

## Novel Hybrid Covalent / Ionic Self-Assembly Technique for Improved Second-Order Nonlinear Optical Films

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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. Here, we investigate the effects of replacing the NLO-active polymer layers with layers of monomeric chromophores containing ionic and covalent bonding sites. Films fabricated exclusively using polyelectrolytes contain some fraction of both randomly oriented and anti-parallel oriented chromophores. We have examined the incorporation of monomeric chromophores into ISAM films in order to increase the net polar orientation of the chromophores and reduce bilayer thickness.

### INTRODUCTION

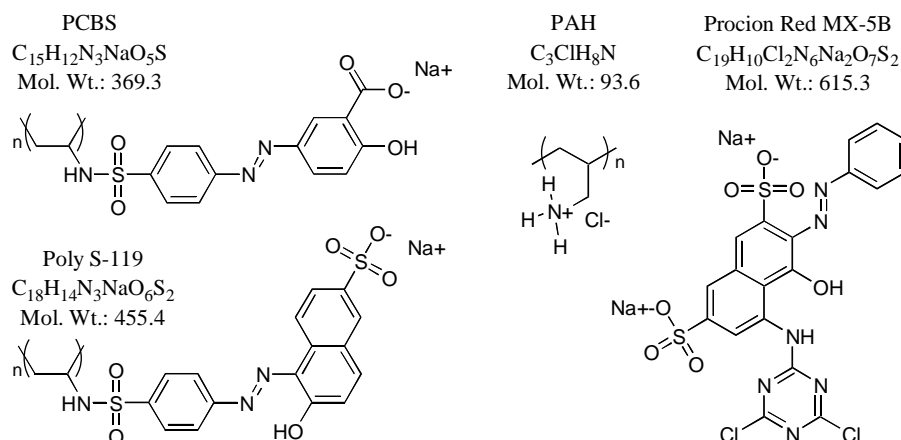
The formation of ionically self-assembled monolayer (ISAM) films, grown monolayer by monolayer by alternately immersing a charged substrate in anionic and cationic polymer solutions, has proven to be an easy, fast, and inexpensive method for creating laterally homogeneous nanostructured thin films[1,2]. Upon each immersion, an exceptionally homogeneous layer is rapidly (less than one minute) adsorbed and the thickness of each monolayer can be controlled to be 0.3 to >5.0 nm by varying the pH and ionic strength of the solutions. 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 devices[3-10]. 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 introduce a hybrid covalent / ionic self-assembly technique that utilizes monomer chromophores with ionic and covalent bonding sites. This novel approach overcomes the disadvantages inherent with polymer chromophores and yields a substantial increase in  $\chi^{(2)}$  by significantly reducing competitive chromophore orientation and random orientation.

## EXPERIMENTAL DETAILS

ISAM films are grown monolayer by monolayer by alternately immersing a charged substrate in anionic and cationic solutions forming a multilayer structure. The immersion process can be repeated indefinitely until a desired thickness or number of bilayers has been achieved. For the studies presented here, 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, with the cationic polymer poly(allylamine hydrochloride) (PAH), as shown in Figure 1. The hybrid covalent / ionic films were produced with PAH along with Procion Red MX-5B (Aldrich), which contains two sulfonic acids for ionic bonding and two potential covalent bonding sites at the chlorines of 2,4-Dichloro-s-triazine. 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. 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.

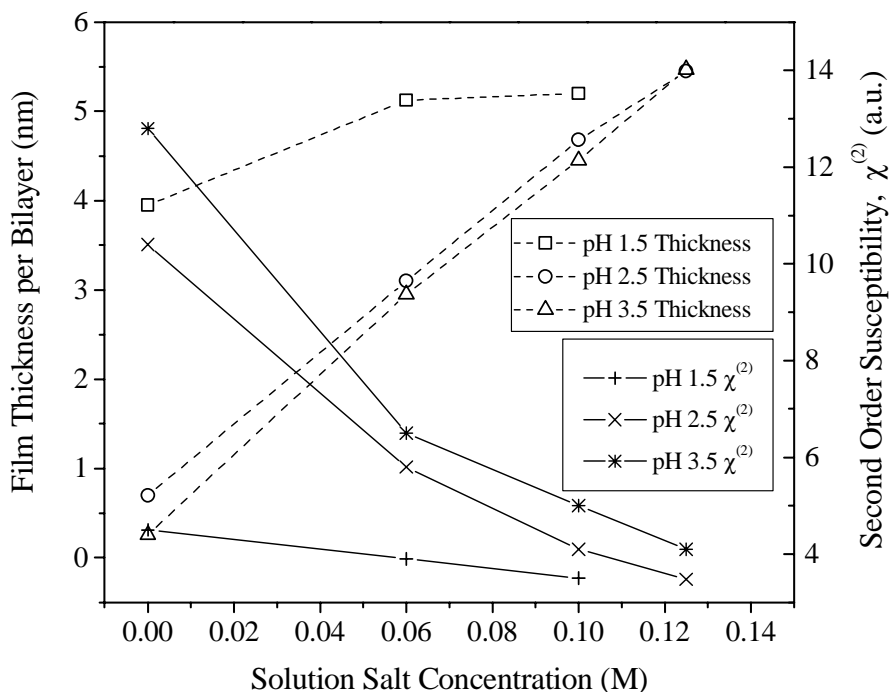
## DISCUSSION

We have shown earlier that the bilayer thickness can be controlled by variation of the pH and ionic strength of the immersion solutions, and that the selection of the polymer cation is vital to achieve any second harmonic generation (SHG) at all [8-10]. 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 2 where the thickness per bilayer and  $\chi^{(2)}$  are shown as a function of anion solution pH and NaCl concentration for Poly S-119 /

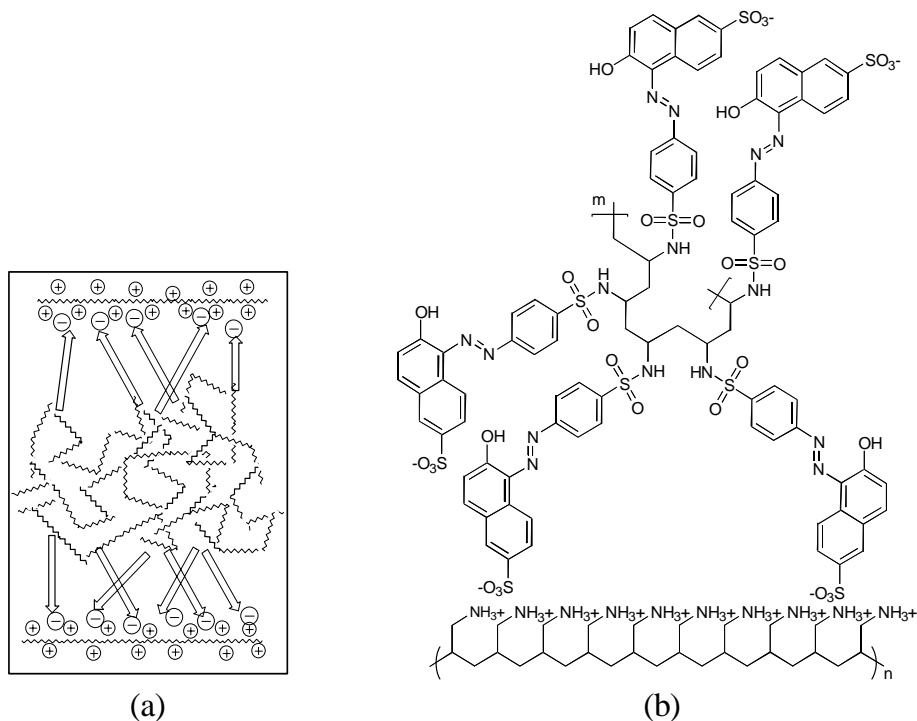


**Figure 1.** Molecules used in NLO film fabrication. PCBS and Poly S-119 chromophores with PAH used for ISAM films. Procion Red MX-5B chromophore with PAH used for Hybrid covalent / ionic films.

PAH ISAM films. It is seen that lowered pH and increased NaCl concentration of the anion solution 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 increased thickness. Similar trends occur for increased pH and NaCl concentration of the cation solution. 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 as illustrated in Figure 3. 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. The opposing dipole orientations cancel one another and lead to an overall reduction in the  $\chi^{(2)}$  of the film. The structure diagram in Figure 3b represents five repeat units of Poly S-119 attached to the linear polymer PAH. This illustrates a fraction of randomly oriented chromophores, and the tendency to interpenetrate neighboring layers. 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.



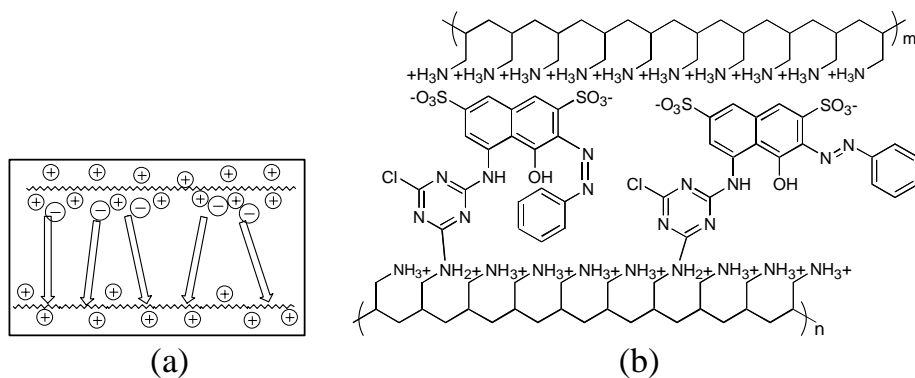
**Figure 2.** Bilayer thickness and  $\chi^{(2)}$  as a function of NaCl concentration and pH of the immersion solutions for Poly S-119/PAH ISAM films.



**Figure 3.** Schematic illustration of (a) a polychromophore between two PAH layers, and (b) five repeat units of Poly S-119 attached to PAH illustrating the conformation of a polychromophore and tendency to form thick (many nanometer) bilayers (b).

### Hybrid covalent / ionic self-assembly

As mentioned above, polyelectrolyte-based ISAM films suffer from lack of orientation of chromophores within the bulk of a monolayer as well as 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, illustrated in Figure 4. These films contain monomeric chromophores, as opposed to polyelectrolytes with NLO sidechains.



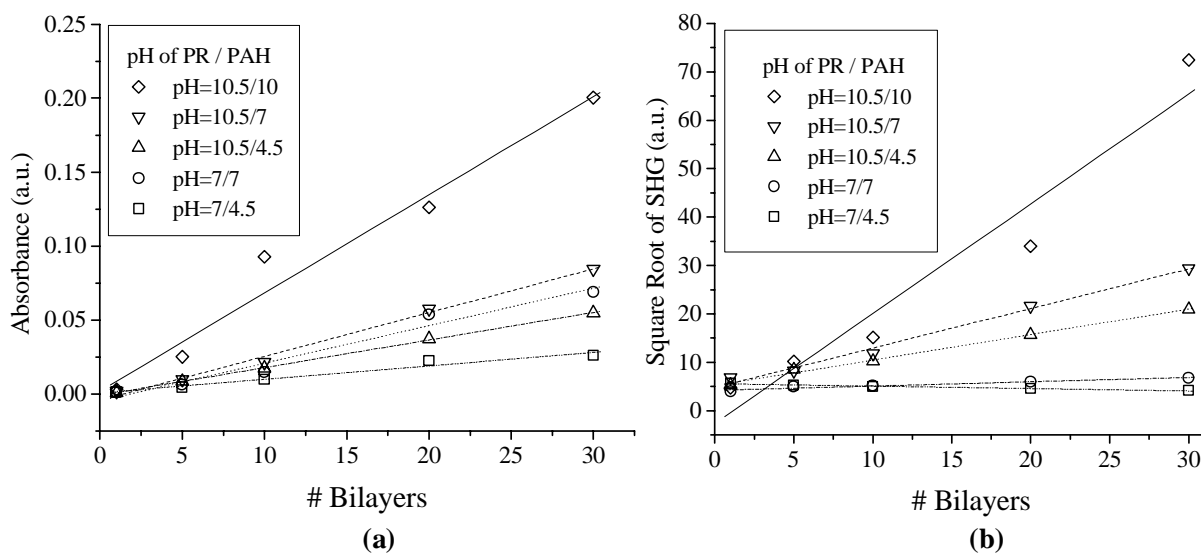
**Figure 4.** Schematic illustration of (a) a monomer chromophore between two PAH layers, and (b) Procion Red MX=5B between two PAH layers illustrating the tendency to form thin (sub-nanometer) bilayers.

When a film with PAH is immersed in a Procion Red (PR) solution, the triazine ring on PR can covalently react with the PAH amines. This occurs preferentially at PR pH values greater than the pKa (9) of PAH. When a film with upper layer of PR is immersed in PAH, protonated amines of PAH can electrostatically attach to the PR sulfonates, preferentially occurring at pH < 9. Table 1 shows the bilayer thickness and absorbance for PAH/PR films at several pairs of pH values. The bilayer thickness indicates the amount of both PAH and PR that have deposited in a bilayer while the absorbance (at 530 nm) represents only the amount of PR in a bilayer. The results are well-explained by the considerations above.

Figure 5(a) shows the absorbance as a function of the number of bilayers. The linearity demonstrates that uniform deposition is obtained in each adsorption step. The square root of the SHG is shown in Figure 5(b) as a function of the number of bilayers. For pH values of 10.5 for PR, the square root of SHG increases linearly with the number of bilayers, demonstrating preferential polar orientation of the PR molecule and sustained orientation as additional layers are added. The case of PAH pH 7 and PR pH 10.5 provides the optimal combination of thin layers with high degree of orientation resulting in a  $\chi^{(2)}$  value of  $35 \times 10^{-9}$  esu.

**Table 1.** Thickness per bilayer and absorbance as a function of pH conditions.

Procion Red pH	PAH pH	Film Absorbance per Bilayer	Film Thickness per Bilayer (nm)
10.5	10	$6.6 \times 10^{-3}$	$4.30 \pm 0.25$
10.5	7	$3.0 \times 10^{-3}$	$0.52 \pm 0.06$
10.5	4.5	$1.9 \times 10^{-3}$	$0.34 \pm 0.02$
7	7	$2.5 \times 10^{-3}$	$0.55 \pm 0.05$
7	4.5	$9.0 \times 10^{-4}$	



**Figure 5.** (a) Absorbance and (b) square root of the SHG intensity as a function of the number of bilayers for several sets of pH conditions in PR/PAH self-assembled films.

## CONCLUSIONS

In continuing efforts to develop a self-assembled organic structure for use in electro-optic devices, we have introduced a novel technique that improves polar ordering and  $\chi^{(2)}$ . By replacing polymer chromophores with monomeric chromophores, we have significantly reduced competitive dipole orientation and eliminated randomly oriented chromophores in the bulk of the anion layer inherent in films produced exclusively with polyelectrolytes. This involves covalently attaching the chromophore at only one of its ends, providing a preferential polar orientation, then ionically attaching the subsequent cationic layer. We found that films fabricated with this hybrid covalent / ionic technique exhibit a substantial increase in  $\chi^{(2)}$  relative to films fabricated using polyelectrolytes with NLO side-chains.

## ACKNOWLEDGEMENTS

This work was supported by NSF grant ECS-9907747

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