

An Ultrathin Polymer Network through Polyion-Complex by Using Sodium Dioctadecyl Sulfate as Monolayer Template

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Two-dimensionally cross-linked ultrathin films of poly(maleic acid-alt-methyl vinyl ether) (MA-MVE) and poly(allylamine) (PAA) were produced by using sodium dioctadecyl sulfate (2C18S) as the monolayer template for Langmuir-Blodgett (LB) deposition. The template molecules were subsequently removed by thermal treatment followed by extraction. The polyion-complexed monolayers of three components, *i.e.*, template 2C18S, co-spread PAA, and subphase MA-MVE, were formed at the air-water interface. Their monolayer properties were studied by the surface pressure-area isotherm. The monolayers were transferred on solid substrates as Y type. The polyion-complexed LB films and the resulting network films were characterized by FT-IR spectroscopy, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). The cross-linking to form a polymer network was achieved by amide or imide formation through heat treatment under a vacuum. SEM observation of the film on a porous fluorocarbon membrane filter (pore diameter 0.1 μm) showed covering of the pores by four layers in the polyion complex state. Extraction by chloroform followed by heat treatment produced hole defects in the film.

Keywords : Network, Monolayer, Langmuir-Blodgett film, Template, Sodium dioctadecyl sulfate.

Introduction

The formations of polyion-complexed monolayers at the air-water interface have been used as a distinctive process in the fabrication of Langmuir-Blodgett (LB) films.¹ By employing these polyion complexes, the preparation of LB films with special functionalities became possible. For example, Kunitake *et al.* succeeded in forming a LB film of a fluorocarbon amphiphile by complexing with potassium poly(styrenesulfonate),² which is otherwise intractable to transfer the monolayer onto a substrate. The LB films of azobenzene amphiphiles as polyion complexes were prepared by spreading monolayers on subphases containing anionic¹ or cationic³ polymers. Ringsdorf *et al.* reported the domain formation of fatty acid monolayers on a poly(ethyleneimine)-containing subphase.⁴ Thin films of poly(imide)^{5,6} and poly(arylenevinylene)⁷ were prepared by the LB method by attaching hydrophobic chains electrostatically to the precursor polymers which, by themselves, are incapable of monolayer formation.

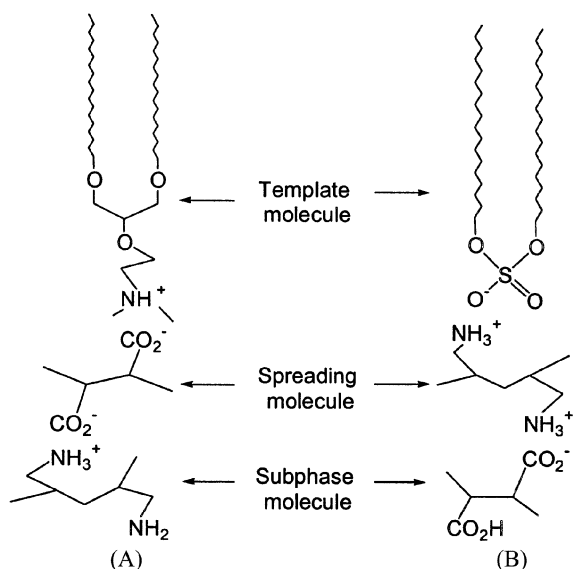
The concept of polyion complexes has been extended to polymer-polymer systems of two different kinds of polymers. Kunitake *et al.* have reported formations of salt bridges between a polymerized ammonium monolayer and an anionic polymer at the air-water interface⁸ and of a two-dimensional polymer network of LB films of a polyamine-polycarboxylate salt.⁹ Higashi *et al.* reported chain-length recognition of poly(acrylic acids) by the monolayer of a

polymer-based amphiphile.¹⁰ We have also used the polyion-complexed system for fabrication of ultrathin network films, especially the polyimide network films which are potentially important in electronic applications.¹¹⁻¹⁹

In this paper, we extend the fabrication technique in dealing with polyion-complexed LB films for polyimide films to a differently charged components system. In particular, we describe two-dimensional polymer network of poly(maleic acid-alt-methyl vinyl ether) (MA-MVE) and poly(allylamine) (PAA), which were prepared from monolayer consisting of three polyion-complexing components. A double chain sulfate, dioctadecyl sulfate (2C18S), was used as the template for enhancing the monolayer stability and deposition efficiency, and was eventually removed from the LB film. In this system, the PAA forms polyion salts with both the template sulfate 2C18S and subphase polymer MA-MVE.

This system which is shown in Scheme 1B is different from the previously described method (Scheme 1A).¹² In the former system, the spreading solution was composed of cationic template molecule and anionic polymer, and the solution was spread on subphase containing cationic polymer such as poly(allylamine). Then, the three-component monolayer was formed at the air-water interface. In this system, we extended the polyion-complexed concept, *i.e.*, anionic template molecule and cationic polymer were employed as spreading components, and cationic water-soluble polymer was dissolved in subphase. By demonstrating this system successfully, we have tried to prove the polyion-complexed system to be generally applicable to LB film fabrication from various combinations of charged components.

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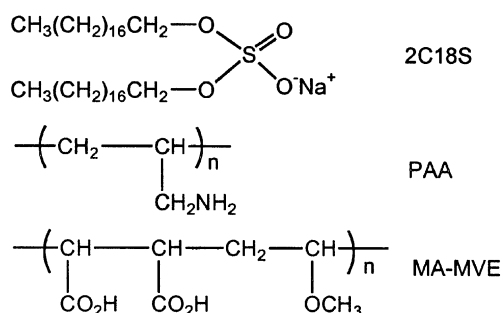


Scheme 1. Components illustration of polyion-complexed monolayer; (A) spreading solution is composed of cationic template molecule and anionic polymer, and cationic polymer is dissolved in subphase. (B) anionic template molecule and cationic polymer are dissolved in spreading solution, and water-soluble anionic polymer is employed as subphase molecule.

Experimental Section

A. Materials. The template sulfate 2C18S, sodium dioctadecyl sulfate, was purchased from Aldrich Chemical Co. and used without further purification. The maleic acid copolymer MA-MVE, poly(maleic acid-alt-methyl vinyl ether), was purchased from Scientific Polymer Products, Inc. in the form of the corresponding maleic anhydride copolymer. The maleic anhydride copolymer was hydrolyzed to the maleic acid copolymer. Poly(allylamine)hydrochloride ($M_w = 1.0 \times 10^4$) 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 amino group in aqueous solution was determined by colloid titration with standard poly(vinyl sulfate) solution using Toluidine Blue O as the indicator.

B. Surface Pressure-Area 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, $150 \times$



Scheme 2. Chemical structures of 2C18S, PAA, and MA-MVE.

600 mm). Isotherms were taken at a compression rate of 0.4 mm/s, and the temperature of the aqueous subphase was maintained at 30.0 ± 0.1 °C. Cosolvent of chloroform and dimethylsulfoxide (7/3, v/v) was employed as spreading solvent. Monolayers were spread on pure water or on aqueous MA-MVE (2×10^{-4} mol/-CO₂H) and incubated for 10 and 30 min, respectively, before starting the compression.

The deposition of the monolayer was performed in the vertical mode by using a computer-controlled film balance (FSD-50) and lifter (FSD-51) system (San-esu Keisoku). The transfer onto solid substrates was carried out at a surface pressure of 30.0 ± 0.2 mN/m and a deposition rate of 4 mm/min. The temperature of the subphase was kept at 30 ± 0.1 °C. The employed substrates were fluorocarbon membrane filter (FP-010, Sumitomo Electric Co.) for scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), and a calcium fluoride plate (Polyscience, Inc.) for FT-IR spectroscopy.

C. Measurements. FT-IR measurements were carried out on a Nicolet 710 FT-IR spectrometer by the transmission method. In order to minimize the influence of water vapor and CO₂ on the spectra, the system was purged by dry air for 1-2 h before measurement. Scanning electron microscopy (SEM; Hitachi S-900) was used to observe the surface morphology of a FP-010 membrane filter (pore diameter, 0.1 μm) covered with the LB films. An acceleration voltage of 2 kV was employed. The sample was sputtered with Pt-Pd before observation. XPS spectra were obtained on an ESCA 5300 X-ray photoelectron spectrometer (Perkin Elmer), which was operated at 12 kV and 25 mA (300 W) with a Mg Kα X-ray source and at less than 7.0×10^{-9} Torr.

Results and Discussion

A. Monolayer Formation and Its Transfer on Solid Substrates. The monolayers were formed by spreading a chloroform/dimethyl sulfoxide (7/3, by volume) solution of 2C18S and PAA (1 : 5, with respect to repeat units) on pure water or on aqueous MA-MVE. The surface pressure-area (π -A) isotherms of Figure 1 show that sulfate 2C18S fixed electrostatically with PAA forms stable monolayers. The collapse pressure was increased from about 40 mN/m of pure water to 60 mN/m of aqueous MA-MVE subphase. This enhancement of monolayer stability means the complex formation of three components at the air-water interface, *i.e.*, the spread PAA already complexed with 2C18S forms another complex with MA-MVE through electrostatic interaction. This additional polyion complex is thought to make the monolayer components stabilize against applied pressure. Different curve shapes of the π -A isotherms were found according to the subphases. While the monolayer collapse have continued with keeping the surface pressure *ca.* 40 mN/m on pure water subphase, the surface pressure of the monolayer on aq. MA-MVE has quickly dropped to *ca.* 30 mN/m just after the monolayer collapse and increased again with the continued barrier compression. The early development of surface pressure at 0.7 nm² of molecular

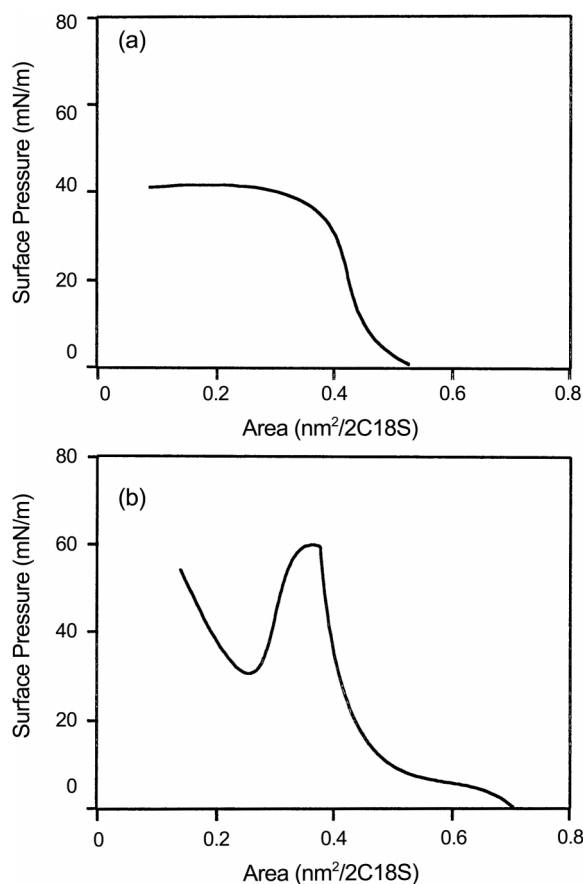


Figure 1. Surface pressure-area isotherms of 2C18S complexed electrostatically with PAA: (a) on pure water; (b) on aqueous MA-MVE at 30 °C.

area in case of aq. MA-MVE subphase is understood as that the subphase polymer MA-MVE makes the spreading molecules much expand by additional polyion complexation.

Monolayer transfer was possible onto various substrates such as a fluorocarbon membrane filter and a calcium fluoride plate. Y-type deposition was found at a surface pressure of 30 mN/m and a transfer rate of 4 mm/min, although the deposition started from upward stroke in the case of the CaF₂ plate. The transfer ratio was close to unity (0.8-1.1) on both the substrates. These monolayers were stable enough to maintain a constant area for drying period when kept at a surface pressure of 30 mN/m, where the monolayers were transferred.

B. Polyion-Complexed LB Film. The formation and composition of the polyion complex in the resulting LB films were confirmed by means of FT-IR and XPS measurements. The FT-IR spectrum of Figure 2(a) shows the bands (1636 and 1575 cm⁻¹) from the amino and ammonium groups in the as-deposited LB film prepared from the aqueous MA-MVE subphase. The strong ammonium band can be understood due to the formation of quarternary ammonium salts between amino and carboxyl groups of PAA and MA-MVE. The broad band around 1575 cm⁻¹ can be also assigned together with the band of 1540 cm⁻¹ as those owing to carboxylate ion group. As shown in Figure

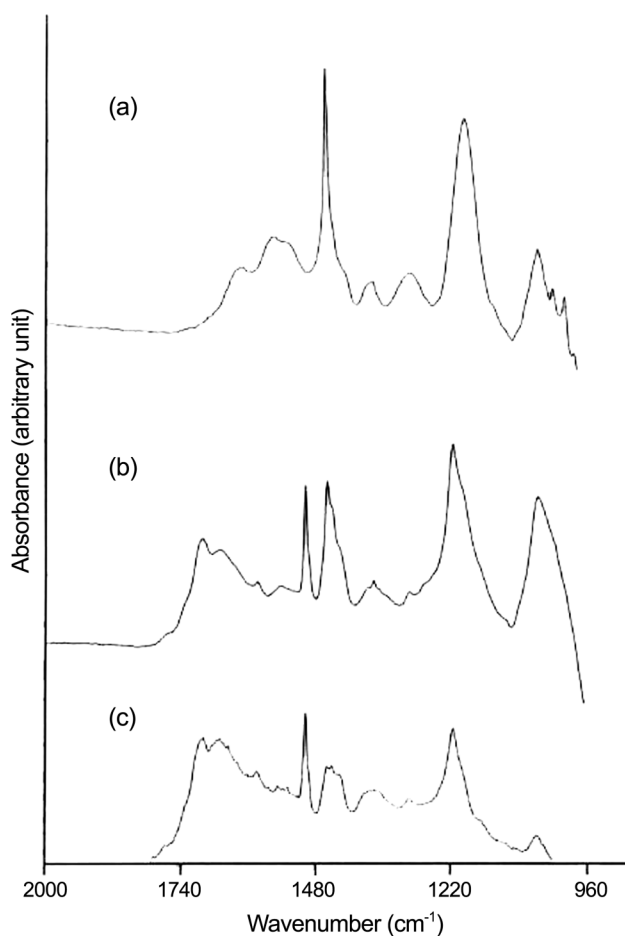
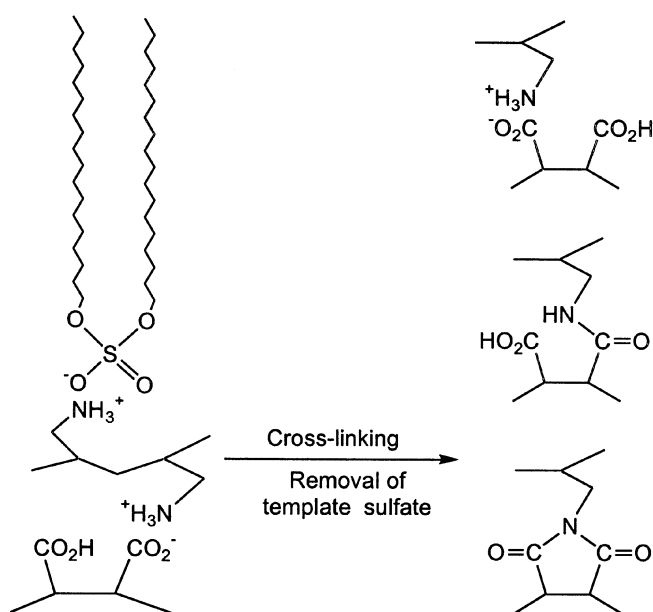


Figure 2. FT-IR spectra of the 2C18S/PAA/MA-MVE LB films (a) in polyion-complex state, (b) after heat treatment, and (c) after template extraction.

2(b), the bands from amino and ammonium groups are decreased when the polyion complex LB film was heat-treated in a vacuum at 180 °C. Along with the decrease of the amino and ammonium groups, the noticeable reduction of carboxylate bands can also be confirmed. The possible complex structure and following network formation are schematically illustrated in Scheme 3. The chemical structures resulted from heat treatment show that the LB films still contain ammonium-carboxylate ionic bond and amide covalent bond besides the imide bond. The spectroscopic analysis of the structures after heat treatment is described in following section.

The composition of the polyion complex LB film was estimated by XPS measurements. The N_{1s} peak of the as-deposited film is made of two components which are attributed to ammonium N (binding energy 399.7 eV) and amino N (397.6 eV), as shown in Figure 3(a). The increase of the ammonium component was found in the film deposited from aq. MA-MVE subphase compared with the film transferred from pure water subphase. This additional increase of ammonium component is due to the formation of polyion complex between PAA and MA-MVE. The extent of MA-MVE incorporation into the LB film was estimated



Scheme 3. Network formation from a polyion complex film through heat treatment. The LB film still contains ammonium-carboxylate ionic bonds and amide bonds besides the imide bonds.

by taking into account the atomic sensitivity factor and the relative area of the N_{1s} and O_{1s} peaks. The XPS results reveal that *ca.* 0.3 equivalent carboxyl groups of subphase polymer MA-MVE are incorporated into the as-deposited film with respect to the repeat unit of PAA.

As a second hand evaluation of the LB film stability, the

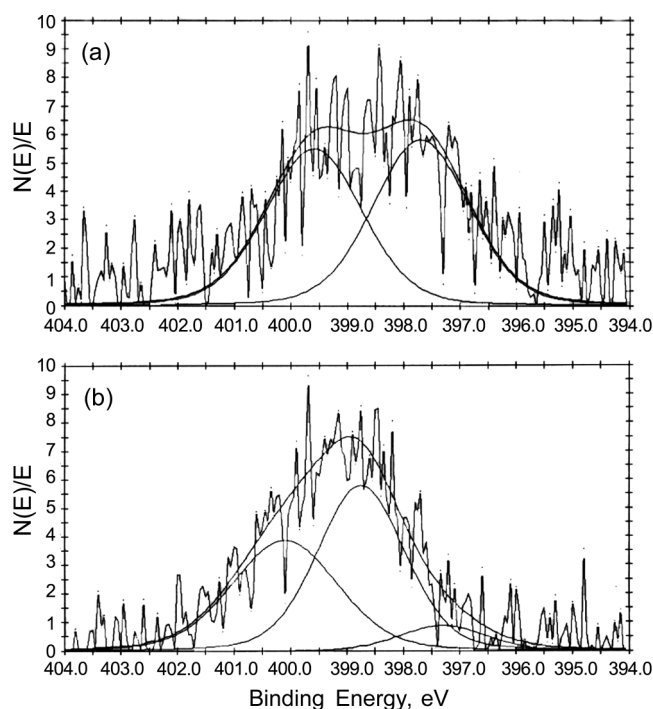


Figure 3. The N_{1s} XPS spectra of the 2C18S/PAA/MA-MVE LB films (a) in polyion-complex state and (b) after heat treatment. The N_{1s} peak of (a) is composed of two components (399.7 eV and 397.6 eV) and the third component at 398.7 eV is developed in that of (b).

covering ability of LB films over the pores of a membrane filter was estimated by direct observation of the LB films by SEM. SEM observation of the LB film on porous fluorocarbon membrane filters (FP-010) showed covering of the pores, which are seen as long and somewhat dark appearances in Figure 4, by four layers in the polyion complex state. This covering ability is not the best case among the three component systems studied so far.^{12,13} The four layers, if anything, belongs to intermediate grade in the stability estimation of LB films. The best case was 2 layers of a template amine/PAA/MA-MVE system at the same substrate condition.¹² Therefore, when we evaluate the relation between polymer structure and covering ability at this point, the flexibility of the polymer backbone is supposed to play an important role for enhancing the covering ability. However, the combination of the spreading molecule and subphase molecule could be reversed in this system. That means the polyion complex technique is able to apply generally to LB films of various combinations from differently charged component molecules.

C. Covalently-Crosslinked LB Film. The polymer network with amide and imide bridges was achieved by heat treatment of the polyion-complexed film at 180 °C in a vacuum for 10 h. The formation of amide and imide bonds could be confirmed by FT-IR spectra. New peaks at 1765 and 1705 cm^{-1} are assigned to asymmetric and symmetric stretching modes, respectively, of the imide group, as shown in Figure 2(b). And, the band due to amide groups could be discerned from the imide bands at 1685 cm^{-1} . Following the partial removal of the template phosphate during the heat treatment, extraction of the residual sulfate was carried out to complete the removal of hydrophobic long tails from the cross-linked network. This skeletonization of the film was performed by immersion in chloroform for 1 day followed by soaking in aqueous NaCl (0.1 M) for 1 day. However, as shown in Figure 2(c), the covalent network structure was kept intact during the skeletonization. The XPS spectrum of Figure 3(b) also supports the formation of the imide and amide groups, since a third peak appears at 398.7 eV in the N_{1s} region. Diminished areas of the ammonium N and amino N peaks are consistent with this supposition. We can estimate the extent of conversion to the amide and imide group from the change of the relative area of each component of the N_{1s} peaks and the O_{1s} peak. About 25 % of maleic acid unit is converted to the covalent amide and imide groups. SEM observation of the heat-treated films on porous fluorocarbon membrane filters (FP-010) showed destruction of the covered films on pores up to 8 layers. Figure 4(c) shows the appearance of the film on the FP-010 filter after extraction of template sulfates. Many hole defects were further produced by the extraction. The hole defects did not increase by immersing the membrane filter in chloroform solvent for 12 hr, which was observed by SEM. The results show that the network LB film can modify the original pores to much smaller pores. In this system, the pores of 0.1 μm diameter could be controlled to pores of less than 10 nm size.

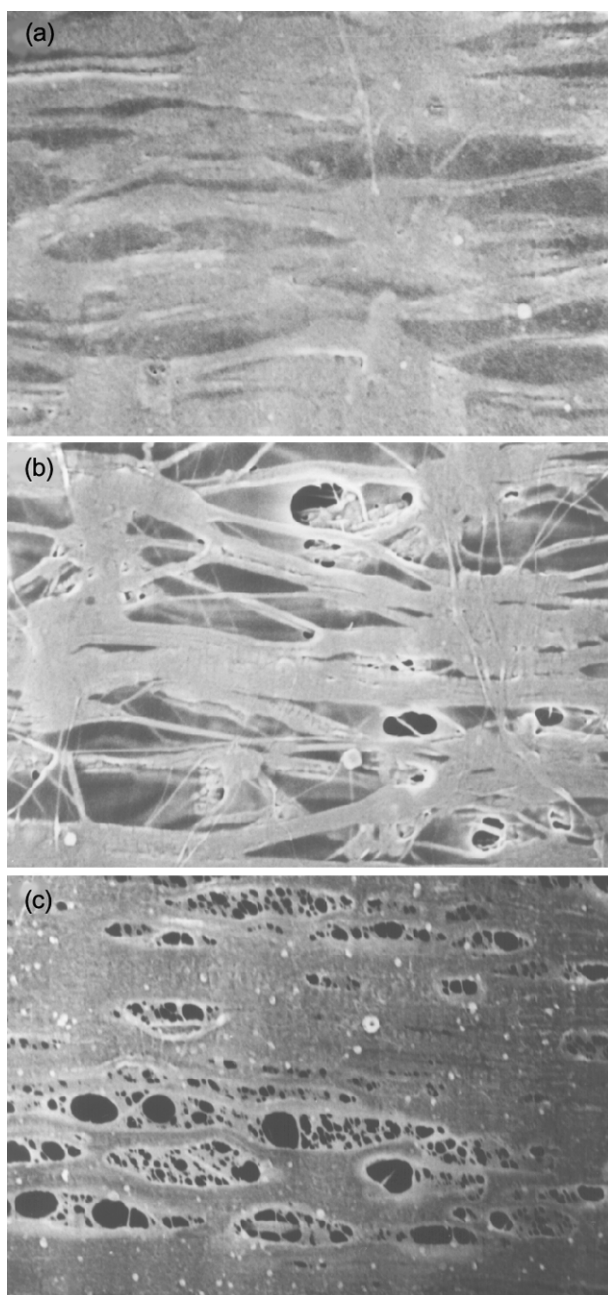


Figure 4. Scanning electron micrographs of LB films of 2C18S/PAA/MA-MVE deposited on fluorocarbon membrane filters (FP-010): (a) as-deposited film of 4 layers; (b) heat-treated film of 8 layers; (c) film of (b) placed in aqueous NaCl and in chloroform for 1 day, respectively. The samples were sputtered with Pt-Pd and observed at 2 kV.

Conclusion

A template synthesis of a two-dimensionally cross-linked network was accomplished by employing a double chain

sulfate as the monolayer template. The template sulfate could be removed by thermal treatment and by extraction. This system provides an extension of a polymer network from two kinds of commercially available polymers which form a polyion complex. And it expands the scope of available polymers for LB film formation by employing a hydrophobic template sulfate, since the use of the template molecule makes the monolayer formation of the polymers possible.

The ultrathin polyimide network shows covering of the substrate pores in less than 10 layers. From the covering and networking of the original pores, we could get a much smaller pores over the original pores. That means this film can be applied to surface modification and size control of the membrane pores. Furthermore, the network structure in the ultrathin films is going to strengthen the physical and chemical stability of the coating films. The application of the network films to thin film devices is expected.

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