Different Surface-Restructuring Behaviors of Poly(methacrylate)s Detected by SFG in Water

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Received June 13, 2001

Understanding polymer surface structures in the liquid environments is very important.[1] Implanted biomedical polymers come in contact with blood or tissue; therefore, to understand biocompatibility, it is crucial to know their surface structures in situ.[2] Since Langmuir described the reorientation of hydrophilic groups on a solid surface in contact with a water drop,[3] much research has been undertaken to understand polymer surface dynamics and structures in water. The most widely used method is to follow changes of the water contact angle as a function of time. Freeze-drying X-ray photoelectron spectroscopy has been developed to study polymer surface restructuring in water, but it cannot provide orientation information of surface functional groups.[4] Most other surface analytical techniques are operable only under ultrahigh vacuum; therefore, molecular level in situ understanding of surface restructuring in water has still not been achieved. The polymer surface changes in water may have a molecular origin, caused by the migration or reorientation of polar (nonpolar) groups, segments, or side chains toward (away from) the aqueous phase to minimize the interfacial free energy. To show that the contact angle measurements have a molecular interpretation, and to understand the relationship between the surface structures of biomedical polymers and biocompatibility, polymer surfaces should be characterized at the molecular level directly in water. Here we show that different surface-restructuring behaviors of poly(methacrylate)s in water have been detected by sum frequency generation (SFG) vibrational spectroscopy.

SFG vibrational spectroscopy has recently been developed into a powerful tool to study surfaces and interfaces.[5] It can provide molecular level information about surface structures without requiring a vacuum. We studied surface changes of poly(methacrylate)s with different alkyl side chains (Table 1) in water by SFG. Contact angle studies of poly(methacrylate)s with different side chains show that their surface structures will change after contact with water;[6] the changes depend on the length of the side chains. It has been suggested that these changes are induced by the reorientation of the surface functional groups or the diffusion between various surface and bulk functional groups. This can be possible only if the polymer molecules are mobile. Backbone mobility is related to the glass transition temperatures (T_g) of poly(methacrylate)s. These T_g's decrease with increasing ester side chain length (Table 1), indicating increased backbone mobility. Compared to polymer backbones, side chains are more mobile and can move at temperatures below T_g. Dynamic mechanical and phosphorescent experiments also show that poly(methacrylate)s have very different mobilities.[7]

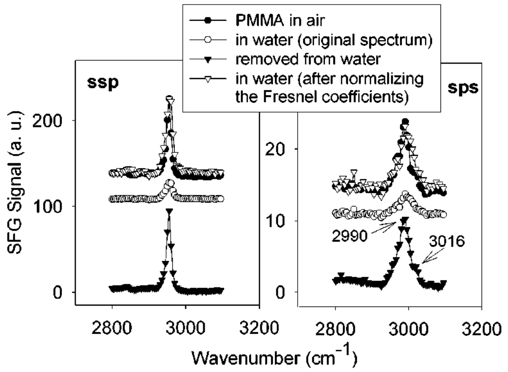

Figure 1. SFG spectra of PMMA before, during, and after contacting water. Left, ssp; right, sps.

Table 1. Polymers Studied and Their Glass Transition Temperatures

name	abbreviation	T_g (°C)
poly(methyl methacrylate)	PMMA	105
poly(*n*-butyl methacrylate)	PBMA	17
poly(*n*-octyl methacrylate)	POMA	−70

Samples were made by spin casting 2 wt % polymer toluene solutions on fused silica at 3000 rpm for 30 s and oven dried at 80 °C for 15 h. The SFG spectra were collected with two input laser beams traveling through the silica substrate and overlapping on the polymer/air or polymer/water interfaces. We have demonstrated that SFG signals were only generated by the polymer/air or polymer/water interfaces, without polymer/substrate or polymer bulk contributions.[8]

The spectra of PMMA before, during, and after contact with water are shown in Figure 1. All of the ssp (s-polarized sum frequency beam, s-polarized visible beam, p-polarized IR beam) spectra are dominated by the symmetric stretch of the ester methyl group at 2955 cm^{-1}. The sps spectra have two peaks: the peak at 2990 cm^{-1} is due to the asymmetric stretches of the alpha methyl and ester methyl groups, and the 3016 cm^{-1} peak comes from the asymmetric stretch of the ester methyl group. Detailed investigations of the PMMA/air interface show that the ester methyl groups tend to stand up on the surface with a relatively narrow angle distribution, and the alpha methyl groups tend to lie down on the surface.[8] Both ssp and sps SFG spectra of PMMA, while in contact with water, are similar to the PMMA/air interface, but with much weaker signals. Calculations show that the weakening of the SFG signals is due mostly to the changes of the Fresnel coefficients of two interfaces. There is almost no change for the ester methyl, alpha methyl, and methylene groups on the PMMA surface after contact with water, indicating that the difference between the advancing and receding water contact angles[1] was not due to surface restructuring in water. We believe, rather, that it is due to small amounts of water absorption at the polymer/water interface, one of the possible explanations suggested by Andrade et al.[9] FTIR experiments indicate that water can penetrate thin PMMA film in seconds and reach equilibrium in 2 min.[10]

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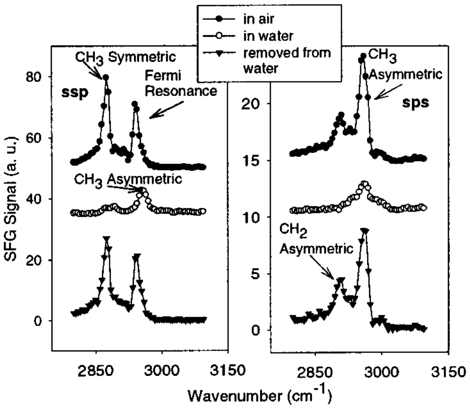

Figure 2. SFG spectra of PBMA before, during, and after contacting water. Left, ssp; right, sps.

Figure 2 shows the spectra of PBMA before, during, and after contact with water. The ssp spectrum of PBMA in air is dominated by the symmetric stretch of the side chain methyl group at 2875 cm^{-1} and Fermi resonance at 2940 cm^{-1}. The sps spectrum is dominated by the asymmetric stretches of the same methyl group at 2960 cm^{-1} and the methylene group at 2910 cm^{-1}. When the PBMA surface is in contact with water, the ssp spectrum is dominated by the asymmetric stretch of the methyl group at 2960 cm^{-1}. Calculations indicate that side chain methyl groups tend to stand up on the surface in air. In water, they tend to lie down on the surface, and the orientation angle changes to larger than 58° versus the surface normal. After the PBMA is removed from water, the SFG spectra recover. The spectra of PBMA in water for 12 h are still similar to the spectra taken immediately after PBMA contacts water. We believe that ester side chain reorientation occurs immediately after immersion.

The SFG spectra of POMA (Figure 3) show that the POMA/air interface is dominated by the methyl and methylene groups. When POMA contacts water, its SFG spectra immediately disappear. After the sample is removed from water, the spectra collected are very different from those before contacting water. We believe that the polymer backbone of POMA changes immediately after contact with water.

Different surface-restructuring behaviors of poly(methacrylate)s have been observed in water. Our results demonstrate that for PBMA, the side chain methyl groups change orientation immediately after the sample contacts water. With prolonged exposure to water, the SFG spectra show no additional changes. The spectra recover after the sample is removed from water. These results indicate that no major changes in the polymer backbone occur. For POMA in water, we believe that the disappearance of the SFG spectra is due to changes in the polymer backbone, since it has a very low T_g and thus is very mobile. This backbone movement would randomize the surface groups and eliminate any SFG signal. Restructuring of the POMA surface is complete and irreversible after the sample is removed from water. The PMMA has a much higher T_g; thus, its structure is more rigid. In addition, the ester methyl group is more hydrophilic than the normal methyl group. Therefore, it is not necessary for the ester methyl group to tilt toward the surface in water to reduce the surface free energy, as the methyl group of the ester chain in PBMA. We show that there is no detectable changes on the PMMA surface in water and believe that the contact angle hysteresis is caused by small amounts of water absorption at the polymer/water interface.

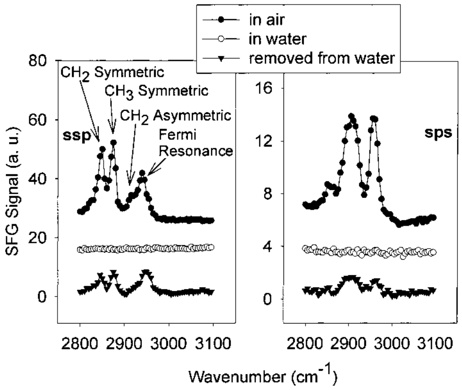

Figure 3. SFG spectra of POMA before, during, and after contacting water. Left, ssp; right, sps.

Conclusions. Polymer/water interfaces have been successfully studied at the molecular level in situ by SFG. Surfaces of poly(methacrylate)s with various alkyl side chains behave differently in water. Previous research has shown that poly(methacrylate)s have different protein adsorption properties.[11] Our studies of surface restructuring in water will help to understand this in detail. Molecular level studies of polymer surface restructuring in water by SFG will provide new insight into the biocompatibility of biomedical polymer materials.

Acknowledgment. This work was supported by the start-up funds from the University of Michigan. We thank Drs. Jonas Kolenda and Zenonas Kuprionis from EKSPLA and Mr. Robert S. Tamosaitis from Altos for their help in the installation of the SFG system.

Supporting Information Available: Detailed description of SFG experimental procedures and some calculations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0164071

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