

Efficient, Thermally Stable, Second Order Nonlinear Optical Response in Organic Hybrid Covalent/Ionic Self-Assembled Films

James R. Heflin,[†] Matthew T. Guzy,[‡] Patrick J. Neyman,[†] Kylie J. Gaskins,[‡] Charles Brands,[†] Zhiyong Wang,[†] Harry W. Gibson,[§] Richey M. Davis,[‡] and Kevin E. Van Cott^{*,‡,||}

Department of Physics, Virginia Tech, Blacksburg, Virginia 24061,
Department of Chemical Engineering, Virginia Tech, Blacksburg, Virginia 24061, and
Department of Chemistry, Virginia Tech, Blacksburg, Virginia 24061

Received January 31, 2006. In Final Form: April 27, 2006

A covalent/electrostatic layer-by-layer self-assembly method was used to achieve polar ordering of a water soluble, reactive dye in the fabrication of nonlinear optical (NLO) films. We observed a quadratic relationship between the second harmonic intensity $I^{2\omega}$ and bilayer number for all films made with Procion Brown MX-GRN, demonstrating that the polar ordering of the chromophores is consistent in each successive bilayer. As the ionic strength of the dye deposition solution was increased to 0.5 M NaCl, the $\chi_{zzz}^{(2)}$ of the films increased by approximately 250% to 50×10^{-9} esu, with a corresponding average chromophore tilt angle of 38° . This was attributed to increased shielding of the dye charges which led to higher chromophore density in the bilayers. The electrooptic coefficient for films of 50 bilayers fabricated at 0.5 M NaCl was 14 ± 2 pm/V. Importantly, these films exhibited excellent thermal stability, with only a 10% decrease in $(I^{2\omega})^{1/2}$ after 36 h at 85°C and then 24 h at 150°C . Furthermore, the $(I^{2\omega})^{1/2}$ recovered completely upon cooling to room temperature. These results with a commodity textile dye point to the potential value of this class of reactive chromophores and this self-assembly method for fabrication of electrooptic materials at ambient conditions from aqueous solutions.

Introduction

The development of organic second-order nonlinear optical (NLO) materials for electrooptic modulation devices is driven by performance benefits vs their inorganic counterparts, such as higher bandwidth, lower driving voltage, more flexible device design, and potentially lower processing cost.¹ Organic NLO materials with high second-order nonlinear susceptibility, $\chi^{(2)}$, require a noncentrosymmetric ordering of polarizable chromophoric molecules. Crystalline lithium niobate (LiNbO_3), which has a $\chi^{(2)}$ of 200×10^{-9} esu and an electrooptic coefficient r_{33} of 32 pm/V,² is often the comparative standard for work in this field. A number of organic chromophore designs and self-assembly strategies have been used to obtain noncentrosymmetric ordering in thin films and waveguides. However, limitations in the NLO performance, the temporal and thermal stability, or the ease of fabrication have limited the development of organic NLO materials into devices.

Guest/host poled polymeric materials with excellent NLO performance have been produced.³ Tradeoffs between NLO performance and the thermal and temporal stability have limited the practical application of these materials thus far, but new NLO polymers and poling conditions are being developed to overcome these limitations.⁴ In an effort to eliminate the need

for poling during the fabrication process and to obtain highly ordered films with chromophores at high densities, several groups have reported strategies based on layer-by-layer self-assembly methods. Heflin et al. showed that layer-by-layer self-assembled films of polyelectrolytes produced in aqueous systems at ambient conditions could exhibit polar order and $\chi^{(2)}$ throughout the bulk of the film.⁵ Although these films had exceptional thermal and temporal stability and were inexpensive to fabricate, the NLO performance was limited by a relatively low degree of noncentrosymmetry that is inherent to the use of these polymers. To obtain higher polar ordering of chromophores in layer-by-layer films, self-assembly methods employing monomeric chromophores deposited by covalent bonds and/or chemisorption have been developed. Recently, Marks et al.^{6–8} have used siloxane-based chemistries and vapor-phase hydrogen bonded assembly to obtain high performance NLO films using film processing conditions that employ dry organic solvents or vacuum oven conditions. To make highly ordered films in aqueous solutions at ambient conditions, we developed a covalent/electrostatic self-assembly method using dyes originally developed for the textile industry.⁹ Polar ordering of Procion Red MX-5B (Figure 1A) was achieved by alternating the mechanism of adsorption between covalent reaction and electrostatic attraction between the reactive dye and a polyelectrolyte layer. Although

* To whom correspondence should be addressed. E-mail: kvancott2@unl.edu.

[†] Department of Physics.

[‡] Department of Chemical Engineering.

[§] Department of Chemistry.

^{||} Current address: Department of Chemical and Biomolecular Engineering, University of Nebraska-Lincoln, Lincoln, Nebraska 68588.

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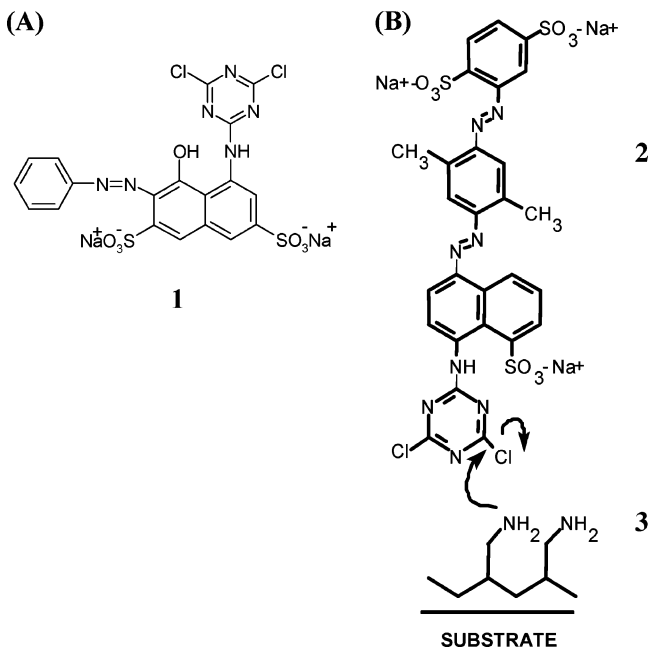


Figure 1. (A) Procion Red MX-5B (1). (B) Covalent deposition of Procion Brown MX-GRN (2) onto an adsorbed layer of poly(allylamine hydrochloride) (3).

this general approach is quite promising, the value of $\chi_{\text{eff}}^{(2)}$ obtained with this system, 11×10^{-9} esu, is well below that of lithium niobate. However, the potential for further improvements in NLO performance using this strategy was clearly evident, since the molecular structure of Procion Red MX-5B is not optimal for NLO.

Improvements in the NLO performance of organic films can be guided by the design equation¹⁰

$$\chi_{\text{zzz}}^{(2)} = NF\beta\langle\cos^3\psi\rangle \quad (1)$$

in which N is the number density of chromophore molecules in the film, F accounts for local field effects, β is the hyperpolarizability of the chromophore, ψ is the tilt angle of the chromophore's dipole moment relative to the surface normal, and the subscript zzz denotes all fields polarized along the polar axis of the material. NLO chromophores with a high β have a strong "push-pull" structure: (electron donor)–(π -electron bridge)–(electron acceptor).³ In our covalent/electrostatic self-assembly method, the conditions of chromophore deposition can affect $\chi_{\text{zzz}}^{(2)}$ through both the amount deposited (N) and the molecular orientation $\langle\psi\rangle$. Since the water-soluble reactive dyes we have used possess strongly acidic moieties, the ionic strength of the solution can affect intermolecular interactions: at high ionic strengths, charge shielding will reduce electrostatic repulsion between dye molecules and facilitate closer packing within the film. A dye that is more linearly anisotropic in structure, such as Procion Brown MX-GRN (2, Figure 1B), may pack more closely on the surface and achieve greater polar ordering than Procion Red MX-5B (1). Furthermore, the β value of Procion Brown MX-GRN has been measured to be 300×10^{-30} esu by hyper-Rayleigh scattering¹¹ and is significantly higher than is expected for Procion Red MX-5B. Thus, we investigated (1) the general applicability of the covalent/electrostatic assembly method for reactive dyes with higher β , (2) how ionic strength affects

the density and molecular orientation of the chromophores, and (3) the temporal and thermal stability of these films. The results of these studies are reported here. They demonstrate the general applicability of this covalent/electrostatic self-assembly method.

Experimental Section

Materials and Methods. The anionic/reactive dye used in this study was Procion Brown MX-GRN (Reactive Brown 23, Figure 1B; Pro Chemical and Dye, Somerset, MA). The NLO-inactive polycation used in this study was poly(allylamine hydrochloride) (PAH) ($M_w \sim 70$ kg/mol, GPC based on poly(ethylene glycol) standard, Aldrich). Deionized water with a specific resistivity > 17 M Ω ·cm was obtained with an ion exchange unit (Barnstead Nanopure II). Fisherfinest Premium glass microscope slides (Fisher Scientific, Pittsburgh, PA) were used as substrates for the films and were prepared using the RCA cleaning procedure.¹²

Dye Purification. Commercially available Procion dyes are not pure materials and contain salts, anti-caking agents, and buffering agents. Solid-phase extraction (SPE) with octadecylsilyl functionalized silica (Alltech High Capacity 75 mL C18 column; Alltech, Deerfield, IL) was used to desalt Procion Brown MX-GRN prior to film fabrication. The dye was dissolved in aqueous 50 mM ammonium acetate at 5–10 mg/mL and filtered with a 0.45 μm filter to remove particulates. The SPE columns were washed with 3 volumes of HPLC grade methanol (Burdick & Jackson), equilibrated with aqueous 50 mM ammonium acetate, and then the filtered dye solutions were applied to the columns. The columns were washed with > 5 volumes of 50 mM ammonium acetate and drained to dryness. The dye was then eluted with HPLC-grade methanol. The methanol and residual ammonium acetate were removed by lyophilization in a Savant SpeedVac system.

Film Deposition. PAH solutions at a concentration of 10 mM on a repeat unit (RU) basis were used in all experiments and the solution pH was held at 7.0. The pH was measured with an Orion SA 720 pH meter. The dye was dissolved in deionized water at a concentration of 5 mg/mL, and the solution pH was held at 10.5. The pH was adjusted using HCl or NaOH as needed and was checked over the course of the deposition process; variations in excess of 0.1 pH units were uncommon. NaCl was used in all cases as the salt for varying the ionic strength of the chromophore solutions. The glass slide immersion time in PAH was 5 min, with the exception of the first layer, which was 10 min. The immersion time for Procion Brown was 5 min. Between immersions, the substrates were vigorously agitated and rinsed with deionized water. Slides were dried using N_2 gas every 10 dips (which gives 5 bilayers on each side of the slide). For any given set of solution conditions, two series of 5 slides were made with a total (both sides) of 2, 10, 20, 40, and 60 bilayers.

Film Characterization. Absorbance measurements at 460 nm, λ_{max} of the films, were taken every 10 bilayers during the deposition process. Upon the completion of dipping for a given slide, 5 absorbance measurements were made along the length of the slide to characterize the homogeneity in the final absorbance value. Point-to-point variations were typically $< 5\%$. Bilayer numbers reported for absorbance measurements account for the film on both sides of the substrate. Film thicknesses were measured using a variable angle spectroscopic ellipsometer (J. A. Woolam Ellipsometer VB-200, with WVASE32 software version 3.361). Details of the ellipsometry procedure are found in the Supporting Information.

Second harmonic generation (SHG) was used to determine the $\chi_{\text{zzz}}^{(2)}$ of the films with the 1064 nm fundamental wavelength of a Q-switched Nd:YAG laser used as the incident light. Since films were deposited on both sides of the substrate, interference of the SHG from the front and rear films was observed as the incident angle is increased. Data for 20, 40, and 60 bilayer (both sides) PAH/Procion Brown films at 0.5 M NaCl are shown in Figure 2. The minima are zero in all cases, demonstrating the homogeneity and equivalence of the front and rear films. The $\chi^{(2)}$ values were

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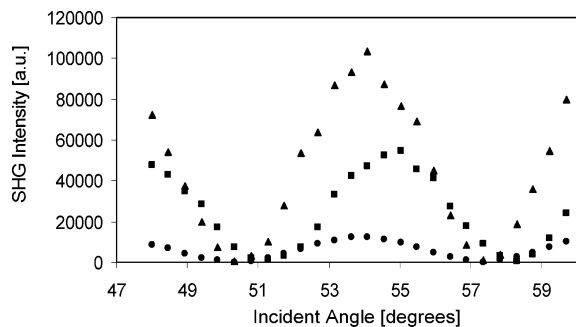


Figure 2. Second harmonic intensity as a function of incident angle for Procion Brown/PAH films consisting of 20 (●), 40 (■), and 60 (▲) bilayers made at [NaCl] = 0.5 M. The shifts in angular position of the peaks is due to differences in substrate thickness.

determined from the maxima of the SHG fringes in comparison to those generated from a quartz wedge. For film thickness much less than the coherence length [$l_c = \lambda/4(n^2\omega - n^{\omega})$, where n is the refractive index], the SHG is expected to have a quadratic dependence on the film thickness.⁵ In this work, all films were less than 100 nm thick, whereas l_c is typically on the order of microns.

The dependence of the second-harmonic intensity $I^{2\omega}$ on film thickness l and an effective $\chi_{\text{eff}}^{(2)}$ is given by⁵

$$(I^{2\omega})^{1/2} \propto l\chi_{\text{eff}}^{(2)} \quad (2)$$

For p-polarized light at a given incident angle θ , $\chi_{\text{eff}}^{(2)}$ is related to the $\chi^{(2)}$ tensor components $\chi_{zxx}^{(2)}$ and $\chi_{zzz}^{(2)}$ by

$$\chi_{\text{eff}}^{(2)} = 3\chi_{zxx}^{(2)} \sin \theta \cos^2 \theta + \chi_{zzz}^{(2)} \sin^3 \theta \quad (3)$$

The ratio of the $\chi^{(2)}$ tensor components as well as the average chromophore tilt angle ψ were determined from the ratio of the p-polarized SHG intensity generated from p-polarized incident fundamental light to that from s-polarized fundamental according to

$$\frac{I_{2\omega}^{\text{p-p}}}{I_{2\omega}^{\text{s-p}}} = \sin^4 \theta \left(\frac{\chi_{zzz}^{(2)}}{\chi_{zxx}^{(2)}} + 3 \cot^2 \theta \right)^2 \quad (4)$$

and

$$\frac{\chi_{zzz}^{(2)}}{\chi_{zxx}^{(2)}} = 2 \cot^2 \psi \quad (5)$$

Thus, $\chi_{\text{eff}}^{(2)}$ is determined from the slope of $(I^{2\omega})^{1/2}$ versus film thickness and $\chi_{zxx}^{(2)}$ is then obtained using eqs 3–5.

The electrooptic coefficient component (r_{33}) for Procion Brown/PAH films was measured using the procedure of Teng and Man¹³ as modified by Han and Wu.¹⁴ In this experiment, modulation of the polarization of light propagating through the film in response to an oscillatory (1 kHz) electric field is measured. Procion Brown/PAH films were deposited on indium tin oxide (ITO)-coated glass substrates, followed by evaporation of an Al top electrode.

Thermal Stability Measurements. An apparatus was constructed to heat the NLO films and allow for in situ measurement of the second harmonic generation. The microscope slide was placed in a grooved section of a heating block, which had a hole for beam propagation. The slide was sandwiched between two plates, and the assembly was placed on ceramic spacers in an aluminum housing. The temperature was monitored by two 4-in.-long, cylindrical thermal resistive device probes to monitor the temperature of the heating plates within 5 mm on either side of the beam propagation hole. The

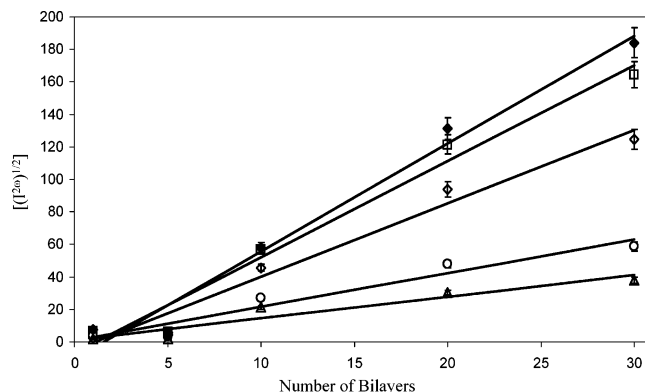


Figure 3. Square root of the second harmonic intensity $[(I^{2\omega})^{1/2}]$ as a function of the number of bilayers deposited for various NaCl concentrations: ◆ = 1.0 M; □ = 0.5 M; ◇ = 0.25 M; ○ = 0.1 M; △ = no added NaCl.

temperature was controlled via an Omega i-Series device and the output sent to a PC via RS-232 communications.

Results and Discussion

A series of films was made by covalently depositing Procion Brown MX-GRN onto the preceding PAH layer at pH 10.5 at concentrations of added NaCl ranging from 0 to 1.0 M. At pH 10.5, the dichlorotriazine moiety reacts readily with the amino moieties of the previously deposited PAH at the film surface at room temperature (Figure 1B). In situ monitoring of the SHG showed that covalent deposition in unstirred solutions was essentially complete within 2 min.¹⁵ After rinsing excess dye from the substrate/film, a PAH layer was then electrostatically deposited at pH 7. We have found that a thorough rinsing step between each monolayer deposition is crucial in obtaining films that are homogeneous. A key feature of this hybrid covalent/electrostatic deposition procedure is that Procion Brown is deposited at a pH above the PAH pK_a value of ~ 9 to ensure covalent reaction to the unprotonated amine groups,¹⁶ whereas the PAH is deposited at a pH below its pK_a , allowing electrostatic interaction with the previous layer's Procion Brown sulfonate moieties. Thus, Procion Brown is preferentially deposited with the dichlorotriazine end directed toward the substrate and the sulfonate end directed away from it (Figure 1B), resulting in a high degree of polar order. For all films, linear growth of the absorbance as a function of the number of bilayers demonstrated uniform layer-by-layer growth, and the resulting films having 30 bilayers on each side of the glass slide were optically homogeneous.

A linear relationship between the square root of the second harmonic intensity $(I^{2\omega})^{1/2}$ and bilayer number signifies that the polar ordering of the chromophores is consistent in each successive bilayer, as shown in Figure 3. The effects of ionic strength on the chromophore density and polar ordering are summarized in Table 1. The $\chi_{zzz}^{(2)}$ for Procion Brown films made with no added NaCl was 20×10^{-9} esu, and the average tilt angle of the Procion Brown chromophores with respect to the surface normal was 43° . As the ionic strength of the Procion Brown deposition solution was increased to 0.5 M NaCl, the $\chi_{zzz}^{(2)}$ increased by approximately 250% to 50×10^{-9} esu. This increase in $\chi_{zzz}^{(2)}$ was concomitant with a decrease in the average chromophore tilt

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Table 1. Procion Brown MX-GRN Film Properties as a Function of NaCl Concentration in the Deposition Solutions

[NaCl] (M)	bilayer thickness (nm)	absorbance/bilayer ($\times 10^{-3}$) ^a	absorbance/nm ($\times 10^{-3}$) ^b	$\langle\psi\rangle$ (degrees)	$\chi_{zzz}^{(2)}$ (10^{-9} esu)
0	0.27 \pm 0.01	1.0 ($R^2 = 0.94$)	3.7	43 \pm 2	20 \pm 2
0.10	0.32 \pm 0.01	1.4 ($R^2 = 0.97$)	4.4	41 \pm 2	28 \pm 2
0.25	0.42 \pm 0.02	2.2 ($R^2 = 0.99$)	5.2	39 \pm 2	49 \pm 2
0.50	0.57 \pm 0.03	2.9 ($R^2 = 0.99$)	5.1	38 \pm 2	50 \pm 2
1.00	0.71 \pm 0.03	4.0 ($R^2 = 0.99$)	5.6	39 \pm 2	42 \pm 2

^a Calculated from slopes determined from linear regression of absorbance vs bilayer number data; R^2 values for each are reported. ^b Calculated from (abs/bilayer)/(bilayer thickness)

angle to 38° with respect to the surface normal. As a comparison, Procion Red MX-5B/PAH films made with no added NaCl had a chromophore tilt angle of 70° such that $\chi_{zzz}^{(2)}$ was only 2×10^{-9} esu despite a $\chi_{\text{eff}}^{(2)}$ of 11×10^{-9} esu.¹⁵

We interpret the data as showing that as the ionic strength of the Procion Brown solution is increased, charge shielding of the sulfonate moieties enables the chromophores to pack closer together on the PAH monolayers, as shown by the increase in the absorbance/bilayer (Table 1). At low packing densities, i.e., at low ionic strengths, the chromophores are more free to interact with the underlying PAH monolayer via electrostatic, hydrogen bonding, and van der Waals interactions, resulting in less polar ordering. With a higher chromophore packing density, there are more sulfonate groups for the next PAH monolayer, and more PAH is also deposited. The combination of higher chromophore and polyelectrolyte deposition per bilayer leads to greater bilayer thickness.

Finally, it is interesting to compare the measured tilt angles in the range 38–43° with the “magic angle” of 39.2° for second-order nonlinear optical processes observed by Simpson and Rowlen.^{17,18} This is not to be confused with the magic angle of chromophore orientation in absorption measurements (54.7°), which is obtained for a random distribution of chromophore orientation. The magic angle in second-order nonlinear optics refers not to a random chromophore distribution (for which $\chi^{(2)}$ is identically zero), but a broad distribution of chromophore orientation angles about the average angle. An SHG orientation measurement yielding a value near the magic angle cannot distinguish between a sharp distribution centered at 39.2° or a broad distribution of orientation angles centered at any angle between 0 and 90°. Although the data are analyzed here within the usual assumption of a narrow tilt angle distribution, we cannot rule out the possibility of a broad distribution in these self-assembled films. However, if the films in the present work had a truly random chromophore orientation, then the measured values of $\chi_{\text{eff}}^{(2)}$ and the electrooptic coefficient (r_{33} , discussed below) would have been zero. The data presented here clearly demonstrate that bulk polar order exists in the films. The existence of a broad tilt angle distribution would not mitigate the large nonlinear optical responses that have been observed in these films.

Films of 50 bilayers made by covalent deposition of Procion Brown with 0.5 M NaCl had an average $r_{33} = 14 \pm 2$ pm/V, whereas films made with no added salt had an average value of $r_{33} = 4.1 \pm 0.3$ pm/V. These values are consistent with the trends noted above for $\chi_{zzz}^{(2)}$ and support the view that increased charge shielding leads to higher chromophore density. Moreover, the value of r_{33} showed no change after the films were soaked in deionized water for 24 h, indicating that the fabrication process left a negligible amount of free salt ions in the films. For comparison, recently reported poled polymer films have reported $r_{33} = 33$ –111 pm/V.⁴ Recent covalent, self-assembled films using an X-shaped chromophore exhibited $r_{33} = 43$ pm/V.⁶

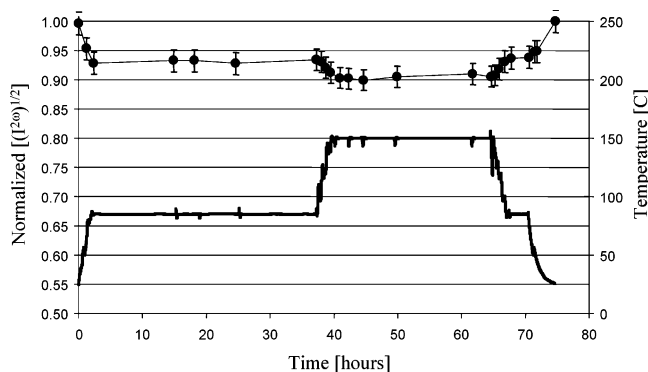


Figure 4. Square root of the SHG intensity (left axis, ●, normalized to 1.0 at the beginning of the experiment) of a Procion Brown/PAH film as a function of time and temperature (right axis, —) during a heating cycle.

Another promising technique, vapor phase deposition of chromophores that are self-assembled by hydrogen bonding, showed $r_{33} = 12$ pm/V.⁸ We note that these reported studies used chromophores that were specifically synthesized as NLO materials. The results that we have obtained with a common commodity textile dye, Procion Brown MX-GRN, are therefore encouraging, and point to the potential utility of this class of reactive dyes and the covalent/electrostatic self-assembly method as an alternative for facile fabrication of electrooptic materials under ambient conditions.

Temporal and thermal stability of electrooptic materials are required for device applications. As discussed above, the stability of poled polymeric NLO materials has been an issue that has limited their development. However, the novel Diels–Alder lattice-hardening process of Haller et al.^{4a} resulted in poled films that retained 80% of their r_{33} values after heating at 85 °C for 500 h. The hydrogen bonded films reported by Facchetti et al. exhibited a stable SHG intensity over more than 300 days when stored at room temperature in a nitrogen atmosphere.⁸ We have found no measurable decay of $\chi^{(2)}$ in Procion Brown/PAH films stored at ambient conditions over a period of more than 420 days. Moreover, the films made with 0.5 M NaCl also have exceptional stability at elevated temperatures (Figure 4). Using an apparatus that allowed in situ measurement of the SHG intensity, we found that, after 36 h at 85 °C, $(I^{2\omega})^{1/2}$ was reduced by 7%. Then the sample was kept at 150 °C for 24 h, and an additional 3% decrease in the $(I^{2\omega})^{1/2}$ was measured, for an overall 10% loss in $(I^{2\omega})^{1/2}$ for the entire process. Upon cooling to room temperature, $(I^{2\omega})^{1/2}$ returned to its initial value over a period of several hours, indicating complete recovery of polar ordering of the chromophores in the film. This small decrease in SHG intensity and complete recovery of polar ordering in these films is similar to observations for layer-by-layer films made with the NLO-active polymeric dye Poly S-119,¹⁹ which have exhibited no measurable decay of $\chi^{(2)}$ over a period of more than six years

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at room temperature. For these Poly S-119 films, as the temperature was increased to 150 °C over 3 h, a 20% decrease in $(I^{2\omega})^{1/2}$ was measured, with no further decay in SHG at 150 °C for 18 h. Like the Procion Brown films in this work, the SHG signals of the Poly S-119 films returned to their initial values upon cooling, demonstrating complete recovery of polar order. This similar behavior of these films made by two different self-assembly processes is not surprising given that the final structures of the films, an organic dye covalently bound to a polymeric backbone with monolayers and bilayers held together by electrostatic interaction, are very similar.

The origin of the small but reversible decrease in SHG intensity upon heating and then cooling the Procion Brown films may be due to thermally driven trans-to-cis isomerization of the two azo bonds in Procion Brown. Isomerization of azo chromophores from their stable trans configuration to the less stable cis form is a well-known phenomenon in multilayer polymeric films^{20–22} and is generally accompanied by a decrease in the chromophore absorbance in the visible and an increase in the UV peak. We have observed a decrease in the visible absorbance at elevated temperature that reversed upon cooling in films made with both Procion Brown and the polyanion poly{1-[4'-(3''-carboxy-4''-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt} (PCBS). A decrease of SHG upon heating could in principle also result from a loss of chromophore orientation due to reaching the glass transition temperature (T_g) of the film (α), or from sub- T_g transitions, commonly denoted as β , γ , and δ transitions.²³ Sub- T_g transitions occur due to hindered rotations of pendent groups and to small-scale backbone motions in polymers. The films in the present work and the earlier layer-by-layer polyelectrolyte films are held together largely by ionic bonds that, for dry films, result in glassy solids with glass transition temperatures well above room temperature. Although there are no published reports on thermal transitions in electrostatic layer-by-layer films and we have not determined these for the films made in the present study, they may be similar to those reported for single-component polyelectrolyte solids. For poly-(diallyldimethylammonium chloride) with a molecular weight of ~200–350 kg/mole, no T_g was observed up to its decomposition temperature of 220 °C, whereas a sub- T_g transition observed at ~130 °C was attributed to a β transition involving the rotation of the five-membered ring about the backbone.²⁴ However, if thermal transitions were responsible for the loss of SHG, there

is no reason chromophore orientation, and hence SHG, should completely recover upon cooling to room temperature. We also note that measurements of the tilt angle according to eq 4 do not yield a discernible variation as a function of temperature, as would be the case should the decrease in the SHG signal at elevated temperature be due to a reduction in the average tilt angle. Thus, we conclude that the trans-to-cis isomerization is the most likely explanation; this possibility is currently being investigated.

Conclusions

In summary, the covalent/electrostatic layer-by-layer self-assembly method is generally applicable for fabricating NLO films at ambient conditions using water soluble, polar, reactive dyes and PAH as the polyelectrolyte/nucleophilic species. The molecular structure of the dye and the film deposition conditions can significantly impact the polar ordering in the film. Increasing the ionic strength of the Procion Brown MX-GRN deposition solution significantly increased the amount of dye deposited, the bilayer thickness, the polar ordering of the chromophore, and the resultant $\chi_{zzz}^{(2)}$. The electrooptic coefficient for the best Procion Brown/PAH films was 14 pm/V, which is ~50% of the value for lithium niobate. The films made under ambient processing conditions have shown excellent temporal stability: no measurable decrease in $\chi_{zzz}^{(2)}$ under ambient conditions for more than 1 year. Additionally, these Procion Brown films exhibited excellent thermal stability, with only a reversible 10% decrease in $(I^{2\omega})^{1/2}$ after 36 h at 85 °C and then 24 h at 150 °C. In contrast to poled polymer materials, the SHG intensity recovered completely upon cooling to room temperature. These results were obtained with a commercially available textile dye that was not designed for NLO applications. Therefore, we view these results as being very promising and indicating that use of dyes specifically designed for NLO properties and compatible with this self-assembly method will lead to films that exceed the NLO performance of lithium niobate. We are presently pursuing this goal.

Acknowledgment. This work was supported by the National Science Foundation through Grant #ECS-9907747. The authors acknowledge the technical assistance of Jason Gaudet.

Supporting Information Available: Experimental details of film characterization by ellipsometry. This material is available free of charge via the Internet at <http://pubs.acs.org>.

LA0602970

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