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FT-IR STUDIES OF STEREO REGULAR PMMA ON SILICA: DRYING EFFECTS

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Introduction

A great amount of work has been done on the configuration of surface adsorbed poly(methyl methacrylate) (PMMA), especially on surfaces to which they have a strong attraction. Some studies have been make on the relationships between configuration and tacticity,[1-3] molecular weight,[4] adsorbed amount,[5] and density of surface hydroxyl groups[4].

The effect of tacticity on the conformation of alumina-adsorbed PMMA in solution and dry spin-coated films were studied by Grohen et al.[1-3] Their results showed that surface-adsorbed PMMA chains adopted a relatively flat configuration, but iso-PMMA (isotactic) adsorbed on aluminum, with a much larger fraction of the bound carbonyl groups, had a flatter configuration than syn-PMMA (syndiotactic) and a-PMMA (atactic). They attributed this phenomenon to the chain segmental rearrangements[6] which may allow iso-PMMA to favor the establishment of interfacial acid-base bonds, while local stiffness of the *tt* state of the syn-PMMA does not.

Compared to interfacial conformation studies of liquid state and dry PMMA films, less work has been done to understand the effect of the drying process that could have a crucial impact on film properties in the dry state. Prest and Luca[7,8] proposed that the preferential alignments of chains on the planes of the films occured as a result of the competing effects of the rapidly increasing relaxation times of the concentrating solution and the time scale of the contraction process as the films dried. As more solvent is lost, the increased viscosity increases the relaxation times of the molecules and reduces their ability to respond to the constantly decreasing film volume. At some point, the longest relaxation times exceed the effective time scale of the collapsing film so that the molecules are no longer able to relax in their new state.

In the present paper, ultra-thin stereoregular PMMA films were adsorbed on silica particles. FT-IR was used to observe the interaction between the surface-bound PMMA and the silica surface following various drying processes.

Experimental

Both isotactic and syndiotactic PMMA samples were prepared by anionic polymerization, initiated by the reaction product of *sec*-butyllithium and 1,1-diphenylethylene. For syndiotactic PMMA, polymerization was conducted in tetrahydrofuran (THF) at −78 °C. The isotactic PMMA was made in toluene at 0 °C. The resulting PMMA samples were reprecipitated from acetone by hexane several times and then dried overnight in a vacuum oven at 70 °C. Molecular mass was measured by gel permeation chromatography (GPC) in THF, relative to standard polystyrene samples. The relative amounts of iso-(mm) syndio-(rr) and hetero-(mr) triads were calculated from the ^{1}H-NMR spectra[9] resonance intensities at 1.2, 0.8 and 1.0 ppm, respectively. The results are shown in Table 1.

Table 1. Characterization of Bulk PMMA

Polymer	Molecular Mass (M_n)	Polydispersity	Tacticity (%, triads)		
			mm	rm	rr
syn-PMMA	71100	1.23	2.3	23.0	74.7
iso-PMMA	89700	2.52	88.9	8.0	3.1

Toluene was used to prepare PMMA solutions. Polymer solutions (10 ml) were transferred into centrifuge tubes containing ~0.3 g fumed silica (CAB-O-SIL M-P5, surface area 200 m²/g, Cabot Corp., Tuscola, IL). The mixtures were shaken for 24 hours at 23 °C. The tubes were centrifuged after adsorption and the supernatant solutions were discarded. The residues were washed with pure toluene three times and a portion of each was directly cast on CaF₂ pellets. The residual amounts were dried in the air, and finally wetted with toluene for another 12 hours, before being cast on CaF₂ pellets. All cast

samples were dried, first in the air, and then dried completely in a vacuum oven overnight at ca. 70 °C. The adsorbed amounts, calculated from thermogravimetric analysis (TGA) results, are listed in Table 2. FT-IR spectra were recorded on a Magna-IR™ Spectrometer 750 (Nicolet Analytical) with 1024 scans under nitrogen at a resolution of 4 cm⁻¹. The surface bound fraction, f_b, was measured by the curve fitting of the carbonyl absorption band.

Table 2. Sample preparation for FT-IR Measurement

Samples	Polymer	Toluene Treatment	Adsorbed Amount(mg/m²)
Syn-tol-d-tol	syn-PMMA	YES	1.29
Syn-tol	syn-PMMA	NO	1.29
Iso-tol-d-tol	iso-PMMA	YES	1.28
Iso-tol	iso-PMMA	NO	1.28

Results and Discussion

The IR absorption bands of the C=O for sample Iso-tol and Syn-tol are shown in Figure 1. Both of the bands are asymmetrical with big shoulders and long tails on the low frequency side, which indicates that both iso-PMMA and syn-PMMA chains have conformations very close to the silica surface (due to high bound fractions). The spectra of each look fairly similar. A curve-fitting technique was used to calculate the bound fraction of the C=O groups on the silica surface. It is well known that, during the adsorption of PMMA onto silica or alumina, the ester groups interact with the surface hydroxyl groups through hydrogen bonding. The formation of H-bonds induces a frequency shift for the O-H and C=O groups.[10] The bands at 1733 and 1716 cm⁻¹ were used in our study of the free and mono-bound C=O absorption. While most researchers used just two frequencies to fit their results to the carbonyl bands, a third band at 1693 cm⁻¹, resulting from the H-bonding of C=O with multiple silanol groups, was proposed by Berquier et al.[11] This interaction was also observed in the adsorption of other ester and ketone-containing molecules.[11] The peak around 1744 cm⁻¹ represents the absorption of C=O in the ester side chains which interact with the silica surface through H-bonding between the methoxyl group and the silanol group (discussed elsewhere).[12] An absorption band at 1628 cm⁻¹, resulting from silica absorption, was subtracted from the C=O absorption bands to correct the baseline. Curve-fitting analysis allows the calculation of the H-bound fraction (f_b) of C=O by equation (1):

$$f_b = \frac{(\varepsilon_{b1}/\varepsilon_f)A_{b1} + (\varepsilon_{b1}/\varepsilon_f)A_{b2}}{(\varepsilon_{me}/\varepsilon_f)A_{me} + A_f + (\varepsilon_{b1}/\varepsilon_f)A_{b1} + (\varepsilon_{b1}/\varepsilon_f)A_{b2}} \tag{1}$$

Where, A_f (free C=O) and A_{b1} (mono bonded C=O) are the peak-fitted integrated intensities of the 1733 and 1716 cm⁻¹ peaks; A_{me} (methoxy bonded) and A_{b2} (multi-bonded C=O) are the intensities of the peaks around 1743 and 1693 cm⁻¹, respectively, and ε_{me}, ε_f, ε_{b1} and ε_{b2} are the corresponding molecular adsorption coefficients. The ratios for $\varepsilon_{b2}/\varepsilon_f$ and $\varepsilon_{me}/\varepsilon_f$ were not found in the literature and the estimates of $\varepsilon_{b1}/\varepsilon_f$ vary from 1.3[3] to 1.5.[13] Ratios equal to 1.5 were used by us for both $\varepsilon_{b2}/\varepsilon_f$ and $\varepsilon_{b1}/\varepsilon_f$ to calculate the bound fraction of C=O. Relative changes are meaningful despite this uncertainty regarding the relative absorptivity of these vibrational bands. The curve-fitting results are listed on the figure. The bound fractions from the curving-fitting for the two adsorbed samples were very similar--0.414 and 0.422 for syn- and iso-PMMA, respectively. The similarity of the bound fraction for syn- and iso-PMMA is different from the results obtained by Grohens et al.[1-3] A much higher bound fraction was obtained by them. for iso-PMMA adsorbed on aluminum compared to adsorbed syn-PMMA. It is known that when PMMA chains adsorbed onto an attractive flat surface, like an oxidized silica wafer or aluminum, the ability of chain segmental rearrangements (*meso* tg state) allows iso-PMMA to favor the establishment of interfacial H-bonds while the syn-PMMA local stiffness of the *tt* state does not.[1,2,6,14] The chains of iso-PMMA are expected to adopt a flatter configuration to have more interacting sites with the surface.
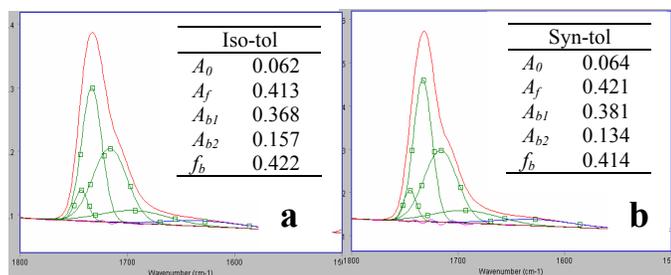
Figure 1. FT-IR spectra and the curve-fitting results of the C=O absorption bands for (a) syn-PMMA and (b) iso-PMMA adsorbed on silica. The samples were cast directly from toluene and dried.

Our present system may be rather different from those with PMMA adsorbed on flat aluminum. The average diameter of the silica particle is ca. 20 nm (claimed by the manufacturer) while the length of our PMMA chain is on the order of 150 nm (calculated through the C-C bonds in the backbone). The bound fraction measured by Grohens et al. for adsorbed iso-PMMA (0.7)[2] is higher than ours (0.422) for a similar adsorbed amount. This could also partially be due to the consequences of the spin-casting process that may lead to chain straightening and flattening, as proposed by the author.[2]

The two adsorbed (and dried) samples discussed above were put back in toluene for ca. 12 h, cast onto CaF_2 pellets, and dried again (samples Syn-tol-d-tol and Iso-tol-d-tol listed in Table 2). The FT-IR spectra were collected and are shown in Figure 2. The curve-fitting results are also listed on the figures. The basic features of the C=O absorption bands for these twice-dried samples are similar to those dried once from toluene, i.e., large shoulders and long tails on the low frequency side. The sizes of the shoulders, however, became larger than those in the single-dried samples. The increase is also greater for the adsorbed iso-PMMA (Iso-tol-d-tol). The bound fraction of the C=O groups, calculated from the curve-fitting results, is 0.563 and 0.450 for samples Iso-tol-d-tol and Syn-tol-d-tol, respectively.
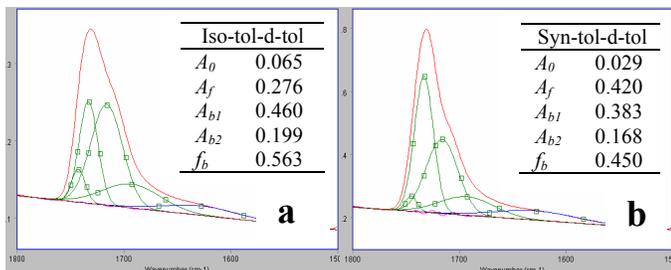

Figure 2. FT-IR spectra and the curve-fitting results of C=O absorption bands for (a) syn-PMMA and (b) iso-PMMA adsorbed on silica. The samples were dried twice from toluene.

This increase for the bound fraction after the second drying indicates the potential of the PMMA segments to relax to a conformation closer to the silica surface after the initial drying. It was suggested by Prest and Luca[7,8] that the conformation of the polymer chains in the dry adsorbed films consists of a number of nonequilibrium states[15] locked in by the drying process. The simulation results by Shaffer and Chakraborty[16] indicated the presence of conformational energy minima and barriers when PMMA segments were adsorbed onto an aluminum surface. When those surface-adsorbed dry PMMA layers were swollen and solvated by the toluene again, the segments acquired extra time to relax to a lower energy configuration, with more interacting sites with the silica surface. Therefore, the relative amount of surface-bound C=O groups increased after the second drying process. As a result of faster relaxation[17] and less chain stiffness[6,14] of the iso-PMMA segments, the bound fraction of the C=O increased much more in the adsorbed iso-PMMA sample (from 0.422 to 0.563) than in the adsorbed syn-PMMA sample (from 0.414 to 0.450). This is also supported by the preferential adsorption of isotactic segments in PMMA chains to the silica surface, as indicated by the experimental results of Carriere et al.[18]

Conclusions

A similar bound fraction was obtained for both iso- and syn-PMMA adsorbed onto silica particles from toluene, followed by drying. The drying process has obvious effects on the configuration of the surface-adsorbed PMMA chains, since a second drying process can increase the bound fraction because of the extra relaxation time acquired for the segments to rearrange in a closer conformation to the silica surface. Under the same conditions, iso-PMMA has a greater ability to relax on a silica surface, thereby resulting in a larger increase in the bound fraction than in syn-PMMA.

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