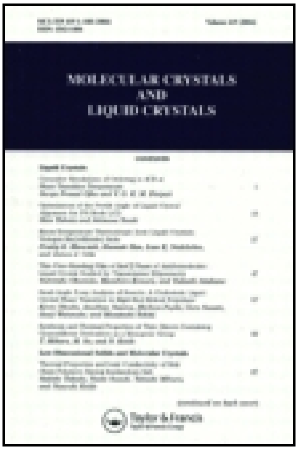

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Polymeric Langmuir-Blodgett Films of Imidazole-Coordinated Metal Complexes

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POLYMERIC LANGMUIR-BLODGETT FILMS OF IMIDAZOLE-COORDINATED METAL COMPLEXES

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Abstract An imidazole-containing amphiphilic polymer (IMA-OVE) was synthesized and the metal-complexing capability of its monolayer at the air-water interface was examined. The polymer was obtained by radical copolymerization of N-(2-(4-imidazolyl)ethyl)maleamic acid (IMA) with n-octadecyl vinyl ether (OVE). Monolayers of IMA-OVE on aq. subphases containing metal ions were studied by measuring surface pressure-area isotherms. The preparation conditions of IMA-OVE Langmuir-Blodgett (LB) films on fluorocarbon membranes and calcium fluoride plates were studied and the physicochemical properties of the LB films were then examined by Raman, XPS, and FT-IR spectroscopy. The concentration of metal ions incorporated into the LB films was the order of Fe^{3+}> Mg^{2+}> Cu^{2+}> K^+.

INTRODUCTION

We have focused on the functionalities of the imidazole group in the living system[1], particularly as ligands to metal ions, and attempted to fabricate imidazole-containing functional Langmuir-Blodgett (LB) films. As examples of imidazole-containing molecules employed for monolayer spreading, 2-heptadecylimidazole[2] was found to fabricate a LB film for the photoinduced proton transfer, and chiral derivatives of N-alkyl imidazole[3] 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 mechanism of the formation of a complex structure between the metal ion and the ligand monolayer at the air-water interface and to explore the possibility of obtaining chemical sensors using the LB films. In this paper, we report the synthesis of a 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

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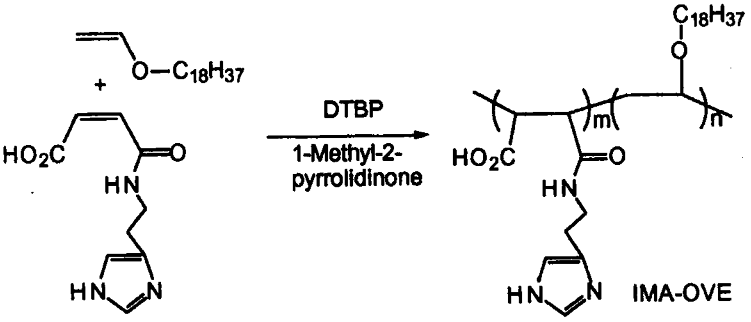
films compared to the low molecular weight correspondent. The high concentration and ordered arrangement of imidazole functional groups on the substrate surface can be obtained by the LB technique and the ordered aggregate structure is supposed to make the film surface much sensitive to detect the metal ion. The monolayer property at the air-water interface was investigated by surface pressure-area isotherms and spectroscopic techniques such as Raman and FT-IR spectra were applied to confirm the molecular structure of the LB films.



EXPERIMENTAL

Materials. The monomer, n-octadecyl vinyl ether (OVE), was synthesized through transetherification between n-octadecyl alcohol and ethyl vinyl ether using mercuric acetate as catalyst.[4] An imidazole-containing monomer, N-(2-(4-imidazolyl)ethyl)maleamic acid (IMA), was prepared by the reaction of maleic anhydride with histamine. Radical copolymerization of OVE and IMA was carried out by using 1-methyl-2-pyrrolidinone as solvent and di-tert-butylperoxide as initiator. The structures of monomers and polymer were confimed by EA, IR, NMR, DSC, TGA, and GPC analyses. KCl (Sigma), $MgCl_2$ (Junsei), $CuCl_2$ (Junsei), and $FeCl_3$ (Katayama) were used as obtained. Aqueous poly(allylamine) (PAA) solution ($Mn=10^4$, 10 wt %) was purchased from Nitto Boseki Co.

Measurement. A film balance system HBM-SS (Kyowa Interface Science) was used for measuring surface pressure as a function of molecular area (trough size, 150 × 600 mm). The deposition of monolayer was performed in vertical mode. The LB transfer was carried out onto solid substrates such as fluorocarbon membrane filters (FP-010) for the XPS measurement and CaF_2 plate (GL Sciences) for transmission FT-IR and Raman measurements. FT-IR measurement was carried out on a Perkin-Elmer FT-IR spectrometer by the transmission method. Raman spectra were obtained with a RENISHAW 2000 He-Ne laser instrument. XPS spectra were obtained on 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.

RESULTS AND DISCUSSION

Monolayer Properties at the Air-Water Interface. Chloroform solution of

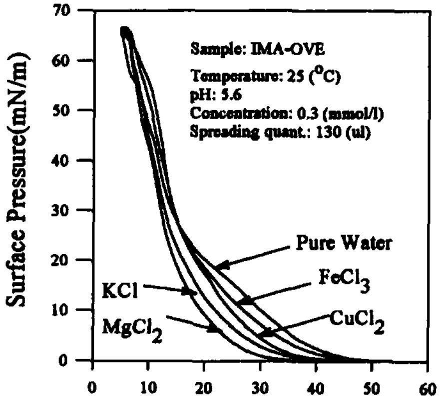
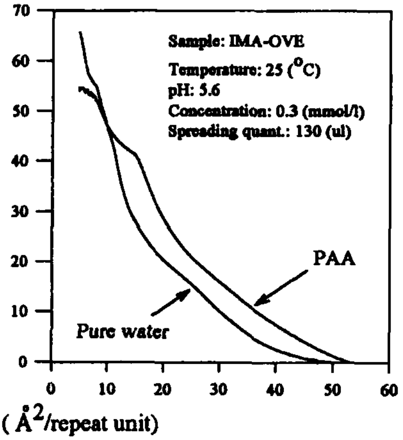


FIGURE 1 π–A isotherms of IMA-OVE on aq. metal subphases.



FIGUE 2 π-A isotherms of IMA-OVE on aq. poly(allylamine).

IMA-OVE was spread on pure water or on aqueous metal ions. The employed metal ions were K^+, Mg^{2+}, Cu^{2+}, and Fe^{3+}. The monolayers showed high stability up to the surface pressure of 60 mN/m. When compared with the case in the absence of the metal ion, all the monolayers showed more condensed phases in the presence of metal ions as shown in Figure 1. The changes of the molecular area from the pure water subphase at 10 mN/m of surface pressure by the addition of metal ions into subphases were -9.8 (Fe^{3+}), -13.8 (Cu^{2+}), -19.1 (K^+), -24.0 (Mg^{2+}) $Å^2$/repeat unit. Specifically, in the presence of magnesium ion, the area reduction was large. This change of molecular areas by the addition of metal ions is attributed to the interaction of imidazole and carboxyl moieties of IMA-OVE with metal ions at the air-water interface and the consequent change of the monolayer organization. Specifically, the hydrogen bonding is considered to be more tightened along with the decrease of the hydration on imidazole groups. Much more than the above effect is the electrostatic interaction between the multivalent metal ions and the carboxylate ions of the polymer. This effect is thought to be pronounced in the subphase containing magnesium ion. The coordination of imidazole nitrogen to transition metal ions as a ligand is another reason of the additional area reduction.

The surface pressure-area isotherms of IMA-OVE on aq. PAA are shown in Figure 2. Differently from the isotherms on metal ion-containing subphases, area expansion by the addition of PAA was observed. The area expansion is attributed to the formation of a polyion complex at the air-water interface and the consequent change of the monolayer organization,[5] i.e., an electrostatic repulsion between the polymer chains with more ionized carboxyls on weakly alkaline PAA subphase (pH 8.4) than on pure water, and a separation of the closely positioning polymer chains of the spread copolymer, PAA, at the air-water interface.[6]

Fabrication and Characterization of LB Films. The monolayer interacting with Fe^{3+} ion at the air-water interface was transferred onto a CaF_2 plate. The Y type deposition occurred at a surface pressure of 30 mN/m and a lifter speed of 100 mm/min. The transfer ratio was 0.88-0.92 during the deposition of 8 monolayers. The molecular structures of LB films were investigated by means of FT-IR and Raman spectra. Four types of carbonyl absorption peaks at 1736 cm^{-1}, 1710 cm^{-1}, 1651 cm^{-1}, and 1541cm^{-1} were observed, which are attributed to carboxyls, amidic carbonyls, and carboxylate ions, respectively. Together with the strong C-H stretching peaks, the carbonyl peaks represent the presence of IMA-OVE in the LB film. The FT-IR and Raman spectra of low frequency (below 600 cm^{-1}) region gave evidences for the imidazole-ferric ion coordination complexes and showed similar peaks pattern in both the spectra. The peaks were complicated and difficult to assign all the peaks to the corresponding vibrational modes. However, we could find the peaks around 390, 410, 840 cm^{-1} due to the imidazole-ferric ion coordination bonds via a model complex from histamine and ferric ion.[7]

The quantitative analysis of metal ion concentration incorportated into the LB films was performed by means of XPS measurements. By taking into account the atomic sensitivity factor and the reative areas of the N 1s, Cl 2p (for K), Cu 2p, Mg 2s, and Fe 2p peaks, we could estimate that the concentration of metal ions incorportated into the LB films was the order of $Fe^{3+} > Mg^{2+} > Cu^{2+} > K^+$ (Table 1).

TABLE 1. The concentration of metal ions incorporated into the LB films.

Copolymer	Metal ion[a]			
	K^+	Mg^{2+}	Cu^{2+}	Fe^{3+}
IMA-OVE	0.09	0.22	0.20	1.14

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

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