

**MICROPOROUS MEMBRANES FROM AN INSOLUBLE POLYIMIDE**

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*Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.*

Poly(amic acid) prepared from 3,3',4,4'-benzophenonetetracarboxylic dianhydride and bis(4-aminophenyl) ether was used for preparation of microporous membranes by the phase inversion process. Membranes coagulated in acetic anhydride were brittle but usable for ultrafiltration. Coagulation of the poly(amic acid) in water or lower alcohols and subsequent thermal cyclocondensation led to extremely brittle polyimides, which limits their use for ultrafiltration process.

In recent years, membrane separation processes have gained widespread acceptance in chemical, pharmaceutical, and food industries. Some techniques, such as ultrafiltration, microfiltration, and membrane distillation utilize microporous membranes; these membranes are also used as substrates for composite membranes in reverse osmosis or in gas separations. Microporous membranes are most often prepared by the phase inversion process developed by Loeb and Sourirajan<sup>1</sup>: a viscous polymer solution is left to coagulate in a nonsolvent bath. By this method microporous membranes have been prepared from a number of polymers<sup>2</sup>. Common polymer membranes, however, cannot be used for separations in organic solvents because of poor chemical stabilities of most polymers. The same holds for the preparation of composite membranes when the selective layer is cast from a solution in organic solvent on a microporous polymer substrate; therefore, new chemically resistant microporous membranes have to be developed. It appears that one of suitable materials for this purpose could be such polyimide which is insoluble in organic solvents. Although dense membranes based on these polyimides are often used for gas separations, vapour permeation or pervaporation, so far only Bo and Kun<sup>3</sup> have reported the preparation of an absolutely insoluble microporous polyimide membrane with open pores. Other prepared microporous polyimide membranes were soluble or were attacked by some organic solvents<sup>4-6</sup>. The aim of this work was to prepare microporous membranes with open pores, stable in all organic solvents, starting from relatively accessible monomers bis(4-aminophenyl) ether and 3,3',4,4'-benzophenonetetracarboxylic dianhydride.

## EXPERIMENTAL

IR spectra were measured with a Perkin–Elmer 577 Grating Infrared Spectrometer (KBr technique) and  $^1\text{H}$  NMR spectra with a Bruker ACF-300 at 300 MHz. Chemical shifts are given in ppm ( $\delta$ -scale).

3,3',4,4'-benzophenonetetracarboxylic dianhydride (Aldrich) was purified by crystallization from acetic anhydride. Bis(4-aminophenyl) ether (Fluka) was purified by crystallization from ethanol.

*Poly(amic acid)*. An equimolar amount of 3,3',4,4'-benzophenonetetracarboxylic dianhydride was added to a vigorously stirred solution of bis(4-aminophenyl) ether in dimethylformamide under nitrogen atmosphere at 20 °C. Poly(amic acid) resulting after 24 h was precipitated in water and dried. Reduced viscosity  $\eta_{\text{red}} = 1.1$  dl/g (0.001 M LiCl in DMF, 25 °C). IR spectrum (KBr):  $\tilde{\nu}$  ( $\text{cm}^{-1}$ ): 1 650 (C=O, amide), 1 530 (NH, amide), 1 500 (arom.), 1 240 (C–O–C).  $^1\text{H}$  NMR spectrum (DMSO): 12.83 sb, 2 H (COOH); 10.53 s, 2 H (CONH); 7.7–8.1 m, 6 H (arom. dianhydride); 7.60 s, 4 H (arom., *ortho* to N); 6.88 s, 4 H (arom., *ortho* to O).

The membranes were prepared by casting a solution of the poly(amic acid) in *N*-methylpyrrolidone on a glass plate as a film 0.35 mm thick. In some cases a small amount of a nonsolvent for the poly(amic acid), either 1-butanol or propionic acid, was added to the casting solution. 30 s after casting, the glass plate with the film was immersed into a precipitation bath containing a nonsolvent for poly(amic acid). If an acetic anhydride precipitation bath was used, pyridine was added to the bath after 15 min (one third of its volume) and the membrane was left in this mixture for 16 h. Then, it was transferred to water bath. If a toluene bath was used, the membrane was transferred into ethanol after 30 min in toluene, then into water, dried in air and heated for 4 h at 350 °C in vacuo. Membranes precipitated in ethanol were transferred into water, dried in air and also heated for 4 h at 350 °C in vacuo. Membranes precipitated in water were heat-treated in the same manner.

Ultrafiltration experiments were carried out in a stirred cell (Amicon Model 52) at 0.1 MPa and 20 °C. The measurements were carried out first with distilled water, then with an 0.1% aqueous solution of Dextran T70 ( $M_w = 74\,300$ ,  $M_n = 36\,300$ ), and finally with an 0.1% aqueous solution of Dextran T500 ( $M_w = 48\,6000$ ,  $M_n = 197\,700$ ; Pharmacia Chemicals). The dextran concentrations were measured by means of a differential refractometer (Waters R4).

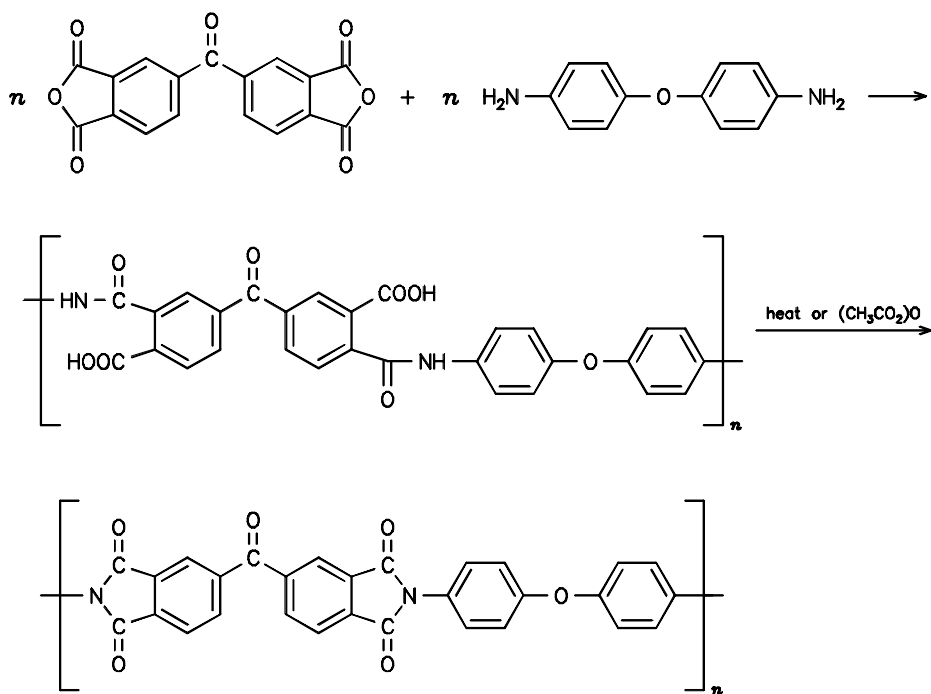
## RESULTS AND DISCUSSION

The polyimide used in the phase inversion process was synthesized from 3,3',4,4'-benzophenonetetracarboxylic dianhydride and bis(4-aminophenyl) ether via poly(amic acid) as it is shown in Scheme 1.

Transformation of the precursor to the fully cyclized product was carried out by thermal treatment (after the phase inversion process) or using acetic anhydride (which is also a nonsolvent in coagulation). Infrared spectra of both chemically and thermally cyclized polymers are identical and they show absorption bands at 1 780, 1 730, 1 380 and 720  $\text{cm}^{-1}$ . These bands are characteristic of polyimides<sup>7–9</sup>. On the other hand, typical absorption bands of the amide C=O group at 1 650  $\text{cm}^{-1}$  may be distinguished only as shoulders of the strong bands of the imide cycle. Absorption bands of C=O group at 1 730  $\text{cm}^{-1}$  and of the amide NH at 1 520  $\text{cm}^{-1}$  disappeared completely. This indicates a very high degree of cyclization. Whereas chemically cyclized polymer dissolves in boiling *N*-methylpyrrolidone, thermally cyclized samples are insoluble in organic solvents. As the insolubility of the polyimide cannot be caused by crystalline phase (the polyimide has entirely amorphous structure<sup>10</sup>), crosslinking seems to take place during

thermal treatment. It is most often brought about by the imine groups resulting from the reaction of a carbonyl group with an amine end group<sup>11</sup>. As the characteristic absorption band of the C=N group is at  $1\,740\text{ cm}^{-1}$  (ref.<sup>12</sup>), possible presence of this group cannot be proved, since this region is dominated by a very intensive band of out-of-plane vibration of the imide C=O groups.

SEM micrographs of cross-sections of prepared membranes are shown in Fig. 1. Membranes coagulated in water, lower alcohols or acetic anhydride had distinctly porous structure. Membranes coagulated in acetic anhydride and cast from a solution without any nonsolvent (Fig. 1a) had some larger cavities. Their structure was asymmetric with pores diminishing towards that surface of the membrane, which was in contact with air during the 30 s evaporation time after casting, i.e., towards the membrane skin. Addition of a nonsolvent (propionic acid or 1-butanol) to the casting solution resulted (depending on amount of the nonsolvent) in diminishing of cavities and an apparent suppression of asymmetry (Fig. 1b). With increasing amount of a nonsolvent, permeability of membranes also increased and their retention ability decreased (Table I) due to the relative increase of pore sizes on the evaporation side of mem-



SCHEME 1

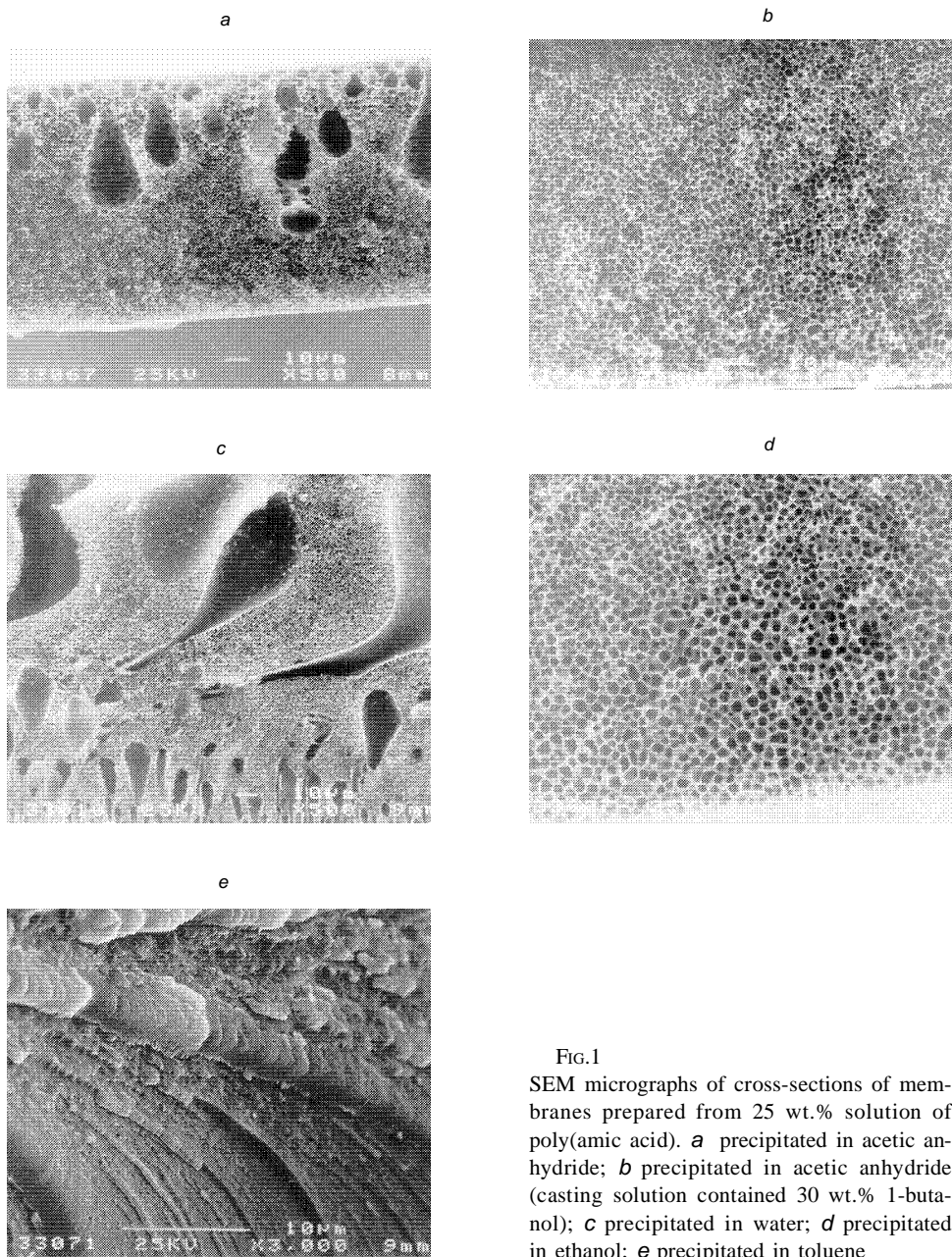


FIG.1

SEM micrographs of cross-sections of membranes prepared from 25 wt.% solution of poly(amic acid). *a* precipitated in acetic anhydride; *b* precipitated in acetic anhydride (casting solution contained 30 wt.% 1-butanol); *c* precipitated in water; *d* precipitated in ethanol; *e* precipitated in toluene

brane. Lower concentration of the polyamic acid in the casting solution resulted in more open structure and more permeable membrane (Table I), which is a common feature of the phase inversion process.

Membranes coagulated in water (Fig. 1c) showed more open structure with large finger-like cavities than membranes prepared from the same casting solution, but coagulated in other nonsolvents.

Membranes coagulated in ethanol exhibited also a negligible amount of asymmetry (Fig. 1d). Membranes from casting solutions with less than approx. 25 wt.% of polyamic acid shrank considerably during coagulation in ethanol and their surface resembled that of an orange peel.

Although, after coagulation in toluene, the cast film became turbid, micrographs of resulting membranes did not show any porosity (Fig. 1e).

All prepared membranes are brittle and their poor mechanical properties might limit their utility in separation techniques. Since the value of reduced viscosity does not indicate low molecular weight, the brittleness seems to be caused by the rigidity of polyimide backbone. Although many microporous membranes have been prepared with satisfactory mechanical strength, porous structure can deteriorate mechanical properties of polymers. This shortcoming of our membranes was partly overcome when a solution of the poly(amic acid) in *N*-methylpyrrolidone containing 20–30 wt.% of a nonsolvent was precipitated in acetic anhydride. In this case the result could be also influenced by chemical cyclization going on in the bath. The membranes precipitated in water and ethanol and in particular those precipitated in toluene were even more brittle, which made impossible their use in ultrafiltration cells. Although SEM micrographs of mem-

TABLE I  
Permeability of 3,3',4,4'-benzophenonetetracarboxylic dianhydride/bis(4-aminophenyl) ether polyimide membranes<sup>a</sup>

Casting solution, wt.%			Pure water flux <sup>b</sup> g/m s	Dextran retention, %	
PA <sup>c</sup>	NMP <sup>d</sup>	BuOH		MW <sup>e</sup>	MW <sup>f</sup>
18	82	–	403	0	0
22	78	–	75	8	42
25	75	–	13	42	92
25	65	10	27	14	72
25	55	20	222	1	22
25	45	30	613	0	6

<sup>a</sup> Coagulated in acetic anhydride; <sup>b</sup> 0.1 MPa; <sup>c</sup> Polyamic acid; <sup>d</sup> *N*-methylpyrrolidone; <sup>e</sup> 70 000; <sup>f</sup> 500 000.

branes precipitated in toluene did not show any porosity (Fig. 1e), the membranes were extremely brittle. SEM micrographs, however, showed fracture surfaces almost identical with those of highly brittle polymers<sup>12</sup>. Although it is clear that a microstructure of a membrane plays an important role in determining mechanical properties, it is possible that the excessive rigidity of the polymer is even a more important factor. The object of a further study should be the preparation of microporous polyimide membranes based on less rigid polymer precursors.

## REFERENCES

1. Loeb S., Sourirajan S.: *Adv. Chem. Ser.* 38, 117 (1962).
2. Kesting R. E.: *Synthetic Polymeric Membranes, A Structural Perspective*. Wiley, New York 1985.
3. Bo D., Kun Z.: *J. Membr. Sci.* 60, 63 (1991).
4. Iwama A., Kazuse Y.: *J. Membr. Sci.* 11, 297 (1982).
5. Yamagishita H., Nakane T., Yakamoto Y., Yoshitome H., Gobo K., Ikeda K.: *Kobunshi Ronbunshu* 43, 795 (1986).
6. Yamagishita H., Nakane T., Yoshitome H.: *Kobunshi Ronbunshu* 49, 1015 (1992).
7. Ishida H., Willinghof S. T., Baer E., Koenig J. L.: *Macromolecules* 13, 826 (1980).
8. Bessonov M. I., Koton M. M., Kudryavtsev V. V., Laius L. A.: *Poliimidy – klass termostoikikh polimerov*, p. 61. Nauka, Leningrad 1983.
9. Navarre M.: *Polyimides: Synthesis, Characterization and Applications*, Vol. 1, p. 429. Plenum, New York 1984.
10. Ree M., Nunes T. L., Lin J. S.: *Polymer* 35, 1148 (1994).
11. Saini K., Carlin C. H., Patterson H. H.: *J. Polym. Sci., Polym. Chem.* 31, 2751 (1993).
12. Lednický F., Pelzbauer Z.: *Int. J. Polym. Mater.* 2, 149 (1973).