

**NOVEL HYBRID COVALENT / IONIC SELF-ASSEMBLY
TECHNIQUE FOR IMPROVED SECOND-ORDER
NONLINEAR OPTICAL FILMS**

P. J. Neyman^a, M. Guzy^b, S. M. Shah^b, R. M. Davis^b, K. E. Van Cott^b, H. Wang^c, H. W. Gibson^c, C. Brand^d, J. R. Heflin^{a,d}

^aDepartment of Materials Science and Engineering,
Virginia Tech, Blacksburg, VA 24061

^bDepartment of Chemical Engineering, Virginia Tech, Blacksburg, VA 24061

^cDepartment of Chemistry, Virginia Tech, Blacksburg, VA 24061

^dDepartment of Physics, Virginia Tech, Blacksburg, VA 24061

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.^{3,4,5} 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. We have shown that films fabricated with an NLO polymer result in significant cancellation of the chromophore orientations.^{8,10} 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 describe a hybrid covalent / ionic self-assembly technique that utilizes monomeric 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

ISAM films are grown monolayer by monolayer by alternately immersing a charged substrate in anionic and cationic solutions to build up 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 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, as shown in Figure 1. 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.

PAH
C₃ClH₈N
Mol. Wt.: 93.6

Procion Red MX-5B
C₁₉H₁₀Cl₂N₆Na₂O₇S₂
Mol. Wt.: 615.3

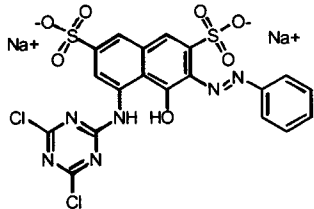
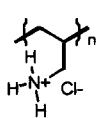


Figure 1. Molecules used in Hybrid covalent / ionic NLO film fabrication.

Results and Discussion

Polymer-polymer ISAM films. We have shown earlier that the bilayer thickness of polymer-polymer ISAM films 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.^{8,9,10} The effect of increased ionic strength typical of polymer-polymer films 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 / 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 orientation and do not contribute to the net SHG. Additionally, 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 partially cancel and lead to an overall reduction in the $\chi^{(2)}$ of the film. Although the layers are believed to be somewhat interpenetrated and to have "fuzzy" rather than distinct interfaces, the model presented here is a useful first approximation. 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.

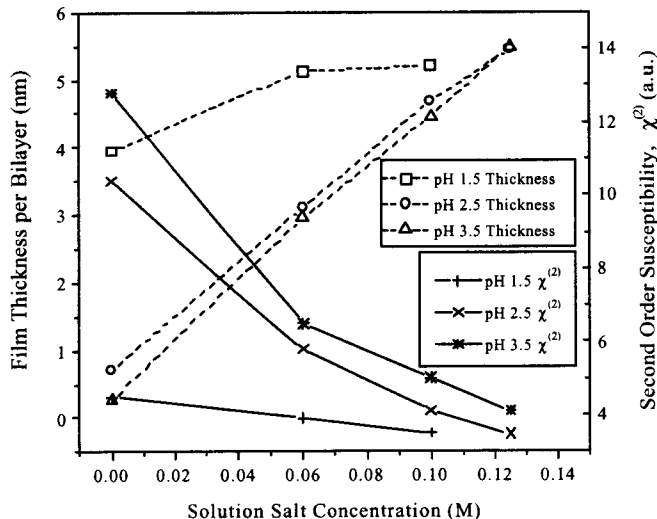


Figure 2. Bilayer thickness and $\chi^{(2)}$ as a function of NaCl concentration and pH of the immersion solutions for Poly S119/PAH ISAM films. This behavior is typical of polymer-polymer ISAM films

Hybrid covalent / ionic self-assembly. In order to overcome the issues associated with polyelectrolyte ISAM NLO films, we have fabricated ionically self-assembled films of a distinctly different structure, illustrated in Figure 4b. These films contain monomeric chromophores, as opposed to polyelectrolytes with NLO sidechains. 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 such that the amines are not protonated. When a film with upper layer of PR is immersed in PAH solution, 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.

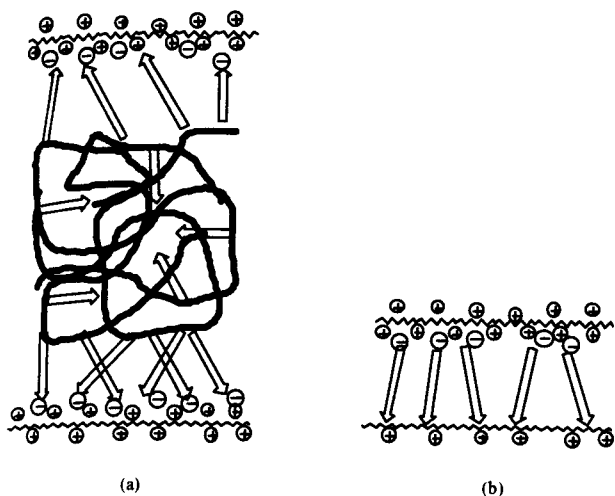


Figure 3. Schematic illustration of (a) a polychromophore between two PAH layers, and (b) Procion Red MX-5B between two PAH layers, illustrating the tendency to form thin (sub-nanometer) bilayers.

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

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

Figure 4 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 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 35×10^{-9} esu.

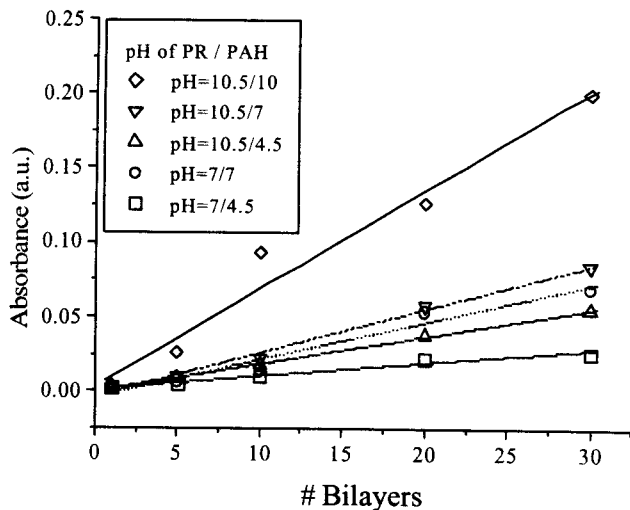


Figure 4. Absorbance and as a function of the number of bilayers for several sets of pH conditions in PR / PAH self-assembled films.

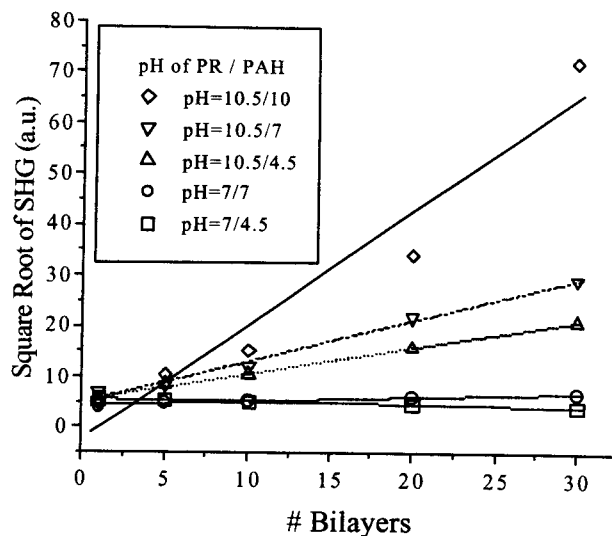


Figure 5. Square root of the SHG intensity as a function of the number of bilayers for several sets of pH conditions in PR/PAH self-assembled films.

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 new approach involves covalent attachment of the chromophore at only one of its ends, providing a preferential polar orientation, then ionic binding of the subsequent cationic layer. We have 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.

References

- (1) G. Decher, J.D. Hong, and J. Schmitt, *Thin Solid Films* **210**, 831 (1992).
- (2) G. Decher, *Science* **277**, 1232 (1997).
- (3) J.R. Heflin, C. Figura, D. Marciu, Y. Liu, and R.O. Claus, *SPIE Proc.* **3147**, 10 (1997); *Appl. Phys. Lett.* **74**, 495 (1999).
- (4) Y. Lvov, S. Yamada, and T. Kunitake, *Thin Solid Films* **300**, 107 (1997).
- (5) X. Wang, S. Balasubramanian, L. Li, X. Jiang, D. Sandman, M.F. Rubner, J. Kumar, and S.K. Tripathy, *Macromol. Rapid Commun.* **18**, 451 (1997).
- (6) K.M. Lenahan, Y. Wang, Y. Liu, R.O. Claus, J.R. Heflin, D. Marciu, and C. Figura, *Adv. Mater.* **10**, 853 (1998).
- (7) M.J. Roberts, G.A. Lindsay, W.N. Herman, and K.J. Wynne, *J. Am. Chem. Soc.* **120**, 11202 (1998).
- (8) C. Figura, P.J. Neyman, D. Marciu, C. Brands, M.A. Murray, S. Hair, M.B. Miller, R.M. Davis, and J.R. Heflin, *MRS Proc.* **598**, BB4.9.1-6 (2000).
- (9) C. Figura, P.J. Neyman, D. Marciu, C. Brands, M.A. Murray, S. Hair, R.M. Davis, M.B. Miller, and J.R. Heflin, *SPIE Proc.* **3939**, 214 (2000).
- (10) P.J. Neyman, M. Guzy, S.M. Shah, R.M. Davis, K.E. Van Cott, H. Wang, H.W. Gibson, C. Brands, J.R. Heflin, *SPIE Proc.* **4461**, 214 (2001).