

Characteristics of Ultrathin Film Prepared through Nano-Sized Langmuir Blodgett Monolayer of Functionalized Polyimide

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Abstract : Techniques measuring Maxwell displacement current (MDC) and LB films surface measuring technique have been applied to the study of monolayers of polyamic acid containing azobenzene. MDCs was generated from monolayers on the water surface by monolayer compression and expansion. It was generated when the area per molecule was about 103\AA^2 and 78\AA^2 just before the initial rise of the surface pressure during the 1st and 2nd mixed monolayer compressions cycle, respectively. It was the maximum of MDCs appeared at the molecular area just before the initial rise of surface pressure in compression cycles, and we have found that the increase of aggregations causes the noticeable increase of the surface roughness.

Keywords : Maxwell displacement current(MDC), polyamic acid, surface pressure, LB films.

1. Introduction

Langmuir-Brodgett(LB) films have been extensively investigated recent years because of their potential applications micro-electronic and opto-electronic devices [1,2]. However, LB films prepared form organic low molecular weight materials are lack of long term stability and thermal stability, which devalue their future application and development. Therefore, polymers have been used to fabricate LB films, and these polymeric LB films may offer much more perspectives for the application because of

their structural stability. How to develop polymeric LB films combining structural stability and high ordered structure is an important topic. Up to now, we have studied extensively the physic chemical properties of organic material thin LB films, such as the photoisomerism, the thermal isomerization kinetics, the novel electrostatic isomerism, and the memory phenomenon, using simple long chain fatty acid containing azobenzene derivatives[3,4].

Recently, much attention has been paid to the polyamic acid and fatty acid containing azobenzene derivatives as a model of visual light processing because of their particularity to functional groups [1-3]. The fatty acid containing azobenzene derivatives undergo reversible *cis-trans* photoisomerization in the

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mixed monolayers, because the condensation of pure azobenzene monolayers is loosened by the introduction of polyamic acid into the monolayers, and the molecular aggregation in pure azobenzene monolayers is also weakened by the introduction of polyamic acid. Therefore it is possible to generate transient displacement current pulses across mixed fatty acid and polyamic acid monolayers, due to the *cis-trans* photoisomerization of azobenzene by alternating irradiation of ultraviolet and visible light[2]. Molecular switching between *cis*- and *trans*-forms in mono and multilayers system containing azobenzene is of particular interest in physics, chemistry and electronics[4], because of the possible applications to optical memories and information storage devices [5-6].

As mentioned above, the introduction of polyamic acid into pure azobenzene monolayers is very effective in the photoisomerization. Unfortunately, many polyamic acids mixed with fatty acid containing azobenzene molecules on a water surface, e. g., polyamic acid monolayer with azobenzenes, give different surface pressure-area(π - A) isotherms by the cyclic application of compression and expansion. That is, the π - A isotherm in the first compression cycle is different from that in the second and succeeding compression cycles. Therefore, we expect that the molecular motion in mixed polyamic acid monolayers due to photoisomerization differs between the first and the second compression cycles[3].

The rearrangement and orientation of hydrophobic chains of prepolymerized amphiphiles at the air/water interface are interfered by polymer main chains, resulting in low order of the polymeric LB films. Rinsdorf and his co-workers[7] have put forward an approach to decouple the interaction between the polymer main chains and side groups by introducing "spacer

group" into the prepolymerized amphiphiles, in this way the order of polymeric LB films is enhanced to some extent. In this experiments, the precursor method was introduced to fabricate LB films[8,9].

In the present paper, we pay attention to the compression cycles and examine the difference in the generation of displacement current induced by the first and the second compressions in polyamic acid monolayer systems on a water surface. We then discuss the surface pressure and MDCs generated across mixed monolayers due to the first and the second compressions of polyamic acid.

2. Experimental

2.1 Materials and Experimental setup

Solvents and apparatus used for the fabrication of the LB films were purified and washed by traditional method. The chemical structures of this molecule are shown in Figure 1. The polyamic acid molecule has one head group (hydrophilic group) and two long saturated alkyl amine chains with a carbonyl group (hydrophobic group). Figure 2 shows a schematic diagram of the experimental setup used here. It was the same as that previously used [10]. Briefly, the setup consisted of a Wilhelmy-type film balance, a type 617 Keithley electrometer and electrodes 1 and 2 which were connected to each other through a sensitive ammeter. Electrode 1 was suspended in the air parallel to the water surface and electrode 2 was immersed in the water subphase. Electrode 1 was a transparent electrode whose working area was 44.5 cm². The spacing between electrode 1 and the water surface was 1.0 mm. The water subphase (pH 5.8) was kept at a temperature of 20±1°C.

The measurement of the surface pressure-area isotherm (π - A) curve and deposition of the polyamic acid long alkyl amine salt were carried out at 20°C using a

NIMA Technology Langmuir-Blodgett Trough 611. The UV/visible absorption spectra were recorded using a Shimadzu UV/Visible spectrophotometer (UV-240). The water subphase was distilled twice and passed through Millipore system.

2.2 MDC measurement

Monolayers composed of polyamic acid was spread from chloroform solutions with a concentration of 0.2 mol/L on the surface of pure water in a Langmuir trough (150 x 730 mm) using a microsyringe. The monolayers formed on the water surface were compressed with constant barrier velocity a of 40.0 mm/min using two moving barriers. After spreading the solution of polyamic acid molecule onto the surface of water, we let it stand 10 min to evaporate the chloroform and to form a stable monolayer on the water surface. The displacement current-molecular area (I - A) isotherm was monitored together with the surface pressure-molecular area (π - A) isotherm during the monolayer compression. In the present experiment, we cyclically compressed and expanded monolayers cyclic and recorded the π - A and I - A isotherms. Charge flowing through the ammeter (ΔQ) was also monitored with the I - A isotherm. The MDC was also measured in a manner similar to that in our previous study[1,3]. In our measuring system, it was possible to detect MDCs with an accuracy of 1 fA because the air gap between the water surface and electrode 1 was a good insulator and the leakage current was eliminated. The resolution of the surface pressure was about 0.08 mN/m.

2.3 Preparation of LB films

Although the polyamic acid lacks of hydrophobicity, the amphiphilic polyamic acid was obtained by incorporation of the amine with a long hydrophobic alkyl chain, namely precursor method. Spreading solution of polyamic acid long alkyl amine salt were

prepared by mixing the solution of polyamic acid at a concentration of 1.0 mmol/L in a mixture of *N,N*-dimethyl acetamide(DMAC) and benzene (1:1 by volume) with the solution of *N*-icosylpyrrolidine in the same solvent system in the ratio of 1 : 2 by volume[7].

The measurement of surface pressure-area (π - A) isotherms and the deposition of the monolayer films were carried out by the commercial Langmuir-trough (NIMA

Technology Langmuir-Blodgett Trough 611) using a Wilhelmy's plate. The compression speed of a moving barrier was kept constant 40mm/min and the dipping speed of substrates was 2mm/min for both down and upward strokes.

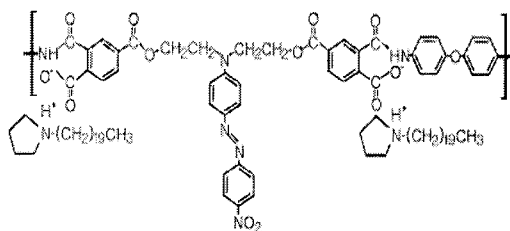


Figure 1. Molecules used in the present study.

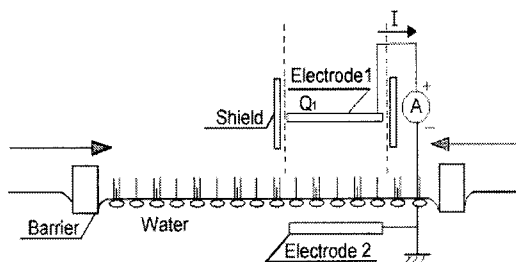


Figure 2. Schematic diagram of the experimental setup used for the present study.

Monolayers on the water surface could be transferred onto various solid substrates by means of the vertical dipping method (LB method) with they-type deposition starting a transfer to the hydrophilic surface in the first up mode. After deposition of the monolayer films onto substrates, imidization was carried out by heating at 160°C for 2 h in *vacuo*.

3. Results and Discussion

3.1 The π -A isotherm of Langmuir films alkyl amines monolayer

The Langmuir films monolayer stability of the amphiphilic polyamic acid alkyl amine salt at the air-water interface was examined by the π -A isotherm. In this study, L films of polyamic acid amine salts possessing the different alkyl chains were examined. The alkyl amine compounds which introduced as the hydrophobic groups on the polymer main chain were $C_{18}H_{37}N6M$ (I.E. NR), $(C_{18}H_{32})_2NCH_3$ (I.E. NR₂) and $N(C_2H_4OCOC_{15}H_{31})_3$ (I.E. NR₃). As shown in Figure 3, the surface pressure rose steeply and the collapse pressure reached as high as 40mN/m.

Figure 3. shows characteristics the L film polyamic acid monolayer of 1.0 mmol/L in a mixture of N,N-dimethyl-acetamide (DMAc) and benzene (1:1 by volume) with the solution of N-icosylpyrrolidine. As a result we can see in this figure the electron transfer increased by sodium ion in the water solution. The feature is that the increased potential for shifted to the right.

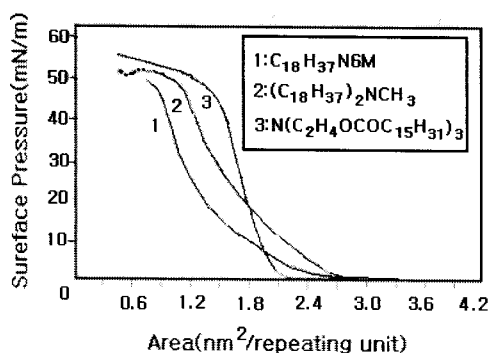


Figure 3. π -A Curves of various alkylamines and polyamic acid.

The low compressibility in the high surface pressure region indicated the formation of a solid-like oriented state of molecules, which was quite stable even under further

compression to 40.0 mN/m.

This results showed that the stable monolayer of the amphiphilic polyamic acid was formed at the air/water interface upon compression. By dipping the substrate perpendicularly though the interface repeatedly at a surface pressure 25 mN/m, the monolayer of the amphiphilic polyamic acid alkyl amine salt could be transferred smoothly onto various substrates. The transfer was performed onto the hydrophilic surfaces in the first up mode. The deposition took place both in up and down modes at the knowing dips, where the transfer ratio calculated from the substrate area and the moving barrier position during deposition was close to 0.95 with good reproducibility in all deposition. Thus, the obtained LB films of polyamic add alkyl amine salt had the Y type structure.

3.2 In the Range of Immeasurably Low Surface Pressure

Figure 4 shows the reversible displacement current generation from the mixed monolayer of polyamic acid by the application of the repeated compression and expansion of surface pressure. Compression curve (top) in Figure 4 shows an I -A isotherm obtained during the course of monolayer compression. The monolayer was compressed in the range of molecule area A from 267 to 50 \AA^2 by moving the two barriers at a speed of 40 mm/min. By decreasing the monolayer-covering area, the displacement current generation was initiated around $267 \text{ \AA}^2/\text{molecule}$ to give a maximum value around $97 \text{ \AA}^2/\text{molecule}$ and was decreased to increase again around the initial rise of the surface pressure. At the beginning of the compression, the MDC was not generated across polyamic acid monolayer[11].

Although the surface pressure change was not detected for molecular areas $A < 90 \text{ \AA}^2$, the MDC was generated at $A < 180 \text{ \AA}^2$ for monolayer compression. In Figure 4, the π -A

isotherm of the same monolayer as examined is also shown as compression curve (bottom). As shown in the figure (bottom), an increase in the monolayer-covering area gave another π -A isotherm (expansion curve) close to compression curve and also the I -A isotherm recorded as expansion curve. The behavior of π -A isotherm of the polyamic acid monolayer was reversible along with the increase and decrease of the monolayer-covering area, and expansion curve was the so-called mirror image of compression curve. The cyclic change of the I -A isotherm was found to be sustained by the repeated decrease and increase cycles of the monolayer-covering area. In Figure 4, regions 1 and 2 were divided at the area per molecule A_i at which the MDC flow was initiated by monolayer compression. The areas (A_i) for polyamic acid molecule used here was as follows: $A_i = 180 \pm 30 \text{ \AA}^2$.

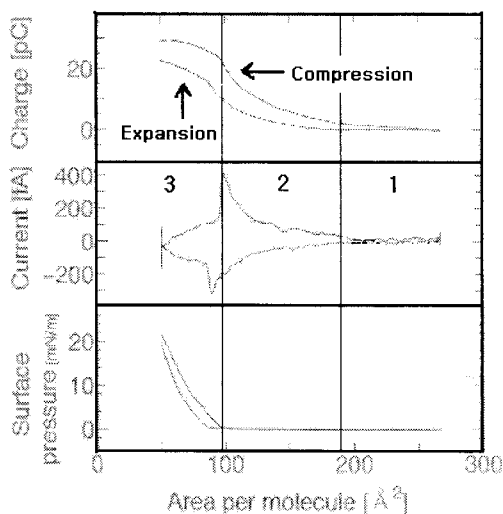


Figure 4. Displacement current, charge and surface pressure-area curves of polyamic acid monolayer on the water surface by the application of the compression and expansion.

The I -A isotherm strongly depended on the polyamic acid molecule. Briefly, for

molecules of polyamic acid monolayer, one large MDC peak appeared during the monolayer compression. The I -A isotherms corresponded well to the trace of the π -A isotherms. Judging from the trace of the MDC obtained in the experiment, we divided the I -A and π -A isotherms as in the figure. In this study, regions 1-3 were examined. The magnitude of the MDC generated in region 3 was inversely proportional to A^2 [12].

3.3 MDC measurement by monolayer compression

Figure 5 shows a typical example of the displacement current generated from the polyamic acid monolayer. Figure 5 represent the π -A, Q-A and I -A isotherms (from bottom to top) obtained during the first and the second monolayer compression, respectively.

Figure 5 shows an experimental result for polyamic acid monolayers. The displacement current was never generated by compression when monolayers were not formed on a water surface[5].

In contrast, the displacement current was generated from the polyamic acid monolayers by the first and the second compression cycles.

Figure 5 was obtained at the molecular area of around 103 \AA^2 and 78 \AA^2 just before the initial rise of the surface pressure during the 1st and 2nd polyamic acid monolayer compression cycles, respectively. Similar experimental results were obtained in the entire range of the molecular area for the first and the second compression cycles. In other words, the displacement current was generated in the whole of the molecular area, although the magnitude of the current changed as a function of molecular area A .

As we can see in the figure, the generation of MDCs through the circuit Q1 for the second monolayer compression cycle is greater than that for the first monolayer cycle in the range of molecular area $A < 78$

\AA^2 . In contrast, in the range of molecular area $A > 78 \text{\AA}^2$, this relationship is just the opposite.

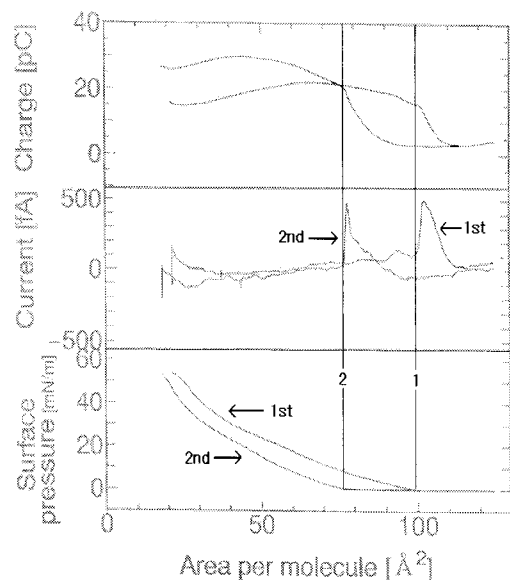


Figure 5. Displacement current and surface pressure–area curves of polyamic acid monolayer on the water surface.

These results are supported from the experimental results shown in Figure 5, where the generation of MDC is quite large in the molecular area before the initial rise of the surface pressure.

In case of the polyamic acid of single material, the surface pressure and MDCs were almost not shifted when compared with those of the mixture[3,13]. After the first compression and expansion, domain was formed by the high aggregation of molecules of polyamic acid[14]. This result suggests that the MDC peak and surface pressure were shifted to the left regardless of spread amount of the polyamic acid.

The MDCs was generated from monolayers on the water surface by Langmuir monolayer compression and expansion(Figure 5).

Displacement current was generated when the area per molecule was about 150\AA^2 and 100\AA^2 . Displacement currents were investigated in connection with monolayer compression cycles. It was found that the maximum of MDC appeared at the molecular area just before the initial rise of surface pressure in compression cycles.

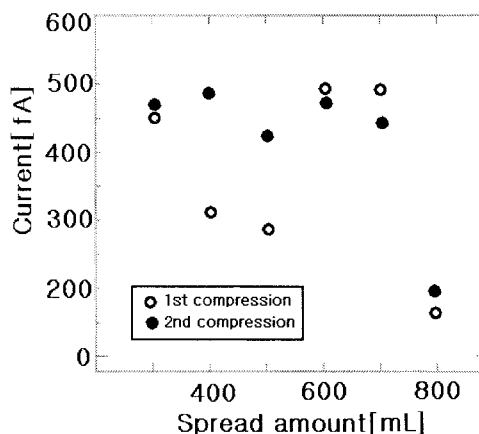


Figure 6. The relationship of displacement current and spreaded amount of polyamic acid on the water surface by the application of the 1st and 2nd compressions.

Figure 6 shows the relationship of displacement current and spreaded amount of polyamic acid by the application of the 1st and 2nd compressions, respectively.

In case of the 2nd compression, we have found that the decrease of displacement currents causes the noticeable increase of spreaded amount of polyamic acid on the water surface, this effect seems to be reasonable stability of the Langmuir films and may be related to the increase of spreaded amount of polyamic acid on the water surface.

The average LB thin film size and the surface roughness of the polyimide thin films were investigated using AFM. Figure 7

shows the surface morphology of the polyimide films on the glass. It can be seen that all AFM images show small surface roughness (2.5~6.0 nm, Figure 7(a)), the LB thin film size in the range of 2.5 ~30 nm (Figure 7(b)) and the existence of both aggregations and pin-holes.

However we have found that the increase of aggregations causes the noticeable increase of the surface roughness. this effect seems to be reasonable and may be related to the increase of the LB size of polyimide thin films.

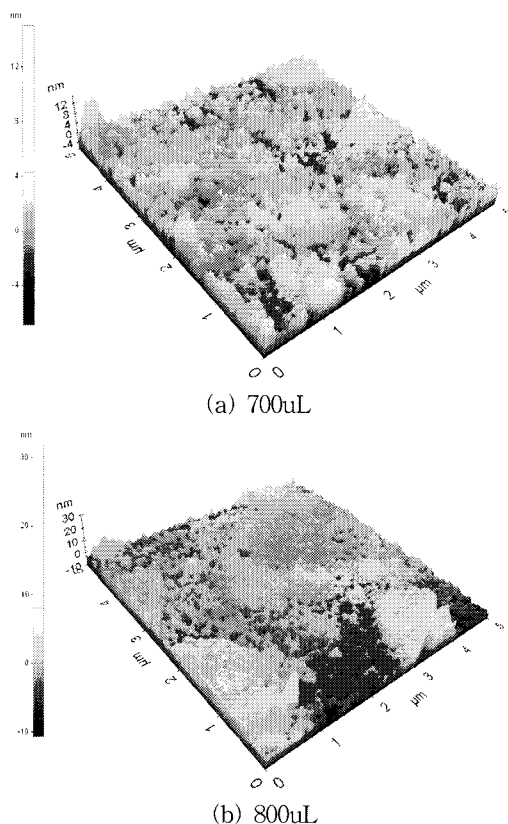


Figure 7. Surface morphology of polyimide thin films structure spreaded in (a) 700uL and (b) 800uL polyamic acid solution using atomic force microscope.

4. Conclusions

The measurement of Maxwell displacement current(MDC) and properties of polyamic acid LB thin films were investigated on the Langmuir and Langmuir–Blodgett monolayers of polyamic acid containing *p*-nitroazobenzene.

1. Displacement current was generated when the area per molecule was about 103\AA^2 and 78\AA^2 . It was found that the maximum of MDC appeared at the molecular area just before the initial rise of surface pressure in compression cycles.
2. We have found that the increase of high aggregations causes the noticeable increase of the surface roughness.
3. In case of the 2nd compression, we have found that the decrease of displacement currents causes to the reasonable stability of the Langmuir films and may be related to the increase of spreaded amount of polyamic acid on the water surface.

Acknowledgement

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