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Citation: [Applied Physics Letters](#) **74**, 495 (1999); doi: 10.1063/1.123166

View online: <http://dx.doi.org/10.1063/1.123166>

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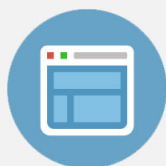
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Thickness dependence of second-harmonic generation in thin films fabricated from ionically self-assembled monolayers

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(Received 29 June 1998; accepted for publication 17 November 1998)

An ionically self-assembled monolayer (ISAM) technique for thin-film deposition has been employed to fabricate materials possessing the noncentrosymmetry that is requisite for a second-order, $\chi^{(2)}$, nonlinear optical response. As a result of the ionic attraction between successive layers, the ISAM $\chi^{(2)}$ films self-assemble into a noncentrosymmetric structure that has exhibited no measurable decay of $\chi^{(2)}$ at room temperature over a period of more than one year. The second-harmonic intensity of the films exhibits the expected quadratic dependence on film thickness up to at least 100 bilayers, corresponding to a film thickness of 120 nm. The polarization dependence of the second-harmonic generation yields a value of 35° for the average tilt angle of the nonlinear optical chromophores away from the surface normal. © 1999 American Institute of Physics. [S0003-6951(99)02904-6]

In order to possess nonzero even-order nonlinear optical susceptibilities, a material must lack a center of inversion at the macroscopic level. As a result of the multitude of potential frequency conversion, optical modulation, and optical switching applications that stem from the $\chi^{(2)}$ second-order susceptibility, several novel methods for creating noncentrosymmetric materials incorporating organic molecules with large β molecular susceptibilities have been developed over the past decade. These include electric-field poled polymers,¹⁻³ Langmuir-Blodgett films,⁴⁻⁶ and covalent self-assembled monolayer structures.⁷⁻⁹ We report here detailed studies of a ionically self-assembled monolayer technique for the creation of noncentrosymmetric organic thin films with substantial $\chi^{(2)}$ values. The advantages of this technique include simple, rapid, inexpensive production, and long-term stability of the induced $\chi^{(2)}$ without the need for additional processing such as electric-field poling or chemical reactions.

Ionically self-assembled monolayer (ISAM) films are a recently developed,¹⁰⁻¹⁸ revolutionary class of materials that allows detailed structural and thickness control at the molecular level combined with ease of manufacturing and low cost. The ISAM method involves the alternate dipping of a charged substrate into an aqueous solution of a cation followed by dipping in an aqueous solution of an anion at room temperature. Using commercial ionic polymer dyes, the ISAM technique has been used to produce a noncentrosymmetric arrangement of nonlinear optical (NLO) chromophores to yield thin films with $\chi^{(2)}$ values comparable to that of quartz. Importantly, the second-harmonic intensity generated by the films exhibits the expected quadratic dependence on film thickness for films as thick as 100 bilayers. This demonstrates that the noncentrosymmetry induced by

the ionic deposition technique is uniformly maintained in each successive bilayer.

The ISAM technique for the deposition of polyelectrolytes was recently demonstrated by Decher and co-workers.¹⁰⁻¹² The films are grown monolayer by monolayer by first immersing an initially charged substrate into an aqueous solution containing an oppositely charged polyelectrolyte. This is followed by rinsing and then by immersion of the substrate into a second polyelectrolyte that is of opposite charge to the first. The dipping process can, in principle, be repeated as many times as desired until a film with the chosen number of bilayers has been produced. For the present study, ISAM films were deposited on glass microscope slide substrates. Noncentrosymmetric, ISAM $\chi^{(2)}$ films were produced using two different polyanions: the polymeric dyes Poly S-119 (see the inset of Fig. 1), which consists of a poly(vinylamine) backbone with an ionic azo-dye chromophore (from Sigma), and poly{1-[4-(3-carboxy-4-

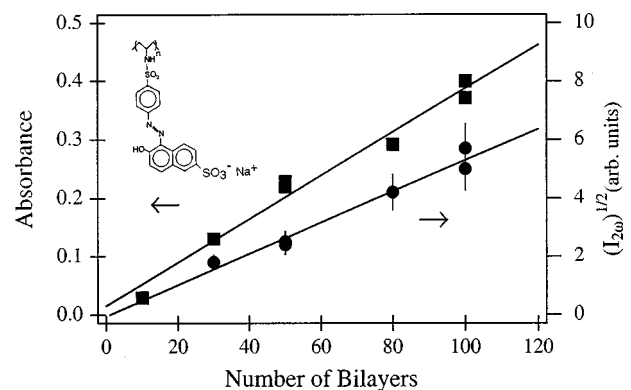


FIG. 1. Absorbance at 500 nm (squares) and square root of second-harmonic intensity, $(I_{2\omega})^{1/2}$, (circles) as a function of the number of Poly S-119/PAH bilayers. The structure of Poly S-119 is shown in the inset.

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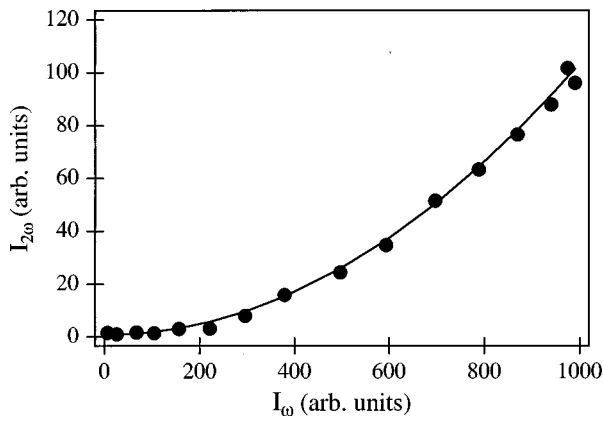


FIG. 2. Dependence of the second-harmonic intensity at 600 nm on the fundamental intensity at 1200 nm for a single-sided 68 bilayer Poly S-119/PAH ISAM film. The best fit yields a power-law dependence with an exponent of 2.02.

hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt} (PCBS, from Aldrich). While either Poly S-119 or PCBS served as the polyanion for the ISAM fabrication, poly(allylamine hydrochloride) (PAH), which has no $\chi^{(2)}$ response, was used for the polycation. The formation of each monolayer is exceptionally rapid with these polymers. Through measurements of absorbance and of film thickness (by ellipsometry) as a function of immersion time, each monolayer is found to be fully deposited in less than 20 s of immersion in the polyelectrolyte. This allows the rapid buildup of self-assembled, multilayer films. This letter focuses on measurements in Poly S-119/PAH films. Similar results have been obtained in PCBS/PAH ISAM films.

The absorption of ISAM films made with Poly S-119/PAH peaks near 480 nm and is transparent for wavelengths greater than 590 nm. In Fig. 1, the absorbance at 500 nm of several films is plotted versus the number of deposited bilayers. The linear growth of absorbance with the number of deposited layers illustrates the homogeneous deposition of the polymer dye with each successive layer. By ellipsometry, each bilayer is found to have a thickness of 1.2 nm.

The second-harmonic generation (SHG) experiments were carried out using both the 1064 nm fundamental wavelength of a Q-switched Nd:YAG laser and the 1200 nm output from a broadband, BBO optical parametric oscillator (OPO). The OPO is pumped by the 355 nm third harmonic of the Nd:YAG and is continuously tunable from 400 to 2500 nm. The incident intensity and polarization on the sample are controlled by a pair of Glan-Laser polarizing prisms.

Since the Poly S-119 films are strongly absorbing at 532 nm, we concentrate here on the measurements using the 1200 nm fundamental wavelength. Figure 2 illustrates the dependence of the SHG signal intensity as a function of the incident fundamental intensity for a single-sided, 68 bilayer Poly S-119 film. The film is rotated 45° away from normal incidence about the vertical axis, and the incident light is p polarized. The solid curve is a best fit to the data of the form $I_{2\omega} = A(I_\omega)^b$, where $I_{2\omega}$ and I_ω are the second-harmonic and fundamental intensities, respectively. The fit yields a value of $b = 2.02$, in excellent agreement with the expected quadratic dependence on fundamental intensity. By comparison

to Maker fringes generated using the $\chi_{xxx}^{(2)}$ (corresponding to d_{11}) coefficient of a quartz wedge, the $\chi_{zzz}^{(2)}$ value for Poly S-119/PAH is found to be 0.70 times the value of quartz, or 1.34×10^{-9} esu. Importantly, the films have exhibited no measurable decay of $\chi_{zzz}^{(2)}$ over a period of more than one year. In contrast to electric-field poled polymers, for example, the noncentrosymmetric order induced by the self-assembly process is a thermodynamically stable state.

The dependence of the second-harmonic intensity on film thickness and $\chi^{(2)}$ is given by

$$I_{2\omega} \propto (l_c \chi_{\text{eff}}^{(2)})^2 \sin^2\left(\frac{\pi l}{2l_c}\right), \quad (1)$$

where l is the sample thickness, $l_c = \lambda/[4(n^{2\omega} - n^\omega)]$ is the coherence length, and $\chi_{\text{eff}}^{(2)}$ is the effective susceptibility determined by the sample geometry and the nonzero components of the $\chi^{(2)}$ tensor. In the limit that the sample thickness is much less than the coherence length, the second-harmonic intensity is quadratic in the film thickness. The thickest film studied here consisted of 100 bilayers for a total thickness of 120 nm. Since l_c is typically of the order $10 \mu\text{m}$, the films are in the $l \ll l_c$ limit and the SHG intensity is expected to grow quadratically with the number of bilayers. In Fig. 1, $(I_{2\omega})^{1/2}$ is plotted versus the number of bilayers for several Poly S-119/PAH films. The data are seen to be in good agreement with the quadratic dependence. This demonstrates that the degree of polar orientation of the chromophores is maintained for each successive layer. If the degree of orientation was decreased for the latter deposited layers, the SHG intensity would yield a subquadratic dependence on the number of bilayers. Two observations of second-harmonic generation in films fabricated using the ISAM technique have been recently reported. Lvov *et al.*¹⁹ found that the second-harmonic intensity began to decrease after just four bilayers. Wang *et al.*²⁰ only report SHG data for a film with five bilayers and do not discuss the dependence of the second-harmonic intensity on the sample thickness. When the sample is oriented at 45° to normal incidence using p -polarized fundamental light, the second-harmonic beam is observed to be strictly p polarized, consistent with dipolar orientation perpendicular to the substrate. The dependence of the second-harmonic intensity on the polarization of the fundamental beam allows determination of the average tilt angle of the NLO chromophores away from the surface normal. For the p -polarized fundamental and p -polarized second harmonic, the effective second-order susceptibility is

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

where θ is the angle of the incident beam with respect to normal incidence and z is perpendicular to the substrate. For an s -polarized incident fundamental beam and p -polarized second harmonic, the effective susceptibility is

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

Therefore, for $\theta = 45^\circ$, the ratio of the second-harmonic intensity for the p -polarized fundamental and p -polarized second harmonic ($I_{2\omega}^{p \rightarrow p}$) to the second-harmonic intensity for the s -polarized fundamental and p -polarized second harmonic ($I_{2\omega}^{s \rightarrow p}$) is

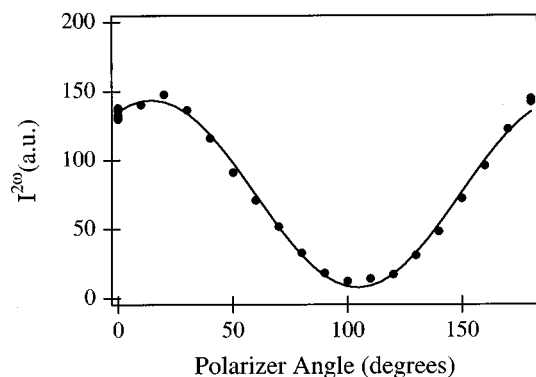


FIG. 3. p -polarized second-harmonic intensity as a function of the polarization of the incident fundamental beam. The polarization angles are labeled such that 15° corresponds to the p -polarized fundamental and 105° corresponds to the s -polarized fundamental.

$$\frac{I_{2\omega}^{p \rightarrow p}}{I_{2\omega}^{s \rightarrow p}} = \frac{1}{4} \left(3 + \frac{\chi_{zzz}^{(2)}}{\chi_{zxx}^{(2)}} \right)^2. \quad (4)$$

The observed p -polarized second-harmonic intensity as a function of the polarization angle of the incident fundamental beam is shown in Fig. 3. The fit to the data yields an intensity ratio of $I_{2\omega}^{p \rightarrow p}/I_{2\omega}^{s \rightarrow p} = 12.5 \pm 1.0$, which corresponds to a susceptibility ratio of $\chi_{zzz}^{(2)}/\chi_{zxx}^{(2)} = 4.1 \pm 0.2$. The average tilt angle $\bar{\psi}$ of the chromophores away from the substrate normal is determined by

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

thus yielding a value of $\bar{\psi} = 35.0^\circ \pm 0.7^\circ$.

The development of ISAM $\chi^{(2)}$ thin films provides significant advantages over the production of organic $\chi^{(2)}$ thin films by alternative methods. Compared to the Langmuir-Blodgett technique, ISAM has the advantages of being a much more rapid fabrication technique and producing films that possess greater chemical, thermal, and mechanical stability due to the ionic, rather than van der Waals, interactions. Moreover, the ISAM technique eliminates the standard electric-field poling process and offers longer-term stability of $\chi^{(2)}$ than electro-optic poled polymers. Furthermore, ISAM produces molecular-level uniform and ordered films with greater homogeneity than spin-coated films.

We have also recently studied the thermal stability of $\chi^{(2)}$ in ISAM films. As the temperature was raised to 150°C , $\chi^{(2)}$ was reduced by 25%. Remarkably, when the temperature was maintained at 150°C for 15 h, the second-harmonic signal remained constant. Furthermore, as the film was cooled back to room temperature, the $\chi^{(2)}$ increased and recovered fully to its initial value prior to heating. The films thus show no indication of loss of polar orientation even at 150°C , in sharp contrast to electric-field poled polymers. These results will be reported in more detail in a separate publication.

We have shown that films deposited using the technique

of ionically self-assembled monolayers can spontaneously assemble into a noncentrosymmetric structure with a substantial $\chi^{(2)}$ value. The uniform orientation of each additional bilayer is demonstrated by the quadratic dependence of the second-harmonic intensity on the number of bilayers. The dependences of the second-harmonic intensity on the fundamental and second-harmonic polarizations indicate that the preferential orientation of the dipoles is perpendicular to the substrate, which is ideal for electro-optic and frequency doubling waveguide applications. Furthermore, ISAM $\chi^{(2)}$ films require no additional processing following film deposition and have shown no decay of $\chi^{(2)}$ over a period of more than one year at room temperature. The ISAM process can be applied to a variety of material structures including polymers that possess separate ionic and NLO-active groups as well as to highly nonlinear, nonpolymeric NLO chromophores that have been chemically modified for compatibility with the ISAM deposition process.

This work was supported by the Army Research Office (DAAG55-97-1-0101), Air Force Office of Scientific Research (F49620-97-C-0047), and by a Cottrell Scholars Award of Research Corporation.

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