Segmental Dynamics of Interfacial Poly(methyl acrylate)-d_3 in Composites by Deuterium NMR Spectroscopy

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Abstract: The interface in composite materials containing an ultrathin layer of poly(methyl acrylate)-d_3 (PMA-d_3) on silica was studied using deuterium NMR. PMA-d_3 was deposited from solution at saturation coverage from toluene onto silica. The samples were dried and composite samples made by hot pressing the PMA-d_3/silica samples with hydrogenated polystyrene (PS) and high (HMW) and low (LMW) molecular weight hydrogenated poly(methyl acrylate) (PMA) as the overlayer. The interfacial layers of PMA-d_3 were studied at the air−polymer−silica and polymer−polymer−silica interfaces using deuterium solid-state quadrupole-echo NMR and the results compared to those for the bulk polymer. It was found that for samples at the air−polymer−silica interface, some of the polymer segments in the surface sample had segmental mobility higher than that of the corresponding bulk PMA-d_3 sample at the same temperature. When overcoated with unlabeled polymer, the interfacial polymer at the polymer−polymer−silica interface showed reduced mobility due to the presence of the overlayer. The adsorbed PMA-d_3, in the composite samples, decreased in mobility in the order of LMW−PMA > HMW−PMA > PS. The PS sample caused the greatest reduction in the PMA-d_3 interfacial mobility. The order was consistent with the segmental mobilities of the polymers used for the overlayers. The lower the mobility of the polymer used for the overlayer, the more restricted were the polymer segments in the adsorbed PMA-d_3 layer.

Introduction

As the size of devices made from multiphase polymeric systems becomes smaller, it becomes critical to understand and characterize the interfacial phenomena in these multiphase systems in a fundamental way. Since the size of the interfacial regions is quite small, many standard characterization techniques are simply not appropriate for chemical and physical analysis of interfacial species, especially in composite systems. Significant progress has recently been made in understanding the behavior of polymers at air−polymer−solid interfaces[1] and can be used as a basis for understanding the behavior of composite systems.

At the air−polymer−solid interface, many techniques have been used to characterize the interfacial polymers such as elipsometry[2−4] and X-ray[5] and neutron reflectometry.[6−8] These techniques basically characterize the structure (often the thickness) of the polymer layer and are typically used to estimate the glass transition temperature through a break in the thickness−temperature curve. Some structural techniques can also be followed as a function of time to yield information on changes, such as those due to diffusion.[7] Results from these studies have, in part, depended on the nature of the system under study. In particular, the affinity of the polymer for the surface, and the presence of a free surface, play significant roles in the behavior of the adsorbed polymer.

There have also been studies that have focused more directly on the dynamics of the polymers in thin films. Some of the techniques probe local free volume and molecular reorientation such as positron annihilation[9] or optical probe reorientation.[10] Others probe larger scale translational diffusion, as in fluorescence photobleaching,[11,12] or segmental dynamics, as in ESR[13] or NMR.[14,15] Often, these techniques have been applied where the polymer was at an interface with air. Much less has been done on composite materials, although the effects of the filler are clearly evident in dynamic mechanical studies of filled systems.[16]

In our laboratory, we have found that the deuterium lineshape method was a valuable tool that could be used for semiquantitative information on interfacial dynamics.[17−19] Using

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this technique, we have identified the existence of a motional gradient in poly(vinyl acetate)-d_3 (PVAc-d_3) and PMA-d_3 on silica. We proposed that the gradient was such that the less mobile regions were those close to the polymer−silica interface, while the more mobile regions existed at the polymer−air interface. In principle, if the more-mobile region was that of the polymer at the air−polymer interface, it would not exist in a system with a thick interface, i.e., a composite sample.

In this study, the dynamics of PMA-d_3 adsorbed on silica was investigated with the deuterated polymer adsorbed as an ultrathin layer on silica with three different polymeric overcoat layers on top of it. The overcoat layers were made from polystyrene (PS) and two PMA samples of differing molecular weights. We exploited the presence of the selective deuterium label on the interfacial polymer to provide contrast so that it could be observed with deuterium NMR without interference from the polymer used in the overlayer. The deuterium NMR technique is not generally hampered by the presence of solid fillers or the optical clarity of the sample but does require the use of high surface area substrates due to the insensitivity of the NMR technique. With this method, we verified that the mobility of the more-mobile segments at the air−polymer interface[17−19] was reduced when the air was replaced with a polymer layer. We also probed the effect of the different overlayer types on the segmental dynamics of the adsorbed polymer layer.

Experimental Section

Methyl acrylate-d_3 was synthesized using methanol-d_4 and acryloyl chloride as starting materials. The monomer was then used to make poly(methyl acrylate)-d_3 via emulsion polymerization. It was this polymer which was adsorbed as the primary layer on the surface. A high molecular weight (HMW) PMA was also made via emulsion polymerization, and a low molecular weight (LMW) PMA was made via solution polymerization. Both the HMW and LMW polymers were fully protonated. The details of the monomer and polymer synthesis can be found elsewhere,[18,19] as can the detailed procedures for the adsorption experiments, line shape simulations, and the ^{2}H NMR experiment.

The PMA-d_3 had a M_w of 1.10×10^6 g/mol and a polydispersity of 2.22, as measured by gel permeation chromatography (GPC) in tetrahydrofuran at room temperature. The data were reported with respect to polystyrene standards. The surface sample at the air−polymer−silica interface was prepared by adsorption of the PMA-d_3 from a toluene solution onto Cab-O-Sil M5 silica (Cabot Corp., Tuscola, IL) with a specific surface area of 200 m^2/g. The dispersion was prepared by mixing the PMA-d_3 solution and silica followed by mechanical shaking. The solid particles were centrifuged and rinsed twice with toluene to remove any polymer not directly bound and then dried in a vacuum oven at 70 °C. The amount of adsorbed PMA-d_3 was determined gravimetrically to be at the saturation coverage of 2.61 mg/m^2 (referred to as $1.0A_m$). This adsorbed amount corresponds to an average polymer layer thickness of 2−3 nm.

Three polymers were used to make the composite samples. The bulk PS had a molecular mass of 1.00×10^5 g/mol and a polydispersity of 3.05, as reported by the manufacturer (Aldrich Chemical, Milwaukee, WI). Two kinds of bulk protonated PMA[19] were used to make composites with the surface sample, HMW−PMA and LMW−PMA. The HMW−PMA had a M_w of 1.05×10^6 g/mol and a polydispersity of 2.20, similar to the bulk and surface PMA-d_3 used. The LMW−PMA had an M_w of 7.14×10^4 g/mol and a polydispersity of 2.52. The composite samples were prepared by hot pressing, by hand, the surface sample in an 8-mm glass tube with the HMW−PMA, LMW−PMA (referred to as HMW− and LMW−PMA composite samples), and PS polymers (referred to as PS composite sample) at 100 °C for 1 min. The ratio of the mass of the polymer overlayer to that in the interfacial adsorbed layer was about 1000/1. A schematic representation of the composite sample is shown in Figure 1.

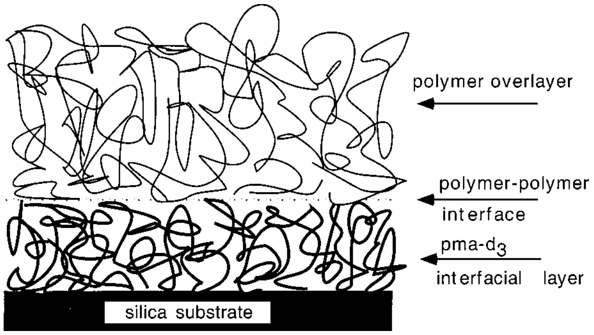

Figure 1. Schematic structure of the composite sample showing the location of the PMA-d_3 interfacial layer.

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 fast digitizer. The ^{2}H resonance frequency was 61.395 MHz. The pulse sequence was $delay-90°_x-\tau-90°_y-\tau-acquisition$. The 90 ° pulse width was 2.7 μs and $\tau = 30$ 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 3000 to 100 000, depending upon the concentration of deuterium in the sample. The distortion of the line shape due to the effect of finite pulse width was estimated to be less than 3% over the spectral range of 80 kHz. Consequently, no correction for this distortion was made. 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. A Hilbert transformation was used to obtain the frequency domain data.

The simulations of the experimental spectra were conducted in the following way. The experimental spectra of the HMW bulk PMA-d_3 were used as basic components that were added up to fit the experimental spectra. These components were chosen because they were obtained under the same experimental conditions as the spectra to be fitted. Consequently, we avoided the time-consuming extrapolation of the spectra to $\tau = 0$.[18] Accordingly, each experimental spectrum from the surface samples could be decomposed into a distribution of the bulk components, each of which is suggestive of a specific motional rate. The precision of the estimate of the amount of each component was about ±2 in the last place.

Results and Discussion

The spectra of bulk PMA-d_3 at 25 °C, Figure 2, show a powder pattern with a splitting of 37.5 kHz between the two “horns”. This corresponds to a reduced quadrupole-coupling constant (QCC) of 50 kHz and is due to the fast rotational motion of the methyl group about its symmetry axis. The features of the bulk spectra, shown in Figure 2, change from a powder pattern at 25 °C, through a broadened pattern with reduced splitting at 44 °C, to a hump-shaped feature at 52 °C, and to a single narrower resonance at 69 °C. A more detailed study of the behavior of the bulk polymer was previously reported,[18] and a full set of the bulk spectra was obtained. The bulk spectra were used as a basis set to “fit” the surface spectra (vide infra). It should be noted that the line shapes observed for the bulk spectra are *single-component*; i.e., all of the different segments in the sample have more or less the same motion. This motion is indeed complicated, but it is similar for all segments throughout the sample.

The change of the line shape, with temperature, is indicative of the change in the segmental motion. As the temperature increases, additional segmental motion results in reduced

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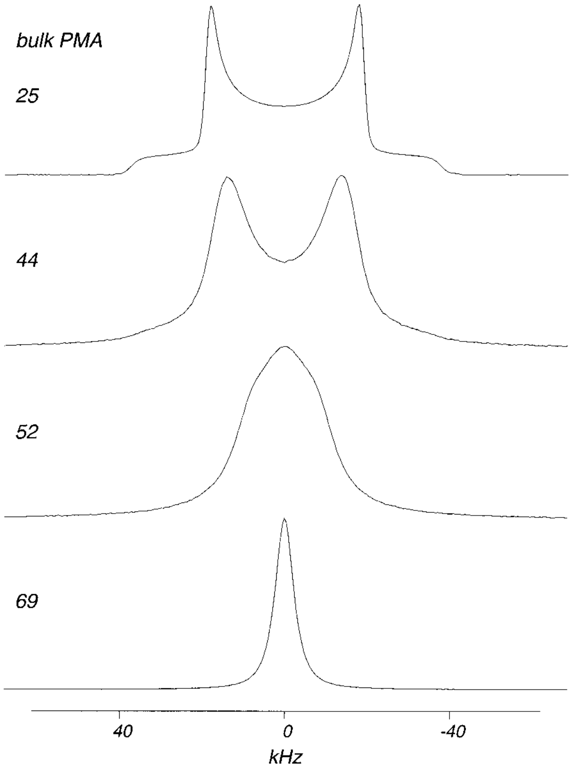

Figure 2. Deuterium NMR spectra of the bulk PMA-d_3 at 25, 44, 52, and 69 °C.

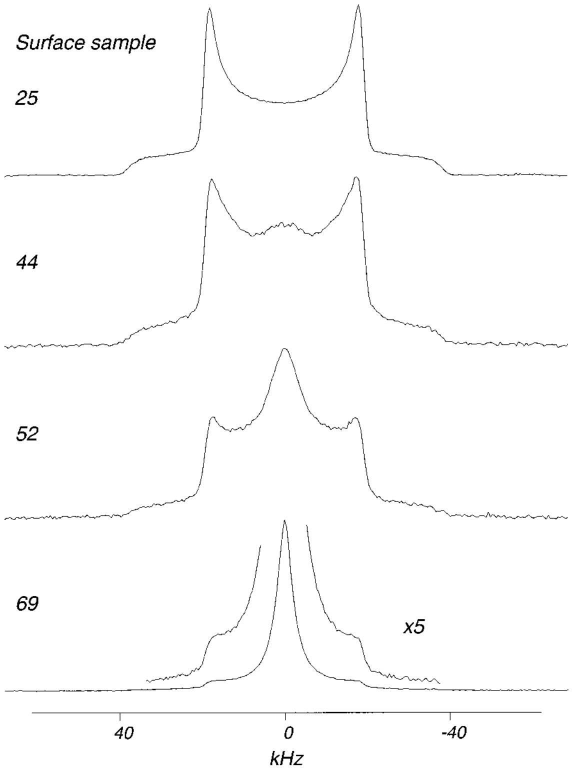

Figure 3. Deuterium NMR spectra of the surface PMA-d_3 sample (1.0A_m) at the air−polymer−silica interface at 25, 44, 52, and 69 °C.

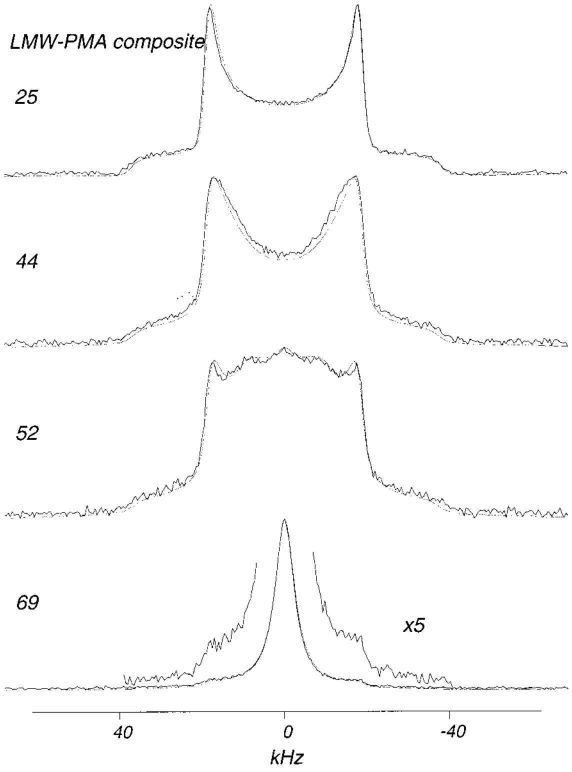

Figure 4. Experimental (solid lines) and simulated (dotted) deuterium NMR spectra of the surface PMA-d_3 sample in the LMW−PMA composite at 25, 44, 52, and 69 °C.

quadrupole splitting. The temperature (really a range of temperatures) at which the powder pattern collapses to a single (broad) resonance could be thought of as the glass-transition temperature, T_g, for the deuterium NMR experiment. The frequency probed by this NMR experiment is on the order of the reciprocal of the residual splitting, or about 40 kHz. Consequently, the NMR T_g would be expected to be considerably higher than the one normally found by calorimetry.[20]

The spectra of PMA-d_3 at the air−polymer−silica interface (surface sample), shown in Figure 3, is more complicated than that of the bulk sample. In simplest terms, the surface spectra can be considered as the superpositions of different components. At 25 °C, the spectrum of the powder pattern is similar to that of the bulk sample. A powder pattern, with a small hump superimposed in the middle, is found at 44 °C. At 52 °C, there is a relatively intense narrower component superimposed on a powder pattern. The narrower component is not observed in the bulk spectrum at the same temperature. At 69 °C, the spectrum is composed primarily of a single narrow resonance, similar to that in the bulk spectrum at the same temperature. A small amount of a powder pattern remains at the base and can be seen on the expanded plot. A comparison of the bulk and surface PMA-d_3 spectra allows us to suggest that the surface samples contain some segments which are more mobile than those in the bulk sample and also some that are less mobile.

The spectra of the composite sample made from LMW−PMA (LMW−PMA composite) are shown in Figure 4. A powder pattern, similar to the bulk and surface-PMA-d_3, is found at 25 °C. At 44 °C, the powder pattern broadens, similar to that of the bulk sample at the same temperature, but without the reduction in splitting. No central component like that at the air−polymer−silica interface is found. At 52 °C, the spectrum consists of a broad hump-shaped feature superimposed on a Pake pattern. At 69 °C, a relatively sharp resonance is found superimposed at a small amount of a Pake pattern. The sharp component is similar to that found in the bulk material at the same temperature. All of the spectra in Figure 4 have a lower signal/noise ratio than those in Figure 3, due to the lower concentration of

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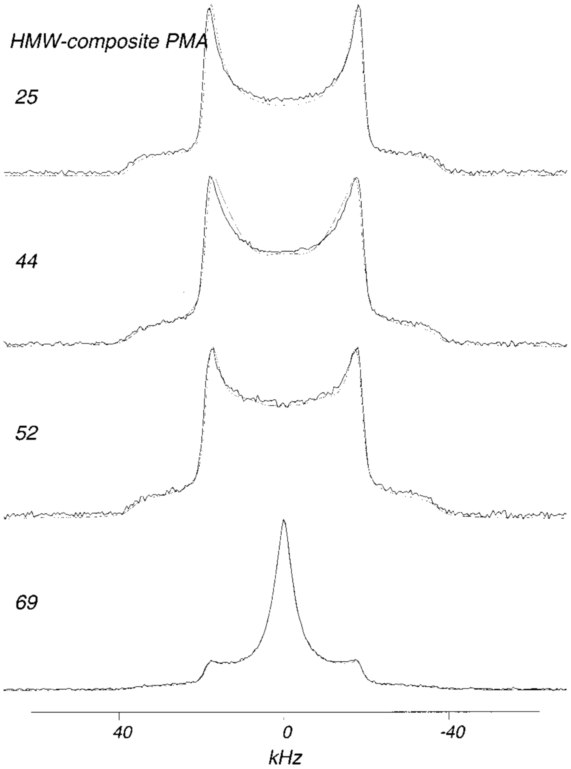

Figure 5. Experimental (solid lines) and simulated (dotted) deuterium NMR spectra of the surface PMA-d_3 sample in the HMW−PMA composite at 25, 44, 52, and 69 °C.

deuterium in the sample. A similar reduction in intensity is found for all of the composite samples reported below.

The spectra of the composite sample made from HMW−PMA (HMW−PMA composite), shown in Figure 5, exhibit a Pake pattern at 25, 44, and 52 °C. The valley between the two horns becomes slightly more filled-in with increasing temperature. At 69 °C, the spectrum appears to be a superposition of a narrow resonance, similar to that of the bulk component at the same temperature, plus on a Pake pattern.

The spectra of the composite made from polystyrene (PS composite), shown in Figure 6, exhibit a powder pattern at 25, 44, and 52 °C. The valley between the two horns becomes slightly more filled with increasing temperature but to a lesser extent than that found in the HMW−PMA composite spectra. At 69 °C, a narrow resonance, similar to that of the bulk spectrum at the same temperature, is superposed on a relatively intense powder pattern.

The simulation results for all of the surface samples are shown in Tables 1 and 2 and on the spectra of the composite samples (Figures 2−6). As is apparent in the spectra, the fits are quite good. We attempted to fit the surface spectra to as few components as possible. Previously, we have shown that the bulk spectra for PMA-d_3, extrapolated to $\tau = 0$, can be fit with a single-component line shape.[18] These "single-component" fits are based on the application of the theory of Freed[21,22] which contains two motional mechanisms (jumps and rotational diffusion), each set to different rates. The separation of the rates in the model roughly accounts for the breadth of the distribution of correlation times that describe the motion of the polymer segments.[23] The notion of a "single-component" refers to the fact that one line shape describes the spectra of the bulk polymer.

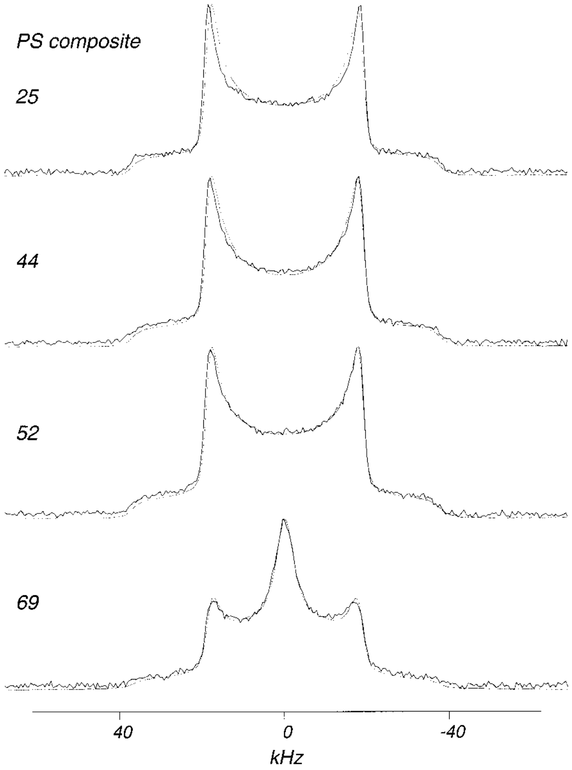

Figure 6. Experimental (solid lines) and simulated (dotted) deuterium NMR spectra of the surface PMA-d_3 sample in the PS composite at 25, 44, 52, and 69 °C.

Table 1. Motional Rate Distribution (%) for PMA-d_3 in Bulk, Adsorbed (1.0A_m), and Different Composite Samples

temp (°C)	component[a]	bulk	1.0A_m	LMw	HMw	PS
25	rigid-A	100	100	100	100	100
44	rigid-A					90
	rigid-B		29	30	33	
	rigid-C			23	67	10
	intermediate-A	100	48	47		
	mobile-A		23			
52	rigid-A					85
	rigid-B				36	
	rigid-C		35	40		10
	intermediate-A			5	12	
	intermediate-B	100	56	55	52	5
	mobile-B		9			
69	rigid-A					29
	rigid-C		15	16	21	
	intermediate-B		32	32	53	59
	mobile-C	100	53	52	26	12

[a] Motional rates for each component are given in Table 2.

Table 2. Various Motional Rates of the Components Used To Simulate the Surface Spectra

component	isotropic diffusion rate (Hz)	jump rate (Hz)
rigid-A	20.0	9.0×10^3
rigid-B	50.0	1.3×10^4
rigid-C	500.0	2.8×10^4
intermediate-A	1.0×10^3	4.5×10^4
intermediate-B	2.5×10^3	1.5×10^5
mobile-A	1.0×10^4	1.6×10^5
mobile-B	2.0×10^4	3.8×10^5
mobile-C	3.5×10^4	5.0×10^5

In contrast, the fitting of the surface spectra, including the composites, is multicomponent, requiring at least two and

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typically three components above the low temperature regime where only powder patterns are observed.

We note that the surface samples probably have a broad distribution of segmental mobilities, which give rise to the line shapes obtained.[18] We have previously shown that the intensity of the different components drop off in the intermediate regime.[18] Thus the fits to the line shapes underestimate the relative amount of material in the intermediate regime. Nevertheless, the fits to the more mobile and less mobile components are should be fairly representative of the behavior and intensity of these components.

From the data in Tables 1 and 2, and the spectra themselves, several features are apparent. A comparison of the spectra/fit data for the bulk and other samples shows that *only* the surface sample at the air−polymer−silica interface contains a component which is more mobile (narrower) than the bulk sample at any given temperature. In all of the composite samples, with polymer−polymer−silica interfaces, similar to filled polymer systems, no portion of the adsorbed layer has the enhanced mobility (narrow component) observed in the surface ($1.0A_m$) system. In our previous reports[7,17] on surface adsorbed PMA or poly(vinyl acetate) (PVAc), the more mobile component in the spectra was proposed to be due to mobile segments in the outer regions−those near the polymer−air interface. Since this component is absent in the spectra of the composite samples, we propose that these mobile segments are eliminated due to their interaction with the polymer overlayer. Thus, results from the composite samples provide support for our previous proposition of a loose mobile structure at the polymer−air interface in the surface sample.

It is also interesting to compare the spectra of the different composite samples. At 25 °C, there is not much difference in the spectra as all of the samples are in the rigid limit and a Pake pattern for methyl rotation results. At 44 °C, more subtle differences are observed. The powder patterns for the composites are broadened, with the most broadening occurring for LMW−PMA and the least for PS. This trend continues at 52 °C with the LMW−PMA composite spectrum showing a definite broad resonance (from a more motionally averaged species) in the middle of the powder pattern. At 69 °C, this center component is evident in all of the composite samples and the relative intensities of the middle components are highest for the LMW−PMA and lowest for the PS composite.

It is possible to rank order the effects of the three polymer overlayers as LMW−PMA < HMW−PMA < PS in terms of their ability to reduce the mobility of the surface PMA-d_3 compared to that at the air−polymer−silica interface. The same conclusions are obvious whether the comparisons are based on the components (amounts and rates) used in the simulations or on a direct comparison of the spectra.

We might consider the reduction in mobility to be caused by either of two effects, the interaction of the two polymers at a “smooth” interface and the possible interpenetration of the overlayer and the adsorbed polymer. We would expect the LMW−PMA to have the maximum interpenetration, followed by the HMW−PMA, with PS being the least with almost no or very little interpenetration. Since PS would not be expected to interpenetrate significantly and it creates the greatest reduction in mobility, interpenetration is perhaps not the most important effect. Layering a polymer on top of the surface polymer will surely have the effect of compressing the surface layer. Consequently, we believe that the mobility of the overlayer is at least partially transferred to the adsorbed PMA-d_3. While the overlayer polymer reduces the mobility of the surface-bound PMA-d_3, in all three cases, the effect of each is different.

There are few other ways to probe the interface in a composite material in such detail. Nevertheless, it is appropriate to make a few comparisons with previous work. For relatively optically transparent systems, molecular probe techniques[10] have been shown to effectively probe translational diffusion in thin to thick films. At film thickness' of roughly 150 nm and above, the behavior in films of poly(isobutyl methacrylate) was found to be indistinguishable from that in bulk polymer. For thinner films, the relaxation distribution was found to broaden. Using isotope labeling, neutron reflectivity can, in principle, be used to get similar information. Lin et al.[7,8] found that the translational interdiffusion coefficients for films less than 5 times the radius of gyration (R_g) of poly(methyl methacrylate) on silicon were decreased compared to bulk. At less that $3R_g$, the effect was particularly dramatic and as much as 2 orders of magnitude slower than bulk. These changes are roughly consistent with the differences in segmental motions in bulk and in composites.

Results from fluorescence photobleaching on primarily polystyrene-containing polymers are somewhat contradictory as to the diffusion of the polymer in the thin layer.[11,12] While it is difficult to make detailed comparisons between systems with such different surface energies as PS and PMA, there is something that can be learned. At the air−polymer−solid interface, Tseng et al.[12] find an increase in translational diffusion coefficient of the polymer with decreasing film thickness, while Frank et al.[11] find a decrease. The former workers attribute this enhanced diffusion coefficient to possible surface segregation of the labeled molecules. Our contention that there is a gradation in mobility at the air−polymer−solid interface supports this enhancement if there is surface segregation. Indeed, in our recent work on the modulated differential scanning calorimetry (MDSC) of adsorbed poly(methyl methacrylate) (PMMA)[24] and PS on silica, we have shown that the graded interfaces result in broadened glass transitions for both adsorbed polymers. While the MDSC experiments are not sufficiently sensitive as NMR in detecting the small amount of the material that we feel enhances mobility, we detect significant differences between PMMA and PS, with the PMMA transitions being shifted to much higher temperatures than in bulk.

Conclusions

The combination of specific isotope labeling with deuterium NMR allows a view of the dynamics of the interface, even with the presence of polymer overlayers. The collapse of the deuterium powder pattern allows a very sensitive probe of motion over a limited range of frequencies. The sensitivity of the technique to a small number of polymer segments with enhanced mobility is rather unique. The results from the composite samples support the proposal that the enhanced mobility is from segments with a mobile structure at the polymer−air interface in the surface sample. These segments with enhanced mobility are suppressed by the presence of the polymer overlayer.

All of the overlayer polymers used in this study have the effect of reducing the mobility of the most mobile surface-adsorbed PMA-d_3 segments. Indeed, the overlayer also reduces the mobility of the inner segments. The chemical nature of overlayer polymer is distinguishable in its effect on the dynamics of adsorbed PMA-d_3. The order, in terms of decreasing mobility,

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is LMW−PMA < HMW−PMA < PS. The order is consistent with the mobility of the polymer used for the overlayer, as estimated from its glass transition temperature. Thus, the dynamics of the overlayer, even in the case of PS−PMA, are transferred to the surface coating.

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