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Dynamics of adsorbed poly(methyl acrylate) and poly(methyl methacrylate) on silica

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Abstract Deuterium NMR and modulated differential scanning calorimetry (MDSC) were used to probe the behavior of ultrathin adsorbed poly(methyl acrylate) (PMA). The spectra for the bulk methyl-labeled PMA- d_3 were consistent with the motions of the polymer segments being spatially homogeneous. For the polymers adsorbed on silica, multicomponent line shapes were observed. The segmental mobility of the surface polymers increased with increased adsorbed amounts. In contrast to the behavior of the polymers in bulk, the adsorbed lower-molecular-mass PMA- d_3 was less mobile than the

adsorbed high-molecular-mass polymer. The presence of a polymer overlayer was sufficient to suppress the enhanced mobility of the more-mobile segments of the adsorbed (inner) polymer. MDSC studies on adsorbed poly(methyl methacrylate) showed that the glass-transition temperature of the thin polymer films increased and broadened compared to the behavior of the polymer in bulk. The presence of a motional gradient with the less-mobile segments near the solid–polymer interface and the more-mobile segments near the polymer–air interface was consistent with the experimental observations.

Introduction

The dynamics of polymers at interfaces are important in a variety of applications, especially when those applications depend on mechanical or surface properties. Unfortunately, the surface properties of interfacial species, like the polymers used in composites, are not easily measured macroscopically. Generally, the interfacial layers are thin, often on the order of 100 Å or less. Microscopic techniques, especially spectroscopic ones, have been successful at probing these interfaces because they can be sensitive to very small amounts of material on the surface. The application of many of these techniques has been reviewed with special emphasis on their use in composite interfaces [1].

Some of the spectroscopic techniques used to study interfaces require either “clean” or flat surfaces, or at least a clear optical path to the interface under study.

These requirements limit the application of the techniques, and make them hard to apply to many materials, including composites. In our laboratory, we have found that NMR techniques can show high sensitivity to certain interfacial phenomena and can probe interfacial materials, such as adsorbed polymers and other surface-active species, such as silane coupling agents [2, 3]. The chief advantages of the NMR technique are that it can be used on opaque materials, different nuclei can be used as probes, and interfacial material can sometimes be selectively probed. The chief disadvantage of the technique is its lower sensitivity, which arises from the Boltzmann factor whereby the NMR energy levels are much closer together than the thermal energies typically available. In addition, for surface NMR, the sensitivity problem is compounded by the need to support the thin films on a solid substrate. Nevertheless, these problems can be overcome

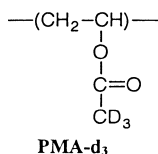
with the choice of appropriate nuclei, high surface-area supports, high-field instruments, and large sample volumes.

In our laboratory, we have chosen deuterium as the nucleus for our surface experiments. Indeed, other nuclei, such as protons or carbon 13 can be used [2, 3], as can stable free radicals in electron spin resonance spectroscopy [4]. We chose deuterium because it has an intermediate quadrupole moment, low natural abundance, and is relatively easy to incorporate into a variety of molecules. Deuterium has a quadrupole moment of intermediate magnitude and, for many species, the spectra of a deuteron bonded to a carbon can be interpreted in terms of the reorientation of the C–D bond. Surface selectivity can also be accomplished through deuterium labeling. The low natural abundance of deuterium is such that, if labeled material is deposited at the interface, the resulting spectrum will be indicative of the behavior at the interface and generally will not be complicated by unlabeled material.

In the present report, we review our laboratory studies of the ^2H NMR spectra of poly(methyl acrylate)- d_3 (PMA- d_3) [5, 6, 7] at the solid–polymer–air and solid–polymer–polymer interfaces. In addition, to verify the NMR results and to get a more complete picture of the surface behavior, we supplement the NMR data with results from modulated differential scanning calorimetry (MDSC) on poly(methyl methacrylate) (PMMA). The goal of the present work is to give an overview of the qualitative behavior of adsorbed polymers on silica.

Experimental

The PMA- d_3 polymers used were prepared as previously reported [5, 6] and only a brief outline is given here. Methyl acrylate- d_3 was synthesized from methanol- d_4 and acryloyl chloride, with about 100% deuteration on the methyl group. Two different molecular mass PMA- d_3 polymers were prepared. The high-molecular-weight (HMW) PMA- d_3 (1,100 kDa, polydispersity 2.2) was prepared from monomer via emulsion polymerization [5, 6]. The low-molecular-weight (LMW) PMA- d_3 was prepared via solution free-radical polymerization (70.5 kDa, polydispersity 2.5) [6]. For MDSC, atactic PMMA was obtained from Aldrich Chemical, Milwaukee, WI (90 kDa, polydispersity 1.5). The surface polymer samples were studied both at the silica–polymer–air interface and also in composites where the polymer-coated silica was compression molded with LMW PMA, HMW PMA, or polystyrene.



The substrate used for NMR and MDSC was Cab-O-Sil silica, grade M5, (Cabot Corporation, Tuscola, IL) which was chosen because of its high specific surface area (200 m²/g). Cab-O-Sil consists of primary particles, which are nonporous and spherical.

The adsorption was carried out from polymer solutions in toluene or benzene/acetonitrile mixtures. The solutions were allowed to equilibrate at 23 °C in centrifuge tubes with known quantities of Cab-O-Sil fumed silica. The samples were then mixed in a mechanical shaker for 48 h, centrifuged, and the coated silica was washed several times with the same solvent(s). The polymer-coated silica was then dried under vacuum at 70 °C for 6 h. The equilibrium concentration of polymer in the supernatant liquid was determined gravimetrically after drying, then also verified by thermogravimetric analysis. For accuracy in determining adsorbed amounts, the solutions were made with concentrations corresponding to the flat portions of the adsorption isotherms [5]. Variations in the adsorbed amounts were made by changing the solvent system from which the polymer was adsorbed.

The NMR spectra were obtained using a Varian VXR-400/S spectrometer equipped with a fixed-frequency wide-line probe (Doty Scientific, Columbia, SC), a high-power amplifier and fast digitizer. The wide-line probe had a coil that could accommodate an 8-mm (diameter) sample. The ^2H -resonance frequency was 61.395 MHz and the quadrupole-echo pulse sequence [8] was used (delay – 90_x^o – τ – 90_y^o – τ – acquisition). The 90°-pulse width was 2.7 μs and an echo time, τ , of 30 μs was typically used. The Fourier transformation was started at the top of the echo and no line broadening was applied to the spectra. The number of scans ranged from 1,000 to 100,000, depending upon the composition of the sample. The distortion of the line shape due to the effect of finite pulse width was estimated to be less than 3% over the spectral range of 80 kHz. Consequently, no correction for this effect was made. The spectra obtained were essentially independent of the temperature cycling of the samples.

The reduced splitting was due to the methyl group's rapid rotation about its symmetry axis. For the deuterium nucleus (spin quantum number, $I=1$), the quadrupolar splitting, $\Delta\nu_q$, between the two different allowed transitions is given by [8, 9]

$$\Delta\nu_q = (3/4)(e^2qQ/h)[3\cos^2\theta(t) - 1 - \eta\sin^2\theta(t)\cos^2\phi(t)], \quad (1)$$

where e^2qQ/h is the quadrupole coupling constant, t is time, and $\theta(t)$ and $\phi(t)$ are the spherical polar angles for the orientation of the principal axis system of the electric field tensor relative to the applied static magnetic field, \mathbf{B}_0 , and η is the asymmetry parameter. For our case with rapid methyl group rotation, the value of η can be taken as 0 and the $3\cos^2\theta(t)$ term can be further decomposed into the following:

$$\langle 3\cos^2\theta(t) - 1 \rangle = (1/2) \langle 3\cos^2\beta(t) - 1 \rangle \langle 3\cos^2\chi - 1 \rangle, \quad (2)$$

where $\langle \rangle$ represents the time average, $\beta(t)$ is the angle between the \mathbf{B}_0 and the rotation axis, and χ is the angle between the rotation axis and the C–D bond. Since χ is 70.5° for a methyl group, the $3\cos^2\chi - 1$ term is reduced and the quadrupolar splitting is reduced to one third of its original value in the absence of other motion. Values for the quadrupole coupling constant of methyl groups are typically of the order of 150–170 kHz [8, 9].

A TA Instruments model 2920 MDSC (New Castle, DE) was used to thermally analyze the coated silica samples. The reference pan was loaded with roughly the equivalent amount of silica that was 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 240 °C, at a rate of 2.5 °C/min, a modulation amplitude of ± 1 °C, and a period of 60 s. The total run time was approximately 4 h per sample. The second heating scan was used to determine the glass-transition data from the reversing heat flow curves so that all of the samples were subjected to a similar thermal history. The reported T_g was found by using the half-height temperature of the transition step. T_g values from at least two separate experiments were averaged for the bulk and all surface samples. A difference of no more than ± 2 °C was observed for experiments performed on different samples of the same material.

Results and discussion

In order to understand the surface dynamics of the polymers, we found it useful to base our understanding on the behavior of the corresponding bulk polymers. In general, we find that the behavior for the bulk polymer is such that single-component line shapes result. In contrast, for the surface-bound polymers, multicomponent line shapes result. The multicomponent line shapes are believed to come from segments, in different locations, with differing mobilities. In turn, we discuss the results of experiments on PMA- d_3 as a function of adsorbed amount, molecular mass, and polymer overlayer. Then we discuss the behavior of similar adsorbed samples of PMMA on silica as probed with MDSC.

PMA- d_3 – bulk

Three experimental deuterium quadrupole-echo spectra for HMW PMA- d_3 are shown in Fig. 1. The spectra at 24 °C (and below, not shown) were Pake powder patterns with reduced splittings as expected for a methyl group undergoing fast motions about its symmetry axis. At these temperatures, the backbone motions are slow enough that they do not appreciably contribute to the spectra and may be considered static for our purposes. At higher temperatures (e.g. at 44 and 52 °C), the powder patterns collapse with a gradual smoothing of the sharp features. Above 52 °C the resonances (not shown) get narrower.

The collapse of the Pake pattern is indicative of the presence of backbone motion in the polymer, which

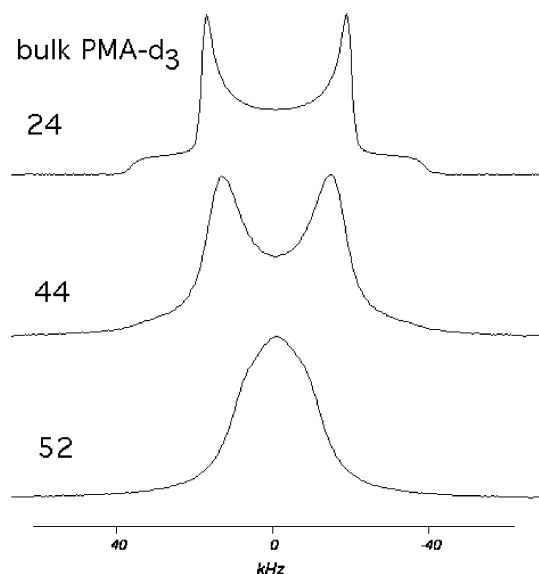


Fig. 1 ^2H NMR spectra of poly(methyl acrylate)- d_3 (PMA- d_3) in bulk at the temperatures (°C) indicated

further narrows the resonance when its rate is comparable with the inverse of the quadrupole splitting. The collapse roughly occurs between 44 and 52 °C and this can be considered the “ $T_g(\text{NMR})$ ”. The $T_g(\text{NMR})$ is about 40 °C above the $T_g(\text{DSC})$ of 10 °C [10] and the difference can be attributed to the differences in time scales of the two experiments with the DSC being of the order of hertz and the ^2H NMR of the order of kilohertz (reciprocal of around 40 kHz). Even though 2D NMR experiments on a wide variety of polymers have shown that the motions of amorphous polymers around the T_g need to be described with a broad distribution of correlation times [11], the $T_g(\text{NMR})$ was still fairly narrow. The polymer behavior was also homogeneous in that the line shapes appeared to have a single component, i.e., all polymer segments exhibited virtually the same motions on the NMR time scale (vide infra).

PMA- d_3 at the silica–polymer–air interface

The adsorption of PMA- d_3 onto silica from a toluene solution resulted in a series of spectra [5], a few of which are shown in Fig. 2, for which a direct comparison with the spectra in Fig. 1 can be made. The adsorbed amount was 2.61 mg polymer/ m^2 silica. At 25 °C, the surface spectrum for PMA- d_3 was almost identical with that of the bulk material, both Pake patterns. In both cases, the backbone of all the polymer segments can be considered rigid. At 44 °C a full Pake pattern is still observed for the surface sample; however, a small motionally narrowed component is evident in the middle. Thus, the surface sample is inherently heterogeneous and consists of some segments which are less mobile, and also more mobile than in bulk. The segments with enhanced mobility are

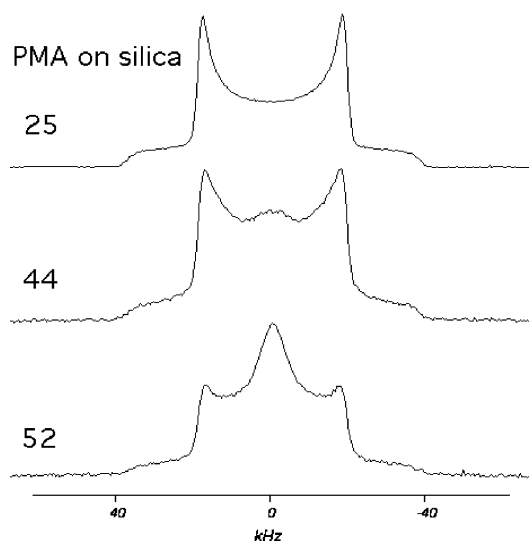


Fig. 2 ^2H NMR spectra of PMA- d_3 on silica at the temperatures (°C) indicated

even more clearly observed in the 52 °C spectra. The corresponding bulk spectrum shows only a narrowed Pake pattern at 44 °C and a broad single resonance at 52 °C.

For simplicity, we choose to confine ourselves to a two-state model with components that are easily identified as more or less mobile than bulk. However, there is undoubtedly a continuous distribution of mobilities in the sample. The deuterium NMR filter suppresses the resonances with intermediate mobility [5, 8]. On one hand, this is a problem in that the spectral intensities are not simply proportional to the number of nuclei with different mobilities, but it is an advantage in that it highlights the extremes, i.e., the more-mobile and less-mobile species are easily observed. Because of these uncertainties, we have chosen not to estimate the relative amounts of the different species with different mobilities.

PMA- d_3 , effect of adsorbed amount

The deuterium NMR spectra of HMW PMA- d_3 at 52 °C in bulk for 1.0 and 0.2 A_m adsorbed amounts are shown

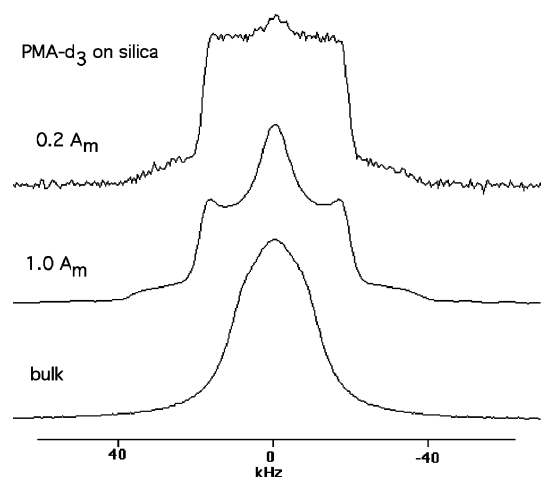
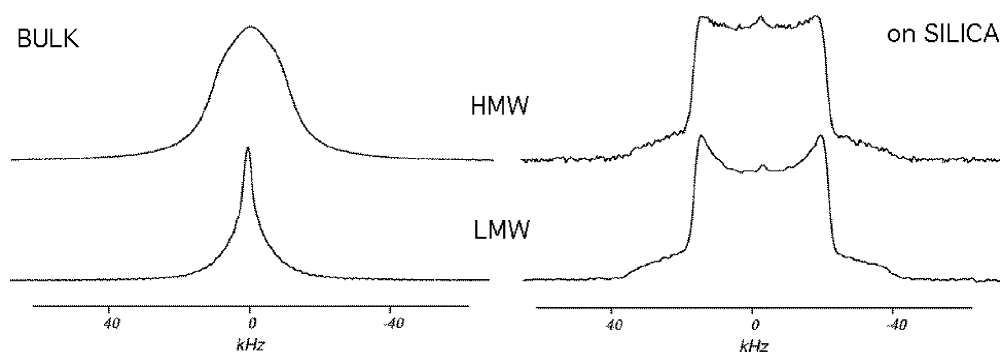


Fig. 3 ^2H NMR spectra of high-molecular-weight (HMW) PMA- d_3 in bulk and at two different adsorbed amounts (in units of A_m) on silica at 52 °C

Fig. 4 ^2H NMR spectra of HMW (upper) and low-molecular-weight (LMW) (lower) PMA- d_3 in bulk (left) and on silica (right) at 52 °C. The adsorbed amounts are 0.23 and 0.31 mg/m^2 for the HMW and LMW materials, respectively



in Fig. 3. The 1.0 A_m designation corresponds to the maximum adsorption amount in toluene (2.61 mg polymer/ m^2). The heterogeneous nature of the adsorbed samples, as compared to bulk, is again quite evident. It is also apparent that the sample with the lower adsorbed amount has relatively fewer of the more-mobile segments. This is indicative of the surface-bound polymers at lower adsorbed amounts having a flatter conformation and more segments at or near the silica surface.

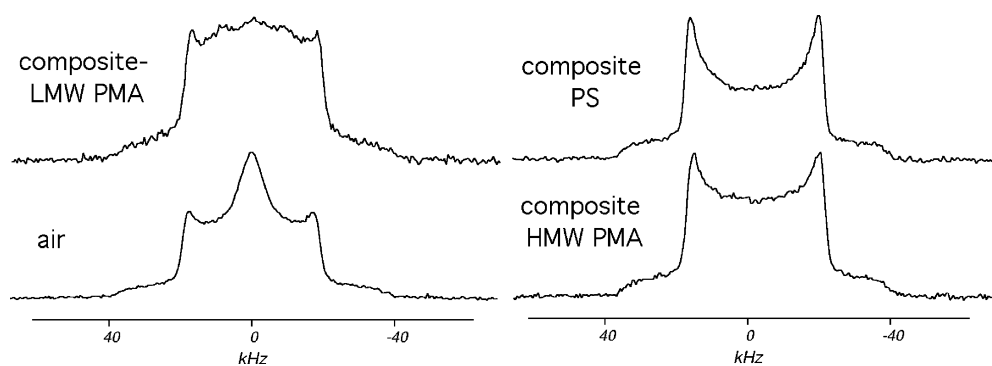
PMA- d_3 , effect of molecular weight

The effect that the surface has on segmental mobility as a function of molecular weight [6] is shown in Fig. 4. For the bulk sample, the LMW PMA- d_3 has a lower T_g (not shown) than the HMW PMA- d_3 . At 52 °C, the LMW polymer has a significantly narrower resonance consistent with it having faster segmental mobility, roughly an order of magnitude faster than the HMW sample [6]. In contrast to their behavior in bulk, at similar adsorbed amounts, the spectra of both adsorbed samples look similar. Closer inspection reveals that the filled-in middle for the HMW sample is indicative of a higher fraction of more-mobile material. This is the opposite of the behavior of the polymer in bulk. The LMW material is more rigid on the surface. In fact, the effect is probably greater than it seems from Fig. 4 because the LMW PMA- d_3 has a slightly higher (1.3 times) adsorbed amount. As we noted previously, this would make the polymer even more mobile than at a lower adsorbed amount.

PMA- d_3 effect of polymer overlayer

In order to test the notion that the more-mobile segments were located at the polymer-air interface, we compression-molded unlabeled (fully protonated) polymers with the silica coated with deuterated polymers to make composite materials. Since the polymers directly adsorbed on the silica were deuterated, and those used as an overlayer were not, the interfacial material in a true

Fig. 5 ^2H NMR spectra of HMW PMA- d_3 at 52 °C at the air interface and in composites compression molded with LMW PMA, HMW PMA, or polystyrene



composite could be probed. The results of the resulting spectra at 52 °C are shown in Fig. 5 [7]. Compared to the PMA- d_3 at the silica–polymer–air interface, the composites yield spectra with a decrease in the intensity of the less-mobile segments (smaller amount of the narrow feature in the center). In fact, it is apparent that the intensity of the central resonance (mobile component) decreased in the order LMW PMA > HMW PMA > polystyrene as the overlayer. Further evidence for this is given at other temperatures as well [7]. Interestingly, this is the order of the T_g s of the polymers used for the overlayer. One can imagine that LMW PMA, or perhaps even HMW PMA might be able to penetrate into the adsorbed PMA- d_3 layer, but certainly not polystyrene. Thus, it is obvious that the interfacial polymer senses the presence of the overlayer even if there is no attractive interaction between the polymers.

PMMA on silica, MDSC results

For comparison with the NMR results, we probed the thermal behavior of adsorbed PMMA samples. The use of MDSC made it possible for us to achieve the baseline stability necessary to observe the transitions for very small amounts of adsorbed polymer. The thermograms

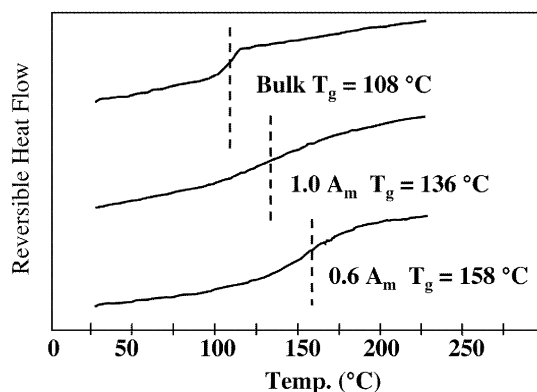


Fig. 6 Modulated differential scanning calorimetry thermograms for bulk and adsorbed (1.0 and 0.6 A_m) samples. The center of the T_g transition is marked with the *dashed line*

for bulk and adsorbed PMMA samples are shown in Fig. 6 [12]. The bulk sample had a T_g which was centered around 108 °C and had a width of about 10 °C, typical for bulk polymers like PMMA. In contrast, the behavior for the adsorbed samples resulted in a shift of the transition to higher temperatures (centered at 136 °C for 1.0 A_m and 158 °C for 0.6 A_m). In addition, the breadth of the transitions for the adsorbed samples was increased substantially to about 60 °C in both cases.

Given that the thermal transitions for the adsorbed polymers are so broad, it is not difficult to rationalize why they have been somewhat elusive. The breadth of the transitions makes stability of the baseline critical and the presence of the substrate affects thermal transport and reduces the concentration of polymer in the sample. The coupling of high-surface-area substrates and MDSC allows meaningful measurements to be made.

The MDSC data are completely consistent with the NMR data. They show that the transition is broader, consistent with the heterogeneous nature of the polymer segments. The higher T_g for the lower-adsorbed-amount samples is consistent with the lower mobility for the lower-molecular-mass polymers in the thin film.

Adsorbed polymer behavior

The NMR data from the different experiments can be understood on the basis of a relatively simple model. The adsorbed polymer may be thought to consist of segments with different mobilities. The differences probably arise from segments that are different distances from the surface of the solid substrate. Segments directly

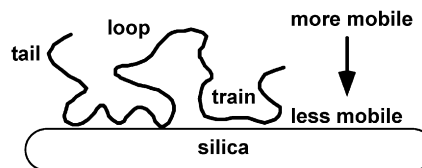


Fig. 7 Schematic representation of the polymer conformation showing trains, loops, and tails. The presence of a motional gradient in the adsorbed polymer is also indicated

attached (or closely associated) with the surface are called trains [13]. Between trains are loops, which are not as close to the surface. Tails are the dangling ends of the molecules. A sketch of this situation is shown in Fig. 7. Since the attraction of the carbonyl group of the polymer and the surface hydroxyls is fairly strong, it is reasonable to propose that the trains are less mobile and the loops and tails are relatively more mobile. The extension of this notion to a more continuous distribution of mobilities leads to the notion of a motional gradient as depicted in Fig. 7. This motional gradient exists within a layer that has a thickness of the order of the size of a single polymer molecule.

The dependencies of the dynamics of the adsorbed polymer on the adsorbed amount, molecular weight, and overlayer are consistent with the model proposed. So are the MDSC results. At lower adsorbed amounts, we envision the polymer to have a flatter conformation and, therefore, shorter, or fewer, loops. If the number of segments in trains in different samples is roughly constant because of similar surface areas, at lower adsorbed amounts, the relative number of less-mobile segments should increase. For the lower-molecular-weight species, the flatter conformation would also result in a larger fraction of the less-mobile segments. It is important to note that the molecular-weight effect in the surface polymer is the opposite of that in the bulk polymer. On the surface, the LMW polymer is less mobile, while in bulk it is more mobile. The coverage of the polymer at the substrate-polymer-air interface with another polymer suppressed the component with enhanced mobility. This is evidence for this fraction being at the air interface. It is interesting to note that this effect occurred even when the polymer overlayer was polystyrene, which should not appreciably interact

with the PMA. The broadened transitions seen in the surface PMMA are also consistent with the model. Unfortunately, we have not been able to identify the fraction with the higher mobility than bulk in the MDSC scans of the surface PMMA. This may be because it is a rather small fraction of an already small adsorbed sample.

Conclusions

Deuterium NMR can be a powerful tool for studying the mobility of adsorbed polymers. The use of labeled methyl groups can give information on the segmental dynamics of the polymer chains through the line shape changes. PMA- d_3 showed spectra which were consistent with a homogeneous distribution of segmental mobility for the bulk polymers. On silica, the distribution of mobilities was found to be quite heterogeneous. On the surface, the polymer chain was proposed to have graded mobility, with segments near the surface being less mobile than bulk and segments near the air interface being more mobile than bulk. The overall effect is to raise the T_g of the surface polymer owing to the attractive interaction between the PMA and silica. This was verified by MDSC as well. The relative amounts of the less-mobile components increase as the adsorbed amount decreases. In contrast to the behavior of the bulk polymers, the LMW surface PMA has a lower mobility than that of the HMW surface PMA. The segments at the air-polymer interface are suppressed when a polymer overlayer is molded over them.

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