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SEGMENTAL DYNAMICS IN POLY(METHYL ACRYLATE)- d_3 ON STRONGLY AND WEAKLY ADSORBING SILICA SURFACES

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Introduction

The segmental dynamics of a polymer on a solid surface appears to be significantly different than that in bulk. The strength of the interaction between polymer segments and a solid surface is likely to be an important factor affecting the segmental mobility of the polymers.

Studies of polymers on a weakly adsorbing surface would provide additional understanding of their motional characteristics on surfaces. In a recent NMR study by Rivillon et al.,¹ chain dynamics was seen to be different for samples, even when there was no specific interaction with the surface. Peanasky et al.² have found a restricted segmental dynamics for the polyphenylmethylsiloxane samples at weakly adsorbing surfaces. Zheng et al.³ observed a significant difference from bulk dynamics on both strongly and weakly interacting interfaces for poly(styrene) (PS) and poly(2-vinylpyridine). Mechanical properties of weakly interacting poly(methyl acrylate) (PMA)-silica composites were seen to become poorer than the ones with stronger interactions.⁴ Contrasting results for PS on silicon surfaces with X-ray reflectivity also highlighted the importance of the surface-polymer interaction for thin films.^{5,6} Wallace et al.⁵ explained that the contrasting results were due to a difference in the surface characteristics. A stronger surface-polymer interaction on a hydrogen-terminated silicon resulted in an increase in glass transition temperature (T_g) for thin films of PS, while Keddie et al.'s work⁶ on a silicon native-oxide surface with the same polymer indicated a decrease in T_g for thin films due to a weaker interaction.

The segmental dynamics of PMA- d_3 on a strongly adsorbing surface was previously studied using the deuterium (^2H) quadrupole-echo NMR and modulated differential scanning calorimetry.⁷⁻⁸ In this study, the segmental dynamics of PMA on a weakly adsorbing surface was investigated with ^2H quadrupole-echo NMR and compared to that in bulk and on a strongly adsorbing surface.

Experimental

A detailed description of the synthesis of the methyl acrylate- d_3 is given somewhere else.⁸ PMA-38K ($M_w = 38000$ g/mol) and PMA-77K ($M_w = 77000$ g/mol) samples, deuterated on methyl groups, were synthesized by atom transfer radical polymerization (ATRP).⁹ The polydispersities were 1.15 and 1.26, respectively. Amorphous untreated fumed silica (M-5 grade, Cabot Corp., Tuscola, IL) was dried in an oven at 450 °C for 24 h before use. Amorphous treated silica (TS-530 grade, Cabot Corp., Tuscola, IL) was dried at 110 °C to prevent the degradation of the treated groups on the silica surface. For TS-530 (weakly adsorbing surface), most of the surface hydroxyl groups on M-5 grade silica (strongly adsorbing surface) were replaced with trimethylsilyl groups. Solutions of PMA in toluene were prepared and mixed with the silica samples in separate tubes to prepare the adsorbed samples. The mixtures were placed on a mechanical shaker for 48 h and were centrifuged for an hour after that. The supernatant liquid was decanted and the solid-containing portion was kept in a vacuum oven for 36 h. Thermogravimetric analysis was used to determine the adsorbed amounts of polymer samples.

NMR spectra were obtained using a VARIAN VXR-400/S spectrometer. The quadrupole echo pulse sequence (delay- 90_y - τ - 90_x - τ -acquisition) was used with the ^2H frequency at 61.39 MHz. 256 scans were used for the bulk polymer and from 4096 to 8192 scans for the adsorbed samples.

Results and Discussion

The powder pattern for a solid sample collapses to a single liquid-like resonance in a ^2H NMR experiment with an increase in temperature. The splitting between the horns (quadrupole splitting) of the powder pattern averages out to zero with rapid isotropic rotational motion at higher temperatures. The broader powder pattern represents a rigid component in the spectra that is mostly from the less-mobile parts of the polymer chains.

^2H NMR spectra of the bulk PMA-38K sample are shown in **Figure 1**. A slightly distorted Pake powder pattern was present at 25 °C due to slight mobility of the chains. A mobile component appeared at 35 °C in the middle

of the powder pattern. At 40 °C, the middle component became even more apparent. However, the spectrum still had the features from the less-mobile components as a broad resonance. The superposition of more-mobile and less-mobile components at 35 and 40 °C is indicative of the heterogeneity of the segmental dynamics in the bulk sample through the glass transition region. The powder pattern collapsed to a single resonance with further increase in temperature. No apparent residual powder pattern was present in the spectrum at higher temperatures.

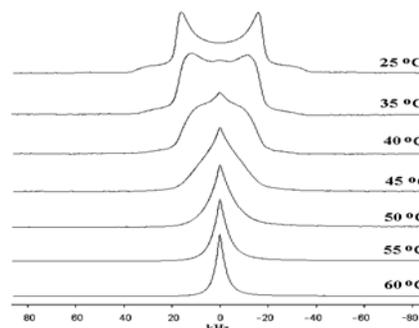


Figure 1. ^2H NMR spectra for the bulk PMA-38K.

^2H NMR spectra of the PMA-38K sample adsorbed on untreated (0.84 mg/m²) and treated silica (0.82 mg/m²) are shown in **Figure 2**. Untreated silica is a strongly adsorbing surface for the polymer due to the surface hydroxyl groups which can form hydrogen bonds with the carbonyl groups of the polymer. A solid-like powder pattern appeared from 35 °C to 45 °C with no significant distortion of the line shape in **Figure 2(a)**. At 55 °C, a motionally-narrowed component appeared in the spectrum. The intensity of the mobile component increased with temperature. However, a significant amount of residual solid powder pattern was present even at temperatures of 60, 70 and 80 °C.

^2H NMR line shapes of the PMA-38K sample adsorbed on a treated silica surface is shown in **Figure 2(b)**. The surface of the untreated silica contained mostly bulky trimethylsilyl groups that were less attractive to the polymer segments. Therefore, the chains were more weakly adsorbed. The powder pattern, compared to a rigid Pake pattern, was slightly distorted at 35 °C due to the mobility of the segments on the surface. At 45 °C, the powder pattern started to collapse and a motionally-narrowed component appeared in the spectra. A further increase in temperature resulted in an increase in intensity of the middle component. The residual solid powder pattern was observed until 70 °C. At 80 °C, a single resonance appeared with no significant residual powder pattern.

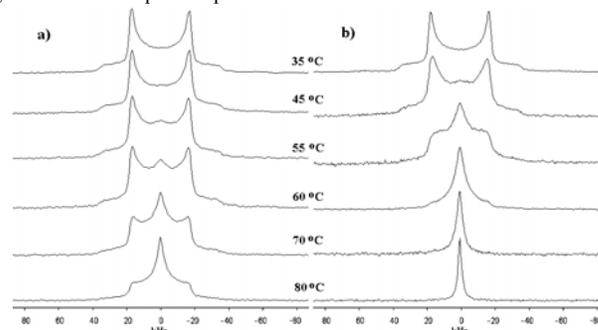


Figure 2. ^2H NMR spectra for the PMA-38K adsorbed on a) untreated (0.84 mg/m²) and b) treated (0.82 mg/m²) silica surface.

The segmental dynamics of the PMA-38K sample appeared to be different on both the strongly and weakly adsorbing surfaces when compared with the bulk. The segmental mobility was restricted on both surfaces. The collapse of the powder pattern in the bulk sample, due to a change in mobility of the segments, occurred at a temperature range of 25 to 50 °C. A similar collapse started for strongly and weakly adsorbing surfaces at 55 and 45 °C, respectively. The collapse to a single resonance occurred for the weakly adsorbing surface by 80 °C, but not for the strongly adsorbing surface at the temperatures studied.

The heterogeneity of the segmental dynamics was obvious in the NMR line shapes of both of the surface samples. Even though the powder pattern for

the bulk PMA-38K sample collapsed to a single resonance with a superposition of different motional characteristics, the contrast between these less-mobile and more-mobile components was more apparent in the spectra of the adsorbed samples. This distinction is most likely due to a conformational heterogeneity of the polymers on the surface. The conformations of the polymers are composed of trains, loops and tails on a surface. Loops and tails are more mobile than trains due to fewer direct interactions with the surface. The mobile component in the spectra is believed to be from the more-mobile loops and tails on the adsorbed surface. The residual powder patterns for the adsorbed samples at higher temperatures are due to the presence of trains that are in more or less direct contact with the surface.

Polymer segments were more mobile on the weakly adsorbing surface than on the strongly adsorbing one. The presence of bulky methyl groups was less attractive to the polymer segments on the weakly adsorbing surface, when compared with the hydroxyl groups of the strongly adsorbing surface. These yielded NMR line shapes that collapsed to single resonance like the bulk sample at higher temperatures. The spectra in **Figure 2** showed that the polymer chains were restricted more on the strongly adsorbing surface. While a distinct motionally narrowed component appeared at 60 °C for untreated silica, it appeared at a much lower temperature of 45 °C for the weakly adsorbing surface. The effect of the strength of the surface-polymer interaction on the segmental dynamics could also be clearly seen at 80 °C. Two distinct motional features existed in the spectra for the strongly adsorbing surface while there was a motionally narrowed component for the weakly adsorbing surface.

A higher molecular mass (HMM) sample, PMA-77K, was also studied with ^2H NMR. The spectra for the bulk PMA-77K sample are shown in **Figure 3** at different temperatures. The temperature region at which the powder pattern collapsed to a single resonance shifted to a higher temperature due to a molecular mass effect. A powder pattern for a solid sample appeared at 35 °C. Around 45 °C, the effect of increasing mobility of the segments was seen in the powder pattern with the narrowing quadrupole splitting. A middle component appeared at 45 °C and it became more prominent at higher temperature. The superposition of more-mobile and less-mobile components also appeared for the bulk PMA-77K sample, but with a much less heterogeneity of the segmental dynamics.

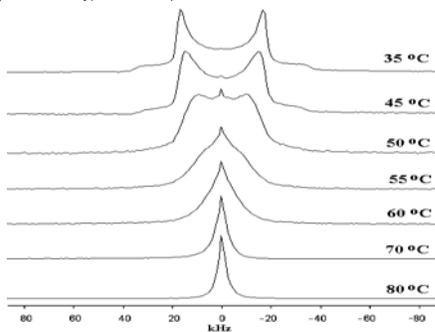


Figure 3. ^2H NMR spectra for the bulk PMA-77K sample.

^2H NMR spectra for the PMA-77K sample adsorbed (0.90 mg/m²) on an untreated silica surface is shown in **Figure 4(a)**. A powder pattern for a rigid sample was present until 60 °C. At 60 °C, a mobile component appeared in the powder pattern and its intensity increased with temperature. A residual powder pattern was also present in the spectra due to the highly restricted train conformations of the segments on the strongly adsorbing surface.

^2H NMR spectra of the PMA-77K sample adsorbed (0.84 mg/m²) on treated silica are shown in **Figure 4(b)**. A motionally narrowed component appeared at 45 °C in the powder pattern and intensity, due to mobile components, increased with temperature. The powder pattern collapsed to a single resonance at 80 °C. No residual powder pattern was present for the PMA-77K sample adsorbed on weakly adsorbing treated silica.

Similar spectral features were observed for the adsorbed PMA-77K sample and the adsorbed PMA-38K samples. Segmental motion appeared to be restricted on both strongly and weakly adsorbing surfaces for both samples. The hindrance to segmental mobility was also greater on the strongly adsorbing surface of the PMA-77K sample.

The onset temperature at which the mobile component appeared in bulk PMA-38K and PMA-77K sample spectra, shifted to a higher temperature for the adsorbed PMA-38K and PMA-77K sample on the strongly adsorbing surface. It was 55 °C for the PMA-38K sample and 60 °C for the PMA-77K sample. The motionally-narrowed component appeared in bulk PMA-38K sample spectra at 35 °C and at 50 °C in the bulk PMA-77K sample spectra. The greater temperature difference for the lower molecular mass PMA-38K sample, at which

the motionally-narrowed component initially appeared, indicated the presence of a higher fraction of segments that were more motionally restricted than

those of the HMM PMA-77K sample. A similar conclusion can be made when a similar comparison is made between bulk and the weakly adsorbing surface spectra for

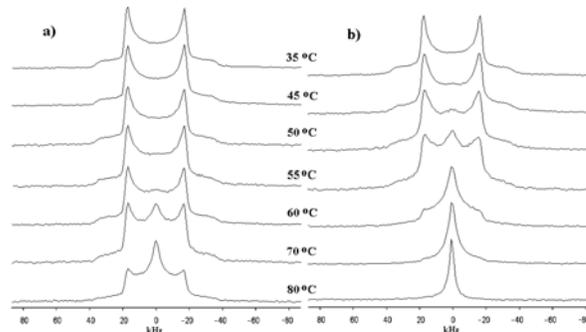


Figure 4. ^2H NMR spectra for the PMA-77K adsorbed on a) untreated (0.90 mg/m²) and b) treated (0.84 mg/m²) silica surface.

each sample. The onset temperature was 45 °C for both the PMA-38K and the PMA-77K sample in the weakly adsorbing surface spectra. However, a component that was more mobile than bulk appeared for the HMM PMA-77K sample in the weakly adsorbing surface spectra. The higher mobility on the surface, than in bulk for the HMM PMA-77K sample, could be due to longer tails and loops that are highly mobile on the surface. A lattice Monte Carlo study indicated the outermost part of the polymer-air interface to be mostly populated with tails.¹⁰ It has also been shown that the length of the tails and loops were affected more by longer chain length, while the length of the trains did not appear to be affected much.¹¹

Conclusions

Restricted segmental mobility, compared to bulk, was observed in general on both strongly and weakly adsorbing surfaces. However, the restriction on the segmental mobility was seen to be more prominent on the strongly adsorbing silica surface. A residual solid powder pattern was present at high temperatures for the strongly adsorbed samples, due to the presence of stronger interaction sites that allowed direct contact with the polymer segments. A residual powder pattern was not present for the weakly adsorbing surface at high temperatures. Segmental dynamics appeared to be much more heterogeneous on silica surfaces than in bulk. The appearance of more-mobile and less-mobile components in the spectra showed the heterogeneity of the segmental mobility on the silica surface. The segments of the HMM sample seemed to be motionally less restricted on the surface than the segments of the LMM sample.

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