

SECOND-ORDER NONLINEAR OPTICAL PROPERTIES OF IONICALLY SELF-ASSEMBLED FILMS

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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 ISAM films are grown monolayer by monolayer by alternately immersing a charged substrate in anionic and cationic solutions.¹ Upon each immersion, a layer is formed by electrostatic attraction. The immersion process can be repeated until a film with the desired number of layers has been produced. The thickness of each individual layer is typically on the order of 1 nm, but can be varied by different pH and salt concentrations in the immersion solutions.¹ 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.^{2,3} Importantly, no electric field poling is required, and the $\chi^{(2)}$ values show excellent temporal and thermal stability. Here, we describe the results of recent nonlinear optical studies of ISAM films.

Results and Discussion

ISAM Polyelectrolyte Film Fabrication

Noncentrosymmetric ISAM $\chi^{(2)}$ films were produced on glass microscope slides using anionic polymeric azo dyes, either poly{1-[4-(3-sulfonato-7-hydroxynaphthylazo)benzenesulfonamido]-1,2-ethanediyl} (PS-119, 1) or poly{1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl} (PCBS, 2). Poly(allylamine hydrochloride) (PAH, 3) was used as the polycation. The formation of each monolayer is exceptionally rapid: <1 minute to reach >80% of the maximum thickness. For PS-119/PAH, lowered pH and increased [NaCl] both lead to dramatic increases in the bilayer thickness from <0.5 to >5.0 nm. This can be understood in terms of a reduction of the Debye length with an increase in the concentration of small counterions.^{1,4}

Non-Linear Optical Properties of Polyelectrolyte-Based ISAM Films

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 one side of the substrate to eliminate interference effects, and the film was rotated 45° away from normal about the vertical axis with incident p-polarized light. The SHG intensity exhibited the expected quadratic dependence on the number of bilayers up to 100 bilayers for PS-119/PAH ISAM films. This illustrates that the degree of polar orientation is maintained for each successive bilayer.

However, nonlinear optical studies of the initial layers showed unusual behavior. Films made from PCBS solutions with pH 7.3 and PAH solutions of pH 7.6 exhibited absorbance (364 nm) that was linear with number of adsorbed layers. 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 the expected quadratic dependence on film thickness and, thus, the number of bilayers. This is shown in Figure 1, where the bilayer susceptibility $\eta^{(2)}$, a quantity normalized to the number of bilayers, is plotted as a function of the number of bilayers. The fit to the data is a function of the form $A/N_b + B$ where N_b 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 $1/N_b$ since the film thickness increases while the SHG intensity remains constant. The second term, independent of N_b , 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.

When pH and/or [NaCl] are varied $\chi^{(2)}$ is inversely correlated with bilayer thickness. These results indicate that the net orientation of chromophores occurs primarily at the interfaces between layers of opposite charge. As the layer thickness is increased through decreased pH or increased [NaCl], the chromophores located within the interior of the layer possess a lower degree of orientation.

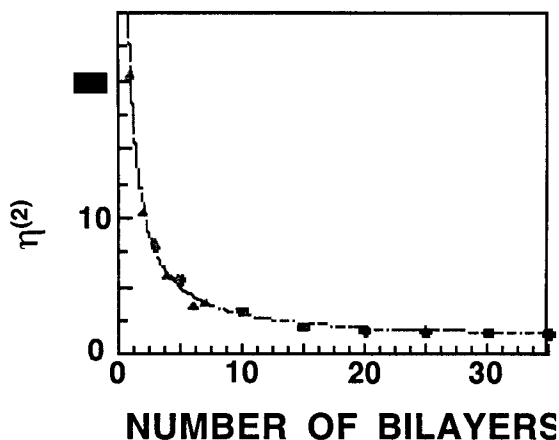


Figure 1. Bilayer susceptibility $\eta^{(2)}$ versus number of bilayers for PCBS/PAH ISAM films measured after each adsorbed bilayer (triangles) and every fifth bilayer (circles). Since the bilayer thickness is constant within this series of films, $\eta^{(2)}$ is proportional to $\chi^{(2)}$.

The growth of individual layers was also measured *in situ* via second harmonic generation. A very rapid rise occurs during the first minute, followed by slower growth over the next several minutes, consistent with the *ex situ* measurements described above. The *in situ* SHG measurements indicate that the noncentrosymmetric ordering occurs immediately upon adsorption, without requiring significant rearrangement of the chromophores.

Since the ISAM process requires a charge reversal of the outer surface of the film in order to provide the basis of attraction for the following adsorbed layer, a simplified representation of the structure of a NLO-active polyanionic layer would be that shown in Figure 2a. The arrows represent the conjugated NLO chromophores terminated with ionic moieties. There are expected to be ionic chromophores oriented both towards the preceding and succeeding cationic layers. If the chromophore populations in each direction were equivalent, there would be no net $\chi^{(2)}$. Since a bulk SHG effect is observed in these films, it is clear that the density and/or average orientation angle must be different for the chromophore populations oriented in opposite directions. Nonetheless, it is expected that there is a significant cancellation in the overall $\chi^{(2)}$ due to oppositely oriented chromophores.

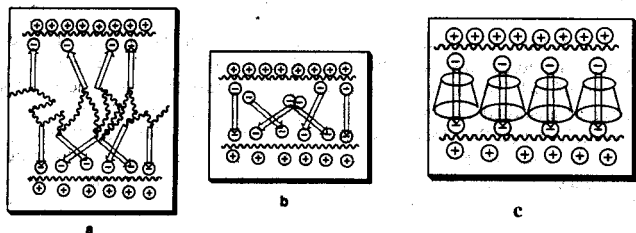
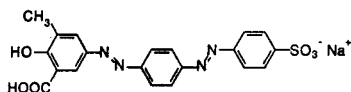


Figure 2. Schematic representations of a) a polyanion with a nonlinear optical chromophore side-chain, b) a non-polymeric, dianionic chromophore with directed orientation and c) a non-polymeric, dianionic chromophore/ β -cyclodextrin pseudorotaxane with directed orientation between two polycationic monolayers.



Fabrication of Hybrid ISAM Films from Dianionic Dye and Polyelectrolyte

In order to overcome the cancellation of orientation observed for nonlinear optical polyelectrolytes depicted in Figure 2a, we have fabricated ionically self-assembled films from non-polymeric, dianionic NLO chromophores with two distinct ionizable functionalities, which provide a means for directing the orientation of the chromophore as it is adsorbed. An example of such a dianionic chromophore is the dye Mordant Orange 10 (MO-10, 4). The sulfonic acid moiety has $pK_a \sim 0$ while that of the carboxylic acid is ~ 5 . Thus, at pH 3, the sulfonic acid will be ionized while the carboxylic acid will remain neutral. When the substrate is immersed in an MO-10 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 2b, was expected to possess a much larger net polar orientation than the polyelectrolytes of Figure 2a.

ISAM films of MO-10 were fabricated from 100 μ M solutions with pH 3.0 and 10 mM PAH solutions with pH 7.0. A 20 bilayer film had a thickness of 13.5 nm, i.e., 0.68 nm/bilayer, as measured by variable angle spectroscopic ellipsometry.

Non-Linear Optical Properties of Hybrid ISAM Films from Dianionic Dye and Polyelectrolyte

The SHG data for the 20 bilayer MO-10/PAH film is compared to that of a 20 bilayer ISAM film of PCBS in Figure 3. In addition to exhibiting 2.5X larger SHG intensity, the MO-10 film is 4X thinner than the PCBS film. The $\chi^{(2)}$ value for the MO-10/PAH ISAM film is calculated to be 1.9×10^{-8} esu. This value is 10X larger than that of quartz and represents a 14X increase in $\chi^{(2)}$ relative to the values obtained for PS-119 ISAM films.²

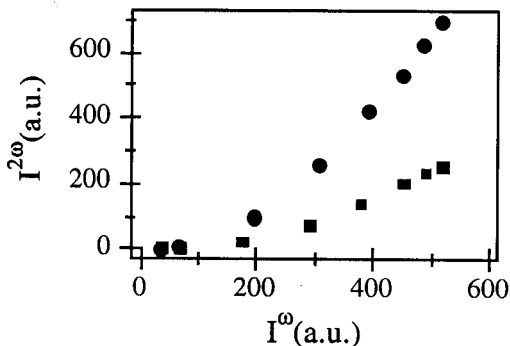


Figure 3. Second harmonic intensity at 532 nm versus fundamental intensity at 1064 nm for MO-10/PAH (circles) and PCBS/PAH (squares) ISAM films.

Fabrication of Hybrid ISAM Films from Dianionic Dye/ β -Cyclodextrin Pseudorotaxane and Polyelectrolyte

Inclusion complexes of cyclodextrins with linear amphiphilic molecules having polar extremities are well known in aqueous media.⁵ Thus, dianionic dyes are ideal guests for formation of pseudorotaxanes,⁶ with the objective of improving the orientation of the chromophore via the rigid sleeve, as suggested in Figure 2c. It should also be noted that cyclodextrins possess asymmetric shapes as indicated and are chiral.

Indeed, as expected, MO-10 does form a pseudorotaxane with β -cyclodextrin based on 1D and 2D NMR and microcalorimetry. The solubility of the dye at pH 3 is improved by a factor of 10 in the presence of the host. ISAM films were prepared from such solutions.

Non-Linear Optical Properties of Hybrid ISAM Films from Dianionic Dye/ β -Cyclodextrin Pseudorotaxane and Polyelectrolyte

The SHG intensity of ISAM films prepared from MO-10 + β -Cyclodextrin/PAH was twice that of films prepared without the cyclodextrin.

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. 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 noncentrosymmetrically ordered structure is largely complete within a couple minutes. The use of non-polymeric dyes with two ionizable substituents provides an enhanced NLO effect through pH controlled orientation. The use of pseudorotaxanes derived from such dyes and cyclodextrins offers further improvement in the NLO behavior.

Acknowledgments

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