

Preparation of Thermal- and Chemical-Resistant Polymeric Membrane via Thermally Induced Phase Separation

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Abstract: Microporous hollow fiber membranes were prepared via thermally induced phase separation process by using the vessel-type melt spinning apparatus. Polypropylene which has good thermal and chemical resistance was used as a membrane material, and soybean oil and dioctylphthalate were used as diluents. Effects of operating parameters were examined on the structure variation of the membrane. As the coagulation bath temperature increased, the fiber melt underwent the slow cooling to have the residence time long enough for liquid-liquid phase separation to result in the cellular structure. The fast cooled one has spherulitic lacy structure, since polymer crystallization inhibited the liquid-liquid phase separation. The membrane with cellular structure has greater pore size and flux than the one with spherulitic lacy structure. The more miscible coagulant with diluent extracted some of the diluent from the outer surface of the hollow fiber to make the more porous surface, but has little effect on the inner surface. It was confirmed that polypropylene membrane made via thermally induced phase separation process had better thermal and chemical resistance than the commercial polysulfone and cellulose acetate membranes.

Introduction

Many separation processes have been so far developed for the effective separation in chemical processes such as distillation, evaporation, extraction, and adsorption, etc. However, these conventional processes have limitations in their efficiencies and energy consumptions. Membrane process is one of the promising separation process which can replace the conventional processes by overcoming their limitations. Membrane process can be applied to many chemical and biological processes.¹ Recently membrane process is gaining much interest for its applications to environmental processes including water treatment, waste water treatment and air pollution control.² Application of polymeric membranes to environmental processes, especially the waste water treatment, is limited by the fact that it should lose its own performances when contacted with organic chemicals or treated at high temperature. Therefore, development of the thermal- and chemical-resistant membranes under these coarse conditions is the hot issue of the membrane technology.

Most of the commercial membranes were prepared via phase inversion method (solvent casting method), in which polymer precipitation was induced by immersion of the polymer solution into the nonsolvent.^{1,3,4} In this case, the available membrane materials were limited to the polymers which have the proper solvents at room temperature. These polymers have to be inherently weak to the chemicals and are not thermally stable, since most of them are amorphous polymers. Therefore, development of thermal- and chemical-resistant membranes is highly required, and employing crystalline polymers and engineering plastics as membrane materials can suffice the needs. Polyolefins, nylons and teflons were tested for their applications to membranes, and some were commercialized.⁵ Fabrication of these polymers into membranes can not be performed by the conventional phase inversion methods, since they do not have the solvents at room temperature. Thermal energy is required to make the homogeneous melt solutions of these polymers with proper diluents. Upon cooling, the melt solution should be phase separated to make

microporous structure. This process is called as thermally-induced phase separation (TIPS) process.⁵⁻⁸

In TIPS process, two kinds of phase separations are involved; solid-liquid phase separation by the polymer crystallization and liquid-liquid phase separation from the thermodynamic instability of the system. From the liquid-liquid phase separation, the melt solution got phase separated into the polymer-rich and polymer-lean phases, and the polymer-lean droplet grows within the liquid-liquid phase separated region until the polymer crystallization freezes the structure. The formation and growth of polymer-lean droplet can be proceeded either by nucleation and growth or by spinodal decomposition followed by coarsening mechanism. Therefore, cooling condition played the most important role in TIPS process, and the desired structure can be obtained by controlling the operation parameters including cooling condition.⁹⁻¹⁴ Takahara^{15,16} and Sieta^{17,18} prepared the polypropylene (PP) hollow fiber membranes with liquid paraffin as a diluent for the application to the blood oxygenator and plasmapheresis.

In this work PP was used as a membrane material and soybean oil (SO) and dioctylphthalate (DOP) were selected as diluents, which can form a homogeneous melt solution with PP at high temperature and cause phase separation upon cooling.^{19,20} PP hollow fiber membranes were prepared via TIPS using melt spinning apparatus. Melt spinning process was developed and optimized by examining the effects of operation parameters.

Experimentals

Materials. Isotactic PP of fiber grade was obtained from Yukong Co. (H236W and H730F) Soybean oil from Cheil Jedang Co., and DOP from Duksan Chemical Co. were used as diluents. Freon 113 from Dong Youn Chemical Co. was used as extractant of diluents. Acetone, dimethylformamide (DMF), tetrahydrofuran (THF), toluene and Tween-80 were purchased from Aldrich Co. All the chemicals used in this work were used as received without further pu-

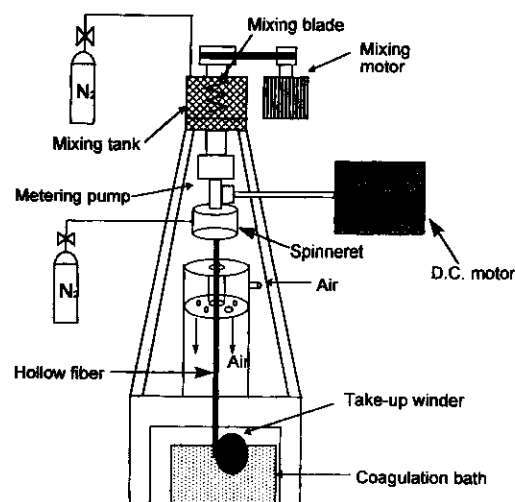


Figure 1. A schematic diagram of the vessel-type melt spinning apparatus for hollow fiber preparation.

rifications. For the comparison tests for thermal- and chemical resistances cellulose acetate membrane (PF100) and polysulfone membrane for diafilter were obtained from Akzo and Amicon Co., respectively.

Hollow Fiber Membrane Fabrication. For the fabrication of PP hollow fiber membranes, melt-spinning apparatus was assembled as shown in Figure 1. Since the conventional extruder was not effective in making a homogeneous melt solution of PP and diluent within the short span of mixing time, vessel-type blender was used for the longer mixing time. PP and diluent were blended in the vessel for 3 hours at 220 °C and 1 kgf/cm². The melt solution was delivered to spinneret at a rate of 25.6 g/min. The spinneret is tube-in-orifice type one; the orifice diameter was 2 mm, inside and outside diameters of the tube were 0.5 and 1.0 mm, respectively. In order to secure the constant supply of the melt solution to the spinneret, a metering pump was installed between the vessel and the spinneret. Nitrogen was introduced to the spinneret for the hollow formation. The spun fiber was partly cooled in the air before it reached the coagulation bath. The spun fiber was completely coagulated and phase separated in the coagulation bath, in which several kinds of coagulants were loaded. Then the fiber was wound on the take-up unit.

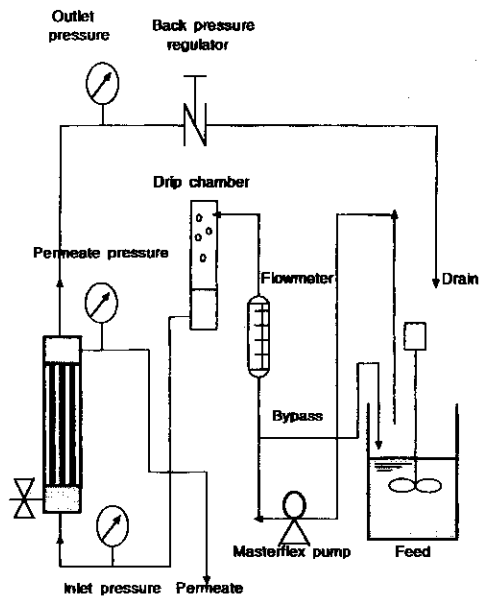


Figure 2. A schematic diagram of the performance test apparatus.

Remaining diluent in the fiber was extracted with Freon 113, and the fiber was dried in convection oven at 40 °C for 12 hours to make the microporous structure.

Performance Tests. The hollow fiber membranes were potted in PMMA tube of 150 cm long with epoxy resin. Since PP is hydrophobic, it must be hydrophilized prior to use. Surfactant, Tween-80, was used for hydrophilization of the membrane by dead end filtration of the 10% surfactant solution through the membrane for an hour. Then it was rinsed for an hour with distilled water before the main test. The performance test apparatus was shown in Figure 2. Molecular weight cut-off (MWCO) of the membrane was measured using dextrans, whose molecular weights were ranged from 38,900 to 2,000,000 at a concentration of 5% in water. Refractive index of each permeate was detected by a refractometer. (RI-930, Jasco Co.) The bubble point pressure of the each membrane was measured by using the apparatus shown in Figure 3. The medium was 30% ethanol aqueous solution.

Chemical resistance of each membrane was measured by treating the membrane with each organic solution of DMF, toluene, or THF in water

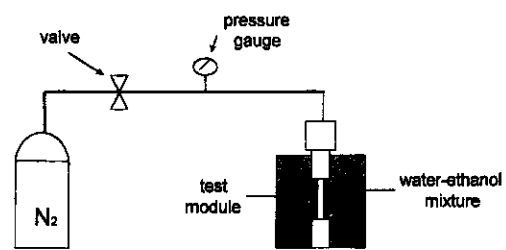


Figure 3. A schematic diagram of the bubble point measuring apparatus.

at a concentration of 3,000 ppm for 60 minutes. Thermal resistance was measured by treating the membrane at 80 °C for 60 minutes. Chemical and thermal resistances of PP membranes were compared with those of commercial CA and PSf membranes.

Results and Discussions

Effects of Coagulation Bath Temperature.

PP/SO=40/60 sample was spun into the coagulation bath filled with distilled water at different temperature. As the temperature of the coagulation bath increased, the cross section of the membrane changed from spherulitic lacy to cellular structure as shown in Figure 4. When the spun melt fiber entered the cold coagulation bath, it was quenched and had no time to allow the liquid-liquid phase separation and droplet growth. It underwent the solid-liquid phase separation via fast crystallization of PP, and it showed the lacy structure with tiny spherulites. As the coagulation bath temperature was warmed up, the structure was shifted to the cellular structure. At higher bath temperature, the melt fiber has time enough to undergo the liquid-liquid phase separation followed by droplet growth before the crystallization of PP begins.²¹⁻²³ As the bath temperature increased, the PP spherulite size as well as cell size increased, since it retarded the both solid-liquid and liquid-liquid phase separation rates. As shown in Figures 5 and 6, flux increased and rejection decreased with the increase of bath temperature due to the structural variations as stated above.

Effects of Kinds of Coagulants. Several kinds of coagulants were tested such as water, acetone, freon 113 and their mixtures. In the coag-

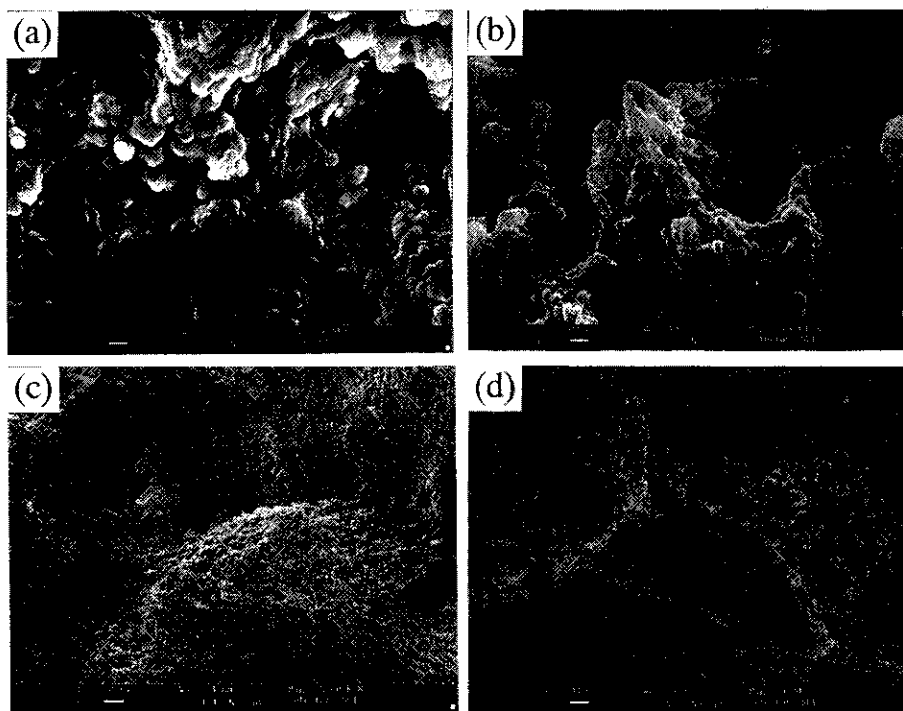


Figure 4. Cross-sectional images of the membrane coagulated at different temperatures : (a) 10 °C, (b) 20 °C, (c) 40 °C, and (d) 60 °C (dope solution : PP/DOP=30/70, coagulant : water).

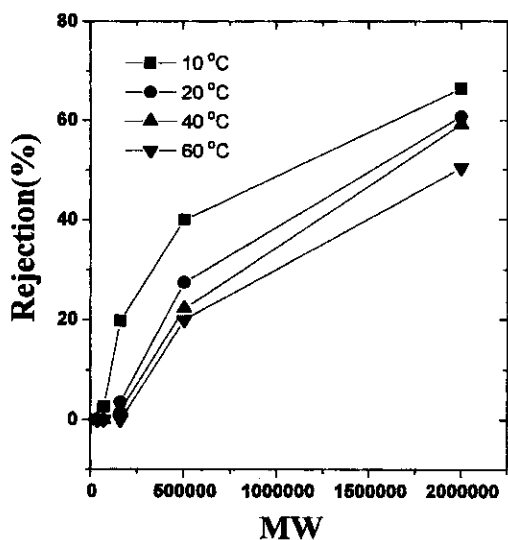


Figure 5. Rejections of the solutes with various molecular weights for the membranes coagulated at different temperatures (dope solution : PP/DOP=30/70, coagulant : water).

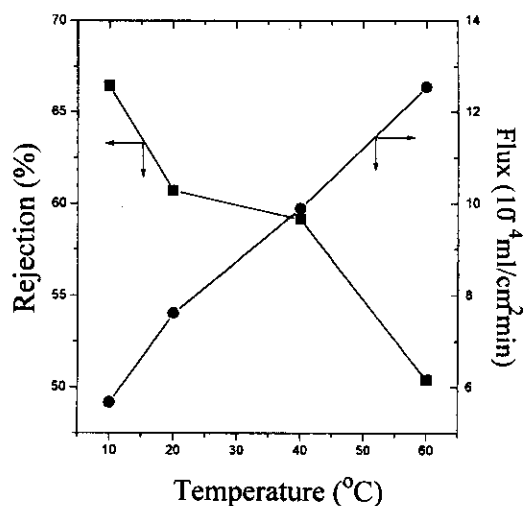


Figure 6. Effects of coagulation bath temperature on the rejection of dextran (MW=2,000,000) and flux (dope solution : PP/DOP=30/70, coagulant : water).

ulation bath the partly cooled fiber melt was completely coagulated. In case the coagulant is the

solvent of the diluent, some of the diluent in the fiber melt was extracted while it passed through the coagulation bath. As show shown in Figure 7.

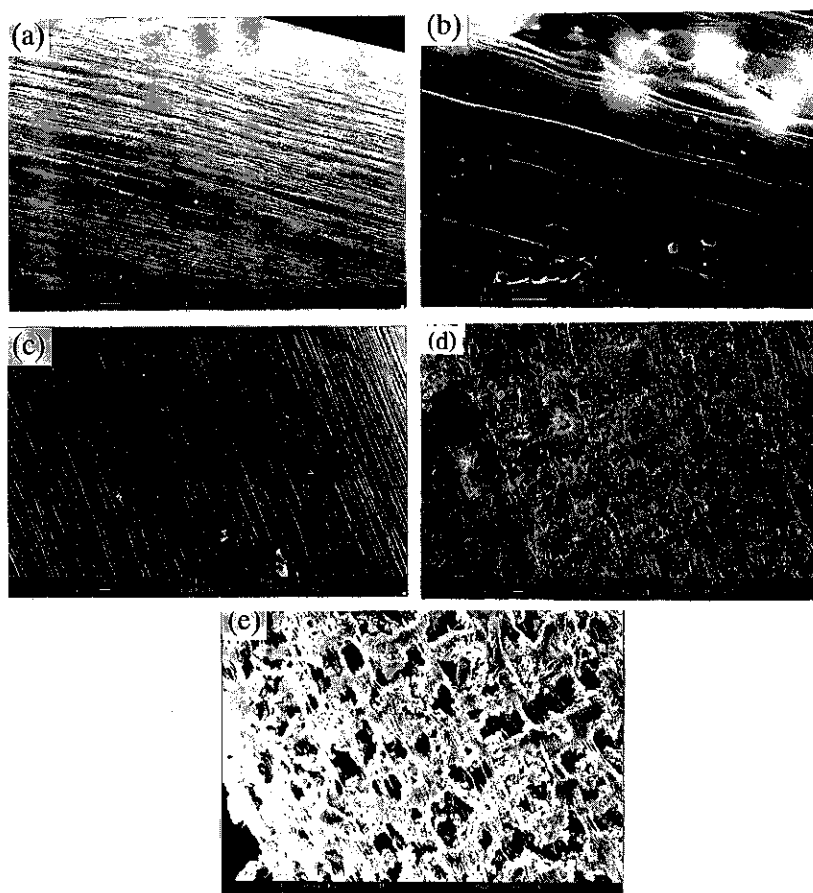


Figure 7. The outer surface images of the membranes coagulated in various coagulants: (a) water, (b) water/acetone=30/70, (c) acetone, (d) freon 113, and (e) freon 113/soybean oil=70/30 (dope solution: PP/SO=30/70, bath temperature: 20 °C).

when water, nonsolvent of diluent, was used as a coagulant, a very dense outer surface was obtained. Acetone is the poor solvent of diluent and it made a less dense outer surface, and mixture of water and acetone made an intermediate dense outer surface between the two cases. Freon 113 is the good solvent of the diluent and some of the diluent at the outer surface was extracted to make porous surface. However, in this case the fibers were stuck together on the winder. When soybean oil was added by 30% to freon 113, it made better porous surface than the case using freon 113 only. Moreover, sticking problem was solved in this case.

Since the inner surface of the hollow fiber melt was not directly contacted with coagulant, the inner surface structures were nearly same to one

another as shown in Figure 8. Since the inner surface was cooled at a slower rate than the outer surface, it has the cellular structure. If the fiber melt was cooled in the air at a slower rate, it can also make the similar outer surface structure to the inner surface structure. However, contact with nonsolvent made very dense surface structure. As the miscibility of coagulant with diluent decreased, bubble point pressure increased and maximum pore diameter decreased (Table I). The water flux showed the same trend as expected. As shown in Figure 9, the membrane coagulated with freon 113 and soybean oil mixture showed the better performance than the others. Therefore, in terms of flux and rejection, freon 113 and soybean oil mixture was the best coagulant in this work.

Chemical and Thermal Resistances. In

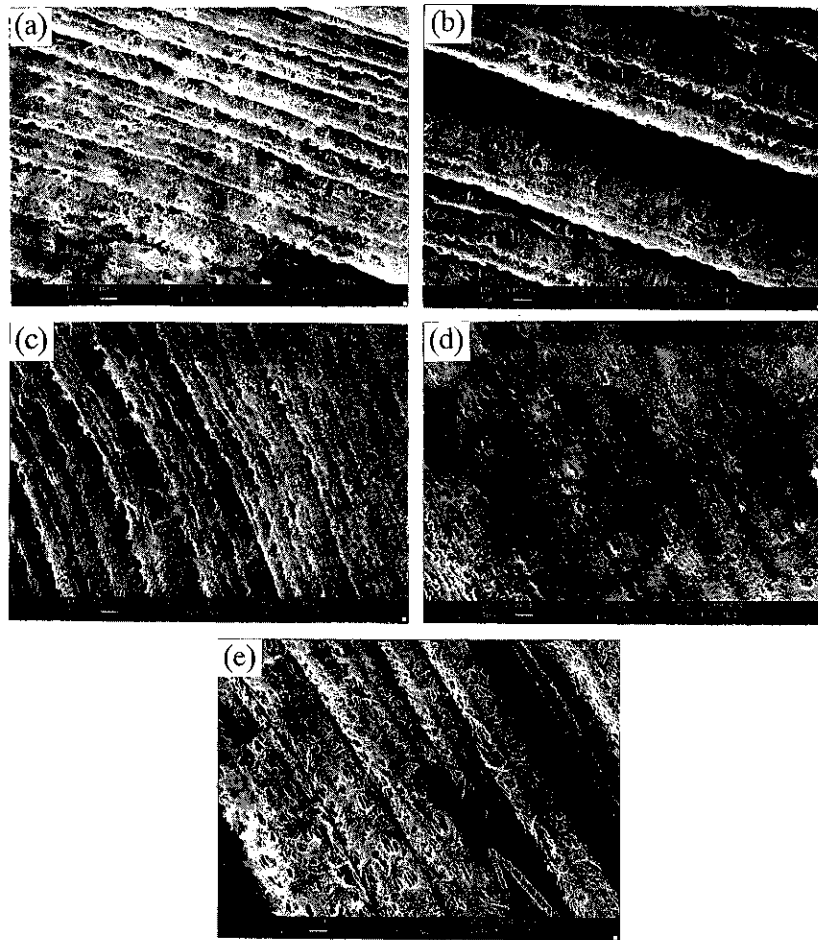


Figure 8. The inner surface images of the membranes coagulated in various coagulants: (a) water, (b) water/acetone=30/70, (c) acetone, (d) freon 113, and (e) freon 113/soyben oil=70/30 (dope solution: PP/SO=30/70, bath temperature: 20 °C).

Table I. Characteristics of the Membranes Treated with Various Coagulants

Content Coagulant	Flux (mL/cm ² min)	Bubble Point Pressure (Kg/cm ²)	D_{max} (μ m)
SO(30)/Freon(70)	2.66×10^{-3}	0.36	3.25
Freon	2.58×10^{-3}	0.37	3.17
Acetone	2.04×10^{-3}	0.39	3.0
Water(30)/Acetone(70)	2.10×10^{-3}	0.40	2.94
Water	1.5×10^{-3}	0.62	1.89

Table II the performance variations of the membranes after the chemical and the heat treatments were summarized. After 60 minutes of chemical treatments in various chemicals, flux of the CA membrane increased. Rejection of dextran (MW=500,000) decreased after the treatment with

DMF. Thermal treatment shrunk the CA membrane to result in the flux decline while maintaining the rejection. PSf membrane was seriously attacked by toluene to result in the no rejection at all. THF treatment decreased the both flux and rejection of the PSf membrane. and DMF decreased the rejection. Thermal treatment also seriously decreased the flux of the PSf membrane without rejection variation. PP membrane was the most thermally resistant among them. since little variations in flux and rejection were observed. It was relatively more stable to chemicals than the rest. Flux decreased slightly after the treatments to DMF and THF with the increases of rejections. It was weak to toluene. since the flux was remarkably reduced. Based on the results of

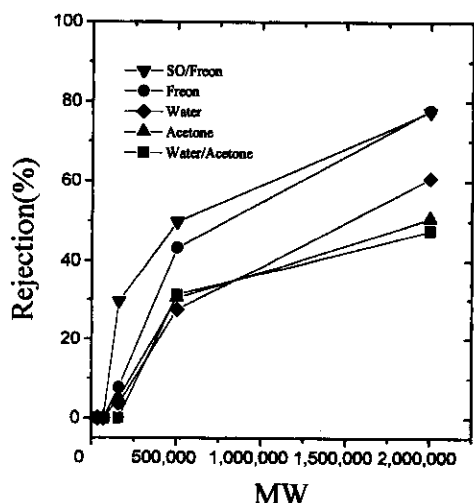


Figure 9. Performances of the membranes coagulated in various coagulants (dope solution: PP/SO=30/70, bath temperature: 20°C).

Table II. Performance Variations of Membranes after Chemical and Thermal Treatments

Membranes	Treatments	Flux [mL/cm ² min]	Rejection (%) (MW=500,000)
CA	original	0.120	98.36
	THF	0.135	99.00
	DMF	0.234	62.56
	Toluene	0.177	98.31
	80 °C	0.084	99.00
PSf	original	0.180	98.87
	THF	0.166	85.12
	DMF	0.191	84.68
	Toluene	0.550	0.500
	80 °C	0.0521	98.09
PP	original	1.517	67.17
	THF	1.092	85.20
	DMF	1.450	75.01
	Toluene	0.079	87.00
	80 °C	1.390	69.10

thermal and chemical resistance tests it can be concluded that PP membrane is more resistant to chemicals and heat than the commercial CA and PSf membranes.

Conclusions

PP hollow fiber membranes were prepared via TIPS process by using a vessel-type melt spinning apparatus. Soybean oil and DOP were used as di-

lucents with PP to result in the microporous structure. As the temperature of the coagulation bath increased, the cross section of the membrane changed from spherulitic lacy to cellular structure, since it had time enough to undergo the liquid-liquid phase separation followed by droplet growth before the crystallization of PP begins. Flux increased and rejection decreased with the increase of bath temperature due to the structural variations. Depending on the miscibility of coagulant with diluent, the outer surface of the membrane structure changed while it passed through the coagulation bath. There was no variation in the inner surface of the membrane, since it was not directly contacted with the coagulant. Freon 113 and soybean oil mixture was the best coagulant. PP membrane performance was little affected by the thermal treatment at 80 °C, while the CA and PSf membranes were deteriorated. PP membrane was relatively more stable to chemicals than the CA and PSf membranes.

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