

In Situ Second Harmonic Generation Measurements of the Growth of 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 a substantial second order nonlinear optical (NLO) response. Here, the deposition of ISAMs has been studied *in situ* via second harmonic generation (SHG). We show that the adsorption and ordering of a noncentrosymmetric nonlinear optical polymer is constant over a wide range of concentrations. Upon immersion in the NLO-active polyelectrolyte solution, the SHG rises sharply over the first minute. Immersion in the NLO-inactive partner polyelectrolyte leads to a reduction in the SHG signal. Furthermore, when the film is removed from the NLO-active solution and allowed to dry, the SHG increases rapidly as the water evaporates. These studies provide greater understanding of the processes by which noncentrosymmetric order is formed in ISAM films and allows design of improved self-assembled nonlinear optical materials.

INTRODUCTION

The formation of ionically self-assembled monolayer (ISAM) films, grown monolayer by monolayer by alternately immersing a charged substrate in anionic and cationic solutions, has proven to be an easy, fast, and inexpensive method for creating laterally homogeneous nanostructured thin films[1,2]. Research is ongoing by many groups to develop ISAM devices including light-emitting diodes, photovoltaics, and electrochromics. A few groups, including ours, have been interested in the use of the ISAM technique for the production of films with a second order nonlinear optical (NLO) response because of the potential for dramatically improved electro-optic devices. These films show substantial $\chi^{(2)}$ values with an excellent temporal and thermal stability[3-7]. In order to better understand the dynamics of the deposition process, it would be advantageous to be able to measure the growth of ISAM films *in situ*. In this paper, we discuss the use of second harmonic generation (SHG) to study the deposition of the films.

EXPERIMENTAL DETAILS

The measurements were done with a standard SHG setup using a 30 picosecond pulsed Nd:YAG laser with a wavelength of 1064 nm and p-polarization. Typical beam radius and pulse energy values were 100 μm and 1 mJ/pulse, respectively. The SHG data were averaged over 100 shots per data point, and the uncertainty in relative $\chi^{(2)}$ values is 10%. Measurements were repeated on at least three samples in each case. The sample holder was constructed such that the sample could be immersed into a 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 also as the sample is removed from the solution. The materials used in these experiments were poly (allylamine hydrochloride) (PAH) and poly {1-4-(3-carboxy -4-hydroxyphenylazo)-benzenesulfonamido-1,2-ethanediyl, sodium salt} (PCBS), both from Aldrich.

The SHG signals generated on either side of the glass substrate interfere with each other. The angle between the sample and the incident beam determines the pathlength difference through the glass. The angle for maximum constructive interference thus differs from one glass slide to the next. However, the *ex situ* measurements depicted in Figure 1 show that for a given sample this angle does not change when additional layers are deposited. Thus, in the studies reported here, the angle was first determined so as to maximize the SHG signal from the bare glass substrate and kept fixed throughout the remainder of each experiment. The SHG signal from the bare glass is due to the fact that the air-glass interface, like any surface, is intrinsically non-centrosymmetric.

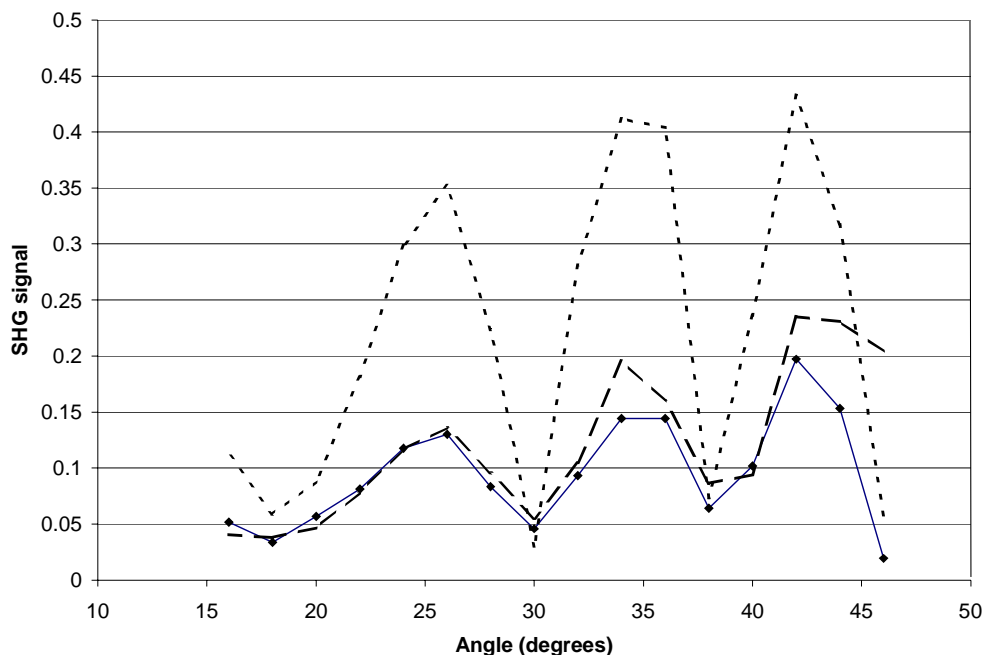


Figure 1. The SHG signal of a glass slide (solid line), single PAH layer (dashed), and a PAH/PCBS bilayer (dotted) as a function of incidence angle between the beam and the substrate normal.

RESULTS

The deposition rate of PCBS on PAH was measured for five different concentrations of PCBS. The concentration of PCBS ranged from 0.037 to 3.0 mM. The PAH concentration was kept fixed at 3 mM, and the pH of both solutions was 7.0. The results, displayed in Figure 2, show that the final SHG value as well as the deposition rate is independent of concentration over this range. It is also clear that the deposition of the PCBS layer is essentially complete in less than a minute.

Figure 3 shows the SHG signal as a function of time for the deposition of the first 5 PCBS layers. The PCBS concentration for this and all subsequent measurements was 0.11 mM. The PAH concentration was 3 mM. The figure shows that the final SHG value is approximately the same for all five layers. It also shows that the deposition for each layer is fast and independent of the layer number. This indicates that in this limit of a small number of PCBS layers, we are strictly dealing with an interface effect and that no bulk SHG signal is generated. This is consistent with our earlier work where *ex situ* measurements of PCBS showed that the SHG signal is essentially constant for the first five bilayers and exhibits the quadratic growth expected of a bulk effect only for greater than twenty bilayers[8]. These results are interpreted in terms of a large interface contribution to the SHG signal that has significant contributions from both the glass-film and film-air interfaces. As the number of deposited layers is increased, the bulk $\chi^{(2)}$ contribution of the film finally becomes dominant.

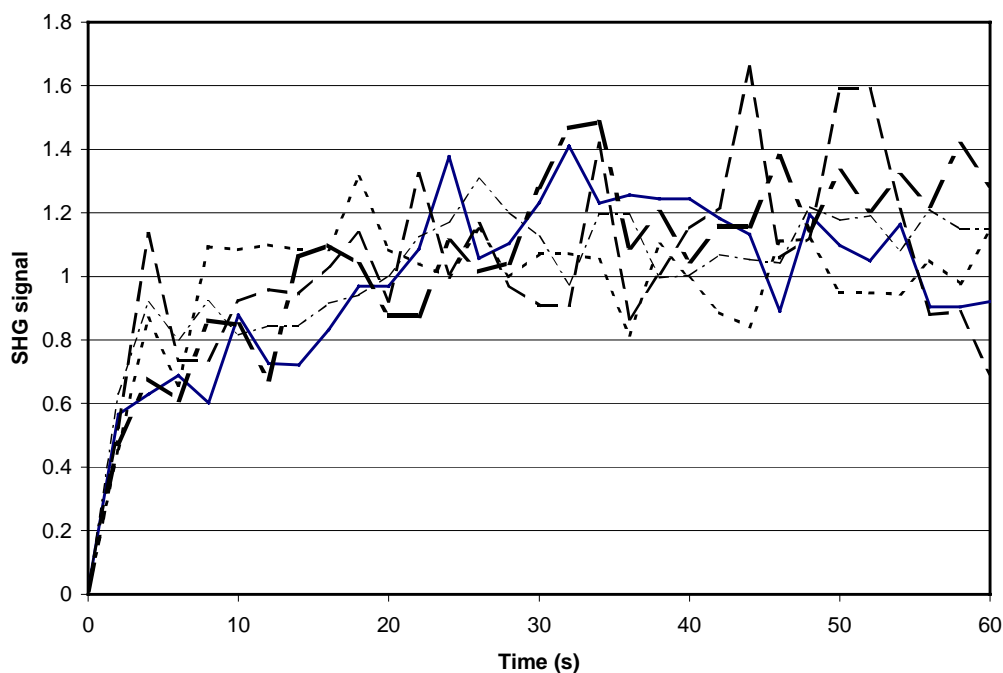


Figure 2. The SHG signal measured in situ as a function of time as a PCBS layer is deposited on a single preceding PAH layer. The figure depicts the SHG signal for five different concentrations of PCBS ranging from 0.037 to 3.0 mM, indicated by solid, dotted, dashed, dash-dotted, and dash-double dotted curves in order of increasing concentration. In all cases the PAH concentration was 3mM.

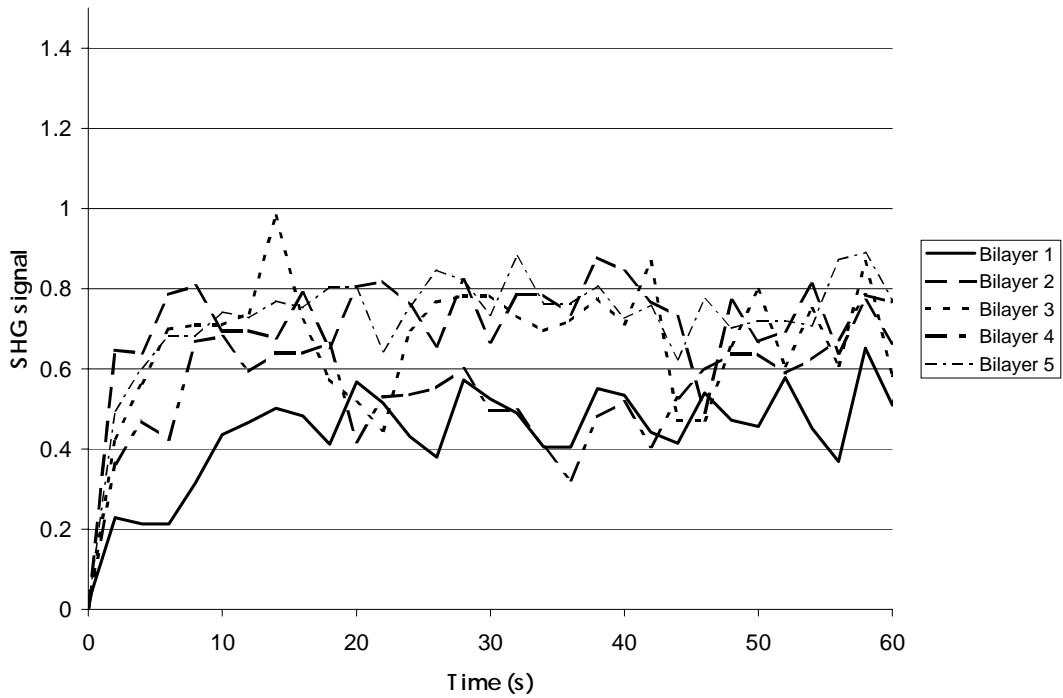


Figure 3. Deposition of PCBS on PAH for the first 5 bilayers as a function of time. The five layers are denoted by solid, dotted, dashed, dash-dotted, and dash-double dotted curves, respectively.

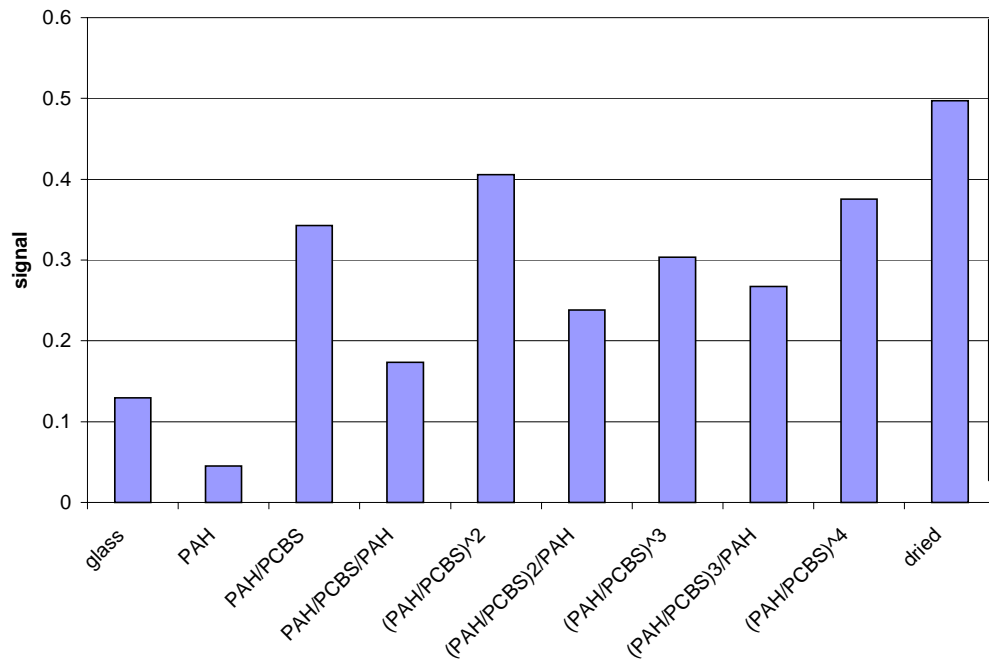


Figure 4. The equilibrium ex situ SHG signal after each layer was deposited for a final five bilayer sample of PAH/PCBS.

The bar chart in Figure 4 shows the *ex situ* SHG values that were taken between depositions, one minute after removal from the solution. It is evident that the measurements done on the “capped layers”, that is, the layers where the outermost polymer is PAH, showed a smaller signal than the previous uncapped signal. We believe this is due to the outermost PAH layer pulling up some of the chromophores of PCBS opposite to the preferred direction (toward the substrate). Because the ISAM fabrication method relies on the formation of ionic bonds with both the preceding and succeeding layers, there is an intrinsic degree of cancellation by chromophores oriented both towards and away from the substrate. When the outer layer is PCBS there is a lesser degree of cancellation while the addition of a PAH layer promotes the orientation of the outermost chromophores away from the substrate. This effect becomes less strong as the number of bilayers increases and the bulk contribution to $\chi^{(2)}$ becomes more significant. Further support for this interpretation of the results is provided by the final bar of Figure 4, which indicates that the SHG of the sample increases as the film dries.

Figure 5 shows the SHG signal as a function of time after removal from PCBS solution. The SHG signal increases rapidly as the water in the film evaporates. In solution, the signal is relatively weak as the solution allows a wide variety of outermost chromophore orientations away from the substrate. As the film dries, these renegade chromophores collapse to orientations more parallel to the surface. Thus, in a simplified view, the outermost layer of PCBS consists of chromophores that are bound to the preceding PAH layer and oriented towards the substrate and other chromophores that are bound to counterions provided by the solution and are oriented primarily parallel to the substrate. This highly asymmetric configuration results in a large SHG signal. The adsorption of an additional PAH layer causes those chromophores previously

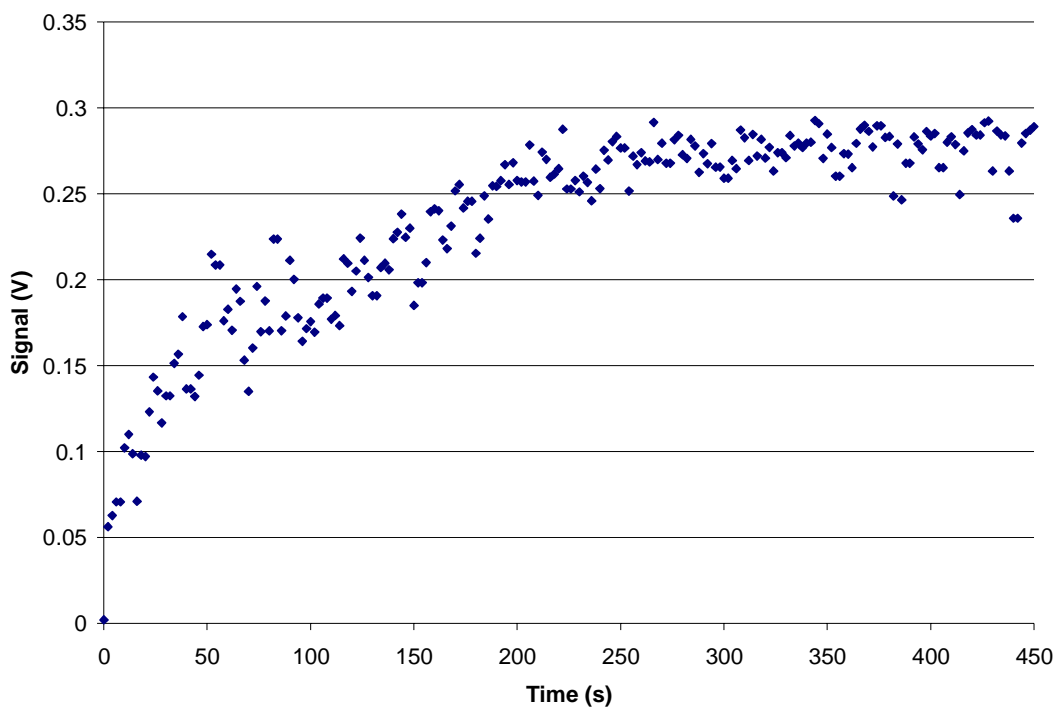


Figure 5. The SHG signal of a PAH/PCBS sample after removal from the PCBS solution as a function of time.

oriented in the plane of the substrate to be pulled to orientations away from the substrate. This cancels the orientation of a fraction of the chromophores oriented towards the substrate and reduces the SHG of the film.

SUMMARY

Ionically self-assembled monolayers are an economically attractive solution for the fabrication of organic thin films for second order nonlinear applications. In this paper, we showed that the generation of a second harmonic signal can be used to observe the NLO chromophore adsorption *in situ*. The deposition rate of PCBS on PAH has been shown to be independent of the PCBS concentration over two orders of magnitude. The deposition rate is the same for all bilayers on a multi bilayer system for small number of bilayers. As the sample dries after removal from the polyelectrolyte solution, the SHG signal increases rapidly as the chromophores reorient.

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