

# Polyether-Segmented Nylon Hemodialysis Membranes. II. Morphologies and Permeability Characteristics of Polyether-Segmented Nylon 610 Membrane Prepared by the Phase Inversion Method

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Received 2 December 1996; accepted 23 January 1997

**ABSTRACT:** The relationships between the morphologies and the permeability characteristics as dialysis membrane of polyether-segmented nylon 610 (PE-Ny610) have been investigated. PE-Ny610 used are poly(propylene oxide) (PPO)-segmented nylon 610 containing 25 wt % PPO (PPO-Ny610) and poly(ethylene oxide) (PEO)-segmented nylon 610 containing 15 wt % PEO (PEO-Ny610). The morphologies in the cross section of the membranes exhibit the cellular porous structures due to liquid-liquid phase separation. On the other hand, the structures of the surfaces are mainly composed of the crystalline spherulite due to liquid-solid phase separation. These morphologies are little affected by the composition ratio of the coagulant, calcium chloride/methanol/water mixture. PEO-Ny610 membranes have shown superior membrane performances to the PPO-Ny610 membrane. The effect of PEO content in PEO-Ny610 on the adhesion of platelet onto the PEO-Ny610 film surface was investigated and it is concluded that PEO-Ny610 having > 10 wt % PEO shows a good nonthrombogenicity equal to PPO-Ny610. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1713–1721, 1997

**Key words:** dialysis membrane; polyether-segmented nylon; nylon 610; morphology; solute permeability; ultrafiltration rate

## INTRODUCTION

In membrane technology and science, the phase inversion method is a very important research object and is widely used to prepare many kinds of membranes, such as dialysis, ultrafiltration, and reverse osmosis membranes. Of course, this method is applied to wet spinning to make hollow fiber membranes. In general, this method is composed of four processes, described below. First is the immersion of polymer solution into a coagulant (nonsolvent). The second is the diffusion of nonsolvent into the polymer solution. The third

and fourth are isothermal phase separation and precipitation of the polymer. In this phase separation, liquid-liquid phase separation, liquid-solid phase separation, or a combination of both are brought about. Cheng, Dwan, and Gryte<sup>1</sup> have reported in detail on the phase behaviors and membrane formation of polyamides such as Ny6, Ny66, Ny610, and Ny6,66,610 terpolymer. They have investigated the binodal miscibility gap of the water-formic acid-terpolymer and the crystallization equilibrium of the homopolymers in formic acid/water system at room temperature. They have concluded that it is almost impossible in these systems for the polyamides having a strong crystallization ability to observe only liquid-liquid phase separation.

Hemodialysis membranes are one of the most

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successful cases in membrane technology and medical treatments. Regenerated cellulose membranes have been used for this purpose, but recently their poor blood compatibility and low permeability for low molecular weight proteins which are toxic for the human body have been pointed out. In order to improve these problems, synthetic polymer membranes have been paid attention to. The synthetic polymers used are polysulfone, ethylene vinylalcohol copolymer, polyacrylonitril, polymethylmethacrylate, and amorphous polyamide. These polymers are all industrial materials and not designed as biocompatible materials.

Recently, polyether-segmented nylon has been studied in detail as a blood-compatible material by Yui et al.<sup>2-7</sup> They have concluded that poly(propylene oxide)-segmented nylon 610 containing 25 wt % polyether (PPO-Ny610) exhibits the least thrombogenicity; that is, the suppression of the adhesion of platelet onto its surface. This polymer has been expected to be applied to medical equipment produced by means of melt compression and has recently been put to practical use as an intravenous catheter.<sup>8</sup>

We have already reported the hemodialysis membrane prepared from PPO-Ny610 by using the phase inversion method,<sup>9</sup> and concluded that the performance of PPO-Ny610 membrane is a little superior to that of regenerated cellulose membrane, but the high permeability characteristics as shown by the polysulfone membrane are not obtained. The reason seems that PPO-Ny610 is relatively hydrophobic and liquid-solid phase separation dominates at the top surface in the coagulation process. In order to confirm the morphology (liquid-solid phase separation) and to improve permeability characteristics, we have investigated membrane morphologies and permeability characteristics of membranes prepared by PPO-Ny610 and PEO-Ny610, which has hydrophilic poly(ethylene oxide) (PEO) as the polyether segment instead of the hydrophobic PPO segment.

## EXPERIMENTAL

### Materials

Polyether segmented nylon 610 (PE-Ny610) was synthesized by means of direct-melt polycondensation at 240–250°C under 5–10 kg/cm<sup>2</sup> pressure for 2 h, and subsequently reduced pressure (<10 mmHg) for 2 h. The detailed method has been reported previously.<sup>9</sup> The monomers used were hexamethylenediamine (Toray, Japan), sebacic

acid (Houkoku Corporation, Japan),  $\alpha,\omega$ -bisaminopropyl-poly(ethylene oxide) (mol wt 2000, Kawaken Fine Chemical, Japan), and bisaminopropyl-poly(propylene oxide) (mol wt 2000, Sun Techno chemical Co. Ltd., Japan). These monomers were used without further purification.

### Swelling Degree

The swelling degrees of PE-Ny610 with water were measured at room temperature by soaking the polymer film in pure water for 3 days. Polymer films used were prepared by hot press  $\sim 200 \mu\text{m}$  thick. After soaking the film in water, its weight was measured and the wet film was dried *in vacuo* at 80°C overnight. This dry film was weighed and the swelling degree was obtained by eq. (1).

Swelling degree (%)

$$= (W_w - W_d)/W_d \times 100 \quad (1)$$

where  $W_w$  is the weight of wet film and  $W_d$  is the weight of dry film.

### Preparation of Membranes

Fifteen grams of PE-Ny610 was dissolved in 85 g of formic acid at room temperature. Membranes were prepared by casting the polymer solution onto a glass plate, then immersing it rapidly into a nonsolvent coagulant bath at 5°C, where the coagulant mixtures of water, calcium chloride, and methanol had several composition ratios. After the complete precipitation (for 30 min), the membranes were taken out of the coagulant bath and immersed in ultrapure water to remove the solvent and to keep the membrane structures.

### Observation of Membrane Morphologies

Wet membranes were immersed into liquid nitrogen. The frozen membranes were fractured in liquid nitrogen and then freeze-dried *in vacuo*. After sputtering platinum onto the membrane, the cross section and the surface were observed by using scanning electron microscopy (SEM) (Jeol F840, Japan).

### Permeability Characteristics of Membrane

Membrane performances were investigated in viewpoints of the ultrafiltration rate (UFR) of water and the permeation of low- and middle-molecular weight substances by using urea and vitamin

B<sub>12</sub>. The detailed methods have been reported previously.<sup>9</sup> Brief measurement methods are mentioned below. UFR was measured with an ultrafiltration cell (Advantec UHP-43), whose effective diameter is 43 mm at the pressure of 250 mmHg using pure water. UFR was calculated from eq. (2).

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

where  $V$  is water flux (mL/h),  $S$  is the membrane area (m<sup>2</sup>), and  $P$  is the operating pressure (mmHg).

The solute permeabilities were measured by using a glass cell which consisted of two compartments. The apparent solute permeability was calculated from eq. (3) under the assumption of neglecting liquid resistance of both sides of the membrane.

$$P = \ln[\Delta C(t_1)/\Delta C(t_2)]/[S(1/v_1 + 1/v_2)(t_2 - t_1)] \quad (\text{cm/min}) \quad (3)$$

where  $t_1$  and  $t_2$  are sampling times of 30 and 150 min, respectively.  $\Delta C(t)$  is the difference between the solute concentrations in the upper and the lower cells at the sampling times,  $t_1$  and  $t_2$ .  $v_1$  and  $v_2$  are the solution volumes (50 cm<sup>3</sup>) in each cell.  $S$  is the membrane area (10 cm<sup>2</sup>).

### *In Vitro* Evaluation of Nonthrombogenicity

As the detailed method was described previously,<sup>9</sup> brief measurement methods are mentioned below. The polymer films used were prepared by casting 5 wt % polymer solution of hexafluoroisopropanol onto a petri dish and evaporating the solvent under atmosphere at room temperature. Citrated platelet-rich human plasmas (PRP) were placed on the polymer films at room temperature under static conditions. After the fixation of the cell on the film surface, the samples were observed under the SEM at a magnification of 1,000, and five micrographs of the film surfaces were taken at random. Adhering platelets in each picture were counted and the numbers summed up for five pictures were the numbers of adhering platelets.

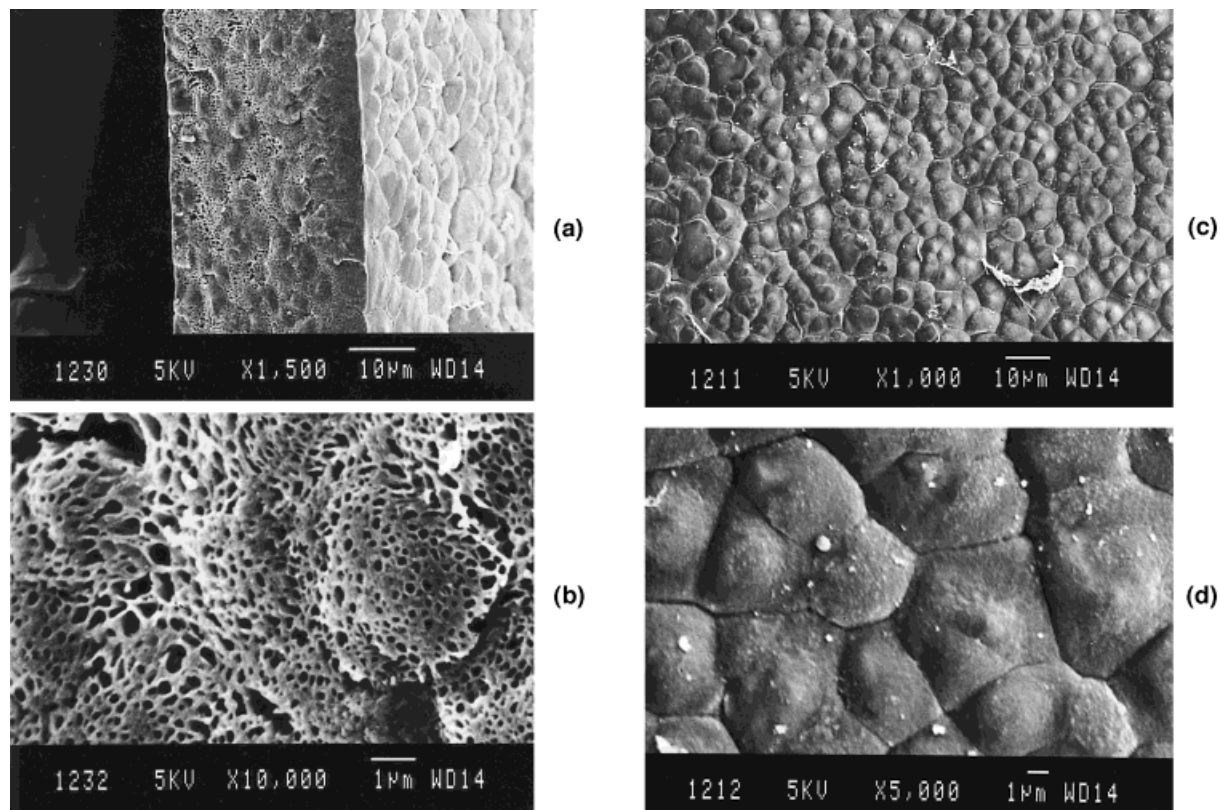
## RESULTS AND DISCUSSION

Previously<sup>9</sup> we reported the membrane formation and the permeability characteristics using PPO-Ny610 as a membrane material. In the report,

we investigated the solvents for PPO-Ny610 and concluded that PPO-Ny610 dissolves in formic acid, methanol saturated with calcium chloride, and so on. To investigate the relationship between the morphologies and permeability characteristics, formic acid for polymer solvent, and calcium chloride/methanol/water mixture as coagulant were used.

The representative morphologies of the PPO-Ny610 membrane are shown in Figure 1, where the composition of the coagulant is calcium chloride/methanol/water 0 : 4 : 6 (wt/wt/wt). Similar morphologies are observed for all the membranes coagulated in the baths whose composition of calcium chloride/methanol/water are 0 : 3 : 7, 1 : 3 : 7, and 2 : 3 : 7 (wt/wt/wt). Therefore, it is concluded that the coagulant composition has little effect on the basic structures of the cross section and top surface of the membranes. The cross section comprises the cellular porous structure and the pores are very small, < 1- $\mu$ m diameter. These results indicate that liquid-liquid phase separation dominates in the coagulation process, and these coagulants give rapid precipitation of polymer from dope solution. In the top surface of the membrane, hard skins, which are composed of very tight polygon plates, are observed in all coagulation conditions. This result means that liquid-solid phase separation occurs at the top layer. These structures in the cross section and top layer are very similar to the ones reported by Cheng, Dwan, and Gryte,<sup>1</sup> except for the pore size. They explained the reason why liquid-solid phase separation occurred at the top surface as follows. In the top surface region, a continuous amorphous polymer-rich gel layer is initially formed. This layer is on the binodal line and highly supersaturated with respect to crystallization. Thus, crystal nucleation occurs in this polymer-rich region. These polymer nuclei grow, and the front meets the adjacent growing spherulites to form the "polygon plate."

Judging from these surface structures, it seems to be difficult for the membrane to exhibit high permeability because the solutes and water cannot permeate through the crystalline region. They permeate through the micropores in an amorphous region which will exist mainly in the boundary region of polygon plates. The top surface structure of PPO-Ny610 membrane suggests that there is not so much amorphous region in the surface. Moreover, considering that PPO-Ny610 is a rather hydrophobic polymer and that the permeation of water is supposed to be the capillary flow, water flow is depressed. Therefore, in PPO-Ny610



**Figure 1** SEM micrographs of PPO-Ny610 membranes. Coagulant is methanol/water 4 : 6 (wt/wt). (a) Cross section, (b) magnified micrograph of cross section, (c) top surface, (d) magnified micrograph of top surface.

membrane, the low ultrafiltration rate and rather low permeability of solutes are anticipated.

The effects of coagulation condition on the permeability characteristics of the PPO-Ny610 membrane were investigated by varying the composition ratio of the coagulant bath, calcium chloride/methanol/water 0 : 3 : 7, 0 : 4 : 6, 1 : 3 : 7, and 2 : 3 : 7 (wt/wt/wt). The results are shown in Table I. It is observed that the UFR increases from 0 to 23 mL/m<sup>2</sup> h mmHg with the increase of calcium chloride in the coagulant. In addition, the increase of UFR is observed when the ratio of

methanol in the coagulant without calcium chloride increases from methanol/water 3 : 7 to 4 : 6 (wt/wt) as shown in Table I. The increase of calcium chloride or methanol means the increase of the solubility of coagulant and brings about the soft coagulation. These results indicate that soft coagulation causes the increase of the UFR. The permeabilities of the low and middle molecular substances were measured using PPO-Ny610 membrane with the UFR > 20 mL/m<sup>2</sup> h mmHg, because the UFR is demanded to be in the range from 20 to 50 mL/m<sup>2</sup> h mmHg for practical use

**Table I** Permeability Characteristics of PPO-Ny610 Membranes

Coagulant (wt/wt/wt) CaCl <sub>2</sub> /MeOH/H <sub>2</sub> O	UFR (mL/m <sup>2</sup> h mmHg)	Urea (10 <sup>-4</sup> cm/min)	Vitamin B <sub>12</sub> (10 <sup>-4</sup> cm/min)
0 : 3 : 7	0	— <sup>a</sup>	—
0 : 4 : 6	39	138	25
1 : 3 : 7	4	—	—
2 : 3 : 7	23	73	10

<sup>a</sup> Not measured.

**Table II** Counts of Adhering Platelet onto PE-Ny610 Surface

PPO-Ny610	PEO(5 wt %)-Ny610	PEO(10 wt %)-Ny610	PEO(15 wt %)-Ny610	PEO(25 wt %)-Ny610	homo Ny610
0	7	3	0	0	397

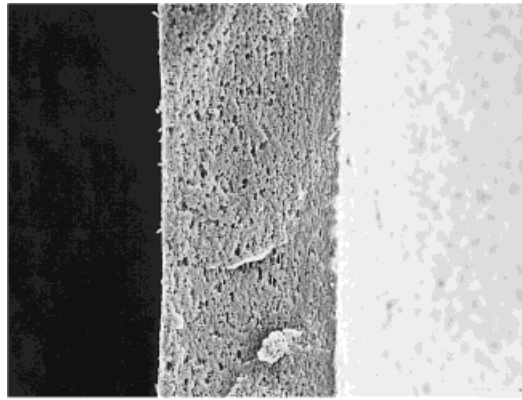
of hemodialysis membrane. Solute permeabilities for urea and vitamin B<sub>12</sub> are  $73 \times 10^{-4}$  and  $10 \times 10^{-4}$  cm/min, respectively; in the case of the membrane with UFR, 23 mL/m<sup>2</sup> h mmHg [coagulant composition : calcium chloride/methanol/water 2 : 3 : 7 (wt/wt/wt)]. The membrane with UFR, 39 mL/m<sup>2</sup> h mmHg [coagulant composition : calcium chloride/methanol/water 0 : 4 : 6 (wt/wt/wt)] has the permeabilities of  $138 \times 10^{-4}$  cm/min for urea and  $25 \times 10^{-4}$  cm/min for vitamin B<sub>12</sub>. These permeabilities are nearly equal to those of regenerated cellulose membrane, but not as high as synthetic hemodialysis membranes.<sup>9</sup>

Since one of the reasons for the inadequate permeability characteristics of PPO-Ny610 membrane is the hydrophobicity of PPO-Ny610 as mentioned above, it is supposed that membrane performances will be improved by replacing the hydrophobic PPO segment with hydrophilic PEO segment. Because of its hydrophilicity, the permeation through the micropores existing in the polygon plate boundaries or the amorphous region in the spherulite will be easier. For hemodialysis membrane, the platelet compatibility is an important factor. When the polyether segment is changed from PPO to PEO, it is important to determine the optimal content of PEO segment suppressing the adhesion of platelet. The effect of PEO content in PEO-Ny610 on the adhesion of platelet onto the polymer surface was investigated. The results are shown in Table II. When PEO content is > 10 wt %, the count of adhering platelets decreases markedly and reaches nearly to the equal level of PPO-Ny610. Therefore, it is concluded that the PEO-Ny610 block copolymers having > 10 wt % PEO are platelet-compatible materials. Therefore, PEO-Ny610 containing 15 wt % of PEO as a membrane material was used in order to investigate the morphologies and permeation characteristics of the membrane.

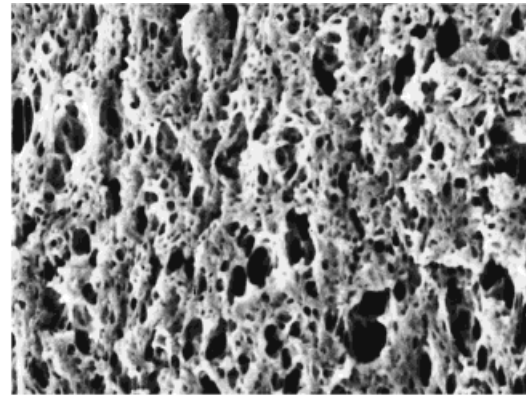
The effect of coagulant composition on the morphologies of the PEO-Ny610 membrane was investigated using the coagulant baths having the composition of calcium chloride/methanol/water 0 : 2 : 8, 0 : 3 : 7, 0 : 4 : 6, 1 : 3 : 7, and 2 : 3 : 7 (wt/wt/wt). The representative structures observed by SEM are shown in Figure 2, where the

composition of the coagulants is calcium chloride/methanol/water 0 : 4 : 6 and 2 : 3 : 7 (wt/wt/wt). The morphologies of the cross sections [Fig. 2(a,b,e,f)] show the cellular porous structure and the similar morphologies are observed in membranes prepared by the other coagulation compositions mentioned above. These results suggest strongly that liquid-liquid phase separation occurs mainly in all the coagulation conditions [calcium chloride/methanol/water 0 : 2 : 8-2 : 3 : 7 (wt/wt/wt)] and that the composition ratio has little effect on the morphologies in the cross section. The micrographs of the top surfaces [Fig. 2(c,g)] show the spherulite structures which are similar to the structures of PPO-Ny610 membranes, but the spherulite (0.5–1 μm diameter) in PEO-Ny610 membrane is significantly smaller than that in PPO-Ny610 (5–7 μm diameter). Careful observation shows that the spherulite has fibrils and there is a slit between the crystalline spherulites [Fig. 2(d,h)]. These results suggest that liquid-liquid phase separations occur at the same time, that is, both liquid-solid and liquid-liquid phase separations are taking place. The liquid-liquid phase separation is enhanced by the increase of the calcium chloride content in the coagulant. The fibril structure between the spherulites due to liquid-liquid phase separation is observed clearly in Figure 2(h), which is obtained by the coagulation in the high calcium chloride content bath, calcium chloride/methanol/water 2 : 3 : 7 (wt/wt/wt). The difference of the top surface structures between the PPO-Ny610 membrane and PEO-Ny610 membrane will be due to differences of the solubility of the polyether segment for the coagulant. While PPO is not soluble in the coagulant, PEO is soluble. From these results, it is concluded that the structure of PEO-Ny610 membrane is preferable to permeate water and solutes in comparison with PPO-Ny610 membrane.

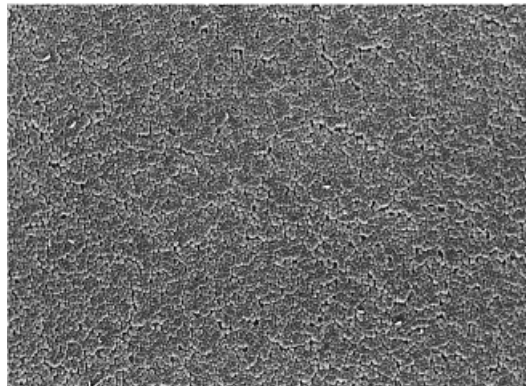
The other significant factor, hydrophilicity, was investigated in a viewpoint of swelling degree for water, and the results are listed in Table III. The swelling degrees of PEO-Ny610 and PPO-Ny610 are 14.5% and 5.2%, respectively. The table indicates that the hydrophilicity of PE-Ny610 is re-



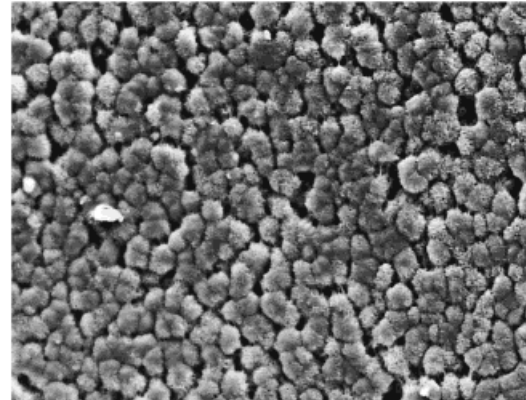
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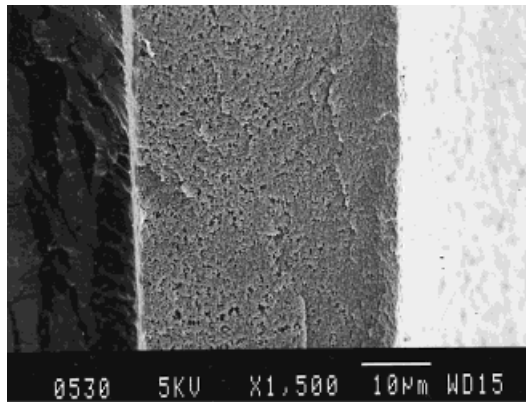
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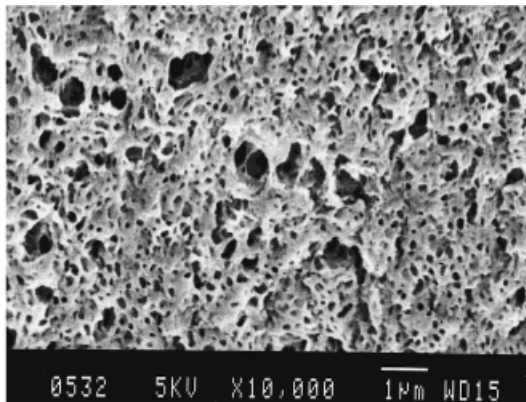
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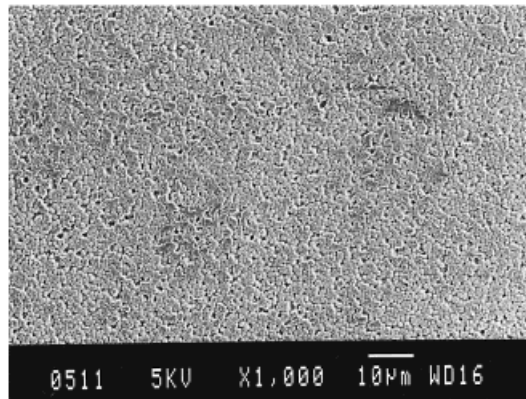
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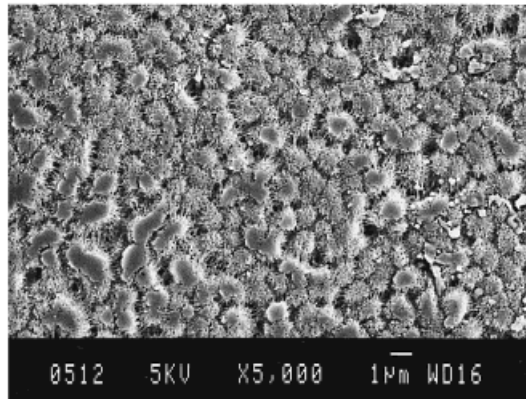
(e)



(f)



(g)



(h)

**Table III Swelling Degree of PE-Ny610 and homo Ny610**

PPO-Ny610	PEO-Ny610	homo Ny610
5.2%	14.5%	2.8%

The contents of polyether are 25 wt % for PPO and 15 wt % for PEO.

markably increased by the replacement of the polyether segment from PPO to PEO. This suggests that hydrogel-like regions composed of PEO segments will be formed in PEO-Ny610, and thus the improvement of the permeability for the low or middle molecular substances due to diffusion are predicted in comparison with PPO-Ny610 membrane.

The results of the permeation characteristics of PEO-Ny610 membranes are listed in Table IV. When the coagulant composition ratio (methanol/water mixture without calcium chloride) is varied in the range from 2 : 8 to 4 : 6 (wt/wt), the UFR increases from 19 to 85 mL/m<sup>2</sup> h mmHg with the increase of methanol content. The addition of calcium chloride into the coagulant [methanol/water 3 : 7 (wt/wt)] induces the increase of UFR from 36 to 74 mL/m<sup>2</sup> h mmHg with the increase of the amount of calcium chloride. These results indicate that the soft coagulation brings about the increase of the UFR, and they are respondent to the top surface structure in the PEO-Ny610 membranes, the degree of liquid-liquid phase separation. The increase of the UFR induced by soft coagulation is similar to the case of PPO-Ny610 membranes shown in Table I, but the UFR of PEO-Ny610 membrane is significantly larger than that of PPO-Ny610 membrane when the same coagulation condition is adopted. For example, when the coagulant is methanol/water 3 : 7 wt/wt, the UFR of PPO-Ny610 membrane is 0 mL/m<sup>2</sup> h mmHg and that of PEO-Ny610 membrane is 36 mL/m<sup>2</sup> h mmHg.

To compare the solute permeabilities of PEO-Ny610 membrane with those of PPO-Ny610 membrane, the PEO-Ny610 membranes with the UFR, 19 and 36 mL/m<sup>2</sup> h mmHg are chosen because

their UFR are close to the UFR of PPO-Ny610 membranes shown in Table I. These PEO-Ny610 membranes were prepared by the coagulation in the baths having the compositions [calcium chloride/methanol/water 0 : 2 : 8 and 0 : 3 : 7 (wt/wt/wt)]. Permeability of urea and vitamin B<sub>12</sub> for PEO-Ny610 membranes are  $> 190 \times 10^{-4}$  cm/min and  $37 \times 10^{-4}$  cm/min, respectively, but those for PPO-Ny610 membranes are  $< 140 \times 10^{-4}$  cm/min and  $25 \times 10^{-4}$  cm/min, respectively, whereas the performances of PEO-Ny610 membrane are superior to those of PPO-Ny610 membrane. Considering that vitamin B<sub>12</sub> is the model substance of the middle molecular toxic substance, higher permeability of vitamin B<sub>12</sub> is desired in clinical hemodialysis membrane.

To compare the difference of morphology and permeability characteristics between the membranes of two block polymers and the membrane of homo Ny610, homo Ny610 membrane was prepared using formic acid as a dope solvent and methanol/water 4 : 6 (wt/wt) mixture as a coagulant. The results of morphologies are shown in Figure 3. The cross section shows that the crystalline particles interlock to form a microporous structure and this suggests that liquid-solid phase separation occurs in the precipitation process. The top surface of the membrane is composed of the polygon plate. These results coincide with the results reported by Cheng, Dwan, and Gryte.<sup>1</sup> From the results of cross section structure in homo Ny610 and PE-Ny610 membranes, the incorporation of polyether segment gives the tendency to cause liquid-liquid phase separation in the coagulation process. The polyether segment disturbs or delays the crystallization of the nylon segment. The permeability characteristic of homo Ny610 membrane is listed in Table V. The UFR of this membrane is significantly small, 0.4 mL/m<sup>2</sup> h mmHg, so that the solute permeability was not measured. The swelling degree for water shown in Table III indicates that homo Ny610 is more hydrophobic than PPO-Ny610. Considering the capillary flow through the micropore in the amorphous region as mentioned above, this hydrophobicity is one of the reasons for the small UFR of Ny610 membrane.

**Figure 2** SEM micrographs of PEO-Ny610 membranes. Coagulant is calcium chloride/methanol/water 0 : 4 : 6 (wt/wt/wt). (a) Cross section, (b) magnified micrograph of cross section, (c) top surface, (d) magnified micrograph of top surface. The magnification in each micrograph is equal to that of the corresponding picture in Figure 1. SEM micrographs of PEO-Ny610 membranes. Coagulant is calcium chloride/methanol/water 2 : 3 : 7 (wt/wt/wt). (e) Cross section, (f) magnified micrograph of cross section, (g) top surface, (h) magnified micrograph of top surface.

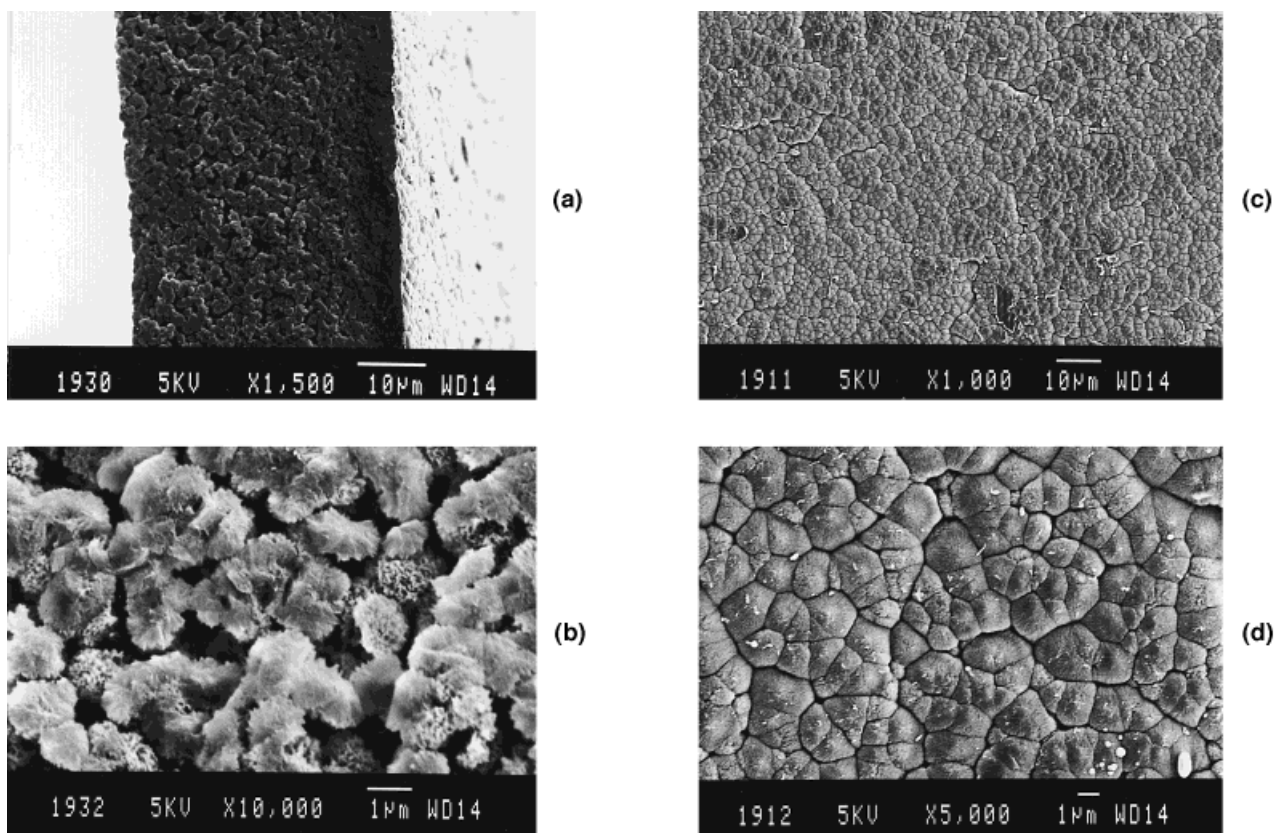
**Table IV** Permeability Characteristics of PEO-Ny610 Membranes

Coagulant (wt/wt/wt) CaCl <sub>2</sub> /MeOH/H <sub>2</sub> O	UFR (mL/m <sup>2</sup> h mmHg)	Urea (10 <sup>-4</sup> cm/min)	Vitamin B <sub>12</sub> (10 <sup>-4</sup> cm/min)
0 : 2 : 8	19	245	37
0 : 3 : 7	36	197	39
0 : 4 : 6	85	— <sup>a</sup>	—
1 : 3 : 7	60	—	—
2 : 3 : 7	74	—	—

<sup>a</sup> Not measured.

It is obvious from the results on PPO-Ny610, PEO-Ny610, and homo Ny610 membranes that the permeability characteristics are affected strongly by the surface top skin layer of the membrane composed of crystal spherulites and the hydrophilicity of the polymer. In semicrystalline polyether-segmented nylon, it is difficult to avoid the formation of this skin layer, and thus the permeation of the low- and middle-

molecular weight substances through the membrane are controlled by the skin layer. Therefore, the rather low permeability performances are exhibited even in hydrophilic PEO-Ny610 membrane. These results also indicate that the membrane having the excellent permeability characteristics will be prepared by the material possessing the low crystallinity or amorphous state.



**Figure 3** SEM micrographs of homo Ny610 membrane. Coagulant is methanol/water 4 : 6 (wt/wt). (a) Cross section, (b) magnified micrograph of cross section, (c) top surface, (d) magnified micrograph of top surface.



**Table V UFR of homo Ny610 Membrane**

Coagulant (wt/wt) MeOH/H <sub>2</sub> O	URF (mL/m <sup>2</sup> h mmHg)
4 : 6	5

## CONCLUSIONS

The asymmetric membranes of polyether-segmented aliphatic nylon were prepared by the phase inversion method. The morphologies and the permeability characteristics of the membranes were investigated. PE-Ny610 used are PPO-Ny610 containing 25 wt % PPO and PEO-Ny610 containing 15 wt % PEO. The polymer solvent and coagulant were formic acid and calcium chloride/methanol/water mixture, respectively. The morphologies of both membranes in the cross section exhibit the cellular porous structures due to liquid-liquid phase separation. On the other hand, the structures of top surfaces are mainly composed of the crystalline spherulite due to liquid-solid phase separation. These morphologies are little affected by the composition ratio of the coagulant, calcium chloride/methanol/water mixture. The permeability of urea is in the range from 73 to  $138 \times 10^{-4}$  cm/min for the PPO-Ny610 membranes and in the range from 197 to  $245 \times 10^{-4}$  cm/min for the PEO-Ny610 membranes. The permeability of vitamin B<sub>12</sub> as a model of toxic middle molecular weight substance through the membrane is in the range from 10 to  $25 \times 10^{-4}$  cm/min for the PPO-Ny610 membrane, and is  $\sim 38 \times 10^{-4}$  cm/min for PEO-Ny610 membrane. The ultrafiltration rates (UFR) in both membranes increase with the increase of the methanol content or the calcium chloride content in the coagulant. This suggests that the soft coagulation brings about the increase of the UFR. PEO-Ny610 membrane has shown superior membrane performances to the PPO-Ny610 membrane because of the top surface morphology of the membrane and the more hydrophilic property of the PEO-Ny610 membranes. These performances are comparable to those of the commercialized regenerated cellulose membrane. The facts that the effect of the

coagulation condition on the solute permeability characteristics is small and that the top surface has a skin layer composed of polygon plates in spite of any coagulation condition indicate that the permeability characteristics are controlled by the skin layer structure at the top surface. Therefore, it will be difficult to improve the solute permeability dramatically using semicrystalline polyether-segmented nylon.

The effect of PEO content in PEO-Ny610 on the nonthrombogenicity was investigated and it is concluded that PEO-Ny610 having  $> 10$  wt % PEO shows a good nonthrombogenicity equal to PPO-Ny610.

The authors thank Tomomich Nakazaki for his help with the synthesis of poly(ethylene oxide)-segmented nylon 610. The authors also thank Dr. N. Yui (Japan Advanced Institute of Science and Technology), Dr. N. Ogata (Sophia University, Japan), Dr. K. Kataoka (Science University of Tokyo, Japan), Dr. T. Okano (Tokyo Women's Medical College, Japan), and Dr. Y. Sakurai (Tokyo Women's Medical College, Japan) for their helpful discussions.

## REFERENCES

1. L. P. Cheng, A. H. Dwan, and C. C. Gryte, *J. Polym. Sci., B*, **33**, 211 (1995).
2. N. Yui, K. Sanui, N. Ogata, K. Kataoka, T. Okano, and Y. Sakurai, *Jpn. J. Art. Org.*, **10**, 1070 (1981).
3. N. Yui, J. Tanaka, K. Sanui, and N. Ogata, *Makromol. Chem.*, **185**, 2259 (1984).
4. N. Yui, K. Sanui, N. Ogata, K. Kataoka, T. Okano, and Y. Sakurai, *J. Biomed. Mater. Res.*, **20**, 929 (1986).
5. T. Aoki, N. Ogata, N. Yui, K. Kataoka, and Y. Sakurai, *Jpn. J. Art. Org.*, **16**, 1395 (1987).
6. N. Yui, K. Kataoka, Y. Sakurai, T. Aoki, K. Sanui, and N. Ogata, *Biomaterials*, **9**, 225 (1988).
7. Y. Takei, N. Yui, A. Maruyama, K. Sanui, Y. Sakurai, and N. Ogata, *J. Biomater. Sci. Polym. Ed.*, **6**, 149 (1994).
8. Y. Yamashita, A. Mochizuki, N. Yui, N. Ogata, K. Kataoka, T. Okano, and Y. Sakurai, *Surface Science of Crystalline Polymers*, Kodansha Scientific, Tokyo, Japan, 1996, p. 195.
9. Y. Seita, A. Mochizuki, M. Nakagawa, K. Takashi, and S. Yamashita, *J. Appl. Polym. Sci.*, **65**, 1703 (1997).