

# Preparation of Porous Hollow Fiber Membranes with a Triple-Orifice Spinneret

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**ABSTRACT:** A triple-orifice spinneret has been applied for the preparation of hollow fiber microfiltration membranes with a high surface porosity. Considering the general rules of diffusion induced phase separation, a low polymer concentration is required at the outer layer to obtain a highly interconnected open-porous structure. Therefore, by using N-methylpyrrolidone (NMP) as the external liquid at the outside orifice of the spinneret, a highly porous surface can be obtained. For a polymer solution containing a low molecular weight additive and with an initial concentration close to the cloud point, this technique shows slightly improvement on the pure water and gas fluxes since the major

resistance of the membrane is located at the substructure and the inner skin. However, for a solution containing a high molecular weight additive and with an initial concentration far from the cloud point, a porous shell surface is obtained, resulting in a significant improvement in water flux. The effect of various external liquids on the morphology has been investigated as well. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2151–2157, 2003

**Key words:** triple-orifice spinneret; membranes; fibers; additives; phase diagrams

## INTRODUCTION

In a dry-wet spinning process, a polymer solution is extruded through a spinneret together with either a bore liquid or gas, followed by an air gap and immersed into a nonsolvent bath which most of the time is water. During the fabrication process, three parameters control the morphology of the hollow fibers to a great extent: composition of the polymer solution, composition of the bore liquid, and air gap conditions. Other parameters, such as composition and temperature of the coagulation bath, spinning speed, and post-treatment, are important as well.

Frequently, additives are added to the polymer solutions to control the membrane morphology. Two types of additives can be used: a compatible high molecular weight additive, for example, polyvinylpyrrolidone (PVP)<sup>1–4</sup>; or a small molecular weight nonsolvent additive, i.e., water, ethylene glycol, or diethylene glycol.<sup>5–8</sup> The inner surface morphology is mostly determined by the composition of the bore liquid. The shell surface morphology can be adjusted by various approaches such as a high temperature bath<sup>4</sup> or a coagulation bath consisting of a mixture of solvent and nonsolvent (e.g., water).<sup>9</sup> These approaches have several drawbacks: a large amount of solvent is needed, which is environmentally unfavor-

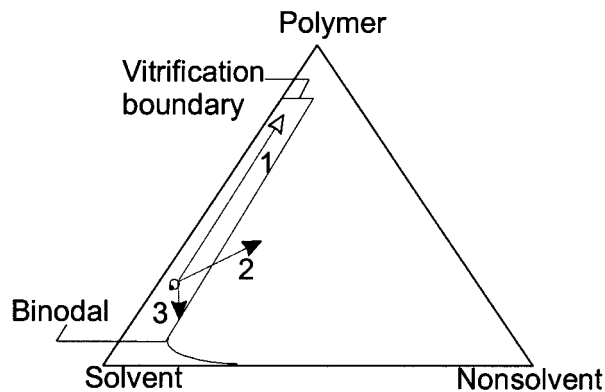
able, and capital intensive. Raising the bath temperature requires precise control of the manufacturing section to guarantee high reproducibility.

In recent years, a triple-orifice spinneret has been developed, in which a polymer solution, a bore liquid, and an external liquid are simultaneously extruded. By variation of this external liquid, different types of morphologies were prepared such as dense membranes for gas separation,<sup>10</sup> pervaporation,<sup>11</sup> and porous membranes for ultrafiltration.<sup>12</sup> This paper describes the use of this spinneret with a solvent as the external liquid to prepare hollow fiber membranes with an open outer skin layer having pores at the micrometer range.

## CONCEPT TO PREPARE POROUS MEMBRANES

During an immersion precipitation process, the composition path at the top of the polymer solution may follow three different routes as shown schematically in a phase diagram for a ternary system of polymer N-methylpyrrolidone (NMP) and nonsolvent (Fig. 1). For a solution with high enough polymer concentration and a high ratio of the outflow of the solvent compared to the inflow of the nonsolvent, the composition of the top part of the solution follows the first route up to the vitrification region. Consequently, the solution vitrifies and forms an asymmetric membrane with a dense top layer. In a case where the ratio of the outflow of the solvent to the inflow of the nonsolvent is relatively low, the composition of the solution at the

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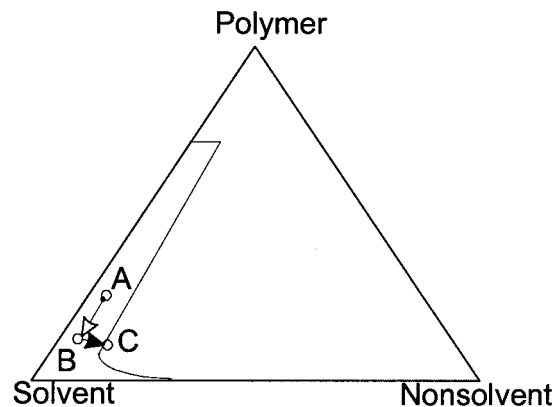


**Figure 1** Phase diagram for a ternary system: polymer/solvent/nonsolvent, showing schematically three different composition paths.

top layer could follow the second path toward the binodal. Immediately, the top layer solution demixes, resulting in a porous membrane with ultrafiltration properties. The third composition path follows a direction where the polymer concentration decreases, which could be achieved by applying a coagulation bath composing of solvent and nonsolvent mixture. Consequently, the phase separation occurs at a region close to the critical point, resulting in an open porous membrane.<sup>13</sup>

Following the arguments given above, the polymer concentration at the top layer just before demixing needs to be low enough to obtain an open porous top layer. One may start with a very low polymer concentration,<sup>14,15</sup> but it is hardly possible to spin fibers at such a low viscosity. However, if we increase the polymer concentration to improve the spinning conditions and use water as a coagulant, the polymer content at the top layer of the polymer solution increases as a result of a relatively large outflow of the solvent with respect to the inflow of water.<sup>16,17</sup> Thus, a membrane with low porosity and small pores is obtained. In order to obtain a highly porous toplayer, the polymer concentration should be low before the occurrence of precipitation. Figure 2 shows a two-step process to solve this problem. To spin hollow fibers according to this process, one needs to employ a triple orifice spinneret where the outer layer contains the solvent. During the contact of the solvent with the polymer solution, solvent diffuses into the polymer solution decreasing the outer layer polymer concentration (representing route A to B in Fig. 2). The fiber is then immersed in water bath at room temperature in which a precipitation occurs, as indicated by route B to C (Fig. 2).

This concept mainly aims to influence the morphology of the skin layer, not the fiber wall morphology. The fiber wall morphology needs to be open enough to minimize the transport resistance as well. Two kinds of additive can realize this: diethylene glycol<sup>5</sup>



**Figure 2** Schematic of the composition change at the top layer of the polymer solution during a two-step immersion precipitation process. A–B: contact with solvent; B–C: immersion in water.

and polyvinyl pyrrolidone.<sup>4</sup> Once the matrix has a minimized resistance, the resistance of the skin layer can be clearly identified and decreased as indicated above.

## EXPERIMENTAL

### Materials

Polysulfone (PSf) (Udel P3500) was purchased from Amoco. PVP (K90,  $M_w$  360,000 g/mol) was from Janssen Chimica. (NMP), diethylene glycol (DegOH), and acetone were purchased from Merck. The solvents are of analytical grade and used without further purification. Tap water was used as a coagulation bath.

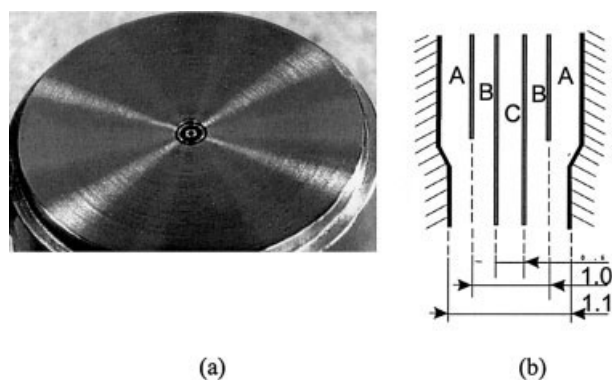
### Solution preparation

Predried polysulfone (one week in an oven at 120°C) was dissolved in NMP with a third component: diethylene glycol or PVP K90. The exact compositions are listed in Table I. The polymer solutions were filtered with a metal filter of 15  $\mu\text{m}$  and degassed before use. The viscosity of the polymer solutions at 25°C was measured with a rotation viscometer (Brabender viscotron, system E17 with spring constant 1699.9). The

**TABLE I**  
Specifications of Spinning Solutions

Terms	Solution 1	Solution 2
$W_{\text{PSf}}$ , wt %	17.0	15
$W_{\text{NMP}}$ , wt %	52.4	70
$W_{\text{additive}}$ , wt %	30.6	15
Viscosity (poise)	53	1100
Cloud point (°C)	$47 \pm 1$ , LCST	—

Two polymer solutions: solution 1: PSf/NMP/diethylene glycol; solution 2: PSf/NMP/PVPK90, no cloud point in the range between 0 and 80°C.



**Figure 3** Schematic of a triple orifice spinneret. Dimension values are in millimeter. (A) bottom view of a spinneret; (B) cross-section view. A, external fluid; B, polymer solution; C, bore liquid.

viscosity was recorded at different rotation speeds or shear rates and extrapolated to zero shear rate.

**Cloud point determination**

The cloud point of a polymer solution was measured by a device developed at the Membrane Technology Group, University of Twente. A polymer solution at certain composition was stored in a standard nuclear magnetic resonance (NMR) tube and the light transmission was measured as a function of the temperature. When phase separation occurs, a steep light transmission change can be observed. The transition temperature is defined as the cloud point of the polymer solution.

**Light transmission determining the delay time**

The delay time of the spinning solutions before the phase separation occurs was determined by preparation of a flat membrane and monitoring the light transmission.<sup>17</sup> The delay time is defined as the time between the immersion of the polymer film and the start of turbidity. The turbidity indicates the onset of phase separation and is detected by a decrease in light transmittance through a polymer solution. The light source was located above the coagulation bath and a light detector below. The signal from the light detector was transferred and recorded by a computer. Delayed demixing is a process taking place during an extended period of time after the moment of immersion of the polymer solution in the nonsolvent bath. Instantaneous demixing is a process in which liquid-liquid demixing immediately occurs upon immersion of the polymer solution in the nonsolvent bath. With this measurement, the kinetics of the immersion phase separation process can be quantified.

**Spinning process**

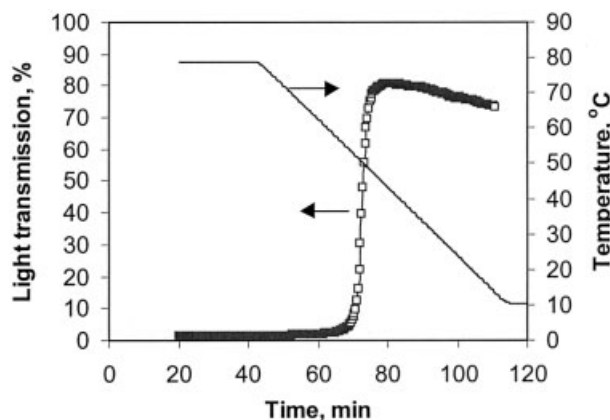
A triple-orifice spinneret was used for spinning the hollow fibers. As shown in Figure 3, a polymer solution, an external liquid, and a bore liquid simultaneously flow out of the spinneret, passing through an air gap of 50 mm and immersing in a water bath at room temperature. The spinning speed was set at 6.0 m/min. The contact time of the first coagulant and the polymer solution in the air gap was 0.5 s. Water forms the coagulation bath, but cannot immediately replace the solvent layer, ending therefore in much longer actual contact time.<sup>10</sup> The flow rate of the first coagulant was controlled at 0.43 cm<sup>3</sup>/min. The bore liquid was a mixture of NMP and water with a weight ratio of 3:1 for polymer solution 1 and 4:1 for solution 2. The fibers were cut into pieces of 60 cm and rinsed with tap water for 48 h. Then the fibers were immersed in a 20 wt % glycerol/water solution for another 24 h and allowed to dry in ambient environment. Membranes from polymer solution 2 were treated with the standard procedure according to literature<sup>4,18</sup> using a solution of sodium hypochlorite solution of 4000 ppm for 48 h to wash out the PVP residue and increase the membrane flux.

**Characterization of the hollow fiber membranes**

Four wet hollow fibers were cut into pieces of 20 cm and potted at the both ends with a nylon tube of 6 mm. The pure water permeability was measured at a pressure of 2.0 bar absolute. The permeation was recorded after one hour prepressurizing. The membrane pore size was measured with Coulter Porometer II for pores larger than 0.05 μm. Smaller pores were characterized by permoporometry.<sup>19</sup>

**Scanning electron microscopy**

Samples for scanning electron microscopy (SEM) (JEOL JSM-T220S) were made by cryogenic breaking



**Figure 4** Cloud point curves of polymer solution 1.

**TABLE II**  
**Delayed Time of Solution 1 and Solution 2 Using**  
**Different First Coagulants**

First Coagulant	Delay Time Before Demixing	
	Polymer Solution 1 (s)	Polymer Solution 2 (s)
NMP	$\infty$	$\infty$
NMP/acetone 50/50	$\infty$	—
Acetone	0	—
Air, humidity 55%	$\sim 1$	39
Water	0	0

of the freshly prepared wet fibers. The samples were allowed to dry under vacuum at 30°C for overnight and coated with a thin gold layer.

## RESULTS AND DISCUSSION

### Characterization of the spinning solution and its phase separation behavior

The solution properties are listed in Table I. Two solutions clearly show different phase separation behavior. Solution 1 contains 30.6% DegOH and was located close to the cloud point, which was  $47 \pm 1^\circ\text{C}$ . This means that by increasing the solution temperature above  $47^\circ\text{C}$ , the solution phase separates, as can be seen in Figure 4. It also indicates that diethylene glycol attributes PSf/NMP solution a lower critical solution temperature (LCST). Solution 2 contains PVP K90, which was miscible with polysulfone in NMP, and shows no phase separation behavior in the range

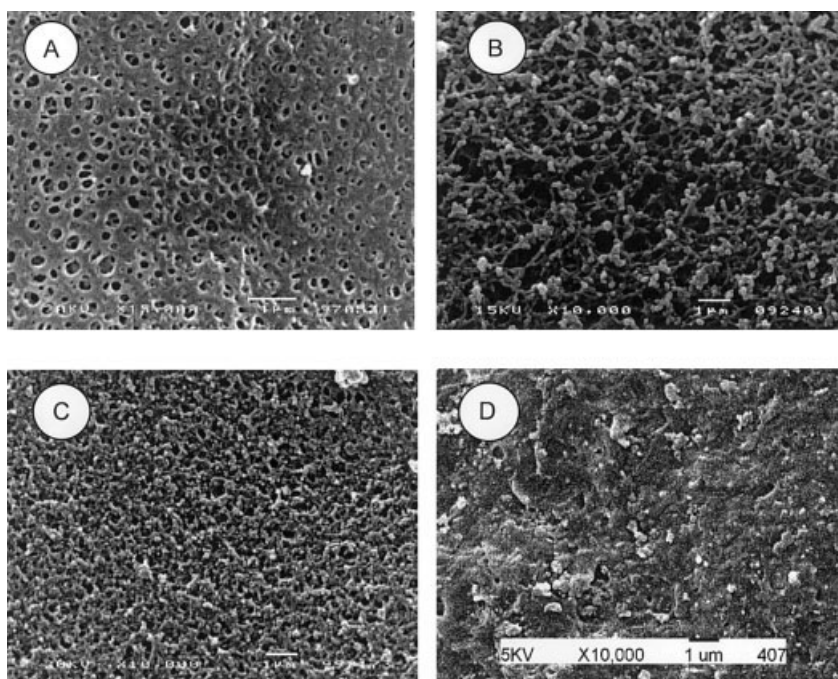
of 0 to  $80^\circ\text{C}$ . PVP as a additive increases the solution viscosity, which was 1100 poise at  $25^\circ\text{C}$ , 20 times higher than that of solution 1, even though the polysulfone concentration was much higher in solution 1.

A solution close to the cloud point (solution 1) may result in an open substructure and an increase in interconnectivity of the membrane pores. The morphology of the surface may have a tremendous effect on the permeation property. The second solution may also give a highly porous substructure due to the presence of a high molecular weight hydrophilic polymer, PVP.<sup>1-20</sup> However, associated with this open substructure, a dense and thick skin layer may be formed as well, giving a high resistance to transport.<sup>3</sup>

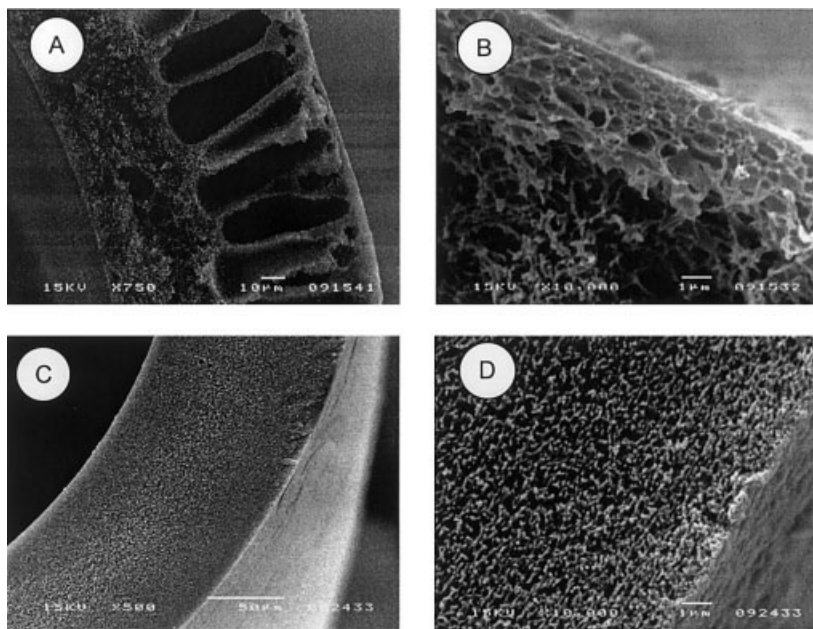
### Kinetics of phase separation

Table II lists the delay time before demixing for different coagulation baths having different solvency strength. The composition of the coagulation bath strongly influences on the delay time. NMP was a good solvent for the polymer, and thus gradually dissolves both polymer solutions. Since water was the strongest nonsolvent, both polymer solutions show instantaneous demixing. An ambient environment with humidity of 55% has a different effect on the delay time. For solution 1, the delay time was 1 s, while it was 39 s for solution 2.

For solution 1, a mixture of NMP and acetone still shows a good solvency up to 50 wt % acetone. However, pure acetone was a mild nonsolvent for polysul-



**Figure 5** Surfaces of PSf hollow fibers spun under different external conditions. (A) air; (B) NMP; (C) NMP/acetone 50/50 wt %; (D) acetone.



**Figure 6** Cross-section of the hollow fibers spun with an external liquid from the outside orifice channel. For A and B, acetone was the external liquid; for C and D, NMP.

fone and it causes instantaneous demixing of solution 1 since it was located close to the cloud point. In later discussion, we show the effect of the solvency of the first coagulants on the porosity and pore interconnectivity of the outside surfaces of membranes obtained from solution 1. Unfortunately, no correlation could be established between morphology and the delay time. The experiments, however, demonstrate the sensitivity of two polymer solutions to different phase separation conditions. Moreover, the infinite delay time of NMP to both solutions confirms that NMP was an excellent dilution solvent. Therefore, NMP was used to alter the polymer solution toward lower polymer concentration from A to B (Fig. 2).

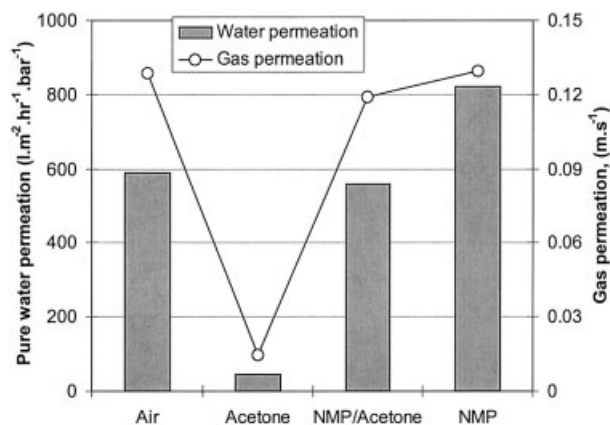
#### Structure and permeation properties of membranes from solution 1

Solution 1 was located so close to the cloud point that demixing occurred immediately after extruding from the spinneret due to the water vapor presented in the air gap. An open porous structure was obtained, as can be seen in Figure 5(A), with a high porosity. When NMP was used in the outer orifice, an extremely open surface with a lacy structure was obtained, as can be seen in Figure 5(B). We reason that the polymer concentration at the outlayer was diluted by NMP and becomes probably low enough to pass the binodal curve close to the critical point, forming an open, loose structure.

Adding acetone to NMP and therefore decreasing the solvency results in a much denser surface structure, as shown in Figure 5(C) and (D). A less open

surface was obtained using a solution of NMP/acetone at a ratio of 50/50 wt %. Moreover, a dense surface was obtained by using acetone alone. The results indicate that with decrease in the solvency of the liquid from the outer orifice, a denser skin was obtained. The morphology was confirmed by a cross-section of various structures as can be seen in Figure 6. The hollow fiber spun using acetone shows a dense surface at the outside as can be seen in Figure 6(A) and (B). Below the top layer a fingerlike structure was observed of about 3/5 of the total thickness, together with an interconnected porous layer. In the top layer, a dense skin of about  $0.5 \mu\text{m}$  consists of closed cells. In contrast, the membrane prepared from NMP as the liquid in the outer orifice shows a symmetric porous, finger-free and interconnected structure [see Fig. 6(C) and (D)].

Figure 7 shows that the permeation properties correspond fairly well to the observed morphology. The gas permeation and water permeation properties indicate that the membrane using acetone as external liquid shows the highest resistance—therefore, the lowest water and gas permeability. Slightly higher fluxes are obtained for the membrane prepared with NMP as the external fluid than the membrane prepared either with NMP/acetone mixture or without external fluids at all. Probably, the outer surface was open enough even without external fluid. The total resistance in this case mainly originates from the substructure and the inner skin layer. Further improvement of the flux can be achieved either by using a solution that forms far more open substructure (for

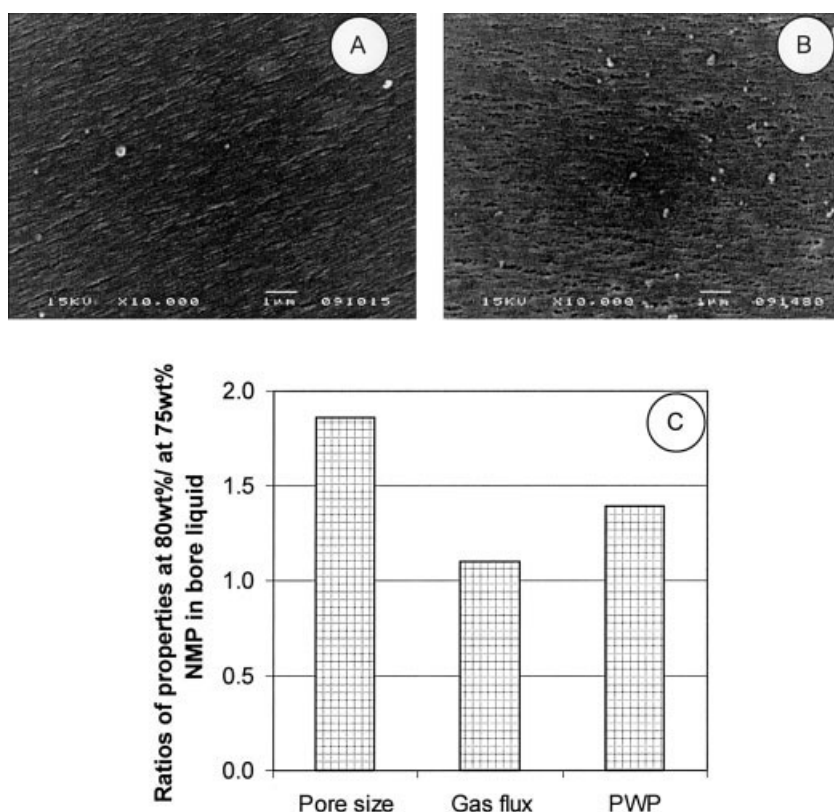


**Figure 7** Effect of different external compounds on the permeation of hollow fiber membranes.

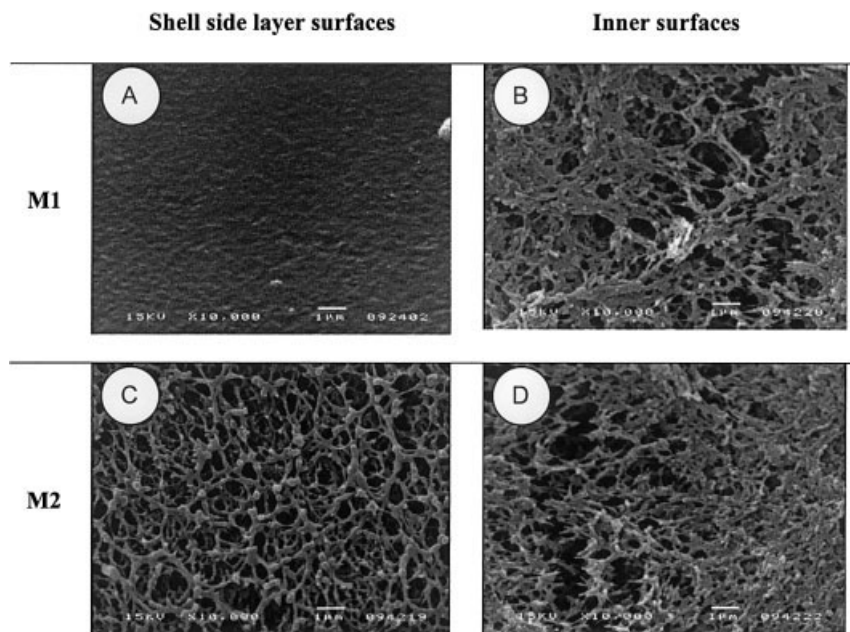
example, solution 2) or using a demixed solution<sup>21</sup> that may generate heterogeneous membranes. Increase of the pore size at the inner surface layer improves fluxes as well. Figure 8 shows a more open inner surface of the membrane prepared with 80 wt % NMP in bore liquid compared to the membrane prepared with 75 wt % solvent. Consequently, the pore size was bigger and slightly higher water and gas permeability [as can be seen in Fig. 8(C)] are obtained.

### Structure and permeation of the membranes from polymer solution 2

Figure 9(A) shows the hollow fiber membranes obtained from solution 2 having an extremely dense skin layer, which was already mentioned by Munari et al.<sup>3</sup> A dense top layer was found by using a polymer solution containing 5–10 wt % PVP, having a pronounced negative effect on the flux. According to the proposed concept, a highly porous surface can be obtained using NMP as the external liquid and Figure 9(C) indeed confirms this. The whole surface consists of a lacy interconnected porous structure and an extremely low transport resistance of the outside skin was expected. This lacy structure was an indication of a rather low polymer concentration at the outer layer before phase separation occurs. Again, NMP dilutes the polymer solution at the top layer during the short period of contact, which results in a loose structure. These membranes also show a quite open inner surfaces, as seen in Figure 9(B) and (D), since the bore liquid NMP content was high, up to 80 wt %. As listed in Table III, the membrane with a dense skin layer shows a water permeability of only 18 L m<sup>-2</sup> h<sup>-1</sup> bar<sup>-1</sup> because of its dense surface at the shell side. However, the membrane prepared using NMP as ex-



**Figure 8** Morphology of the inner surface for membranes prepared with 75 wt % (A) and 80 wt % (B) NMP in bore liquid and ratios of properties, (C) (pore size, gas flux, pure water permeability) of two membranes from solution 1 using NMP as the external liquid. Pore size of membrane (A) is 52 nm and of membrane (B) is 97 nm.



**Figure 9** Structure of the shell side surface and inner surface of hollow fiber membranes prepared from solution 2. M1, without NMP; M2, with NMP as the external liquid. Bore liquid, 80 wt % NMP.

ternal liquid has a water permeability of  $4700 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  and the average pore size of 1.2–1.3  $\mu\text{m}$ .

layer but an open substructure, such as a solution of PSf and PVP.

**CONCLUSIONS**

This work describes the application of the triple-orifice spinneret in the preparation of microfiltration membranes with a highly porous surface. Dilution solvents, i.e., NMP and NMP/acetone (50/50 wt %), can be used as the external liquids during spinning, but not acetone, a mild nonsolvent for polysulfone. A simple way to obtain a highly porous top layer independent of polymer solution in spinning process is to apply a good solvent as the external liquid using a triple-orifice spinneret. A polymer solution close to the cloud point does not show significant improvement in permeability since the surface pores are open enough and not the controlling parameter for transport. However, a porous surface can be obtained for a polymer solution far from the cloud point, forming a dense skin

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**TABLE III**  
Effect of NMP on the Properties of a PSf/PVP Blend Membrane Prepared from Solution 2

External Liquid	PWP <sup>a</sup> ( $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ )	Pore Size ( $\mu\text{m}$ )
N/A	18	Dense layer
NMP	4700	1.2–1.3

Membrane 1 formed by passing through a short air gap, and the pore size was measured by permoporometry. Membrane 2 formed by using NMP as the external liquid, and the pore size was measured by Coulter Porometer II.

<sup>a</sup> PWP: pure water permeability.