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DYNAMICS OF ADSORBED PMA-D₃ - EFFECT OF SUBSTRATE

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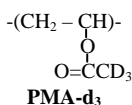
Introduction

In the last few years, our group has focused much of our attention on studying the dynamics of polymers adsorbed at interfaces. Much of our work, to date has been on labeled poly(vinyl acetate)-d₃ (PVAc-d₃)¹ and poly(methyl acrylate)-d₃ (PMA-d₃)² on silica. We have been able to probe the effects of adsorbed amount,³ molecular mass,^{4,5} and the effect of overlayer.⁶ These studies have provided a view of the adsorbed polymer consistent with a motional gradient in the layer with the more mobile segments being those at the air-polymer interface and the less-mobile segments at the substrate-polymer interface. However, we have not probed the effect of the interaction with the substrate.

In the present work, we describe the dynamics of PMA-d₃ adsorbed on different substrates with a focus on how the substrate affects the dynamics of the polymer. In particular, we examine silica- and alumina-based substrates. For silica we explored the behavior of PMA-d₃ on Cab-O-Sil silica, both in its native and hydrophobic form. For alumina we have probed the behavior on both alumina powder and also anopore membranes. We find that the dynamics of the adsorbed polymer depends on the nature of the substrate.

Experimental

The synthesis of PMA-d₃ has been reported elsewhere in detail.⁷ Briefly, methyl acrylate was made by the addition of methanol-d₃ to methacryloyl chloride in toluene. The resulting monomer was polymerized via atom transfer radical polymerization (ATRP). The molecular masses were measured with light scattering and the ones reported in this preprint were around 40 kDa.



The silica used was Cab-O-Sil M5 (untreated, 200 m²/g, from Cabot Corp.) and TS-530 (treated). The TS-530 was treated by the manufacturer, resulting in trimethylsilyl groups on the surface. Anopore membranes were from Whatman and came with either 0.2 and 0.02 μm pore size. The alumina used (Alfa Aesar, Ward Hill, MA) was α-aluminum oxide of 1.0 micron powder with a surface area of 14 m²/g. Samples with adsorbed polymers were prepared by dissolving the polymer in toluene, mixing it with the substrate, waiting, and then drying. It was not always possible to prepare samples with the same adsorbed amounts.

The spectra reported were taken using a Varian VXR 400/S operating at 61 MHz for deuterium. The spectra were taken with the quadrupole echo sequence (π/2)_x - τ - (π/2)_y - τ - echo. The times, τ, were typically on the order of 30 μs.

Results and Discussion

The spectra for PMA-d₃ on different substrates (and bulk) are shown in Figure 1 at 55 °C. At this temperature, the spectrum of the bulk polymer was consistent with a broad single resonance from a material that could be considered rubbery. On untreated silica, the spectrum was mostly a Pake pattern, consistent with glassy polymer segments. For that sample, a small amount of extra intensity in the middle of the spectrum was indicative of a small number of segments, which had additional mobility. The spectrum for the PMA-d₃ on the treated (hydrophobic) silica was intermediate between the spectra for bulk and silica(untreated)-adsorbed polymer. The nature of these spectra can be understood based on a stronger H-bonding interaction between the untreated silica, from the surface hydroxyls, and the carbonyl groups of the polymer. Reaction of the surface silanols in the treated silica eliminated

most of the possibility for H-bonding and, consequently, the effect on polymer dynamics was minimized.

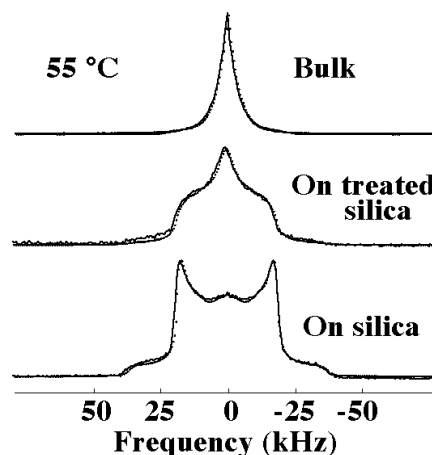
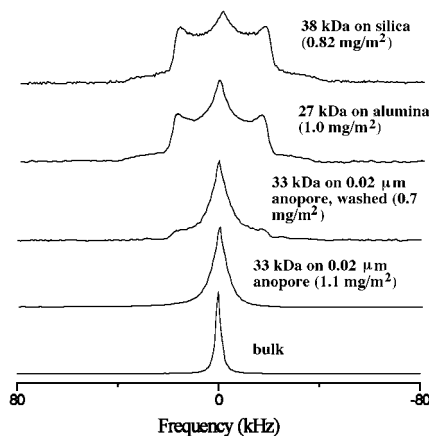


Figure 1. ²H NMR spectra of PMA-d₃ (38 kDa) in bulk, on treated silica (at 0.84 mg/m²) and on untreated silica (at 0.82 mg/m²) at 55 °C. The small squares represent the fits (hard to discern separately) to the spectra.

The behavior of adsorbed PMA-d₃ at 65 °C on alumina-like substrates compared with that on silica and in bulk is shown in Figure 2. On anopore, a relatively narrow spectrum was obtained, but upon washing, a small amount of more tightly-bound PMA-d₃ was obvious. In comparison, the polymer on alumina was more tightly bound, but not bound as strongly as the polymer on untreated silica.



Conclusions

It is obvious from the spectra that the interaction of PMA-d₃ with the substrate influences the spectra. All substrates reduce the mobility of the polymer compared to bulk. Untreated silica resulted in the most motionally restricted polymer, followed by alumina, then anopore, and then treated silica. NMR provides an exceptional way to probe the polymer surface interactions.

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