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Segmental Dynamics of Bulk and Silica-Adsorbed Poly(methyl acrylate)-d_3 by Deuterium NMR: the Effect of Molecular Weight

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ABSTRACT: Deuterium solid-state quadrupole-echo NMR was used to study the effect of molecular weight on the segmental dynamics of bulk and adsorbed poly(methyl acrylate)-d_3 (PMA-d_3). It was found that the bulk PMA-d_3 with lower molecular weight was more mobile and more heterogeneous in motion than the high molecular weight species. Surface samples with coverages up to saturation coverage in toluene, adsorption maximum in toluene (A_m), were prepared by adsorption of PMA-d_3 with two different molecular weights onto silica from different solvent systems. After drying, the spectra were collected from the surface species at the solid−air interface. For the adsorbed polymers, the low molecular weight PMA-d_3 segments on silica were more rigid than those of the high molecular weight PMA-d_3. For both molecular weights, the surface polymers exhibited a wider range of mobilities than the bulk polymers.

Introduction

Many applications of polymers involve their use in multiple phases, such as composites, reinforced rubbers, and adhesives. In those applications, solid phases, such as glass fibers, inorganic fillers, or other substrates, are involved in the system. Consequently, the interaction of the polymer and the other phase plays an important role in the physical properties of the system.

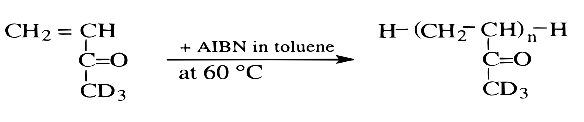
The properties of polymers at interfaces have been reviewed.[1−4] Most of the studies have dealt with aspects of the surface structure. A number of techniques have been used to study the structure of polymers at interfaces, such as nuclear magnetic resonance (NMR),[4−7] electron spin resonance,[8] small-angle neutron scattering,[9] X-ray and neutron reflectometry,[10] ellipsometry,[11] and force−distance measurements.[12] Most of these focused on the properties of polymers at solid−liquid interfaces and were concerned mainly with the thickness of the adsorbed layer, density profile, or estimation of the fraction of segments in trains, loops, and tails. Direct measurements of the dynamics of polymers at surfaces (e.g., molecular motion) have not received much attention,[4] although there are a few papers which are related (to some extent) to the mobility of adsorbed polymer molecules.[9,10,13−15]

There are many important factors in determining the physical properties of adsorbed polymers. The molecular weight of the polymer is one of them. The Scheutjens−Fleer model,[16] using mean-field theory, predicts that the fraction of the trains (segments closely associated with the surface) decreases with increasing molecular weight. De Gennes modeled the adsorption of homopolymers on surfaces deposited from good solvents using scaling theory.[17] Three different regimes, i.e., dilute, semidilute, and plateau regions, were considered. In the plateau region, the surface was fully covered and scaling theory predicted that the thickness of the adsorbed layer was proportional to the chain length. Thus, the longer the chain length, the higher the fraction of segments in loops and tails. Since molecular weight plays an important role in the structure of adsorbed polymers, the dynamics should be affected by this as well.

In our previous study of high molecular weight PMA-d_3,[13] we showed that a silica surface had a restrictive effect on many of the segments of the adsorbed polymer, although a small fraction of the segments had increased mobility. Mobility appeared to be distributed in the adsorbed layer—mobility decreased as coverage decreased. It seemed important to extend that study to a lower molecular weight polymer. In this paper, we report the study of the dynamics of two different molecular weight samples of PMA-d_3 on a silica surface. The effect of molecular weight on dynamics was the main concern when surface samples with different molecular weights were compared. This was done by using both low and high molecular weight PMA-d_3 samples. The deuterium NMR line-shape method[18] was used to analyze the spectra, using the deuterated methyl group serving as a reporter group.

Experimental Section

Methyl acrylate-d_3 monomer was synthesized with methanol-d_4 and acryloyl chloride as starting materials. The level of deuteration of the monomer was found by proton NMR to be about 100%. The details of the monomer synthesis and high molecular weight (HMw) PMA-d_3, made from emulsion polymerization, can be found elsewhere.[13] The HMw PMA-d_3 had a M_w of 1.10×10^6 and a polydispersity of 2.20. A low molecular weight (LMw) poly(methyl acrylate)-d_3 was prepared from methyl acrylate-d_3 via free-radical polymerization. The polymerization was conducted by adding 50 mL of toluene and 10 mL of monomer to 0.03 g of 2,2′-azobis(isobutyronitrile) (AIBN) as the initiator and heating at 60 °C for 2 h. The yield of the polymer was 80%, based on the amount of monomer used. The reaction scheme is as follows:



$$\mathrm{CH_2{=}CH{-}C({=}O){-}Cl} + \mathrm{CD_3OD} \xrightarrow{\text{at } 0\ ^\circ\mathrm{C}} \mathrm{CH_2{=}CH{-}C({=}O){-}CD_3} + \mathrm{DCl}$$

$$\mathrm{CH_2{=}CH{-}C({=}O){-}CD_3} \xrightarrow[\text{at } 60\ ^\circ\mathrm{C}]{\text{+ AIBN in toluene}} \mathrm{H{-}(CH_2{-}CH(C({=}O)CD_3))_n{-}H}$$

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The LMw PMA-d_3 had a M_w of 7.05×10^4 and a polydispersity of 2.50 as measured by gel permeation chromatography (GPC) in tetrahydrofuran (THF). A protonated PMA was also made for isotherm experiments by the above procedure. It had a M_w of 7.14×10^4 and a polydispersity of 2.52. The data were reported with respect to polystyrene standards, and no universal calibration correction was made.

All of the surface samples were made by adsorption of PMA-d_3 onto silica, Cab-O-Sil M5 fumed silica (Cabot Corp., Tuscola, IL), with a surface area of 200 m^2/g. The adsorption isotherms were measured by determining the amount of polymer in solution after adsorption.[13] LMw surface samples, with different coverages on silica, were prepared with an equilibrium concentration of 11 mg/mL where the adsorption was in the plateau region. Different coverages were obtained using mixed-solvent systems of different compositions. The samples with different surface coverages were washed and dried under vacuum at 70 °C overnight. The HMw surface samples were prepared following the same procedure, using the HMw PMA-d_3.

The NMR spectra were obtained on a Varian VXR-400/S spectrometer equipped with a wide-line probe (Doty Scientific, Columbia, SC), a high-power amplifier, and a fast digitizer. The ^{2}H resonance frequency was 61.395 MHz. The quadrupole-echo pulse sequence was used (delay$-90°_x-\tau-90°_y-\tau-$acquisition). The 90° pulse width was 2.7 μs, and $t = 30$ ms. The Fourier transformation was started at the top of the echo. The number of scans ranged from 3000 to 100 000, depending upon the coverage. 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. All of the spectra shown in this paper were processed with Felix (Biosym, San Diego, CA). There was no line broadening applied to the spectra.

The spectra of HMw PMA-d_3 were simulated as previously described.[13] Spectra collected at different t values were exponentially extrapolated to $t = 0$ point by point. These spectra were then simulated using a computer program written by Schneider and Freed[19] and adapted by us for ^{2}H NMR.[20] The model simulates the spectra by solving the stochastic Liouville equation for rotational motions, including those in the intermediate regime. The simulations predicted the change in line shape of a Pake powder pattern due the reorientation of the methyl group. For the methyl deuterons with nearly axially symmetric electric field gradients, the line shape was dominated by the quadrupole coupling, $\Delta\nu_q$, between the two different allowed transitions given by[21]

$$\Delta\nu_q = (3/4)(e^2qQ/h)(3\cos^2\theta(t) - 1) \qquad (1)$$

where e^2qQ/h is the quadrupole coupling constant, t is time, and θ is the angle between the principal axis of the electric field gradient tensor and the applied static magnetic field, $\mathbf{B}_0$. The rapid methyl group rotation about its symmetry axis allows the time average (represented by $\langle\,\rangle$) of the $3\cos^2\theta(t) - 1$ term to be further decomposed into

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

where $\beta(t)$ is the angle between $\mathbf{B}_0$ and the symmetry axis and χ is the angle between the rotation (symmetry) axis and the C$-$D bond. Since χ is 70.5° for a methyl deuteron, the $3\cos^2\chi - 1$ term is reduced and the quadrupolar splitting is reduced to $^1/_3$ of its original value. Values for the quadrupole coupling constants (QCC) of methyl groups are typically on the order of 150$-$170 kHz.[22] Accordingly, the simulations were based on a residual QCC of 50 kHz corresponding to a splitting between the two horns of 37.5 kHz. A combination of two simultaneous motions at widely different rates was required to simulate the HMw PMA-d_3 spectra: continuous diffusion and discrete jumps.

The spectra from the surface or LMw polymer were often observed to be the superposition of different components. Extrapolations of these spectra to $t = 0$ were not done due to time limitations, and those spectra were simulated by the addition of the appropriate amounts of different HMw spectra taken at the same echo time ($t = 30$ ms). Thus, the set of spectra taken for the HMw species (for which the motional rates were determined) formed the basis set used to fit the LMw and surface spectra. The precision in the amounts of the required components was typically on the order of ±2% for each amount.

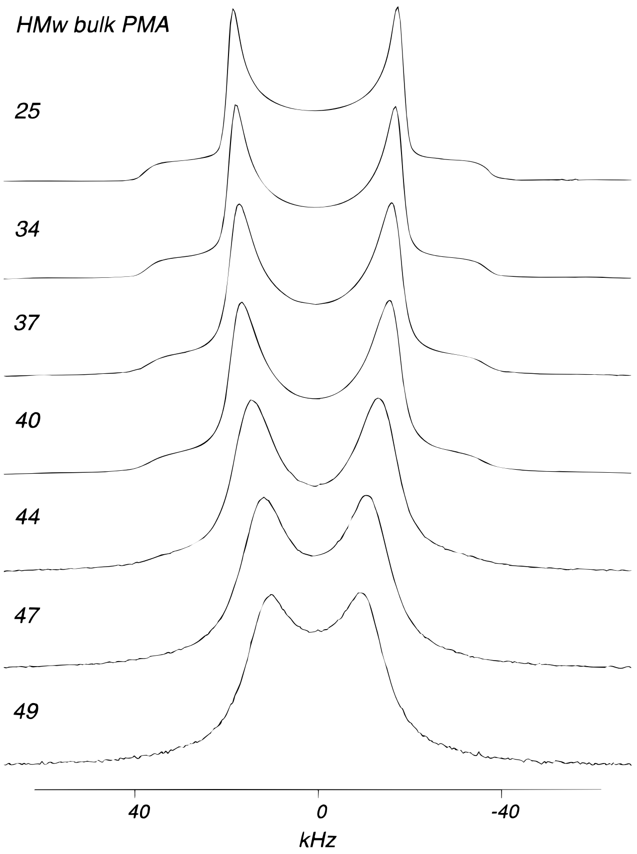

Figure 1. Experimental ^{2}H NMR spectra of the HMw bulk PMA-d_3 sample at 25$-$49 °C.

Results and Discussion

Bulk Deuterium NMR Spectra. The HMw and LMw PMA-d_3 spectra for the bulk polymers are shown in Figures 1$-$3. A larger number of spectra were collected for the HMw bulk sample as these were used as the basis for the spectral simulations for the LMw surface samples. Both the HMw and LMw bulk samples showed Pake patterns at 25 °C. Both had a reduced splitting of about 37.5 kHz between the two horns, corresponding to a reduced QCC of 50 kHz. The splitting for these patterns was reduced from the static value by the fast rotational motion of the methyl group. With increasing temperature, the features of the HMw bulk spectra (Figure 1 and 2) went from a rigid Pake pattern at 25 °C (with some broadening and reduction in splitting due to the fast methyl motion), through a hump-shaped feature at 52 °C, to a relatively narrow resonance at 69 °C. The changes in the line shapes demonstrated that there were changes in the motional rates at different temperatures. Some of these HMw spectra were previously simulated through extrapolation to $\tau = 0$, based on a single-component line shape, although the motion was clearly complex.[13]

The simulation of the HMw spectra with the Freed model was possible only by using the two different simultaneous modes incorporated within the model

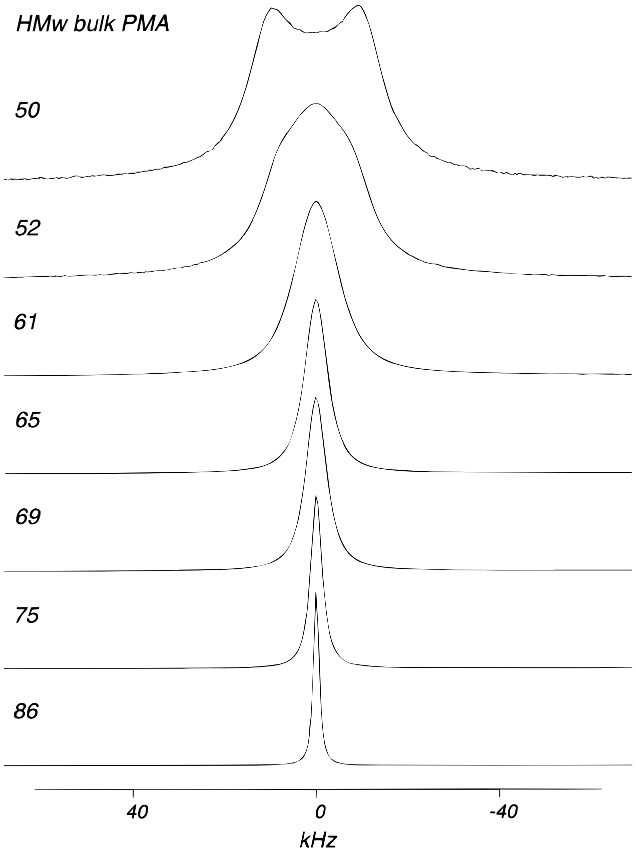

Figure 2. Experimental ^{2}H NMR spectra of the HMw bulk PMA-d_3 sample at 50−86 °C.

(continuous diffusion and jumps) at two widely different rates. The two rates are representative of, say, a distribution of correlation times.[23] More detailed simulations of the motion have been done for 1-dimensional (1-D) spectra,[24,25] for example, those taking the decay of the magnetization with t into account. For this work, it seemed sufficient to characterize the spectra with the Freed model, reserving the accurate determination of the distribution of correlation times for 2-dimensional (2-D) NMR studies.[26] In any case, it is important to note that the spectra for the HMw bulk polymer are consistent with the spectra that can be simulated with one set of motional parameters. Indeed, the spectra themselves all appear to consist of one component. We conclude from this that the segmental dynamics are *homogeneous*; i.e., all of the segments have the same kind of molecular motion on the time scale of the 1-dimensional ^{2}H spectra.

For the LMw bulk sample, a superposition of different components (Figure 3) was found at all temperatures except at 25 °C and below (not shown). This is in contrast to the findings for the HMw bulk sample. At 37 and 40 °C, a narrow component was superimposed on a two-horn Pake pattern in each LMw bulk spectrum. At 44 and 47 °C, the narrow component was superimposed on a hump-shaped feature. At 52 and 69 °C, the line shape consisted of a relatively narrow resonance. The width of the 69 °C spectrum for the LMw bulk sample was narrower than that of the HMw bulk sample. In general, the LMw bulk spectra had a higher fraction of the narrow component in the spectra and narrower features at higher temperatures. The superposition features of the LMw bulk spectra indicated *inhomogeneity* in the mobility of that sample.

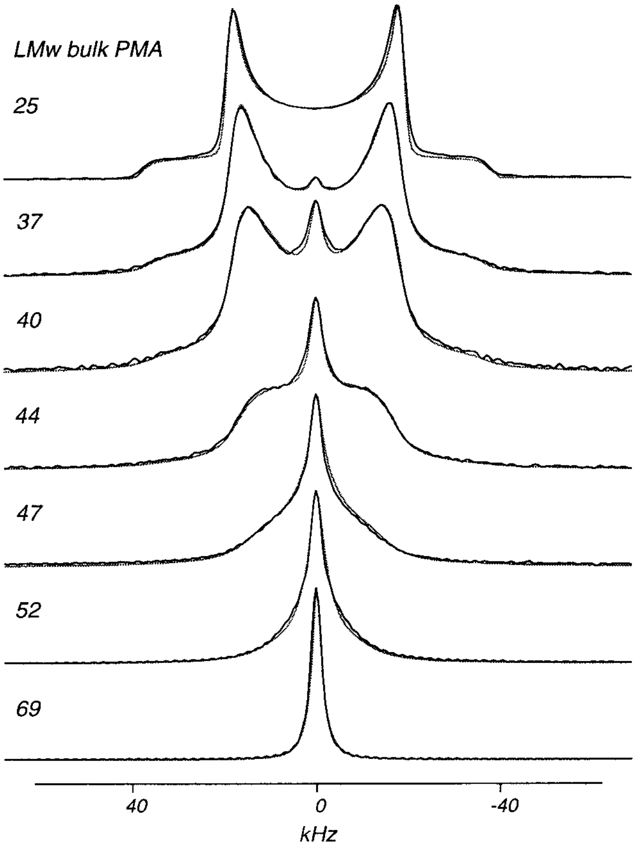

Figure 3. Experimental (solid line) and simulated (dotted) ^{2}H NMR spectra of the LMw bulk PMA-d_3 sample at 25−69 °C.

It is worthwhile to compare the LMw bulk spectra with the HMw bulk spectra at the same temperatures to demonstrate the effect of molecular weight on the dynamics of bulk PMA-d_3. At 37 and 40 °C, the LMw bulk spectra exhibited a small narrow component superimposed on the powder pattern, not found in the HMw bulk spectra. The LMw bulk spectra at 44 and 47 °C had a narrow component superimposed on a hump-shaped feature, while the HMw bulk spectra showed only a broadened Pake pattern. At 52 and 69 °C, the LMw bulk spectra were narrower than the HMw bulk spectra. All of these observations were consistent with the single-component HMw bulk sample having a lower mobility than the multicomponent LMw bulk sample.

The difference in line shape between the HMw and LMw bulk spectra was presumably due to the chain end effect of the polymers. Chain ends would be expected to have a higher mobility[27] than the other parts of the molecule. Since the LMw bulk sample had many more chain ends, the inhomogeneity in the motional rate of the sample resulted in a composite line shape. Also, the chain ends may have caused the other segments of the LMw bulk sample to be more mobile than the HMw bulk sample. Both possibly contributed to the inhomogeneous line shape. We also note that the broader component in the LMw spectra at 37 °C, and higher, was narrower than those for the HMw species at the same temperatures. Thus, neither component in the LMw spectra was the same as that for the HMw species at the same temperature.

The effect of the inhomogeneity of the line shape is also demonstrated in Figures 4 and 5, where the

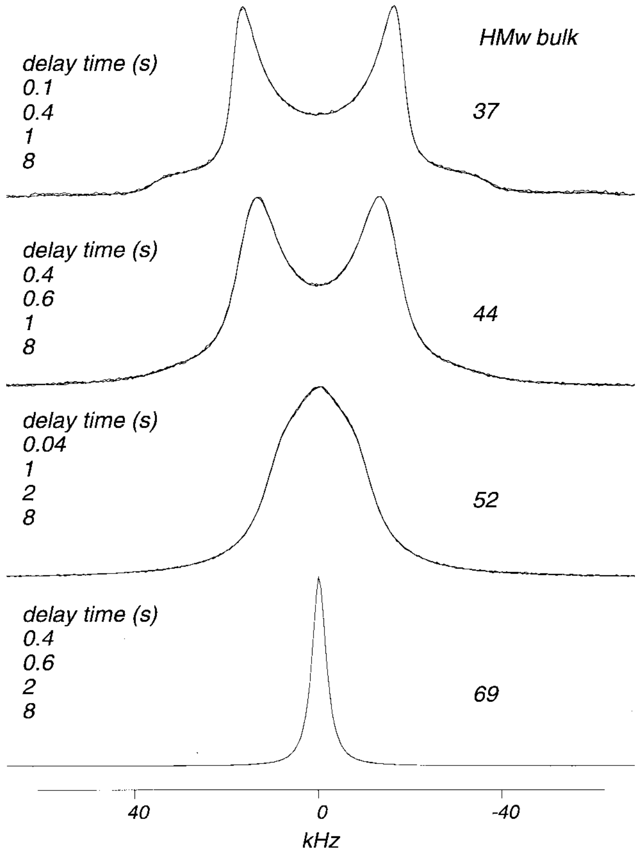

Figure 4. Dependence of the experimental ^{2}H NMR spectra of the HMw bulk PMA-d_3 sample at various temperatures (°C) on the relaxation delay. (The spectra for each delay are virtually indistinguishable for each set.)

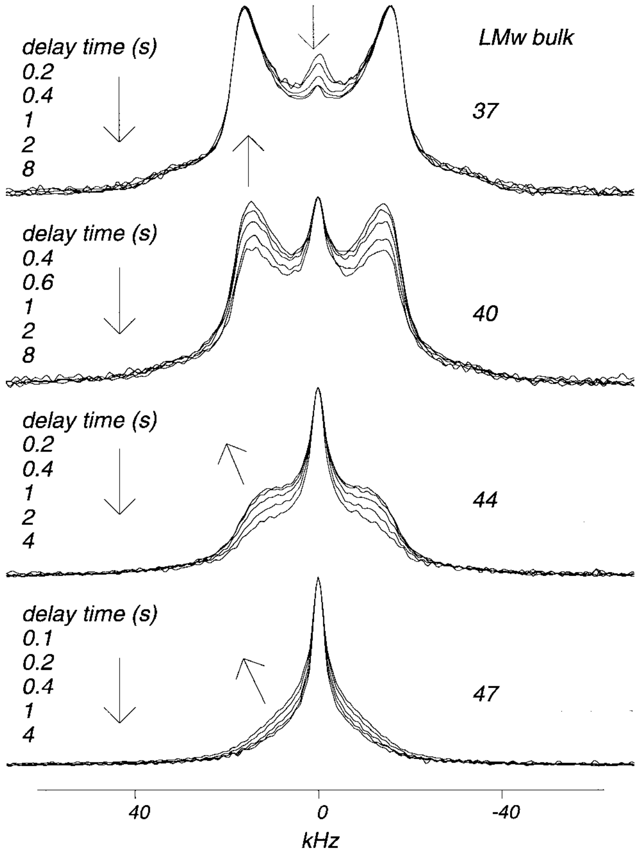

Figure 5. Dependence of the experimental ^{2}H NMR spectra of the LMw bulk PMA-d_3 sample at various temperatures (°C) on the relaxation delay. The arrows indicate the order of the spectra relative to increasing the delay time.

relaxation delay between each scan in the pulse sequence varied. The HMw bulk sample (Figure 4) showed no difference in the line shape at any temperature with a changing relaxation delay in the NMR quadrupole-echo sequence. This was indicative of the *homogeneous* relaxation (T_1) behavior of the line shape. In contrast, the LMw bulk sample (Figure 5) showed a relative enhancement of the narrow component in the center of the Pake pattern at all temperatures with decreasing delay time. The effect of the delay time on the line shape was due to the different T_1 values caused by the different motional rates of the different components. In general, under extreme narrowing conditions, T_1 decreases as the motional rate decreases. Eventually, the T_1 value reaches a minimum and increases as the motional rate decreases. The T_1 minimum occurs roughly when the motional rate is in the vicinity of the Larmor frequency. In our previous study[13] of HMw bulk PMA-d_3, we found that the motional rates below 86 °C (excluding the methyl rotation) were always slower than the Larmor frequency of 61 MHz. Consistent with this effect, the narrow component in Figure 5 had a shorter T_1 corresponding to a higher motional rate. Thus, the narrow component relaxed faster. As a result, the fraction of the narrow component in each of the LMw bulk spectra became relatively more intense as the delay time in the NMR sequence decreased. Again, the results clearly showed a significant molecular weight effect on line shape and mobility.

It was found that the LMw bulk spectra could be modeled with a superposition of HMw bulk components. The amounts of each of the HMw components used to simulate each LMw spectrum are shown in Table 1, and the simulations are shown as dashed spectra in Figure 3. The simulations were consistent with a segmental motional *inhomogeneity* in the LMw bulk sample; i.e., different segments moved differently. We were not able to simulate the line shapes for the LMw surface sample above 25 °C, using the Freed simulation program,[20] without adding more than one independent component together. In effect, to get good fits, at least three components were required, and many different components were needed to span the range of the LMw samples. As shown in the table, the distribution moved to higher temperature (more mobile) components as the temperature increased. Once again, we remind the reader that the number of components used in the simulation is simply a guide to characterize the complexity of the spectra and range of motional components.

Table 1. Simulation Parameters for the LMw PMA-d_3 Bulk Spectra[a]

		LMw spectrum temperature						
isotropic diffusion/ discrete jump (Hz)[b]	HMw temp[c], °C	25 °C	37 °C	40 °C	44 °C	47 °C	52 °C	69 °C
$2.0 \times 10^1/9.0 \times 10^3$	25	100						
$5.0 \times 10^2/2.8 \times 10^4$	40		90					
$1.0 \times 10^3/4.5 \times 10^4$	44			82	48	27		
$2.5 \times 10^3/1.5 \times 10^5$	52		9.5	17	49			
$1.0 \times 10^4/1.6 \times 10^5$	56					67	88	
$8.5 \times 10^4/9.5 \times 10^5$	75		0.5	1	3	6	12	100

[a] Percent of given component. [b] Rates from the Freed simulation model. [c] Temperature of the HMw spectrum used for the simulation.

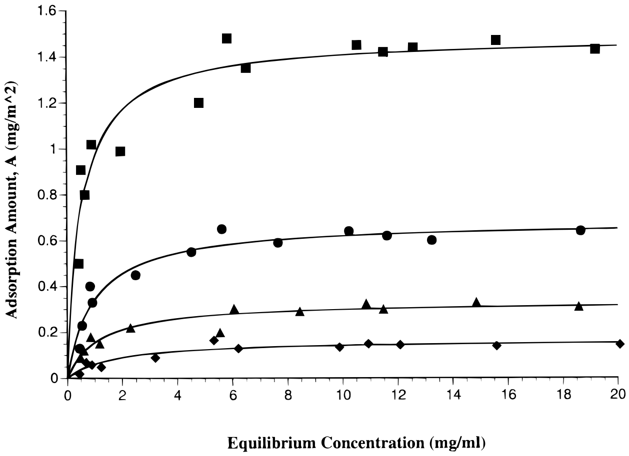

Figure 6. Adsorption isotherms for LMw PMA in toluene (■) and benzene/acetonitrile (v/v) mixtures: 8.1/1.9 (●); 7.5/2.5 (▲); 5.5/4.5 (◆).

Table 2. Surface Coverages and Thicknesses for HMw and LMw PMA on Silica

	equivalent amount	$1.0A_m$	$0.4A_m$	$0.2A_m$	$0.1A_m$
HMw	coverage[a]	2.61	1.05	0.47	0.23
	thickness[b]	2.14	0.86	0.39	0.19
LMw	coverage[a]	1.45	0.64	0.31	0.15
	thickness[b]	1.18	0.52	0.25	0.12

[a] Milligrams of polymer per square meter of silica. [b] In nanometers. Based the assumptions that the density of the surface polymer was the same as that of the bulk polymer and that the coverage was uniform and complete.

Table 3. Molecular Weight Distribution in the Liquid Phase after LMw Samples Adsorption

	bulk	$1.0A_m$	$0.4A_m$	$0.2A_m$	$0.1A_m$
M_w (g/mol)	76 000	76 000	75 000	78 000	75 500
polydispersity	2.49	2.50	2.52	2.53	2.48

The true distribution responsible for the spectra is probably broad and continuous.

Adsorption Isotherms. Adsorption isotherms for the hydrogenated LMw PMA for various solvent mixtures are shown in Figure 6. It was found that amounts of less than saturation coverage of a single solvent (toluene) were more accurately adsorbed from the solvent mixtures (acetonitrile/benzene) than from lower concentrations of a single solvent.[16] The saturation coverages for each LMw surface sample are shown in Table 2 along with the data on the high molecular weight samples from our previous study.[13] The reference values of $1.0A_m$ coverage for the LMw and HMw samples, the maximum adsorbed amount in toluene, were determined to be 1.45 and 2.61 mg/m^2, respectively. The other LMw and HMw surface samples were referred to relative to these.

The molecular weight distribution of the polymer in the supernatant liquids with concentrations of 11 mg/mL was measured by GPC for each coverage and compared to that of the original solution. The concentrations of 11 mg/mL for the proper coverage for this study were determined based on the adsorption isotherms. As seen in Table 3, the molecular weights and polydispersities of the original sample and supernatant liquids were virtually the same. In fact, the distributions themselves (not shown) were essentially the same. In these experiments, the fractions of the polymer left in the supernatant liquids with the equilibrium concentration of 11 mg/mL were calculated to be from 86 to 35%, depending upon the solvent used. Thus, any preferential adsorption should have been observed if it occurred. Accordingly, we believe that little or perhaps no preferential adsorption occurred. Since high molecular weight homopolymers are known to preferentially adsorb, we conclude that the system is probably not at true equilibrium. This situation may be expected in the case of a strong adsorption at the interface.[13]

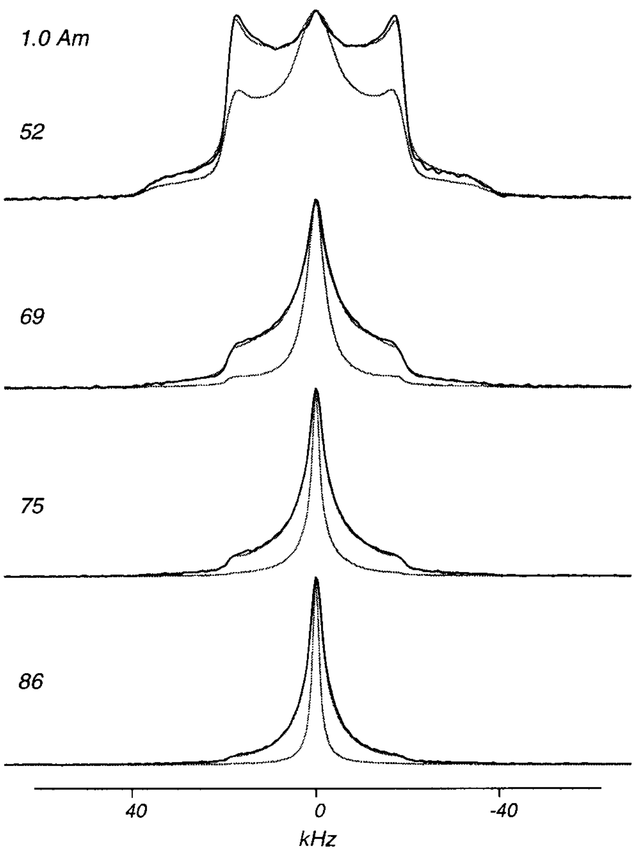

Figure 7. Experimental (solid curve) and simulated (dashed) ^{2}H NMR spectra for the $1.0A_m$ LMw surface samples. Also shown, for comparison, are the corresponding HMw (inner dotted) surface spectra.

Surface PMA-d_3. ^{2}H NMR spectra for the LMw surface samples are shown in Figures 7–10, with experimental spectra as solid curves and simulated spectra as the dashed curves which were good fits to the experimental ones. Also shown, for comparison, are the corresponding HMw surface spectra (inner dotted curves) at the same temperatures. At 52, 69, 75, and 86 °C, the LMw surface spectra consisted of composite line shapes whose components could be simulated by a superposition of the HMw bulk spectra components. It was also observed that the lower the coverage, the broader the central component and the larger the amount of rigid component required. In general, the results showed that the lower the coverage, the lower the mobility of the adsorbed polymers. The effect of coverage on the line shape of the LMw surface samples was qualitatively similar to that for the HMw surface samples.[13]

The simulation results for the LMw surface samples are shown in Figures 7–10 as dotted curves, and the amounts of the components required are given in Table 4. The simulated spectra fit the experimental ones very well. We attempted to fit the spectra with a minimum number of components, although we recognize that

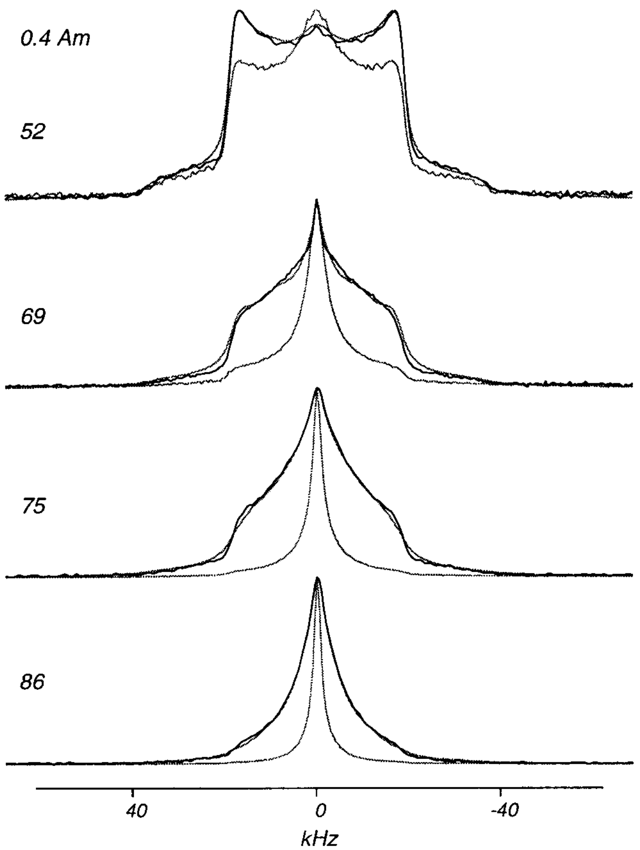

Figure 8. Experimental (solid curve) and simulated (dashed) ^{2}H NMR spectra for the 0.4A_m LMw surface samples. Also shown, for comparison, are the corresponding HMw (inner dotted) surface spectra.

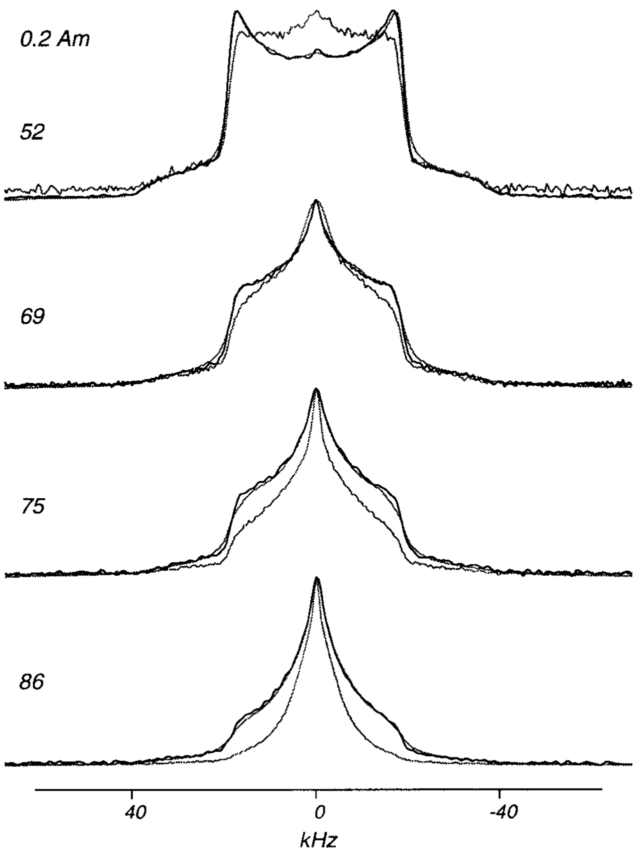

Figure 9. Experimental (solid curve) and simulated (dashed) ^{2}H NMR spectra for the 0.2A_m LMw surface samples. Also shown, for comparison, are the corresponding HMw (inner dotted) surface spectra.

there likely was a continuous distribution of mobilities. Nevertheless, fitting based on a small number of discrete components will allow a comparison of the amounts and rates for representative classes of motional species. All of the LMw surface samples required a minimum of three components, which could be considered as rigid, intermediate, and mobile on the deuterium NMR time scale. The motional rates of the components (and hence spectral components) were chosen so as to correspond to those for the HMw bulk PMA-d_3 spectra.[13] To calculate the relative amounts of each component, the intensity factor from our previous study[13] was taken into account. This factor relates to the dephasing that occurred during the quadrupole-echo sequence. From the data in Table 4, it was observed that the composition of the spectra drifted from rigid to mobile components as the temperature or the coverage increased.

It was important to determine if the effect of molecular weight on the dynamics of the bulk PMA-d_3 was the same as that for the adsorbed PMA-d_3. First, each LMw surface spectrum was compared with the corresponding HMw surface spectrum having equivalent surface coverage. As shown in Figures 7−10 for 52, 69, 75, and 86 °C, there was always a higher fraction of the rigid component in each LMw surface spectrum than in the corresponding HMw surface spectrum. In other words, on a relative basis, there was always a smaller fraction of the narrow component superposed on each LMw surface spectrum.

A comparison of the simulation results (or, qualitatively, of the spectra themselves) for the LMw (Table 4) and HMw[13] surface spectra is in order. When compared at similar fractions of the adsorbed amount in toluene (A_m), the LMw surface segments were more rigid than their corresponding HMw surface segments. If a comparison is to be made at similar adsorbed amounts (mg/m^2), one should compare the spectra of 1.0-, 0.4-, and 0.2A_m LMw with 0.4-, 0.2-, and 0.1A_m HMw, respectively. Even though each LMw sample had a slightly larger adsorbed amount, the LMw samples still had lower mobility segments. This mobility difference is the opposite of that found for bulk PMA-d_3.

Table 4. Motional Rate Distributions (%) for LMw Surface Samples at Different Temperatures Based on Various Components

temp (°C)	component[a]	1.0A_m	0.4A_m	0.2A_m	0.1A_m
52	rigid	51	48	51	52
	intermediate	46	50	49	48
	mobile-1	3	2		
69	rigid	21	24	28	31
	intermediate	66	71	68	66
	mobile-1		5	4	3
	mobile-2	13			
75	rigid	14	20	23	28
	intermediate	55	71	70	67
	mobile-1		9	7	5
	mobile-2	31			
86	rigid	11	16	20	27
	intermediate	39	61	65	67
	mobile-1		23	15	6
	mobile-2	50			

[a] Motional rates for each component are given in Table 5.

Polymer segments that are closer to the silica surface are expected to have lower mobility due to the restric-

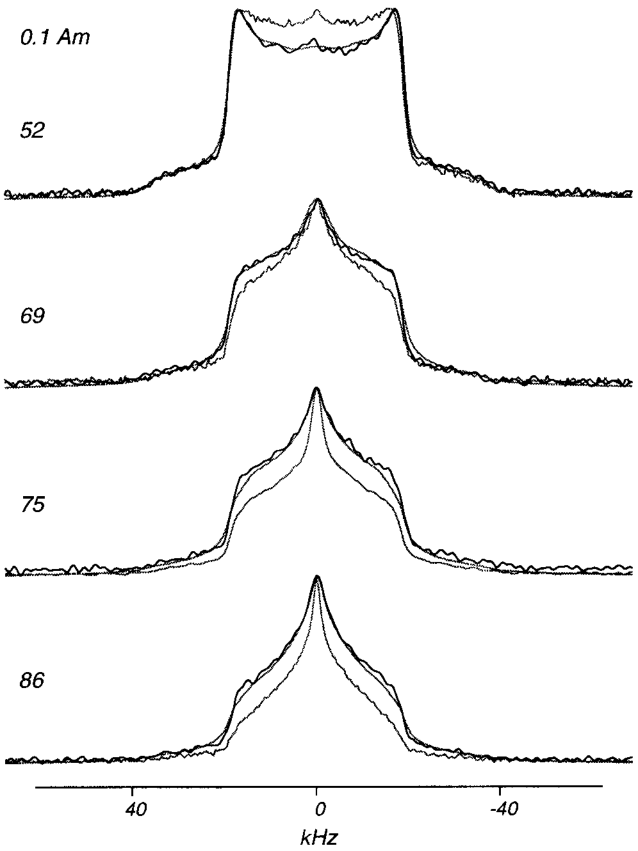

Figure 10. Experimental (solid curve) and simulated (dashed) ^{2}H NMR spectra for the 0.1A_m LMw surface samples. Also shown, for comparison, are the corresponding HMw (inner dotted) surface spectra.

Table 5. Motional Rates of Components Used to Simulate HMw and LMw Surface Spectra

component	isotropic diffusion rate (Hz)	jump rate (Hz)	HMw sample[a] (°C)
rigid	500	2.8×10^4	40
intermediate	2.5×10^3	1.5×10^5	52
mobile-1	2.0×10^4	3.8×10^5	65
mobile-2	3.5×10^4	5.0×105	69

[a] Temperatures at which the motional rates listed match the bulk spectrum.

tion in motion caused by the surface. Accordingly, it is proposed that the configuration of the adsorbed PMA-d_3 with lower molecular weight was flatter than that of PMA-d_3 with higher molecular weight.

Assuming that the adsorbed layers were continuous films with a homogeneous density of 1.22×10^9 mg/m^3, the thickness of the adsorbed layers in the surface samples could be estimated and are shown in Table 2. These thicknesses seem to be quite thin, especially for the low adsorbed amount samples. If they are representative, the polymers must have adapted relatively flat configurations upon adsorption. These configurations would be consistent with the NMR results, in that the lower molecular weight chains had lower mobility on the surface due to their strong interaction with the substrate.

Conclusions

The low molecular weight (LMw) bulk PMA-d_3 yielded spectra which consisted of more than one component. This was evident from the spectra themselves, their simulations, and their behavior under different recycling delays. In contrast, this was not the case for the HMw bulk sample where a single component was found under all conditions tested. The bulk LMw PMA-d_3 had a higher mobility than the bulk HMw PMA-d_3. We concluded that the inhomogeneity for the LMw sample was due to the much larger concentration chain ends in that polymer.

In general, the surface restricted the mobility of the adsorbed polymers. The mobility of the adsorbed PMA-d_3 segments decreased as the surface coverage decreased. The adsorbed polymers exhibited a heterogeneity in mobilities, probably due to different segments at different distances from the silica surface moving at different rates.

The adsorbed LMw PMA-d_3 segments were more restricted, i.e., had lower mobility, than the adsorbed HMw segments. It was proposed that the configurations of the adsorbed LMw PMA-d_3 polymers were flatter than those of the adsorbed HMw PMA-d_3.

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References and Notes

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(23) We recognize that while it appears that all segments undergo similar motions from the standpoint of a 1-D spectrum, it may not be so. 2-D exchange and related experiments are needed to confirm this point. We expect the motion of the HMw PMA-d_3 to be described by a broad distribution of correlation times. However, the 1-D ^{2}H spectrum can be successfully simulated by assuming that the polymer seg-

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