Macromolecules **1993,** *26,* 1789–1792

Efficient Second-Harmonic Generation from Thick All-Polymeric Langmuir–Blodgett Films

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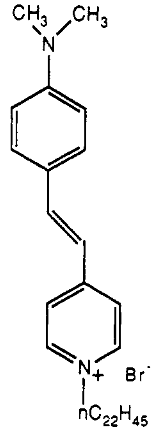
Received August 11, 1992
Revised Manuscript Received January 21, 1993

Introduction. It was recognized about 20 years ago that Langmuir–Blodgett (LB) films, being ordered at the *molecular* level, might have applications in optoelectronics, microelectronics, and molecular electronics.[1] Since then, good progress has been made toward several goals in these various fields.[2-4] In the majority of cases the LB films have been prepared from low-molecular-weight amphiphiles. Such films are, however, very fragile and unlikely to be suitable for commercial devices. Moreover, it has been demonstrated recently that both during[5] and after[6] the deposition of the LB multilayers the films have a tendency to become disordered. These problems are likely to be much less serious if the amphiphiles are preformed polymers, and this prompted us several years ago to initiate a study of monolayers of preformed polymers at the air–water interface[7-10] and of the LB films prepared from these monolayers.[8-10]

An application of LB films in optoelectronics which has attracted much attention is second-harmonic generation (SHG).[11] This requires films that contain SHG chromophores, i.e., moieties containing a π-electron system with donor and acceptor groups at opposite ends. Many compounds have been studied as SHG chromophores, but so far hemicyanines, for example, compound 1, have one of the highest second-order *molecular* hyperpolarizabilities (i.e., β-values).[12] In addition to containing SHG chromophores, an SHG material must also have a significant *macroscopic* second-order susceptibility, i.e., a significant $\chi^{(2)}$ value. This requires the material to have a noncentrosymmetric arrangement of the SHG chromophores. The noncentrosymmetric arrangement can in principle be achieved easily with LB films. For example, alternating multilayers of the Y-type with just one of the components containing an SHG chromophore will be noncentrosymmetric. If both layers have chromophores, they must be arranged so that the signals from each layer do not cancel out. Simple theory predicts that if each bilayer is deposited to a consistently high quality, the intensity of the SHG signal, $I_{2\omega}$, should increase as the *square* of the number of active bilayers. Clearly it is vital to achieve this quality of LB film if SHG signals of high intensity are to be obtained. So far several *nonpolymeric* LB films consisting of 100 or more bilayers have been described which display the desired quadratic dependence.[13-15] Very few polymeric multilayers have been prepared which display the quadratic relationship. The best of those in which just *one* of the amphiphiles was polymeric consisted of only 32 bilayers,[16] while the best in which *both* were polymeric contained only 10 bilayers,[17] though a recent publication implies that a film of 22 bilayers was satisfactory.[16] In this paper we report the preparation of *all-polymeric* LB films which can be used efficiently for SHG. For films containing up to ca. 150 bilayers (total thickness 0.6 μm) the intensity of the second-harmonic signal from light of wavelength 1.064 μm was proportional to the square of the number of active layers. For a film consisting of 120 bilayers it was shown that the intensity of the signal was unchanged after the film had been heated at 60 °C for 72 h or had been left at 20 °C for 3 months.



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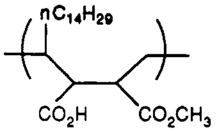

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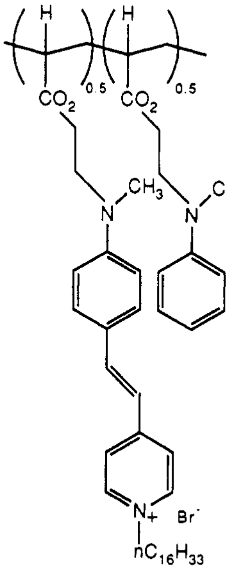

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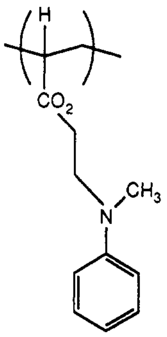

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Experimental Section. The polymers used in this study have been described previously.[10,18] The computer-controlled Langmuir troughs, both single[10] and double[19] compartment models, and the general procedures for the measurement of isotherms[10] and for the preparation of LB multilayers[10] have been described before. Polymer 2 was spread from a solution in chloroform; polymer 3 was spread from a solution in ethyl acetate. The subphase was double-distilled deionized water to which, when polymer 3 was used, cadmium chloride was added (2.5 × 10^{-4}). The LB film were deposited onto silanized Pyrex glass microscope slides.

X-ray reflectivity experiments were carried out as before[10] except that a Philips diffractometer PW1730 was used. Ellipsometry was carried out using reflection and a multiple angle of incidence technique at wavelengths of 543.5 and 632.8 nm.[20] Data for both wavelengths were analyzed for real, scalar film refractive index and thickness only. The scalar index at 632.8 nm was 1.48. At 543.5 nm the scalar index was best fitted as 1.52. Due to absorption

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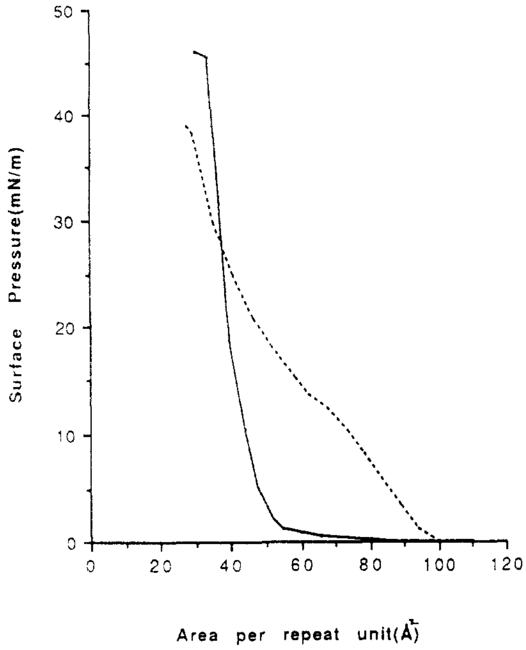

Figure 1. Isotherms for polymer 2 (···) and polymer 3 (—). Conditions as given in text.

within the hemicyanine the magnitude of the complex refractive index would be higher at this wavelength. Films for SHG measurement were stored in the dark until the measurements were made. SHG was measured using the 1.064-μm radiation from a Q-switched Nd:YAG laser. Pulses of less than 1-mJ energy with 10-ns duration were focused to an ca. 100-μm spot size on the sample. Incident and detected light were p-polarized and SHG was resolved in complete scans and angle of incidence onto the samples as described previously.[21]

Results and Discussion. Preliminary experiments on alternating LB films suggested that polymers 2 and 3 were potentially a suitable pair for the preparation of thick Y-type multilayers for SHG.[22]

Properties of Polymers 2 and 3. Polymer 2, the "active" polymer, has been studied before.[18,23] It was prepared from polymer 4 ($\bar{M}_n$ = 11 000, $\bar{M}_w$ = 40 000; by GPC relative to polystyrene standards) by formylation (Vilsmeir–Haack reaction[24]) and then reaction of the aldehyde group with *N*-hexadecyl-γ-picolinium bromide in the presence of piperidine. As only half the pendant groups in polymer 4 were formylated, only 50% of the side groups in polymer 2 contained a hemicyanine chromophore. Incomplete substitution may well be an advantage because it has been reported that, possibly due to aggregation, a pure monolayer of hemicyanine 1 gives a weaker SHG signal than a monolayer which is 50% compound 1 and 50% arachidic acid.[25] The longest wavelength maximum of hemicyanine 1 in chloroform solution is at 494 nm while that for polymer 2 in chloroform is at 475 nm and in an LB film 463 nm. This suggests a small amount of aggregation of the chromophores, not surprising given that they are held in close proximity by the polymer backbone.

A monolayer of polymer 2 on pure water (see Figure 1) had an isotherm indicating a surface area per chromophore at zero pressure of 58 Å². The isotherm was essentially unchanged when cadmium chloride was present in the subphase. Polymer 2 deposited readily onto silanized glass at 30 mN/m to give Y-type multilayers. An X-ray reflectivity study showed one Bragg peak corresponding to a bilayer spacing of 38.7 Å.

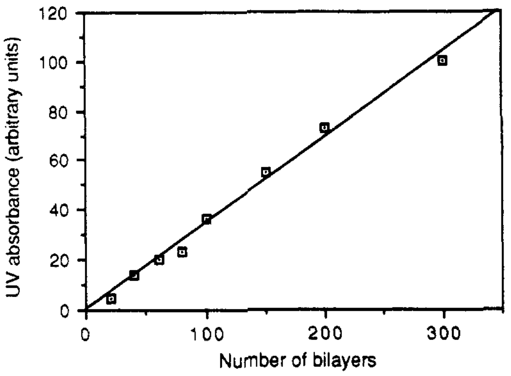

Figure 2. Plot of the intensity of UV absorbance at 463 nm versus the number of bilayers in the LB film.

Polymer 3 ($\bar{M}_n$ = 9000, $\bar{M}_w$ = 15 000; by GPC relative to polystyrene standards), the "passive" polymer, is one of a type we have studied extensively.[10] When spread on a subphase containing cadmium chloride, it gave excellent steep isotherms (see Figure 1) with a surface area per repeat unit at zero pressure of 39 Å² and it transferred readily onto silanized glass at 30 mN/m to give excellent multilayers which on X-ray reflectivity displayed three Bragg peaks indicating a bilayer spacing of 36.5 Å.

Properties of Alternating Multilayers Prepared from Polymers 2 and 3. Alternating LB multilayers were prepared from polymers 2 and 3 using a double Langmuir trough as described earlier.[19] The films were deposited onto silanized Pyrex glass microscope slides. Deposition from each trough was carried out at a surface pressure of 30 mN/m, polymer 2 being deposited (deposition ratio 1.00 ± 0.05) on the upstroke and polymer 3 (deposition ratio 1.00 ± 0.05) on the downstroke. A range of multilayers were prepared with thicknesses of up to 300 bilayers.

An X-ray reflectivity study of a film of 60 bilayers showed one Bragg peak corresponding to a bilayer thickness of 40.5 Å. The UV absorbance at 463 nm plotted against the number of bilayers in the films (see Figure 2) was a straight line, suggesting that the deposition process produced uniform films. Ellipsometric measurements on the multilayers (see Figure 3) were in agreement with this. The latter indicated an average bilayer thickness of 42.5 Å, a value in good agreement with the X-ray study, and that the films had a refractive index of 1.52 to light of wavelength 0.543 μm.

A reference standard conversion efficiency from a quartz crystal was used to quantify the SHG measurements. A Y-cut quartz wedge of 20-mrad angle was used, with the amplitude of the interference fringes due to the d_{11} coefficient of the quartz measured as the crystal was linearly translated along the z crystal axis. The results are plotted out in Figure 4. Experiments using a second reference detection arm for normalization of SHG signals with respect to laser pulse energy found laser stability to be within ±2% and an overall uncertainty in $I_{2\omega}$ of ±5%. Pulse-to-pulse noise was therefore concluded not to be a limiting factor to data reproducibility. It is apparent that $I_{2\omega}$ increases in proportion to the square of the number of active layers up to ca. 150 bilayers. The slight scatter of the points is reasonable given that each measurement was made on a completely different film; i.e., a single film was *not* built up progressively with SHG measurements being made at various thicknesses. The modest amount of scatter indicates the extent to which the films can be reproduced. Beyond 150 bilayers the intensity of the signal still increases, but subquadratically.

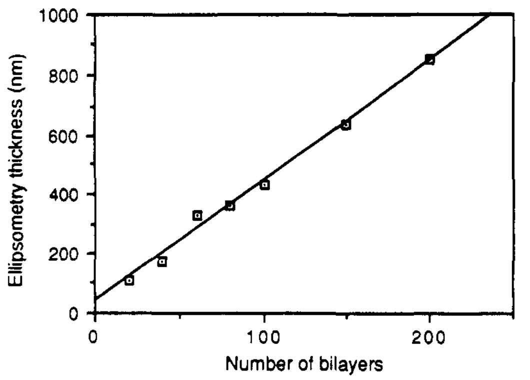

Figure 3. Plot of the LB film thickness determined by ellipsometry versus the number of bilayers in the film.

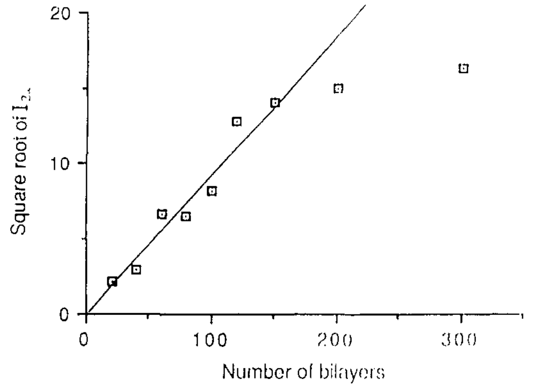

Figure 4. Plot of the square root of $I_{2\omega}$ versus the number of bilayers in the LB film. $I_{2\omega}$ is expressed as intensity relative to quartz multiplied by 10^3. Values of $I_{2\omega}$ have an error of ±5%. The further variations reflect the reproducibility of film preparation.

As a check on the stability of the film, the film consisting of 120 bilayers was heated in the dark at 60 °C for 72 h. The intensity of the SHG light was then remeasured. It was found to be the same (±10%) as that obtained before heating. A similar result was obtained when a film consisting of 100 bilayers was kept in the dark at 20 °C for 3 months. No experiments were made at higher temperatures because the acid and ester moieties in the passive polymer 3 rapidly cyclize to give anhydride moieities and methanol at ca. 100 °C. Accordingly, we are currently studying alternative passive polymers.

Since the SHG signal is close to the longest wavelength maximum in the UV spectrum of the chromophore, $I_{2\omega}$ may be partly resonance enhanced. This and the lack of other properties such as the local field effect within the multilayer make it difficult to accurately assess the molecular chromophore response (β). A study of the angle of incidence for maximum SHG and the angular full width at half-maximum of the SHG response can allow an estimate of chromophore tilt using a one-dimensional model of chromophore nonlinear response. The conventional model for an LB film is that chromophores are titled from the perpendicular to the film with a very narrow angular distribution.[26] Such a study of the angular dependence of SHG suggests that the chromophores are titled at an angle ca. 65–70° from the perpendicular.

The slope of the graph of SHG response with film thickness for these films corresponds to an effective nonlinear susceptibility $\chi^{(2)}_{\mathrm{pp}}$ = 7 pm V^{-1}. This response leads to a conversion efficiency *per monolayer* of the hemicyanine polymer of 6×10^{-6} relative to the quartz fringes for the hemicyanine copolymer layers within the bulk structure. For comparison, the conversion efficiency for a single monolayer of a monomeric hemicyanine has been reported as 25×10^{-6} relative to quartz.[25]

The form of the angular dependence of the SHG signal observed from the copolymeric hemicyanine films does not exactly correspond to the predictions based on the one-dimensional chromophore response and the assumed uniform molecular tilt angle. With the second harmonic on resonance in the material, the chromophore response is not adequately described by a single coefficient. The influence of the polymer backbone may also broaden the angular spread of chromophore tilt angles. However, a calculation based on the one-dimensional response of a nonlinear chromophore, a uniform tilt of 70°, and an effective nonlinear susceptibility $\chi^{(2)}_{\mathrm{pp}}$ ~7 pm V^{-1} leads to a chromophore response of $\chi^{(2)}_{\mathrm{zzz}}$ ~40 pm V^{-1}. This compares to published data in the region of 100 pm V^{-1}.[27]

It is interesting to note that while the SHG signal becomes subquadratic at greater than 150 bilayers, the UV spectroscopic and ellipsometric measurements still indicate a uniform layer structure. It is clear that SHG measurements are the most sensitive test of film order.

Conclusions. We have shown for the first time that all-polymeric LB films can be prepared which generate a second-harmonic signal with the intensity displaying the desired quadratic dependence on thickness up to a thickness of ca. 150 bilayers. The thickness, 0.6 μm, is greater than the wavelength of the second harmonic (0.532 μm) as required for the successful application of LB films in devices, but systems with optical transmission in suitable wavelength regions are required for specific applications. We have previously shown in preliminary studies that an LB film prepared from a polymer very similar to polymer 3 had an optical attenuation of 10 dB/cm.[28] Other workers have since reported values of ~3[29] and 1 dB/cm[16] for polymeric LB films.

Acknowledgment. We thank the SERC for financial support (Z.A.-A.) and a Quota Studentship (D.W.).

References and Notes

(1) Vincent, P. S.; Roberts, G. G. *Thin Solid Films* **1980**, *68*, 135. Roberts, G. G. *Adv. Phys.* **1985**, *34*, 475. Sugi, M. *J. Mol. Electron.* **1985**, *1*, 3.
(2) Stegeman, G. I. In *Organic Materials for Non-Linear Optics II*; Hann, R. A., Bloor, D., Eds.; *Royal Society of Chemistry*: London, 1990; pp 311–323.
(3) Roberts, G. G. In *Langmuir–Blodgett Films*; Roberts, G. G., Ed.; Plenum: New York, 1990; Chapter 7, pp 317–411.
(4) Peterson, I. R. In *Molecular Electronics*; Ashwell, G. J., Ed.; Research Studies Press, John Wiley and Sons: New York, 1992; Chapter 3, pp 117–206.
(5) Grundy, M. J.; Musgrove, R. J.; Richardson, R. M.; Roser, S. J.; Penfold, J. *Langmuir* **1990**, *6*, 519.
(6) Stroeve, P.; Rabolt, J. F.; Hilleke, R. O.; Felcher, G. P.; Chen, S. H. *Mater. Res. Soc. Symp. Proc.* **1990**, *166*, 103. Shimomura, M.; Song, K.; Rabolt, J. F. *Langmuir* **1992**, *8*, 887.
(7) Hodge, P.; Towns, C. R.; Thomas, R. K.; Shackleton, C. *Langmuir* **1992**, *8*, 585.
(8) Hodge, P.; Khoshdel, E.; Tredgold, R. H.; Vickers, A. J.; Winter, C. S. *Br. Polym. J.* **1985**, *17*, 368.
(9) Hodge, P.; Davis, F.; Tredgold, R. H. *Philos. Trans. R. Soc. London* **1990**, *330*, 153.
(10) Davis, F.; Hodge, P.; Towns, C. R.; Ali-Adib, Z. *Macromolecules* **1991**, *24*, 5695.
(11) Prasad, P. N.; Williams, D. J. *Introduction to Non-Linear Optical Effects in Molecules and Polymers*; John Wiley: New York, 1991.
(12) Girling, I. R.; Cade, N. A.; Kolinsky, P. V.; Earls, J. D.; Cross, G. H.; Peterson, I. R. *Thin Solid Films* **1985**, *132*, 101.
(13) Decher, G.; Tieke, B.; Bosshard, C.; Günter, P. *J. Chem. Soc., Chem. Commun.* **1988**, 933.
(14) Era, M.; Nakamura, K.; Tsutsui, T.; Saito, S.; Niino, K.; Takehara, K.; Isomura, K.; Taniguchi, H. *Jpn. J. Appl. Phys.* **1990**, *29*, L2261.

(15) Ashwell, G. J.; Dawnay, E. J. C.; Kuczynski, A. P.; Martin, P. J. *Proc. SPIE Int. Soc. Opt. Eng.* **1991**, *1361*, 589.

(16) Penner, T. L.; Armstrong, N. J.; Willard, C. S.; Schildkraut, J. J.; Robello, D. R. *Proc. SPIE Conf. NLO Properties IV* **1991**, *1560*, 377.

(17) Anderson, B. L.; Hall, R. C.; Higgins, B. G.; Lindsay, G.; Stroeve, P.; Kowel, S. T. *Synth. Met.* **1989**, *28*, D683.

(18) Young, M. C. J.; Jones, R.; Tredgold, R. H.; Lu, W. X.; Ali-Adib, Z.; Hodge, P.; Abbasi, F. *Thin Solid Films* **1989**, *182*, 319.

(19) Tredgold, R. H.; Evans, S. D.; Hodge, P.; Hoorfar, A. *Thin Solid Films* **1988**, *160*, 99.

(20) Azzam, R. M. A.; Bashara, N. M. *Ellipsometry and Polarized Light*; North-Holland Personal Library, Elsevier Science Publications: Amsterdam, The Netherlands, 1977.

(21) Bishop, M.; Clarke, J. H. R.; Davis, L. E.; King, T. A.; Mayers, F. R.; Mohebati, A.; Munn, R. W.; Shabat, M. M.; West, D.; Williams, J. O. *Thin Solid Films* **1992**, *210/211*, 185.

(22) Hodge, P.; Ali-Adib, Z.; West, D.; Mohebati, A.; King, T. *Organic Materials for Non-Linear Optics III*; Ashwell, G., Allen, S., Eds.; Royal Society of Chemistry: London, 1993; in press.

(23) Young, M. C. J.; Lu, W. X.; Tredgold, R. H.; Hodge, P.; Abbasi, F. *Electron. Lett.* **1990**, *26*, 993.

(24) Jutz, C. *Adv. Org. Chem.* **1976**, *9*, 225.

(25) Girling, I. R.; Cade, N. A.; Kolinsky, P. V.; Jones, R. J.; Peterson, I. R.; Ahmad, M. M.; Neal, D. B.; Petty, M. C.; Roberts, G. G.; Feast, W. J. *J. Opt. Soc. Am. B* **1987**, *4*, 950.

(26) Allen, S. *Inst. Phys. Conf. Ser.* **1989**, *103*, 163.

(27) Ashwell, G. J. In *Molecular Electronics*; Ashwell, G. J.; Ed.; Research Studies Press, Wiley: London, 1992; p 25.

(28) Tredgold, R. H.; Young, M. C. J.; Hodge, P.; Khoshdel, E. *Thin Solid Films* **1987**, *151*, 441.

(29) Hickel, W.; Duda, G.; Jurich, M.; Kröhl, T.; Rochford, K.; Stegeman, G. I.; Swalen, I. D.; Wegner, G.; Knoll, W. *Langmuir* **1990**, *6*, 1403.