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Synthesis and Langmuir-Blodgett (LB) Film Properties of Functional α,ω-diamine Amphiphilic Materials

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SUMMARY: We have investigated the synthesis and ultrathin film forming properties of α,ω-diamine derivatives. The amphiphiles were synthesized as precursors to the formation of ionene polymers. Two materials were investigated: oligothiophene and azobenzene functional groups. These type of materials are of great interest for the preparation of ultrathin film layers with applications for photochemical regulation of liquid crystal (LC) orientation, optical storage media, and electroluminescent displays. Azobenzene and its derivatives are well known photochemical systems exhibiting the reversible *cis-trans* photoisomerization. Conjugated oligothiophene derivatives, exhibit interesting optical and electronic properties for applications such as light emitting diodes (LED)s, Schottky diodes, and thin film field-effect transistors (TFT). The two amphiphiles behaved very differently as Langmuir monolayers and LB films. Dye aggregation was observed with the azobenzene derivatives compared with the oligothiophenes.

Introduction

The investigation of functionalized oligomers has recently gained much attention due to their analogous properties with monodispersed polymer systems and interesting electro-optical and display properties.1) The oligomers themselves become telechelic when functionalized at the end groups or can act as macromonomers. The telechelic functionality is attractive for further polymerization reactions and utility in copolymer architectures. As amphiphiles, oligomers are capable of surface activity, thereby allowing manipulation at interfaces for molecular ordering or film formation. The application of molecular and macromolecular assembly techniques2) has proven to be an excellent alternative to casting and evaporation techniques in preparation of ultrathin films for electro-optical and display applications. The Langmuir-Blodgett-Kuhn (LBK) technique

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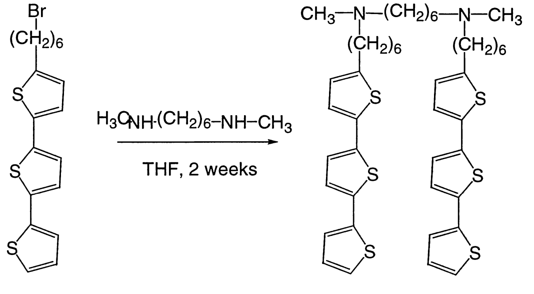
is still one of the most viable techniques for inducing order at the monomolecular layer level.[3] The formation of highly ordered multilayers is preceded by careful investigations of Langmuir monolayer film and adsorption behavior at the air-water interface. In this report, we focus on the synthesis, characterization, and LB studies of functional diamine amphiphiles. These amphiphiles consists of two types: oligothiophene and azobenzene dyes. Their aggregation, monolayer, and multilayer film properties are compared.

Conjugated oligothiophene derivatives, exhibit interesting optical and electronic properties,[4] for applications such as light emitting diodes (LEDs)[5], Schottky diodes[6], and thin film field-effect transistors[7]. The α,ω alkyl derivatives of sexithienyl are another class of compounds that have been reported to form well-ordered structures.[8] Oligothiophenes are also electrochemically active species, which makes them ideal for sensors and oxidative reactions in solutions or films.[9] We have reported the synthesis of functional oligothiophenes, (Figure 1) [10] as precursors for the formation of ionene polymers.[11] It is our objective to investigate functionalization of oligothiophene derivatives to achieve amphiphilicity and application to molecular and macromolecular assembly techniques in thin films.



5-(6-bromohexyl)-2,2’;5’,2" -terthiophene

N, N’-dimethyl-N,N’-bis(6-(2,2’;5’,2";5",2"’;5"’,2"" -terthiophene)hexyl)-1,6-hexanediamine

Fig. 1: Synthesis scheme for the terthiophene diamine derivative *N,N'*-dimethyl-*N,N'*-bis (6-(2,2’;5’,2"; 5",2"’;5"’,2""-terthiophene) hexyl)-1,6-hexadiamine.

We also describe the synthesis and characterization of diamine amphiphiles with azobenzene dye moieties. These types of materials are of great interest for the preparation of ultrathin film layers with applications for photochemical regulation of liquid crystal (LC) orientation and optical storage media.[12,13,21] Azobenzene and its derivatives are well known photochemical systems exhibiting the reversible *cis-trans* photoisomerization.

The Z isomer can be induced upon irradiation with UV light towards π-π* excitation and reversed upon heating or irradiation with visible light for the n-π* state. For photochromic command surface layer applications, the surface should contain highly photoreactive units. There have been several studies in our groups on the photoisomerization of azobenzene derivatives in molecularly thin films such as LB and self-assembled films.[13 - 14)]

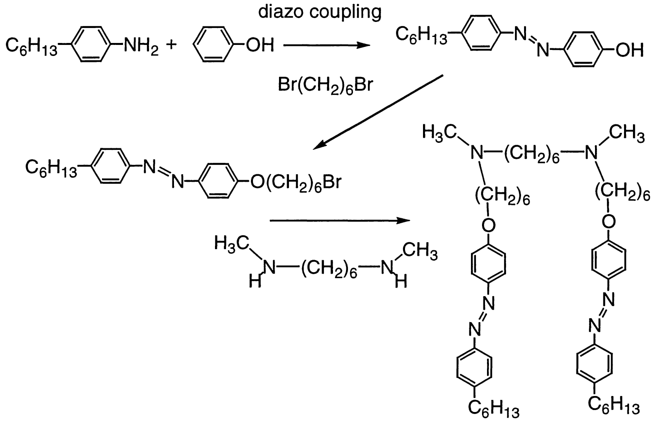


Fig. 2: Synthesis scheme of *N,N'*-dimethyl-*N,N'*-bis-(6-(4',4"-hexylazo benzene) hexyloxy)-1,6-hexanediamine.

Experimental

Materials. All essential chemicals and reagents were purchased from Aldrich Chemical Co. and used as received. Purification of solvents was done with standard distillation techniques and addition of drying agents. All of the reactions were carried out under nitrogen atmosphere. For monolayer experiments, Milli-Q quality water (greater than 18 MΩ) was used as subphase (pH=5.7). HPLC grade chloroform was used as spreading solution (0.5 mg/ml concentration) and added dropwise to the surface of the trough.

Instrumentation. NMR (Bruker 400 MHz), IR (Bruker Vector 22), UV-vis (Perkin Elmer Lambda 20), ellipsometry (Microphotonics SE400), Atomic Force Microscopy (AFM) (PicoScan Molecular Imaging). For monolayer investigations, the KSV LB 2000

Dipping trough was used under a laminar flow hood and vibration free platform. Surface pressure area isotherms, isobaric creep measurements, and compression-expansion cycles (hysteresis) were investigated.

Synthesis of 5-(6-bromohexyl)-2,2':5',2"-terthiophene. Terthiophene (4.7g, 19.3mmol) was dissolved in THF (150mL) and cooled to -78°C in a dry ice and methanol bath. n-BuLi (7.72mL, 19.3mmol) was then added using a syringe. This mixture was allowed to stir for 45 minutes, after which, 1,6-dibromohexane (11.79g, 48.3mmol., 1.5X) was added using a syringe and the reaction allowed to sit overnight and come to room temperature. The product was purified primarily by recrystalization from hexane giving a product that ranged in color from greenish-yellow to brown in color. This product was characterized by NMR ($CDCl_3$) δ 1.5(m, alkyl C3-C4); δ 1.7(p, alkyl C2); δ 1.9(p, alkyl C5); δ 2.8(t, alkyl C1); δ 3.4(t, alkyl C6); δ 6.7(t, thienyl); δ 7.0(m, thienyl); δ 7.14(dd, thienyl); δ 7.23(dd, thienyl). UV($CHCl_3$) λmax=361 nm.

Synthesis of *N,N'*-dimethyl-*N,N'*-bis (6-(2,2';5',2"; 5",2"';5"',2""-terthienyl) hexyl)-1,6-hexanediamine. The reaction with a diamine derivative was followed according to literature.[15] This product was characterized by ^{1}H-NMR($CDCl_3$), δ(7.18, dd, 2H), δ(7.12, dd, 2H), δ(6.97, m, 8H), δ(6.94, d,2H), δ(2.77, m, 12H), δ(2.62, s, 6H), δ(1.87, m, 8H), δ(1.64, p, 4H), δ(1.37, m, 12H) and UV-vis in $CHCl_3$, λ_{max}=364nm.

Synthesis of 4-(6-bromohexyloxy)-4'-hexylazobenzene. This begins with preparation of the 4-Hydroxyphenylazophenol derivative (prepared by azo-coupling of phenol with hexylaniline). To 4.0 g (14.4 mmol) of 4-hydroxy-4'-hexylazobenzene, 3.2 g (23.2 mmol) of potassium carbonate in 20 ml of DMF was added dropwise to 34.5 g (0.141mol) of 1,6-dibromohexane and stirred magnetically at 90 °C for 10 h. To the stirred reaction mixture, ethyl acetate was added and the precipitate was filtrated. The solution was washed with water and dried over anhydrous sodium sulfate, followed by removal of the solvent, a red liquid product with excess of 1,6-dibromohexane was obtained. The removal of 1,6-dibromohexane by heating in vacuo gave a crystalline mass which was recrystallized from ethanol to yield 5.8 g of the 4-(6-bromohexyloxy)-4'-hexylazobenzene. Mp 53 °C. ^{1}H-NMR ($CDCl_3$) (ppm): 0.89 (3H, t, CH_3-C), 1.3-1.9

(16H, m, C-CH_2-C), 2.67 (2H, t, CH_2-arom), 3.44 (2H, t, CH_2-Br), 4.05 (2H, t, O- CH_2), 6.99 (2H, d, H arom), 7.30 (2H, d, H-arom), 7.81 (2H, d, H-arom), 7.91 (2H, d, H-arom).

Synthesis of *N,N'*-dimethyl-*N,N'*-bis-(6-(4',4"-hexylazo benzene) hexyloxy)-1,6-hexanediamine. The reaction involved also involved the literature procedure utilizing the bromoalkylazobenzene derivative and *N*, *N*-dimethyl-1, 6-hexanediamine and characterized by NMR, IR, and UV-vis.16) ^{1}H-NMR($CDCl_3$)(ppm): 0.90(6H, t, C-CH_3), 1.87-1.33(40H, m, C-CH_2-C), 2.37(6H, s, CH_3-N), 2.69(4H, t, CH_2-arom), 4.04(4H, t, O-CH_3), 7.01(4H, d, H-arom), 7.30(4H, d, H-arom), 7.81(4H, d, H-arom), 7.91(4H, d, H-arom) and UV-vis in $CHCl_3$, λ_{max}=352nm.

Results and Discussion

The diamine derivatives were synthesized and characterized. Sufficient purity was established by NMR, UV-vis, IR, and elemental analysis. The monolayer properties were then investigated at the air-water interface.

1. Diamine-azobenzene Monolayers. Figure 3 shows a typical isotherm with a compression rate of 1.5 $Å^2$ /molecule x min. at 24°C. The monolayer of the diamine-azobenzene showed a steep rise in surface pressure without a phase transition. The molecular cross-section area of about 43 $Å^2$, indicates that the side chains are closely packed accounting for the two azobenzene moieties of the diamine. The limiting area varied with the rate of compression (0.1 to 10 $Å^2$ /molecule x min) to within 1.2 $Å^2$. The collapse pressure, which is about 46 mN/m, does not significantly change with the compression rate. As the spreading amount is increased, the limiting molecular area decreased to within 1 $Å^2$. The trends of limiting molecular area change dependent on barrier speed and spreading amount has been previously observed on azobenezene amphiphiles.17) With π-A isotherms at different temperatures; 14°C, 24°C and 34 °C, the shape of the curves and the limiting molecular areas did not change significantly but the collapse pressure slightly increased with higher temperature.

Compression-expansion experiments were carried out to evaluate the stability of monolayer up to various surface pressures. Repeated cycles (hysteresis) showed a *non-*

instantaneously reversible behavior$^{18)}$ with a compression-expansion rates of up to 7.5 Å^2 /molecule x min. This was observed between 10-25 mN/m However at pressures very near the collapse, the expansion cycle did not follow the trace of the compression indicating that the monolayer could not form an observable gaseous phase , i.e. is exhibiting the formation of nearly collapsed domains. Considering all these results, the diamine-azobenzene is capable of forming a closely packed monolayer at the air-water interface.

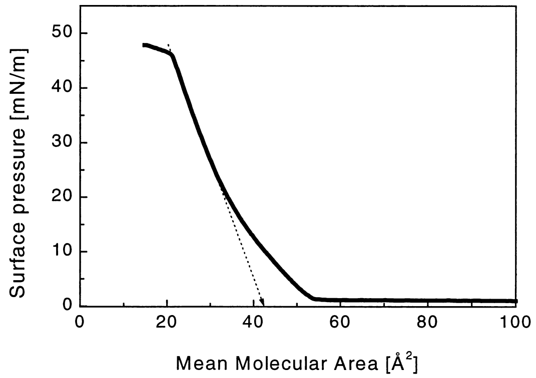


Fig. 3: A typical isotherm of the diamine-azobenzene with a compression rate 1.5 Å^2 /molecule x min. at 24°C. The monolayer molecular cross-section area is about 43 Å^2

2. Diamine-terthiophene Monolayers. Figure 4 shows the isotherm recorded at a compression rate of 1.5 Å^2 /molecule x min. at 24°C. Similar to the diamine-azobenzene monolayer it showed a steep rise in surface pressure without a phase transition. The molecular cross-section is about 38 Å^2, but varied significantly with the rate of compression (0.1 to 10 Å^2 /molecule x min) to within 3 Å^2 . No particular collapse pressure was identifiable but only a minimal inflection point near 15 mN/m and 25 Å^2. Usually, the collapse pressure provides valuable information on the stability of a monolayer; the higher the collapse pressure, the more stable the monolayer. The absence of a defined collapse point indicate a less stable monolayer compared to the diamine-azobenzene. This is likely considering the absence of an alkyl chain on the hydrophobic terthiophene group. The isotherms are also dependent on different spreading amounts. When 200 μl of spreading amount was spread, the limiting molecular area decreased significantly to 34 Å^2 The π-A isotherms also showed strong temperature dependence, shifting to lower limiting areas with decreasing temperature. However, compression-expansion isotherms were observed to be *reversible* at pressures below 15 mN/m but became *irreversible* beyond. This behavior is contrary to what would be expected with an unstable monolayer. Nevertheless, all this characteristics indicate the formation of a poor monolayer for the diamine-terthiophene despite a reversible hysteresis observed.

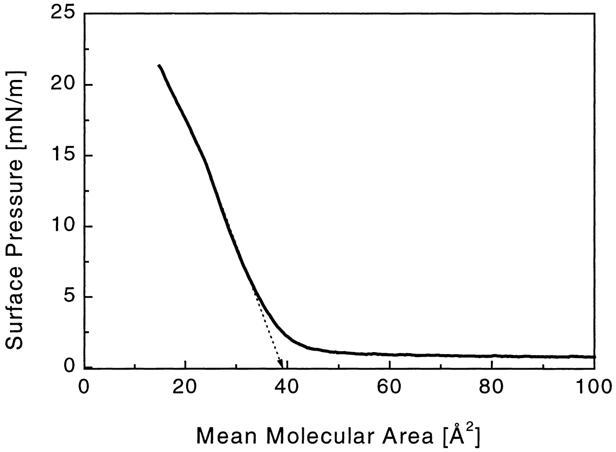


Fig. 4: The diamine-azobenzene monolayer isotherm recorded at a compression rate of 1.5 Å^2/molecule x min. at 24°C. The molecular cross-section is about 38 Å^2

To compare the stability between the two diamines, isobaric creep measurements were performed. Figure 5 shows the time -relative area (A/A_0) plots at constant surface pressure 11 mN/m, and 40 mN/m for diamine-terthiophene and diamine-azobenzene, respectively. At constant pressure, the mean molecular area of the diamine-azobenzene decreased to 16%, whereas that of diamine-terthiophene decreased up to 23%. This clearly indicates that the monolayer of diamine-terthiophene is much less stable than that of diamine-azobenzene. This also indicates that multilayer deposition is possible for the diamine-azobenzene with the LB technique. The role of the diamine is unclear compared to other hydrophilic groups, e.g. carboxylic acid. Comparison of monolayer film behavior can be made on the basis of the absence of H-bonding for the diamine.17)

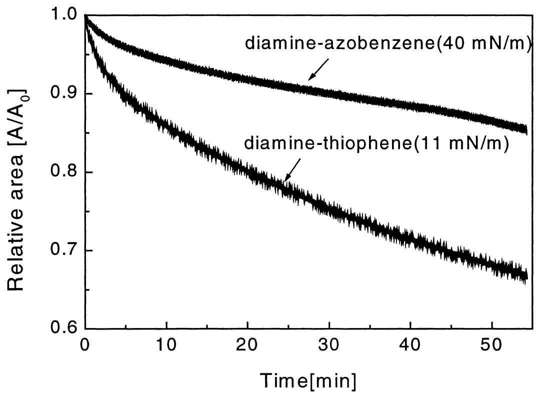


Fig. 5: Relative area (A/A_0) of the diamines versus time at constant pressures: 11 mN/m, and 40 mN/m for diamine-terthiophene and diamine-azobenzene, respectively

3. Langmuir-Blodgett (LB) Film Studies.

Damine-azobenzene LB Films. Monolayers of diamine-azobenzene was transferred onto a hydrophilic substrate at a constant pressure of 32 mN/m. The transfer ratio of first layer was between 1.0 to 1.2 (on several attempts), but the second layer had a negative transfer ratio indicating poor deposition on the downstroke mode, i.e. perhaps dissolution. This preference for z-type deposition has also been observed with carboxylic acid head groups.19) We are currently attempting to deposit z-type multilayers only by the selective upstroke mode. Comparison of the UV-visible absorption spectra of diamine-azobenzene in chloroform solution and of an LB film monolayer showed H-aggregate behavior based on the absorption blue shift of 17 nm, i.e. aggregate formation whose molecular plane is parallel to its long axis. This behavior was observed typical of monolayers with azobenzene functional groups.17) The aggregation behavior can be both thermally17), electrochemically20), and photochemically21) modified. In this case the diamine, amphiphilicity did not affect the initial H-aggregation behavior. However, further studies can be made to their aggregation behavior compared with the carboxylic head group and the above-mentioned parameters.

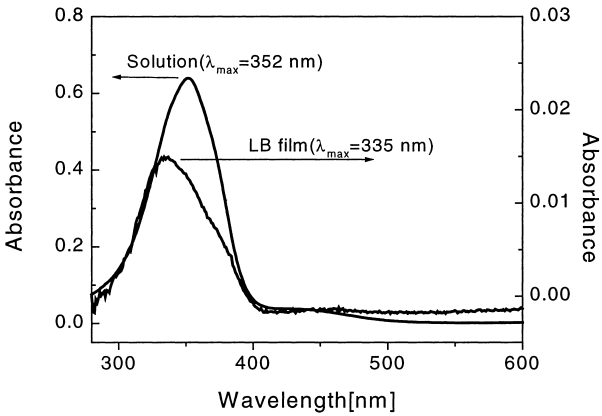


Fig. 6: UV-visible absorption spectrum of diamine-azobenzene in chloroform solution and LB monolayer film.

Diamine-Terthiophene LB Films. To build up stable LB films of diamine-terthiophene, it was necessary to use stearic acid mixed at various molar ratios (molar ratio 1:0.5, 1:1, and 1:2).[22)] The π-A isotherm of 1:1 diamine:stearic acid mixture showed ideal mixing behavior with a 32 $Å^2$ limiting molecular area and 45 mN/m collapse pressure, indicating that the mixture formed a good monolayer. The LB films were transferred onto a glass and Si substrate at a constant surface pressure of 35 mN/m. Transfer ratio was within 0.95-1.1 during deposition. Figure 7 and 8 show the linearity of the thickness and absorbance behavior of the diamine-terthiophene LB films with increasing number of layers. The average thickness of the mixed LB film is about 2.68 nm. This thickness is higher than an ideal orthogonal orientation of the terthiophene group but is well within the thickness of a monolayer of stearic acid. The UV-vis absorption maximum of the diamine-terthiophene in chloroform solution and the mixed LB films has almost the same value. This indicates that the molecule of diamine-terthiophene domains probably formed disordered layers between well ordered stearic acid molecules, repressing aggregation behavior for the terthiophene groups. The domain structure for a 5 layer thick film was also investigated by AFM.

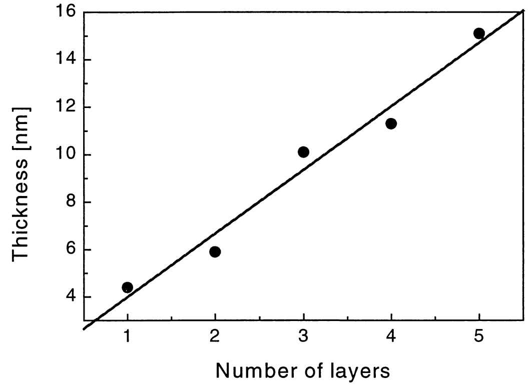


Fig. 7: The optical thickness versus number of layers of diamine-azobenzene - stearic acid mixed LB films. The films were deposited on a Si wafer.

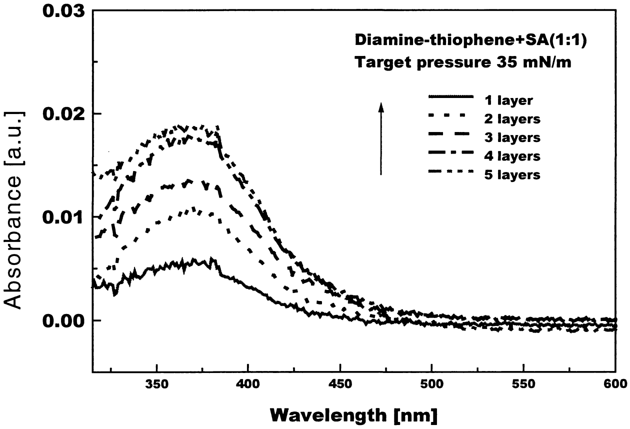
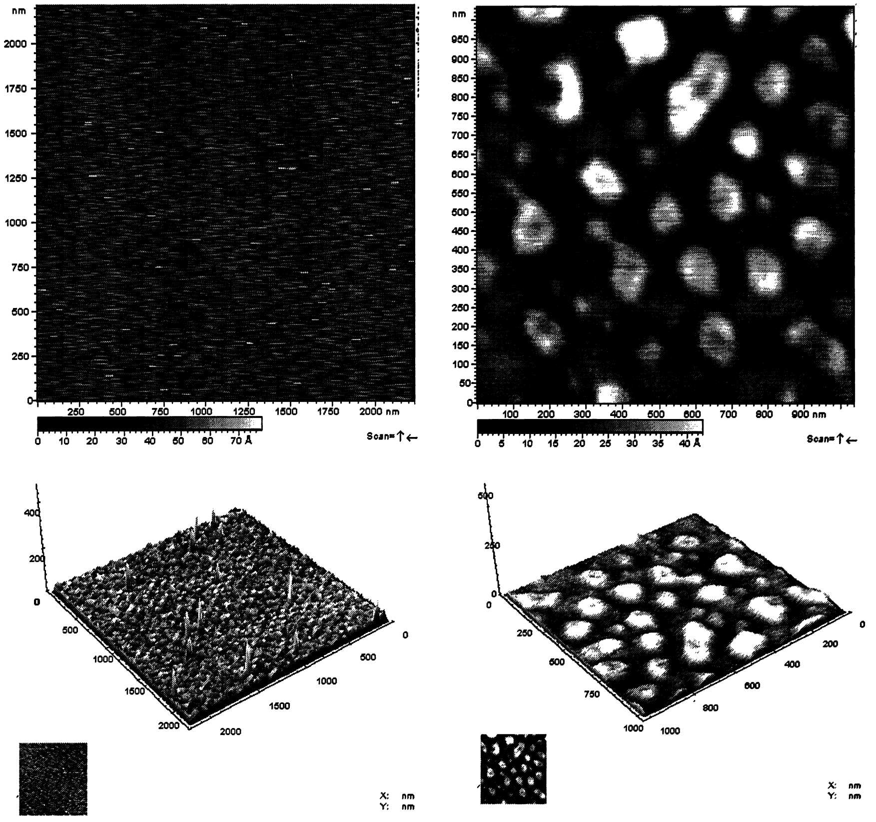


Fig. 8: The UV-visible absorption spectra of diamine-terthiophene-stearic acid mixed LB films. The absorption increased with the number of layers but no aggregation (shift) was observed compared to solution and with increasing number of layers.

4. AFM Images. We directly observed the aggregation behavior of the molecules and film morphology by AFM under magnetic AC or MAC mode. For the diamine-azobenzene monolayer, we observed a relatively uniform film with a roughness almost equivalent to 10% of the monolayer thickness. The relatively featureless micrograph is consistent with a good monolayer spreading behavior and LB film deposition.[20)] For the diamine-terthiophene-stearic acid films, the formation of phase-segregated stearic acid domains is observed with the height difference. The domains of stearic acid are higher by 2.0 to 2.5 nm relative to the diamine-terthiophene domains. This is consistent with the thicknesses obtained by ellipsometry. Further investigations are being made.



a) Diamine-azobenzene b) Diamine-terthiophene

Fig. 9: AFM Images. a) For the diamine-azobenzene monolayer, RMS = 10% of the monolayer thickness which is 3.8 nm. b) For the diamine-terthiophene-stearic acid films, the formation of phase-segregated stearic acid domains is observed with the height 2.0 to 2.5 nm relative to the diamine-terthiophene domains.

Conclusion

We have synthesized two functional α,ω-diamine derivatives as (monomers) precursors for ionene polymers: oligothiophene and azobenezene functional groups. The two amphiphiles behaved very differently as Langmuir monolayers and LB films. Dye aggregation was observed with the diamine-azobenzene derivatives while diamine-terthiophene monolayers were found to be relatively unstable. The azobenzene can only be deposited as LB films in the z-type mode, whereas stearic acid mixed monolayers were necessary for the terthiophene amphiphiles. AFM images confirmed the monolayer aggregation and LB film behavior of the amphiphiles. Futher studies will also be made to relate their film morphology and mutilayer ordering towards photoisomerization (diamine-azobenzene) and electrochemistry (diamine-terthiophene)

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