

# Langmuir-Blodgett Films of Perfluoroalkyl Monomaleate Copolymers on a Porous Substrate

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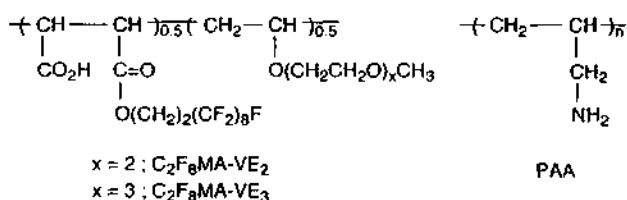
Stable polyion-complexed polymeric monolayers were prepared by spreading perfluoroalkyl monomaleate copolymers,  $C_2F_8MA-VE_2$  and  $C_2F_8MA-VE_3$ , on a aqueous poly(allylamine) subphase. The monolayer properties have been studied by the surface pressure-area ( $\pi$ -A) isotherms. The  $C_2F_8MA-VE_3$  containing longer oligoethyleneglycol pendant showed more expanded monolayer phase than the  $C_2F_8MA-VE_2$ . The polyion-complexed monolayers were transferable on various substrates, and the resulting Langmuir-Blodgett (LB) films were characterized by FT-IR spectroscopy and scanning electron microscopy (SEM). Two-dimensional crosslinking to form a polymer network was achieved by amide formation through heat treatment under vacuum with concurrent removal of perfluoroalkyl tails. SEM observation of this film on a porous membrane filter showed that the four layer film was sufficiently stable to cover the filter pore size of 0.1  $\mu$ m. The  $C_2F_8MA-VE_3$  revealed better covering capability than the  $C_2F_8MA-VE_2$ . Immersion of this film in water or in benzene did not cause any change in its appearance and in FT-IR spectra.

## Introduction

The Langmuir-Blodgett (LB) technique provides a unique approach to achieve supramolecular architectures of layered assemblies of suitably designed organic molecules. The LB films have been used as sophisticated molecular devices useful to test molecularly controlled processes of energy transfer, charge carrier motion, energy conversion, molecular recognition, and separation.<sup>1</sup> But, the LB films have problems to be solved for their practical applications, which are in part due to the inherent instability and the defects of the layered assemblies.<sup>2</sup> Specifically, when we consider its use for separations, the mechanical stability of the film should be importantly taken into account, because the separation must happen through the films that are built up on stable, porous supports. As a breakthrough to improve the mechanical stability, the use of preformed polymers has been investigated extensively in the recent years.<sup>3,4</sup> Since the copolymers of maleic anhydride and their derivatives were spread to monolayers,<sup>5</sup> polyacrylates,<sup>6</sup> polymethacrylates,<sup>7</sup> polymers of aromatic backbones<sup>8</sup> or with aromatic side chains,<sup>9</sup> condensation polymers,<sup>10</sup> water-soluble polymers,<sup>11</sup> rod-like polymers,<sup>12</sup> and poly(vinyl alkylals)<sup>13</sup> were employed to fabricate stable monolayers and LB films. Specifically, Kunitake *et al.* have reported stabilization of monolayers and LB films by electrostatic interaction of ionic polymers with oppositely-charged amphiphiles<sup>14</sup> and by covalent crosslinking of ionically interacting polymers.<sup>15</sup> Very recently, concurrent removal of alkyl tails along with a crosslinking of LB films was achieved by heat treatment.<sup>16</sup>

In this paper, we describe improved stability of LB films on a porous substrate by employing perfluoroalkyl monomaleate copolymers as spreading polymers. The polymers are designed to have hydrophobic perfluoroalkyl chains and hydrophilic carboxyls and oligoethers as pendants, *i.e.*, i) the fluorocarbon chains are expected to give more close packing than hydrocarbon ones, ii) the carboxyls can form polyion complexes with subphase polymer, poly(allylamine), through

carboxylate/ammonium salt formation, and possible covalent crosslinking 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.



## Experimental

**Materials.** The monomer, 2-(perfluorooctyl)ethyl monomaleate( $C_2F_8MA$ ), was prepared by applying the known procedure<sup>16a</sup>. Maleic anhydride (4.2 g, 43.0 mmol) and 2-(perfluorooctyl)ethanol(4.0 g, 8.6 mmol) were dissolved in dried tetrahydrofuran (10 ml) and refluxed for 38 h. The reaction solution was poured into large volume of water (500 ml) and stirred for 5 h. After filtering the precipitate, the crude product was recrystallized from acetone: white powder; yield 89%; mp. 83-84°C; IR (KBr,  $\text{cm}^{-1}$ ) 1720 (C=O, ester), 1700 (C=O, carboxylic acid), 1640 (C=C), 1200 (C-O), 1140 (C-F); <sup>1</sup>H-NMR (acetone- $d_6$ , ppm) 1.2-2.5 (broad m, 2H), 3.7-4.1 (t, 2H), 5.8 (s, 2H). The comonomers, diethyleneglycol methyl vinyl ether ( $VE_2$ ) and triethyleneglycol methyl vinyl ether ( $VE_3$ ), were synthesized through transesterification according to the literature.<sup>17</sup>  $VE_2$ : viscous liquid; yield 52%; IR (NaCl,  $\text{cm}^{-1}$ ) 2895 (C-H), 1615 (C=C), 1200, 1105 (C-O); <sup>1</sup>H-NMR ( $\text{CDCl}_3$ , ppm) 3.2 (s, 3H), 3.4-4.3 (m, 10H), 6.2-6.7 (q, 1H).  $VE_3$ : viscous liquid; yield 53%; IR (NaCl,  $\text{cm}^{-1}$ ) 2895 (C-H), 1620 (C=C), 1200, 1115 (C-O); <sup>1</sup>H-NMR ( $\text{CDCl}_3$ , ppm) 3.3 (s, 3H), 3.5-4.5 (m, 14H), 6.3-6.8 (q, 1H).

The copolymerization of the perfluoroalkyl 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. The reaction solution was poured into water and the precipitate was collected.  $C_2F_8MA-VE_2$ : yield 73%;  $\eta_{inh}=0.15$  dL/g (0.5 g/dL in THF at 25°C); IR (NaCl,  $cm^{-1}$ ) 2970 (C-H), 1722 (C=O), 1440 ( $CH_2$ ), 1380, 1340 ( $CH_3$ ), 1300-1000 (C-O, C-F);  $^1H-NMR$  ( $CF_3CO_2H$ , ppm) 1.3-2.5 (broad s, 6H), 2.5-3.1 (broad s, 3H), 3.1-3.8 (broad s, 9H), 3.8-4.7 (broad s, 2H).  $C_2F_8MA-VE_3$ : yield 78%;  $\eta_{inh}=0.17$  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);  $^1H-NMR$  ( $CF_3CO_2H$ , 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 copolymers was estimated to be 1:1 by  $^1H-NMR$  spectra. Poly(allylamine) hydrochloride ( $\bar{M}_n=10^4$ ) 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 indicator.<sup>18</sup>

**Surface Pressure ( $\pi$ -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 molecular area (trough size, 150×600 mm). Isotherms were taken at a compression rate of 0.5 mm/s. Tetrahydrofuran was employed as spreading solvent. Monolayers were spread on pure water or on aqueous PAA ( $2 \times 10^{-4}$  mol/L- $NH_2$ ) and incubated for 10 min before starting the compression.

The deposition of the monolayer was performed in the vertical mode. The employed substrates were fluorocarbon membrane filters (FP-010, Sumitomo Electric Co.) for scanning electron microscopy (SEM) observations and  $CaF_2$  plates (GL Sciences) for FT-IR measurements. The transfer onto the substrates was carried out at a surface pressure of 25 or 30 mN/m and deposition rates of 10 mm/min (upward stroke) and 50 mm/min (downward stroke).

**Measurements.** DSC and TGA curves were obtained by using Du Pont 910 and 951 thermal analyzers, respectively. 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 dry air for 1-2 h before measurement. Scanning electron microscopy (SEM; JSM 35CH) was used to observe the surface morphology of the FT-010 membrane filter (pore diameter, 0.1  $\mu m$ ). An acceleration voltage of 15 kV was employed. The samples were sputtered with Au before observation.

## Results and Discussion

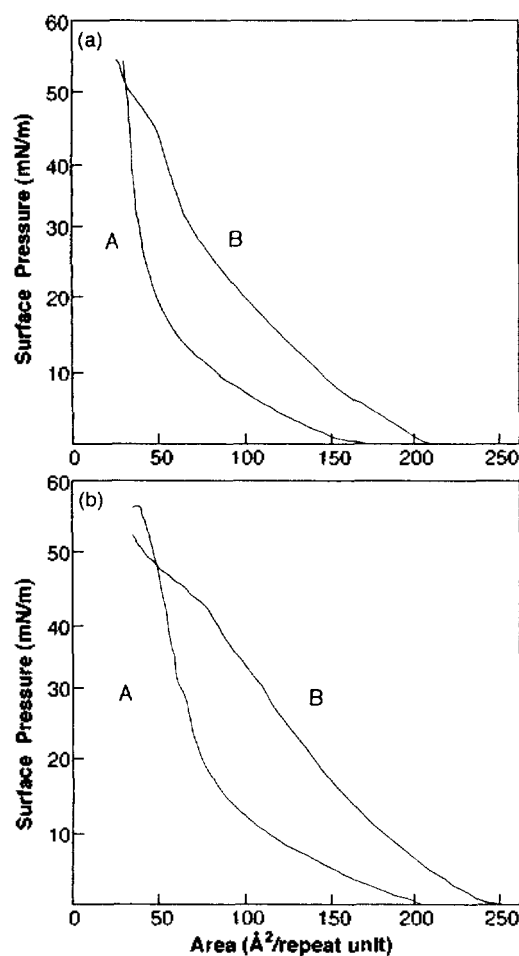
### Thermal Properties of the Fluorocarbon Copolymers.

The results on the thermal behaviors of  $C_2F_8MA-VE_2$  and  $C_2F_8MA-VE_3$  determined by DSC and TGA curves are summarized in Table 1. Compared to *ca.* 50°C of  $T_g$  of conventional hydrocarbon-side-chained amphiphilic polymers,<sup>19</sup> the fluorocarbon copolymers show higher  $T_g$  over 100°C. The increase of  $T_g$  is attributed to the rigidity of fluorocarbon chains and strong interactions between the chains. However, thermal degradation begins at relatively low temperature of around 150°C. This is supposed to be related with possible anhydride formations within the maleate units and between

**Table 1.** Thermal Properties of the Fluorocarbon Copolymers Measured by DSC and TGA

Polymer	$T_g$ (°C) <sup>a</sup>	Degradation Temp. (°C) <sup>b</sup>			Residue at 700°C (%)
		5%-loss	20%-loss	40%-loss	
$C_2F_8MA-VE_2$	117	160	215	262	1.1
$C_2F_8MA-VE_3$	100	140	211	234	5.5

<sup>a</sup>Determined from DSC curves measured on Du Pont 910 differential scanning calorimeter with a heating rate of 10°C/min under nitrogen atmosphere. <sup>b</sup>Determined from TGA curves measured on Du Pont 951 thermogravimetric analyzer with a heating rate of 10°C/min under nitrogen atmosphere.



**Figure 1.** Surface pressure-area isotherms of (a)  $C_2F_8MA-VE_2$  and (b)  $C_2F_8MA-VE_3$ . A: on pure water. B: on aqueous PAA at 30°C. The concentration of the amino group of PAA is  $2 \times 10^{-4}$  M.

the different copolymer chains, but further examination has not been carried out. When the temperature was raised up to 700°C, the residues of  $C_2F_8MA-VE_2$  and  $C_2F_8MA-VE_3$  were 1.1% and 5.5%, respectively. Any noticeable differences of  $T_g$  and degradation behavior between  $C_2F_8MA-VE_2$  and  $C_2F_8MA-VE_3$  were not observed.

**Monolayer Formation and Its Transfer on Solid Substrates.** Tetrahydrofuran solutions of the copolymers,  $C_2F_8MA-VE_2$  and  $C_2F_8MA-VE_3$ , were spread on pure water

**Table 2.** Conditions Employed for Monolayer Deposition<sup>a</sup>

Polymer	Surface pressure (mN/m)	Deposition speed (mm/min)		Deposition type	Transfer ratio (1st-6th L)
		Downward	Upward		
C <sub>2</sub> F <sub>8</sub> MA-VE <sub>2</sub>	30	50	10	Y (FP-010)	1.06-1.00
	25	50	10	Y (CaF <sub>2</sub> )	1.14-0.80
C <sub>2</sub> F <sub>8</sub> MA-VE <sub>3</sub>	30	50	10	Y (FP-010)	1.10-0.90
	25	50	10	Y (CaF <sub>2</sub> )	1.06-0.85

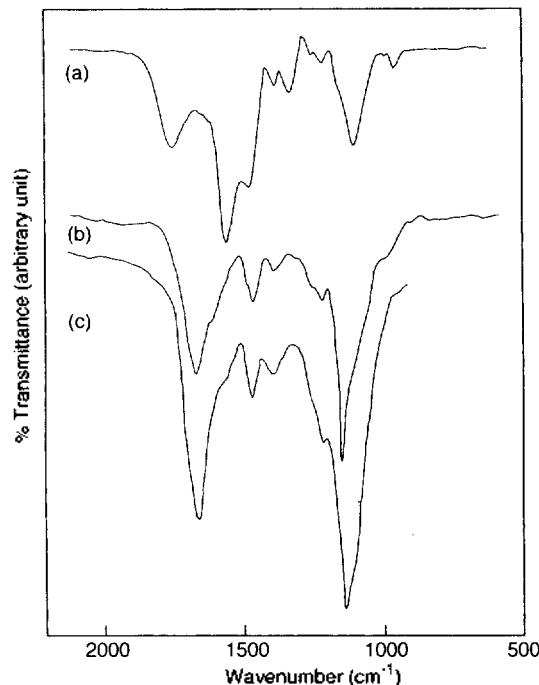
<sup>a</sup>Other common conditions: spreading solvent; THF. drying period; 10 min. Temp. 30°C.

or on aqueous PAA.  $\pi$ -A Isotherms of Figure 1 show that the copolymers form stable monolayers. These monolayers give expanded phases. When compared with the isotherm on pure water, a more expanded area is revealed on aqueous PAA. This change between the two isotherms is attributed to the formation of a polyion complex at the interface and the consequent change of the monolayer organization, as already described for other systems.<sup>14-16</sup> The C<sub>2</sub>F<sub>8</sub>MA-VE<sub>3</sub> containing longer oligoethyleneglycol pendant showed more expanded monolayer phase than the C<sub>2</sub>F<sub>8</sub>MA-VE<sub>2</sub>. No noticeable expansion of the isotherm is observed with increasing incubation times from 10 min to 2 h.

The polyion-complexed monolayer could be transferred onto solid substrates such as a porous fluorocarbon membrane filter (FP-010) and a CaF<sub>2</sub> plate (GL Sciences). The conditions employed for monolayer transfer are summarized in Table 2. In all cases, the Y type deposition was found at a surface pressure of 25 or 30 mN/m and a transfer rate of 50 (downward) or 10 (upward) mm/min. In that process, no deposition was observed at the first downward stroke in the case of CaF<sub>2</sub> plate, and rapid downward stroke was necessary to avoid the loss of deposited layers. The transfer ratio was 1.14 to 0.80. The monolayers on pure water also show Y type deposition. However, when a surface pressure of 30 mN/m was applied to the monolayers for 1 h, their area gradually decreased by about 10% in both the copolymers. This is contrasting with the behavior of the polyion-complexed monolayer, which becomes so stable that any noticeable area decrease is not observed during the transfer period of up to 3 h.

**Polyion-Complexed Film.** The formation and structure of a polyion complex could be confirmed by means of FT-IR. Figure 2(a) of C<sub>2</sub>F<sub>8</sub>MA-VE<sub>2</sub>/PAA system shows two characteristic carbonyl peaks at 1725 cm<sup>-1</sup> and 1575 cm<sup>-1</sup>, which are attributed to ester and carboxylate salt, respectively. The appearance of a shoulder peak at around 1660 cm<sup>-1</sup> is due to the carbonyl stretching mode of amide bond already formed before heat treatment or the N-H bending mode, showing incorporation of PAA into the film. The spectra of the same pattern were also obtained in case of C<sub>2</sub>F<sub>8</sub>MA-VE<sub>3</sub>/PAA system.

SEM micrographs of Figure 3 show the surface morphology of the porous fluorocarbon membranes (FP-010). We can readily observe that the original pores, which are seen as longish and somewhat dark appearance (Figure 3(a)), of the substrate membrane. When the monolayer was deposited on FP-010 from pure water subphase, the large defects with sizes of ca. 1  $\mu$ m are seen as dark spots even in 4 layers, which are indicated as arrows. However, good covering of



**Figure 2.** Transmission FT-IR spectra of LB films (15×2 layers) of C<sub>2</sub>F<sub>8</sub>MA-VE<sub>2</sub>/PAA on a CaF<sub>2</sub> plate: (a) as-deposited film; (b) heat-treated at 180°C for 10 h in a vacuum; (c) immersed in benzene for 24 h.

the pores is found in the 4 layer film which was transferred from aq. PAA subphase (Figure 3(c)). It can be supposed that the covering capability is enhanced through the polyion complexation at the air-water interface. The C<sub>2</sub>F<sub>8</sub>MA-VE<sub>3</sub>/PAA system was better in the covering capability, which was evidenced through the degree of the hole-defects observed by SEM, than the C<sub>2</sub>F<sub>8</sub>MA-VE<sub>2</sub>/PAA one. Satisfactory coverage of the pores by a 4 layer film indicates that this LB film has a good self-supporting ability.

**Amide-Crosslinked Film.** The polyion complex film was subsequently subjected to heat treatment at 180°C in a vacuum of 10<sup>-2</sup> mmHg for 10 h. The formation of amide bonds can be confirmed by FT-IR spectra. Strong peak at 1659 cm<sup>-1</sup> as shown in Figure 2(b) can be mainly assigned to carbonyl stretching mode of the amide group. Concurrently, the peak of carboxylate (1575 cm<sup>-1</sup>) is weakened. This reaction results in detachment of ester alcohol tails, as evidenced by decreased intensity of the peak due to ester carbonyl group (1725 cm<sup>-1</sup>) (Scheme 1A). The detached fluorocarbon alcohols are believed to be removed from the film,

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## The Effect of Alkali Metal Ions on Nucleophilic Substitution Reactions of Aryl 2-Furoates with Alkali Metal Ethoxides in Ethanol

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Rate constants have been measured spectrophotometrically for the nucleophilic substitution reactions of *p*- and *m*-nitrophenyl 2-furoates (**4** and **5**, respectively) with alkali metal ethoxides (EtO<sup>-</sup>M<sup>+</sup>) in absolute ethanol at 25°C. The reactivity of EtO<sup>-</sup>M<sup>+</sup> toward **4** is in the order EtO<sup>-</sup>K<sup>+</sup> > EtO<sup>-</sup>Na<sup>+</sup> > EtO<sup>-</sup>Li<sup>+</sup> > EtO<sup>-</sup>K<sup>+</sup> + 18-crown-6 ether. This is further confirmed by an ion pairing treatment method. The present result indicates that (1) ion paired EtO<sup>-</sup>M<sup>+</sup> is more reactive than dissociated EtO<sup>-</sup>; (2) the alkali metal ions (K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup>) behave as a catalyst; (3) the catalytic effect increases with increasing the size of the metal ion. A similar result has been obtained for the reaction of **5**, however, the catalytic effects shown by the metal ions are more significant in the reaction of **5** than in that of **4**.

### Introduction

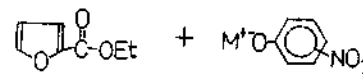
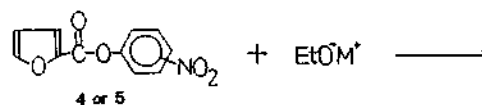
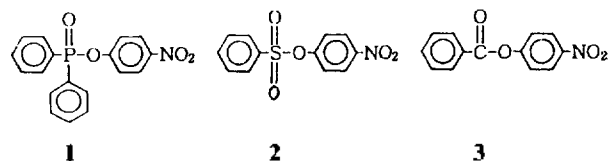
The effect of metal ions on acyl-transfer reactions has been intensively studied due to their important roles in biological processes.<sup>1-3</sup> However, most investigations have been focused on divalent metal ions such as Mg<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, ... etc.,<sup>4,5</sup> and studies of alkali metal ions have been initiated only recently.<sup>6-9</sup>

Buncel and his coworkers found significant effect of alkali metal ions on the reactions of alkali metal ethoxides (EtO<sup>-</sup>M<sup>+</sup>) with *p*-nitrophenyl diphenyl phosphinate (**1**) and with *p*-nitrophenyl benzenesulfonate (**2**) in absolute ethanol.<sup>6,7</sup> In the reaction of the phosphinate ester (**1**) alkali metal ions behave as a catalyst, and the catalytic effect increases with increasing the charge density of the metal ion (e.g., Li<sup>+</sup> > Na<sup>+</sup> > K<sup>+</sup>).<sup>6</sup> On the contrary, Li<sup>+</sup> ion exhibits inhibitory effect while K<sup>+</sup> ion shows largest catalytic effect in the reaction of the sulfonate ester (**2**).<sup>7</sup> Recently, we have found that the alkali metal ions exhibit inhibitory effect on the reaction of the phosphinate ester (**1**) with alkali metal phenoxides (ArO<sup>-</sup>M<sup>+</sup>),<sup>8</sup> but no effect on the reaction of a carboxylic ester (**3**) with EtO<sup>-</sup>M<sup>+</sup> in absolute ethanol.<sup>9</sup> In this way, the effect of alkali metal ions appears to be significantly dependent on the type of substrates and nucleophiles as well as on the size of alkali metal ions.

Several explanations have been suggested to rationalize the catalytic or inhibitory effect of the alkali metal ions.<sup>6-8</sup> However, their roles in the acyl-transfer reactions are not fully understood.<sup>10,11</sup> In order to investigate the role of alkali metal ions in acyl-transfer reactions, we have chosen the following reaction system.

### Experimental

**Materials.** The aryl 2-furoates (**4** and **5**) were prepared by a known procedure<sup>12</sup> using *p*- or *m*-nitrophenol and 2-furoyl chloride in the presence of triethylamine in dried ether. Their purity was checked by means of melting points and spectral data such as IR and <sup>1</sup>H-NMR characteristics. Absolute ethanol was prepared by the method described in the literature<sup>12</sup> under a nitrogen atmosphere. Solutions of alkali metal ethoxides were prepared by dissolving the corresponding alkali metal in the absolute ethanol under a nitrogen



- 4** : *p*-nitrophenyl 2-furoate  
**5** : *m*-nitrophenyl 2-furoate  
 M': K<sup>+</sup>, Na<sup>+</sup>, Li<sup>+</sup>, K<sup>+</sup> + 18C6

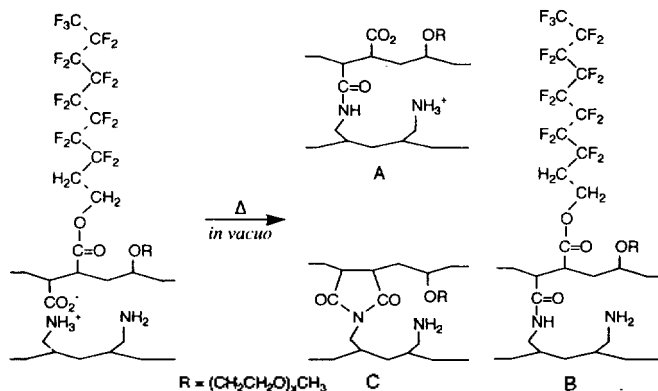
Scheme 1.



**Figure 3.** Scanning electron micrographs of LB films of  $C_2F_5$ -MA-VE<sub>3</sub> deposited on fluorocarbon membrane filters (FP-010): (a) FP-010 only; (b) as-deposited film of 4 layers from pure water subphase; (c) as-deposited film of 4 layers from aq. PAA subphase; (d) heat-treated (c) of 4 layers. The samples were sputtered with Au and observed at 15 kV. The defects are indicated with arrows.

because the heat treatment is carried out under a high temperature and a high vacuum. Another possibility of amide formation is from condensation reaction of carboxylate/ammonium salt (Scheme 1B). But, stoichiometric analysis for those different amide groups did not further proceed. The peaks due to imide bonds (Scheme 1C), which were observed in the related previous systems,<sup>16</sup> were not discriminately seen in FT-IR spectra of present system. The reason for the difference is not clear at this point.

Figure 3(d) is SEM micrograph of the LB film on the porous membrane (FP-010) after heat treatment. By compar-



**Scheme 1.** Amide formations from polyion complex film through heat treatment.

ing with Figure 3(c), we can see that the formation of the amide bond *i.e.*, crosslinking and detachment of ester alcohol tails, does not give further defects to the covered film. This means that only 4 molecular layers of the polymer network are enough to cover the pores of the membrane filter. Immersion of this film in water or in benzene for 1 day did not cause any change in its appearance. Its FT-IR spectrum after immersion (Figure 2(c)) does not give any indication of structure changes.

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