

Second-Order Nonlinear Optical Responses of Ionically Self-Assembled Films: Polycation Variations and Dianionic Chromophores

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ABSTRACT

Ionically self-assembled monolayer (ISAM) films have been 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. Ordinarily, the NLO-inactive polycation solution parameters are chosen the same as for the NLO-active polyanion solution. Here, we study the effects of varying the polycation solution parameters separately from the polyanion solution. We also investigate 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. We have examined the incorporation of dianionic chromophores into ISAM films in order to increase the net polar orientation of the chromophores and reduce bilayer thickness.

Keywords: second order nonlinear optics, organic thin films, self assembly

1. 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 examining 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 devices³⁻⁹. 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. This cancellation occurs by two mechanisms: competitive orientation due to the ionic bonding of the polymer chromophore with the subsequent polycation layer, and random orientation of the chromophores within the bulk of each polyanion layer. A reduction in film thickness accompanied by an increase in net polar ordering is one possible avenue to obtain the $\chi^{(2)}$ necessary for efficient electro-optic devices. In this paper, we discuss two yet unexplored approaches to obtain these characteristics. One approach involves the variation of solution parameters of several cationic polymers separately from the polyanion solution in order to reduce the competitive chromophore orientation at the layer interfaces and to reduce the thickness of the inactive polycation layer. We have found that the complexity of ISAM films does not allow large $\chi^{(2)}$ values in polyion-based films, and that the selection of the polymer cation is vital to achieve second harmonic generation (SHG) at all. The second and highly promising approach involves the incorporation of monomeric chromophores into ISAM films in order to eliminate both competitive chromophore orientation and random chromophore orientation inherent with polymer chromophores. We will discuss some drawbacks of incorporating dianionic molecules into ISAM films however, and introduce a novel approach of hybrid ionic / covalent self-assembly which overcomes these disadvantages and yields a substantial increase in $\chi^{(2)}$.

2. 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 varying 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 dyes Poly S-119 (from Aldrich) and PCBS (from Sigma) which have a poly(vinyl amine) backbone with an ionic azo-dye chromophore as shown in Figure 1. The cationic polymers in these bilayers were poly(allylamine hydrochloride) (PAH), Poly L-Lysine (PLL) and poly(diallyldimethylammonium chloride) (PDDA) shown in Figure 2. The dianionic chromophore films were produced with PAH along with Mordant Orange 10 (Aldrich) which has a sulfonic acid on one end and a carboxylic acid on the opposite end.

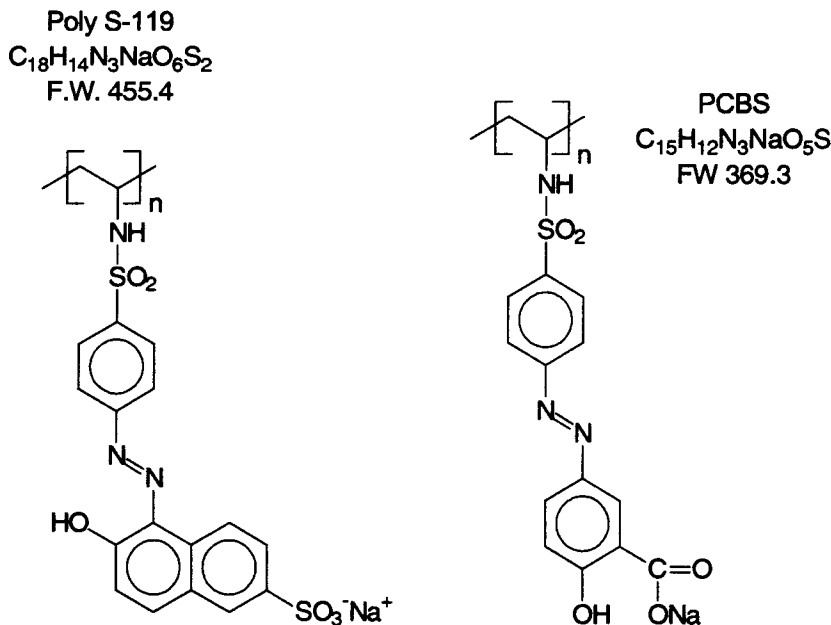


Figure 1. Polyaniions poly S-119 and PCBS used in ISAM NLO film fabrication

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. 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. Typical spot radius and pulse energy values from the OPO output were 100 μ m and 3 mJ/pulse, respectively. 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 as well as the cation variations incorporating PCBS, measurements were made at the Nd:YAG fundamental wavelength. Typical spot radius and pulse energy values for this configuration were 30 μ m and 7mJ/pulse, respectively. The film was left on both sides, and the sample was rotated from 30° to 60° away from normal incidence using a stepper motor controlled rotation stage.

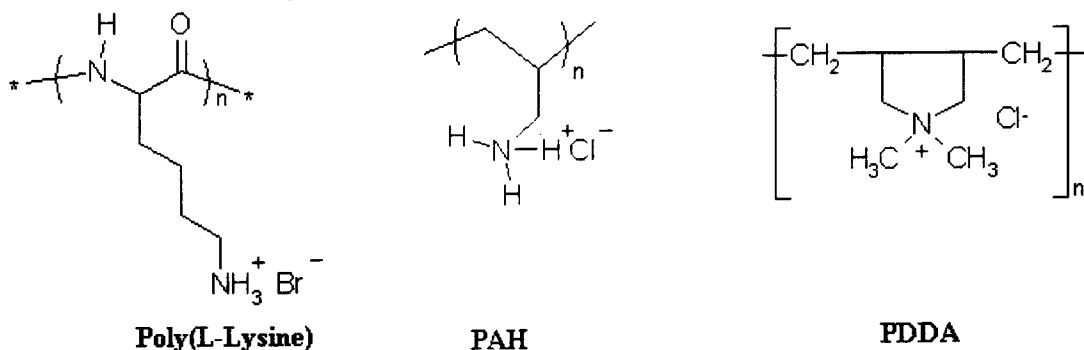


Figure 2. NLO-inactive polycations PLL, PAH, and PDDA used in ISAM film fabrication

3. DISCUSSION

3.1 Background

We have shown earlier that the bilayer thickness can be controlled by variation of the pH and ionic strength of the immersion solutions^{8,9}. Utilizing Debye-Huckel theory, we showed that the free ion concentration in solution is the determining factor for film thickness. For example, in a polyanion solution, 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 3 where the thickness per bilayer is shown as a function of pH and NaCl concentration for Poly S-119/PAH ISAM films. It is seen that lowered anion 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 4. Since increased bilayer thickness corresponds to decreased $\chi^{(2)}$, 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 5a. The opposing dipole orientations cancel one another and lead to an overall reduction in the $\chi^{(2)}$ of the film. Thus, polyelectrolyte-based ISAM films suffer from lack of orientation of chromophores within the bulk of a monolayer and partial cancellation of the preferentially oriented chromophores at the lower interface by chromophores at the upper interface.

3.2 Optimization of the polycation layer.

Optimization of the solution parameters, to date, has involved changing the pH and the salt concentration of the ionic solutions simultaneously. As mentioned in the previous section, there is increasing evidence that ISAM layers are quite interpenetrated rather than stratified. When the film is in a dipping solution, the phase at the surface of the film is altered due to the solution parameters, thus the degree of interpenetration is also altered. The pH of the dipping solution also dictates the degree of ionization of the polyelectrolytes as well as the free ion concentration which increases with decreased pH of the anionic solution, and increases with increased pH of the cationic solutions. We refer to the free ion concentration as the concentration of ions of opposite charge to the polyelectrolyte in solution. The free ion concentration of the solutions can also be increased by the addition of NaCl. As we have shown previously, increased

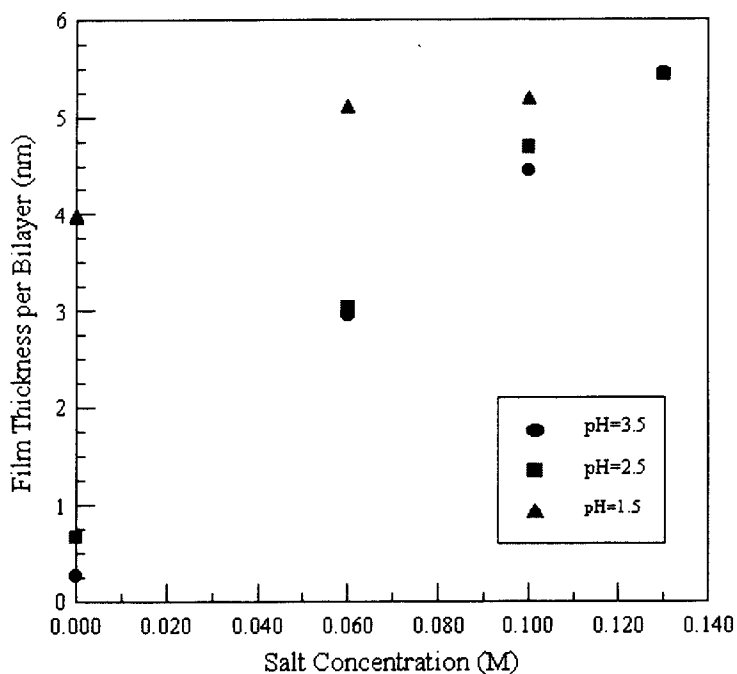


Figure 3. Bilayer thickness as a function of pH and salt concentration of the immersion solutions for Poly S-119/PAH ISAM films.

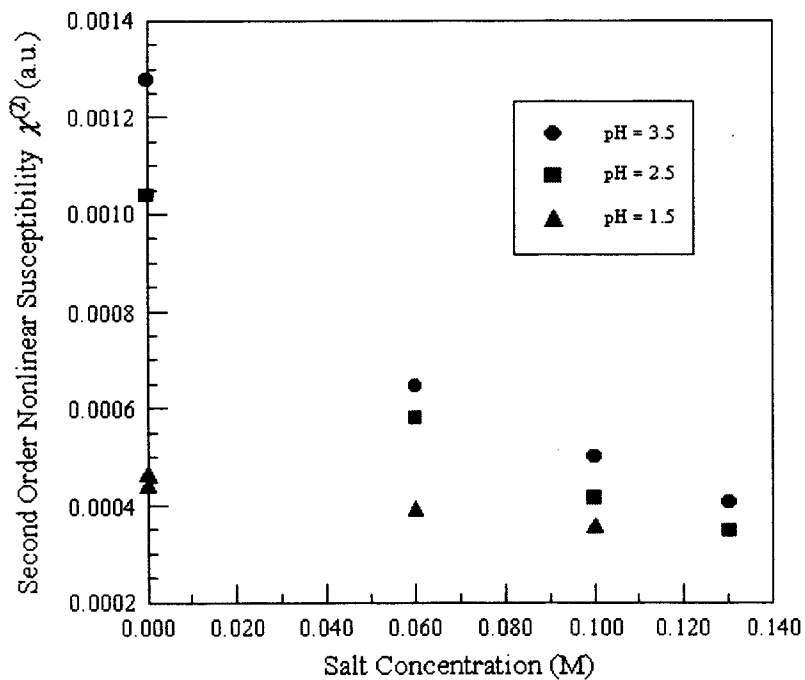


Figure 4. $\chi^{(2)}$ as a function of solution parameters. When compared with Figure 3, it is evident that $\chi^{(2)}$ decreases with increasing thickness per bilayer.

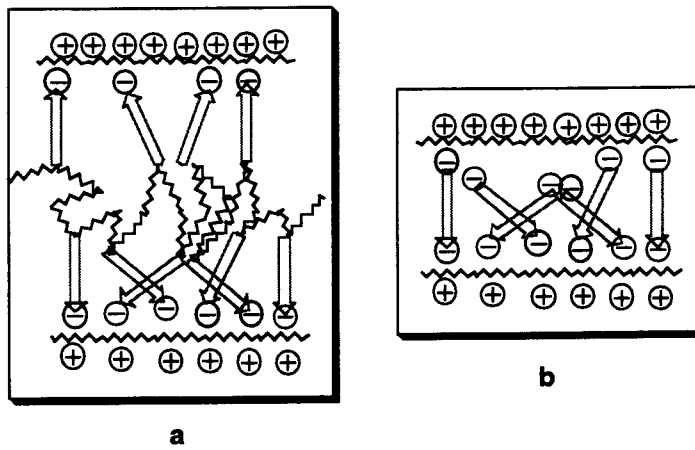


Figure 5. Schematic illustrations of the first few monolayers of a) a conventional ISAM film incorporating a polar side-chain polymer and b) a dianionic chromophore ISAM $\chi^{(2)}$ film.

free ion concentration leads to a more loopy polymer conformation which leads to greater interpenetration, increased monolayer thickness, and decreased net chromophore orientation.

3.2.1 Variation of polycation solution parameters.

We chose pH 7 for the polyanion PCBS which yields a relatively thin monolayer with minimal "bulk" chromophore fraction and minimal interpenetration of the subsequent polycation (PAH) layer. We then varied the pH of PAH without the addition of NaCl. The absorbance as a function of the number of bilayers, shown in Figure 6, shows constant chromophore deposition throughout the growth of the film which is also indicative of reproducible bilayer thickness. Further, we observed quadratic growth of the SHG with film thickness, as shown in Figure 7, demonstrating that each successive bilayer has the same degree of chromophore orientation. The film with the greater cation pH exhibited greater SHG, which was as expected. The greater cation pH yields a more loopy polymer conformation which results in a thicker polycation layer and therefore also promotes a thicker polyanion layer. The latter point is illustrated by the larger PCBS absorbance observed in Figure 6 for the PAH pH 10 films relative to the PAH pH 7 films. The increased amount of PCBS deposited per bilayer leads to the larger SHG signal in the high pH case.

We further studied the properties of the films by determining the tilt angle of the chromophores away from the normal to the substrate by measuring the ratio of the SHG intensity for p-polarized versus s-polarized incident fundamental beams. The analysis for the determination of the tilt angle is as follows. The intensities, $I_{2\omega}$, of p-polarized SHG from p- and s-polarized beams incident at an angle θ away from the normal to the film surface may be expressed as

$$I_{2\omega}^{p \rightarrow p} = (3\chi_{zz}^{(2)} \sin \theta \cos^2 \theta + \chi_{zz}^{(2)} \sin^3 \theta)^2 E_{\omega}^4, \quad (1)$$

$$I_{2\omega}^{s \rightarrow p} = (3\chi_{zz}^{(2)} \sin \theta)^2 E_{\omega}^4. \quad (2)$$

where the E_{ω} 's are the electric field strength of the incident p- or s-polarized beams. In addition, since the net dipole orientation of these films is normal to the surface, the non-vanishing susceptibility tensor elements for a collection of N molecules may be written as

$$\chi_{zz}^{(2)}(-\omega; \omega_1, \omega_2) \propto \frac{1}{2} N \langle \cos \psi \sin^2 \psi \rangle \beta_{zz} f(\omega) f(\omega_1) f(\omega_2), \quad (3)$$

$$\chi_{zz}^{(2)}(-\omega; \omega_1, \omega_2) \propto N \langle \cos^3 \psi \rangle \beta_{zz} f(\omega) f(\omega_1) f(\omega_2), \quad (4)$$

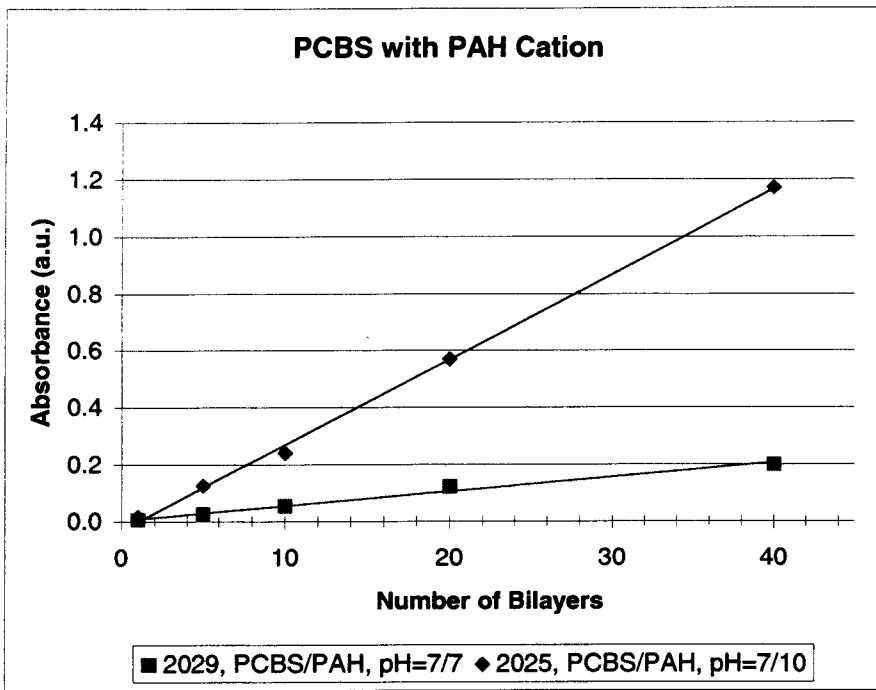


Figure 6. Absorbance at 370nm of ISAM films with PCBS at pH=7 and PAH at pH=7 and 10 as a function of the number of bilayers.

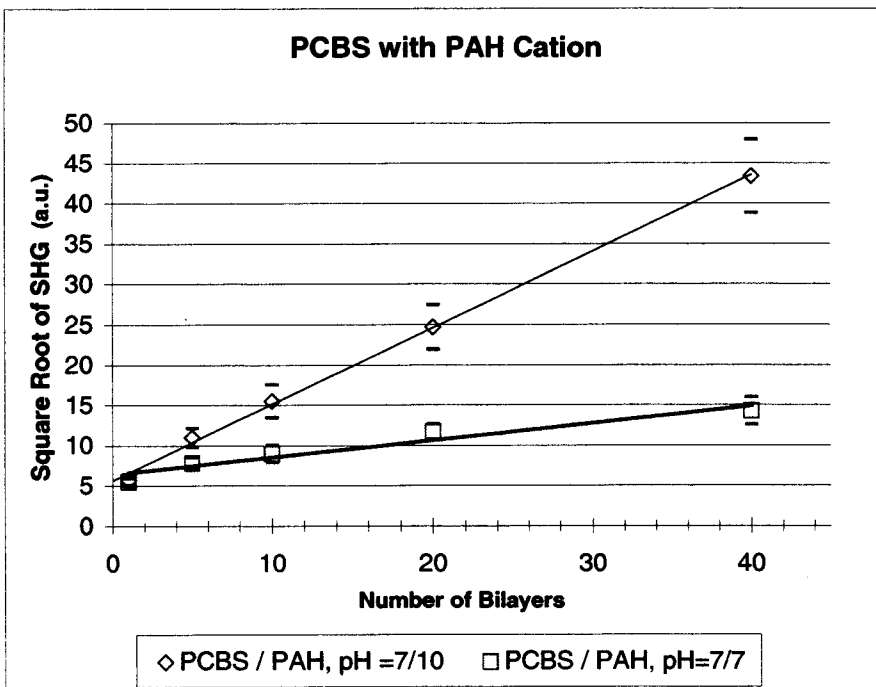


Figure 7. Square root of the SHG of ISAM films with PCBS at pH=7 and PAH at pH=7 and 10 as a function of the number of bilayers.

where ψ is the molecular tilt angle away from normal, β_{zzz} is the hyperpolarizability along the molecular axis, and the f 's are local field factors. If the distribution of ψ 's is peaked sharply about a particular angle Ψ , the average values of these products may be taken as products of functions of the average value Ψ . Then, the ratio of the susceptibilities may be written as

$$\frac{\chi_{zz}^{(2)}}{\chi_{zxx}^{(2)}} = 2 \cot^2 \Psi. \quad (5)$$

Incorporating (1) and (2) into (5) allows the average tilt angle to be expressed as a ratio of SHG intensities:

$$\Psi = \cot^{-1} \sqrt{\frac{1}{2} \left[\csc^2 \theta \sqrt{\frac{I_{2\omega}^{p \rightarrow p}}{I_{2\omega}^{s \rightarrow p}}} - 3 \cot^2 \theta \right]}. \quad (6)$$

Figure 8 shows the dependence of the SHG intensity on the polarization of the incident 1064 nm fundamental beam for a 20 bilayer film made with PCBS at pH=7 and PAH at pH=10. Similar data is shown in Figure 9 for a 20 bilayer films with PCBS and PAH both at pH=7. In both cases, the maxima correspond to p-polarized incident light and the minima to s-polarized incident light. The ratio of the maxima to the minima is larger for the films made with PAH at pH=10 indicating a smaller tilt angle away from the preferred direction normal to the substrate.

Table 1 shows the measured tilt angles for the PAH pH 7 and pH 10 films with 20 bilayers. Also included in the table are the film thickness per bilayer as measured by variable angle ellipsometry and the $\chi^{(2)}$ values as determined by comparison with Maker fringes from a quartz wedge. The thicker films formed at pH 10 have a smaller tilt angle away from the surface normal. This is perhaps not surprising since the length of the azo chromophore side-chain is approximately 1.5 nm. For the 0.2 nm bilayer thickness of the PAH pH 7 case, the chromophore must lie largely in the plane of the substrate and therefore have a large tilt angle relative to the surface normal. It is also interesting to note that while the thickness of the PAH/PCBS bilayer increases by a factor of 45 for the higher PAH pH, the thickness of the PCBS component, as determined by the absorbance data of Figure 6, increases by only a factor of 6. Thus, while the thicker PAH layers also secondarily promote thicker PCBS layers by providing a larger number of binding sites, the PAH component comprises a larger fraction of the film in the pH 10 thicker film case. This clearly has a deleterious effect on the $\chi^{(2)}$ values since the fraction of NLO-active (PCBS) polymer is decreased. There are, therefore, several competing effects regarding $\chi^{(2)}$ as the polycation pH is increased. The amount of PCBS adsorbed upon each layer deposition is increased and the average tilt angle of the chromophores away from the direction of the net polar order (perpendicular to the substrate) is decreased. Both of these would tend to increase the $\chi^{(2)}$ value. However, as we have reported previously in the study of varying the polyanion and polycation pH values simultaneously, thicker layers of the NLO-active polymer lead in fact to decreased $\chi^{(2)}$ values.⁹ This is because the chromophores within the "bulk" of the monolayer tend towards random orientation. Furthermore, in the present case of increasing the PAH pH while maintaining the PSBS pH fixed, the fraction of NLO-inactive PAH incorporated into each bilayer increases relative to PCBS. These latter two effects work towards a decreased $\chi^{(2)}$ value at the higher PAH pH value. It is clear from Table 1 that these effects are dominant.

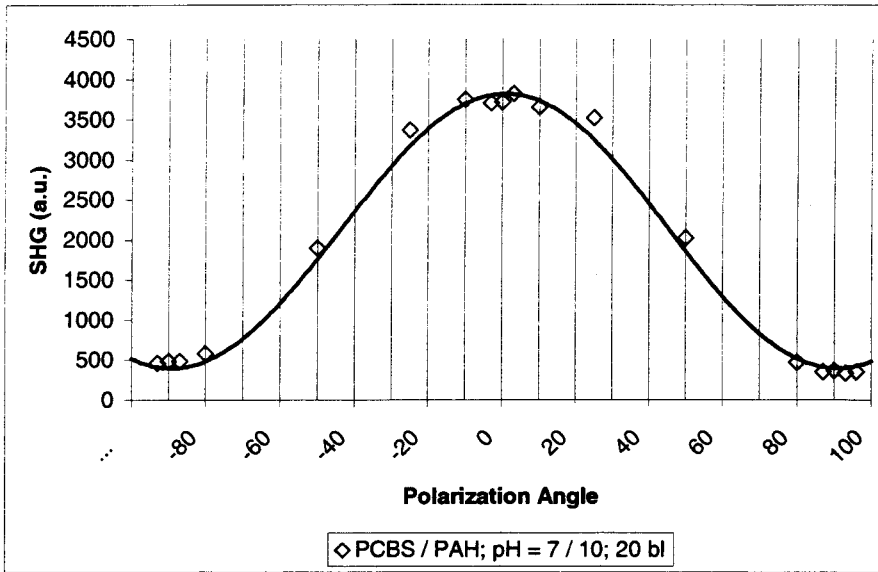


Figure 8. SHG intensity as a function of the incident polarization for a 20 bilayer film with PCBS at pH=7 and PAH at pH=10.

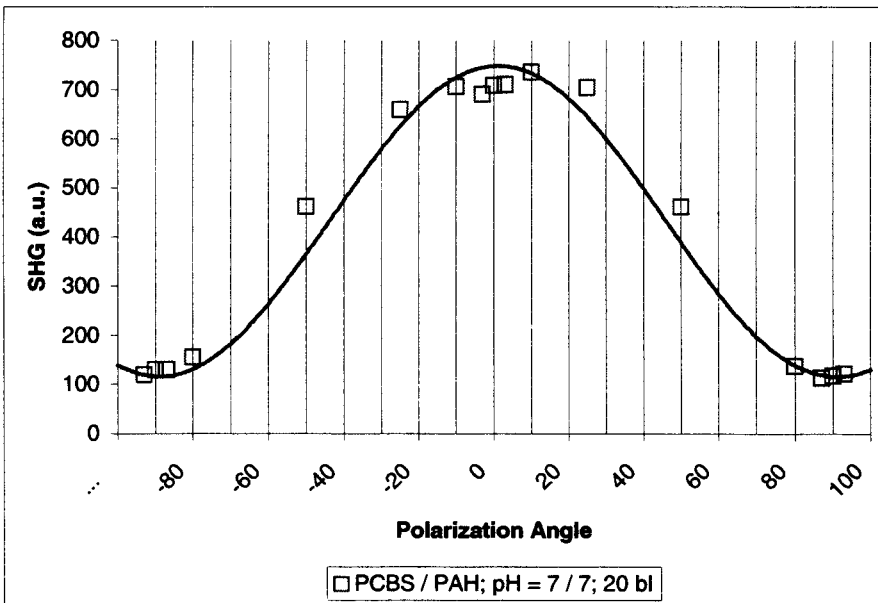


Figure 9. SHG intensity as a function of the incident polarization for a 20 bilayer film with PCBS at pH=7 and PAH at pH=7.

Cation pH	Tilt Angle	Bilayer Thickness	$\chi^{(2)}$ (10^{-9} esu)
10	37°	9.2 nm	0.95
7	63°	0.2 nm	9.1

Table 1. Chromophore tilt angle, bilayer thickness, and $\chi^{(2)}$ values for 20 bilayer PCBS/PAH films with PAH pH values of 7 and 10.

3.2.2 Variation of the polycation

We further explored the role of the polycation within the NLO ISAM film by replacing PAH with other polycations. We used separately poly(diallyldimethylammonium chloride) (PDDA) and poly (L-Lysine) (PLL), illustrated above in Figure 2. Films made with each of these polycations showed linear growth of absorbance with number of bilayers demonstrating that a constant rate of PCBS deposition per bilayer was achieved, as shown in Figure 10. However, Figure 11 reveals that after the first bilayer, the SHG intensity remained essentially constant as the number of bilayers was increased. Thus, although PCBS is well-incorporated into ISAM films with PDDA and PLL, net polar ordering is not achieved with these polycations as it is with PAH. A primary distinction between PAH and the other two polycations is the ability of PAH to form hydrogen bonds. We speculate that the directionality of hydrogen bonding plays an essential role in achieving net polar order in NLO ISAM films made from polyanions such as PCBS and poly S-119. While the usage of polycations other than PAH failed to produce films with a bulk $\chi^{(2)}$, they did produce high-quality ISAM films which reveals their potential in other applications such as LEDs, photovoltaics, and electrochromic devices.

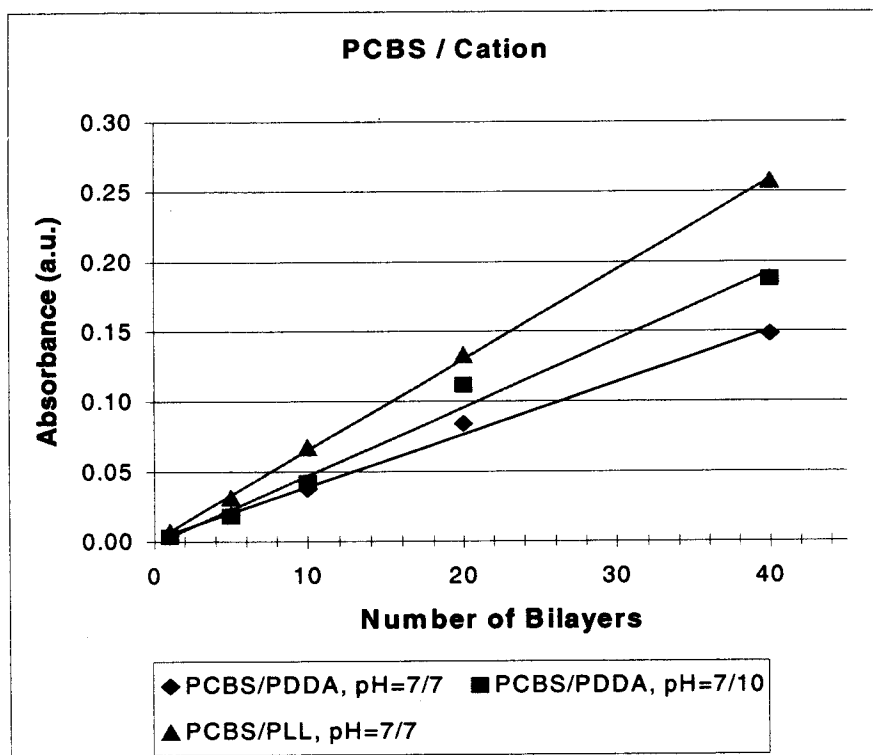


Figure 10. Absorbance at 370nm as a function of the number of bilayers for PCBS with PDDA at pH 7 and 10 and PLL at pH 7.

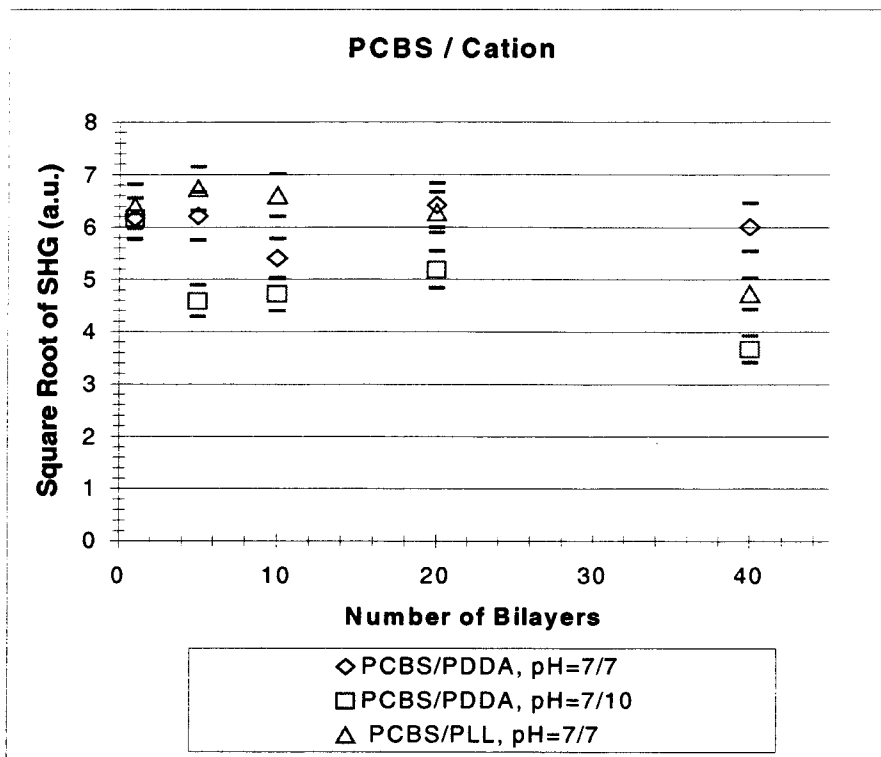


Figure 11. Square root of SHG intensity as a function of the number of bilayers for PCBS with PDDA at pH 7 and 10 and PLL at pH 7.

3.3 Incorporation of the dianionic molecule Mordant Orange 10.

As mentioned in section 3.1 and illustrated in Figure 5a, polyelectrolyte-based ISAM films suffer from lack of orientation of chromophores within the bulk of a monolayer and partial cancellation of the preferentially oriented chromophores at the lower interface by chromophores at the upper interface. 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 12. 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 5b, is expected to possess a much larger net polar orientation than that of Figure 5a.

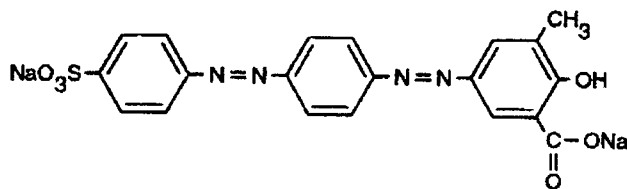


Figure 12. The dianionic chromophore Mordant Orange 10.

Figure 13 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 of 2 bilayers 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 also possesses a non-zero $\chi^{(2)}$ and generates second harmonic. The interference fringes in Figure 13 have a periodicity of $\sim 7^\circ$ in the vicinity of 45° 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 maximum ~ 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.

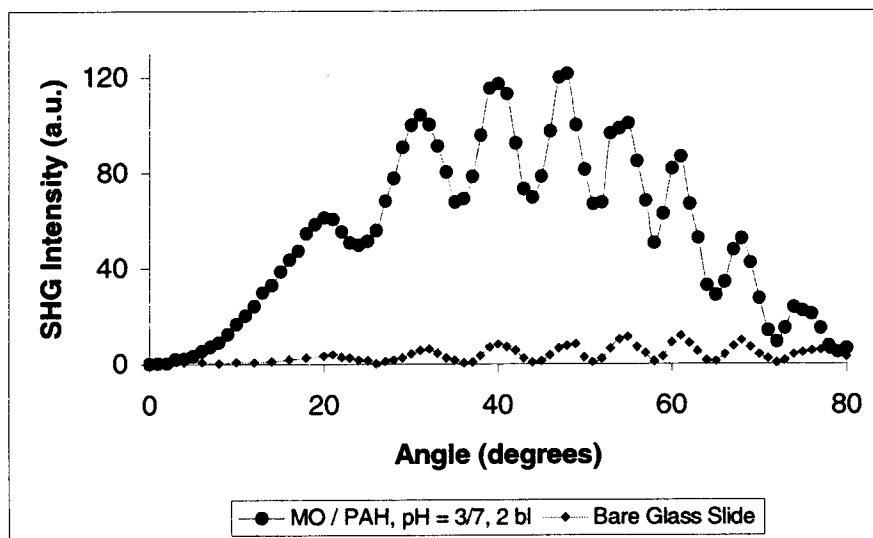


Figure 13. SHG interference fringes from a bare glass slide (lower curve) and a slide with Mordant Orange 10 film on one side. The amplitude of the fringes in both cases indicates SHG from the glass-air interfaces. The periodicity of the fringes corresponds to SHG from interfaces 1 mm apart (the thickness of a microscope slide)

Figure 14 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 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. As seen in Figure 14, the SHG intensity increases with the number of bilayers indicating a bulk $\chi^{(2)}$ effect does exist. However, as verified in Mordant Orange ISAM films with larger numbers of bilayers, the SHG intensity does not grow quadratically with the number of bilayers. Thus the degree of polar ordering in these systems does not remain constant as the number of layers is increased. Because the outermost monolayer of Mordant Orange is only tethered to the preceding PAH layer by a single ionic bond for each molecule, each chromophore can be dissociated during the following immersion into PAH and either be removed from the film entirely or subsequently readsorb with opposite orientation. Further studies into these effects are ongoing. Most recently, we have developed a novel hybrid covalent/ionic deposition technique that is highly promising. We have observed quadratic growth in SHG in this system, as well as $\chi^{(2)}$ values 18 times that of quartz (35×10^{-9} esu). These results will be reported separately.

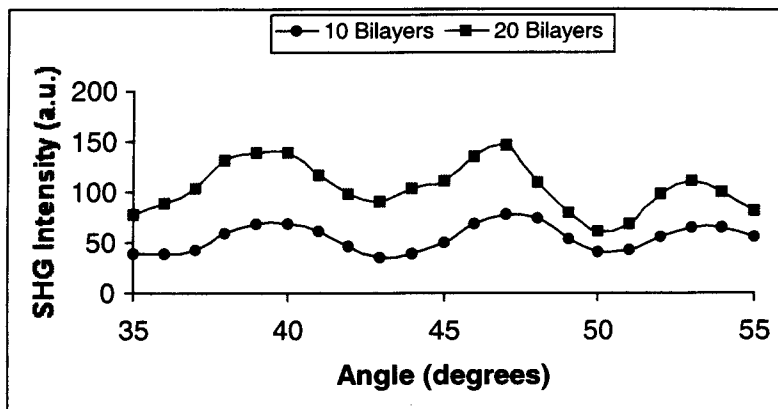


Figure 14. SHG intensity for a 10 bilayer and a 20 bilayer Mordant Orange 10/PAH ISAM film. The $\chi^{(2)}$ of the 20 bilayer film was 1.9×10^{-8} esu.

4. CONCLUSIONS

In continuing efforts to develop a full understanding of the structure of ionically self-assembled monolayers and, in particular, its relation to polar ordering and $\chi^{(2)}$, we have systematically studied the effect of varying the NLO-inactive polycation. Using PAH as a polycation with PCBS as the active NLO polyanion, we have found that increasing the polycation pH from 7 to 10 yields an increase in the bilayer thickness of a factor of 45. While most of the increased thickness is due to an increase in the thickness of PAH, there is a concomitant increase in the thickness of PCBS by a factor of 6. While the average chromophore tilt angle away from the preferred direction is decreased and the total SHG intensity is increased for the higher pH value, the $\chi^{(2)}$ value is significantly decreased due to the random orientation of chromophores within the thicker PCBS layers and to the larger fraction of PAH content relative to PCBS. We have also found that the polycations PDDA and PLL do not exhibit bulk $\chi^{(2)}$ effects, suggesting that hydrogen bonding plays a vital role in obtaining the polar order. We have also reported 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 a substantial increase in $\chi^{(2)}$ relative to films fabricated using polyelectrolytes with NLO side-chains.

5. ACKNOWLEDGEMENTS

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