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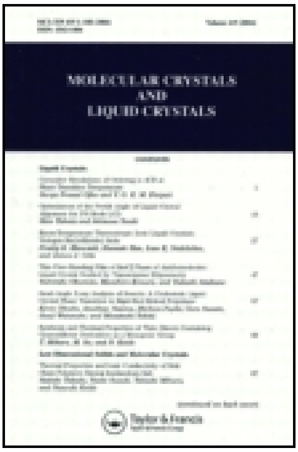

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Monolayer Properties of a Perfluoroalkyl Maleate Copolymer on Aqueous Metal Ion Subphases

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MONOLAYER PROPERTIES OF A PERFLUOROALKYL MALEATE COPOLYMER ON AQUEOUS METAL ION SUBPHASES

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Abstract Electrostatic interactions between polymers and metal ions at the air-water interface and in resulting LB films were investigated. The polymer was prepared from radical copolymerization of 2-(perfluorooctyl)ethyl monomaleate with triethyleneglycol methyl vinyl ether. The metal ions examined were Na^+, Cs^+, Mg^{2+}, Fe^{2+}, Al^{3+}, and Fe^{3+}. The surface pressure-area isotherms show that all the monolayers on aqueous metal ions reveal more expanded phases than that on pure water. From the FT-IR (reflection and transmission) spectra, the formation of carboxylate salts and the relative pendent orientation of the polymer in LB film could be estimated. Quantitative analysis of metal ion concentration incorporated into the LB film was carried out by XPS measurement.

INTRODUCTION

Metal ion-containing Langmuir-Blodgett(LB) films have shown unique electric, electronic, and magnetic properties[1]. However, even the principles governing the type and efficiency of deposition of monolayers interacting with metal ions remain poorly understood. Recently, Puggelli et al. reported interactions between monolayers and metal ions at the air-water interface, which was focused on the conditions for the transferability as LB multilayers[2]. Another report is found to be studied on dynamic contact angle and deposition efficiency for transfer of docosanoic acid onto mica from $CdCl_2$ subphase as a function of pH [3].

On the other hand, as a breakthrough to improve the mechanical stability of intrinsically fragile LB films, the use of preformed polymers has been investigated extensively in the recent years[4]. Specifically, Kunitake et al. have reported stabilization of monolayers and LB films by electrostatic interaction of ionic polymers with oppositely-charged amphiphiles[5] and by covalent crosslinking of ionically interacting polymers[6]. However, the interactions of those ionizable polymers with metal ions at the monolayers and in their LB films have not been reported.

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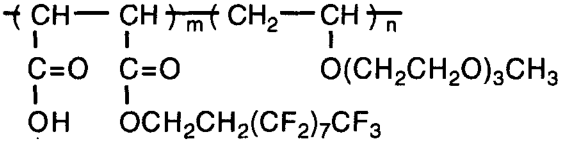
In this paper, we report interactions between polymers and metal ions at the air-water interface and in their LB films. The polymer is designed to have pendants of hydrophobic perfluoroalkyl chain, and hydrophilic carboxyls and oligoethers, i.e., i) the fluorocarbon chains are expected to give more close packing than hydrocarbon ones, ii) the carboxyls can form carboxylate salts with subphase metal ions and give pseudo-crosslinking by interchain electrostatic interaction with multivalent metal ions, iii) the pendent oligoethers are expected to give a flexibility to the polymer backbone and to enhance the monolayer stability. The metal ions examined were Na^+, Cs^+, Mg^{2+}, Fe^{2+}, Al^{3+}, and Fe^{3+}. The monolayer properties at the air-water interface were examined by surface pressure-area (π-A) isotherms. The structural characterization of the LB films was carried out by means of FT-IR. Quantitative analysis of metal ion concentration incorporated into the LB films was carried out by XPS measurement.



$$\left(\begin{array}{ll} CH - & CH \\ | & | \\ C{=}O & C{=}O \\ | & | \\ OH & OCH_2CH_2(CF_2)_7CF_3 \end{array}\right)_m \left(\begin{array}{ll} CH_2 - & CH \\ & | \\ & O(CH_2CH_2O)_3CH_3 \end{array}\right)_n$$

$C_2F_8MA\text{-}VE_3$

EXPERIMENTALS

Materials

The synthetic procedure of monomer, 2-(perfluorooctyl)ethyl monomaleate(C_2F_8MA), was described previously[7]. The comonomer, triethyleneglycol methyl vinyl ether (VE_3), was synthesized through transetherification according to the literature[8]. The copolymerization of the monomaleate monomer was carried out in a pressure bottle at 60 °C for 24 h by using the vinyl ether comonomer as an excess. AIBN was used as initiator. $C_2F_8MA\text{-}VE_3$[7]: yield 78%; η_{inh}=0.17 dL/g (0.5 g/dL in THF at 25 °C); IR (NaCl, cm^{-1}) 2900 (C-H), 1725 (C=O), 1450 (CH_2), 1322 (CH_3), 1300-1000 (C-O, C-F); ^{1}H-NMR (CF_3CO_2H, ppm) 1.3-2.5 (broad s, 6H), 2.5-3.1 (broad s, 3H), 3.1-3.9 (broad s, 13H), 3.9-4.7 (broad s, 2H). The composition of the copolymer was estimated to be 1:1 by ^{1}H-NMR spectra. NaCl (Junsei), CsCl (Sigma), $MgCl_2$ (Junsei), $FeCl_2$ (Junsei), $AlCl_3$ (Junsei), and $FeCl_3$ (Katayama) were used as obtained.

π-A isotherm and LB transfer of monolayer

A computer-controlled film balance system FSD-50(San-esu Keisoku) was used for measuring surface pressure as a function of molecular area (trough size, 150 x 600 mm) and together with FSD-51 lifter for monolayer transfer. Isotherms were taken at a

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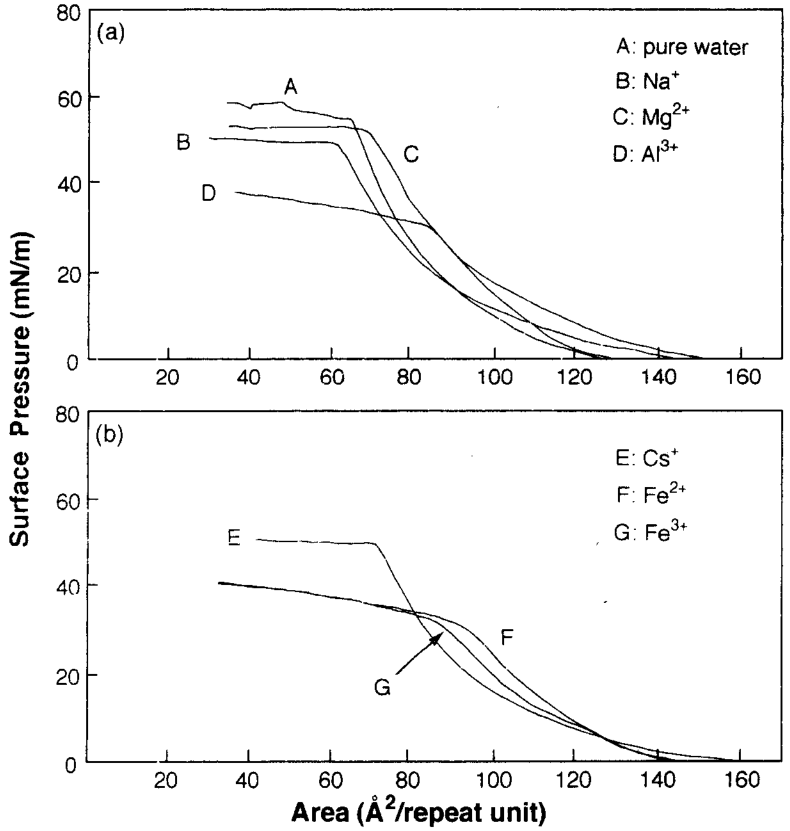

FIGURE 1 π-A isotherms of C_2F_8MA-VE_3 on aq. metal ion subphases.

compression rate of 0.4 mm/sec, and the temperature of the aqueous subphase was maintained at 20.0 ± 0.1 °C. Monolayers were spread on pure water or on aqueous metal ions (1.0 x 10^{-3} N) and incubated for 30 min before starting the compression. The employed substrates were slide glass deposited sequentially with Cr (200 Å) and Au (1000 Å) for the reflection FT-IR and XPS measurements and CaF_2 plates(GL Sciences) for the transmission FT-IR measurement.

Measurements

FT-IR spectra were obtained on a Perkin-Elmer FT-IR spectrometer by the reflection and the transmission methods. In order to minimize the influence of water vapor and CO_2 on the spectra, the system was purged by dry air for 1-2 h before measurement. XPS spectra were obtained on an ESCA 5300 X-ray photoelectron spectrometer(Perkin-Elmer), which was operated with a Mg Kα X-ray source and at less than 4.0 x 10^{-10} Torr. The sample stage was cooled to below -100 °C by an internal thermal conductor connected to an external cryogenic Dewar.

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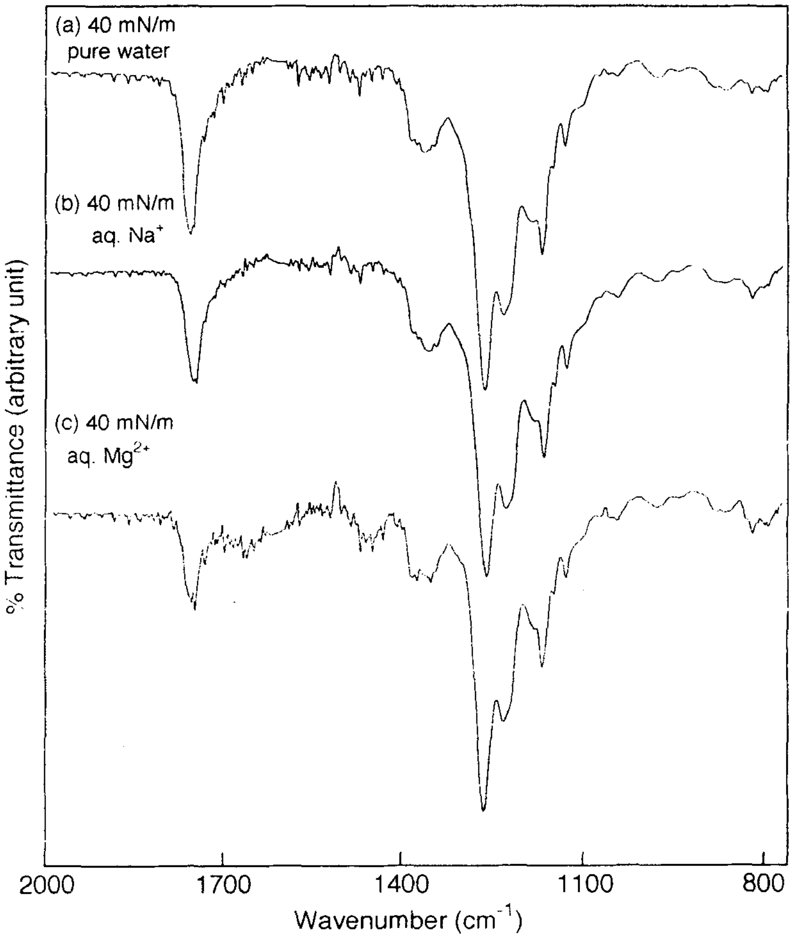

FIGURE 2 Reflection FT-IR spectra of LB films of $C_2F_8MA\text{-}VE_3$.

RESULTS AND DISCUSSION

Monolayer formation and its transfer onto solid substrates

Methyl pentafluoropropionate solution of the copolymer $C_2F_8MA\text{-}VE_3$ was spread on pure water or on aqueous metal ions. π-A isotherms of Figure 1 show that the copolymer forms stable monolayers. The monolayers give expanded phases. When compared with the isotherm on pure water, more expanded area is revealed on aqueous metal ions. This change between the two isotherms is attributed to the interaction of the copolymer with metal ions at the interface and the consequent change of the monolayer organization, similarly as described for other polymer-polymer polyion-complexing systems[5-7]. The copolymer showed lowered collapse pressure of the monolayers when spread on aq. Fe^{2+}, Al^{3+}, and Fe^{3+} subphases. It is supposed that the lowered monolayer stability is due

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to the lowered pH (3.5 of $FeCl_3$ and 4.8 of $AlCl_3$) and the possible multiple complexation with carboxylate ions and a consequent decrease in hydrophilicity of the copolymers.

The monolayers interacting with Na^+ or Mg^{2+} ion at the interface were transferred onto solid substrates such as a silde glass deposited with Au/Cr and a CaF_2 plate. In all cases, the Y type deposition was found at a surface pressure of 10 or 40 mN/m and a transfer rate of 50 or 10 mm/min. Whenever the monolayers were transferred at 10 mN/m, rapid dipping run of 50 mm/min was necessary in order not to lose the deposited molecular layers during the downward strokes. The transfer ratio was 1.09 to 0.79.

Metal ion-containing LB film

The formation and structure of a polymer complex with metal ions could be confirmed by means of FT-IR. Figure 2(c) shows two characteristic carbonyl peaks at 1725 cm^{-1} and 1575 cm^{-1}, which are attributed to ester and carboxylate salt, respectively. It means the incorporaton of Mg^{2+} into the film. However, the peak due to carboxylate salt was not strong in case of LB films deposited from aq. Na^+ subphase. The result was also supported by quantitative analysis of metal ion concentration incorporated into the LB films by means of XPS measurements. By taking into account the atomic sensitivity factor and the relative area of the C 1s, Na 1s, and Mg 2p peaks, it was estimated that ca. 4.1 repeat units of the polymer C_2F_8MA-VE_3 contained one Na^+ ion, while one Mg^{2+} ion interacted with 2.7 carboxyls. Figure 3 shows the Na 1s and Mg 2p peaks on XPS spectra. But, contribution of the oligoether-metal ion interaction to the incorporation of metal ion into the LB films is supposed to be negligible, which is evidenced from the

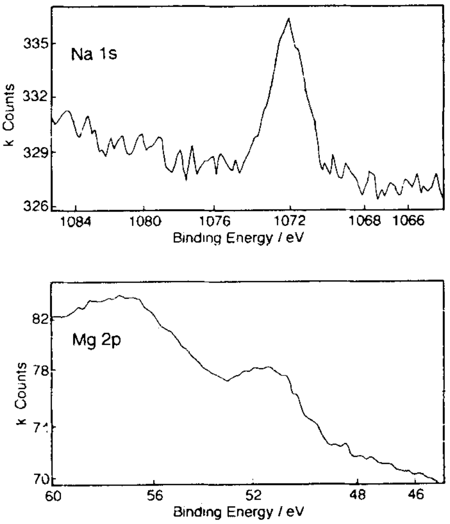

FIGURE 3 XPS spectra of Na 1s and Mg 2p of LB films.

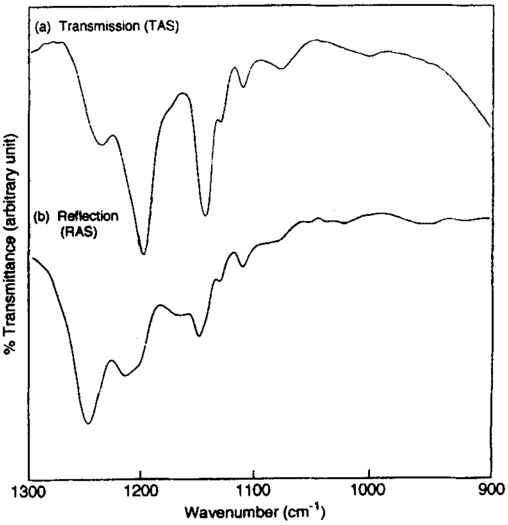

FIGURE 4 Transmission and reflection FT-IR spectra of LB films.

ether peaks showing no noticeable changes in Fig. 2. Compared with Figure 4(b), more intensive ether and fluorocarbon peaks are seen in Figure 4(a). From the difference of relative intensities of the transmission and the reflection spectra, we can deduce that, while the pendent oligoether chains lie on the substrate surface, the fluorocarbon chains are uprisen against the substrate surface. The spectra patterns were same in all the LB films obtained from various metal ion subphases. Therefore, it is supposed that the orientation of the oligoethers is irrespective of the existance of the metal ions.

ACKNOWLEDGMENT

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