

Thermal Stability and Immersion Solution Dependence of Second Order Nonlinear Optical Ionically Self-Assembled Films

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ABSTRACT

Polymeric films fabricated from ionically self-assembled monolayers (ISAMs) spontaneously form in a noncentrosymmetric structure requisite for a nonzero second order nonlinear optical (NLO) susceptibility, $\chi^{(2)}$, without the need for electric field poling. ISAM NLO films exhibit excellent long-term temporal stability of $\chi^{(2)}$, having shown no decay over a period of nearly three years. They are also remarkably stable at elevated temperatures. While $\chi^{(2)}$ decreases by 20% as the temperature is raised to 150° C, total recovery of the susceptibility is observed upon cooling, demonstrating that the decrease is not due to an irreversible randomization of the chromophore alignment. The thickness, orientational order, and NLO response are found to be strongly dependent on the pH and ionic strength of the solutions from which the films are deposited. The largest $\chi^{(2)}$ values are observed in films with the smallest bilayer thickness. This suggests that polar orientation is obtained primarily at the interfaces between adjacent layers rather than throughout a full monolayer.

Keywords: second order nonlinear optical susceptibility, ionically self-assembled monolayers, thermal stability, pH, ionic strength

1. INTRODUCTION

Since the first demonstration of electro-optic poled polymers,¹ there have been intense research and development efforts to make these materials suitable for commercial application. This is spurred, for example, by the potential for less expensive electro-optic modulators with larger bandwidths and lower drive voltages than the presently dominant LiNbO₃ technology. While significant progress has been achieved over the past decade, one of the most difficult challenges remains the tendency of the nonlinear optical chromophores to relax to random orientation, especially at the elevated temperatures that are typical of many device applications. The crux of this difficulty is that the polar orientation obtained by electric field poling is a thermodynamically-unstable state of the system. In attempts to circumvent this challenge, several approaches have been explored that spontaneously exhibit the required noncentrosymmetric ordering without the need for an external force. These include Langmuir-Blodgett films²⁻⁴ and covalently self-assembled monolayer

structures.⁵⁻⁷ More recently, several groups⁸⁻¹³ have shown that a thin-film fabrication method based on the sequential adsorption of alternating thin layers of oppositely-charged polyelectrolytes can yield noncentrosymmetric structures with substantial $\chi^{(2)}$ values. The fabrication technique for these polymeric thin films, referred to here as ionically self-assembled monolayers (ISAMs), was first demonstrated by Decher and co-workers in 1991.¹⁴⁻¹⁶

We have shown previously^{8,13} that ISAM films fabricated using a commercial polyelectrolyte dye have $\chi^{(2)}$ values comparable to that of quartz with no measurable decrease in $\chi^{(2)}$ over more than a year. Furthermore, as the film thickness was increased through the adsorption of additional bilayers, the second harmonic intensity exhibited the expected quadratic dependence, demonstrating that the degree of orientational order is the same in each sequential bilayer. This is a critical demonstration since one major potential application for ISAM $\chi^{(2)}$ films is in electro-optic waveguides, which requires film thickness on the order of a micron or more. Here, we show that the degree of ordering within ISAM $\chi^{(2)}$ films is a strong function of the pH and salt concentration of the immersion solutions from which the films are fabricated. These results provide insight into the nature of the polar ordering obtained in these films and are valuable in developing approaches for increasing the $\chi^{(2)}$ values. We also show that the NLO response exhibits remarkable thermal stability. No decrease in the $\chi^{(2)}$ value occurs after a heating cycle to 150° C for twenty hours.

2. EFFECT OF pH AND SALT CONCENTRATION ON $\chi^{(2)}$

ISAM films are grown monolayer by monolayer by alternately immersing a charged substrate in anionic and cationic solutions. Upon each immersion, an exceptionally homogeneous layer is rapidly formed by electrostatic attraction to the oppositely charged surface. The thickness of each individual layer is typically on the order of 1 nm. The immersion process can be repeated until a film with the desired thickness or number of layers has been produced. For the studies presented here, ISAM films were deposited on glass microscope slide substrates. Noncentrosymmetric, ISAM $\chi^{(2)}$ films were produced using the anionic polymer dye Poly S-119 (from Sigma), which consists of a poly(vinyl amine) backbone with an ionic azo-dye chromophore.¹³ Poly (allylamine hydrochloride) (PAH) was used for the polycation. The concentration of each solution was 10 mM. The pH was adjusted by the addition of HCl. In some cases, NaCl was also added to separately adjust the ionic strength. The films were immersed in one solution for three minutes, rinsed with deionized water, dried, and subsequently immersed in the opposite charge solution for three minutes.

Second harmonic generation (SHG) measurements were made using the 1200 nm output from a broadband BBO optical parametric oscillator pumped by the 355 nm third harmonic of a Q-switched Nd:YAG laser. The beam was weakly focused into the sample to a spot size of a few hundred microns. The film was polished off of one side of the substrate to eliminate interference effects, and the film was rotated 45° away from normal incidence about the vertical axis with incident p-polarized light.

It has been found that the thickness of ISAM layers can be dramatically varied by different pH and salt concentrations in the immersion solutions.¹⁷ As an example, Figure 1 illustrates the dependence of the peak absorbance (480 nm) as a function of the number of bilayers for four NaCl concentrations ranging from 0.0 to 0.13 M at a fixed pH of 3.5. In each case, the excellent linear

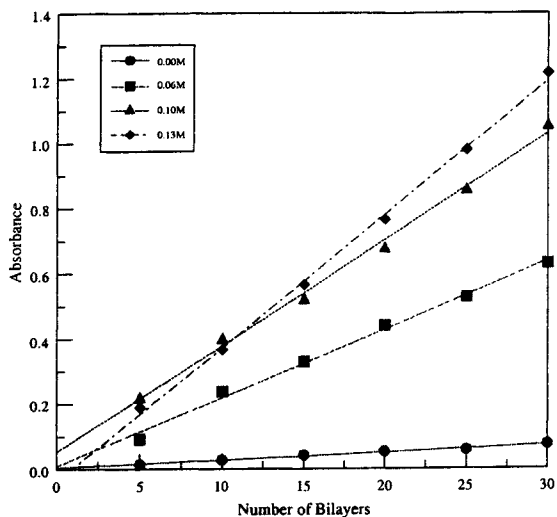


Figure 1. Peak absorbance versus number of bilayers of Poly S-119/PAH ISAM films for varying salt concentration at a pH of 3.5.

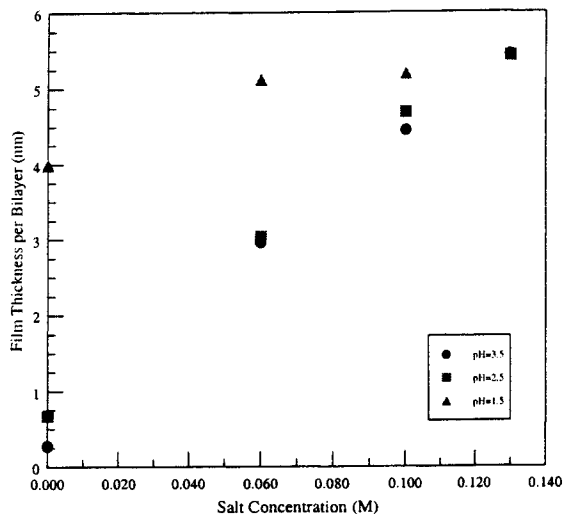


Figure 2. Bilayer thickness versus salt concentration for three pH values.

dependence demonstrates the excellent homogeneity of ISAM film formation from layer to layer. However, the larger slope for decreased pH values indicates that more chromophore is incorporated into each layer. This is confirmed by direct measurements of thickness. In all our studies, thickness and absorbance have yielded excellent linear dependence for a given set of polymeric components. A similar set of films was made for pH values of 1.5 and 2.5. The measured film thickness per Poly S-119/PAH bilayer is shown for the full set of films in Figure 2. It seen that at each pH value, the film thickness increases with increased salt concentration. The dependence of film thickness on salt concentration decreases with increasing acidity however. The ability to control the bilayer thickness from 0.3 to greater than 5 nm simply by adjusting the parameters of the immersion solutions illustrates the extreme power and versatility of the ISAM fabrication technique.

The conformation of a polyelectrolyte in solution is determined by the Debye length κ^{-1} .¹⁸ The Debye length is the characteristic length scale for electrostatic interactions in solution and is given by

$$\kappa^{-1} = \sqrt{\frac{kT}{2c_s z^2 e^2}} \quad (1)$$

where c_s is the total ionic strength (concentration of small ions) and z is the counterion valency. In solutions with added NaCl and for low polymer concentrations, the ionic strength is the total concentration of Na^+ and H^+ ions as given by

$$c_s = c_{\text{NaCl}} + 10^{-\text{pH}} \quad (2)$$

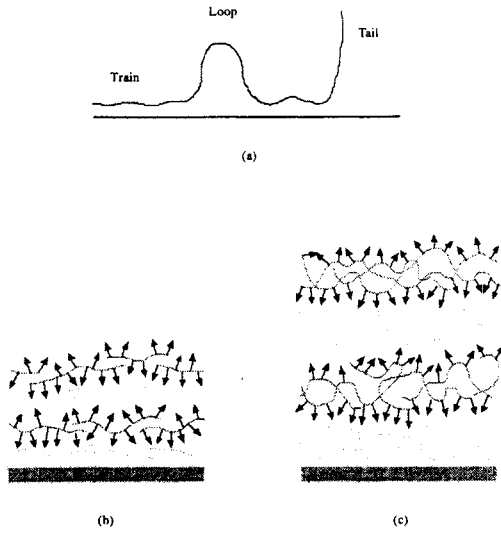


Figure 3. a) Conformation of polymer as trains, loops and tails. b) At low ionic strength, polymer forms predominantly trains. c) At higher ionic strength, polyelectrolyte charges are screened, allowing polymer to loop and coil.

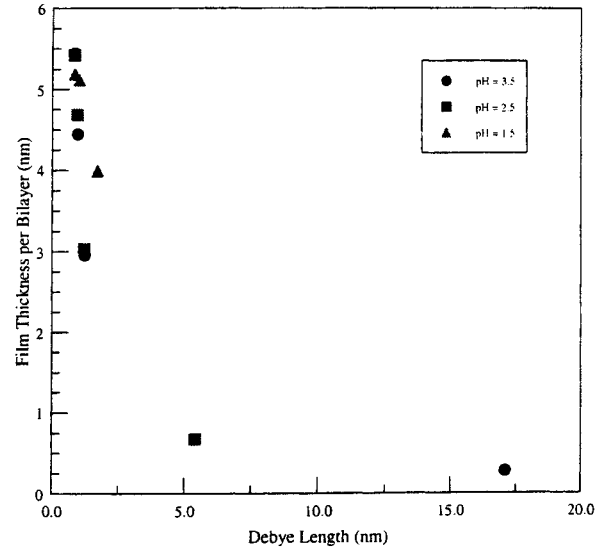


Figure 4. Film thickness versus Debye length for Poly S-119 ISAM films.

As the Debye length is reduced, the repulsion of neighboring ions on the polymer is reduced due to electrostatic screening by the counterions. This, in turn, allows more curvature in the polymer backbone or, correspondingly, a reduction in the chain stiffness as characterized by the persistence length. At low ionic strengths, when the electrostatic screening is low, the polyelectrolyte adopts an extended conformation and adsorbs onto the surface with a predominance of trains (see Figure 3). At higher ionic strength, the fraction of adsorbed polymer segments in the form of loops increases, resulting in a thicker adsorbed layer.¹⁸ As seen in Figure 2, lower pH and increased NaCl both lead to dramatic increases in bilayer thickness, consistent with this description. Further confirmation of the relationship between Debye length, polyelectrolyte conformation, and film thickness is illustrated in Figure 4. The data of Figure 2 are seen to collapse onto a master curve in which Debye length is inversely correlated with the film thickness.

In the limit that the film thickness is much less than the coherence length l_c , the second harmonic intensity is related to the film thickness and $\chi^{(2)}$ through $I_{2\omega} \propto (l\chi^{(2)})^2 I_\omega^2$. Since the film thickness varies with the solution parameters but the number of bilayers is known for every film, it is valuable to define an additional quantity $\eta^{(2)}$ that we refer to as the bilayer susceptibility through

$$I_{2\omega} \propto (N_b \eta^{(2)})^2 I_\omega^2 \quad (3)$$

where N_b is the number of bilayers in the film. $\eta^{(2)}$ is thus a measure of the effectiveness of the NLO response per bilayer deposition cycle, an important consideration in the fabrication of ISAM films.

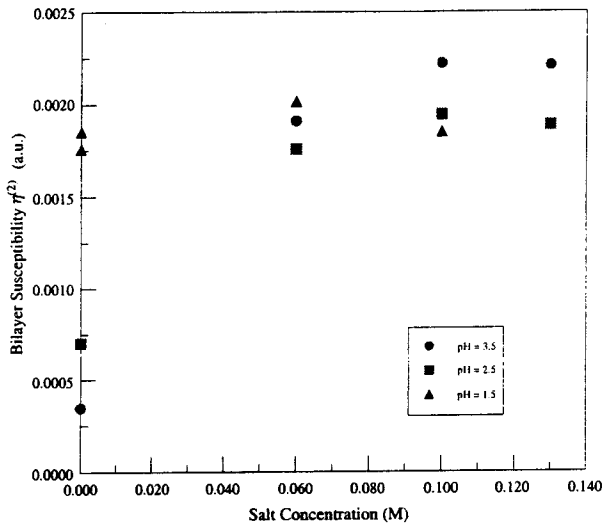


Figure 5. Bilayer susceptibility versus salt concentration for several pH values. Increase corresponds to increase in SHG intensity for same number of bilayers.

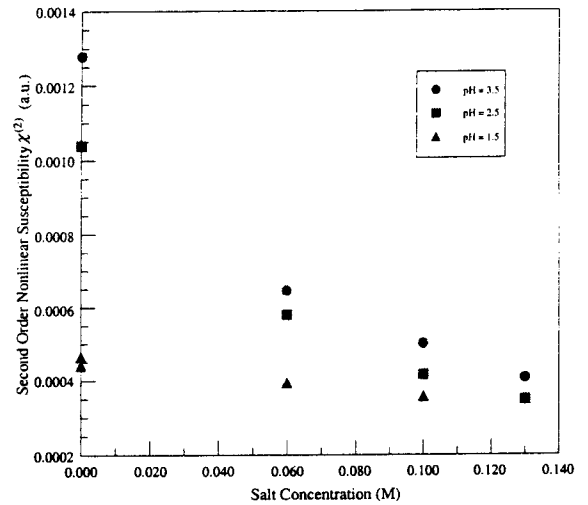


Figure 6. Second order susceptibility $\chi^{(2)}$ versus salt concentration for several pH values. Decrease is due to increase of thickness faster than SHG intensity.

For two films with equal numbers of bilayers, $\eta^{(2)}$ is directly proportional to the square root of the SHG intensity. The values of $\eta^{(2)}$ for the same series of films presented in Figure 2 are plotted in Figure 5. A general trend is observed that the SHG intensity increases with decreased pH and increased NaCl concentration. These values are seen to plateau more rapidly than those for the bilayer thickness in Figure 2, however. In fact, the $\chi^{(2)}$ values for this set of films, plotted in Figure 6, show the reverse trend. $\chi^{(2)}$ decreases with with decreased pH and increased NaCl concentration. The interpretation of these results is displayed in simplified form in Figures 3b and c. For the lowest bilayer thickness values, the polymer backbone assumes an extended conformation and the majority of the NLO chromophores are located at the interfaces between adjacent layers. While the growth of ISAM films requires chromophores to be oriented both towards and away from the substrate, a net polar orientation is obtained through a predominance in one direction over the other and/or a smaller average tilt angle away from the normal in one direction. The asymmetry is achieved during the formation of each layer due to the strong anisotropy between the electrically charged surface to which the polymers is adsorbed and the neutral, isotropic immersion solution. In thicker films (Figure 3c), the chromophores that are incorporated into the interior of a monolayer (which are not shown in Figure 3c) are less likely to be oriented as a result of weaker interactions with the preceding and subsequent layers of opposite charge. Since the bilayer susceptibility does increase with increased thickness, there is clearly some polar orientation obtained in the additional adsorbed material. This degree of orientation is simply stronger, however, at the layer interfaces than within the "bulk" of a monolayer, resulting in a decreased $\chi^{(2)}$ as the bilayer thickness is increased.

3. THERMAL STABILITY OF $\chi^{(2)}$ IN ISAM FILMS

Thermal and temporal stability of polymer NLO films is one of the most critical issues for the development of commercial devices. Poled polymers exhibit increased decay rates of $\chi^{(2)}$ as the

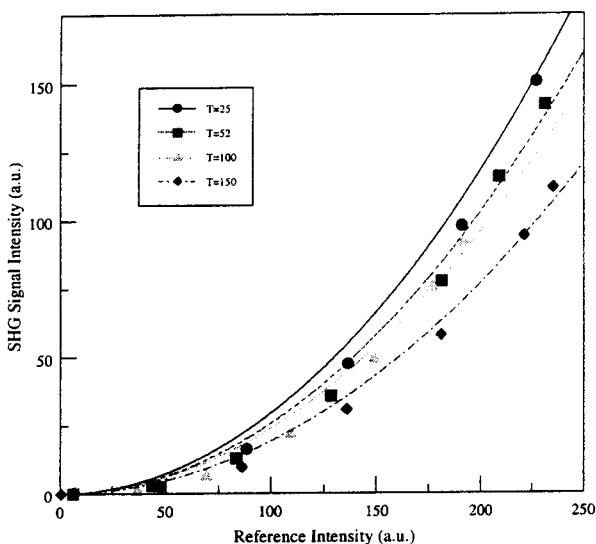


Figure 7. SHG intensity in a Poly S-119 ISAM film while heating to 150° C over three hours.

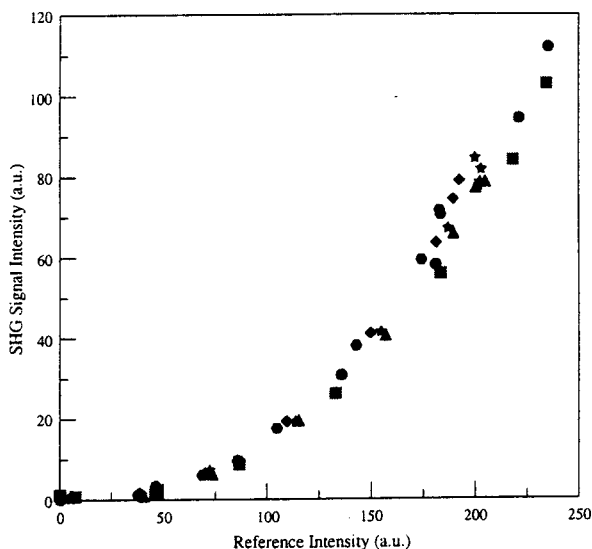


Figure 8. SHG intensity measured at several times during heating for twenty hours at 150° C constant temperature.

temperature approaches the glass transition temperature T_g . Above T_g , the $\chi^{(2)}$ immediately decays to zero. This is due to randomization of the chromophore orientation due to increased orientational mobility. ISAM films do not suffer from similar drawbacks since the polar orientation is spontaneously obtained and is thermodynamically stable. To evaluate the thermal stability of ISAM $\chi^{(2)}$ films, a Poly S-119/PAH film was heated to 150° C over a period of three hours. Figure 7 shows the SHG data taken at several temperatures during the heating cycle. The decrease in the SHG intensity corresponds to a 20% decrease in $\eta^{(2)}$ and, correspondingly, $\chi^{(2)}$ under the assumption of constant film thickness.

Once the temperature reached 150° C, the sample was maintained at this temperature for twenty hours and the second harmonic intensity was measured several times during this interval. As seen in Figure 8, nearly identical SHG data were obtained throughout this time period. ISAM films clearly exhibit exceptional thermal stability of $\chi^{(2)}$ for twenty hours at 150° C. Even more remarkably, as the sample was cooled to room temperature, the SHG signal *increased* as shown in Figure 9. Within 24 hours, the $\chi^{(2)}$ value had *completely recovered* to its value prior to the heating cycle. The decrease in the SHG intensity observed upon sample heating is clearly not due to chromophore randomization as is the case in poled polymers. In fact, the glass transition temperature of Poly S-119/PAH ISAM films was measured to be 140° C. The observation that chromophore orientation is maintained even above T_g demonstrates the potential advantage of ISAM films in NLO polymer device applications. The partial decrease in the SHG signal that is observed as the sample temperature is increased is believed to be due to breaking of a fraction of the ionic bonds that maintain the chromophore orientation. As the temperature is lowered, these bonds are reformed and the SHG intensity and $\chi^{(2)}$ return to their initial values. The complete recovery of the $\chi^{(2)}$ value suggests but doesn't prove that the diffusion of the chromophore-containing Poly S-119 during the heating cycle above T_g is highly constrained.

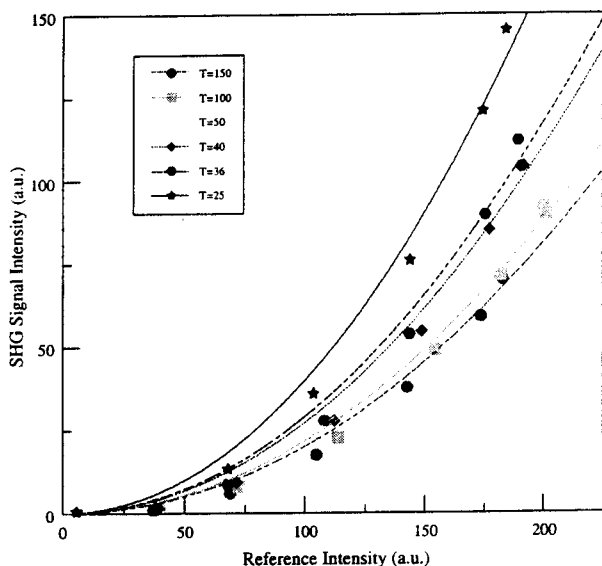


Figure 9. SHG intensity as ISAM film is cooled from 150° C to room temperature. SHG intensity *increases*.

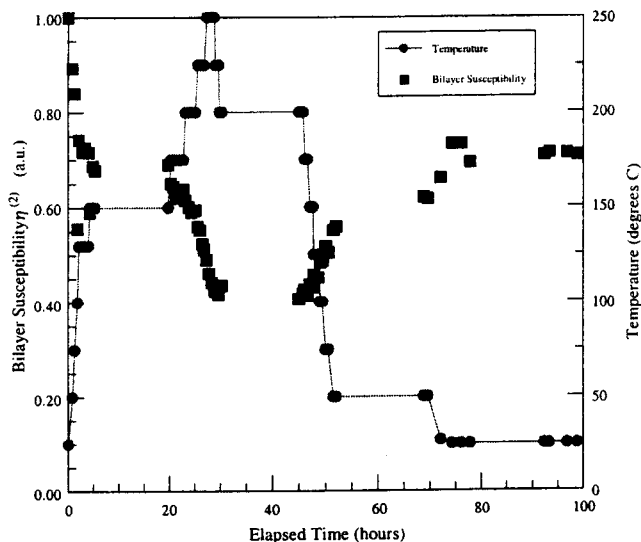


Figure 10. Bilayer susceptibility and temperature as a function of time for more extreme heating cycle.

As a further test of the thermal stability, a more extreme heating cycle was also run. This heating cycle, shown as the solid line in Figure 10, included fifteen hours at 150° C, one hour at 250° C, and fifteen hours at 200° C. The bilayer susceptibility $\eta^{(2)}$ (we use $\eta^{(2)}$ here rather than $\chi^{(2)}$ because it is not known whether the film thickness varies with temperature) followed a similar trend to that observed in the 150° C heating cycle described above. $\eta^{(2)}$ decreased as the temperature was raised, remained fairly stable at constant temperature, and increased as the temperature was lowered. However, in this more extreme example, the value of $\eta^{(2)}$ does not fully recover to that prior to the cycle. In this case, the final value of $\eta^{(2)}$ (or $\chi^{(2)}$) is 30% lower than the initial value. Figure 11 shows the optical absorption spectrum of this ISAM film prior to and following this heating cycle. As seen in the figure, the decrease in $\eta^{(2)}$ is accompanied by a 23% decrease in the optical absorption of the NLO chromophore. Thus, nearly all of the decrease in $\eta^{(2)}$ can be attributed to decomposition of the chromophore rather than a loss of chromophore orientation. This is not particularly surprising since azo chromophores do not typically have high thermal stabilities. Our results suggest that ISAM films containing NLO chromophores with high decomposition temperatures could exhibit highly stable $\chi^{(2)}$ values for temperature excursions upwards of 250° C, even when the T_g of the film is significantly lower. The ability of ISAM films to maintain chromophore alignment well above T_g is a result of the internal ionic bonds, which maintain a continuous force towards chromophore alignment.

4. SUMMARY

Ionically self-assembled monolayers offer an attractive approach for the fabrication of organic thin films for second-order nonlinear optical applications. Because the polar chromophore orientation is a direct result of the self-assembly process, ISAM films exhibit excellent temporal and thermal

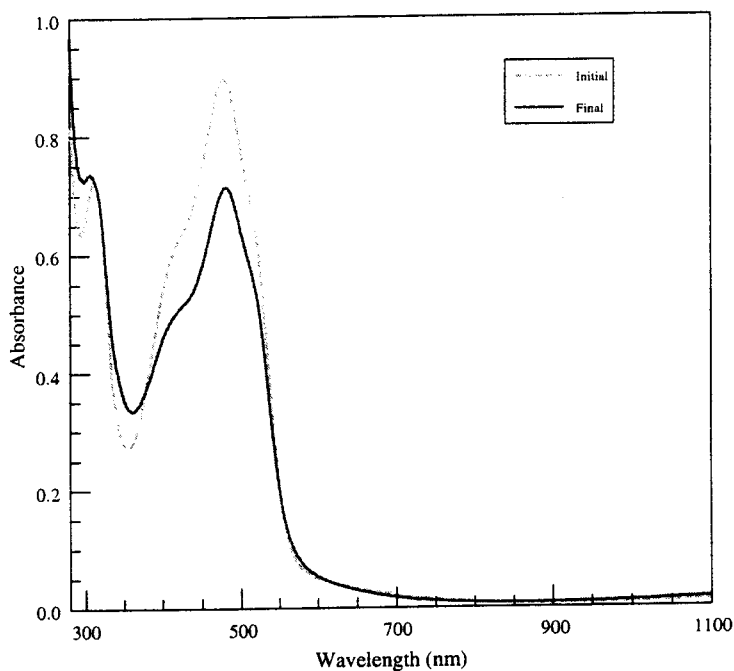


Figure 11. Absorbance spectra of Poly-S-119/PAH ISAM film before and after heating cycle including excursion to 250° C. Decrease in absorbance corresponds to thermal decomposition of Poly S-119 azo chromophore.

stability. In this paper, we have discussed the role of polymer conformation, as determined by pH and salt concentration, on the film thickness and the NLO susceptibility. While the film thickness is substantially increased with increased ionic strength, the $\chi^{(2)}$ value exhibits a corresponding decrease. The NLO response is determined primarily by chromophores at the layer interfaces. Chromophores located within the bulk of a layer possess a much lower degree of preferential orientation. An understanding of the structure of ISAM NLO films provides opportunities for the design of architectures with enhanced $\chi^{(2)}$ values, which is the essential next step in the development of ISAM films for electro-optic device applications. We have also described studies of the thermal stability of ISAM NLO films. These films exhibit no decay of the $\chi^{(2)}$ value after three years at room temperature and twenty hours at 150° C, which is above the glass transition temperature of the film.

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