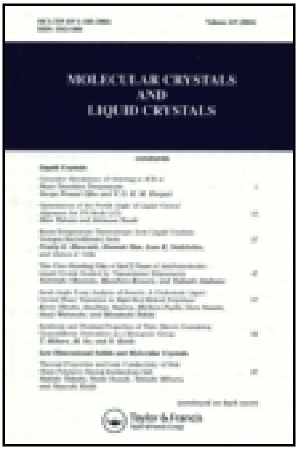

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Absolute Molecular Orientation of Noncentrosymmetric Self-Assembled Tolan Langmuir-Blodgett Films

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The absolute molecular orientation of tolan derivative 4-docosylamino-4′-nitorotolan (DCANT) Langmuir-Blodgett films transferred by a horizontal lifting method was determined by the phase measurement of second-harmonic generation (SHG). The absorption spectra of the multilayers indicated DCANT molecules aligned in an in-plane anisotropy. In the phase measurement of SHG, the absolute molecular orientation of the DCANT multilayer was determined in comparison with the interference pattern of a poled polymethylmethacrylate film doped with p-nitroaniline, whose absolute molecular orientation was known. The results indicated the DCANT molecules aligned in parallel each other and the absolute molecular orientation was perpendicular to the direction of compression at the air/water interface, which was probably achieved during the compression process in a long and narrow trough.

Keywords: Second-harmonic generation; 4-docosylamino-4′-nitorotolan (DCANT); Langmuir-Blodgett; absolute molecular orientation; phase measurement

INTRODUCTION

The design and fabrication of molecular assemblies have a great interest, and the orientation of component molecules in those assemblies has been the subject of a number of studies [1,2]. Langmuir-Blodgett (LB) technique has been intensively applied to assemble amphiphilic molecules because of its surface specificity and applicability to a various combination of substrates [2-6]. Although amphiphilic molecules are aligned at the air/water interface, it is generally believed that molecules are isotropically distributed in the plane of the monolayer [7]. Noncentrosymmetric assemblies can be obtained in the X-type or Z-type multilayers transferred by a horizontal lifting method or in the alternating Y-type multilayers by a vertical dipping method. The Y-type deposition usually creates a centrosymmetric assembly, where a second-harmonic generation (SHG) disappears due to the cancellation of electric dipoles. However, it is reported that docosylamino-5-nitropyridine (DCANP) multilayers transferred onto a substrate by the vertical dipping method exhibit a noncentrosymmetric structure due to the shear flow during deposition [8]. An in-plane polar anisotropy of DCANP multilayers was confirmed by SHG measurements which provided the average orientation of molecules based on the oriented gas model [8,9].

In our previous work [6], we observed an in-plane polar anisotropy in 4-docosylamino-4'-nitorotolan (DCANT, shown in Fig.1) multilayers transferred by the horizontal lifting method. Since the shear flow during deposition could not be expected in the horizontal lifting, we assumed that the in-plane polar anisotropy of DCANT multilayer was due to the process of the compression of monolayer in a long and narrow trough.

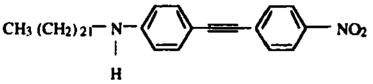

FIGURE 1 Chemical structure of 4-docosylamino-4'-nitorotolan (DCANT).

In this paper, we applied phase measurements of SHG [10-13] to determine the absolute molecular orientation of DCANT multilayers on substrates. The absolute molecular orientation, *i.e.*, the direction of the first hyperpolarizability (β), which cannot be obtained directly from conventional SHG measurements, provides the insight into the basic chemical interactions at surfaces and interfaces [10]. During the transfer of DCANT molecules at the air/ water interface to the substrate, we prepared two different substrate configurations, that is, 180° rotated in-plane each other. Behavior of DCANT molecules in floating monolayer was clarified by comparing the absolute molecular orientation on the substrate and the deposition configuration.

EXPERIMENTAL

DCANT was synthesized by coupling the corresponding alkylamino-iodobenzene with 4-ethynylnitrobenzene. A solution of DCANT in toluene was spread onto distilled water in a long and narrow trough (6 x 180 cm) at the room temperature. The monolayers of DCANT were slowly compressed (3 x 6 cm^2/min) to form a rigid condensed monolayer with a limiting area of 30 $Å^2$/molecule (Lauda film balance) [6]. Two microscope glass plates, (A) and (B), were marked with a line to distinguish the direction of the plates, as shown in Fig. 2. The monolayer

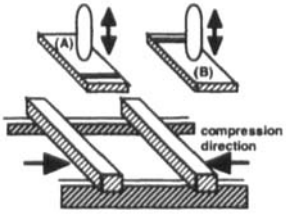

FIGURE 2 Horizontal lifting method. The microscope glass plates are marked with the line to distinguish the direction of plates.

was successively transferred onto one side of the glass plate (A) by 8 layers at 10 mN/m by the horizontal lifting method without changing the direction of the plate. The direction of plate (B) was set to be opposite to the plate (A) in plane, and the monolayer was also successively transferred onto the plate (B) by 8 layers.

Polarized absorption spectrum of the DCANT multilayer was measured by HITACHI Spectrometer Model 340. The linear polarized lights irradiated the DCANT multilayer at the normal incident with parallel and perpendicular to the direction of the compression.

Fig. 3 shows an optical arrangement of phase measurement of SHG. The light source was a p-polarized Q-switched Nd:YAG laser (Spectra-Physics GCR230-10 operating at 10 Hz repetition rate and 10 ns pulse width, λ=1064 nm), and p-polarized second-harmonic (SH) signal (λ=532 nm) was detected by a photomultiplier tube. The interference of SH signal was generated between the two SH active films (a reference and a sample), and was modulated by rotating a glass plate inserted between the two films. The interference patterns obtained between DCANT multilayers and the reference were compared with those obtained between the standard film and the reference. Poled polymethylmethacrylate films doped with p-nitroaniline (PNA/PMMA) were used as the reference and the standard film because the direction of the dipole moment of PNA in PMMA could be controlled by a polarity of poling electric field. PMMA was completely dissolved in chloroform (CHCl3) and mixed with 0.5 wt% of PNA. The solution was casted on a glass substrate at 3000 rpm for 10 sec to make a thin film. The PNA/PMMA film was settled in a vacuum oven heated at 60 °C for more than 24 hours in order to remove residual solvent, then it was heated at 110 °C (above Tg of PMMA) on a hot plate for 30 min. An electric field was also applied to the PNA/PMMA films at 110 °C for 30 min and the films were quickly cooled down to the room temperature with the electric filed. The thickness of the PNA/PMMA film was approximately 1 µm, which was smaller than the coherence length of the fundamental and SH lights. In an absorption spectrum of PNA/PMMA film, the phase shift was not influenced by the existence of an absorption band [12], since there was no absorption band at 532 nm [14]. The fundamental beam irradiates the reference film at an incident angle of θ_1 to generate the SH beam, and both the fundamental beam and SH beam ($(SH)_{ref}$) from the reference irradiate the glass plate at an incident angle of θ_2, which is varied for changing the optical paths for both beams. The fundamental beam passing through is incident on the sample at an incident angle of θ_3 to generate an SH beam ($(SH)_s$), which interferes with $(SH)_{ref}$.

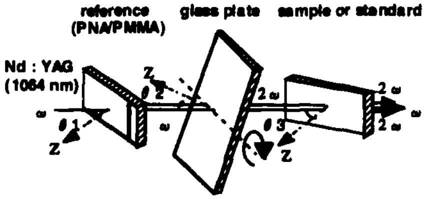

FIGURE 3 Optical arrangement of the phase measurement of SHG.

RESULTS AND DISCUSSION

The absorption spectra of DCANT multilayers were measured with linear polarized lights, parallel or perpendicular to the direction of the compression, as shown in Fig. 4. There is a strong absorption band near 440 nm and the absorbance obtained by parallel polarization (p) is

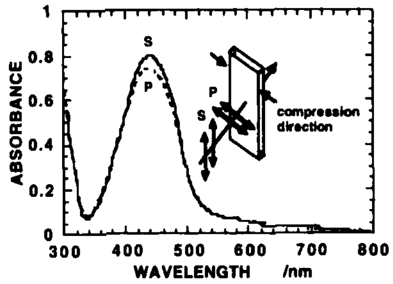

FIGURE 4 Absorption spectra of DCANT multilayers measured with linear polarized light. The polarized lights irradiate the multilayer parallel (p) or perpendicular (s) to the direction of compression.

smaller than that obtained by perpendicular polarization (s). This result indicates that an anisotropy is present in the DCANT multilayer and the direction of the transition dipole moment is perpendicular to the direction of the compression. The value of the dichroic ratio for the DCANT multilayer at 440 nm is 0.925 (Ap/As).

Fig.5 shows the interference pattern obtained by the phase measurement of SHG. Poled PNA/PMMA films were used as the reference and the standard. The absolute molecular orientation of PNA in the poled PNA/PMMA is also shown in Fig.5 (μ). Firstly, in the case that both reference and sample are poled PNA/PMMA films, we set the incident angle of θ_1 and θ_3 to 45°, and varied θ_2 from 0° to 60°. In this configuration, the interference pattern (dotted

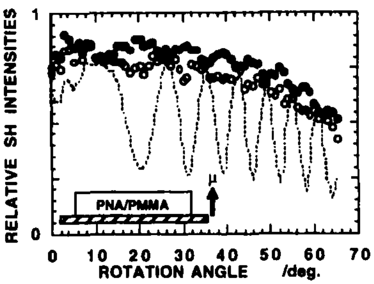

FIGURE 5 Interference patterns obtained for DCANT multilayers and poled PNA/PMMA film (as a standard). Dotted line, poled PNA/PMMA film; Open circle, DCANT multilayer (A); Closed circle, DCANT multilayer (B).

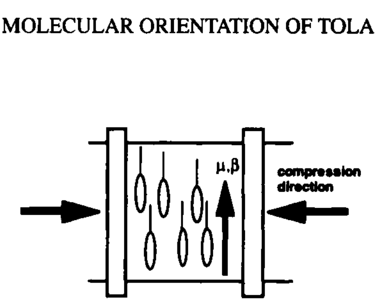

FIGURE 6 Model of DCANT molecular orientation in floating monolayer.

line) is modulated between the two poled PNA/PMMA films. Secondly the DCANT multilayer A is placed in the sample position, and the incident angle of θ_3 is set at normal incidence, because the DCANT multilayer has an in-plane polar anisotropy [6]. The incident angle of the fundamental beam to the reference (θ_1) is set at 30°, since the SH intensity of poled PNA/PMMA film can be tuned to optimize the interference with the sample. Then the DCANT multilayer B is placed in the same configuration as the sample A. In Fig.5, we can observe the phase shift by π in the interference patterns of DCANT multilayers A (open circle) and B (closed circle). Moreover, the interference pattern is shifted by π when the direction of the sample is inversed for both samples. These results indicate that the DCANT molecules align in parallel each other and the absolute molecular orientation of DCANT multilayer is not affected by the deposition process at the air/water interface. The absolute molecular orientation of the DCANT multilayer is estimated from the comparison of both interference patterns of DCANT multilayer and the poled PNA/PMMA film (as a standard film). Fig. 6 shows the model of DCANT molecular orientation in floating monolayer in a long and narrow trough, and the DCANT molecules align perpendicular to the direction of compression. In the case of DCANP molecules, a highly tilted arrangement of the alkyl chains can be suggested from the molecular packing density at collapse point [8], and an in-plane anisotropy with C_{1h} symmetry is already present in the floating monolayer film where the molecules are preferentially aligned parallel to the barriers of LB trough [7]. DCANT molecule has also a long alkyl chain, which shows the tilted molecular packing by compression, and the absolute molecular orientation of DCANT is probably achieved during the compression process in the long and narrow trough [7,15,16].

CONCLUSION

DCANT molecules were transferred to the substrate by the horizontal lifting method without changing the molecular orientation. The absolute molecular orientation of DCANT on the substrate could be measured by the phase measurement of SHG using the poled PNA/PMMA films as the reference and the standard. DCANT molecules aligned in parallel each other in the long and narrow trough. The absolute molecular orientation was perpendicular to the direction of compression, and was probably achieved during the compression process.

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