

Control of Second-Order Nonlinear Optical Susceptibility in Ionically Self-Assembled Films by pH and Ionic Strength

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ABSTRACT

Ionically self-assembled monolayers have been recently shown to spontaneously produce the noncentrosymmetric ordering that is required for a second order nonlinear optical (NLO) response. The precise thickness of each monolayer is determined by variables such as the pH and ionic strength of the immersion solutions. We show here that the relationship between polymer conformation and layer thickness dramatically affects the magnitude of the NLO response. The largest $\chi^{(2)}$ values are found in the thinnest films, indicating that the NLO response is determined primarily by chromophores located at the layer interfaces, as opposed to those within the bulk of a layer.

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, ISAM films can be fabricated with substantial $\chi^{(2)}$ values.³⁻⁶ Importantly, no electric field poling is required, and the $\chi^{(2)}$ values show excellent temporal and thermal stability. A valuable degree of flexibility offered by ISAM film fabrication is control of the individual layer thickness over more than an order of magnitude by variation of the solutions from which the films are formed.⁷ In this paper, we discuss how this variation of thickness and polymer conformation also determines the NLO response of the films.

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 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. 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

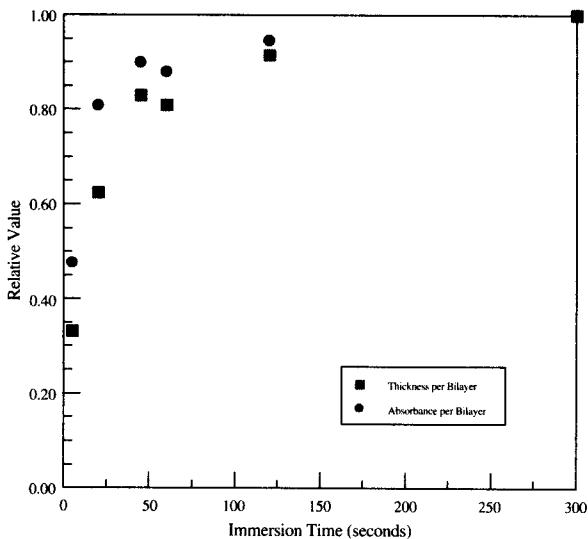


Figure 1. Relative film thickness and absorbance for thirty-bilayer Poly S-119/PAH ISAM films.

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.

Second harmonic generation (SHG) measurements were made using 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, as has been observed in some reports.^{4,6}

EFFECTS OF pH AND SALT CONCENTRATION

It has been found that the thickness of ISAM layers can be dramatically varied by different pH and salt concentrations in the immersion solutions.⁷ As an example, Figure 2 illustrates the dependence of the peak absorbance (480 nm) as a function of the number of bilayers for pH values of 1.5, 2.5, and 3.5. In each case, the excellent linear dependence demonstrates the excellent homogeneity of ISAM film formation from layer

to layer. However, the larger slope for decreased pH values indicates that more chromophore is incorporated into each layer. This is confirmed by direct measurements of thickness. In all our studies, thickness and absorbance have yielded excellent linear dependence for a given set of polymeric components.

The conformation of a polyelectrolyte in solution is determined by the Debye length κ^{-1} .⁸ The Debye length represents the effective electrostatic interaction range between charges on the polymer and is given by

$$\kappa^{-1} = \sqrt{\frac{kT}{2c_s z^2 e^2}}$$

where c_s is the total ionic strength (concentration of small ions) and z is the counterion valency. In solutions with added NaCl, the ionic strength is the total concentration of Na^+ and H^+ ions. As the Debye length is reduced, the repulsion of neighboring ions on the polymer is reduced due to electrostatic screening by the counterions. This, in turn, allows more curvature in the polymer backbone, or correspondingly, a reduction in the persistence length. When the electrostatic screening is low, the polyelectrolyte adopts an extended conformation and adsorbs onto the surface with a predominance of trains (see Figure 3). At higher ionic strength, the polymer adsorbs with a larger number of loops, resulting in a thicker adsorbed layer. The effects of pH and the addition of NaCl to the immersion solutions are shown in Figure 4. It is seen that lowered pH and increased salt concentration both lead to dramatic increases in the bilayer thickness, consistent with the above description. Further confirmation of the relationship between Debye length, polyelectrolyte conformation, and film thickness is illustrated in Figure 5. The data of Figure 4 are seen to collapse onto a master curve in which Debye length is inversely correlated with the film thickness. The relative $\chi^{(2)}$ values of the films represented in

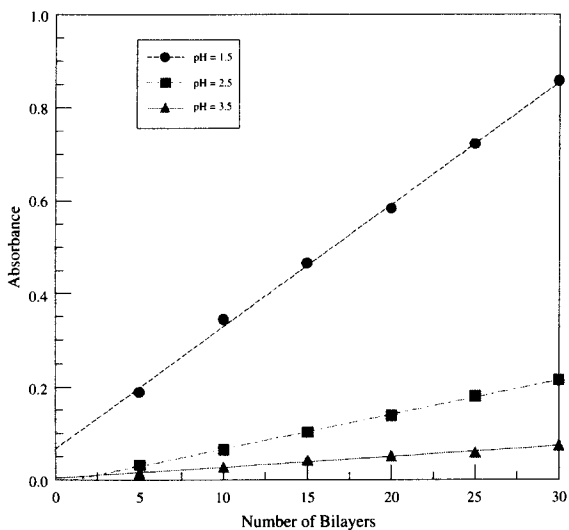


Figure 2. Absorbance at 480 nm versus the number of Poly S-119/PAH bilayers for varying solution pH values with no added NaCl.

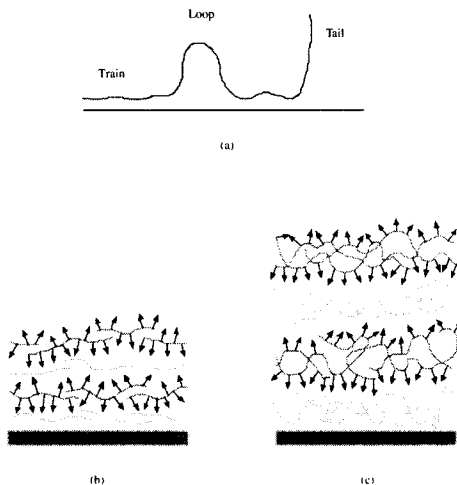


Figure 3. a) Adsorbed polymer conformation consists of three structures: trains, loops, and tails. b) For low ionic strength, polymer adsorbs predominantly in train conformation. c) At high ionic strength, screening of polyelectrolyte charges allows polymer to loop and coil, resulting in thicker layers. Arrows in a) and b) represent NLO chromophore dipoles.

Figures 4 and 5 are shown in Figure 6. $\chi^{(2)}$ is observed to decrease with increased ionic strength (decreased pH or increased salt concentration.) The $\chi^{(2)}$ of a sample relative to a reference is determined from

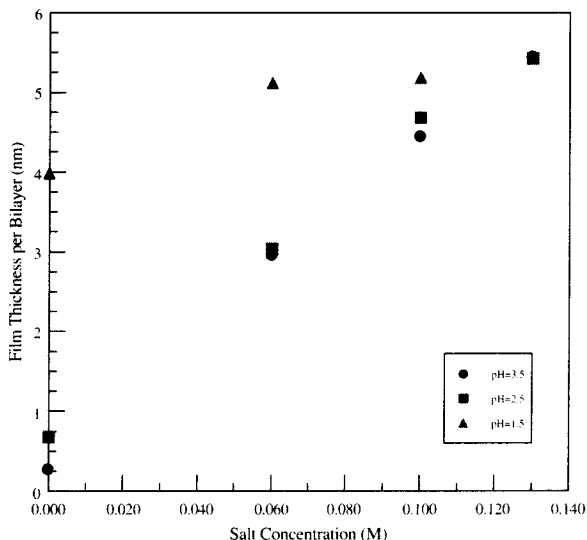


Figure 4. Film thickness per bilayer as functions of NaCl concentration and pH.

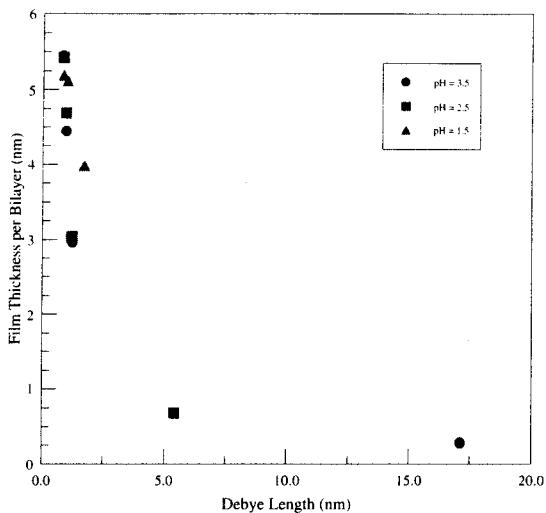


Figure 5. Film thickness per bilayer versus Debye length. Decreased Debye length corresponds to stronger electrostatic screening and adsorption of a thicker polymer layer containing a greater fraction of loops.

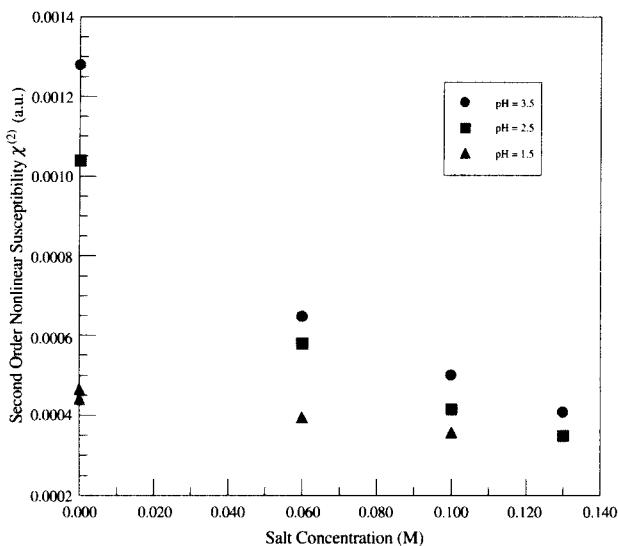


Figure 6. $\chi^{(2)}$ values for Poly S-119/PAH ISAM films as a function of pH and salt concentration.

$$\chi_s^{(2)} = \sqrt{\frac{I_s}{I_r} \frac{l_r}{l_s}} \chi_r^{(2)}$$

where s and r refer to sample and reference, respectively, I is the SHG intensity and l is the film thickness. While the SHG intensity does exhibit a slight increase with increased ionic strength and film thickness, it does not grow nearly as rapidly as the square of the film thickness. These results are interpreted in terms of the illustrations of Figure 3. First, the formation of ISAM layers requires charge reversal of the surface after each immersion. Thus, there must be anionic chromophore units directed towards the cationic layers both above and below. This leads to a partial cancellation of the NLO susceptibility. The cancellation is believed to be incomplete, however, due to a larger number density and/or a lesser average tilt angle of chromophore units at the lower anionic/cationic interface relative to the upper interface. This asymmetry results from the difference during layer formation of the highly charged substrate surface relative to the electrostatically-screened immersion solution. As the layer thickness is increased (Figure 3c), chromophore units are incorporated into the “bulk” of the monolayer and are randomly oriented. These additional chromophores are not shown in Figure 3 for clarity. Since chromophore alignment is obtained predominantly at the interfaces between anionic and cationic layers, increasing the thickness of the layer results in the addition of randomly oriented chromophore and a reduction in the $\chi^{(2)}$ value.

SUMMARY

Ionic self-assembled monolayers offer an attractive approach for the fabrication of organic thin films for second-order nonlinear optical applications. In this paper, we have discussed the role of polymer conformation, as determined by pH and salt concentration, on the film thickness and the NLO susceptibility. While the film thickness is substantially increased with increased ionic strength, the $\chi^{(2)}$ value exhibits a corresponding decrease. The NLO response is determined primarily by chromophores at the layer interfaces. Chromophores located within the bulk of a layer possess a much lower degree of preferential orientation. An understanding of the structure of ISAM NLO films provides opportunities for the design of architectures with enhanced $\chi^{(2)}$ values.

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