

# Polyether-Segmented Nylon Hemodialysis Membranes. IV. Membrane Morphologies and Permeability Characteristics of Dialysis Membrane Composed of Poly(ethylene oxide)-Segmented Ny69/M10

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**ABSTRACT:** Dialysis membrane was prepared by a phase inversion method using a new polyether-segmented nylon which dissolves in common organic solvents such as dimethylsulfoxide. The polyether-segmented nylon contained poly(ethylene oxide) block and nylon block (random copolyamide: Ny69/M10) prepared by sebacic acid, azelaic acid, *m*-xylenediamine, and hexamethylenediamine. The morphologies and permeability characteristics of the membranes were investigated. It was shown by scanning electron microscope observation that the membrane had a fingerlike structure when dimethylsulfoxide was used as a polymer solvent, and a spongelike structure when an additive such as calcium chloride was added to the polymer solution. The high permeability for the solutes such as urea and vitamin B<sub>12</sub> were observed in comparison with the polyether-segmented Ny610 membranes prepared by a phase inversion method. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1731–1737, 1997

**Key words:** dialysis membrane; phase inversion method; solute permeability; membrane morphology; polyether-segmented nylon

## INTRODUCTION

Recently, hemodialysis membrane has been demanding high permeability characteristics and good blood compatibility. The polyether-segmented nylon 610 (PE-Ny610), known as the non-thrombogenic material, had a possibility to give a good hemodialysis membrane. We have already reported on the investigation of PE-Ny610 membranes using poly(tetramethylene oxide)-segmented nylon 610 (PTMO-Ny610), poly(propylene oxide) segmented nylon 610 (PPO-Ny610), and poly(ethylene oxide)-segmented nylon 610 (PEO-Ny610).<sup>1,2</sup> In that article it was clarified that PPO-Ny610 and PTMO-Ny610 dissolve only

in specific solvents, such as formic acid, hexafluoroisopropanol, and methanol saturated with calcium chloride because of their high crystallinity.<sup>1</sup> On the basis of this result, the membranes were prepared by using formic acid as a polymer solvent and calcium chloride/methanol/water mixtures as a coagulant, and it was concluded that these materials showed liquid-solid phase separation at the top surface of the membrane in the membrane formation process, and these membranes did not exhibit enough permeation characteristics. These membrane morphologies coincided with the results reported by Cheng, Dwan, and Gryte.<sup>3</sup> They concluded that aliphatic polyamides such as nylon 66 and nylon 610 had a tendency to give liquid-solid separation in phase inversion. The liquid-solid phase separation is known to be induced strongly by the high crys-

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tallinity of the polymer. Since such membranes have large spherulites in them, high membrane performance is not expected. Therefore, it is important to prevent the top surface from having the skin layer composed of crystalline polygon plates. To avoid liquid-solid phase separation using the PE-Ny as a membrane material, the linear nylon block which gives high crystallinity must change to a nylon block with low crystallinity or stable amorphous state. This modification will also bring about the improvement of the polymer solubility for common organic solvents such as DMSO, dimethylformamide, dimethylacetamide, and *N*-methylpyrrolidone. We have reported previously<sup>4</sup> that the synthesis of a new polyether-segmented nylon 69/M10 had a bending structure in the main chain and concluded that PEO(10%)-Ny69/M10(1 : 9) was the most preferable material for dialysis membranes from the viewpoints of solubility, thermal properties, and nonthrombogenicity. We report the membrane preparation by the phase inversion method using this polymer and the morphologies and permeability characteristics of the membranes.

## EXPERIMENTAL

### Materials

The polyether-segmented nylon, PEO-Ny69/M10, was synthesized according to the method described previously.<sup>4</sup> PEO-Ny69/M10 consists of 10 wt % of poly(ethylene oxide) block (PEO,  $M_n = 2000$ ), and 90 wt % of nylon block (random copolyamide of Ny69 and NyM10), where 6 is hexamethylenediamine, 9 is azelaic acid, *M* is *m*-xylenediamine, and 10 is sebacic acid. The nylon block was prepared by the polycondensation of 10 wt % nylon 69 salt and 90 wt % of nylon M10 salt, and thus the block was a random copolyamide. The relative viscosity of the obtained polyether-segmented nylon was 6.28 in *m*-cresol at 30°C.

### Preparation of Membranes

PEO-Ny69/M10 was dissolved in formic acid, dimethylsulfoxide (DMSO), and DMSO containing calcium chloride with several ratios at 80°C. Membranes were prepared by casting the polymer solution onto a glass plate, then immersing it rapidly into a coagulant bath at 5°C, where the coagulants were the mixtures of methanol/water with the several-composition ratio. After complete precipi-

tation (for 30 min), membranes were taken out of the coagulant bath and immersed in ultrapure water to remove the solvent and to keep the membrane structures.

### SEM Observation

The wet membranes were immersed into liquid nitrogen. The frozen membranes were fractured in liquid nitrogen and then 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).

### Membrane Performance

As has been reported,<sup>4</sup> the membrane performances were investigated in viewpoints of the ultrafiltration rate (UFR) of water and the permeation of low- and middle-molecular weight substances, urea and vitamin B<sub>12</sub>, respectively. Brief measurement methods are described below. UFR was measured with an ultrafiltration cell (Advantec UHP-43) at the pressure of 250 mmHg using pure water and was calculated from eq. (1).

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

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. (2) under the assumption of neglecting liquid resistance of both sides of the membrane.

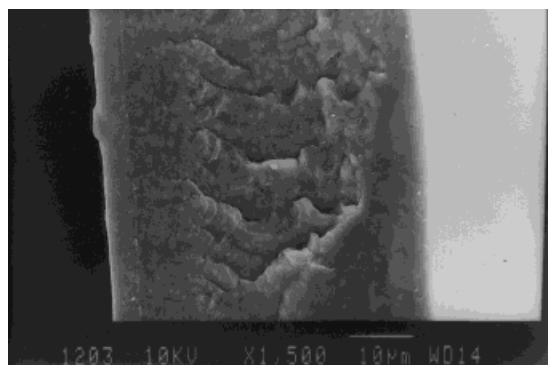
$$P = \ln[\Delta C(t_1)/\Delta C(t_2)] / [S(1/v_1 + 1/v_2)(t_2 - t_1)] \quad (\text{cm/min}) \quad (2)$$

where *t*<sub>1</sub> and *t*<sub>2</sub> 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 time, *t*<sub>1</sub> and *t*<sub>2</sub>. *v*<sub>1</sub> and *v*<sub>2</sub> are the solution volumes (50 cm<sup>3</sup>) in each cell. *S* is the membrane area (10 cm<sup>2</sup>).

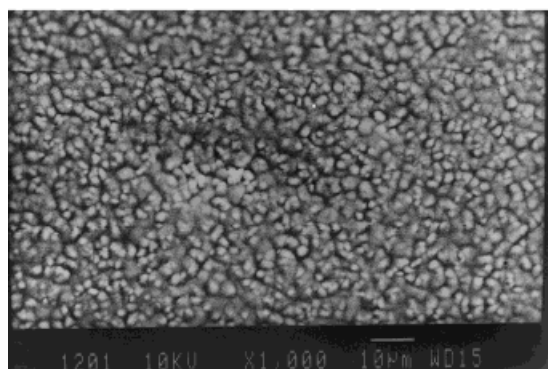
## RESULTS AND DISCUSSION

### Membranes Cast from Formic Acid Solution

The morphologies of the membranes prepared by formic acid as a polymer solvent, which is the



(a)

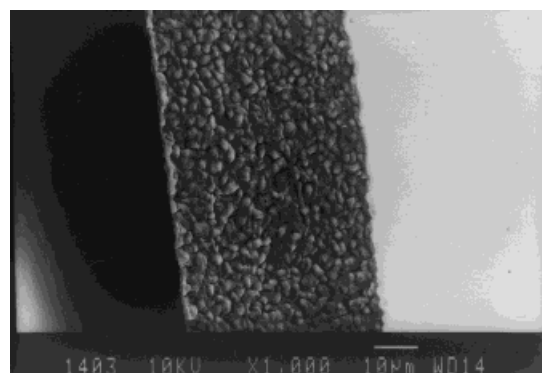


(b)

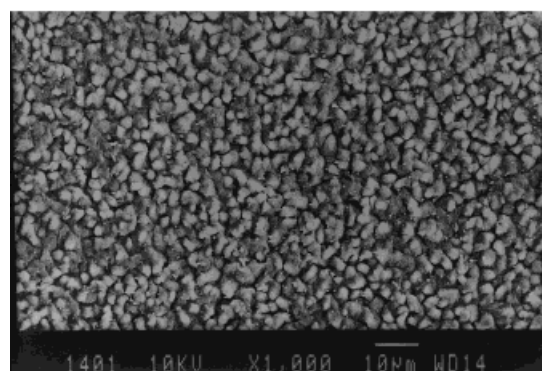
**Figure 1** SEM micrographs of PEO-Ny69/10 membrane. Solvent: formic acid; polymer concentration: 20 wt %; coagulant: methanol/water 30 : 70 (wt/wt). (a) Cross section, (b) top surface.

most common organic solvent for nylon, were investigated by using SEM. The coagulant is methanol/water mixtures and the composition ratio is varied from 30 : 70 to 70 : 30 (wt/wt). The representative morphologies of the membranes are shown in Figures 1 and 2, where the composition ratios of coagulants are 30 : 70 and 70 : 30 (wt/wt), respectively. The structures of the membranes in cross sections are the spherulite ones and the increase of the methanol ration in the coagulant brings about the obvious spherulite structure in the cross section. These results indicate that in the phase inversion process, liquid-solid phase separation occurs dominantly. It is known that liquid-solid phase separation takes place mainly when a slow precipitation occurs in the process. The reason for the predominant liquid-solid phase separation will be explained as follows. As formic acid is a very good solvent for

PEO-Ny69/M10 and prevents the rapid formation of hydrogen bonding between the amide groups of the polymer in the membrane formation process, the extremely gentle coagulation occurs and the crystallization proceeds. Moreover, the increase of the methanol ratio in coagulant means the decrease of the coagulating ability of the bath, so that slower coagulation is brought about. Thus, the spherulite structure in cross section is emphasized. It is predicted by the previous results observed in polyether-segmented Ny610 (PE-Ny610) membranes that PEO-Ny69/M10 membranes having these surface morphologies will not give high permeability characteristics. In fact, the permeability of vitamin B<sub>12</sub> is not good, as shown in Table I, and these values are close to those of PEO-Ny610 membrane containing 15 wt % of PEO, shown in Table II.



(a)



(b)

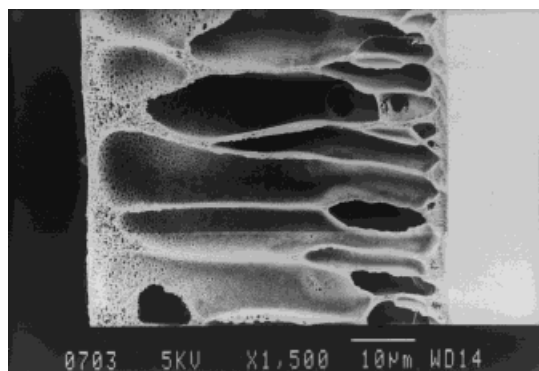
**Figure 2** SEM micrographs of PEO-Ny69/10 membrane. Solvent: formic acid; polymer concentration: 20 wt %; coagulant: methanol/water 70 : 30 (wt/wt). (a) Cross section, (b) top surface.

**Table I Permeability Characteristics of PEO-Ny69/M10 Membranes**

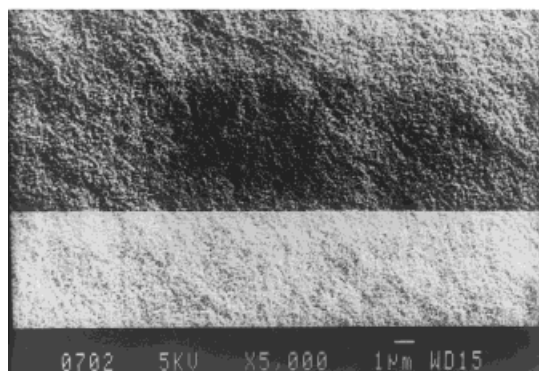
Coagulant Composition MeOH/H <sub>2</sub> O (wt/wt)	UFR (mL/m <sup>2</sup> h mmHg)	Vitamin B <sub>12</sub> (10 <sup>-4</sup> cm/min)
3/7	3	— <sup>a</sup>
5/5	16	42
7/3	53	63

<sup>a</sup> Not measured.**Membranes Cast from DMSO Solution**

The results mentioned above suggest that a good solvent for the polymer brings about liquid-solid phase separation and that a poor solvent should be used to realize liquid-liquid phase separation or rapid coagulation. In a previous report, we reported that PEO-Ny69/M10 dissolved in hot DMSO and gave a stable solution.<sup>4</sup> The fact that DMSO cannot dissolve the polymer at room temperature indicates that DMSO is a poor solvent for this polymer. Hence, the preparation of the membrane was investigated by using DMSO as a solvent and methanol/water mixtures as a coagulant whose composition ratios were varied from 30 : 70 to 70 : 30 (wt/wt). The morphologies of the membranes were observed by SEM. The representative micrographs of the membrane prepared by using the coagulant [methanol/water 30 : 70 (wt/wt)] is shown in Figure 3. The micrograph of the cross section [Fig. 3(a)] indicates that DMSO solution gives the fingerlike structure. The SEM observation of the top surface [Fig. 3(b)] indicates that the membrane has no polygon plate surface, unlike the top surface structure of the PE-Ny610 membranes. Almost all the same morphologies in the cross section and the top surface were observed in the membranes prepared



(a)



(b)

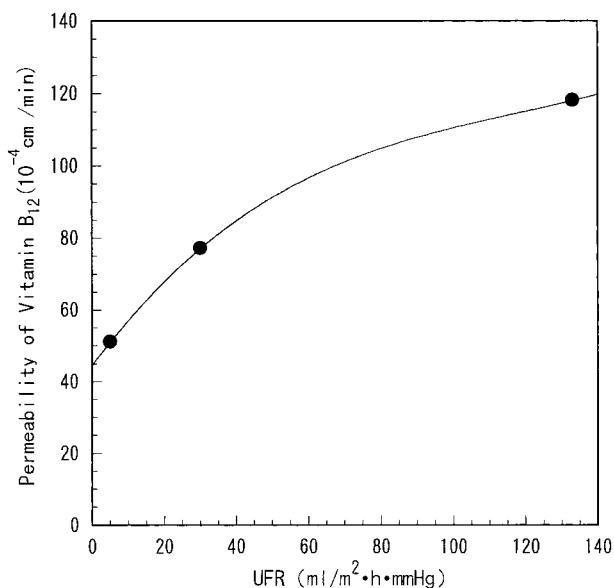
**Figure 3** SEM micrographs of PEO-Ny69/10 membrane. Solvent: DMSO; polymer concentration: 16 wt %; coagulant: methanol/water 30 : 70 (wt/wt). (a) Cross section, (b) top surface.

by the coagulants with other composition ratios. These results indicate that liquid-liquid phase separation occurs dominantly in the coagulating process, and the composition ratio of the coagulant has little effect on the formation of membrane structure.

**Table II Permeability Characteristics of PEO-Ny69/M10**

Membrane	Coagulant (wt/wt) 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)
PEO-Ny69/M10	30 : 70	5	354	51
	50 : 50	30	391	77
	70 : 30	133	379	118
PEO-Ny610 <sup>a</sup>	20 : 80	19	245	37
	30 : 70	36	197	39

<sup>a</sup> PEO content is 15 wt %. These results have been reported previously (ref. 2).



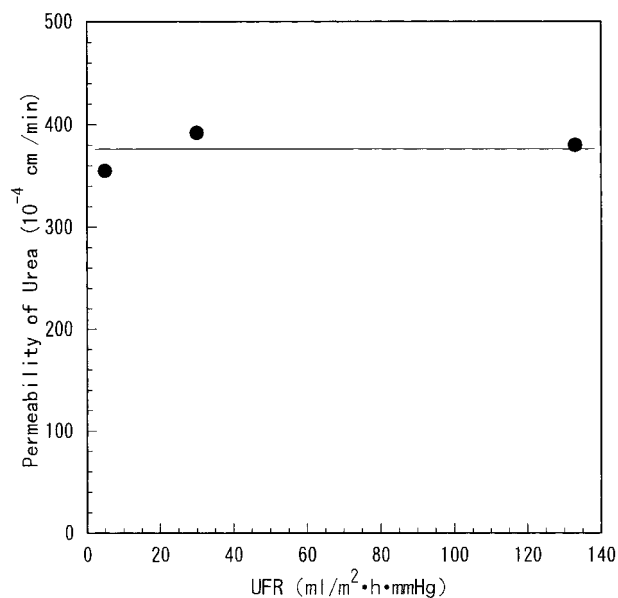
**Figure 4** Relationship between permeability of vitamin B<sub>12</sub> and UFR. The permeability characteristics used are shown in Table II.

Permeability characteristics of the PEO-Ny69/M10 membranes with the finger structure are discussed below. The solutes used were urea and vitamin B<sub>12</sub> as low- and middle-molecular weight substances, respectively. The results are listed in Table II together with the results of PEO-Ny610, which have been reported.<sup>2</sup> On the basis of the table, the solute permeabilities are plotted against the UFR and the results are shown in Figures 4 and 5. The UFR of the PEO-Ny69/M10 membrane increases from 5 to 133 mL/m<sup>2</sup> h mmHg with an increase of the methanol content in the coagulant in the range of methanol/water ratio from 30 : 70 to 70 : 30 (wt/wt). This result and the fact that the increase of the methanol ratio in the coagulant increases the solubility of the coagulant indicate that the mild coagulation brings about the increase of the UFR. The increase of the UFR caused by the soft coagulation have been observed in PPO-Ny610 and PEO-Ny610 membranes, as has been reported previously.<sup>1,2</sup> Next, the solute permeabilities are described. The permeability of vitamin B<sub>12</sub> for the PEO-Ny69/M10 membrane increases from 51 to 118 × 10<sup>-4</sup> cm/min with the increase of the UFR from 5 to 133 mL/m<sup>2</sup> h mmHg. On the other hand, in the PEO-Ny610 membrane, the permeability of vitamin B<sub>12</sub> is not affected by the UFR and stays constant, ~ 40 × 10<sup>-4</sup> cm/min. The permeabilities of urea are almost all constant for any membranes with various UFRs. For the PEO-Ny69/M10 mem-

brane, the permeability of urea is ~ 380 × 10<sup>-4</sup> cm/min, and for the PEO-Ny610 membrane, it is ~ 250 × 10<sup>-4</sup> cm/min. Therefore, it is concluded that the permeability characteristics of PEO-Ny69/M10 membrane is significantly superior to that of PEO-Ny610 membrane. The reason is explained by their morphologies. While the PEO-Ny69/M10 membranes have fingerlike structures in the cross section and have the smooth top surface (no crystalline polygon plate in the top surface), the PEO-Ny610 membranes have cellular porous structures in the cross section and polygon plate top surface, which are not preferable membrane structures for the solute permeation as described previously.<sup>2</sup>

#### Effect of Additives on the Membrane Structure

The fingerlike structure membrane has several weak points, for example, weak mechanical properties, and leakage because of the existence of a macro void close to the thin active layer. Therefore, the spongelike structure is preferable for hemodialysis membranes. It is well known that the third components (additives) are added to the polymer solution in order to improve or change the membrane morphologies and permeability characteristics. These additives are usually inorganic salts such as lithium chloride, calcium chloride, and magnesium perchlorate, and low molec-



**Figure 5** Relationship between permeability of urea and UFR. The permeability characteristics used are shown in Table II.

**Table III Effect of Calcium Chloride as an Additive on Membrane Morphology**

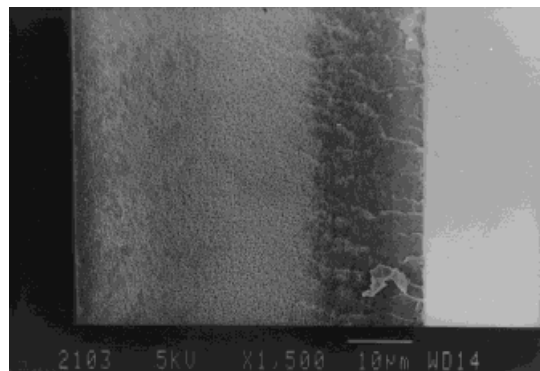
Coagulant [methanol/ water (wt/wt)]	Amounts of Additives		
	30 Parts	50 Parts	100 Parts
30 : 70	finger	finger	sponge
50 : 50	finger	finger	sponge
70 : 30	finger	finger	sponge

ular weight organic substances such as urea. In this study, the effect of calcium chloride as an additive on the membrane morphologies was investigated, where the amount of additive was presented as the weight ratio to the polymer weight in the polymer solution, and is varied from 30 to 100 parts. One hundred parts means that the amount of calcium chloride added is equal to the weight of the polymer in the solution. The results are listed and shown in Table III and Figure 6. Table III indicates that the spongelike structure is observed when the amount of the additives is 100 parts and that the effect of the additive is hardly observed in the case that the amount of the additive is <50 parts. Figure 6 shows the representative cross-section view which is obtained by using 100 parts of calcium chloride as the additive. The cross section of the membrane has a gradient spongelike structure, that is, the region close to the top surface has a dense structure and the region close to the bottom surface which contacted with the glass plate is a loose structure. The top surface of the membrane is smooth and has no structure. The permeability characteristics of the PEO-Ny69/M10 membrane prepared by using the polymer solution with 100 parts of calcium chloride as the additive and methanol/water 30 : 70 mixtures as the coagulant were evaluated. The permeability coefficient of vitamin B<sub>12</sub> for the membrane was  $71 \times 10^{-4}$  cm/min, when the UFR was 31 mL/m<sup>2</sup> h mmHg. The relation between this permeability coefficient and the UFR corresponds to the results obtained in the fingerlike membranes as shown in Figure 4.

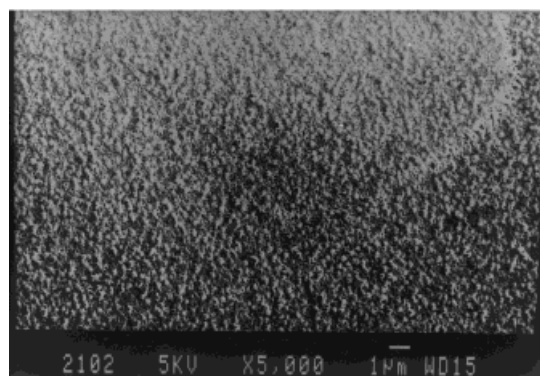
## CONCLUSION

A dialysis membrane was prepared by a phase inversion method and its structures and permeability characteristics were investigated using a new polyether-segmented nylon which dissolves

in common organic solvents such as DMSO. The polyether-segmented nylon consists of 10 wt % of poly(ethylene oxide) block and 90 wt % of nylon block (random copolyamide: Ny69/M10). It is shown by SEM observation that the membrane has a fingerlike structure when DMSO is used as a polymer solvent and that it has a spongelike structure when an additive such as calcium chloride is added to the polymer solution. The top surfaces of the both membranes are smooth and they do not have polygon plate skin layers. The composition ratio of the coagulant (methanol/water mixture) has little effect on the morphologies. The finger and spongelike structures indicate that liquid-liquid phase separation occurs dominantly in the membrane formation process. On the other hand, when formic acid is used as a polymer solvent, spherulite polygon plate structure and spherulite are observed at the top surface of the



(a)



(b)

**Figure 6** SEM micrograph of PEO-Ny69/M10 membrane. Solvent: DMSO; additive: calcium chloride 100 parts; polymer concentration: 16 wt %; coagulant: methanol/water 30 : 70 (wt/wt). (a) Cross section, (b) top surface.

membrane and in the cross section, respectively. In this case, liquid-solid phase separation occurs, because formic acid is a good solvent, and thus the extremely mild coagulation has taken place. The permeability coefficient of PEO-Ny69/M10 membrane prepared by using DMSO solution without an additive for urea is nearly constant and stayed in the range of  $355\text{--}395 \times 10^{-4}$  cm/min in spite of the variation of UFR. The permeability coefficient of it for vitamin B<sub>12</sub> is increased from 50 to  $120 \times 10^{-4}$  cm/min, with an increase of the UFR from 5 to 133 mL/m<sup>2</sup> h mmHg. These membrane performances are superior to PEO-Ny610 membrane performances.

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