

Microporous Membranes Prepared from Blends of Polysulfone and Sulfonated Poly(2,6-dimethyl-1,4-phenylene oxide)

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ABSTRACT: Membranes were prepared from solutions containing Udel-type polysulfone (PSf) and sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO). Polymer solutions in 1-methyl-2-pyrrolidone were cast on a nonwoven textile and precipitated in a water bath. The permeabilities and selectivities of the prepared membranes depended on the concentrations of both polymers in the casting solution. The higher the concentration of PSf, the lower were the permeabilities to water and average pore sizes of the membranes. On the other hand, a very small amount of SPPO in the casting solution (about 1–4 wt % relative to the casting solution weight) brought about a considerable increase in water permeabilities and had a small influence on the average pore sizes. The effects were most pronounced if SPPO with a degree of sulfonation of 20–40% was used. The considerable increase in water permeabilities was explained by separation of the PSf and SPPO phases during precipitation in water and by the concentration of hydrophilic SPPO on the surface of the membrane and its pores. The determinations of the oriented concentration potentials proved the presence of a negative surface charge in the membranes. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 134–142, 2001

Key words: membrane; ultrafiltration; polysulfone; sulfonated poly(2,6-dimethyl-1,4-phenylene oxide)

INTRODUCTION

Polysulfone (PSf) is an attractive material for preparation of microporous membranes because it possesses excellent film- and membrane-forming properties, as well as high thermal and chem-

ical stability. Microporous membranes from PSf are prepared by the wet phase inversion process, which includes the following steps: dissolving PSf in an aprotic solvent, usually 1-methyl-2-pyrrolidone (NMP) or dimethylformamide to a homogeneous solution; casting the prepared solution onto an inert support as a thin film or extruding the solution in the form of a hollow fiber; and immersing the cast or extruded solution into a nonsolvent with respect to PSf (usually water) in which the initially homogeneous solution is separated into a polymer-poor and a polymer-rich phase from which the membrane pores and polymer matrix surrounding the pores are generated.

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A second water-soluble polymer is often added to the PSf casting solution with the aim to obtain membranes with a more desirable pore structure (i.e., high porosity, well-interconnected pores, no macrovoids in the sublayer) and/or to increase the viscosity of the casting solution. Poly(1-vinyl-2-pyrrolidone) (PVP) is most often used as a water-soluble polymer^{1–6}; poly(ethylene glycol)s,^{1,7} sulfonated PSf,^{8,9} and carboxylated PSf¹⁰ were also tested.

The role of PVP in the casting solution during membrane formation [in this case, membranes of poly(ether sulfone), a polymer with similar properties to Udel-type PSf] was systematically studied.^{11–14} Steady-state experiments with dilute solutions showed that after immersion of the cast film into a water bath the solution separates into two phases: one phase consists of poly(ether sulfone), solvent, and water while the other consists of PVP, solvent, and water. The continuous poly(ether sulfone)-rich phase forms the membrane matrix while the continuous PVP-rich phase forms interconnected pores. The separation process of the polymers is mainly controlled by diffusion of both polymers. However, mutual diffusion of the two polymers is a very slow process compared to the diffusion of small molecules of solvent and water. Solidification of the resulting membrane will therefore occur before all PVP can diffuse out of the poly(ether sulfone) phase, and some PVP molecules remain trapped in the PSf matrix, especially near to the surface and on the pore surface of the resulting membrane. These entrapped molecules make the membrane surface more hydrophilic.

In this work sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) was used as a hydrophilic additive to PSf casting solutions instead of PVP. The aim was the preparation of microporous PSf membranes having similar qualities to those prepared with PVP, yet bearing electric charges.

EXPERIMENTAL

Low-Degree Sulfonation of PPO

The PPO ($M_w = 55,000$ by light scattering, Spolana Neratovice, Czech Republic) was dissolved in chloroform to a 3% solution. Chlorosulfonic acid in chloroform (5% solution) was slowly added with stirring to the PPO chloroform solution at 25°C. When a drop of the PPO solution withdrawn with a pipette did not precipitate in NMP (SPPO prod-

ucts with a degree of sulfonation of ≈ 10 –20%) or in methanol (SPPO products with a degree of sulfonation of ≈ 20 –45%), the reaction was stopped and the reaction mixture was precipitated into petroleum ether. The precipitated sulfonated product was removed by filtration, extracted thoroughly with distilled water, and dried under a vacuum at room temperature.

All values of the sulfonation degrees were based on the sulfur content obtained by elemental analysis. A sulfonation degree of 100% means that all aromatic rings in the PPO bear one sulfonic acid group.

Medium-Degree Sulfonation of PPO

Chlorosulfonic acid in chloroform (5% solution) was slowly added with stirring to a 3% PPO chloroform solution at 25°C until the SPPO precipitated from the solution. The precipitate was dissolved in methanol, and a powdery product was obtained from the solution using a spray drier (Buechi 190). The degree of sulfonation of the products was 60–76%.

High-Degree Sulfonation of PPO

Sulfur trioxide (8.0 g) in 5% 1,2-dichloroethane solution was slowly added to the equimolar amount of PPO suspended in 1,2-dichloroethane (12.0 g in 200 mL). The reaction mixture was stirred for 4 h and the product was filtered off, washed with 1,2-dichloroethane, and dried in a flow of dry nitrogen at room temperature. The sulfonated polymer was immediately used for the preparation of membranes, because it undergoes crosslinking within several days and becomes unstable. The degree of sulfonation of the product was 99%.

Membrane Preparation

The membranes were prepared from solutions containing Udel-type PSf (nominal MW 75,000, Janssen Chimica), SPPO, and NMP. The solutions were cast on a nonwoven textile as a 0.35 mm thick film, and after 30 s the films were immersed into a water precipitation bath.

Membrane Characterization

The morphology of the prepared membranes was investigated using a Jeol 6400 F microscope for scanning electron microscopy (SEM). The membranes dried in air were immersed into liquid

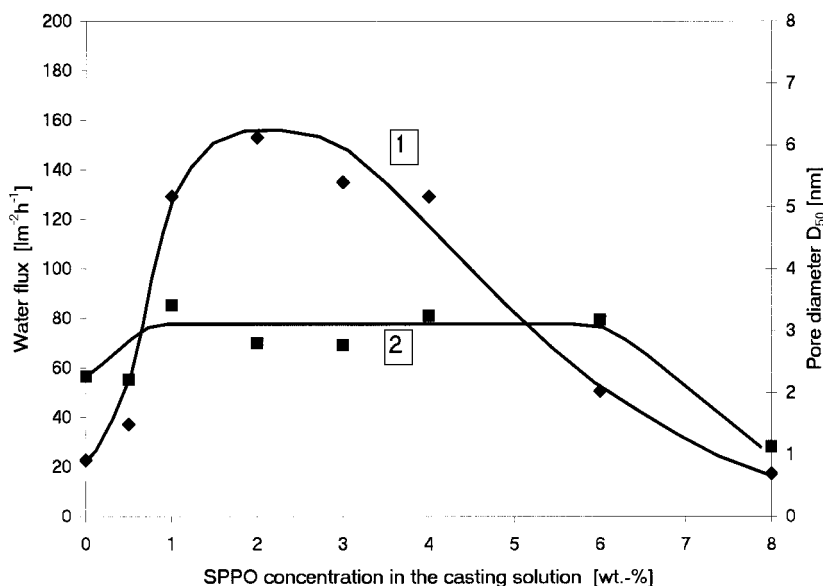


Figure 1 The dependence of the water flux at 0.05 MPa (curve 1) and the average pore diameter D_{50} (curve 2) on the SPPO (60% degree of sulfonation) concentration in the casting solution (20 wt % PSf concentration in the casting solution).

nitrogen, broken, placed onto a metal holder, and coated with a gold/palladium layer (80/20) by sputtering under a vacuum.

Atomic force microscopy (AFM) micrographs were obtained with a multimode AFM Nanoscope IIIa (Digital Instruments). Silicon microcantilevers (OTESPA-70) with a resonance frequency of about 270 kHz were used for the tapping mode. The amplitude of the free oscillations was kept at 2 V, and the amplitude of set-point oscillations was about 1.1 V. The scan size was 350×350 nm. The contrast covered 20 nm in height and was 40° in phase. The micrographs were obtained with membranes dried in air.

The permeabilities and rejections of the prepared membranes were determined at 0.05 MPa in a stirred ultrafiltration cell (type 8010, Amicon). The ultrafiltration experiments were carried out first with distilled water, then with a single solution of a test mixture (0.1 wt % aqueous solution of a dextran mixture with 650–215,000 MW). The molecular size distribution of dextrans in the permeates, retentates, and original solutions was determined by gel-permeation chromatography (GPC). From the GPC results, the average pore diameter (D_{50}), maximum pore diameter (D_{100}), and corresponding molecular weights were calculated assuming a logarithmic normal distribution of the pore size.¹⁵ The pore density and porosity were calculated from the average pore diameter

and the water permeability by the Sampson equation.¹⁶

The oriented concentration potentials were determined in a cell made of organic glass and consisting of two independently thermostatted compartments. A pair of saturated calomel electrodes and a digital voltmeter with high input impedance was used for the potential measurements. Solutions in contact with the membranes were 1.0/0.01M in KCl. The orientation with the skin toward the more concentrated solution was denoted as positive (+) and vice versa. The procedure is described in detail in the literature.^{17–19}

RESULTS AND DISCUSSION

The effect of the addition of SPPO (60% degree of sulfonation) to the PSf casting solution is shown in Figure 1. Curve 1 shows that the addition of a relatively small amount of SPPO (1–4 wt % relative to the casting solution) considerably increased the permeability of the resulting membranes to water. On the other hand, the addition of a higher amount of SPPO (more than about 4 wt %) had the opposite effect, probably as a consequence of the increased total casting solution concentration. The pore size of the prepared membranes was only slightly influenced by the

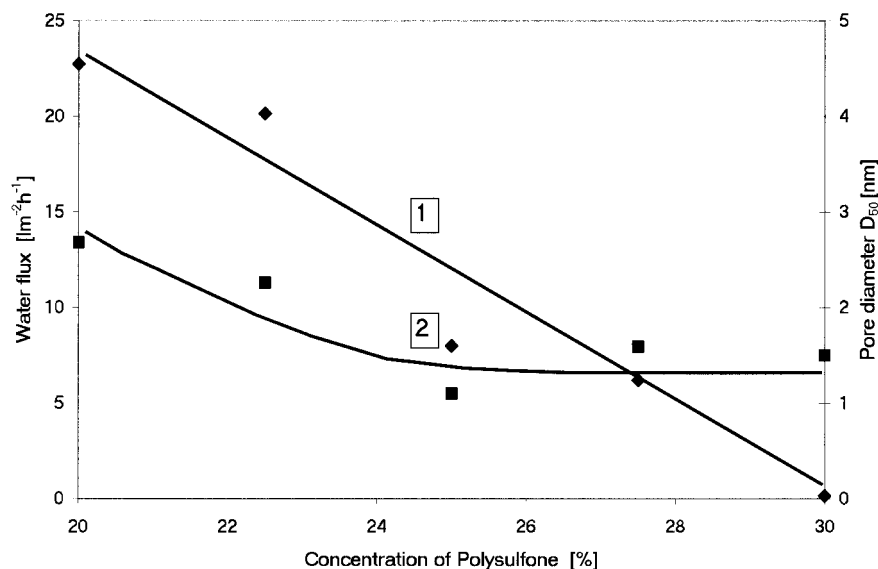


Figure 2 The dependence of the water flux at 0.05 MPa (curve 1) and the average pore diameter D_{50} (curve 2) on the PSf concentration in the casting solution.

addition of SPPO to the casting solution (Fig. 1, curve 2).

To see the difference between the influence of the total polymer concentration in the casting solution and the influence of SPPO, the same dependences are depicted in Figure 2 as in Figure 1. However, an increase in the polymer concentration in the casting solution was brought about by an increase in the PSf concentration, not by the addition of SPPO. The addition of further PSf to the PSf casting solution caused the water fluxes and average pore diameters of the resulting membranes to decrease, which was in contrast to the effects of the SPPO addition.

Figure 3 presents SEM micrographs of cross sections of PSf/SPPO membranes. The membranes are the same as those in Figure 1, which were prepared from a 20 wt % PSf solution without SPPO [Fig. 3(a)] or with 1, 4, or 8 wt % of SPPO [Fig. 3(b–d)]. The membranes with 0 or 8 wt % [Fig. 3(a,d)] of SPPO had very low water fluxes, and the membranes with 1 or 4 wt % of SPPO [Fig. 3(b,c)] exhibited very high water fluxes (Fig. 1). It can be seen on the micrographs that all membranes had an asymmetrical skinned structure and that an increasing concentration of SPPO caused a finger structure to become less pronounced and a spongy structure to form between the primary coagulation layer and the substructure. Figure 3(c,d) shows that small beads appeared in the pores of membranes containing higher amounts of SPPO.

These beads were probably SPPO particles excluded from the PSf matrix. Both PSf and SPPO are separately soluble in NMP, but phase separation may occur after mixing both polymer solutions. In the casting solutions used for the preparation of membranes from Figures 1 and 3, distinct phase separation occurred if the concentrations of PSf, SPPO (60% degree of sulfonation), and NMP in the casting mixture were about 20, 8, and 72 wt %, respectively, or if the concentrations in the mixture increased during the phase inversion. On the other hand, if the concentration of SPPO was low, both polymers were miscible in NMP. The role of SPPO in the casting solution in membrane formation was then similar to that of PVP.^{11–14} In this case, after immersion of the cast film into a water bath, the solution separated into two phases: one phase predominantly consisted of PSf, NMP, and water while the other consisted of SPPO, NMP, and water. Mutual diffusion of the two polymers was however a very slow process compared with the diffusion of small molecules like NMP and water. Vitrification of the resulting membrane therefore occurred before all SPPO could diffuse out of the PSf matrix phase and some SPPO molecules remained trapped in the PSf matrix, especially in the primary coagulation layer and at the surface of pores of the resulting membrane. These entrapped molecules made the membrane more hydrophilic and caused an increase in the water flux of the blended membranes. The presence of en-

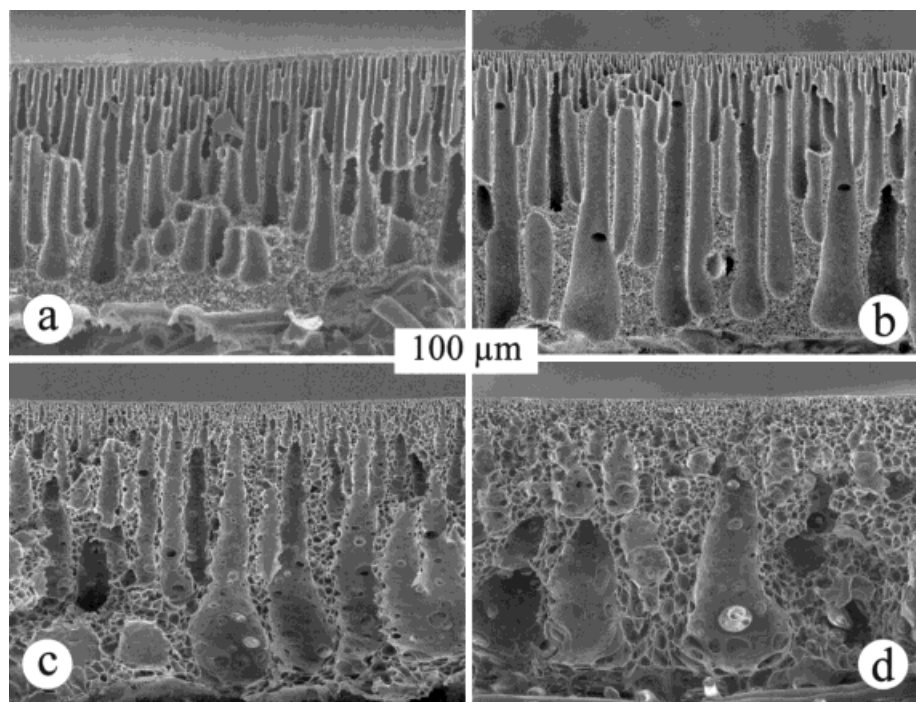


Figure 3 SEM micrographs of cross sections of membranes prepared from 20 wt % PSf solution in NMP containing (a) 0, (b) 1, (c) 4, and (d) 8 wt % SPPO (60% degree of sulfonation).

trapped SPPO molecules near the membrane surface and on the pore surface can be confirmed by concentration potential measurements.

The concentration potential (E_c) can be observed and measured on every electrically charged permselective membrane in contact with two differently concentrated solutions of the same electrolyte.^{17–19} The value of E_c depends only on the concentrations of the solutions adjacent to the membrane and on the molality of the fixed ions in the membrane. The values of the fixed ions in the membrane are, of course, directly proportional to the concentration of fixed ions in the membrane polymer and (using microporous membranes) inversely proportional to the membrane porosity. If the membrane is isotropic, charged sites are distributed homogeneously in the membrane cross section and the value of E_c is independent of orientation of the membrane toward the solutions. If, however, the membrane is anisotropic (e.g., skinned), the values of E_c depend on the membrane orientation: a higher E_c is observed if the porous sublayer is in contact with the more concentrated solution.

Figure 4 shows that the E_c values depended on the concentration of SPPO in the membrane casting solution and on the relative porosity of the skin layer. It can be seen that

1. membranes of pure PSf have both absolute values of E_c higher than zero, although not significantly, which means that the membrane bears a very small charge;
2. all E_c values are orientation dependent (Fig. 4, curves 1 and 2 are different), which proves the asymmetric structure of the prepared membranes; and
3. membranes prepared from the casting solutions that also contain a sulfonated polymer exhibit higher values of E_c than the membrane of neat PSf, although their porosity is much higher. Therefore, at least a part of the SO_3^- groups of SPPO are at or near the surface of the membrane pores, where they can influence the values of the concentration potential and other membrane properties.

The dependence of the water permeability and medium pore size on the concentration of PSf (the main matrix polymer) in the casting solution is shown in Figure 5. The concentration of SPPO (with 60% sulfonation degree) was kept constant at 4 wt %. It can be seen that with the increasing concentration of the matrix polymer in the casting solution, the water permeability and medium

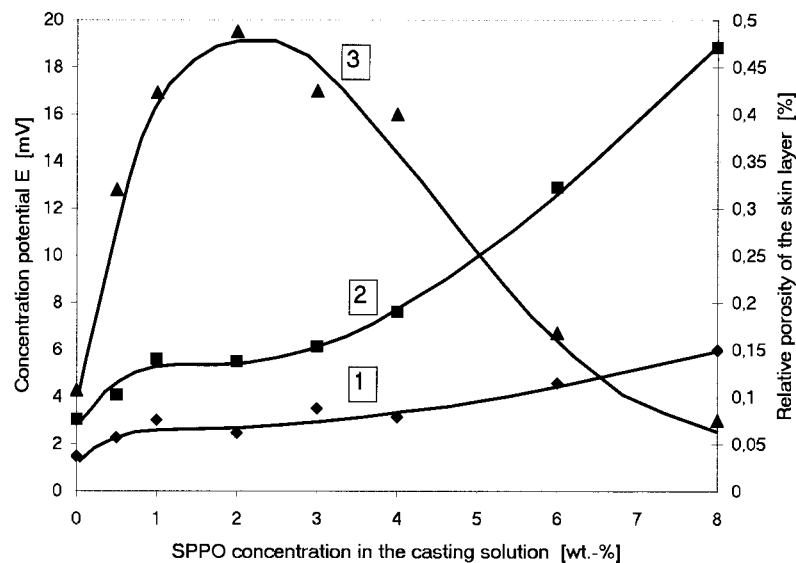


Figure 4 The dependence of the oriented concentration potentials E (♦, curve 1; ■, curve 2) and relative porosity of the skin layer (curve 3) on the SPPO (60% degree of sulfonation) concentration in the casting solution (always 20 wt % PSf concentration in the casting solution).

pore size decreased, as was nearly always observed with the phase inversion membranes.

Figure 6 demonstrates the dependence of the water flux on the degree of sulfonation of SPPO added to the casting solution. The concentration of PSf (20 wt %) and that of SPPO (2 wt %) were kept constant. No membranes could be prepared with SPPO with a degree of sulfonation lower than about 10%; as such, SPPO was not soluble in

NMP at room temperature. The highest water flux was exhibited by membranes prepared from solutions to which SPPO with a degree of sulfonation of about 20–40% was added. Such a SPPO was soluble in NMP but insoluble in water. Samples of SPPO with a degree of sulfonation higher than about 85% were water soluble. Membranes prepared from casting solutions containing highly sulfonated SPPO exhibited very low permeability.

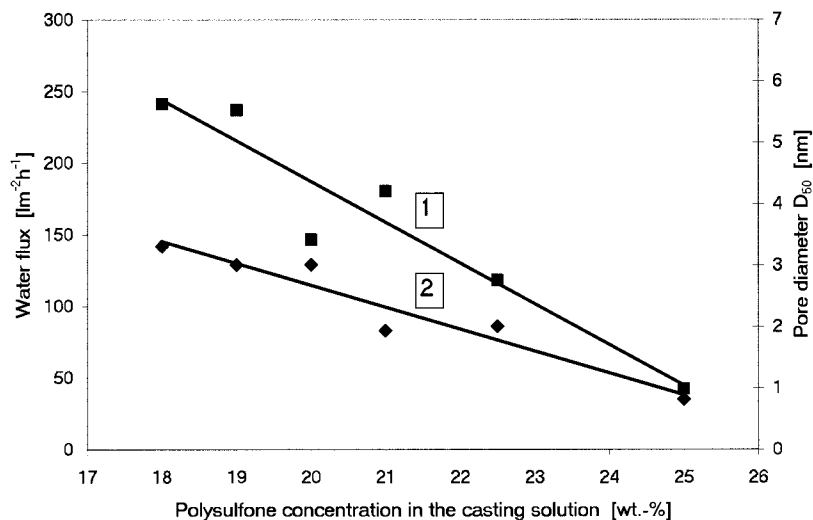


Figure 5 The dependence of the water flux at 0.05 MPa (curve 1) and the average pore diameter D_{50} (curve 2) on the PSf concentration in the casting solution. (4 wt % concentration of SPPO with a 60% degree of sulfonation in the casting solution).

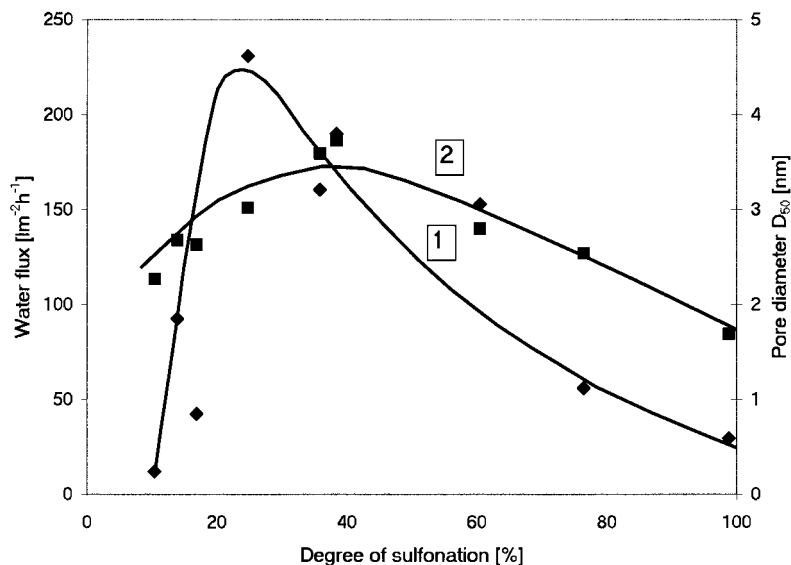


Figure 6 The dependence of the water flux at 0.05 MPa (curve 1) and the average pore diameter D_{50} (curve 2) on the degree of sulfonation of SPPO. All membranes were prepared from solutions containing 20 wt % PSf and 2 wt % SPPO.

ties to water, which was virtually the same as the membranes prepared from solutions containing no SPPO. The values of the concentration potentials of membranes prepared from casting solutions containing highly sulfonated SPPO were also virtually the same as those of membranes prepared from solutions containing no SPPO. It is highly probable that, after immersion of a cast film into a water bath, all highly sulfonated SPPO from the casting solution was transferred into the water and had no effect on the properties of the resulting membranes.

Figure 7 presents SEM micrographs of membranes prepared by the addition of 2 wt % SPPO with different sulfonation degrees to the PSf solution. The degree of sulfonation increases in the series in Figure 7(a–f). It can be seen that the membranes prepared from solutions containing more sulfonated SPPO had a more pronounced finger structure [Fig. 7(e,f)] while a highly porous spongy structure formed beneath the primary coagulation layer was observed in the membranes prepared from solutions containing less sulfonated SPPO [in particular, Fig. 7(a,b)]. The difference in membrane morphology was evidently brought about by the SPPO compatibility with PSf and its affinity to water. Highly sulfonated PPO (99% degree of sulfonation) is rather incompatible with PSf (its casting solutions with PSf in NMP were turbid) and it is well soluble in water. In this case, the SPPO blend component could not

act as a structure-influencing agent. During coagulation, a typical PSf structure was generated and the resulting membrane was not very permeable (cf. Fig. 6). On the other hand, at a low degree of sulfonation of SPPO, both polymers were more compatible (it is possible to prepare clear solutions of PSf in NMP containing high concentrations of SPPO) and SPPO was insoluble in coagulation water. In this case, SPPO was precipitated into the membrane matrix and new membrane morphologies were observed, which were different from typical PSf structures.

Detailed AFM images of the skin side of dried membranes prepared from 20 wt % PSf solutions containing no SPPO and 4 wt % SPPO are shown in Figures 8 and 9, respectively. The height images had a rather corrugated surface. Additional details could be seen on the phase images that distinguished two different materials: brighter areas were polymers while dark spots corresponded to air in the valleys as follows from the coincidence with the height images. The valleys must have been deep (note that the phase difference of oscillations was more than 40°) and they probably cohered with pores in the skin, also because their size (up to about 12 nm) roughly corresponded to the maximum pore size calculated from water and dextran permeation data. In Figure 9 (and also in the images of similar membranes, not shown here) it is not possible to distinguish both the polymers, PSf and SPPO.

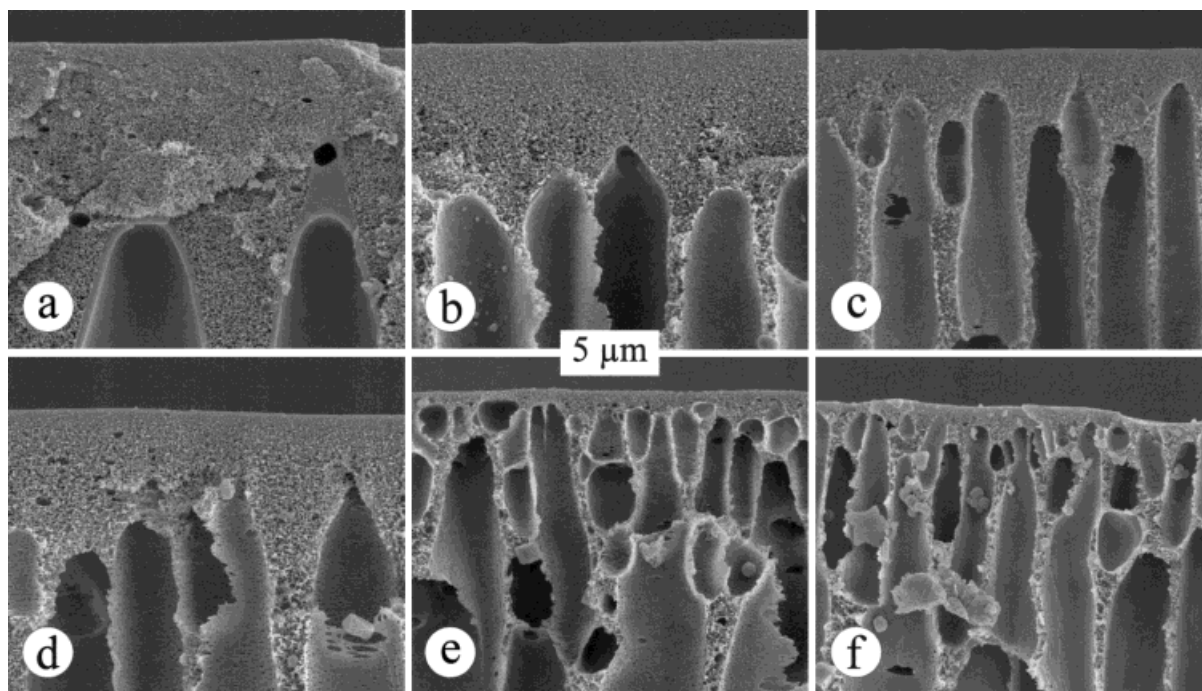
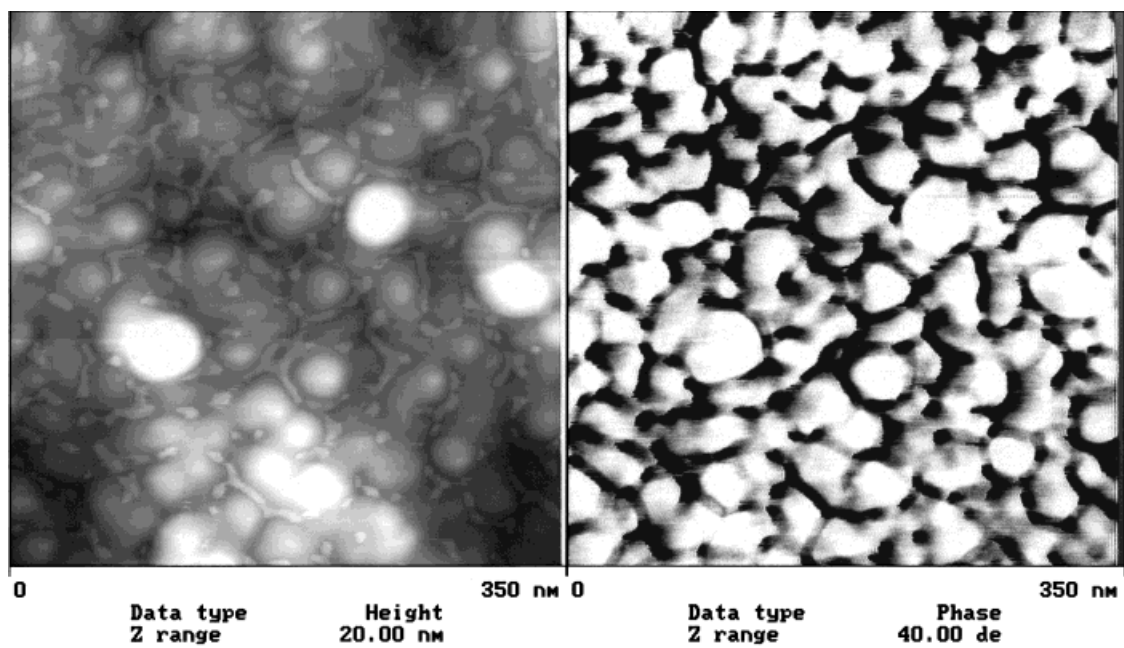


Figure 7 SEM micrographs of cross sections of membranes prepared from solutions containing 20 wt % PSf and 2 wt % SPPO with degrees of sulfonation of (a) 10, (b) 17, (c) 36, (d) 60, (e) 76, and (f) 99%.



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Figure 8 AFM height and phase images of the skin surface of a membrane prepared from a 20 wt % PSf solution (with no SPPO).

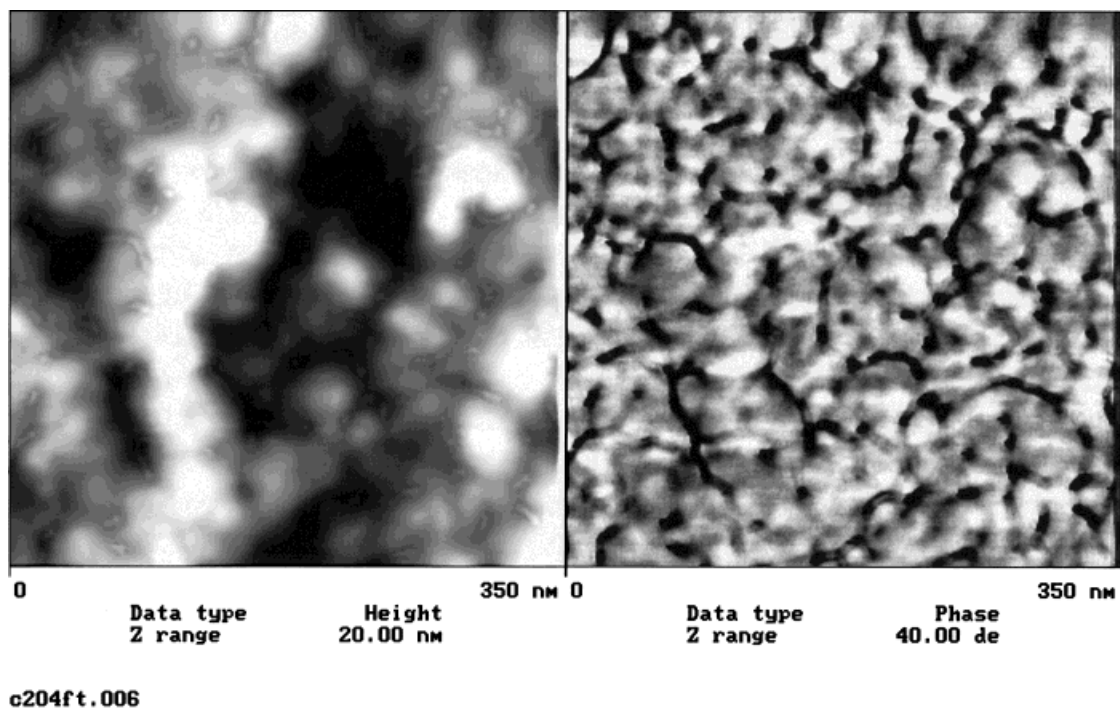


Figure 9 AFM height and phase images of the skin surface of a dried membrane prepared from a solution containing 20 wt % PSf and 4 wt % SPPO with a degree of sulfonation of 60%.

CONCLUSIONS

Polysulfone microporous membranes, which are highly permeable to water, can be prepared if the casting solution contains, in addition to PSf, a small amount of SPPO with a degree of sulfonation in the range of about 20–40%. The presence of negative surface charges in such membranes was proved by determinations of the oriented concentration potentials.

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REFERENCES

- Cabasso, I.; Klein, E.; Smith, J. K. *J Appl Polym Sci* 1976, 20, 2377.
- Cabasso, I.; Klein, E.; Smith, J. K. *J Appl Polym Sci* 1977, 21, 165.
- Tweddle, T. A.; Kutowy, O.; Thayer, W. L.; Sourirajan, S. *Ind Eng Chem Prod Res Dev* 1983, 22, 320.
- Munari, S.; Bottino, A.; Capannelli, G.; Moretti, P.; Petit Bon, P. *Desalination* 1988, 70, 265.
- Munari, S.; Bottino, A.; Camera Roda, G.; Capannelli, G. *Desalination* 1990, 77, 85.
- Machado, P. S. T.; Habert, A. C.; Borges, C. P. *J Membr Sci* 1999, 155, 171.
- Kim, J.-H.; Lee, K.-H. *J Membr Sci* 1998, 138, 153.
- Pozniak, G.; Bryjak, M.; Trochimczuk, W. *Angew Makromol Chem* 1995, 233, 23.
- Chen, M.-H.; Chiao, T.-C.; Tseng, T.-W. *J Appl Polym Sci* 1996, 61, 1205.
- Lau, W. W. Y.; Jiang, Y. *Polym Int* 1994, 33, 413.
- Boom, R. M.; van den Boomgaard, T.; Smolders, C. A. *J Membr Sci* 1994, 90, 231.
- Boom, R. M.; van den Boomgaard, T.; Smolders, C. A. *Macromolecules* 1994, 27, 2034.
- Boom, R. M.; Reinders, H. W.; Rolevink, H. H. W.; van den Boomgaard, T.; Smolders, C. A. *Macromolecules* 1994, 27, 2041.
- Wienk, I. M.; Boom, R. M.; Beerlage, M. A. M.; Bulte, A. M. W.; Smolders, C. A.; Strathmann, H. *J Membr Sci* 1996, 113, 361.
- Weigel, T.; Makschin, W.; Albrecht, W.; Groebe, V.; Paul, D. *Acta Polym* 1991, 42, 366.
- Velicangil, O.; Howell, J. A. *J Phys Chem* 1980, 84, 2298.
- Kúdela, V.; Richau, K.; Schwarz, H.-H.; Paul, D. *Collect Czech Chem Commun* 1992, 57, 2145.
- Schwarz, H.-H.; Richau, K. *J Membr Sci* 1989, 43, 39.
- Richau, K.; Bleha, M.; Paul, D. *Sep Purif Technol*, submitted.