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DYNAMICS OF POLY(VINYL ACETATE)- d_3 ON SILICA

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Introduction

Poly(vinyl acetate) (PVAc) is an important polymer in applications because of both its bulk and surface characteristics. Its chain architecture gives it a low T_g and, generally, good qualities for processing and applications, which include paints, adhesives, thin films and surface coatings.

In this study, we investigate the surface dynamics of PVAc adsorbed onto silica with deuterium nuclear magnetic resonance (^2H NMR). For dynamics studies, ^2H NMR is an excellent technique because it uses an innocuous probe that can report on correlation times (τ_c) from approximately 10^{-8} s to 10 s.¹ We report the use of two-dimensional exchange NMR (2D-X) and a side-chain methyl- d_3 probe to investigate surface dynamics with τ_c 's in the range of 10^{-6} to over 1 s.

Experimental

Vinyl acetate- d_3 was prepared via the interchange reaction of deuterated acetic acid- d_3 and vinyl propionate. The vinyl acetate- d_3 was then polymerized in a $\text{K}_2\text{S}_2\text{O}_8$ / sodium-dodecyl sulfate/ H_2O emulsion. The resulting polymer had molecular mass and polydispersity of 1200 kg/mol and 2.2, respectively.²

A monolayer of PVAc- d_3 was adsorbed onto Cab-O-Sil silica M5 (200 m^2/g , Cabot Corp., Tuscola, IL) from a toluene solution at room temperature. The resulting sample had 0.36 mg PVAc/mg of silica, which corresponds to a monolayer.²

The ^2H NMR spectra were acquired at 61.3 MHz on a modified VXR-400S spectrometer with, typically, a 2-3 s relaxation delay between scans and $2.7 \mu\text{s}$ 90° pulses.³ The relaxation delay was approximately two T_1 's. Fully relaxed spectra showed small increases in the diagonal intensity. A five pulse 2D-X sequence was used with a $2 \mu\text{s}$ t_1 echo, a $25 \mu\text{s}$ t_2 echo, and varying mixing times (τ_m).³

Results and Discussion

Methyl deuterons quickly reorient about their C_3 axis, resulting in a compressed powder pattern with an apparent quadrupolar coupling of about 40 kHz. This value is slightly less in PVAc because of the asymmetry caused by the carbonyl oxygen.⁴ For such quickly rotating methyl- d_3 groups, 2D-X experiments report on the C_3 axis motion, only. For PVAc, the methyl- C_3 axis reorients both from a side-chain rotation and backbone reorientations.

The 2D-X spectra at various temperatures and τ_m 's are shown in Figures 1-6. The intensity along the diagonal represents the C_3 axis of methyl- d_3 groups that were static during τ_m ; intensity in the 2D plane (exchange) represents C_3 axis that reorient with τ_c 's on the order of τ_m (ms); and, the central intensity represents methyl- d_3 groups that are reorienting isotropically with $\tau_c < 10^{-6}$ s.

The prominent diagonal, small exchange, and isotropic intensity in the spectra suggest that the PVAc monolayer is composed of both a rigid ($\tau_c > 10$ s) and a quickly reorienting ($\tau_c < 10^{-4}$ s) fraction. There is little motion between these two extremes (exchange). This bimodal nature is further supported by the lack of exchange as τ_m is increased, and also by the increased isotropic intensity and lack of increased exchange as temperature increases. Presumably, the static fraction is from chains on the silica surface and the fast fraction from chains at the air surface.

It is interesting to note that the bulk polymer samples show complete exchange for the times and temperatures shown in this report. Thus, the majority of PVAc segments on the surface are much more rigid than those in bulk.

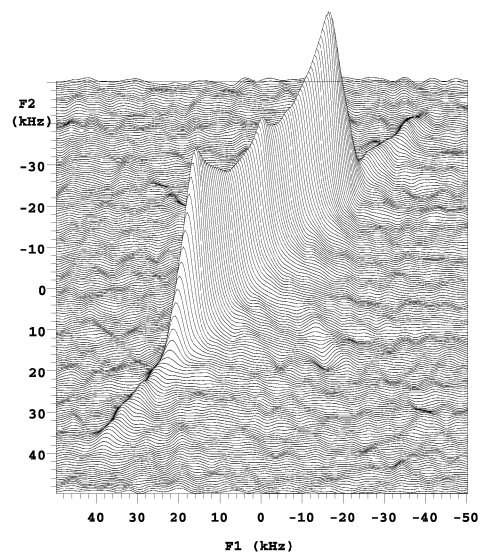


Figure 1. 2D-X spectrum of a monolayer of PVAc- d_3 on silica at 61 °C and $\tau_m = 1$ ms.

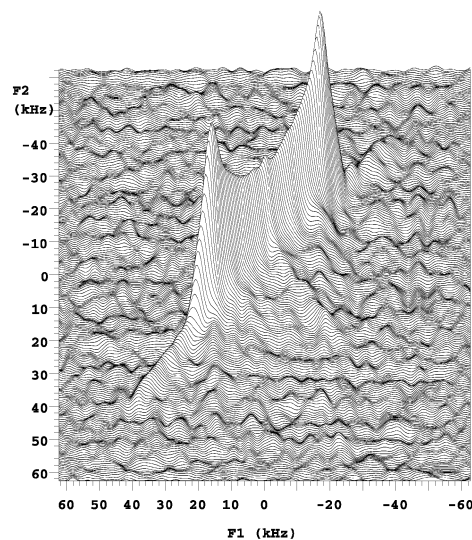


Figure 2. 2D-X spectrum of a monolayer of PVAc- d_3 on silica at 61 °C and $\tau_m = 300$ ms.

Conclusions

The 2D-X NMR can be applied to very thin layers of polymers and yield information about polymer reorientation. A more thorough analysis needs to be done to extract the motional rates and angular excursion from this data. However, it is clear from the spectra that the majority of surface PVAc species are much less mobile than in bulk.

Acknowledgements

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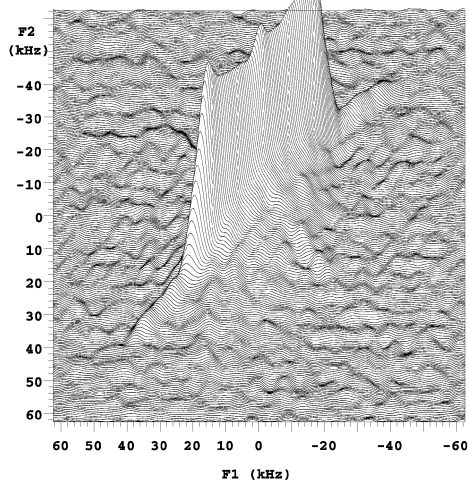


Figure 3. 2D-X spectrum of a monolayer of PVAc- d_3 on silica at 69 °C and $\tau_m = 1$ ms.

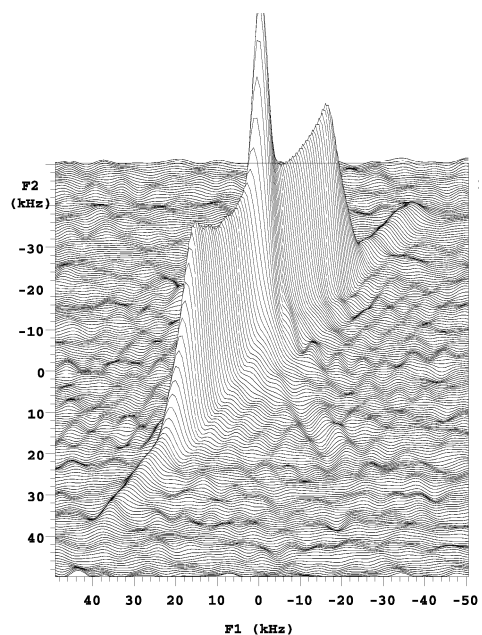


Figure 5. 2D-X spectrum of a monolayer of PVAc- d_3 on silica at 82 °C and $\tau_m = 1$ ms.

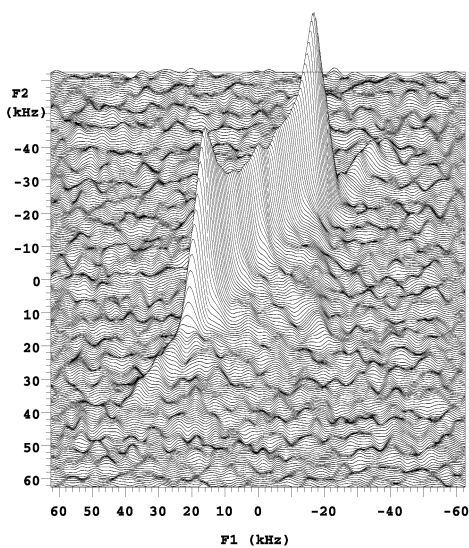


Figure 4. 2D-X spectrum of a monolayer of PVAc- d_3 on silica at 69 °C and $\tau_m = 300$ ms.

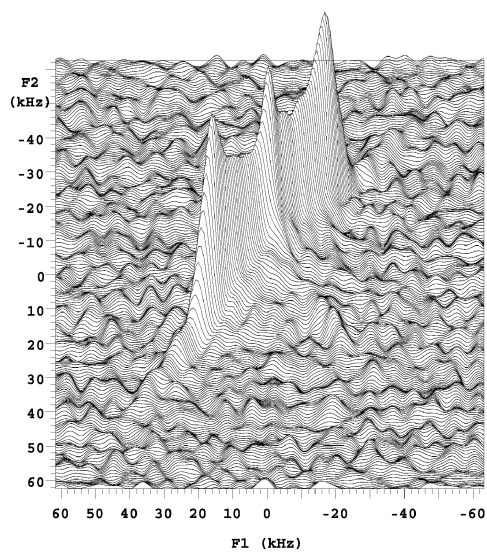


Figure 6 2D-X spectrum of a monolayer of PVAc- d_3 on silica at 82 °C and $\tau_m = 300$ ms.

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