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Deuterium NMR of Adsorbed Poly(methyl acrylate)-d<sub>3</sub>

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## Introduction

The dynamics of polymers at interfaces are important in a variety of applications, especially where those applications depend on the mechanical or surface properties. Unfortunately, the surface properties of interfacial species like polymers used in composites are not easily measured macroscopically. Microscopic techniques, especially spectroscopic ones, have been successful.

In our laboratory we have been successful in applying NMR to determine the behavior of adsorbed polymers.<sup>1,2</sup> NMR has several advantages for this kind of study, the principal ones being that it can be used on opaque materials, different nuclei can be used as probes, and interfacial material can sometimes be selectively probed. The chief disadvantage is that the inherent insensitivity of NMR is compounded by filling the sample with the substrate.

Deuterium NMR has been the nucleus of choice in our laboratory. It has a moderate quadrupole moment and, for polymers, the spectra for deuterium bonded to a carbon can be representative of the behavior of the reorientation of the C-D bond. Surface selectivity can also be obtained through the use of a deuterium label, if the label is at the interface. We have applied these techniques to poly(vinyl acetate)-d<sub>3</sub> adsorbed on silica<sup>3</sup> and postulated that a motional gradient existed within a single molecule on the surface. In that case, polymer segments near the polymer-silica interface (in or close to trains) moved more slowly than polymer segments near the air-polymer interface (loops and tails). More recently we have extended these studies to poly(methyl acrylate)-d<sub>3</sub> (PMA) on silica<sup>4</sup> and found that a similar trend had been found for that polymer, although its detailed nature depended on the relative amount of polymer adsorbed.

In the present work, we report studies of the dependence of the dynamics of PMA-d<sub>3</sub> on both the amount of polymer adsorbed and also the molecular weight of the polymer used. We find that both affect the behavior of the adsorbed polymer probably due to the conformation of the polymer on the surface.

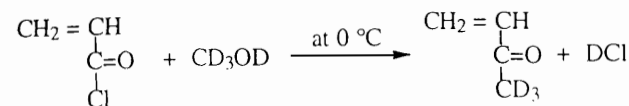
## Experimental

Methyl acrylate-d<sub>3</sub> was synthesized from methanol-d<sub>4</sub> and acryloyl chloride.<sup>4</sup> 12 ml of methanol-d<sub>4</sub> (Aldrich Chemical, Milwaukee, WI), used as received, was added to 25 ml of freshly distilled acryloyl chloride (Aldrich) at 0 °C for 60 minutes. Distilled water was added to the reaction mixture to separate the excess methanol-d<sub>4</sub>. The aqueous phase was separated and the organic phase was dried over calcium hydride. The yield of the product, methyl acrylate-d<sub>3</sub>, was 80%. The monomer was then distilled under vacuum. The level of deuteration of the monomer was found to be about 100% by proton NMR.

High molecular weight PMA-d<sub>3</sub> (HMw) was prepared from the monomer via emulsion polymerization. The emulsion was prepared by adding 100 ml of water and 20 ml of the monomer to 0.028 g of potassium persulfate and 0.33 g of sodium dodecylsulfate. The reaction temperature was kept at 60 °C for 2 hours. The yield of the polymer was 80%, based on the amount of monomer used. The M<sub>w</sub> and polydispersity of as measured by gel permeation chromatography (GPC) in tetrahydrofuran (THF) were measured to be 1.10 x 10<sup>6</sup> g/mol and 2.22, respectively.

Low molecular weight (LMw) PMA-d<sub>3</sub> was prepared from methyl acrylate-d<sub>3</sub> via free radical polymerization. The polymerization was conducted by adding 50 ml of toluene and 10 ml of the monomer to 0.03 g of 2,2'-azobis(isobutyronitrile) (AIBN) as the initiator and heating to 60 °C for 2 hours. The yield of the polymer was 80%, based on the amount of monomer used. The

LMw PMA-d<sub>3</sub> had a M<sub>w</sub> of 7.05 x 10<sup>4</sup> g/mol and a polydispersity of 2.50. The reaction scheme is shown below.



All of the adsorption experiments were conducted by first preparing solutions of the polymer in toluene or solvent mixtures of benzene/acetonitrile. The solutions were allowed to equilibrate at 25 °C in centrifuge tubes with known quantities of Cab-O-Sil M5 fumed silica (Cabot Corp, Tuscola, IL), with a surface area of 200 m<sup>2</sup>/g, in a mechanical shaker for 48 h. The tubes were centrifuged and the coated silica was washed several times with the same solvents. The polymer-coated silica was then dried under vacuum at 70 °C for 6 h. The equilibrium concentration of polymer in the supernatant liquid was determined gravimetrically after drying. The amount of polymer adsorbed was calculated based on knowledge of the initial and final concentrations of the polymer and the amount of silica used. The adsorption isotherm measurements were made using the protonated PMA sample. Surface samples with different adsorbed amounts of the deuterated polymer on silica were prepared with an equilibrium concentration of approximately 15 mg/ml.

The NMR spectra were obtained on a Varian VXR-400/S spectrometer equipped with a wideline probe (Doty Scientific, Columbia, SC), a high power amplifier and fast digitizer. The <sup>2</sup>H resonance frequency was 61.395 MHz. The quadrupole-echo pulse sequence was used (delay - 90°x - τ - 90°y - τ - acquisition). The 90° pulse width was 2.7 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 1,000 to 100,000, depending upon the coverage. The distortion of the line shape due to the effect of finite pulse width was estimated to be less than 3% over the spectral range of 80 kHz. Consequently no correction for this effect was made. All of the spectra shown in this paper were processed with Felix (Biosym, San Diego, CA). There was no line broadening applied to the spectra.

Spectral simulations of the deuterium line shapes were based on a rigid component, a Pake powder pattern, with reduced splitting between the two horns of 37.5 kHz, corresponding to a residual quadrupole coupling constant (QCC) of 50 kHz. The reduced splitting was due to methyl group's fast rotation about its symmetry axis. For the deuterium nucleus (spin quantum number, I = 1), the quadrupolar splitting, Δν<sub>q</sub>, between the two different allowed transitions is given by:<sup>34</sup>

$$\Delta\nu_q = (3/4)(e^2qQ/h)(3\cos^2\theta(t) - 1 - \eta\sin^2\theta(t)\cos^2\phi) \quad (1)$$

where e<sup>2</sup>qQ/h is the quadrupole coupling constant, t is time, and θ and φ are the spherical polar angles for the orientation of the principle axis system of the electric field tensor relative to the applied static magnetic field, B<sub>0</sub>, and η is the asymmetry parameter. For our case with rapid methyl group rotation, the value of η can be taken as 0 and the 3cos<sup>2</sup>θ(t) - 1 term can be further decomposed into the following:<sup>35</sup>

$$\langle 3\cos^2\theta(t) - 1 \rangle = (1/2) \langle 3\cos^2\beta(t) - 1 \rangle (3\cos^2\chi - 1) \quad (2)$$

where the <> represents the time average, the β(t) is the angle between the B<sub>0</sub> and the rotation axis, and the χ is the angle between the rotation axis and the C-D bond. Since χ is 70.5° for a methyl group, the (3cos<sup>2</sup>χ - 1) term is reduced and the quadrupolar splitting is reduced to one third of its original value in the absence of other motion. Values for the QCC of methyl groups are typically on the order of 150 - 170 kHz.<sup>36</sup>

## Results and Discussion

Shown in Figure 1 are the deuterium NMR spectra of HMw PMA-d<sub>3</sub> at 52 °C for different coverages. The coverage labelled 1.0 Am is that corresponding to the maximum adsorption amount in toluene. Also shown for comparison is that for bulk PMA-d<sub>3</sub>. The bulk spectrum shows the beginnings of collapse to an isotropic, narrow resonance. This resonance is homogeneous in terms of all of the polymer segments having similar motion. In contrast, the surface adsorbed species have heterogeneous behavior. We believe that this is representative of a continuous distribution of mobilities on the surface. However, due to the intensity profile as a function of correlation times,<sup>5</sup> the spectra show the characteristics of a two-component line shape.

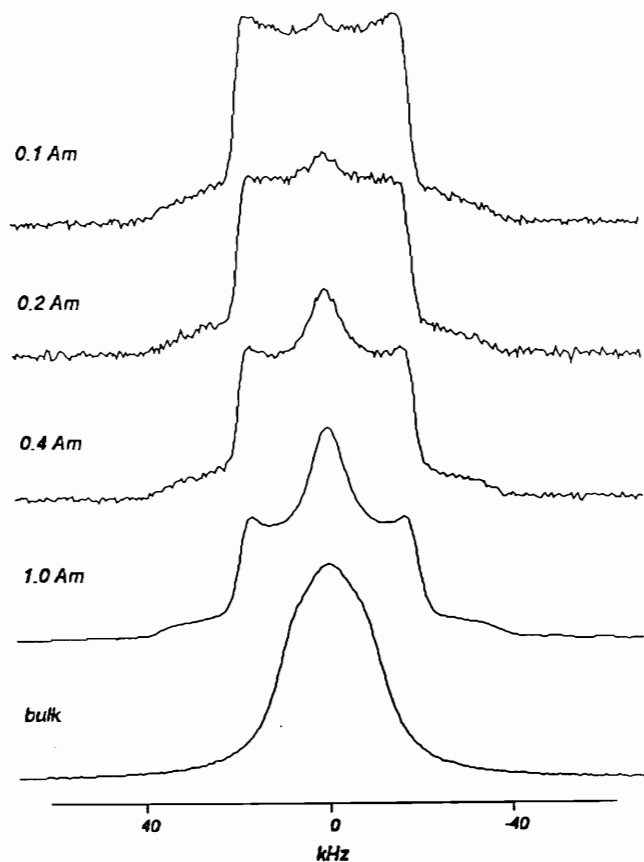


Figure 1. Deuterium NMR spectra of HMw PMA-d<sub>3</sub> as a function of coverage on silica at 52°C.

It is obvious from the spectra that there is a fraction of segments on the surface that are *more* mobile than bulk, as well as a fraction that are *less* mobile than those in bulk. We assign these to the polymer segments near the air and silica interfaces, respectively. As the adsorbed amount decreased, the relative amount of material with decreased mobility increased. This is consistent the surface polymer having with fewer segments in loops and tails as the adsorbed amount decreased.

The effect of segmental mobility as a function of molecular weight is shown in Figure 2 at relative coverages of 1.0 Am for each of the polymers. In general, the lower molecular weight polymer has more segments of lower mobility than the one with higher molecular weight. This is consistent with the assumption that loops in the lower molecular-weight polymer were smaller.

Thus, on average, the segments in the lower molecular-weight polymer are closer to those segments attached to the silica. This is in contrast to the behavior of bulk polymers where lower molecular-weight polymer segments have higher mobility than those of the higher molecular-weight polymer segments.<sup>6</sup>

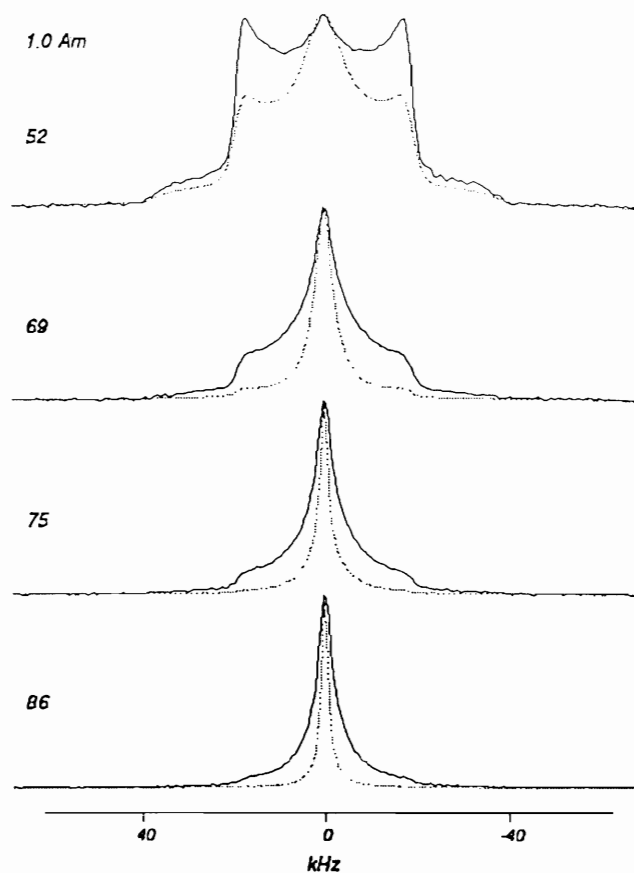


Figure 2. Deuterium NMR spectra of LMw (solid) and HMw (dashed) PMA-d<sub>3</sub> as a function of temperature on silica at a coverage of 1.0 Am.

## Conclusions

A heterogeneous distribution of segmental mobility is found for PMA-d<sub>3</sub> segments adsorbed on silica. Less mobile segments are found at the polymer-silica interface, while more mobile material is found at the air-polymer interface. A motional gradient is believed to exist within a single polymer molecule. The relative amounts of the less mobile component increases as the adsorbed amount decreases. In contrast to the behavior of the bulk polymers, the LMw surface PMA has a lower mobility than that of the HMw polymer.

## Acknowledgements

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