

Hybrid Covalent/Ionic Self-Assembly of Organic Second Order Nonlinear Optical Films

J.R. Hefflin, P.J. Neyman, C. Brands

*Department of Physics, Virginia Tech, Blacksburg, VA 24061-0435
rhefflin@vt.edu*

M.T. Guzy, S.M. Shah, R.M. Davis, K.E. Van Cott

Department of Chemical Engineering, Virginia Tech, Blacksburg, VA 24061-0211

H. Wang, H.W. Gibson

Department of Chemistry, Virginia Tech, Blacksburg, VA 24061-0212

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. Previously, the ISAM films for NLO response consisted of bilayers of oppositely charged polymers whose thickness can be controlled through variation of pH and ionic strength of the immersion solutions. Here, we present an approach that replaces the NLO-active polymer layers with layers of monomeric chromophores containing ionic and covalent bonding sites. We have examined the effect of the pH of the immersion solutions on the orientation of the monomeric chromophores and demonstrated bulk polar ordering with $\chi^{(2)}$ values six times larger than quartz.

©2000 Optical Society of America

OCIS codes: 190.4710; 310.6860

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]. 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. These films show substantial $\chi^{(2)}$ values with excellent temporal and thermal stability [2]. Films fabricated with an NLO polymer result in significant cancellation of the chromophore orientations. In this paper, we describe 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.

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. 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 using 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. Poly(allylamine hydrochloride) (PAH), was used to provide both the nucleophilic primary amine groups for reaction with the triazine ring and the protonated amine groups for electrostatic interaction with the sulfonic acid groups of PR (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.

3. Results

When the film thickness is much less than the second harmonic coherence length of the material, the SHG intensity should exhibit a quadratic dependence on the film thickness or, correspondingly, number of bilayers. Figure 2 shows the square root of the peak second harmonic intensity as a function of the number of bilayers for the sets of films fabricated with different PAH and Procion Red pH values. The linear dependence of the square root of the SHG intensity on the number of bilayers for the films fabricated with Procion Red pH 10.5 demonstrates that the SHG signal is due to polar ordering in each successive bilayer of the film. If the degree of ordering decreased in successive bilayers

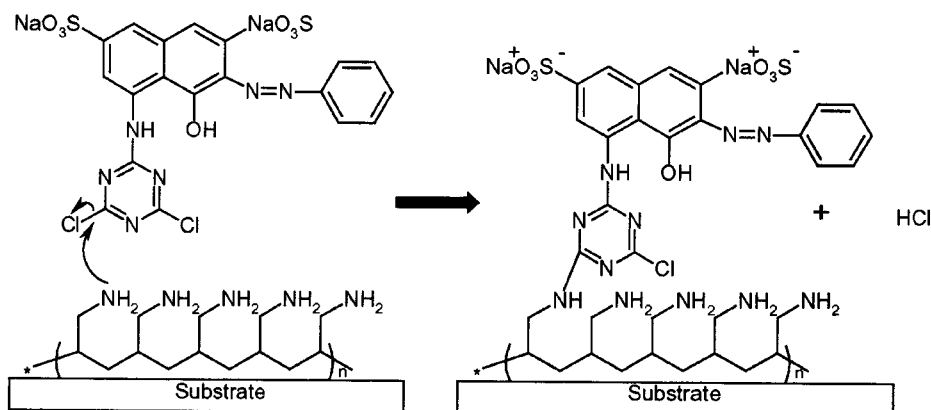


Figure 1. Reaction between PR molecule and a previously absorbed monolayer or PAH

or if the SHG signal was due to interface effects, the SHG intensity would have a subquadratic dependence on the number of bilayers. The PR solution pH directly affects the degree of protonation of the previous deposited PAH layers. At a pH above the pK_a of the side chain amines of PAH, the majority of the amines will be unprotonated and thus able to react with the triazine ring of PR. Additionally, the reactivity of the triazine ring on PR increases with increasing pH. These two effects result in reactive deposition being favored as the pH is increased. The large SHG observed in the PR pH 10.5 case is confirmation of the expected preference of covalent over electrostatic attachment of Procion Red to PAH (i.e., orientation of the triazine ring towards the PAH layer and the sulfonates away from it.) A $\chi^{(2)}$ value of 11×10^{-9} esu is obtained for the PAH/PR pH 7/10.5 films is obtained, demonstrating the effectiveness of this novel hybrid covalent/ionic self-assembly technique.

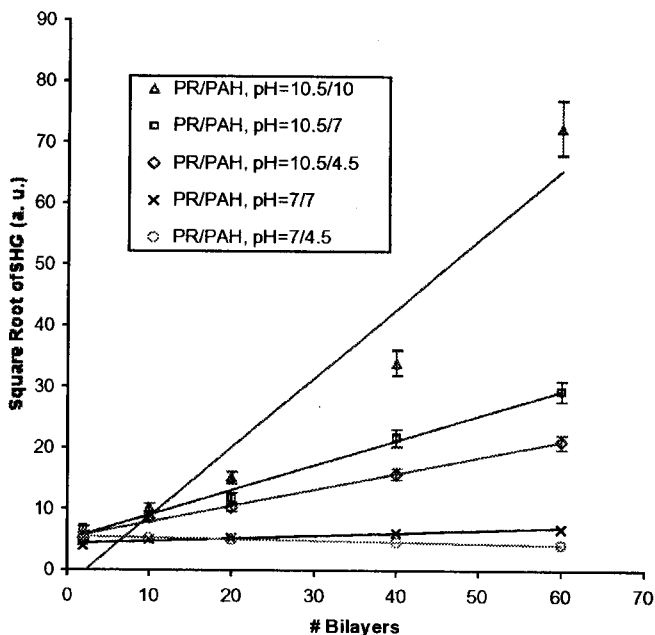


Figure 2. Square root of the SHG intensity as a function of the number of bilayer for various Procion Red/PAH pH conditions.

4. 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).