structure, all 8 cations are associated with 6-ring oxygens; 4 Ca^{2+} ions are moved *ca.* 0.22 Å into the large cavity from the (111) plane of the O(3) oxygens, and 4 Na^+ ions are displaced *ca.* 0.58 Å into the sodalite unit from the (111) plane of the O(3). About 5.65 diiodine molecules are sorbed per unit cell each I_2 molecule make close approaches in its axial direaction to a framework oxygen atom and to an iodine atom in an adjacent molecules, with an I-O distance of 3.29 Å and I-I distance of 2.72, and I-I-O=178°. The structure also indicates that diiodine molecule forms charge transfer complexes with framework oxygen.

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Free-Standing Langmuir-Blodgett Films of Maleic Acid-Vinyl Ether Copolymers across 1 μm Pores

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A coverage of about 1 μm-sized pores of a membrane filter by four monolayers of maleic acids copolymers and poly(allylamine) (PAA) was attained by Langmuir-Blodgett (LB) technique through a covalent cross-linking followed a polyion complexation at the air-water interface. The copolymers were prepared to have side chains of hydrocarbon tail, carboxyl, and/or oligoether in the repeat unit. The surface pressure-area isotherms showed that the monolayers on an aqueous PAA have more expanded area than on pure water. The monolayers were transferable on a calcium fluoride substrate and a fluorocarbon membrane filter as Y deposition type, and the resulting LB films were characterized by FT-IR spectroscopy and scanning electron microscopy. A polymer network produced through interchain amide formation was confirmed in as-deposited films. The films were heat-treated in order to complete the cross-linking. SEM observation of the heat-treated film on a porous membrane filter showed that the four layer film was sufficiently stable to cover the filter pore of about 1 μm. Immersion of the film in water or in chloroform did not cause any change in its appearance on SEM and in FT-IR spectra.

Introduction

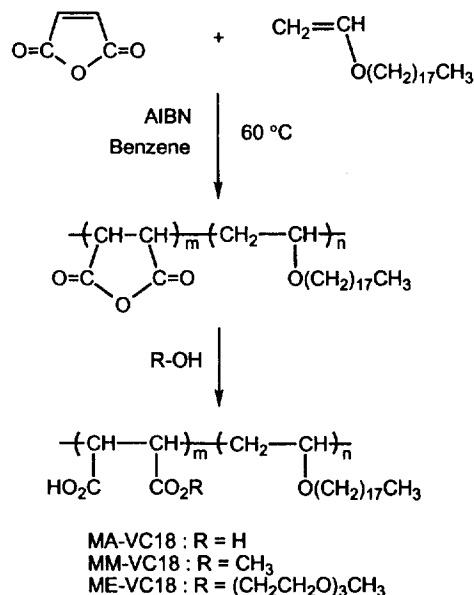Langmuir-Blodgett (LB) films transferred onto porous membrane substrates are of interest, because the surface-modified composite films can produce new functionalities.[1] For example, selective permeations of gases or biomolecules through the molecularly-thin organized films may be useful for separation[2] and sensor[3] applications. For this purpose, the mecha-
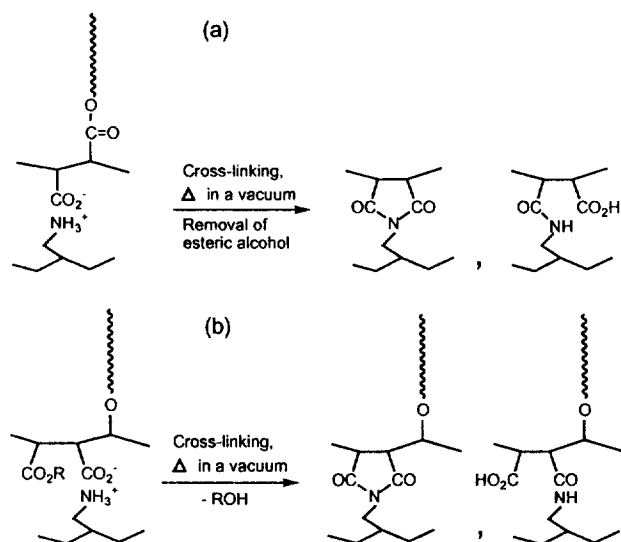
Scheme 1. Representative cross-linking reactions in the polyion-complexed LB films: (a) in case of the long hydrocarbon side chain attached to the backbone by an ester linkage; (b) in case of the side chain attached to the backbone by an ether linkage.

Scheme 2. Preparation scheme of the copolymers, MA-VC18, MM-VC18, and ME-VC18.

nical stability of the LB film should be importantly taken into account, because the permeations must happen through the free-standing LB films that are built up on stable, porous supports.[4] However, very little in the literature refers to such LB films, presumably owing to fabrication problems. Okahata *et al.* have used a porous glass plate with extremely small pore size of 5 nm as the LB substrate.[5] It has involved polymerization or cross-linking at the air-water interface to stabilize the LB films before deposition. Hodge *et al.* showed that good coverage of an alumina filter of 0.2 μm pore size with 80% probability was possible with as few as six monolayers of preformed polymers.[6] The polymers were cross-linked by UV exposure after deposition. Kunitake *et al.* have demonstrated stabilization of the LB films by electrostatic interaction of ionic polymers with oppositely-charged amphiphiles[7] and by covalent cross-linking of ionically interacting polymers,[8] and covered 0.1 μm pores of a fluorocarbon membrane filter by four monolayers. A LB technique employing an tert-amine as monolayer template was investigated for a formation of the two-dimensional network from differently-charged two kinds of water-soluble polymers.[9,10] The polyion-complexed networks on porous substrates, however, showed hole-defects on the covered films during a thermal treatment for covalent cross-linking. For gas separation through the LB films, several groups have used polymer membrane filters as substrates, however, they have always deposited more than ten monolayers for a defect-free coating.[11~15]

In the course of searching polymer systems for free-standing LB films on porous substrates, we have demonstrated that polyion-complexed monolayers of maleate or itaconate copolymers with poly(allylamine) (PAA) at the air-water interface have revealed good transferabilities and network formations on porous substrates, and, in the best case, four monolayers were enough to cover the 0.1 μm pores of a fluorocarbon membrane filter with more than 95% probabi-

lity.[16~19] A characteristic of the polymer systems was that concurrent detachment of the hydrocarbon or the fluorocarbon chains from the backbones occurs along with the network formation by covalent cross-linking. The representative reactions for network formation in the LB films are shown in Scheme 1a.

In this paper, we report an extention of the polymer systems for free-standing LB films on porous substrates, which are represented in Scheme 1b. The polymers have following structural characteristics, *i.e.*, i) the long hydrocarbon side chains are attached to the polymer backbones as ether bonds, thus, the hydrocarbon chains will remain after cross-linking reactions in the LB films, ii) the carboxyls can form polyion complexes with subphase polymer, PAA, through carboxylate-ammonium salt formation, and covalent cross-linkings by amide or imide formation, iii) the pendent oligoethers are expected to give a flexibility to the polymer backbone and to enhance the monolayer stability. As structurally related copolymers, derivatives of maleic anhydride copolymers were used to fabricate the LB films for various applications such as stability improvement,[20] surface tension reduction,[21] second-harmonic generation,[22] optical waveguides,[23] and control film of the Schottky barrier height of GaP semiconductor.[24]

Experimental

Materials. The spreading polymers, MA-VC18, MM-VC 18, and ME-VC18, were synthesized as described below. Poly (allylamine) hydrochloride (Mn = 10⁴) was purchased from Nitto Boseki Co. and treated with a strong anion exchange resin (Amberlite IRA-402) to obtain free poly(allylamine) (PAA). The concentration of the amino group in aqueous solution was determined by colloid titration with standard poly(vinyl sulfate) solution using Toluidine Blue O as an indicator.[25]

Synthesis of Monomer. The monomer, n-octadecyl vinyl ether (VC18), was synthesized through transetherification

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between n-octadecyl alcohol and ethyl vinyl ether by using mercuric acetate as catalyst.[26] Mercuric acetate (0.05 g, 0.15 mmol) was added to a mixture of n-octadecyl alcohol (2.0 g, 7.4 mmol) and ethyl vinyl ether (13 mL, 0.14 mol), and refluxed for 48 h at bath temperature of 55 °C. After removal of excess ethyl vinyl ether by rotary evaporator, the residue was eluted through a silica gel (70-230 mesh ASTM) column with a solvent mixture of ethyl acetate and hexane (1 : 10, by volume). After removal of the solvent, the product was obtained. VC18: mp 28-30 °C; yield 75%; IR (NaCl, cm^{-1}) 2896 (C-H), 1618 (C=C), 1200, 1115 (C-O); ^{1}H NMR (CDCl$_3$, ppm) 0.91 (t, 3H), 1.10-1.62 (broad s, 32H), 3.80 (t, 2H), 3.85-4.50 (m, 2H), 6.25-6.72 (q, 1H).

Polymerization and Modification. The synthetic scheme of the copolymers are shown in Scheme 2. The radical copolymerization of maleic anhydride (MAH; 0.5 g, 5.0 mmol) with the vinyl ether monomer, VC18 (0.5 g, 1.7 mmol), was carried out in a pressure tube at 60 °C for 24 h by using benzene (5.0 mL) as solvent. 2,2'-Azobis(isobutyronitrile) (4.2 mg, 0.025 mmol) was used as a radical initiator. The benzene solution was degassed by freeze-thaw-cycles under nitrogen before sealing the pressure tube. After completion of the reaction, the reaction solution was poured into ice-cooled water and stirred for 12 h. The precipitate was collected and washed with water. The composition of the copolymer was determined from integration ratio of ^{1}H NMR peaks and found to be nearly 1 : 1 molar ratio. The number-average molecular weight was 9.5×10^4 (Mw/Mn=2.05) as determined by gel permeation chromatography (polystyrene calibration). MAH-VC18: yield 73%; IR (KBr, cm^{-1}) 2920, 2855 (C-H), 1822, 1745 (C=O), 1470 (CH$_2$), 1390, 1350 (CH$_3$), 1250-920 (C-O); ^{1}H NMR (CDCl$_3$, ppm) 0.91 (t, 3H), 1.10-1.70 (broad s, 34H), 2.05-2.55 (broad m, 2H), 3.10-3.85 (broad m, 3H). The derivatives of the parent copolymer, MA-VC18, MM-VC18, and ME-VC18, were prepared by the reaction with an excess of water, methanol, and triethyleneglycol monomethyl ether for 48 h at bath temperature of 60 °C (water, methanol) and 85 °C (triethyleneglycol monomethyl ether), respectively. The products were extracted with chloroform in case of the reaction with water, while the excess methanol was evaporated in the reaction with methanol. On the other hand, in case of the reaction with triethyleneglycol monomethyl ether, the product was precipitated into cold water. The conversion of the anhydride units to the acid and the esters was almost completed as confirmed by ^{1}H NMR and IR spectra. MA-VC18: yield 88%; IR (KBr, cm^{-1}) 2918, 2850 (C-H), 1695 (C=O), 1466 (CH$_2$), 1392, 1350 (CH$_3$), 1250-1000 (C-O); ^{1}H NMR (CDCl$_3$, ppm) 0.90 (t, 3H), 1.11-1.72 (broad s, 34H), 2.05-2.50 (broad m, 2H), 3.30-3.84 (broad m, 3H), 9.80 (broad s, 2H). MM-VC18: yield 92%; IR (KBr, cm^{-1}) 2920, 2855 (C-H), 1727 (C=O), 1473 (CH$_2$), 1390, 1352 (CH$_3$), 1300-1010 (C-O); ^{1}H NMR (CDCl$_3$, ppm) 0.91 (t, 3H), 1.10-1.70 (broad s, 34H), 2.05-2.55 (broad m, 2H), 3.10-3.88 (broad m, 3H), 4.40 (s, 3H). ME-VC18: yield 78%; IR (KBr, cm^{-1}) 2920, 2855 (C-H), 1738 (C=O), 1470 (CH$_2$), 1390, 1350 (CH$_3$), 1330-1000 (C-O); ^{1}H NMR (CDCl$_3$, ppm) 0.90 (t, 3H), 1.10-1.71 (broad s, 34H), 2.03-2.51 (broad m, 2H), 3.15 (s, 3H), 3.30-4.35 (broad m, 15H).

π-A Isotherm and LB Deposition of Monolayer. A film balance system HBM-SS (Kyowa Interface Science) was used for measuring surface pressure as a function of molecu-

lar area (trough size, 150×600 mm). Isotherms were taken at a compression rate of 0.5 mm/s. Chloroform was employed as spreading solvent. Monolayers were spread on pure water or on aqueous PAA (2×10^{-4} mol/-NH$_2$) and incubated for 10 min before starting the compression.

The deposition of the monolayer on the substrates was performed in the vertical mode. The employed substrates were a fluorocarbon membrane filter (Sumitomo Electric Co.) for scanning electron microscopy (SEM) observation and a calcium fluoride plate (GL Sciences) for FT-IR measurement. The transfer onto the substrates was carried out at a surface pressure of 30 or 40 mN/m and deposition rates of 5 or 10 mm/min (upward stroke) and 10 or 25 mm/min (downward stroke).

Measurements. Molecular weight distribution of the copolymers was determined by a Waters GPC system equipped with μ-Sytyragel columns. FT-IR measurements were carried out on a Bomem MB-102 FT-IR spectrometer by the transmission method. 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. Scanning electron microscopy (SEM; JSM 35CH) was used to observe the surface morphology of a fluorocarbon membrane filter (Sumitomo Electric Co.). An acceleration voltage of 15 kV was employed. The samples were sputtered with Au before observation.

Results and Discussion

Formation and Stability of Monolayer. Chloroform solutions of the copolymers, MA-VC18, MM-VC18, and ME-VC18, were spread on pure water or on aqueous PAA. Surface-pressure (π-A) isotherms of Figure 1 show that the monolayers are stable up to a surface pressure of 40 mN/m. While the monolayers of ME-VC18 gave expanded phases, those of MA-VC18 and MM-VC18 had rather condensed isotherms. When compared with the isotherm on pure water, a more expanded area is revealed on aqueous PAA. This change between the two isotherms is clear in cases of MA-VC18 and MM-VC18, while, in case of ME-VC18, the change is very little. 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,[7] *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 (pH 6.2), and a separation of the closely positioning polymer chains of the spread copolymers accompanied with an unfolding of the electrostatically complexed subphase polymer, PAA, at the air-water interface.[27] In case of ME-VC18 which showed already expanded phase on pure water, an additional area expansion by polyion complex did not occur. No noticeable change of the isotherm was observed with increasing incubation times from 10 min to 2 h.

A stable monolayer against surface pressure at the air-water interface is a prerequisite for obtaining a stable LB film. The monolayer stability against surface pressure was investigated at 30 mN/m of surface pressure at 25 °C. Figure 2 shows the trend of spontaneous area loss in the monolayers of the copolymers on pure water and on aqueous PAA subphases. The largest area loss was found to be 10% of original area in the monolayers of MA-VC18. However, even in case
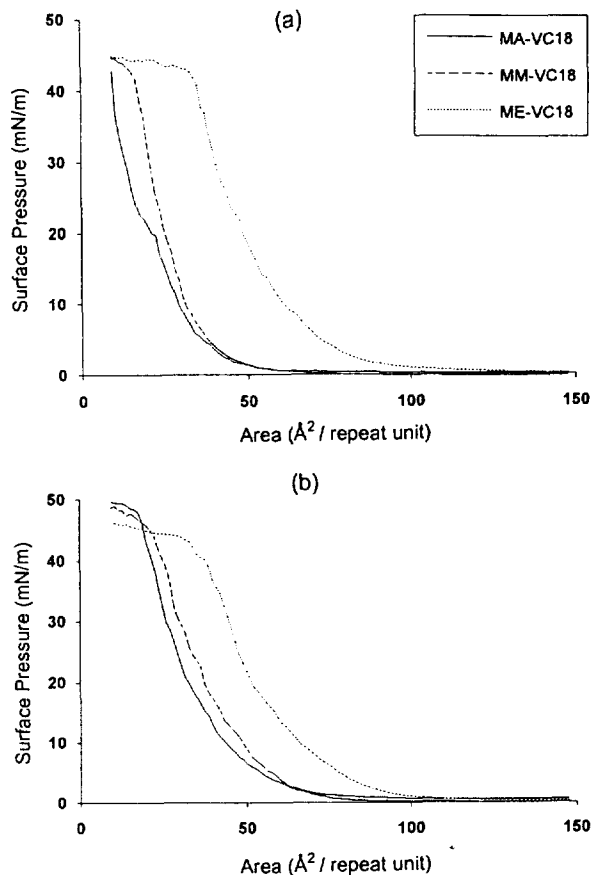
Figure 1. Surface pressure-area isotherms of the copolymers measured at a speed of 0.4 mm/sec: (a) on pure water and (b) on aqueous PAA subphases. The concentration of the amino group of PAA was 2×10^{-4} M.

of MA-VC18, the monolayers became stable after *ca.* 40 min, and no further area loss was observed. Thus, the area reduction is thought to be attributable to a reorganization of the monolayer and not due to the collapse of monolayer or the dissolution into the subphase. The most stable monolayer was obtained in MM-VC18 system. Slight area expansion was obseved in ME-VC18 monolayer on aqueous PAA, but the reason is not clear at this point. The monolayer stability was the order of MM-VC18>ME-VC18>MA-VC18.

LB Transfer of Monolayer. All the monolayers on pure water and on aqueous PAA were transferable onto solid substrates such as a porous fluorocarbon membrane filter and a calcium fluoride plate. The conditions employed for monolayer transfer are summarized in Table 1. In all cases, the Y type deposition occurred at a surface pressure of 30 or 40 mN/m and transfer rates of 5 or 10 (downward) and 10 or 25 (upward) mm/min. In that process, no deposition was observed at the first downward stroke in the case of the calcium fluoride plate. The transfer ratio was 1.2 to 0.7. The monolayer transfer was started after that time the monolayer area did not show any more decrease at a given surface pressure.

As-deposited LB Film. The structures of the LB films on calcium fluoride plates were estimated by means of FT-IR spectra. The FT-IR spectra of ME-VC18 LB films depos-
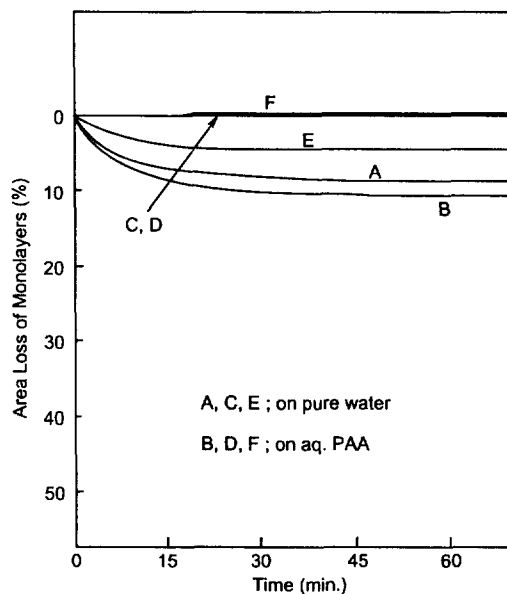

Figure 2. Area loss of monolayers of the copolymers at the air-water interface during incubation at 30 mN/m and at 25 °C. MA-VC18 (A) on pure water and (B) on aqueous PAA. MM-VC18 (C) on pure water and (D) on aqueous PAA. ME-VC18 (E) on pure water and (F) on aqueous PAA. The concentration of the amino group of PAA was 2×10^{-4} M.

Table 1. Conditions employed for monolayer deposition[a]

Polymer	Subphase	Surface pressure (mN/m)	Lifter speed (mm/min) down	up	Transfer ratio (1st-6th L)
MA-VC18	H₂O	40	5	10	1.2-0.9
	PAA[b]	40	10	25	1.1-0.8
MM-VC18	H₂O	30	10	25	1.0-0.9
	PAA	30	10	25	1.2-0.7
ME-VC18	H₂O	40	10	25	0.8-1.1
	PAA	30	10	25	1.2-1.0

[a] Common conditions: spreading solvent, chloroform; drying period, 10 min; temp, 25 °C; deposition type, Y; substrates, fluorocarbon membrane filter and calcium fluoride plates. [b] The concentration of the amino group of PAA was 2×10^{-4} M.

ited from pure water (Figure 3a) and aqueous PAA subphases (Figure 3b, c) were obtained. The two characteristic carbonyl bands at 1729 cm^{-1} and 1590 cm^{-1} of Figure 3a are attributable to ester and carboxylic acid, and carboxylate groups, respectively. Strong absorption bands at 2918 cm^{-1} and 2850 cm^{-1} are assigned to long hydrocarbon side chains, and those of 1259 cm^{-1}, 1175 cm^{-1}, 1097 cm^{-1}, and 1023 cm^{-1} to C-O linkages. When the LB films of ME-VC18 was fabricated from aqueous PAA subphase, the spectrum of Figure 3b was obtained. The incorporation of PAA into the LB film could be confirmed from the peaks due to the amino groups of PAA, *i.e.*, strong bands of 3377 cm^{-1}, 3244 cm^{-1} (-NH₂ st), 1635 cm^{-1} (-NH₂ δ, overlapped with C=O st of amides), 1539 cm^{-1} (-NH₃⁺ δ), and 1082 cm^{-1} (C-N st, overlapped with C-O st of ethers). The band of 1729 cm^{-1} in

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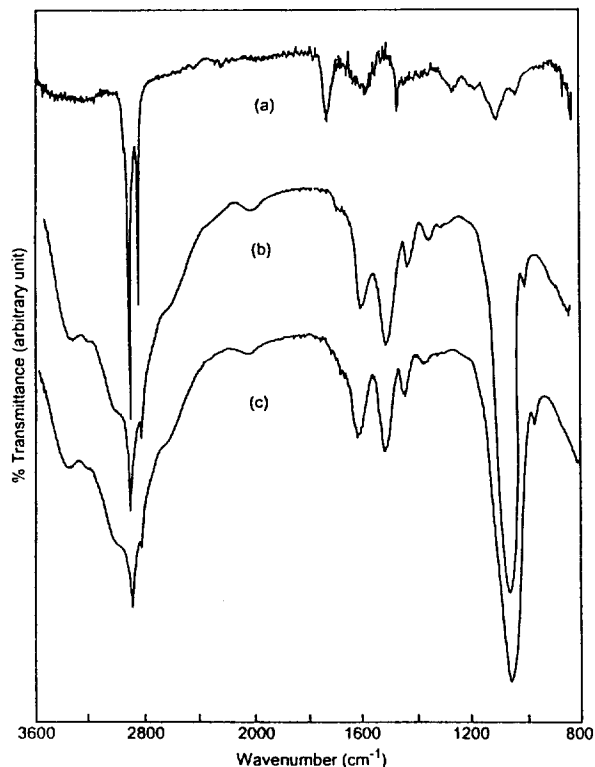*Bull. Korean Chem. Soc.* **1995**, Vol. 16, No. 12   1171

Figure 3. Transmission FT-IR spectra of LB films (15×2 layers) of ME-VC18 on calcium fluoride plates: (a) as-deposited film from pure water subphase; (b) as-deposited film from aqueous PAA subphase; (c) heat-treated film at 150 ℃ for 10 h in a vacuum.

Figure 4. Scanning electron micrographs of LB films of MM-VC18 deposited on fluorocarbon membrane filters: (a) the membrane filter only; (b) as-deposited film of 6 monolayers from pure water subphase; (c) as-deposited film of 4 monolayers from aq. PAA subphase. The samples were sputtered with Au and observed at 15 kV.

Figure 3a nearly disappears in Figure 3b, and the amide carbonyl band of 1635 cm⁻¹ appears instead as overlapped with aforementioned ammonium bending band. The spectra of the similar pattern were also obtained in cases of MA-VC18 and MM-VC18 system. It means that the formation of amide linkage between the copolymer and PAA has already occurred before the sequent heat treatment for thermal cross-linking is performed. We have no experimental evidence to determine whether the cross-linking reaction began on the monolayer at the air-water interface or after its transfer onto the substrate. But, in view of the report on the possible polycondensation reactions of amino acid esters on monolayers at the air-water interface,[28] the amide formation at the air-water interface was able to proceed in the present polymer systems. Compared with the previous polymer systems shown in Scheme 1a, the relatively small expansion of monolayer area on aq. PAA in the present polymer system is supposed to be related with the condensation reaction at the air-water interface. This was also different from the previous polymer systems which had the long hydro- or fluorocarbon side chains as an ester linkage of maleates or itaconates as shown in Scheme 1a.[16,19] In the previous systems, the cross-linking reaction had occurred during the heat treatment of the as-deposited LB film. The formation of the amide bond is believed to be accelerated in the present polymer systems because of the relatively small esteric alcohol side groups. The quantitative analysis of the incorporated PAA was not performed. However, from the compari-
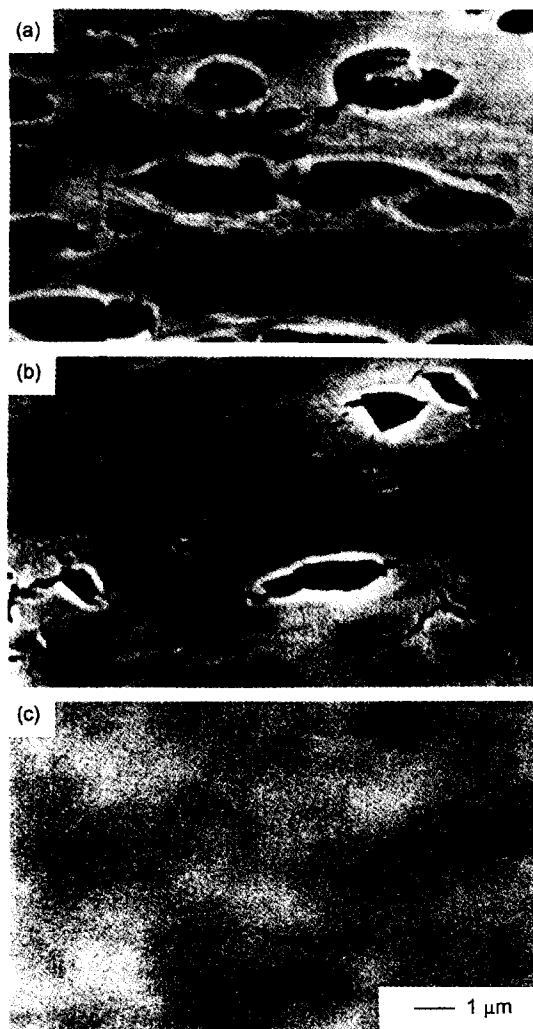
son of the peak intensities of FT-IR spectra with those of the quantitatively analyzed polymer systems,[8] it was estimated that more than 2 amino units of PAA per one maleate unit were incorporated into the LB films. The network formation in the as-deposited LB films was the order of MM-VC18>ME-VC18>MA-VC18, which was evidenced from the relative carbonyl peaks of their FT-IR spectra.

SEM micrographs of Figure 4 show the surface morphology of the porous fluorocarbon membranes. We can readily observe that the original pores, which are seen as longish and somewhat dark appearance (Figure 4a), of the substrate membrane. When the monolayer of MM-VC18 was deposited on the substrate membrane from pure water subphase, the large defects with sizes of *ca.* 2 μm are seen as dark spots even in 6 monolayers (Figure 4b). The cracks of the covered film on the pores are also found. However, good covering of the pores is found in the 4 monolayer film which was transferred from aqueous PAA subphase (Figure 4c). No

more focusing was made from the smoothly covered film surface. It is supposed that the covering capability is enhanced through the polyion complexation and covalent cross-linking at the air-water interface. The MM-VC18/PAA system was better in the covering capability than the other MA-VC 18/PAA or ME-VC18/PAA one.

Heat-treated LB Film. In order to complete the covalent cross-linking in the LB films, the as-deposited LB film was subsequently subjected to heat treatment at 150 ℃ in a vacuum of 10^{-2} mmHg for 10 h. Compared with the FT-IR spectrum of Figure 3b, only a slight increase of band intensity of 1635 cm^{-1} was observed together with an intensity decrease of 1539 cm^{-1} in Figure 3c. It means that a further formation of amide linkage was only a little carried out during the heat treatment, that is, the amide formation proceeded mostly before the heat treatment. The intensities of the bands of 2926 cm^{-1} and 2846 cm^{-1} due to C-H stretchings were not reduced after the heat treatment. This is because the long hydrocarbon side chains were not involved in the amide formation owing to their attachment to backbones as ether linkage. The bands due to imide bonds, which had occurred in the related previous systems,[8,20] were not discernible from the amide peaks of Figure 3b and 3c. The reason for the difference is not known at this point.

SEM micrograph of the LB film on the porous membrane was taken after the heat treatment. The appearance of the micrograph was same to Figure 4c, *i.e.*, the heat treatment did not give any defects to the covered film. This is supposed to be due to already formed polymer networks before the heat treatment. Immersion of this film in water or in chloroform for 1 day did not cause any change in its appearance observed by SEM. And the FT-IR spectrum after the immersion did not give any indication of structure changes. This means that only 4 monolayers of the polymer network are enough to cover the *ca.* 2 μm pores of the membrane filter and resist against solvents.

Conclusions

Free-standing two-dimensional networks on the pores with a few μm range were made by LB deposition preceded by polyion-complexed monolayers at the air-water interface. Compared with the previous maleate copolymer systems which had employed this LB technique, the present copolymer systems showed following differences, i) network formation by cross-linking proceeded almost before the heat treatment, and this was believed to give the monolayer better covering capability, ii) the cross-linking occurred mostly through the formation of interchain amide bonds, however, the probability of the imide formation can not be ruled out, iii) hydrocarbon side chains still remained even after heat treatment. The present results indicate that the network formation in the stage of monolayer at the air-water interface is important in order to cover the porous substrate with a small number of LB monolayers as possible.

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