regions of thermal activity that we believe can be regarded as transitions of the polymer segments in different environments, and hence with different mobilities, on the silica surface. Transition *a*, at the high-temperature end, can be assigned to those segments having the lowest segment mobility, i.e., those segments connected to or very near the silica surface (trains).[36] The transition labeled *c* has a similar transition temperature to that of the bulk sample, likely corresponding to the segments with mobilities similar to those of the bulk sample, but still not far from those of the surface (loops). Transition *b* is likely related to the intermediate mobile segments between the two above.

The behaviors of each of the homopolymers and the copolymers are different. Because of the weaker interaction between the PS chains and silica,[15,33] most of the thermal activity of the adsorbed PS sample (Figure 2) was located in transition *c*, but a small amount of activity was also found in regions *a* and *b*. Therefore, most of the segments of adsorbed PS were bulklike, with a few segments showing more restricted motion due to their interaction with the silica. In contrast to this behavior, the more strongly adsorbing PMMA exhibited much more intensity for the adsorbed polymer in the transition *a* region (Figure 3). The more restricted chain segments, with their intensities shown in region *a*, were responsible for stretching out the thermal transition to higher temperatures, resulting in increased $T_g$'s. The larger number of segments in the *a* region of PMMA was responsible for the greater increase in the average $T_g$ for adsorbed PMMA (60 °C)[23] than for adsorbed PS (10 °C)[22] for similar adsorbed amounts.

For the adsorbed copolymers, the positions of transitions *a*, *b*, and *c* did not change much with variations in composition, but their relative intensities did. The shifting of the intensity from transition *c* to *a* with increased MMA composition is consistent with a more motionally restricted copolymer due to the stronger binding of the MMA units. A rough analysis suggests that the relative intensities of the *a* transition increase from about 9 to 96% as the compositions change from PS to PMMA. The transition for the behavior of adsorbed PS to adsorbed PMMA via the copolymers appears to be fairly smooth. The uncertainties in the baseline, overlap, and transition shapes make the intensities very difficult to quantify with certainty. Nevertheless, it is clear that with increasing MMA content adsorbed copolymers can be characterized as having a higher $T_g$ and more segments with lower mobility.

Other direct measurements of the thermal behavior of adsorbed polymers have been made. In controlled-pore glass, PS dissolved in *o*-terphenyl was observed to have two glass transitions, one higher and one lower than bulk.[37] PMMA in silica gel composites showed increased $T_g$'s. Local thermal analysis[38,39] has also shown differences in thin films of PS and PMMA and how they are affected by interaction with the substrate, though their films were considerably thicker than those reported here. These studies and recent simulations[40] are consistent with the nature of the glass transition being dependent upon the film thickness and, indeed, upon the differences in dynamics within the film itself.

It is useful to consider these results within the context of what other researchers have found with respect to the shift in $T_g$ with adsorption of a polymer onto a solid surface. The research cited in the Introduction was clear with respect to adsorbed PS on silica (and, perhaps, likely low-MMA content copolymers) having a lower $T_g$ than that of bulk. Clearly, we have observed little thermal behavior below the bulk $T_g$, with most of the thermal activity being at higher temperatures. Compared to the other studies cited, our systems have adsorbed amounts that are much smaller (1–5 nm average thickness). One exception is the work of Reiter,[8] whose thin films (as thin as 3.5 nm) dewetted at temperatures lower than $T_g$(bulk). Our sample preparation process was in a region where this dewetting likely occurred for PS, so at least for PS, the films are likely to have holes in them.

The interplay between the effects of the substrate and air interfaces is apparently such that the interaction of the silica surface dominates at such low adsorbed amounts, raising the average transition temperature of the adsorbed polymer. Nevertheless, even at these low adsorbed amounts, different regions of different mobility provide direct evidence for multistate models.[4] The similarity of the intensities in Figure 7 in the *a* and *b* regions with increased adsorbed amounts suggested that the quantities of more rigid and intermediate segments were fixed at a fairly low level. When the adsorbed amounts were larger, as in the 4.26 mg/m$^2$ sample in Figure 7, the dominance of the *c* transition (similar to that of the bulk polymer) was easily observed. Unfortunately, with the current technique, samples prepared with much greater adsorbed amounts begin to have polymer chains bridging between particles so that their behavior is no longer representative of chains restricted on a single solid substrate. Interestingly, this rough thickness corresponds to the estimation of the immobilized layer predicted at the solid substrate (5 nm).[4] It may be that the constraints of the silica on the chains prevent them from extending outward at much smaller adsorbed amounts. Thus, they can be considered constrained without the enhanced mobility and lower $T_g$ than those in other studies.

## Conclusions

The adsorption of a series of polystyrene-*random*-poly(methyl methacrylate) (PS-*r*-PMMA) copolymers, with different compositions, from toluene onto silica was studied. Because of the different interactions of MMA and styrene units with toluene and the stronger MMA unit–silanol interaction with the silica surface, the adsorbed amounts of the copolymers increased monotonically as the MMA compositions increased.

Modulated differential scanning calorimetry (MDSC) was able to provide direct evidence of fractions with different mobilities in the adsorbed polymers. The segment mobility profiles for the surface supported films showed (i) one layer with mobile segments similar to the bulk polymer, (ii) an intermediate layer, and (iii) one layer with more rigid segments, at about 100, 130, and 160 °C, respectively. Through observation of the relative changes in the sizes of the different transitions, we concluded that when the MMA content in the copolymers increased, then the mobile fraction decreased while the rigid fraction increased. When the adsorbed amount increased, the more mobile fraction in the films also increased, and the rigid and intermediate fractions remained relatively constant. In all of the cases studied, the vast majority of the thermal activity occurred at temperatures greater than the $T_g$ of the bulk polymers. Little evidence was found of polymer segments with higher mobility than bulk, which we ascribe to the adsorbed amounts being much smaller than those of others. In this regime, the interaction of the polymer with the solid surface dominates that of the polymers with air.

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