Metal Ion-Containing Langmuir-Blodgett Films of a Monooctadecyl Itaconate Copolymer

Jong Hyun Son, Giseon Choi, Burm-Jong Lee*, and Kazue Kurihara†

Department of Chemistry, Inje University, Kimhae 621-749, Korea
†Department of Applied Physics, Nagoya Univ., Nagoya 464-01, Japan
Received November 28, 1994

The incorporation of metal ion into the Langmuir-Blodgett (LB) film of an itaconate copolymer was investigated. The polymer was prepared *via* radical copolymerization of monooctadecyl itaconate with triethyleneglycol methyl vinyl ether. The metal ions employed were Na^+, Cs^+, Mg^{2+}, Fe^{2+}, Al^{3+}, and Fe^{3+}. The surface pressure-area isotherms indicated that all the monolayers studied on subphases with metal ions showed more expanded areas than that observed on pure water. The monolayers showed an irreversible collapse behavior. The collapse pressure of the monolayers was low on subphases containing trivalent metal ions. From the FT-IR spectra by reflection and transmission modes, the formation of carboxylate salts and the uprisen orientation of the pendant against substrate surface in the polymer LB film were determined. It was estimated by XPS measurement that *ca.* 13.1 repeat units of the polymer contain one Na^+ ion, while one Mg^{2+} ion corresponds to 5.9 carboxyls.

Introduction

Metal ions have been incorporated into the Langmuir-Blodgett (LB) films mostly in two aspects.[1] One is to improve the intrinsic fragility of LB films and the transferability on solid substrates. Namely, it has been focused on obtaining high quality LB films. In spite of the much attention in metal ion-containing LB films, the principles governing the type and efficiency of deposition of monolayers interacting with metal ions remain yet poorly understood. Recently, Puggelli *et al.* reported interactions between monolayers and metal ions at the air-water interface and focused on the conditions for the transferability as LB multilayers.[2] Ye *et al.* 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] Another aspect of incorporation of metal ions into the LB film is to utilize the quantum size effects of metallic particles in molecularly organized thin films. For example, Talham *et al.* obtained organometallic LB films of manganese octadecyl phosphonate and confirmed a short-range antiferromagnetic order in the film.[4] Nano-particles of metal halides, metal oxides, and metal sulfides were obtained by using LB films as molecular templates.[5~9] Those were achieved through the reaction of metal ions with the corresponding gaseous reagents in the LB films. Roulliay *et al.* employed ion-exchange technique to obtain $Cd_2P_2S_6$ particles.[10] Another progress is to make quantum-sized metal particles. Barraud *et al.* introduced silver metal between the organic layers by reduction of silver behenate LB film with hydrazine vapor.[11] Very recently, Jiang *et al.* obtained 2 nm sized silver particles through direct movement of silver arachidate monolayers at the air-water interface on to aqueous hydrazine subphase.[12]

Meanwhile, as a breakthrough to improve the mechanical stability of intrinsically fragile LB films, the use of preformed polymers as spreading molecules has been extensively investigated in the recent years.[13] Specifically, Kunitake *et al.* have reported stabilization of monolayers and LB films by electro-

static interaction of ionic polymers with oppositely-charged amphiphiles[14] and by covalent crosslinking of ionically interacting polymers.[15,16] We have reported stabilized LB films of monoalkyl maleate copolymers by polyion-complexing with poly(allylamine) which were coverable the μm sized pores of a porous substrate with a few multilayers.[17,18] However, the interactions of those ionizable polymers with metal ions at the monolayers and in their LB films have not yet known.

In this paper, we report interactions between polymers and metal ions at the air-water interface and in their LB films. The polymer structure is based on an itaconate copolymer and designed to have pendants of hydrophobic long alkyl chain, and hydrophilic carboxyls and oligoethers. The carboxyls can form carboxylate salts with subphase metal ions and give pseudo-crosslinking by interchain electrostatic interaction with multivalent metal ions. The pendant 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 performed by XPS measurement.

Experimental

Materials. The monomer, monooctadecyl itaconate (C_{18} ITA), was prepared by applying the procedure of the corresponding maleate.[18] Itaconic anhydride (5.44 g, 0.055 mole) and 1-octadecanol (3.00 g, 0.011 mole) were dissolved in dry tetrahydrofuran (20 mL) and refluxed for 56 h. The reaction solution was poured into large volume of water (600 mL) and stirred for 5 h. After filtering the precipitate, the crude product was recrystallized from acetone: white powder; yield 85%; mp 70-74 ℃ ; IR (KBr, cm^{-1}) 3400 (O-H), 1710 (C=O), 1640 (C=C), 1210, 1180 (C-O); ^1H NMR (chloroform-d, ppm)

Metal Ion-Containing Polymer LB Films

*Bull. Korean Chem. Soc.* **1995**, *Vol. 16, No. 4* 317

0.92 (t, 3H), 1.13-1.66 (broad s, 30H), 3.34 (s, 2H), 3.91-4.24 (t, 2H), 5.80 (s, 1H), 6.42 (s, 1H), 9.15-9.75 (broad s, 1H). The synthesis of comonomer, triethyleneglycol methyl vinyl ether (VE_3), was carried out according to the known procedure.[19] VE_3: viscous liquid; yield 53%; IR (NaCl, cm^{-1}) 2895 (C-H), 1620 (C=C), 1200, 1115 (C-O); ^{1}H NMR (CDCl$_3$, ppm) 3.3 (s, 3H), 3.5-4.5 (m, 14H), 6.3-6.8 (q, 1H).

The copolymerization of C_{18}ITA (0.50 g, 0.0014 mole) with VE_3 (0.39 g, 0.0021 mole) was carried out in a pressure bottle at 60 °C for 24 h by using the vinyl ether comonomer as an excess. 2,2'-Azobis-(isobutyronitrile) (1 mole % of the itaconate monomer) was used as initiator. The benzene solution (10 mL) was degassed by freeze-thaw cycles under nitrogen before sealing the pressure bottle. The reaction solution was poured into ice-cooled methanol and the precipitate was collected. The composition of the copolymer was determined from integration ratio of ^{1}H NMR peaks and found to be nearly 1 : 1. The number-average molecular weight was 1.1×10^4 (Mw/Mn=4.0) as determined by gel permeation chromatography (polystyrene calibration). C_{18}ITA-VE_3: yield 72%; IR (KBr, cm^{-1}) 3450 (O-H), 2910, 2850 (C-H), 1735 (C=O), 1470 (CH$_2$), 1390, 1350 (CH$_3$), 1320-1010 (C-O); ^{1}H NMR (chloroform-d, ppm) 0.91 (t, 3H), 1.18-1.71 (broad s, 42H), 3.26 (s, 3H), 3.35-3.75 (m, 8H), 4.01 (s, 2H). The metal halides, 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 measurement of surface pressure as a function of molecular area (trough size, 150×600 mm) and together with FSD-51 lifter for monolayer transfer. Isotherms were taken at a 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 halides (1.0×10^{-3} N) and incubated for 30 min before starting the compression. The pH of the aqueous metal halide was 6.7 (NaCl), 6.1 (CsCl), 6.2 (MgCl$_2$), 4.3 (FeCl$_2$), 4.8 (AlCl$_3$), and 3.5 (FeCl$_3$), respectively.

The monolayer transfer onto the substrates was carried out by the vertical mode at surface pressures of 10 to 40 dyne/cm and deposition rates of 10 mm/min (upward stroke) and 50 mm/min (downward stroke). 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. DSC and TGA curves were obtained by using DuPont 910 and 951 thermal analyzers, respectively. Molecular weight distribution of the copolymer was determined by a Waters GPC system equipped with µ-Sytyragel columns. FT-IR spectra were obtained on a Perkin-Elmer FT-IR spectrometer by the reflection and the transmission methods. The p-polarized radiation was introduced on the sample at 80° off the surface normal. In order to minimize the influence of water vapor and CO$_2$ on the spectra, the system was purged by decarbonated dry air for 1-2 h before measurement. XPS spectra were obtained on Perkin-Elmer ESCA 5300 X-ray photoelectron spectrometer, which was operated with a Mg Kα X-ray source and at less than 4.0×10^{-10} Torr. The sample stage was cooled to below −100 °C by an internal thermal conductor connected to an external
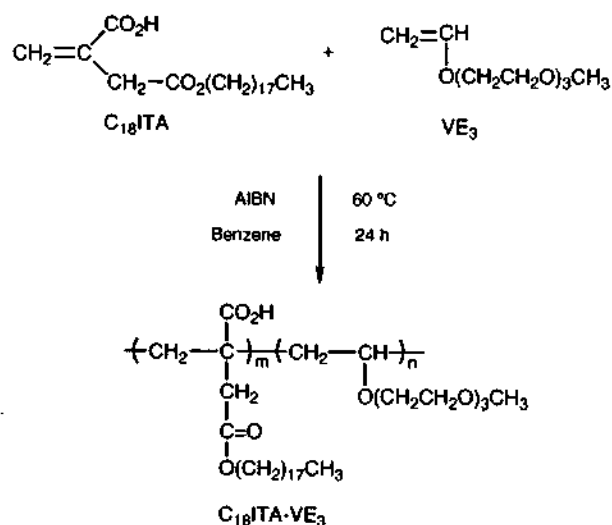
Scheme 1. Preparation of C_{18}ITA-VE_3 by radical copolymerization.

Table 1. Thermal Properties of the Itaconate Copolymer Measured by DSC and TGA

Polymer	Tg (°C)[a]	Degradation Temp. (°C)[b]		
		5%-loss	20%-loss	40%-loss
C_{18}ITA-VE_3	42	155	220	270

[a]Determined by DSC at a heating rate of 10 °C/min under nitrogen atmosphere. [b]Determined by TGA at a heating rate of 10 °C/min under nitrogen atmosphere.

cryogenic Dewar.

Results and Discussion

Synthesis of copolymer C_{18}ITA-VE_3. The monomers, C_{18}ITA and VE_3, were synthesized from esterification and transetherification, respectively. A radical copolymerization of C_{18}ITA with VE_3 gave rise to the copolymer which has nearly 1 : 1 composition as confirmed from ^{1}H NMR. The resulting composition is attributable to the structural combination of an electron-poor (C_{18}ITA) and an electron-rich (VE_3) vinyl monomers.[20] Specifically, the vinyl ethers such as VE_3 do not likely homopolymerize with radical initiators. Scheme 1 shows radical copolymerization of the two monomers.

The thermal behaviors of C_{18}ITA-VE_3 determined by DSC and TGA curves are summarized in Table 1. Low Tg of 42 °C is probably due to long hydrocarbon side chains. Thermal degradation begins at relatively low temperature of around 150 °C. This is supposed to be related with possible anhydride formations within the itaconate units or between the different copolymer chains, as described previously in fluoroalkyl maleate systems.[18] Further examination on degradation mode, however, did not proceed.
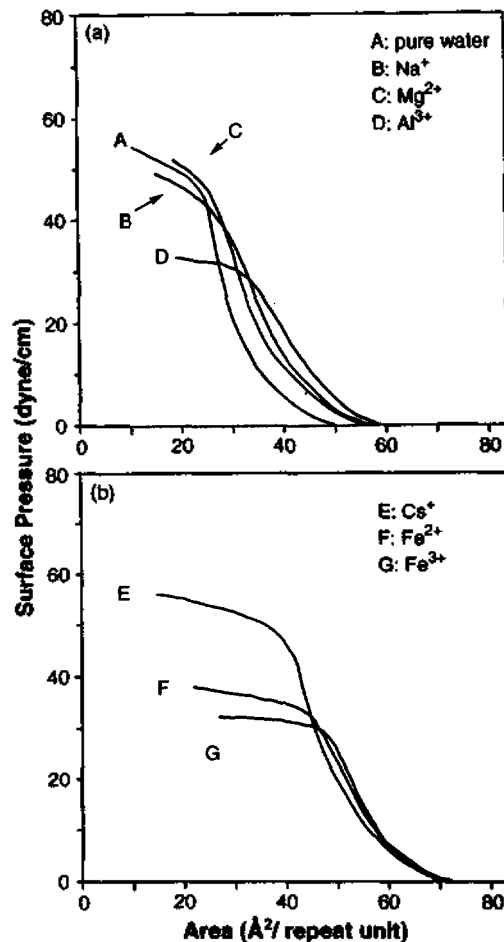
Monolayer behaviors on air-water interface. Chloroform solution of the copolymer C_{18}ITA-VE_3 was spread on pure water or on aqueous metal halides. Figure 1 represents π-A isotherms obtained by sequent compression and expan-

318 *Bull. Korean Chem. Soc.* **1995**, *Vol. 16, No. 4*

Jong Hyun Son et al.
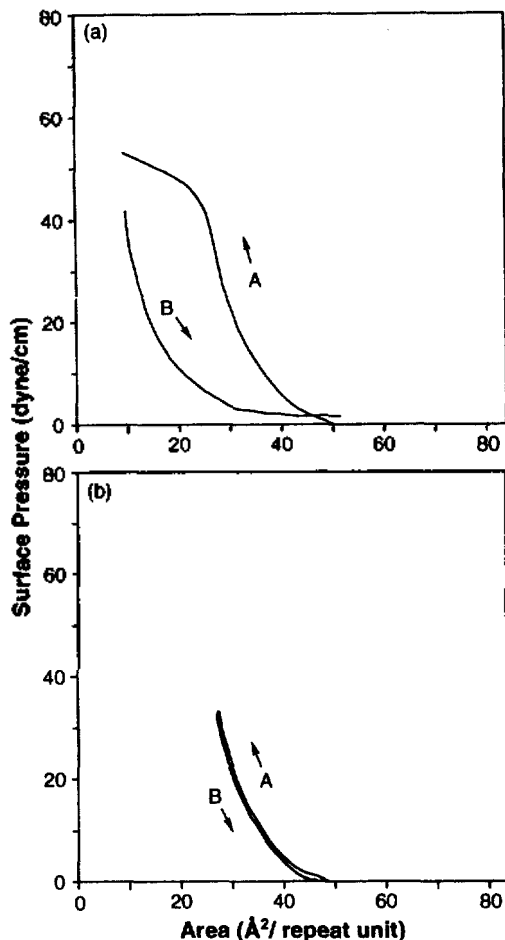
Figure 1. Surface pressure-area isotherms of $C_{18}ITA-VE_3$ measured at a speed of 0.4 mm/sec. A; monolayer compression. B; monolayer expansion. (a) compression-expansion cycle over the collapse pressure and (b) below the collapse pressure.

Figure 2. Surface pressure-area isotherms of $C_{18}ITA-VE_3$ on aq. metal halide subphases. The concentration of metal ions is 1.0×10^{-3} N.

sion of the monolayers on pure water at a speed of 0.4 mm/sec. The compression curve of Figure 1a shows that collapse of monolayer begins at surface pressure of *ca.* 50 dyne/cm which is comparatively high among the preformed polymers. It means that the copolymer forms stable monolayers. The monolayers give expanded phases at low surface pressures. Reversible behavior was observed only below the collapse pressure, *i.e.*, the expansion curve reproduced the initial compression (Figure 1b). Once the film has collapsed the polymer did not respread along the same isotherm curve (Figure 1a). This behavior belongs to the case of irreversible collapse, as stated by Gaines.[21]

Figure 2 shows *n*-A isotherms of $C_{18}ITA-VE_3$ on subphases with metal ions. When compared with the isotherm obtained on the pure water, more expanded area is revealed on aqueous metal ions. The large expanded area is attributable to the interaction of the copolymer with metal ions at the interface and the subsequent change of the monolayer organization, similarly as described for the polymer-polymer polyion-complexing systems.[15-17] The copolymer showed lowered collapse pressure of the monolayers when spread on aq. multivalent metal ions, particularly on aq. trivalent metal ions such as Al^{3+} and Fe^{3+}. It is supposed that the lowered

monolayer stability is due to a decrease in hydrophilicity of the copolymers, which can be resulted from the lowered pH (3.5 of $FeCl_3$ and 4.8 of $AlCl_3$) of the subphases and the multiple coordination of carboxylate groups to the multivalent metal ion. In case of ferrous and ferric ions, the lowered extent of the collapse pressure was remarkable regardless of valent numbers. This is possibly related with oxidation of ferrous to ferric ions, in addition to the effects of pH (4.3 of $FeCl_2$) and multiple complexation with carboxylate groups as mentioned above. The size effect of metal ion on *n*-A isotherm was not noticed.

Monolayer transfer onto solid substrates. The monolayers interacting with Na^+ or Mg^{2+} ion at the air-water interface were transferred onto solid substrates such as a slide glass deposited with Au/Cr and a CaF_2 plate. The conditions employed for monolayer transfer are summarized in Table 2. The Y type deposition was obtained at a surface pressure of 30 or 40 dyne/cm and a lifter speed of 50 or 10 mm/min. In that process, no deposition was observed at the first downward stroke in both cases of CaF_2 and Au/Cr substrates. It was necessary a rapid downward stroke of 50 mm/min to avoid the loss of deposited layers. When the deposition pressure was 10 dyne/cm, the deposition type changed to Z type. The reason for the change of deposition

Metal Ion-Containing Polymer LB Films

Bull. Korean Chem. Soc. **1995**, *Vol. 16, No. 4*   319

Table 2. Conditions Employed for LB Deposition[a]

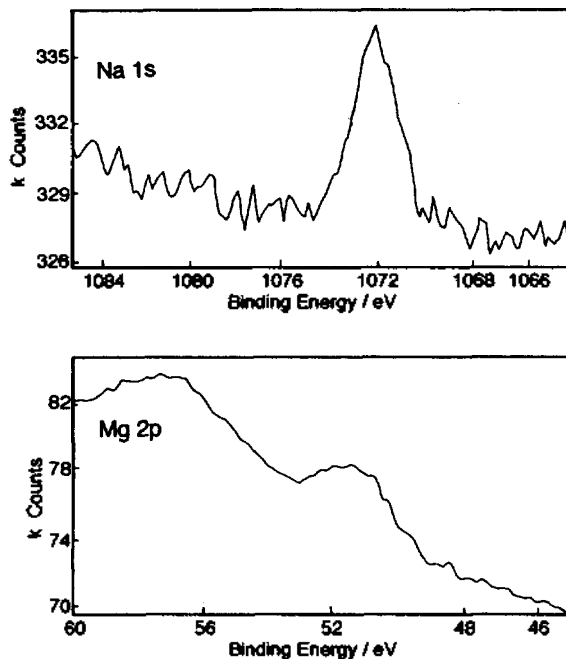| Polymer	Surface pressure (dyne/cm)	Lifter speed (mm/min)		Deposition type (substrate)	Transfer ratio (1st-6th layer)
		Down	Up		
$C_{18}ITA-VE_3$	30	10	10	Y(CaF₂)	1.14-0.80
	40	10	50	Y(Au/Cr)	1.10-0.84
	10	10	50	Z(Au/Cr)	0.93-0.71

[a]Common conditions: spreading solvent, chloroform; drying period, 15 min; temp, 20.0±0.1 ℃.
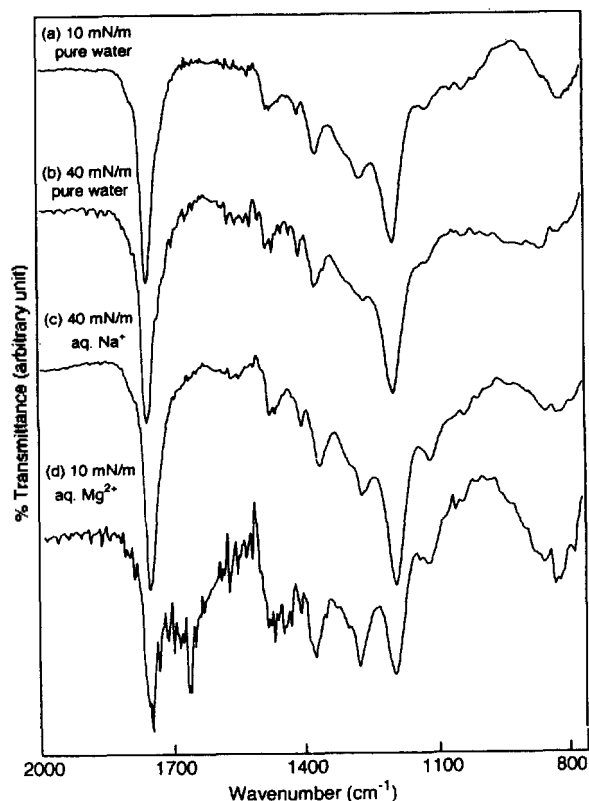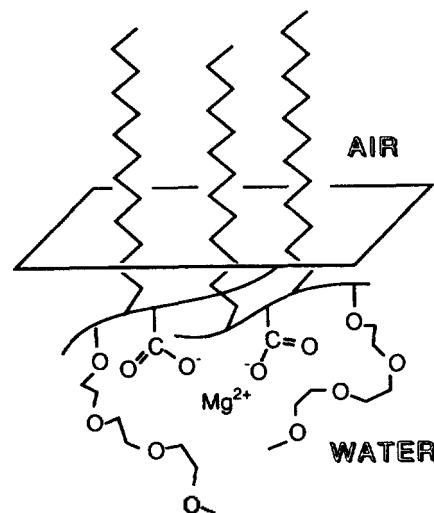

Figure 3. Reflection FT-IR spectra of LB films of $C_{18}ITA-VE_3$ (5 layers) on Au/Cr plates.

Figure 4. XPS spectra of Na 1s and Mg 2p of LB films of $C_{18}ITA-VE_3$ (5 layers) on Au/Cr plates.

Scheme 2. Schematic illustration of the possible interaction of the polymers with Mg^{2+} ions at the air-water interface.

type is not clear at this point. The transfer ratio was 1.14 to 0.71. The monolayers formed on the aqueous solutions with Fe^{2+}, Fe^{3+}, and Al^{3+} were not stable enough to keep an applied pressure during monolayer transfer, *i.e.*, the monolayer area was spontaneously decreased at the deposition pressure.

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 3a and 3b represent very similar carbonyl and ether peaks in the spectra of LB films which were, respectively, obtained at deposition pressures of 10 dyne/cm and 40 dyne/cm. The structural differences of LB films generated by the Y and Z type depositions which formed at different deposition pressure were not able to detect by means of reflection FT-IR spectroscopy. Figure 3d shows two characteristic carbonyl peaks at 1735 and 1665 cm⁻¹, which are attributed to ester and carboxylate salt, re-

spectively. It means the incorporaton of Mg^{2+} as carboxylate salt into the film. However, the peak due to carboxylate salt was not strong in case of LB films deposited from aq. Na^+ subphase. Figure 3b and 3c show the FT-IR spectra obtained from the LB films deposited from pure water and aq. Na^+ subphases, respectively, which have very similar peak patterns. 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 is estimated that *ca.* 13.1 repeat units of the polymer $C_{18}ITA-VE_3$ contain one Na^+ ion, while one Mg^{2+} ion corresponds to 5.9 carboxyls. Figure 4 shows

320 Bull. Korean Chem. Soc. 1995, Vol. 16, No. 4

Jong Hyun Son et al.
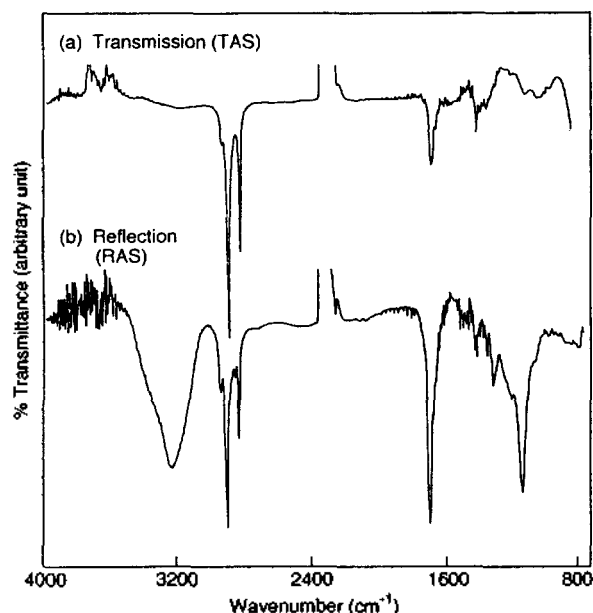
Figure 5. (a) Transmission and (b) reflection FT-IR spectra of LB films of C₁₈ITA-VE₃ (5 layers).

the Na 1s and Mg 2p peaks on XPS spectra. A contribution by the oligoether-metal ion interaction to the incorporation of metal ion into the LB films is supposed to be accounted, which is evidenced from the ether peaks showing changes of intensity and wavenumber in Figure 3. But, quantitative examination on the extent of metal ion incorporation into the LB film by the interaction with pendant oligoethers did not proceed. Scheme 2 illustrates the possible interaction of the polymers with Mg^{2+} ions at the air-water interface.

Figure 5 shows two FT-IR spectra of LB films of C₁₈ITA-VE₃ transferred at 40 dyne/cm from pure water subphase, which were obtained by transmission and reflection methods, respectively. Compared with reflection spectrum of Figure 4b, relatively intense methylene peaks are seen in transmission spectrum of Figure 4a. On the contrary to the methylene peaks, hydroxy, carbonyl, and ether peaks are much stronger in the reflection spectrum. From the difference of relative intensities of the transmission and the reflection spectra, we can deduce that the long hydrocarbon side chains are up-risen against the substrate surface.[22] Other pendants including carboxyls also seem to have not totally parallel orientation to substrate surface. The spectra patterns were same in all the LB films obtained from various aq. metal ion sub-

phases. Thus, the effects of metal ion incorporation on the pendant orientation of polymers in the LB film were not observed.

References

1. Roberts, G. Langmuir-Blodgett Films; Plenum Press: New York, 1990.
2. Bettarini, S.; Bonosi, F.; Gabrielli, G.; Martini, G.; Puggelli, M. Thin Solid Films 1992, 210/211, 42.
3. Aveyard, R.; Binks, B. P.; Fletcher, P. D. I.; Ye, X. Thin Solid Films 1992, 210/211, 36.
4. Byrd, H.; Whipps, S.; Pike, J. K.; Ma, J.; Nagler, S. E.; Talham, D. R. J. Am. Chem. Soc. 1992, 116, 295.
5. Byrd, H.; Pike, J. K.; Talham, D. R. Thin Solid Films 1994, 243, 510.
6. Yi, K. C.; Fendler, J. H. Proc. of 5th Mole. Elect. Symp.(Korea) 1994, 11.
7. Wang, J. Y.; Uphaus, R. A.; Ameenuddin, S.; Rintoul, D. A. Thin Solid Films 1994, 242, 127.
8. Taylor, D. M.; Lambi, J. N. Thin Solid Films 1994, 243, 384.
9. Amm, D. T.; Johnson, D. J.; Matsuura, N.; Laursen, T.; Palmer, G. Thin Solid Films 1994, 242, 74.
10. Perez, H.; Ruaudel-Teixier, A.; Roulliay, M. Thin Solid Films 1992, 210/211, 410.
11. Leloup, J.; Maire, P.; Ruaudel-Teixier, A.; Barraud, A. J. Chim. Phys. 1985, 82, 695.
12. Ji, S. X.; Fan, C. Y.; Ma, F. Y.; Chen, X. C.; Jiang, L. Thin Solid Films 1994, 242, 16.
13. Embs, F. W.; Funhoff, D.; Laschewsky, A.; Licht, U.; Ohst, H.; Prass, W.; Ringsdorf, H.; Wegner, G.; Wehrmann, R. Adv. Mater. 1991, 3, 25.
14. Shimomura, M.; Kunitake, T. Thin Solid Films 1985, 132, 243.
15. Lee, B. J.; Kunitake, T. Langmuir 1992, 8, 2223.
16. Lee, B. J.; Kunitake, T. Langmuir 1994, 10, 557.
17. Jeong, H.; Lee, B.-J.; Kwon, Y.-S. Thin Solid Films 1994, 244, 710.
18. Jeong, H.; Lee, B.-J.; Kwon, Y.-S. Bull. Korean Chem. Soc. 1994, 15, 650.
19. Watanabe, W. H.; Conlon, L. E. J. Am. Chem. Soc. 1957, 79, 2828.
20. Cho, I.; Lee, B.-J. J. Polym. Sci., Polym. Lett. Ed. 1984, 22, 487.
21. Gains, Jr, G. L. Langmuir 1991, 7, 834.
22. Ikeura, Y.; Kurihara, K.; Kunitake, T. J. Am. Chem. Soc. 1991, 113, 7342.