JOURNAL OF MATERIALS SCIENCE **37** (2002) 4839–4843

Surface modification using polymer Langmuir-Blodgett films

Y. KADO, A. AOKI, T. MIYASHITA*
Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Katahira 2-1-1, Aobaku, Sendai, Miyagi 980-8577, Japan
E-mail: miya@tagen.tohoku.ac.jp

We describe a simple and effective approach to introduce a functional group into polymer film on a solid surface using reactive polymer LB films. *N*-dodecylacrylamide copolymers containing terminal amino groups in the side chains as the reactive moiety form a stable monolayer, and the monolayer was transferred onto a solid support to modify the solid surface using the Langmuir-Blodgett method. The transferred coatings were characterized with fluorescence, IR spectroscopies, and X-ray diffraction. The reactivity of the terminal amino group incorporated in the LB films was investigated in detail using fluorescein isothiocyanate (FITC) as a fluorescent probe. The chemical reaction between amino groups in the LB films and FITC in the bulk solution was completed within approximately 30 minutes and the chemical bond formation was confirmed by infrared spectroscopy. Furthermore, the fluorescent image of the multilayers reacted with FITC were observed with fluorescent microscopy. This method is effective for tailoring functional organic ultrathin films on solid substrates.

1. Introduction

Recently, bottom-up approaches for constructing ordered nanoscale structures in organic molecular assemblies have been of interest and various techniques for the preparation of organic ultrathin films have been studied [1–10]. Organic thin films are attractive materials for their processability, ease of functionalization, their light weight, flexibility, and so on. However their processing technologies are immature and further development is expected. Various organic films, for example, a spin-coating film [3], self-assembled monolayers (SAM) [1, 4, 5], grafting polymers [6–8] and multilayers of ionic polymers via electrostatic interactions [9, 10], have been investigated. Most applications of these films have been extended to optics [10], microelectronics devices [3, 11, 12], sensors [3, 13], optical memory devices [14, 15], and so on. On the other hand, the Langmuir-Blodgett (LB) technique is an excellent method for providing organized molecular assemblies with controlled molecular orientation and well-defined molecular arrangement. Furthermore, the well-ordered multilayers can be produced onto a solid substrate. Thus it is possible to control thickness of films easily by the number of deposited layers.

In our previous papers [16–18], we reported that *N*-dodecylacrylamide (DDA) polymer forms stable LB films with a monolayer thickness of 1.7 nm. Moreover, due to the high stability of the DDA monolayer, the copolymers of DDA with various functional comonomers also form stable monolayers and LB films [19]. As a precursor copolymer LB film for introduction of functional groups by substitution reaction, the copolymer of DDA with *N*-acryloxysuccinimide (SuOA) was prepared. SuOA has an active ester moiety which acts as a good sacrificial group in substitution reactions and the active ester can be replaced with primary amine derivatives in organic solvents or water [20–22]. We succeeded in the introduction of a naphthyl chromophore into the polymer monolayer by the reaction of 1-(1-naphthyl)ethylamine with the succinimide group in the pDDA-SuOA monolayer on an aqueous phosphate buffer surface. However, the amino derivatives were not able to incorporate into the pDDA-SuOA LB film on a solid surface by contact with a solution containing the amino derivatives, because the succinimide group is isolated in densely packed alkyl chains of the LB films.

In this paper, we describe the surface modification and coating technique via chemical reaction with reactive polymer Langmuir-Blodgett film (LB film) containing terminal amino groups (Fig. 1). Generally the amino group is widely used as a reactive moiety which allows reaction with various functional groups such as epoxide [23, 24], isothiocyanate [25], succinimide ester [19], and so on. The technique for the coating of a solid substrate with LB films and the introduction of various functional groups would be significant for the fabrication of molecular nano devices.

Reactive polymer LB films containing amino groups were prepared and their reactivities were investigated in

*Author to whom all correspondence should be addressed.

detail using fluorescein isothiocyanate (FITC) as a fluorescent probe by several spectroscopic methods [25, 26]. The reactive LB films could introduce FITC with by an immersion method. Apparently the amino groups in the LB films were found to show high reactivity with FITC. Furthermore, the fluorescent image of the LB multilayers reacted with FITC was observed by fluorescence microscopy.

2. Experimental

2.1. Materials

2,2'-(Ethylenedioxy)bis(ethylamine) (DADOO), fluorescein isothiocyanate (FITC) isomer I were purchased from Aldrich. Octadecyltrichlorosilane was purchased from ShinEtsu Chemical Co., Ltd. Na_2CO_3 and $NaHCO_3$ were purchased from Nacalai Tesque. *N*-Dodecylacrylamide (DDA), *N*-hydroxysuccinimide (SuOA), and the copolymers (pDDA-SuOA) were prepared as described in previous papers [19]. DDA copolymers with DADOO (pDDA-DADOO) (Fig. 1) were synthesized as follows: A chloroform solution of pDDA-SuOA (ca. 0.1 M) was dropped into a chloroform solution of DADOO (ca. 5 M) under stirring and the mixture was stirred at room temperature for 2 days. The resulting copolymers were reprecipitated with acetonitrile several times and dried under vacuum. The mole fractions (n) of DADOO in the copolymers were determined by ^{1}H NMR spectroscopy. Fluorescein isothiocyanate (FITC) solution was dissolved in an aqueous buffer solution of 0.1 M Na_2CO_3-$NaHCO_3$ (pH 9.6).

2.2. Measurements

Measurements of surface pressure (π)–area (A) isotherms and the deposition of monolayers were carried out with a computer-controlled Langmuir trough system (FSD-50, 51 USI) at 20°C. The copolymers were dissolved in chloroform at a concentration of about 1 mM (monomer unit) and spread on a pure water (Milli-Q grade water; resistivity >17 M$\Omega \cdot$cm). The compression speed was 1400 mm^2/min. The polymer monolayers were transferred onto solid substrates by the vertical dipping method at a dipping speed of 10 mm/min under surface pressure of 35 mN/m at 20°C. Glass substrates were cleaned using an O_3 cleaner, and were treated with octadecyltrichlorosilane to make the surface hydrophobic. PDDA LB films with 10 layers were precoated on substrates and then pDDA-DADOO LB films were deposited on them.

Fluorescence spectra were measured using Hitachi U-4000. The reactive LB films on the substrates were immersed in an FITC solution, and rinsed with the buffer and distilled water three times alternately to remove unreacted species from the LB film surface. Finally, they were dried with pure N_2 gas. Light below 480 nm was cut off with a filter. Fourier transform infrared (FT-IR) spectra were measured with JASCO FT/IR-230. A CaF_2 substrate was used after washing with $CHCl_3$ and acetone. X-ray diffraction (XRD) measurements were carried out with MAC Science M18XHF^{22}-SRA. The film thickness was determined from their Bragg peaks [27]. The fluorescent images of the LB films reacted with FITCs was observed with a fluorescence microscope (Olympus Vanox). Fluorescence images were taken through a 380–490 nm excitation filter with a 200 W high pressure mercury lamp.

3. Results and discussion

3.1. Monolayers and LB films formation

PDDA-DADOO copolymers with various copolymer compositions ($n = 0.07$, 0.12, and 0.22) were prepared. Number-average molecular weights of the copolymers with $n = 0.07$, 0.12, and 0.22 were 3.02×10^4, 3.17×10^4, and 3.17×10^4, respectively. Dispersions of these copolymers were almost 1.5. Solutions (1.0 mM, 200 mm^3) of the copolymers in chloroform were spread on a water surface to measure surface pressure (π)-area (A) isotherms at 20°C (Fig. 2). The

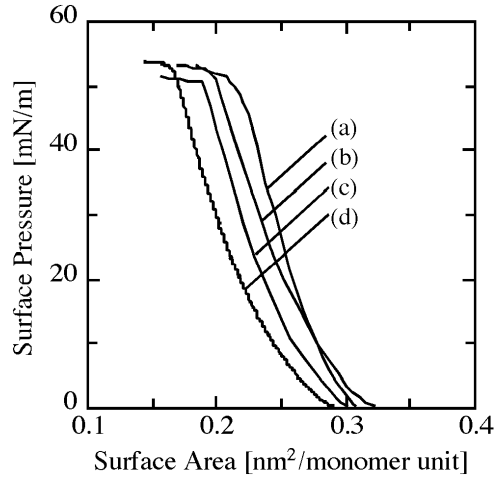

Figure 2 Surface pressure-area isotherms of pDDA-DADOO copolymers with various mole fractions (n) of DADOO unit at 20°C: (a) pDDA homopolymer; (b) $n = 0.07$; (c) $n = 0.12$; (d) $n = 0.22$.

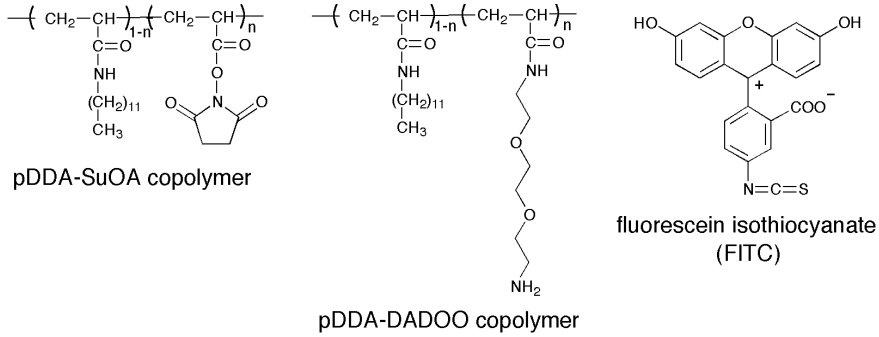

Figure 1 Chemical structures used in this work.

isotherms indicate that all of the copolymers form stable monolayers with a steep rise in surface pressure and a high collapse pressure. The limiting surface areas became smaller with increasing mole fraction of DADOO units. Since the limiting surface area of the DDA monomer unit is known to be 0.28 nm^2 [16], the surface area of the DADOO unit in the copolymer monolayer is estimated to be approximately 0.06 nm^2/monomer unit from the π-A isotherms. On the basis of this value, we suggest that the DADOO unit exists in the subphase. The condensed copolymer monolayers can be transferred onto hydrophobized glass slides at a surface pressure of 35 mN/m by down- and up-ward strokes, yielding Y–type LB films.

To determine thicknesses of the LB films X-ray diffraction measurements were carried out. The film thicknesses of pDDA ($n = 0$) and pDDA-DADOO copolymer ($n = 0.07$, 0.12, and 0.22) LB films were determined to be 1.67, 1.74, 1.84, and 1.94 nm per monolayer, respectively. The film thickness increases with increasing mole fraction of DADOO units. This result also suggests that the DADOO unit in the pDDA-DADOO monolayer on a water surface exists in the subphase. Therefore the DADOO unit was placed in the hydrophilic part of the LB films and interposed between the hydrophobic part of the pDDA-DADOO LB films and the film thickness of the hydrophilic part of the LB films increased with mole fraction of DADOO unit. This is in accordance with the results of π-A isotherms.

3.2. Reactivity of amino groups in LB films

The terminal amino group is known to react with many functional groups such as epoxide, isothiocyanate, succinimide ester, and so on. The reactivity of the terminal amino group of the LB film deposited on a glass surface was examined by the reaction with fluorescein isothiocyanate (FITC) as a fluorescent probe (Fig. 3). An aqueous FITC solution (pH 9.6) has the absorption maximum at 490 nm and the fluorescent maximum at 520 nm. The pDDA-DADOO LB films with two layers on a glass surface were immersed in the FITC solution for approximately 30 min, and their fluorescent spectra were measured (Fig. 4). Apparently the fluorescent spectra suggest that the introduction of the fluorescent probe into the monolayer and two-layer LB film was carried out. The amino group in the monolayer LB film on a glass surface is exposed on the surface, while the amino group in the two-layer LB film exists inside of

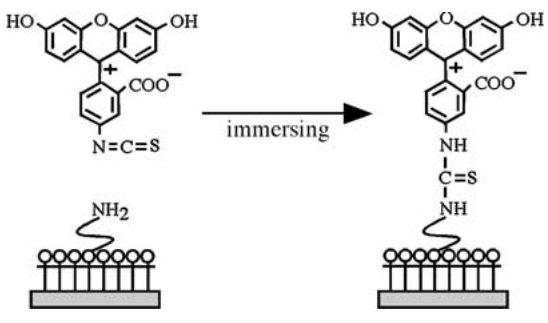

Figure 3 Schematic representation of the reaction between the terminal amino groups in the pDDA-DADOO LB films and FITC via chemical attachment.

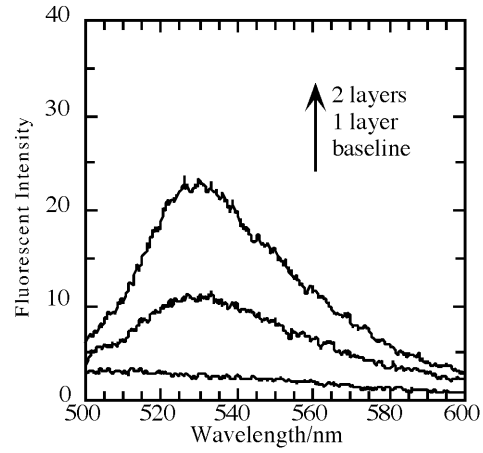

Figure 4 Fluorescence spectra of pDDA-DADOO ($n = 0.12$) LB films (monolayer and two layers).

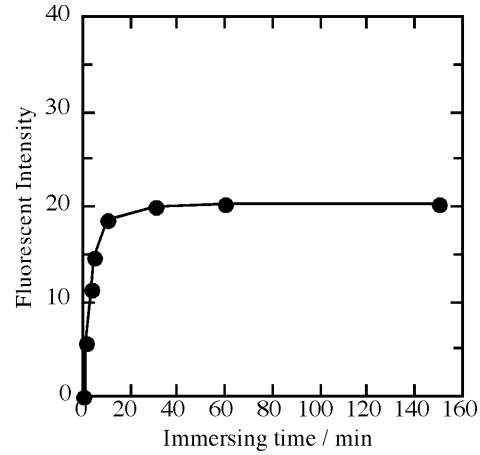

Figure 5 Changes in fluorescent intensities at 530 nm of the pDDA-DADOO ($n = 0.12$) LB films with 2 layers as a function of the immersing time.

the LB film due to the head-to-head bilayer structure. However, the fluorescent spectra observed with the two-layer LB film were twice as intense as those for the monolayer LB film. These results indicate that FITC is allowed to react with internal amino groups in the LB films. In the previous study, the active ester group in pDDA-SuOA LB film was found not to react in the LB film, because the reactive group is placed in the hydrophobic part and is surrounded with condensed alkyl chains. The reactive group (the terminal amino group) in the present LB film has sufficient reactivity even in the LB film. This is because the amino group exists in the hydrophilic part of pDDA-DADOO LB film and has sufficient free volume to react with FITC.

The time profile of the reaction in the LB films was measured by monitoring the fluorescent intensity at 530 nm as a function of immersing time (Fig. 5). The intensity increased rapidly in the initial 10 minutes, and became saturated after 30 minutes, indicating the completion of the reaction of amino groups with FITC. Accordingly, the immersing time of 30 minutes was chosen for subsequent experiments.

We tried to introduce FITC into the LB films with more than two layers. Fig. 6 shows the fluorescent intensity at 530 nm for the LB film with various deposited layers after contact with FITC solution for 30 min. The

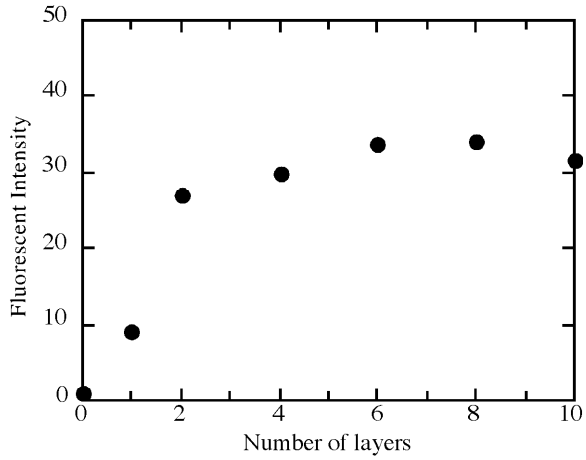

Figure 6 Change in fluorescent intensities at 530 nm of the pDDA-DADOO ($n = 0.12$) LB films as a function of the number of layers.

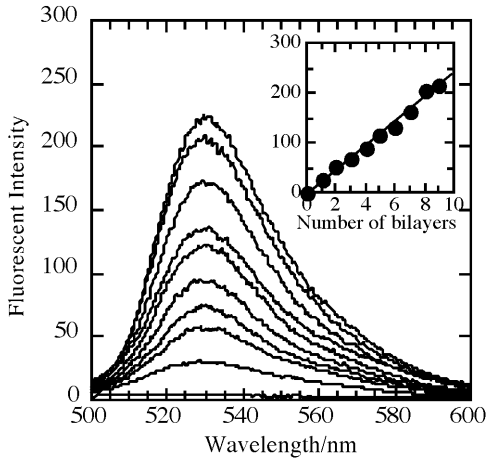

Figure 7 Fluorescence spectra of pDDA-DADOO ($n = 0.22$) LB films as a function of number of immersing cycles.

intensity was almost saturated after two-layers, indicating that the FITC molecule can gain access to the amino group in the LB film through a monolayer or two layers. It is concluded that the introduction of FITC into a two-layer LB film in most effective. Therefore, a two-layer LB film was deposited onto a glass surface and then contacted with FITC solution, then finally rinsed with water. This operation was repeated and the fluorescence spectra were measured as a function of the number of depositions of two-layers (Fig. 7). Apparently, the fluorescent intensity increases with the number of layers, which is different from the result in Fig. 6.

The chemical attachment of amino groups with FITC was observed with FT-IR spectra change of the pDDA-DADOO LB films before and after the reaction with FITC (Fig. 8). A pDDA-DADOO LB film with two layers was deposited on a CaF_2 substrate, the LB films were immersed in the FITC solution for 10 minutes, rinsed 3 times with buffer solution and water, respectively, and dried with N_2 gas. This operation cycle was repeated 15 times and the resulting LB film with 60 layers was measured. The characteristic absorption bands in the FT-IR spectra are listed in Table I. A decrease in the absorption band around 3500 cm^{-1} (N─H stretching vibration of amine) indicates the consumption of the amino group in the LB film due to the reaction with FITC. The appearance of an absorption

TABLE I Assignment of selected absorption in the infrared spectra of pDDA-DADOO LB films before and after the reaction

Wavenumber (cm^{-1})			
Before the reaction	After the reaction	Assignment	
3504		Amine	N─H stretch
3297	3295	Amide	N─H stretch
	3204	─CS─NH─	N─H stretch
3073	3072	Amide	N─H stretch

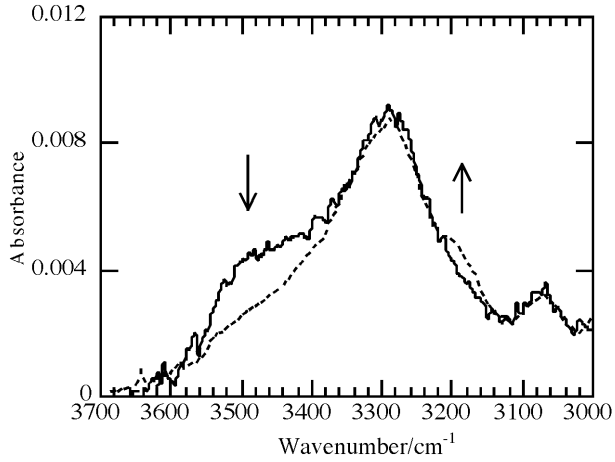

Figure 8 FT-IR spectra of pDDA-DADOO ($n = 0.22$) LB films with 60 layers before the reaction (solid line) and after the reaction with FITC (dotted line).

band around 3200 cm^{-1}, which is assigned to N─H stretching vibration of ─NH─CS─, indicates the formation of ─NH─CS─bonds. In addition, the absorption band around 2000 cm^{-1} which is assigned to unreacted ─N═C═S groups was not observed in the IR spectra of the LB film after the reaction with FITC. These results suggest that the amino group in the LB films reacts with FITC by the addition reaction of $-NH_2$ to ─N═C═S as shown in Fig. 3.

4. Conclusions

The coating of a solid surface with polymer monolayer or two-layer LB film containing reactive terminal amino groups was achieved. By the reaction with the amino group the introduction of a functional group was confirmed using a fluorescent probe. This coating method with the reactive copolymer LB film is applicable to functionalization of surfaces.

References

1. Y. XIA and G. M. WHITESIDES, *Angew. Chem. Int. Ed.* **37** (1998) 550.
2. S. HUANG, A. W. H. MAU, T. W. TURNEY, P. A. WHITE and L. DAI, *J. Phys. Chem.* B **104** (2000) 2193.
3. S. H. LEE, J. KUMAR and S. K. TRIPATHY, *Langmuir* **16** (2000) 10482.
4. X.-Y. ZHU, V. BOIADJIEV, J. A. MULDER, R. P. HSUNG and R. C. MAJOR, *ibid.* **16** (2000) 6766.
5. K. TAMADA, T. ISHIDA, W. KNOLL, H. FUKUSHIMA, R. COLORADO, JR., M. GRAUPE, O. E. SHMAKOVA and T. R. LEE, *ibid.* **17** (2001) 1913.
6. O. PRUCKER and J. RÜHE, *Macromolecules* **31** (1998) 592.
7. O. PRUCKER, C. A. NAUMANN, J. RÜHE, W. KNOLL and C. W. FRANK, *J. Am. Chem. Soc.* **121** (1999) 8766.

8. Y. CHEN, E. T. KANG, K. G. NEOH and K. L. TAN, *J. Phys. Chem.* **104** (2000) 9171.
9. R. ADVINCULA, E. AUST, W. MAYER and W. KNOLL, *Langmuir* **12** (1996) 3536.
10. A. TOUTIANOUSH, F. SAREMI and B. TIEKE, *Mater. Sci. Eng.* **C8-9** (1999) 343.
11. G. XU, Z. BAO and J. T. GROVES, *Langmuir* **16** (2000) 1834.
12. C. J. BRABEC, N. S. SARICIFTCI and J. C. HUMMELEN, *Adv. Funct. Mater.* **11** (2001) 15.
13. M. IDE, A. MITAMURA and T. MIYASHITA, *Bull. Chem. Soc. Jpn.* **74** (2001) 1355.
14. M. THEANDER, T. GRANLUND, D. M. JOHANSON, A. RUSECKAS, V. SUNDSTRÖM, M. R. ANDERSSON and O. INGANÄS, *Adv. Mater.* **13** (2001) 323.
15. H. BECKER, T. D. WILKINSON and R. H. FRIEND, *Adv. Mater. Opt. Electron* **9** (1999) 9.
16. T. MIYASHITA, Y. MIZUTA and M. MATSUDA, *Langmuir* **9** (1993) 1110.
17. T. MIYASHITA, P. QIAN and M. MATSUDA, *J. Am. Chem. Soc* **115** (1993) 5624.
18. T. MIYASHITA and Y. YATSUE, *J. Phys. Chem.* **99** (1995) 16047.
19. K. ARISUMI, F. FENG, T. MIYASHITA and H. NINOMIYA, *Langmuir* **14** (1998) 5555.
20. F. M. WINNIK, *Polymer* **31** (1990) 2125.
21. T. E. WILSON, W. SPEVAK, D. H. CHARYCH and M. D. BEDNARSKI, *Langmuir* **10** (1994) 1512.
22. A. POLLAK, H. BLUMENFELD, M. WAX, R. L. BAUGHN and G. M. WHITESIDES, *J. Am. Chem. Soc.* **102** (1980) 6324.
23. S. Y. CHOI, Y.-J. LEE, Y. S. PARK, K. HA and K. B. YOON, *ibid.* **122** (2000) 5201.
24. T. HUGEL, M. GROSHOLZ, H. C.-S. CHAUMANN, A. PFAU, H. GAUB and M. SEITZ, *Macromolecules* **34** (2001) 1039.
25. H. MAEDA, N. ISHIDA, H. KAWAUCHI and K. TUZIMURA, *J. Biochem.* **65** (1969) 777.
26. D. PRODNIKOV and A. MIRZABEKOV, *Nucleic Acid Res.* **24** (1996) 4535.
27. M. SCHAUB, C. FAKIROV, A. SCHMIDT, G. LIESER, G. WENZ, G. WEGNER, P.-A. ALBOUY, H. WU, M. D. FOSTER, C. MAJRKZAK and S. SATIJA, *Macromolecules* **28** (1995) 1221.

Received 12 February
and accepted 22 June 2002