

IN SITU SECOND HARMONIC GENERATION MEASUREMENTS OF THE GROWTH OF NONLINEAR OPTICALLY IONICALLY SELF-ASSEMBLED MONOLAYERS

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Introduction

The ability to control the structure and composition of matter on the nanometer length scale affords opportunities both for enhanced material properties and for novel phenomena. The formation of ionically self-assembled monolayers (ISAMs) is a particularly elegant and simple approach to nanocomposites.^{1,2} Several groups, including our own, have recently shown that with appropriate choices of component materials, noncentrosymmetric ISAM films can be fabricated with substantial $\chi^{(2)}$ values.³⁻⁹ Importantly, no electric field poling is required, and the $\chi^{(2)}$ values show excellent temporal and thermal stability. Here, we describe nonlinear optical studies of the layer-by-layer formation of ISAM films, including *in situ* second harmonic generation (SHG) measurements as a layer is adsorbed onto the surface.

ISAM Film Fabrication

ISAM films are grown monolayer by monolayer by alternately immersing a charged substrate in anionic and cationic solutions. Upon each immersion, an exceptionally homogeneous layer is rapidly formed by electrostatic attraction to the oppositely charged surface. The thickness of each individual layer is typically on the order of 1 nm. The immersion process can be repeated until a film with the desired thickness or number of layers has been produced. For the studies presented here, ISAM films were deposited on glass microscope slide substrates. Noncentrosymmetric, ISAM $\chi^{(2)}$ films were produced using the anionic polymer dye poly{1-[4-(3-carboxy-4-hydroxyphenylazo)benzene-sulfanamido]-1,2-ethanediyl} (PCBS, from Aldrich), which consists of a poly(vinyl amine) backbone with an ionic azo-dye chromophore. Poly (allylamine hydrochloride) (PAH) was used for the polycation. As shown in Figure 1, the formation of each monolayer is exceptionally rapid. The figure shows the absorbance and thickness for a series of films consisting of thirty bilayers each as a function of the immersion time in each solution. In less than one minute, the absorbance and thickness each reach values greater than 80% of the maximum value. Films immersed for thirty minutes in each solution produced values roughly 10% less than those immersed for 300 seconds.

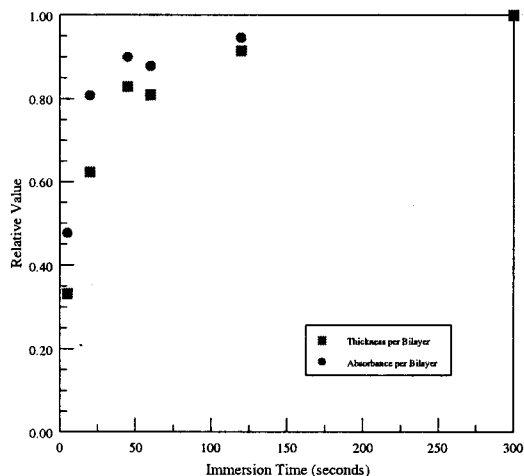


Figure 1. Relative film thickness and absorbance for thirty-bilayer Poly S-119/PAH ISAM films as a function of immersion time in the solutions.

Results and Discussion

Second harmonic generation (SHG) measurements were made using the 1064 nm fundamental or the 1200 nm output from a broadband BBO optical parametric oscillator pumped by the 355 nm third harmonic of a Q-switched Nd:YAG laser. The beam was weakly focused into the sample to a spot size of a few hundred microns. The film was polished off of one side of the substrate to eliminate interference effects, and the film was rotated 45° away from normal incidence about the vertical axis with incident p-polarized light. As described in ref. 3, the SHG intensity exhibited the expected quadratic dependence on the number of bilayers up to 100 bilayers for Poly S-119/PAH ISAM films. The quadratic growth of the SHG intensity is particularly important because it illustrates that the degree of polar orientation is maintained for each successive bilayer. If the degree of orientation was decreased for the latter deposited layers, the SHG intensity would have a subquadratic dependence on the number of bilayers.

While the data presented in ref. 3 shows the expected quadratic dependence of SHG intensity on the number of deposited layers (and, correspondingly, thickness) for the range of 30 to 100 bilayers, nonlinear optical studies of the initial layers showed unusual behavior. Two films of PCBS and PAH were grown and measured at intermediate points during the fabrication process. Both films were made from solutions with PCBS pH of 7.3 and PAH pH of 7.6. The absorbance and SHG of the first film was measured after the adsorption of each PCBS layer up to a total of seven bilayers. The second film was measured after every fifth PCBS layer up to a total of 35 bilayers. The absorbance at the 364 nm peak is shown in Figure 2 for each of the two film series. The absorbance and thickness of the film are seen to be linear with number of adsorbed layers.

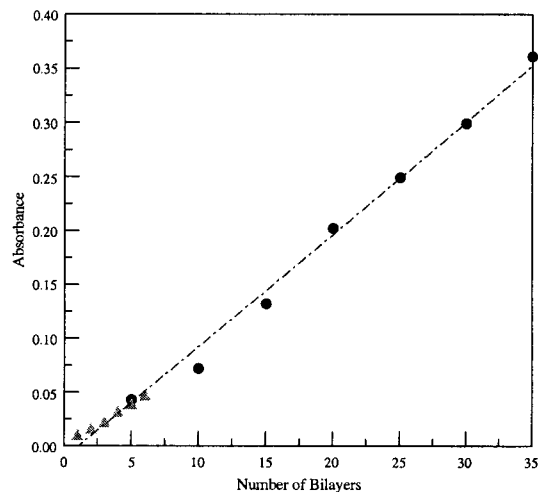


Figure 2. Absorbance at 364 nm for PCBS/PAH ISAM films measured after each adsorbed bilayer (triangles) and every fifth bilayer (circles).

The SHG intensity as a function of the number of PCBS layers is shown in Figure 3. The SHG intensity is expected to be quadratic in the film thickness and, thus, the number of bilayers. It is found, however, the SHG signal from the first PCBS layer is substantially larger than that of successive layers. Only after approximately 20 bilayers does the SHG intensity begin to exhibit quadratic growth.

The calculated $\chi^{(2)}$ from the data of Figure 3 is largest for the single-bilayer film and decreases monotonically with a nonzero asymptotic value. This is shown in Figure 4, where the bilayer susceptibility $\eta^{(2)}$ is plotted as a function of the number of bilayers. The bilayer susceptibility is a quantity normalized to the number of bilayers rather than the thickness of the film. In the case of constant bilayer thickness, such as the case here, it is proportional to $\chi^{(2)}$. The fit to the data is a function of the form $A/N_0 + B$ where N_0 is the number of bilayers. The first term corresponds to a contribution to $\chi^{(2)}$ from just the first bilayer. If the additional bilayers produced no net $\chi^{(2)}$, the $\chi^{(2)}$ of the film would decrease as $1/N_0$ since the film thickness increases while the SHG intensity remains constant. The second term, independent of N_0 ,

represents a "bulk" $\chi^{(2)}$ response in which the degree of polar order is constant in each successive layer starting with the second. The value of A/B from the fit is 10, indicating that the effective $\chi^{(2)}$ of the first bilayer is ten times larger than that successive layers.

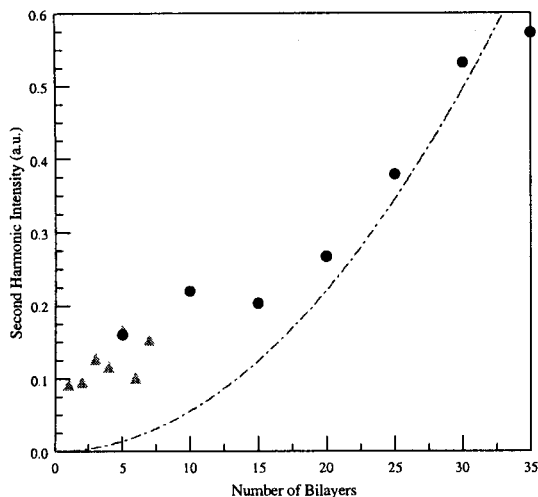


Figure 3. Second harmonic intensity versus number of bilayers for PCBS/PAH ISAM films measured after each adsorbed bilayer (triangles) and every fifth bilayer (circles).

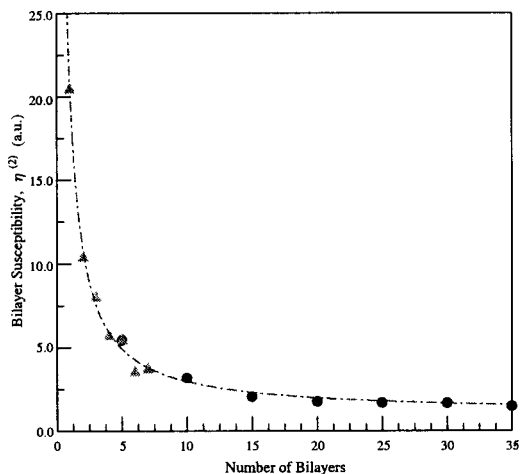


Figure 4. Bilayer susceptibility $\eta^{(2)}$ versus number of bilayers for PCBS/PAH ISAM films measured after each adsorbed bilayer (triangles) and every fifth bilayer (circles). Since the bilayer thickness is constant within this series of films, $\eta^{(2)}$ is proportional to $\chi^{(2)}$.

The growth of individual layers has also been measured *in situ* via second harmonic generation. 10 mM solutions of PCBS and PAH were made at pH=7.0 and placed in glass cells 6 cm wide and 1 cm deep. A cleaned glass microscope slide was suspended from above in the optical path and the cells were inserted from underneath to immerse the slide in the solutions. The measurements were made with 30 ps pulses at 1064 nm fundamental wavelength from a modelocked Nd:YAG laser. The slide was first immersed in PAH to provide a cationic outer surface. The slide was then rinsed with deionized water and immersed in PCBS. The observed growth in the second harmonic intensity as a function of immersion time is illustrated in Figure 5. A very rapid rise occurs during the first minute, followed by a slower growth over the next several minutes. This behavior is consistent with that shown in Figure 1, in which the slides were immersed for the specified time in each

solution, removed and measured *ex situ*. The *in situ* SHG measurements indicate that the noncentrosymmetric ordering occurs immediately upon adsorption, without requiring significant rearrangement of the chromophores.

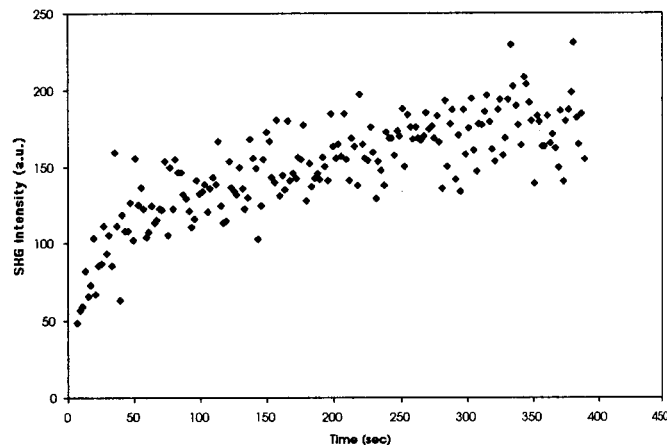


Figure 5. *In situ* measurement of the second harmonic intensity of the deposition of a PCBS layer on a glass slide that has had one layer of PAH previously adsorbed.

Conclusions

Ionically self-assembled monolayers provide a novel route to the fabrication of polymer films with intrinsic noncentrosymmetry. These films possess exceptional temporal and thermal stability of $\chi^{(2)}$ relative to poled polymers.⁹ It has been found that the first bilayer provides an exceptionally large contribution to the second harmonic signal while the successive layers produce smaller contributions that show the expected quadratic scaling with thickness. *In situ* SHG measurements show that formation of the noncentrosymmetric ordered structure is largely complete within a couple minutes.

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