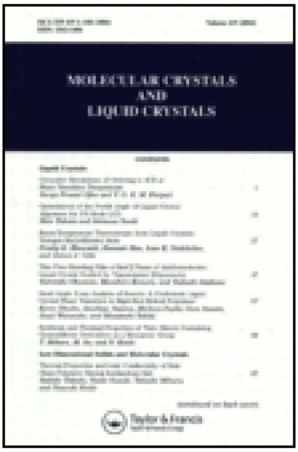

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Second- and Third-Harmonic Generation by Z-Type Langmuir-Blodgett Multilayer Films

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SECOND- AND THIRD-HARMONIC GENERATION BY Z-TYPE LANGMUIR-BLODGETT MULTILAYER FILMS

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Abstract Z-type Langmuir-Blodgett films are prepared from an amphiphilic diacetylene derivative which has been polymerized. The high structural fidelity of these films is verified by optical second and third harmonic generation.

Keywords: harmonic generation, z-type langmuir blodgett films, multilayers

INTRODUCTION

The Langmuir-Blodgett technique is a well established method for the layer by layer preparation of organized organic structures. In the usual embodiment of this method, an amphiphilic molecule is transferred from the air/water interface onto a solid substrate as the substrate is passed through the interface. Transfer occurs on both the downward and upward passages of the substrate, leading to a centrosymmetric (Y-type) structure of the transferred amphiphile film. Such centrosymmetric structures are unsuitable for applications such as piezo- and pyro-electricity and second order nonlinear optics, which require a non-centrosymmetric structure.

Non-centrosymmetric Langmuir-Blodgett films may be obtained if two different amphiphiles are used for the up and down transfer strokes, or if a single amphiphile itself transfers only on one of the strokes. Amphiphiles fulfilling the latter condition have occasionally been found,[1-3] although such behaviour (Z-type deposition) cannot usually be predicted in advance.

Recently, a strategy to ensure that insoluble monolayers at the air/water interface transfer as non-centrosymmetric Langmuir-Blodgett films has been described.[4] Amphiphilic molecules are prepared which preferably contain two amide groups at specified distances from the polar head group. When a substrate is dipped through the monolayer, these amphiphiles invariably transfer only on the upstroke, characteristic of Z-type deposition.

These multilayers were analyzed by infrared spectroscopy, ellipsometry and low-angle X-ray diffraction, yielding information about the reproducibility of each transferred layer.[4] Another technique, highly sensitive to small deviations from complete translational symmetry between the layers, is optical second harmonic generation (SHG). This technique was used to analyze multilayers formed by amphiphiles with large second-order nonlinearity.[3,4]

We have extended this work to Z-type multilayers of amphiphilic polydiacetylene (PDA) derivatives.[5] Due to the extremely large third-order nonlinearity of polydiacetylene, these films can be analyzed simultaneously by both SHG and third-harmonic generation (THG).[6] Consequently, these parallel measurements probe both the number of molecules in each transferred layer, and the structural and symmetrical fidelity of each successive layer.

EXPERIMENTAL

The synthesis of 10,12-nonacosadiynol-S-lysine, its spreading as a Langmuir film,, and photopolymerization to give a substituted PDA (see Figure 1) has been described earlier.[5] Langmuir-Blodgett films are prepared by dipping fused silica slides coated with an octadecyl trichloro silane (OTS) monolayer through the Langmuir film. As evidenced by the transfer ratios, the first layer transferred on the downstroke, which is followed by transfer only on successive upstrokes. Thus, the PDA films are considered to consist of a Y-type bilayer, followed by successive Z-type layers.

Nonlinear optical measuements were performed in reflection by focussing a pulsed, linearly polarized, Nd-YAG laser (1064nm, 8ns pulse width, 5mJ pulse energy) using a 15cm focal length lens onto the slides at 45° incidence. A short focal length lens must be used to eliminate complications caused if there is significant THG by air.[6-8] An aperture was positioned to transmit only the reflection from the front face of the slide, after which the residual fundamental was blocked by a Schott BG-39 filter. The SHG and THG (at 532 and 355 nm respectively) were recorded by a photon counting system, after passing through a monochromator. In this arrangement, the observed THG signal was typically much stronger than the SHG, consistent with the small second-order, but large third-order susceptibilty of these polydiacetylenes.

RESULTS AND DISCUSSION

In Figure 1, the square root of the relative SHG and THG signals is plotted against the number of layers. The SHG is measured as a p-polarized signal generated by p-polarized laser input, and THG is s-polarized following s-polarized input. Note that each measurement is taken with a different sample, rather than by successively adding layers to the one sample.

It is seen that a linear dependence on the number of layers is obtained in both SHG and THG, indicating high quality Z-type multilayer formation. This behaviour also means that the substrate signal is either negligible (THG), or at least of the same phase as the film. In the SHG data, the linear plot is drawn starting from the first bilayer, which is not Z-type. We did note, however, that the SHG from the bilayer is larger than that of both the plain substrate, and a substrate covered only with OTS, indicating that the first bilayer is NOT perfectly centrosymmetric. This may be due to the attached water molecules on the second layer, which is assumed[5] to be the reason for the subsequent Z-type transfer, and may also indicate different molecular orientations of the first and second PDA molecular layers.

Measurements using other input-signal polarization combinations yielded much smaller SHG and THG signals. In SHG the p-polarized signal using s-input was about 5 times smaller than for p-input; and the s-polarized output signals were negligible. In THG the p-in, p-out signal was about 10 times smaller than s-in, s-out. These results are consistent with a model used previously,[6] where the SHG comes essentially from the head groups, which are almost normal to the film, while the THG comes from the polymer backbone which lies in the plane of the film.

From the magnitude of the THG signals, relative to the fused silica substrate,we can estimate the $|\chi^{(3)}|$ of the polymer. In a reflection measurement in this geometry, a substrate thickness of about 200Å contributes to the THG.[6] We observed that the OTS covered substrate and the PDA bilayer covered sample had THG intensities of about 4 and 100 times that of fused silica respectively. Taking the known[7,9] susceptibility of fused silica ($3\mathrm{x}10^{-14}$ esu) and the thickness of each polymer monolayer[5] as 45Å, we estimate the $\chi^{(3)}$ per unit volume to be about $1\mathrm{x}10^{-12}$ esu for PDA and $6\mathrm{x}10^{-13}$ esu for OTS (thickness 20Å). These $\chi^{(3)}$ values are in good agreement with earlier results[10,11] on analogous systems, taking into account the fact that in these long chain substituted molecules, only a small volume fraction of the polymers contributes to $\chi^{(3)}$.

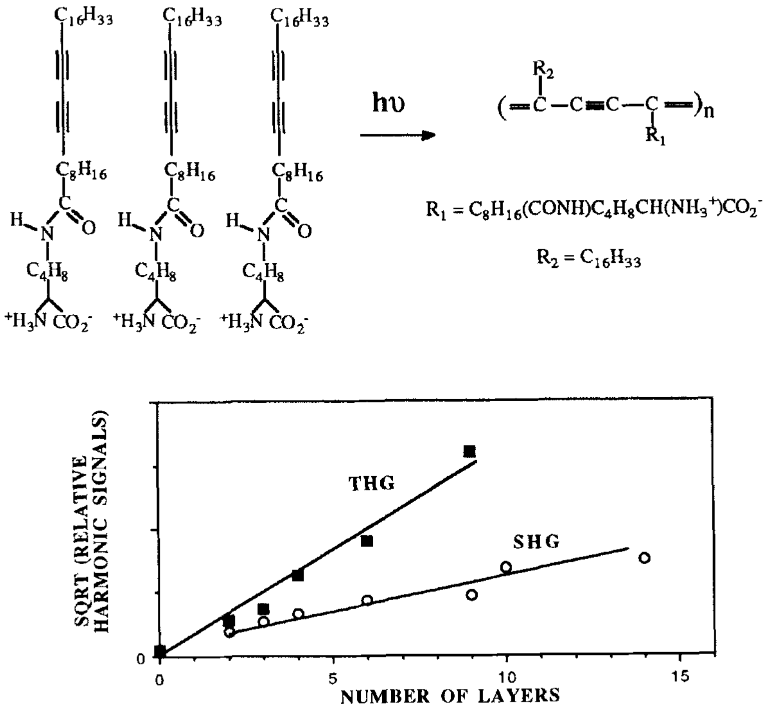

Figure 1. Molecular structure of the amphiphilic diacetylene monomer and PDA polymer (top). Plot of relative SHG and THG from PDA films (bottom). THG was much stronger than SHG, however here the latter has been expanded to fit on the same scale. The zero data point for THG was obtained for an OTS covered substrate.

REFERENCES

1. P.S. Vincett, W.A. Barlow, F.T. Boyle, J.A. Finney and G.G. Roberts, Thin Solid Films 60, 265 (1983).
2. M.F. Daniel, O.C. Lettington and S.M. Small, Thin Solid Films 99, 61 (1983).
3. L.M. Hayden, S.T. Kowel and M.P. Srinivasan, Opt. Comm. 61, 351 (1987).
4. R. Popovitz-Biro, K. Hill, E. Shavit, D.J. Hung, M. Lahav, L. Leiserowitz, J. Sagiv, H. Hsiuing, G.R. Meredith and H. Vanherzeele, J. Am. Chem. Soc. 112, 2498 (1990).
5. R. Popovitz-Biro, D.J. Hung, E. Shavit, M. Lahav and L. Leiserowitz, Thin Solid Films 178, 203 (1989).
6. G. Berkovic, R. Superfine, P. Guyot-Sionnest, Y.R. Shen and P.N. Prasad, J. Opt.Soc. Am. B 5, 668 (1988).
7. F. Kajzar and J. Messier, Phys. Rev. A 32, 2352 (1985).
8. K. Kubodera and H. Kobayashi, Mol. Cryst. Liq. Cryst. 182A, 103 (1990).
9. B. Buchalter and G.R. Meredith, Appl. Opt. 21, 3221 (1982).
10. F. Kajzar, J. Messier, J. Zyss and I. Ledoux, Opt. Comm. 45, 133 (1983).
11. J.-C. Baumert, G.C. Bjorklund, D.H. Jundt, M.C. Jurich, H. Looser, R.D. Miller, J. Rabolt, R. Sooriyakumaran, J.D. Swalen and R.J. Tweig, Appl. Phys. Lett. 53, 1147 (1988).