Microstructure of Charged Mosaic Membranes Constructed by Phase Growth

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SYNOPSIS

A template pattern with alternating poly(4-vinylpyridine) (P4VP)/poly(vinyl alcohol) (PVA) lamellae was fabricated upon a cross-linked PVA film by casting of poly[4-vinyl-pyridine (4VP)-g-vinyl alcohol (VA)] graft copolymer. After a treatment involving the binding of a PVA film with the graft copolymer and also domain fixing of the PVA phases, a dilute solution of poly[acrylic acid (AA)-benzyl N,N-dimethyldithiocarbamate (DMTC)] copolymer/P4VP binary blend was cast on this template surface. The microstructure of binary blend was observed from scanning electron microscopy (SEM) by wet-etching of films after domain fixing of one component of the binary blend. The poly(AA-DMTC) copolymer/P4VP binary microdomains formed by phase growth were oriented perpendicularly to the film surface. We also fabricated these charged mosaic regions on a microporous poly(vinyl chloride) (PVC) membrane, and carried out the surface analysis by X-ray photoelectron microscopy (XPS). Finally, we examined the transport of KCl through the charged mosaic composite membranes. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In previous works,[1,2] we reported that the charged mosaic microdomains (strong acid/strong base) could be constructed on a microporous membrane as substrate by means of an epitaxial process of phase growth. The cylindrical microdomains of strong acids seemed to pass uninterrupted and yet perpendicularly through the membrane. However, the micropores near the upper side of poly(vinyl chloride) (PVC) membrane were difficult to coat completely with the first casting of graft copolymer in the fabrication process of such charged mosaic composite membranes. Therefore, these composite membranes sometimes had problems forming the voids in the charged mosaic regions. As a result of dialytic separation of KCl and sucrose, the diffusion coefficient of sucrose was strongly dependent on the cross-link density of the charged regions. However, the diffusion rate of sucrose could be controlled with the thickness of the charged regions.

In this study, we devised a useful domain fixing to increase the cross-link density of the anion charged region. In order to make clear the microstructure of charged mosaic regions, a template pattern with alternating poly(4-vinylpyridine) (P4VP)/poly(vinyl alcohol) (PVA) lamellae was fabricated upon a cross-linked PVA film by casting of poly[4-vinylpyridine (4VP)-g-vinyl alcohol (VA)] graft copolymer. After a treatment involving the binding of a PVA film with the graft copolymer and domain fixing of the PVA phases, the solution of poly[acrylic acid (AA)-benzyl N,N-dimethyldithiocarbamate (DMTC)] copolymer/P4VP binary blend was cast on this template surface. The microstructure of the binary blend (charged mosaic regions) was observed from scanning electron microscopy (SEM) by wet-etching of films after domain fixing of one component of the binary blend. Subsequently we fabricated the charged mosaic regions on a microporous PVC membrane, and carried out the surface analysis by X-ray photoelectron microscopy (XPS).

EXPERIMENTAL

Polymer Synthesis and Characterization

The well-defined poly(4VP-g-VA) graft copolymers were prepared using a poly(vinyl acetate) (PVAc)

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macromonomer, free radical copolymerization of this macromonomer with 4VP monomer, and its alkaline hydrolysis. The details concerning the synthesis and purification of such graft copolymers have been given elsewhere.[1]

The P4VP [the viscosity-average molecular weight ($\bar{M}_v$; 2.98 × 10^4) was prepared by free radical polymerization and fractionated using a water–methanol system.[2]

The poly(AA-DMTC) copolymers were synthesized by the following method. Free radical copolymerization of AA (20 mL) with p-chloromethylstyrene (CMS; 4 mL) was carried out in tetrahydrofuran (THF)/water: 20/30 (mL/mL) initiated by 2,2'-azobisisobutyronitrile (AIBN; 300 mg) at 60°C for 24 h in the addition of 2-aminoethanethiol hydrochloride (400 mg) in a sealed glass ampoule under high vacuum. After polymerization, the solution was adjusted to pH 3 adding HCl. This solution was poured into an excess of acetone. Poly(AA-CMS) copolymer was purified three times from a water–acetone system. It was well known that the reaction of CMS with dimethyldithiocarbamic acid quantitatively formed a dithiocarbamate group.[3] This copolymer (6 g) was reacted with dimethyldithiocarbamic acid sodium salt (2 g) in DMF/water: 16/19 (mL/mL) at room temperature for 8 h using a brown flask. The DMTC content was determined by ^{1}H NMR (60 MHz Hitachi high-resolution NMR R-24B) in D$_2$O/DMSO-d_6 mixture at δ = 3.5 (methyl proton) and 1.4–3.0 ppm (methylene protons of backbone). The $\bar{M}_v$ of poly(AA-DMTC) copolymer, ACS7 (2.45 × 10^4; DMTC 2.6 mol %), was obtained by using the following equation for PAA[4]: intrinsic viscosity $[\eta] = 42.2 \times 10^{-3} \bar{M}_v^{0.64}$ (mL/g) in 2 M NaOH aqueous solution at 25°C.

Crosslinking of Anion and Cation Charged Regions

The moisture content of each charged region was inferred from the equilibrium volume swelling degree (Q) of cross-linked homopolymer films of quaternized P4VP, VP1, and poly(AA-DMTC) copolymer, ACS7, respectively. The details concerning the cross-linking method of P4VP films have been given elsewhere.[1]

It was found that the ACS7 film insufficiently cross-linked by UV irradiation; that is, when the irradiated film was immersed in water, more than 60 wt % dissolved out and a highly swollen gel remained. We added photosensitizer and cross-linking agent in this film to increase the cross-link density. The ACS7 film, 300-μm thick, was cast from water/

1-propanol, 1/1 (v/v) with a small amount of 4,4'-bis(dimethylamino)benzophenone, varying the feed mole ratio of diethylene glycol dimethacrylate (DGDM) or N,N'-methylene bisacrylamide (MBA) to [DGDM]. The UV beam was irradiated to films for 2 h in a nitrogen atmosphere (250 W high-pressure mercury lamp, Ushio Denki UI 250D). The equilibrium length swelling degree (L) of film was expressed by $(L_w - L_d)/L_d$ (%), where L_d and L_w are the lengths of the sample in the dry and in the swollen state in water.

Fabrication of Charged Mosaic Regions

The template pattern was constructed on the cross-linked PVA film as follows. A 0.8 wt % water/1-propanol, 1/1 (v/v) solution (containing 1 v % of 50 wt % glutaraldehyde aqueous solution of G22H graft copolymer was cast on the surface of a cross-linked PVA film. This cross-linked PVA film was prepared by the cross-link treatment with glutaraldehyde-HCl of PVA films (PVA: Kanto Chemical Co. ING.; degree of polymerization, 2000; degree of saponification, 78–82 mol %). After evaporating the solvent, binding of the PVA film with G22H and domain fixing of PVA phases were carried out at the same time in HCl vapour for 2 h. After neutralization of this template film with ammonia vapour and subsequent washing with water, a 1.0 wt % water/1-propanol, 1/1 (v/v) mixture [containing 5 v % of triethylamine (Et$_3$N), DGDM [(DGDM)/ (DMTC) = 2 mol/mol], 4,4'-bis(dimethylamino)-benzophenone] of VP1/ACS7, 1/1 (wt/wt) binary blend was cast on the surface of the template pattern under the saturated vapour of the casting solvent. The microstructure of the template pattern was not disturbed during the casting process due to domain fixing of the continuous PVA phases. A small amount of Et$_3$N was added to prevent the formation of a polyion complex between polymer blends having opposite charges. After drying this composite film in vacuo, poly(AA-DMTC) domains were cross-linked with the irradiation of UV beam for 2 h. Next, the P4VP domains were both cross-linked and quaternized with 1,4-diiodobutane (DIB) vapour for 1 h at 40°C under reduced pressure. The film was embedded in an epoxy resin and cut perpendicular to the film interface into ultra-thin sections (about 70–100 nm thick) using an ultra microtome (Reichert–Nissei Co., Ultracut N). These specimens were exposed with the vapour of osmium tetraoxide (OsO$_4$). Morphological results were obtained with transmission electron microscopy (TEM; Hitachi H-500 TEM) at 75 kV.

On the other hand, the SEM observation is one of the best characterizations to judge the orientation of microdomain structures. Therefore, P4VP domains of this composite film were cross-linked only with DIB vapour. Subsequently, the film was broken in liquid nitrogen and poly(AA-DMTC) domains of upper layer were wet-etched by soaking in water. The morphological results were obtained on a JEOL-T220 SEM.

Fabrication of Charged Mosaic Composite Membranes

We used microporous PVC (Mitsubishi Yuka Co., Ltd., average pore size $\bar{D} = 0.4$ and 100 μm thick) with a modified surface as a support membrane. The PVC membrane surface was modified via the following chemical reactions: hydrolysis of the microporous PVC membrane, oxidation of the double bond formed, and hydrolysis of the epoxy groups formed. As a result, the content of hydroxyl groups for this modified membrane was ca. 20 mol % at the membrane surface from the XPS analysis.

We constructed the charged mosaic regions on this modified PVC membrane by means of the phase growth and domain fixings mentioned in the former section. In brief, a 0.6 wt % of PVA aqueous solution (containing 1 v % of 50 wt % glutaraldehyde aqueous solution) was cast on the surface of the modified PVC membrane (0.25 mL/25 cm^2) to stop up the microporous holes. After evaporating the solvent, binding of the microporous membrane with PVA and cross-linking of PVA film were carried out at the same time in HCl vapour for 2 h. After washing this membrane with water, a 1.0 wt % water/1-propanol solution (containing glutaraldehyde) of G22H graft copolymer was cast on the PVC surface covered with the cross-linked PVA. We also carried out the formation of the template pattern by casting directly on the modified PVC membrane. Not only the binding of the support membrane but also the domain fixing of PVA phases were performed with HCl treatment. After neutralization of this template film with ammonia vapour and subsequent washing with water, a 1.5 wt % water/1-propanol, 1/1 (v/v) mixture [containing 5 v % of Et$_3$N, (DGDM)/(DMTC) = 2.0 mol/mol, 4,4'-bis(dimethylamino)-benzophenone] of VP1/ACS7, 1/1 (wt/wt) binary blend was cast on the surface of the template pattern (0.25 mL/25 cm^2) under the saturated vapour of the casting solvent. The poly(AA-DMTC) domains were cross-linked with the irradiation of UV beam. The P4VP domains were both cross-linked and quaternized with DIB vapour. After neutralization of this membrane with ammonia vapour and washing of this membrane with ammonia vapour and wash-

ing with water, the residual P4VP domains were quaternized with methyl iodide vapour for 2 h at room temperature.

The film surface at stepwise processes concerning the preparation of the charged mosaic composite membranes were analyzed by XPS measurements. The sample film was dried under vacuum for 2 days at room temperature. The film (7 × 20 mm^2) was coated on a copper sample holder with double-sided adhesive tape and copper wire, and was dried in an argon atmosphere at ambient temperature.

Spectra were recorded on a Spectoros XSAM 800 apparatus using Al Kα exciting radiation. Typical operating conditions were: X-ray gun, 14 kV and 20 mA; pressure in the analysis chamber, 5×10^{-8} Torr. A liquid-nitrogen-cooled sample holder was used throughout the experiments. A value of 285.0 eV was used for the C1s core level of the hydrocarbon. Overlapping peaks were resolved into their individual components by use of a DEC PDP11/03L curve resolver. These studies have shown that the line shapes are approximately Gaussian for individual components.

The sample was rotated relative to the fixed energy analyser by angle σ, which is the angle between the normal to the sample and the slits in the analyser. Spectra were recorded at polar angle $\sigma = 68°$ with respect to the sample surface to achieve effective sample depth of ≈ 2 nm, where the mean free length (λ) is dependent on the $\frac{1}{2}$ power of kinetic energy. The average values for λ as a function of kinetic energy for the polymer systems are ≈ 14, ≈ 22, ≈ 23, and ≈ 29 Å for kinetic energies of ≈ 969, ≈ 1170, ≈ 1202, and ≈ 1403 eV, respectively.[5]

The film surfaces at stepwise processes concerning the preparation of the charged mosaic composite membranes were observed by the SEM images. On the other hand, the morphology of the template pattern was observed as follows. An ultra-thin film specimen of poly(4VP-g-VA) graft copolymer G22H was prepared for electron microscopy by placing one drop of a 1 wt % water/1-propanol, 1/1 (v/v) solution on a microscopy grid coated with cross-linked PVA film. The surface morphology of this specimen is considered to correspond to that of the template pattern on the microporous membrane. This specimen was exposed to OsO$_4$ vapour. The morphological results were obtained on the TEM.

Transport of KCl Through Charged Mosaic Composite Membranes

The transport of KCl aqueous solution through the charged mosaic composite membranes was investi-

gated by a dialysis method. The details concerning the measurement method and apparatus of such dialysis have been given elsewhere.[2]

RESULTS AND DISCUSSION

Photo-cross-linking of the poly(AA-DMTC) anionic domains was carried out under the irradiation of UV beam. Figure 1 shows the relationship between the length swelling degree L and feed mole ratio of cross-linking agents to DMTC groups, varying the cross-linking agents (DGDM and MBA). The values of the volume swelling degree Q were calculated from the observed L values with the assumption of isotropic swelling of gels. In both cases of DGDM and MBA as cross-linking agents, the observed L shows the minimum value at near the (cross-linking agent)/(DMTC) = 2.0 (mol/mol). It is also found that the DGDM works effectively on the network formation compared with MBA. In Figure 1, the closed signs indicate the swelling degree in 0.1 M NaCl aqueous solution. In an electrolyte solution, the L values decrease steeply due to poor degree of the ion-dissociation of carboxyl groups. The Q value is estimated to be ca. 250% in 0.1 M NaCl under the condition of (DGDM)/(DMTC) = 2.0 (mol/mol).

The result of cross-linking for P4VP cationic domains was quoted from a previous work.[2] Figure 2 shows the relationship between the equilibrium swelling degree Q and cross-link density of quaternized P4VP films. The cross-linked film (85-μm
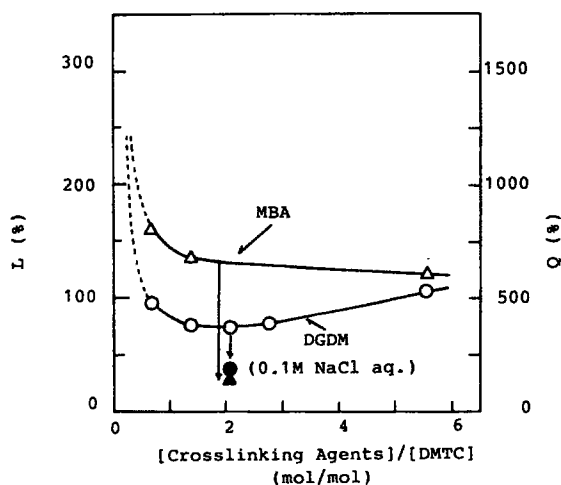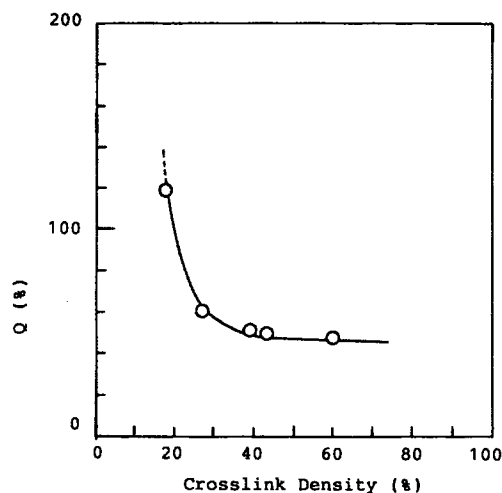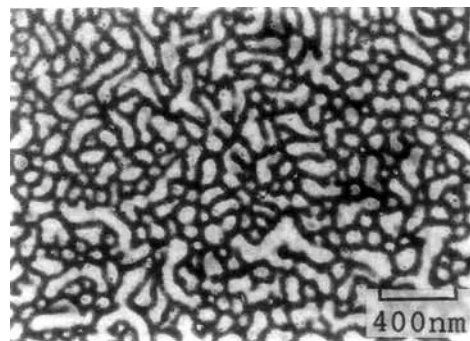

Figure 2   Relationship between equilibrium swelling degree (Q) and cross-link density of 4VP units.

thick) was obtained from quaternization of P4VP film with DIB vapour at 60°C, varying the reaction time. The swelling degree of the quaternized P4VP films was almost constant (Q = 50%), regardless of the increment of cross-link density of 4VP units (more than 40%). So, anionic domains were somewhat loose compared to cationic domains in our charged mosaic regions.

Figure 3 shows a TEM micrograph of graft copolymer G22H ($\bar{M}_n$ = 1.00 × 10^5; P4VP, 61 mol %) cast on the cross-linked PVA support film. The dark portions are P4VP domains selectively stained with OsO$_4$. The surface of specimen G22H shows P4VP/PVA lamellar-like microdomains. The average domain distances of P4VP and PVA lamellae ($\bar{D}_{P4VP}$ and $\bar{D}_{PVA}$) were 50 and 62 nm, respectively. The surface morphology of this specimen corresponded

Figure 1   Relationship between length swelling degree (L) and feed mole ratio of cross-linking agents to DMTC groups, varying cross-linking agents (DGDM and MBA).

G22H Graft Copolymer

Figure 3   TEM micrograph of G22H graft copolymer specimen cast from water/1-propanol mixture.

to that of the template pattern on the cross-linked PVA film.

Figure 4 shows a TEM micrograph of poly(AA-DMTC) copolymer ($\bar{M}_v$ = 2.45 × 10^4; DMTC, 2.6 mol %)/P4VP ($\bar{M}_v$ = 2.98 × 10^4) binary blend, 1/1 (wt/wt) specimen cast from water/1-propanol mixture in the presence of Et$_3$N. The dark portions are P4VP domains selectively stained with OsO$_4$. The morphology appears to exhibit macrophase separation. Both domain sizes were on the order of 10^3 nm magnitude. The solution of this binary blend forms a precipitate in the absence of Et$_3$N. Direct casting of binary polymer blends composed of anionic and cationic polyelectrolytes from solution is not feasible because interactions between the oppositely charged segments lead to poly–ion complex formation; consequently, phase separation does not occur.

The charged mosaic regions were prepared by casting of poly(AA-DMTC)/P4VP binary blend on the template pattern using the cross-linked PVA film as a support. In order to obtain information concerning the microdomain orientation of the charged regions, the poly(AA-DMTC) domains of the upper layer were wet-etched with water after domain fixing of P4VP. Figure 5(a) shows the SEM micrograph of the charged regions in the surface of the upper layer. It is found from this image that quaternized P4VP domains are oriented perpendicularly to the film surface with the shape of lamellar structure. Figure 5(b) shows the cross-sectional view of the wet-etched film. The thickness of the charged regions composed of G22H graft copolymer and binary blend films is ca. 0.7 μm as judged from this micrograph. The lamellar domains of P4VP (average

(a) Surface of Charged Mosaic Regions

(b) Vertical Sectional View

Figure 5   SEM micrographs of charged mosaic regions constructed on cross-linked PVA film: (a) surface; (b) vertical sectional view.

domain distance = 75 nm) and poly(AA-DMTC) (85 nm) seem to pass perpendicularly through the film. The sizes of charged regions became somewhat large compared to those of the template pattern. It can be seen from Figure 5(a) and (b) that poly(AA-DMTC)/P4VP binary blend forms a microphase-separated structure by phase growth. P4VP and poly(AA-DMTC) segments in binary blend may be absorbed to P4VP and PVA phases on the template G22H, respectively. These binary components seem to orient perpendicularly to the film surface by repeating of such absorption (phase growth).

Figure 6(a) shows TEM micrograph of a vertical section of the charged mosaic film. The interface between the template and charged regions can be sighted from the difference of domain sizes. Micrograph (b) indicates the enlargement of template part on micrograph (a). The domain sizes of charged regions (binary blend) are almost the same as those observed from the SEM image. Both domains of charged regions seem to pass perpendicularly but interrupted through the film. Ultra-thin sections were floated upon water after cutting using a microtome. In this preparation step, the specimen led to swelling. So, the microdomain structures in the charged regions may be disturbed during the dry process. In order to make a clearer TEM image, a highly skilled technique will be required in the preparation of TEM samples.
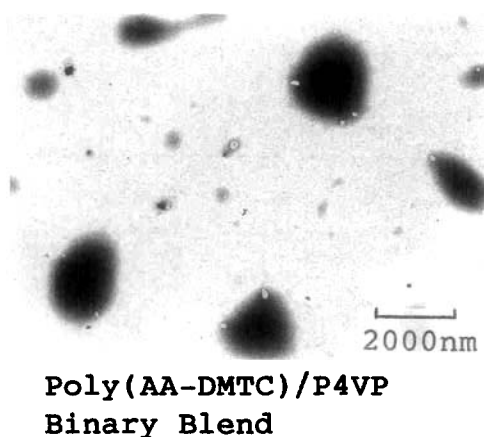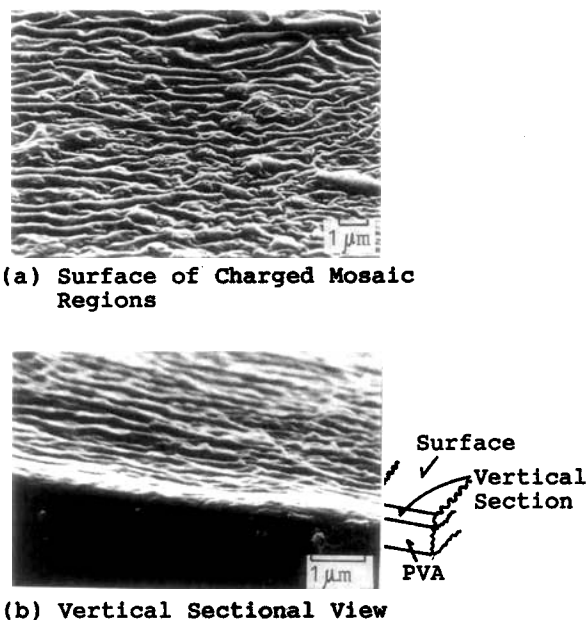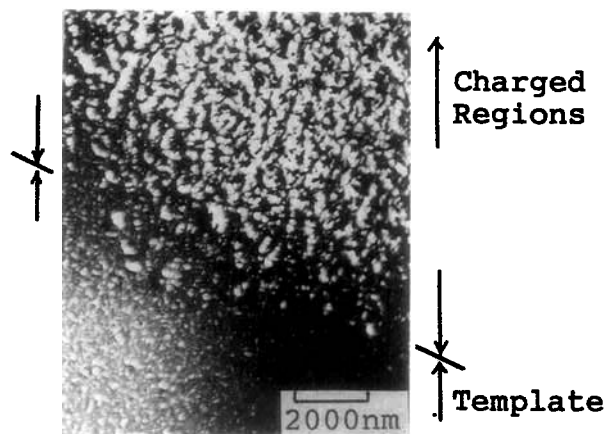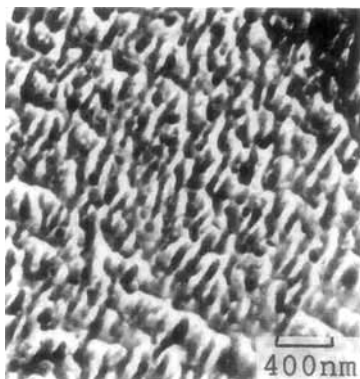

Poly(AA-DMTC)/P4VP Binary Blend

Figure 4   TEM micrograph of poly(AA-DMTC)/P4VP binary blend specimen cast from water/1-propanol.

(a) Vertical Section

(b) Enlargement of
Template Part

Figure 6   TEM micrographs of charged mosaic regions.
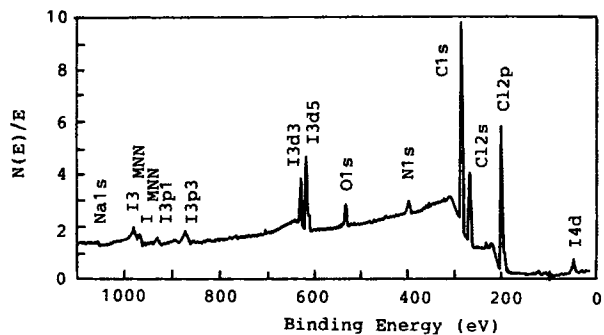

Figure 7   Typical XPS survey scan of composite film M5.

Subsequently we constructed the charged mosaic regions on the modified PVC membrane. The film surface at each stepwise process was analyzed by XPS measurements. Figure 7 shows a typical XPS survey scan at a sampling depth of $\approx$ 2 nm of the composite film M5. Element composition of composite films are listed in Table I. Figure 8 shows SEM micrographs of vertical sectional views for the composite films, where micrographs (a), (b), and (c) indicate the vertical sectional views of M2, M4, and M5, respectively. It was found from the XPS data of M1 and M2 that the modified PVC membrane (PVC-M) has 20 mol % of hydroxyl groups at the membrane surface. The surface of the template pattern prepared from casting of G22H directly on PVC-M (M3) has 8% of chlorine. It is suggested that the microporous holes on PVC-M were not stopped up with the casting film of G22H graft copolymer. The PVC-M membrane is composed of hydrophilic surface and hydrophobic bulk. A water/1-propanol mixture was employed as the casting

Table I   Element Composition of Composite Films at Each Stepwise Process

| Code	Component of Membrane[a] Template/Support	Element (atm %)[b] C	O	Cl	N	I
M1	/PVC	68 (67)	1	30 (33)		
M2	/PVC-M	67	7	24	1	
M3	G22H/PVC-M	76 (78)	11 (6)	8	5 (9)	1
M4	/PVC-M + PVA	66 (67)	28 (33)	6		
M5	G22H/PVC-M + PVA	77 (78)	12 (6)	2	8 (9)	1

[a] PVC-M; the modified PVC membrane.
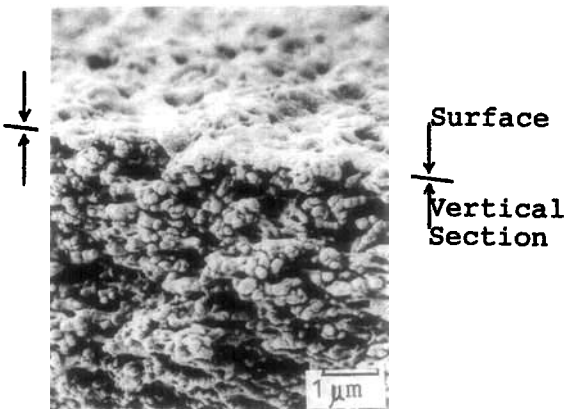[b] The values in parentheses indicate the calculated atomic percentages.

solvent of the template (G22H). This casting solution seems to have permeated into the area of the bulk of the PVC-M membrane. Then, we tried another approach in which the PVC-M surface was
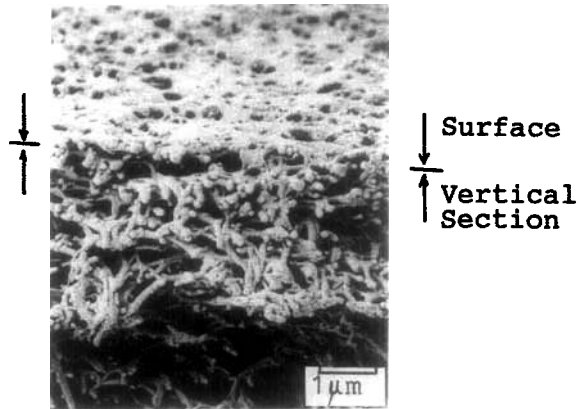
(a) M2
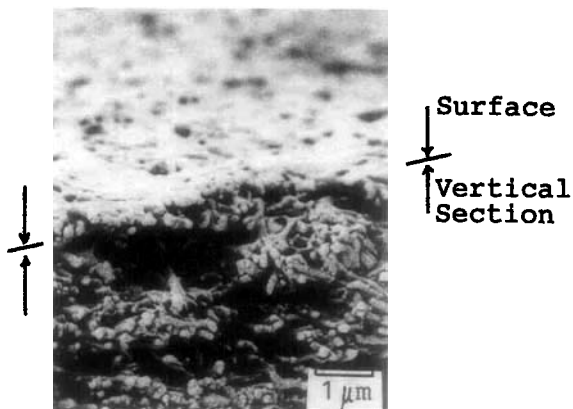
(b) M4

(c) M5

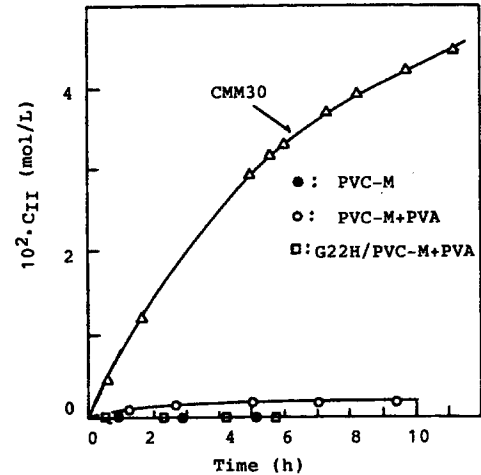**Figure 8** SEM micrographs of vertical sectional views of composite films: (a) M2; (b) M4; (c) M5.

Figure 9 Dialysis separation of KCl through charged mosaic composite membrane CMM30: the initial concentration (C_I) in the dialysand was 0.1 M KCl aqueous solution. The dialysate side was filled with the same volume of water. Both compartments were immersed in a water bath thermostated at 25°C. (●) PVC-M; (□) G22H/PVC-M + PVA; (○) PVC-M + PVA.

coated with the cross-linked PVA (M4 film). It was found from the XPS data and Figure 8(b) that the microporous holes on PVC-M were coated to a considerable extent. The M5 film indicates the template pattern from casting of G22H on the above pre-membrane. From the results of XPS data and Figure 8(c), the surface of the PVC-M was coated with G22H graft copolymer for the most part.

Figure 9 shows the results of dialysis separation of KCl through the charged mosaic composite membrane CMM30. The initial concentration (C_I) in the dialysand was 0.1 M KCl aqueous solution. The dialysate side was filled with the same volume of water. Both compartments were immersed in a water bath thermostated at 25°C. The concentration (C_{II}) of KCl in the dialysate is plotted against the dialysis time. Neither KCl is transported to the dialysate side (compartment II) through both PVC-M and the template pattern membrane prepared from casting of G22H on the cross-linked PVA surface. A small amount of KCl transport is observed in the PVC-M membrane coated with the cross-linked PVA. In the charged mosaic composite membrane CMM30 [charged region; poly(AA-DMTC)/quaternized P4VP binary blend], the volume changes in each cell indicated a flow from compartment I to compartment II, implying a negative osmosis characteristic of the charged mosaic membrane. Moreover, the KCl concentration in the dialysate in-

creases rapidly with time and reaches the saturated concentration after 12 h. It was necessary to measure the selective transport of KCl/saccharoid through the charged mosaic composite membrane in order to make clear the cross-link density-dependence of charged mosaic regions.

CONCLUSION

Charged mosaic regions were constructed on the microporous modified PVC membrane as a support. Cationic quaternized P4VP and anionic poly(AA-DMTC) microdomains were oriented perpendicularly to the support surface by phase growth. As a result of domain fixings, the water contents of cationic and anionic domains were inferred to be 50 and 250%, respectively. This charged mosaic composite membrane showed the KCl transport from a dialysis measurement. It will be necessary to accumulate the data concerning the selective transport, for example, the KCl/saccharoid system. The in-formation obtained from these investigations will be reported in the near future.

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