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Photopatterning of a fluorescent polymer Langmuir–Blodgett film by crosslinking reaction

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Abstract

A fluorescent two-dimensional network patterning was fabricated with polymer LB films. An amphiphilic polymer consisting of *N*-dodecylacrylamide, *N*-11-acryloylundecyl-4-vinylpyridinium salt and 1-pyrenylacrylamide forms a stable monolayer, which is transferred onto solid substrates yielding LB films. The absorption and emission spectra of the LB films indicate that pyrene chromophore exists in the LB film. On irradiation, photo-crosslinking reaction of the acryloyl group, which is aligned on each interlayer hydrophobic tail surface of LB films occurs efficiently. Consequently, the irradiated polymer LB film becomes insoluble in organic solvents due to the formation of the two-dimensional polymer network in the LB film. The patterned fluorescent polymer LB film was confirmed by the fluorescence microscopy.

Keywords: Photopatterning; Crosslinking reaction; Langmuir–Blodgett film

1. Introduction

Spatial arrangement of functional molecules on substrates has been greatly investigated for the application to molecular devices and DNA chips. There are several methods such as microcontact printing using self-assembled monolayers (SAMs) of alkanethiols on metal substrates [1–4] and photoactivation of photolabile protecting groups [5–7] to construct spatial arrangement of functional molecules on the substrates. On the other hand, Langmuir–Blodgett (LB) technique has some attractive features preparing ultra-thin films at a molecular level with high molecular orientation on solid substrates [8]. Moreover, as the thickness of each monolayer can be easily controlled in several nanometer scale using the LB technique, various hetero-deposited LB films constructed by the successive deposition of different kind of monolayers on substrates have been fabricated in order to realize artificial photosynthetic systems [9] and molecular devices [10]. However, the LB technique has a lack of ability to control in-plane structures of LB films except the phase separation of mixed LB films using hydrocarbon and fluorocarbon amphiphiles [11]. We have tried to employ the LB method as one of the techniques of molecular arrangement in the nanotechnology for soft-material devices. It is significant to apply the LB technique to photolithography. The photolithography has been developed to form fine pattern films on substrates using light and has widely been used for the production of microelectronics. Therefore, the combination of the LB technique with the photolithography enables us to control the spatial arrangement of functional molecules. So far, polymerizable monomer LB films [12,13] and crosslinkable polymer LB films [14–16] have been developed for the application to resist films and thermally stable films. They were demonstrated to make fine patterns with a high resolution using photolithography.

Recently, we have succeeded in the preparation of a preformed polymer LB film containing a crosslinkable group, which produces a two-dimensional network polymer LB film by crosslinking at UV light irradiation [17–19]. In the linear polymer main chains of the LB film, only a small degree of crosslinking reaction produces an insoluble film. This phenomenon results in higher sensitivity of photolithography compared with photopolymerization of monomer LB films. Polymer LB films have received much attention because of their stable thermal and mechanical properties compared with conventional LB films such as long-alkyl chain fatty acids. We reported previously that preformed *N*-dodecylacrylamide (DDA) polymer has excellent spreading behavior and form stable polymer LB films [12]. Furthermore, we have also succeeded in the introduction of various functional groups such as redox species [20] and aromatic chromophores [21,22] into the polymer LB

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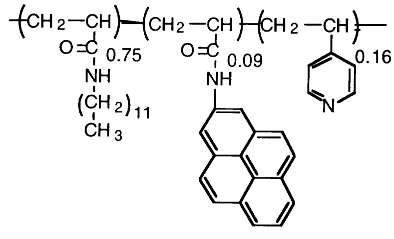
films as a comonomer of DDA. Thus, we tried to introduce an acryloyl group as a crosslinking group and a fluorescent chromophore as a functional group simultaneously into the amphiphilic DDA polymer.

In this study, the introduction of pyrene as a functional group into a crosslinkable polymer LB film has been carried out. Pyrene is a well-known fluorescent chromophore, which is used as a probe molecule for the photophysical study in the LB films. The fluorescent image of the patterned LB film consisting of crosslinkable amphiphilic poly(*p*-phenylenevinylene) has been reported by Wegner et al. [23,24]. The fluorescent imaging of polymer films using photoacid lithography has also been reported [25–28]. We have designed a fluorescent crosslinkable amphiphilic polymer forming a stable monolayer on the water surface and demonstrated the photopatterning of a fluorescent polymer LB film.

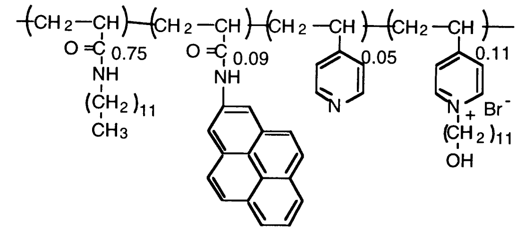
2. Experimental

A fluorescent crosslinkable amphiphilic copolymer consisting of three monomer units, that is, DDA, 1-pyrenylacrylamide (PyA) and *N*-(11-acryloylundecyl)-4-vinylpyridinium salt, was synthesized by the modified method described in the previous study [17] (Fig. 1). The DDA copolymer **1** containing PyA and 4-vinylpyridine (vpy) was prepared by free radical polymerization in THF at 60°C for 24 h with 2,2′-azobis(isobutyronitrile). The fraction of the vpy moiety in the resulting copolymer **1** was quaternized with 11-bromo-1-undecanol under reflux in 2-propanol for 48 h to yield copolymer **2**. Copolymer **3** was obtained by reacting acryloyl chloride with the hydroxyl groups in the quaternized copolymer **2** in the presence of triethylamine in chloroform at room temperature. Copolymer **3** was washed with water to remove unreacted acryloyl chloride and triethylamine and then purified twice by precipitation from chloroform solution into a large excess of acetonitrile. The mole fractions of the copolymers were determined by ^{1}H NMR spectroscopy. All other chemicals were of reagent grade and used without further purification.

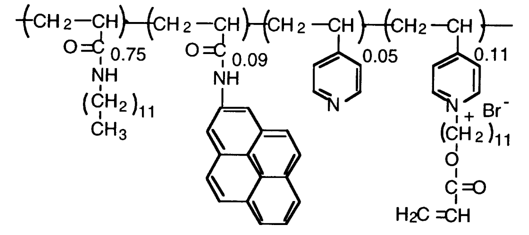
The measurement of surface pressure–area (π–A) isotherms and deposition of the monolayers were carried out with a computer-controlled Langmuir trough FSD-11(USI) at 20°C. Distilled and deionized water (Milipore Milli-Q) was used for the subphase. Chloroform was used as a solvent for spreading monolayers on a water surface. A quartz substrate and a silicon wafer (100) were employed as a substrate for LB films. The monolayer of the polymers were transferred onto both substrates by the vertical dipping method at a dipping speed of 10 mm min^{-1} and surface pressure of 40 mN m^{-1} at 20°C.



copolymer **1**



copolymer **2**



copolymer **3**

Fig. 1. Chemical structure of amphiphilic polymers containing a fluorescent chromophore and a crosslinkable group.

UV absorption spectra and fluorescent spectra were measured with a UV–Vis absorption spectrometer (Hitachi U-3000) and fluorescent spectrometer (Hitachi F-4500), respectively. The photopatterning of a fluorescent crosslinkable polymer LB film was carried out as follows: the polymer LB film was irradiated through a test mask using a 500 W xenon lamp (USHIO) filtered with an IR filter. The irradiated LB films were developed in chloroform for typically 1 min and dried with N_2 gas. The fluorescent images of the patterned LB films were observed using a fluorescent microscope (Olympus Vanox) equipped with a camera. Fluorescent images were taken through a 380–415 nm excitation filter, 455 nm beam splitter and above 455 nm emission filter using a 200 W high pressure mercury lamp.

3. Molecular design of a fluorescent crosslinkable amphiphilic polymer

4-Vinylpyridine was used as an introducing site of a crosslinkable group because the amount of introduction of vpy into the DDA copolymer was quite flexible. Acryloyl group acts as a crosslinkable group for photopatterning. PyA is chosen as a fluorescent chromophore because the detectable fluorescence intensity is observed at a few mole fraction of PyA in the DDA polymer LB films in previous studies [21,22]. Although the mole fractions of DDA, vpy and PyA in the copolymer can vary infinitely, the amphiphilic

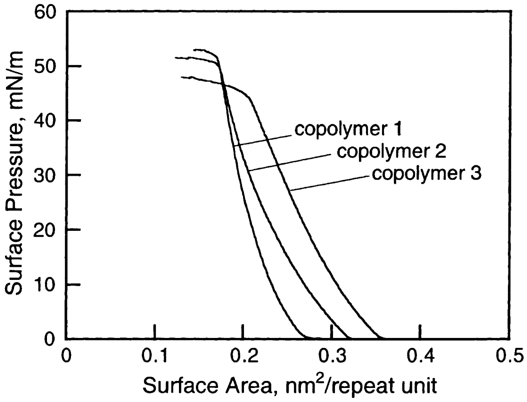


Fig. 2. Surface pressure and molecular area isotherms of copolymers **1**–**3** at 20°C.

balance is a crucial factor to obtain a stable monolayer on the water surface. The mole fraction ratio should be determined to optimize the amphiphilic balance. According to the previous results of the copolymerization of DDA with vpy and PyA [17,22], high mole fractions of vpy and PyA were incorporated into the copolymer compared with that of DDA. The mole fractions of DDA, vpy and PyA in the resulting copolymer **1** were determined to be 0.75, 0.16 and 0.09, respectively, by ^{1}H NMR spectrum. The pyridine moiety in the copolymer **1** was then quaternized by 11-bromo-1-undecanol, yielding 70% determined by ^{1}H NMR spectrum. The hydroxyl moiety in the copolymer **2** was almost perfectly esterified by acryloyl chloride to obtain the copolymer **3**.

4. Monolayers of the copolymers at the air–water interface

The copolymes were spread onto the water surface from the chloroform solution to measure the monolayer behavior. The π–A isotherms show that all the copolymers form stable monolayers on a water surface with a high collapse pressure above 45 mN m^{-1} (Fig. 2). The limiting surface area, which was obtained by the extrapolation of the linear part of π–A curves into zero surface pressure, was different from each other. The collapse pressure decreases and the limiting surface area increases with the order of the copolymers **1**, **2** and **3**. The surface pressure of the copolymer **1** monolayer steeply raised, indicating the condensed monolayer, whereas the surface pressure of the monolayers of copolymers **2** and **3** raised gradually, showing an expanded monolayer.

As a possibility of the monolayer structure of copolymer **1** on a water surface, the molecular orientation of alkyl side chains of the DDA moiety stand up from the water surface and amide moiety in the copolymer **1** is placed on the water surface because of amphiphilic property can be supposed. The pyrenyl moiety in the copolymer **1** would be incorporated into alkyl side chains due to the hydrophobicity and the hydrophilic pyridine moiety would be placed under a water subphase. The orientation is consistent with the results reported previously [19,24]. After the quaternization of pyridine moiety with 11-bromoundecanol, the copolymer **2** monolayer becomes the expanding monolayer, whereas the limiting area is similar to that of the copolymer **1**. This result indicates that the *N*-hydroxyundecyl pyridinium moiety is still held under the water subphase because of the hydrophilicity of hydroxyl and pyridinium groups. On the other hand, the limiting area of the copolymer **3**, where the hydroxyl group is esterified by acryloyl chloride, shifts toward the large surface area. This result means that the acryloylundecyl side chain stands up from the water subphase. Therefore, we propose the orientation of the copolymer **3** monolayer on the water surface as illustrated in Fig. 3. All the monolayers of three copolymers were transferred on a quartz slide and a silicon wafer as a Y-type LB film with a transfer ratio of unity.

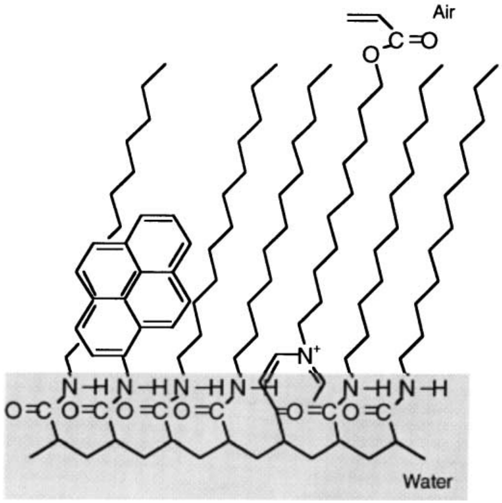


Fig. 3. Schematic representation of the monolayer structure of copolymer **3** on a water surface.

5. Photolithographic and fluorescent properties of the LB films of copolymer 3

The UV absorption spectra of the LB film of copolymer **3** with 18 layers on a quartz slide with various exposure times are shown in Fig. 4. Before light irradiation, the absorption around 260, 290 and 350 nm can be assigned to the π–π^* transition of the phenyl and pyrene groups. The absorption of acryloyl group at 230 nm is buried into the aromatic absorption of pyrene group. The concentration of pyrenyl moiety per monolayer is determined to be 6.5×10^{-11} mol cm^{-2} from the absorption at 350 nm using the molar absorbance coefficient of pyrene group (4.6×10^4 mol^{-1} dm^3 cm^{-1}). This means that one pyrenyl moiety occupies an area of 2.6 nm^2 in the LB films. This value is in reasonably good agreement with the surface area for pyrene

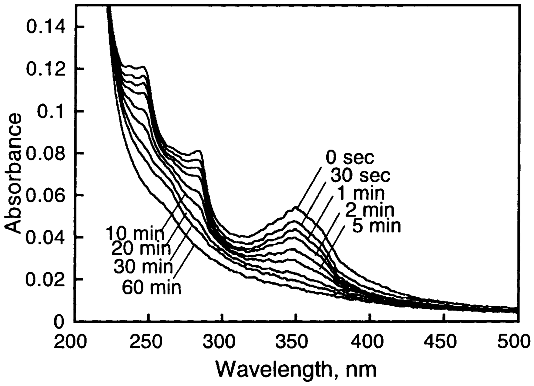


Fig. 4. UV absorption spectra for the LB films of copolymer **3** with 18 layers on a quartz substrate at different irradiating times.

group (2.4 nm^2), which is determined from the π–A isotherm for the copolymer **3** monolayer.

On irradiation, the absorption of pyrene group decreases with exposure time, indicating that the pyrenyl moiety is bleached by the light irradiation. The photobleaching of pyrene may be caused by photooxidation or decomposition of the photoexcited pyrene. After exposure for 60 min, the absorption of pyrene group disappears completely. However, the absorption of pyrene group remains during the light exposure within several minutes. After white light irradiation with a xenon lamp, the LB film becomes insoluble in chloroform, whereas it is soluble before light irradiation. The difference of the solubility against chloroform between the non-irradiated and irradiated polymer LB films indicates that the linear polymer LB films are crosslinked at several points in the polymer chains, forming an insoluble two-dimensional polymer network. Therefore, we expect that the fluorescent crosslinkable polymer LB film will be patterned by photo-crosslinking reaction.

The fluorescent emission spectra of the LB films of the copolymers **1** and **3** are shown in Fig. 5 together with the excitation spectra. The emission bands at 390 nm and the broad band around 420 nm for the LB film of the copolymer **1** (Fig. 5(A)) can be assigned to a typical fluorescence of the excited monomer and the excimer, respectively. On the other hand, the emission intensity around 400–450 nm based on the monomer and the excimer apparently decreases and the broad emission around 500 nm relatively becomes clear (Fig. 5(B)). This emission is attributed to the exciplex from the excited pyrene and the pyridinium cation.

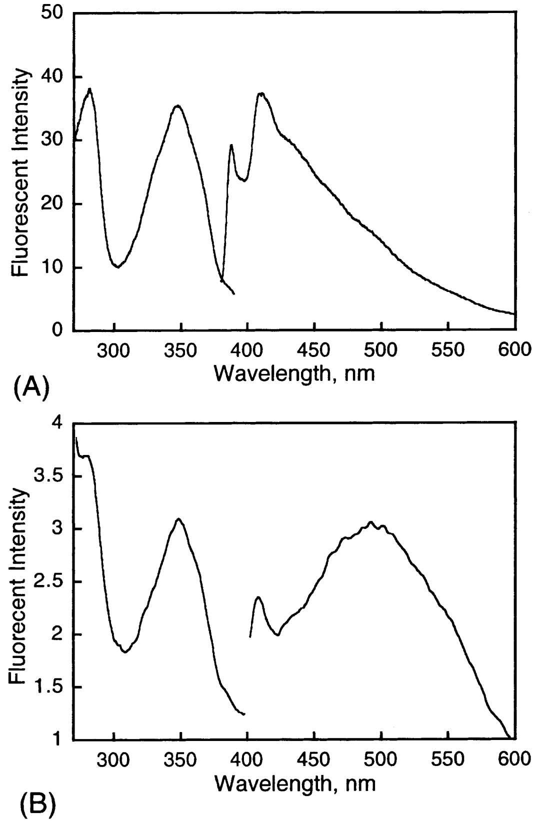


Fig. 5. Fluorescence spectra of the LB films of copolymer **1** (A) and copolymer **3** (B) with 18 layers on quartz substrates. The excitation spectra of (A) and (B) monitored at 410 and 500 nm, respectively.

Next, the photopatterning on the LB films was carried out. The fluorescent microscopic image of the patterned copolymer **3** LB film with 39 layers is shown in Fig. 6. The LB film was patterned as follows: 500 W xenon light was irradiated on the fluorescent crosslinkable polymer LB film through a test mask for 5 min. The irradiated LB film was immersed in a chloroform solution for 1 min to develop the pattern of the LB film. The negative tone pattern was formed. The fluorescent microscopic observation indicates that green color patterns are drawn at the maximum resolution of 2 μm line-and-space. The patterns show that the irradiated part of the LB film is not dissolved and the masked region of the LB film is dissolved only in chloroform. Hence, the crosslinking reaction occurs and some pyrene chromophores in the LB film survive during the light exposure for the photo-crosslinking reaction. The green color shows the exciplex emission based on the pyrenyl moiety in the crosslinked polymer LB film above 455 nm. The surface structure of the patterns was observed to be uniform with no cracks evidently, indicating any aggregation of pyrene moiety in the copolymer LB film, any shrinkage of the LB films caused by a crosslinking reaction and any swelling of the LB films following development with chloroform are negligible. Therefore, we demonstrated that the fluorescent patterns of pyrene were drawn by the incorporation of the pyrene chromophore into the crosslinkable polymer LB film as a comonomer.

In conclusion, we prepared DDA amphiphilic polymer with a crosslinkable acryloyl group and a fluorescent pyrene chromophore as comonomers and fabricated the fluorescent crosslinkable polymer LB film. We demonstrated that the fluorescent images of the polymer LB films were produced by the photolithographic method using a photo-crosslinking reaction. The photolithographic method for producing functional patterns using the crosslinkable LB film can be

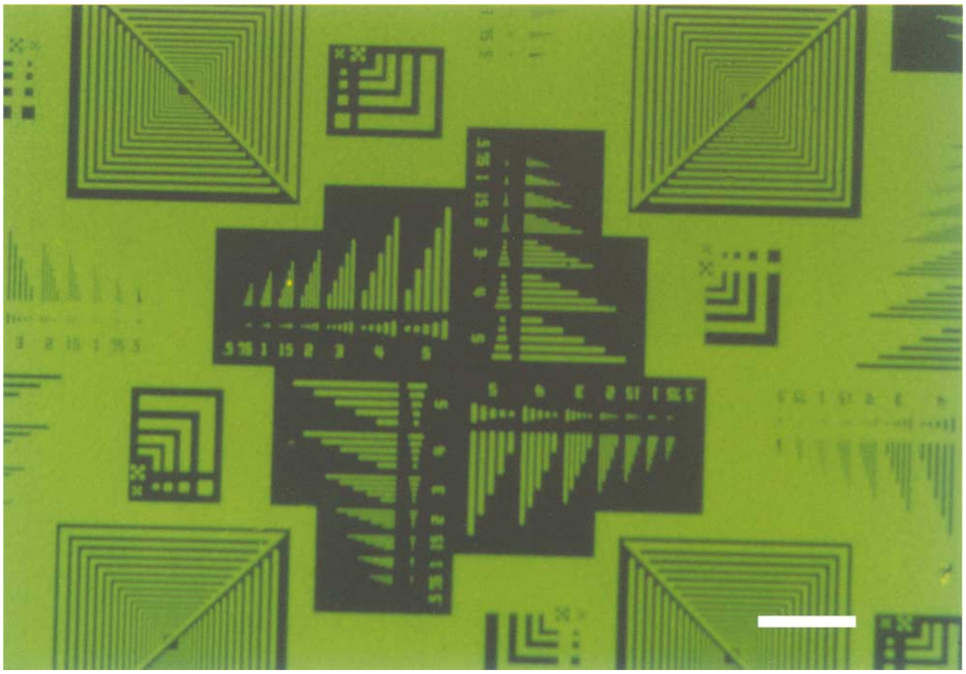


Fig. 6. Fluorescent microscopic photograph of a patterned pyrene polymer LB film with 39 layers on a silicon wafer. An excitation wavelength at 405 nm and an emission wavelength above 455 nm. The patterning condition: the exposure time, 5 min; the developing time, 1 min. White scaling bar represents 100 μm.

extended to pattern various functional groups, such as redox species and donor/acceptors instead of fluorescent chromophore, pyrene. The combination of the LB technique and the photolithography has versatile for spatial arrangement of various functional LB films.

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