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Frank D. Blum  
*Missouri University of Science and Technology*

Crystal E. Porter

Wuu-Yung Lin

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## GRADUATED SEGMENTAL MOBILITY IN POLYMER LAYERS ON SILICA

Frank D. Blum, Crystal E. Porter<sup>a</sup> and Wu-Yung Lin

Department of Chemistry and Materials Research Center  
University of Missouri-Rolla  
Rolla, MO 65409-0010

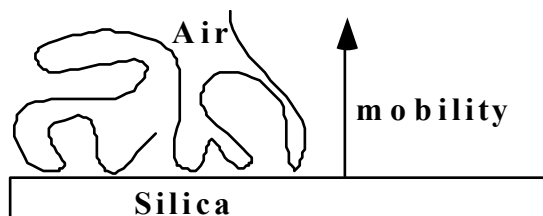
### Introduction

The behavior of thin polymer layers on oxide substrates has gotten a great deal of attention as the size of materials, and hence polymer films, has gotten smaller. Indeed, the properties of adsorbed polymers are such that they can be different from those of bulk polymers, especially when the films are very thin. A wide variety of studies have been made on adsorbed polymers and sometimes the results seem contradictory.

One of the properties often measured in thin films is the apparent glass-transition temperature,  $T_g$ . In principle, many techniques are sensitive to phenomenological changes occurring around  $T_g$  and, therefore, can be compared to each other.

For polymer thin films there are two surfaces (often different) to consider. For example, a thin polymer film on a solid substrate, such as silica, has a polymer-silica interface and a polymer-air interface. In principle, these two interfaces would be expected to have different properties. In addition, it is not always clear if either of these would dominate the properties measured.

In this paper, we provide support for the existence of graduated segmental mobility in thin polymer films. As examples we cite the behavior observed from both deuterium NMR of poly(methyl acrylate)- $d_3$  (PMA- $d_3$ ) and modulated differential scanning calorimetry (MDSC) of poly(methyl methacrylate) (PMMA), both on silica powder. In Figure 1, we depict a surface with which the polymer has a favorable interaction. We propose that the segments at the polymer-air interface have enhanced mobility while those



at the polymer-silica interface have reduced mobility.

**Figure 1.** Schematic representation of an adsorbed polymer on silica.

### Experimental

Labeled PMA was made by the polymerization of methyl acrylate- $d_3$  (MA- $d_3$ )<sup>1</sup> which was made from methanol- $d_4$  and acryloyl chloride. The PMA- $d_3$  had a  $M_w$  of  $1.10 \times 10^6$  g/mol and a polydispersity of 2.22, as measured by gel permeation chromatography (GPC). The surface sample was prepared by adsorption of the PMA- $d_3$  onto silica from toluene at saturation coverage, 2.61 mg/m<sup>2</sup>. PMMA (Aldrich;  $M_n=58K$ , PD=1.5) was adsorbed from toluene solution for the MDSC experiments.

In order to increase the sensitivity of both the NMR and MDSC experiments, the polymers were adsorbed from solution onto Cab-O-Sil, amorphous fumed silica (Cabot Corp., Tuscola, IL.) with a surface area of 200m<sup>2</sup>/g. Typically, the dispersions were allowed to equilibrate and were shaken in a mechanical shaker for 48 hr at ambient temperature. The treated silica was centrifuged and rinsed 3 times with the appropriate solvent to remove any excess polymer that may have been present. The polymer/silica samples were then dried under vacuum at ambient temperature and then 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 solution. The amount adsorbed was verified using thermal gravimetric analysis.

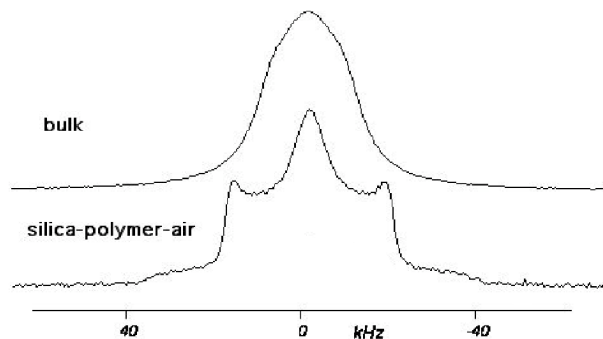
The NMR spectra were obtained on a Varian VXR-400/S spectrometer equipped with a wideline probe (Doty Scientific, Columbia, SC), a high power amplifier, and fast digitizer. The <sup>2</sup>H resonance frequency was 61.395

MHz. The pulse sequence was  $delay - 90_x^\circ - \tau - 90_y^\circ - \tau - acquisition$ . The 90° pulse width was 2.7  $\mu$ s and  $\tau = 30 \mu$ s. The number of scans ranged from 3,000 to 100,000, depending upon the amount of deuterium in the sample.

A TA Instruments 2920 MDSC was used to analyze the PMMA/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 to 240 °C at a rate of 2.5 °C/min with a modulation amplitude of  $\pm 1$  °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.

### Results and Discussion

Shown in Figure 2 is a representative example of the deuterium quadrupole echo NMR spectrum of PMA- $d_3$ , in this case taken at 52 °C. For the bulk sample, the spectrum has features that are "homogeneous" in that all segments in the sample appear to exhibit the same spectral features. The spectrum shown is one that is in the NMR- $T_g$  range. In contrast, the spectrum for the interfacial labeled polymer at the air-polymer-silica interface has features that are "heterogeneous" with respect to different segments having different mobilities. In the figure, it is obvious that two extremes dominate the spectrum, a rigid component (Pake powder pattern, more rigid than bulk), and a mobile component (narrowed central resonance, more mobile than bulk). While the extremes dominate the spectrum, there is also other evidence of a broad distribution of mobilities between these two extremes; the effects of this distribution are not as evident in the line shapes because of how the quadrupole echo intensities depend on correlation times.



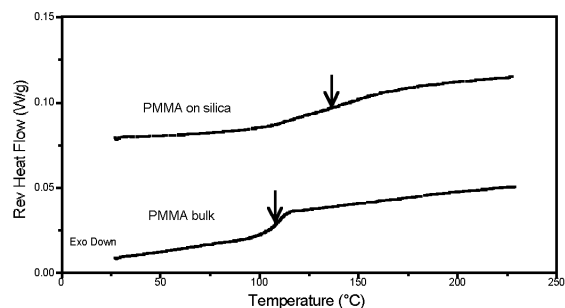
**Figure 2.** Deuterium quadrupole NMR patterns for the bulk and silica adsorbed polymer at 52 °C.

We propose that the segments with the enhanced mobility are those segments at the polymer-air interface. This region would be unconstrained by high-density (condensed phase) material like that in the middle of the film or at the solid-polymer interface. We note that the amount of material from this fraction is small (about 8%). The amount looks larger because its intensity is compressed into a narrower resonance. A similar result was also obtained for poly(vinyl acetate)- $d_3$ .<sup>2</sup> In addition, when a thin layer of interfacial PMA- $d_3$  is overcoated with unlabelled polymer, the component representative of the fraction with enhanced mobility is eliminated.<sup>3</sup>

Given that there is a range of mobilities present in thin films such as those in PMA- $d_3$  on silica, it seems reasonable to attempt to observe the thermal transitions with MDSC. The stability of the MDSC instrument and its higher sensitivity make it possible to see the thermal transitions in the films. Because of the availability of the polymer, we chose to do the MDSC experiments with PMMA. Shown in Figure 3 are the thermograms for two PMMA samples, bulk and adsorbed.<sup>4</sup> First for the bulk PMMA sample, the center of the  $T_g$  transition is at 108 °C and it has a width of roughly 10 °C. This is typical of synthetic polymers. In contrast, the transition for the adsorbed PMMA is 136 °C and has a width of about 60 °C. Clearly the trend from thermal analysis is consistent with that from NMR. The broadened transition is indicative of the distribution of mobilities on the sample.

We note that at the present time we do not easily observe the presence of the more mobile material in the MDSC scans of the surface PMMA. It may be that this material has a broad enough transition that is not clearly

distinguishable from the baseline. However, we also observed that the onset of the thermal transition is similar for both the bulk and surface polymer. Thus most of the thermal activity observed is from the less mobile segments.



**Figure 3.** MDSC thermograms for bulk (lower) and adsorbed (upper) PMMA.

### Conclusions

The results described are consistent with an interfacial polymer layer that has a motional gradient. The NMR spectra of PMA- $d_3$  show the motional heterogeneity with fractions that are more mobile and less mobile than bulk. In addition, the NMR glass transition is observed to occur over a much broader temperature range for the surface material than for the bulk material. The more-mobile material is believed to be at the polymer-air interface and the less-mobile material at the polymer-silica interface.

The motional gradient is also evident in the MDSC results for bulk and adsorbed PMMA. The MDSC thermograms of the adsorbed polymer seem to be dominated by the less-mobile material with the higher glass transition. The breadth of the transition for the adsorbed polymer also supports the main theme of this paper.

We believe that the motional gradients identified may be responsible for some of the uncertainty in the literature regarding the glass transitions of thin polymer films. While it is beyond the scope of this work to analyze other specific examples, it is obvious that different experiments may be sensitive to the presence of different components of the polymer film. If the experiment is sensitive to the more-mobile fraction, a lower  $T_g$  may be found, while those experiments sensitive to the less-mobile segments may support higher  $T_g$ 's. Clearly, more work needs to be done on surface systems to elucidate these effects.

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