In Situ Measurement of the Second Harmonic Signal of Adsorbing Nonlinear Optical Ionically Self-assembled Monolayers.

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ABSTRACT

Ionically self-assembled monolayers (ISAMs) have recently been shown to spontaneously exhibit a polar ordering that gives rise to substantial second order nonlinear optical response. The deposition of ISAMs has been studied *in situ* via second harmonic generation. This is a particularly sensitive probe of the growth of nanometer-thick films since the centrosymmetry of the immersion solutions, the substrate, and the container yields no SHG contribution from these bulk components. Upon immersion in the NLO-active polyelectrolyte solution, the SHG rises sharply over the first minute. When a film is immersed into salt water, the SHG decreases significantly only to be restored when the salt solution is replaced with deionized water.

INTRODUCTION

Ionically self-assembled monolayer (ISAM) films are grown, one monolayer at a time, by immersing a charged substrate alternately in anionic and cationic solutions. This has been shown to be an easy, economic, and fast method for creating laterally homogeneous, nanostructured thin films. [1,2] These films can be used to provide nanoscale control of thickness, composition and orientation in devices such as light-emitting diodes, photovoltaics, and electrochromics. One application we have been focusing on is the fabrication of films with a second order nonlinear optical response. These films show substantial $\chi^{(2)}$ values with outstanding thermal and time stability. [3-7] To increase the understanding of the formation of the ISAM films it is beneficial to be able to measure the growth of the layer *in situ*. In this paper, we describe studies of the deposition process using second harmonic generation (SHG) as a probe. We also compare the deposition process of a polymer with that of a monomer.

EXPERIMENTAL DETAILS

The measurements were done with a standard SHG setup employing a 30 picosecond pulsewidth modelocked Nd:YAG laser. The fundamental wavelength is 1064 nm and is p-polarized. Typical values for beam radius and pulse energy values were 100 μm and 1 mJ/pulse respectively. The SHG data are averaged over 10 shots and 100 shots per data point for *in situ* and *ex situ* measurements, respectively. The sample holder was

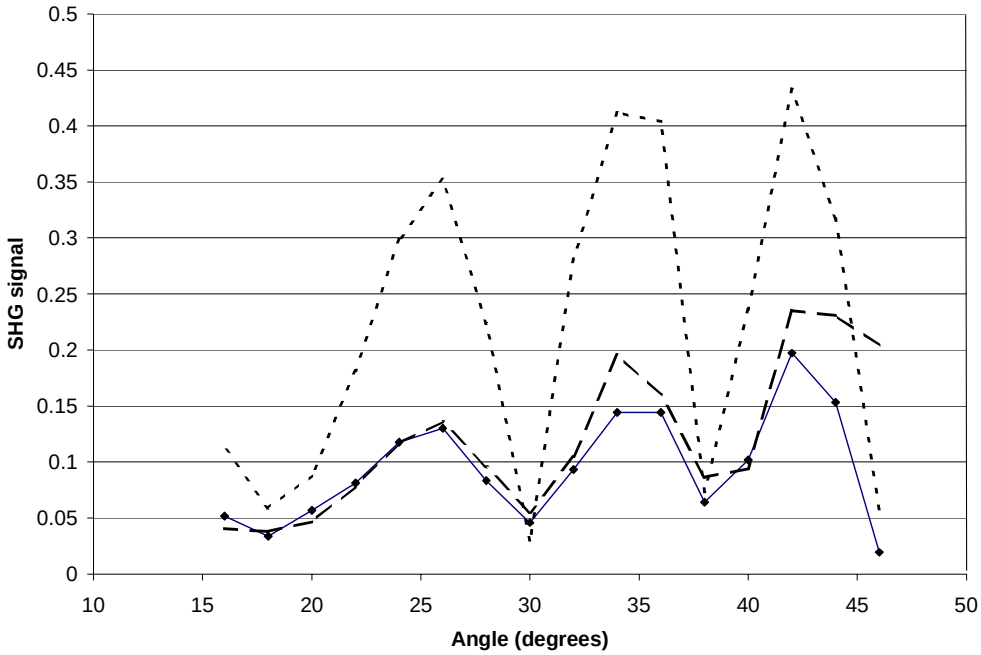

Figure 1. The second harmonic signal as a function of incidence angle. The solid line represents the glass slide, which has some SHG signal due to the fact that the interface is non-centrosymetric. The dashed and the dotted lines represent the same slide after depositing PAH and PCBS layers, respectively.

constructed so that the sample could be immersed in solution without moving the sample with respect to the incoming laser beam. This enabled us to measure the SHG signal while the layer is growing and the SHG signal between the deposition steps, always monitoring the same spot on the sample. [8] The optically active material used in these experiments was poly{1-4-(3-carboxy -4–hydroxyphenylazo)-benzenesulfoamido-1,2-ethanediyl, sodium salt} (PCBS). The optically inactive material used as counterion was poly (allylamine hydrochloride) (PAH). Both materials were purchased from Aldrich.

The SHG signals generated by the film on either side of the sample interfere with one other. The phase of the interference is determined by the thickness of the glass slide, the angle of incidence of the laser beam, and the refractive indices of the glass slide and the surrounding media. The thickness of the layers is negligible compared to the thickness of the glass slide, therefore one would expect that interference pattern of SHG versus angle of incidence is independent of layers deposited when the measurements are made *ex situ*. Figure 1 shows this to be true for the bare substrate, a PAH layer, and a PAH/PCBS bilayer. It is clear that signal strength is much stronger after deposition of PCBS, but the angular position of the maxima and minima is unaltered by depositing additional layers. The SHG signal observed from a bare glass slide is due to the fact that the air-glass interface, like any other interface, is intrinsically non-centrosymetric.

The interference between the SHG signals generated on opposite sides of the substrate is determined by the propagation distance through the glass, which is $h = 1\ \text{mm} / \cos\theta'$ where 1 mm is the thickness of the slide and θ' is the refracted angle in the glass. The interference pattern is thus dependent on the refractive index of the surrounding

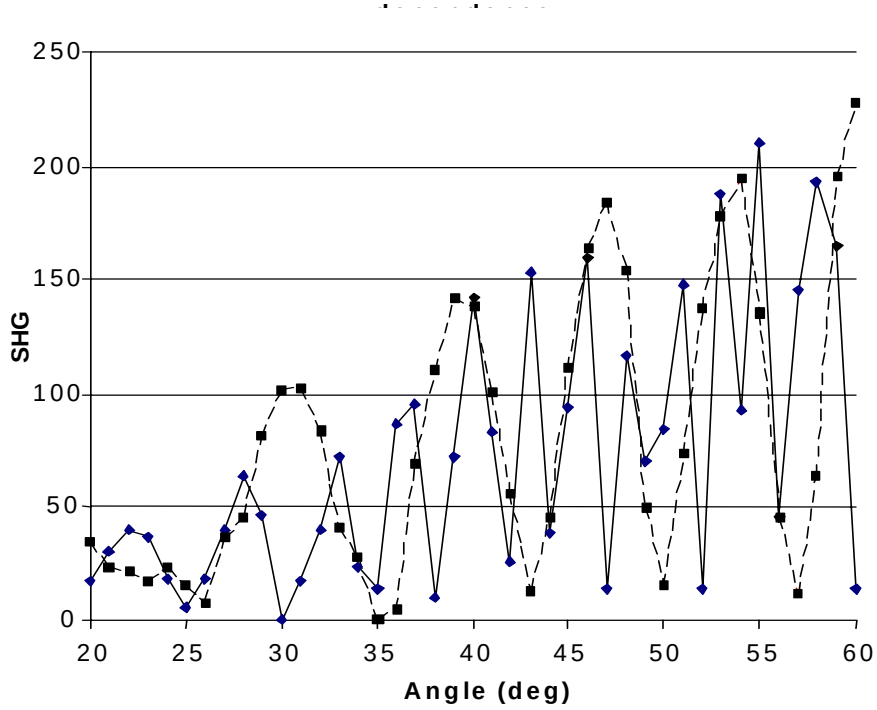

Figure 2. The SHG as a function of incident angle for a PAH/PCBS sample. The solid and dashed lines represent the sample in water and in air, respectively.

medium since that determines θ'. Figure 2 compares the interference patterns of a sample in air with that of the same sample in water. It is clear that the peaks are shifted closer together when the sample is in aqueous solution. This is due to the fact that the refractive index difference between water and glass is smaller than the refractive index difference between air and glass.

Figure 3 shows the calculated SHG interference pattern as a function of external incident angle for a glass slide (n = 1.5, 1 mm thickness) in air (n = 1.0) and water (n = 1.33). The calculation confirms the experimental finding that the peaks are closer together as the refractive index of the surrounding medium increases. In the remainder of this paper, the angle of maximum interference was determined for each glass slide in air and in aqueous solution. These angles were then used for the remainder of the experiment.

RESULTS

The deposition rate of PCBS on PAH was measured for three concentrations from 0.5 mMol down to 0.0025 mMol as shown in Figure 4. . The concentration of PAH was kept at 10 mMol. A decrease in the equilibrium SHG intensity was observed with decreasing concentration, indicating a decreased amount of adsorbed PCBS. The rate of adsorption is similar for each concentration.

In polyelectrolyte ISAM films, it is known that pH and salt concentration have a strong impact on thickness and SHG of the films. [7] Figure 5 shows that immersion of a

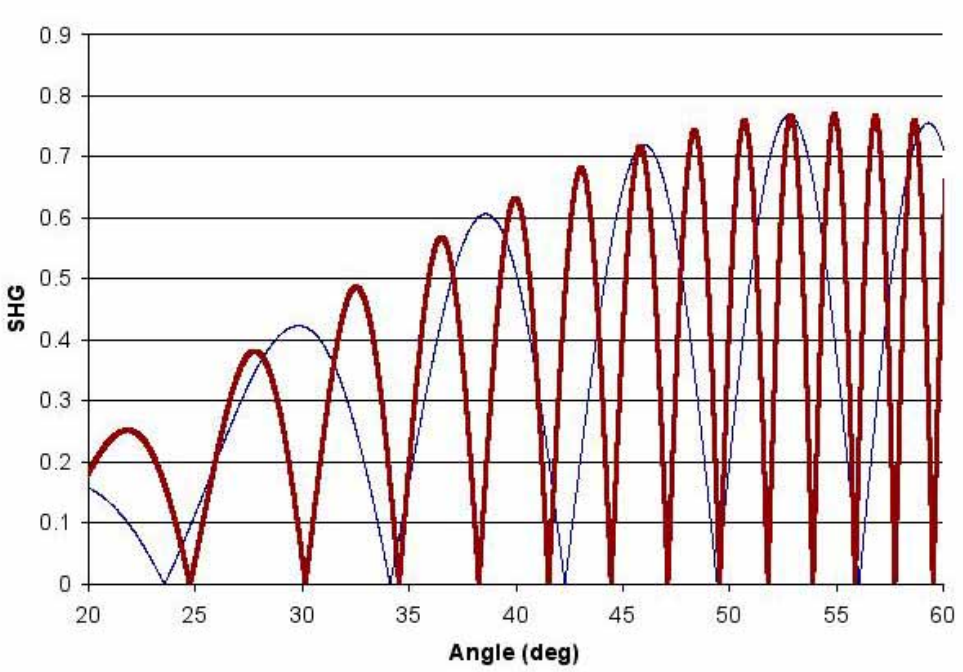

Figure 3. Calculated angular dependence of SHG interference fringes for thin films on opposite sides of the substrate immersed in water (thick curve) and in air (thin curve).

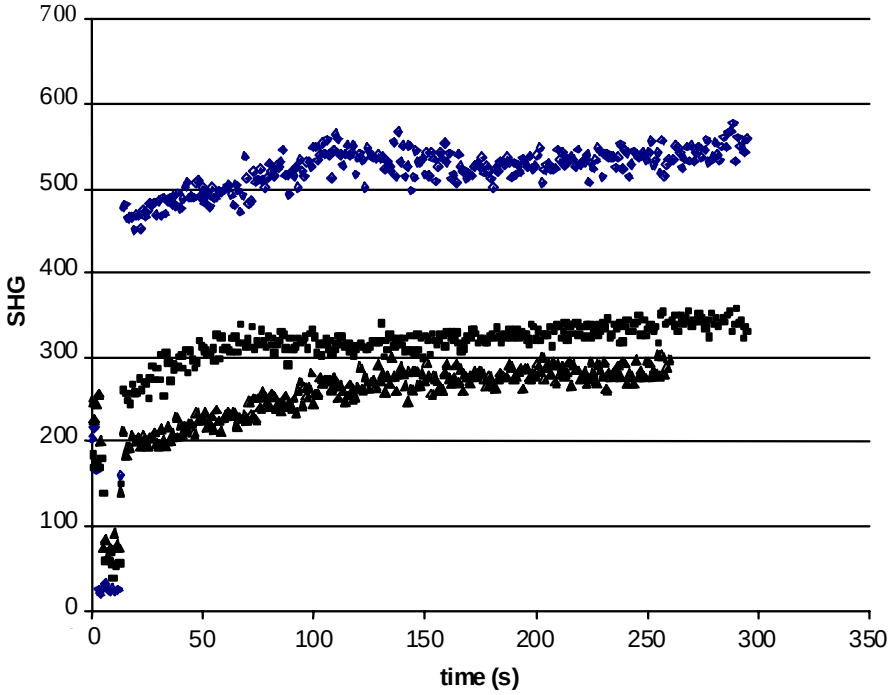

Figure 4. SHG signal as function of time during PCBS deposition on PAH for low concentrations of PCBS. The concentrations, top to bottom, are 0.5 mM, 0.05 mM, and 0.0025 mM.

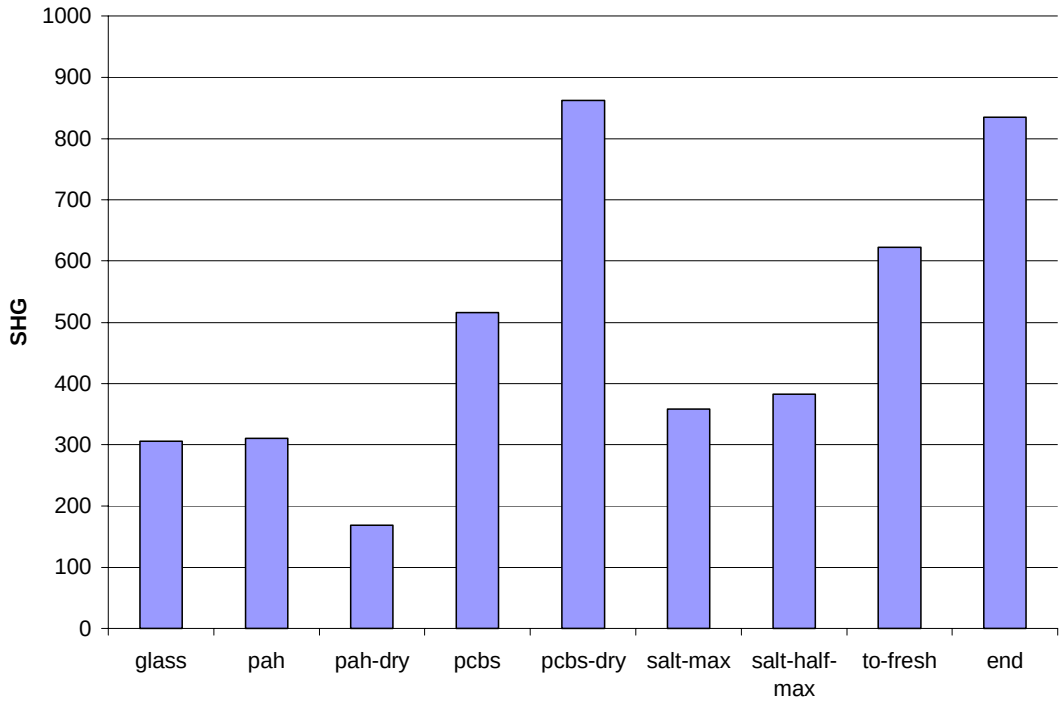

Figure 5. Final values of the *ex situ* SHG signal for different deposition steps. Immersion in salt solution results in a rapid decrease in signal, which is restored when the sample is immersed in deionized water.

PAH/PCBS bilayer in a saturated salt solution leads to decreased SHG intensity. This is believed to be due to the incorporation of salt ions into the monolayer, resulting in decreased polar order of the chromophores. Reducing by half the salt concentration of the ambient solution has hardly any effect on the SHG. However, when the sample is immersed in deionized water, the salt ions diffuse out of the film and the film conformation and therefore the SHG is fully restored. In situ measurements show that most of the restoration takes place in the first minute.

We have recently developed a novel, hybrid covalent/ionic approach to fabricating second order NLO ISAM-like films based on monomeric chromophores. [9] Procion Red (PR, Aldrich) was chosen as a prototype system, possessing a triazine ring which can covalently couple into the preceding PAH layer and two sulfonate groups which can promote electrostatic adsorption of the successive PAH layer. Figure 6 shows the *in situ* SHG as a function of time during the deposition of Procion Red on PAH. This deposition is essentially complete in two minutes.

SUMMARY

In this study, we showed that both Procion Red and PCBS can be deposited on PAH in roughly minute. Also, PAH can be deposited on Procion Red in less than a minute. The concentration of the PCBS solution can be lowered to 0.5 mMol without loss of signal or deposition speed. Lower concentrations reduce the SHG signal but significant deposition has been recorded at concentrations as low as 0.0025 mMol. Immersion in salt solution

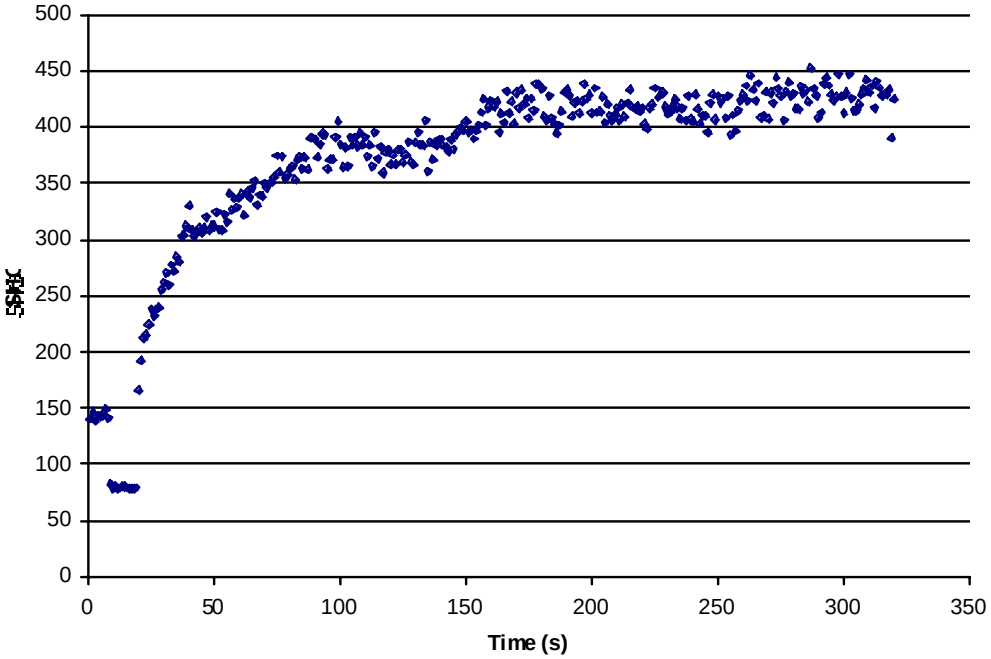

Figure 6. The SHG signal as function of time during deposition of procion red on PAH.

immediately decreases the SHG signal due to inclusion of salt ions in the film. Subsequent immersion into deionized water causes the salt ions to diffuse out of the layer causing near complete restoration of the SHG signal

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