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Formation of Langmuir–Blodgett thin film of a novel *N*-dodecylphthalimide

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Abstract

The aim of this work is to investigate the Langmuir–Blodgett (LB) thin film preparation of a novel *N*-dodecylphthalimide (NDP). Langmuir properties of this new molecule are studied at the air–water interface recording isotherm graph. Atomic Force Microscopy and Quartz Crystal Microbalance measurement systems are employed to study the LB film deposition process. This newly synthesized NDP molecule can be used as an LB film material and a uniform LB film monolayer at the water surface can be transferred with a transfer ratio of over 0.90 onto a glass or quartz crystal substrates.

Keywords: Phthalimide; Langmuir–Blodgett thin film; Langmuir properties

1. Introduction

Phthalimide and *N*-substituted phthalimides have an interesting class of organic compounds because of their potential application in a wide range of several fields such as medicine, pharmacology, biology, chemistry and physics etc. *N*-substituted phthalimide derivatives were first examined by Chapman et al. [1] for their hypolipidemic activity and it was found that *N*-butyl- and *N*-pentylphthalimides were effective in reducing serum cholesterol levels by 46% and 42%. Couple of years later, *N*-arylphthalimides have been used and the most potent product, *o*-(*N*-phthalimido) acetophenone, was shown to lower both serum cholesterol and triglyceride levels by 57% and 44% and it was shown that replacement of one of the oxygen atoms of the carbonyl groups by NH in phthalimide was effective in reducing serum cholesterol (44%) [2].

Another phthalimide and its derivatives are used in the synthesis of antimicrobial activity, antiandrogens and other agents for treating tumour necrosis factor [3]. Some of phthalimide derivatives are widely used as herbicides and for reducing bacterial contamination. These materials are acting like bleaching detergents, anion exchange resins, antidepressants, heat resistant polymers, flame-retardants [3]. Lee and his group synthesized phthalimide-based polymeric drugs with anticancer drugs such as 5-fluorouracil (5-FU) for the improvement of the biological profile of 5-FU. Such polymers have been found to be efficient carriers of 5-FU, retaining its antitumor activity while decreasing its toxicity. They also reported the synthesis and antitumor activity of polymers containing camptothecin based on the tetrahydrophthalimide template. 3,6-endo-methylene-1,2,3,6-tetrahydrophthalimidoacetamidoglycine camptothecin ester (ETPA-gly-CPT) from camptothecin and 3,6-endo-methylene-1,2,3,6-tetrahydrophthalimidoacetamido glycine are synthesized and their homo- and copolymer with acrylic acid (AA) were prepared by photopolymerization method. The content of ETPA-gly-CPT in poly(ETPA-gly-CPTco-AA) was found to be 40 wt.%. The range of IC50 values obtained from the in vitro test for ETPA-gly-CPT, poly(ETPA-gly-CPT), and poly(ETPA-gly-CPTco-AA) were from 9.4 to 99.8 ng/ml against cancer cell lines. In a normal cell, the cytotoxicity of monomer was stronger than those of its homopolymer and its copolymer [4]. Recently, the synthesis and hypolipidemic activity of five *N*-phthalimidomethyl glycosides have been reported by Sena et al., their results show a lower diminution of cholesterol, but higher decrease in triglyceride levels [5]. Also phthalimides are widely used in many countries for foliage protection of fruit and ornamental plants [6].

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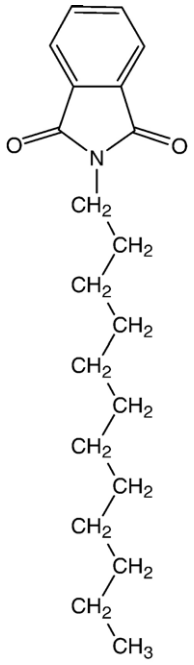

Fig. 1. The chemical structure of material.

N-l-phenylphthalimide, *N*-adamantylbenzamide and *N*-1-adamantyl phthalimide derivatives are synthesized by Derpoorten et al. and these compounds are used against HIV-l and HIV-2 in CEM cells [7].

There is very limited information in the literature on the study of phthalimide-based materials as a Langmuir–Blodgett thin film. However the 3-morpholinylphthalimide and phthalanhydride derivative films deposited on hydrophobic substrates

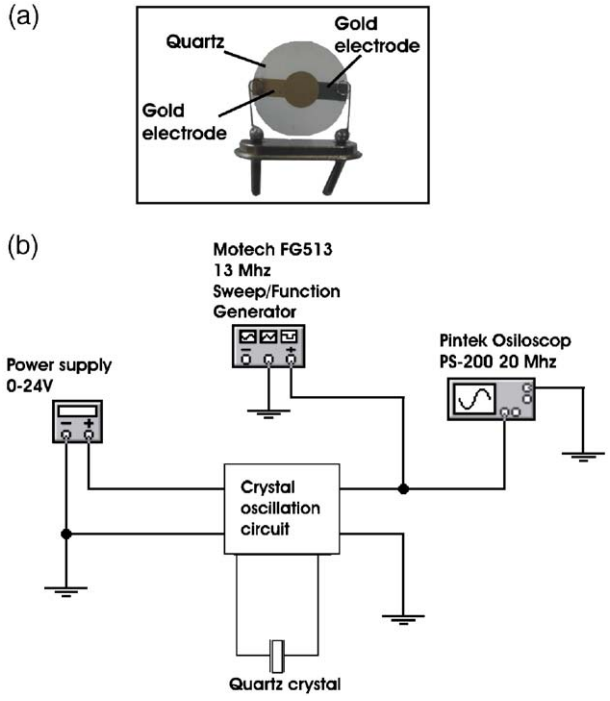

Fig. 2. a) Quartz crystal sandwiched between two electrodes. b) The QCM measurement system.

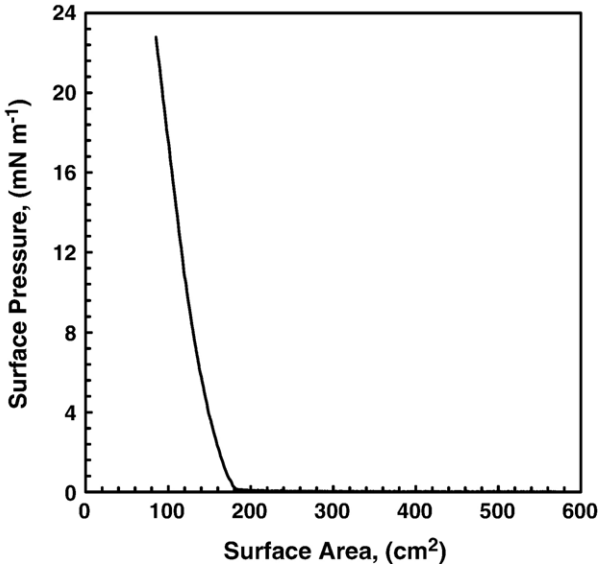

Fig. 3. Isotherm graph of NDP.

or substrates covered with Langmuir–Blodgett (LB) films are studied using linear dichroism measurements, X-ray diffraction, and electron microscopy methods [8].

Langmuir monolayers of a soluble fluorine containing poly (amide–imide)s were studied at the air/water interface and the monolayers were generally stable and were transferred onto solid substrates to produce Langmuir–Blodgett (LB) multilayers [9]. 2,3-bis(*N*-(3-thiopropyl)phthalimido)-7,8,12,13,17,18-hexakis(octylthio)-5,10,15,20-tetraaza-porphyrinato (TAP) copper (LI) and nickel(II) derivatives were studied at the water–air interface and the improved ordering in the LB film fabrication reached with the unsymmetrical substitution as being due to the presence of the hydrophilic phthalimide moieties [10].

In the present work, an investigation of Langmuir properties for a newly synthesized *N*-dodecylphthalimide (NDP) material will study and make an organisation of this molecule as an LB monolayer at the air–water interface. Ultra-thin Langmuir–Blodgett films will be fabricated onto a glass and quartz crystal substrates with a computer controlled LB film trough. Quartz Crystal Microbalance and Atomic Force Microscopy will be used to investigate the reproducibility of an LB film using NDP material.

2. Experimental details

LB films were prepared at a quartz and glass substrates using a NIMA 622 type alternate layer LB trough for QCM and AFM measurements. Fig. 1 shows the chemical structure of the NDP material that was synthesized from the reaction of phtaloyl-dichloride (5 mmol from Merck) and dodecylamine (5 mmol from Fluka) in tetrahydrofurane (100 ml) at the room temperature. For the neutralization of released HCI, triethylamine (15 mmol from Merck) was added drop wise to the reaction media in the first 30 min of the reaction. After a waiting time of 24 h, the triethylamine salts were filtered off and the solvent was evaporated under reduced pressure. The highly pure product was obtained by the recrystallisation of the crude product from the hexane as white needles.

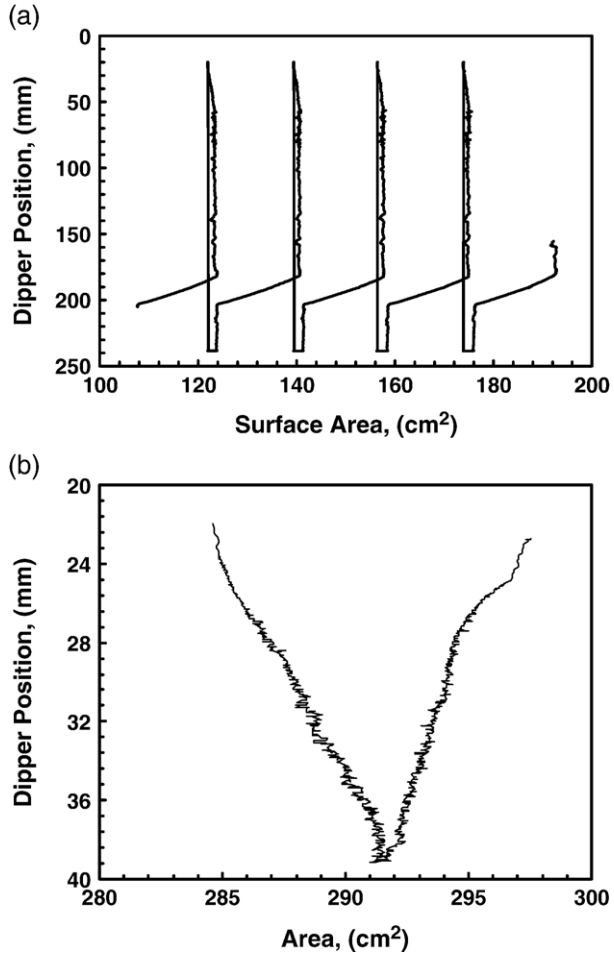

Fig. 4. Deposition graph of NDP film; a) glass substrate, b) quartz substrate.

NDP was dissolved in chloroform with a concentration of 0.4 mg ml^{-1}. The solution was spread onto the water surface using a microlitre syringe and approximately 15 min were allowed for the chloroform to evaporate. The Π-A isotherm graph of NDP was recorded as a function of surface area at

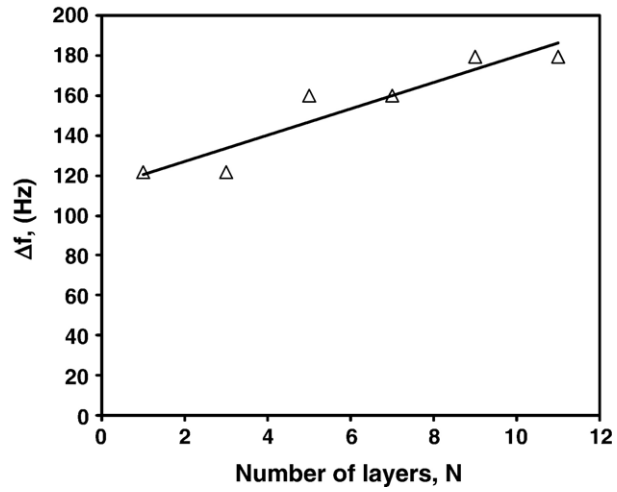

Fig. 5. A plot of the change in the resonant frequency as a function of number of layers.

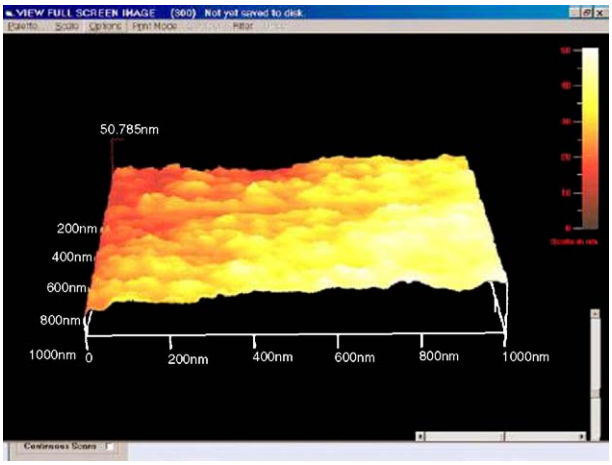

Fig. 6. AFM imagine for 15 layer LB film sample.

pH 6.0. Isotherm graph was taken several times at room temperature using Lauda Ecoline RE 204 model temperature control unit and the results were found to be reproducible.

Monolayers at the water surface were sequentially transferred onto glass and quartz crystal substrates by the alternate layer LB deposition procedure. Fig. 2 shows the QCM measurement system. QCM measurements were performed at room temperature using an in-house designed oscillating circuit and standard quartz crystal with a nominal resonance frequency of 9 MHz. The frequency was measured with a MOTECH FG-513 model function generator and TEKTRONIX TDS 210 model digital oscilloscope. Atomic Force Microscopy pictures were taken by using a Quesant 350 Scanning Probe Microscope. The scale is set in such a way that light colours correspond to higher structures. The images were taken by using a standard silicon nitride tip (constant force 12 N m^{-1}) in the contact mode.

3. Experimental results

The surface pressure as a function of surface area called isotherm (Π-A) graph of NDP molecule was recorded at room temperature and is given in Fig. 3. The surface pressure starts rising around 170 cm^2 shown in Fig. 3. After this point, Π-A isotherm graph has a fast surface pressure increasing during a reduction of the surface area. The surface pressure for the deposition of LB film monolayer at solid phase region is selected at 15 mN m^{-1} and all deposition processes were carried out at this surface pressure value.

The reduced surface area change of the float monolayer during the deposition onto a glass substrate for 5 monolayers is shown in Fig. 4(a). It can be seen that the average reduction of the area for each layer was almost the same during the deposition process of monolayers onto a glass substrate. This can be explained that the similar amount of materials is deposited onto glass substrates. For each monolayer, the average reduced area is calculated ~16.5 cm^2/monolayer and the transfer ratio, τ, for a glass substrate is found to be over 90%.

Fig. 4(b) indicates the reduced surface area during the deposition process for two layers of NDP molecules for QCM crystal. The transfer ratio for a QCM substrate is found to be similar to the glass substrate. These results are supported by the transfer ratio obtained from LB film system and the transfer ratio of each deposition for both substrates is calculated >0.90. These results indicate that a stable monolayer of NDP formed on the water subphase and a uniform LB deposition occurred

onto a glass or QCM crystal substrates. Similar study was carried out by Onah et al. for a soluble fluorine containing poly(amide–imide)s, PAI(1–4). Their results showed that the LB monolayer at the water–air interface is stable and is transferred onto solid substrates to build up Langmuir–Blodgett (LB) multilayers [9].

The deposition of LB film layer is also monitored to check reproducibility of LB film by QCM measurement system that can detect a small mass change. This ability helps to check reproducibility of multilayer LB film. QCM system consists of a thinly AT-cut quartz sandwiched between two electrodes and this quartz crystal resonates at an extremely well-defined frequency when it is placed in an electronic circuit shown in Fig. 2. This frequency called resonant frequency depends on the area of the electrodes and thickness of the quartz.

The linear relationship between mass change Δm and change of frequency Δf is first shown by Sauerbrey [11].

$$\Delta f = \frac{2f_0^2 \Delta m}{\rho_q v_q A} \tag{1}$$

f_0: initial resonant frequency of quartz crystal, ρ_q: density of quartz, v_q: propagation speed of acoustic waves in the quartz, A: electrode area.

For an LB film, frequency change related with the mass of the bilayer. Therefore Δf should be directly proportional with the number of layer.

$$\Delta f = \frac{2f_0^2 \Delta m}{K_q} N \tag{2}$$

N is the number of deposition layers, Δm is the mass per unit area per layer. $K_q = \rho_q v_q$. As a result of this equation, LB film reproducibility can be controlled by a change of frequency against number of layers.

Resonant frequency of quartz crystal coated LB film layers using NDP molecule was recorded as a function of number of layers. Fig. 5 displays a linear relationship that can be explained an equal mass per unit area deposited onto the quartz crystal during the transfer of each bilayer. The mass deposited on the quartz crystal per bilayer is found to be 29 ng using Eq. (2). These results show that a newly synthesized NDP molecule can be used as a thin film material such as other phthalimide molecules [8,10].

The surface morphology of 15 layer NDP LB film deposited onto an optically flat hydrophilic glass substrate is carried out using an atomic force microscope in contact mode. Fig. 6 shows the AFM picture of LB film deposited at a rate of 1000 mm min^{-1} and AFM image indicates a smooth, compact, uniform and void free morphology with a root-mean-square (rms) value between 1.5 and 2.0 nm.

4. Conclusion

A novel *N*-dodecylphthalimide molecule synthesized from the phtalic anhydride and dodecylamine in toluene as an LB film material is investigated at the air–water interface using a Langmuir–Blodgett thin film deposition technique. Isotherm graph for NDP molecule is recorded and NDP monolayer at the water surface was successfully deposited onto a glass and quartz crystal substrate with the transfer ratio of over 0.90. Our AFM and QCM results show that a uniform LB film can be fabricated from a novel NDP material. Our future work will be focused on the potential application of this NDP material such as bio- or gas sensor properties.

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