Polyether-Segmented Nylon Hemodialysis Membrane. VI. Effect of Polyether Segment on Morphology and Surface Structure of Membrane

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ABSTRACT: Amorphous nylon, poly(iminoisophthaloyliminomethylene-1,3-cyclohexylenemethylene) (NyBI) and poly(ethylene oxide) (PEO)-segmented NyBI (PEO–NyBI) membranes were prepared by a phase-inversion method using water/dimethyl sulfoxide (DMSO) mixtures as coagulants. The influence of the PEO segment and coagulant compositions on the morphology of the membranes was investigated. The cloud-point curves in the polymer/DMSO/water ternary system showed that PEO–NyBI and NyBI had the same coagulation processes, that is, instantaneous liquid–liquid phase separation occurred, resulting in a fingerlike structure in the cross section of the membranes. The membrane morphologies observed under a scanning electron microscope (SEM) agreed with the prediction. The PEO segment had little or no effect on the membrane morphologies which were prepared in the coagulants with a low DMSO concentration, and it promoted the change of the phase-separation style from the instantaneous to the delayed one in the case of the DMSO-rich coagulant. The PEO segment, however, significantly influenced the ultrafiltration rate. Additionally, the relationship between the surface composition of the PEO–NyBI membrane and the coagulation condition was also investigated by use of electron spectroscopy for chemical analysis (ESCA) and static secondary ion mass spectrometry (SSIMS). A small enrichment of the PEO segment at the top surface of the membranes was observed with the increase of the DMSO concentration in the coagulant. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1645–1659, 1998

Key words: polyether-segmented nylon; membrane; phase-inversion method; clouding point; morphology; surface structure; SEM; ESCA; SIMS

INTRODUCTION

We have reported the effect of the coagulation conditions of the phase-inversion method on the morphology of the polyether-segmented nylon (PE–Ny) membranes, which are semicrystalline polymers, and the permeability characteristics.[1–4] The typical semicrystalline PE–Ny, polyether-segmented nylon610 (PE–Ny610), brings about a solid–liquid phase separation during the membrane-formation process and produces a skin layer composed of rigid crystalline spherulites due to their high crystallinity. This skin layer is the cause of the low permeability characteristics as

those of a hemodialysis membrane.[1,2] To avoid bringing about the solid–liquid phase separation or forming the spherulite surface, a new poly-ether-segmented nylon with a low crystallinity, poly(ethylene oxide)-segmented nylon 69/M10 (PEO–Ny69/M10) was designed. This nylon segment is a random copolyamide, and its abbreviations are 6 = hexamethylenediamine, M = *m*-xylenediamine, 9 = azelaic acid, and 10 = sebacic acid. PEO–Ny69/M10 had a lower crystallinity than that of PEO–Ny610 and dissolved in hot dimethyl sulfoxide (DMSO).[3] PEO–Ny69/M10 gave rise to a solid–liquid phase separation predominantly when formic acid was used as a solvent for the polymer. When hot DMSO was used as the solvent, PEO–Ny69/M10 gave rise to the liquid–liquid phase separation and fingerlike or spongelike structures in the cross sections of the membranes without the skin-layer structure at the top surface were obtained. The PEO–Ny69/M10 membrane obtained by the liquid–liquid phase separation exhibited high permeability characteristics for urea and vitamin B_{12}.[4] However, since the polymer solution was not so stable, the coagulation condition was limited, because the polymer had rather high crystallinity and the decrease of the solution temperature caused the gelation of the polymer solution. Moreover, the PEO–Ny69/M10 membrane did not show good compatibility with the leukocyte in the *ex vivo* extracorporeal circulation in a rabbit model, and, thus, it was concluded that PEO–Ny69/M10 was not suitable for a hemodialysis membrane material.[5]

To obtain a high-performance dialysis membrane from PE–Ny, the membrane-formation process governed by liquid–liquid phase separation is preferable. Therefore, we reached the conclusion that an amorphous polymer was suitable for this purpose. It is widely accepted that the bulky and asymmetric monomers give an amorphous polymer. On the basis of this fact, we designed a new PEO- or poly(tetramethylene oxide)-segmented amorphous nylon whose nylon segment is composed of asymmetric bulky dimaine, bis-1,3-aminomethylcyclohexane, and isophthalic acid as the hemodialysis membrane material. It has been reported that the new polyether-segmented nylon whose polyether was poly(tetramethylene oxide) was synthesized and the hollow-fiber membrane prepared from it exhibited high permeability characteristics and good blood compatibilities.[6] In this article, for the PEO-segmented amorphous nylon, the effect of the PEO segment on the mem-
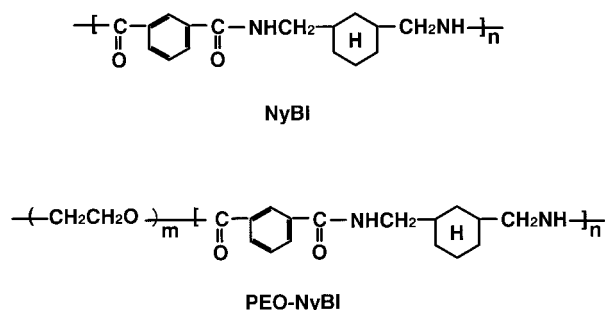

Figure 1 Chemical structures of NyBI and PEO–NyBI.

brane morphology, permeation rate of water, and the effect of the coagulation condition on the surface structures are discussed.

EXPERIMENTAL

Materials

The new PEO-segmented amorphous nylon and the corresponding homo-nylon, poly(iminoisophthaloyliminomethylene-1,3-cyclohexylenemethylene), are abbreviated PEO–NyBI and NyBI, respectively, and their chemical structures are shown in Figure 1. The abbreviated B stands for bis-1,3-aminomethylcyclohexane which contains *cis* and *trans* forms, and I is for isophthalic acid. The polymers were synthesized according to the method described in the previous article.[1,6] The molecular weight of PEO [α,ω-bis(aminopropyl)–PEO] was 1000, and the PEO content in the PE–Ny was 10 wt %. Bis-1,3-aminomethylcyclohexane, isophthalic acid, and PEO were purchased from Mitsubishi Gas Chemical Co. (Tokyo, Japan), A. G. International Chemical Co., Inc. (Tokyo, Japan), and Kawaken Fine Chemicals Co., Ltd. (Tokyo, Japan), respectively. These materials were used without further purification.

Cloud Point

The cloud points of the DMSO solutions of PEO–NyBI and NyBI were determined by a titration method. To about 8 g of a polymer solution that was weighed accurately, water was added slowly at 25°C with stirring until the solution became milky white. The weight of water added was calculated from the total weight of the demixing solution, and then the composition at the cloud point was obtained.

Preparation of Membranes

PEO–NyBI and NyBI were dissolved in DMSO at room temperature to make a 19 wt % solution. Membranes were prepared as follows: The polymer solution was cast onto a glass plate, then immersed rapidly into a coagulant bath at 25°C. The coagulants used was the mixture of water/DMSO at various composition ratios. After complete precipitation (after 60 min), the membrane was taken out of the coagulant bath and immersed in ultrapure water to remove the solvent and maintain the membrane structure.

SEM Observation

The wet membranes were immersed into liquid nitrogen. The frozen membranes were fractured in liquid nitrogen and then dried *in vacuo*. After spattering platinum onto the membrane, the cross section and the surface were observed under a scanning electron microscope (SEM) equipped with a field emission gun at an accelerated voltage of 5 kV (JSM-840F, JEOL Ltd., Japan).

Measurement of UFR

As had been reported,[1] the membrane performances were investigated from the viewpoint of the ultrafiltration rate (UFR) of pure water. A brief measurement method is described below. UFR was measured by using an ultrafiltration cell (Advantec UHP-43) with an effective membrane area of 11.5 cm^2 at a pressure of 250 mmHg and was calculated from eq. (1):

$$UFR = V/SP \ (\text{mL m}^{-2}\text{ h}^{-1}\text{ mmHg}^{-1}) \quad (1)$$

where V is water flux (mL/h), S is the membrane area (m^2), and P is the operation pressure (mmHg).

Surface Analysis

The outermost surface of the PEO–NyBI membranes were analyzed by electron spectroscopy for chemical analysis (ESCA) and static secondary ion mass spectrometry (SSIMS). The surface analysis by ESCA (PHI 5600ci, Perkin–Elmer, USA) was carried out under the condition described below. The X-ray source was monochromatized Al Kα (1486.7 eV). The X-ray gun was operated at 14 kV and the anode power was 20 W. The base pressure was maintained at less than

10^{-9} Torr. Pass energies of 187.5 and 29.25 eV were chosen for survey spectrum acquisition (0–1000 eV) and high-resolution spectrum acquisition (O1s, N1s, and C1s), respectively. The survey scans were carried out in order to survey the element species existing on the surface. The photoelectron take-off angle (TOA) was 40° for all the measurements, where TOA was defined as the angle between the sample plane and the axis of the analyzer. This angle corresponds to 70 Å of the sampling depth. A low-energy electron flood gun (emission current: 0–20 mA; electron energy: 5–20 eV) was used in order to minimize sample charging. Quantification of the ESCA signals was performed using the provided software, PHI 5600ci. All the binding energies were referenced by setting the CH$_x$ peak maximum in the resolved C1s spectra to 285.0 eV.

The surface analysis by SSIMS was as follows: The apparatus was the same one as for ESCA, PHI 5600ci, equipped with a quadruple mass analyzer. The Xe$^+$ ion of 3 keV was used as a primary ion and was rastered over a 3×1.5-mm^2 area with an average current density of 1 nA/cm^2. Charge neutralization was achieved with a low-energy flood gun. The sampling depth was about 10 Å.

RESULTS AND DISCUSSION

Properties of PEO–NyBI

As shown in Figure 1, the nylon (NyBI) segment was prepared by polycondensation of a bulky and nonlinear diamine, bis-1,3-(aminomethyl)cyclohexane, with isophthalic acid. The diamine contains *cis* and *trans* forms as described in the Experimental section. These facts anticipate that PEO–NyBI is an amorphous polymer. The thermal analysis by a differential scanning calorimetry for PEO–NyBI reveals a glass transition point at 159°C, and there is no endothermic peak derived from the melting point. Moreover, PEO–NyBI dissolves easily in DMSO at room temperature. These results indicate that PEO–NyBI is an amorphous multiblock copolymer. Therefore, the DMSO solution of PEO–NyBI brings about the liquid–liquid demixing within a wide range of coagulation conditions when the membrane is prepared by the phase-inversion method.

PEO–NyBI is composed of two different segments in its polymer chain as mentioned above, and they have different solubilities in water and in DMSO. The solubility parameters of each seg-

Table I Solubility Parameter of Polymers and Solvents

Polymers and Solvents	Solubility Parameter $(\text{MPa})^{1/2}$
PEO	20.2 ± 2[a]
NyBI	22.9[b]
DMSO	29.7[a]
Water	47.9[a]

[a] [7].
[b] Calculated from group contributions to cohesive energy density based on van Krevelen's values (*Polymer Handbook* [7]) and the density of NyBI was supposed to be 1.05.

ment and the solvents are shown in Table I. This table indicates that NyBI has a better affinity to DMSO than PEO has. Indeed, NyBI dissolves in DMSO easily at room temperature, but the solubility of PEO in DMSO is low at room temperature. On the other hand, water is a nonsolvent for NyBI and a good solvent for PEO. The solubility of PEO in water does not coincide with that predicted from its solubility parameter. This behavior of PEO is known as amphiphilicity. These facts anticipate that the membrane morphologies and permeation characteristics of PEO–NyBI membranes are more strongly influenced by the coagulant composition than are those of a homo-NyBI membrane.

Solution Properties of PEO–NyBI

The cloud points of NyBI and PEO–NyBI solutions were measured in the polymer/DMSO/water ternary system, and their ternary phase diagram is shown in Figure 2. The cloud points of both polymers are caused by the liquid–liquid phase separation, which was confirmed by the fact that the phase-separated solutions produced two transparent clear solutions after aging for several hours. Figure 2 indicates that both cloud-point curves are close to the polymer–solvent axis and their curves overlap. It is generally well known that the binodal curve is nearly equal to the cloud-point curves as long as no compositions near the critical point are considered.[8,9] Moreover, it is said that the existence of a binodal curve closer to the polymer–solvent axis indicates the occurrence of the instantaneous liquid–liquid phase separation, resulting in a fingerlike structure membrane.[10,11] These facts suggest that the membranes of NyBI and PEO–NyBI have a fingerlike structure when water is adopted as a coagulant.

Furthermore, the result showing that the cloud-point curve of PEO–NyBI overlaps with that of NyBI anticipates that the PEO segment has a small or no effect on the coagulation process or the membrane morphology.

Membrane Morphology

The effects of the PEO segment on the morphologies of NyBI and PEO–NyBI membranes are described below together with the effect of the composition of the coagulant on the membrane morphology, where the coagulants were composed of water and DMSO at the ratios of 10 : 0, 8 : 2, 6 : 4, and 4 : 6 (wt/wt). The SEM pictures of the cross sections and top surfaces of NyBI and PEO–NyBI membranes are shown in Figures 3–5. The results obtained with the pure water coagulant [Fig. 3(A) and 4(A)] indicate that both membranes have the same structure with the typical fingerlike structure predicted from the cloud-point curve mentioned above. Moreover, it is confirmed from these structures that the instantaneous liquid–liquid phase separation occurs in the membrane-formation process. The pictures of the top surfaces [Fig. 5(A,C)] also show that both membranes have smooth surfaces and that the spherulites observed in the polyether-segmented nylon610 membranes[2] never exist at the surfaces. Consequently, these results showing that there is no difference between the NyBI and PEO–NyBI membrane morphologies in the cross sections and the top surfaces suggest that the PEO segment
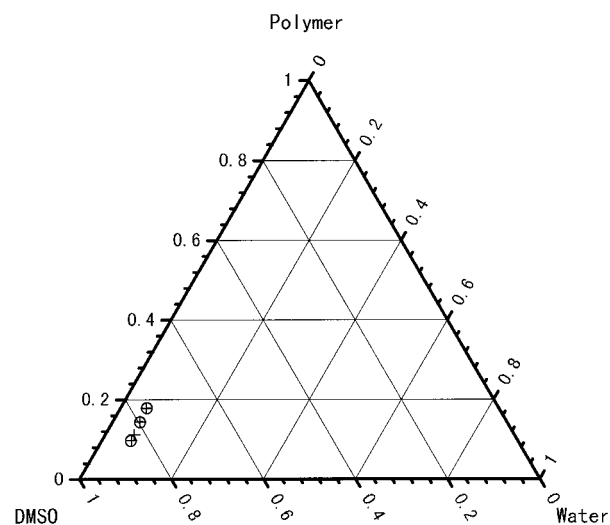

Figure 2 Polymer/DMSO/water ternary-phase diagram: (○) NyBI; (+) PEO–NyBI; 25°C.
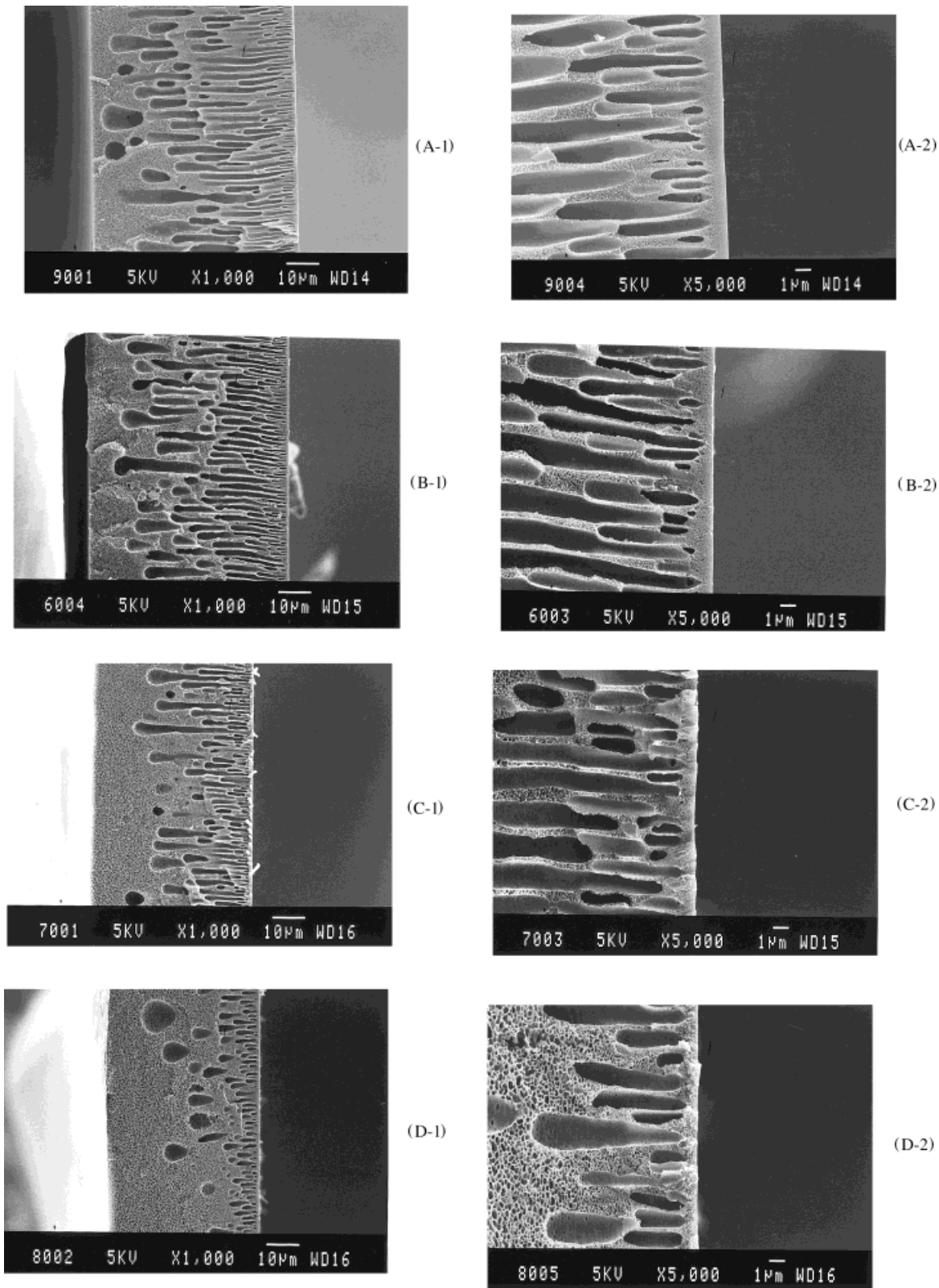
Figure 3   Cross section of NyBI membranes: (A) coagulant : water; (B) coagulant : water/DMSO = 8 : 2 wt/wt; (C) coagulant : water/DMSO = 6 : 4 wt/wt; (D) coagulant : water/DMSO = 4 : 6 wt/wt; (1) cross section; (2) cross section close to top surface at high magnification.
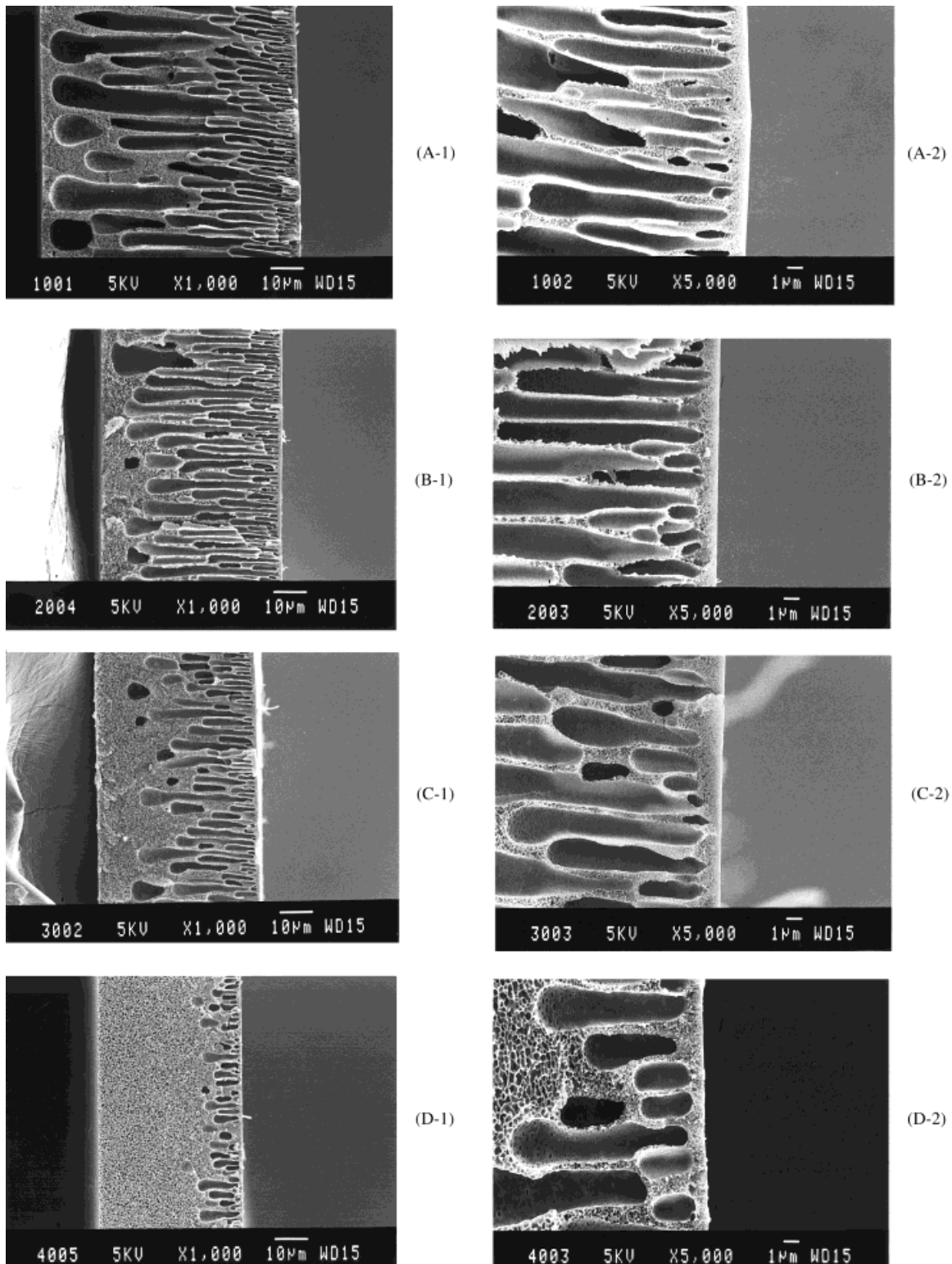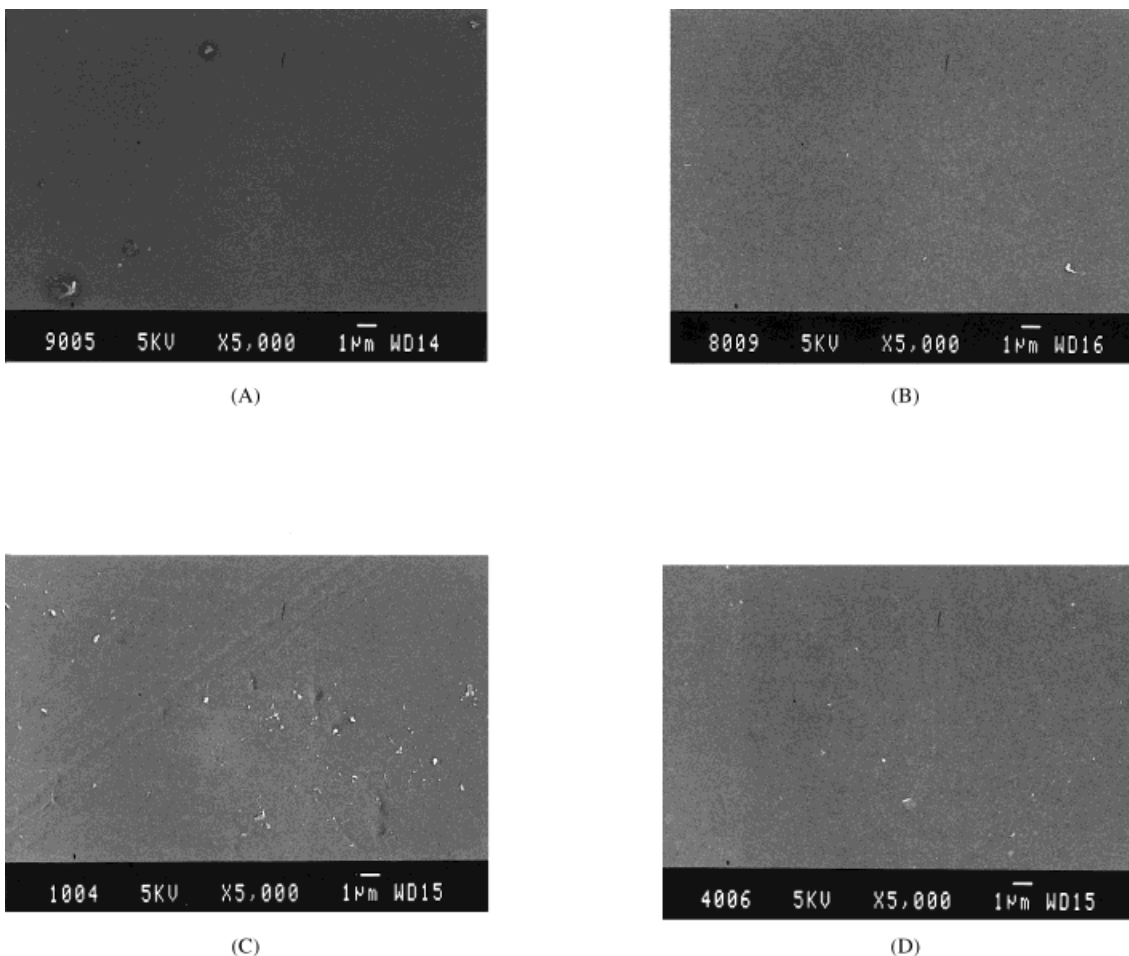
Figure 4 Cross section of PEO–NyBI membranes: (A) coagulant : water; (B) coagulant : water/DMSO = 8 : 2 wt/wt; (C) coagulant : water/DMSO = 6 : 4 wt/wt; (D) coagulant : water/DMSO = 4 : 6 wt/wt; (1) cross section; (2) cross section close to top surface at high magnification.

Figure 5 Top surface of NyBI and PEO–NyBI membranes: (A) NyBI, coagulant : water; (B) NyBI, coagulant : water/DMSO = 4 : 6 wt/wt; (C) PEO–NyBI, coagulant : water; (D) PEO–NyBI, coagulant : water/DMSO = 4 : 6 wt/wt.

has little or no influence on the phase-inversion process when water is used as the coagulant.

Next, the effect of the composition in the coagulant is discussed. Smolders et al. reported [12,13] that the addition of the solvent to the coagulant caused the delayed phase separation, resulting in a spongelike structure. Their investigation is described as follows: In the cellulose acetate/dioxane/water ternary system, when water was used as the coagulant, instantaneous phase separation occurred, resulting in a fingerlike structure, but when dioxane was added to the coagulant, delayed phase separation took place and a membrane with a spongelike structure was obtained. Their results suggest that the addition of DMSO to the coagulant would also change the coagulation style from the instantaneous to the delayed phase separation in our case, because DMSO is a

good solvent for NyBI and the NyBI segment in PEO–NyBI.

The addition of DMSO to the coagulant was investigated in the range of the water/DMSO ratio from 10 : 0 to 4 : 6 wt/wt. When the coagulant composition ratio was 2 : 8 wt/wt, it was difficult to obtain a membrane because of a too slow coagulation. In the range of low DMSO concentration, up to 6 : 4 wt/wt, the pictures of the cross sections of the NyBI and PEO–NyBI membranes show the typical fingerlike structure and indicate that instantaneous liquid–liquid phase separation has occurred [Figs. 3(A–C) and 4(A–C)]. Careful observation exhibits the facts that are described below. When water is used as the coagulant, the macrovoids extend close to the bottom surface of the membrane, which is in contact with a glass plate in the membrane-preparing process (the left

side in the pictures). On the other hand, the spongelike structure region near the bottom surface expands and the macrovoids become smaller and shorter and exist near the top surface (the right side) with the increase in the DMSO concentration in the coagulant to 6 : 4 wt/wt as shown in Figures 3(C) and 4(C). These pictures of the cross sections in the range of a water/DMSO ratio from 10 : 0 to 6 : 4 wt/wt reveal that the NyBI and PEO–NyBI membranes have almost the same morphologies for each coagulation condition. Moreover, the thicknesses of the skin layers existing in the top surfaces of both membranes are nearly equal, about 0.5 μm [Figs. 3(A-2), 3(B-2), 3(C-2), 4(A-2), 4(B-2), and 4(C-2)] when the DMSO concentration in the coagulant is $\leq$ 40 wt %.

From these results, it is concluded that the PEO segment has little or no effect on the morphologies in the case of coagulants with low DMSO concentration. In the case of a DMSO-rich coagulant, water/DMSO = 4 : 6 wt/wt, the main structure in the cross section is a spongelike one as predicted, although the small fingerlike macrovoids remain near the top surface as shown in Figures 3(D-1) and 4(D-1). Moreover, Figures 3(D-2) and 4(D-2) indicate that the pore size in the spongelike structure becomes larger than that of the membranes prepared in the coagulant with $\leq$ 40 wt % of DMSO [Figs. 3(A–C) and 4(A–C)]. A careful comparison of Figure 3(D-1) with Figure 4(D-1) reveals that the spongelike region in the PEO–NyBI membrane is larger than that in the NyBI membrane and that the NyBI membrane has larger macrovoids than those of the PEO–NyBI membrane. These results suggest that the change of the phase-separation style from the instantaneous to the delayed one is promoted by the PEO segment, especially in the DMSO-rich coagulant, and a perfect transition of the phase-separation style will exist in a coagulant whose composition is about water/DMSO = 3/7 wt/wt. Moreover, the top skin layers of the NyBI and PEO–NyBI become thinner than those of the membranes prepared in DMSO-poor coagulants and the thickness is about 0.3 μm. The top-surface structures (Fig. 5) of these membranes are not affected by the coagulant compositions and have smooth surfaces like the membranes coagulated in water when observed at a magnification of 5000 [Fig. 5(A–D)].

As mentioned above, the SEM observation demonstrated the promotion of the change of the phase-separation style by the PEO segment with increase of the DMSO concentration in the co-

agulant. The reason is believed to be as follows: When the DMSO concentration in the coagulant increases, the inflow of water to the polymer solution is small and, thus, the onset of the liquid–liquid phase separation is delayed. The phase separation produces a polymer-rich phase and a polymer-lean phase. Generally, the inflow of water into the polymer-rich phase continues and the precipitation occurs, resulting in the membrane formation. In the DMSO-lean coagulants, $\leq$ 40 wt %, the inflow of water to the polymer-rich phase is sufficiently fast or large so that there is little or no difference in the precipitation process between NyBI and PEO–NyBI. Consequently, the NyBI and PEO–NyBI membranes have almost the same structures in the cross sections for each coagulation condition. In the case of the DMSO-rich coagulant, water/DMSO = 4/6 wt/wt, since the inflow of water to the polymer-rich phase is significantly slow, or small, the phase containing PEO–NyBI can remain in a stable state for a longer time than that containing NyBI against the water inflow, because the former includes the hydrophilic PEO segment which can diminish the influence of the inflow of water to precipitate the polymer. Thus, the precipitation apparently is more delayed. Therefore, the PEO segment acts to promote the change of the phase-separation style from the instantaneous to the delayed one in the DMSO-rich coagulant so that the morphological difference between the NyBI and PEO–NyBI membranes is observed as shown in Figures 3(D-1) and 4(D-1).

Permeability Characteristics of NyBI and PEO–NyBI Membranes

To investigate the effects of the coagulation condition and PEO segment on the permeability characteristics, the UFRs of the membranes for pure water were measured. The results are shown in Figure 6, where the UFRs are plotted against the water concentration in the coagulant. The UFR of the PEO–NyBI membrane is higher than that of the NyBI membrane within the whole range of the coagulant composition. The reason is attributed mainly to the stronger hydrophilic property of PEO–NyBI due to the PEO segment than that of NyBI, because both membranes have almost the same membrane morphologies in each coagulation condition as described above. The UFRs of both membranes decrease simply with the decrease of the water concentration from 100 to 40 wt % in the coagulant. In the case of the PEO–
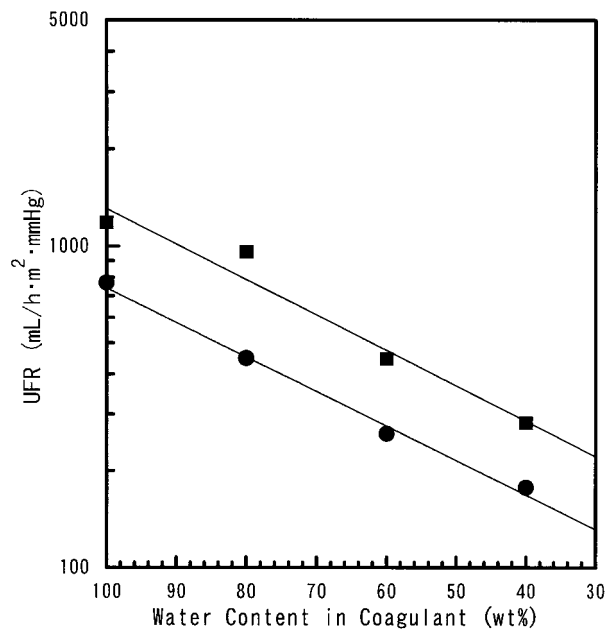
Figure 6 Permeation characteristics of NyBI and PEO–NyBI membranes: (●) NyBI membrane; (■) PEO–NyBI membrane; 37°C.

NyBI membrane, the UFR decreases from 1125 to 260 mL h^{-1} m^{-2} mmHg^{-1}, and in the case of the NyBI membrane, it decreases from 750 to 160 mL h^{-1} m^{-2} mmHg^{-1}.

The fact that the permeation behavior is affected by the phase-separation styles was reported by Reuvers et al.[14,15] They made it clear in terms of the calculated paths and experimental data that the instantaneous liquid–liquid phase separation gave a finely porous, thin skin layer and a fingerlike structure sublayer with ultrafiltration characteristics and that the delayed phase separation causes a dense, relatively thick skin top layer with reverse osmosis or pervaporation characteristics. Therefore, the phenomena whereby the UFR in the NyBI and PEO–NyBI membranes decreases with increase of the DMSO concentration agree with Reuvers' results, that is, the decrease of the UFR is induced by the change of the structure of the top skin layer due to the change of the coagulation style. However, not all of our results obey their theory. The thickness of the skin layers seems to be equal in spite of the increase of the DMSO concentration to 40 wt % in the coagulant and the thickness becomes thinner when the DMSO concentration is 60 wt % when observed under SEM as described above.

To clarify the reason for the decrease of the UFR in terms of the morphological aspect, further investigations of the morphologies of the cross sections and the top surfaces of the membranes were performed for NyBI membranes by means of the SEM observation at a higher magnification, ×50,000. The pictures of the top surfaces and cross sections near the top surfaces are shown in Figure 7, where the membranes were prepared using coagulants with the compositions; water/DMSO = 10 : 0 and 4 : 6 (wt/wt). The pictures show that the top surfaces of both membranes are composed of small nodules about 10–20 nm [Fig. 7(A-1, B-1)] and that the membrane prepared in water/DMSO = 4 : 6 wt/wt coagulant has a clearer nodule structure than that prepared in water/DMSO = 10 : 0 wt/wt. Moreover, the pictures of the cross sections shown in Figure 7(A-2, B-2) show that the fine morphologies of the membranes are different from each other. The cross section of the membrane prepared in the coagulant water/DMSO = 6 : 4 wt/wt has a more porous structure than that prepared in the water/DMSO = 10 : 0 wt/wt. The latter membrane is composed of clear particles which are packed uniformly [Fig. 7(A-2)], while the former membrane reveals a porous and spongelike structure at the cross section near the top surface [Fig. 7(B-2)]. These overviews might anticipate that the former membrane (coagulated in DMSO/water = 6 : 4 wt/wt) would have a higher UFR than that of the latter membrane (coagulated in water), but the result does not agree with this prediction as mentioned above. Careful observation of the cross section at the top layer indicates the difference between the two membranes. In the case of the membrane coagulated in water [Fig. 7(A-2)], it can be observed that the top layer in the cross-section view is composed of nodules which are packed very tightly, and the boundary between the nodules can be observed. On the other hand, the membrane coagulated in water/DMSO = 4 : 6 wt/wt [Fig. 7(B-2)] has a gradient structure where the pore decreases in size the closer it gets to the top surface and at last changes to a dense skin structure with 20–30 nm thickness. In this skin layer, neither nodules nor a boundary can be observed. This structural change from the layer packed with the particles to the dense layer induces the decrease in UFR. From these observation, it is concluded that the UFRs are decided by the top skin layer with a thickness of less than 40 nm and that SEM observation at a higher magnification is needed to confirm the difference of the top layer.
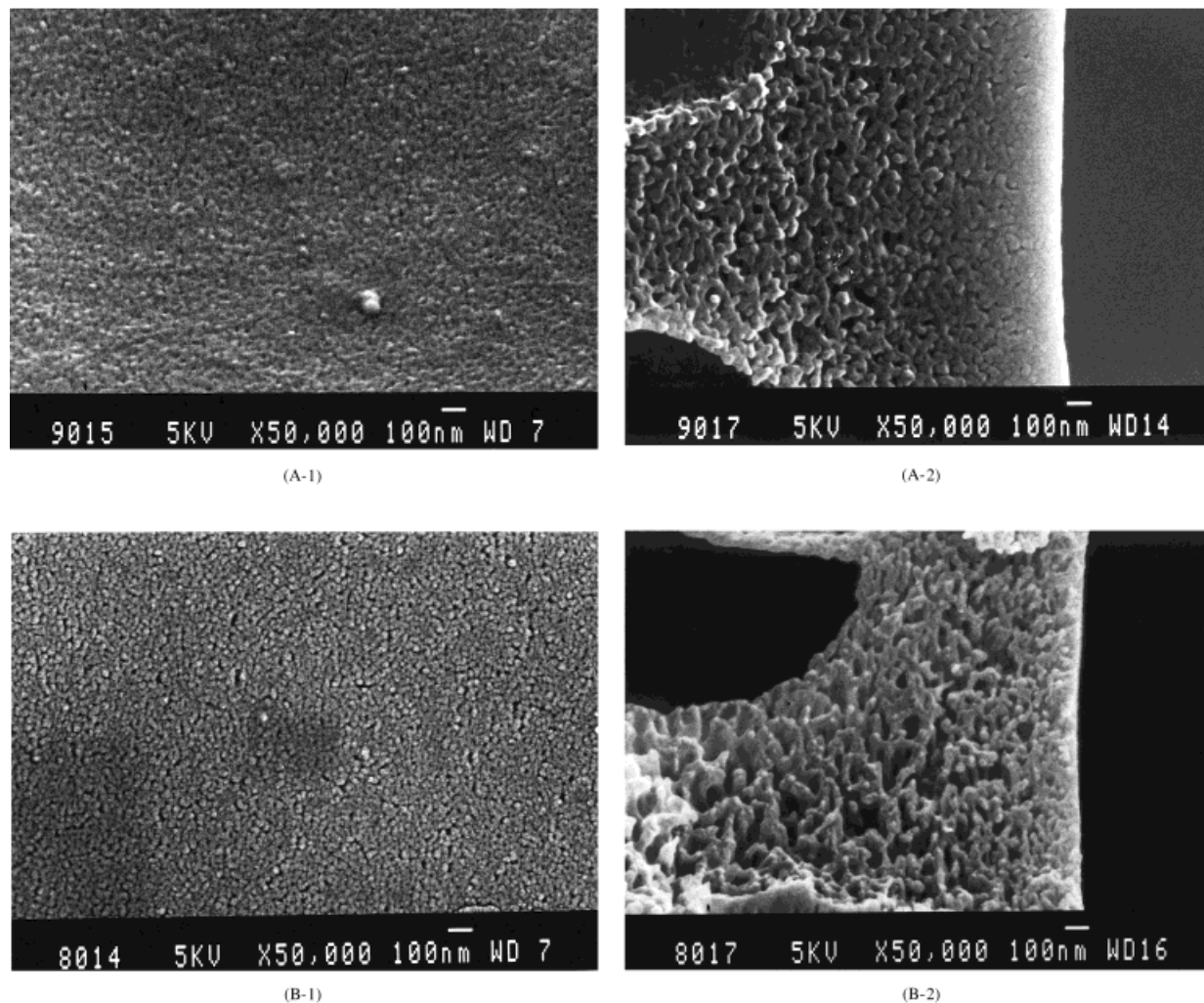
Figure 7 SEM pictures of NyBI membranes at high magnification: (A) coagulant is water; (1) top surface; (2) cross section close to top surface. (B) coagulant is water/DMSO = 4 : 6 wt/wt; (1) top surface; (2) cross section close to top surface.

Surface Analysis of the Membrane

As described above, SEM observation suggested that the PEO segment affected the morphology of the membrane prepared in a DMSO-rich coagulant. To obtain further evidence that the PEO segment affects the morphology of the membrane, or the change of the phase-inversion style, we investigated the relationship between the coagulation condition and the outermost surface composition of the membrane in terms of the enrichment of PEO or the nylon segment using ESCA and SSIMS. It is well known that in the block or graft copolymers composed of both hydrophilic and hydrophobic segments the enrichment of one segment at the outermost surface is observed. The

phenomenon is governed by the environment in contact with the surface of the copolymer. When the surface is in contact with air (dry condition), the hydrophobic segment is concentrated at the outermost surface, and the hydrophilic segment is concentrated at the surface when in contact with water (wet condition) to minimize the surface free energy. Since PEO–NyBI is a multiblock copolymer, the enrichment of the PEO or NyBI segments at the outermost surface is anticipated by the change of the coagulant composition, because DMSO is a good solvent for the NyBI segment but a poor solvent for the PEO segment and water is a good solvent for the PEO segment but a nonsolvent for the NyBI segment, as mentioned above.
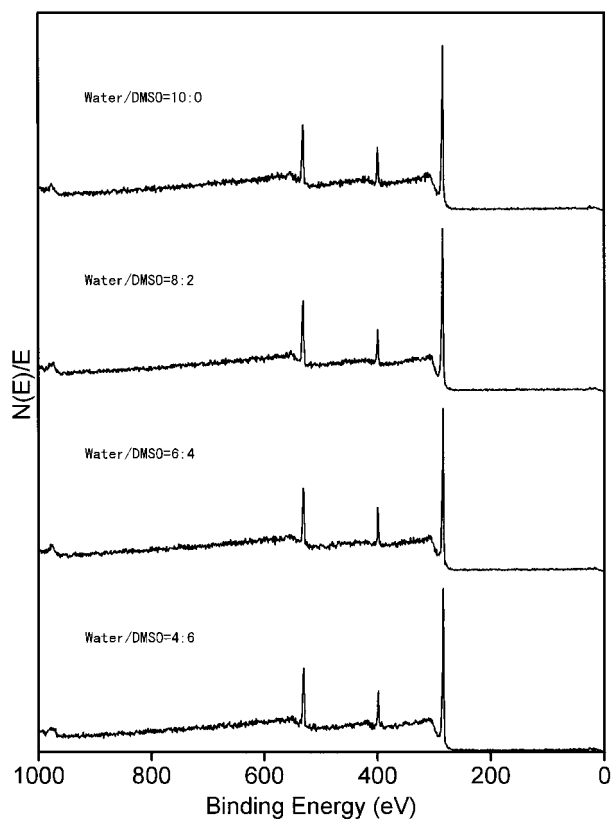
Figure 8 Survey scan of ESCA for PEO–NyBI membranes.

The survey scans of ESCA for the PEO–NyBI membranes are shown in Figure 8. It is revealed from the spectra that the elements detected are just only carbon, oxygen, and nitrogen and these results indicate that there is no contamination at the surfaces of all the membranes. On the basis of the ratio of carbon to nitrogen obtained by the narrow scans of ESCA, the chemical compositions of the outermost surface are calculated and the PEO content determined at 9–12 wt % as shown in Table II. The table shows that the PEO contents in the outermost surfaces of the membranes prepared in coagulants at a low DMSO concentration, ≤ 40 wt %, are 10 ± 1 wt %. These results indicate that the top surfaces of these membranes have almost the same chemical composition and their compositions are close to that of the bulk PEO–NyBI, 10 wt %, determined on proton-NMR, as determined by ESCA analysis. In the case of a coagulant with 60 wt % DMSO, the PEO content in the outermost surface is 12 wt % as listed in the table and this result suggests a slight enrichment of PEO, that is, the segregation of PEO is influenced by the concentration of the poor sol-

vent, DMSO, for the PEO segment in the coagulant.

However, these results in the ESCA analysis are not obvious evidence that the phase-separation style changed by the coagulant composition reflects the segregation of the segment of PEO–NyBI. The reason for this uncertainty is attributed to the low sensibility of ESCA and the fact that ESCA cannot determine the chemical species but atoms. On the other hand, SIMS can analyze the top layer with a very high sensitivity and, moreover, can characterize the chemical structure of the outermost surface by the analysis of the fragmentation pattern. Therefore, more detailed information about the segregation at the outermost surface can be obtained.

The positive MASS spectra of the PEO homopolymer and the NyBI membrane are shown in Figure 9, and they represent the references for analyzing the surface structure of the PEO–NyBI membrane. Since the NyBI membrane is composed of a homopolymer, the outermost surfaces of all the membranes should have the same chemical composition in spite of the different coagulation conditions. Thus, only one membrane prepared with the use of water as the coagulant was investigated. The main ion structure assignments of the positive SIMS spectra in the high mass range for PEO and the NyBI membrane are summarized in Table III. When the fragmentation patterns of PEO are compared with those of NyBI, the peak at $m/z^+ = 45$ with high intensity observed in the PEO fragmentation is not detected in the NyBI fragmentation and it is assigned as $^+CH_2CH_2$—OH, while the peak at $m/z^+ = 104$ with high intensity observed in the NyBI fragmentation is not detected in PEO and is assigned as $\cdot Ph$—$C\equiv O^+$. On the basis of these results, it is concluded that the peak strength ratio of $m/z^+ = 104$ to $m/z^+ = 45$ in the spectra of the PEO–NyBI membranes indicates a qualitative surface composition.

Table II   Surface Composition of PEO–NyBI Membrane by ESCA

Coagulation Condition [Water/DMSO (wt/wt)]	PEO Concentration (wt %)
100 : 0	11
80 : 20	9
60 : 40	10
40 : 60	12
Bulk[a]	10

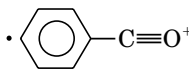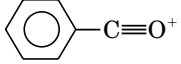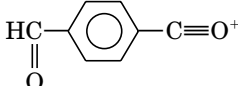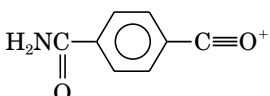[a] Calculated from the measurement of ^{1}H-NMR.
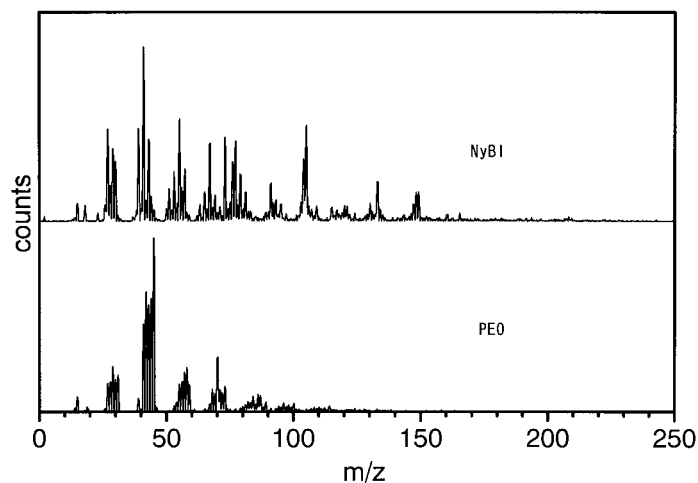
Figure 9 Positive SIMS spectra for surface of PEO and NyBI membrane. NyBI membrane was prepared using water as the coagulant.

The spectra of PEO–NyBI membranes are shown in Figure 10. The peak ratios for each PEO–NyBI membrane are listed in Table IV. The ratio, 104(NyBI)/45(PEO), for the membranes prepared in a coagulant with a low DMSO concen-tration, $\leq$ 40 wt %, decreases slightly from 0.66 to 0.52 with increase of the DMSO concentration in the coagulant. This result indicates that the PEO content of these membranes at the outer-most surface slightly increases with increase of

Table III   Assignment of Main Cation Peaks in the SIMS Spectra of PEO and NyBI

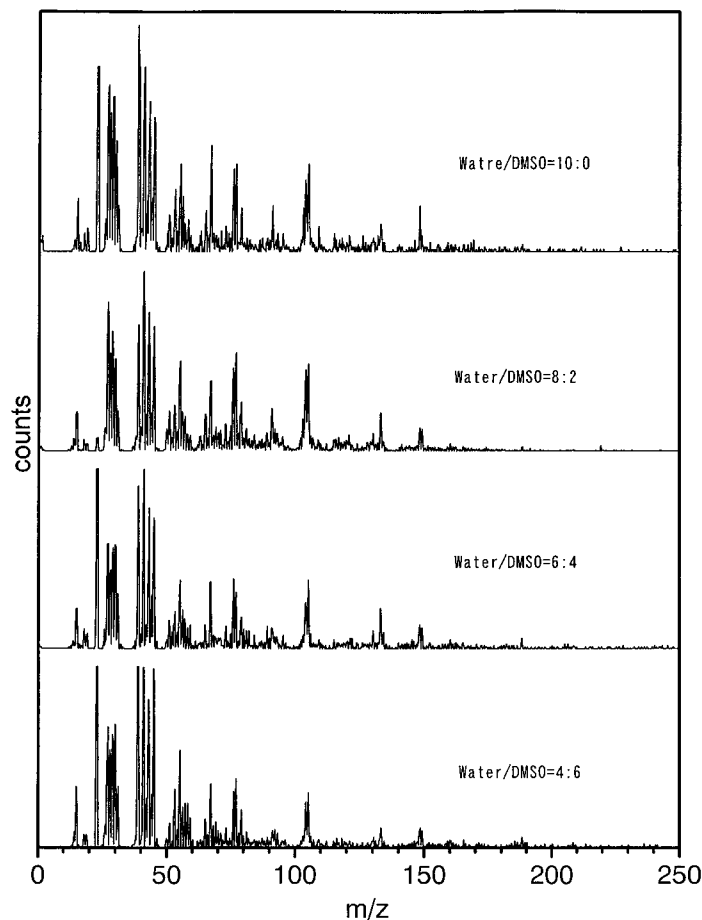| NyBI Homo		PEO Homo	
m/z	Structure	m/z	Structure
27	$H_2C{=}CH^+$	15	CH_3^+
41	$H_2C{=}CH{-}CH_2^+$	31	$^+H_2C{-}OH$
55	$H_2C{=}CH{-}C{\equiv}O^+$	45	$^+H_2C{-}H_2C{-}OH$
		73	$CH_3{-}CH_2{-}O{-}CH_2{-}CH_2^+$
77	⬡· $^+$		
91	⬡ $+$		
104	$\cdot$⬡$-C{\equiv}O^+$		
105	⬡$-C{\equiv}O^+$		
133	$\overset{\displaystyle HC}{\underset{O}{\|}}$⬡$-C{\equiv}O^+$		
148	$\overset{\displaystyle H_2NC}{\underset{O}{\|}}$⬡$-C{\equiv}O^+$		

Figure 10 Positive SIMS spectra for surface of PEO–NyBI membranes. As the peak with the largest intensity derived from the polymer is plotted as the maximum count in the y-axis, the peaks of m/z^+ at 23 and 40 assigned as Na^+ and K^+, respectively, are overscaled. Na^+ and K^+ are attributed to the contamination.

the DMSO concentration in the coagulant because the decrease of the ratio means an increase of the PEO fragment, $m/z^+ = 45$. In the case of the DMSO-rich coagulant, 60 wt %, the ratio becomes rather small or about 0.30. This result strongly indicates that the PEO content at the top surface

Table IV   Counterratio of NyBI to PEO Segments at PEO–NyBI Membranes

Coagulant Composition Water/DMSO (wt/wt)	Counterratio $(105/45)^a$
100 : 0	0.66
80 : 20	0.54
60 : 40	0.52
40 : 60	0.30

^{a} The peak $m/z^+ = 105$ was derived from the Ny segment. The peak $m/z^+ = 45$ was derived from the PEO segment.

of the membrane prepared in the coagulant, water/DMSO = 4 : 6 wt/wt, is obviously higher than that of the former three membranes coagulated in the low DMSO concentration. This knowledge corresponds to the result of ESCA analysis whereby the enrichment of the PEO segment was observed in the membrane prepared in the DMSO-rich coagulant, 60 wt % DMSO. The coagulant composition which induces the apparent change of the PEO content in the outermost surface agrees with the coagulant composition which brings about the morphological difference between the NyBI and PEO–NyBI membranes. However, the fact of the enrichment of the PEO segment conflicts with the prediction to which the common microphase-separation mechanism mentioned above would lead, that is, the common mechanism predicts the enrichment of the NyBI segment at the top surface of the membrane.

The reason for the marked increase of the PEO content at the outermost surface of the membrane prepared in the coagulant, water/DMSO = 4 : 6 wt/wt, is supposed to be as follows: In the membrane-formation process, the polymer solution separates into a polymer-rich and a polymer-poor phase, and then the polymer precipitates due to the in-flow of water to the polymer-rich phase, resulting in the formation of the membrane. In this polymer-rich phase, the segregation of the PEO and NyBI segments in PEO–NyBI will occur because they have different affinities to water and to DMSO. Consequently, it is predicted that the kinetic competition between the precipitation and the segregation takes place in the membrane-formation process. When the instantaneous phase separation occurs, or the DMSO poor coagulants, $\leq$ 40 wt %, are used, the polymer will precipitate from the polymer-rich phase rapidly before the segregation of PEO–NyBI occurs. Therefore, the change of the strength ratio of the NyBI fragment peak ($m/z^+ = 104$) to the PEO fragment peak ($m/z^+ = 45$) with increase of the DMSO concentration in the coagulant is small. When the DMSO concentration in the coagulant becomes high, 60 wt %, the precipitation of the polymer in the polymer-rich phase is slow enough to complete the segregation of the two segments because of the low water in-flow to the polymer-rich phase, that is, since the polymer-rich phase is surrounded by the DMSO-poor phase, which is mainly water, the PEO segment is concentrated at the surface to minimize the surface energy of the phase. Once the segregation in the polymer-rich phase occurs, the polymer precipitates and then the outermost surface of the PEO–NyBI membrane with the enrichment of the PEO content is formed. These speculations that the precipitation occurs faster than the segregation of the two segments in PEO–NyBI in the low DMSO coagulant and that the segregation occurs faster than the precipitation in the DMSO-rich coagulant agree with the explanation that has been considered as the reason for the results of the morphological change of the cross section induced by the coagulant composition and PEO segment described above. These results indicate that the analyses by ESCA and SIMS are very important and useful methods not only to characterize the outermost surface but also to investigate the phase-inversion process.

CONCLUSIONS

The asymmetric membranes were prepared from amorphous homo-nylon, NyBI, and polyether-seg-mented nylon, PEO–NyBI. The influences of the PEO segment on the morphology of the PEO–NyBI membranes formed by the phase-inversion method were investigated using the water/DMSO mixtures as coagulants. The cloud-point curves for NyBI and PEO–NyBI were investigated. The results indicating that the curves overlap and are close to the polymer–solvent axis in the ternary phase diagram indicate that both polymers give rise to the same coagulation processes and predict that the instantaneous liquid–liquid phase separation occurs, resulting in a fingerlike structure. The membrane morphologies observed agreed with the prediction and the same structures were observed for PEO–NyBI and NyBI membranes prepared in water as the coagulant. The addition of DMSO to the coagulant brought about the change of the phase-separation style from the instantaneous liquid–liquid phase separation to the delayed one. The NyBI and PEO–NyBI membranes prepared under the same coagulation condition, coagulants with $\leq$ 40 wt % of DMSO, have the same morphology with the fingerlike structure. The increase of DMSO concentration to 60 wt % in the coagulant produces a spongelike structure with small macrovoids for each membrane and causes a morphological difference between the NyBI and PEO–NyBI membranes. The small macrovoids remain slightly near the top surface in the PEO–NyBI membrane, while the rather big macrovoids still exist in the sponge region in the NyBI membrane, that is, the change of phase-separation style from the instantaneous to the delayed phase separation is promoted by the PEO segment in the DMSO-rich coagulant.

The relationship between the UFR and the DMSO concentration in the coagulant was investigated. Decreases of the UFRs with the increase of DMSO concentration were observed in both membranes. The UFR of the PEO–NyBI membrane was higher than that of the NyBI membrane within the whole range of the coagulation conditions, and this phenomenon is attributed to the hydrophilicity of the PEO segment. Moreover, the relationship between the surface analysis of the PEO–NyBI membrane and the coagulation condition was studied using ESCA and SIMS. The small enrichment of the PEO segment at the outermost surface of the membrane prepared in water/DMSO = 4 : 6 wt/wt coagulant was observed by ESCA. The SSIM measurement reveals, obviously, the same tendency, that is, the ratio of the fragment peak derived from the NyBI segment to the one from the PEO segment increased mark-

edly in the DMSO-rich coagulant, 60 wt %. These surface analyses indicate that the effect of the PEO segment on the morphology of the membrane appears when a coagulant with high DMSO concentration, ≥ 60 wt %, is adopted.

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