

A Poly(4,4'-oxydiphenylene-pyromellitimide) Membrane with Novel Pore Structure

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ABSTRACT: A poly(4,4'-oxydiphenylene-pyromellitimide) (PI) membrane with unique microporous structure has been developed. The PI membrane can be prepared from homogeneous poly(4,4'-oxydiphenylene-pyromellitic acid) (PAA) solutions containing tetrahydrofuran (THF), methanol (MeOH) and toluene in a particular ratio, by coating onto a copper foil, followed by drying and thermal cure. Microporous structure formed by this process has been found to be isotropic asymmetric. The resulting PI membranes showing both good mechanical properties and lower dielectric constant due to the micropores may be useful for various microelectronics applications.

Introduction

Polymeric porous membranes prepared by phase separation process such as the phase inversion or thermally induced phase separation (TIPS) process show a variety of microporous structures. In order to represent these microporous structures, a particular terminology has been proposed. Tanny¹ classified membranes with gradient pore size profiles as anisotropic membranes, while anisotropic membranes with thin skin layers were called asymmetric membranes. On the contrary, Caneba² referred to the above asymmetric membrane (i.e., skinned membranes with an internal pore size gradient) as anisotropic asymmetric membranes. According to Caneba's terminology, which is considered to be more clear, polymeric porous membranes can be logically classified into four different categories. These may be represented by terms such as isotropic, anisotropic, isotropic asymmetric, and anisotropic asymmetric structures, respectively, as illustrated in Fig. 1. As well known, membranes produced by the phase inversion process (so-called Loeb's membranes) have an anisotropic asymmetric structure.³ On the other hand, membranes produced by the thermally induced phase separation (TIPS) method⁴ (first introduced by Castro⁵) show isotropic or anisotropic structure. Polymeric membranes with an isotropic asymmetric structure have not been reported.

In the course of our investigation related to polyimide membranes, we have discovered that microporous poly(4,4'-oxydiphenylene-pyromellitimide) (PI)⁶ membranes with an isotropic asymmetric structure can be prepared from poly(4,4'-oxydiphenylene-pyromellitic acid) (PAA) solutions containing a mixed solvent composed of tetrahydrofuran (THF), methanol (MeOH) and toluene through a simple process.

Aspects of these microporous PI membranes and their possible applications will be presented.

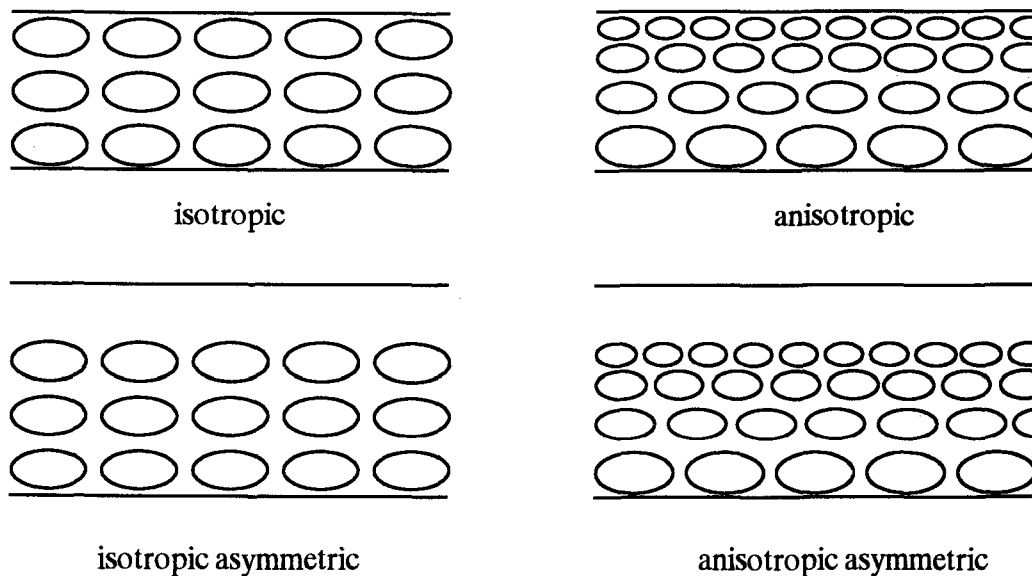
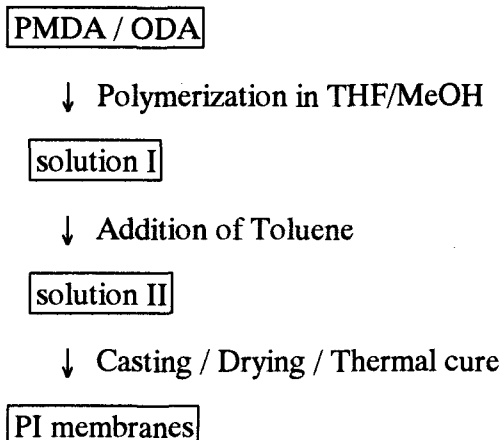


Figure 1. Classification of microstructures in polymer membranes.

Experimental Section

Microporous PI membranes were prepared according to Scheme 1. The polymerization procedure⁷ is as follows: Into a three-necked flask fitted with a mechanical stirrer and thermometer were charged 20.02 g (0.100 mol) of 4,4'-oxydianiline (ODA), 286.8 g of THF and 71.7 g of MeOH. Stirring was begun and after the ODA had dissolved, 22.24 g (0.102 mol) of pyromellitic dianhydride (PMDA) powder was added gradually to the stirring solution of the diamine over 40 min. The temperature of the solution was maintained between 20 °C and 25 °C during the addition of PMDA. The stirring was continued at room temperature for 20 min and the temperature was maintained for 24 h. Into the resulting homogenous solution, (which is denoted by solution I) 30.3 g of toluene was added dropwise for 3 hours with stirring and

Scheme 1. Preparation of Microporous PI Membranes



the temperature was maintained for 24 hours. The solid content and M_w^8 of the resulting homogeneous solution (which is denoted by solution II) was 13 wt% and 110000, respectively.

The solution was coated on a copper foil using an automatic film applicator at a speed of 40 mm/sec. The coated film was dried at 40 °C for 30 minutes and at 80 °C for 6 hours. The PAA films were cured thermally from room temperature to 300 °C at a heating rate of 10 °C/min and temperature was held at 300 °C for 3 hours in a nitrogen atmosphere. Copper was then removed by etching from the resulting laminate to yield flexible PI membranes which exhibited IR spectra in accordance with assigned structure.⁹

Results and Discussion

Figure 2 shows the cross sectional view¹⁰ of the resulting microstructure for the PI membrane prepared from solution II. Typical isotropic asymmetric structure are confirmed because the thickness of nonporous layers is almost the same as that of porous layers which appear to be isotropic. The micropores are formed because the phase separation is induced during the drying process in the PAA film cast from solution II. As reported previously,¹¹ the phase separation does not occur during the drying process in the PAA film cast from the PAA solution composed of THF/MeOH alone¹² (corresponding to solution I), and a transparent PI film with no voids can be obtained by thermal cure.

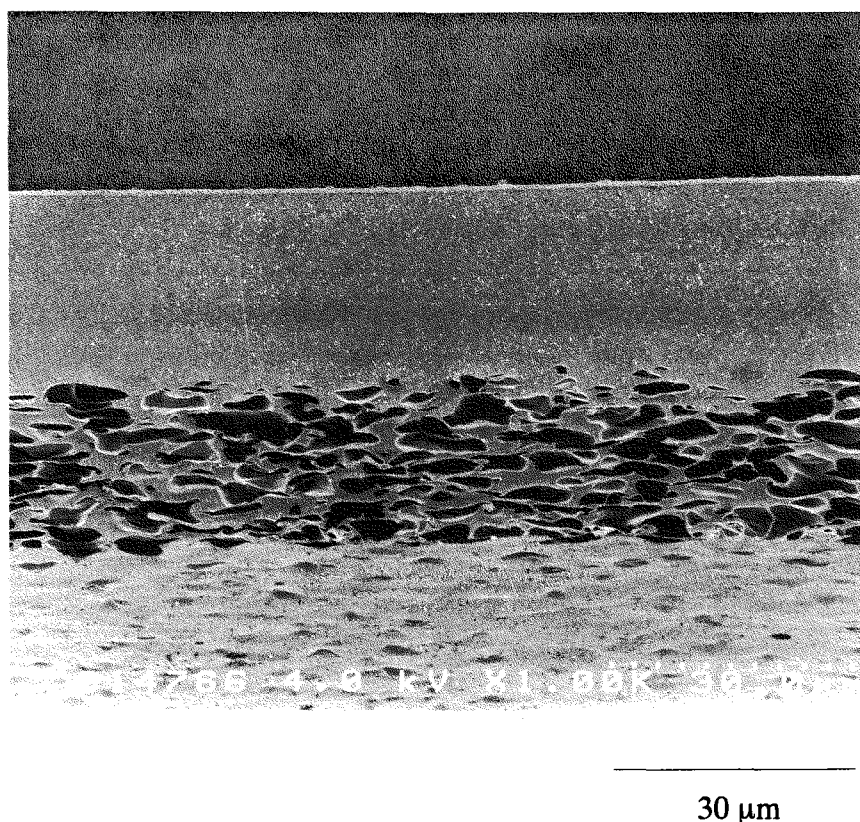


Figure 2. Scanning electron micrograph of the cross section of the PI membrane.

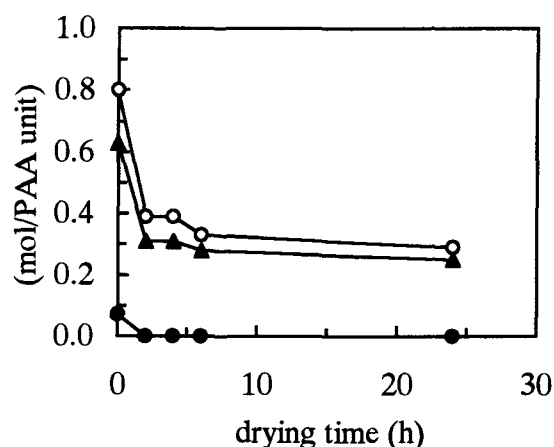


Figure 3. Solvents remaining in dried PAA films at 80 °C:
(O) THF; (●) MeOH; (▲) toluene.

In order to clarify which of the solvents remains in the PAA films during the drying, the solvent composition of the dried films, which were prepared under various drying conditions from the solution I and II, was determined by $^1\text{H-NMR}$ measurements.¹³ The sample films were dissolved in $\text{DMSO-}d_6$ for the NMR measurements. The results, shown in Figure 3, clearly indicate that the evaporation behavior of THF is quite different between solution 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 toluene, which is a typical non-solvent for the PAA, remains in the dried PAA film even if the drying is continued at 80 °C for 24 h. Consequently, the toluene trapped in the dried film should induce the phase separation in a manner as shown in Figure 4, which leads to the formation of the isotropic asymmetric microporous structure. At present, the reason of this interesting phenomenon is not known.

In sharp contrast, when N-methyl-2-pyrrolidone (NMP) or N,N-dimethylacetamide (DMAc) (boiling point: 202 and 166 °C, respectively) is used as a solvent for polymerization of PMDA with ODA, even if toluene is added to the resulting PAA solution, the porous PI membranes could not be obtained under any drying condition. Apparently, the boiling point of the solvents in the solution I needs to be lower than that of toluene in order to induce the phase separation.

The PI membranes with such unique microporous structure will be used for microelectronics applications. Generally speaking, PI has proved to be the most suitable

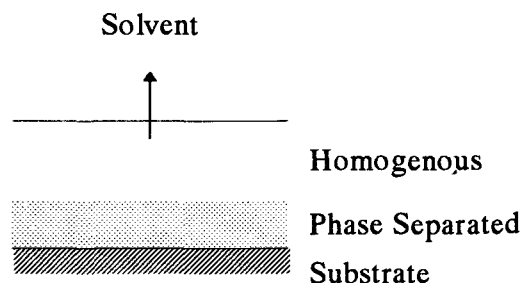


Figure 4. Schematic diagram of the formation of microporous structure.

Table 1. Properties of the PI membrane

thick- ness (μm)	apparent density (g/cm^3)	pore volume (%)	mechanical properties ^a			dielectric constant ^b
			tensile strength (kg/mm^2)	tensile modulus (kg/mm^2)	elon- gation (%)	
50	1.15	19	12.5	300	42	2.65

^a Mechanical properties were measured at 20 °C according to JIS (Japanese Industrial Standard) K 7127 on a INTESCO model 2020. ^b To the PI membrane laminated with the copper foil, a silver paste was applied in a circular form 62 mm in diameter and the resulting laminate was dried at 80 °C for 10 hours to produce a capacitor of the PI membrane interposed between the copper and silver paste. Using an impedance analyzer (Hewlett Packard 4194A) the electrostatic capacitance of the capacitor was measured at 1 MHz.

high performance polymer for this application due to the favorable processability and excellent properties including thermal stability, good mechanical strength and chemical resistance. Although PI meets most of the material requirement, it has been desired to reduce the dielectric constant.¹⁴ One solution will be the use of a microporous structure. In Table 1, basic properties of the present membrane are summarized. Obviously, the microporous structure leads to lowering of the dielectric constant. Thanks to the non-porous layer, the membrane had good mechanical properties in spite of the higher pore volume as shown in the Table. Thus, the present membranes may be suitable for microelectronics applications.

In the preparative process of the present membrane, solvents dissolving polymers should be evaporated from the cast film in order to induce microphase separation. By contrast, the phase inversion process using a coagulant bath requires the exchange of solvent and nonsolvent. Thus, the present process is different from the phase inversion method and from the thermally induced phase separation (TIPS), which needs cooling, although all these processes depend on a phase separation.

References and Notes

- (1) Tanny, G. B. *J. Appl. Polym. Sci.* **1974**, *18*, 2149.
- (2) (a) Caneba, G. T.; Soong, D. S. *Macromolecules* **1985**, *18*, 2538.
(b) Caneba, G. T.; Soong, D. S. *Macromolecules* **1985**, *18*, 2545.
- (3) Loeb, S.; Sourirajan, S. *Adv. Chem. Ser.* **1963**, *38*, 117.
- (4) (a) Song, S.-W.; Torkelson, J. M. *Macromolecules* **1994**, *27*, 6389.
(b) Lloyd, D. R.; Kinzer, K. E.; Tseng, H. S. *J. Membrane Sci.* **1990**, *52*, 239.
(c) Kim, S. S.; Lim, G. B. A.; Alwattari, A. A.; Wang, Y. F.; Lloyd, D. R. *J. Membrane Sci.* **1991**, *64*, 41.
- (5) *Chem. Eng. News* **1978**, *56* (Dec 11), 23-24.
- (6) Sroog, C. E. *J. Polym. Sci., Macromolecular Reviews* **1976**, *11*, 161.
- (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) Mw was determined using a Hitachi GPC system equipped with a Hitachi RI detector and a Hitachi Kasei column (GL-S300MDT-5) in DMF/LiBr/H₃PO₄/THF at 35 °C. Molecular weight calculations were based on polystyrene standards.
- (9) Infrared (IR) spectra were recorded on an FTIR spectroscopic system (Perkin Elmer system 2000).
- (10) 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.
- (11) (a) Echigo, Y.; Iwaya, Y.; Tomioka, I.; Furukawa, M.; Okamoto, S. *Macromolecules*, **1995**, *28*, 3000.
(b) Echigo, Y.; Iwaya, Y.; Tomioka, I.; Yamada, H. *Macromolecules*, **1995**, *28*, 4861.
- (12) It should be noted here that THF or MeOH alone does not dissolve PAA.
- (13) ¹H-NMR spectra were recorded on an NMR spectroscopic system (Varian 300 MHz) at 20 °C.
- (14) Since the velocity of pulse propagation is inversely proportional to the square root of the dielectric constant of the medium, reductions in the dielectric constant of the insulating material, translate directly into improvements in machine cycle time. The most common method to reduce the dielectric constant of PI may be a chemical modification such as copolymerization using fluorinated monomer or blending with a low dielectric polymer. When these techniques are applied, the dielectric constant may be reduced to some extent. However, it seems not easy to reduce the dielectric constant significantly with maintaining other excellent properties of PI.