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ARTICLE

Plasticization of Adsorbed Poly(vinyl acetate) on Silica by Deuterium Solid-State NMR

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ABSTRACT: Deuterium nuclear magnetic resonance spectroscopy and temperature modulated differential scanning calorimetry (TMDSC) were used to probe the segmental dynamics of methyl-labeled poly(vinyl acetate)-d_3 (PVAc-d_3) adsorbed on Cab-O-Sil silica in the presence and absence of a plasticizer, dipropyleneglycol dibenzoate. Unlike the effect of this plasticizer on the bulk polymer, where the reduction in the glass transition temperature (T_g), was proportional to the amount of plasticizer added, the effectiveness of the plasticizer on the adsorbed polymer depended on the amount of polymer adsorbed. For samples with very small amounts of adsorbed polymer (i.e., 0.81 mg/m^2), there was little or no effect of plasticizer on the dynamics of the adsorbed polymer. For samples with more adsorbed polymer (i.e., 1.42 or 1.81 mg/m^2), the efficiency of the plasticizer was easily measurable on a fraction of the adsorbed polymer that can be considered loosely bound. The ^{2}H NMR line shape changes obtained from the adsorbed samples were fitted to a small jump model (based on the vertices of a "soccer-ball" shaped polyhedron) to obtain the distributions of jump rates contributing to the spectra. The same samples were also studied using TMDSC, and the results were consistent with the NMR results in terms of the effects of the plasticizer on the amount of polymer adsorbed. On the basis of the TMDSC experiments, the plasticizer tends to have a greater effect on the more loosely-bound polymer and lesser effect on a fraction that is more-tightly bound. Compared to the bulk polymer, where the glass transition range was on the order of 10 K, the range for the adsorbed polymer was more around 60 K.

Introduction

Polymers have been used extensively in composite materials in conjunction with other materials like fibers and fillers, where they are generally adsorbed on filler surfaces. The interfacial interactions of the polymers with the fibers/fillers play a pivotal role in the physical, mechanical, and chemical properties of the systems. Interfaces in polymer systems are very important, not just in polymer blends and composites, but also in laminates, multilayer coatings, rubber-toughened materials, photoresists, and semiconductor insulator junctions, especially as devices get smaller.[1−3] For example, in microelectronics applications, there is a large difference between the performance of ultrathin (~50 nm) and thick resist films (> 400 nm). This difference may be explained in terms of differences in the microstructure of the interface and the microdynamics of the polymer molecules therein.[4] Both of these properties vary on a scale comparable to the sizes of the polymer chains and are an interesting subject for study.

Significant progress has been made in the understanding of the behavior of polymeric thin films on surfaces. Polymer dynamics have been studied in a variety of geometries, including the following: polymer thin films supported on substrates like silicon or silicon oxide,[5−7] those freely standing,[8,9] or those confined in nanoscopic pores.[10,11] The changes in the apparent glass transition temperature (T_g) of supported thin polymer films with decreasing thickness (generally known as the T_g-nanoconfinement effect) have been widely studied during the last 15 years. A range of experimental methods were used including: ellipsometry,[6,7,12,13] X-ray reflectivity,[6,14] calorimetry,[10,15−19] dielectric spectroscopy,[20,21] positron lifetime spectroscopy,[22,23] infrared spectroscopy,[24−26] atomic force microscopy,[27] Brillouin light scattering,[9] mechanical,[28] nuclear magnetic resonance (NMR),[29−41] and electron spin resonance (ESR).[42,43]

Reiter[5] and Keddie et al.[6] showed that there was a significant depression in the T_g upon reduction in the thickness of polystyrene (PS) films on hydrogen-passivated silicon substrates, if the polymer and the substrate had no favorable enthalpic interactions; i.e., the PS films had a strong tendency to dewet. Studies were conducted by Keddie et al.[6,7] on ultrathin polymer films supported on substrates. Attractive interactions between poly(methyl methacrylate) (PMMA) and silica surfaces were found to increase the T_g due to the presence of hydroxyl units on the silica.[7] Strong attractive interactions between poly(2-vinylpyridine) and silica with hydrophilic surfaces showed that in the presence of favorable enthalpic interactions between the polymer and the substrate, the apparent T_g shifted to higher temperatures with decreasing film thickness.[14] Other experiments on supported films have revealed either an increase[7,12,16,44,45] or a decrease[8,9,21,46] in thin film T_g with reduction in film thickness. Although many studies (some are mentioned above) focus on the thickness dependence of T_g, it is also important to understand other aspects of nanoconfined polymer systems. For example, polymeric photoresists contain small-molecule photoactive compounds, plasticizers, and processing aids. These components interact with the polymer chains and affect the segmental mobility that, in turn, alters the T_g of the system.

Plasticizers, or low molecular mass diluents, are often blended with polymers to increase flexibility by effectively lowering the

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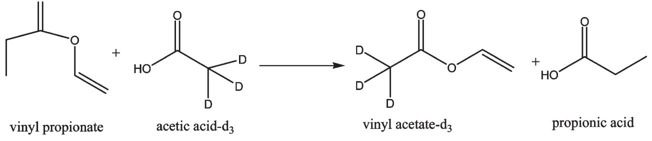
T_g.[47] The mechanism of plasticization is not understood in great detail, but a conventional model envisions a dynamic interaction between the polymer and a diluent, resulting in reduced chain−chain interactions, reduced local viscosity, and increased chain mobility.[48] The severity of constraints on local motion is alleviated by these small molecule plasticizers, thereby reducing the degree of intermolecular cooperativeness associated with the local motion.[49] Any change in the local friction, such as variation in the available free volume or the configurational entropy,[50,51] changes the dynamics of the chain molecules. Numerous reports describe the effect of plasticizer on the dynamics of polymer chains in bulk, but only a limited number of studies deal with supported plasticized thin films. Research from the Torkelson group focused the effect of small molecule diluents on the T_g of polymer films by using fluorescence spectroscopy.[52,53] They reported that the decreases or increases in the T_g found in a nanoconfined polymer system were suppressed by adding diluents that were considered plasticizers.

Our research group has been concerned with the dynamics of much smaller amounts of adsorbed polymers (i.e., smaller distance scales, on the order of 1−10 nm) than those considered in most of the studies mentioned above. We found that deuterium NMR spectroscopy is a valuable tool that can be used to obtain quantitative information about the interfacial dynamics of these adsorbed polymers.[31−34,37,54] Previous studies of adsorbed polymers have probed the effects of amounts adsorbed,[32] molecular mass,[33,37] and the composition of monomers (copolymers)[18] on the interfacial dynamics of polymer chains on silica. In this study, we investigated the effect of small molecule plasticizers on the segmental dynamics of adsorbed PVAc-d_3 by using ^{2}H NMR and temperature modulated differential scanning calorimetry (TMDSC). This investigation was aided by previous studies of PVAc-d_3 in bulk in the presence of the same plasticizer[55] and for PVAc-d_3 on silica.[31]

Experimental Section

Synthesis of Deuterated Vinyl Acetate Monomer. A vinyl interchange reaction catalyzed by mercury was used to synthesize vinyl acetate-d_3 from acetic acid-d_3 and vinyl propionate.[31,55] Acetic acid-d_3 (Aldrich, Milwaukee, WI) (0.167 mol) and vinyl propionate (Landcaster Synthesis Inc., Windham, NH) (0.33 mol) were added to a reaction flask under nitrogen. Mercuric acetate (Aldrich) (4.01 mmol) and concentrated sulfuric acid (98%, Fisher, Pittsburgh, PA) (0.42 mmol) along with a trace amount of hydroquinone (Eastman Kodak Co., Rochester, NY) were added to the above reagents and the mixture was stirred at 85−90 °C for 3−4 h. Solution-state ^{1}H NMR was used to monitor the progress of the reaction. The reaction was quenched by the addition of 6.68 mmol sodium acetate (Aldrich) and the resultant vinyl acetate-d_3 was collected by distillation under reduced pressure. Distillation using a spinning band column, gave a pure product (45% yield based on acetic acid used).



Synthesis of Deuterated Poly(vinyl acetate). PVAc-d_3 was synthesized using a conventional emulsion polymerization technique. The monomer, methyl-deuterated vinyl acetate (3.5 g) was mixed with double distilled water (3.4 g) in a round-bottom flask. Initiator $K_2S_2O_8$ (3 mg) and surfactant sodium dodecyl sulfate (7 mg) were added to the above mixture followed by purging with nitrogen gas. The polymerization was carried out at 70 °C for about 3−4 h with stirring using a magnetic bar. Adding sodium chloride, which destabilized the emulsion, precipitated the polymer. A white solid PVAc-d_3 was obtained with a yield of 70% based on the amount of the monomer. A protonated polymer, with a molecular mass similar to the deuterated one, was purchased from Scientific Polymer Products (Ontario, NY).

Table 1. Molecular Mass Measurements for the Protonated and Deuterated PVAc

sample	molecular mass (kg/ mol)	polydispersity
PVAc	240	2.0
PVAc-d_3	236	2.2

Table 2. Adsorbed Amounts of the Surface-Adsorbed Samples

sample designation	adsorbed amount of PVAc on silica (mg/m^2)
P81	0.81 ± 0.02
P142	1.42 ± 0.02
P181	1.81 ± 0.02

Molecular Mass Determination. Molecular mass was measured using gel permeation chromatography (GPC), in tetrahydrofuran (THF), with an Optilab DSP differential refractometer (Wyatt Technology, Santa Barbara, CA) and a DAWN EOS Light Scattering Instrument (Wyatt Technology) at 690 nm, attached to a gel permeation instrument. Measurements were performed at room temperature using THF as the solvent, with a flow rate of 0.5 mL/min. The dn/dc value was taken as 0.057.[56] The molecular mass data for the protonated and deuterated PVAc samples is given in Table 1.

Preparation of Adsorbed Samples. Samples of adsorbed polymer with dipropyleneglycol dibenzoate (plasticizer) were prepared by first preparing PVAc/plasticizer/toluene solutions of known compositions in a test tube. These solutions were mixed thoroughly for 12 h, followed by the addition of 0.2 g of silica (Cab-O-Sil M5, 200 m^2/g). These mixtures were then equilibrated in a shaker bath for about 72 h at room temperature. Toluene was removed by passing air through the adsorbed polymer−silica mixture, while the sample was agitated. Air was continuously bubbled into the sample until most of the toluene was removed. The drying was completed under vacuum at about 40 °C. Nonplasticized, adsorbed samples were prepared in the same way, except for the addition of plasticizer.

Three sets of samples were made with different adsorbed amounts; these adsorbed amounts and sample designations are shown in Table 2. For each set of samples, varying plasticizer contents (0, 5, and 10% based on the mass of polymer alone) were prepared. The sample designations list the adsorbed amount of polymer and the percentage of plasticizer in the sample (e.g., P141PL5 denotes the sample with 1.41 mg PVAc/m^2 silica with 5% plasticizer). The procedure for preparing the plasticized bulk samples can be found elsewhere.[55]

Characterization of the Samples by TGA and MDSC. Thermogravimetric analysis (TGA) (TA Instruments, New Castle, DE) was used to verify the amount of polymer and plasticizer present. A heating scan rate of 10 °C/min in air was used for all measurements. The thermal transitions in the T_g region were measured with a TA Instruments model 2920 MDSC (TA Instruments). An empty pan was used as reference in the MDSC experiments for all of the samples. Two heating scans and one cooling scan were taken from −40 to +150 °C, at a rate of 2.5 °C/min, modulation amplitude of ±0.5 °C, and a period of 60 s. A mass of approximately 8−12 mg of samples was used and the cell was purged with nitrogen gas at 50 mL/min during the scans. The second heating scan was used to determine the T_g data for the reversing heat flow curves so that all of the samples were subjected to a similar thermal history. The results are shown as the derivative of the differential reversing heat flow rate (dQ_{rev}/dT) vs temperature (T).

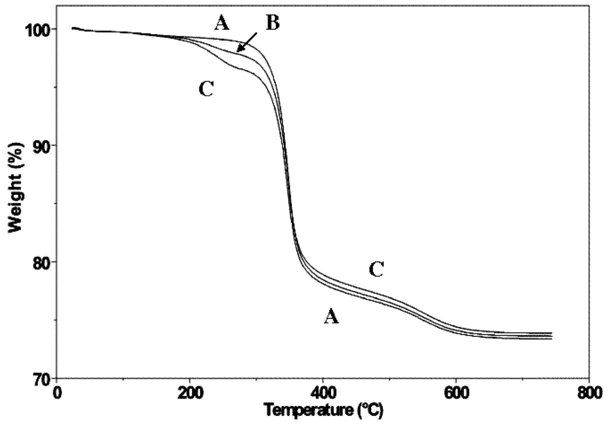


Figure 1. Representative thermogravimetric (TGA) thermograms for the 1.81 mg PVAc/m^2 silica samples with different plasticizer amounts: (A) P181PL0, (B) P181PL5, and (C) P181PL10. The P181PL5 (trace B) is in between the traces labeled A and C.

Characterization of the Samples by Solid State ^{2}H NMR. The NMR spectra were obtained using a Varian VXR-400/S spectrometer equipped with a fixed-frequency wide-line probe (Doty Scientific, Columbia, SC), a high power amplifier and fast digitizer. The wide line probe had a coil that could accommodate an 8 mm (diameter) sample. The quadrupole-echo pulse sequence (delay$-90_y-\tau-90_x-\tau-$acquisition) was used with a ^{2}H frequency at 61.39 MHz. The 90° pulse width was 2.8 μs and an echo time (τ_{echo}) of 30 μs was used. The Fourier transform was started from the top of the echo and no line broadening was applied to the spectra. The number of scans collected for bulk samples ranged from 4000 to 10000 depending on the temperature of operation and the amount of polymer adsorbed. The spectra obtained were processed by using the Mestrec software package (Santiago de Compostela University, Spain) and the spectra from a given set were scaled to the same height for easier comparison.

Simulation Studies of the Experimental Spectra. The experimental NMR line shapes were simulated using a FORTRAN based program known as MXQET.[57,58] In this study, the simulation was based on jumps on a truncated icosahedron (soccer ball).[59] The vertices were defined as the jump sites (60 sites) for the symmetry axis of the methyl group (effective C$-$D bond vector). We have previously shown that the soccer-ball model, with jumps of about 21 degrees were consistent with the experimental spectra.[59] Other simpler shapes, such as a tetrahedron, octahedron, or dodecahedron had jumps that were too large; i.e., their simulations had features of large jumps. This model is still simple enough to be reasonable in terms of computational effort. The soccer ball model provided a set of line shapes that mimicked the experimental ones, based on a reduced quadrupole-coupling constant of 59 kHz and an asymmetry parameter of 0.12 to account for the methyl group's rotation about its symmetry axis.[31,55] The pulse spacings and widths were the same as those used in the experiments with a small Gaussian broadening of 0.1 kHz. The experimental line shapes were then fitted with a superposition of the simulated spectra by using a mathematical routine (MATLAB, The Mathworks, Inc., Natick, MA).[59] The weighting factors of each of the simulated spectra were found by minimizing the differences between the experimental spectra and the sum of the simulated ones. A constrained least-squares fit was applied to find the positive weighting factors of a series of spectra.

Results

The amounts of polymer adsorbed on the silica surface and the amount of plasticizer present in the adsorbed samples were determined using TGA. The thermograms for three different plasticized samples for P181 (P181PL0, P181PL5, and P181PL10) are shown in Figure 1. These samples have 1.81 mg PVAc/m^2 silica with 0, 5, and 10% plasticizer, respectively. The initial mass loss was due to the loss (or degradation) of the plasticizer and the latter one was due to the decomposition of the polymer. The remaining mass at 600 °C was from the silica. The calculated amounts of adsorbed polymer on silica are shown in Table 2. Weight losses from 200 to 290 °C were used to estimate the amount of plasticizer in the adsorbed samples.[55] The plasticizer contents determined in this way were in good agreement with the amounts expected based on the initial compositions. Similar quality results were found for the P81 and P141 series samples.

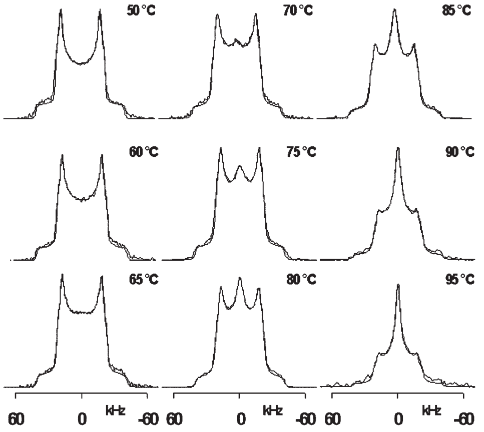


Figure 2. Experimental (black) and simulated (gray) ^{2}H NMR spectra for the 0.81 mg/m^2 PVAc-d_3 on silica with 0% plasticizer (P81PL0), as a function of temperature.

Quadrupole echo NMR spectra for the adsorbed PVAc-d_3 samples with different plasticizer amounts, were collected as a function of temperature. Both the experimental and the simulated spectra are shown in the figures. The intensity of each spectrum was adjusted to a constant maximum height. The experimental deuterium spectra for the 0% plasticized sample with 0.81 mg PVAc-d_3/m^2 silica (P81PL0) are shown in Figure 2. At 50 °C and below, the spectra showed Pake powder patterns with quadrupole splittings of 44 kHz between the bases of the two horns. This corresponds to a reduced quadrupole-coupling constant (QCC) of 59 kHz, consistent with the value for a methyl group undergoing a fast rotational motion about its symmetry axis. The spectrum of the powder pattern, at 50 °C, is similar to that of the nonplasticized bulk PVAc-d_3 sample previously studied.[31] The horns curve inward as they go upward from the base to give a lower final splitting of 35 kHz between the horns. This shape is due to the interaction of the methyl deuterons with the carbonyl group.[31] For other similar systems, it has been proposed that the deuterons (or protons) nearest to the oxygen are slightly distorted from a normal methyl group.[31] The effect can be adequately simulated with the inclusion of a small asymmetry parameter. At 65 °C, the splitting between the horns was reduced slightly, indicating an increase in mobility of some of the components, while at 70 °C, there were signs of a small central resonance. The spectrum at 75 °C looked like a powder pattern, with a small peak superimposed in the middle. As the temperature increased, the relative intensity of the central component increased, while the intensity of the outer horns decreased. By 80 °C, the central resonance stood above the outer horns. With higher temperatures, the central resonance (characteristic of faster segmental motions) became narrower and more intense. Even at 95 °C, the spectrum still showed evidence of the residual powder pattern and an intense central resonance, again suggestive of a distribution of the mobilities of polymer segments in the adsorbed sample. While

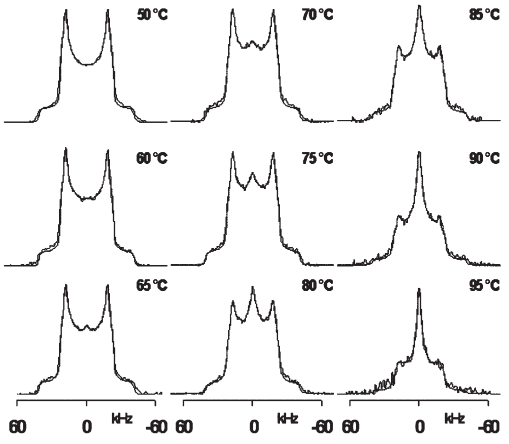


Figure 3. Experimental (black) and simulated (gray) ^{2}H NMR spectra for the 5% plasticized 0.81 mg/m^{2} PVAc-d_3 on silica (P81PL5), as a function of temperature.

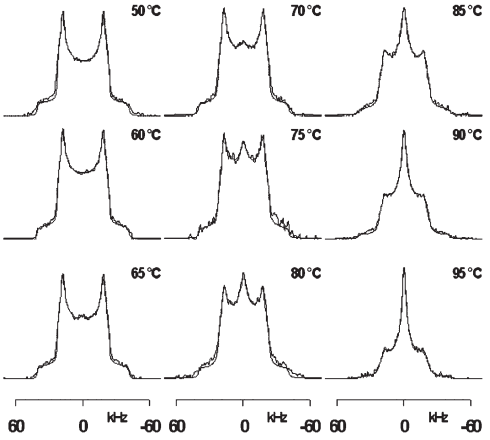


Figure 4. Experimental (black) and simulated (gray) ^{2}H NMR spectra for the 10% plasticized 0.81 mg/m^{2} PVAc-d_3 on silica (P81PL10), as a function of temperature.

the distribution of mobilities and heterogeneity in the spectra made it difficult to assign a single T_g for the adsorbed samples, an attempt has been made to characterize the system with two temperatures, T_{onset} and T_{mid}. T_{onset} is estimated as the temperature where a discrete middle (motionally narrowed) component is first observed and T_{mid} is the temperature at which the intensities of both the narrow and powder pattern components are roughly equal. For this sample, T_{onset} was about 70 °C and T_{mid} was about 95 °C. These values are consistent with our earlier estimates for unplasticized PVAc-d_3 on silica.[31,60] The ends of the glass transitions for the absorbed samples were difficult to estimate as small amounts of powder patterns were found even at the highest temperatures studied. Nevertheless, the T_{onset} and T_{mid} can give a measure of width of the transition from the NMR perspective.

The ^{2}H NMR spectra for the 5% (P81PL0) and 10% plasticized PVAc-d_3 for the P81 samples (0.81 mg PVAc-d_3/m^{2} silica) are shown in Figure 3 and Figure 4, respectively. The spectra had line shapes quite similar to those for the 0% plasticized sample (P81PL0), i.e., the powder pattern collapsed and was replaced by a broad resonance with a sharper, pointed center. This result suggested that, *for the P81 samples, the addition of plasticizer did not result in any significant changes in the line shapes*. Therefore, the mobility of the polymer chains remained relatively constant for those samples. The glass transition region can be characterized with $T_{onset} = 70$ and $T_{mid} = 95$ °C.

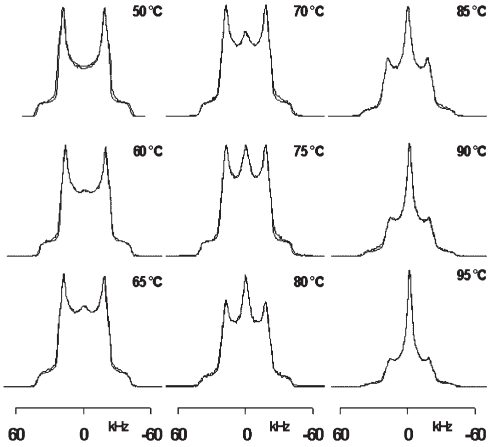


Figure 5. Experimental (black) and simulated (gray) ^{2}H NMR spectra for the 0% plasticized 1.42 mg/m^{2} PVAc-d_3 on silica (P142PL0), as a function of temperature.

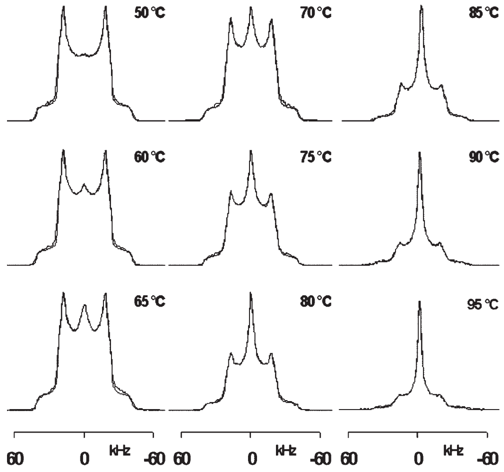


Figure 6. Experimental (black) and simulated (gray) ^{2}H NMR spectra for the 5% plasticized 1.42 mg/m^{2} PVAc-d_3 on silica (P142PL5), as a function of temperature.

The spectra obtained from a higher adsorbed-amount sample (1.42 mg/m^{2}) with 0% plasticized PVAc-d_3 (P142PL0) are shown in Figure 5. The spectrum at 50 °C had a Pake powder pattern similar to that of the 0% plasticized P81PL0 sample. There was a slight hint of the central resonance (i.e., the mobile component for the spectrum at 60 °C) and its intensity increased as the temperature increased. The line shape was different from that of the corresponding P81PL0 sample; e.g., the central component appeared at a lower temperature. Thus, the P142PL0 sample had more mobile components than the P81PL0 sample did at any given temperature. The glass transition region can be characterized with $T_{onset} = 66$ and $T_{mid} = 90$ °C.

For the 5% (P142PL5) and 10% (P142PL10) plasticized adsorbed samples with 1.42 mg/m^{2} PVAc-d_3 samples, the line shapes are shown in Figure 6 and Figure 7. There was a significant change in the line shapes for these samples, as compared to that of the 0% plasticized sample (P142PL0). At 50 °C, the line shape was similar to the Pake pattern except that a small amount of the central component showed up for both samples. As the temperature increased, the central component for the 10% plasticized sample (P142PL10) increased in intensity, faster than that of the 5% plasticized sample (P142PL5). The polymer chains in the 10% plasticized sample were. therefore, more mobile than those in the 5% plasticized sample. The spectrum of both samples at 95 °C had their residual powder pattern reduced considerably, as

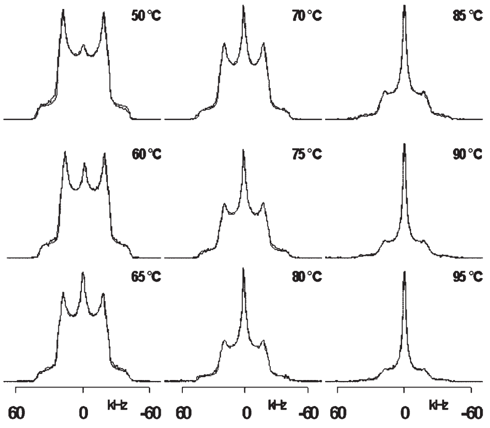


Figure 7. Experimental (black) and simulated (gray) ^{2}H NMR spectra for the 10% plasticized 1.42 mg/m^2 PVAc-d_3 on silica (P142PL10), as a function of temperature.

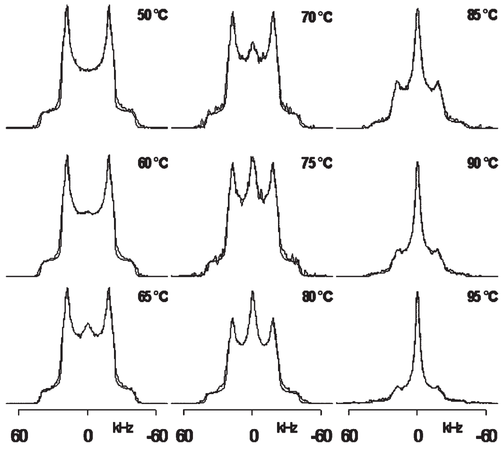


Figure 8. Experimental (black) and simulated (gray) ^{2}H NMR spectra for the 0% plasticized 1.81 mg/m^2 PVAc-d_3 on silica (P181PL0), as a function of temperature.

compared to the corresponding P81 samples. The line shape changes for these samples suggested that the mobility of the polymer chains had increased considerably due to the presence of the plasticizer. The ranges of the T_gs assigned for the 5% and 10% plasticized samples were 60 and 83 °C and 51 and 78 °C (T_{onset}, T_{mid}), respectively.

A sample with more PVAc-d_3 adsorbed, P181 (1.81 mg.m^2), was also studied as a function of added plasticizer. The ^{2}H NMR spectra for these samples are shown in Figures 8, 9 and 10. The spectrum at 50 °C for the 0% plasticized sample (P181PL0) was indicative of a powder pattern. The central mobile components started showing up after 60 °C, grew gradually, and led to the collapse of the powder pattern, giving a sharp narrow resonance at 95 °C. In contrast, the spectrum at 95 °C for the nonplasticized P81PL0 sample showed the presence of a large amount of residual, less-mobile component. For the P181PL0 sample, at the same temperature, only a small amount of the nonmobile component was present. The T_g for the P181PL0 sample can be assigned as ranging from 63 and 85 °C (T_{onset}, T_{mid}).

The ^{2}H NMR spectra for the 5% (P181PL5) and 10% (P181PL10) plasticized samples (Figures 9 and 10, respectively) appear to be highly mobile as compared to those of the corresponding nonplasticized sample. In the case of the 5% plasticized sample, the spectrum had a hint of the central component at 50 °C, while the 10% plasticized sample had a higher intensity of the central component present. The line shape changes in the 10% plasticized sample were similar to those in the bulk PVAc-d_3,[55] except that a very small amount of residual nonmobile component was still present at the base of the spectrum, representing the segments strongly attached to the silica surface. The T_gs for the 5% and 10% plasticized P181PL5 and P181PL10 samples were at much lower temperatures, ranging from 57 to 76 °C and from 45 to 62 °C (T_{onset}, T_{mid}), respectively. Thus, the plasticizer depressed the T_gs to a greater extent for the P181 samples than for the other samples with smaller adsorbed amounts.

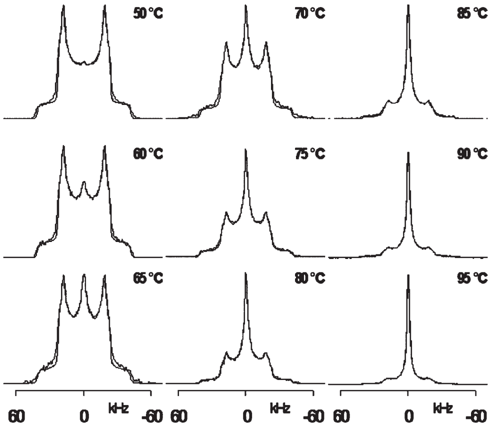


Figure 9. Experimental (black) and simulated (gray) ^{2}H NMR spectra for the 5% plasticized 1.81 mg/m^2 PVAc-d_3 on silica (P181PL5), as a function of temperature.

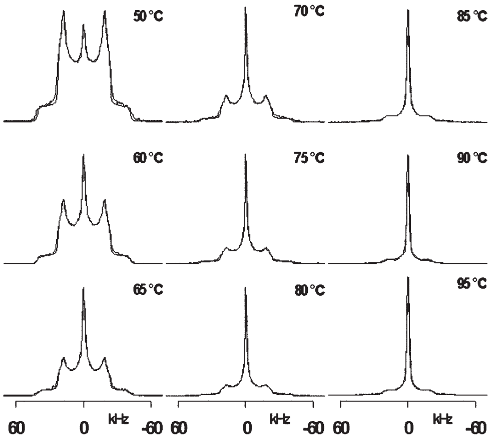


Figure 10. Experimental (black) and simulated (gray) ^{2}H NMR spectra for the 10% plasticized 1.81 mg/m^2 PVAc-d_3 on silica (P181PL10), as a function of temperature.

Table 3. NMR Glass Transition Temperature Ranges[a] for Samples of Different Adsorbed Amounts and Plasticizer Contents[60]

	P81 (0.81 mg/m^2)			P142 (1.42 mg/m^2)			P181 (1.81 mg/m^2)		
sample	T_{onset}	T_{mid}	width	T_{onset}	T_{mid}	width	T_{onset}	T_{mid}	width
0% plasticized	70	95	25	66	90	24	63	85	22
5% plasticized	70	95	25	60	83	23	57	76	19
10% plasticized	70	95	25	51	78	27	45	62	17

[a] T_{onset} is where a narrowed component in the spectrum is first observed and T_{mid} is an estimate of the middle of the transition where the two components are roughly of equal intensity.

The ranges of the glass transition temperatures from the quadrupole echo NMR experiments or T_g(QE-NMR) for all of the different plasticized and adsorbed samples are summarized in Table 3. Again, in this table, the T_{onset} is the temperature at which a distinct central resonance is observed. The T_{mid} (for middle) is the temperature at which the spectrum corresponds to that for the 95 °C spectrum for the P81PL0 sample where about half of the spectral intensity is in the narrower central resonance and the other

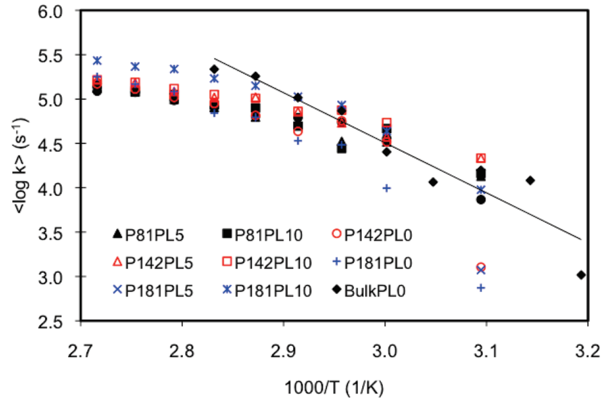


Figure 11. Averages of the log jump rate values, ⟨log k⟩, as a function of temperature for the different samples at different adsorbed amounts (P81, P142, P181) and different amounts of plasticizer. For reference, the data for the bulk sample, without plasticizer, is also shown.

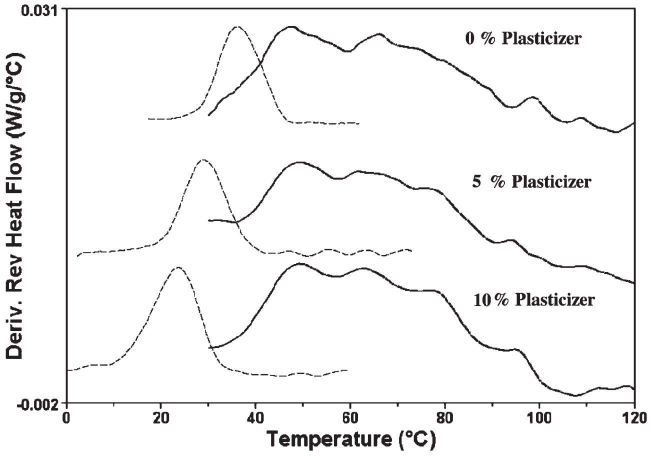


Figure 12. Derivative heat flow curves for the P81 surface (0.81 mg/m^2) (—) and bulk[55] (----) PVAc samples with different plasticizer contents: top, 0%; middle, 5%; bottom, 10%.

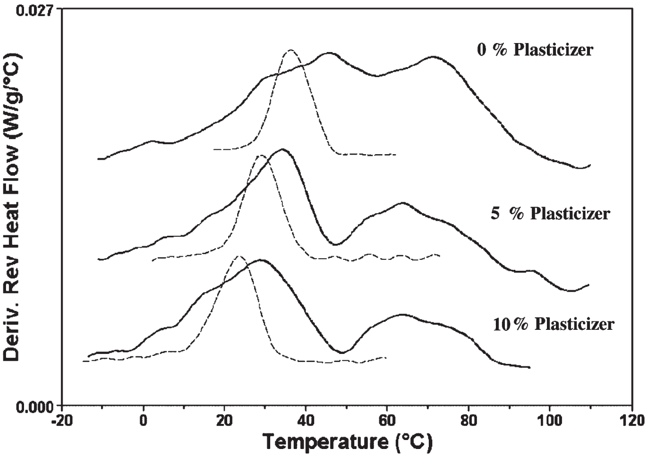


Figure 13. Derivative heat flow curves for the P142 surface (1.42 mg/m^2) (—) and bulk[55] (----) PVAc samples with different plasticizer contents: top, 0%; middle, 5%; bottom, 10%.

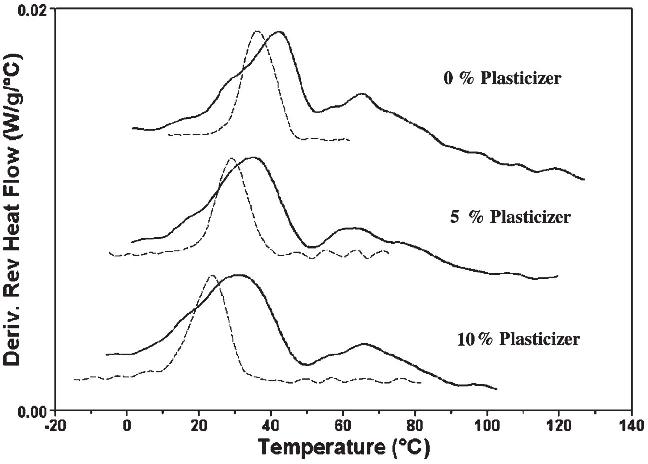


Figure 14. Derivative heat flow curves for the P181 surface (1.81 mg/m^2) (—) and bulk[55] (----) PVAc samples with different plasticizer contents: top, 0%; middle, 5%; bottom, 10%.

half is in the residual power pattern. These temperatures are for a rough estimate of the T_g range only. It is difficult to estimate an ending temperature for the adsorbed samples as a rigid fraction was always present in the temperature range studied.

The simulations of the experimental ^{2}H NMR line shapes are shown as lighter curves in Figures 2−10. The fits were good to excellent, in most cases, and hence (in most cases) were superimposed on the experimental spectra. A series of jump rates from 100 Hz to 1.0×10^{11} Hz were selected so that different spectra (with different jump rates) could be used to fit the experimental spectra in a reasonable amount of time. Bar graphs of the distributions of component spectra used to fit the experimental spectra, as a function of temperature and plasticizer content, are given in the Supporting Information. For simplicity, the jump rates were divided into three groups (or regimes) with respect to their powder pattern intensities, namely slow, intermediate and fast.[59] The distributions of these are also given in the Supporting Information. The MSQET program was used to calculate the time correlation functions for each of the basis-set spectra for our jump model.[58] As observed in our study for the bulk samples,[55] good fits required a broad distribution of spectra with widely different jump rates, covering about 5 orders of magnitude in jump rate. A master correlation function for each experimental spectrum was constructed by superposition of the correlation functions for the component spectra. These master time correlation functions were integrated to yield an average correlation time, or $\langle\tau_c\rangle$.[61] The average correlation times were calculated and plotted as a function of temperature and plasticizer content and are included in Supporting Information. However, with a broad distribution of jump rates (or correlation times), $\langle\tau_c\rangle$ was dominated by the long correlation times. A more representative set of values is the weighted average of the logarithm of the jump rate, ⟨log k⟩. These are plotted in Figure 11 as a function of temperature and plasticizer content. It should be noted that for the lower temperature data, the powder patterns are not very sensitive measures of motion and this accounts for the broad spread in the data above $1000/T$ of about 3. The variation of ⟨log k⟩ with inverse temperature was not a simple function as it represents a superposition of a broad range of different motional species. For the P81 samples, there was little difference in correlation times, with the addition of plasticizer. For the P142 and P181 samples, the ⟨log k⟩ increased with differences in both the adsorbed amount and the plasticizer content. For reference, the ⟨log k⟩ values for the bulk (not plasticized) polymer are also plotted along with the apparent Arrhenius behavior for the bulk polymer.[55]

Thermal analysis experiments were performed using temperature modulated differential scanning calorimetry (TMDSC). Glass transition curves for the different adsorbed amounts with two different plasticizer contents are shown in Figures 12−14. The thermograms for the bulk plasticized samples are plotted along with those for the adsorbed samples for comparison.[55]

Table 4. MTDSC Glass Transition Temperature Ranges[a] for Samples of Different Adsorbed Amounts and Plasticizer Contents[60]

	P81 (0.81 mg/m^2)			P142 (1.42 mg/m^2)			P181 (1.81 mg/m^2)		
sample	T_A	T_B	width	T_A	T_B	width	T_A	T_B	width
0% plasticized	47	66	47	46	72	61	42	65	60
5% plasticized	49	64	43	34	64	63	35	63	64
10% plasticized	50	63	45	29	64	67	31	66	66

[a] T_A is top of the peak for the loosely-bound material and T_B is that for the tightly-bound material.

The derivative of the reversible heat flow rate was plotted as a function of temperature for the different PVAc samples. The bulk samples showed relatively narrow transitions. For the adsorbed samples, the thermal behavior was fairly complex, as observed from the derivative mode thermograms. The transition curve for the P81PL0 (0.81 mg/m^2, 0% plasticized) sample was very broad, compared to that of the bulk polymer. The transition region of the adsorbed sample was quite broad and ranged from 30 to 90 °C. The thermograms for the 5% (P81PL5) and 10% (P81PL10) plasticized samples were similar to that for the 0% plasticized sample. Thus, the plasticizer did not affect the transition curve, i.e., there was no appreciable change in the mobility of the polymer chains due to the addition of the plasticizer. It is important to note that, while there were no significant differences between the thermograms for the adsorbed samples, the effect of plasticizer was significant for the bulk samples. To characterize the behavior more quantitatively, we have listed the temperatures of the low temperature peak, called T_A which is representative of loosely-bound polymer and T_B for the transition around the next highest peak which we use to characterize the more-tightly bound polymer.[62] The width of the transition was taken as the full width at half height of the derivative signal. These values for all of the samples are given in Table 4. For this adsorbed sample, none of the TMDSC traces varied much with added plasticizer.

For the P142PL0 (Figure 13, 0% plasticizer) sample, the transition region extended to the lower temperatures, the range being 15 to 90 °C, when compared to the corresponding P81PL0 sample with a smaller adsorbed amount. The presence of two significant humps was also observed for the adsorbed samples, allowing the T_A and T_B to be estimated. When the plasticizer content in the P142 adsorbed sample increased, the relative area under the hump at higher temperatures decreased, indicating that the plasticizer increased the mobility of the chains. The T_A portions changes systematically with plasticizer, and the T_B changed only from 0 to 5% plasticizer. The decrease in T_A was similar to that found at the maximum (T_g) for the bulk PVAc samples.[55]

For the adsorbed sample with 1.81 mg/m^2 (P181), the samples also showed a two-component behavior. The T_A peak again shifted to lower temperatures similar to that for the bulk samples. The relative amounts of both components and also the position of the T_B peak were relatively constant. It should be noted that it is difficult to characterize these transitions with just two numbers, but we do feel that they are representative of the trends observed.

Discussion

For the ^{2}H NMR spectra of PVAc-d_3 at lower temperatures, a Pake powder pattern was observed. For a ^{2}H nucleus (nuclear spin quantum number, $I = 1$), the quadrupolar splitting, $\Delta\nu_q$ is given by,[55,61,63]

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

where e^2qQ/h is the quadrupole coupling constant, θ and φ are spherical polar angles for the orientation of the principle-axis system of the electric-field tensor relative to the applied static magnetic field, $\boldsymbol{B}_0$, and η is the asymmetry parameter of the quadrupolar tensor. In general, the spherical polar angles vary with time, t. For a C-D bond or a methyl group in particular, the $3\cos^2\theta(t) - 1$ term can be expanded to

$$\langle 3\cos^2\theta(t) - 1\rangle = (1/2)\langle 3\cos^2\delta(t) - 1\rangle(3\cos^2\chi(t) - 1) \tag{2}$$

where $\langle\rangle$ represents the time average, $\delta(t)$ is the angle between the $\boldsymbol{B}_0$, and the rotation axis, and χ is the angle between the rotation axis and the C-D bond. Since χ is 70.5° for a methyl deuteron, the $3\cos^2\chi - 1$ term is reduced and the quadrupolar splitting is reduced to $^1/_3$ of its original value. Full values for QCC of the methyl groups are typically on the order of 150−170 kHz.[63]

The solid-state deuterium NMR line shapes were mainly dominated by the electric quadrupolar interactions. These spectra were very sensitive to the reorientation of the labeled methyl groups on the polymer chain. An extensive amount of information can be obtained about the dynamics of polymer chains from the coupling of the C−D bond axes with the cooperative motion of the polymer chains. The Pake powder patterns for PVAc-d_3 samples collapsed to motionally narrowed resonances with increased temperatures due to the increase in the segmental mobility of the polymer. The spectra in the intermediate regime consisted of the superimpositions of both. These changes in the line shapes of the adsorbed samples were different from those of the bulk samples.[55] Instead of a distinct transition from a powder pattern to single resonance, the intensity of the central resonance increased gradually with temperature.

The glass transition for adsorbed PVAc clearly occurs over a broad range of temperatures, and characterizing this range (based on the ^{2}H QE-NMR or MTDSC results) is challenging. No spectra were observed for any surface polymer that did not include at least a small number of glassy polymer segments (rigid components). Consequently, it is difficult to estimate the end of the transition for the adsorbed polymer. Accordingly, T_{mid} was defined temperature as being where the signal height of the central resonance of the spectrum was three times (roughly equal intensities) that of the height of the horns (e.g., the 95 °C spectrum in Figure 2). We have identified this temperature for each of our samples. The rough range of the T_g from NMR should be about twice the range identified by T_{onset} and T_{mid}.

The line shapes were reasonably well described by the soccer-ball jump model. This model seems to be able to mimic the relatively small jumps expected in PVAc. The correlation times calculated from the model and shown in Figure 11, were consistent with those expected for deuterium line-shape changes. The correlation functions were nonexponential and fit to a stretched exponential where the width parameter, β, was determined from:

$$C(t) = \exp(t/\tau_{kww})^{\beta} \tag{3}$$

The fitted width parameters (β) were moderately broad (between 0.16 and 0.35) which was consistent with the broad distribution of spectra required for spectral simulations. For comparison, the bulk polymer spectra were fit with β values between 0.2 and 0.4.[55]

One of the most interesting aspects of this study is evident in Figure 15. This figure shows the quadrupole-echo NMR spectra for the P81, P142, and P181 adsorbed samples (with different plasticizer amounts) at 65 °C. For the P81 (0.81 mg/m^2 samples), the spectra with 0%, 5% and 10% plasticizer were remarkably similar. This clearly indicates that, *at smaller adsorbed amounts, the plasticizer has little effect on the adsorbed polymer*. For the P142 (1.42 mg/m^2) samples, the central component increased as the plasticizer content increased. This effect was even stronger for the P181 (1.81 mg/m^2) PVAc-d_3 sample. These results demonstrated that the plasticizer became affective when the

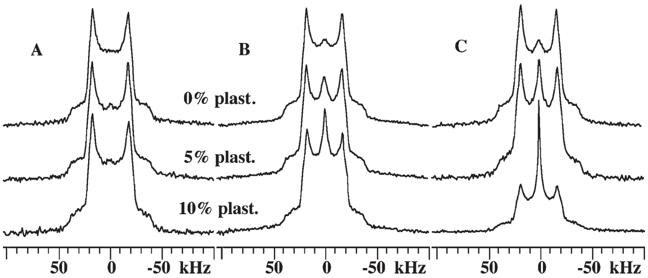


Figure 15. ^{2}H NMR spectra for different adsorbed amounts A (P81, 0.81 mg/m^2), B (P142, 1.42 mg/m^2), C (P181, 1.81 mg/m^2), with 0%, 5%, and 10% plasticizer at 65 °C.

amount of PVAc adsorbed was greater than a minimum amount (somewhere in between 0.81 and 1.42 mg/m^2).

The results obtained from the thermal analysis of the adsorbed samples were also consistent with the NMR data. None of the TMDSC thermograms for the P81 (0.81 mg/m^2) samples, at different plasticizer loadings, showed any significant effects from the plasticizer. The TMDSC transition curves for the adsorbed samples were broader, compared to those of the bulk samples, indicating the heterogeneity in the distribution of mobility of the polymer chains. Zhang and Blum[18] reported the presence of distinct humps in the TMDSC derivative transition curves, for styrene-methyl methacrylate copolymers, and assigned the hump closer to the bulk T_g to a more-mobile component (loosely bound) while the other hump represented the less-mobile (tightly bound) polymer chains attached to silica.[18] Blum et al.[31] made a quantitative treatment of the humps in the TMDSC derivative curves for PMMA and determined the contributions from both loosely and tightly-bound components.

All of the thermograms of the adsorbed polymers showed at least two components that have been characterized by the T_A (loosely bound) and T_B (tightly bound) as shown in Table 4. For the P81 sample, the two humps were roughly of equal intensity, though the full transition was quite broad and complicated. Neither of these components was significantly affected by the presence of the plasticizer. The other samples also had at least two distinct components with the loosely-bound component growing in intensity as the adsorbed amount increased. For the P142 and P181 samples, the position of the loosely-bound component shifted to lower temperature and increased in intensity with addition of plasticizer. The position of the tightly-bound component remained roughly the same with increased plasticizer content. The TMDSC curves, like the NMR line shapes, suggested that the effectiveness of the plasticizer in reducing the T_g decreases when the adsorbed amount decreases.

A comparison of the NMR (for T_{onset}) and TMDSC (for T_A) experiments is shown in Figure 16 along with the data for the bulk polymer T_gs from both experiments. It should be pointed out that the bulk PVAc does not show either such a broad transition region or the kind of heterogeneity seen in the adsorbed polymers.[55] The figure shows the approximate invariance of both NMR and TMDSC for the P82 sample. It also shows the similarity of the effect of plasticizer for the P142 and P181 samples with the bulk samples. The differences between the two experiments is due to their different time scales which can be accounted for through a time−temperature superposition.[55]

At adsorbed amounts below a certain level (at least 0.82 mg/m^2 in this case), the PVAc does not allow the plasticizer to function. Most of the polymer is tightly bound at this adsorbed amount and there may be some loops and tails that have some additional mobility (loosely bound), but they may be not sufficiently far away from the surface to allow plasticizer penetration. It should be noted that different experiments give different measurements of length scales.[1,62] For example, FTIR experiments are only sensitive to distances around the length of a chemical bond,[26,64] whereas, the NMR and TMDSC experiments are sensitive to a much longer distance scale.[1,62] Mechanical measurements made on PVAc-containing composites were not sensitive to such a small amount of tightly-bound polymer (about 1% of the amount of polymer studied).[28]

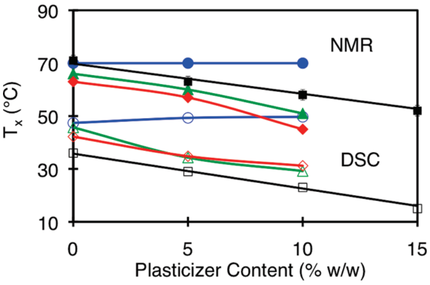


Figure 16. Comparison of the T_g estimates from NMR (filled symbols, from T_{onset}) and TMDSC (open symbols, from T_A) for the P82 (circles), P142 (triangles), P181 (diamond), and bulk (squares).[55]

For PVAc, the amount of tightly-bound polymer amounts to less than 0.81 mg/m^2 as this sample shows both tightly-bound and loosely-bound polymer, but the loosely-bound polymer has a higher T_g than that in the other samples. For this sample, the effect of plasticizer is minimal. One possibility is that the plasticizer molecules can be immobilized in the rigid polymer−silica interfacial layer and, thus, have very little effect on mobility. Another possibility is the formation of a separate polymer and plasticizer domains; i.e., plasticizer may not be embedded but instead excluded from the polymer chains for the tightly-bound components. In this scenario, the polymer segments do not have the free space (“holes” according to free volume theory) to undergo the long-range segmental motions and, thus, may lead to the ineffectiveness of the plasticizer to reduce the T_g in these samples. For the samples with more polymer adsorbed, there are more mobile components in a thicker polymer layer, with more loops and tails. These interfacial layers behave more like bulk polymer, and hence, the plasticizer is more effective in these layers. To answer these questions, studies of the plasticizer itself would be very useful, as shown by Bingermann et al.[65]

There are very few studies of the plasticization of either thin films or small amounts of polymer on solid substrates. The work of Ellison et al.[52] showed that for a thin film of either free-standing polystyrene or poly(2-vinylpyridine), the changes in T_g due to film thickness were minimized with the addition of a plasticizer, dioctyl phthalate or diluent, pyrene. For supported films of PMMA on an attractive substrate, the increases in T_g were also diminished with added plasticizer.[66] The mechanism proposed was that the plasticizer (or diluent) reduced the size of the cooperative rearranging region (CRR) of the polymer, thereby reducing the length scale for the effect of the free interface on the more inner polymer segments. In our case, the results are different for small-adsorbed amounts as it appears that the plasticizer is excluded from the tightly-bound polymer. This is due to the strong hydrogen bonding between the polymer and silica. At higher adsorbed amounts, the loosely-bound polymer, being more bulk like, probably allows the plasticizer to have a more bulk-like effect. Clearly, there are also likely differences in the two studies/systems due to the geometry of the confined polymer (film vs adsorbed on silica) and the polymer thickness (10 nm vs a few nanometers).

Conclusions

The combination of deuterium labeling with ^{2}H QE-NMR spectroscopy and TMDSC are powerful tools for studying the mobility of polymer chains and obtaining information about the segmental dynamics of polymer chains through changes in line shapes. The partial collapse of the deuterium powder pattern provided a very sensitive probe of the motion of polymers as a function of temperature. Applying these techniques to adsorbed polymers with added plasticizer yields some intriguing results. Perhaps the most interesting of these is that *there must be a minimum amount of polymer adsorbed before the plasticizer can be effective*. We have shown that the effect of plasticizer in reducing the T_g of PVAc was significant for samples with 1.4 mg/m^2 or more PVAc on silica, while it was negligible for the 0.81 mg/m^2 sample. The powder pattern line shapes for the 0.81 mg/m^2 samples did not change much with an increase in plasticizer content, while they changed significantly for the samples with more adsorbed polymer.

The NMR line shapes and TMDSC thermograms give a consistent, yet complementary, report of the effect of the interaction of the PVAc with the silica substrate. The glass transition region is shown to broaden significantly and also shift to higher temperature due to the interaction. It is particularly interesting to note that the amount of PVAc that seems to form the tightly bound polymer is less than that for PMMA, even though the latter has a smaller CRR. Obviously, the reasons for these differences need to be explored further as does the nature of the plasticizer, especially when it does not effectively plasticize the adsorbed PVAc. Both the NMR and TMSDC experiments show that the glass transition region for these adsorbed polymers is as broad as 60 K.

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Supporting Information Available: Text giving experimental information and figures showing the bar graphs representing the component spectra, tables of the component spectra used in the simulations, and a figure showing the plot of the average correlation times as a function of temperature. This material is available free of charge via the Internet at http://pubs.acs.org.

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(60) The glass transition region for the adsorbed samples was generally over a broad range of temperatures due to a wide distribution of

segmental mobility of polymer chains in the sample. For the sake of comparison of the different plasticized samples and to explain the effect in a more quantitative way we have assigned the T_g to a range of temperature over which the quadrupole powder pattern collapsed. In order to be more precise, the range extended from the temperature, where the central resonance appears up while its midpoint at a temperature where the signal intensity of the central resonance is about the same that of the powder pattern. The T_gs for all the adsorbed samples were assigned in the same way.

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