Formation of Anisotropic Membranes via Thermally Induced Phase Separation

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1. Introduction

Thermally induced phase separation (TIPS) is one of the major methods for making microporous membranes[1]. The TIPS process is based on the phenomenon that the solvent quality decreases when the temperature is decreased. Thus, by cooling the polymer diluent solution, phase separation occurs.

In separation applications, an anisotropic (a gradation of cell size from small at the feed-side to large at the permeate-side of the membrane) or asymmetric (a relatively dense skin on a microporous support) membrane structure is desirable. However, isotropic structures have been mostly produced by the TIPS process, that is, the pore size does not vary with direction in the membrane.

In this work, anisotropic and asymmetric polypropylene membranes were produced by TIPS process.

2. Principle of formation of anisotropic or asymmetric structure

Typical phase diagram in the TIPS process is shown in Fig.1. The faster cooling rate is, the shorter a time interval from onset of the phase separation to polymer solidification (time interval A shown in Fig.1) becomes. Thus, the high cooling rate brings about the smaller pores. Production of anisotropic or asymmetric structure can be achieved by imposing the

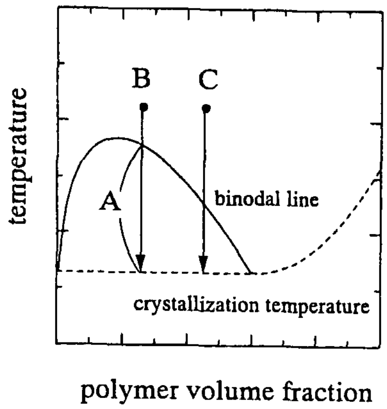

Fig.1 Typical phase diagram.

cooling rate gradient across the membrane.

Alternative production of anisotropic or asymmetric TIPS membrane was achieved by inducing a polymer concentration gradient in the membrane solution. Examples of conditions at bottom and top surfaces are shown in Fig.1 as point B and C, respectively. The time interval from onset of the phase separation to polymer solidification is shorter at the top surface (point C) than that at the bottom (point B). Furthermore, the higher polymer concentration leads to slower droplet coarsening owing to the lower volume fraction of the droplet phase. Due to these two factors, the anisotropic structure can be obtained.

3.Experimental

The polymer and diluent used are isotropic polypropylene (iPP, Aldrich Chemical Co., Mw = 250000) and diphenyl ether. The preparation of a homogeneous polymer-diluent solid sample was similar to that described previously[2]. The anisotropic or asymmetric membranes were prepared by two methods (method A and B). In method A, the anisotropy was produced by the polymer concentration gradient in the membrane solution, while the cooling rate gradient was imposed in method B. In both methods, the solid sample with 100 μm thickness was put in a glass bottle, sealed by a glass cap and heated at 433.2 K to cause melt-blending. In method A, the glass cap was taken off and evaporation of diluent was allowed from the exposed surface (top surface) into the air at 433.2 K. After evaporation, the entire assembly was cooled in room temperature air. In method B, the cooling rate gradient was imposed across the sample. After the melt-blended sample was obtained, the top surface of the sample was immersed in cool water (298.2 K or 333.2 K) for 1 or 3 sec. Then the assembly was placed at room temperature.

Solute rejection was measured using a stirred cell. The solutes used were vitamin B_{12} (molecular weight:1355), lysozyme (14600), ovalbumin (45000), γ-globulin (160000), ferritin(440000).

4.Results and discussion

Figure 2 shows the cross sections of the membranes obtained by contacting only the top surface of the sample with water. Right sides of the membranes correspond to the surfaces contacted with water. Three kinds of membranes were prepared by changing water temperature and contact time. As reference, isotropic membrane prepared with no cooling rate gradient is also added in Fig.2. In these membranes, pore sizes at the top surfaces are evidently smaller than at the bottom surfaces. In SEM observation at higher magnification, top surfaces were found to have skin layers with about 1 μ m. Thus, these membranes were asymmetric membranes.

Figure 3 shows the solute rejection results for the asymmetric membranes. The isotropic membrane used for comparison purpose had no rejection. In the asymmetric membranes, lower water temperature and longer contact time in the preparation condition led to the higher solute rejection. The rejection coefficient of lysozyme of molecular weight of 14600 reached more than 0.95 in the membrane prepared by contacting with 298 K water for 3 sec. This indicates that the asymmetric polypropylene membrane prepared in this work can be regarded as ultrafiltration membrane.

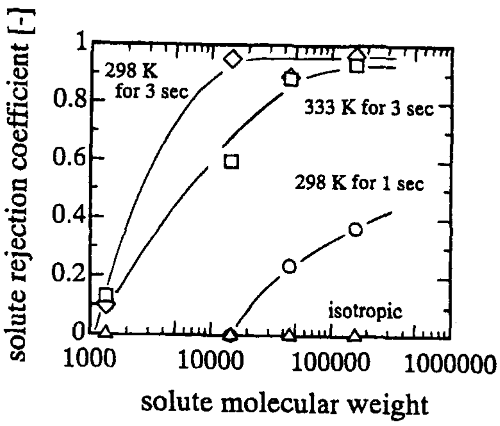

Fig.3 Relation between solute rejection coefficient and solute Stokes diameter.
Membranes were prepared by imposing the cooling rate gradient.
△: cooled at room temperature (isotropic)
○: cooled at 298 K for 1 sec
□: cooled at 333 K for 3 sec
◇: cooled at 298 K for 3 sec

5.Conclusion

Production of asymmetric structure was achieved by imposing the cooling rate gradient across the membrane. The membranes had the skin layers of about 1 μm thickness at the surfaces contacted with water. The asymmetric membrane showed the solute rejection coefficient of more than 0.95 in lysozyme of molecular weight of 14600. This result clearly showed that the asymmetric membrane can be regarded as ultrafiltration membrane. Formation of anisotropic membrane by the polymer concentration gradient will be mentioned in the presentation.

References

1) For example, A.J.Castro, US Patent 4,247,498 (1981)

2) S.S. Kim and D.R.Lloyd, *J. Membrane Sci.*, **64**, 13 (1991)

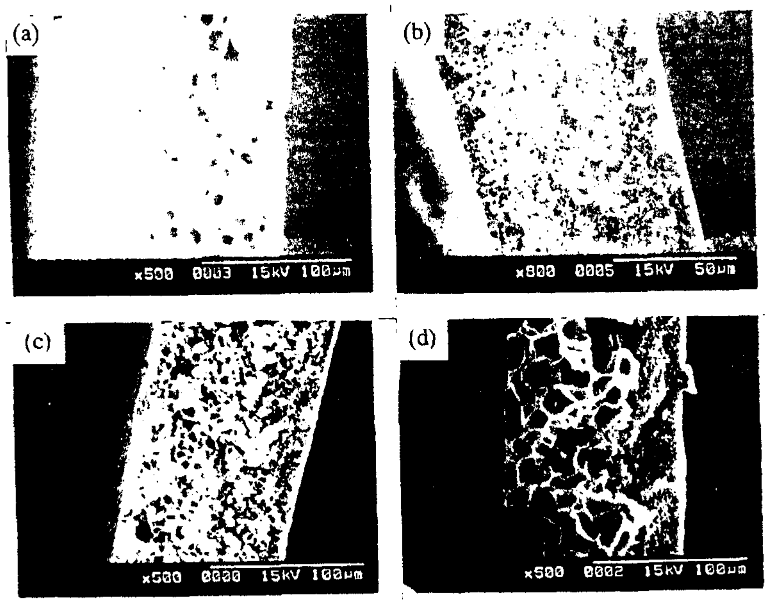

Fig.2 Cross sections of membranes obtained by contacting only the top surface with water.
Right sides of the membranes correspond to the surfaces contacted with water.
(a) isotropic membrane
(b) cooled at 298 K for 3 sec
(c) cooled at 333 K for 3 sec
(d) cooled at 298 K for 1 sec