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The effect of molecular mass on the segmental dynamics of poly(methyl acrylate) (PMA) adsorbed on silica was studied using deuterium quadrupole-echo nuclear magnetic resonance (NMR) and modulated differential scanning calorimetry. Samples adsorbed on silica (all about 1.5 mg PMA/m^2 silica) were shown to have more restricted segmental mobility, and higher T_g's, than the corresponding bulk PMA samples. Around the glass-transition region, adsorbed samples exhibited segmental mobility, which could be classified as heterogeneous due to a superposition of more-mobile and less-mobile components present in the deuterium NMR spectra. This heterogeneity was consistent with a motional gradient with more-mobile segments near the polymer-air interface and the less-mobile species near the polymer-silica interface. The mobility of the adsorbed 77 kDa PMA sample was the lowest among the four different molecular-mass samples studied. Samples studied with masses both larger and smaller than 77 kDa had larger mobile-component fractions in the adsorbed polymer. The additional mobility was attributed to the presence of either longer tail and loop conformations in the higher molecular-mass samples or the inherent mobility of the tails in the lower molecular-mass samples on the surface. © *2006 American Institute of Physics.* [DOI: 10.1063/1.2219739]

INTRODUCTION

Studies of polymers at the polymer-substrate interface have significantly enhanced our understanding of composite systems. The interactions between polymers and substrates are diverse and, consequently, so are the effects of fillers on different polymers. Theoretical and experimental studies of interfaces have led to a better understanding of colloid-polymer interactions.[1] The interactions between a polymer film and a substrate may cause profound changes in the thermal and mechanical properties of the polymers. The interaction may differ for thin films in diverse systems, and these differences may also play a role in the development of physical properties.

The concept of a surface glass-transition temperature (T_g) of polymers adsorbed on solid substrates is useful to characterize some of the profound changes that adsorbed polymers undergo. Optical and scattering experiments have shown that, due to the nature of the surface and its interaction with polystyrene (PS), the T_g can be increased as in the case of H-passivated silicon[2] or decreased[3–11] as for many other surfaces. In other systems, stronger interactions of the substrate with the polymer, e.g., of poly-2-vinylpyridine films[12] on silicon oxide and poly(methyl methacrylate) (PMMA)[13] adsorbed on a silica surface, resulted in increases in T_g's, as compared to bulk. Other techniques such as secondary ion mass spectrometry,[14] fluorescence recovery after patterned photobleaching,[15] nuclear magnetic resonance (NMR),[16–21] and dielectric spectroscopy[22] have all indicated

significant deviations from bulk dynamics for thin films supported on solid surfaces. These effects are also apparent in mechanical properties. Tsagaropoulos and Eisenberg[23] observed two T_g's for silica-filled polymers using a dynamic mechanical analyzer. In addition to bulklike behavior, a second transition at higher temperature was attributed to the segments with reduced mobility due to an interaction with the filler. Blum *et al.* also demonstrated that the interaction of poly(methyl acrylate) (PMA) with a glass substrate affects the dynamics in such a way that adhesion in thin films is changed.[24]

Several experimental techniques have also been used to understand the molecular-mass dependence of the T_g of thin polymer films on solid substrates. Miyazaki *et al.*[10] and Fukao *et al.*[7,25] showed evidence of the molecular-mass dependence of the T_g for thin PS films using x-ray reflectivity and dielectric relaxation spectroscopy, respectively. Several other researchers have also observed a molecular-mass-dependent surface T_g.[6,8,9] However, the molecular-mass dependence of T_g, in thin supported films, is in question because of other studies reporting no dependence.[4,5,7,11,26]

NMR spectroscopy has been used to probe the dynamics on surfaces.[27,28] A strong polymer-surface interaction was shown to restrict the mobility of poly(vinyl acetate),[16] PS-b-2-vinylpyridine,[29] and PMA[17,18,21] polymers on silica and alumina using solid-state deuterium NMR experiments. These experiments identified the dependence of the mobility of the adsorbed polymer on the adsorbed amount,[16,17] the presence of an overlayer,[21] and the molecular mass.[18] In the latter case, only two widely different molecular masses were
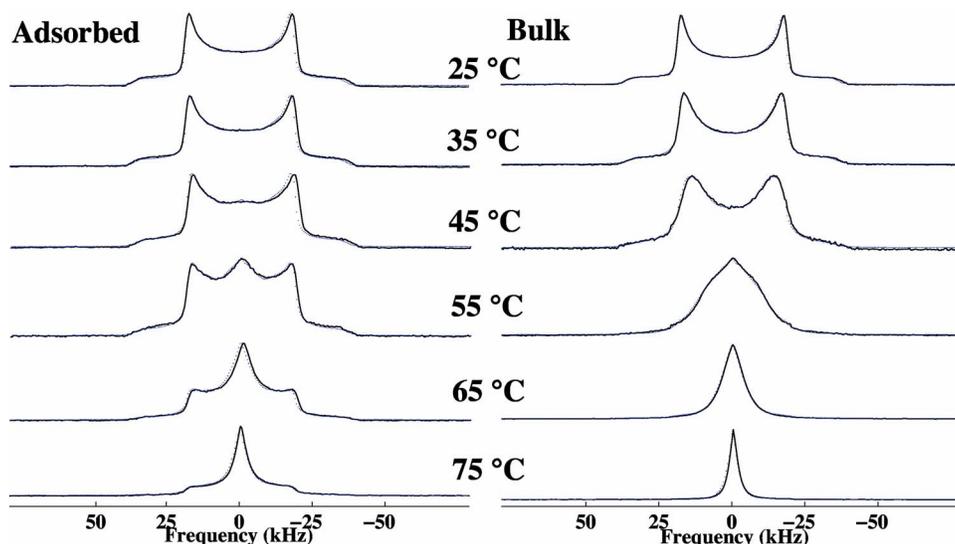

FIG. 1. Experimental (–) and simulated (···) ^{2}H NMR spectra for bulk and adsorbed (1.52 mg/m^2) PMA-165 K samples as a function of temperature.

studied.[18] For these broadly spaced masses, a lower mobility was observed for the lower molecular-mass PMA sample on the surface.

In this paper, we report detailed studies of the effect of molecular mass on the segmental dynamics of adsorbed PMA on silica. The large polydispersity and the big differences in molecular masses of the samples in the previous study[18] have been overcome by the use of PMA-d_3 of much lower polydispersity. Four relatively narrow molecular-mass PMA-d_3 samples, with molecular masses ranging from 5000 to 165 000 g/mol, were synthesized. These samples, adsorbed on silica, were studied using the ^{2}H quadrupole-echo NMR and modulated differential scanning calorimetry (MDSC) techniques. Taken together, these two techniques provide complementary information about adsorbed polymers.[30] In this case, the results of these techniques were consistent with the notion that, for this system, a molecular-mass region exists where there is a minimum of the polymer mobility on the surface.

EXPERIMENT

A detailed description of the synthesis procedure of methyl acrylate-d_3 is given elsewhere.[31] PMA-d_3 samples were synthesized by atom transfer radical polymerization.[32] Amorphous fumed silica (M-5 grade, Cabot Corp., Tuscola, IL) was dried in an oven at 450 °C for 24 h before use. Solutions of PMA in toluene were prepared and mixed with silica in separate tubes. The mixtures were then placed on a mechanical shaker for 48 h and centrifuged for 1 h. The supernatant liquid was decanted and the solid-containing portion was kept under vacuum for 36 h. Thermogravimetric analysis (TGA) was used to determine the adsorbed amounts of the polymer based on the masses of the samples before and after the polymer was burned off. Samples made with known amounts of polymer with mixed silica were used as controls for the TGA experiments.

The molecular masses and polydispersities (PDs) of the PMA samples were measured using gel permeation chromatography (GPC), an Optilab DSP interferometer refractometer, and a Dawn EOS light-scattering instrument (Wyatt

Technology, Santa Barbara). The molecular masses and PDs found were as follows: PMA-5 K (M_w=5600 g/mol, PD=1.02), PMA-38 K (M_w=38 000 g/mol, PD=1.15), PMA-77 K (M_w=77 000 g/mol, PD=1.26), and PMA-165 K (M_w=165 000 g/mol, PD=1.42). An additional PMA-400 K protonated sample was prepared and used in the MDSC experiments.

Calorimetric measurements were made using a MDSC (TA Instruments, New Castle, DE) with a modulation rate of ±0.5 °C every 50 s and a heating rate of 3 °C/min. Universal analysis software (TA Instruments) was used to process the collected MDSC data. The thermograms were shown as the derivative of the heat flows. The derivative mode makes the broad transitions much easier to observe than in the simple heat-flow curves.

Deuterium NMR spectra were obtained using a Varian VXR-400/S spectrometer. The quadrupole-echo pulse sequence (delay-90$_y$-τ-90$_x$-τ-acquisition) was used with the ^{2}H frequency at 61.39 MHz. A 90° pulse width of 2.7 μs and an echo time (τ) of 30 μs were used. For the bulk samples, 256 scans were taken, while 4096–8192 scans were required for the adsorbed samples.

The experimental NMR line shapes were fitted using a series of simulated line shapes with different jump rates that were produced with the MXQET[33,34] program. A series of simulated line shapes (94 in this case) were generated using a jump model based on jumps corresponding to the vertices of a truncated icosahedron (soccer ball). The jumps were allowed to occur from one site to one of its three-nearest neighbors with equal probability. The truncated icosahedron, with its 60 vertices, represents a balance between the need to have small angle jumps and the limits of computation time. A mathematical routine was applied to fit the experimental line shapes to a superposition of simulated spectra with MATLAB (The Mathworks, Inc., Natick, MA). Details of the line shape simulation are given elsewhere.[31]

RESULTS

The ^{2}H NMR spectra for adsorbed PMA on silica are shown in Figs. 1–4 for the polymers of different molecular
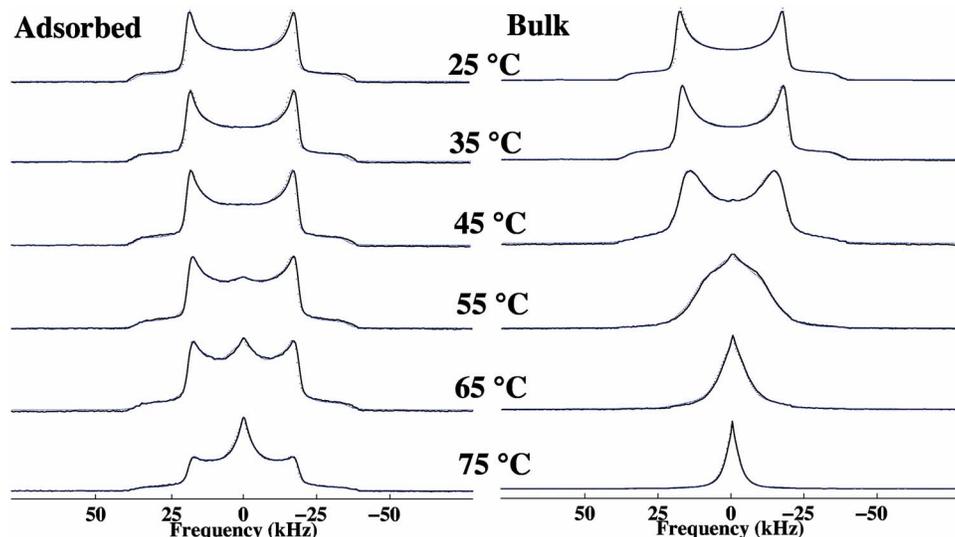
FIG. 2. Experimental (–) and simulated ($\cdots$) ^{2}H NMR spectra for bulk and adsorbed (1.46 mg/m^2) PMA-77 K samples as a function of temperature.

masses. All of the adsorbed samples had similar adsorbed amounts. The fits from the simulated surface spectra are superimposed as dotted lines. The simulations very accurately fit the experimental spectra and are almost indistinguishable from them in most cases. For comparison, the spectra of the bulk polymers at the same temperatures are also shown, although the details and simulations of these spectra have been reported.[31]

The spectra for the adsorbed and bulk PMA-165 K samples are shown in Fig. 1. At 25–45 °C the spectra for the adsorbed polymer (1.52 mg/m^2) consisted of a Pake powder pattern which broadened slightly with temperature. The spectrum at 45 °C showed a subtle hint of a central resonance which built up with temperature. By 75 °C, the central resonance appeared to dominate the spectra, but there was still a significant amount of broad component in the "wings" of the spectrum. The superposition of significant amounts of the broad (less-mobile) and central components (more-mobile) at the same temperatures motivated us to label this behavior as "heterogeneous." In contrast, the bulk spectra for this polymer showed a gradual broadening of the Pake patterns as they collapsed with temperature to narrow central reso-

nances. At 55 °C there was no distinct presence of a Pake pattern. In contrast to the surface spectra at 75 °C, there was no evidence of a broad component in the spectrum of the bulk material.

The deuterium NMR spectra of the adsorbed (1.46 mg/m^2) and bulk PMA-77 K samples are shown in Fig. 2. The spectra for the adsorbed sample showed no significant line shape changes until 55 °C, where a motionally narrowed (more-mobile) component was present in the powder pattern of the adsorbed sample. Again, a significant amount of residual powder pattern was present at higher temperatures. The Pake pattern for the bulk sample disappeared at 55 °C, and a further increase in temperature resulted in a narrower resonance with no broader components.

The NMR spectra of the adsorbed (1.45 mg/m^2) and bulk PMA-38 K sample are shown in Fig. 3. No significant change in the ^{2}H NMR spectra of the adsorbed sample occurred at 25 and 35 °C. A more-mobile component appeared at 45 °C for the adsorbed samples, and its intensity increased with temperature. A significant amount of residual powder pattern was also present for the adsorbed PMA-38 K sample at higher temperatures. For the bulk sample, the Pake pattern
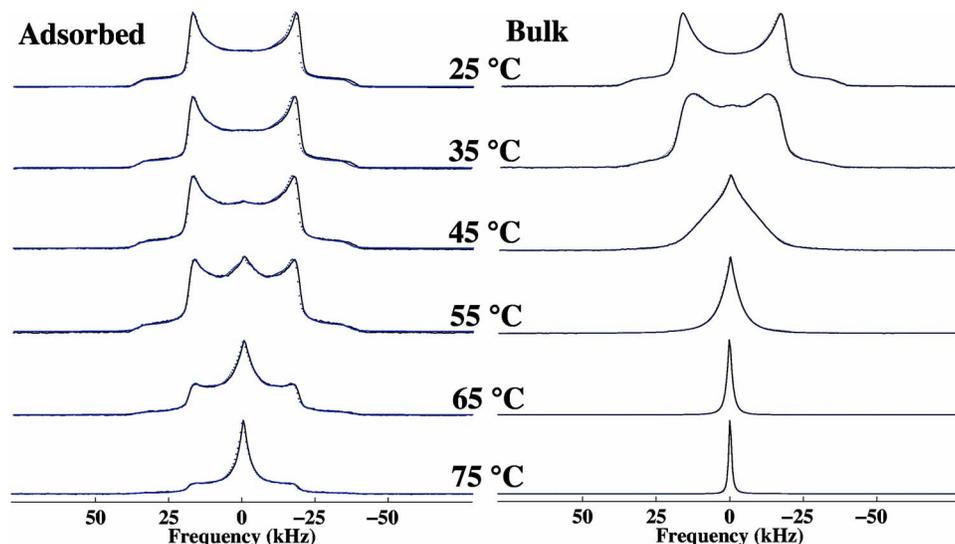

FIG. 3. Experimental (–) and simulated ($\cdots$) ^{2}H NMR spectra for bulk and adsorbed (1.45 mg/m^2) PMA-38 K samples as a function of temperature.
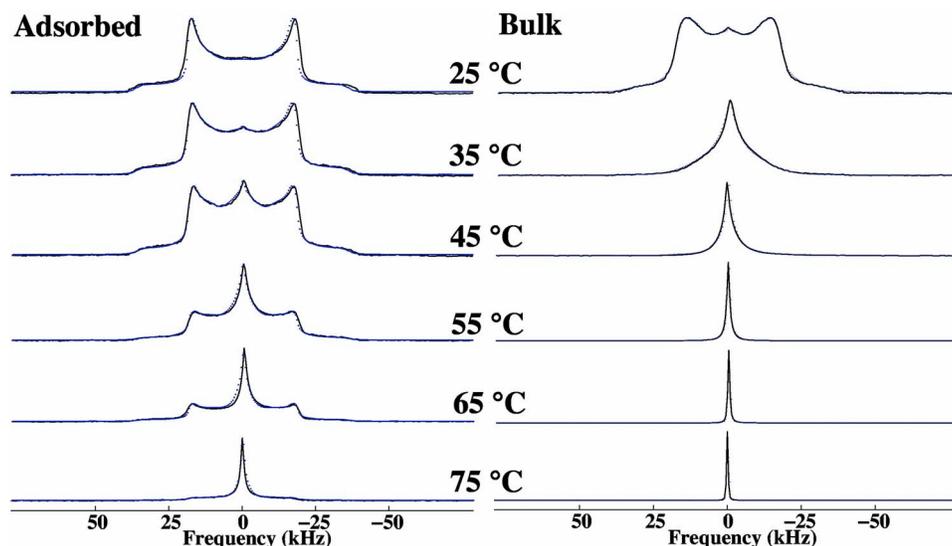
FIG. 4. Experimental (–) and simulated (···) ^{2}H NMR spectra for bulk and adsorbed (1.46 mg/m^2) PMA-5 K samples as a function of temperature.

disappeared at 35 °C. There was evidence of a small amount of heterogeneity due to chain ends, but not as much as that found in the surface spectra. The spectra contained only a central component at higher temperatures. We note that while the spectra for the bulk PMA-38 K and PMA-165 K samples were rather different, their surface spectra were almost identical.

The deuterium NMR spectra of the adsorbed (1.46 mg/m^2) and bulk PMA-5 K samples are shown in Fig. 4. At 25 °C, the adsorbed PMA-5 K sample exhibited a Pake powder pattern, with the middle slightly filled in, indicating the rigidity of the segments at this temperature. A larger middle component, due to more-mobile segments on the surface, was obvious at 35 °C for the sample. The intensity of the broad component in the adsorbed sample decreased gradually with temperature. However, a residual powder pattern was still present in the adsorbed sample spectra even at a temperature of 75 °C. For the bulk PMA-5 K sample at 25 °C, a central component overlapped with a broader component similar to that for the bulk PMA-38 K sample at 35 °C. Again, the spectra had no broad component at higher temperatures.

In order to facilitate further comparison, Fig. 5 shows the spectra for each molecular mass for the adsorbed PMA-d_3 at 55 °C and bulk PMA-d_3 at 35 °C. For the bulk polymer at 35 °C, there was a progression with molecular mass from a Pake powder pattern for PMA-165 K and PMA-77 K to a partially collapsed pattern for PMA-38 K and to a somewhat narrower central resonance for PMA-5 K. For the surface samples at 55 °C, the progression with molecular mass was not monotonic. The PMA-165 K sample showed a superposition of a Pake pattern, plus a central resonance. The PMA-77 K had a similar spectrum except that the intensity of the central resonance was smaller. For PMA-38 K, the intensity of the central resonance was now *larger* with a relative intensity similar to that for the PMA-165 K sample. Finally, the PMA-5 K exhibited a central resonance that was much larger than those for the other samples.

The MDSC scans for the adsorbed and bulk polymers are shown in Fig. 6, where the derivatives of the reversible heat flow data with respect to temperature are plotted. It is easy to see that the MDSC curves for the surface polymers were shifted to significantly higher temperatures and are much broader than those for the bulk polymers. The highest
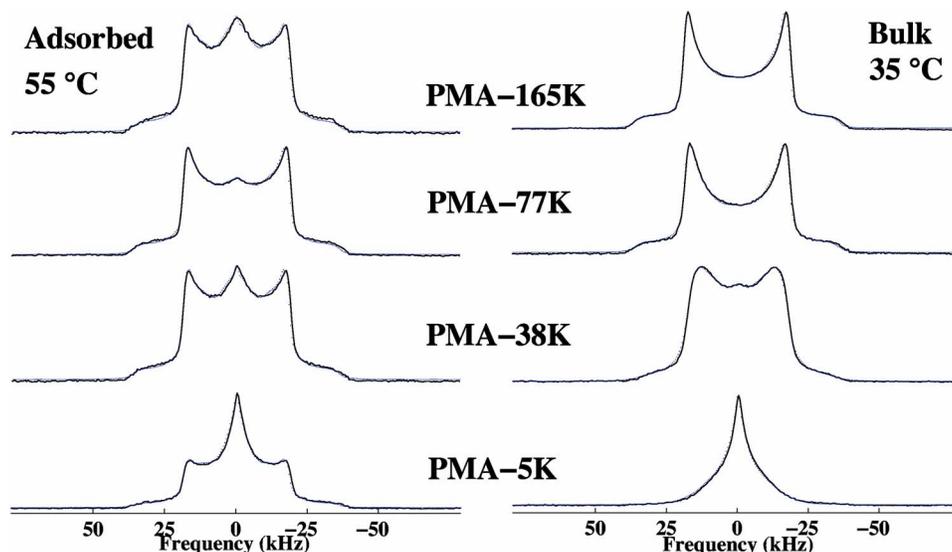

FIG. 5. Comparison of ^{2}H NMR spectra of different molecular mass bulk (35 °C) and adsorbed (55 °C) PMA.
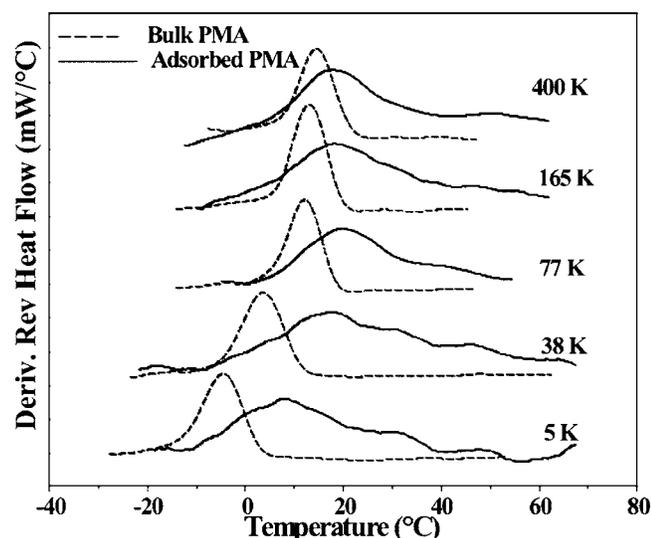
FIG. 6. MDSC thermograms (derivative mode) for bulk and adsorbed PMA with different molecular masses.
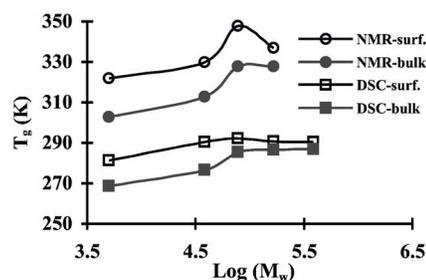

FIG. 7. The change of T_g with molecular mass for the adsorbed (open symbols) and bulk (filled symbols) PMA samples from MDSC and NMR experiments.

points of the peaks in the derivative curves were reported as the T_g's and are listed in Table I. The transition widths at the half-heights for the derivative MDSC curves are also listed in Table I for both the bulk and surface-adsorbed samples. The MDSC widths for different samples/runs were determined to be from 5.6 to 9.3 °C for the bulk samples, while those for the adsorbed PMA samples were between 19 and 31 °C. For comparison with other data, these values are plotted in Fig. 7.

The Boltzmann-corrected intensity curves for the NMR experiments are shown in Fig. 8. The minima in the intensity curves were used as an estimate of the NMR T_g's and are also listed in Table I, along with the widths at half-height. Consistent with the MDSC data, the T_g's increased and became much wider for the adsorbed polymer. The intensity curves for the adsorbed samples were also wider and shallower than those for the bulk samples.[31] The values for the T_g's determined in this way are also shown in Fig. 7 for the bulk and surface polymers.

The NMR line shapes, at each temperature, were fitted based on a series of simulated spectra generated from the MXQET program with different jump rates, k_i. A "best-fit" spectrum was obtained using a matrix routine in MATLAB.[31] The distributions of the jump rates, $w(k_i)$, used to fit the adsorbed-sample spectra are shown in Fig. 9. Our basis set of

spectra consisted of 94 spectra[31] with jump rates which can be classified as the slow ($10^2 - 10^4$ Hz), intermediate ($10^4 - 10^6$ Hz), and fast ($10^6 - 10^{11}$ Hz) regimes. The adsorbed sample spectra required mostly slow and intermediate components for good fits. As expected from the spectra, significant amounts of slow components were required even at higher temperatures for the adsorbed samples. With increases in temperature, the jump rate distributions shifted to the fast side. There were several small, but important, contributions to the fits from the fast regime at higher temperatures.

The average correlation times were calculated at each temperature based on the fits and these are shown in Fig. 10 along with the values for the corresponding bulk samples.[31] In general, the correlation times for the adsorbed samples were longer than those for the bulk samples. We note that correlation times for the adsorbed polymers are much closer together than the corresponding values for the bulk polymers. In other words, the adsorbed samples are more similar to each other than the bulk samples are. In general, for the adsorbed polymers, the PMA-5 K sample had the faster correlation times and the PMA-77 K, the slowest.

The weight-averaged overall correlation functions for each of the experimental spectra, $C(t)$, were estimated by adding the correlation functions of the component spectra, $C(t,k_i)$, or

$$C(t) = \sum_{i=1}^{94} w(k_i)C(t,k_i). \qquad (1)$$

It has previously been shown that the correlation functions for the basis set of spectra could all be fitted to a Kohlrausch-Williams-Watts (KWW) function (stretched exponential)

TABLE I. T_g measurements (°C) and widths (°C) from MDSC and ^{2}H NMR for the bulk and absorbed (1.5 mg/m^2) PMA.

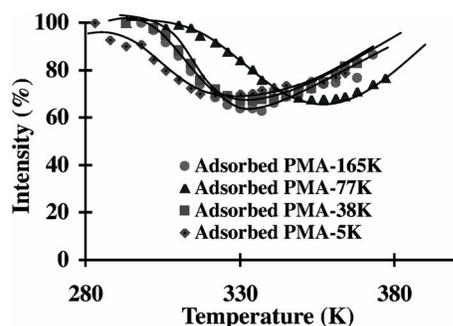|	DSC				NMR			
	Bulk		Adsorbed		Bulk		Adsorbed	
Polymer	T_g	Width	T_g	Width	T_g	Width	T_g	Width
PMA-5 K	−4.5	7.41	8.4	25	30	37.5	49	59
PMA-38 K	3.5	8.93	17.7	20	40	34.6	57	50
PMA-77 K	12.3	6.37	19.5	31	55	34	80	55
PMA-165 K	13.4	5.64	18.0	26	55	33.9	64	50
PMA-400 K	14.2	5.58	17.5	25				

FIG. 8. The Boltzmann-corrected intensity curves obtained from the NMR experiments. A similar curve for the bulk samples was shown in Ref. 31.

FIG. 10. Average correlation times for bulk and adsorbed PMA samples from the NMR line shape fitting.

with a fixed width parameter, $\beta=0.63$.[31] Similar to the experimental spectra for the bulk polymer, the overall correlation functions could also be fitted to a stretched exponential, or

$$C(t) = \exp[-(t/\tau)^{\beta}]. \qquad (2)$$

These fitted curves of $C(t)$ were then integrated to obtain the average correlation times for the spectra.

The change in the β parameter of Eq. (2) with temperature, for bulk and adsorbed samples, is shown in Fig. 11. The value of $\beta(0 \leq \beta \leq 1)$ indicates the breadth of the distribution of correlation times.[35] The smaller β is, the broader the distribution of correlation times is. While there is some scatter in the data, the adsorbed samples have smaller β's, and the differences between the bulk and surface samples were greater at higher temperature. The smaller β values, corresponding to broader distributions, provided more evidence for the heterogeneous nature of the motions of the adsorbed polymer.

DISCUSSION

The deuterium NMR spectrum of aliphatic C–D bonds is dominated by quadrupole interactions on the order of 167 kHz.[36] For a methyl group undergoing fast, continuous rotation about its symmetry axis, the quadrupole splitting is reduced to 1/3 of its static value. Random orientations of the methyl groups, with respect to the magnetic field, are re-
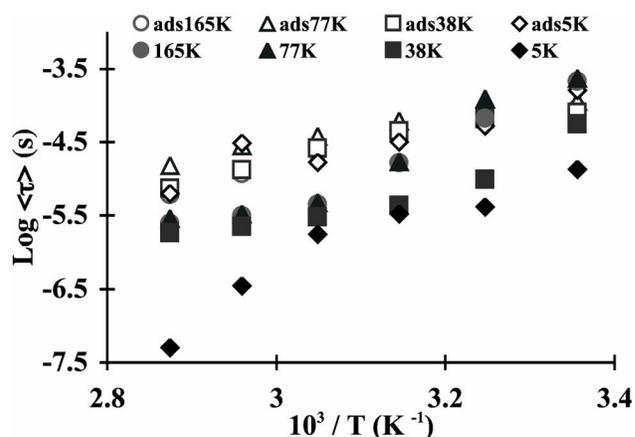
flected as a powder pattern in the ^{2}H NMR spectrum. Segmental mobility may average the quadrupole couplings and ultimately lead to the collapse of the powder pattern into a single resonance. This could occur, for example, for rubbery polymers when the motion is on the scale of, or faster than, the quadrupole interactions.

Segmental dynamics of surface-bound polymers are a function of the configuration of the polymer and the proximity of the segments to the surface. Randomly adsorbed polymers are believed to consist of segments in trains, tails, and loops on the surface.[37] In our case, trains, in direct contact with the silica surface through hydrogen bonding, are likely responsible for the broader (residual powder pattern) components in the spectra at higher temperature. Loops are the segments between trains, and tails are the ends of the polymer concluding with the first train segment. The appearance of a middle (motionally narrowed) component, in the NMR spectra for an adsorbed sample, is likely initially attributed to segments in tails and loops, located further away from the restrictions caused by the surface.

Segments in the bulk PMA samples of high molecular mass behaved in what we have previously referred to as a "homogeneous" manner, i.e., all of the segments in those samples exhibited more or less the same dynamics.[16,17] We
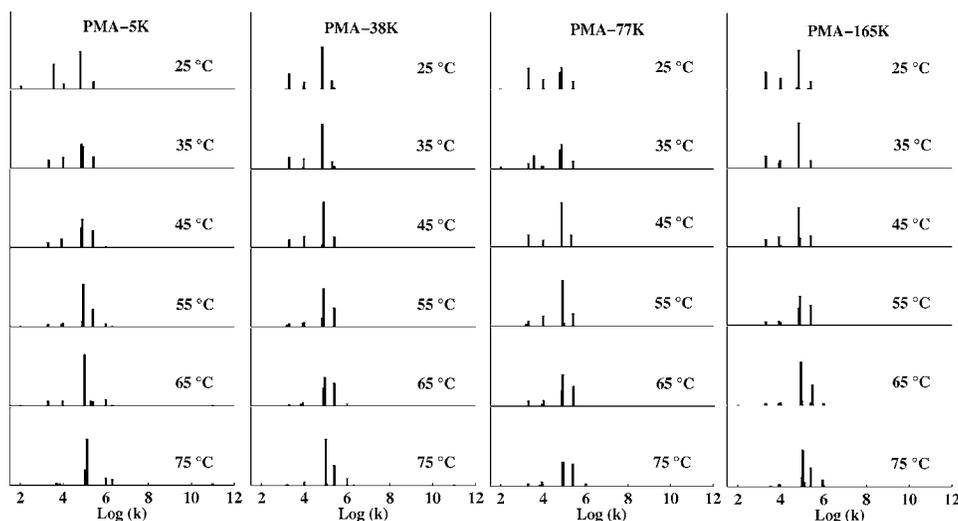

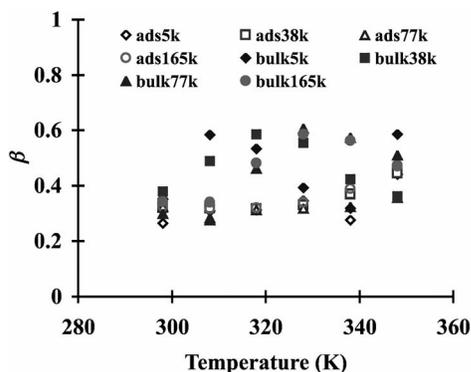FIG. 9. Distributions of jump rates used to simulate the NMR line shapes of the adsorbed samples.

FIG. 11. The change of β in Eq. (2) with temperature for bulk (filled) and adsorbed (open) PMA samples.

note that lower molecular-mass samples in bulk contain some "heterogeneities,"[31] due to a difference in mobilities between the chain middles and ends. The more-mobile chain ends were responsible for the appearance of a central component in the spectra, superimposed on a powder pattern due to the less-mobile chain middles. The mobility of the bulk polymers, on the whole, decreased with increased molecular mass with a leveling off around masses greater than about 50 kDa.

In contrast to the behavior of the bulk polymer, the NMR spectra of *all* the adsorbed samples showed the presence of at least two motionally distinct components and, consequently, some inherent "heterogeneity" of the segmental dynamics on the surface. We have previously characterized this heterogeneity as due to a motional gradient in the adsorbed polymer,[16] which occurred in samples with both high and low molecular masses in similar, but not identical, ways. The broadness and shallowness of the intensity loss curves (Fig. 8) for the adsorbed samples, as compared to those of the bulk ones,[31] were indications of a broader distribution of the segmental dynamics or more heterogeneity on the surface. This heterogeneity was also apparent in the distribution of jump rates (Fig. 9) and width parameters (β, Fig. 11) for the adsorbed samples. For the surface spectra, slow jump rate spectra were always required for a good fit to the experimental spectra. These slow components were not required at higher temperatures for the bulk-sample spectra.[31]

The heterogeneity in the surface-adsorbed PMA was also evident in the broader glass transition widths in the MDSC thermograms of the adsorbed samples. The heterogeneity of dynamics on the surface has been attributed to the presence of a motional gradient on the surface.[16,17] Segments closer to the surface were believed to be relatively immobile, while those at the polymer-air interface were more mobile. The fact that the segments at the air interface were more mobile was confirmed with NMR studies using an unlabeled polymer overlayer.[21] An intermediate mobility was attributed to the segments in between these two extremes. Recent MDSC experiments on PMMA adsorbed on silica showed that a separate "tightly bound" fraction could be identified and quantified.[38] A similar heterogeneity for much thicker polymer films has also been observed.[39]

The NMR line shapes and MDSC thermograms of the bulk and adsorbed PMA samples clearly indicated a more

highly restricted segmental mobility of the surface polymers. At high temperatures, the presence of a narrow single resonance for the bulk samples indicated rubberlike behavior. However, at similar temperatures for all of the silica-adsorbed PMA samples, a significant amount of residual powder pattern was present in addition to the narrow rubbery component. The residual powder pattern, associated with segments closely interacting with the surface,[21] is an indication of the surface-imposed restriction. In addition, the MDSC thermograms for all of the adsorbed samples showed higher T_g's than those for the bulk polymers, consistent with the restricted mobility on the surface.

The change of T_g with molecular mass in NMR and differential scanning calorimetry (DSC) experiments are summarized in Fig. 7 for the adsorbed samples. Both experiments indicated that the T_g's for the adsorbed PMA-77 K sample were the highest. The change in T_g with molecular mass was greater for the NMR data. In general, the NMR-T_g's were higher and NMR-T_g widths were broader than the DSC-T_g's. The differences were attributed to the difference in the frequencies of the experiments.[31]

For each PMA sample, the average correlation times were slower on the surface, confirming the net restricted mobility. At lower temperatures, there is little difference in the estimated correlation times with temperature because the experiment is not sensitive to the nature of the slower motions. The widths of the distributions of correlation times were consistent with the notion of the heterogeneity of the surface polymer due to the motional gradient present. It is most important to note that the most rigid sample on the silica surface was the PMA-77 K sample with the slowest correlation times.

The NMR and MDSC experiments clearly show the molecular-mass-dependent mobility on the silica surface for the adsorbed PMA samples. The sample with the lowest relative amount of mobile component was the adsorbed PMA-77 K sample as clearly shown in Fig. 5. The middle component was more intense in the adsorbed PMA-165 K sample spectrum than it was on the adsorbed PMA-77 K sample. This observation was consistent with previous work,[18] where a PMA-1100 K surface-adsorbed sample had a larger fraction of faster component than a PMA-70 K sample. Interestingly, while it is a small effect, the MDSC thermal transition for the adsorbed PMA-77 K sample had the highest temperature for the peak in the derivative curve in Fig. 6. The increase in surface T_g and the fraction of mobile component with molecular mass, above 77 000, is believed to be due to the longer tail and loop conformations on the surface.

For all samples, the adsorbed PMA samples were less mobile than in bulk. The adsorbed PMA-5 K sample had the highest mobility both in bulk and on the surface. The PMA-38 K sample followed suit, as did the PMA-77 K sample. However, there was a difference in effect for the PMA-165 K sample. This sample had a similar mobility to that of the PMA-77 K sample in bulk, but a *higher* mobility than that sample on the surface. To the best of our knowledge, this is the first time that this effect has been observed.

We believe that an interplay must exist on the surface between surface-imposed restrictions (adsorption strength,

conformational preference) and the dynamics of the polymer. It has been shown that the length of adsorbed polymer loops, in dilute solution, increases with increased molecular mass.[40] These longer loop configurations would be expected to be retained as the systems were dried. Longer loops should also have higher mobility and shorter loops, with segments closer to the silica surface, would be less mobile. On this basis, the mobility should increase with increasing molecular mass. In contrast, the inherent mobility of the end groups, and their decreased concentration with increasing molecular mass, causes the mobility to decrease with increasing molecular mass. These two competing (and opposite) effects seem to cross around the minimum mobility molecular mass.

It should be pointed out that the thicknesses of the adsorbed PMA used in this study are, on average, on the order of a few nanometers, although the uniformity of the adsorbed polymer's thickness is not currently known. In any case, the thickness of the adsorbed PMA is considerably thinner than those used in the other studies,[2–12,25,26] allowing us to study effects that would be masked in much thicker films. Adsorbed amount (or thickness) of polymer has been shown to be an important factor in determining the dynamics of PMA.[17] Clearly, differences in the adsorbed amounts could play a role in the differences in dynamics observed, however, the adsorbed amounts of the different molecular-mass polymers used in this study were quite similar and within a range where the spectral changes with adsorbed amounts were not large.[17] Previous studies showed that a molecular-mass effect, similar to the one reported here, also occurred at different adsorbed amounts,[18] although only two relatively polydisperse samples were studied. We, therefore, conclude that the major effect observed, minimum in molecular mobility at a particular molecular mass, is valid in the adsorbed amount range studied here and in other works.[17,18] Another important point is that the strongly adsorbing surface used in this study contrasts with the weakly adsorbing substrates used in some previous investigations.[3–10] Thus, a similar molecular-mass effect may or may not be observed on these weakly adsorbing surfaces, which, we believe, need to be studied in detail in the future.

CONCLUSIONS

Restricted segmental mobility, compared to bulk, was observed for all adsorbed samples in the glass-transition region. The presence of more-mobile and less-mobile components in the spectra resulted from the heterogeneity of the segmental mobility (motional gradient) of PMA on silica. The differences in the behavior directly due to molecular mass are less apparent for adsorbed PMA than bulk PMA, e.g., the spectra for the different molecular-mass adsorbed PMA samples at the same temperature look more alike than those for the bulk PMA. Nevertheless, there are also keen differences in the adsorbed PMA samples as a function of molecular mass.

The highest surface mobility was found for the lower molecular-mass sample (PMA-5 K), in spite of a significant increase in the T_g's for the adsorbed sample compared to the bulk samples. The PMA-77 K exhibited the lowest mobility

on the surface. At molecular masses higher than 77 000, the segments of those samples were less motionally restricted on the surface than those of the lower molecular-mass ones. In the regime studied, the average thicknesses of the adsorbed polymer samples were on the order of the radius of gyration of the polymer coils. Clearly, this molecular-mass effect is due to the interplay of many factors including adsorbed amount (thickness), chain-end mobility, loop length, and configuration of the adsorbed polymer. Further study to clarify these inter-relationships is warranted.

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