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DYNAMICS OF BULK AND ADSORBED POLY(VINYL ACETATE)

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Introduction

We have recently completed a series of experiments on methyl-labeled poly(vinyl acetate)- d_3 , (PVAc- d_3)¹ and poly(methyl acrylate)- d_3 (PMA- d_3).²³⁴ The systems have been studied as a function of the adsorbed amount, molecular weight, and presence of a protonated overlayer. Using deuterium line shape analysis, we have found that around the glass transition temperature, the adsorbed polymers show the presence of a motional gradient. Polymer segments near the silica-polymer interface have less mobility than the bulk polymer and those near the polymer-air interface are more mobile than those of the bulk polymer. A schematic representation of the motional gradient is shown in Figure 1.

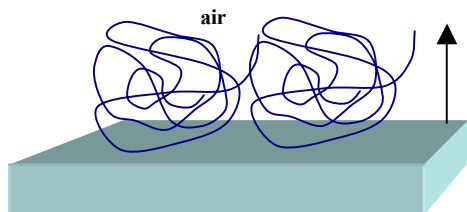


Figure 1. Schematic representation of motional gradients in adsorbed polymers.

In the present work, we report the results of 2-dimensional deuterium NMR exchange (2dX) experiments on PVAc- d_3 in bulk and adsorbed on silica. The results of these experiments can be used to identify the dynamics of the adsorbed polymer so that the nature of the motional gradient can be identified. We find that the dynamics of the adsorbed polymer around the glass transition can be described by a bimodal distribution of reorientation times.

Experimental

The synthesis of the labeled PVAc- d_3 has already been described elsewhere.¹ This material had a fairly high molecular mass, 1,200,000 Da and a polydispersity of 2.2. The polymer was adsorbed onto Cab-O-Sil silica M5 (200 m²/g) from a toluene solution. The adsorbed amount was 0.36 mg polymer/g silica that corresponded to roughly a monolayer of coverage when the toluene was present. The adsorbed samples were dried in a vacuum oven at ca. 70 °C.

The deuterium NMR spectra were obtained at 61.3 MHz on a modified VXR-400S spectrometer, using a typical 2dX pulse sequence,⁵ with approximately 2 T₁'s as relaxation delays, a 93 kHz B₁ field, and varying mixing times. The results were fit to multicomponent distributions of correlation times.

Results and Discussion

Shown in Figure 2 is the 2dX spectra for PVAc- d_3 in bulk at 43 °C with a mixing time of 50 ms. The spectra show a significant amount of exchange under these conditions. The fitting of a series of these spectra for the bulk polymer at different temperatures resulted in the correlation time distributions shown in Figure 3. It is observed that the distribution of segmental correlation times is found to be a broad, but single modal distribution. This is consistent with our original notion that the motion of the segments in bulk could be described as "homogeneous." Of course, we note that this homogeneous behavior involves a distribution of correlation times that can be as much as three decades in breadth. Nevertheless, all of the segments in the bulk sample have basically the same motions.

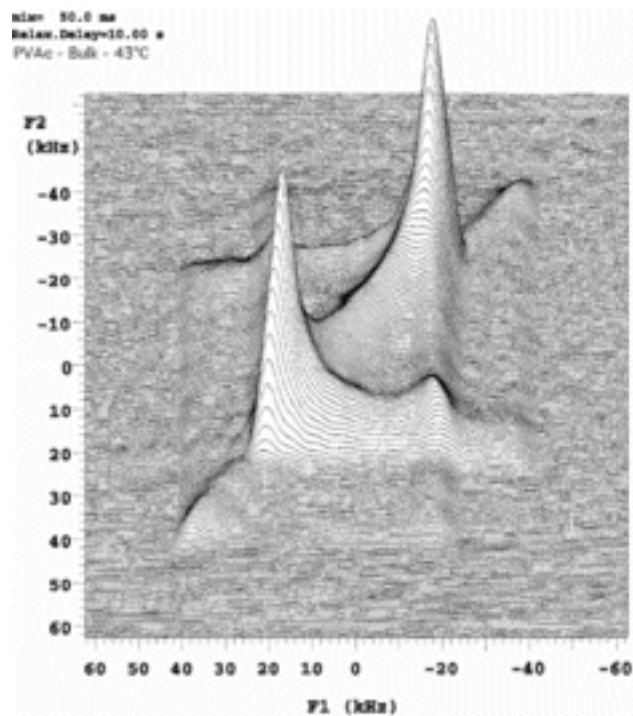


Figure 2. 2dX spectrum of PVAc- d_3 in bulk at 43 °C with a mixing time of 50 ms.

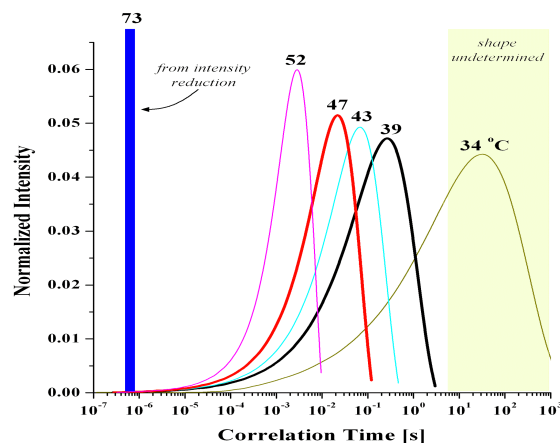


Figure 3. Distributions of correlation times for PVAc- d_3 in bulk as a function of temperature.

Shown in Figure 4 are the 2dX spectra for PVAc- d_3 on silica at 61 °C and a mixing time of 100 ms. Even at this temperature that is much higher than that for the bulk polymer in Figure 2, and longer mixing times, much less exchange is found. Most of the intensity is along the diagonal. For a variety of mixing times and different temperatures, the correlation time distributions that fit the data are shown in Figure 5. Interestingly, these data can be fitted by a bimodal distribution of correlation times. The two modes are well separated in frequency and the fast mode is faster than that of the bulk polymer at similar temperatures. The slower mode is much slower than that of the bulk polymer. Again, this information is consistent with the previously studied systems based on line-shape analyses. It can also be said that, based on the bimodal distribution, the surface polymer can be considered to be "heterogeneous" with respect to segmental dynamics. In other words, the behavior of the polymer segments depends on the position of the segments relative to the silica surface.

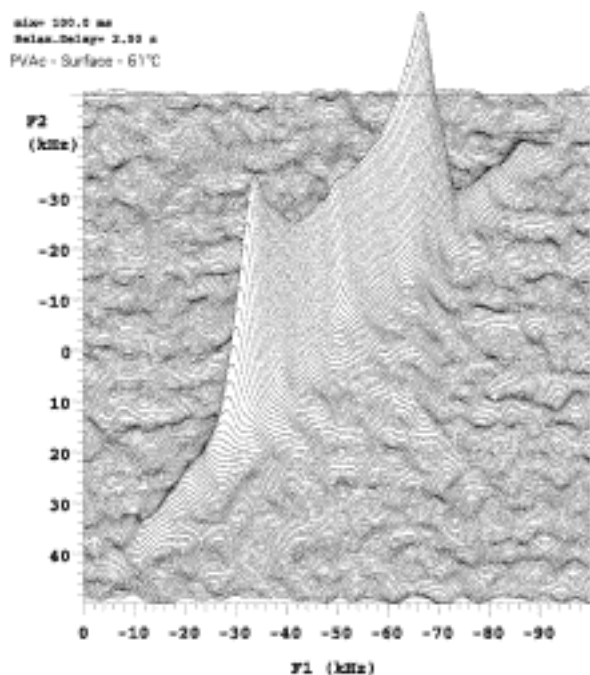


Figure 4. 2dX of PVAc- d_3 in bulk at 61 °C and a mixing time of 100 ms

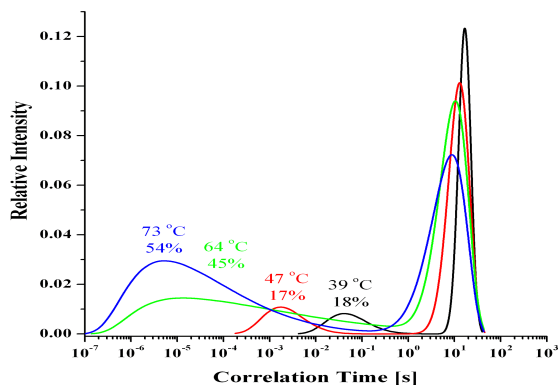


Figure 5. Distributions of correlation times for PVAc- d_3 adsorbed on silica as a function of temperature.

Based on both the line-shape analyses and the correlation times, the two modes for the surface polymer can be assigned to the rubbery and glassy components of the adsorbed species. These two seem to be clearly separated and the amounts of the rubbery species increase with increases in temperature. Thus, the picture that emerges is one where there are separated rubbery segments (near the air interface) and glassy segments (near the silica interface). In order to have this kind of system, there must be a relatively sharp distinction between the two layers.

Conclusions

The 2D exchange spectra of PVAc- d_3 can be used to quantify the segmental dynamics, including its behavior on silica surfaces. Especially interesting behavior is found around the glass transition temperature. In bulk, a broad distribution of correlation times fits the data. On silica, a bimodal distribution of correlation times fits the data. These two nodes may be associated with rubbery and glassy segments.

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