Polyether-Segmented Nylon Hemodialysis Membranes. I. Preparation and Permeability Characteristics of Polyether-Segmented Nylon 610 Hemodialysis Membrane

YUKIO SEITA, AKIRA MOCHIZUKI, MITSUHIDE NAKAGAWA, KATSUHIRO TAKANASHI, SHUZO YAMASHITA

Research and Development Center, Terumo Corporation, Inokuchi 1500, Nakaimachi, Ashigarakami-gun, Kanagawa
259-01, Japan

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ABSTRACT: The effect of the coagulation condition in the phase inversion method on the permeability characteristics of poly(propylene oxide) or poly(tetramethylene oxide)-segmented nylon 610 (PPO-Ny610 or PTMO-Ny610) hemodialysis membranes, the stability of the membrane performance, and the mechanical strength were investigated. The polymers were dissolved in a solvent such as formic acid and methanol saturated with calcium chloride, and thus PPO-Ny610 and PTMO-Ny610 membranes were prepared using formic acid and a calcium chloride/methanol/water mixture as a polymer solvent and a coagulant, respectively. It is concluded that PPO-Ny610 membrane has better permeability characteristics than PTMO-Ny610 membrane, and possesses additional properties for hemodialysis membranes such as mechanical properties and permeability stability in the drying and sterilizing processes. Furthermore, the blood compatibilities of PPO-Ny610 and PTMO-Ny610 membranes were superior to regenerated cellulose membranes on the basis of the result of platelet adhesion test. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 1703–1711, 1997

Key words: dialysis membrane; polyether-segmented nylon; solute permeability; protein adsorption; ultrafiltration rate

INTRODUCTION

Today, various polymers are widely applied in clinical fields as biomedical materials. With the progress of prosthetic surgery, blood-compatible polymers have been increasingly demanded, and a large number of investigations have been carried out. In the field of hemodialysis, various polymers such as cellulose, cellulose acetate, polysulfone, polyacrylonitrile, nylon, polymethylmethacrylate, and ethylene–vinylalcohol copolymer have been applied to practical use as membrane materials, but all of these polymers are not designed as blood-compatible materials.

In the basic research of blood-compatible materials, much interest has been devoted to the surface structure and properties of block-copolymers by the Tokyo Women's Medical College group. Okano et al. studied in detail and reported about the amphiphilic block-copolymers composed of 2-hydroxyethyl methacrylate (HEMA) and styrene (St).[1–5] The block-copolymers were found to have microphase-separated structures composed of hydrophilic domains (polyHEMA block) and hydrophobic domains (polySt block). Its film surface showed an excellent blood compatibility. Moreover, the unique interactions with cells on the HEMA-St block-copolymer surface have been observed. Yui et al. have studied systematically on the nonthrombogenicity of various polyether-segmented nylons in terms of estimating platelet ac-

Correspondence to: A. Mochizuki.
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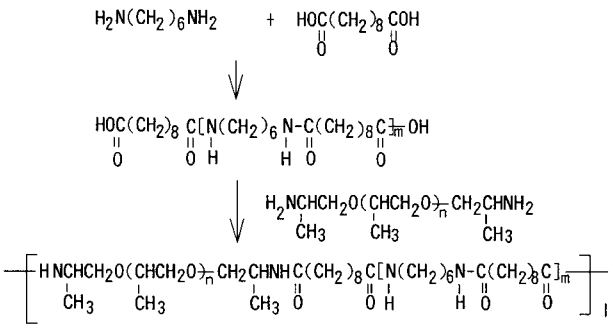

Figure 1 Synthetic route of PPO-Ny610 by melt polycondensation.

tivation on their surfaces.[6–11] They found that the platelet activation was affected by the surface structure of the block-copolymers, which have the crystalline-amorphous microphase-separated structure, and concluded that poly(propylene oxide) (PPO) segmented nylon 610 containing 25 wt % PPO, (PPO-Ny610), and poly(tetramethylene oxide) (PTMO)-segmented nylon 610 containing 45 wt % PTMO, (PTMO-Ny610), showed the least thrombogenicity. While HEMA-St block-copolymer has a decisive defect (poor mechanical properties), polyether-segmented nylon 610 (PE-Ny610), such as PPO-Ny610 and PTMO-Ny610, has excellent mechanical properties. Yamashita et al.[12] paid attention to this blood-compatible copolymer as a material of an intravenous catheter, and have succeeded in applying PPO-Ny610 to practical use.

We have paid attention to these blood-compatible block-copolymers as materials of hemodialysis membrane. In this paper, we have reported on the membrane formation by the phase inversion method, the permeability characteristics, the stability of the membrane performance, and the mechanical properties of PE-Ny610 membrane.

EXPERIMENTAL

Preparation of PPO-Ny610 and PTMO-Ny610

The synthetic routes of PPO-Ny610, having 25 wt % PPO, and PTMO-Ny610, having 45 wt % PTMO, are schematically shown in Figures 1 and 2, and the method is as follows. The aqueous solution of the salt of nylon 610 and sebacic acid corresponding to the amount of α,ω-bisaminoisopropyl poly(propylene oxide) (diamino-PPO, $M_w = 2000$, Sun Techno Chemical Co. Ltd., Japan) (25 wt %) or α,ω-bisaminopropyl poly(tetramethylene oxide) (diamino-PTMO, $M_w = 2100$, BASF Aktiengeselschaft, Germany) (45 wt %) were reacted in an autoclave at 240°C for 2 h under 10 kg/cm^2 pressure with stirring, followed by adding diamino-PPO or diamino-PTMO, and the reaction was continued for 2 h under the same condition. After release of the pressure, the reaction was continued under reduced pressure at 240°C for 2 h. The melted polymer was extruded from the autoclave and pelletized after cooling with water. The number average molecular weights of synthesized PPO-Ny610 and PTMO-Ny610 were 31,000 and 29,000, respectively, which were calculated from the concentration of end groups.

Solubility of PE-Ny610

Translucent films of PE-Ny610 obtained by the melt process were immersed in various solvents, shown in Table I, at 70, 90, and 100°C, and the solubility was evaluated.

Preparation of Membranes

Dried PE-Ny610 was dissolved in formic acid at 60°C, whose concentration was 22 wt %. Immediately after the formic acid solution of PE-Ny610 kept at 60°C was cast onto a glass plate controlled at 30°C, it was immersed in the coagulant (calcium chloride/methanol/water) mixture for 30 min and the membrane thus obtained was washed in ultrapure water.

Glycerin Treatment of Membranes

The PPO-Ny610 membranes were plasticized by glycerin to dry up the membranes. The method was that the membranes were soaked in the glycerin solution whose concentrations were 5, 10, and 20 wt % for 5 min, and then dried up at 60°C in the air oven.

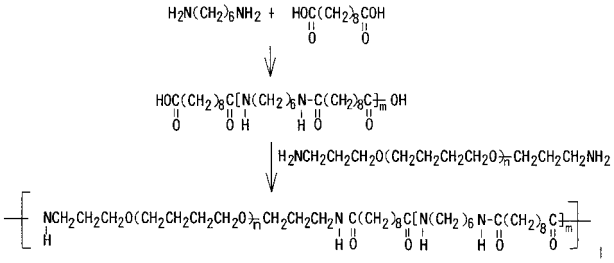

Figure 2 Synthetic route of PTMO-Ny610 by melt polycondensation.

Table I Solubility of PE-Ny610

	70°C	90°C		100°C	
Solvent[a]	PPO-Ny610	PTMO-Ny610	PPO-Ny610	PTMO-Ny610	PPO-Ny610
DMF	○	△	◎	○	◎
NMP	○	◎	◎	◎	◎
EG	—	—	—	—	○
DMSO	—	—	○	△	—
MeOH	○	—	—	—	—
MeOH saturated with $CaCl_2$	solved	—	—	—	—
Formic acid	solved	—	—	—	—
Hexafluoroisopropanol	solved	—	—	—	—

(◎) highly swelled; (○) medium-swelled; (△) low-swelled.
[a] DMF, *N,N*-dimethylformamide; NMP, *N*-methylpyrrolidone; EG, ethyleneglycol; DMSO, dimethylsulfoxide; MeOH, methanol.

Evaluation of Permeability Characteristics of Membranes

Ultrafiltration Rate (UFR)

The measurement of UFR was carried out by using a membrane holder (Advantec UHP-43), whose effective inner diameter is 43 mm, at 250 mmHg and 37°C. UFR was calculated from eq. (1).

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

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

Solute Permeability

A glass cell consisting of two compartments was used. The volume of each compartment is 50 mL. A membrane whose effective area was 10.0 cm^2 was clamped between two compartments. One of the compartment was filled with ultrapure water and the other was filled with urea, vitamin B_{12}, or myoglobin solution, where their concentrations were 100 mg/dL, 5 mg/dL, and 5 mg/dL, respectively. These solutes were used singly. The solutions in the compartments were stirred with a magnetic stirrer during the measurements at room temperature and were sampled at 30 min and 150 min after the start of the test. The determinations of the concentrations of the solutes were carried out by using the urease-indophenol method for urea and the measurement of the direct ultraviolet absorbance for vitamin B_{12} and myoglobin. The apparent solute permeability was calculated from eq. (2) under the assumption of neglecting liquid resistance of both sides of the membrane.

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

where t_1 and t_2 are sampling times (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_1 and t_2. V_1 and v_2 are the solution volume (cm^3) in each cell and they are 50 cm^3. S is the membrane area (cm^2) and 10 cm^2.

Adsorption of β_2-Microglobulin

The 43-mm diameter membrane was soaked in 20 mL of the Ecum (extracorporeal ultrafiltration method) solution where the concentration of β_2-microglobulin was 13.5 mg/L with stirring at 37°C. Ecum solution was the dialysate obtained from the clinical hemodialysis. After 2, 3, 4, and 5 h, 1 mL of the solution was sampled and its concentration was determined by latex photometric immunoassay. The adsorption amount of β_2-microglobulin onto the membrane was calculated by the decrease of the concentration in the solution.

Adsorption of Myoglobulin

The 43-mm diameter membrane was soaked in 100 mL of the myoglobin solution where the concentration was 10 mg/dL with stirring at 37°C. After 30, 60, 90, and 150 min, 1 mL of the solution was sampled and its concentration was determined by the measurement of the ultraviolet ab-

sorbance at 408 nm. The adsorption amount of myoglobin onto the membrane was calculated by the decrease of the concentration in the solution.

Evaluation of *in Vitro* Nonthrombogenicity

The evaluation of nonthrombogenicity *in vitro* was carried out by the adhesion of platelet onto the membrane surface. Citrated platelet-rich human plasmas (PRP), which had been collected from volunteer donors, were placed on the membrane or a polymer film and kept for 30 min at room temperature under static condition. After rinsing the membranes three times with phosphate buffer, they were soaked in aqueous glutaraldehyde solution to fix the cells. The membranes were freeze-dried after washing. The samples were observed under the scanning electron microscope (SEM) at a magnification of 1,000, and five micrographs of the membrane surface were taken at random. Each picture had an area of 100 μm $\times$ 80 μm. Adhering platelets in each picture were counted and the numbers summed up for five pictures are the numbers of adhering platelets.

RESULTS AND DISCUSSION

First of all, the solubility of PE-Ny610 for organic solvents was investigated to prepare PE-Ny610 hemodialysis membranes. For this purpose, the transparent films of PE-Ny610 obtained by heat press at 240°C were immersed in various organic solvents at controlled temperature for 5 min. The results are shown in Table I. Formic acid, hexafluoroisopropanol (HFIP), and methanol (MeOH) saturated with calcium chloride dissolved the PE-Ny610, and dimethylformamide (DMF), *N*-methylpyrrolidone (NMP), dimethylsulfoxide (DMSO) and methanol did not dissolve the PE-Ny610, but could swell them at high temperature (>70°C). On the basis of these results, formic acid and calcium chloride/methanol/water mixture were chosen as a polymer solvent and as a coagulant, respectively, and asymmetric membranes of PE-Ny610 were prepared by the phase inversion method. The thickness of the PTMO-Ny610 membranes obtained is in the range of 45–56 μm and that of the PPO-Ny610 membrane is in the range of 37–50 μm.

The permeability characteristics of PTMO-Ny610 and PPO-Ny610 are discussed below. To evaluate the membrane performance, it was important to choose model substances which permeated through the membrane. As the first evaluation, urea and vitamin B_{12}, as low- and middle-molecular weight substances, respectively, were chosen. Moreover, it was important to adjust the UFR when the membrane performances in dialysis were compared. For hemodialysis membranes, it is expected that the UFR is in the range of 10–50 mL/m^2 h mmHg. So, to prepare the membrane having the UFR with this range, the effects of the coagulant composition ratio on the UFR were investigated using calcium chloride/methanol/water mixture as a coagulant. The results for PTMO-Ny610 membrane and PPO-Ny610 membrane are listed in Tables II and III, respectively. Table II indicates that the increase of the methanol and calcium chloride content in the coagulant brings about the increase of the UFR from 1.1 to 65 mL/m^2 h mmHg. Since calcium chloride/methanol mixture is a solvent for PE-Ny610 as mentioned above, the increase of the calcium chloride/methanol in the coagulant means that a mild coagulation occurs, that is, the polymer in the dope precipitates slowly in phase inversion. The results suggest that the suitable ratio of the coagulant composition (calcium chloride/methanol/water) in the case of the membrane formation of PTMO-Ny610 is in the range of 2 : 2 : 20–1 : 4 : 20 (wt/wt/wt), which can adjust the UFR in the range of 20–50 mL/m^2 h mmHg. Table II shows that the solute permeability also increases with the increase of calcium chloride/methanol content in the coagulant. The permeability of urea is in the order of 10^{-3} cm/min, and the permeability of vitamin B_{12} is in the order of 10^{-4} cm/min.

The results of the PPO-Ny610 membrane in Table III indicate that the preferable coagulation condition is largely different from that of PTMO-Ny610 membranes, and that the water content in the coagulant is remarkably low to obtain the appropriate UFR. The composition ratio of the coagulant, calcium chloride/methanol/water, giving suitable UFR is in the range of 1–2 : 1–3 : 5–7 (wt/wt/wt). Comparing this composition ratio with the ratio adopted for the preparation of PTMO-Ny610 membrane, the coagulant for PPO-Ny610 is much softer than that for PTMO-Ny610, but the basic tendency for UFR and solute permeabilities are the same as the PTMO-Ny610 membranes. That is, the increase of the good solvent ratio in the coagulant increases the UFR and the solute permeabilities. Furthermore, the solute permeabilities of PPO-Ny610 membranes have better than those of PTMO-Ny610 membranes

Table II Permeability Characteristics of PTMO-Ny610 Membranes

Experimental	Coagulant $CaCl_2$/MeOH/H_2O (wt/wt/wt)	UFR (mL/m^2 h mmHg)	Solute Permeability	
			Urea (10^{-4} cm/min)	Vitamin B_{12} (10^{-4} cm/min)
1	0 : 0 : 1	1.1	0	—
2	2 : 1 : 20	9.0	11	—
3	1 : 1 : 20	27	16	2.6
4	1 : 4 : 20	65	42	6.8
5	regenerated cellulose	3.0	100	20

Coagulant temperature = 5°C.

and are close to those of commercialized regenerated cellulose membrane. The difference of the coagulation condition between PPO-Ny610 membrane and PTMO-Ny610 membrane is due to the difference of the content of the polyether in PE-Ny610. In the membrane formation, PPO-Ny610 can coagulate stronger and faster than PTMO-Ny610, because the content of nylon block in PPO-Ny610 is higher than that in PTMO-Ny610. In addition, as polyether dissolves well in methanol, polyether block prevents the PE-Ny610 from precipitating in the investigated coagulants. Therefore, a strong coagulant is needed for PTMO-Ny610. This strong coagulation will reduce the pore size of the membrane formed in phase inversion, whereas the solute permeability of large molecules such as vitamin B_{12} in PTMO-Ny610 membrane must have been smaller than that in PPO-Ny610 membrane. Based on these results, we focused on PPO-Ny610 membrane and carried out further investigation on it.

The effects of the coagulant composition and temperature of the coagulant in the phase inversion method on the permeability characteristics of PPO-Ny610 membrane were investigated in detail, where formic acid and calcium chloride/methanol/water mixture with 2 : 1 : 5, 2 : 3 : 7, and 1 : 3 : 5 (wt/wt/wt) were used as polymer solvents and coagulants, respectively. The results are shown in Table III and Figure 3. The increase of methanol ratio in the coagulant brings about the increase of the UFR at each coagulant temperature, 5, 10, and 15°C (Fig. 3). The rise of the temperature also causes the increase of the UFR, especially in the case of the methanol-rich coagulants. For example (Table III, no. 3 and 9), the UFR increases from 28 to 63 mL/m^2 h mmHg with the rise of coagulant temperature from 5 to 15°C using the coagulant with calcium chloride/methanol/water 1 : 3 : 5 (wt/wt/wt). The solute permeabilities for urea, vitamin B_{12}, and myoglobin are discussed. Table III indicates that the permeabilities of these solutes increase with increase of the UFR and that the permeabilities of PPO-Ny610 membranes are several times larger than those of PTMO-Ny610 membranes, when the membranes having the same UFR are compared. For example, the permeability for urea and vitamin B_{12} in PPO-Ny610 membrane with 28 mL/m^2 h mmHg of UFR (Table III, no. 3) are 106×10^{-4} and 22×10^{-4} cm/min, respectively, while the coefficients of PTMO-Ny610 membrane with 27 mL/m^2 h mmHg (Table II, no. 3) are 16×10^{-4} and 2.6×10^{-4} cm/min, respectively. From these results it is concluded that the PPO-Ny610 membrane has good permeability characteristics and is superior to regenerated cellulose membrane when the appropriate coagulation condition is adopted.

Since a hemodialyzer usually uses hollow fiber membranes, they must be bundled with polyurethane to make a membrane module. To avoid the side reaction of isocyanate with water, the membranes must be dried up. The drying process sometimes causes the decisive decrease of the permeability characteristics of the membrane in a manufacturing process. The reason for the decrease is the crush of the micropore in the membrane. To maintain the membrane performance in the drying process, it is often carried out that the water in the membrane is substituted with organic liquid such as glycerin before drying (glycerin treatment). On the basis of these facts, the stability of the PPO-Ny610 membrane performance in drying processes was investigated. The effects of a heat treatment, a glycerin treatment, and drying temperature on the retention of the UFR in PPO-Ny610 membranes are discussed below. The results are shown in Figure 4, where the retention of the UFR exhibits the percent of the UFR based on the nontreated membrane (original

Table III Permeability Characteristics of PPO-Ny610 Membranes

Experiment	Coagulant $CaCl_2$/MeOH/H_2O (wt/wt/wt)	Coagulant Temperature (°C)	UFR (mL/m^2 h mmHg)	Solute Permeability		
				Urea (10^{-4} cm/min)	Vitamin B_{12} (10^{-4} cm/min)	Myoglobin (10^{-4} cm/min)
1	2 : 1 : 5 (= 14 : 7 : 35)	5	7.9	40	—	—
2	2 : 3 : 7 (= 10 : 15 : 35)	5	13	72	—	—
3	1 : 3 : 5 (= 7 : 21 : 35)	5	28	106	22	1.1
4	2 : 1 : 5 (= 14 : 7 : 35)	10	6.9	27	—	—
5	2 : 3 : 7 (= 10 : 15 : 35)	10	17	115	24	3.3
6	1 : 3 : 5 (= 7 : 21 : 35)	10	54	137	29	7.2
7	2 : 1 : 5 (= 14 : 7 : 35)	15	7.5	42	—	—
8	2 : 3 : 7 (= 10 : 15 : 35)	15	27	88	23	3.4
9	1 : 3 : 5 (= 7 : 21 : 35)	15	63	129	34	8.3
10	regenerated cellulose	—	27	100	20	—

membrane). First, the effect of the heat treatment on the UFR of the PPO-Ny610 membrane is discussed. The membrane is treated as follows. The membrane is soaked in water at 60°C (heat treatment), soaked in the 20 wt % glycerin solution (glycerin treatment), and then is dried up at 60°C in an air oven. The heat treatment keeps the UFR of the membrane more than 75% of the UFR of the original membrane. On the other hand, when the heat treatment is not carried out, the same drying process reduced the UFR of the membrane to $\sim$ 20% of the original UFR. These results indicate that the heat treatment at 60°C is very effective to maintain the UFR. The retention of the UFR through the heat treatment is due to the fixation of the micropores in the membrane formed in the phase inversion process. This result indicates that the heat treatment is necessary before drying. Next, using the membranes with the heat treatment at 60°C, the effects of the drying temperature and the concentration of the glycerin on the retention of the UFR are discussed. When the membranes were dried at 40°C, there was no remarkable change of UFR in spite of varying the glycerin concentration in the treatment solution, but the drying over 60°C brings about the decrease of the UFR. Especially, the glycerin treatments with 5 and 10 wt % glycerin solutions bring about the drastic decrease of the UFR, and the retentions of both membranes are under 50%. In contrast with these results, the treatment of 20 wt % glycerin solution keeps the UFR of the membrane 75% of the original UFR, even in the drying at 60°C. The concentration of glycerin in the treatment solution is preferable to be over 20 wt %, considering the effectiveness of drying in a practical manufacturing process, where higher drying temperature is desirable. Thus, the effect of the drying temperature on the UFR of the membrane treated with 20 wt % glycerin solution is described. The rise of the drying temperature from 40 to 100°C causes the significant decrease of the UFR, the retention of the UFR decreases to $\sim$ 40% at 100°C. These results indicate that the extremely high temperature of drying must be avoided and the preferable drying temperature is 60°C. It is concluded that the heat treatment at 60°C in water, the treatment with 20 wt % glycerin, and drying at 60°C are applicable to practical use for the membrane drying process.

The mechanical properties of hemodialysis membranes are very important in the assembly of dialyzers and the point of safety in clinical use. The mechanical properties of the regenerated cel-

lulose membrane are by far better than those of synthetic hemodialysis membranes due to its high crystallinity. The mechanical properties of PPO-Ny610 membranes are shown in Table IV together with ethylene–vinylalcohol copolymer membrane[13] which is one of the synthetic hemodialysis membranes already applied in clinical use. Table IV indicates that the PPO-Ny610 membranes have the mechanical properties close to ethylene–vinylalcohol copolymer membrane, and that the mechanical properties depend on the methanol content and temperature of the coagulant. Lower methanol content in the coagulant (calcium chloride/methanol/water 2 : 1 : 5) at 15°C or lower temperature (5°C) of the coagulant (calcium chloride/methanol/water 2 : 3 : 7) give the tensile strength of over 40 kg/cm^2. As a result, it is concluded that PPO-Ny610 membranes have enough mechanical strength for hemodialysis membranes.

The adsorption of myoglobin and β_2-microglobulin onto PPO-Ny610 membrane was investigated and the results are shown in Figures 5 and 6. The amount of adsorbed myoglobin onto PPO-Ny610 membrane was significantly less than regenerated cellulose membrane (Fig. 5). In regenerated cellulose membrane, the amount of absorbed myoglobin increases to 2.2 mg for 150 min, but in PPO-Ny610 membrane, it stays below 0.2 mg for 150 min. The adsorption of β_2-microglobulin onto PPO-Ny610 membrane after dipping in Ecum solution was larger than that of regenerated cellulose membrane, as shown in Figure 6. These results suggest that PPO-Ny610 membrane removes β_2-microglobulin more effectively in clinical use than regenerated cellulose membrane because PPO-Ny610 membrane adsorbs β_2-microglobulin better than regenerated cellulose membrane.

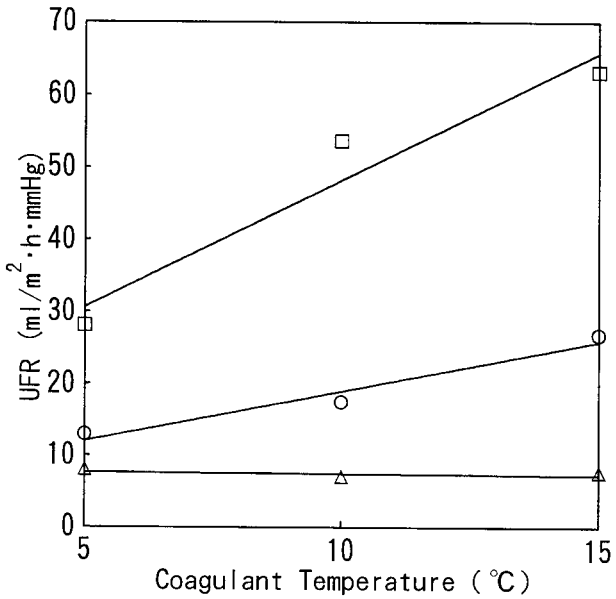

Figure 3 Effect of coagulant composition on UFR of PPO-Ny610 membrane. Coagulant composition ratio ($CaCl_2$/MeOH/H_2O): (△) 2 : 1 : 5, (○) 2 : 3 : 7, (□) 1 : 3 : 5 (wt/wt/wt).

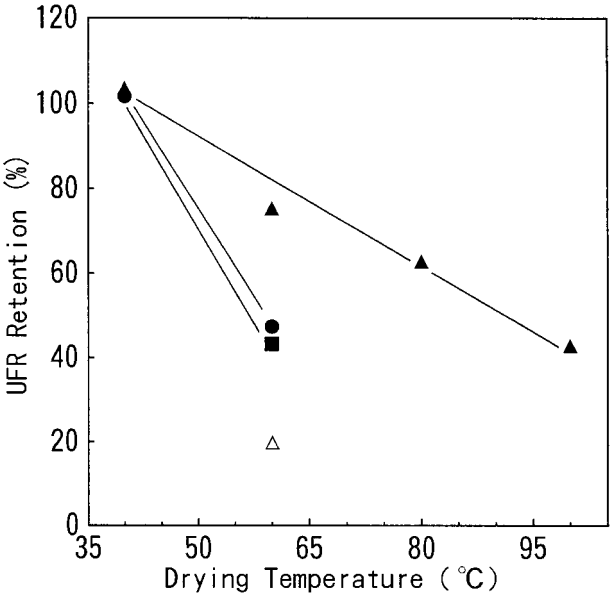

Figure 4 Effect of heat and glycerin treatments on UFR of PPO-Ny610 membranes. The glycerin concentrations in the treatment solution are (▲) 20 wt %, (●) 10 wt %, and (■) 5 wt %, and each membrane is treated with hot water (at 60°C) (heat treatment). (△) glycerin (20 wt %)-treated membrane without heat treatment at 60°C.

The nonthrombogenicity of PE-Ny610 was investigated by the adhesion of platelets onto the polymer surface, and the result is shown in Figure 7. The count of platelets adhered onto the surface of PE-Ny610 membrane was less than that of regenerated cellulose membrane and polypropylene film, which is a positive control. It is expected that PE-Ny610 membrane shows good nonthrombogenicity in clinical use.

CONCLUSION

PE-Ny610, known as a blood-compatible material, has been investigated as a hemodialysis membrane material. First of all, we have investigated

Table IV Mechanical Properties of PPO-Ny610 Membranes

Coagulant $CaCl_2/MeOH/H_2O$ (wt/wt/wt)	Coagulant Temperature (°C)	Strength at Break (kg/cm^2)	Elongation at Break (kg/cm^2)
2 : 1 : 5 (= 14 : 7 : 35)	15	53	22
2 : 3 : 7 (= 10 : 15 : 35)	15	27	15
2 : 3 : 7 (= 10 : 15 : 35)	5	43	42
1 : 3 : 5 (= 7 : 21 : 35)	15	20	8
EVA membrane[a]		32	30

[a] Ethylene/vinylalcohol copolymer membrane; ref. 13.

the solubility of PE-Ny610 for organic solvents to prepare PE-Ny610 hemodialysis membranes. Formic acid, HFIP, and methanol saturated with calcium chloride dissolve PE-Ny610 and DMF, NMP, DMSO, and methanol swell it at high temperature (>70°C). From these results, formic acid and calcium chloride/methanol/water mixture are selected as a polymer solvents and a coagulant, respectively.

PTMO-Ny610 and PPO-Ny610 membranes were prepared by the phase inversion method and their permeability characteristics were investigated. In both membranes, the tendencies that the UFR's and solute permeabilities increase when the mild coagulation was applied were observed. Comparing the solute permeability of PTMO-Ny610 membrane with that of PPO-Ny610 membrane, PPO-Ny610 membrane has better performance than PTMO-Ny610 membrane. PPO-Ny610 membrane has comparatively larger pores through which vitamin B_{12} can permeate than PTMO-Ny610. This must be due to the difference of the polyether content between PPO-Ny610 and PTMO-Ny610. As polyether dissolves in methanol, polyether block prevents the PE-Ny610 from precipitating. Therefore, a stronger coagulation condition is needed for PTMO-Ny610 and will reduce the pore size of the PTMO-Ny610 membrane.

PPO-Ny610 membranes possess the following properties together with good permeability characteristics and performance for the adsorption of proteins: (1) no remarkable permeability decline in the drying process, and (2) good mechanical

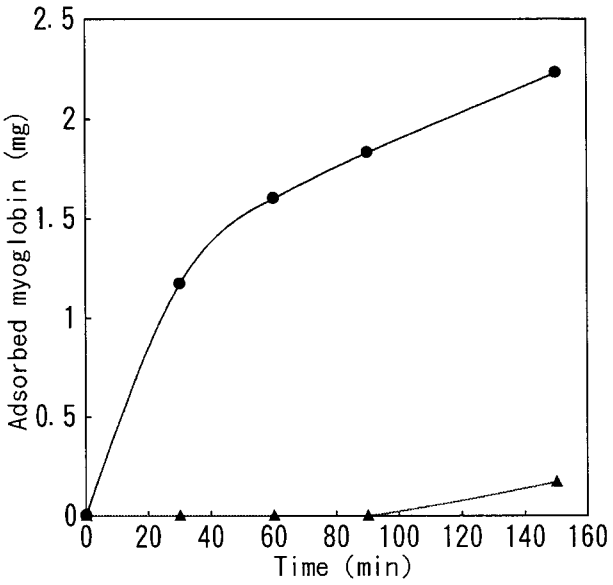

Figure 5 Adsorption of myoglobin onto membranes. (▲) PPO-Ny610 membrane, (●) regenerated cellulose membrane.

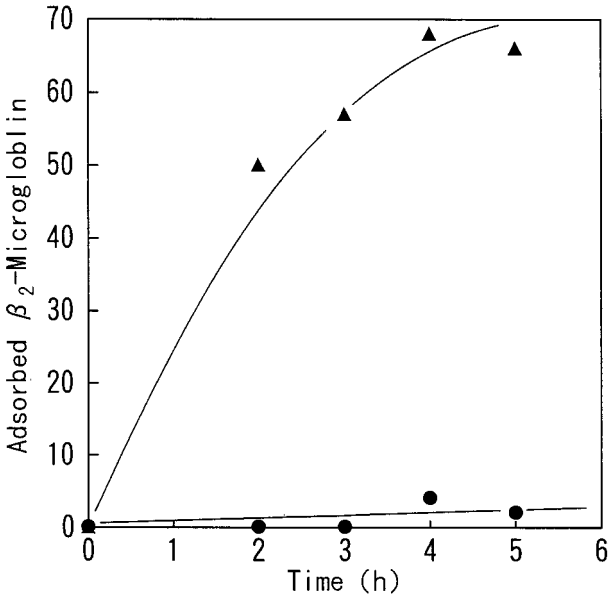

Figure 6 Adsorption of β_2-microglobulin onto membranes. (▲) PPO-Ny610 membrane, (●) regenerated cellulose membrane.

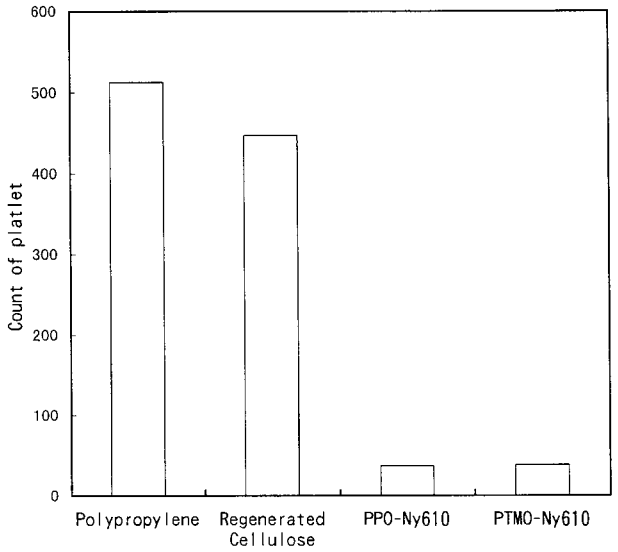

Figure 7 Count of adhering platelet onto polymer surface.

properties. Furthermore, PE-Ny610 membranes prepared by the phase inversion method have shown good nonthrombogenicity from the result of the platelet adhesion test on the membrane surface.

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