

01 Jan 2006

## Segmental Dynamics of Poly(Vinyl Acetate)- D<sub>3</sub> Absorbed on Silica by Solid State 2HNMR: Effect of Small Molecule Plasticizer

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### Recommended Citation

R. R. Nambiar and F. D. Blum, "Segmental Dynamics of Poly(Vinyl Acetate)- D<sub>3</sub> Absorbed on Silica by Solid State 2HNMR: Effect of Small Molecule Plasticizer," *Polymer Preprints*, American Chemical Society (ACS), Jan 2006.

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# SEGMENTAL DYNAMICS OF POLY(VINYL ACETATE)-d<sub>3</sub> ADSORBED ON SILICA BY SOLID STATE <sup>2</sup>H NMR: EFFECT OF SMALL MOLECULE PLASTICIZER

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## Introduction

There has been significant progress in understanding the behavior of polymeric thin films on surfaces. The change in the apparent glass transition temperature ( $T_g$ ) of supported thin polymer films with thickness ( $T_g$  – nanoconfinement effect) has been widely studied over the last fifteen years. While many studies focused on the thickness dependence of  $T_g$ , there are other aspects which are important to understand in a nanoconfined polymer system. 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, which, in turn, affects the  $T_g$  – nanoconfinement effect.

Plasticizers or low molecular mass diluents are often blended with polymers to increase flexibility by effectively shifting the  $T_g$  to lower temperatures.<sup>1</sup> The mechanism of plasticization is not understood in great detail, but the conventional model envisions a dynamic interaction between the polymer and diluent, resulting in reduced chain-chain interactions, reduced local viscosity and increased chain mobility.<sup>2</sup> In this paper we report the effect of plasticizer on the dynamics of poly(vinyl acetate) (PVAc) chains adsorbed on silica surfaces using solid-state deuterium nuclear magnetic resonance (NMR) and modulated differential scanning calorimeter (MDSC).

The deuterium NMR technique is an excellent tool to probe interfacial phenomena and study the dynamics of polymer chains on surfaces.<sup>3,4</sup> In our lab, we have used deuterium NMR extensively for characterizing different types of polymers like poly(methyl acrylate)<sup>5,6,7</sup> and PVAc<sup>8</sup> on silica surfaces. The methyl groups of PVAc have been deuterated in order to probe the mobility of their segments. Random orientations of the methyl groups, with respect to the static magnetic field, result in powder patterns in the <sup>2</sup>H NMR spectrum for segments with little or no motion. Segmental mobility averages the quadrupole couplings and ultimately leads to the collapse of the powder pattern into a single resonance for rubbery polymers when the motion is on the scale of or faster than the quadrupole interactions.

## Experimental

Vinyl acetate-d<sub>3</sub> was prepared via the interchange reaction of acetic acid-d<sub>3</sub> and vinyl propionate. A mixture of 0.167 mol of acetic acid-d<sub>3</sub>, 0.33 mol of vinyl propionate, 4.01 mmol of mercuric acetate, 0.42 mmol of concentrated sulfuric acid and a trace amount of hydroquinone were stirred in a three neck flask at 85–90 °C for 3–4 h. About 6.68 mmol of sodium acetate was added after reaction appeared to be complete and then the resultant vinyl acetate-d<sub>3</sub> was collected by distillation under reduced pressure. The product was then purified using a spinning band column. The yield was about 45% based on the amount of acetic acid used.<sup>9</sup>

Vinyl acetate-d<sub>3</sub> was polymerized in a K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/sodium-dodecyl sulfate/water emulsion. The resulting polymer had a molecular mass and polydispersity of 240 kg/mol and 2.2, respectively. The molecular masses were measured using an OPTILAB DSP Interferometer Refractometer and a DAWN EOS Light Scattering Instrument (Wyatt Technology, Santa Barbara), connected to a gel permeation instrument.

Toluene was used as the solvent for adsorption of poly(vinyl acetate) on silica. The calculated amounts of PVAc and dipropylene glycol dibenzoate (plasticizer) were dissolved in toluene and mixed thoroughly for 12 h followed by the addition of 0.2 g of silica (Cab-O-Sil M5 200 m<sup>2</sup>/g). This mixture was then equilibrated for about 72 h at room temperature. Toluene was removed by passing air through the adsorbed polymer-silica mixture, which was simultaneously agitated. Air was continuously bubbled into the sample until most of the toluene was removed. The mixture was then dried under vacuum at about 40 °C. Non-plasticized, adsorbed samples were also prepared in the same way to have a comparative study. Three different sets of adsorbed

amounts with varying plasticizer contents (0, 5, 10% based on the mass of polymer alone) were prepared.

**Table 1. Adsorbed Amounts Of The Surface Adsorbed Samples.**

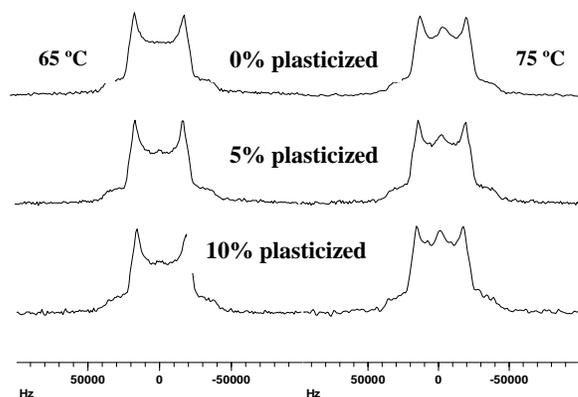
Sample Name	Adsorbed amount
Low adsorbed	0.81 mg/m <sup>2</sup> ± 0.04
Medium adsorbed	1.42 mg/m <sup>2</sup> ± 0.05
High adsorbed	1.81 mg/m <sup>2</sup> ± 0.05

The NMR spectra were obtained on a Varian VXR-400/S spectrometer equipped with a wide-line probe (Doty Scientific, Columbia, SC). The <sup>2</sup>H resonance frequency was 61.395 MHz, and the pulse sequence was delay-90°-τ-90°-τ-acquisition. The pulse width used was 2.8 μs and τ = 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 4000 to 10000. All of the spectra shown were processed by using the Mestrec software package (Santiago de Compostela University, Spain).

A TA Instruments model 2920 Modulated Differential Scanning Calorimetry (New Castle, DE) was also used for thermal analysis of the plasticized PVAc samples. Two heating scans and one cooling scan were taken from –40 °C to 150 °C, at a rate of 2.5 °C/min, modulation amplitude of ± 0.5 °C and a period of 60 s.

## Results and Discussion

The adsorbed samples of PVAc on silica with different amounts of plasticizer were prepared according to the above procedure. Thermogravimetric analysis was used to confirm the amount of plasticizer present in the adsorbed samples and also to calculate the adsorbed amounts. Quadruple echo NMR spectra for these adsorbed samples were taken as a function of temperature. The spectra of the low adsorbed amount sample (**Figure 1**) at 65 °C and 0% plasticized showed a powder pattern with a splitting of about 44 kHz between the bases of the two horns as expected for methyl groups rotating about their symmetry axis. As the plasticization of the sample increased there was a hint of a slight central component. The central component indicated segments of enhanced mobility due to the presence of plasticizer. The spectra at 75 °C had a larger central component and lower quadruple splittings compared to the ones at 65 °C which were due to the increase in mobility of polymer chains with increased temperature. The spectra of the plasticized sample at 75 °C had similar shapes to those of the non-plasticized one. This clearly indicates that at lower adsorbed amounts there is not much reduction in the glass transition temperature due to the presence of plasticizer.



**Figure 1.** <sup>2</sup>H NMR spectra for a low adsorbed amount of PVAc (0.8 mg/m<sup>2</sup>) with plasticization percentages of 0, 5, 10% at 65 °C and 75 °C.

In the spectra for the medium adsorbed amount sample (**Figure 2**) at 65 °C and 75 °C, the magnitude of the central component increased with an increase in the plasticizer amount. This shows that the effect of plasticizer was more pronounced in reducing the  $T_g$  for the medium adsorbed amount sample than for the low adsorbed amount one. The effect of plasticizer is even more

appreciable in the case of the higher adsorbed PVAc sample (Figure 3). The increase in the intensity of the central mobile component of the line shapes was considerably more in the case of the high adsorbed amount samples than in the medium adsorbed amount sample when the amount of plasticizer increased. Thus, our results show that the effect of plasticizer is more significant with increased adsorbed amounts of PVAc on a silica surface.

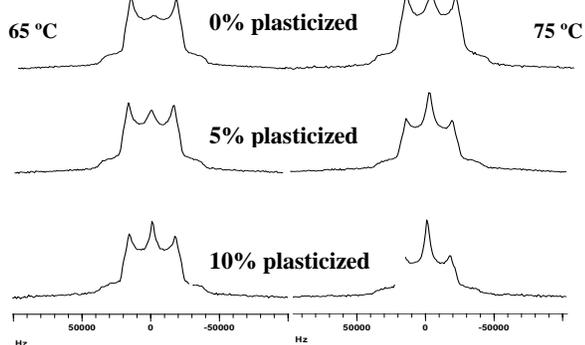


Figure 2.  $^2\text{H}$  NMR spectra for a medium adsorbed amount of PVAc ( $1.4 \text{ mg/m}^2$ ) with plasticization percentages of 0, 5, 10% at  $65^\circ\text{C}$  and  $75^\circ\text{C}$ .

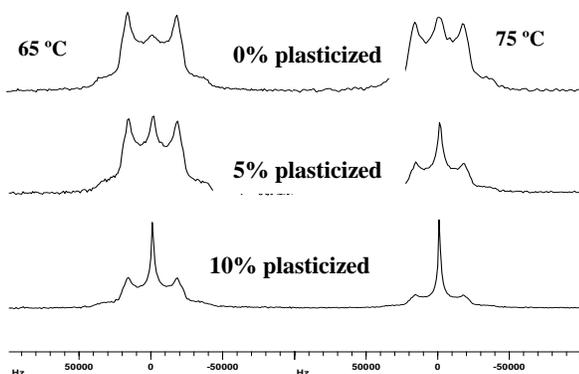


Figure 3.  $^2\text{H}$  NMR spectra for a high adsorbed amount of PVAc ( $1.8 \text{ mg/m}^2$ ) with plasticization percentages of 0, 5, 10% at  $65^\circ\text{C}$  and  $75^\circ\text{C}$ .

The MDSC derivative curves for the low adsorbed amount samples with different amounts of plasticizer are shown in Figure 4. The curves for the adsorbed samples are more complex and broader compared to that of the bulk sample. We observe that there are some major transitions, one in the temperature range of  $40\text{--}60^\circ\text{C}$  (that represents the bulk-like segments) while the other is in the range of  $60\text{--}80^\circ\text{C}$  (that represents the less mobile segments closer to the surface). There is not much difference in the curves for the three plasticized amounts, which is consistent with the  $^2\text{H}$  NMR data above. The MDSC curves (not shown here) for the other two adsorbed amounts showed gradual decrease in the  $T_g$  as the plasticized amounts increased.

In order to explain the effect of plasticizer amounts on the mobility of polymer chains (Figure 5), we propose the following model. At lower adsorbed amounts, the conformation of the adsorbed polymer molecule should be relatively flat, resulting in a higher fraction of rigid segments. Also, the segments have a strong interaction with the silica surface due to the carbonyl group on the polymer molecule. Hence, in lower adsorbed amount samples, there are fewer mobile segments compared to higher adsorbed amount samples. One possibility is that the plasticizer molecule can be immobilized in the polymer-silica interfacial layer, in the case of lower adsorbed amounts, and thus have very little effect on mobility even with a high plasticized amount. Another possibility is the formation of a separate polymer and plasticizer domain, i.e., plasticizer is not embedded in the polymer chains of the low adsorbed amount sample. This may also lead to the ineffectiveness of the plasticizer to reduce the  $T_g$  in these samples. For the higher adsorbed amount samples, there are more mobile components due to the presence of a thicker polymer layer. These interfacial layers behave more like bulk and, hence, the plasticizer is more effective in these layers.

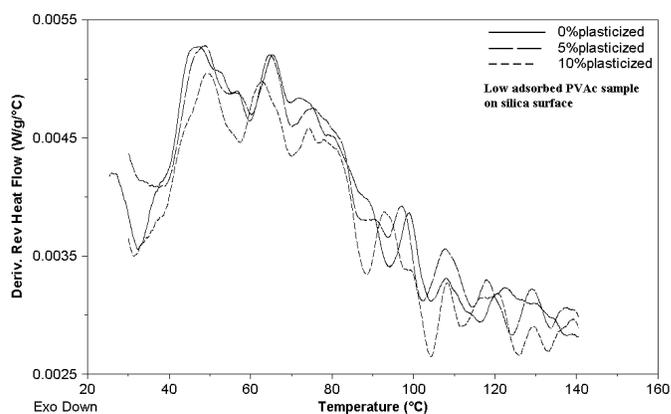


Figure 4. MDSC derivative heat flow curves for a low adsorbed amount PVAc sample on silica with different plasticized amounts.

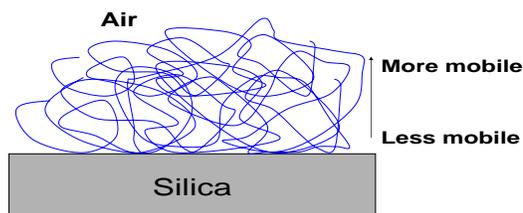


Figure 5. Schematic representation of the motional gradient in the PVAc-silica composite sample (surface bound).

## Conclusions

The combination of deuterium labeling and  $^2\text{H}$  NMR spectroscopy 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 provides a very sensitive probe of the motion of polymers as a function of temperature. We have shown that the effect of plasticizer in reducing the glass transition temperature of PVAc is significant for a high adsorbed amount sample of PVAc on silica, while it is ineffective for the low adsorbed sample. The powder pattern line shape for the low adsorbed amount samples did not change much with an increase in plasticizer content, while it changed significantly for a high adsorbed amount sample. A better understanding of this effect could be obtained with further studies. Also, the mobility of the polymer backbone decreased with a decrease in the adsorbed amount even in plasticized sample.

**Acknowledgements.** We acknowledge the National Science Foundation (NSF) and the University of Missouri-Rolla for financial support of this research.

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