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Preparation of porous membrane by combined use of thermally induced phase separation and immersion precipitation

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Abstract

By immersion in the cooled nonsolvent, PMMA porous membrane was prepared by the combined use of thermally induced phase separation (TIPS) and immersion precipitation. As nonsolvent, water with low mutual affinity with cyclohexanol (diluent) and methanol with high affinity were used. In the case of water, the porous structure was formed by TIPS immediately after the immersion. Near the top surface contacted with the nonsolvent, the thin skin layer was formed due to the outflow of the diluent. After the long immersion period, macrovoids were formed near the top surface due to the penetration of the nonsolvent. Thus, TIPS and the immersion precipitation occurred serially. On the contrary, TIPS and the immersion precipitation occurred simultaneously in the case of methanol because the inflow of methanol was fast. Therefore, the membrane obtained after the short immersion period had the larger pores near the top surface due to the nonsolvent induced phase separation and the smaller pores near the bottom surface due to TIPS. These two modes of the phase separations were confirmed by the changes in light transmittance through the polymer solutions. © 2002 Published by Elsevier Science Ltd.

Keywords: Thermally induced phase separation; Immersion precipitation; Microporous membrane

1. Introduction

Polymeric porous membranes have been mainly prepared by phase separation of polymer solutions [1,2]. Phase separation can be induced by the removal of thermal energy or existence of nonsolvent. The former is thermally induced phase separation (TIPS), while the latter is nonsolvent induced phase separation (NIPS). In the TIPS process, a polymer is dissolved in a diluent at high temperature and then by cooling the solution, phase separation is induced. The diluent is removed by extraction, evaporation or freeze-drying to obtain the porous membrane [3–10]. The NIPS process is classified into air-casting of a polymer solution, precipitation from a vapor phase and immersion precipitation. In the air-casting process, the polymer is dissolved in a mixture of a volatile solvent and a nonvolatile nonsolvent. The evaporation of the solvent induces the phase separation. In the precipitation from the vapor phase, a nonsolvent vapor penetrates into a polymer solution, which induces the phase separation. The immersion precipitation has been most widely used in the NIPS process. A polymer solution is cast on a support and immersed in a nonsolvent bath. The phase separation occurs due to the exchange of solvent and nonsolvent.

The porous membranes have been prepared by either of the methods described above. In this work, a new method for the combined use of TIPS and the immersion precipitation is proposed. Two kinds of nonsolvents such as water and methanol were used and the effect of nonsolvent on the porous membrane structure was studied. As far as we know, this is the first work on the membrane formation in the combined use of TIPS and NIPS.

2. Experimental

2.1. Materials

Polymer was poly(methyl methacrylate) (PMMA, $M_w = 10\,100$, $M_n = 48\,300$, Aldrich Chemical Co.) and diluent was cyclohexanol (Nakalai Tesque Co., Japan). Nonsolvents were water and methanol (Wako Pure Chemical Industries, Japan).

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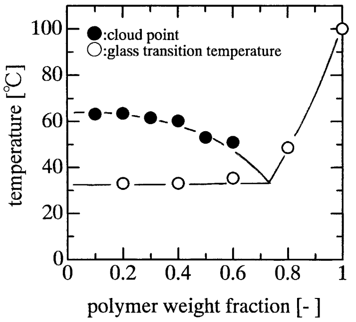

Fig. 1. Phase diagram in PMMA/cyclohexanol system: (•) cloud point, (○) glass transition temperature.

2.2. Phase diagram

2.2.1. Phase diagram for TIPS process

Homogeneous PMMA–cyclohexanol sample was prepared by a method reported by Kim and Lloyd [5]. The sample was placed between a pair of microscope cover slips and a Teflon film of 100 μm thickness with a square opening was inserted between the cover slips. The sample was heated on a hot stage (Linkam, LK-600PH) at 80 °C and cooled to 25 °C at a controlled rate of 1 °C/min. Cloud points were determined visually by noting the appearance of turbidity under an optical microscope (Olympus, BX 50).

A DSC (Perkin Elmer, DSC-7) was used to determine the glass transition temperature. The solid sample was sealed in an aluminum DSC pan, maintained at 20 °C for 3 min and then heated up to 120 °C at the rate of 10 °C/min.

2.2.2. Phase diagram of three component system at 70 °C

Four kinds of homogeneous PMMA/cyclohexanol solutions with polymer concentrations of 3, 5, 7 and 10 wt% were prepared in a test tube at 70 °C. Then, a small amount of water was successively added to the solution. Cloud point was determined visually by noting the appearance of turbidity.

2.3. Membrane preparation

2.3.1. TIPS process

The PMMA–cyclohexanol sample of 20 wt% polymer concentration was sealed with two cover slips. For adjusting membrane thickness, the Teflon film of 300 μm thickness was inserted between the cover slips. The sample was heated on the hot stage at 80 °C to cause melt-blending and then quenched to 40 °C at the cooling rate of 130 °C/min for the phase separation. After the retention for 10 min at 40 °C, the sample was freeze-dried to remove the diluent.

2.3.2. Immersion precipitation

The cover slips with sample of 20 wt% polymer concentration was heated at 80 °C as described above. After only the upper cover slip was removed, the sample was immersed in water at 70 °C for 15 h. Then, the membrane sample was freeze-dried.

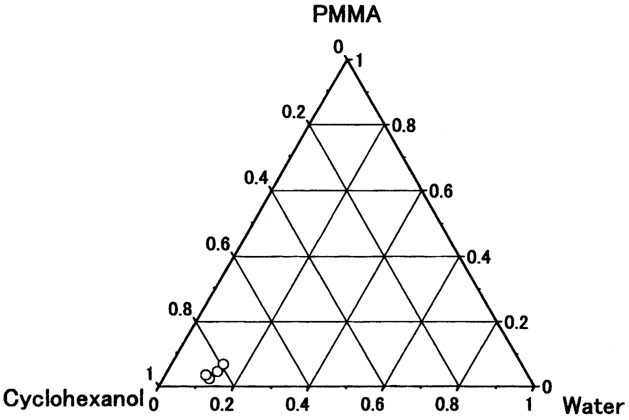

Fig. 2. Phase diagram in PMMA/cyclohexanol/water system at 70 °C: (○) cloud point.

2.3.3. Combined use of TIPS and immersion precipitation

After the cover slips with the sample of 20 wt% polymer concentration was heated at 80 °C, the upper cover slip was removed and the sample was immersed in nonsolvents such as water or methanol at 40 °C. The immersion period was varied. In this process, the cooling at 40 °C and the penetration of the nonsolvent occur simultaneously. When water was used as nonsolvent, the sample was freeze-dried for the removal of water. In the case of methanol, the membrane was dried at room temperature.

2.4. Light transmittance measurement and SEM observation

When the phase separation occurs, the polymer solution becomes turbid, which reduces the light transmittance through the polymer solution. Thus, the light transmittance measurement gives information about the phase separation [11,12]. Experimental procedure was similar to that described in Section 2.3.3. The sample with one cover slip on the bottom side heated at 80 °C was immersed in water or methanol at 40 °C. The time-course of the light transmittance through the polymer solution was monitored by a polymer dynamics analyzer (Otsuka Electronics Co., DYNA-3000).

The microporous membranes prepared by the various methods were fractured in liquid nitrogen and mounted vertically on a sample holder. The sample was coated with Pt/Pd. A SEM (Hitachi Co., S-2300) with an accelerating voltage set to 15 kV was set to examine the membrane cross-sections.

3. Results and discussion

Fig. 1 shows the phase diagram of the relation between PMMA weight fraction and temperature. In all the

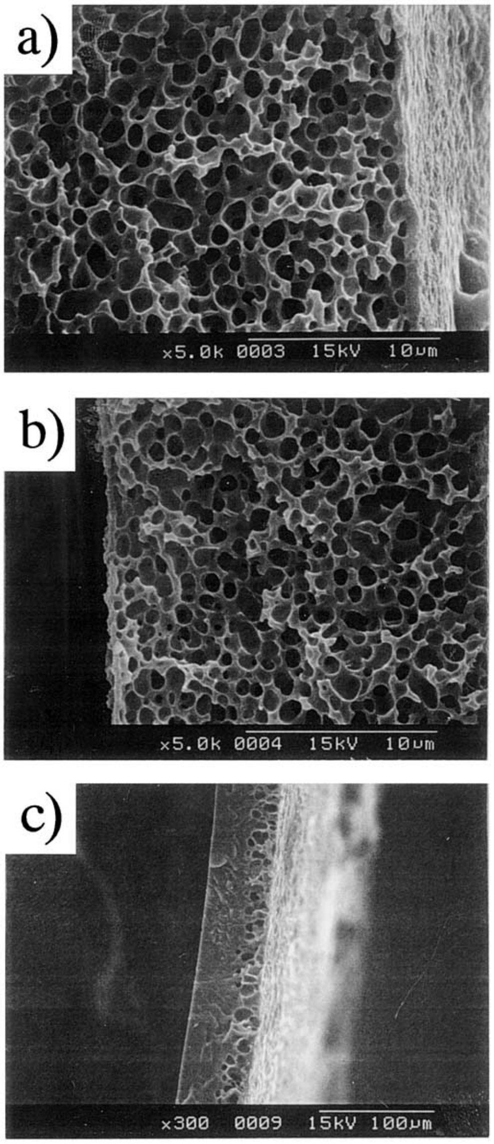

Fig. 3. Porous structures prepared by normal TIPS and immersion precipitation. Polymer concentration = 20 wt%. TIPS: temperature = 40 °C, experimental period = 10 min. Immersion precipitation: nonsolvent = water, temperature = 70 °C, immersion time = 15 h: (a) structure prepared by TIPS near one side, (b) structure prepared by TIPS near other side, (c) whole cross-section of porous membrane prepared by immersion precipitation. Right side corresponds to top surface.

experiments for the preparation of membranes, initial polymer concentration was fixed at 20 wt%. In this polymer concentration, the cloud point and the glass transition temperature were 63 and 33 °C, respectively. As described above, the normal immersion precipitation was carried out at 70 °C. This temperature is above the cloud point and TIPS does not occur. The temperature of the nonsolvent was 40 °C in the combined use of TIPS and the immersion precipitation. This temperature was between the cloud point and the glass transition temperature. Thus, the polymer structure can be changed during the immersion in the nonsolvent because the polymer is not in the glassy state.

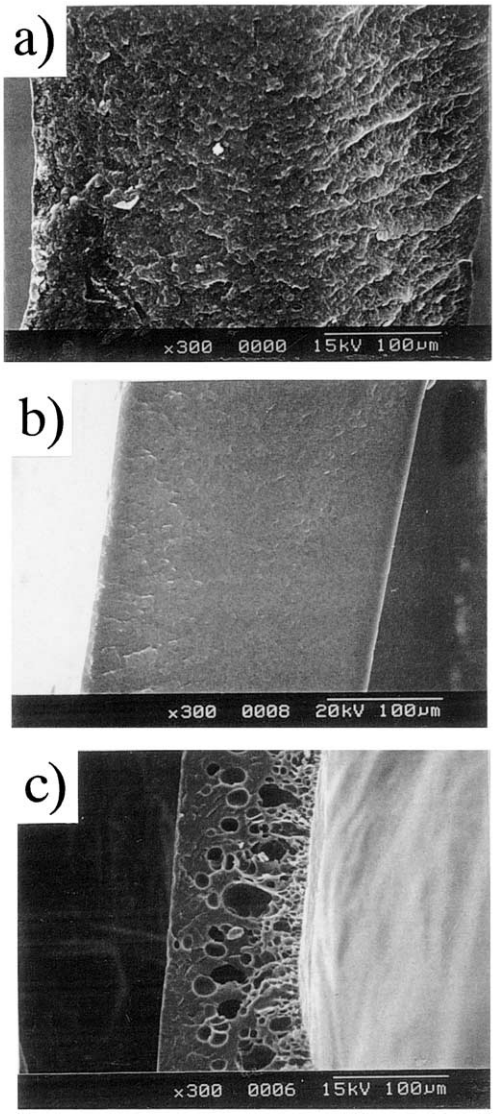

Fig. 4. Whole cross-sections of membranes prepared in the combined use of TIPS and immersion precipitation. Nonsolvent: water, nonsolvent temperature: 40 °C, polymer concentration = 20 wt%. Right side corresponds to top surface: (a) immersion period = 1 min, (b) immersion period = 10 min, (c) immersion period = 24 h.

Phase diagram of ternary system of PMMA/cyclohexanol/water is shown in Fig. 2. In this system, about 15 wt% water induces the phase separation.

Fig. 3(a) and (b) shows porous structures near both the surfaces of the membrane prepared by TIPS. The cellular structures, which are typical in membranes prepared by liquid–liquid phase separation of TIPS, were formed near both surfaces. The pore structure was isotropic, that is, the pore size at one side is almost the same as that at the other side because the cooling conditions at both sides were similar. The cross-section of the membrane prepared by immersion precipitation is shown in Fig. 3(c). Near the top surface contacted with nonsolvent, macrovoids were formed. This is also the typical structure in membranes prepared by the immersion precipitation.

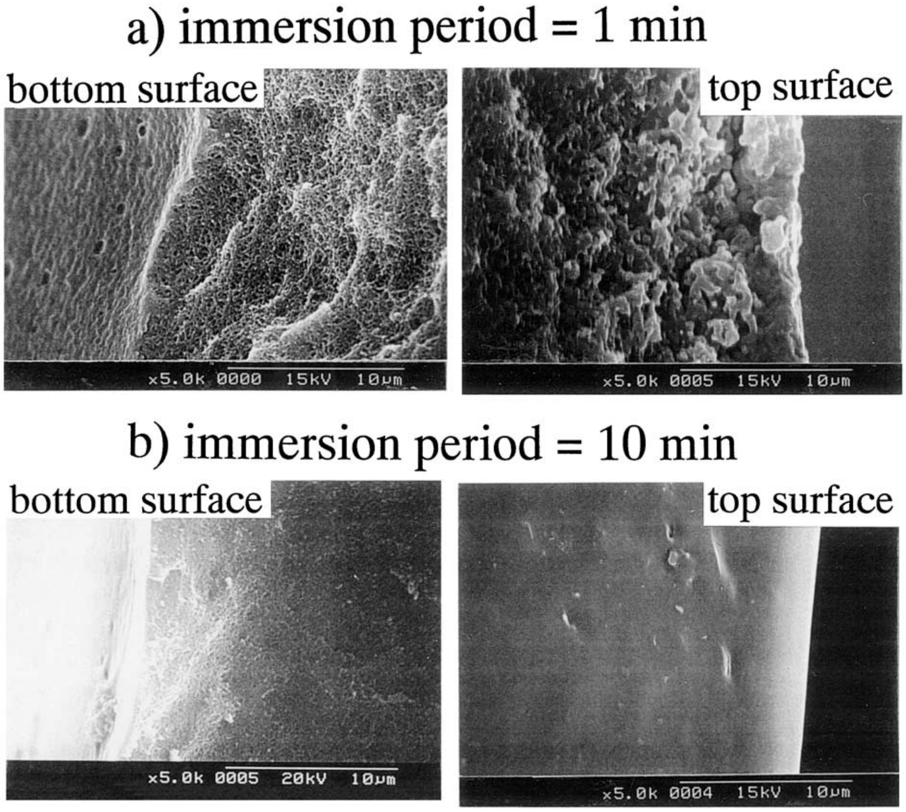

Fig. 5. Structures near top and bottom surfaces of membrane shown in Fig. 4(a) and (b): (a) immersion period = 1 min, (b) immersion period = 10 min.

Whole cross-sections of the membranes prepared in the combined use of TIPS and the immersion precipitation are shown in Fig. 4. Water was used as the nonsolvent. When the immersion period was 1 min, pores were formed in almost the whole cross-sections. However, most of the pores disappeared after 10 min. The immersion for 24 h brought about the formation of macrovoids near the top surface.

Figure 5 shows structures near top surface contacted with nonsolvent and near bottom surface contacted with the cover slip of the membranes shown in Fig. 4(a) and (b). When immersed for 1 min, thin skin layer was formed near the top surface. Therefore, the asymmetric structure with dense skin layer was obtained. As the immersion period increased to 10 min, the thickness of the skin layer became thick near the top surface and the pore size near the bottom surface decreased.

Formation of membrane structures shown in Figs. 4 and 5 is explained as follows. The membrane was prepared by the immersion in the cooled nonsolvent. Heat transfer is generally about two order faster than mass transfer in liquids [13]. Thus, just after the immersion in the cooled nonsolvent, TIPS occurs rather than NIPS. The membrane shown in Fig. 5(a) nearly corresponds to that in this stage. As shown in Table 1, the difference in the solubility parameters between cyclohexanol (diluent) and water (nonsolvent) is large, which indicates the low mutual affinity between the diluent and the nonsolvent. In this case, a high ratio of diluent outflow versus nonsolvent inflow is achieved and in fact only the diluent diffuses out of the polymer solution [1]. Thus, the composition near the top surface shifts to the high polymer concentration region, which is the one phase region without the occurrence of the phase separation. The membrane structure at this stage is shown in Fig. 5(b). Near top surface, the skin layer without pores was formed due to the high polymer concentration brought about by the diluent outflow. The schematic composition change in this process is shown in Fig. 6(a). In the phase diagram of Fig. 1, only the cloud points above the temperature of nonsolvent (40 °C) were shown. In the low polymer concentration region in Fig. 1, the glass transition temperatures were about 33 °C and were nearly constant. This means that the temperature at which the cloud point and the glass transition curve intersect is 33 °C [15]. Thus, in the high polymer concentration region, the cloud point is below 40 °C, which indicates that the polymer solution can become homogeneous at 40 °C with the increase in the polymer concentration. After the further

Table 1
Solubility parameters

Diluent or nonsolvent	Solubility parameter δ (MPa$^{1/2}$)[a]
Cyclohexanol	22.4
Water	47.9
Methanol	29.6

[a] Ref. [14].

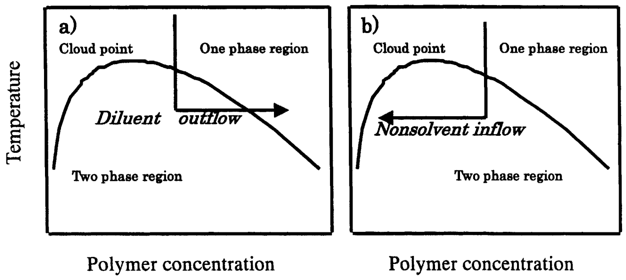

Fig. 6. Schematic composition change: (a) nonsolvent = water, (b) nonsolvent = methanol.

immersion in the nonsolvent, the nonsolvent diffuses into the polymer solution and the NIPS occur. Thus, the obtained membrane structure shown in Fig. 4(c) is similar to that by the normal immersion precipitation. These experimental results indicate that TIPS and NIPS occurred serially, when water was used as nonsolvent. Table 2 shows the membrane thickness in three immersion periods. The thickness decreased with increase in the immersion period, which supports that the diluent outflow is higher than the nonsolvent inflow.

Fig. 7 shows the cross-sections of the membranes prepared in the combined use of TIPS and the immersion precipitation using methanol as nonsolvent. As shown in Table 1, the solubility parameter of methanol is close to that of cyclohexanol. Therefore, the nonsolvent inflow is higher than the diluent outflow, which is in contrast to the case of water. This is confirmed by the increase of the membrane thickness with the increase of the immersion period, as shown in Table 2. Even when immersed for 1 min, the large pores were formed near the top surface due to the inflow of methanol. As can be seen in the enlarged photograph near the bottom surface of Fig. 7(b), TIPS produced small pores near the bottom surface. Thus, the obtained membrane had the asymmetric structure with the larger pores near the top surface. This asymmetry is opposite to the membrane shown in Fig. 5(a). Fig. 6(b) shows the schematic composition change in this case. In the case of methanol, TIPS and NIPS occurred simultaneously. This is also in contrast to the case of water. After 10 min immersion, pores near the top surface became larger and the large pores were formed even in the inner region due to the deeper penetration of methanol. The pore size near the bottom surface also increased.

Table 2
Membrane thickness (μm)

Immersion period	Water (nonsolvent)	Methanol (nonsolvent)
1 min	394	286
10 min	249	328
24 h	118	547

Fig. 8 shows the time-courses of the light transmittance through the polymer solution immersed in the nonsolvent bath in the case of the combined use of TIPS and the immersion precipitation. The ordinates of these figures are the relative light transmittances, which are the transmittances divided by the initial value. When water was used as nonsolvent, the light transmittance initially decreased by

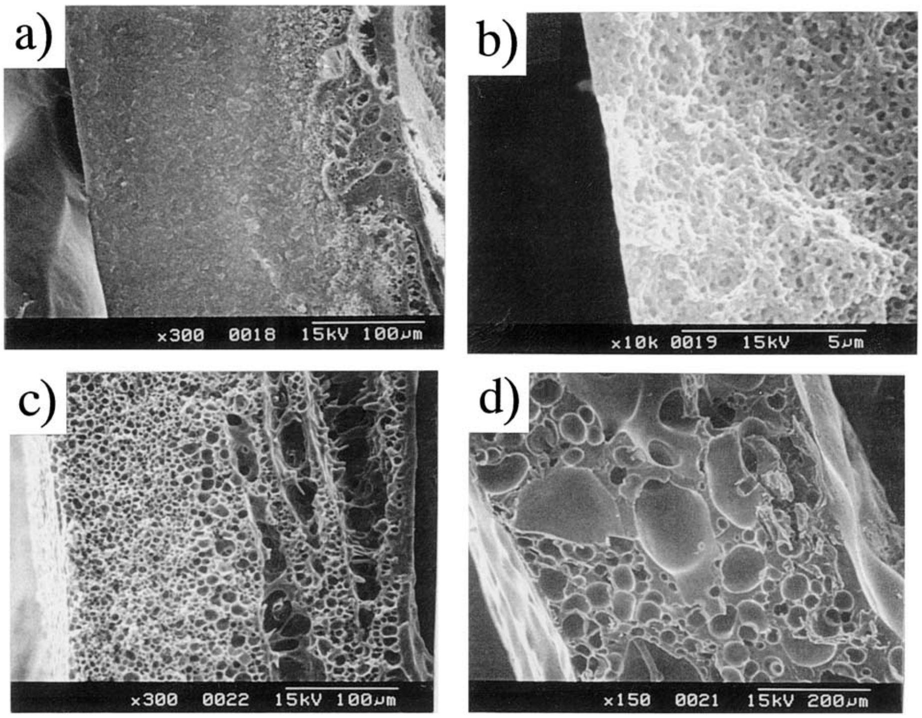

Fig. 7. Cross-sections of membranes prepared in the combined use of TIPS and immersion precipitation. Nonsolvent: methanol, nonsolvent temperature: 40 °C, polymer concentration = 20 wt%. Right side corresponds to top surface: (a) immersion period = 1 min, (b) structure near bottom surface of membrane shown in (a), (c) immersion period = 10 min, (d) immersion period = 24 h.

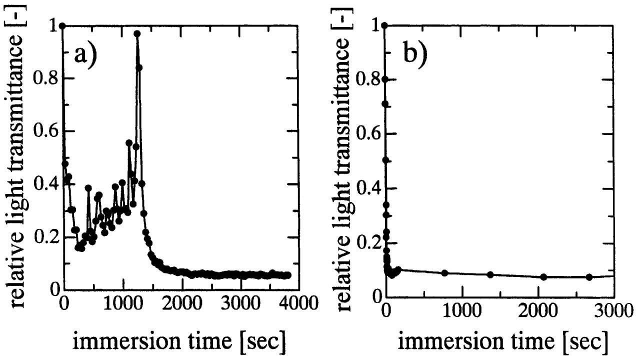

Fig. 8. Time-course of light transmittance through polymer solution immersed in nonsolvent bath: (a) nonsolvent = water, (b) nonsolvent = methanol.

TIPS process. Then the outflow of the diluent made polymer solution homogeneous and the light transmittance increased and nearly returned to the initial value. Finally, the inflow of nonsolvent induced the phase separation, which again led to the decrease in the light transmittance. Thus, this change of the light transmittance supports the serial occurrence of TIPS and NIPS. In the case of methanol, the transmittance initially decreased and then hardly changed. This is because of the simultaneous occurrence of TIPS and NIPS.

4. Conclusion

PMMA membranes were prepared in the combined use of TIPS and the immersion precipitation. When water was used as nonsolvent, the porous structure was formed by TIPS immediately after the immersion. Near the top surface, the thin skin layer was formed due to the outflow of the diluent. Thus, the obtained membrane was asymmetric. When the immersion time was 10 min, the thickness of the skin layer became thick. The further immersion led to the NIPS because large amount of nonsolvent penetrated into the polymer solution. Thus, TIPS and NIPS occurred serially.

In the case of methanol, even after 1 min immersion, large pores attributable to the NIPS were formed near the top surface, while small pores were formed by TIPS near the bottom surface. Therefore, TIPS and NIPS occurred simultaneously, which is in contrast to the result in the case of water.

The light transmittance through the polymer solution was measured when immersed in the nonsolvent bath. From the obtained time-course of the transmittance, the serial and simultaneous occurrences of TIPS and NIPS were confirmed in the cases of water and methanol, respectively.

References

[1] Mulder M. Basic principles of membrane technology. Dordrecht: Kluwer; 1996.
[2] van de Witte P, Dijkstra PJ, van den Berg JWA, Feijen J. J Membr Sci 1996;117:1.
[3] Lloyd DR, Kinzer KE, Tseng HS. J Membr Sci 1990;52:239.
[4] Tsai FJ, Torkelson M. Macromolecules 1990;23:775.
[5] Kim SS, Lloyd DR. J Membr Sci 1991;64:13.
[6] Vadalia HC, Lee HK, Myerson AS, Levon K. J Membr Sci 1994;89:37.
[7] Mehta RH, Madsen DA, Kalika DS. J Membr Sci 1995;107:93.
[8] Cha BJ, Char K, Kim JJ, Kim SS, Kim CK. J Membr Sci 1995;108:219.
[9] Matsuyama H, Berghmans S, Lloyd DR. Polymer 1999;40:2289.
[10] Matsuyama H, Yuasa M, Kitamura Y, Teramoto M, Lloyd DR. J Membr Sci 2000;179:91.
[11] Kim JH, Lee KH. J Membr Sci 1998;138:153.
[12] Reuvers AJ, Smolders CA. J Membr Sci 1987;34:67.
[13] Komiyama H. Rate processes (in Japanese). Tokyo: Asakura Syoten; 1990.
[14] Barton AFM. Handbook of solubility parameters and other cohesion parameters. Boca Raton: CRC Press; 1991.
[15] De Rudder J, Berghmans H, Arnauts J. Polymer 1999;40:5919.