Wet-Phase-Separation Membranes from the Polysulfone/N,N-Dimethylacetamide/Water Ternary System: The Formation and Elements of Their Structure and Properties

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ABSTRACT: Asymmetric and porous polysulfone (PSf) membranes were prepared by wet phase separation. Binary (PSf)/N,N-dimethylacetamide (DMA) solutions with polymer concentrations of 12.5–30 wt % were cast in thicknesses of 80–700 μm and immersed in a coagulation bath of pure water. The morphology of the formed membranes' cross sections consisted of a cellular structure and macrovoids; the cellular structure density was highest when the cast solution contained about 21 wt % PSf, regardless of the cast thickness. The membranes' pure water permeability decreased as the cast thickness increased. The instantaneous onset of the turbidity, regardless of the PSf content and cast thickness, its steep growth, and relatively high end value were the main characteristics of the turbidity phenomena taking place during the formation of the protomembranes. Again, the membrane-forming system with a PSf/DMA solution with about 21 wt % polymer, regardless of the cast thickness, had the highest turbidity end value. The shrinkage of the cast solutions into the corresponding protomembrane was also examined quantitatively. Inverse experiments showed that the direction of the gravitation field had no influence on the shrinkage of the membrane-forming ternary system or the membranes' morphology and its water permeability. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1667–1674, 2005

Key words: membranes; morphology; phase separation

INTRODUCTION

Polysulfone Udel (PSf) is one of the classic polymers used for membrane preparation by wet phase separation (WPS).[1–10] The usual solvents for dissolving PSf are N-methyl-2-pyrrolidone and N,N-dimethylacetamide (DMA), both of which are aprotic and polar. Furthermore, they are completely miscible with water, which is a nonsolvent for PSf. Here we report the preparation of a variety of asymmetric and porous PSf membranes from a PSf/DMA/water ternary system by means of WPS. The membrane-forming region in the PSf/DMA/water ternary system began when the PSf/DMA solution contained more than 10 wt % polymer. The membranes were prepared from PSf/DMA solutions with various polymer concentrations, and the solutions were cast in different thicknesses on a glass plate; they were immersed in a coagulation bath consisting of pure water. Although the turbidity and shrinkage phenomena taking place during the membranes' formation in the PSf/DMA/water ternary system by WPS, the membranes' pure water permeabilities, and the formed membranes' cross-sectional morphology have already been presented in our previous works,[11–14] this article presents them in greater detail. Here, some further correlations among them are established, too. Parallel experiments were also conducted, through which the influence of the direction of the gravitation field on the PSf membrane-formation mechanism could be examined.

In the membranes' cross-sectional morphology, examined by scanning electron microscopy (SEM), the cellular structure and the macrovoids were the fundamental structural features, regardless of how the wet phase inversion was accomplished, with respect to the directions of the gravitation field or the direction of the primary mass transport of the components. In the article, we speak only of the cellular structure; the formation of macrovoids and the syneresis pressure–coalescence mechanism of PSf membrane formation will be presented elsewhere.

EXPERIMENTAL

PSf (weight-average molecular weight = 22.000 Da; 18,224-3, Aldrich, St. Louis, MO) membranes were prepared by WPS from two-component solutions of various PSf contents (12.5, 15.0, 18.0, 21.0, 25.0, and 30.0 wt %) in DMA (60145, Riedel-de Haën, Seelze, Germany). The solutions were cast with a rectangular

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knife (ca. 26 cm long) with accurately manufactured slits (unevenness < 5 μm) onto a ground glass plate (29 cm $\times$ 27 cm) with maximal unevenness of less than 5 μm. We presumed that the casting velocity was so low that a die-swelling effect could not occur, and the nominal dimension of the cast knife slit was the thickness of the cast solution. Accordingly, the thicknesses of the cast solutions were 80, 100, 150, 200, 300, 400, 500, 600, and 700 μm. Each ground glass plate with a cast PSf/DMA solution was immediately transferred (within 5 s) to a coagulation bath, which always consisted of pure deionized water. The formed flat-sheet protomembranes were left in the coagulation bath for 10 min and then were transported into another bath with slightly agitated deionized water, in which they were left for 24–30 h. As such, they were used for further characterization.

For the examination of the influence of the gravitation field direction on the membranes' formation mechanism, inverted experiments were performed, in which the direction of the primary mass transport was inverted. In the normal WPS experiment, the nonsolvent (solvent) was transported down from the coagulation bath, that is, in the direction of the gravitation field (up from the cast solution in the direction opposite to the gravitation field), into the cast solution (to the coagulation bath). During the inverse experiment, we achieved the inverse transportation of the solvent and nonsolvent by turning the glass plate around with the cast PSf/DMA solution before its immersion into (contact with) the coagulation bath.

The turbidity phenomena taking place during the transformation of the membrane-forming ternary system into the protomembrane were followed by a simple turbidity measurement setup described elsewhere.[15,16]

The thickness of the formed PSf membranes was determined with a Minimer HD1 magnetic probe (Setron, Bistrica ob Dravi, Slovenia); an average of 10 measurements at evenly spaced points on the flat-sheet membrane was taken as the membrane thickness.

The pure water flux (PWF) for the membranes was determined in an Amicon 8400 dead-end measuring cell (Millipore, Billerica, MA) under ultrafiltration conditions and with pressurized nitrogen as the driving gas.

We prepared samples for the examination of the morphology of the membranes' cross sections under a scanning electron microscope (JSM-840A, JEOL, Tokyo, Japan) by drying the membranes and then breaking them in liquid nitrogen. After they were mounted on the sample holder, the samples were dried again and sputtered before their examination by SEM.

The number of cells per unit of area of the membranes' cross-sectional morphology was determined by the simple counting of the cells in the chosen mea-

sured area. Micrographs of the cross-sectional morphology were adequately magnified to suit this purpose; the area for counting the cells was chosen so that the number of counting cells fell between 100 and 200.

RESULTS AND DISCUSSION

Cross-section morphology

Micrographs of the membranes' cross sections are presented in two magnifications so that the membranes can be seen in their entirety and so that some details can be seen; the particular magnifications were chosen at random.

In Figures 1 and 2, SEM micrographs of the PSf membranes' cross-sectional morphologies are presented. They were prepared by WPS of the ternary PSf/DMA/water system. A very important conclusion can be drawn from Figure 2: the direction of the gravitation field had no influence on the PSf membranes' cross-sectional morphology. Despite the complexity of the membranes' cross-sectional morphology, the micrographs of the normal experiment and the inverse experiment showed practically identical results. However, there were differences in the cross-sectional morphologies because of the variation in the PSf content in the cast solution and the variation in the cast thickness (Fig. 1). The main characteristic features of all the cross-sectional morphologies were a cellular structure and macrovoids. The mechanism of the macrovoid (finger-like structure) formation is the subject of another article. As is known from the literature[17] and as was pointed out in our previous work,[12,13,18] the cellular structure was formed by the nucleation and growth (NaG) of the polymer-lean phase. Because of the primary mass transport, by which the solvent and nonsolvent were transported in opposite directions out of and into the cast solution, respectively (the direction of this mass transport was perpendicular to the cast-solution/coagulation-bath interface), thermodynamic instability in the ternary PSf/DMA/water system was induced. It was resolved by secondary mass transport, by which the matter (all three components, i.e., PSf, DMA, and water) was transported in all directions in the space; phase separation in the narrower sense took place by the elementary process of NaG of the polymer-lean phase. The solvent and nonsolvent were transported from all directions to the formed and growing nuclei, and the polymer also shifted out of the nuclei's surroundings in all directions. The space around the formed and growing nuclei became richer and richer in the polymer because the solvent and nonsolvent were transported against the concentration gradient to the increasingly larger nuclei of the polymer-lean phase. Its composition was directed toward the composition of the equilibrium polymer-rich phase. To achieve a firm polymeric
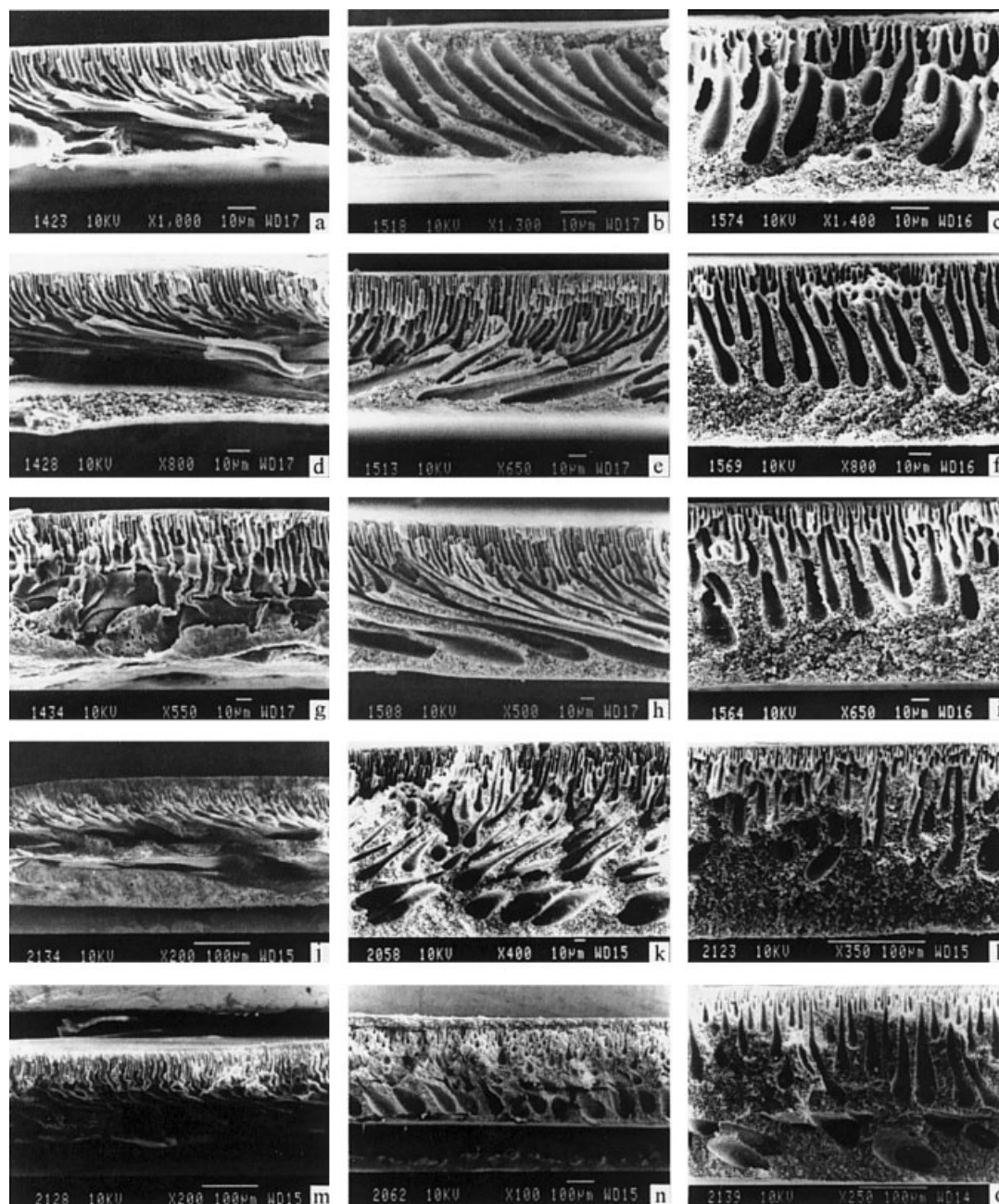
Figure 1 Micrographs of the cross-sectional morphologies of the PSf membranes prepared from cast solutions with different concentrations of the polymer (12.5, 18, and 25 wt %, from left to right) and different cast thicknesses (80, 150, 250, 400, and 600 μm, from top to bottom).

membrane, the surroundings of the growing nuclei had to undergo some form of solidification, namely, gelation, vitrification (glass transition), or crystallization. It was not necessary that the surroundings of the forming and growing nuclei achieve a thermodynamically equilibrated composition; it could solidify earlier when the solidification line in the ternary phase diagram was surpassed, and in its composition, there was not (yet) an equilibrium content of the polymer. In such a way, the growing nuclei of the polymer-lean phase were frozen in the continuously solidified poly-

mer-rich phase, and the cellular structure of the protomembrane was formed. The forms of solidification of the nonequilibrium polymer-rich phase were for the cellular structure of the membranes very important for the membranes' PWF, as we show later. Usually, the polymer-lean phase was leached out of the cells of the protomembrane's cellular structure by water, and the membrane was thus produced.

The cellular structure was always present in the PSf membranes' cross-sectional morphology, regardless of the presence of macrovoids and channels. When the
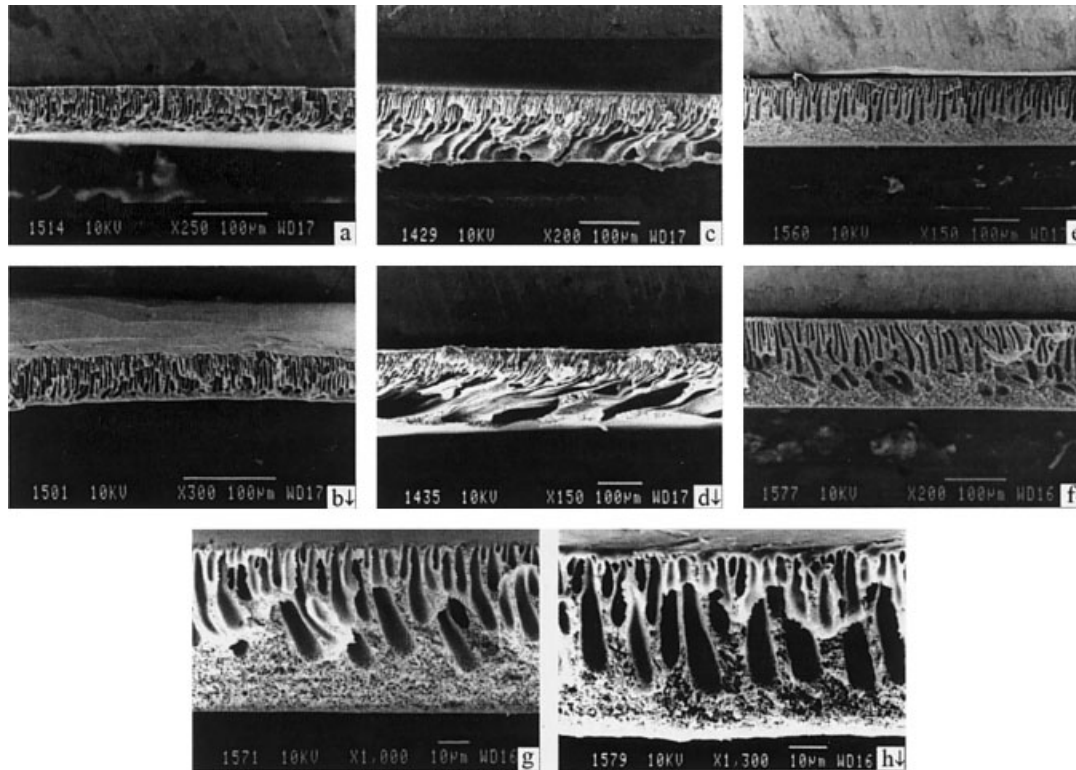
Figure 2 Micrographs of the cross-sectional morphologies of the PSf membranes prepared (a,c,e,g) in the normal experiments and (b,d,f,h) in the inverse experiments. The PSf concentrations in the cast solutions and the cast thicknesses were (a,b) 18 wt % and 100 μm, (c,d) 12.5 wt % and 300 μm, (e,f) 25 wt % and 300 μm, and (g,h) 25 wt % and 100 μm.

membranes were prepared from more concentrated solutions of PSf in DMA, this structure was obvious, but when the membranes were prepared from solutions containing 15 or even 12.5 wt % polymer, the parts with the cellular structure could be found by a careful inspection of the surroundings of the great macrovoids (megamacrovoids) on the lower part of the membranes' cross-sectional morphology. Cells were packed very closely to one another, and they had round to oval shapes, in some places turning into polygonal shapes that gave the impression that after their formation as round cells they were forced to undergo some (slight) deformation. They also showed slight asymmetry in their shape: the cells near the upper part of the membranes were slightly smaller than the cells at the bottom. Regardless of this slight asymmetry, we determined the average number of cells per unit of area (Fig. 3). This parameter also measured the (relative) dimensions of the cells. The number of cells per unit of area (the dimensions of the cells) increased (decreased) as the content of PSf in the cast solution increased[19] up to 21 wt %; thereafter, it decreased (increased) with a further increase in the PSf content in the cast solution. The maximum number of cells was best expressed when the membranes were prepared from a 80-μm-thick cast solution; the expressiveness of the maximum was diminished

against the 300-μm-thick membranes when the number of cells became almost independent of the cast composition. On the other hand, Figure 3 shows that the number of cells per unit of area (the dimensions of the cells) decreased (increased) as the thickness of the cast solution increased. For now, we have no explanation for this cell density dependence on the cast-solution composition and thickness. Some opposing pro-
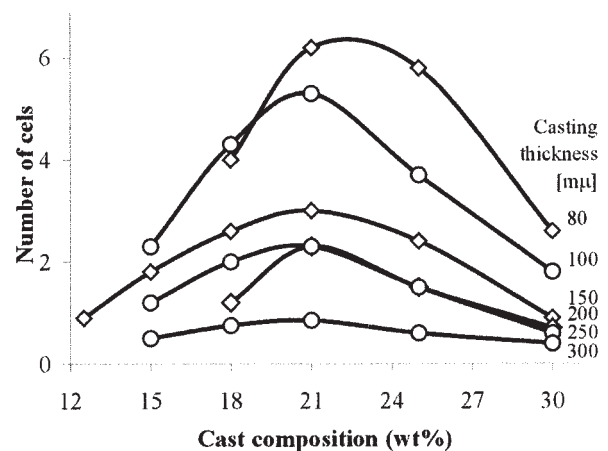

Figure 3 Number of cells per cross-sectional morphology area versus the cast composition and cast thickness.

cesses connected to the rate of appearance of nuclei, the growth of nuclei, the mass-transport dependence on the viscosity, and the surface tension of the participating phases were probably in force.[9] The results are presented because of the clear correlation with the turbidity end value (see the next section).

Turbidity phenomena

In Figure 4(a–c), the time dependence of the turbidity of various PSf/DMA/water membranes forming ternary systems is presented. Their main characteristics were an instantaneous turbidity onset, a high rate of turbidity growth, and, in comparison with other polymer/solvent/nonsolvent membrane-forming systems, a high or even highest end value of turbidity.[10–13,16]

In the PSf/DMA/water membrane-forming system, the elementary process of the secondary mass transport, namely, phase separation in a narrower sense, took place by NaG of the polymer-lean phase. According to the turbidity phenomena, which reflected the light scattering on the phase boundaries, the nuclei of the polymer-lean phase and thus the phase boundaries were formed immediately after the contact of the cast solution with water in the coagulation bath (an instantaneous onset of the turbidity). This property did not depend on the cast composition or thickness, and it (probably) reflected the fact that the binodal in the PSf/DMA/water ternary phase diagram was very near the solvent–polymer axis. The high rate of turbidity growth showed the high rate of polymer-lean phase nuclei formation. Some dependence of the turbidity growth rate on the cast composition and thickness was observed, but our turbidity measurement setup was not sensitive enough to clearly distinguish such small differences. The high end value of the turbidity showed a large quantity of phase boundaries at the moment at which some form of solidification of the continuous polymer-rich phase took place and froze NaG of the polymer-lean phase mode of phase separation. A firm protomembrane with a cellular structure was formed; the cells were, of course, filled with the polymer-lean phase. As for the dependence of the turbidity end value on the cast composition (at a constant cast thickness), the former was practically always maximal in the process of wet phase inversion with the cast solution containing 21 wt % PSf. (Fig. 4). These maximums coincided with the maximum number of cells per area of the cross-sectional morphology (Fig. 3). These correlations confirmed the connection of the cellular structure formation with NaG of the polymer-lean phase, which manifested itself in the turbidity phenomena during the WPS process. Although the cell-counting method could be burden with some suspicion because of the anisotropic cell density, the presented correlation was through many data so straightforward that it deserved presentation.
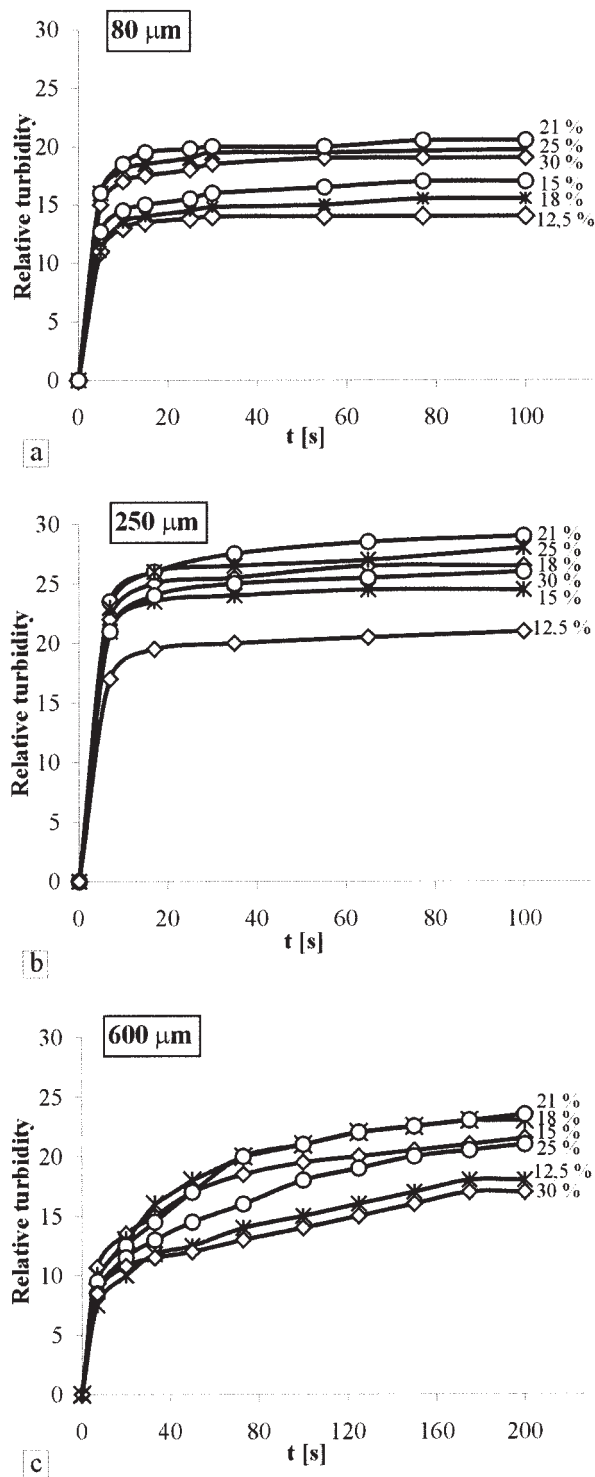
Figure 4 Turbidity of the membrane-forming PSf/DMA/water ternary system versus time. The cast thicknesses were (a) 80, (b) 250, and (c) 600 μm. The compositions of the cast solutions were 12.5, 15, 18, 21, 25, and 30 wt %, regardless of the cast thickness.

Longitudinal syneresis (shrinkage) of the membrane-forming system

Previously,[11,13] we described the conditions and circumstances in which the shrinkage or longitudinal

Knife slit (μm)	Solution composition (wt %)					
	12.5	15	18	21	25	30
80	17.5 ± 1.3	25.0 ± 3.9	30.8 ± 3.1	35.5 ± 0.9	39.1 ± 2.4	43.5 ± 2.1
100	26.9 ± 4.7	35.4 ± 1.9	42.6 ± 1.8	46.4 ± 1.5	52.0 ± 1.3	59.6 ± 2.5
100(↓)		33.7 ± 1.8	41.9 ± 1.7		51.5 ± 1.5	56.7 ± 1.9
150	40.1 ± 8.0	56.1 ± 6.0	63.9 ± 2.2	66.6 ± 2.6	75.1 ± 1.9	88.4 ± 1.5
200	47.1 ± 4.7	67.3 ± 5.0	72.8 ± 3.2	78.0 ± 2.7	90.3 ± 3.9	101.9 ± 2.9
250	71.4 ± 16.3	78.1 ± 7.2	91.0 ± 3.7	99.0 ± 2.7	100.3 ± 1.3	112.8 ± 0.5
300	115.9 ± 17.2	125.3 ± 5.1	130.5 ± 4.9	132.8 ± 2.0	139.8 ± 1.5	152.1 ± 1.1
300(↓)		121.8 ± 4.7	130.1 ± 4.3		138.2 ± 1.7	

syneresis of a membrane-forming system containing three components could take place. Because the cast solution contained about 30 wt % PSf at most, the membrane prepared by WPS had to be thinner than the initial cast solution. The longitudinal syneresis, experimentally determined as the difference between the slit dimension on the cast knife and the thickness of the formed (proto)membrane, determined by the magnetic probe or from SEM micrographs, somehow reflected the overall or average porosity. Less longitudinal syneresis meant that a lot of empty space was formed during the process of WPS, whereas greater syneresis meant the opposite. Of course, the longitudinal syneresis said nothing about the quality of the membrane porosity: the cellular, bicontinuous (spinodal), and beadlike porosity could not be distinguished by syneresis determination because for the mentioned porosities, the ratio between the empty volume and the volume of the entire membrane was practically independent of the porosity quality.

For WPS by the PSf/DMA/water system at the membrane-forming compositions of PSf in DMA (>10 wt %), cellular porosity was always formed. This fact was also reflected in the longitudinal syneresis, which was, by its values of 80–40%, moderate in comparison with some other ternary membrane-forming systems.[13] In Table I, the thicknesses and their standard deviations for PSf (proto)membranes are presented. The membranes were prepared from PSf/DMA solutions with more than 10 wt % polymer and with various nominal cast thicknesses. The longitudinal syneresis (shrinkage) was almost 80% of the cast thickness for the (proto)membranes prepared from cast solutions with 12.5 wt % PSf and was about 50–40% of the cast thickness when the (proto)membranes were prepared from cast solutions with 30 wt % PSf. The (proto)membranes' thicknesses monotonically increased with an increase in the concentration of PSf in the cast solution and with an increase in the cast thickness. No abrupt change occurred. The shrinkage of the membranes prepared by inverted experiments had practically the same value as the shrinkage of the

normal experiment membranes (see Table I). At this point, we need to say something about transversal (lateral) syneresis. It existed because it could be seen with the naked eye in some systems during the membranes' formation. Self-peeling from the glass plate and the rolling of the membranes also indicated that transversal syneresis existed to different extents in different layers of the membrane-forming system. When the membranes were rolled up (this was the case for our PSf/DMA/water system), the upper layer of the membrane-forming system experienced greater transversal syneresis than the layer close to the glass plate. We had some indication that unequal lateral syneresis in different layers of the membrane-forming system caused some macrovoids to be oblique in the cross-sectional morphology of some membranes. This effect of macrovoid obliqueness was especially expressed when the membrane-forming system was hindered in its transversal syneresis by, for example, being somewhat stacked on the supporting glass plate. The folding of the surfaces of the membranes prepared from PSf/DMA solutions with less than 15 wt % polymer also had its origin in irregular lateral syneresis.

PWF

Table II presents PWF through PSf membranes prepared from PSf/DMA solutions with different polymer contents and with various cast thicknesses under ultrafiltration conditions. At this point, even with good laboratory practices concerning the membranes' PWF, the scattering of the results sometimes became as great as 50%. With some exceptions, very clear and simple tendencies were expressed: PWF decreased as the cast thickness increased and as the content of the polymer in the cast solution increased. However, the membranes prepared from thin (80 and 100 μm) and low-polymer-content (12.5 wt %) solutions were exceptions. The PWF decrease was relatively rapid. Again, the differences in PWF through normal experiment membranes and through inverse experiment

TABLE II
PWF (L m^{-2}/h^{-1}) Under Ultrafiltration Conditions of PSf Membranes Prepared from Solutions with Different Polymer Contents and with Various Cast Thicknesses and Data Concerning Inverted Experiments (↓)

Knife slits (μm)	Solution composition (wt %)					
	12.5	15	18	21	25	30
	25.1	5.7	0.0	0.0	0.0	0.0
	882.8	—	163.0	11.4	0.0	0.0
80	1263.0	—	298.8	—	8.3	0.0
	—	—	543.2	—	12.3	0.0
	0.0	0.0	0.0	0.0	0.0	0.0
	728.9	570.4	14.9	1.7	0.0	0.0
100	1079.7	1059.3	36.7	3.2	0.0	0.0
	—	1575.4	66.5	5.7	0.0	0.0
	9.8	0.0	0.0	0.0	0.0	0.0
	1337.7	760.5	31.8	0.0	0.0	0.0
100(↓)	1612.7	1358.0	70.1	3.1	0.0	0.0
	—	1874.0	115.4	5.6	0.0	0.0
	19.2	0.0	0.0	0.0	0.0	0.0
	488.9	237.6	6.5	0.0	0.0	0.0
150	624.7	516.1	13.6	0.9	0.0	0.0
	724.3	760.5	25.0	3.1	0.0	0.0
	25.4	0.0	0.0	0.0	0.0	0.0
	1136.3	182.0	0.0	0.0	0.0	0.0
200	1747.4	516.1	4.5	0.0	0.0	0.0
	2028.0	624.7	7.1	0.0	0.0	0.0
	3.8	0.0	0.0	0.0	0.0	0.0
	584.0	122.2	0.0	0.0	0.0	0.0
250	719.8	264.8	0.0	0.0	0.0	0.0
	842.0	488.9	7.7	0.0	0.0	0.0
	2.1	0.0	0.0	0.0	0.0	0.0
	163.0	31.2	0.0	0.0	0.0	0.0
300	190.1	84.9	0.0	0.0	0.0	0.0
	210.5	163.0	0.0	0.0	0.0	0.0
	0.0	0.0	0.0	0.0	0.0	0.0
	217.3	25.8	0.0	0.0	0.0	0.0
300(↓)	312.4	71.3	0.0	0.0	0.0	0.0
	414.2	126.3	0.0	0.0	0.0	0.0

Pressure difference (Δp); first line: $\Delta p = 0.0$ bar; second line: $\Delta p = 2.0$ bar; third line: $\Delta p = 4.0$ bar; fourth line: $\Delta p = 6.0$ bar.

nectedness is the second decisive factor for any medium permeability through the membranes' cellular structure. For the PSf membranes, the cells' interconnectedness by macrovoids was very important. Because the membranes prepared from PSf/DMA solutions with lower contents of the polymer had macrovoids extending from the top to the bottom surface (Figs. 1 and 2), their PWF was relatively high under ultrafiltration conditions. The macrovoids gradually became shorter when the content of PSf in the cast solution increased (Figs. 1 and 2) and thus caused the PWF under ultrafiltration conditions to disappear. Now the cells' interconnectedness through the dense polymer controlled the matter permeation. The elementary processes of solidification—gelation, glass transition (vitrification), and crystallization—could alone or in any combination form a variety of microporosities in the continuous phase. However, these distinctions could probably not be detected by PWF variation alone, and so other, more subtle methods had to be used for differentiating among a variety of microporosities. Our experimental results enabled the interpretation of the disappearance of PWF. It was caused by the disappearance of the cells' interconnectedness due to the shortening of macrovoids in the PSf membranes with a cellular structure; the latter occurred as a result of the increasing content of PSf in the cast solution.[19]

CONCLUSIONS

In the ternary system PSf/DMA/water, the most prominent features of the polymeric asymmetric and porous membranes' formation by WPS were their cross-sectional morphology, with its cellular structure and macrovoids, as well as the turbidity phenomena with their instantaneous onset, high rate of growth, and relatively high end value. The cellular structure was the result of NaG of the polymer-lean phase and the subsequent solidification of the surrounding polymer-rich phase; the formation of nuclei was reflected in the turbidity phenomena because an interphase surface on which light was scattered was formed. The cellular structure density, that is, the number of cells per cross section area, and the end values of the turbidities were maximal when the PSf membranes were prepared from cast solutions containing about 21 wt % polymer, regardless of the cast thickness. Longitudinal and transversal syneresis took place during the transformation of the cast solutions into protomembranes: the latter was 40–80% thinner than the former, this depending on the content of the polymer in the cast solution. Syneresis was, as could be expected, greater when the PSf content in the cast solution was smaller. The membrane permeability for pure water was in an analogous relation with the cast composition and thickness: the membranes prepared from thinner cast solutions and with fewer polymers were more water-permeable. Water transport through the porous mem-

membranes were practically negligible (except for membranes of low thickness and concentration). Although the magnification of the SEM micrographs was not completely appropriate, we can speculate that the cross-sectional morphology of the various membranes would have revealed that there was no appreciably thick layer of a dense polymer material or skin on top of the membranes that could be the decisive limiting barrier for PWF. As pointed out in our previous work,[13] in the porosity spectra, the cellular structure belongs to a quite closed structure for any media flux because the permeating media have to pass through the dense polymer, which is a matrix (continuous phase) of the cellular structure. This continuous phase, made during the elementary process of NaG of the polymer-lean phase and after some form of solidification of the polymer-rich phase, surrounds the forming and growing nuclei. The degree of the cells' intercon-

branes depended on the skin properties and on the interconnectedness of the cellular structure. Solution–diffusion transport took place through the skin and through the solid polymer, forming the matrix (continuous phase) of the cellular structure, in which the cellular interconnectedness was low or even absent. Such transport was much smaller than hydrodynamic transport through the cellular structure, in which the cells were connected with the empty space. From the inverse experiments, in which the directions of the solvent and nonsolvent primary mass transport were changed for the sake of investigating the gravitational field direction's influence on the membranes' formation, we concluded that there was no difference in the membranes' cross-sectional morphology, in their water permeability, and in their longitudinal syneresis. Membrane formation by WPS in the PSf/DMA/water ternary system was invariant with respect to the gravitation field direction.

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