

Enhanced Second Order Nonlinear Optical Susceptibilities in Ionically Self-Assembled Films Incorporating Dianionic Molecules

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ABSTRACT

Ionically self-assembled monolayer (ISAM) films have been recently shown to spontaneously produce noncentrosymmetric ordering that gives rise to a substantial second order nonlinear optical (NLO) response. Typically, the ISAM films for NLO response are an assemblage of bilayers of oppositely charged polymers whose thickness can be controlled through variation of pH and ionic strength of the immersion solutions. Here, we study the effects of replacing the NLO-active polymer layers with layers of dianionic molecules. Films fabricated exclusively using polyelectrolytes contain some fraction of both randomly oriented and anti-parallel oriented chromophores. The incorporation of dianionic molecules within the ISAM films affords greater $\chi^{(2)}$ due to increased net polar orientation of the chromophores.

INTRODUCTION

The formation of ionically self-assembled monolayer (ISAM) films, grown monolayer by monolayer by alternately immersing a charged substrate in anionic and cationic polymer solutions, has proven to be an easy, fast, and inexpensive method for creating laterally homogeneous nanostructured thin films [1,2]. 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 [3-9]. These films show substantial $\chi^{(2)}$ values with excellent temporal and thermal stability. In addition, the study of the structure of the ISAM films via second harmonic generation (SHG) affords valuable insight for other applications. Films fabricated with an NLO polymer result in significant cancellation of the chromophore orientations. A reduction in film thickness accompanied by an increase in polar ordering is one possible avenue to obtain the $\chi^{(2)}$ necessary for electro-optic devices. In this paper, we discuss the advantages of incorporating dianionic molecules into ISAM films in order to achieve an enhanced second order nonlinear optical susceptibility.

EXPERIMENTAL DETAILS

ISAM films are grown monolayer by monolayer by alternately immersing a charged substrate in anionic and cationic solutions forming a multilayer structure. Upon each immersion, an exceptionally homogeneous layer is rapidly (less than one minute) formed by electrostatic attraction to the oppositely charged surface. The thickness of each monolayer is on the order of 1 nm, and can be controlled to be 0.3 to >5.0 nm by the pH and ionic strength of the solutions. The immersion process can be repeated indefinitely until a desired thickness or number of bilayers has been

achieved. For the studies presented here, ISAM films were deposited on cleaned glass microscope substrates. The polymer-polymer bilayers were produced using the anionic polymer dye Poly S-119 (from Sigma), which consists of a poly(vinyl amine) backbone with an ionic azo-dye chromophore, and the cationic polymer poly(allylamine hydrochloride) (PAH). The dianionic chromophore films were produced with PAH along with Mordant Orange 10 (Aldrich) which has a sulfonate on one end and a carboxyl on the opposite end.

Measurements were performed with a standard SHG setup using a 10-nanosecond pulse width, Q-switched Nd:YAG laser with a fundamental wavelength of 1064 nm. Typical beam radius and pulse energy values were 100 μm and 3 mJ/pulse, respectively. The SHG data were averaged over 100 shots per data point, and the uncertainty in relative $\chi^{(2)}$ values is 10%. For the polymer-polymer films, to obtain a second harmonic wavelength outside the absorbing region of Poly S-119, the measurements were made using the 1200 nm output from a broadband BBO optical parametric oscillator (OPO) pumped by the 355nm third harmonic of the laser. The film was polished from one side of the substrate. The film was rotated 45° away from normal incidence about the vertical axis with incident p-polarized light, and the second harmonic was measured as a function of the incident fundamental beam intensity. For the study of the incorporation of dianionic chromophores, measurements were made at 1064 nm.

DISCUSSION

We have shown earlier that the film thickness can be controlled by variation of the pH and ionic strength of the immersion solution [8,9]. Utilizing Debye-Huckel theory, we showed that the free ion concentration in solution is the determining factor for film thickness. For example, increased H^+ or Na^+ ion concentrations (through lowered pH or added NaCl) provide greater electrostatic screening between neighboring charges on the polyanion. This allows greater curvature of the polymer backbone such that an increased fraction of the polymer segments adsorbs as loops, resulting in a thicker adsorbed layer. The effect of increased ionic strength is shown in Figure 1 where the thickness per bilayer is shown as a function of pH and NaCl concentration for

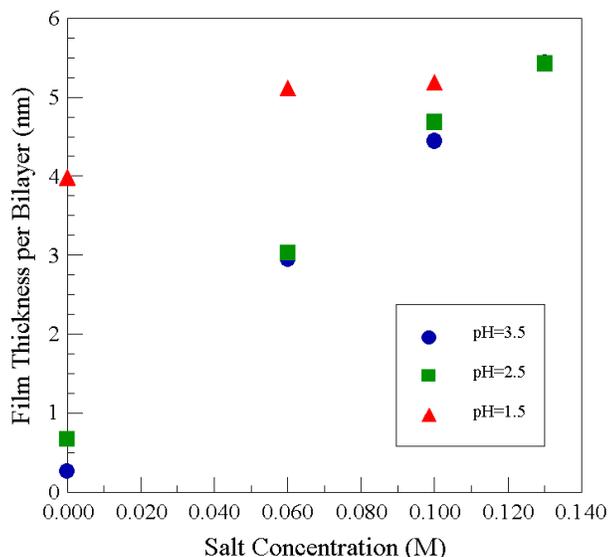


Figure 1. Bilayer thickness as a function of pH and salt concentration of the immersion solutions for Poly S-119/PAH ISAM films.

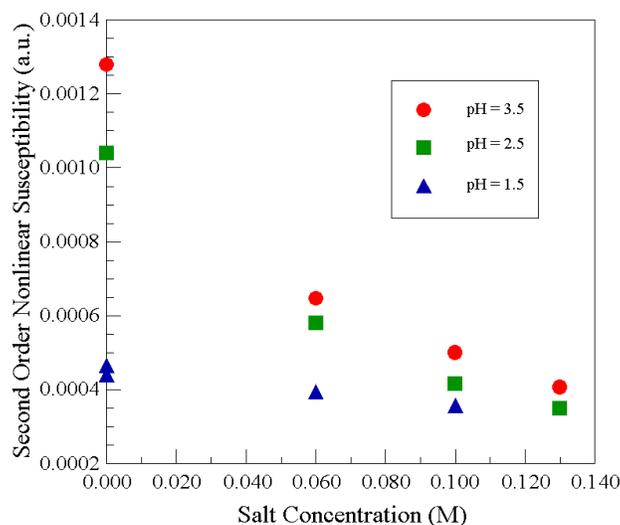


Figure 2. $\chi^{(2)}$ as a function of solution parameters. When compared with Figure 1, it is evident that $\chi^{(2)}$ decreases with increasing thickness per bilayer.

Poly S-119/PAH ISAM films. It is seen that lowered pH and increased NaCl dramatically increase the bilayer thickness. However, the SHG produced by these films increases much less rapidly than the bilayer thickness. As a result, $\chi^{(2)}$ decreases with decreased pH and increased salt concentration, as shown in Figure 2. This indicates that not all of the adsorbed chromophores contribute equally to the SHG, otherwise $\chi^{(2)}$ would remain constant. Rather, $\chi^{(2)}$ is determined primarily from the chromophores at the monolayer interfaces. Those chromophores within the “bulk” of an individual layer have essentially random orientations. It should also be noted that there is increasing evidence that ISAM layers are quite interpenetrated rather than stratified so that the models described here are first approximations to the very complex physical system. Due to the nature of the formation of ISAM films utilizing two polymers, the NLO-active polyelectrolyte must have chromophores oriented in opposite directions in order to provide binding to the preceding and following oppositely-charged layers. This is schematically illustrated in Figure 3a. The opposing dipole orientations cancel one another and lead to an overall reduction in the $\chi^{(2)}$ of the film. Thus,

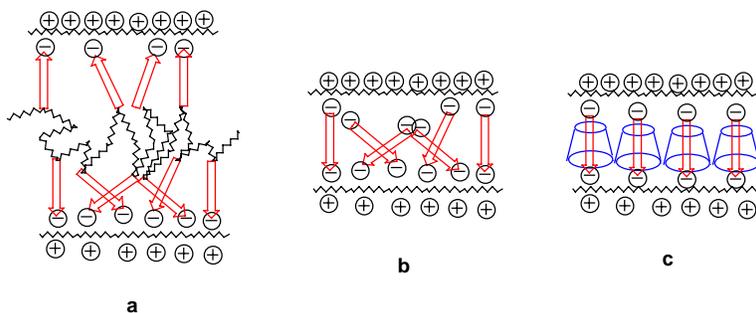


Figure 3 Schematic illustrations of the first couple monolayers of a) a conventional ISAM film incorporating a polar side-chain polymer and b) a dianionic chromophore ISAM $\chi^{(2)}$ film and c) a dianionic chromophore with a cyclodextrin rigid sleeve.

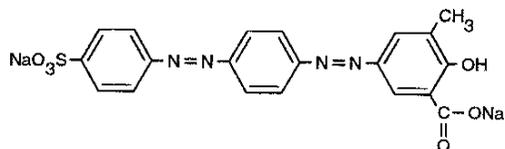


Figure 4. The dianionic chromophore Mordant Orange 10.

polyelectrolyte-based ISAM films suffer from lack of orientation of chromophores within the bulk of a monolayer and partial cancellation by chromophores at the upper and lower interfaces. In order to overcome these issues, we have fabricated ionically self-assembled films of a distinctly different structure. These films contain dianionic NLO chromophores, as opposed to polyelectrolytes with NLO sidechains. An example of such a dianionic chromophore is the dye Mordant Orange 10 (from Aldrich) depicted in Figure 4. The use of a chromophore with two distinct ionic functionalities provides an important method for directing the orientation of the chromophore as it is adsorbed. The sulfonic acid moiety has a pKa in the vicinity of 0 while that of the carboxylic acid is 5. Thus, at a pH of 3, the sulfonic acid will be ionized while the carboxylic acid will remain neutral. When the substrate is immersed in a Mordant Orange aqueous solution at pH=3, the sulfonate will be preferentially adsorbed towards the preceding polycationic layer. Subsequent immersion in the polycationic solution at pH 7 will lead to ionization of the carboxy groups, allowing adsorption of the next polycationic layer. The structure obtained by such a procedure, illustrated schematically in Figure 3b, is expected to possess a much larger net polar orientation than that of Figure 3a.

Figure 5 shows the SHG signal as a function of the incident angle of the fundamental beam with respect to the substrate normal for a representative Mordant Orange 10/PAH ISAM sample from which one side of the film has been polished off. The fringes with non-zero minima result from interference of the SHG from the film with the SHG from the air-glass interface on the opposite side. The lower curve in the figure shows the SHG signal from a bare glass slide. Because the air-glass interface is inherently noncentrosymmetric, it possesses a non-zero $\chi^{(2)}$ and generates second harmonic. The Maker fringes in Figure 5 have a periodicity of $\sim 7^\circ$ in the vicinity of 45°

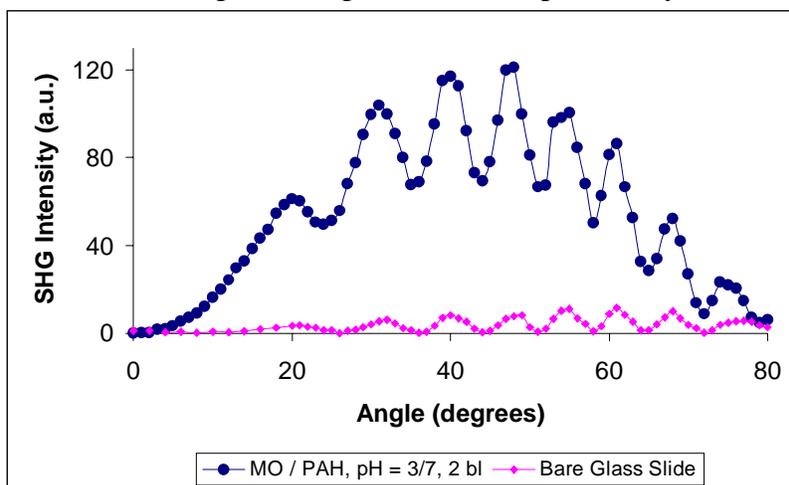


Figure 5. Maker fringes from a bare glass slide (lower curve) and a slide with Mordant Orange 10 film on one side. The amplitude of the fringes in both cases indicates SHG from the glass-air interfaces. The periodicity of the fringes corresponds to SHG from interfaces 1 mm apart (the thickness of a microscope slide)

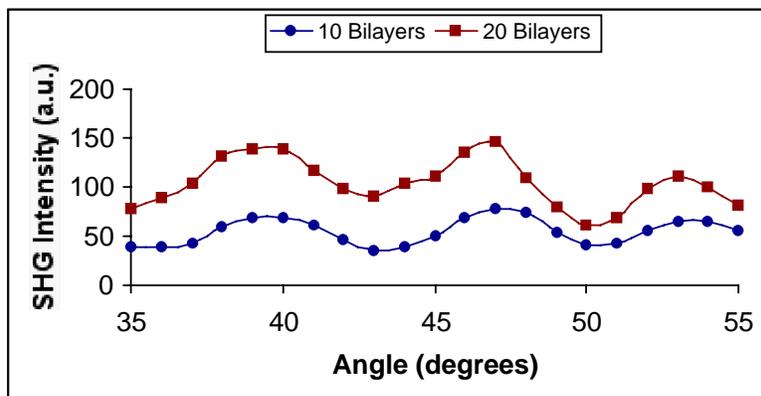


Figure 6. SHG intensity for a 10 bilayer and a 20 bilayer Mordant Orange 10/PAH ISAM film. The $\chi^{(2)}$ of the 20 bilayer film was 1.9×10^{-8} esu, an order of magnitude greater than that of a typical ISAM polymer film.

incidence. 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 θ' is the refracted angle in the glass. Using the angles of consecutive maxima or minima, the coherence length ($l_c = \Delta h / 2$) for this periodicity is determined to be $32 \mu\text{m}$, which is typical of glass for a wavelength of 1064 nm. The two air-glass interfaces on the bare slide create an SHG signal with max ~ 10 counts in the vicinity of 45° incident angle. This corresponds to a second harmonic electric field amplitude, proportional to the square root of the SHG, of $1.5 \text{ counts}^{1/2}$ for each of the glass-air interfaces. The fringes for the sample with a film on one side can then be interpreted as a field amplitude of $9.5 \text{ counts}^{1/2}$ from that side and $1.5 \text{ counts}^{1/2}$ from the opposite side. This results in an SHG maximum of 121 counts $[(9.5 + 1.5)^2]$ and a minimum of 64 counts, in excellent agreement with the data.

Figure 6 shows the results for 10 bilayer and 20 bilayer films fabricated with a 0.1 mM Mordant Orange solution at pH 3.0 and a 10 mM PAH solution at pH 7.0. With a bilayer thickness

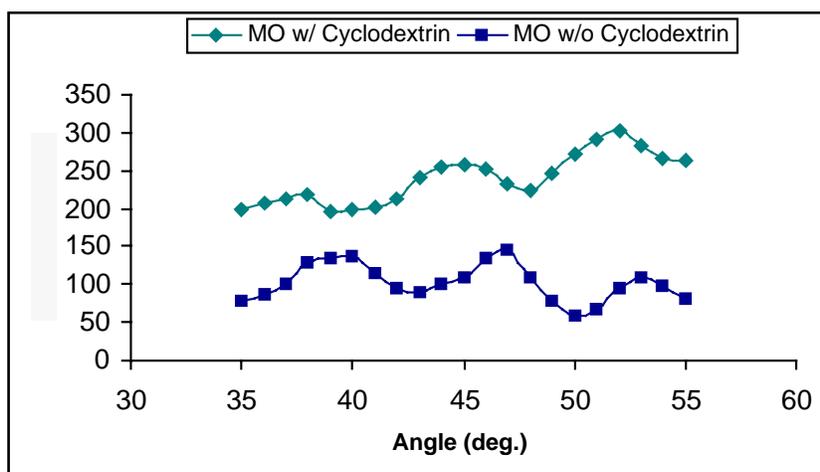


Figure 7. SHG intensity for Mordant Orange 10 complexed with β -Cyclodextrin (top), and Mordant Orange without β -Cyclodextrin.

of 0.68 nm measured by variable angle ellipsometry, the $\chi^{(2)}$ of the 20 bilayer film was determined to be 1.9×10^{-8} esu, an order of magnitude greater than that of a typical ISAM polymer film. The SHG intensity increases with the number of bilayers indicating a bulk $\chi^{(2)}$ effect. However, it does not grow quadratically with the number of bilayers, requiring further optimization studies.

One optimization technique being studied involves the complexation of β -cyclodextrin with the Mordant Orange 10 molecules. Cyclodextrins are cyclic sugars that thread onto Mordant Orange 10 as illustrated schematically in Figure 3c. One effect of the complexation was an increase in solubility of Mordant Orange 10 at pH=3 from 10^{-4} M to 10^{-3} M. Figure 7 shows the SHG intensity for 20 bilayer films of Mordant Orange with and without β -cyclodextrin. The complexation with cyclodextrin results in a two-fold increase in SHG intensity.

CONCLUSIONS

We have developed a novel procedure for the fabrication of noncentrosymmetric ionically self-assembled films that dramatically reduces the cancellation inherent in films produced exclusively with polyelectrolytes. The procedure involves the use of dianionic nonlinear optical chromophores with two distinct ionic moieties with different pKa values. In this way, the chromophore can be ionized on only one of its ends as it is adsorbed onto the surface, providing a preferential polar orientation. We have demonstrated the principle of this procedure using the Mordant Orange 10 chromophore and found that the fabricated films exhibit an order of magnitude increase in $\chi^{(2)}$ relative to films fabricated using polyelectrolytes with NLO side-chains.

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