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Polymeric Langmuir–Blodgett films containing imidazole-coordinated metal complexes

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Abstract

The binding property and complex structure of an imidazole-containing polymer with metal ions were investigated at the air–water interface and in the LB films. An amphiphilic polymer, poly(*N*-(2-(4-imidazolyl)ethyl)maleimide-*alt*-1-octadecene) (IM-O), was synthesized by the reaction of poly(maleic anhydride-*alt*-1-octadecene) with histamine. A dimethylsulfoxide/chloroform solution of IM-O was spread on pure water or aqueous metal ion (K^+, Mg^{2+}, and Fe^{3+}) subphases. The monolayers were not collapsed until the surface pressure of 40 to 50 mN/m. The surface pressure–area isotherms of IM-O monolayers did not show noticeable difference according to the kinds of subphase. The images of Brewster angle microscopy revealed straight lines after monolayer collapse. The ferric ion-complexed monolayer was transferred onto solid substrates as Y-type. The molecular structure and orientation in the LB films were investigated by means of FT-IR and surface-enhanced Raman spectroscopy. The surface morphology of the LB film was obtained by atomic force microscopy. The quantitative analysis of metal ion concentration incorporated into the LB films was accomplished by means of XPS measurements. The mechanical stability of the LB films was indirectly estimated by SEM observation of the surface morphology of the porous FP-010 membrane covered with the LB films. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Monolayer; LB film; Metal-ion

1. Introduction

Molecularly thin films of polymer–metal complexes have attracted interest because of their potential application to sensors, catalytic systems, and molecular electronic devices [1]. The Langmuir–Blodgett (LB) technique can provide highly ordered molecular films, which in turn can produce multilayers of properly designed structures and thickness [2]. Recently, the incorporation of metal ions in LB films has been investigated in various fields of potential applications [3–5]. However, not much effort has been made regarding the coordination properties of polymeric monolayers spread on aqueous subphases containing metal ions [6–10].

We have however, focused on the functionalities of the imidazole group in the living system, particularly as ligands to metal ions [11–14], and attempted to fabricate imidazole-containing LB films in order to realize the imidazole–metal coordination at the monolayer system [15]. Octadecyl urocanate (OU) showed characteristic monolayer behavior at the air–water interface. The molecular surface area of the OU monolayer was expanded on acidic and basic subphases compared with that on pure water subphases. Meanwhile, the monolayers on subphases containing metal ions showed condensed phases due to imidazole–metal interactions. Additionally, the $[2+2]$ photochemical cyclization between the OU molecules in the LB film was demonstrated. As other examples of using imidazole-containing amphiphiles for monolayer spreading, 2-heptadecylimidazole [16] was used to fabricate a LB film for the photoinduced proton transfer, and chiral derivatives of *N*-alkyl imidazole [17] were spread on metal ion-containing subphases and their two-dimensional aggregation morphology was investigated by fluorescence microscopy.

The aims of the present work are to study the formation and structure of a coordination complex between the metal ion and the ligand monolayer in the LB films and to explore the possibility of obtaining ion sensors using the LB films. Particularly, we report in this paper, the synthesis of an amphiphilic polymeric imidazole, which can be spread to stable monolayers on water surface and the interaction of the polymer with metal ions at the air–water interface. The polymer was expected to fabricate stable LB films compared

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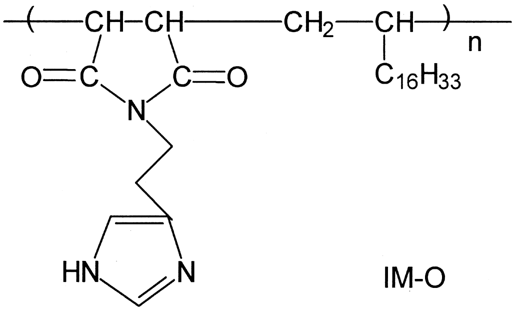
to the low molecular weight correspondent. The high concentration and ordered arrangement of imidazole functional groups can be obtained on the substrate surface by the LB technique and the ordered aggregate structure is supposed to make the film surface much sensitive to detect the metal ion. The monolayer property at the air–water interface was investigated by surface pressure–area (π–A) isotherms and Brewster angle microscopy (BAM). Spectroscopic techniques such as surface-enhanced Raman and FT-IR were applied to confirm the molecular structure and orientation in the LB films. The metal ion concentration in the LB film was determined by X-ray photoelectron spectroscopy (XPS), and mechanical stability of the LB film was indirectly estimated by scanning electron microscopy (SEM) by observing the LB film covered over a porous substrate.

2. Experimental

2.1. Materials

The amphiphilic polymer, poly(*N*-(2-(4-imidazolyl)ethyl)maleimide-*alt*-1-octadecene) (IM-O), was synthesized by the reaction of poly(maleic anhydride-*alt*-1-octadecene) with histamine. Yield 60%; FT-IR (KBr, cm^{-1}) 3103 (aromatic C–H), 2926, 2852 (aliphatic C–H), 1770, 1693 (imide C=O), 1464 (CH_2), 1357 (C–N), other imidazole-originated peaks; ^1H NMR (DMSO-d_6, ppm) 0.80 (t, 3H), 0.90–1.8 (broad s, 32H), 3.02–3.80 (m, 6H), 6.72 (s, 1H), 7.50 (s, 1H). KCl (Sigma), $MgCl_2$ (Junsei), and $FeCl_3$ (Katayama) were used as obtained.



IM-O

2.2. π–A isotherm and LB deposition of monolayer

A film balance system (Nippon Laser and Electronics, NLE-LB200-MWC) was used for measuring surface pressure as a function of molecular area (trough size, $80 \times 585\ mm^2$). Isotherms were taken at a compression rate of 30 mm min^{-1}. A dimethylsufoxide /chloroform (1/9, v/v) mixture was employed as the spreading solvent. The deposition of the monolayer was performed by the vertical mode. The LB depositions were carried out onto solid substrates such as fluorocarbon membrane filters (FP-010, Sumitomo Electric Co.) for SEM and XPS, CaF_2 plates (GL Sciences) for transmission FT-IR spectroscopy, and the Ag colloidal film on mica (60 nm particle size) for surface-enhanced Raman spectroscopy (SERS). SERS spectra were also obtained from the self-assembled IM-O film. The transfer onto the substrates was carried out at a surface pressure of 30.0 ± 0.2 mN/m and a lifter speed of 60 mm min^{-1}. Specifically, the Z-type monolayer was obtained at the speed of 1 mm min^{-1} in the case of the Ag colloidal film on mica.

2.3. Measurements

The FT-IR measurement was carried out on a Perkin–Elmer FT-IR spectrometer by the transmission method. BAM was carried out with a BAM 1 + (NSF) equipped on a NIMA 611D Langmuir trough. The lateral resolution was 10 μm. SERS spectra were obtained with a 1877 Triplemate (Spex) coupled with CCD detector (liq. N_2 cooled). The laser source was Innova 70 (Coherent Co.) The Ar ion laser and power was 10 mW. Atomic force microscopy (AFM; Nanoscope®, Digital Instruments Co.) was used for the observation of the surface morphology of the LB film. The tapping mode was applied to avoid damage on the LB films onto silicon wafers. XPS spectra were obtained on a V.G. Scientific X-ray photoelectron spectrometer, which was operated with a Mg Kα X-ray source and at less than 7.0×10^{-10} Torr. A SEM (JSM 35CH) was used to observe the surface morphology of the FT-010 membrane filter (pore diameter, 0.1 μm). An acceleration voltage of 15 kV was employed. The samples were sputtered with Au before observation.

3. Results and discussion

3.1. Monolayer property of IM-O at the air–water interface

A dimethylsulfoxide/chloroform solution (1/9, v/v) of IM-O was spread on pure water or aqueous metal ion subphases. The employed metal ions were K^+, Mg^{2+}, and Fe^{3+} (1.0×10^{-4} N, pH approximately 7.0). The monolayers revealed high stability up to the surface pressure of 40 to 50 mN/m as shown in Fig. 1. The monolayers of IM-O on aq. subphases containing metal ions showed almost the same isotherms as that on pure water. The monolayer areas were slightly reduced on metal ion-containing subphases compared with that of pure water at the same surface pressure. The extent of area decrease due to imidazole–metal ion interactions was relatively small, compared with the previous OU monolayer systems [15]. The main reason for the difference is thought to be the molecular mobility difference caused by the molecular weight. That is, the OU is a low molecular weight compound while IM-O is obtained from the maleic anhydride copolymer of $M_n = 30,000–50,000$.

The macroscopic images of the IM-O monolayer were monitored at the air–water interface by BAM. Fig. 2

shows the images at different surface pressures of 0 mN/m, 50 mN/m, and after monolayer collapse. No noticeable images were detected before the monolayer collapse. After the collapse point, spotted straight lines appeared normal to the direction of applied surface pressure. It was understood that the monolayer has a homogeneous phase and responds uniformly against the direction of applied surface pressure.

3.2. Molecular structure and orientation in the LB film

The molecular structures of LB films were investigated by means of FT-IR and SERS measurements. Since the most abundant ion incorporated in the LB film was ferric ion as described later, we investigated only the interaction between the imidazole group and ferric ion. The LB transfer was carried out on a CaF_2 plate for transmission FT-IR measurement. The Y-type deposition occurred at a surface pressure of 30 mN/m and a lifter speed of 60 mm/min. The transfer ratio was 0.85–1.02 during the deposition of 20 layers. Together with the strong C–H stretching peaks, the carbonyl peaks in the FT-IR spectra represented the presence of IM-O in the LB film.

The SERS spectra of monolayer films transferred from pure water and metal ion-containing subphases indicated the formation of metal coordinated complexes. The monolayer interacting with the Fe^{3+} ion at the air–water interface was transferred onto a Ag colloidal film on mica (60 nm particle size). The Z-type deposition occurred at a surface pressure of 30 mN/m and a lifter speed of 1 mm min^{-1}. Fig. 3 shows the SERS spectra taken from the self-assembly monolayer (pure water subphase) and LB monolayer (1 mM $FeCl_3$ subphase). In the case of pure water subphase, the spectrum shows large background peaks with a small S/N ratio. From this result, we believe that the IM-O monolayer in the air–water interface is not well adsorbed to the surface of the Ag colloidal film. Because of the negative charge of citrate ions in the surface of the original Ag colloidal film, imidazole groups possessing lone pair electrons on five-membered rings show repulsive interactions with the colloidal film surface. Thus, it is thought that the fluorescence quenching does not take place effectively. In the case of the $FeCl_3$ subphase, however, very different spectral feature was observed. The ferric cation of positive charge could form a complex with the imidazole group and then easily adsorb to the negatively charged surface of the Ag colloidal, which yields effective fluorescence quenching and enhanced S/N ratio.

Strong peaks due to in-plane modes of the imidazole ring were observed in the wavelength range from 1000 to 1600 cm^{-1} in the monolayer system from pure water subphase, meaning vertical orientation of the imidazole ring against the film surface. In the case of the $FeCl_3$ subphase, however, the spectrum of the IM-O LB film shows relatively enhanced peaks of out-of-plane (OOP) modes in the wavelengths at 612 and 772 cm^{-1}. These

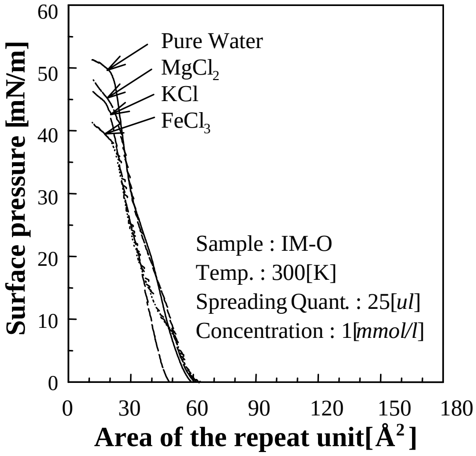


Fig. 1. Surface pressure–area isotherms of IM-O on aq. metal ion subphases. The concentration of metal ions was 1.0×10^{-4} N.

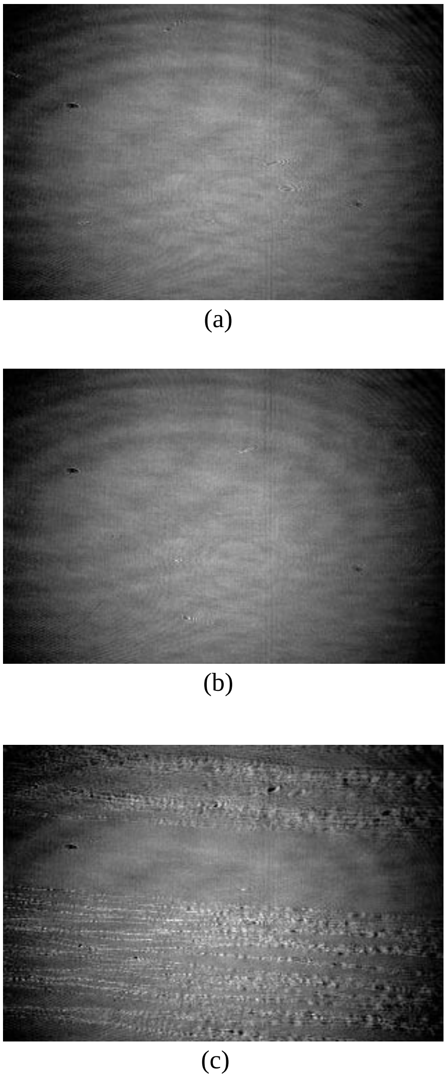

(a)
(b)
(c)

Fig. 2. BAM images of IM-O on pure water subphase at 25°C: (a) at 0 mN/m; (b) 50 mN/m; and (c) after monolayer collapse.

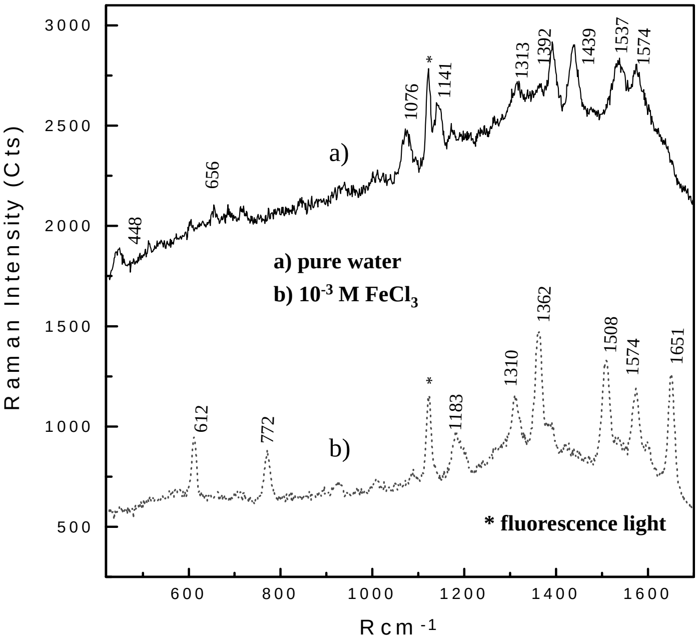


Fig. 3. SERS spectra of: (a) self-assembled monolayer; and (b) LB monolayer of IM-O on mica-supported Ag colloidal film.

enhanced OOP modes indicate flat orientation of the imidazole ring to the surface due to the ferric complex-induced rearrangement. Also, the relative intensity of the in-plane ring-breathing mode at 1076 cm^{-1} is weakened, and the C=O stretching mode at 1651 cm^{-1} is observed only in the case of the metal ion-containing subphase. The results suggest that the metals coordinate also with oxygen of imide carbonyls. Based on the above results, we suppose that two imidazole groups and one carbonyl oxygen participate together in the formation of the ferric complex as ligands, and the horizontal orientations of imidazole rings are induced in order to make the distance between oxygen and the imidazole ring closer.

The surface morphology of the IM-O LB films, which were transferred at 30 mN/m onto silicon wafers, was obtained by an AFM. The AFM images were taken from the domain structure in the 5×5 μm scale and showed molecularly uniform structure. The root-mean-square values of roughness and thickness of the IM-O monolayer LB film are ca. 2.4 and ca. 20 Å, respectively.

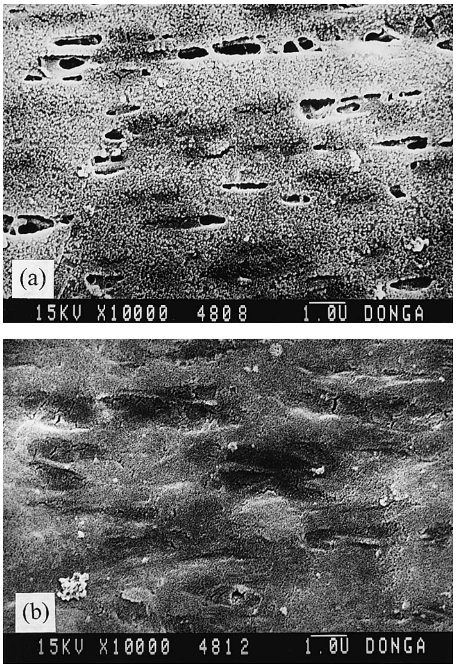


Fig. 4. SEM micrographs of LB films of IM-O deposited on fluorocarbon membrane filters (FP-010): (a) as-deposited film of 4 monolayers from pure water subphase and (b) as-deposited film of 4 monolayers from aq. $FeCl_3$ subphase (1.0×10^{-4} N).

3.3. Metal ion concentration and LB film stability

The quantitative analysis of metal ion concentration incorporated into the LB films was performed by means of XPS measurement. By taking into account the atomic sensitivity factor and the relative area of the N 1s, K 2p, Mg 2p, and Fe 2p peaks, we could estimate that the concentration of metal ions was the order of $Fe^{3+} > Mg^{2+} > K^+$

Table 1
The concentration of metal ions incorporated into the LB films

Polymer	Metal ion[a]		
	K^+	Mg^{2+}	Fe^{3+}
IM-O	2.96	2.99	3.34

[a] The value means the number of metal ion per repeat unit of the polymer. The concentration of the metal ions was determined by taking into account the atomic sensitivity factor and the relative area of the N 1s, K 2p, Mg 2p, and Fe 2p peaks of XPS spectra.

(Table 1). The most abundant ion incorporated in the LB film was ferric ion. The calculated number of the ions per repeat unit of IM-O polymer was close to 3 even in alkali or alkali earth metals. This means that the ions are not totally transferred only as the states of electrostatic or coordinated binding with IM-O polymer. The hydrated ions around the hydrophilic moiety of the IM-O monolayer are supposed to be transferred together with the binding ions.

The stability evaluation of the LB film was indirectly performed by counting the least number of LB monolayers necessary to cover the pores of membrane filter substrates. Fig. 4 shows the SEM micrographs, when the LB film did not contain the metal ions, the LB film was rarely seen over the pores, i.e. the LB films were collapsed into the pores. However, the metal ion-containing LB films could be placed over the pores with a few layers. The self-supporting LB films over the pores tell the enhanced mechanical stability of the LB films by incorporation of metal ions. This self-supporting capability of the LB films on porous substrates should be important for practical applications toward sensors and selective permeation of gases or biomolecules.

Acknowledgements

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