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Hydrogen Bonding on the Surface of Poly(2-methoxyethyl acrylate)

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Hydrogen bonding plays an important role in polymer science. For instance, the self- and inter-association types of hydrogen-bonding interactions have been used to evaluate the miscibility between polymers containing hydrogen-bond donors (such as, hydroxyl, etc.) and acceptors (carbonyl, pyridine, etc.).[1] These studies, however, mainly focused on the interaction in the polymer bulk; little attention has been paid to the hydrogen bonding on the polymer surface, although it is crucial to understand the properties of the polymer surface. This situation has been ascribed to the lack of effective surface-sensitive probes for the polymer surface. By using time-of-flight secondary ion mass spectrometry, X-ray photoelectron spectroscopy, and atomic force microscope techniques, one is now able to probe the chemical structures at the polymer surface.[2−5] However, it is still difficult to correlate these results to the exact surface structure on a molecular level.

As a second-order nonlinear vibrational spectroscopic technique, sum frequency generation (SFG) is intrinsically surface-specific[6] and is widely employed to investigate the molecular structures on various interfaces including polymer surfaces.[7] SFG especially succeeded in studying the hydrogen bonding on air/liquid, liquid/liquid, and liquid/solid interfaces.[8] However, direct SFG observation of the hydrogen bonding on the polymer surface is limited, while much information regarding its bulk has been obtained by infrared measurements.[1] Recently, Tanaka et al. reported that poly(2-methoxyethyl acrylate) (PMEA) shows excellent blood compatibility in comparison with other polymers.[9−11] These results implied that the blood compatibility may be related to "freezing bound water" in PMEA observed by differential scanning calorimetry (DSC). Although it is expected that the water structure on the PMEA surface is one of the most important factors affecting the blood compatibility, the interaction between the water molecules and the PMEA surface is still unclear.

In the present study, we investigated the surface molecular structure of a PMEA thin film by SFG in order to understand its excellent biocompatibility and first observed that the majority of carbonyl groups on the PMEA surface are hydrogen-bonded with water or ethanol solvent molecules, while the PMEA bulk is still dominated by the free carbonyl group.

PMEA ($M_w \sim 8.5 \times 10^4$) was synthesized by radical polymerization[9] and was deposited by spin coating from its toluene solution on the flat surface of a CaF_2 prism or the surface of a 200-nm-thick gold film evaporated on a slide glass (see Supporting Information). The thickness of the PMEA was ca. 50 nm, determined by ellipsometry.[12] The PMEA was immersed in a solution containing a hydrogen-bond donor group such as water, ethanol, or 2,2-bis(*p*-hydroxyphenyl)propane (bisphenol A). After being dried under a flow of purified Ar gas for ca. 1 min, the PMEA samples were characterized by SFG (CaF_2 substrate), infrared reflection absorption (IRRA), and Raman spectroscopy (gold substrate). The SFG system using a tunable broadband infrared pulse (3700−1000 cm^{-1}, 200 cm^{-1} fwhm) and a narrow-band visible pulse (800 nm, <10 cm^{-1} fwhm) has been described elsewhere.[13] In the present sample geometry, the SFG signal is mainly contributed by the polymer/air interface. The IR frequency for the SFG system was calibrated by the bending modes of water vapor. The IRRA spectra were obtained with an FTIR equipped with a grazing reflection accessory by co-adding 32 interferrograms. The chemical compositions of the PMEA bulk and surface are obtained by deconvolution of these IRRA and SFG spectra, respectively.

Figure 1 shows (A) IRRA and (B) SFG spectra of PMEA (a) before and (b−d) after immersion into different kinds of solutions in the IR frequency region between 1800 and 1620 cm^{-1}. The IRRA spectra in a wider region (3700−1000 cm^{-1}) are given in the Supporting Information. The IRRA and SFG spectra of PMEA show an intense band at 1740 cm^{-1} (Figure 1A-(a) and 1B-(a)), which can be assigned to the C═O stretching of the carbonyl group in the bulk and on the surface of PMEA, respectively.

Almost the same IRRA spectrum was obtained after the PMEA was immersed into Milli-Q water, and no IR band due to water absorption could be found in the IRRA spectrum, as shown in Figure 1A-(b) (see also Supporting Information), indicating that water molecules were not absorbed in the PMEA bulk here. On the other hand, the SFG spectrum was completely changed after contact with water for 10 s (Figure 1B-(b)). The SFG spectra were almost the same with an increase of immersion time. The center of the SFG peak moved to 1722 cm^{-1}, and the SFG peak at 1740 cm^{-1} decreased to a shoulder. An identical SFG spectrum was obtained after the PMEA was immersed in deuterated water (D_2O), suggesting that this peak is due to structure change on the PMEA surface induced by water molecules but not due to the bending mode of water. It is a well-known fact that the IR band of C═O stretching in a polymer will shift to a lower frequency when the hydrogen bonding is formed with hydrogen-bond donors.[1] Recently, Chen and co-workers studied the interfacial structure between poly(ethylene terephthalate) (PET) and (3-aminopropyl)trimethoxysilane by SFG and reported a 10 cm^{-1} red-shift in the ester carbonyl-stretching mode of the PET surface due to the hydrogen bonding with the amino group from silane.[14] In the present work, water molecules form hydrogen bonding with the carbonyl group on the PMEA surface and induce a large red-shift (18 cm^{-1}). This is a first direct evidence for the formation of hydrogen bonding on the PMEA polymer surface with water molecules. The fitting results showed that the majority of the carbonyl groups on the PMEA surface were hydrogen bonded with water, while no hydrogen bonding could be observed in its bulk. This peak does not change much with an increase of immersion time in water. On the other hand, the hydrogen-bonded carbonyl species were found to be very limited on the surface of poly(methyl methacrylate) (PMMA) and poly(*n*-butyl methacrylate) (PBMA) after contact with water under the same conditions; PMMA and PBMA are poly(acrylate)s with less biocompatibility than PMEA. Detailed experiments correlating the "freezing bound water" in PMEA observed by DSC and the

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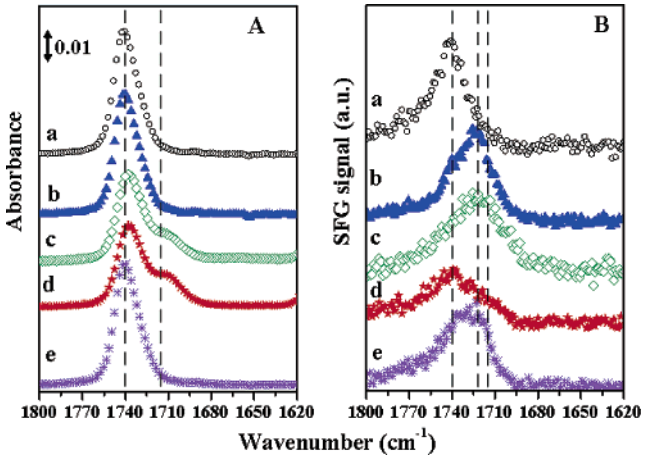

Figure 1. (A) IRRA and (B) SFG spectra of PMEA film in the C═O stretching region (a) before and after immersion in (b) water for 10 s and (c) bisphenol A aqueous solution for 10 min. (d) Bisphenol A in hexane−$CHCl_3$ (9:1, v/v) solution for 2 min and (e) after being rinsed by ethanol after (d).

surface hydrogen bonding are still in progress; hydrogen bonding between the PMEA surface and water molecules is expected to play a role in its blood compatibility.

It is interesting to compare the hydrogen bonding on the PMEA surface with that of other molecules containing hydrogen-bonding donors. Recently, it was found that PMEA could absorb a large amount of bisphenol A, which contains two phenol units constrained by a spatial conformation.[12,15,16] As shown in Figure 1A-(c), a shoulder was observed at 1715 cm^{-1} in the IRRA spectrum after 10 min of immersion in a bisphenol A aqueous solution, which has been attributed to the C═O stretching of the carbonyl of PMEA hydrogen-bonded with the hydroxyl group of bisphenol A.[1,15] A similar behavior was also observed by Raman scattering measurements (Supporting Information). On the other hand, the SFG spectrum after contact with a bisphenol A aqueous solution (Figure 1B-(c)) was quite different from that of the as-prepared PMEA (Figure 1B-(a)) but similar to that of PMEA in water (Figure 1B-(b)). A broad SFG peak was observed around 1722 cm^{-1}, while the SFG intensity on the lower frequency side slightly increased in comparison with that immersed in pure water.

Since water can also adsorb on the PMEA surface by hydrogen bonding (Figure 1B-(b)), the adsorption of bisphenol A was also investigated in a non-proton solution (hexane/chloroform, 9:1). The IRRA spectra show nearly identical behavior in bisphenol A non-proton and aqueous solutions (Figure 1A-(c,d)). The SFG spectrum (Figure 1B-(d)) was obviously different, and the ratio of the free carbonyl group seemed to be higher than that observed in bisphenol A aqueous solution (Figure 1B-(c)). Deconvolution showed that three components at 1740, 1722, and 1715 cm^{-1} were present in the SFG spectra after immersion in either bisphenol A aqueous or non-proton solutions, as shown by three dotted lines in Figure 1B. On the basis of the discussion given for Figure 1B-(b), the peak component at 1722 cm^{-1} is attributed to the surface carbonyl group hydrogen-bonded with water coabsorbed. The peak component at 1715 cm^{-1} can be assigned to that hydrogen-bonded with bisphenol A, which locates at almost the same position as that observed in the PMEA bulk. The peak shift from the free carbonyl (1740 cm^{-1}) induced by bisphenol A (25 cm^{-1}) was greater than that by water (18 cm^{-1}), suggesting a stronger hydrogen-bonding interaction between bisphenol A and PMEA. However, even for immersion in a non-proton solution containing bisphenol A, some surface carbonyl sites are still terminated by hydrogen bonding with water (Figure 1B-(d)), which may come from water vapor or a trace amount of water in the non-proton solution. As a result of the coadsorption of bisphenol A and water molecules, the majority of the carbonyl groups on the PMEA surface were terminated by hydrogen bonding. This is in contrast to that observed in the PMEA bulk, where the free carbonyl groups are the dominating species (Figure 1A-(c,d)).

When the bisphenol A-treated PMEA was rinsed by ethanol, the IRRA spectra showed that the bisphenol A was entirely removed from the PMEA (Figure 1A-(e) and Supporting Information).[12] Nevertheless, an SFG peak was still observed around 1722 cm^{-1} in addition to the free carbonyl peak at 1740 cm^{-1} (Figure 1B-(e)) after the rinse treatment. It is likely that the ethanol and/or water molecules can produce hydrogen bonding with the carbonyl on the PMEA surface after the bisphenol A molecules are removed by ethanol.

In summary, interfacial hydrogen bonding between water molecules and PMEA was observed for the first time. The majority of the carbonyl groups on the PMEA surface are hydrogen-bonded after contact with water, in comparison with that in its bulk. The SFG measurement is able to distinguish the different kinds of hydrogen bonding on the PMEA surface. We are continuing to elucidate the relationship between the surface hydrogen bonding and biocompatibility of PMEA.

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Supporting Information Available: Sample preparation conditions, IRRA spectra in a wider region corresponding to Figure 1A, and Raman spectra for bisphenol A adsorption /desorption in PMEA; IRRA and SFG spectra of the PMEA in the C−D stretching region after contact with a deuterated bisphenol A aqueous solution are also provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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