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Communications to the Editor

A Novel Preparative Method of Microporous Poly(4,4′-oxydiphenylenepyromellitimide) Membranes

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Introduction. Microporous polymeric membranes[1] have been applied to a variety of uses in the water treatment, gas separation, electronics, medical, food, and other industries. As a method for preparing these membranes, the phase inversion process introduced first by Loeb et al.[2] is well-known and has been utilized for commercial production. Using this technique, microporous membranes from a variety of polymers have been prepared successfully.

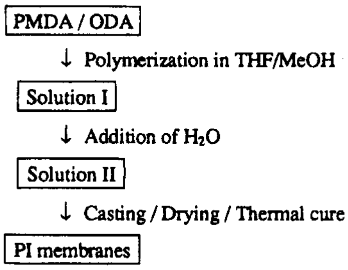
Concerning poly(4,4′-oxydiphenylenepyromellitimide) (PI),[3] which is one of the most useful polyimides because of its high thermal stability and good mechanical strength, a microporous membrane by the phase inversion process was presented first by Dupont's researcher.[4] The resulting microstructure of the PI membrane was asymmetrical and the pore volume was relatively low, as is the case with other polymeric membranes prepared by this process. As an alternative method to prepare microporous polymeric membranes, the thermally induced phase separation (TIPS) method introduced first by Castro[5] has been developed using a variety of polymer–solvent systems in which vinyl polymers are used commonly.[6] According to this process, microporous polymeric membranes with uniform cell size and higher pore volume can be prepared. However, it seems difficult to apply this process, in which cooling is utilized, for preparing microporous PI membranes. Consequently, there appeared no methods for preparing a PI membrane with uniform cell size and higher pore volume, which must be useful in various applications, especially as porous layers in composite membranes for reverse osmosis, ultrafiltration, and gas separation.

In view of the above, a method for preparing microporous PI membranes has been investigated. As a result, we have discovered that, from a homogeneous poly(4,4′-oxydiphenylenepyromellitamic acid) (PAA) solution containing a mixed solvent of tetrahydrofuran (THF), methanol (MeOH), and H_2O, microporous PI membranes with both uniform cell size and higher pore volume can be made by a simple process. As will be shown, a basic concept of this process is quite novel.

In this paper, aspects of the preparative method and basic properties of the resulting PI membranes are presented.

Experimental Section. Microporous PI membranes were prepared according to Scheme 1. The polymerization procedure[7] is as follows: Into a three-necked flask fitted with a mechanical stirrer and thermometer were charged 20.02 g (0.100 mol) of ODA, 286.8 g of THF, and 71.7 g of MeOH (THF/MeOH = 8/2 by weight). Stirring was begun, and after the ODA had dissolved, 22.24 g (0.102 mol) of PMDA powder was added gradually to the stirring solution of the diamine over 40 min. The temperature of the solution was maintained between 20 and 25 °C during the addition of PMDA. The stirring was continued at room temperature for 20 min. Thereafter, the temperature was maintained at room temperature for 24 h. The solid content and weight-average molecular weight (M_w)[8] of the resulting solution (which is denoted by solution I) were 10 wt % and 155 000, respectively.

Scheme 1. Preparation of Microporous PI Membranes



With stirring, 118.2 g of H_2O (THF/MeOH/H_2O = 80/20/33 by weight) was added dropwise into the solution I for 3 h. During the addition of H_2O, the temperature of the solution was maintained between 10 and 15 °C using a cooling bath. Thereafter, the solution was allowed to stand at 5 °C for 72 h. The solid content and M_w of the resulting homogeneous solution (which is denoted by solution II) was 8 wt % and 92 000, respectively.[9]

The PAA solution was coated on a glass plate using an automatic film applicator (Yasuda Seiki Co., Ltd.) at a speed of 40 mm/s and to a thickness of 300 μm. The coated film was dried at room temperature (20 °C) for 30 min and at 80 °C for 2 h. Thereafter, the thus formed films were removed from the glass plate to yield opaque PAA films. The PAA films were cured thermally from room temperature to 300 °C at a heating rate of 1 °C/min, and the temperature was held at 300 °C for 3 h in a nitrogen atmosphere to yield flexible PI membranes with a thickness of 50 μm, which exhibited IR spectra in accordance with assigned structure.[10]

The H_2 gas permeability of the resulting PI membranes was measured at 20 °C using an apparatus prepared for this study. Figure 1 shows a schematic diagram of the apparatus equipped with a Film Flow Meter SF-1100 (STEC Inc.).[11]

Results and Discussion. Figure 2 shows the cross-sectional view[12] of the resulting microstructure for the PI membrane (which is denoted by membrane A) prepared from solution II. A honeycomb structure with higher pore volume and uniform cell size was observed. The formation of such microporous structures is because the phase separation is induced during the drying process in the PAA film casted from solution II. On the contrary, as reported previously,[13] the phase separation does not occur during the drying process in the PAA film

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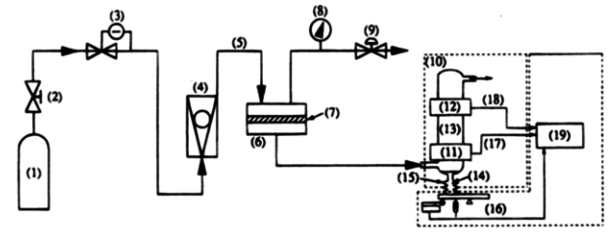

Figure 1. Schematic diagram of the apparatus for gas permeation: (1) gas cylinder; (2) line regulator; (3) needle valve; (4) flow meter; (5) sample gas; (6) permeation cell; (7) PI membrane; (8) pressure gauge; (9) pressure relief valve; (10) flow measurement unit; (11) start detector; (12) stop detector; (13) volume measurement tube; (14) soapy water; (15) accordion fold; (16) bubble generator lever; (17) start signal; (18) stop signal; (19) data processor.

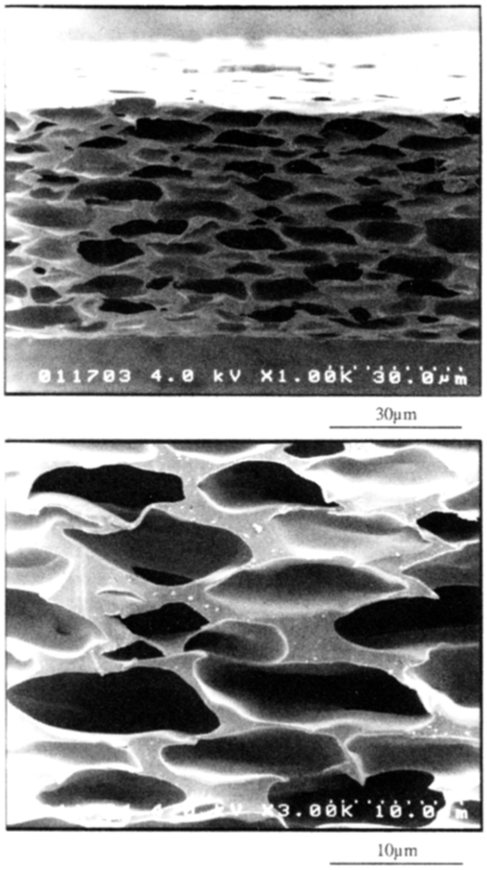

Figure 2. Scanning electron micorgraphs of the cross section of the PI membrane (membrane A). The membrane was prepared from a 8 wt % PAA solution containing THF, MeOH, and H_2O (THF/MeOH/H_2O = 80/20/33 by weight).

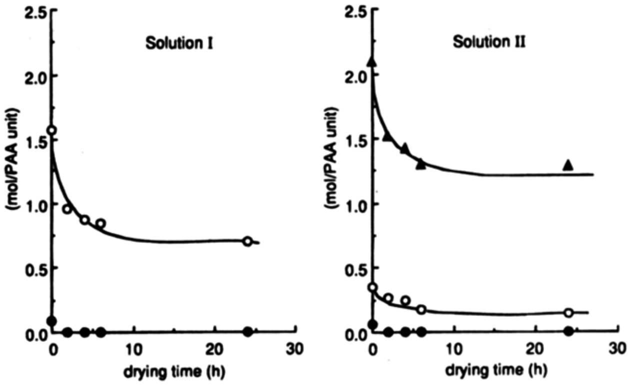

Figure 3. Solvents remaining in dried PAA films at 80 °C: (○) THF; (●) MeOH; (▲) H_2O.

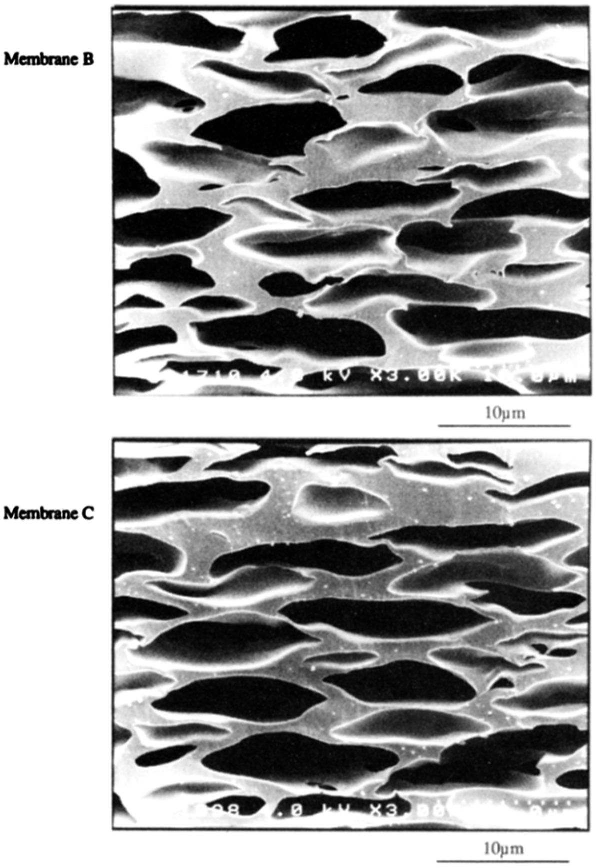

Figure 4. Scanning electron micrographs of the cross section of the PI membranes (membranes B and C). Membranes were prepared from 8 wt % PAA solutions containing THF, MeOH, and H_2O (THF/MeOH/H_2O = 80/20/30 and 80/20/25 by weight).

casted from the PAA solution composed of THF/MeOH alone[14] (which is corresponding to solution I), and a transparent PI film with no voids can be obtained by thermal cure.

In order to clarify which of the solvents remains in the PAA films during the process of drying, the solvent composition of dried films, which were prepared under various drying conditions from both solutions I and II, was determined by ^{1}H-NMR measurements.[15] The sample films were dissolved in DMSO-d_6 to perform the NMR measurements. The results, which are shown and compared in Figure 3, clearly indicate that the evaporation behavior of THF is quite different between solutions I and II, while that of MeOH is almost the same in both solvent systems. Furthermore, in the case of the solution II, it was found that a significant amount of H_2O, which is a typical non-solvent for the PAA, is still remaining in the dried PAA film even if the drying is continued at 80 °C for 24 h. Consequently, the thus trapped water in the dried film should induce the phase separation which leads to the formation of the microporous structures.

In sharp contrast, when NMP or DMAc (boiling point: 202 and 166 °C, respectively) is used as a solvent for solution I, even if H_2O is added to the PAA solution, the porous PI membranes were not able to be obtained under any drying condition.[16] From these results, it was considered that the boiling point of the solvents in solution I needs to be lower than that of H_2O in order to induce the phase separation.

In order to examine effects of H_2O on the pore formation, additional PI membranes were prepared from 8 wt % PAA solutions in which weight parts of

Table 1. Properties of the Membrane Sample

			mechanical properties[b]			
thickness (μm)	apparent density (g/cm^3)	pore volume[a] (vol %)	tensile strength (kg/mm^2)	tensile modulus (kg/mm^2)	elongation (%)	H_2 gas permeability (cm^3(STP)/cm^2·s·cmHg)
50	0.48	66	2.3	52	28	5.5

[a] Calculated value from the apparent density and the true density (1.43 g/cm^3). [b] Mechanical properties were measured at 20 °C according to JIS (Japanese Industrial Standard) K 7127 on a INTESCO Model 2020.

THF/MeOH/H_2O were 80/20/30 and 80/20/25. (These membranes are denoted by membrane B and membrane C, respectively.) The contents of H_2O which is remaining in the dried PAA films of membranes B and C were found to be almost similar to that of membrane A. As the cross-sectional view of the resulting microstructure for membranes B and C is shown in Figure 4, there appeared no significant difference in the cell size among membranes A–C. These results indicate that the pore formation in the present method depends on the contents of H_2O remaining in the dried PAA films.

Properties of membrane A are summarized in Table 1. The higher gas permeability of the membrane indicates that continuous micropores are formed through the present method. In addition, as shown in Table 1, the membrane had good mechanical properties in spite of the higher pore volume. For comparison, microporous PI membranes with thicknesses of 40 μm were prepared from a NMP solution by the traditional phase inversion method. The H_2 gas permeability of the resulting membrane was found to be less than 1×10^{-5} cm^3(STP)/cm^2·s·cmHg, which was consistent with the value in the patent literature.[4] As is well-known, so-called skin layers are formed through the phase inversion method, so that the gas permeability of the resulting membrane may be extremely low in comparison with the present membrane in which the skin layers are not formed.

Actually, in the present method, solvents dissolving polymers should be evaporated from the casted film in order to induce microphase separation. On the contrary, the phase inversion method using a coagulant bath needs the exchange of solvent and nonsolvent. In this sense, the present method is quite different from the phase inversion method, although both methods need nonsolvents. Furthermore, the present method is different from the traditional TIPS method, which needs cooling, although a concept of both methods can be represented by a term of "thermally induced phase separation".

Finally, it should be noted that the present PI membranes are useful in various applications.

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(7) Polymerization-grade pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) were purchased from commercial sources and were used as received. THF and MeOH were reagent-grade materials and were used as received.

(8) M_w was determined using a Hitachi GPC system equipped with a Hitachi RI detector and a Hitachi Kasei column (GL-S300MDT-5) in DMF/LiBr/H_3PO_4/THF at 35 °C. Molecular weight calculations were based on polystyrene standards.

(9) M_w of solution II is lower than that of solution I. This is due to the hydrolysis of PAA. However, it should be noted that M_w of solution II is still high enough to prepare PI membranes, so that the hydrolysis does not cause a serious problem if the solution is used within 72 h after an addition of water.

(10) Infrared (IR) spectra were recorded on an FTIR spectroscopic system (Perkin-Elmer system 2000).

(11) The diameter of sample membranes shaped into a disk was 47 mm. The value of gas permeability was calculated from relations between gas flow rates and pressures.

(12) Analyses by scanning electron microscopy (SEM) were performed using a Hitachi S-4000. Cross sections of sample membranes were prepared by a freeze-fracturing method under liquid nitrogen, and the membrane samples were gold sputtered before analyses.

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(14) It should be noted here that THF or MeOH alone does not dissolve PAA.

(15) ^{H}-NMR spectra were recorded on an NMR spectroscopic system (Varian 300 MHz) at 20 °C.

(16) It should be noted that, when NMP or DMAc is used, hydrolysis of PAA proceeds faster compared to the present solvent system.

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