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**THERMAL CHARACTERIZATION OF PMMA THIN FILMS ON SILICA USING MODULATED DIFFERENTIAL SCANNING CALORIMETRY**

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**Introduction**

The number of studies of thin polymer films has increased over recent years as technological processes incorporate the use of nanomaterials.<sup>1,2</sup> An enhanced understanding of these films would enable us to predict bound-polymer behavior and thus improve the efficiency of processes and the quality of products. This is especially true as the thickness of the films approach molecular dimensions.

The glass transition temperature of a polymer is one of the most important properties for characterization because it indicates how the polymer might perform macroscopically.<sup>3</sup> When a polymer is confined, such as on the surface of a substrate, its behavior is influenced by molecular interactions between the polymer and the substrate.<sup>4,5</sup> These interactions may effect the polymer's glass transition temperature and warrant scientific investigation.

This study uses modulated differential scanning calorimetry (MDSC) to examine the glass transition of poly(methyl methacrylate) adsorbed onto silica. We varied the amount of polymer adsorbed, as well as the solvent from which the polymer was adsorbed, and found that the  $T_g$  center and its breadth increased with decreased coverage. To our knowledge, this is the first reported analysis of such very thin polymer films using MDSC.

**Experimental**

**Adsorption.** PMMA (Aldrich; Mn=58K, P.D.=1.5) solutions of various concentrations were prepared using either toluene or a 5:1 benzene/acetonitrile solvent system. After dissolution, the solutions were allowed to equilibrate with known quantities of amorphous fumed silica (Cabot Corp., Tuscola, IL.) that had a surface area of 200m<sup>2</sup>/g. The samples were shaken in a mechanical shaker for 48 hr at 22°C. The treated silica was centrifuged and rinsed 3 times with the appropriate solvent to remove any excess polymer that may have been present. The PMMA/silica samples were then dried under vacuum at 70°C for 12 hours.

The initial and equilibrium solution concentration and the amount adsorbed were determined gravimetrically after drying a known volume of the solution. The amount adsorbed was verified using thermal gravimetric analysis.

**Characterization.** A TA Instruments 2920 MDSC was used to thermally analyze the coated silica samples. The reference pan contained roughly the equivalent amount of silica as was in the sample pan so that the thermal behavior of the adsorbed polymer was emphasized. Two heating scans and one cooling scan were taken from 25°C to 240°C at a rate of 2.5°C/min with a modulation amplitude of ±1°C and a period of 60 sec. The mass of the sample was approximately 7 to 8 mg and the cell was purged with nitrogen gas at 50mL/min during the scans.

The second scan was used to determine the glass transition temperature from the reversing heat flow curves. The  $T_g$  region was found by using the half-height, or midpoint, of the transition step. The isotherms shown in the figures were purposely shifted on the heat axis to aid in seeing the transition for the different samples.

**Results and Discussion**

**Coverage Effects.** Figure 1 shows the adsorption isotherm for PMMA adsorbed onto silica from toluene. The plateau region revealed that the maximum adsorbed amount (defined as 1.00A<sub>m</sub> coverage) was at approximately 0.80 mg/m<sup>2</sup>. Lower coverage values were determined relative to this maximum amount.

The thermograms of bulk, 1.00A<sub>m</sub> and 0.48A<sub>m</sub> coverage on silica are shown in figure 2. The center of the transition for bulk PMMA was about 108°C and the  $T_g$  span from onset to end was about 10°C. The  $T_g$  center for the adsorbed polymer at saturation coverage in toluene was higher at approximately 137°C and the temperature span had broadened significantly to

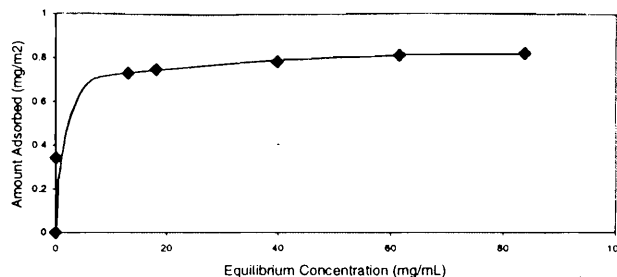


Figure 1. Adsorption Isotherm for PMMA (Mn=58,000; P.D.=1.5) adsorbed onto silica.

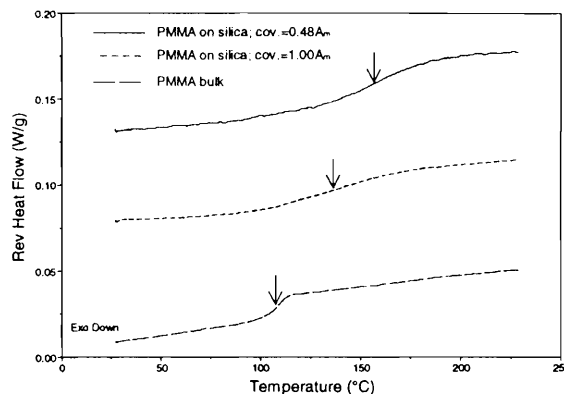


Figure 2. MDSC thermograms of PMMA adsorbed onto silica. Rate = 2.5°C/min; amplitude = ±1°C; period = 60s. The top thermogram is from 0.48A<sub>m</sub> coverage (——), the middle is from 1.00A<sub>m</sub> coverage (-----) and the bottom is from bulk PMMA (.....). The arrows are estimates of the center of the transitions.

about 60°C. The glass transition shift for the 0.48A<sub>m</sub> coverage was even higher at about 156°C and had the same span as the full coverage sample of approximately 60°C. These results are summarized in Table 1.

Previous studies have shown that the glass transition temperature can increase and broaden due to polymer chain confinement that result from intermolecular interactions,<sup>6,7</sup> in particular, hydrogen bonding.<sup>8,9</sup> Since it is known that the adsorption mechanism for PMMA on silica is through hydrogen bonding,<sup>9-11</sup> we believe that the apparent  $T_g$  elevation was the result of segmental restrictions due to being bound to silica. As the adsorbed amount decreased, the molecules were more likely to spread-out along the surface more<sup>4</sup> and hence, segmental attachment to the substrate increased which resulted in a higher  $T_g$ . In addition, the heterogeneity of the surface polymer resulted in a broader transition.

Table 1. Glass Transition Data for Bulk and Surface Adsorbed PMMA

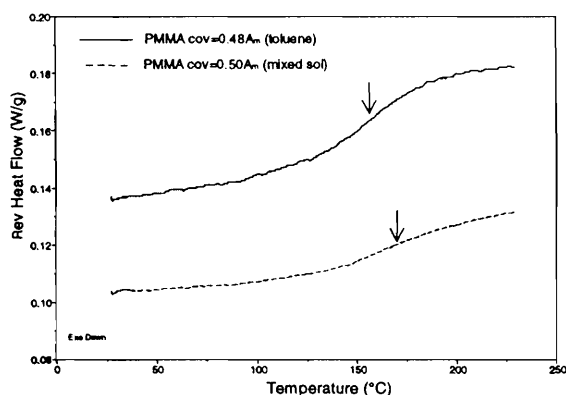
Sample	Center of Transition (approx.)	Width of Transition (approx.)
Bulk PMMA	108°C	10°C
Full coverage <sup>a</sup>	137°C	60°C
0.48A <sub>m</sub> coverage <sup>a</sup>	156°C	60°C
0.50A <sub>m</sub> coverage <sup>b</sup>	168°C	68°C

<sup>a</sup>Adsorbed from toluene

<sup>b</sup>Adsorbed from 5:1 benzene/acetonitrile solution

**Solvent Effects.** Figure 3 shows the thermograms of 0.48A<sub>m</sub> and 0.50A<sub>m</sub> coverages of PMMA on silica that were adsorbed from toluene and benzene/acetonitrile solvents, respectively. The polymer adsorbed from toluene had a glass transition center of about 156°C with a span of roughly 60°C while the sample adsorbed from the mixed solvent system had a T<sub>g</sub> center of around 168°C and a span of approximately 68°C.

The decrease in the amount of PMMA adsorption at maximum using the co-solvent system resulted from the interactions between the polymer and the solvent with the substrate. This was primarily due to an increase in solvent polarity from the presence of acetonitrile.<sup>12</sup> The increased polarity also made the solvent thermodynamically better than toluene which should increase the polymer coil size in solution and result in a more extended configuration in the chain at the surface. We propose that the increased number of segmental contacts resulting from the flattened conformation restricted the mobility of the polymer and thus, shifted the T<sub>g</sub> to a higher temperature and caused broadening.



**Figure 3.** MDSC thermograms of PMMA adsorbed onto silica. Rate = 2.5°C/min; amplitude = ±1°C; period = 60s. The top thermogram (0.48A<sub>m</sub> cov.) was adsorbed from toluene (—). The bottom thermogram (0.50A<sub>m</sub> cov.) was adsorbed from a 5:1 benzene/acetonitrile solution (-----). The arrows are estimates of the center of the transitions.

### Conclusions.

We have shown that the thermal behavior of thin films of poly(methyl methacrylate) on silica varied as a function of the adsorbed amount and the solvent used. The glass transition temperature increased and broadened at 1.00A<sub>m</sub> coverage and 0.48A<sub>m</sub> coverage compared to bulk. The T<sub>g</sub> also increased as solvent quality increased. We suggest that the increase and broadening in T<sub>g</sub> results from segmental confinement of the attached polymer. Both the increase in the glass transition and its breadth for PMMA were consistent with previous studies by deuterium NMR of poly(methyl acrylate) on silica.<sup>13</sup>

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