

Membrane Formation via Thermally Induced Phase Separation in Polypropylene/Polybutene/Diluent System

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Received 22 December 2000; accepted 19 September 2001

ABSTRACT: Porous membranes were prepared from a polymer blend system by the thermally induced phase separation (TIPS) process. The polymer blend system was isotactic polypropylene (iPP)/polybutene (PB) and the diluent was diphenyl ether (DPE). Two types of porous membranes were prepared by the extractions of DPE alone and both DPE and PB after the phase separation. The effect of the addition of PB to the iPP solution on the phase diagram was investigated and the phase separation kinetics was measured by the light scattering method. The addition of PB resulted in the higher solute rejection property and lower water permeance. By the further extraction of PB from the porous iPP/PB membrane prepared by the extraction of DPE, the water permeance was approximately doubled, maintaining almost the same rejection property. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1701–1708, 2002; DOI 10.1002/app.10550

Key words: thermally induced phase separation; polymer blend; polypropylene; polybutene; light scattering

INTRODUCTION

Thermally induced phase separation (TIPS) is a method of making microporous membranes.^{1–11} TIPS is applied to a wide range of polymers that could not be used in the traditional phase inversion membrane formation due to the solubility problems. A variety of thermally stable, chemically resistant membranes were produced by the TIPS process on a commercial scale.

In the TIPS process, only one polymer component and diluent, that is, two-component system, have been mainly used. Few studies have re-

ported on the formation of porous membranes from a two-polymer blend and diluent system. Castro produced microporous membranes by TIPS process from several two polymer blend/diluent systems such as polypropylene/chlorinated polyethylene/diluent, polyethylene/chlorinated polyethylene/diluent, and others.¹ The membrane formation from hydroxylate polypropylene/polypropylene/diluent system was reported by Chung and Lee.¹²

In contrast to the small number of works on the TIPS process, polymer blend was widely used to improve thermal, rheological, and mechanical properties.¹³ Also in the field of membrane, ultrafiltration^{14,15} and gas separation membranes^{16–18} were prepared from polymer blend systems. The advantage of the use of polymer blend in the TIPS process is that pore size can be controlled by

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Journal of Applied Polymer Science, Vol. 84, 1701–1708 (2002)
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the addition of second polymer due to the change of thermodynamics and kinetic properties. Furthermore, the properties of membrane materials such as hydrophilicity can be changed in the blend system, as shown in the study of Chung and Lee.¹² If only the one polymer component can be dissolved in a certain diluent, the polymer can be rinsed away and high porosity will be achieved in the porous membrane.

In this work, polypropylene/polybutene blend membrane was produced by the TIPS process. The phase diagram and the pore growth kinetics were investigated. Because only polybutene (PB) could be rinsed away by toluene, two types of porous membranes were prepared by the extractions of diluent alone and both diluent and polybutene after the phase separation. The membrane properties such as the solute rejection and water permeability were compared for the two membranes.

EXPERIMENTAL

Materials

Polymers used were isotactic polypropylene (iPP, $M_w = 250,000$; Aldrich Chemical Co.) and PB (>90% polyisobutene, $M_n = 1290$; Aldrich Chemical Co.). Diphenyl ether (DPE; Nakalai Tesque Co., Kyoto, Japan) was used as the diluent without further purification. Extractants for DPE and for PB were methanol and toluene, respectively.

Phase Diagram

Homogeneous two-polymer (iPP + PB) diluent samples were prepared by a method previously described.⁷ The sample was placed between a pair of microscope cover slips. To prevent diluent loss by evaporation, a Teflon film of 100 μm thickness with a square opening was inserted between the coverslips. The sample was heated on a hot stage (Linkam, LK-600PH) at 453 K and cooled to 298 K at a controlled rate of 10 K/min. The temperature of the stage was manipulated by a Linkam L-600A controller. Cloud points were determined visually by noting the appearance of turbidity under an optical microscope (Olympus BX50, Tokyo, Japan).

To obtain the spinodal points, the sample on the hot stage was quenched and maintained at various desired temperatures below the cloud point at the maximum cooling rate of 130 K/min.

If the isolated droplets started to form gradually in the scattered position, the temperature was considered in the metastable region between the binodal and the spinodal.¹⁹ On the other hand, when the interconnected structure was immediately formed all over the position, the temperature was considered in the unstable region below the spinodal. Thus, the spinodal point, which is the border between the metastable region and unstable region, was determined from the results at various different temperatures.

A DSC (Perkin–Elmer, DSC-7) was used to determine the dynamic crystallization temperature. The solid sample was sealed in an aluminum DSC pan, melted at 453 K for 3 min, and then cooled at a 10 K/min to 298 K. The onset of the exothermic peak during the cooling was taken as the crystallization temperature.

Kinetic Study

The light scattering measurement was carried out to obtain the structure growth data with a polymer dynamics analyzer (Otsuka Electronics Co., Hiraka, DYNA-3000).²⁰ The hot stage was located between a He-Ne laser (5 mW) and a detector. The sample sealed with two coverslips was placed on the stage and heated at 453 K. Then it was quenched to the desired temperature at a cooling rate of 130 K/min. It was confirmed that the light scattering occurred after the temperature reached the set value. The time interval for the measurement was 0.22 s.

Droplet growth kinetics was measured by the optical microscope in the relatively later stage of the phase separation. The sample sealed with two coverslips was heated at 453 K and cooled to 298 K at a cooling rate of 10 K/min. After the temperature reached the cloud point, the droplet size was observed under a microscope. The image from the microscope was converted to a video signal. The video signal was passed through a video timer and into a videocassette recorder. To obtain the average droplet size of the polymer-lean phase, an image analysis (Mitani Co., Fukui, Japan, Win ROOF) was used.

SEM Observation

The sample sealed with two coverslips was heated at 453 K and quenched in ice water. Then diphenyl ether was extracted from the membrane with methanol and the methanol was evaporated. In some cases, PB in the membrane was further

extracted with toluene. The microporous membrane was fractured in liquid nitrogen and coated with Au/Pd. A SEM (Hitachi Co., Tokyo, Japan, S-800) with an accelerating voltage set to 15 kV was used to examine the membrane cross sections.

Solute Rejection Experiment

Membranes used for the filtration experiment were prepared as follows. The homogeneous polymer-diluent sample was placed between a pair of copper plates (length: 150 mm, width: 150 mm, thickness: 0.5 mm). For adjusting membrane thickness, the Teflon film of 150 μm thickness with a square opening in the center was inserted between the copper plates. The copper plates were heated at 453 K in an oven for 15 min to cause melt-blending. Then the copper plates were quenched in ice water. After cooling, diphenyl ether was extracted from the membrane with methanol and the methanol was evaporated. In some cases, PB in the membrane was further extracted with toluene.

The apparatus and procedure for the filtration experiment were the same as those described previously.²¹ The filtration experiment was conducted by using a stirred cell (Advantec Co., UHP-25K). The feed solution was pressurized by nitrogen gas at 0.1 atm for iPP membrane and at 0.5 atm for iPP/PB blend membrane. Solutes used were lysozyme from egg white (Seikagaku Co., 6 \times crystallized, $M_w = 14,600$, Stokes radius: 1.69 nm²²), ovalbumin (Sigma Chemical Co., Grade V, 98% purity, $M_w = 45,000$, Stokes radius: 2.53 nm²²), ferritin from horse spleen (Nacalai Tesque Co., $M_w = 440,000$, Stokes radius: 6.77 nm²²) and polystyrene latex particle (Duke Scientific Co., radius: 50 nm). The feed solutions were prepared by dissolving the proteins in a 0.05 mol/dm³ phosphate-buffered solution (disodium hydrogen phosphate + potassium dihydrogen phosphate, pH 7.0). The protein concentrations were 0.1 g/dm³ for lysozyme, 0.2 g/dm³ for ovalbumin, and 0.002 g/dm³ for ferritin. The latex particle was dispersed in an aqueous nonionic surfactant (0.01% Triton X-100) at a concentration of 1.03×10^{11} particles/dm³. The solute concentrations in filtrate were measured by using a UV spectrophotometer (Hitachi Co., U-2000) at the wavelengths of 280 nm for lysozyme and ovalbumin, 275 nm for ferritin, and 385 nm for latex particle. Before the filtration experiments, aqueous propanol solution (50 wt %) was passed through the mem-

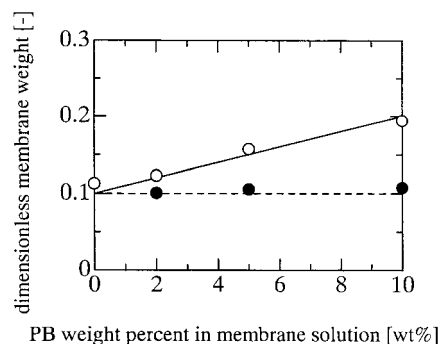


Figure 1 Membrane weight after the extraction. (○) DPE extraction; (●) DPE + PB extraction. The solid and dashed lines denote the predicted values when all DPE and DPE + PB are extracted, respectively. Membrane was prepared as follows. The homogeneous polymer-diluent sample was placed between a pair of glass plates (thickness: 2.8 mm) and after melt-blending, the glass plates were cooled at room temperature.

brane to fill pores of the membrane with the solution.

RESULTS AND DISCUSSION

Extraction Behavior

Figure 1 shows the membrane weight after the extraction. The ordinate is the dimensionless weight, which is defined as the membrane weight after the extraction divided by the initial membrane weight. The axis denotes the weight percentage of PB added to the iPP solution, in which the iPP weight percentage was fixed to be 10 wt %. First, DPE was extracted by methanol and then PB was extracted by toluene. The data in both cases are shown in Figure 1. The solid and dashed lines denote the predicted values when all DPE and DPE + PB are extracted. The experimental results in DPE extraction (○) and in DPE + PB extraction (●) agreed with the predicted solid line and dashed line, respectively. This indicates that almost all DPE and PB could be effectively extracted. Further, the agreement between the experimental data and the predicted lines suggests that the concentration of iPP and PB in the polymer-lean phase is quite low. When the polymer concentration in the polymer-lean phase is high, in which the polymers can flow out in the extraction process, the experimental data is expected to be lower than the predicted line. Therefore, almost all iPP and PB exist in the

Table I Shrinkage Results After the Extraction of DPE and PB

Membrane Type ^a	Extractant	Relative Membrane Area ^b	Relative Membrane Thickness ^b	Relative Membrane Volume ^b
iPP alone	Methanol	94.0%	97.9%	92.0%
iPP alone	Methanol + toluene	88.7%	95.7%	84.9%
iPP/PB blend ^c	Methanol	97.4%	100%	97.4%
iPP/PB blend ^c	Methanol + toluene	77.6%	88.9%	68.9%

^aMembrane preparation condition was the same as that used in the membranes for the solute rejection experiment.

^bValues relative to the initial values of membranes before the extraction.

^ciPP : PB ratio = 1 : 1.

polymer-rich phase and form the membrane matrix.

The shrinkage results after the evaporation of extractants are summarized in Table I. In both cases of iPP alone and iPP/PB blend, the shrinkage degree of the membranes after the extraction of DPE were low. On the other hand, after the extraction of PB, the iPP/PB blend membrane shrunk well and the resultant volume was 69% of the initial volume. Even after the immersion in toluene, the iPP membrane did not shrink so much.

Phase Diagram

Figure 2 shows the phase diagrams. The cloud point curve and the dynamic crystallization temperature are shown in Figure 2(a) when iPP concentration was fixed at 10 wt % and additional PB concentration was changed. The cloud points decreased with the increase of PB concentration because the total polymer concentration increased. In the polymer concentration region higher than the critical point, the increase of the

polymer concentration usually leads to the decrease of the binodal line in the upper critical solution temperature-type phase diagram.²³ The crystallization temperature slightly decreased as the PB concentration increased. However, such degree of decrease was very small and the crystallization temperature was not influenced so much by the addition of PB. Because PB is the amorphous polymer, only iPP can crystallize. As shown in Table II, the heat of crystallization slightly decreased with the increase of PB content. This means that the crystallinity of iPP decreased by the addition of PB.

Figure 2(b) shows the phase diagrams when the ratio of PP to PB was fixed. The cloud points at the same total polymer concentration decreased with the increase of the PB fraction. This cannot be explained by the increase of the total polymer concentration, which was the main cause for the result shown in Figure 2(a). First, we must consider the change of the compatibility between the polymer and the diluent. The solubility parameters for iPP, polyisobutene, and DPE were

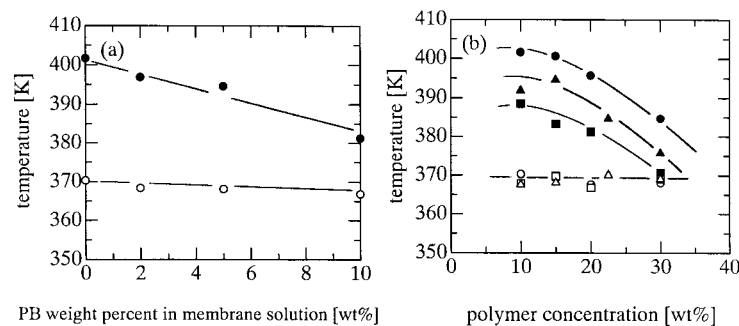


Figure 2 Phase diagrams for polymer blend/diluent system. (a) Constant iPP concentration (10 wt %). (●) cloud point; (○) crystallization temperature. (b) Constant ratio of PP to PB. (●) cloud point (iPP alone), (▲) cloud point (iPP : PB = 2 : 1), (■) cloud point (iPP : PB = 1 : 1), (○) crystallization temperature (iPP alone), (△) crystallization temperature (iPP : PB = 2 : 1), (□) crystallization temperature (iPP : PB = 1 : 1)

Table II Heat of Crystallization

PB Weight Percent	0	2	5	10
Heat of crystallization [J/g-iPP]	107	101	87.9	82.7

iPP concentration was fixed to be 10 wt%.

reported as 18.8,²⁴ 16.5,²⁴ and 20.7 MPa^{1/2},²⁵ respectively. When the PB fraction in the polymer blend increases, the solubility parameter difference between the polymer blend and the diluent becomes large and thus the compatibility decreases, which suggests that the cloud point should be shifted to the high-temperature position.⁶ Because this expectation is opposite to the experimental result, the result cannot be explained by the change of the compatibility. The addition of PB brings about the decrease of the average molecular weight because the molecular weight of PB is much lower than that of iPP. When the molecular weight is lower, the cloud point is shifted to the lower temperature position due to the entropy effect.²³ This may be the reason for the decrease of the cloud point brought about by the increase of PB fraction.

The spinodal points were 0.7 and 0.5°C lower than the binodal points in the cases of iPP alone (15 wt %) and iPP (10wt %) + PB (5 wt %) system, respectively.

Kinetic Study

An example of the light scattering measurement is shown in Figure 3. The time shown in this figure corresponds to the elapse of time after the phase separation occurs. Clear maxima of the

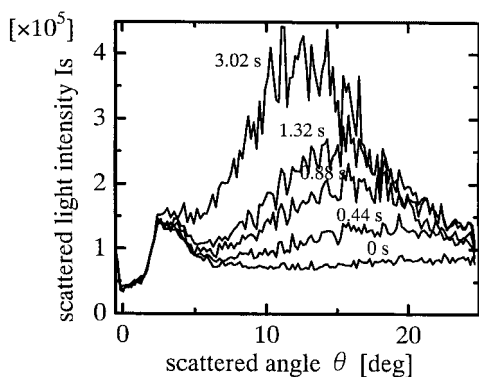


Figure 3 An example of light scattering measurement. IPP 10 wt % + PB 5 wt %, quench depth = 1.3 K.

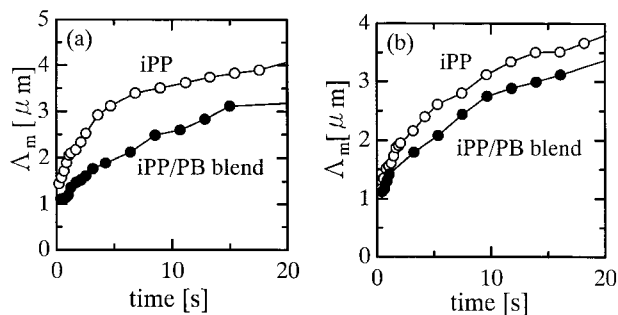


Figure 4 Time course of Λ_m in both iPP alone (15 wt %) and iPP/PB systems (iPP 10 wt % + PB 5 wt %). (a) Quench depth: 1.2 K for iPP alone and 1.3 K for iPP/PB blend, (b) quench depth: 2.2 K for iPP alone and 2.3 K for iPP/PB blend.

scattered light intensity I_s were observed each time. This indicates that the phase separation mechanism is not the nucleation and growth mechanism (NG mechanism) but the spinodal decomposition (SD).²⁶ The peaks of I_s shifted to a smaller angle with time, which means that the phase-separated structure was growing in this time scale.²⁰

The scattered angle is related to the wave number as:

$$q = (4\pi n/\lambda_0)\sin(\theta/2) \quad (1)$$

where n is the solution refractive index and λ_0 is the wavelength of light *in vacuo*. The relation between q_m , which is the wave number where maximum scattered light intensity appears, and the average interphase periodic distance Λ_m is given by

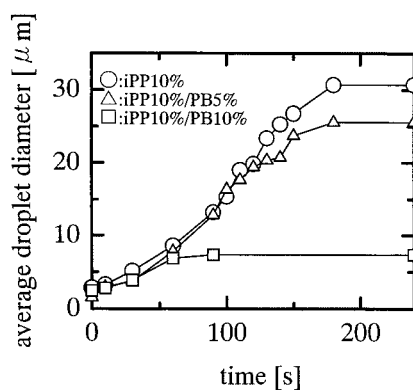


Figure 5 Time course of average droplet diameter. Cooling rate was 10 K/min.

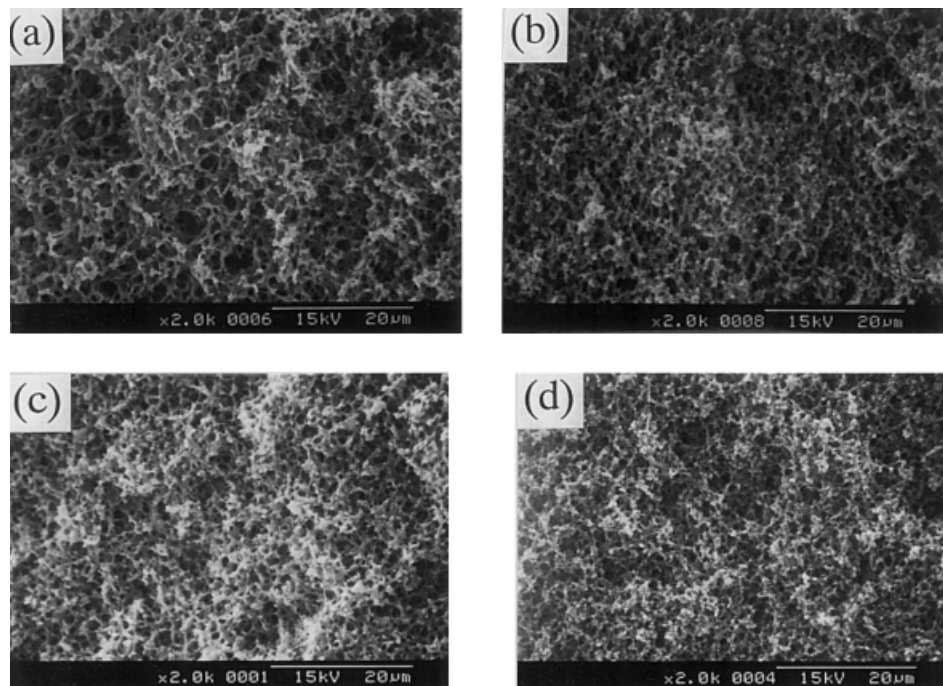


Figure 6 Cross sections of the membranes. (a) iPP alone (10 wt %, DPE extraction), (b) iPP 10 wt % + PB 5 wt % (DPE extraction), (c) iPP 10 wt % + PB 10 wt % (DPE extraction), (d) iPP 10 wt % + PB 10 wt % (DPE + PB extraction).

$$q_m = 2\pi/\Lambda_m \quad (2)$$

By using eqs. (1) and (2), the time course of Λ_m can be obtained from the light scattering experiment result. Figure 4 shows the time course of Λ_m in both iPP alone and iPP/PB blend systems (iPP : PB = 2 : 1). At almost the same quench depth, which is defined as the difference between the spinodal temperature and the experimental temperature, the larger Λ_m was obtained in the iPP system than in the iPP/PB blend system. In both two-quench depth cases, the difference of Λ_m hardly changed as time passed. This means that at the early stage of SD, Λ_m is lower in the blend system and, however, the growth rate of Λ_m in the later stage was almost the same in the two systems. Λ_m in the early stage of SD can be related as radius of gyration R_g as²⁷:

$$\Lambda_m \propto R_g \{(T_s - T)/T\}^{-2/3} \quad (3)$$

where T_s and T are the spinodal temperature and experimental temperature, respectively. In the iPP/PB blend system, the average molecular weight is smaller than in the iPP system, as described above. Thus, the smaller R_g value in the

blend system led to the smaller Λ_m in the early stage of SD.

Average droplet diameter determined from the optical micrograph is plotted with time in Figure 5. In these experiments, temperature was not fixed and gradually decreased at a constant cooling rate of 10 K/min. The droplet sizes increased

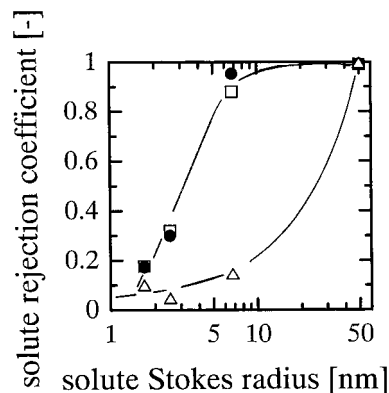


Figure 7 Relation between apparent solute rejection coefficient and solute Stokes radius. (Δ) iPP alone (10 wt %, DPE extraction), (\square) iPP 10 wt % + PB 10 wt % (DPE extraction), (\bullet) iPP 10 wt % + PB 10 wt % (DPE + PB extraction).

Table III Water Permeance of Membranes Prepared in Various Conditions

Membrane Type	Extracted Species	Water Permeance [$\text{m}^3/(\text{m}^2 \text{ s Pa})$]
iPP alone (10 wt %)	DPE	3.29×10^{-9}
iPP/PB blend (iPP10 wt % + PB 10 wt %)	DPE	2.35×10^{-10}
iPP/PB blend (iPP10 wt % + PB 10 wt %)	DPE + PB	4.51×10^{-10}

initially with time and reached constant values in all polymer cases. When temperature crossed the cloud point in the cooling process, phase separation occurred and the droplet growth continued until the temperature reached the crystallization temperature. By the addition of PB, the constant droplet size clearly decreased. As shown in Figure 2(a), the region between the cloud point and the crystallization temperature decreased with the increase in amount of PB. Thus, in the polymer blend with the higher PB content, the droplet growth soon stopped and the resultant droplet size was smaller.

SEM Observation

Figure 6 shows the cross sections of the membranes. As the PB content in the blend membrane increased [Fig. 6(a)–(c)], the pore size decreased because of the increase in the total polymer concentration. This result agreed with the result in Figure 5, although the cooling conditions in the two cases were different. It is expected that after the PB extraction, the thickness of the polymer fibrils becomes thinner due to the effusion of PB from the matrix phase, which probably leads to the larger pores. However, between the membrane structures after the PB extraction [Fig. 6(d)] and before the PB extraction [Fig. 6(c)], a clear difference cannot be recognized at this magnification.

Solute Rejection

Figure 7 shows the relation between the apparent solute rejection coefficient R_a and the solute Stokes radius. The apparent rejection coefficient is defined as $(1 - C_s/C_0)$, where C_0 and C_s are the solute concentrations in the feed and filtrate phases. In Table III, the pure water permeance are summarized in three cases. The water permeance is defined as the volumetric flow rate divided by the membrane area and the pressure difference. From Figure 7 and Table III, the addition of PB increased the solute rejection coefficient remarkably and lowered the water per-

meance due to the formation of the smaller pores, as shown in Figure 6. By the extraction of PB, the water permeance was approximately doubled, maintaining the same solute rejection property. This indicates that the use of the polymer blend system in the TIPS process has the advantage of obtaining the higher permeability by the extraction of one polymer component. The extraction of PB brings about the enlargement of pores, whereas the membrane shrinkage shown in Table I brings about the pore size reduction. If the former effect compensates for the latter, almost the same solute rejection properties are obtained in the cases after and before the PB extraction, as shown in Figure 7. The higher water permeance in the extraction of PB may be due to the formation of small pores, through which only water molecules can permeate and the larger solute cannot permeate. Further detailed investigation is necessary to confirm this.

CONCLUSION

Porous membranes were prepared from iPP/PB blend system by the TIPS process. The addition of PB to the iPP solution lowered the cloud point, whereas the dynamic crystallization temperature hardly changed. The kinetic studies by the light scattering showed that the structure formed at the early stage of the spinodal decomposition was smaller in the blend system than in the iPP system. However, the structure growth rate in the latter stage was almost the same in both systems. When the polymer solution was cooled at the constant cooling rate of 10 K/min, the droplet sizes increased first and reached constant value. The constant droplet sizes decreased with the increase of the PB content because of the smaller region between the cloud point and the crystallization temperature.

The addition of PB increased the solute rejection and lowered the water permeance owing to the formation of smaller pores. The extraction of

PB from the membrane was effective to improve the water permeance.

REFERENCES

1. Castro, A. J. U.S. Pat. 4,247,498, 1981.
2. Caneba, G. T.; Soong, D. S. *Macromolecules* 1985, 18, 2538.
3. Hiatt, W. C.; Vitzthum, G. H.; Wagener, K. B.; Gerlach, K.; Josefiak, C. in *Microporous Membranes via Upper Critical Temperature Phase Separation*; Lloyd, D. R., Ed.; ACS Symposium Series 269; American Chemical Society: Washington, DC, 1985; p 229.
4. Lloyd, D. R.; Kinzer, K. E.; Tseng, H. S. *J Membr Sci* 1990, 52, 239.
5. Tsai, F.-J.; Torkelson, J. M. *Macromolecules* 1990, 23, 775.
6. Lloyd, D. R.; Kim, S.-S.; Kinzer, K.E. *J Membr Sci* 1991, 64, 1.
7. Kim, S.-S.; Lloyd, D. R. *J Membr Sci* 1991, 64, 13.
8. Vadhia, H. C.; Lee, H. K.; Myerson, A. S.; Levon, K. *J Membr Sci* 1994, 89, 37.
9. Mehta, R. H.; Madsen, D. A.; Kalika, D. S. *J Membr Sci* 1995, 107, 93.
10. Matsuyama, H.; Berghmans, S.; Lloyd, D. R. *J Membr Sci* 1998, 142, 213.
11. Matsuyama, H.; Berghmans, S.; Lloyd, D. R. *Polymer* 1999, 40, 2289.
12. Chung, T. C.; Lee, S. H. *J Appl Polym Sci* 1997, 64, 567.
13. Utracki, L. A. *Polymer Alloys and Blends*; Carl Hanser Verlag: Munich, 1989.
14. Nunes, S. P.; Peinemann, K. V. *J Membr Sci* 1992, 73, 25.
15. Blicke, C.; Peinemann, K. V.; Nunes, S. P. *J Membr Sci* 1993, 79, 83.
16. Chiou, J. S.; Paul, D. R. *J Appl Polym Sci* 1987, 34, 1037.
17. Bikson, B.; Nelson, J. K.; Muruganandam, N. *J Membr Sci* 1994, 94, 313.
18. Park, C.; Jo, W. H.; Park, H. C.; Kang, Y. S. *Polymer* 2000, 41, 1765.
19. van de Witte, P.; Dijkstra, P. J.; van den Berg, J. W. A.; Feijen, J. *J Membr Sci* 1996, 117, 1.
20. Matsuyama, H.; Kudari, S.; Kiyofuji, H.; Kitamura, Y. *J Appl Polym Sci* 2000, 76, 1028.
21. Matsuyama, H.; Yuasa, M.; Kitamura, Y.; Teramoto, M.; Lloyd, D. R. *J Membr Sci* 2001, 179, 91.
22. Matsuyama, H.; Iwatani, T.; Kitamura, Y.; Teramoto, M.; Sugo, N. *J Appl Polym Sci* 2001, 79, 2456.
23. Flory, P. J. *Principles of Polymer Chemistry*; Cornell Univ. Press: Ithaca, NY, 1953.
24. Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 4th ed.; John Wiley and Sons: New York, 1999.
25. Barton, A. F. M. *Handbook of Solubility Parameters and Other Cohesion Parameters*, 2nd ed.; CRC Press: Boca Raton, FL, 1991.
26. Hashimoto, T.; Sasaki, K.; Kawai, H. *Macromolecules* 1984, 17, 2812.
27. Lal, J.; Bansil, R. *Macromolecules* 1991, 24, 290.