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6. AUTHOR(S)
W.N. Herman, M.J. Roberts, J.D. Stenger-Smith, A.P. Chafin, R.A. Hollins, G.A. Lindsay, K.J.Wynne

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PERSISTENT IN-PLANE ORDER THROUGH 90 BILAYERS IN AN ACCORDION POLYMER LB FILM

W.N. Herman

U.S. Navy, NAWC AD
EO Sensors Branch
Patuxent River, MD 20670

M.J. Roberts, J.D. Stenger-Smith, A.P. Chafin, R.A. Hollins, G.A Lindsay

U.S. Navy, NAWC WD
Chemistry and Materials Branch
China Lake, CA 93555

K.J. Wynne

U.S. Office of Naval Research,
Physical S&T Division
Arlington, VA 22217

Introduction

Processing-assisted ordering techniques that do not require electric field poling are gaining increased interest in nonlinear optical (NLO) polymer research. Langmuir Blodgett (LB) processing[1] offers advantages over electric-field poling in that it can be done at room temperature (hence the *kT* Brownian motion is much less) without the strong electric fields that can lead to film damage during corona poling. We report second harmonic generation (SHG) measurements on multiple heterolayer films of two interleaved amphiphilic accordion polymers fabricated by LB deposition. Accordion NLO polymers have the chromophores arranged in a syndioregic (head-to-head) fashion in the mainchain and are inherently more stable than sidechain polymers because both ends of the chromophore are attached to the polymer backbone. The two polymers in the alternating layers contain the same cinnamamide chromophore but differ in that the hydrophilic group (OH) and hydrophobic group (aliphatic chains) on either side of the chromophore are reversed from one polymer to the other in order to yield a net dipolar order with heterolayer Y-type deposition. In earlier work,[2,3] we reported SHG results on a similar pair of polymers, except one had a 12-C aliphatic chain and the other a 16-C chain. Alternating ABAB... type LB films of these polymers exhibited *mm2* point group symmetry at 24 bilayers, but ∞*mm* symmetry by 92 bilayers. Here we present SHG azimuthal data on 20,40, and 90 bilayer ABAB... Y-type LB films where both polymers contain 12-C aliphatic chains. We find in-plane order associated with the *mm2* point group that persists even at 90 bilayers, as well as a quadratic dependence of the generated second harmonic on the number of bilayers.

Experimental

Polymer Structures. The chemical structures of the polymers incorporating amphiphilic molecules[4] used in building up the ABAB... multilayer films are shown in Figure 1. The synthesis of these polymers will be presented elsewhere.
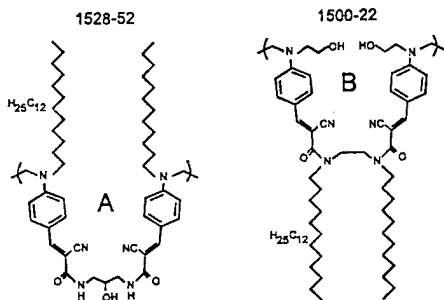

Figure 1. Polymer structures. Polymer A has a 12-carbon lipophilic group on the donor side of the cinnamamide chromophore, while polymer B has a similar lipophilic group attached to the acceptor side of the chromophore.

LB film fabrication. Heterolayer LB Films were deposited using a two-compartment circular LB trough from NIMA (Coventry, UK) that is kept in a Class 100 clean room. The films were deposited at 24 °C in air under amber lighting (blue-UV blocked) to eliminate the possibility of photo-oxidation of the polymers. Monolayers of the polymer A were spread from chloroform solutions of concentrations near 0.5 mg/mL. Polymer B spreading solutions contained about 5% pyridine as an aid for solubilization. The compressed monolayers were aged for about 5 minutes at 20 mN/m to assure densification and to assure no leakage of polymer from the compression area. Films were deposited on hydrophobic microscope slides. Polymer A was deposited at a rate of 2 mm/min on the downstroke and polymer B was deposited at 3 mm/min on the upstroke. With the deposition of each 10 bilayers, the trough was cleaned and new monolayers of the polymers were spread before the deposition of the next 10 bilayers.
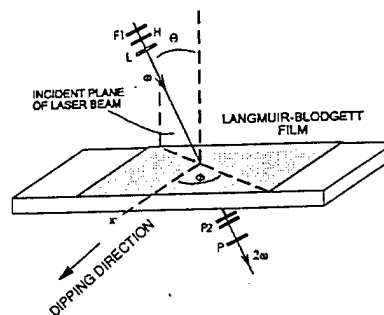

Figure 2. Configuration and reference axes for azimuthal SHG scans. F1 and F2: narrow-band filters, L: 150 mm lens; P: Glan-Thompson prism. The angle of incidence Θ of the laser beam was fixed at 45° and the azimuthal angle varied from 0 - 360° in 1-2° steps.

Second-Harmonic Generation Setup. The experimental setup for observing second-harmonic generation from these films is shown in Figure 2. The sample was positioned at the waist of a focused (150 mm lens) fundamental beam (1319 nm) produced by a diode-pumped Q-switched Nd:YAG laser. The pulse width was 14 ns and the repetition rate 1 kHz. The fundamental beam was polarized inside the laser cavity and a half-wave plate was used to control the polarization of the beam incident on the sample. The second-harmonic signal was detected by a Hamamatsu R928 photomultiplier tube in conjunction with a Stanford Research SR250 boxcar averager, which was operated using active baseline subtraction. To account for laser power fluctuations, part of the fundamental beam was split off and sent through a lithium iodate crystal to produce a reference second harmonic signal. The sample was mounted on a computer-controlled Oriel rotation stage and data were collected by computer at 1-2° increments of the azimuthal angle Φ. The angle of incidence of the laser beam was fixed at Θ = 45°.

Results and Discussion

Complete 360° SHG scans were recorded for each of six different polarization combinations of the fundamental and detected second harmonic. The s-s (s-polarized fundamental with detection of the s-polarized component of the 2nd harmonic) combination was zero and the p-s combination very small, nearly in the noise of the detection system. The results of the remaining four combinations — p-p, 45°-p, s-p, and 45°-s — are shown in Figure 3 for a 20 bilayer film. The azimuthal scans for 40 and 90 bilayer films were qualitatively similar. To establish a reference, an additional azimuthal scan at a 45° angle of incidence was made on an X-cut quartz crystal using a p-p combination. The azimuthal data was then fit using a theoretical expression[5] that included the effect of reflections of the second harmonic, which were found to be non-negligible. All the azimuthal scans in Figure 3 can be simultaneously fit using the *d*-coefficient matrix for point group *mm2*,[2]

$$\vec{d} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{31} & 0 \\ 0 & 0 & 0 & d_{32} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{bmatrix}, \quad (1)$$

in a new laboratory coordinate system obtained by a rotation of the x-axis shown in Figure 2 by an angle Ω about the normal to the film to align the new x-axis with the long dimension of the p-p ellipse. When transformed back to the original lab frame, the effective d-coefficients take the forms,

$$d_{eff}^{p-p} = t_{1p}^2 t_{2p} \left[d_{33} s_2 s_1^2 + f(\Phi)(s_1 c_1^2 + 2c_2 s_1 c_1) \right] ,$$

$$d_{eff}^{s-p} = t_{1s}^2 t_{2p} s_2 g(\Phi) \quad , \quad d_{eff}^{45-s} = t_{1p}^2 t_{2s} s_1 c_1 h(\Phi) + t_{1p} t_{1s} t_{2s} s_1 g(\Phi) , \quad (2)$$

$$d_{eff}^{45-p} = \tfrac{1}{2}(d_{eff}^{p-p} + d_{eff}^{s-p}) + t_{1p} t_{1s} t_{2s}(s_2 c_1 + c_2 s_1) h(\Phi) ,$$

where

$$g(\Phi) \equiv d_{31} \sin^2(\Phi - \Omega) + d_{32} \cos^2(\Phi - \Omega) ,$$

$$f(\Phi) \equiv d_{31} \cos^2(\Phi - \Omega) + d_{32} \sin^2(\Phi - \Omega) , \quad (3)$$

$$h(\Phi) \equiv \tfrac{1}{2}(d_{31} - d_{32}) \sin[2(\Phi - \Omega)] .$$

The t's are Fresnel transmission coefficients for (1) the fundamental and (2) second harmonic, respectively, and $s_m = \sin(\Theta_m)$, $c_m = \cos(\Theta_m)$, $m = 1,2$, where Θ_1 and Θ_2 are the angles of refraction of the fundamental and second-harmonic, respectively, in the film. It is important to note, unlike the case of a poled polymer, that $d_{32} \neq d_{31}$ in Eq.(1) and this feature is responsible for the lack of isotropy in the plane that is evident in Figure 3.

For the 20 bilayer film in Figure 3, as well as the 90 bilayer film, the long axis of the p-p oval was found to deviate by $\Omega \approx 10°$ from the dipping direction ($\Phi=0$). The 40 bilayer film, on the other hand, deviated ~18°. These deviations from the dipping direction suggest that the polymer chains are not being picked off the water vertically onto the substrate during the dipping process.
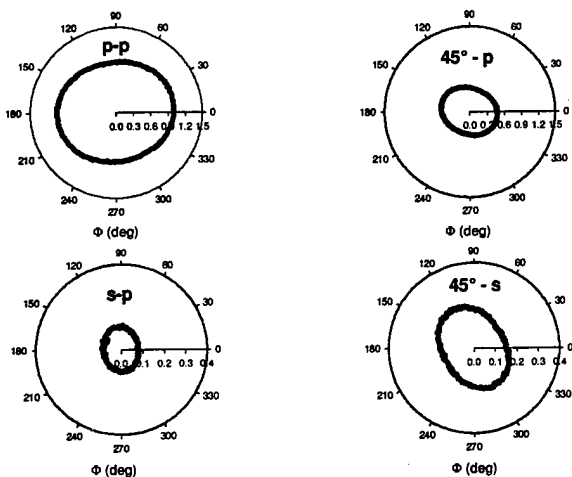
Figure 3. Azimuthal 360° SHG scans for a 20 bilayer film. The long axis of the ellipse in the p-p scan (p-polarized fundamental with detected p-polarized second harmonic) lies about 10° from the dipping direction.

The square root of the maximum SHG for the p-p (value when $\Phi=\Omega$) and s-p (value when $\Phi=\Omega+\pi/2$) cases are plotted in Figure 4. A clear quadratic dependence of SHG on the number of bilayers is evident for the p-p case, while there appears to be a slight decrease in the s-p case. From the expression for the effective d-coefficients in Eq.(2), the s-p maximum is determined by d_{31} and the p-p maximum by a combination of d_{31} and d_{33}. In Figure 4, there may be a slight decrease in d_{31} accompanied by an increase in d_{33} at 90 bilayers, although this point is within experimental error. Assuming 15Å thickness per monolayer and refractive indices of 1.61 and 1.66 at 1300nm and 650 nm, respectively, the theoretical fits give $d_{33}/d_{31} \approx 0.75$ at 20 bilayers increasing to 1.2 at 90 bilayers. On the other hand, the ratio d_{32}/d_{31}, which determines the in-plane anisotropy, was in the range 0.9 to 0.93 for all three samples. In a previously studied[3] 92 bilayer film involving mixed 12-C and 16-C lipophilic chains, the ratio d_{33}/d_{31}

had reached ~3 with $d_{32}/d_{31} \approx 1$ indicating the possibility of a smooth transition from point group $mm2$ to ∞mm .

For a chromophore with a single dominant hyperpolarizability component $\beta_{\xi\xi\xi}$ along a 1D charge transfer axes ξ, oriented at the spherical angles θ , ϕ with respect to the molecular Z-axis, the structure of d in Eq.(2) dictates[6] that the odd orientational averages depending on ϕ, such as $<\cos \phi>$, $<\sin \phi \cos^2\phi>$, etc., are zero, leaving

$$d_{33} \propto <\cos^3 \theta > \beta_{\xi\xi\xi} ,$$

$$d_{15} = d_{31} \propto <\cos \theta \sin^2 \theta > <\cos^2(\phi - \Omega)> \beta_{\xi\xi\xi} , \quad (4)$$

$$d_{24} = d_{32} \propto <\cos \theta \sin^2 \theta > <\sin^2(\phi - \Omega)> \beta_{\xi\xi\xi} ,$$

A sufficient condition for the odd averages to vanish occurs if for every chromophore with $\phi=\Omega+\phi_p$, there is another at $\phi=\Omega-\phi_p$ and two more at $\phi=\Omega\pm\phi_p+\pi$. For accordion polymers with the chromophores linked together in the mainchain forming V's, this can occur for the chains aligned along $\Phi=\Omega$ with equal tilts to the left and to the right of the chain direction. If we assume delta function distributions for both ϕ and θ and the previously assumed thickness and indices, then d_{32}/d_{31} determines ϕ_p to be in the range 43 - 44°, and the ratio $d_{33}/(d_{31}+d_{32})$ determines a tilt angle θ that varies from ~58° at 20 bilayers to ~51° at 90 bilayers. This implies the interesting circumstance that the chromophores "stand up" (perpendicular to the substrate) more with increasing thickness of the LB film.
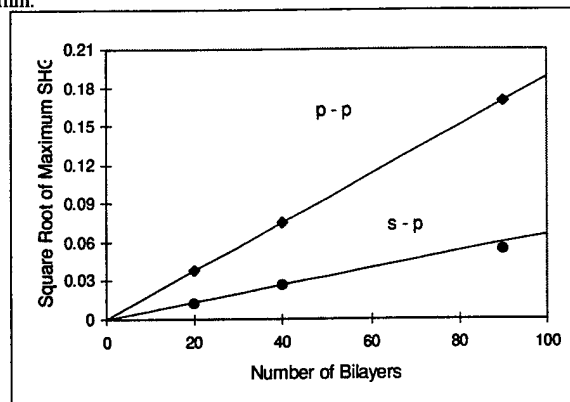
Figure 4 . Quadratic dependence of SHG on number of bilayers.

Conclusions

From SHG azimuthal data on 20,40, and 90 bilayer ABAB... Y-type accordion polymer LB films, where both polymers contain 12-C lipophilic chains, we find in-plane order associated with the $mm2$ point group that persists even at 90 bilayers, as well as a quadratic dependence of the generated second harmonic on the number of bilayers. A simple molecular model was presented that provides a sufficient condition for observing point group $mm2$. This model suggests, in the limit of a delta function distribution, the possibility that the chromophore tilt angle might decrease with increasing number of bilayers. Additional films with thickness greater than 90 bilayers are needed to test this possibility.

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