Preparation of Cross-Linked Ultrathin Films Based on Layer-by-Layer Assembly of Polymers

Izumi ICHINOSE, Suguru MIZUKI, Shinji OHNO, Hiroaki SHIRAISHI, and Toyoki KUNITAKE[†]

Department of Chemical Engineering & Technology, Faculty of Engineering, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan

(Received March 29, 1999)

ABSTRACT: Ultrathin cross-linked polymer films were prepared by means of two different assembly techniques. As one of the two approaches, alternate adsorption of poly(allylamine hydrochloride) (PAH) and glutaraldehyde, terephthalaldehyde, and valeraldehyde was studied. Cross-linked polymer layers regularly grow via condensation of glutaraldehyde with the adjacent polymer layers, as confirmed by UV, FT-IR, and XPS measurements. The resulting multilayer film has a nano-porous structure with density of 0.65 g/cm³, and unit thickness of ca. 45 Å. The hydrophobic interaction at the PAH surface modified with the aldehyde group appears to be crucial to the successful assembly. In the second approach, multilayer films were similarly prepared from PAH and (methyl vinyl ether)-alt-(monomethyl maleate) copolymer (MMC). Linear film growth is achieved only in limited pH ranges, pH 7–8 for MMC and pH 6 for PAH, to give unit bilayer (PAH + MMC) thickness of 26–33 Å. Upon heating in vacuo, more than half of the amino groups in PAH form the imide linkage with monomethyl maleate units of MMC. The cross-linked ultrathin polymer films prepared on a microporous polymer support display selective permeation of methyl orange against myoglobin.

KEY WORDS Alternate Adsorption / Ultrathin Film / Cross-linked Polymer / Permeability / Polymer Network / Quartz Crystal Microbalance / Layer-by-Layer Assembly /

Fabrication of ultrathin cross-linked polymers has been actively studied during the past several decades for the purpose of preparation of ultrathin separation devices. Earlier examples of two-dimensional polymer networks based on the Langmuir-Blodgett (LB) technique include polymerization of long alkyl derivatives with vinyl and diacetylene units,¹ cross-linking of octadecyl urea multilayers by formaldehyde,² and formation of polyion complexes at the air-water interface.³ More recently, we prepared LB films of polyion complexes of polymer amines and polymer acids, and converted them to cross-linked films via thermal imide formation.^{4,5}

Other examples of the 2D-polymer network are based on alternate adsorption of linear polymers and cross-linking agents. In the initial studies, Meyers and Royer reported that poly(ethyleneimine) adsorbed on the surface of alumina beads was immobilized by adsorption of glutaraldehyde and additional adsorption of poly(ethyleneimine).⁶ Surface modification and alternate adsorption of reactive polymers have been advocated by Beyer et al.⁷ An amino-silanized glass plate readily reacts with a poly(methyl vinyl isocyanate-co-maleic anhydride). The modified surface containing isocyanate and anhydride groups can be further functionalized using hydroxyl and amino compounds. Alternate adsorption of this reactive polymer and 2-aminoethanol gives regular film growth with a thickness increase of 14–61 Å.⁷ We recently reported a preparative technique of extensively bridged organic/inorganic ultrathin films by means of alternate complexation of metal alkoxides and hydroxyl polymers.⁸

Greater mechanical stability is more anticipated for cross-linked polymer films prepared using alternate condensation than cross-linked layers prepared by the LB technique, because each polymer layer is covalently bound to upper and lower layers. Furthermore, pore-size control in polymer network, which is essential for its use as separation membranes, will be achieved by adjusting the degree of bridging and/or by molecular design of cross-linking agents. Such studies are, however, very few as far

as we know.

We describe here additional approaches for the preparation of cross-linked polymer films based on alternate assembly. One is reactive adsorption of poly(allylamine hydrochloride) (PAH) and glutaraldehyde, and the second one is electrostatic alternate adsorption of poly(allylamine hydrochloride) (PAH) and (methyl vinyl ether)-alt-(monomethyl maleate) copolymer (MMC) and subsequent cross-linking (Figure 1).

EXPERIMENTAL

Materials

Poly(allylamine hydrochloride) (PAH; MW 99,300; Am. Polym. Standard), sodium poly(styrenesulfonate) (PSS; MW 88,000; Am. Polym. Standard), poly(ethyleneimine) (PEI; MW 70,000; Waco Chem.), poly(L-lysine hydrochloride) (PLy; MW 30,000 – 70,000; Aldrich Chem.), glutaraldehyde (25 wt% in water; Kishida Chem.), terephthalaldehyde (Tokyo Kasei), and valeraldehyde (Tokyo Kasei) were used as purchased. MMC ((methyl vinyl ether)-alt-(monomethyl maleate) copolymer) was prepared in these laboratories. (Methyl vinyl ether)-co-(maleic anhydride) copolymer (3 g, MW 50,000; Sci. Poly. Products) was stirred in 500-ml methanol at 40 °C for 2 weeks. After disappearance of infrared peaks of maleic anhydride, solvent was removed in vacuo to give MMC as white powder.

[†] To whom correspondence should be addressed.

Figure 1. a) Schiff base formation in PAH/glutaraldehyde film, b) imide formation in PAH/MMC film, c) schematic illustration of cross-linking in layer-by-layer polymer assembly.

Quartz Crystal Microbalance

A quartz crystal microbalance (QCM; 9 MHz) device manufactured by USI System, Fukuoka, was used for monitoring layer-by-layer film growth. Before each measurement, a silver-coated QCM electrode was washed, and one or two precursor layers were assembled by using the previously reported method.⁹ PSS (3.0 mg/ml; pH 7), PAH (1 mg/ml; pH 6), and PEI (1.5 mg/ml; pH 9) were used for the precursor film.

QCM frequency decrease of 1 Hz corresponds to a mass increase of 0.87 ng in our system.^{10,11} Thickness (d) of an adsorbed film on one side of the electrode is given as follows

$$2d(\text{\AA}) = -\Delta F(\text{Hz}) / 1.832 \rho (\text{g/cm}^3) \quad (1)$$

where ρ is the density of adsorbed film and ΔF is the frequency shift of QCM. The kinetic process of adsorption was monitored by using an *in situ* QCM technique elaborated by Ebara *et al.*¹² and Lvov *et al.*¹¹

Other Measurements

Fourier transform infrared (FT-IR) reflection spectra and X-ray photoelectron spectra (XPS) were obtained by using a Nicolet 710 FTIR spectrometer and Perkin Elmer PHI 5300 ESCA system, respectively.^{13,14} Scanning electron micrographs were obtained with a Hitachi S-900 instrument at an acceleration voltage of 25 kV. UV absorption spectra were obtained by using JASCO V-550 spectrometer.

RESULTS AND DISCUSSION

Alternate Assembly of PAH and Aldehydes

Glutaraldehyde, which has two aldehyde groups, can bind to

the upper and lower PAH layers via Schiff base formation to produce 3-D polymer networks. Preliminary experiments revealed that this Schiff base formation rapidly proceeded in acidic solution. Therefore, we adjusted PAH and glutaraldehyde solutions to pH 5 by adding aqueous HCl. A (PAH/PSS) precursor film was adsorbed on a silver-coated QCM resonator in order to provide a uniformly smooth surface.¹¹ The negatively charged surface was immersed in PAH solution (1 mg/ml, pH 5) for 20 min, rinsed in pure water for 1 min, and dried by flushing with nitrogen gas. After measuring QCM frequency, the electrode was immersed in glutaraldehyde solution (1 mg/ml, pH 5) for 20 min, rinsed, and dried with nitrogen gas.

Figure 2 shows frequency decrements ($-\Delta F$) of QCM resonator during alternate adsorption of PAH and glutaraldehyde. The frequency linearly decreased up to at least the 10th adsorption cycle. The averaged frequency shifts are 57 ± 24 Hz for PAH, and 49 ± 18 Hz for glutaraldehyde. Since the frequency decrease of 1 Hz corresponds to a mass increase of 0.87 ng in our system, these values correspond to 10.0×10^{-10} unit mol of PAH (57 Hz; 49 ng as free-base) and 4.9×10^{-10} mol of glutaraldehyde (49 Hz; 53 ng), respectively. The molar ratio, PAH/glutaraldehyde = 2.0, agrees with the functional stoichiometry between the two components. The thickness of the glutaraldehyde layer is estimated as 13 Å from equation (1) using the frequency shift (49 Hz) and the assumed density of 1.0 g/cm³. This is, however, much larger than the CPK molecular length of glutaraldehyde (7 Å). Therefore, glutaraldehyde must have reacted not only with the surface amino group but also with the inner amino group of the PAH layer. Terephthalaldehyde, which has two aldehyde groups in a molecule, shows similar assembly behavior. For the combination of PAH solution (1 mg/ml; pH 5) and terephthalaldehyde (0.5 mg/ml; pH 5), the average frequency shifts were 55 Hz for PAH and 62 Hz for terephthalaldehyde, respectively. The molar ratio again becomes 2.1.

In general, Schiff base formation of amine and aldehyde is in equilibrium with hydrolysis, and is hindered by a large excess of water. In the present case, however, the reaction proceeded completely on the PAH surface that was exposed to water. In contrast, if methanol or ethanol is used as solvents of glutaraldehyde (or terephthalaldehyde), the adsorption of dialdehyde compounds is remarkably diminished. Furthermore, when poly(L-lysine hydrochloride) (PLy; 1 mg/ml; pH 5 in water) was used in place of PAH, adsorptions of each component were gradually saturated with increasing adsorption cycles. Equilibrium of the condensation reaction between PAH and glutaraldehyde may be shifted toward the Schiff base formation by the hydrophobic environment of PAH layer. PLy with a polypeptide chain is probably not able to form hydrophobic layer even after reaction with glutaraldehyde.

We have examined alternate adsorption of PAH and valeraldehyde that has one aldehyde group. The QCM plots of PAH (1 mg/ml; pH 5) and valeraldehyde (1 mg/ml; pH 5) are also shown in Figure 2. Though the slope is smaller than that of glutaraldehyde, the frequency decrease is linear. The molar ratio estimated from the average frequency shifts was PAH/valeraldehyde = 1.2. In case of mono-functional valeraldehyde, excess valeraldehyde must be adsorbed in order to render the subsequent PAH adsorption possible. We suggest here that the hydrophobic interaction play an important role on the adsorption process. When PAH and valeraldehyde form Schiff base, the PAH layer is covered with alkyl chains. This hydrophobic environment must promote adsorption of excess

valeraldehyde to make the outermost layer hydrophilic. This factor causes bilayer adsorption of valeraldehyde, and excess valeraldehyde can react with aqueous PAH. Valeraldehyde did not undergo alternately adsorption with PAH when ethanol was used as solvent. This indicates that hydrophobic interaction is an essential factor for these assemblies.

Cross-linking in PAH/Glutaraldehyde Film

Figure 3 shows a scanning electron micrograph (SEM) of a PAH/glutaraldehyde film prepared on a silver-coated QCM resonator. The film has a 500-Å thickness, and peeling off of surface layers are partially observed. The total QCM frequency shift during film preparation was 1200 Hz. Based on the frequency shift and the thickness (500 Å), the film density is estimated to be 0.65 g/cm³ from equation (1). This is smaller than those of other alternate films. For example, the density of alternate films of PAH/PSS and PAH/protein was 1.2 g/cm³.¹¹ The thickness increase for each adsorption cycle is 45 Å, as calculated from this density (0.65 g/cm³) and frequency shift (106 Hz) for both PAH and glutaraldehyde adsorption. Figure 4 shows UV-Vis absorption spectra of PAH/glutaraldehyde assembly. For this measurement, a quartz substrate with (PAH/PSS)₂ precursor film was alternately immersed into PAH solution (1 mg/ml; pH 5) and glutaraldehyde solution (1 mg/ml; pH 5) for 20 min. Spectra were recorded at every two cycle after glutaraldehyde adsorption, and were corrected by subtracting absorption of the precursor film. Absorption maxima near 268 nm are attributed to Schiff base and are enhanced with the number of the adsorption cycle. This regular film growth should be based on the condensation of PAH and glutaraldehyde. The absorption near 235 nm is to be attributed to carbonyl group of glutaraldehyde. Some of the aldehyde group remain unreacted after glutaraldehyde adsorption. The 235-nm absorption slightly decreased after PAH adsorption, but it did not completely disappear. The presence of unreacted aldehyde units was also confirmed by FT-IR measurements for a PAH/glutaraldehyde film (40 cycles) on a (PAH/PSS)₂ precursor film adsorbed on a glass. The reflection FT-IR spectra gave broad peaks near 1720 cm⁻¹ and 1647 cm⁻¹, due to stretching bands of carbonyl groups and Schiff base, respectively. The peak area of the Schiff base absorption is three times larger than that of the carbonyl peak. This indicates that most of glutaraldehyde molecules act as bi-functional aldehydes. Figure 5 shows an XPS spectrum of PAH/glutaraldehyde assembly (30 cycles) prepared on a glass plate. After correction of the charge up shift on the basis of binding energy of carbon, the N_{1s} region peaks were curve-fitted using binding energies of ammonium nitrogen (401.3 eV), free amine (399.2 eV) and Schiff base amine (398.2 eV).^{14,15} The atomic ratio is NH₃⁺ : NH₂ : Schiff base nitrogen = 3 : 6 : 4, as estimated from the relative peak area. The PAH nitrogen in the cross-linked film mostly exists as free amino group, and some of them are protonated. Schiff base nitrogen is no more than 30 %.

As mentioned before, the molar ratio estimated from QCM data was PAH/glutaraldehyde = 2.0, which suggests stoichiometric condensation between two components. XPS data are, however, inconsistent with this assumption, and showed that the PAH amino groups used for Schiff base formation was less than 30 %. However, UV and FT-IR spectra indicated a large part of the aldehyde groups were included as Schiff base. Considering the equilibrium nature of this reaction, we presume that glutaraldehyde adsorbed on PAH layer must be partially desorbed during the next PAH adsorption procedure. In this case, the amount of the stably adsorbed glutaraldehyde becomes smaller

Figure 2. QCM frequency shifts of alternate assembly of PAH and aldehyde compounds. (a) PAH: 1 mg/ml; pH 5, glutaraldehyde: 1 mg/ml; pH5, (b) PAH: 1 mg/ml; pH 5, valeraldehyde: 1 mg/ml; pH 5. The period of adsorption for each cycle was 20 min. The first two P marks indicate a (PAH/PSS) precursor film.

Figure 3. Scanning electron micrograph of PAH/glutaraldehyde assembly on a silver-coated resonator. Total frequency shift: 1200 Hz.

Figure 4. UV-Vis absorption changes due to growth of PAH/glutaraldehyde assembly. The sample was prepared on a quartz plate with (PAH/PSS)₂ precursor. Absorbance due to the precursor layer is corrected for each measurement.

than that estimated from the QCM frequency shift, and mass of PAH becomes correspondingly larger. Figure 6 shows a schematic illustration of PAH/glutaraldehyde cross-linked film. Part of the aldehyde groups are not involved in Schiff base, and free and protonated amino groups are present in the PAH layer. The film has a network structure, in which glutaraldehyde forms bridges for every four PAH monomer units in average to give nano-sized porosities. The lower film density (0.65 g/cm³) revealed from SEM observation supports such a porous structure.

Figure 5. XPS spectrum of a PAH/glutaraldehyde assembly. The sample obtained by 30 adsorption cycles. The outermost surface is glutaraldehyde layer.

Figure 6. Schematic illustration of a cross-linked PAH/glutaraldehyde film.

Alternate Assembly of PAH and MMC

As mentioned above, we prepared LB films of polyion complexes of polymer amines and polymer acids by employing double chain amphiphiles, and converted them to two-dimensional polymer networks via thermal imide formation.⁵ Multilayer films of cross-linked polymers are obtainable after extraction of amphiphiles. The films, however, possessed many pin-hole defects, probably due to low mechanical strength of each component layer. In order to improve the film quality, we prepared PAH/MMC multilayers by means of electrostatic layer-by-layer adsorption.¹⁶ Since PAH and MMC are a combination of weak acid and weak base, the assembly behavior is expected to be strongly dependent on pH conditions.

A silver-coated QCM resonator with a poly(ethyleneimine)/PSS precursor film was immersed into PAH solution (1 mg/ml) for 20 min, rinsed in pure water for 1 min, and dried by flushing with nitrogen gas. The electrode was then immersed into MMC solution (1 mg/ml) for 20 min, rinsed, and dried with nitrogen gas. The QCM frequency was recorded at each adsorption step after drying. Figure 7a shows QCM frequency shifts during alternate adsorption of PAH (pH 6; in water) and MMC (pH 4, in water). Under these conditions, the frequency decrement ($-\Delta F$) upon PAH adsorption becomes larger with adsorption cycles, whereas MMC adsorption gives corresponding frequency increases. These data imply that increasing amounts of PAH are adsorbed on the MMC surface, which, however, are mostly desorbed in the next MMC adsorption step. The MMC layer may not be uniform, and the polyion-complex produced will not give a regular film structure. *In situ* QCM measurements^{11,12} showed

Figure 7. QCM frequency shifts due to alternate adsorption of PAH and MMC. a) PAH: 1 mg/ml dissolved in pure water; pH 6, MMC: 1 mg/ml dissolved in pure water; pH 4. b) PAH: 1 mg/ml; pH 5, MMC: 1 mg/ml; pH 5. pH of both solutions was adjusted with acetic acid/sodium acetate buffer. c) PAH: 1 mg/ml dissolved in pure water; pH 6, MMC: 1 mg/ml; pH 7. pH of MMC solution was adjusted with phosphoric acid/potassium phosphate buffer.

that both of PAH and MMC adsorptions were not saturated within 20 min. In particular, PAH adsorption continued without saturation. In typical electrostatic alternate assembly, such as sodium poly(styrenesulfonate) and PAH, adsorption becomes saturated when the surface charge is reversed by overcompensation. Since PAH and MMC are weak acid and base, the charge reversal due to overcompensation is apparently not complete. The lack of saturation may be attributed to low, variable charge densities in adsorbed polymers. This situation did not change, even if pH of the polymer solutions was adjusted by acetate buffer. The amount of adsorbed polymers gradually increased at pH 5, as shown in Figure 7b. Regular growth of PAH/MMC assembly was achieved for the cases of PAH (pH 6) without buffer and MMC of pH 7-8 (phosphate buffer), as shown in Figure 7c. Averaged frequency shifts during ten adsorption cycles are 110 Hz for PAH and 37 Hz for MMC, respectively. Using a polymer density of 1.2 g/cm³, these frequency shifts correspond to thickness increases of 25 Å (PAH) and 8 Å (MMC). The molar ratio of monomer unit estimated from the

average frequency shifts is PAH/MMC = 11. For solutions of PAH (pH 6) and MMC (pH 8), the thickness based solely on QCM data is 17 Å (PAH) and 9 Å (MMC), and the molar ratio is PAH/MMC = 7. These data are not definite, however, due to the possible desorption process.

The pH dependency of polymer adsorption was more clearly seen for the assembly of poly(L-lysine hydrochloride) (PLy) and MMC. PLy undergoes coil-helix transition at pH 10-11, when the positive charge becomes less than one for four lysine residues.¹⁷ The alternate adsorption of PLy (1 mg/ml; pH 7) and MMC (pH 7) gave linear QCM frequency shifts up to at least 10 cycles with frequency decreases of ca. 2000 Hz. Frequency shift for one PLy adsorption, however, becomes 500-1500 Hz for the combination of PLy (pH 10) and MMC (pH 7). Similar pH dependency has been reported for the alternate adsorption of PAH and poly(acrylic acid) by Rubner et al.,¹⁸ where regular multilayer films were obtainable at the neutral pH condition as in our PAH/MMC assembly.

Cross-linking in PAH/MMC Film

Figures 8 and 9 show FT-IR and XPS spectra before and after heating of the PAH/MMC film. The sample was prepared on a gold-evaporated glass plate using PAH solution (pH 5) adjusted with HCl and MMC solution (pH 4) without buffer (10-min adsorption; 10 cycles). The film before heating gives two carbonyl peaks at 1739 cm⁻¹ and at near 1572 cm⁻¹ due to ester and carboxylate groups of MMC, respectively (Figure 8a). The peak at 1441 cm⁻¹ is assigned to N-H bonding of the PAH layer. Upon heating this film at 125°C for 13 h under reduced pressure, the ester and carboxylate peaks were weakened, and new strong peaks appeared at 1774 cm⁻¹ and 1707 cm⁻¹. These should be attributed to asymmetric (1774 cm⁻¹) and symmetric (1707 cm⁻¹) stretching modes of carbonyl group of the imide moiety.⁵ It is known that maleic anhydride unit gives characteristic peaks near 1770 cm⁻¹ and near 1850 cm⁻¹. A broad peak near 1850 cm⁻¹ in Figure 8b corresponds to the maleic anhydride unit formed from MMC. A strong peak at 1774 cm⁻¹ is probably a superposition of imide and anhydride peaks.

The formation of imide was also confirmed by XPS spectra. The N_{1s} region peak before heating can be deconvoluted to ammonium nitrogen (401.3 eV), free amine (398.9 eV) and imide nitrogen (400.0 eV), as shown in Figure 9a. Since chloride ion was not detected in the energy region, the counterion of ammonium nitrogen of PAH layers must be carboxylate groups of MMC layers. Diminution of the peak area of ammonium nitrogen and enhancement of the imide peak after heating indicates the progress of imide formation. We can estimate the extent of imide conversion to be 50 % of the amino groups of PAH. It is not clear why the imide peak is observed for the as-assembled film. Exposing the film to X-ray under ultra-high vacuum may induce imide formation. Otherwise, this reaction should proceed only slowly at room temperature. The conversion is much accelerated by heating. Cross-linking in the PAH/MMC film is schematically drawn in Figure 10. The film assembled by electrostatic alternate adsorption is composed of polymer layers with molecular thickness, and contains carboxylate/ammonium ion pairs. This pre-organization is favorable for efficient imide formation by heating and slow cross-linking occurring even at room temperature.

Permeability of Polymer Networks

We carried out permeation experiments in order to examine the network property of the cross-linked PAH/MMC film. One side

Figure 8. FT-IR spectra of a PAH/MMC film a) before and b) after heating. The sample was prepared on a gold-coated glass plate with (PAH/PSS)₂ precursor: PAH: 1 mg/ml; pH 5, MMC: 1 mg/ml dissolved in pure water; pH 4. pH of PAH solution was adjusted by adding aqueous HCl.

Figure 9. XPS spectra of a PAH/MMC film a) before and b) after heating. The sample was prepared identical conditions with those of Figure 8.

of a polycarbonate membrane filter (Millipore GTTPO 1300; pore diameter 0.2 μm) was covered with 2-nm Pt, and was treated with 3-mercaptopropionic acid (1 mM; in ethanol). The negatively charged surface was immersed into PAH solution (1 mg/ml; pH 10) for 5 min, rinsed with hydrochloric acid (pH 3). Then, the

Figure 10. Schematic illustration of cross-linking of the PAH/MMC assembly.

Figure 11. UV-Vis absorption spectra of myoglobin/methyl orange mixture and the filtered solutions through PAH/MMC films. Permeation solution: myoglobin; 12.5 μ M, methyl orange; 0.1 mM.

membrane filter was immersed in PSS solution (3 mg/ml; pH 3) for 5 min, and rinsed with pure water. After repeating these procedures four times, all the pores of the membrane filter were covered by PAH/PSS multilayer.¹⁹ Four cycles of the PAH/MMC layer was adsorbed on the filter together with precursor films by using the conditions of Figure 7c (PAH; pH 6, MMC; pH 7). The membrane filters were set to a folder and the permeation solution was filtered at a constant pressure. We selected an aqueous mixture of myoglobin (SIGMA; 12.5 μ M) and methyl orange (0.1 mM) as a permeation solution. Myoglobin and methyl orange have absorption peaks at 410 nm and at 463 nm, respectively. Figure 11 shows UV-Vis spectra of permeation solution and filter solution. The as-assembled film shows high permeability at a pressure of 1.5 kg/cm². The permselectivity is not so high, where 78 % of myoglobin permeated against 90 % of methyl orange. On the other hand, enhancement of permselectivity and diminishment of permeability were observed after drying this film for one week at room temperature. Then, myoglobin was detected only as a shoulder of methyl orange peak, as filtered at 3.0 kg/cm². When two-fifths by volume of the solution was filtered, the myoglobin

concentration in the permeation solution was increased 20 % against the original solution. Myoglobin is an elliptical molecule with 3–4 nm diameter, and the molecular length of methyl orange is ca. 2 nm. The porous multilayer can discriminate these sizes.

CONCLUDING REMARKS

We demonstrated here two preparative techniques of ultrathin cross-linked polymer films. Alternate adsorption of PAH and glutaraldehyde gave nano-porous films with density of 0.65 g/cm³. Glutaraldehyde molecules can bridge 25 % of the PAH monomer unit, and free and protonated amino groups remain intact in the PAH layers. Schiff base formation and hydrophobic interaction are essential for this assembly. On the other hand, highly cross-linked films were obtainable from PAH/MMC multilayers based on electrostatic layer-by-layer adsorption. In this case, the medium pH directly affects the thickness of component layers. Therefore, the pH adjustment can be a useful means to control the cross-linking density.

Recently, Regen and his co-workers reported that LB films of calix[6]arene-based surfactants showed a remarkable gas permeation selectivity,²⁰ amounting He/N₂ selectivity of over 170. The Regen approach would be a powerful tool for recognition and/or selective permeation of gas and small molecules. This methodology is, however, not effective, when the size of target molecules becomes larger. The use of cross-linked polymer films will give a solution on this problem if the pore size is adjustable.

Acknowledgments. We are grateful to Mr. Keita Kuroiwa and Mr. Yoshihiro Iwasaki for their help in figure preparation.

REFERENCES

1. A. Laschewsky, H. Ringsdorf, and G. Schmidt, *Thin Solid Films*, **134**, 153 (1985).
2. C. Rosilio and A. Ruau-del-Teixier, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 2459 (1975).
3. T. Kunitake, N. Higashi, M. Kunitake, and Y. Fukushima, *Macromolecules*, **22**, 485 (1989).
4. T. Ueno and T. Kunitake, *Chem. Lett.*, 1927 (1990).
5. B. J. Lee and T. Kunitake, *Langmuir*, **10**, 557 (1994).
6. W. E. Meyers and G. P. Royer, *J. Am. Chem. Soc.*, **99**, 6141 (1977).
7. D. Beyer, T. M. Bohanon, W. Knoll, and H. Ringsdorf, *Langmuir*, **12**, 2514 (1996).
8. I. Ichinose, T. Kawakami, and T. Kunitake, *Adv. Mater.*, **10**, 535 (1998).
9. I. Ichinose, H. Tagawa, S. Mizuki, Y. Lvov, and T. Kunitake, *Langmuir*, **14**, 187 (1998).
10. G. Sauerbrey, *Z. Phys.*, **155**, 206 (1959).
11. Y. Lvov, K. Ariga, I. Ichinose, and T. Kunitake, *J. Am. Chem. Soc.*, **117**, 6117 (1995).
12. Y. Ebara and Y. Okahata, *J. Am. Chem. Soc.*, **116**, 11209 (1994).
13. I. Ichinose, N. Kimizuka, T. Kunitake, *J. Phys. Chem.*, **99**, 3736 (1995).
14. D. Briggs and M. P. Seah, "Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy," Wiley, New York, 1983.
15. A cast film was prepared from a 2:1 mixture of n-propylamine and glutaraldehyde. The N_{1s} region XPS spectrum gave a large peak at 398.2 eV, that was attributed to Schiff base nitrogen.
16. G. Decher and J. D. Hong, *Ber. Bunsenges. Phys. Chem.*, **95**, 1430 (1991).
17. A. Shibata, H. Kayama, and I. Ueda, *Biochim. Biophys. Acta.*, **1119**, 211 (1992).
18. D. Yoo, S. Shiratori, and M. F. Rubner, *Macromolecules*, **31**, 4309 (1998).
19. H. Shiraishi, I. Ichinose, and T. Kunitake, *Polymer Prepr. Jpn.*, **46**, 473 (1997).
20. R. A. Hendel, E. Nomura, V. Janout, and S. L. Regen, *J. Am. Chem. Soc.*, **119**, 6909 (1997).