

# In Situ Second Harmonic Generation Measurements of the Formation of Ionically Self-assembled Monolayers

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## ABSTRACT

Recently, ionically self-assembled monolayers (ISAMs) of polymers with nonlinear optical chromophores have been shown to spontaneously exhibit a preferential ordering during the deposition process. This gives rise to a substantial second order nonlinear optical (NLO) response. Here, we use this second harmonic generation (SHG) to our advantage in the *in situ* study of the deposition of ISAMs. Upon immersion in the NLO-active polyelectrolyte solution, the SHG rises sharply over the first minute, demonstrating a rapid adsorption process. Immersion in the NLO-inactive partner polyelectrolyte leads to an instantaneous reduction in the SHG signal. We also show that the adsorption and ordering of a noncentrosymmetric nonlinear optical polymer increases with increasing PCBS concentration. These studies provide deeper understanding of the processes by which noncentrosymmetric order is formed in ISAM films and allows design of improved self-assembled nonlinear optical materials.

## 1. INTRODUCTION

The fabrication of ionically self-assembled monolayers (ISAM) has proven to be an easy, fast, and economically attractive method for creating laterally homogeneous nanostructured thin films[1,2]. ISAM films are grown one monolayer at a time by alternately immersing a charged substrate in anionic and cationic solutions. Research done by many groups has shown that the ISAM method can produce devices such as light-emitting diodes, photovoltaics, and electrochromics with nanostructural control. A few groups, including ours, are researching the application of ISAM technique for the production of films with a second order nonlinear optical (NLO) response. These films show substantial  $\chi^{(2)}$  values with an excellent temporal and thermal stability[3-7]. It would be beneficial, for a better understanding of the deposition process, to be able to measure the growth of the ISAM layer *in situ*. In this paper, we discuss the use of second harmonic generation (SHG) as a unique probe of the deposition of the films.

## 2. EXPERIMENTAL DETAILS

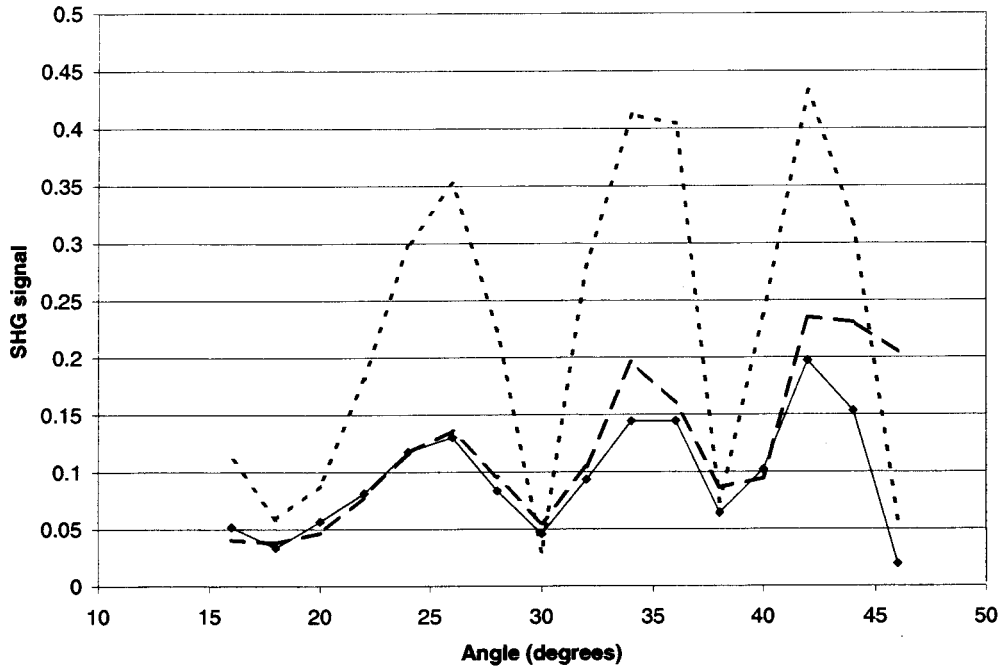
The measurements were done with a standard SHG setup using a 30 picosecond pulsed Nd:YAG modelocked laser with a wavelength of 1064 nm and p-polarized incident light. Typical beam radius and pulse energy values were 100  $\mu\text{m}$  and 1 mJ/pulse, respectively. The SHG data are averaged over 10 shots per data point for the *in situ* measurements and 100 shots for *ex situ* measurements. Measurements were repeated on at least three samples in each case. The sample holder was constructed such that the film substrate is not moved with respect to the incoming laser beam at any time during the experiment. This enabled us to measure the SHG signal while the layer is growing and also as the sample is removed from the solution, always monitoring the same spot on the sample. 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.

In general, the SHG signals generated by the film on either side of the sample interfere with one other, with a phase that is determined by the propagation distance between them. The pathlength difference through the glass substrate is determined by the angle between the sample and the incident beam and the thickness of the glass. The angle for maximum constructive interference is therefore dependent on the thickness of each particular glass slide. Figure 1 shows that this angle is independent of the deposited layers. Although the angle of maximum interference is not dependent on the deposited layer it is dependent on the refractive index of the surrounding material, since this determines the refracted angle in the glass. Figure 2 shows the measured SHG interference fringes for ISAM films on both sides of a glass microscope slide as a function of the external incident angle. The relevant length scale for the interference between SHG signal from opposite sides of the glass slide is the pathlength of the beam through the slide. This distance is  $h = 1 \text{ mm} / \cos \theta'$  where 1 mm is the thickness of the slide and  $\theta'$  is the refracted angle in the glass which is determined from the external incident angle by Snell's Law. Figure 3 shows the result of 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 in water ( $n=1.33$ ). It is evident that when the sample is in aqueous solution the peaks are shifted and closer together as a result of the larger refracted angle in the glass.

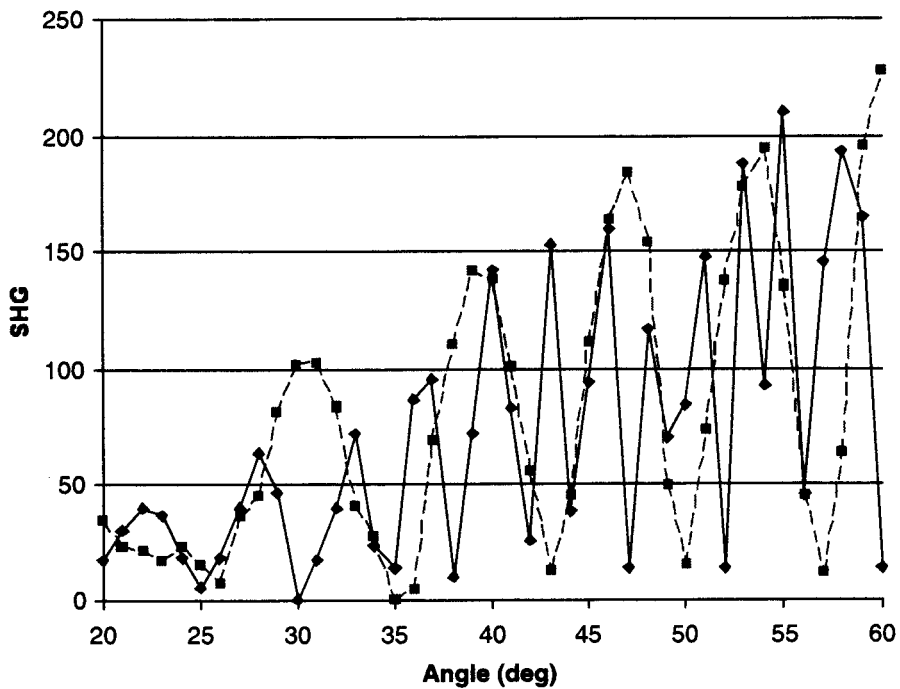
Thus, in the studies reported here, the angle for maximal constructive interference was first determined for both the air-glass as well as the water-glass interface and these angles were used for the remainder of each experiment. The SHG signal from the bare glass substrate is due to the fact that the air-glass interface, like any surface, is intrinsically non-centrosymmetric.

## 3. RESULTS

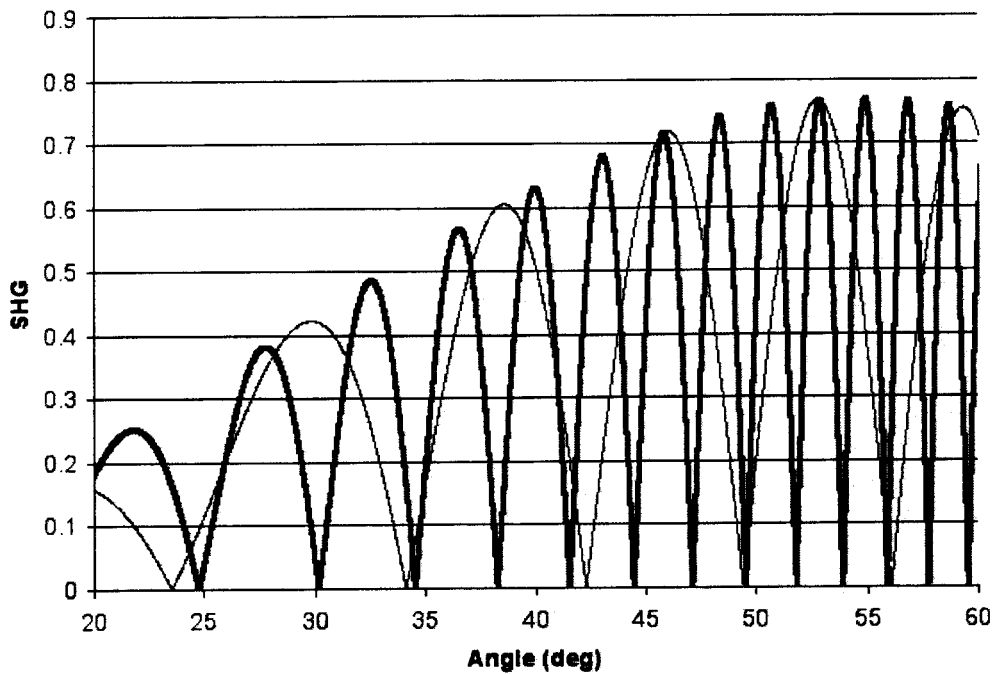
The deposition rate of PCBS on PAH was measured for three different concentrations of PCBS. The PCBS concentration ranged from 0.0025 to 0.5 mM while the concentration of PAH was kept constant at 10 mM. The pH of both solutions was kept at 7.0. The results displayed in



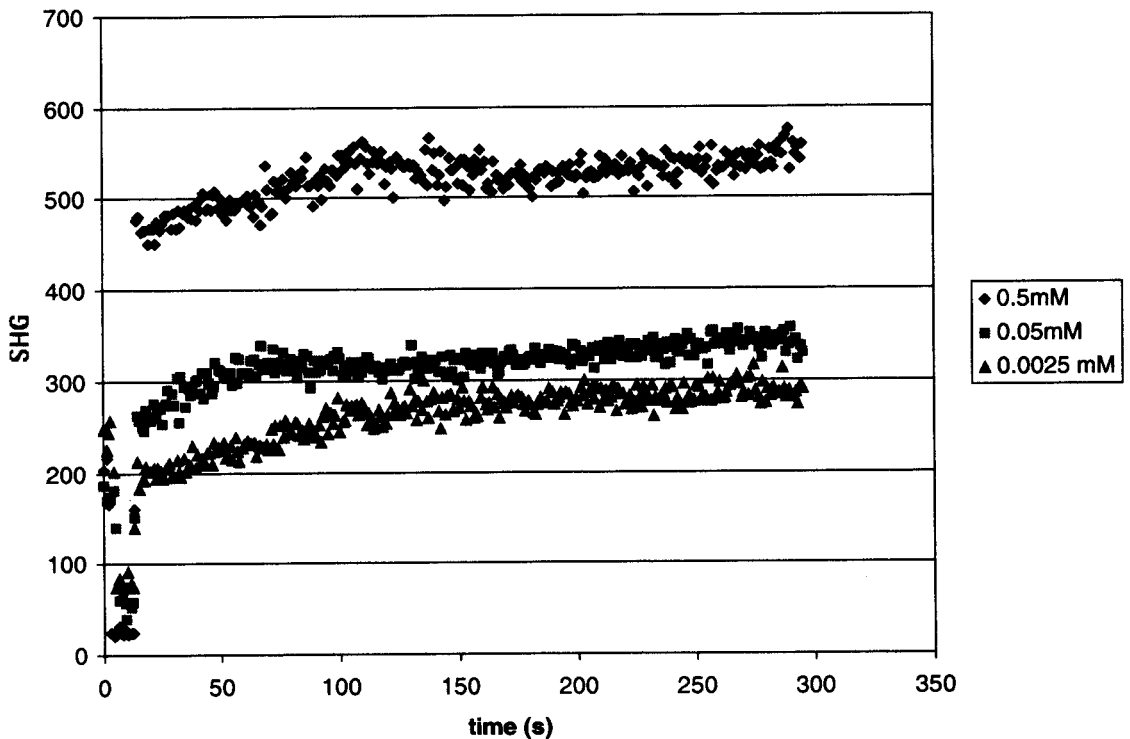
**Figure 1.** The SHG signal of a glass slide, single PAH layer, and a PAH/PCBS bilayer as a function of incidence angle between the beam and the substrate normal are denoted with a solid, dashed, and dotted line respectively. All measurements are taken on ex situ dry films.



**Figure 2.** The SHG signal of an ISAM film measured in aqueous solution (solid line) and dry (dashed line) as a function of incident angle.



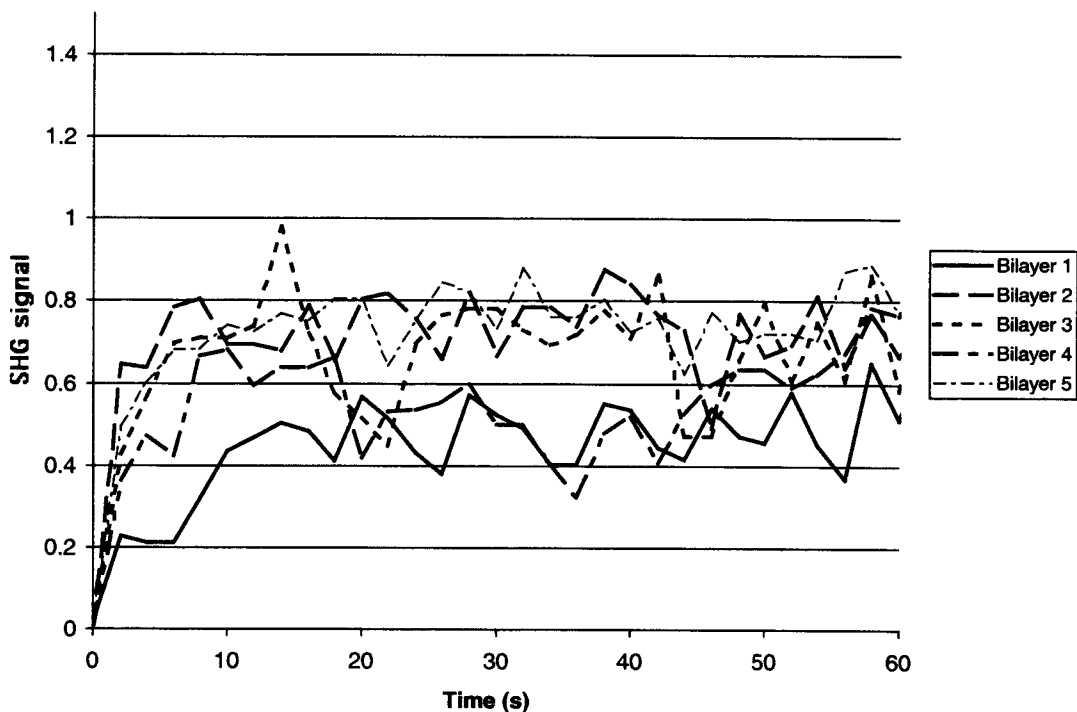
**Figure 3.** Calculated angular dependence of SHG interference fringes for thin films on opposite sides of the substrate immersed in water (thick curve) and in air (thin curve).



**Figure 4.** The *in situ* SHG signal measured as a function of time while a PCBS layer is deposited on a single PAH layer. The PCBS concentrations were 0.0025, 0.05, and 0.5 mM from bottom to top, respectively. The PAH concentration was kept constant at 10 mM.

Figure 4, show that the final SHG value of the film decreases with decreasing PCBS concentration. The deposition rate also decreases with decreasing PCBS concentration although the deposition is complete in about a minute in all cases. It is remarkable that significant adsorption occurs with relative rapidity even at a concentration as low as 0.0025 mM.

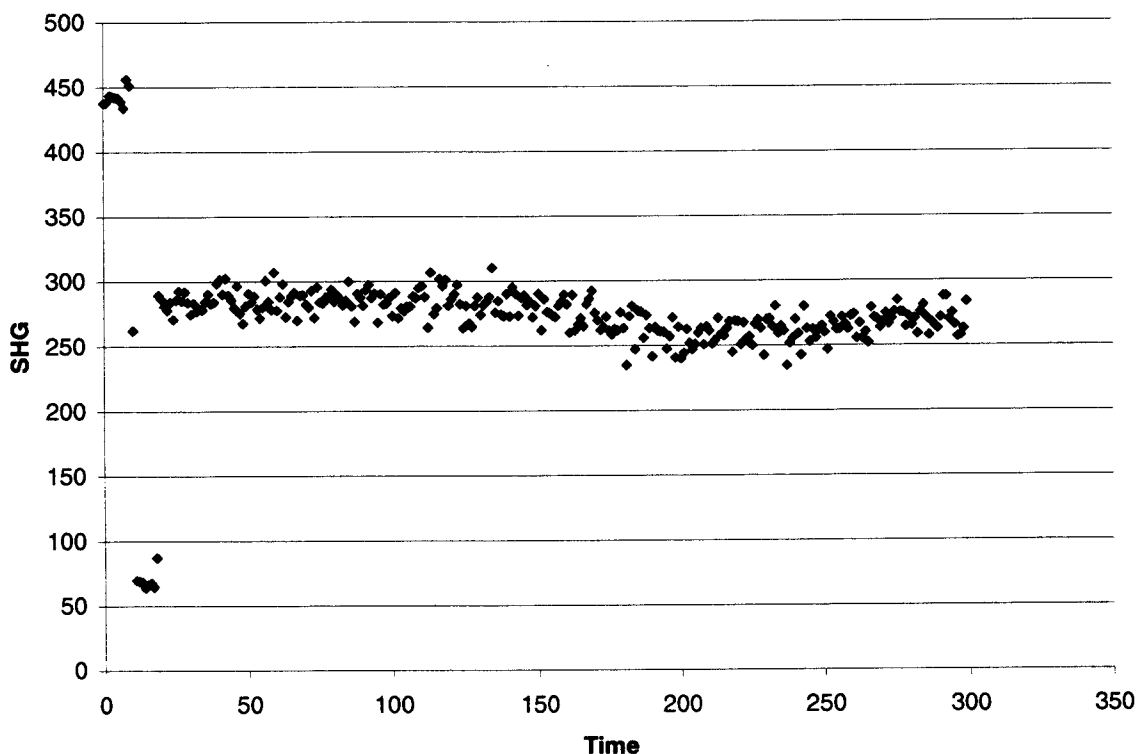
Figure 5 shows the SHG signal as a function of time for the deposition of five consecutive PCBS layers with PAH layers deposited between each one. The PCBS concentration for this measurement was 0.11 mM. The PAH concentration was 3 mM. The figure shows that the final SHG value is approximately the same for all five layers. It also shows that the deposition rate for each layer is large and independent of the layer number. This indicates that for small numbers of PCBS layers the interface effects are dominant and that little or no bulk SHG is generated. This is in agreement with our earlier *ex situ* measurements of PCBS on PAH which 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.



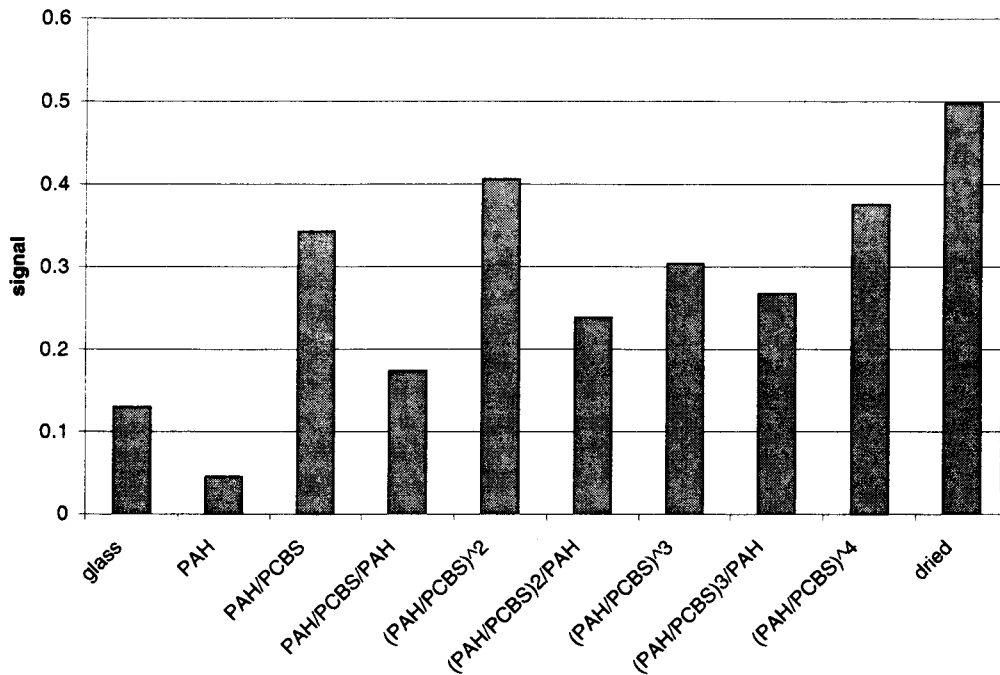
**Figure 5.** Deposition of PCBS on PAH for the first 5 bilayers as a function of time. The five layers are denoted by solid, dotted, dashed, dash-dotted, and dash-double dotted curves, respectively.

As discussed in more detail below, the addition of a PAH layer to a PCBS layer ("capping") leads to a decrease in the SHG signal. While the capping due to PAH deposition in some of our measurements on other materials took times up to a minute, we observed that the capping effect of 10 mM PAH on a PCBS layer is faster than the minimum resolution of our measurements of a few seconds. This can be seen in Figure 6 where the SHG signal from the dry PCBS layers is 440 counts. Immediately after immersion into the PAH solution, the SHG falls to 280 counts.

SHG measurements were also made for each layer after the substrate was removed from the solution and allowed to dry. The final *ex situ* SHG values taken after each deposition are shown in Figure 7. The signal from the measurements made on the "capped" layers, that is, the layers where the outermost polymer is PAH, is smaller than the previous uncapped signal. We believe that as the outer PAH layer is deposited it pulls up some of the chromophores of PCBS opposite to the preferred direction (which is towards the substrate). Because the ISAM fabrication method relies on the formation of ionic bonds with both the preceding and succeeding layers, some degree of cancellation by chromophores oriented both towards and away from the substrate is inevitable in polymeric systems. For the outermost PCBS layer, the situation is more symmetric if a capping layer is present than if it is not, thus resulting in the observed lower SHG signal for capped layers. This effect becomes less strong as the number of bilayers increases and the bulk contribution to  $\chi^{(2)}$  becomes more significant.



**Figure 6.** The SHG as a function of time for 10 mM PAH deposited on a PCBS layer.



**Figure 7.** The equilibrium *ex situ* SHG signal after each layer was deposited for a final four bilayer sample of PAH/PCBS.

#### 4. SUMMARY

Ionically self-assembled monolayers are an inexpensive and rapid approach to the fabrication of highly stable organic thin films for second order nonlinear optical applications. In this paper, we employed the generation of a second harmonic signal to observe the NLO chromophore adsorption *in situ*. The adsorption of polymeric monolayers with typical thickness on the order of 1 nm has been observed in real time to occur on a time scale faster than one minute. The deposition amount and rate of PCBS on PAH has been shown to increase with increasing PCBS concentration. For small number of bilayers, the deposition rate is unchanged for all bilayers on a multi-bilayer system when the immersion solution parameters are kept fixed.

#### 5. ACKNOWLEDGEMENTS

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