Synthesis and Second Harmonic Generation Studies of Langmuir−Blodgett Monolayers of 4-(*N*-Docosyl-*N*-methylamino)-β-nitrostyrene

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Received January 10, 1994. Revised Manuscript Received June 30, 1994[®]

The nonlinear optical chromophore 4-amino-β-nitrostyrene was derivatized to yield a Langmuir−Blodgett (LB) film forming amphiphillic molecule 4-(*N*-docosyl-*N*-methylamino)-β-nitrostyrene (DMANST). The Z-type LB monolayers of DMANST was transferred onto hydrophilic silica substrates and characterized by optical second harmonic generation (SHG) measurements. The SHG results reveal that the LB film of pure DMANST deposited onto a silica substrate consists of molecular inhomogeneities on a scale larger than a wavelength. The presence of a strong SHG signal for both the p- and s-polarized fundamental beams, at the normal incidence, suggests the lack of in-plane symmetry in the monolayer of pure DMANST on the silica surface. The LB film of DMANST mixed with docosanoic acid shows a SHG behavior that is pertaining to the $C_{\infty v}$ symmetry. This indicates that the symmetry in the film plane is restored in monolayers of DMANST mixed with docosanoic acid. The chromophore tilt angle of DMANST mixed with docosanoic acid is calculated to be 42° with respect to the film normal.

Introduction

Some organic materials possess nonlinear optical (NLO) responses that far exceeds that from inorganic counterparts which are presently being used as active components in electrooptic (EO) devices.[1−6] Organic materials also offer the flexibility to modify their structure and ease to process them. Organic materials, therefore, are considered to be potential candidates for their utilization into photonic and optoelectronic devices.[1−6]

4-Amino-β-nitrostyrene (ANST)[7] and its *N*-alkyl derivatives (for example, DEANST)[8] are a well-known group of compounds for their optical and NLO properties.[7−10] For example, the hyperpolarizability, β, of some (dialkylamino)-β-nitrostyrenes[7,10] is approximately 13 times larger than that of *p*-nitroaniline,[11] a NLO chromophore very often used as a standard. However, one difficulty with the compounds of *N*-alkyl derivatives of ANST is that they crystallize in a centrosymmetric space group, thus showing no second-order NLO activity in the crystalline form.[8] Therefore, the macroscopic three-dimensional arrangement of these compounds has to be controlled as to avoid centrosymmetry in order to employ them in the second-order NLO measurements.[13,14] The Langmuir−Blodgett (LB) method of depositing monomolecular layers of amphiphilic compounds, from an air−subphase interface to a solid substrate, is one of the techniques which allows fabrication of thin molecular layers of materials without introducing an inversion center in the film.[14−16]

In this paper we report the synthesis, characterization, and second harmonic generation (SHG) studies of LB films of an ANST derivative, 4-(*N*-docosyl-*N*-methylamino)-β-nitrostyrene (DMANST). We deposited monolayers of pure DMANST and DMANST diluted with docosanoic acid onto hydrophilic silica glass substrates using a vertical Z-mode transfer and characterized them by UV−visible and SHG measurements. It is shown that a pure monolayer of DMANST on silica substrates consists of molecular structures which are larger than the SHG wavelength. Upon dilution with docosanoic acid the size of molecular domains decreases and LB films begin to exhibit SH response conforming to the $C_{\infty v}$ symmetry. The DMANST chromophore in the films mixed with docosanoic acid is found to be at a 42° tilted with respect to the film normal.

[®] Abstract published in *Advance ACS Abstracts,* August 15, 1994.

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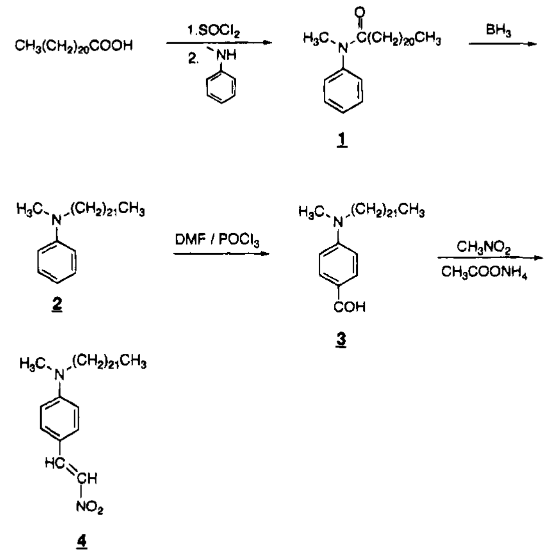

Figure 1. Synthetic scheme of DMANST.

Material Synthesis

The synthesis of DMANST was accomplished via the route shown in Figure 1. All starting materials, docosanoic acid (99%), thionylchloride (99%), *N*-methylaniline (99%), borane–tetrahydrofuran complex and phosphorous oxychloride (99%) were purchased from Aldrich Chemicals and used without further purification.

***N*-Methyl-*N*-phenyldocosanamide (1).** A mixture of docosanoic acid (50 g, 0.15 mol) and thionyl chloride (40 mL, 0.55 mol) was refluxed for a period of 16 h under nitrogen atmosphere, and excess thionyl chloride was removed under reduced pressure. Then *N*-methylaniline (21.4 g, 0.20 mol) in 100 mL of tetrahydrofuran was added dropwise into the acid chloride, during a period of 30 min, and the resulting mixture was refluxed for 16 h under nitrogen atmosphere. The solution was cooled down to the room temperature and poured into a 1:1 mixture of ethanol/water (300 mL). The solid product was isolated by filtration. The crude product was recrystallized in ethanol to obtain white crystalline solid; yield 88%, mp 61 °C. ^{1}H NMR ($CDCl_3$) δ 0.8 (t, 3H), 1.2 (s, 36H), 1.5 (m, 2H), 2.0 (t, 2H), 3.2 (s, 3H), 7.1 (d, 2H), 7.3 (d, 1H), 7.4 (d, 2H).

***N*-Docosyl-*N*-methylaniline (2).** *N*-Methyl-*N*-phenyldocosanamide (30 g, 0.07 mol) was added to a 1 M solution of borane in tetrahydrofuran (300 mL), and the mixture was refluxed for 20 h. This mixture was cooled down to room temperature. Then a solution of 6 M HCl (60 mL) was added dropwise during a period of 30 min, and the resulting mixture was refluxed for 10 min and neutralized by adding an aqueous sodium hydroxide. The white crude product was extracted from ether, dried in a rotary–evaporator and recrystallized from ethanol; yield 82%, mp 51 °C. ^{1}H NMR ($CDCl_3$) δ 0.8 (t, 3H), 1.2 (s, 38H), 1.5 (m, 2H), 2.9 (s, 3H), 3.2 (t, 2H), 6.6 (d, 3H), and 7.2 (d, 2H).

4-(*N*-Docosyl-*N*-methylamino)benzaldehyde (3). Phosphorous oxychloride (30 mL, 0.32 mol) was added dropwise into 150 mL of cold dimethylformamide in a dry ice bath under nitrogen atmosphere. Then the solution was brought up to room temperature and kept at room temperature for about 30 min. Next, *N*-docosyl-*N*-methylaniline (20 g, 0.05 mol) was added to the above mixture and stirred at a temperature of ~90 °C for 2 h. After the solution was cooled to −20 °C, water (15 mL) was added to the solution. The resulting solution was then poured into a saturated solution of sodium acetate in a 1:1 mixture of ethanol and water. After stirring the suspension for about 1 h at room temperature, pale yellow crystals were collected by filtration. The resulting product was washed with a ethanol/water solution (4:1); yield 61%, mp 68 °C. ^{1}H NMR ($CDCl_3$) δ 0.8 (t, 3H), 1.2 (s, 38H), 1.6 (m, 2H), 3.0 (s, 3H), 3.4 (t, 2H), 6.6 (d, 2H), 7.7 (d, 2H), and 9.7 (s, 1H).

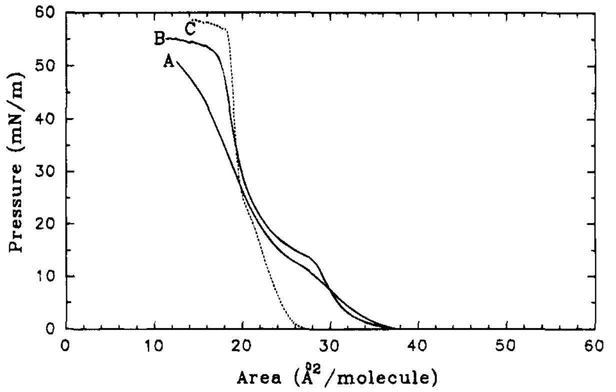

Figure 2. Surface pressure vs molecular area isotherm of (A) pure DMANST, (B) DMANST diluted with docosanoic acid (molar fraction of DMANST = 0.2), and (C) pure docosanoic acid at 293 K.

4-(*N*-Docosyl-*N*-methylamino)-*β*-nitrostyrene (4). A mixture of 4-(*N*-docosyl-*N*-methylamino)benzaldehyde (6 g, 14 mmol), ammonium acetate (0.5 g, 6 mmol), and nitromethane (40 mL) was refluxed for 20 h, cooled to room temperature, and filtered with a suction pump. The solid product was first recrystallized from acetone and then from a 1:1 mixture of acetone/chloroform. The final product is a red crystalline powder; yield 57%, mp 92 °C. ^{1}H NMR ($CDCl_3$) δ 0.8 (t, 3H), 1.2 (s, 38H), 1.6 (m, 2H), 3.0 (s, 3H), 3.4 (t, 2H), 6.6 (d, 2H), 7.4 (d, 2H), 7.5 (s, 1H), and 8.0 (s, 1H). Anal. Calcd for $C_{31}H_{54}N_2O_2$: C, 76.49; H, 11.18; N, 5.75. Found: C, 76.08; H, 11.08; N, 5.66.

The elemental analysis was carried out at Galbraith Laboratories Inc. Melting temperatures of all materials were determined by using a Fisher-Jones melting point apparatus. Proton NMR spectra were recorded on a Varian Gemini-300 spectrometer. UV–visible spectra were recorded by using a Shimadzu UV-3101 PC spectrometer.

Preparation of Langmuir–Blodgett Monolayers

The LB monolayers were fabricated in a custom-built computer-interfaced Teflon LB trough. Solutions in chloroform were spread dropwise onto a subphase of doubly distilled deionized water. The solvent was allowed to evaporate about 15 min before compression began. The film was slowly compressed (~5 Å^2 molecule^{-1} min^{-1}) while the surface pressure was continuously monitored. Typical pressure (π) vs molecular area (A) isotherm of pure DMANST, docosanoic acid, and various molar ratios of DMANST and docosanoic acid are shown in Figure 2. At 20 °C the highest pressure which the pure monolayer of DMANST at the air–water interface could tolerate without collapsing into a bulk phase is about 51 mN m^{-1}. The pressure–area isotherm of pure DMANST is irreversible below the collapse pressure. However, as the molar fraction of docosanoic acid increases the isotherm becomes reversible. This indicates the dominance of formation of molecular domains/aggregates in pure DMANST films. All films were transferred in the vertical Z-mode onto hydrophilic glass substrates at 20 °C at a constant pressure of 30 mN m^{-1}. Deposition speed was 0.5 cm min^{-1}. In a series of depositions it was found that the deposition ratio of a pure DMANST monolayer varies from run to run (0.95–1.45). However, monolayers of DMANST mixed with docosanoic acid can be deposited with a deposition ratio of almost 1 (0.98). The samples of Z-type monolayer only on one side of the substrate was prepared by carefully removing the film from the other side of the substrate by washing it with chloroform.

SHG Measurements

The SHG measurements on LB films were made with a Q-switched and mode-locked Nd^{3+}:YAG laser operating in the TEM$_{00}$ mode. Each Q-switched pulse contains about 40 mode-locked pulses having a pulse width of approximately 150 ps. The entire pulse train was utilized for the SHG experiments. When the signal levels were low as many as 500 pulse trains were accumulated for each data point. The pulses having an energy of approximately 45 μJ/pulse were focused onto the sample using a 100 cm focal length lens. The LB films were mounted on a motor-driven rotational stage, and the second harmonic signal was recorded as a function of the angle of rotation. The SH signal was guided through a series of interference filters to filter out the fundamental beam ($\lambda = 1064$ nm) and focused onto a photocathode of photomultiplier tube (Hamamatsu 2014); the resulting signal was amplified and collected with a boxcar integrator (EG&G Model 4420). The desired input and output polarizations were achieved by employing a polarizer–analyzer combination in conjunction with a half-wave plate. SHG measurements of all films were made under identical experimental conditions. The SHG signal from the LB film was normalized relative to the second harmonic Maker fringes from a 1 mm thick quartz plate ($d_{11} = 1.2 \times 10^{-9}$ esu).

Results and Discussion

In general, most of the LB films which have been investigated by the SHG possess either $C_{\infty v}$ symmetry (in-plane isotropic)[17–20] or herringbone (in-plane anisotropic)[21–24] structures. In the latter case, the in-plane anisotropy arises due to the preferential alignment of molecules along the dipping direction (The film frame is defined such that z is the surface normal and y is the dipping direction which lies in the film plane; x is perpendicular to both y and z[22,23]) during the film transfer.[21] Hence, the predominant NLO susceptibility, $\chi^{(2)}$, tensor component in herringbone type LB films is the one along the dipping direction ($\chi^{(2)}_{yyy}$). The other $\chi^{(2)}$ tensor component ($\chi^{(2)}_{yxx}$) is much smaller than the major component, $\chi^{(2)}_{yyy}$.

In the case of LB films that have a $C_{\infty v}$ symmetry their SHG activity is mainly due to the $\chi^{(2)}_{zzz}$ component of the second-order NLO susceptibility. The other nonzero $\chi^{(2)}$ tensor component, $\chi^{(2)}_{zxx}$ (where $\chi^{(2)}_{zxx} = \chi^{(2)}_{zyy} = \chi^{(2)}_{xzx} = \chi^{(2)}_{yzy}$, by assuming Kleinman conditions[25]) are much smaller than the $\chi^{(2)}_{zzz}$ component. If the LB film possesses a $C_{\infty v}$ symmetry either the Z-type or the X-type deposition has to be followed to obtain a noncentrosymmetric multilayer LB film since the Y-type deposition very often introduces an inversion center in the film.[15].

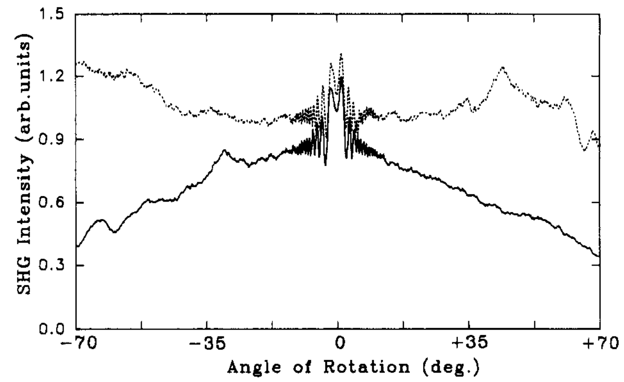

Figure 3. Second harmonic intensity from a monolayer (coated on both sides of the substrate) of DMANST as a function of the angle of rotation for different input and out put polarizations (solid line = P_{in}/P_{out}; broken line = S_{in}/S_{out})

The SHG behavior of a Z-type monolayer of pure DMANST is shown in Figure 3. It is clear that if the fundamental beam is polarized in the plane of incidence the SHG signal from monolayer peaks out at the normal incidence and gradually decreases as we deviate from the normal incidence. If the fundamental beam is polarized in the plane perpendicular to the plane of incidence, the SHG signal shows no apparent variation with the angle of incidence (in our experimental geometry the incidence angle is the one between the surface normal and the direction of beam propagation). These results cannot be explained by assuming either the $C_{\infty v}$ symmetry or the herringbone structure for the film. The lack of well contrasted interference fringes in monolayer deposited on both sides of the substrate indicate the presence of molecular inhomogeneities on a scale larger than the SHG wavelength.[26,27]

At the normal incidence the SHG activity arises due to only the $\chi^{(2)}_{xxx}$ component (when both the fundamental and the SH beams are p-polarized) and $\chi^{(2)}_{yyy}$ component (when both the fundamental and the SH beams are s-polarized) of the NLO susceptibility tensor. If the monolayer possesses the $C_{\infty v}$ symmetry, no SHG signal is expected at the normal incidence for above indicated input–output polarization combinations. Therefore, the SHG measurements show the breakdown of the symmetry in the plane of the film in pure DMANST monolayer on silica surface.

In the case of the $C_{\infty v}$ symmetry the $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}$ tensor components can be determined by measuring the p-polarized SHG intensity in the film generated by p- and s-polarized fundamental beams, respectively.[19,21] When DMANST is diluted with docosanoic acid, the SHG signal from the film gradually changes to conforming to the $C_{\infty v}$ symmetry as the molar percentage of docosanoic acid increases. The p-polarized SHG intensity of monolayer of DMANST mixed with docosanoic

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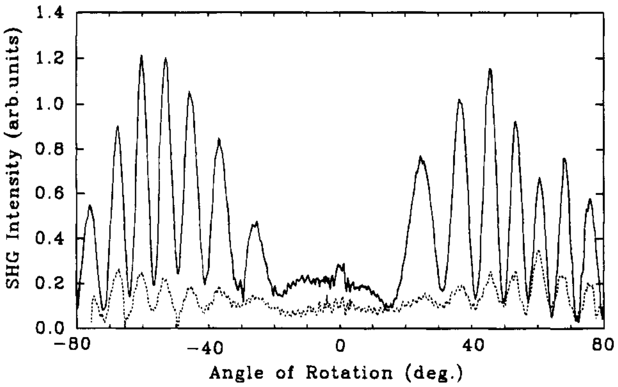

Figure 4. Second harmonic intensity from a monolayer (coated on both sides of the substrate) of DMANST mixed with docosanoic acid (molar fraction of DMANST = 0.2) as a function of the angle of rotation for different input and out put polarizations (solid line = P_{in}/P_{out}; broken line = S_{in}/P_{out})

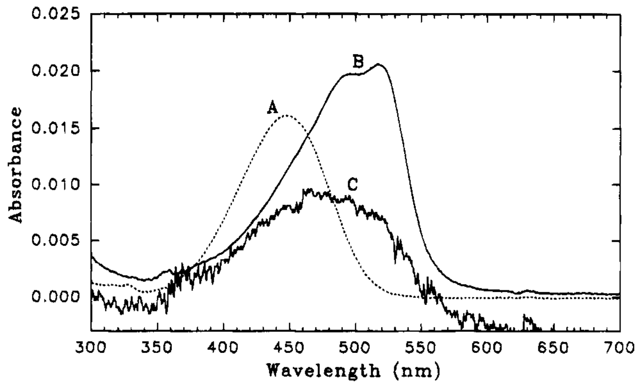

Figure 5. UV–visible spectra of DMANST: (A) in chloroform solution, (B) a Z-type monolayer on a hydrophilic silica substrate, and (C) a Z-type monolayer of DMANST mixed with docosanoic acid (molar fraction of DMANST = 0.2). Spectra of transferred monolayers were recorded by using a bare substrate as a reference.

acid, coated on only one side of the substrate, is found to be zero at the normal incidence and peak outs around ±60° for both p- and s-polarized fundamentals as the angle of incidence is scanned. Also, the SHG output from monolayers that are coated on both sides of the substrate generates distinct interference fringes[27] and the angle of incidence is varied (Figure 4). These results indicate the dominance of $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}$ tensor components over the in-plane components $\chi^{(2)}_{xxx}$ and $\chi^{(2)}_{yyy}$. Therefore, the symmetry in the film plane (azimuthal symmetry) is lifted indicating a drastic change in the orientation of DMANST chromophores upon the dilution with docosanoic acid. Hence, we note that hereafter the analysis of the SHG results are made by assuming a $C_{\infty v}$ symmetry for the monolayers, although that Kleinman's conditions[25] are not satisfied for the monolayers of DMANST mixed with docosanoic acid (as shown in Figure 5, the optical spectrum of monolayer transferred onto hydrophilic silica substrate exhibits a considerable absorption of the second harmonic light).

The SHG measurements (made at an incidence angle of 45°) on a monolayer of DMANST mixed with 80% of docosanoic acid, deposited only on one side of the substrate yield a value of 2.2×10^{-8} esu for $\chi^{(2)}_{zzz}$ and a value of 8.9×10^{-9} esu for $\chi^{(2)}_{zxx}$. Therefore the ratio of $\chi^{(2)}_{zxx}/\chi^{(2)}_{zzz}$ (=0.40) is clearly indicative of the invalidity of Kleinman symmetry[26] conjecture for these monolayers. It should be noted that we have assumed a refractive index of 1.5 for n_{ω} and a refractive index of 1.7 for $n_{2\omega}$ (based on typical refractive indexes assumed for monolayers with similar absorption profile[28]) in calculating above indicated NLO coefficients. By assuming that molecular NLO susceptibility has only one nonzero component (i.e., $\beta = \beta_{\xi\xi\xi}$ where ξ is the molecular axis), we obtain a value of 42° for the tilt angle θ (angle between the film normal and the molecular axis) of DMANST chromophores with the use of relationships $\chi^{(2)}_{zzz} = N\beta_{\xi\xi\xi}\langle\cos^3\theta\rangle$ and $\chi^{(2)}_{zxx} = 0.5N\beta_{\xi\xi\xi}\langle\cos\theta\sin^2\theta\rangle$. (It should be noted that we have neglected the local field factors and assumed that all the chromophores have the same tilt angle).[19] Therefore, it is concluded that molecular inhomogeneities in LB films of pure DMANST is diminished and chromophores under go substantial orientational changes upon dilution with docosanoic acid.

Conclusions

We have fabricated Z-type monolayer LB films of the newly synthesized amphiphilic molecule 4-(*N*-docosyl-*N*-methylamino)-β-nitrostyrene (DMANST). A monolayer of pure DMANST, transferred onto a hydrophilic silica substrate, consists of molecular inhomogeneities on a scale larger than the optical wavelength used. Molecular inhomogeneities of LB films of DMANST can be greatly reduced by mixing with a fatty acid, an example being docosanoic acid. The SHG behavior of LB monolayers DMANST mixed with docosanoic acid can be explained by assuming a $C_{\infty v}$ symmetry for the film. This indicates that a drastic change in the orientation of DMANST chromophore can be achieved by mixing them with a long-chain fatty acid.

Acknowledgment. This research was supported by the Defense Initiative Organization, the Office of Innovative Science and Technology and the Air Force Office of Scientific Research, Directorate of Chemical Sciences through Contract F49620-91-C-0053.

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