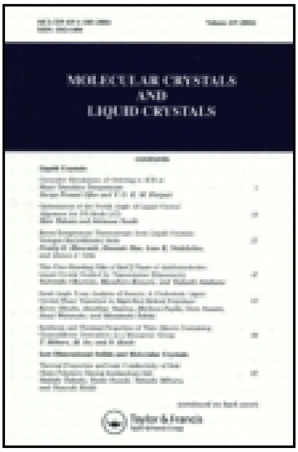

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Nonlinear Optical Effect and Optical Characteristics of Langmuir-Blodgett Films : n-Octadecyl 4-(4′-Nitrophenylazo)-1-Naphthyl Ether

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NONLINEAR OPTICAL EFFECT AND OPTICAL CHARACTERISTICS OF LANGMUIR-BLODGETT FILMS:
n-OCTADECYL 4-(4'-NITROPHENYLAZO)-1-NAPHTHYL ETHER

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Abstract n - Octadecyl 4 - (4'-nitrophenylazo) -1 - naphthyl ether, ONNE, was synthesized and the optical characteristics of ONNE was studied. Noncentrosymmetric Z-type Langmuir-Bodgett (LB) films of ONNE were prepared and the second harmonic generation, SHG, intensity of the films were measured. The structural characteristics of floating monolayer and LB film of ONNE were discussed with the π - A isotherm, UV - visible absorption spectroscopy and ellipsometry. The polarized UV - visible absorption spectroscopy and SHG intensity suggest molecular orientation in LB film.

INTRODUCTION

The second-order nonlinear optical(NLO) phenomena in Langmuir-Blodgett(LB) films have attracted much attention over the past few years.[1-5] Possibility of exploiting LB film as a potential candidate for application for NLO devices draws much interests[3, 5] Asymmetric orientation of film can be obtained when the substrate is being withdrawn(Z-type) or immersed(X-type) through the monolayer prepared on the water. In many cases, such molecular assemblies are not thermodynamically stable and tend to relax the imposed order.[6] For a multilayer structure in which the noncentrosymmetric arrangement of molecules is attained, the second harmonic generation (SHG) efficiency should increase quadratically with number of layers.[7] This feature is difficult to achieve, because the angle from the surface normal distributes within some range, and the relaxation processes of the molecular order randomize the molecular orientations. In this paper, we introduce naphthyl group instead of a phenyl ring of a 1-alkoxy-4'-nitro azobenzene. The naphthyl group may increase π-π interaction and molecular stacking in LB film. We synthesized n-octadecyl

4-(4'-nitrophenylazo)-1-naphthyl ether, ONNE. We will show the SHG behavior of Z-type film with varying number of layer. Intrinsic difference in SHG intensity of perpendicular and horizontal polarization with respect to the dipping direction will be shown. The LB films are characterized by the use of UV-visible spectroscopy and spectroscopic ellipsometry.

EXPERIMENTALS

Figure 1 shows the molecular structure of ONNE used in this study. The molecular structure was characterized with 500MHz NMR.

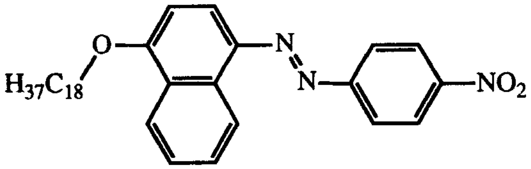

FIGURE 1. Molecular structure of n-octadecyl 4-(4'-nitrophenylazo)-1-naphthyl ether, ONNE.

Noncentrosymmetric Z-type LB films of ONNE were prepared from a moving-wall type LB film deposition apparatus (Nippon Laser & Electronics, NL-LB-240S-MWA). ONNE in $CHCl_3$ solvent (10^{-3}mol/l) was spread on ultrapure water (18MΩ-cm) as a subphase. A monolayer was compressed to 15mN/m, before deposition onto solid substrate, with the compression ratio of 10.3Å^2/molecule. The monolayer was transferred on fused quartz substrates and *Si*(100) wafer only in the up-stroke, respectively. The UV-visible absorption spectra of ONNE in the LB films and in $CHCl_3$ (10^{-5}mol/l) were measured with the diode array type spectrophotometer (Hewlett-Packard, HP8452A). The refractive index, extinction coefficient and monolayer thickness of the Z-type LB films deposited on a *Si* wafer were obtained from the spectroscopic ellipsometer (Rudolph, S-2000). The second harmonic generation of the ONNE in LB films was observed using a Q-switched Nd:YAG laser (Continuum, NY81-10) operating at 532nm with 10ns and a repetition rate of 10Hz. p- and s-Polarized laser light was passed through the LB films at a incident angle between 0° to 50°. The p- and s-polarized second harmonic photons with the wavelength of 266nm were detected with the photomultiplier tube (PRI, P292R) and the PMT signal was processed with the 2-channel gated photon counter (SRS, SR400). The incident light of 532nm was removed by a monochromator (McPherson

2-meter UV-scanning monochromator).

RESULTS AND DISCUSSION

The π-A isotherm of ONNE shows take off area at 65Å^2/molecule and a limiting area of 32Å^2/molecule (Figure 2). Since the monolayer spreaded on the water aggregated in 30 minutes after delivering the chloroform solution of ONNE on the water surface, the transfer of floating monolayer onto the solid surface was performed within 30 minutes. Sometimes, arachidic acid was mixed with ONNE to reduce the aggregation. The aggregation behavior was significantly reduced by mixing with arachidic acid, but the transfer ratio was reduced from 0.86~0.92 for pure ONNE film to 0.52~0.6 for 1:1 mixture of arachidic acid and ONNE. The take off area of 1:1 mixture was 60Å^2/molecule, which was smaller than that of ONNE. The limiting area was 30Å^2/molecule, which was 2Å^2/molecule smaller than that of ONNE. The reduction in area/molecule of mixed monolayer was due to the small area/molecule for the arachidic acid.

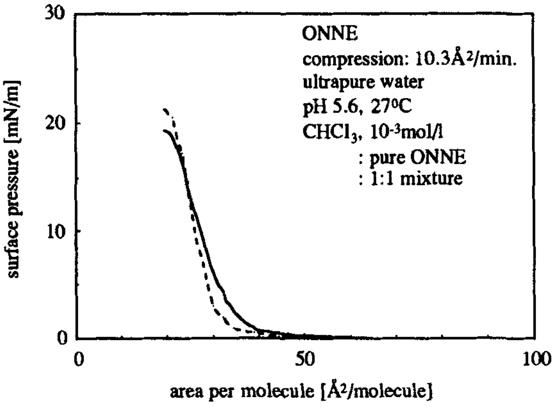

FIGURE 2. The π-A isotherms of pure ONNE and 1:1 mixture of arachidic acid.

Absorption maximum of ONNE obtained from $CHCl_3$ was 440nm, which was also the absorption maximum of LB film. A shoulder at 540nm might represents J-aggregate absorption, since the J-aggregate absorption occurred at low energy region. The peak intensity observed at 540nm was significantly reduced for 1:1 mixture film. Relative intensity of 540nm shoulder versus 440nm peak did not change much as the number of layer increased. Figure 3 represents the UV-visible absorption spectrum of the 5 layer ONNE LB film deposited on a fused quartz plate and that of $CHCl_3$ solution with a concentration of 10^{-5}mol/l.

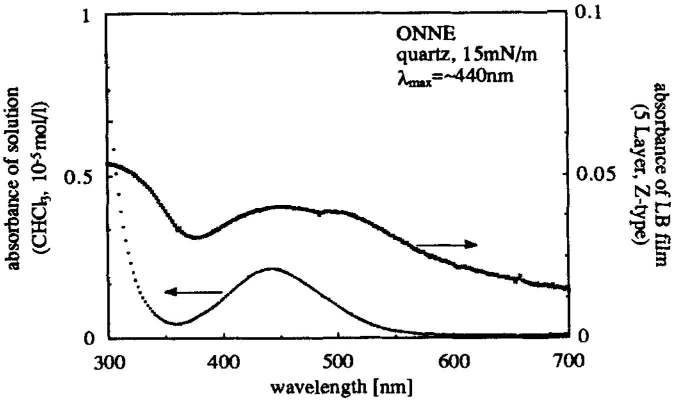

FIGURE 3. UV - visible absorption spectrum of the 5 layer ONNE LB film deposited on fused quartz plate and that of $CHCl_3$ solution with a concentration of 10^{-5}mol/l.

Thickness of one layer ONNE film was 24±1Å, which was two thirds the length of ONNE, 36Å. The small limiting area and thin thickness strongly suggest that azo chromophores significantly overlap between each other. The calculated area per azo chromophore is 64Å^2, which is twice as large as that of limiting area. Thickness of 1:1 mixture film was 36±1Å, which is close to the length of ONNE. We do not have any evidence for the tilting angle of alkyl chain. Refractive index calculated for ONNE LB film was 1.3±0.1 and that for 1:1 mixture film was 1.5±0.1. It is interesting to note that the refractive index of arachidic acid is 1.5.

Polarized visible absorption spectra showed that the dichroic ratio(A_s/A_p) was 0.6 for three layer ONNE film (Figure 4), where as A_s is the intensity of absorption of polarized light parallel to the dipping direction and A_p is that of polarized light perpendicular to the dipping direction. Since the dichroic ratio was smaller than 1.0, the tilted azo chromophore lie parallel to the moving barrier. For 1:1 mixture, dichroic ratio approached to 1, which indicated that orientation of the azo chromophores are random with respect to the dipping direction. The dichroic ratio gradually became unity as the number of layer increased up to 7 layers. The dichroic ratio of 7 layer LB film was 0.96, which indicated that the orientation of azo chromophore became random, as the number of layer was increased.

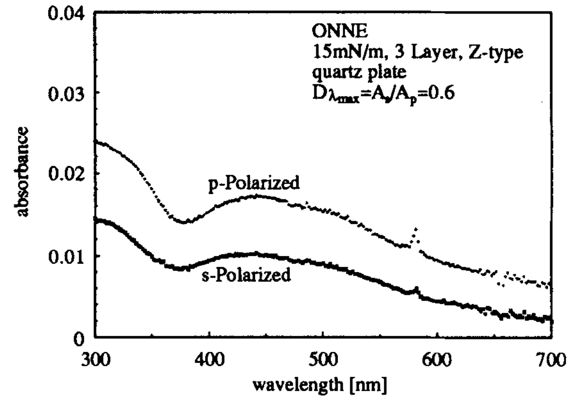

FIGURE 4. Polarized UV-visible absorption spectrum of 3 layered Z-type ONNE LB film deposited under the surface pressure of 15mN/m on the fused quartz plate

SHG signal intensity of p-polarized light was about ten times greater than that of s-polarized light at 0° incidence angle as shown in Figure 5. This indicates that the ONNE molecules orient perpendicular to the dipping direction. This results are consistent with the results obtained with polarized UV-visible spectroscopy.

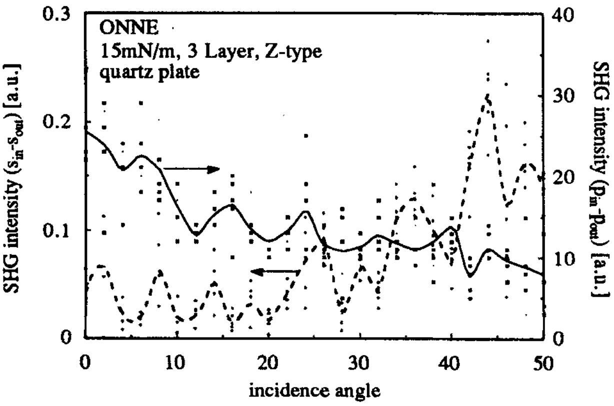

FIGURE 5. Variation of SHG intensity from an 3 layers of the Z-type ONNE LB film as a function of the incidence angle and as a function of the input and output polarization. The sample was rotated around the y-axis (dipping direction).

The fringe patterns are quite similar as the previous results.[8-11] However, the SHG intensity was quite low. This may due to the stacking between ONNE molecules and a random orientations of the chromophores. The SHG intensity of 1:1 mixture LB film was significantly lower than the pure ONNE LB film. The SHG intensity dependence on the number of layer has not observed, presumably became disorder and instability as number of layer increased.

CONCLUSION

ONNE can be layered on solid surface. ONNE chromophores in the LB film formed J-aggregate. The polarized UV-visible absorption and the SHG intensity observed from LB film indicated that in-plane orientations of azo chromophores were perpendicular to the dipping direction.

Acknowledgments

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