Polyimide Asymmetric Membranes: Elaboration, Morphology, and Gas Permeation Performance

N. Leblanc, D. Le Cerf, C. Chappey, D. Langevin, M. Métayer, G. Muller

UMR 6522 CNRS, University of Rouen "Polymères, Biopolymères, Membranes,"
76821 Mont-Saint-Aignan Cedex, France

ABSTRACT: Asymmetric 2,2-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA)-2-methyl-1,3-phenylenediamine (mPDA) polyimide membranes were prepared according to a phase-inversion mechanism by using different solvent/nonsolvent blends. The membrane formation mechanism and the final performances of the asymmetric membranes have been found both nonsolvent and solvent nature dependent. From the visualization of cross sections of asymmetric membranes by scanning electron microscopy and the study of the permeation of two gases (N_2, CO_2) through asymmetric membranes, a relationship between elaboration conditions and asymmetric membranes characteristics could be drawn. The organization of polymer chains in solution strongly affects the final polymer arrangement and thus the final performances of the membrane. The influence of preliminary solvent evaporation before immersion has been shown to be dependent on the structure of the asymmetric membrane: finger-like or sponge-like structures. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1838–1848, 2003

Key words: asymmetric membranes; polyimide; wet phase inversion; elaboration conditions; morphology; gas permeation

INTRODUCTION

Polyimides are a class of starting materials having excellent chemical and physical properties and are well suited for the elaboration of gas-separation membranes and notably asymmetric membranes.[1,2]

Membrane formation by immersion precipitation can be modeled on the basis of thermodynamic and kinetic considerations as shown by various authors for ternary membrane-forming systems composed of a nonsolvent, a solvent, and a polymer.[3,4,5] Macrovoids are often generated during the phase-inversion technique. The presence of these macrovoids has harmful consequences to such high-pressure operations as gas separation. Therefore, attempts are necessary to avoid macrovoids during the membrane formation process.[6,7] Macrovoids are more easily formed as the doped solution is fluid. Decreasing the fluidity of the doped polymer solution would lead to a macrovoid-free asymmetric membrane. This can be achieved by gelation, resulting in an increase of the polymer solution concentration. Moreover, by controlling the solution composition during the inversion process, the membrane would have a uniform and a macrovoid-free structure with interconnected pores, in favor of a low mass-transport resistance as well as high mechanical strength.

The studied polyimide (2,2-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride–2-methyl-1,3-phenyldiamine; 6FDA–mPDA) has a primary structure with bulky groups (CF_3), offering a higher gas permeability and selectivity than polyimides free of fluorinated dianhydride moieties.[8] The solvent dependence of the 6FDA–mPDA polyimide solutions and dense films as a function of solvent conditions have been described recently.[9,10] It has been shown that conformation of polyimide in solution (isolated chains or aggregates formation) is highly dependent on solvent quality and that the permeation properties of films are affected by the presence of residual solvent. Moreover, the quality of solvent has no influence on the final properties of the dense films, probably because of the reorganization of the polymer chains during the film curing.

In a recent study, we have examined the relationship between the nature of nonsolvent and solvent and the structure of 6FDA–mPDA asymmetric membrane.[11] Different solvent/nonsolvent blends were used which differ, respectively, by their compatibility toward the 6FDA–mPDA polyimide. From the analysis of demixing curves, we have shown that the mutual affinity between solvent/polyimide and nonsolvent/solvent can be quantified by determining the interaction parameters between nonsolvent/solvent
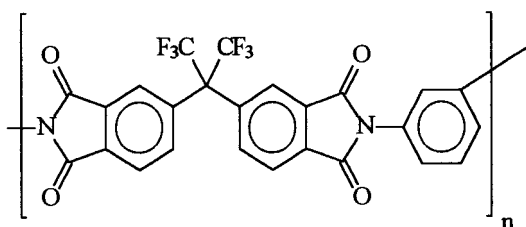
Figure 1 6FDA–mPDA primary structure.

χ_{12}, nonsolvent/polymer χ_{13}, and solvent/polymer χ_{23} from the Flory–Huggins theory.[12,13]

We have also shown than the kinetics of membrane formation was both nonsolvent and solvent dependent. More precisely, the time for forming a membrane increases with growing coagulant size and is more dependent on the nature of the nonsolvent than that of the solvent. No significally different coagulation times were observed for different casting solution in N-methyl-2-pyrrolidone (NMP), dimethylformamide (DMF), and N-N-dimethylacetamide (DMAc) immersed in the same nonsolvent. Only with dioxane as solvent, the formation of membrane needs very long times, which have been related to the high-fusion temperature of dioxane (T_f = 11.8°C). Exchanges of nonsolvent/dioxane could be actually very reduced by the coagulation bath temperature (6°C). The formed superficial layer limits nonsolvent and solvent flow ratio, hence, a longer substructure formation and consequently an increased membrane formation global time. In conclusion, the morphology of membranes depends on elaboration conditions.

In this article, our objective was an attempt to establish a correlation between the resulting morphology and permeation performances and the elaboration conditions of membranes. We have investigated the influence of the nature of the initial solution (conformation of polymer chains) and of a preliminary evaporation step on the separation properties of membranes.

EXPERIMENTAL

Materials and methods

6FDA–mPDA has a primary structure (Fig. 1) with bulky CF_3 groups responsible for a large free volume.[14] Polycondensation of a 6FDA and a mPDA obtained the polyimide. It exhibits a weight molar mass of 50,000 g mol^{-1} (obtained by laser light scattering) with a polydispersity of 1.9 (size exclusion chromatography data). It is an amorphous polymer with a glass transition temperature of 305°C (thermogravimetry analysis). The polymer was dried at 120°C for 24 h in an oven prior to use and stored under vacuum in the presence of P_2O_5.

NMP, DMAc, 1-4-dioxane, DMF, and dichloromethane (CH_2Cl_2) were used as solvents, acquired from Merck, Normapur reagent quality. All solvents were dried over molecular sieve beads (4 Å) and filtered through 0.45-μm Acrodisc CR PTFE filters (Gelman).

Water, methyl alcohol, ethyl alcohol, and isopropyl alcohol were used as nonsolvents. The water was deionized by Milli Q process. Alcohols were from Merck (NJ), Normapur reagent quality. All nonsolvents were filtered through 0.45-μm Millipore HA filters (Billerica, MA) (for water) and through 0.20-μm Millipore FG filters (for alcohols).

The permeating gases (Air Liquide, N_2, and CO_2) were at least 99.998% pure and were used without further purification.

Asymmetric membrane preparation

The casting solutions were prepared at ambient temperature. Materials necessary for solutions preparation were dried at 80°C for 12 h in an oven prior to use and stored under vacuum in the presence of P_2O_5. The composition of the casting solution was 25 wt % polyimide. An argon gaseous flow was deposited on the polymer solutions because some solvents were hygroscopic. Solutions were homogenized by vortexing and were used the day of their preparation.

The asymmetric flat 6FDA–mPDA membranes were made by using a wet-phase inversion process. They were prepared by casting solvent/6FDA–mPDA solutions (4 mL) on a glass plate by using a doctor blade set to ensure a final membrane thickness of 100–120 μm. Then they were solidified into a sloping nonsolvent bath that permits the maintainance of a homogeneous immersion speed for each system. The temperature of the coagulation bath and initial solution was 6°C and the glass plate was ambient temperature. Only solutions with dioxane were made at ambient temperature because of solvent fusion temperature (T_f = 11.8°C). In this case, solutions were cast at ambient temperature, but immersed in a 6°C nonsolvent bath. Coagulation occurs at different times as a function of the nonsolvent/solvent system. After a residence time of 30 min in the coagulation bath the film detached itself of the glass plate. All membranes were washed for 48 h in water, and then for 48 h in methyl alcohol, air-dried for 24 h, and finally dried in an oven at 200°C for 4 h to remove all solvents.

Silicone rubber coating

To seal the membrane defects, a solution of silicone (Rhodorsil RTV-2) was deposited on each membrane.[15] The coated membranes were then cured in an oven at 60°C for 24 h. The CO_2 and N_2 permeabilities of this poly(dimethylsiloxane) at 35°C were 2200 and 275 Barrers, respectively.
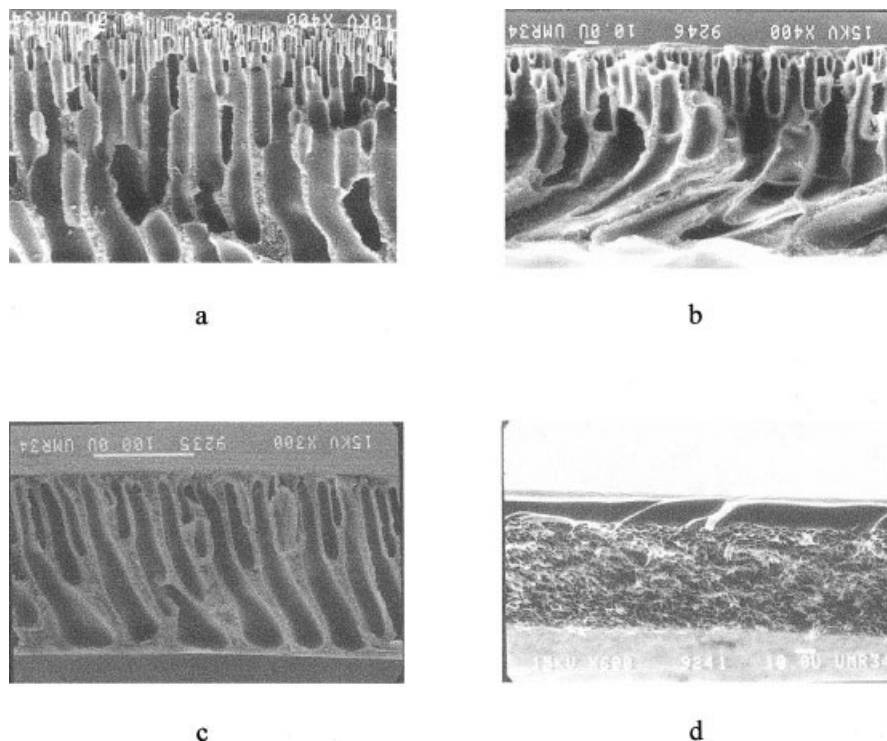
Figure 2 Cross sections of water/solvent/6FDA–mPDA membranes prepared with NMP (a), DMAc (b), DMF (c), dioxane (d).

Asymmetric membrane structure

The cross section of the asymmetric membranes was observed with a scanning electron microscope (SEM; JEOL JSM 35 CF) (JEOL, Peabody, MA). The membranes were cryogenically fractured in liquid nitrogen and then coated with gold.

Gas permeation measurements

Permeances, at 35°C by using the variable pressure method,[16] of the asymmetric membranes to carbon dioxide and nitrogen were measured and compared with the intrinsic permeability of dense films, reported in a previous work.[10] The permeance coefficient P'_i of the membrane to the gas i was obtained from the slope of the steady state of the curve $p_2 = f(t)$, assuming $p_2 \ll p_1$ (p_1 and p_2, upstream and downstream pressure, respectively). Selectivity $\alpha(CO_2/N_2)$ was expressed in terms of the ratio of the corresponding permeances:

$$\alpha(CO_2/N_2) = P'_{CO_2}/P'_{N_2}$$

The gas selectivity of the asymmetric polyimide membranes was calculated from the individual pure gas permeances.

The apparent skin layer thickness (e) and the superficial porosity (δ) of a defect-free asymmetric membrane were calculated from the permeance coefficient by using:[17]

$$P'_i = \frac{1}{e}\left(P_i + \frac{K}{\sqrt{M_i}} r\delta\right)$$

where P_i is the gas permeability coefficient of the dense membrane, K is a Knudsen coefficient, r is the pore diameter range, δ is the surface porosity, and M_i is the molar weight of gas i. For CO_2 and N_2 measurements, the final expressions of the apparent skin layer thickness and the superficial porosity become

$$e = \frac{1}{P'_{CO_2}}\left[P_{CO_2} + 309\left(\frac{P_{CO_2} - \alpha_{CO_2/N_2}P_{N_2}}{387.3\alpha_{CO_2/N_2} - 309}\right)\right]$$

$$r\delta = \frac{(P_{CO_2} - \alpha_{CO_2/N_2}P_{N_2})}{(387.3\alpha_{CO_2/N_2} - 309)}$$

The evaluation of the membrane porosity is valid for membranes porosity is valid for membranes presenting a selectivity superior or equal to Knudsen selectivity. In our case, this selectivity is equal to 0.80.

RESULTS AND DISCUSSION

Asymmetric membranes structure as a function of elaboration conditions

Figures 2, 3, 4, and 5 show photographs that illustrate how the final membrane structure is influenced by the solvent choice for a given nonsolvent. For different
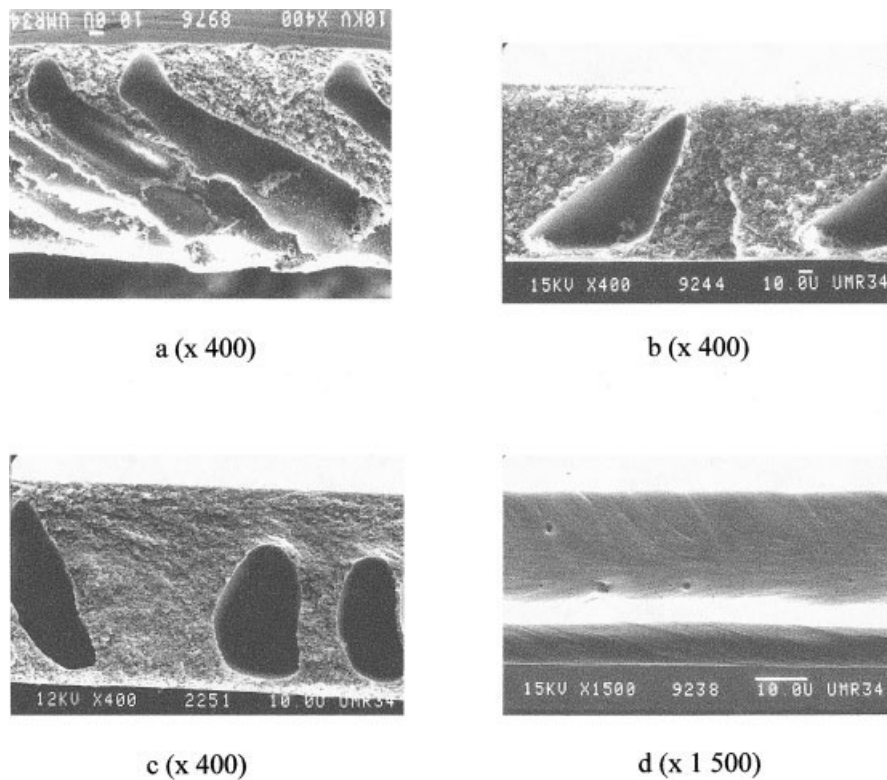
Figure 3 Cross sections of methyl alcohol/solvent/6FDA–mPDA membranes prepared with NMP (a), DMAc (b), DMF (c), CH_2Cl_2 (d).
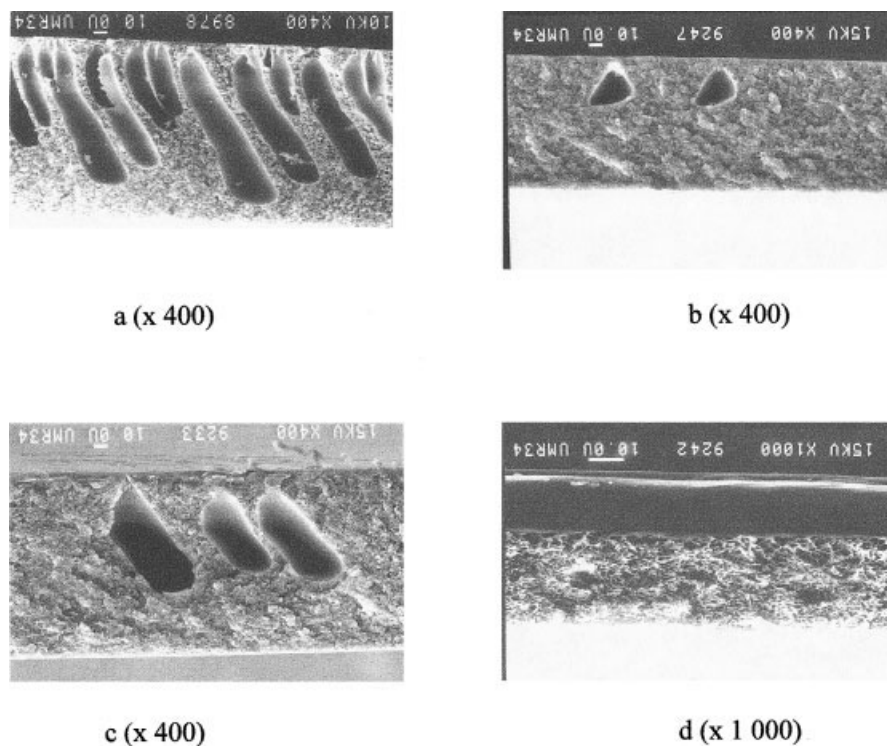

Figure 4 Cross sections of ethyl alcohol/solvent/6FDA–mPDA membranes prepared with NMP (a), DMAc (b), DMF (c), dioxane (d).
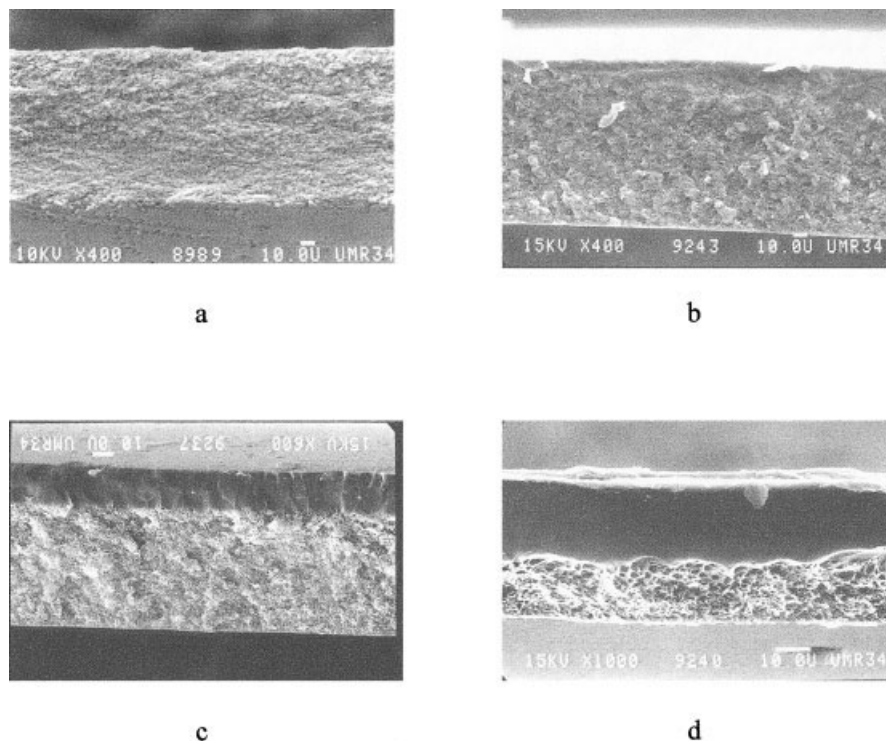
Figure 5 Cross sections of isopropyl alcohol/solvent/6FDA-mPDA membranes prepared with NMP (a), DMAc (b), DMF (c), dioxane (d).

solvents tested, changing the nonsolvent bath gives the same behavior. The transition from instantaneous to delayed time of demixing obtained by varying the type of nonsolvent for each solvent is also accompanied by the disappearance of macrovoids. On the other hand, it appears that morphology depends particularly on nonsolvent as coagulation kinetic. Indeed, using NMP, DMAc, or DMF as solvents for an identical nonsolvent, the membrane morphology is practically unchanged. Differences in interaction parameters in function of the solvent used are not large enough to modify the precipitation conditions. Only membranes obtained with DMF present substructures with less macrovoids, and a more important superficial layer than one of the membranes obtained with NMP and DMAc. The structural characteristics of membranes coincide with demixing curves and membranes formation times, presented in a recent work.[11] An overconcentration in polyimide at the interface film bath limits the macrovoids appearance.

Membranes elaborated from dioxane do not present macrovoids and show only a spongelike structure with a thick superficial layer and without apparent porosity. These membranes are characteristic of a slow liquid–liquid-phase separation process.

The cross section of a membrane prepared with a CH_2Cl_2/6FDA–mPDA solution coagulated in methyl alcohol is presenting in Figure 3d. Structure is very close to that of a dense film with no asymmetry and only microholes are present. No exchange between nonsolvent and CH_2Cl_2 took place and evaporation of the volatile solvent induced a dense film formation.

Figure 5 presents photographs of membranes obtained with 6FDA–mPDA in different solvents and coagulated in isopropyl alcohol. Transversal sections reveal that a denser and thicker skin layer appears in the order DMAc < DMF < dioxane. For NMP, no apparent dense skin exists in comparison with other solvents. These photographs prove how the solvent nature is important in the elaboration of asymmetric membrane.

In our previous study, we have reported the influence of nonsolvent nature on membrane elaborated from NMP/6FDA–mPDA solutions. Gas permeation measurements have revealed that no real dense skin was veritably formed. The solvent nature and its mutual affinity with nonsolvent and polymer seem to control the existence of the dense skin layer.

It seems then that the solvent nature controls membrane morphology with the same importance as nonsolvent. The photographs reveal that the membrane skin layer thickness increases with decreasing mutual affinity of solvent and polymer. Indeed, polyimide affinity is lower for DMF and dioxane solvents in comparison with NMP or DMAC. For solvents DMF and dioxane we obtain the thickest dense skin layers. The following hypothesis on the different solvation effect can then be theorized. The presence of favorable polymer–polymer interactions when polyimide is solvated in poor solvents involves a very fast gelation

and results in real dense skin. Permeation measurements would give useful information in favor of this assumption.

In brief, SEM images show that the important driving factor for membrane formation seems to be the local polymer concentration in the top layer of the polymer solution film, which is directly related to the affinity among polymer, solvent, and nonsolvent and kinetic parameters. Actually, the higher the polymer concentration before nucleation in the skin is, the more numerous and the smaller are the structural units.[17,18] The thickness of the skin layer gradually increases until the diffusion of solvent from the sublayer solution through the dense skin layer into the coagulation bath is restrained.[6]

Influence of solvent evaporation prior to membrane elaboration on gas transport performances

For establishing a relation between the dense skin quality and the nature of the initial solution, it is necessary to ensure that the dense skin is actually created. One method is to control the solvent outflow, which can be technically realized by an evaporation stage prior to immersion.[19,20] This evaporation is operated to increase the surfacing polymer concentration of the casting solution on the glass plate. The compactness of the superficial layer formed during the phase inversion process is then more important. By using this process, the aim is to limit the dense skin layer thickness to optimize the gaseous flow.

In Figure 6, we have reported data showing how a prior evaporation stage could affect the formation times. Prior evaporation of solvent results in larger formation times than without evaporation. This can be attributed to the increase of the 6FDA–mPDA concentration at the solution–air interface, which reduces the exchanges between nonsolvent and solvent during the solution immersion in the coagulant.

Figure 7 presents photographs of membranes elaborated from the same ternary system, with and without prior evaporation stage. The expected increase of the dense skin thickness is not observed and no significant structural difference exists when the evaporation stage is realized prior to coagulation. It can only be noted that NMP, DMAc, and DMF evaporation seems to favor the apparition of fingerlike structure, although the propagation of macrovoids should be attenuated. Macrovoids are in fact smaller but more numerous. One explanation is probably the strong hygroscopy of DMF and its sensibility to the atmosphere water.[21] Actually, the solution becomes slightly turbid during solvent evaporation. The precipitation is then initiated by air humidity, and membranes formation time is then reduced. At this stage, no real conclusion can be established concerning the prior solvent

evaporation effect. Gas permeation tests would be useful to give indications on the dense skin compactness of membranes elaborated after the solvent evaporation stage.

All asymmetric membranes were silicone coated to seal eventual defects prior to gas permeation tests. Permeametric performances of membranes elaborated from the same ternary system without and with solvent evaporation prior to coagulation are presented in Figure 8. We have distinguished on the different graphs of this figure performances of membranes as a function of their structures: a fingerlike and a spongelike structure.

Fingerlike structure membranes

We have reported in Figure 8 the permeametric characteristics [$P'(N_2)$, $P'(CO_2)$, $\alpha(CO_2/N_2)$] of membranes prepared with different nonsolvents and solvents. In general, it appears that membranes obtained by coagulation of the casting solution in water or methyl alcohol have no interesting permeametric properties. Membranes prepared with DMAC and DMF obtained by coagulation in ethyl alcohol present few macrovoids. Permeances decrease but not enough to improve selectivity. The presence of some macrovoids is sufficient to perturb membrane performances as indicated by the selectivity very close to those of silicone. Actually, membranes obtained with rapid coagulation are usually more permeable to CO_2 and N_2 but have a slightly lower selectivity. One explanation for this lower selectivity might be that the thin top layer formed contains some defects and that the silicone coating cannot correctly seal all the defects. Hence, membranes containing macrovoid morphology do not permit the obtaining of reproducible permeametric properties.

It appears that the prior solvent evaporation stage for membranes containing original macrovoids brings no improvement of the gas permeation performances. This stage does not permit the creation of a superficial layer compact enough to eliminate defects apparition. However, the test results show that gaseous flows through membranes obtained after solvent evaporation are a little bit slower. This decrease can be attributed to a sucker membrane resistance on gas passage. The structure of the membrane is then more compact. However, no selective skin is formed when the solvent is evaporated because no increase in selectivity is observed. Actually, the presence of macrovoids in membrane structure always seems to involve the presence of defects in the superficial layer. This observation is in agreement with the data reported by Icard[21] and Pedro Bom[22] and confirms that the presence of macrovoids does not favor a high selectivity.
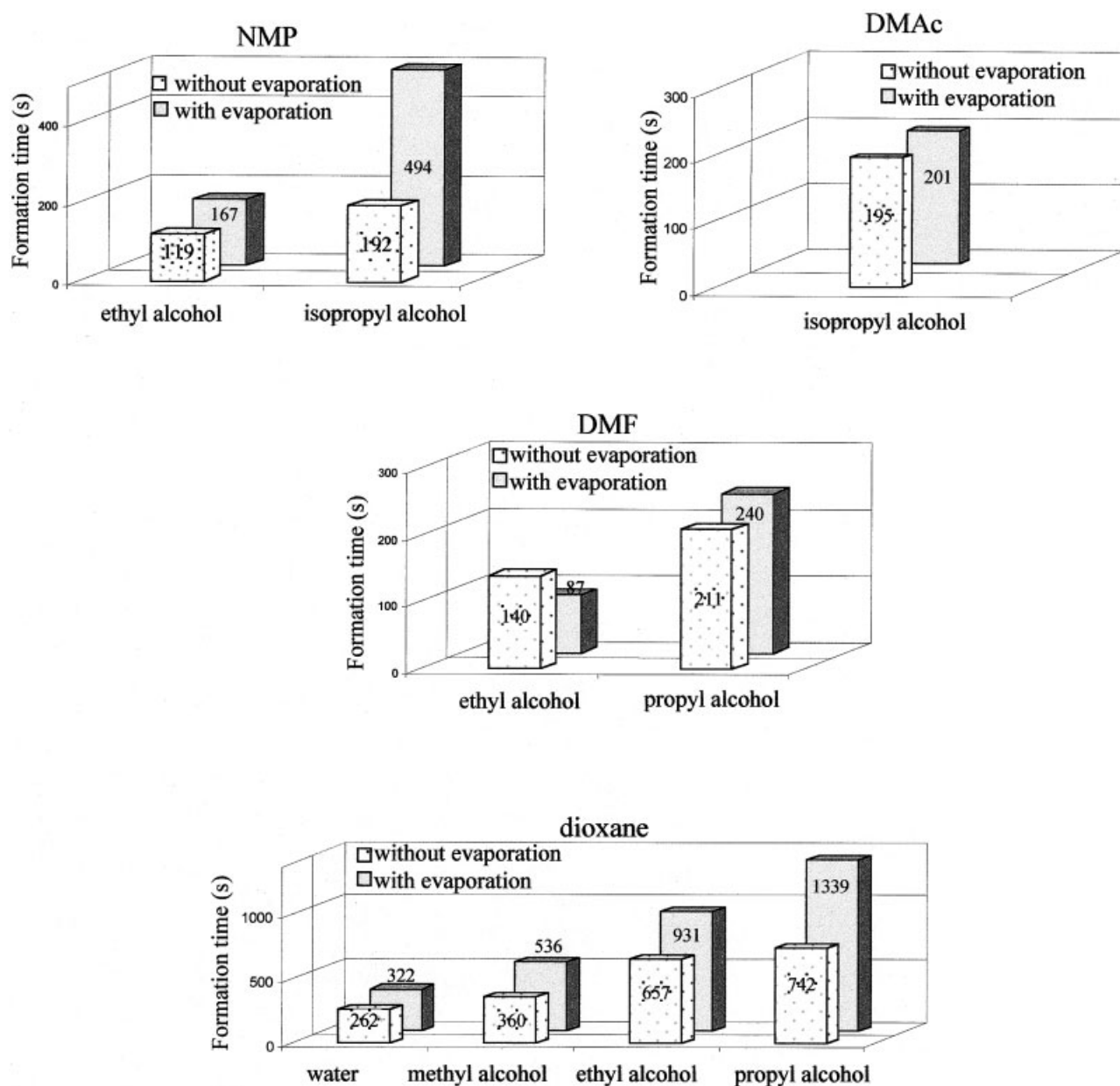
**Figure 6** Prior evaporation effect (5 min) on membranes formation time.

Spongelike structure membranes

Membranes prepared with dioxane have lower permeances than the previous ones. $P'(CO_2)$ and $P'(N_2)$ decrease with increasing affinity of alcohols and dioxane. Less permeable membranes are obtained with isopropyl alcohol. Moreover, microscopy observation indicates that the skin layer becomes thicker and thicker according to the order: methyl alcohol, ethyl alcohol, and propyl alcohol. Therefore, the presence of a dense skin layer seems to be responsible for the decrease of permeances.

The effect of solvent evaporation stage is more visible on membranes free of macrovoids (coagulation in isopropyl alcohol for NMP and DMF and with diox-

ane). Two situations can be distinguished. CO_2 permeances of membranes obtained after prior evaporation of DMF and dioxane increase without decrease of selectivity. The formed superficial layer then has a good quality. Its quality seems to be superior because an increase of $\alpha(CO_2/N_2)$, accompanied by a permeance increase, means that the dense skin is thinner but more compact. Selectivity of ethyl alcohol/dioxane/6FDA–mPDA [$\alpha(CO_2/N_2) = 32.2$)] and isopropyl alcohol/dioxane/6FDA–mPDA [$\alpha(CO_2/N_2) = 32.3$)] then become superior to the theoretical selectivity of 6FDA–mPDa dense film [$\alpha(CO_2/N_2) = 22.0$]. This simultaneous increase of permeances and selectivity due to prior solvent evaporation has been equally
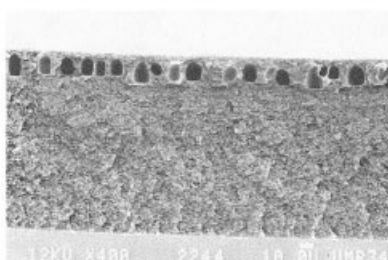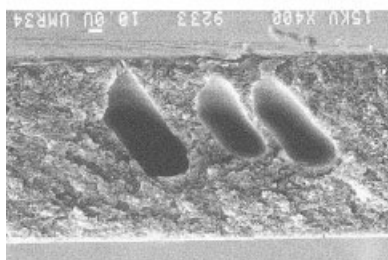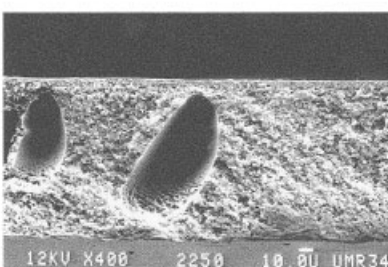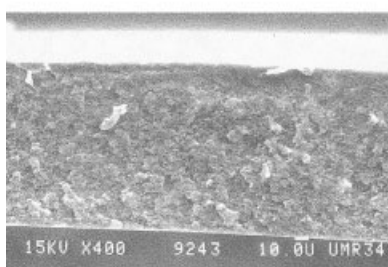
without prior evaporation
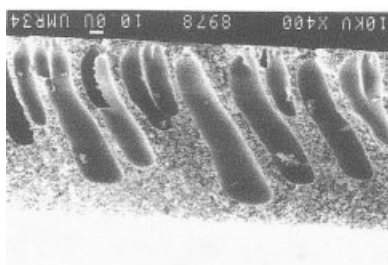
with prior evaporation (5 minutes)
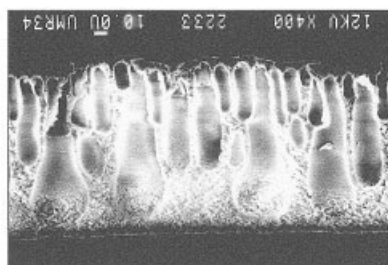
ethyl alcohol / NMP / 6FDA-mPDA

ethyl alcohol / DMF / 6FDA-mPDA

propyl alcohol / DMAc / 6FDA-mPDA

Figure 7 Cross sections of membranes elaborated from the same ternary system, with (right photographs) and without (left photographs) prior evaporation stage.

observed for the membrane methyl alcohol/dioxane/6FDA–mPDA, which has a compact structure.

The effect of prior solvent evaporation in the case of isopropyl alcohol/NMP/6FDA–mPDA membrane differs from what is observed with membranes elaborated from DMF and dioxane. CO_2 and N_2 permeances decrease, and the selectivity is then improved and tends toward the theoretical selectivity of a dense film. The decrease of permeances is either the result of a dense skin creation or the result of an increased compactness of the membrane structure.

Relationship between the solvent nature and the quality of dense skin

Using isopropyl alcohol as nonsolvent, membranes are no more influenced by the presence of macrovoids. Performances of these membranes can also be compared to evaluate solvent effect on the skin quality. Selectivity close to that of the 6FDA–mPDA dense film was obtained for NMP and DMF solvents. The membrane isopropyl alcohol/DMF/6FDA–mPDA has, however, lower permeances, indicating a more com-
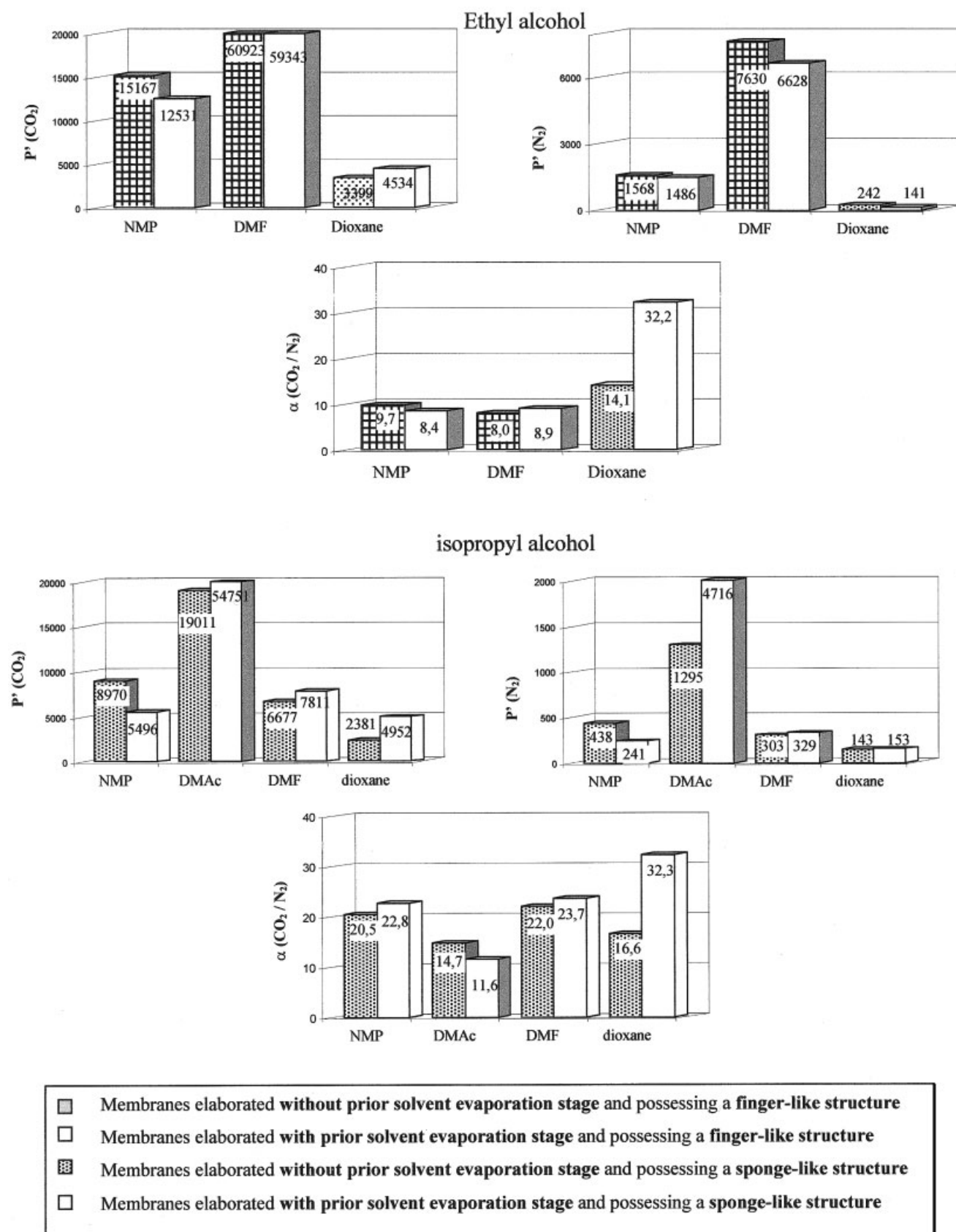
Figure 8 Permeametric performances comparison of membranes elaborated without and with prior solvent evaporation.
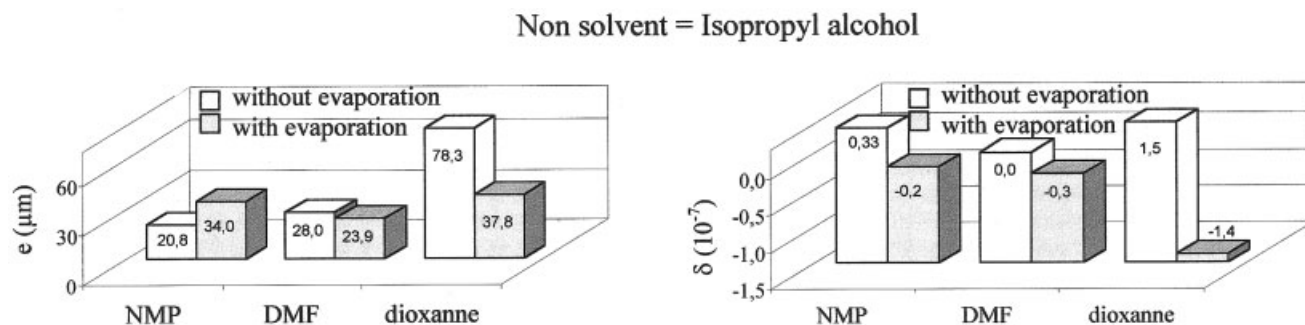
Non solvent = Isopropyl alcohol

Figure 9 Dense skin layer structural characteristics comparison of asymmetric membranes elaborated without and with prior solvent evaporation (5 min). Coagulation is in isopropyl alcohol.

pact structure. Selectivity is thus increased. Membrane prepared with dioxane presents very low permeances too, but its selectivity is lower than that of isopropyl alcohol/DMF/6FDA–mPDA membrane. The effect of residual dioxane presence disappears, which confirms earlier data.[10] One explanation could be that diazote preferentially operates on remaining dioxane molecules, whereas carbon dioxide is not affected. This effect has already been observed on 6FDA–mPDA dense films.

In conclusion, analysis of all permeametric characteristics shows that the membranes prepared with DMF and NMP permit the obtainment of selectivity close to that of the dense film, while limiting the decrease of the gaseous flow. Indeed, permeances and selectivity were better with these two solvents than with dioxane. As for membranes prepared with DMAc, they do not present good permeametric performances.

Structural characteristics of asymmetric membranes dense skins

In Figures 9 and 10 the dense skin structural characteristics are represented [equivalent skin thickness (e) and superficial porosity (δ)] of defect-free asymmetric membranes elaborated without and with a prior solvent evaporation stage. These structural characteris-

tics are evaluated from the permeance coefficients of asymmetric membranes and CO_2 and N_2 permeability coefficients of dense 6FDA–mPDA membranes. Superficial porosity is compared to one of a 6FDA–mPDA dense film, taken as reference. A negative value of δ means that the dense skin compactness of the asymmetric membrane is superior to one of the dense films. Only structural characteristics of asymmetric membranes possessing interesting permeametric performances are presented (i.e., membranes containing no macrovoids).

For membranes coagulated in isopropyl alcohol (Fig. 9), we observe the decrease of e when the solvent is evaporated for DMF and dioxane solvents, whereas e increases for NMP. However, δ decreases for the three solvents. A decrease of δ also occurs in the case of methyl alcohol/dioxane/6FDA–mPDA and ethyl alcohol/dioxane/6FDA–mPDA membrane (Fig. 10). The skin tends then to the compactness with prior evaporation, whatever solvent or nonsolvent there is. These results show that the membrane selectivity is not regulated by the dense skin thickness but by its homogeneity (absence of default). A superior selectivity is in fact obtained with membranes elaborated after dioxane or DMF evaporation even though their respective dense skin thickness is lowest. The final polymer arrangement during asymmetric membranes formation then plays a key role.
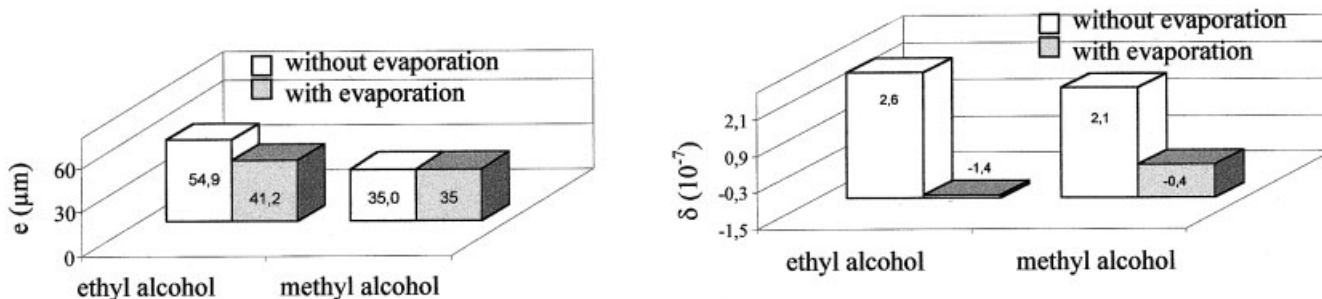

Figure 10 Dense skin layer structural characteristics comparison of asymmetric membranes elaborated without and with prior dioxane evaporation (5 min). Coagulation is in methyl and ethyl alcohol.

For example, the use of isopropyl alcohol as nonsolvent leads to a superficial porosity of asymmetric membranes very close to the one of the dense films. Moreover, we can see that with this nonsolvent, the isopropyl alcohol/DMF/6FDA–mPDA membrane presents a dense skin layer with a quality equivalence to that of a dense film. Indeed, isopropyl alcohol/dioxane/6FDA–mPDA membrane presents the lowest permeances. However, these characteristics are not the consequence of a better quality skin than the one of the isopropyl alcohol/DMF/6FDA–mPDA membrane, but only of a superior thickness of this skin layer.

In the case of NMP prior evaporation, it appears that the increase of the isopropyl/NMP/6FDA–mPDA membrane selectivity is due to the equivalent skin thickness increase. The prior NMP evaporation then brings little improvement to the dense skin quality. It is actually a higher density of the global structure, which permits reaching the theoretical dense film selectivity.

CONCLUSION

The relationship between elaboration conditions, structure, and performances of fluorinated polyimide asymmetric membranes has been investigated.

The coagulation time of the casting solution is highly dependent on nonsolvent/solvent and solvent/polymer systems used. The membrane structure and thickness are visualized by using SEM. The membrane structure depends on the affinity between solvent and polymer. The ratio of nonsolvent inflow and solvent outflow directly influences the formation of the membrane. A poor affinity between solvent and polymer increases the coagulation time and favors a final structure with a thicker skin layer and a smaller porosity in the sublayer.[23,24]

The study of the permeation of two gases (N_2 and CO_2) through the different silicone-coated asymmetric membranes permits the simultaneous determination of the membranes permeances and selectivity. An order of selectivity properties can be established as a function of elaboration conditions. The influence of prior evaporation stage is dependent on the structure of the asymmetric membrane. Fingerlike structure membranes always present few macrovoids and consequently no good permeametric properties. On the other hand, the slowing down of the coagulation gives a more compact dense skin for spongelike structure membranes. Permeances decrease but selectivities are close to the theoretical selectivity of a dense film.

A complementary study on elaborated membranes from solvents blends is investigated. We particularly study the blend of a volatile solvent (CH_2Cl_2) with a nonvolatile solvent (NMP, DMF) with an evaporation stage.

References

1. Deschamps, A.; Driancourt, A.; Mileo, J. C. in Polyimides and Other High-Temperature Polymers; Abadie, J. M.; Sillion, B. Eds.; Proceedings of, 2nd European Technical Symposium on Polyimides and High-Temperature Polymers; Elsevier: Amsterdam, 1991; p. 497.
2. Stern, S. A. J Membr Sci 1994, 94, 1.
3. Wijmans, J. G; Kant, J.; Mulder, M. H. V.; Smolders, C. A. Polymer 1985, 26, 1539.
4. Bulte, A. M. W.; Naafs, E. M.; Van Eeten, F.; Mulder, M. H. V.; Smolders, C. A.; Strathmann, H., Polymer, 1996, 37(9), 1647.
5. Mchugh, A. J.; Miller, D. C., J Membr Sci 1995, 105, 121.
6. Reuvers, A. J.; Altena, F. W.; Smolders, C. A., J Polym Sci, Part B: Polym Phys 1994, 32, 1009.
7. Mulder, M., Basic Principles of Membrane Technology, 2nd ed.; Kluwer Academic: Dordrecht, Netherlands, 1996.
8. Tanaka, K.; Kita, H.; Okano, M.; Okamoto, K., Polymer, 1992, 33, 585.
9. Joly, C.; Le Cerf, D.; Chappey, C.; Langevin, D.; Muller, G., Polym Int 1997, 44, 497.
10. Joly, C.; Le Cerf, D.; Chappey, C.; Langevin, D.; Muller, G., Sep Purif Techn 1999, 16/1, 47.
11. Leblanc, N.; Le Cerf, D.; Chappey, C.; Langevin, D.; Métayer, M.; Muller, G., Sep Purif Techn 2001, 22–23, 277.
12. Zeman, L.; Tkacik, G., J Membr Sci 1988, 36, 119.
13. Hourdet, D.; Muller, G.; Vincent, J. C.; Avrillon, R.; Robert, E., in Abadie, J. M.; Sillion, B., Eds; Polyimides and Other High-Temperature Polymers, Proceedings of 2nd European Technical Symposium on Polyimides and High-Temperature Polymers; Elsevier: Amsterdam, 1991; p. 507.
14. Kim, T. H.; Koros, W. J.; Husk, G. R., Sep Sci Tech 1988, 23, 1611.
15. Marchese, J.; Ochoa, N.; Pagliero, C., J Chem Tech Biotechnol 1995, 63, 329.
16. Glatz, F. P.; Mulhaupt, R.; Schultze, J. D.; Springer, J.; Membr J.; Sci 1994, 90, 151.
17. Perez, S., Ph.D. Thesis, University of Paris VI, France, 1991.
18. Yilmaz, L.; Mc Hugh, A. J., J Appl Polym Sci 1986, 31, 997.
19. Huang, R. Y. M.; Feng, X., J Appl Polym Sci 1995, 57, 613.
20. Matsuyama, H.; Teramoto, M.; Uesaka, T., J Membr Sci 1997, 135, 271.
21. Icard, B., Ph.D. Thesis, University of Grenoble I, 1996.
22. Pedro Bom, R., Ph.D. Thesis, University Grenoble I, 1993.
23. Kurdi, J.; Tremblay, Y., J Appl Polym Sci 1999, 73(8), 1471.
24. Chun, K. Y.; Jang, S. H.; Kim, H. S.; Kim, Y. W.; Han, H. S.; Joe, Y. I., J Membr Sci 2000, 169, 197.