

## **Chapter Four:            Enhancements for Second-Order Nonlinear Susceptibility in ISAM Films**

The excellent design characteristics associated with ISAM films, the ease of fabrication, and the remarkable thermal stability/recovery of the second order nonlinear optical susceptibility of the films encourage their use for device application. Unfortunately, with  $\chi^{(2)}$  comparable to quartz, some improvement needs to be made to the nonlinear susceptibility to make ISAM films practical for application.

The second order NLO response of chromophores depends on several properties of the molecules. This may be tailored as described in Chapter One, by choosing conjugation length and appropriate donor/acceptor groups to suit the spectral characteristics desired. Furthermore, ISAM film structure may also be modified through the choice of pH and salt concentrations in dipping solutions, which can result in an enhancement of  $\chi^{(2)}$  (though moderate advancements only have been made in this manner at this point).

It is of extreme interest to determine additional methods which might allow larger  $\chi^{(2)}$  values in ISAM films. Two possibilities discussed here involve utilizing cyclodextrin molecules to complex with the polymeric chromophores to improve chromophore orientation and using dianionic chromophore molecules instead of polymers to avoid interface-interface competition that decreases the net order of the film.

### **4.1        Increased Second Order Susceptibility Through Tailored Chromophores**

Some initial work has been undertaken in synthesis of new polymers to improve  $\chi^{(2)}$  response of ISAM films. Several 'Polydye' polymer chromophores have been synthesized by Y. Liu and Y. Wang at FEORC (VPI-SU) and have been shown to form ISAM films.

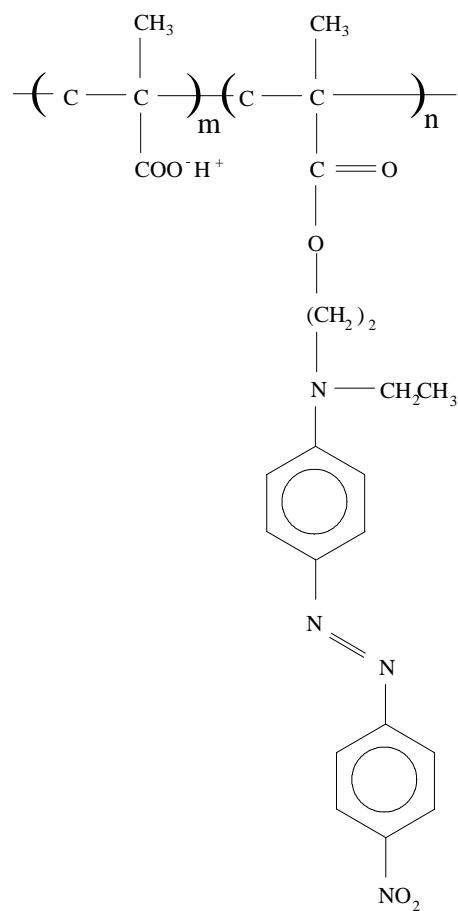


Figure 4.1.1: Structure of Polydye1 molecule. Note that chromophore-chromophore spacing is much larger than in other polymer dyes studied. Also note that ionic bond site is not located at end of chromophore, but rather on polymer backbone.

Of particular interest is Polydye 1, a poly(methacrylic acid) backbone with a sidechain azo dye chromophore (Figure 4.1.1). This chromophore should have a strong hyperpolarizability, as it has a long conjugation length and strong donors ( $\text{NCH}_2\text{CH}_3$ ) and acceptors ( $\text{NO}_2$ ). Of possible concern is the ionic bond site, a carboxylic acid group located not on the end of the chromophore but on the poly(methacrylic acid) backbone.

Polydye 1 was incorporated into an ISAM film using poly(diallyldimethylammonium chloride), PDDA, as the nonlinear inactive polycation. A 15 bilayer Polydye 1/PDDA ISAM film showed reasonable quadratic intensity dependence (Figure 4.1.2), with second harmonic intensities comparable to a 68 bilayer PS-119/PAH ISAM film used as a reference standard in our experiments. The smaller number of bilayers results in a bilayer susceptibility  $\eta^{(2)}$  that is approximately 5 times that of the PS-119/PAH standard. If the two films have similar bilayer thicknesses, this corresponds to an equivalent increase in  $\chi^{(2)}$ .

Orientation measurements indicate that Polydye 1 chromophores possess an average angle of  $26^\circ$ , much smaller than the  $\sim 40^\circ$ - $50^\circ$  angles observed for PS-119/PAH and PCBS/PAH ISAM films. This is thought to be due to Polydye 1's long polymer backbone. Chromophores on the polymer are spread out, which decreases the steric forces that may tend to increase the orientation angle in the other polymers.

## 4.2 Cyclodextrin-Complexed ISAM Films

As discussed previously, materials must possess a net non-centrosymmetry in order to possess second order non-linear optical properties. An important parameter of this noncentrosymmetry is the orientation of the chromophores at the interface: the greater the tilt angle, the less  $\chi^{(2)}$  is observed.

Several parameters have been shown to affect this orientation angle. In general, increased ionic strength and/or increased acidity in solution have been shown to decrease the orientation angle. This is thought to

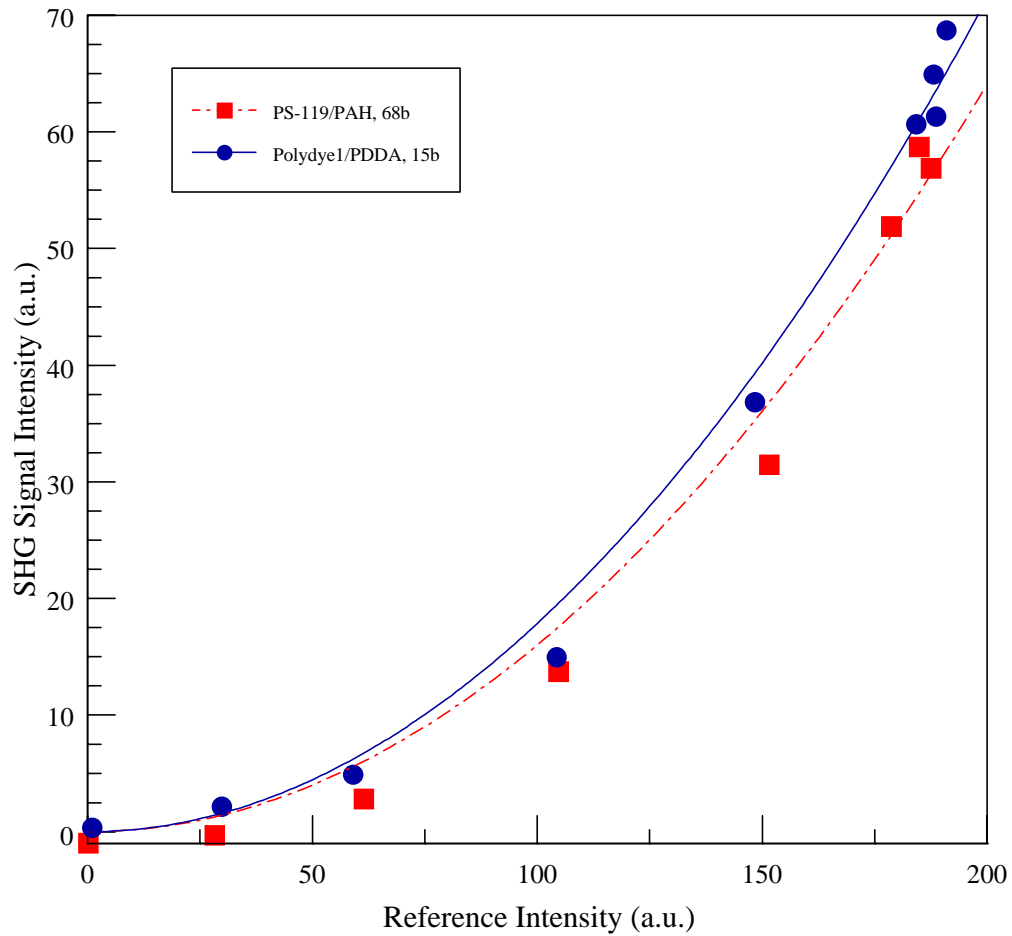


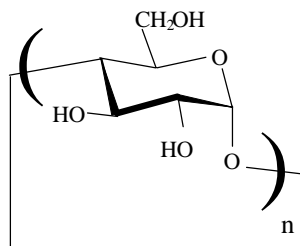
Figure 4.1.2: Second harmonic generation in Polydye1/PDDA ISAM film. Second harmonic intensity is shown to be quadratic with intensity of fundamental. Shown for comparison is PS-119/PAH ISAM film, used as our standard for comparison. Though the SHG is similar, the Polydye1/PDDA film has only 15 bilayers while the PS-119/PAH film has 68 bilayers.

be due to the accompanying increase in electrostatic screening, which decreases the chromophore-chromophore repulsion (due to like charges on the chromophore ends). This reduction allows chromophores to assume more upright orientations. It may be possible to use rigid sleeve-like molecules called cyclodextrins to improve  $\chi^{(2)}$  by physically ‘forcing’ a more normal chromophore orientation.

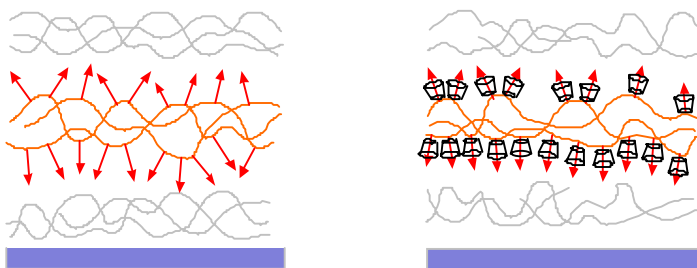
Cyclodextrins are a family of cyclic oligosaccharides that have been of increasing interest due to their ability to easily complex with rod-like molecules (rotaxanes) and chain or ring-like molecules (catananes). The three major types,  $\alpha$ ,  $\beta$ , and  $\gamma$  are comprised of 6, 7, and 8 glucopyranose repeat units (Figure 4.2.1a). The molecules form a conical cylinder whose interior region is lined by hydrogen atoms and glycosidic oxygen bridges. When in aqueous solution, this apolar cavity is filled with energetically unfavored water molecules which are easily substituted by guest molecules which are less polar than water. This is the basis for ‘molecular encapsulation’<sup>1</sup>. This complexation has several important consequences to poorly soluble guest molecules. Of particular interest, solubility of the guest increases, as the cyclodextrin is in general very soluble in aqueous solution. Also of interest, the UV-VIS spectra of the guest may be strongly modified by the complexation.

If cyclodextrins can be made to complex with chromophore sidechains<sup>2</sup> (forming pseudorotaxanes) during ISAM deposition, they may be able to assist chromophore orientation. The large size of the cyclodextrins would allow them to bridge irregularities in the polymer film at the surface. The cyclodextrins would tend to sit flat on the surface, forcing the encapsulated chromophore to orient normal to the surface (Figure 4.2.1b,c). This should then result in an increased second-order non-linear susceptibility.

For initial tests, PAH was used as then NLO-inactive polycation, with the NLO-active polyanion PS-119 chosen to complex with the cyclodextrins. Three ISAM variations were produced – PS-119/PAH without cyclodextrins for use as a reference, PS-119:CD $\alpha$ /PAH, and PS-119:CD $\beta$ /PAH. Cyclodextrins were provided by H. Gibson and H. Wang of the Department of Chemistry, Virginia Tech. 10.0mM PS-119 solutions at pH 2.5 with 0.05M NaCl were used. Cyclodextrins  $\alpha$  and  $\beta$  were added to the PS-119



(a)



(b)

(c)

Figure 4.2.1: Cyclodextrins and CD-polymer complexes. (a) Cyclodextrin structure.  $n=6,7,8$  for  $\alpha,\beta,\gamma$  types cyclodextrins, respectively. (b) Chromophores in ISAM films tend to have large ( $\sim 45^\circ$ ) orientation angles. (c) When incorporated into ISAM films, cyclodextrins are expected to help decrease the orientation angle, increasing  $\chi^{(2)}$ .

solutions at a 1:1 cyclodextrin:chromophore concentration. Threading would be expected to occur in solution, and film immersion times were kept at 3 minutes.

All films grow in absorbance linearly with the number of bilayers adsorbed. Both PS-119/PAH and PS-119:CD $\alpha$  show identical absorbance per bilayer at  $A/N_b=0.0142$ . PS-119:CD $\beta$ /PAH is 2% less, at  $A/N_b=0.0139$ .

Both PS-119:CD $\alpha$ /PAH and PS-119:CD $\beta$ /PAH are shown to possess a slightly larger second harmonic signal (and bilayer susceptibility  $\eta^{(2)}$ ) than the reference non-cyclodextrin PS-119/PAH film (Figure 4.2.2). Variations are small, however, and may be due to minor variations in absorbance. Chromophore orientation measurements indicate that both cyclodextrin  $\alpha$  and  $\beta$  as well as non-cyclodextrin reference PCBS/PAH films have identical average tilt angles to within the sensitivity of our measurement technique. Values of  $\bar{\psi} = 55^\circ \pm 0.5^\circ$  are obtained for all films.

Recently completed proton NMR has determined that a very low fraction of pseudorotaxanes form with PS-119. This is likely due to the large biphenyl located at the end of the PS-119 chromophore. The biphenyl is roughly  $5\text{\AA}$  across, while the  $\alpha$  and  $\beta$  cyclodextrins investigated have diameters of  $\sim 5.0\text{\AA}$  and  $\sim 6.3\text{\AA}$ , respectively.

Also of concern is the close chromophore-chromophore spacing on the PS-119 backbone. Even uncomplexed chromophores are expected to experience large steric forces from adjacent chromophores, forcing larger orientation angles. If cyclodextrins could be made to thread on the PS-119 chromophore, the tight spacing would likely worsen the chromophore orientation.

Despite these disappointing first trials, it is still believed that a more judicious choice of a chromophore partner for the cyclodextrins could yield films with enhanced orientational alignment.

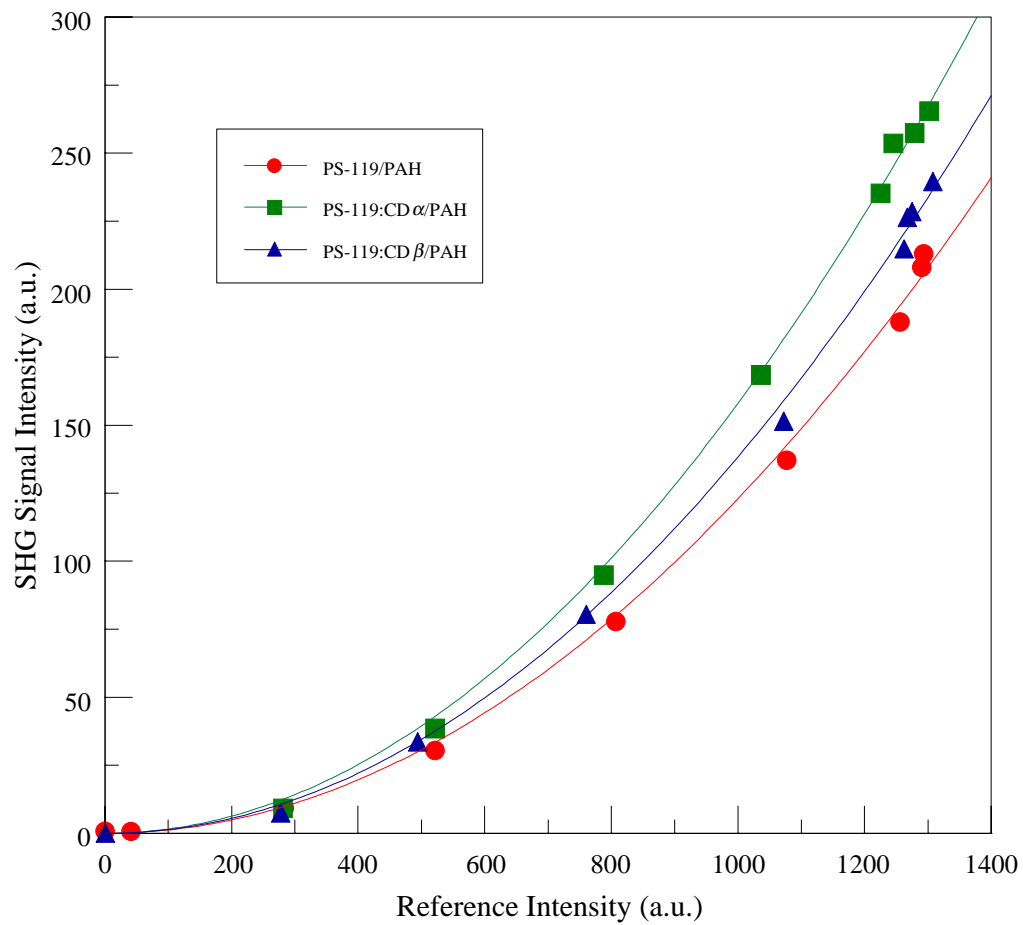


Figure 4.2.2: Second harmonic signal intensity for cyclodextrin-complexed PS-119/PAH films. Both cyclodextrins show a small improvement in SHG signal over the non-complexed reference film.

### 4.3 Polymer-Dye Systems and Decreased Interface-Interface Competition

ISAM deposition requires some amount of chromophores to be oriented outward (away from the layer) at each interface in a layer. However, since ISAM films exhibit SHG, the cancellation due to oppositely oriented chromophores at opposing interfaces must not be complete. While there is, in fact, a non-zero  $\chi^{(2)}$  observed for ISAM films and therefore a noncentrosymmetry associated with the films, there can be no doubt that this competition is a serious limiting factor to large  $\chi^{(2)}$  in ISAM films. In Chapter 3.5 significant decreases in  $\eta^{(2)}$  were observed when the top chromophore layer was ‘capped’ with a layer of NLO-inactive polymer. This decrease is associated with the decreased tilt angle  $\bar{\psi}$  of the (formerly) outermost layer as newly adsorbed polymer binds, pulling charged side groups (chromophores) upward.

The ‘losses’ in  $\chi^{(2)}$  due to interface competition and unoriented intra-layer chromophore can also be seen through corona-poling experiments with ISAM films. A 367 bilayer PS-119/PAH film was poled with a 270kV/m field for 1 hour at 165°C. Quadratic intensity dependences are observed in both poled and unpoled films (Figure 4.3.1). Immediately after poling, ISAM films show an increase in  $\chi^{(2)}$  by a factor of 50 over unpoled films. This indicates that there must be a large amount of unoriented chromophore (in the intra-layer region, away from the interfaces) and that there must be some large amount of competition between interfaces.

As a possibility for avoiding this competition, a polyelectrolyte-ionic dye system was investigated. This involves the ISAM deposition of a polycation followed by a similar deposition step involving a dianionic chromophore (such as that shown in Figure 4.3.2a). This chromophore would bond to the surface, theoretically leaving a charged group at its opposite end extending into the bulk phase to effect charge reversal, limiting film deposition. In order to give the molecule a preferential alignment, two different anionic groups with different pKa values are used. The chromophore shown in Figure 4.3.2a, Mordant Yellow 10 (Aldrich) possesses a sulfonate group at one end and a carboxylic acid group at the other. The sulfonate group has a pKa of  $\sim -1$  to 0, and is well-charged even at high acidities near pH 3. At this pH,

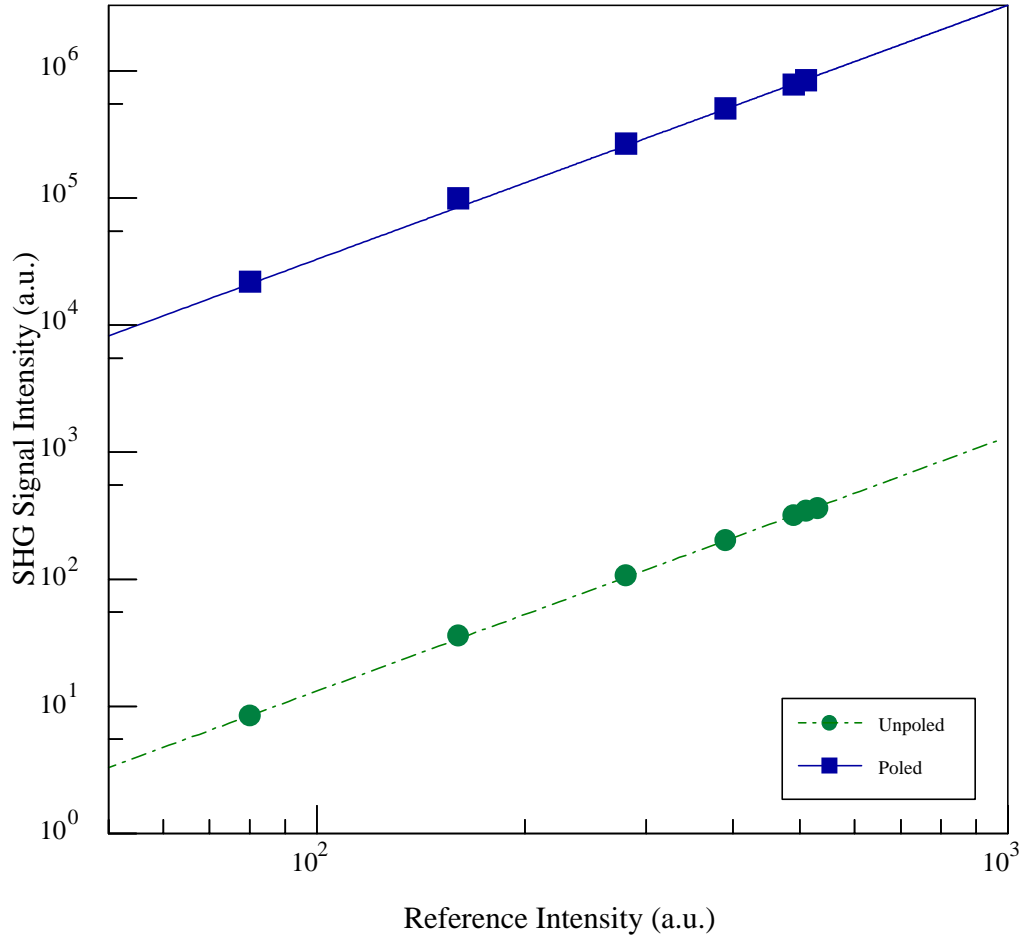


Figure 4.3.1: Second harmonic intensity for poled and unpoled PS-119/PAH ISAM films. Film was poled with 270kV/m field at 165°C for 1 hour. Increase in second harmonic corresponds to an increase in  $\chi^{(2)}$  by a factor of 50.

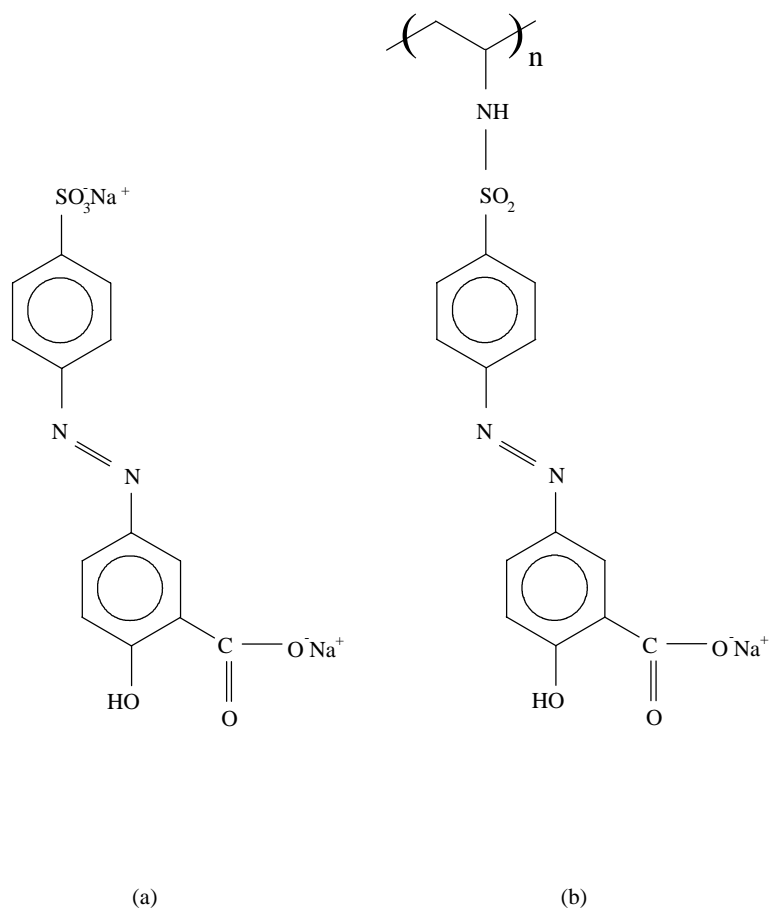


Figure 4.3.2: Dianinic chromophore molecular structure. (a) Mordant Yellow 10, and (b) PCBS, used as a comparison. Both available from Aldrich. Both molecules are conjugated over the entire length of the chromophore.

however, the carboxylic acid with pKa ~4-5 is very poorly charged. As such, the Mordant Yellow 10 chromophore should behave as a molecule with only one charged end when it is in a pH 3 solution. The following step, deposition of the NLO-inactive polymer (PAH), is then made at a higher pH of 7.5. At this pH the PAH (with pKa 11) and the exposed carboxylic acid on the Mordant Yellow 10 are both well charged, allowing deposition of the PAH layer. Deposition may continue in this manner until the desired number of layers is reached.

Mordant Yellow 10 (MY-10) was obtained from Aldrich at 85% purity and further purified by H. Wang (Dept. of Chemistry, VPI-SU) as follows. Stock MY-10 was dissolved in just enough hot water to completely dissolve the chromophore. The solution was allowed to cool to room temperature, at which time Mordant Yellow precipitated out, leaving impurities in solution. These were then drained, and this process repeated twice. After the last iteration, the precipitated chromophore was dissolved in a 50% ethanol solution. As this cooled MY-10 crystallized out and was ready for use.

All films were produced from 10mM solutions. As a comparison, PCBS/PAH films were produced under similar conditions. The chromophore side-chain of the PCBS polymer (Figure 4.3.2b) closely resembles that of Mordant Yellow 10, and its absorbance spectra likewise is very similar (Figure 4.3.3). Since PCBS has a carboxylic acid group, the pH of PCBS solution was maintained at 7.5. At lower pH PCBS became insoluble and precipitated out of solution. A 10mM solution of PAH at pH 7.5 was used for the polycation. The pH of the PAH solution was stabilized using Imidazole(Fischer) as a buffer with concentration of 12.5mM.

Both MY-10/PAH and PCBS/PAH films show linear increase in absorbance with added numbers of bilayers (Figure 4.3.4). The MY-10/PAH film shows a small absorbance per bilayer at its absorption peak that is comparable to those shown by the zero salt, high pH PS-119/PAH films reported earlier. We determined that the small absorbance in those cases was due to strong electrostatic interactions in the solution, which forced the polymer to maintain a train-like conformation. The layers were very thin as a result, which

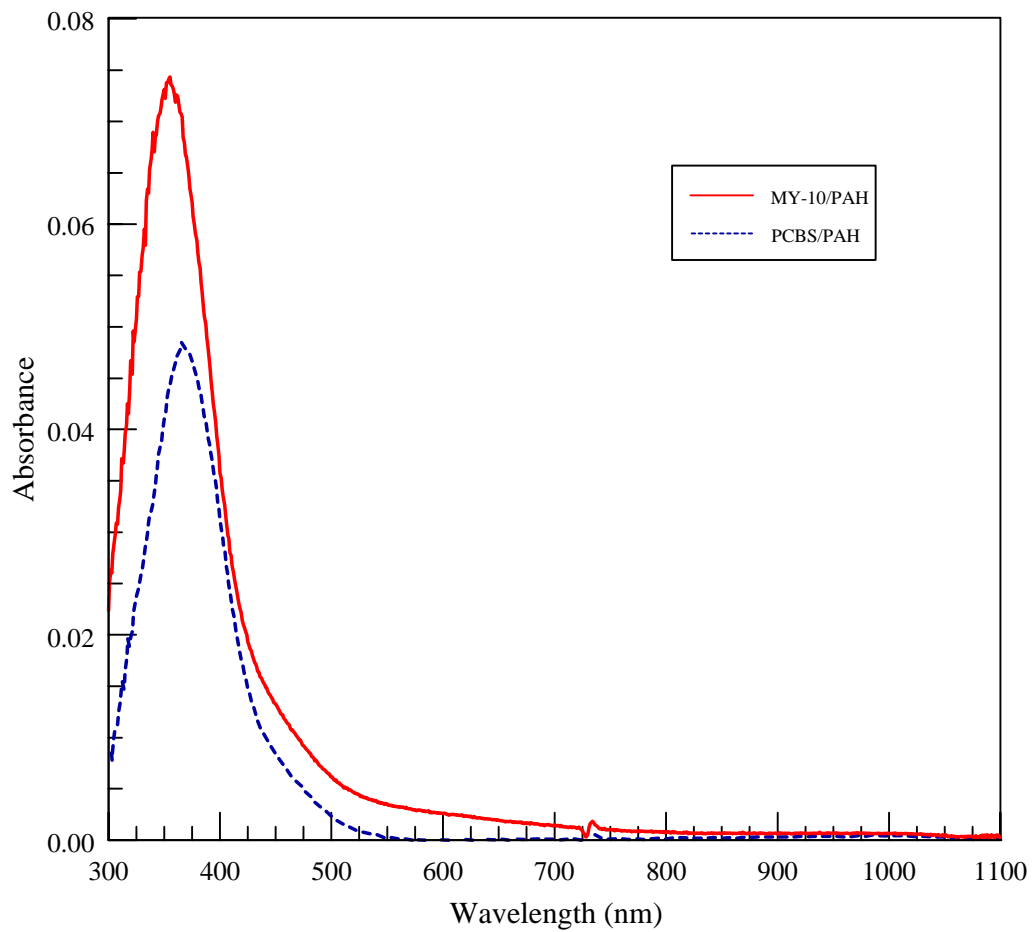


Figure 4.3.3: Absorbance spectra of Mordant Yellow 10/PAH and PCBS/PAH ISAM films

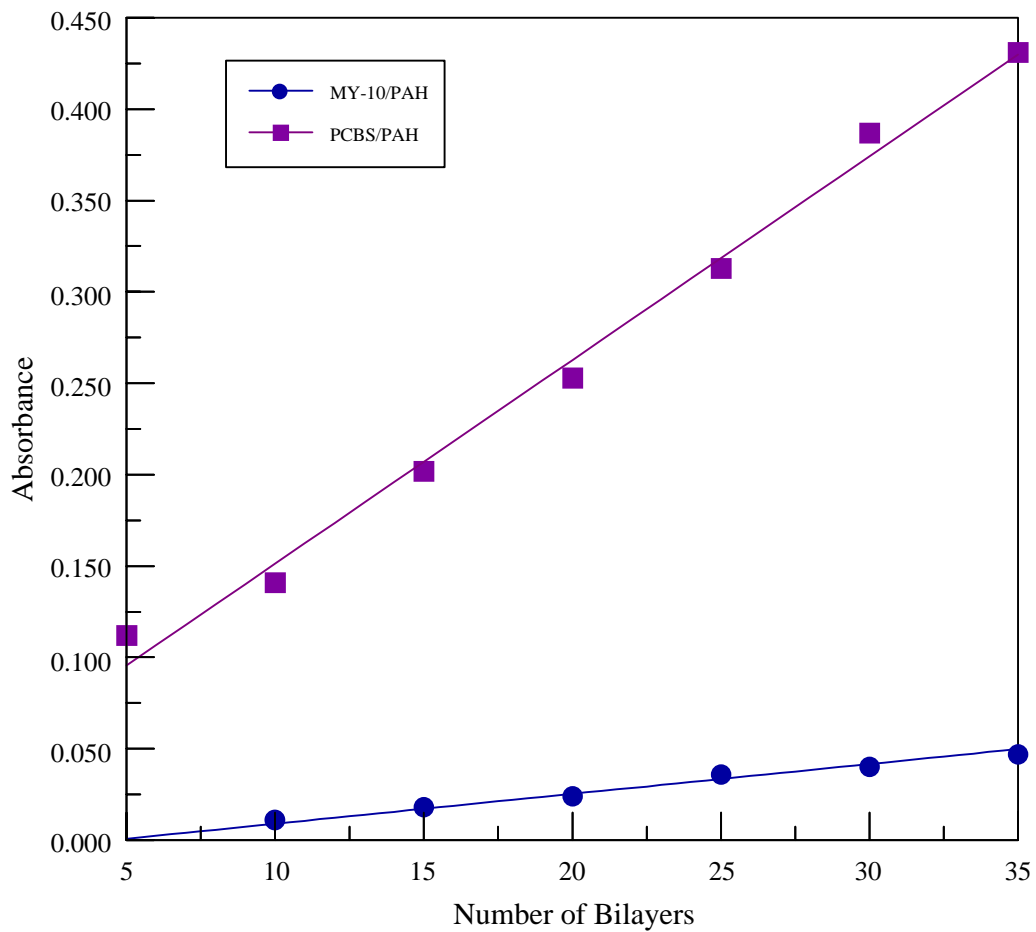


Figure 4.3.4 Absorbance vs. number of bilayers for MY-10/PAH and PCBS/PAH ISAM films. Films are produced under similar dipping conditions. Constant absorbance per bilayer is indicated for both films.

decreased the amount of chromophore that could be adsorbed. Because Mordant Yellow 10 is a molecule and not a chromophore, all chromophore adsorbed should be right at the interface. PCBS/PAH shows a much larger absorbance per bilayer. We associate this with the formation of a polymer layer containing unoriented intra-layer chromophores. Many PCBS chromophores are expected to be adsorbed though only a few may actually form ion pairs at the interface. MY-10 chromophores acting singly must form ion pairs with each chromophore adsorbed. No intra-layer randomly-oriented region is thought to be possible.

Second harmonic generation measurements of MY-10/PAH ISAM films yield much smaller signals than expected. Quadratic dependence on fundamental intensity is evident (Figure 4.3.5), but second harmonic intensity does not grow quadratically with the number of bilayers adsorbed. Orientation angle measurements suggest an orientation angle near  $50^\circ$ , but these measurements are suspect as SHG intensities were very small and subject to significant fluctuations, resulting in uncertainty in the orientation angle of  $\pm 5^\circ$ .

Since absorbance measurements indicate that the amount of chromophore being deposited in each additional layer remains constant, the poor behaviour of the second harmonic intensity suggest that chromophore orientation is not being maintained. This may be due to several parameters which may affect the polymer/dye system. If the pH is not sufficiently low, the carboxylic acid group on the Mordant Yellow 10 may be charged, removing our mechanism for 'preferential alignment' at the deposition stage. It is also possible that the interpenetration noted with ISAM films is causing severe disorientation with the dianionic molecule. If this is so, then the chromophores may be bonding at one end (the sulfonate end), but within the PAH layer, so that the net orientation may be well away from the surface normal. Several other groups have also cited longer immersion times for polymer-dye adsorption than the three minutes used for these tests<sup>3,4</sup>. The kinematics of polyelectrolyte adsorption could likely take place on a different time scale than those of molecular adsorption.

The principle behind the ordered deposition of dianionic dyes seems sound. Several variations of their formation should be tried to determine if  $\chi^{(2)}$  can be improved. Different combinations of anionic and

cationic pH values should be tested to see if better control of the sulfonate versus the carboxy group can be achieved. Also, higher Mordant Yellow 10 concentrations and longer immersion times should be checked to ensure that Mordant Yellow 10 adsorption has equilibrated.

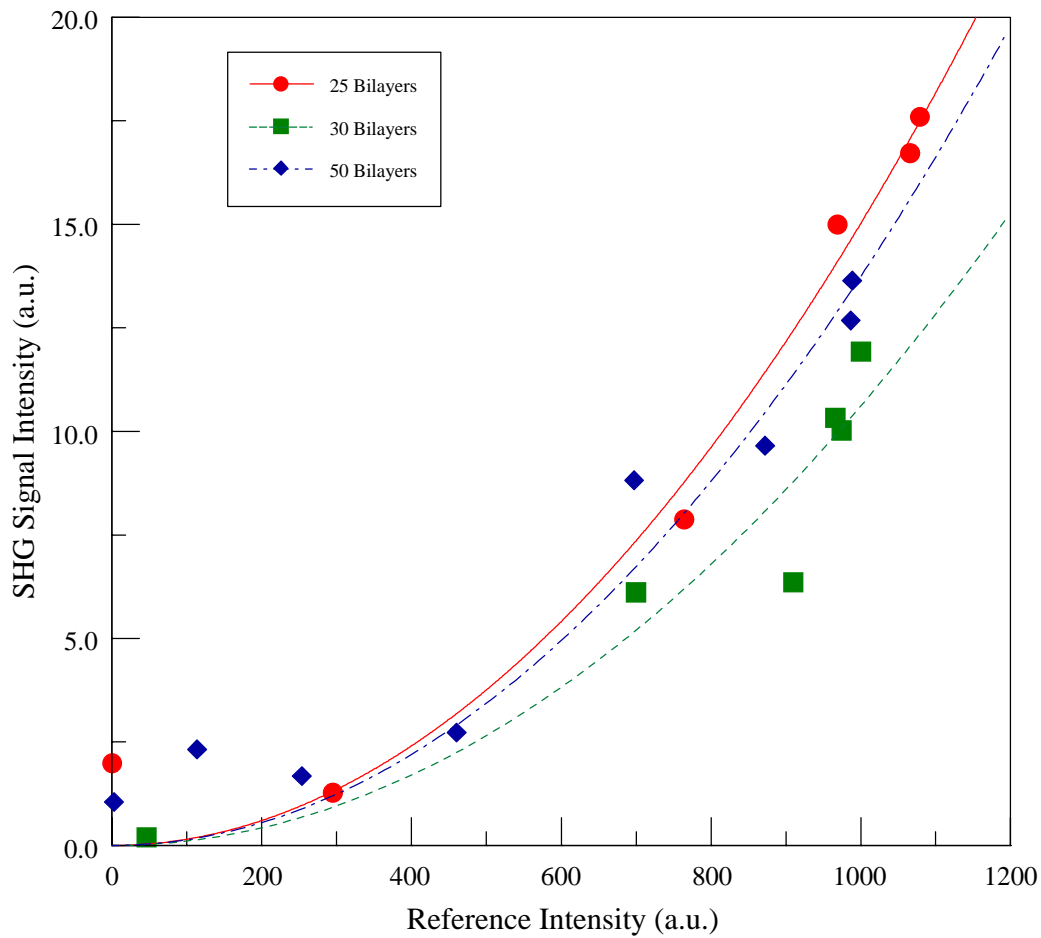


Figure 4.3.5: Second harmonic generation in Mordant Yellow 10/PAH ISAM films. Quadratic SHG is observed, though some amount of error is present due to small intensities measured.

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<sup>1</sup> J. Szejtli, *Chem. Rev.*, **98**, (1998) p1743-1753

<sup>2</sup> S. Nepogodiev, J. F. Stoddart, *Chem. Rev.*, **98**, (1998) p1959-1976

<sup>3</sup> K. Ariga, Y. Lvov, T. Kunitake, *J. Am. Chem. Soc.*, **119**, (1997) p2224-2231

<sup>4</sup> G. Mao, Y. Tsao, M. Tirrell, H. T. Davis, *Langmuir*, **11**, (1995) p942-952