Sum Frequency Generation (SFG) Studies of Molecular Structure on the Organic Film Surface

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It is well known that the surface/interface of materials usually exhibit properties and behaviors that are considerably different from its bulk phase. The functionality of the solid surface modified by an organic thin film, such as a self-assembled monolayer (SAM), *Langmuir-Blodgett* (LB) ultra-thin film or polymer thin film, depends significantly on its surface molecular structure.[1,2] Therefore, elucidation and control of the surface molecular structure is essential to understand the novel functionality introduced by the modification.

As a 2nd-order non-linear optical spectroscopic technique, sum frequency generation (SFG)[3] is attracting much attention in surface science due to its high surface selectivity, sensitivity and versatile applicability and is now used at the gas/solid, gas/solution and solution/solid interfaces in various environments (UHV, air, liquid, etc.).[4-8] A great deal of valuable structure information at the interface has been acquired by the non-linear optical method, which is difficult to obtain by conventional vibrational spectroscopy.

In the present study, the interfacial molecular structures of the poly(acrylate) polymer thin films[9-12] and the LB films of fatty acid[13,14] formed on solid substrates have been investigated by using a broadband SFG system.

(1) Interfacial Structures of Poly(acrylate) Thin Films

The interfacial structure changes on a poly(2-methoxy ethyl acrylate) (PMEA) thin film induced by the absorption of bisphenol A (BPA), which is suspected to be an endocrine disrupter, has been investigated by SFG and infrared reflection absorption (IRRA) measurements in comparison with those observed in poly(methyl methacrylate) (PMMA) and polystyrene (PS) thin films. By controlling the thickness of the intermediate PS film between the PMEA and Au substrate, we are able to explore the molecular structure at the different PMEA interfaces of air/PMEA (free) and PMEA/PS (buried). The SFG results suggest that the OCH_3 groups at the PMEA interfaces are likely to stand up and that the interfacial ordering on the PMEA is increased by the BPA absorption in a reversible way.[9]

The interaction between BPA and other poly(acrylate) polymers have also been investigated by IRRAS and SFG measurements.[11] We found this behavior strongly depends on the glass transition temperature (T_g) of the polymers.[10] The hydrogen bonding interaction between the polymers and BPA in the bulk and on the surface of polymers have been investigated for the first time.[12]

(2) *Surface Structure of the Fatty Acid LB Films*

Although the bulk structures of LB films have been extensively investigated, a number of issues about their surface molecular structures are still not clear.[1,2] SFG been applied to explore the interfacial structures of the LB films of fatty acids both in air and in solution.[13-16]

It was found that the SFG peaks observed for the LB films of fatty acids on the hydrophilic substrates are mainly attributed to the terminal CH_3 group in its outmost layer and their intensities are independent of thickness of the LB films. By combining the normal and deuterated fatty acids, it has been demonstrated that one is able to probe any layer in the "bulk" of the thin films by SFG measurements.[14,15] It was found that the outermost layer structures of the even-numbered LB films are changed after the films are pulled up from the water sub-phase.[13] On the other hand, the *in situ* SFG measurements demonstrated that the outmost layer structures of the LB bilayer of stearic acid in the water sub-phase is affected significantly by the divalent metal cation (such as Cd^{2+}) in the buffered solution.[14]

Furthermore, we have employed the SFG technique to investigate the CdS nanoparticle induced structural changes within the fatty acid multilayer films for the first time.[16]

As described in the report, SFG spectroscopy has its significant advantages on the conventional vibrational spectroscopy and can provide much structural information on the various interface/surface. This information will be very useful to understand and to control the properties and reactions on the surface or interface.

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