

Hollow Fiber Formation Using Lewis Acid : Base Complex in the Polymer Solution

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ABSTRACT: In the present work, hollow fiber formation was investigated by using Lewis acid : base complexes in the polymer solution. The studied systems consisted of poly(ether sulfone); *N*-methyl-2-pyrrolidone (NMP) as solvent and Lewis base, and acetic, propionic, *n*-caproic, and adipic acids as additives and Lewis acids. Bore liquid was formed by water/NMP solutions, as well as vaseline; whereas water was used as external precipitation bath. The spinneret and precipitation bath distance (i.e., air gap) also varied. The membranes were characterized by scanning electron microscopy and pure gas permeation tests. The influence of the complex dissociation rate was observed mainly when a reduction to water inflow from the bore liquid to the polymer solution occurred, because in this case, dissociation rate was inhibited. Therefore, stability was favored in the sublayer for a longer period, allowing macrovoid formation. These results are also evidenced by the permeability coefficients, which increased as fast as the polymer solution reaches water (i.e., the kinetics of precipitation was accelerated). © 20012001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 908–917, 2001

Key words: hollow fiber; Lewis acid : base complex; membrane formation; poly(ether sulfone)

INTRODUCTION

In the gas separation process using membranes, the driving force is the partial pressure difference of the components between the feed and the permeate sides. The usual transport mechanism assumes that the permeation of a gas molecule through dense membranes occurs in three major steps: sorption of the gas molecules in the polymer, diffusion through the membrane, and desorption at the low-pressure side. The study of membrane polymer materials with high permeability and selectivity values, as well as good me-

chanical and thermal resistance, is quite important to turn the membrane process more competitive. Nevertheless, it has been reported that the conditions that lead to high selectivity generally lead to low permeability and vice versa.^{1,2} Hence, it is of great interest that the development of membranes offers low-transport resistance and high selectivities (i.e., anisotropic morphology membranes) with an ultrathin dense skin of highly selective polymer materials. In the phase-inversion process by immersion precipitation, a polymer solution is immersed into a precipitation bath, which is a nonsolvent to the polymer, or a mixture of nonsolvent/solvent.³ It is the major technique used to obtain anisotropic membranes. However, great difficulties were often reported in obtaining defect-free dense membranes with an ultrathin skin using this technique.

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Fritzsche et al.⁴⁻⁹ studied the use of Lewis acid : base complexes in the polymer solution to obtain membranes by the immersion precipitation technique. When the nonsolvent reaches the polymer solution, the complex molecules are fast dissociated, and it was assumed that the kinetics of precipitation accelerate. High permeability was reported to associate with a gradual reduction in pore density toward the skin.

In a recent paper, Pereira et al.¹⁰ investigated the influence of Lewis acid : base complex on the polymer solution characteristics and, consequently, on the membrane properties. A relationship was found between the miscibility gap and the permeability, when liquid : liquid demixing was performed prior to the vitrification phenomenon. The results showed that such a relationship occurred mainly at lower polymer concentration and when water was used as precipitation bath. In the case of Lewis acid : base complex, these parameters are especially important provided that they influence the mass transfer rate and, consequently, the complex dissociation rate. Hence, the importance of binodal location increases. The analysis showed that the results of cloud point determination (concerning miscibility gap), light transmission measurements (concerning the kinetics of precipitation), and viscosity measurements are clearly connected.

In the present work, hollow fiber membranes were prepared by using the phase inversion process by immersion-precipitation technique and polymer solutions composed of Lewis acid : base complexes. The main objective was to enhance the knowledge in membrane formation when these complexes are present in the solution. Compared to the synthesis of flat membranes, the presence of two precipitation fronts during hollow fiber formation provides a larger range of possibilities to investigate further the relationship between precipitation kinetics and morphological characteristics.

EXPERIMENTAL

Hollow fiber membranes were prepared by using poly(ether sulfone) (PES; Ultrason E6020 from BASF, São Paulo, Brazil) as polymer. Lewis acid : base complexes were formed by *N*-methyl-2-pyrrolidone (NMP), as solvent, from Merck (Rio de Janeiro, Brazil), and carboxylic acids, as additives, acetic (AA), propionic (PA), *n*-caproic (CA),

Table I Compositions of the Investigated Polymer Solutions

Polymer Solution	Acid : NMP Molar Ratio	Composition (wt %)
PES/AA/NMP	1 : 1	25/28.3/46.7
	1 : 1	30/26.4/43.6
	1 : 2	30/16.3/53.7
PES/PA/NMP	1 : 1	30/29.9/40.1
	1 : 2	30/19.0/51.0
PES/CA/NMP	1 : 2	30/25.9/44.1
PES/AD/NMP	1 : 4	25/20.2/54.8
	1 : 4	30/18.9/51.1

and adipic (AD) acids were purchased from Rio Lab (Rio de Janeiro, Brazil). Distilled water was used as the external precipitation bath. Water/NMP at different compositions (10/0, 7/3, 5/5, 3/7, and 1/9 w/w), as well as pure Vaseline (from Rio Lab), were used as bore liquids. Vaseline works as an inert fluid to the polymer solution (i.e., does not promote its precipitation in the experimental time interval). The acid : NMP molar ratios applied were 1 : 1 and 1 : 2. Table I shows the compositions of all the polymer solutions used in the present work.

During spinning, the polymer solution was pressurized to the spinneret, whereas the bore liquid was pumped toward it. The distance between the spinneret and the precipitation bath, the air gap (average RH = 65%), varied from null to 35 cm. After spinning, the membranes were kept in water at 60°C for residual solvent extraction. The liquid exchange method used by van't Hof¹¹ and Li¹² was also applied in this work to avoid collapsing pores due to water superficial tension. These authors verified reduction in pore collapsing by scanning electron microscope (SEM) and gas permeation measurements. Following this procedure, the membranes were immersed in ethanol for 2 h. In the following step, they were immersed into *n*-hexane for 2 h, and, subsequently, exposed to the environment until solvent completed evaporating.

The morphologies of the fibers were observed by SEM (Jeol JSM-5300). The samples were broken after immersion into liquid nitrogen to avoid the structure deformation and metallized with gold (Jeol JFC-1500). Figure 1 shows a scheme of the spinning setup. Pure gas permeation tests (CO₂ and N₂) were also carried out, using the setup represented schematically in Figure 2. It consisted of a permeation cell, where the fiber was

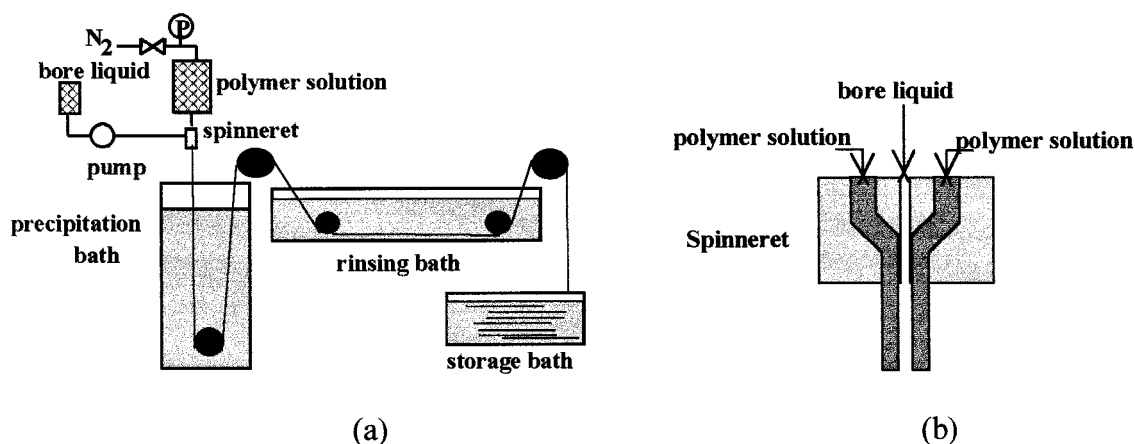


Figure 1 (a) Schematic representation of the spinning apparatus; (b) spinneret cross section.

placed, and a vacuum pump for cleaning the equipment before each experiment. A calibrated pressure transducer and a bubble soap flowmeter were used to measure low- and high-permeate fluxes, respectively.

RESULTS

Lewis Acid : Base Pair

The hollow fiber morphologies and gas permeation results obtained by using different Lewis acid : base pairs in the polymer solution are dis-

cussed here. In this case, spinning was carried out by using polymer solutions composed of PES at 30 wt % and Lewis acid : base at 1 : 1 and 1 : 2M ratios and by using water/NMP (1/9 w/w) as bore liquid. The polymer solutions with AA, PA, or CA were spun at room temperature (25°C). In the presence of AD, the polymer solution was spun at 50°C because of its high viscosity. The air gap varied from null to 4 cm.

Hollow fibers obtained by using monocarboxylic acids in the polymer solution presented a structure of closed cells and low incidence or complete lack of macrovoids, as can be seen in Figure 3, to the fiber resultant from spinning of PES/AA/NMP (30/26.4/43.6 wt %), acid : NMP molar ratio = 1 : 1.

The presence of macrovoids near the internal surface of the fiber indicates that the polymer solution was stable in this region for a longer period. This is evident provided that when stability occurs for a longer period, a nucleus of the polymer-lean phase may grow, leading to macrovoid formation. Stability of this region is confirmed, because light transmission results of these solutions, presented elsewhere^{10,13} using water/NMP at the same composition as the precipitation bath, showed that these solutions did not precipitate for a period of at least 2 h. Macrovoid formation and delay in precipitation are the result of high-solvent concentration in the precipitation bath, which reduces the water activity and, consequently, the water inflow to the polymer solution. As demonstrated in the previous paper, water inflow is very important in the complex dissociation rate and, consequently, precipi-

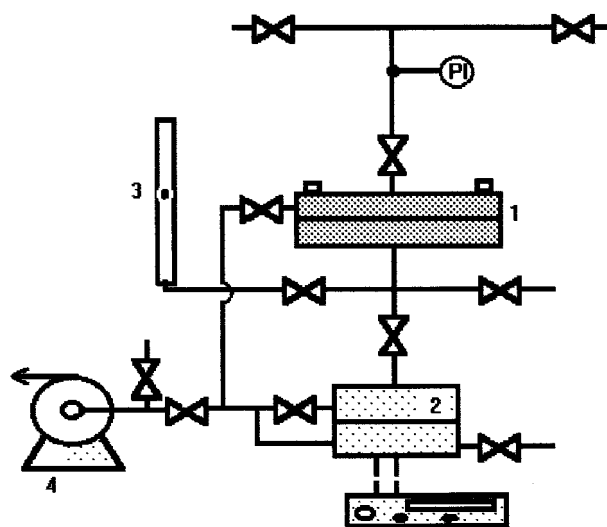


Figure 2 Gas permeation setup. (1) permeation cell; (2) pressure transducer; (3) bubble soap flowmeter; (4) vacuum pump.

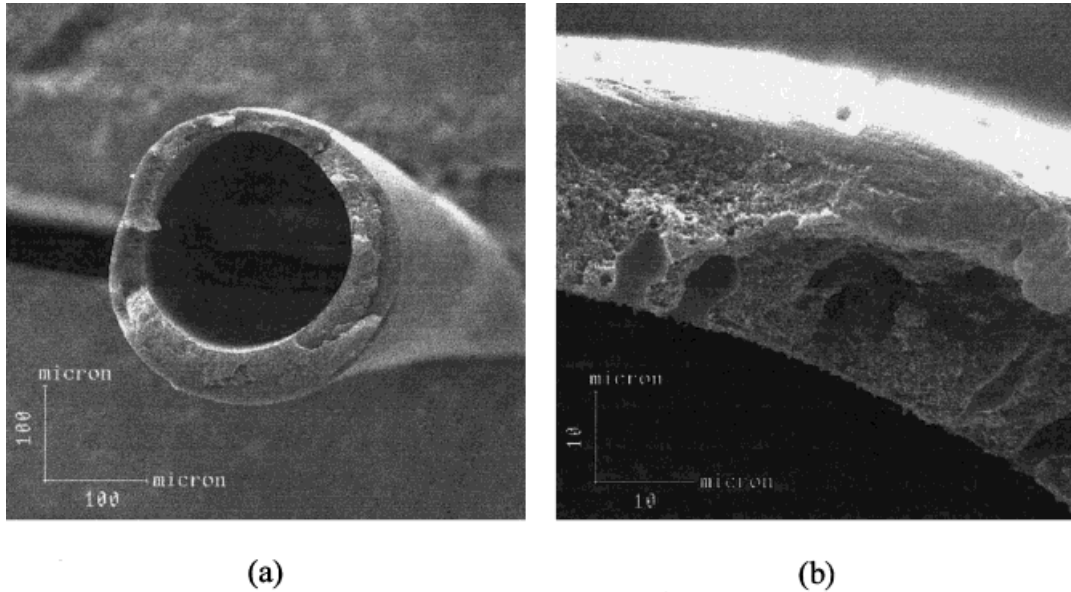


Figure 3 Photomicrographs of the hollow fiber cross sections obtained using PES/AA/NMP (30/26.4/43.6 wt %). Air gap: 4 cm; bore liquid: water/NMP (1/9 w/w). Cross section magnitude: (a) 200 \times ; (b) 2000 \times .

tation of the solution. Furthermore, the concentration difference of NMP in the bore liquid (90 wt %) and all the investigated polymer solutions (40.1–53.7 wt %) may increase the driving force for solvent inflow from the bore liquid to the polymer solution, which also corroborates the stability of the solution.

When AD, which is a dicarboxylic acid, was used in the polymer solution, the hollow fibers presented higher incidence of macrovoids near the inner surface, as can be seen in Figure 4. Once again, because of low mass transfer rate between bore liquid (water/NMP = 1/9 w/w) and the polymer solution, the inner region was kept stable for

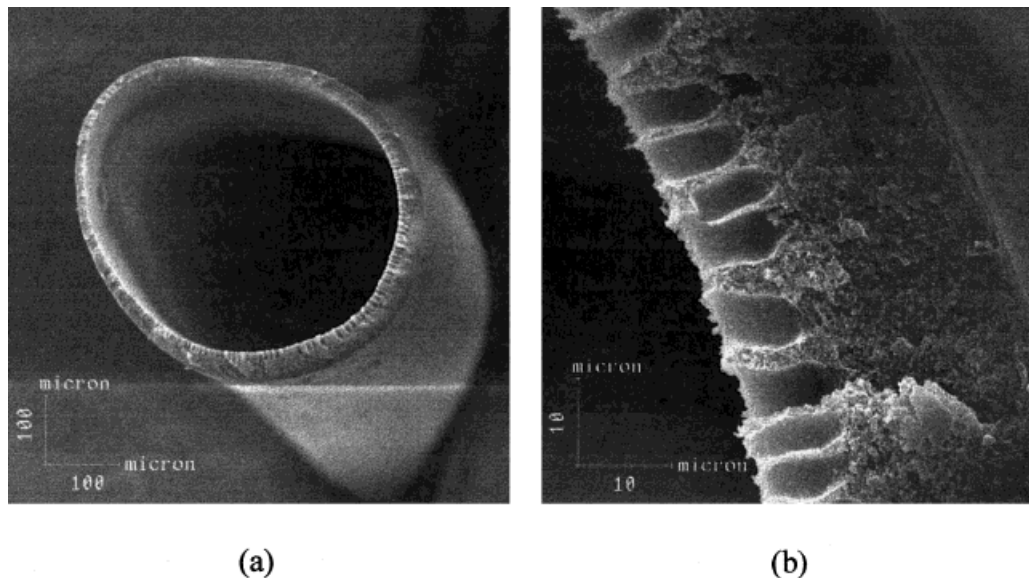


Figure 4 Photomicrographs of the hollow fiber cross sections obtained by PES/AD/NMP (30/18.9/51.1 wt %). Air gap: null; bore liquid: water. Cross section magnitude: (a) 50 \times ; (b) 2000 \times .

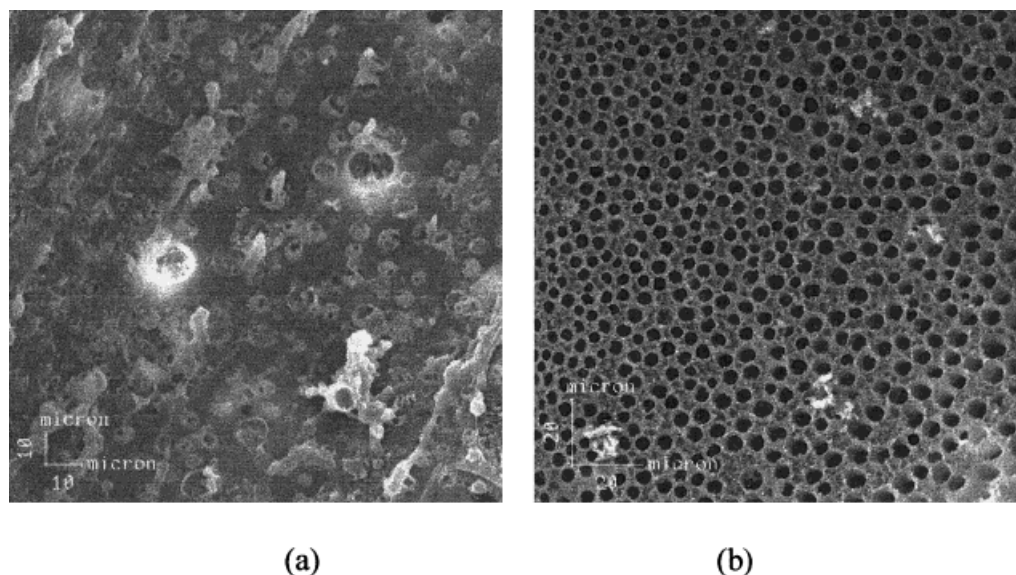


Figure 5 Photomicrographs of the hollow fibers inner surfaces obtained by using (a) PES/AA/NMP (30/26.4/43.5 wt %); (b) PES/AD/NMP (30/18.9/51.1 wt %). Air gap: 4 cm; bore liquid: water/NMP (1/9 w/w).

a longer period, which may promote nuclei growth. This effect was intensified in the presence of AD, probably because of the high viscosity of such a solution.^{10,13} The extremely high viscosity (even at higher temperature) of this polymer solution also diminishes the inflow of water from the external precipitation bath favoring the stability and nuclei growth. As a consequence, the internal surface presents, on average, larger pore size when compared to the hollow fibers resultant

Table II Gas Permeation Results of the Hollow Fibers Obtained by Using PES/acid/NMP at PES = 30 wt % and Acid : NMP Molar Ratio = 1 : 2 (AA, PA, and CA), and 1 : 4 (AD); Bore Liquid : Water/NMP (1/9 w/w) and Precipitation Bath : Water

Acid	Air Gap (cm)	P/e CO ₂ (GPU)	α CO ₂ /N ₂
CA	0	90	0.8
	4	9	0.6
AD	0	2520	0.8
	4	2160	0.8
AA	0	377	1.0
	4	258	1.0
PA	0	^a	^a
	4	^a	^a

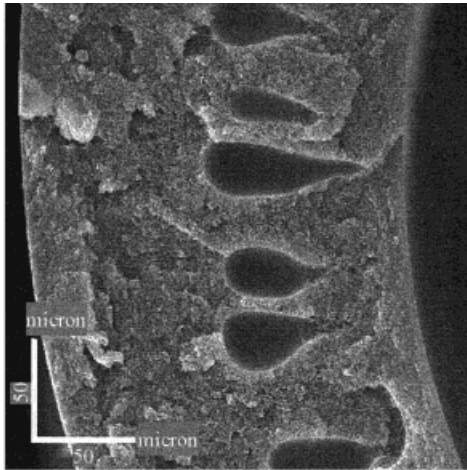
^a Not measured due to low mechanical resistance of the hollow fiber.

from monocarboxylic acids solutions, as one may observe in Figure 5.

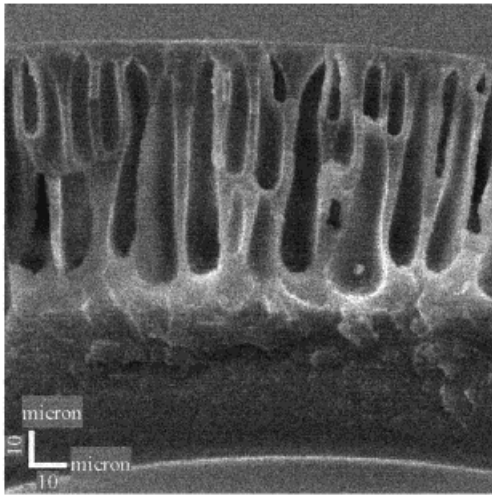
In all cases, the presence of closed cells and macrovoids near the inner surface were similar and independent of the investigated gap and acid : NMP molar ratio. As discussed previously, it may be assumed that the precipitation front comes mainly from the outer side of the polymer solution (i.e., from the external precipitation bath or because of absorption of water vapor from the environment during the exposition time before immersion). However, by SEM analysis, it is difficult to observe pores in the outer surface of the fiber and, hence, to establish accurately the influence of exposition to the environment (i.e., air gap influence, as well as acid : NMP molar ratio variation). Therefore, gas permeation seems to be more appropriate to evaluate

Table III Gas Permeation Results of the Hollow Fibers Obtained by Using PES/acid/NMP at PES = 30 wt % and Acid : NMP Molar Ratio = 1 : 1 (AA and PA); Bore Liquid : Water/NMP (1/9 w/w) and Precipitation Bath : Water

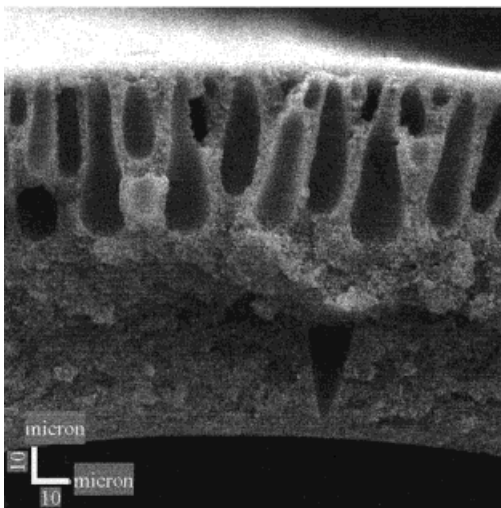
Acid	Air Gap (cm)	P/e CO ₂ (GPU)	α CO ₂ /N ₂
AA	0	1560	0.8
	4	1325	0.9
AP	0	1340	0.8
	4	980	0.8



(a)



(b)



(c)

those variables' influence. Table II shows the gas permeation results of the membranes prepared in the present work.

From Table II, one may observe that the permeability coefficient was always higher to the membranes obtained using air gap null. In the case of Lewis acid : base complex in polymer solution, its dissociation rate seems to be intensified after immersion in the external precipitation bath because of a high-solvent outflow and water inflow. As faster water reaches the polymer solution, so does the dissociation of the complexes. Consequently, the kinetics of precipitation accelerates, resulting in lower packing density and, consequently, higher permeability coefficients. However, in all cases, the selectivity values were smaller than unity, indicating formation of small defects on the surface, which did not allow determination of the polymer permeability but the permeability through the membranes pores. The presence of pores or small defects on the surface can also be favored by the fast kinetics of precipitation.

These results show a remarkable difference in precipitation of solutions with Lewis acid : base complex. As the literature reports,^{14,15} fibers are prepared from solutions without such complexes and similar miscibility gap, and the longer the exposition time to the environment before immersion, the higher the permeability coefficient, because of previous instability promoted by water in the region close to the outer interface before immersion.

The sequence of the permeability coefficient obtained did not show agreement with the binodal location of these systems, which indicates that when PES concentration is 30 wt %, the viscous effects seem to be preponderant to the nuclei growth and independent of the acid chain length. This result is analogous to the flat membranes obtained from the same polymer solutions precipitated in water presented in the previous paper.¹⁰ When acid : base molar ratio = 1 : 1 was applied (Table III), then the same analysis is reasonable.

Air Gap Influence on Morphology

The influence of air gap on the morphology was more evident when water was used as bore liquid.

Figure 6 Photomicrographs of the hollow fiber cross sections obtained by using PES/AA/NMP (25/28.3/46.7 wt %). Bore liquid: water; air gap: (a) null, (b) 3 cm, (c) 6 cm.

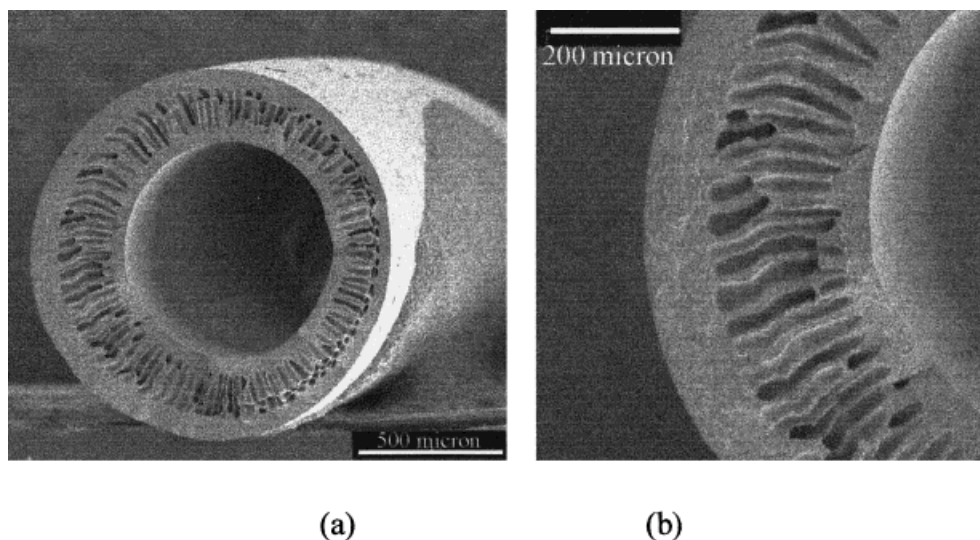


Figure 7 Photomicrographs of the hollow fiber cross sections obtained by using PES/AD/NMP (25/20.2/54.8 wt %). Air gap: 35 cm; bore liquid: water. Cross section magnitude: (a) 200 \times ; (b) 2000 \times .

In this case, by using PES/AA/NMP (25/28.3/46.7 wt %) as polymer solution and varying air gap from null to 6 cm, macrovoid formation was always observed, as shown in Figure 6.

When null air gap was used, the macrovoids are formed close to the inner region, and they seem to be initiated from the inner surface. In the very first instants of precipitation, it is expected that the polymer concentration in the region close to each surface be the same, because both contact pure water as precipitation baths. However, as solvent flows from the solution toward the precipitation bath, the solvent concentration increases significantly only in the bore liquid, because of its smaller volume when compared to the outer bath. This fact reduces the mass transfer rate and allows longer stability when compared to the precipitation front progressing from the outer bath. This situation favors nuclei growth and macrovoid formation in the region near the inner surface. On the other hand, as air gap increases to 3 cm, the outer layer remains stable for a longer period, and the concentration variation promoted by the precipitation front from the inner side may reach deeper layers. This situation creates conditions to macrovoid formation initiated near the outer surface. When air gap is even higher (6 cm), this effect is more evident. These results show a competition between mass transfer and precipitation front, progressing from external and internal precipitation baths, which strongly affect the cross-section morphology of the hollow fibers.

Using AD as Lewis acid, the same PES concentration (25 wt %) macrovoids start from the inner surface, even when the air gap was as long as 35 cm, as can be seen from Figure 7. In this case, the polymer solution was spun at room temperature and presents a higher viscosity than the previous system composed of AA. Compared to PES/AA/NMP solution, a longer exposition time to the environment before immersion into the precipita-

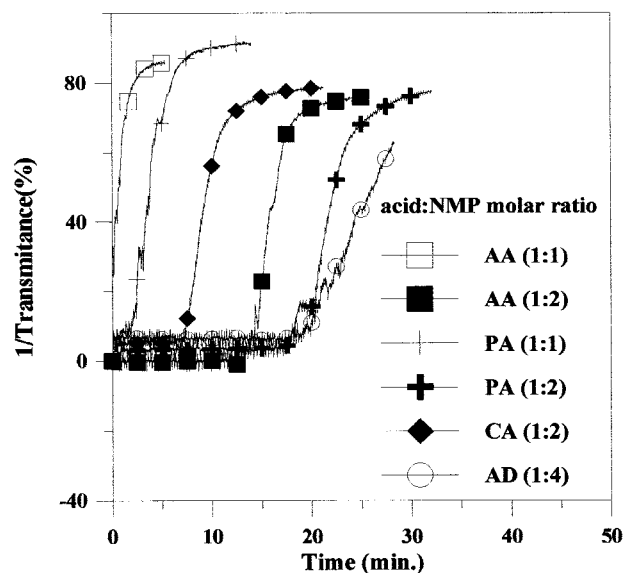


Figure 8 Light transmission decay when the polymer solutions (25 wt % PES) were exposed to the environment for a long period.

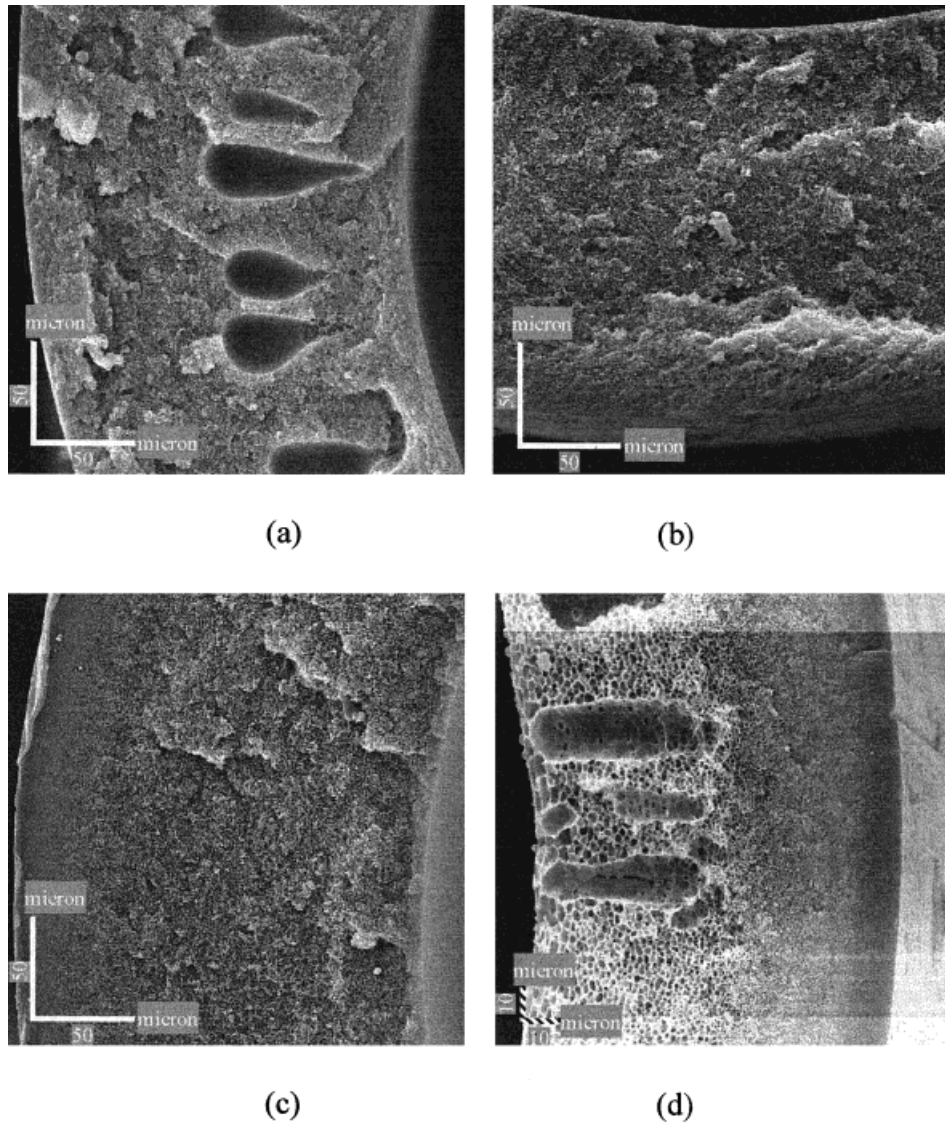


Figure 9 Photomicrographs of the hollow fibers cross sections obtained by using PES/AA/NMP (25/28.3/46.7 wt %). Air gap: null; bore liquid (water/NMP, w/w): (a) 10/0, (b) 7/3, (c) 5/5, (d) 3/7.

tion bath was used (approximately 35 s, instead of 2.2 s in the case of previous solution with 6 cm of air gap). According to another part of this study,^{10,13} this PES/AD/NMP solution starts its precipitation after approximately 20 min, when exposed to the environment. This means that the solution region near the external surface remains stable during the investigated exposition time. Compared to PES/AA/NMP solution, the time scale of stability is rather different, mainly because of the extremely high viscosity of PES/AD/NMP solution, which reduces the mass transfer between the polymer solution and both internal and external environments. Figure 8 shows the

light transmission of these solutions when exposed to the atmosphere. Hence, the much longer stability period of PES/AD/NMP solution near the outer surface allows time enough for nuclei growth from the inner surface and promotes macrovoid formation.

Effect of Bore Liquid Concentration

The effect of bore liquid was further investigated using PES/AA/NMP (25/28.3/46.7 wt %) as polymer solution. Null air gap was used, and spinning was carried out at room temperature (25°C).

Figure 9 shows the photomicrographs of the

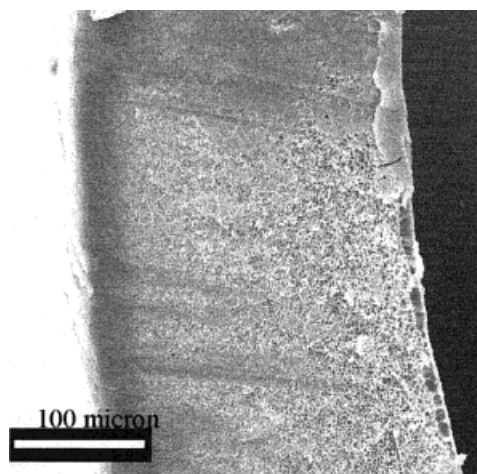


Figure 10 Photomicrographs of the hollow fiber cross sections obtained by using PES/AA/NMP (25/28.3/46.7 wt %). Air gap: null; bore liquid: Vaseline.

cross sections of the hollow fibers obtained as a function of bore liquid composition (water/NMP = 10/0, 7/3, 5/5, and 3/7). One may observe that an initial increase of the solvent concentration in the bore liquid reduced the presence of macrovoids. As expected, the presence of solvent reduces mass transfer between polymer solution and internal precipitation bath. Thus, precipitation is delayed and water inflow may reach inner layers. In the case of solutions with Lewis acid : base complex, this effect is especially important because it will affect the dissociation and, consequently, the kinetics of precipitation and macrovoid formation. In the highest concentration of solvent (70 wt %), the macrovoids appear again, which means, despite the water inflow, that the region near the inner surface was kept stable for a longer time, as analyzed in the previous section. This oscillatory behavior was reported before by Machado et al.¹⁶ Following the authors, this behavior can be understood, considering mass transfer resistances in the nascent membrane, controlling both precipitation rates and morphology. As macrovoid formation can be attributed to delayed demixing in sublayers of the polymer solution, it was concluded that the oscillatory occurrence of macrovoids is dependent not only on precipitation at the interface, but also on precipitation rate variation of regions underneath the interface.

To obtain more insights about the precipitation behavior of the investigated polymer solution, Vaseline was used as a bore liquid. In this case, it may be expected that the mass transfer is inhibited from

the inner surface. Figure 10 shows the photomicrograph of the cross section of the fibers obtained. Although the precipitation is promoted only from the outer surface, there are no macrovoids near the inner surface, as it occurred when a high concentration of solvent (NMP) in the bore liquid was used. These results indicate that the nuclei also grew because of the inflow of solvent from the bore liquid to the inner region, which contributes to a longer stability period in this region. It is also appropriate to emphasize that the absence of macrovoids also occurred in the case of the flat membranes prepared from the same polymer solution, using water as precipitation bath. This becomes clear if one considers that the use of an inert fluid in the bore works analogous to the glass plate support for flat membrane casting, allowing only one precipitation front during membrane formation.

Table IV shows the gas permeation results of the hollow fibers obtained by using PES/AA/NMP (25/28.3/46.7 wt %), acid : NMP molar ratio = 1 : 1, null air gap, water, and Vaseline as bore liquid. According to these results, when Vaseline was used, the permeability coefficient decreased strongly. In this case, because the mass transfer is not promoted from the inner surface, the dissociation of the complexes may only occur because of water inflow from the outer surface. Consequently, it may be expected that the precipitation rate decreases, and a less porous structure is formed. Once again, this result is in agreement with the flat membrane permeabilities presented in previous work,¹⁰ which is reasonable, because the use of Vaseline in the bore liquid is the condition that more closely approaches the mass transfer conditions in flat membranes. Besides that, the flat membranes presented permeability coefficients even lower. This is clear because the contact to the precipitation bath is faster in the case of spinning; thus, the dissociation of the complexes is favored. Furthermore, the results indicate that a second precipitation front, originated from the bore liquid, also accelerates complex dissociation, leading to a higher permeability coefficient.

Table IV Gas Permeation Results of the Hollow Fibers Obtained by Using PES/AA/NMP (25/28.3/46.7 wt %), Acid : NMP Molar Ratio = 1 : 1, and Different Bore Liquid Composition. Precipitation Bath: Water; Air Gap : Null

Bore Liquid	P/e CO ₂ (GPU)	α CO ₂ /N ₂
Water	1800	0.7
Vaseline	289	0.9

CONCLUSION

The presence of a high solvent in the bore liquid and high viscosity of the polymer promoted stability in the region near the internal surface, and consequently, macrovoid formation. It emphasizes the importance of water inflow in the case of polymer solutions constituted of Lewis acid : base complexes, because reduction of water inflow seemed to inhibit complex dissociation. Another proof of this effect was suggested by observing the effect of air gap on the permeability coefficient which was always higher to the membranes obtained using air gap null (i.e., as faster water reaches the polymer solution, so does the dissociation of the complexes). Furthermore, when pure Vaseline was used as bore liquid, the macrovoids were absent and lower permeability coefficients were obtained.

Symbols

AA	acetic acid
AD	adipic acid
CA	caproic acid
e	membrane thickness (L)
GPU	gas permeation unit [$L^3(STP)/L^2\theta(F/L^2)$]
SEM	scanning electron microscopy
NMP	<i>N</i> -methyl-2-pyrrolidone
P	permeability [$L^3(STP)L/L^3\theta(F/L^2)$]
PA	propionic acid
PES	poly(ether sulfone)

Greek symbol

α	selectivity
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