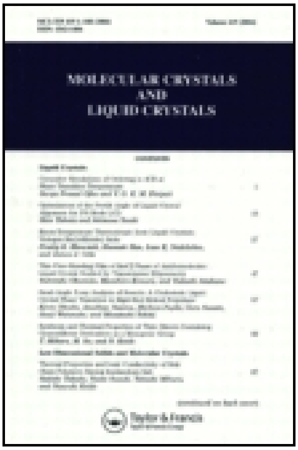

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Structure Analysis of Langmuir and Langmuir-Blodgett Films with Metal Complexes

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Structure Analysis of Langmuir and Langmuir-Blodgett Films with Metal Complexes

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We fabricated IMI-O polymer containing imidazole group that forms a complex structure between the monolayer and the metal ions at the air-water interface. Also, the monolayer behavior at the air-water interface and Langmuir-Blodgett (LB) films by complex formation have been investigated by π-A isotherm and the scanning Maxwell-stress microscope.

Keywords: Ion complex; LB films; SMM; Surface potential

INTRODUCTION

The increasing interest into technical applications of LB films emphasizes the need to pay special attention to the mechanical stability of the film structure[1]. This interest is supported by the opportunity of forming similar layered structures by the consecutive deposition of monomolecular layers of various surface-active substances[2].

The scanning Maxwell-stress microscope (SMM) is a variant of AFM operated in the noncontact mode, which can image the distribution of surface charge and potential over ultra-thin films with a nanometer scale resolution. SMM allows simultaneous observation of electrically imaged topography and electric properties as above based only on the harmonic analysis of forced oscillations of the cantilever driven by an external AC-voltage[3]. In this work, we attempted to fabricate IMI-O polymer containing imidazole group that can form a complex structure with the metal ions at the air-water interface. Also, we investigated the application of the SMM to structural-functional study of LB films of metal-polymer complexes as well as the molecular ordering.

EXPERIMENTAL

We synthesized the amphiphilic polymer, poly(N-(2-(4-imidazolyl) ethyl) maleimide-alt-1-octadecene) (IMI-O), by reaction of poly(maleic anhydride-alt-1-octadecene) with histamine to form a metal complex structure at the air-water interface (Fig. 1(a))[4]. The chloroform was employed as the spreading solvent (1mmol/l). The metal ions were Fe^{3+}, K^{+} and Mg^{2+} of 1mmol/l. The π-A isotherms were investigated by NL-LB200-MWC (NLE, Moving-wall type, 80mm×585mm). The deposition on the substrates was carried out at a surface pressure of 30mNm. The images of the LB films were obtained by using SMM imaging in the repulsive mode in air with commercial system (Nanoscope III, Digital Instruments, USA).

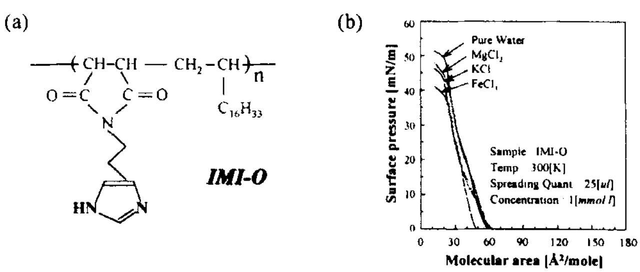

FIGURE 1 (a) Molecular structure and (b) surface pressure-area isotherms for IMI-O monolayer on various subphase.

RESULTS AND DISCUSSION

Metal complexed LB films are expected to be improved with respect to stability and structural defects because of the stability of metal complexed monolayer films at the air-water interface[5]. The molecular structure by complex formation was verified by Raman and FT-IR spectroscopy. In Fig. 1(b), the monolayer on subphases containing metal ions showed almost the same isotherms as that on pure water. The monolayer areas were slightly reduced on metal ion subphases compared with that of pure water at the same surface pressure and the surface pressures at the collapse point were observed to be different from each other. It is thought that these phenomena occurred due to the molecular weight and interaction of metal ions.

Figure 2 shows the Brewster Angle Microscopy (BAM) images as the surface pressure increases to examine the morphologies of the Langmuir films on subphase of the pure water and the metal ion (Mg^{2+}). The difference of BAM images between the pure water and the metal ion is attributed to the interactions of the copolymers with metal ions at the air-water interface and the consequent change of the monolayer organization.

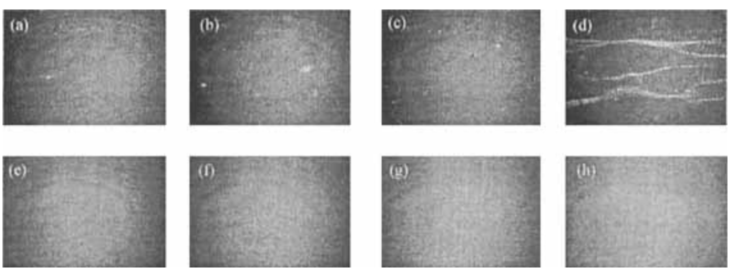

FIGURE 2 The BAM image of IMI-O monolayer. (a) 10mN/m, (b) 20mN/m, (c) 40mN/m and (d) 50mN/m on subphase of pure water, (e) 10mN/m, (f) 20mN/m, (g) 30mN/m and (h) 45mN/m on subphase of Mg^{2+}.

Figure 3 shows the SMM topography and surface potential images of metal complexd LB film deposited on a silicon substrate. The SMM surface potential image clearly shows the existence of micron-sized domains in the LB film, having a good correspond with the topographical features. The height of the hump, however, reaches 20nm, so that this portion is most likely to be a collapsed residue rather than a monolayer. The fact that the surface potential is lower over the hump by 30mV relative to the surrounding region should reflect the charge distribution inside the collapsed monolayer. The use of other metal ions showed essentially similar potential distribution on the surface. It is thought that this phenomenon was one of the special potential distributions formed by effect of ion complex at the air-water interface.

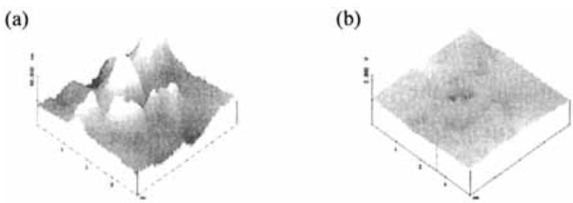

FIGURE 3 Topography (a) and surface potential (b) of Fe^{3+} IMI-O monolayer LB film observed by SMM. (4μm x 4μm).

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