

Membrane Formation via Thermally-Induced Phase Separation from Polypropylene/Fatty Acids Systems

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Microporous polypropylene membranes were prepared via thermally-induced phase separation from mixtures of polypropylene/soybean oil, polypropylene/oleic acid, and polypropylene/linoleic acid. The phase diagram of each system was obtained by thermal analysis and cloud point measurements. It was proved that each system has a liquid-liquid phase separation region at concentrations less than the monotectic composition. A cellular structure was obtained for each system, which is the typical structure for liquid-liquid phase separation via slow cooling. Fine structure with tiny polypropylene spherulites was obtained via quenching process. Mobility of diluent was related with its rejection during the polypropylene spherulite formation. A melt spinning apparatus was designed to produce microporous hollow fiber membranes. The mechanical strength of the hollow fiber seemed to be related to solution viscosity. Polypropylene/soybean oil samples had much greater solution viscosity than the other systems, and formed fibril structures with enhanced mechanical strength.

Key words : microporous membranes, membrane formation and structure, phase separation, thermally-induced, hollow fiber, melt spinning

1. Introduction

The thermally-induced phase separation (TIPS) process has been utilized for making microporous membranes¹⁻³⁾. Various polymers and diluents have been used for the TIPS process, and some of them have been commercialized^{4,5)}. Polypropylene (PP) is one of the most popular TIPS membrane materials because of its many advantages over other polymers⁶⁾. The choice of diluent is important since it determines the interactions with the polymer and consequently the phase separation mechanism⁷⁻⁷⁾. PP/mineral oil undergoes solid-liquid phase separation, which results in a spherulitic structure via PP crystallization⁸⁾. PP/

n, n-bis (2-hydroxyethyl) tallowamine (TA) undergoes liquid-liquid phase separation when the initial composition is less than the monotectic composition^{2, 4, 9)}. Liquid-liquid phase separation can result in a cellular structure via nucleation and growth or coarsening after spinodal decomposition^{4, 10, 11)}.

A cellular structure with connecting pores is useful for ultrafiltration and microfiltration membranes. Ultrafiltration and microfiltration processes are often used in biological processes, medical devices, and food processes; therefore, the toxicity of the diluent as well as the polymer is critical. Soybean oil is an appropriate candidate for these purposes, since PP/soybean oil system

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Table 1. Constituents of soybean oil

Constituents	Composition (%)
Linoleic acid	50.7
Oleic acid	28.9
Palmitic acid	9.8
Linoleic acid	6.5
Stearic acid	2.4
Arachidic acid	0.9
Palmitoleic acid	0.4
Lauric acid	0.2
Myristic acid	0.1
Others	0.1

undergoes liquid-liquid phase separation and the soybean oil has little toxicity. Moreover, soybean oil is available at cheaper price than previously reported diluents for PP.

Flat membranes were fabricated on a hot stage apparatus and hollow fiber membranes were made via melt spinning process from the PP/soybean oil mixture. Pure oleic acid and linoleic acid, the constituents of soybean oil, were also used as diluents. Thermal analysis and cloud point measurement were performed for each PP/diluent system to help understand the phase separation mechanism and the resulting structure.

2. Materials and Methods

PP was supplied by Daehan Yuhwa Co., Korea, and its weight average molecular weight was 400,000, and melt index was 2 g/10 min. Soybean oil was purchased from Cheil Food Chemicals Co., Korea, and its constituents are listed in Table 1. Oleic acid was purchased from Kanto Chemical Co., Japan, and linoleic acid from Sigma Chemical Co., Trichlorotrifluoroethane (Freon 113) was from Ulsan Chemical Co., Korea. A Perkin Elmer DSC 4 was used for the thermal analyses. A Mettler FP 82 hot stage and FP 80 central processor were used for flat membrane fabrication and cloud point measurement. A vessel extrusion apparatus was manufactured for hol-

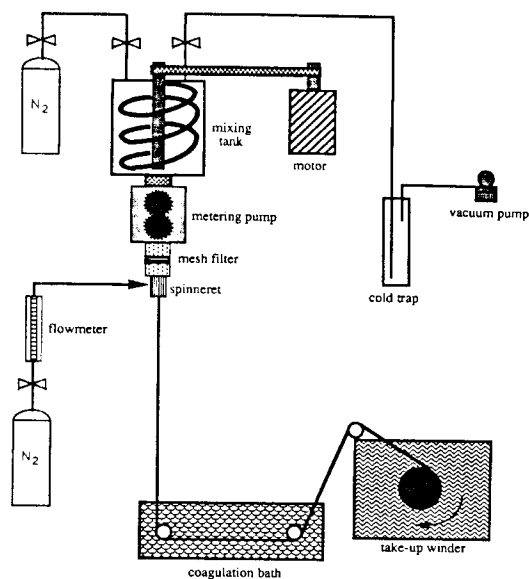


Fig. 1 A schematic diagram of vessel extrusion process.

low fiber spinning. The structure of each membrane was examined by using a scanning electron microscope (Hitachi S-510). A Ubbelohde capillary viscometer of diameter 1.13 mm was used to measure the efflux times of pure diluents. The tensile strength of each hollow fiber was measured by Instron (Model #4201) using a load cell of 5 Kg at a crosshead speed of 10 cm/min. Melt index of each PP/diluent mixture was measured using an apparatus made by Nihon Rigaku Kogyo Co. (Model #204-65 T) with the total load of 2.16 Kg.

3. Fabrication of Flat Membranes

Measured amounts of PP and diluent were mixed in a test tube and purged with nitrogen. The test tube was flame sealed and placed in an oven preset at 200° C for 24 hours to make a homogeneous melt solution. The test tube was quenched in ambient water to recover the homogeneous sample. The chopped sample was placed between a pair of microscope cover slips sealed with teflon tape, placed on a hot stage apparatus preset at 200° C

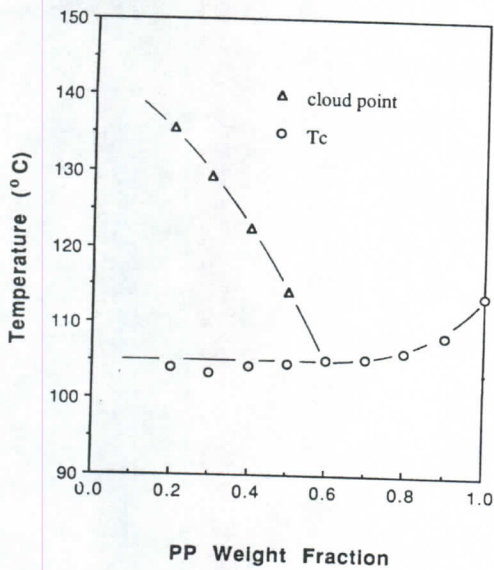


Fig. 2 Phase diagrams of PP/soybean oil system determined at 10°C/min cooling.

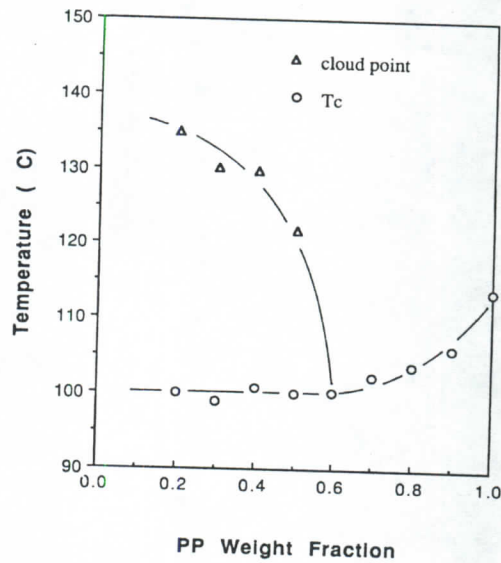


Fig. 3 Phase diagrams of PP/oleic acid system determined at 10°C/min cooling.

for 3 minutes, and cooled at a rate of 10°C/min or quenched to 25°C. The film sample was peeled from the cover slips and immersed in Freon 113 for diluent extraction. The sample was dried in a vacuum oven to make a flat TIPS membrane.

4. Melt Spinning of Hollow Fiber Membranes

Hollow fibers were prepared via melt spinning. Difficulties in premixing of PP and the liquid diluents and feeding through the hopper prevented use of a conventional extruder. Therefore, vessel extrusion apparatus was designed as shown in Figure 1. Measured amounts of PP and diluent were placed in the vessel and heated to 220°C under the nitrogen purged atmosphere. The spiral mixing blade was employed to enhance the sample homogeneity, and the mixing time was 4 hours. Under the nitrogen pressure the metered amount of homogeneous melt was fed to a spinneret by a gear pump. A spinneret of tube-in-orifice type was manufactured; its inner diameter was 3 mm

and outer diameter was 5 mm. Another stream of nitrogen was introduced into the spinneret to make a lumen at the center of the fiber. The spinneret temperature was varied from 165 to 185°C according to the composition and the molecular weight of PP.

The hollow fiber melt was partly cooled in the air, and it entered the coagulation bath where it was completely solidified and stretched. The Freon 113 in the coagulation bath was used as a diluent extractant as well as a coagulant, and diluent at the outer surface of the fiber was partly extracted while it passed through the coagulation bath. The hollow fiber was wound on a take-up winder at a specified melt-draw ratio. The remaining diluent was completely extracted in Freon 113 for 24 hours. Finally, it was dried in a vacuum oven for the removal of the remaining solvent and diluent.

5. Phase Diagrams

The crystallization temperatures of the PP/soybean oil, PP/oleic acid, and PP/linoleic acid

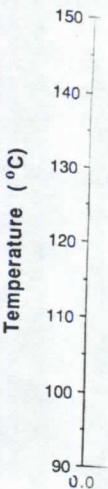


Fig. 4

systems were determined at 10°C/min cooling. The phase diagrams show the cloud point and Tc as a function of PP concentration, which are used to determine the phase separation region for PP/soybean oil, PP/oleic acid, and PP/linoleic acid systems. The cloud point and Tc for 60 wt. % of PP and 40 wt. % of diluent system, and 70 wt. % of PP and 30 wt. % of diluent system, and 70 wt. % of PP and 30 wt. % of linoleic acid system are shown in Figure 4.

6.

PP/soybean oil system was prepared at a concentration of 40 wt. % of PP and 60 wt. % of soybean oil. The phase diagram was determined at a rate of 10°C/min cooling. Since 40 wt. % of PP and 60 wt. % of soybean oil concentration system went liquid-liquid phase separation, the PP crystallization temperature was determined.

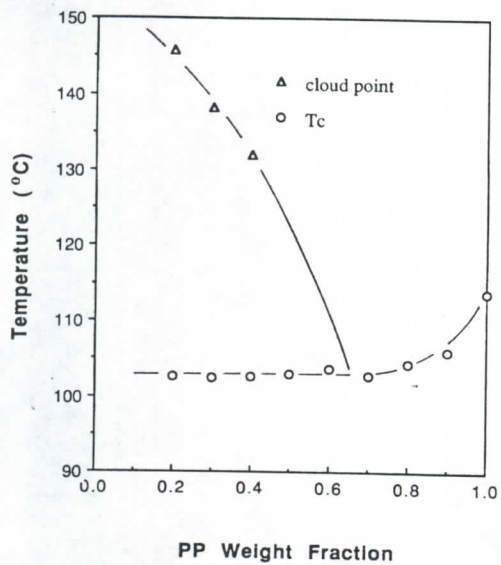


Fig. 4 Phase diagrams of PP/linoleic acid system determined at 10°C/min cooling.

systems were measured by DSC at a cooling rate of 10°C/min. As shown in Figures 2,3, and 4, each phase diagram has a flat crystallization curve at concentration less than the monotectic composition, which is a characteristic of liquid-liquid phase separation. The monotectic point of the PP/soybean oil system is located around 60 wt. % of PP and 105°C at a cooling rate of 10°C/min, 60 wt. % of PP and 100°C for the PP/oleic acid system, and 70 wt. % of PP and 103.5°C for the PP/linoleic acid system.

6. Structure Analysis

PP/soybean oil, PP/oleic acid, and PP/linoleic acid samples were prepared in flat form with PP concentration of 40 wt.%. They were cooled at a rate of 10°C/min or directly quenched to 25°C. Since 40 wt.% of PP is less than the monotectic concentration, each slowly cooled sample underwent liquid-liquid phase separation followed by PP crystallization after it reaches the monotectic temperature. Therefore, a cellular structure was

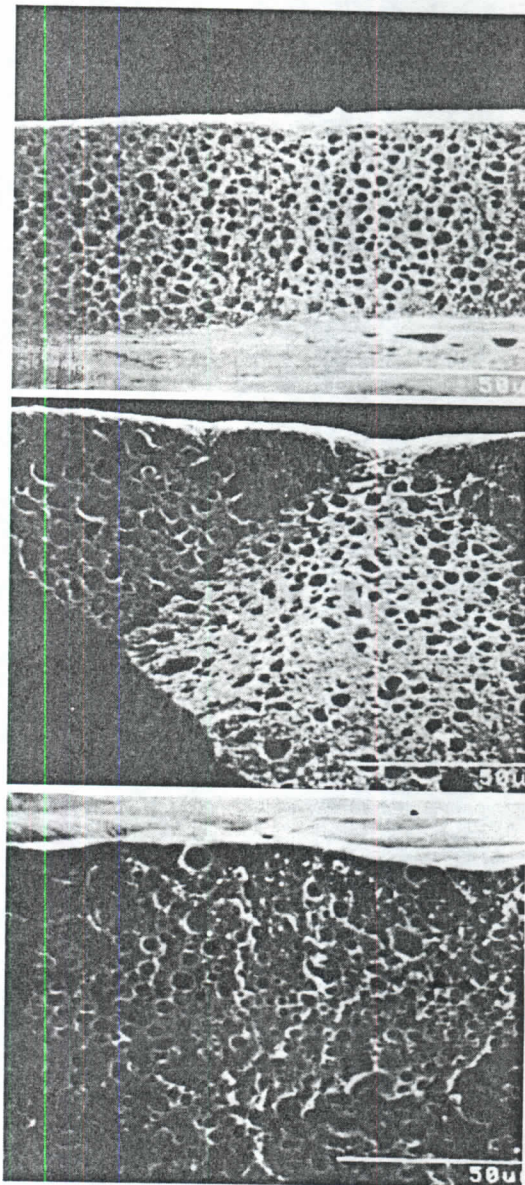


Fig. 5 Cross sectional views of flat membranes cooled at rate of 10°C/min from 200°C to 25°C (top : PP/soybean oil, middle : PP/oleic acid, bottom : PP/linoleic acid).

obtained for every case as shown in Figure 5. The cellular structure was obtained via nucleation and growth or coarsening after spinodal decomposition, and it is a characteristic structure of liquid-

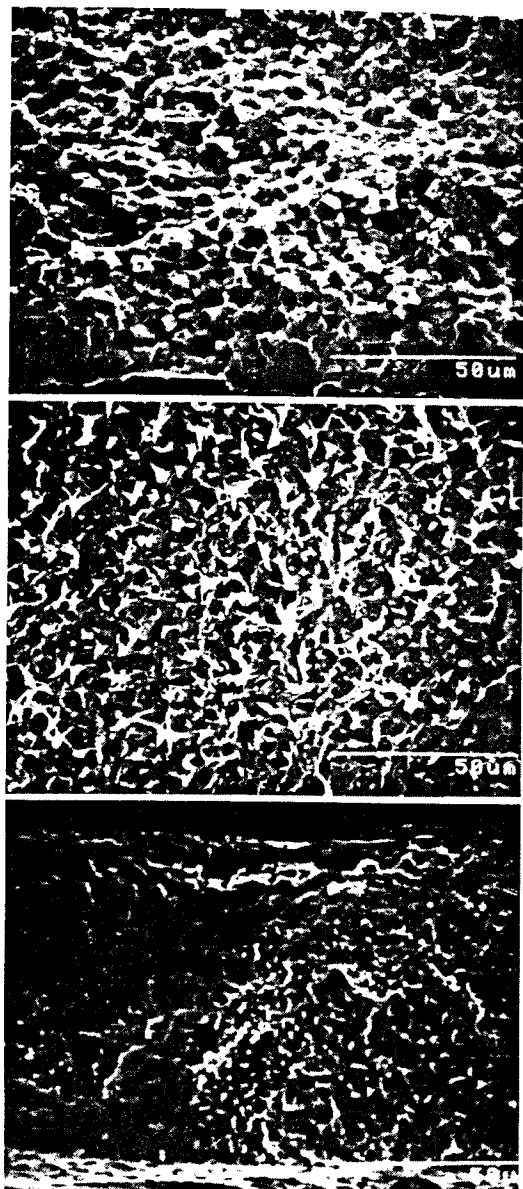


Fig. 6 Cross sectional views of flat membranes quenched from 200°C to 25°C (top : PP/soybean oil, middle : PP/oleic acid, bottom : PP/linoleic acid).

liquid phase separation^{7,14}.

When the same sample were directly quenched from 200°C to 25°C water, they formed a fine structure with tiny PP spherulites as shown in Figure

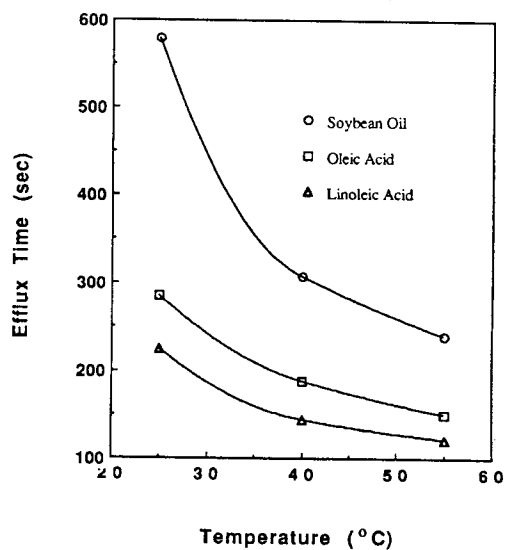


Fig. 7 Efflux time of each diluent through Ubbelohde type capillary viscometer.

6. Since every sample was under the thermodynamic conditions of liquid-liquid phase separation and PP crystallization, simultaneous liquid-liquid and solid-liquid phase separations could be expected for every sample. The PP/soybean oil sample formed tiny spherulites with micropores within the spherulites, while PP/oleic acid and PP/linoleic acid samples have dense PP spherulites free of such tiny micropores. Micropores within the tiny spherulite are frequently observed in solid-liquid phase separation systems^{4, 8}. The micropores result from unrejected diluent due to its low mobility¹³. Diluent mobility was indirectly measured by measuring the efflux time of each pure diluent through a Ubbelohde capillary viscometer over a temperature range of 25 to 55°C. Soybean oil has greater efflux time than the other diluents used in this study as shown in Figure 7. Due to the experimental difficulties in bath temperature control, efflux times at the TIPS temperature were not measured. However, trend can be extrapolated to TIPS temperature. Soybean oil was less rejected from the growth front of the PP spherulites than oleic acid and linoleic acid due to

Table 2. Spinning conditions for hollow fiber membrane formation

Coagulant	Freon 113
Vessel Temperature	220°C
Spinning Temperature	170°C
Spinning Speed	8.0 cm/min
Nitrogen Flow Rate	3 cm ³ /min
Distance between spinneret and coagulation bath	40 cm
Melt-draw ratio	1000

its low nobility.

The hollow fibers were prepared from PP/soybean oil, PP/oleic acid, and PP/linoleic acid samples (30 wt.% of PP) with the spinning conditions listed in Table 2. As shown in Figure 8, each sample formed a microporous structure. When the structures of the hollow fiber membranes were compared with those of the quenched flat membranes (Figure 6), the former has more porous structure than the latter. The difference in porous structure came from two factors; axial stretching of the hollow fibers and immediate contact with extracting solvent before the completion of the phase separation.

For flat membrane fabrication, there was no shear stress for stretching, whereas the spun hollow fiber was stretched at a melt-draw ratio specified in Table 2. Therefore, more pores could be formed via axial stretching of hollow fiber membranes. The melt-draw ratio is defined as the ratio of take-up speed to spinning speed. More details of melt-draw ratio effect are discussed elsewhere^{14, 15}. The phase separation and solidification of flat membranes were completed without any contact with extracting solvent, and extraction of diluent was performed after the completion of structure formation via TIPS. The hollow fiber melt contacted extracting solvent before the completion of phase separation and solidification of the melt. Three processes occurred in the bath; phase separation of the sample by cooling, extraction of the diluent, and phase separation via counter diffusion of diluent and solvent. These

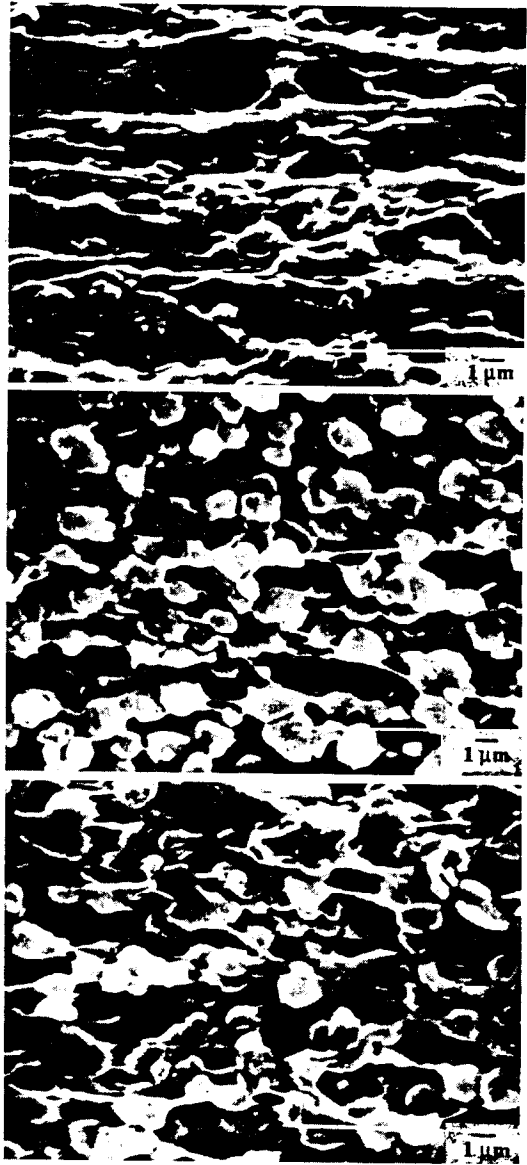


Fig. 8 Microporous structures of hollow fiber membranes (top : PP/soybean oil, middle : PP/oleic acid, bottom : PP/linoleic acid).

factors cause the structures of the hollow fiber membranes to be different from those of the flat membranes.

The mechanical strength of the hollow fiber made from PP/soybean oil mixture was much

Table 3. Melt index of each PP/diluent mixture (30 wt. % of PP) at 190°C and tensile strength of each hollow fiber

Sample	PP/soybean oil	PP/oleic acid	PP/linoleic acid
Melt index* (g/10 min)	19.6	44.5	46.3
Tensile Strength** (Kg./mm ²)	2.64	1.56	0.95

*Melt index of PP/diluent mixture at 190°C Total load : 2.16 Kg

**Tensile strength of hollow fiber after removal of diluent Local cell : 5 Kg, Crosshead speed : 10 cm/min

higher than those from PP/oleic acid and PP/linoleic acid mixtures as shown in Table 3. The difference can be explained in terms of the fibril structure of the fibers. As shown in Figure 8, there were many fibrils in the hollow fibers made from the PP/soybean oil mixture, and those from PP/oleic acid and PP/linoleic acid mixtures have tiny isolated PP spherulites without connecting fibrils. The presence of the fibrils between the PP spherulites enhanced the mechanical strength of the fiber. Formation of the fibrils is related to the viscosity of the PP/diluent melt. During the solidification, the hollow fiber melt can be stretched in the spinning direction with appropriate melt viscosity to make fibrils. However, the fibrils cannot resist the shear stress in the spinning direction if the melt viscosity is low.

The melt index of each PP/diluent mixture (30 wt.% PP) was measured according to ASTM D-1238-88 to show that the melt indices of the PP/oleic acid and PP/linoleic acid sample were much higher than that of PP/soybean oil sample at 190°C (Table 3). Therefore, low melt viscosities of PP/oleic acid and PP/linoleic acid samples failed to form the fibril structures to result in the poor mechanical strengths. PP/soybean oil system is more recommendable for making microporous hollow fiber membranes than the other PP/diluent systems reported here.

6. Conclusions

Microporous structures for ultrafiltration and microfiltration were obtained from PP/soybean

oil, PP/oleic acid, and PP/linoleic acid systems in both flat and hollow fiber types. Thermal analysis and cloud point measurement proved that these systems have liquid-liquid phase separation behavior, and the location of binodal region is much related to the diluent polarity. A cellular structure was obtained for each system at a cooling rate of 10°C/min confirming the liquid-liquid phase separation. Diluent mobility determined the size of the micropores within the PP spherulites. Stretching of the hollow fibers by melt-drawing enhanced the porosity of the membranes. Simultaneous phase separation and diluent extraction also affected the structure of the membranes. Melt viscosity influences the formation of fibrils between the spherulites and the mechanical strength of the hollow fiber.

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