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DEUTERIUM NMR STUDIES OF SEGMENTAL DYNAMICS OF ANOPORE-ADSORBED POLY(METHYL ACRYLATE)

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Introduction

Studies of segmental dynamics of polymers at interfaces provide a basis for understanding the properties of composite materials. Interfacial phenomena in multi-phase systems need to be understood as devices made from multi-phase polymeric systems become smaller.

Various techniques have been used to investigate interfacial polymers at the air-polymer-solid interface; for example, ellipsometry,¹ X-ray,² and neutron reflectometry.³ These techniques typically characterize the structure (often the thickness) of the polymer layer and are normally used to determine the glass-transition temperature (T_g) through a break in the thickness-temperature curve.

There have been a few reports where the dynamics of polymers at the surface-air interface has been probed directly or inferred by NMR⁴ or ESR⁵. Using deuterium quadrupolar echo techniques on poly(vinyl acetate)- d_3 , Blum et al.⁶ showed that a deuterated methyl group could be used to probe the dynamics of adsorbed polymers. Lin and Blum^{7,8} observed that molecular mass affected segmental dynamics in both bulk and silica-adsorbed poly(methyl acrylate) (PMA- d_3). As temperature increased, both high and low molecular mass samples showed increased motional rates, with significantly faster motional rates in the high molecular mass samples. They also reported that lower adsorbed amounts exhibited relatively slower motional rates than higher adsorbed amounts did.

Anopore is an inorganic membrane that is produced by anodic oxidation of aluminum.⁹ Since the process is electrochemical, the conditions can be controlled and reproducible pore structures with narrow pore-size distributions can be obtained. They are available in 4.7 cm discs, 60 μm thick, with 0.2 or 0.02 μm diameter pore sizes. The anopore membranes are usually used for filtration purposes. Anopore has been used as a confining substrate in studies of polymer adsorption.¹⁰⁻¹² However, not much is known about the adsorption mechanism or the state of the polymer in them.

In this paper, we examine the adsorption of PMA- d_3 on anopore by ^2H NMR. We look at the process of adsorption, the effect of adsorbed amounts, and the effect of pore size. The results show little difference in the effect of pore size, or adsorbed amounts on the mobilities of PMA- d_3 segments.

Experimental

Deuterated poly(methyl acrylate) (PMA- d_3) was synthesized in our lab by a method described elsewhere.¹³ The samples used had molecular masses of 33 and 37 kDa. For practical purposes, we consider these two molecular masses to be equivalent in terms of the behavior studied.

Anopore was obtained from Whatman Inc. The membrane was cut into 4 x 10 mm pieces and adsorption was carried out by immersing these small pieces in a 6% mass solution of PMA- d_3 in chloroform for 5 min. A lower concentration solution (3%) was also used and yielded a lower adsorbed amount. The samples were then removed from solution and dried in the open air for 45 min. A sample of 33 kDa PMA- d_3 on 0.2 μm pore-size anopore was washed in chloroform after adsorption but before drying. The adsorbed amounts were determined using thermogravimetric analysis (TGA).

NMR spectra were obtained using a Varian VXR-400/S spectrometer. The quadrupole-echo pulse sequence (delay-90 $^\circ$ -tau-90 $^\circ$ -tau-acquisition) was used with a ^2H frequency at 61.39 MHz. The 90 $^\circ$ pulse-width was 2.7 μs with an echo time of 30 μs . For the bulk sample, 128 scans were collected, while for the adsorbed samples, 4096 to 16384 scans were collected. Spectra were made for all samples at temperatures from 25 to 65 $^\circ\text{C}$ at 5 $^\circ\text{C}$ intervals.

Theoretical simulations of the spectra were made, based on the Multiple Axis Quadrupolar Exchange program written by Greenfield, et al.¹⁴

Results and Discussion

Adsorption isotherms for PMA- d_3 are shown in **Figure 1**. Samples were taken from adsorption at 5-min intervals in two portions: (a) directly dried after patting with tissue paper, and (b) washed in chloroform before drying. The adsorbed amount was observed to remain relatively constant after 5 min.

After the 30-min adsorption, some pieces of anopore were left in solution and tested for the adsorbed amount after 12 hours. The adsorbed amount was found to be the same. Thus, equilibration seems to occur rather fast.

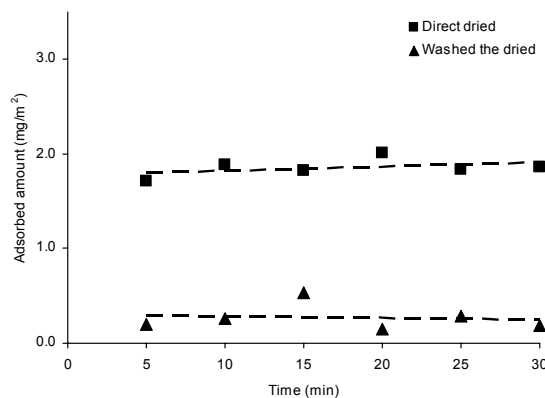


Figure 1: Adsorption isotherms for PMA- d_3 adsorbed on 0.2 mm pore-size anopore.

Variable temperature ^2H NMR spectra for bulk and the sample of 33 kDa PMA- d_3 adsorbed on 0.02 μm pore-size anopore are given in **Figure 2**. The adsorbed amount was found to be 1.1 mg/m^2 . The spectra for the bulk sample show the emergence of a middle peak at 35 $^\circ\text{C}$. The middle peak indicates the presence of segments with higher mobility. As the temperature increased, the middle peak got more intense as the outer 'horns' collapsed. The adsorbed sample began showing the middle peak at 50 $^\circ\text{C}$, which got more intense as the outer 'horns' collapsed at higher temperatures.

The spectra shown in **Figure 3** are for the adsorbed samples of 37 kDa PMA- d_3 and 33 kDa PMA- d_3 , both on 0.2 μm pore-size anopore. The adsorbed amounts were 1.4 mg/m^2 and 4.2 mg/m^2 , respectively. Both sets of spectra showed the emergence of a middle peak at 50 $^\circ\text{C}$ that got more intense at higher temperatures. **Figure 4** was obtained from the washed sample of 33 kDa PMA- d_3 adsorbed on 0.2 μm pore-size anopore. The spectra showed a residual powder pattern, even at higher temperatures where none was obvious in the bulk sample. The spectrum marked with x 5 has been magnified 5 times to illustrate the residual powder pattern at 75 $^\circ\text{C}$. This can be attributed to restricted motion due to adsorption. A lower adsorbed amount results in the polymer adsorbing in configurations that are more flat, hence there is more restricted motion of the segments.

The similarity in the variable temperature spectra for all adsorbed samples, except for the one that was washed, indicates that the nature of adsorption is the same regardless of the pore size. For the adsorbed amounts studied (1.1-4.2 mg/m^2), the variable temperature spectra also showed little difference.

The simulated spectra were based on a Pake powder pattern with a reduced quadrupolar coupling constant (QCC) of 50 kHz. The simulated spectra are not shown. The simulations generally required a combination of two types of motion, each at different rates along different axes. The motional rates increased with temperature, from $5.00 \times 10^2 \text{ s}^{-1}$ (for both kinds of motion) for the least mobile, to $5.00 \times 10^5 \text{ s}^{-1}$, for the fast motion.

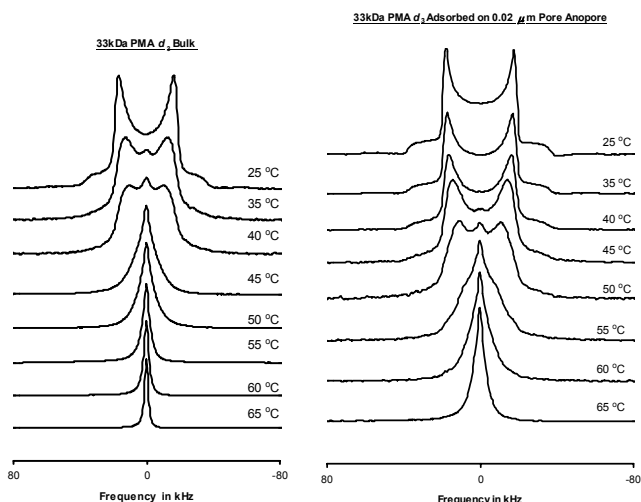


Figure 2. Variable temperature ^2H NMR spectra for 33 kDa PMA- d_3 in bulk (left) and when adsorbed (1.1 mg/m^2) on anopore of $0.02 \mu\text{m}$ pore-size (right).

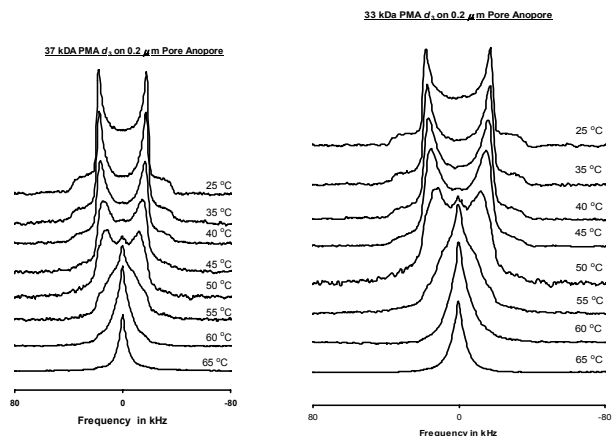


Figure 3. Variable temperature ^2H NMR spectra for 37 kDa PMA- d_3 adsorbed (1.4 mg/m^2) on anopore of $0.02 \mu\text{m}$ pore-size (left) and 33 kDa PMA- d_3 adsorbed (4.2 mg/m^2) on anopore of $0.2 \mu\text{m}$ pore-size (right).

33 kDa PMA d_3 on $0.2 \mu\text{m}$ Pore Anopore (Washed)

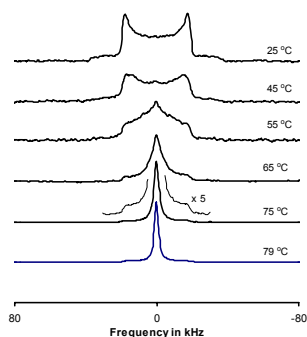


Figure 4. Variable temperature ^2H NMR spectra for 33 kDa PMA- d_3 adsorbed (0.6 mg/m^2) on anopore of $0.2 \mu\text{m}$ pore-size. The $75 \text{ }^\circ\text{C}$ has been magnified five times to show the residual powder pattern.

Conclusions

The bulk PMA- d_3 shows NMR T_g at around $35 \text{ }^\circ\text{C}$, by using the deuterium line-shape method. The adsorbed samples show heterogeneous behavior with most of the material having mobilities that are slower than those in bulk. There is no significant difference in the effect on adsorption between the 0.02 and $0.2 \mu\text{m}$ pore-sizes of anopore, and from 1.1 to 4.2 mg/m^2 adsorbed amounts, the effect on the mobility is the same. We are currently investigating the reasons for the similarity of the spectra.

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