Segmental Dynamics of Bulk and Adsorbed Poly(methyl acrylate)-d_3 by Deuterium NMR: Effect of Adsorbed Amount

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ABSTRACT: Deuterium solid-state quadrupole-echo NMR techniques were used to probe the dynamics of bulk and silica-adsorbed methyl-labeled poly(methyl acrylate)-d_3 (PMA-d_3). For bulk PMA-d_3, collapse of the ^{2}H NMR powder pattern indicated a sudden increase in segmental motion at about 50 °C. This temperature was 40 °C above the reported glass transition temperature (T_g) of bulk PMA and was due to the higher frequencies to which the "NMR" T_g was sensitive. Surface samples with different adsorbed amounts exhibited different behavior at the silica−polymer−air interface and consisted of superpositions from different components. At lower temperatures, a mobile component not found in the bulk PMA-d_3 was observed while, at higher temperatures, a rigid component still existed. The mobile component was attributed to polymer segments near the polymer−air interface and the rigid component to segments nearer to the polymer−silica interface. As the adsorbed amount increased, the relative amounts of mobile components increased. The results were consistent with an interface graded in mobility with a broad distribution in the adsorbed layer. The mobilities were generally reduced at lower adsorbed amounts.

Introduction

Interfacial phenomena are important in determining the properties of materials involving multiple phases. For example, the mechanical properties of composite materials are not simply the superpositions of the properties of the individual components. The properties of the interfacial layer must be considered in order to understand the mechanical properties of composite materials. However, these are not easily estimated from mechanical property measurements. Interfacial phenomena are also important in a variety of applications such as polymeric stabilization of colloidal dispersions, adhesion, and chromatography.

There has been good progress in understanding the structure of polymers at interfaces,[1,2] and a variety of techniques have been used. Nuclear magnetic resonance,[3−6] electron spin resonance,[7−9] infrared spectroscopy,[10−11] microcalorimetry,[12] and surface-enhanced Raman scattering[13−15] have been used to detect physical or chemical changes in adsorbed molecules. Other techniques probe the thickness or density profiles of the adsorbed layer, such as small angle neutron scattering,[16] X-ray and neutron reflectometry,[17,18] photon correlation spectroscopy,[19] ellipsometry,[20−22] and force−distance measurements.[23−25] However, the information on interfacial properties usually given by these techniques is still incomplete, especially with respect to the dynamics of adsorbed polymers.

The dynamics of adsorbed polymers may be probed or inferred from experiments on a variety of different length scales. For example, X-ray reflectometry[26,27] or ellipsometry[28] probes the behavior of the polymer through its entire thickness. Expansion of the films with temperature can then be related to the glass transition. Even at thicknesses less than the unperturbed radius of the polymer coil, the measurements represent an averaging over the behavior of different segments. Fluorescence recovery[29] has been used on thin films to probe the diffusion of chains. The translational motion of entire chains appeared to be retarded with decreasing film thicknesses. In contrast, NMR[2] or ESR[9] have been used to probe local segmental motions and differences from different parts of the same chain can be probed.

Recently, Blum et al.[30] used deuterium quadrupole-echo techniques on poly(vinyl acetate)-d_3 (PVAc) adsorbed on silica. The deuterated methyl group was used to demonstrate that a distribution of segmental mobilities existed in a single adsorbed layer with at maximum adsorbed amount from toluene. A motional gradient was inferred, with more mobile material at the polymer−air interface and the less mobile material at the substrate−polymer interface. It seems relevant to extend this study to different adsorbed amounts and to a different polymer.

In this paper, the segmental motion of PMA-d_3 on a silica surface was investigated as a function of adsorbed amount using the deuterium line shape method.[31] In this system there is a strong physical interaction between the adsorbed polymer and the substrate. We envision that during sample preparation, the polymer ultimately adsorbs as a relatively uniform thin film. We have been able to probe the system down to adsorbed amounts as low as 0.1 of the amount of the maximum adsorbed amount in toluene. With this variation in coverage, we were able to get a more detailed picture of the dynamics of the segments of the adsorbed polymers.

Experimental Section

Methyl acrylate-d_3 was synthesized from methanol-d_4 and acryloyl chloride. A 12 mL aliquot of methanol-d_4 (Aldrich Chemical, Milwaukee, WI), used as received, was added to 25 mL of freshly distilled acryloyl chloride (Aldrich) at 0 °C for 60 min. Distilled water was added to the reaction mixture to separate the excess methanol-d_4. The aqueous phase was separated and the organic phase dried over calcium hydride. The yield of the product, methyl acrylate-d_3, was 80%. The monomer was then distilled under vacuum. PMA-d_3 was prepared from the monomer via emulsion polymerization. The emulsion was prepared by adding 100 mL of water and 20 mL of the monomer to 0.028 g of potassium persulfate and 0.33 g of sodium dodecyl sulfate. The reaction temperature was kept

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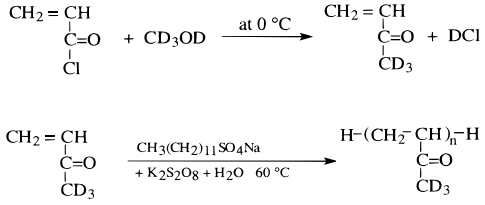
at 60 °C for 2 h. The yield of the polymer was 80%, based on the amount of monomer used. The reaction scheme is



The deuterated polymer had an M_w of 1.10×10^6 and a polydispersity of 2.22 as measured by gel permeation chromatography (GPC) in tetrahydrofuran (THF). A protonated PMA was made for the isotherm measurements by the above procedure. It had an M_w of 1.05×10^6 and polydispersity of 2.20. The data were reported with respect to polystyrene standards and no universal calibration correction was made.

All of the adsorption experiments were conducted by first preparing solutions of the polymer in toluene or solvent mixtures of benzene/acetonitrile. The solutions were allowed to equilibrate in centrifuge tubes with known quantities of Cab-O-Sil M5 fumed silica (Cabot Corp, Tuscola, IL), with a surface area of 200 m^2/g, in a mechanical shaker for 48 h at 25 °C. The tubes were centrifuged and the coated silica washed several times with the same solvents. The polymer-coated silica was then dried in vacuum at 70 °C for 6 h. The equilibrium concentration of polymer in the supernatant liquid was determined gravimetrically after drying. The amount of polymer adsorbed was calculated from the knowledge of the initial and final concentrations of the polymer and the amount of the silica used. The adsorption isotherm measurements were made using the protonated PMA sample. Surface samples with different adsorbed amounts of the deuterated polymer on silica were prepared with an equilibrium concentration of approximately 15 mg/mL.

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 a fast digitizer. The ^2H resonance frequency was 61.395 MHz. A quadrupole-echo pulse sequence was used (delay$-90°_x-\tau-90°_y-\tau-$acquisition). The 90° pulse width was 2.7 μs. 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 1000 to 80000, depending upon the adsorbed amount. 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. Spectra of the bulk and surface samples were collected at various temperatures from 25 to 86 °C. All of the spectra shown in this paper were processed with Felix (Biosym, San Diego, CA), and scaled to the same height for easier comparison.

Theoretical simulations of the deuterium spectra of the bulk sample were made based on a computer program written by Schneider and Freed[32] and adapted by us for ^2H NMR.[33] Since the simulation program does not correct for the anisotropic transverse relaxation effect on the line shape,[31] efforts were made to compensate for it. For each temperature, eight spectra were collected with various τ values between the two pulses of the solid state quadrupole echo sequence. These spectra were used to extrapolate the spectra to $\tau = 0$. The extrapolation was linear on a logarithmic scale and conducted using a commercial Fortran IMSL (IMSL Products, Houston, TX) subroutine, RLINE. The RLINE subroutine used a least-squares linear regression for minimization. Each extrapolated spectrum was then simulated using the Freed simulation program. The simulations were based on a rigid component which was a Pake pattern with reduced splitting between the two horns of 37.5 kHz, corresponding to a residual quadrupole coupling constant (QCC) of 50 kHz. The reduced splitting was due to fast methyl group 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[34]

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

where e^2qQ/h is the quadrupole coupling constant, t is time, θ and φ are the spherical polar angles for the orientation of the principle 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 $3\cos^2\theta(t) - 1$ term can be further decomposed into the following:[35]

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

Here the $\langle\ \rangle$ represents the time average, the $\beta(t)$ is the angle between the $\mathbf{B}_0$ and the rotation axis, and the 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 QCC of methyl groups are typically on the order of 150−170 kHz.[36]

The simulation of the distribution of the motion rates in the adsorbed layer was conducted in the following way. The spectra of the bulk polymer at various temperatures with a $\tau = 30$ μs were used as the basic components to be added to fit the experimental spectra which were collected with the same τ. The precision in the amounts of the required components was typically on the order of ±2% in the amount of each. Essentially each experimental spectrum for the surface samples was simulated by adding up appropriate bulk components to match it. Accordingly, each experimental spectrum from surface samples could be decomposed into a distribution of bulk components, each of which was indicative of specific motional rates.

Results and Discussion

Adsorption Isotherms. The adsorption isotherms for hydrogenated PMA for various solvent mixtures are shown in Figure 1. It was found that amounts of less than the maximum adsorption amount in a single solvent (e.g. toluene) were more accurately adsorbed from cosolvent systems (e.g. benzene/acetonitrile) than those obtained from a pure solvent system at a lower concentration.[2] The adsorbed amount for each surface sample is shown in Table 1. The reference value, the maximum adsorbed amount, A_m, in toluene was determined to be 2.61 mg/m^2. The other surface samples were labeled relative to this one.

The molecular weight distributions of the polymer in the supernatant liquids with equilibrium concentrations of 15 mg/mL were measured by GPC for each adsorbed amount and compared to the distribution in the original solution. As seen in Table 2, the molecular weights and polydispersities of the original sample and supernatant liquids were about the same. In fact, the distributions themselves (not shown) were almost identical. In these experiments, the fractions of the polymer adsorbed from the original solutions with the equilibrium concentrations of 15 mg/mL were calculated to be from 25 to 76%, depending upon the solvent used. Thus, preferential adsorption could have been observed. Accordingly, we believe that little and perhaps no preferential adsorption occurred. We suspect that this may be due to a relatively strong adsorption case where the kinetics of exchange may be slow.[2]

Bulk PMA-d_3 Dynamics. Three series of ^2H NMR spectra of bulk PMA-d_3 as a function of τ are shown in Figures 2−4. The three temperatures shown were for samples of significantly different mobility—so that the τ-effect can be demonstrated for different motional regimes. At each of these temperatures as τ increased, the intensity in the center and shoulder positions of the spectra decreased relative to that of the horns. For the

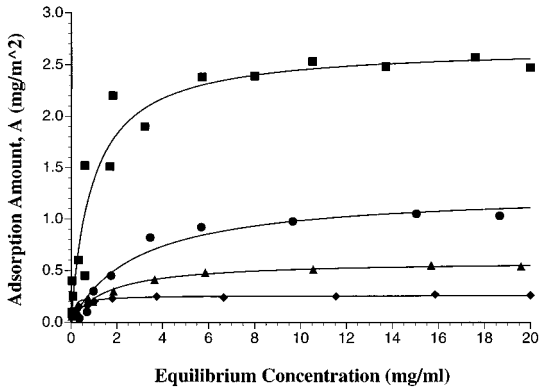


Figure 1. Adsorption isotherms for poly(methyl acrylate) in toluene (■) and in various benzene/acetonitrile (v/v) mixtures: 4.5 (●); 2.0 (▲); 1.0 (◆).

Table 1. Adsorbed Amounts of the Surface Samples

surface amount[a]	2.61	1.05	0.47	0.23
equivalent amount[b]	$1.0A_m$	$0.4A_m$	$0.2A_m$	$0.1A_m$

[a] In mg of polymer/m^2 of silica. [b] Relative to A_m, maximum adsorption amount in toluene.

Table 2. Comparison of PMA Molecular Weights and Polydispersities in the Liquid Phase before and after Adsorption

	equivalent adsorbed amount[a]				original solution
	$1.0A_m$	$0.4A_m$	$0.2A_m$	$0.1A_m$	
10^{-5} M_w	1.16	1.15	1.18	1.15	1.10
polydispersity	2.27	2.21	2.25	2.24	2.22

[a] Relative to A_m, maximum adsorption amount in toluene.

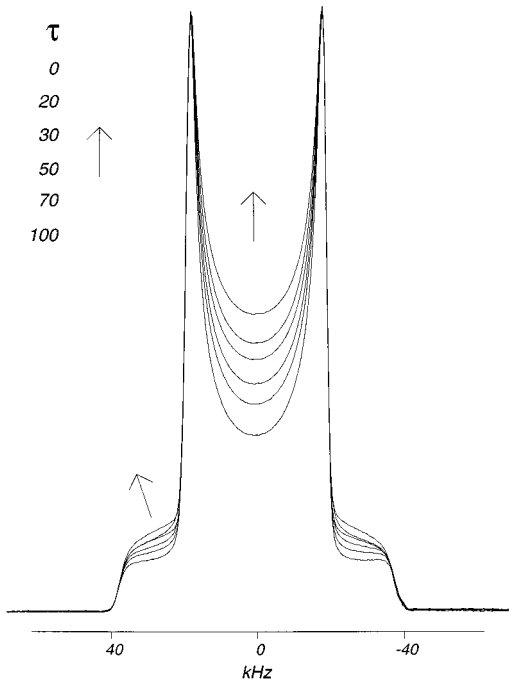


Figure 2. Dependence of the experimental deuterium NMR spectra for bulk PMA-d_3 at 25 °C on τ (in μs), along with the extrapolated spectrum to $\tau = 0$. The arrows indicate the direction of increasing τ values.

spectra at 37 and 44 °C, the splitting between the two horns lessened as τ increased. At temperatures higher than 69 °C, the line shapes (not shown) did not change with τ. The origin of this "τ-effect" on the line shape is that the T_2 relaxation times were anisotropic in the solid samples.[31] Different frequencies in the quadrupole-echo

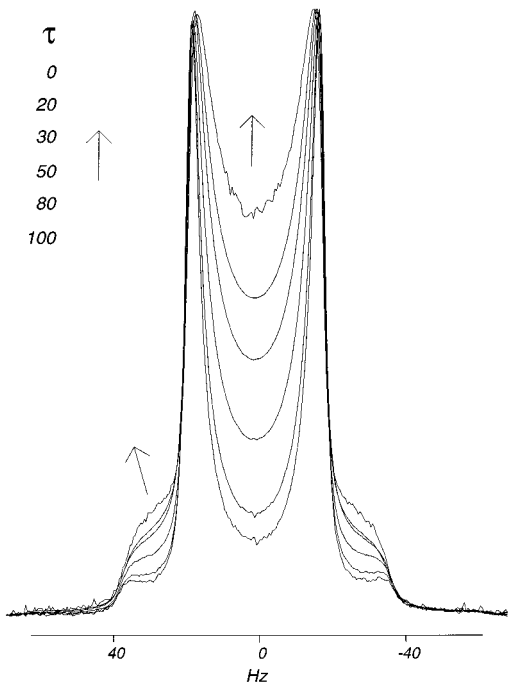


Figure 3. Dependence of the experimental deuterium NMR spectra for bulk PMA-d_3 at 37 °C on τ (in μs), along with the extrapolated spectrum to $\tau = 0$. The arrows indicate the direction of increasing τ values.

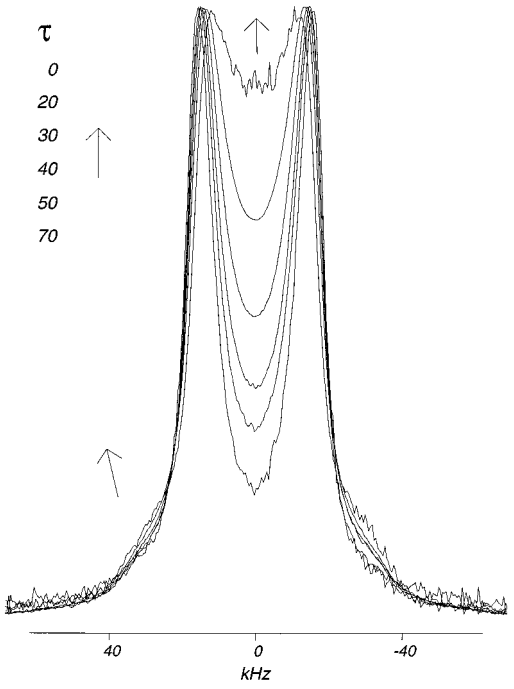


Figure 4. Dependence of the experimental deuterium NMR spectra for bulk PMA-d_3 at 44 °C on τ (in μs), along with the extrapolated spectrum to $\tau = 0$. The arrows indicate the direction of increasing τ values.

spectrum had different T_2 values and consequently different spin intensity refocussed at different τ's.

The variation of the total integrated intensities of the bulk spectra with τ equal to 30 μs at various temperatures is shown in Figure 5. The intensity of the spectrum at 25 °C was normalized to 100. The other intensities were reported relative to the intensity at 25 °C. The normalized spectra were all measured under the same conditions except for the temperature. A poly(α-methyl styrene)-d_3 sample,[37] which exhibited the same spectrum as a function of temperature, was used

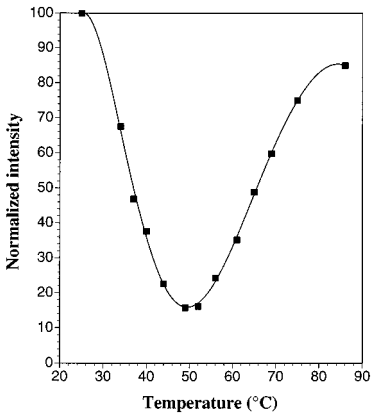


Figure 5. The normalized intensity of bulk PMA-d_3 collected with $\tau = 30$ μs at various temperatures. The spectral intensities were normalized to the intensity of the spectrum at 25 °C which was set to 100.

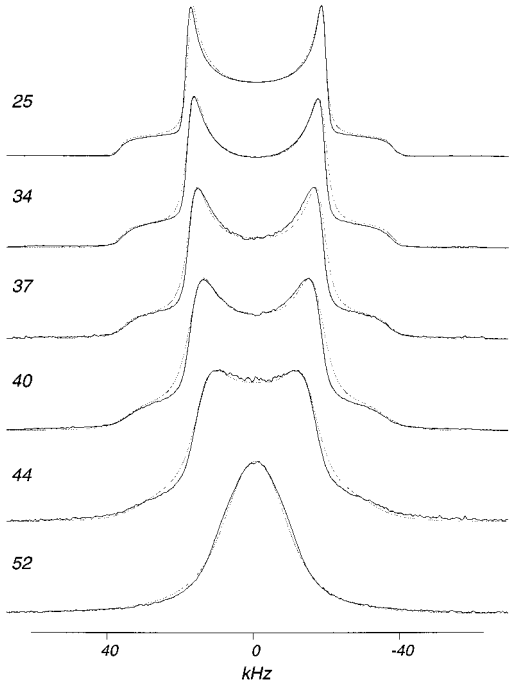


Figure 6. Experimental deuterium NMR (solid curves) extrapolated to the $\tau = 0$ and simulated spectra (dotted curves) for the bulk sample at temperatures from 25 to 52 °C.

to verify that there was no significant intensity reduction (within 2%) caused by the NMR instrumentation over the temperature range studied.

The experimental spectra of the bulk sample with $\tau = 0$ are shown in Figures 6 and 7 as solid curves. The bulk sample showed a Pake pattern at 25 °C with a reduced splitting between the two horns of 37.5 kHz. This corresponded to a reduced quadrupole coupling constant (QCC) of 50 kHz and was due to the rapid rotational motion of the methyl group. At 25 °C this methyl motion controls the shape of the spectrum. Backbone motions were apparently too slow to affect the spectrum much. With increasing temperature, the spectral features broadened and splitting was reduced due to the onset of backbone motion on the deuterium NMR time scale. Between 44 and 52 °C, the spectrum collapsed from a "Pake" pattern to a single (although broad) resonance.

The simulated spectra, shown in Figures 6 and 7 as dotted lines, fit their corresponding extrapolated spectra quite well. The spectra were modeled with a combination of isotropic rotational diffusion and discrete jump motions with multiple (50) equivalent jump sites. This method of simulation allowed us to use the Freed model with two kinds of motion at very different rates. The methyl rotation was implicitly included in the simulation through a reduction of the quadrupole coupling constant to 50 kHz.

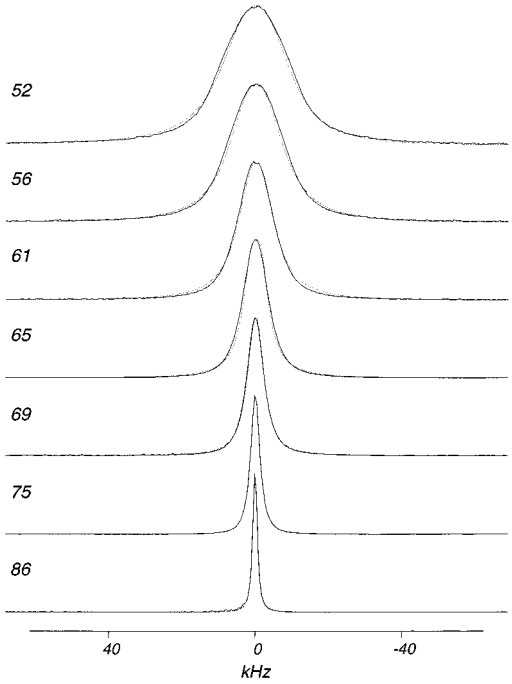


Figure 7. Experimental deuterium NMR (solid curves) extrapolated to the $\tau = 0$ and simulated spectra (dotted curves) for the bulk sample at temperatures from 52 to 86 °C.

Using deuterium 2D exchange techniques, Spiess et al.[36,38,39] found that the backbone motion of polystyrene above its DSC T_g could be modeled as isotropic rotational diffusion with a distribution of correlation times. Also, they found that the motions at the ester methyl group in poly(methyl methacrylate) (PMMA), below its DSC T_g, could be modeled with rocking motions with a 180° jump within the OCO plane, accompanied by some localized backbone motions. More recent work on poly(ethyl methacrylate) (PEMA), using 3D difference-correlated NMR,[40] showed the presence small angle fluctuations plus larger angle reorientations.

The detailed information from Spiess et al.[36,38−40] for PS, PMMA, and PEMA was obtained primarily from ^{2}H exchange spectra. To simulate a 1-D spectrum, this level of detail was not required, and indeed it is not generally available. The line shape changes in Figures 3 and 4 were undoubtedly due to a distribution of the motional rates in the bulk sample. Nevertheless, for our purposes, it was sufficient to model the motion as the superposition of two types (fast and slow components) at rather different rates. This was consistent with the behavior demonstrated for PEMA[40] although we know a broader distribution of correlation times exists.

The motional rates for both the isotropic rotational diffusion and discrete jump motions increased as the temperature increased (Figure 8). At low temperatures the spectra were effectively static and the reorientation rates were basically in the slow motion limit. There was a sudden increase in the motional rates around 50 °C corresponding to where the Pake pattern collapsed. The collapse of the two-horn feature into a single resonance

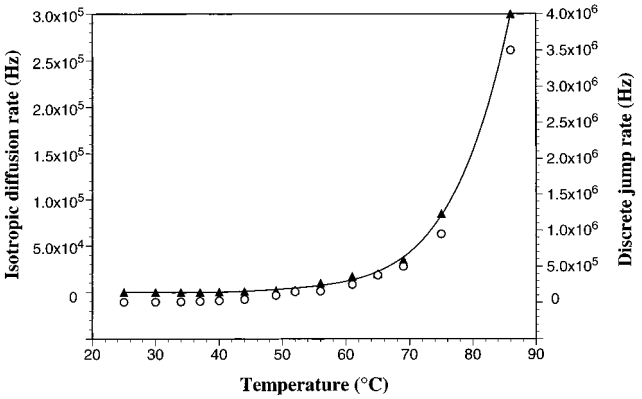


Figure 8. Motional rates for the simulated bulk spectra at various temperatures based on jump motion (○) plus isotropic diffusion (▲). See text for simulation method.

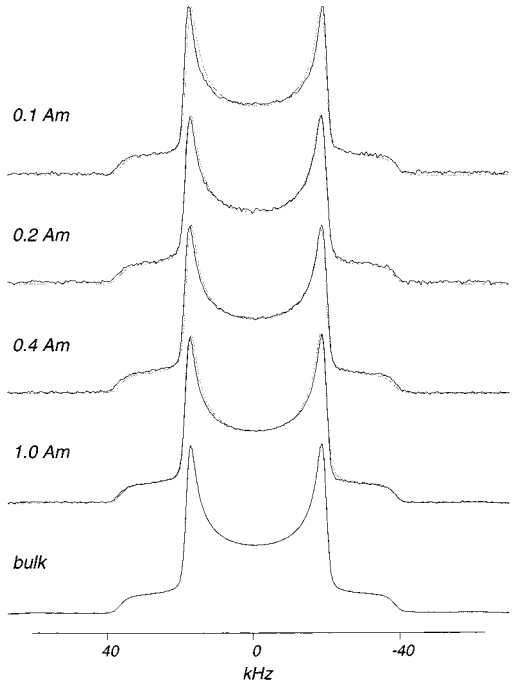


Figure 9. Experimental (solid curves) and simulated (dotted curves) ^{2}H NMR spectra at 25 °C for the bulk and surface samples of 1.0A_m, 0.4A_m, 0.2A_m, and 0.1A_m adsorbed amount.

was indicative of a dramatic change in the dynamics of the polymer. This was consistent with the so- called NMR T_g of PMA-d_3. The reported DSC T_g for PMA was 10 °C.[41] The difference between the NMR and DSC T_g was presumably due to the NMR time scale. This time scale is roughly the reciprocal of the residual quadrupole splitting of about 37.5 kHz. For DSC, the time scale can be taken on the order of seconds.

Surface PMA-d_3 Dynamics. All of the spectra for the surface samples shown in Figures 9−14 are composed of superpositions of different components indicating that the dynamics in the adsorbed layer were heterogeneous. The change in the line shapes for the surface samples with temperature was different from those of the bulk sample. Instead of a distinct transition from a powder pattern to a single resonance, the intensity of the mobile components (the central resonance) increased gradually with temperature. At 25 °C (Figure 9), the basic line shape of the Pake pattern did not change as a function of adsorbed amount. At 44 °C (Figure 10), a narrow component was observed for the surface samples, but was not observed for the bulk

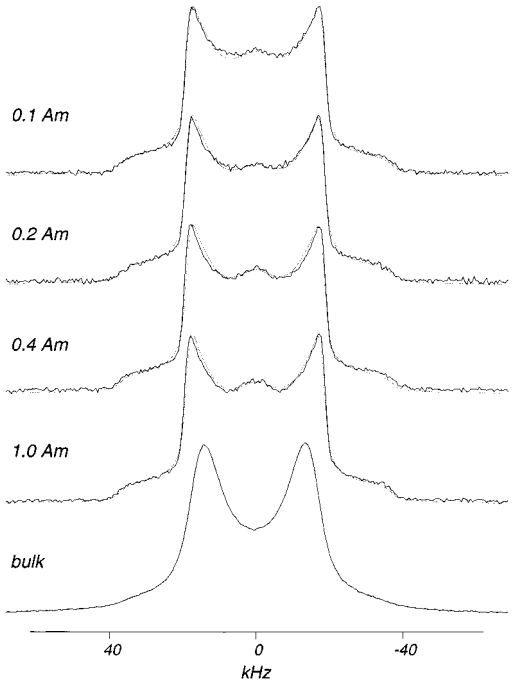


Figure 10. Experimental (solid curves) and simulated (dotted curves) ^{2}H NMR spectra at 44 °C for the bulk and surface samples of 1.0A_m, 0.4A_m, 0.2A_m, and 0.1A_m adsorbed amount.

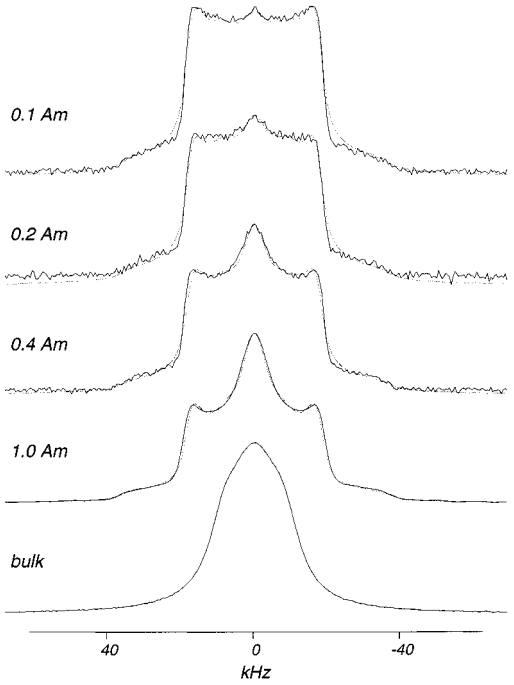


Figure 11. Experimental (solid curves) and simulated (dotted curves) ^{2}H NMR spectra at 52 °C for the bulk and surface samples of 1.0A_m, 0.4A_m, 0.2A_m, and 0.1A_m adsorbed amount.

sample. This was indicative of some portion of the polymer having enhanced mobility as compared to bulk. Blum et al.[26] found similar behavior for PVAC-d_3 on silica. They proposed that this more mobile component was associated with segments near the polymer−air interface. At 52 °C (Figure 11), the surface spectra showed a narrow component which had a higher relative intensity with higher adsorbed amounts. Also, the surface spectra retained a residual rigid powder pattern component, while the bulk spectrum had none at this temperature. At 69 °C (Figure 12), this trend continued with a distinct Pake pattern in the surface samples superimposed on a narrow component. At first glance,

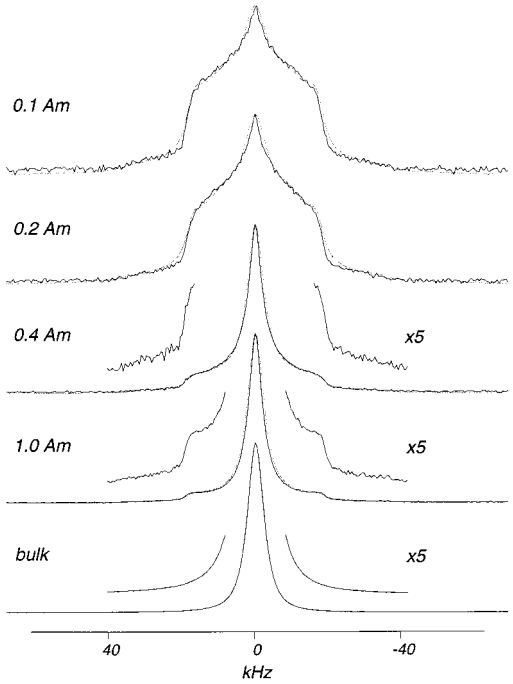


Figure 12. Experimental (solid curves) and simulated (dotted curves) ^{2}H NMR spectra at 69 °C for the bulk and surface samples of 1.0A_m, 0.4A_m, 0.2A_m, and 0.1A_m adsorbed amount.

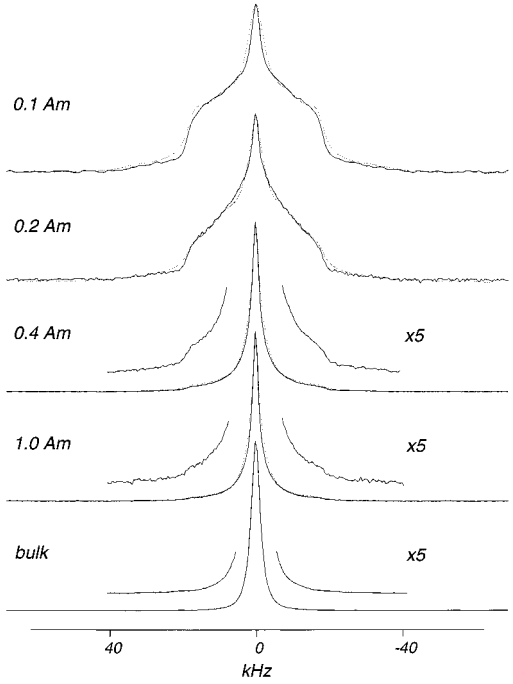


Figure 13. Experimental (solid curves) and simulated (dotted curves) ^{2}H NMR spectra at 75 °C for the bulk and surface samples of 1.0A_m, 0.4A_m, 0.2A_m, and 0.1A_m adsorbed amount.

the spectra at 75 °C (Figure 13) show only a narrow component. However, increasing the vertical scale revealed the appearance of a small amount of residual powder pattern. By 86 °C (Figure 14), only a small hint of a Pake pattern spectrum for the surface samples was observed upon high magnification of the wings. Only at the lowest adsorbed amount (0.1A_m) were the clear shoulders of a Pake pattern obvious.

The simulation results for the surface samples at above 25 °C are shown as dotted lines in Figures 9−14. The components on which the simulations were based are given in Tables 3 and 4. We attempted to fit the

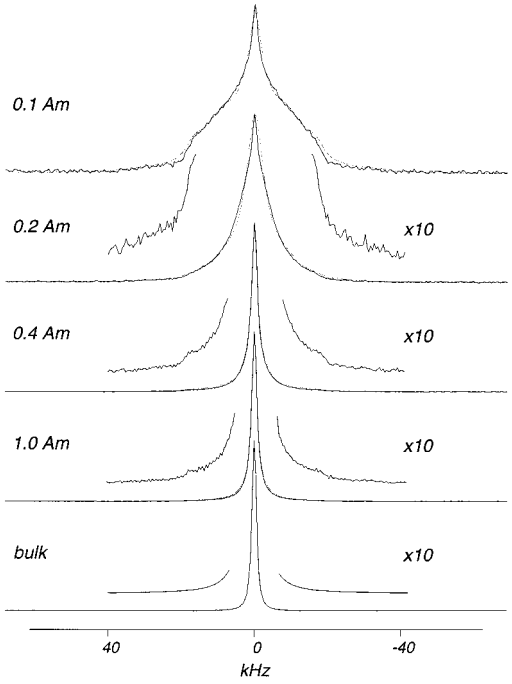


Figure 14. Experimental (solid curves) and simulated (dotted curves) ^{2}H NMR spectra at 86 °C for the bulk and surface samples of 1.0A_m, 0.4A_m, 0.2A_m, and 0.1A_m adsorbed amount.

Table 3. Motional Rate Distribution (%) for the 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
25	rigid-0	100	100	100	100
44	rigid-1	29	29	29	29
	intermediate-1	48	48	48	48
	mobile-1	23	23	23	23
52	rigid-2	36	37	37	41
	intermediate-2	56	59	61	58
	mobile-2	8	4	2	1
69	rigid-2	15	18	23	23
	intermediate-2	32	52	71	72
	mobile-2			6	5
	mobile-3	53	30		
75	rigid-2	9	12	13	24
	intermediate-2	37	49	80	70
	mobile-3	45	39	7	6
	mobile-4	9			
86	rigid-2	3	7	7	12
	intermediate-2	30	42	71	81
	mobile-3	33	51	22	7
	mobile-4	34			

[a] Motional rates for each component are given in Table 4.

Table 4. Motional Rates of the Components Used to Simulate the Surface Spectra

component	isotropic diffusion rate (Hz)	jump rate (Hz)
rigid-0	20	9.0×10^3
rigid-1	50	1.3×10^4
rigid-2	500	2.8×10^4
intermediate-1	1.0×10^3	4.5×10^4
intermediate-2	2.5×10^3	1.5×10^5
mobile-1	1.0×10^4	1.6×10^5
mobile-2	2.0×10^4	3.8×10^5
mobile-3	3.5×10^4	5.0×10^5
mobile-4	3.0×10^5	3.5×10^6

spectra with a minimum number of components, although we recognize that there undoubtedly was a continuous distribution of mobilities. Nevertheless, fitting based on a small number of discrete components allowed a comparison of the amounts and rates for

representative types of different motional species. Most of the surface samples required three components to fit the spectra, and these could roughly be classified as slow, intermediate, and fast on the deuterium NMR time scale. The motional rates of the components (and hence spectral components) were chosen to correspond to those for the bulk PMA-d_3 spectra. To calculate the relative amounts of each component, the intensity factor in Figure 5 was taken into account.

Several observations can be made from the simulations and their components listed in Table 3. The composition of the spectra drifted from rigid to mobile components as either the temperature or adsorbed amount was increased. In contrast to bulk PMA-d_3, the amounts of mobile component changed gradually. Clearly the amount of mobile component was significantly reduced for the lower adsorbed amounts ($0.2A_m$ and $0.1A_m$ samples) below 86 °C. Even at 86 °C, the $0.1A_m$ sample still had a small mobile component of 12.0%, and a rigid component of 6.6%. We note that these fractions should not be taken as the same as the "polymer-bound fractions", estimated by solid- and liquid-echo proton NMR,[42,43] where the presence of solvents created a very mobile component which did not exist in our "dry" samples.

Our results are qualitatively different than those of Reiter,[26] Orts et al.,[27] and Keddie et al.[28] for PS adsorbed on silicon(oxide). For those systems, the apparent T_g was lower for the surface polymer than the bulk one. When the system was changed to PMMA on silicon (oxide) such as that studied by Wu et al.[44] using neutron scattering and Keddie et al.[45] using ellipsometry, different results were found. The apparent T_g of the thin films increased with decreased film thickness. Clearly the nature of the mobility of the polymer in the thin film was affected by its interaction with the substrate. More strongly attached segments, resulting in lower mobility of the polymer, would be expected to result in a higher T_g. Unfortunately, this *may* be complicated by differences in the chain conformations between the surface and bulk polymers. Mobility estimates from thickness measurements may be in error. In contrast, the ^{2}H NMR experiment provided a direct probe of mobility and, demonstrated that the situation is more complex than simply either increased or decreased mobility of the surface polymer.

In order to explain the effect of mobility on adsorbed amounts, we propose the following model. At lower adsorbed amounts, the confirmation of the adsorbed polymer molecule should be relatively flat, resulting in a higher fraction of rigid segments at lower adsorbed amounts. At higher temperatures and higher adsorbed amounts, a small fraction of the polymer segments have *enhanced* mobility compared to bulk. This is the material near the polymer−air interface whose amount decreases with decreasing adsorbed amounts. At lower adsorbed amounts, the segmental motions of all segments are reduced because of their proximity to the surface. This is probably not simply due to their distance from the surface, but more likely because they are closer (via contour length) to directly adsorbed and immobile segments. Those segments close to the solid surface (e.g. trains) have even *more restricted* mobility than in bulk. The strong interaction of the carbonyl group with the surface is probably responsible for the reduced mobility (which, for example, is not observed in PS/silica). This is especially apparent with lower adsorbed amounts where, even at the highest temperature, a significant fraction of rigid material remains.

Finally, we note that in the systems studied here, the polymer molecule is thought to adsorb as a random coil perturbed somewhat by the interface. Under these conditions, the adsorption corresponds to a thickness representative of a single molecule. The differences in segmental motions observed here arise from within a single molecule. Thus, within a single adsorbed molecule, graded interfacial mobility exists with the more mobile segments at the polymer−air interface and the less mobile segments at the polymer−silica interface.

Conclusions

The bulk PMA-d_3 sample exhibited a T_g(NMR) at about 50 °C by the deuterium NMR line shape method, which was 40 °C above the reported DSC glass transition temperature of 10 °C. The behavior of the bulk polymer was "homogeneous" in that the spectrum was comprised of a single spectral component. Even though a distribution of correlation times existed, the motion in the bulk PMA-d_3 sample was successfully modeled with a combination of isotropic rotational diffusion plus discrete jump motions. In contrast, the surface-bound PMA-d_3 species were "heterogeneous" in that the spectra were superpositions from species with different mobilities in the adsorbed layer. These were successfully modeled based on rigid, intermediate, and mobile components, though a more continuous distribution of species with different mobilities were thought to exist. In general, the surface had a restricting effect on the motion of the adsorbed molecules above its NMR T_g. A small amount of material, assigned to that near the polymer−air interface had a greater mobility than bulk. In general, the mobility of the backbone decreased as the surface adsorbed amount decreased. The partial collapse of the deuterium NMR quadrupole splitting pattern provides a sensitive means of probing surface mobilities as a function of temperature.

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