

SECOND-ORDER NONLINEAR OPTICAL PROPERTIES OF IONICALLY SELF-ASSEMBLED FILMS CONTAINING DIANIONIC CHROMOPHORES

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Introduction

Since the first demonstration of electro-optic poled polymers,¹ there have been intense research and development efforts to make these materials suitable for commercial application. This is spurred, for example, by the potential for less expensive electro-optic modulators with larger bandwidths and lower drive voltages than the presently dominant LiNbO₃ technology. While significant progress has been achieved over the past decade, one of the most difficult challenges remains the tendency of the nonlinear optical chromophores to relax to random orientation, especially at the elevated temperatures that are typical of many device applications. The crux of this difficulty is that the polar orientation obtained by electric field poling is a thermodynamically-unstable state of the system. In attempts to circumvent this challenge, several approaches have been explored that spontaneously exhibit the required noncentrosymmetric ordering without the need for an external force. Several groups^{2,6} have shown that a thin-film fabrication method based on the sequential adsorption of alternating thin layers of oppositely-charged polyelectrolytes can yield noncentrosymmetric structures with substantial $\chi^{(2)}$ values. The fabrication technique for these polymeric thin films, referred to here as ionically self-assembled monolayers (ISAMs), was first demonstrated by Decher and co-workers in 1991.⁷⁻⁹

We have shown previously² that ISAM films fabricated using a commercial polyelectrolyte dye have $\chi^{(2)}$ values comparable to that of quartz with no measurable decrease in $\chi^{(2)}$ over more than three years. Furthermore, as the film thickness was increased through the adsorption of additional bilayers, the second harmonic intensity exhibited the expected quadratic dependence, demonstrating that degree of orientational order is the same in each sequential bilayer. This is a critical demonstration since one major potential application for ISAM $\chi^{(2)}$ films is in electro-optic waveguides, which requires film thickness on the order of a micron or more. We have also shown that the degree of ordering within ISAM $\chi^{(2)}$ films is a strong function of the pH and salt concentration of the immersion solutions from which the films are fabricated.¹⁰ These results provide insight into the nature of the polar ordering obtained in these films and are valuable in developing approaches for increasing the $\chi^{(2)}$ values. The NLO response also exhibits remarkable thermal stability. No decrease in the $\chi^{(2)}$ value occurs after a heating cycle to 150°C for twenty hours.¹¹ Here, we present results describing a novel approach to ionic self-assembly of noncentrosymmetric films that provides a substantial increase the $\chi^{(2)}$ value.

Fabrication of Ionically Self-Assembled Films

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, but can be varied between 0.5 nm and >5.0 nm through control of the pH and ionic strength of the immersion solutions.¹⁰ 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. In some of our earlier studies, noncentrosymmetric, ISAM $\chi^{(2)}$ films 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. Poly (allylamine hydrochloride) (PAH) was used for the polycation. The formation of each monolayer is exceptionally rapid. In less than one minute, the absorbance and thickness each reach values greater than 80% of the maximum value.

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 1a. The arrows represent the conjugated NLO chromophores terminated with ionic moieties. There are expected to be ionic chromophores oriented both towards the preceding cationic layer and towards the succeeding cationic layer. If the chromophore populations in each direction were equivalent, there would be no net $\chi^{(2)}$. Since a bulk second harmonic generation (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.

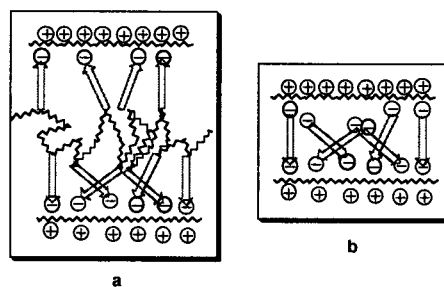


Figure 1. a) Schematic representation of a polyanion with a nonlinear optical chromophore side-chain between two polycationic monolayers. b) A dianionic chromophore with directed orientation between two polycationic monolayers.

In order to overcome the cancellation for nonlinear optical polyelectrolytes depicted in Figure 1a, we have fabricated ionically self-assembled films of a distinctly different structure. These films comprise 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 2. 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 1b, possesses a much larger net polar orientation than that of Figure 1a.

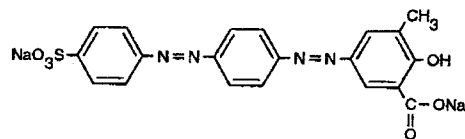


Figure 2. The dianionic chromophore Mordant Orange 10.

Results and Discussion

Second harmonic generation (SHG) measurements were made using the 1064 nm fundamental output 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. 2, 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.

In order to develop an improved understanding of the structure of noncentrosymmetric ISAM films containing polyelectrolytes with NLO sidechains, we examined the dependence of film thickness and $\chi^{(2)}$ on the pH and ionic strength of the immersion solutions. It has been found that the thickness of ISAM layers can be dramatically varied by different pH and salt concentrations in the immersion solutions.¹² For the case of Poly S-119/PAH, the effects of pH and the addition of NaCl to the immersion solutions are

shown in Figure 3. It is seen that lowered pH and increased salt concentration 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.^{10,13} The resultant reduced electrostatic screening between neighboring polyelectrolyte charges causes a change from an extended polymer conformation to one with greater curvature in the backbone, thus yielding a thicker adsorbed layer.

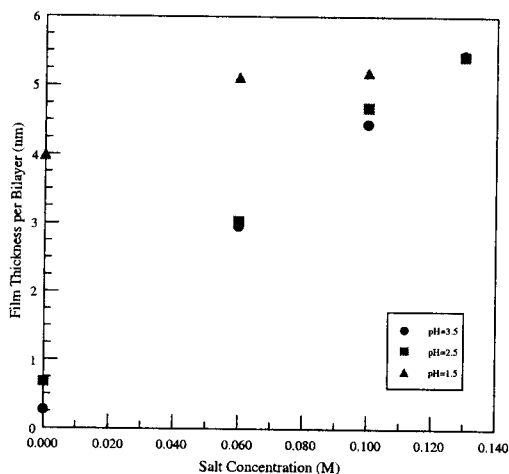


Figure 3. Bilayer thickness versus salt concentration for pH values of 3.5 (circles), 2.5 (squares), and 1.5 (triangles).

Figure 4 shows the relative $\chi^{(2)}$ values for the same set of films presented in Figure 3. $\chi^{(2)}$ is seen to be inversely correlated with bilayer thickness. This is true even though the total SHG signal observed from each film increases with bilayer thickness. It is found, however, that the bilayer thickness increases significantly faster than the SHG intensity, leading to a net decrease in $\chi^{(2)}$. 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 concentration, the chromophores located within the interior of the layer possess a lesser degree of orientation.

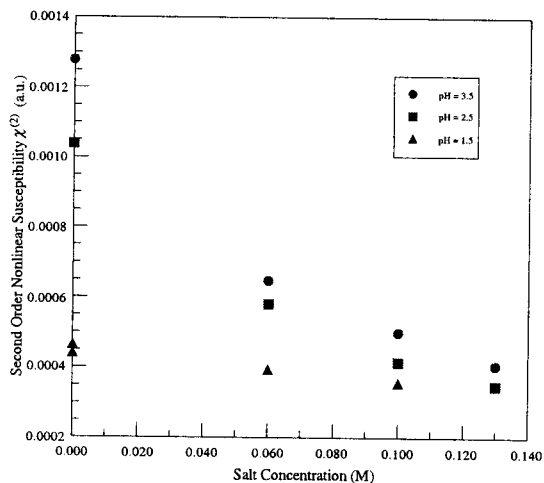


Figure 4. Relative second order susceptibility $\chi^{(2)}$ versus salt concentration for pH values of 3.5 (circles), 2.5 (squares), and 1.5 (triangles).

We now turn to films fabricated from the dianionic chromophore Mordant Orange, which has a relatively low solubility at a pH of 3. ISAM films were fabricated from 100 μ M Mordant Orange solutions with pH=3.0 and 10 mM PAH solutions with pH=7.0. The 100x lower concentration used for Mordant Orange relative to the polyelectrolytes is expected to lead to a substantially reduced amount of chromophore adsorbed into each layer. The thickness of a 20 bilayer Mordant Orange/PAH ISAM film was determined to

be 13.5 nm by variable angle spectral ellipsometry. The SHG data for the 20 bilayer Mordant Orange/PAH film is compared to that of a 20 bilayer ISAM film of poly{1-[4-(3-carboxy-4-hydroxyphenylazo)benzene-sulfanamido]-1,2-ethanediyl (PCBS, from Aldrich) in Figure 5. PCBS ISAM films have $\chi^{(2)}$ values comparable to those of Poly S-119 films. In addition to exhibiting a 2.5 times larger SHG intensity, the Mordant Orange film is four times thinner than the PCBS film. The $\chi^{(2)}$ value for the Mordant Orange/PAH ISAM film is calculated to be 1.9×10^{-8} esu. This value is ten times larger than that of quartz and represents a factor of fourteen increase in $\chi^{(2)}$ relative to the values obtained for Poly S-119 ISAM films in reference 2.

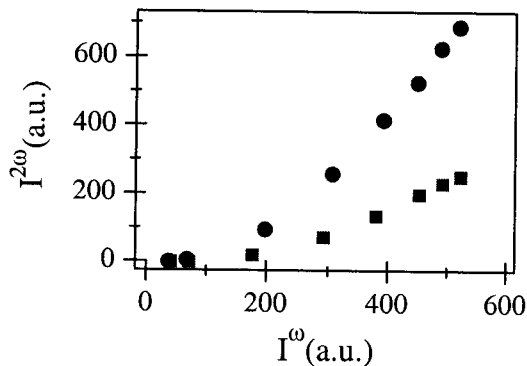


Figure 5. Second harmonic intensity at 532 nm versus fundamental intensity at 1064 nm for Mordant Orange/PAH (circles) and PCBS/PAH (squares) ISAM films.

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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