Preparation and Performance Testing of Sulfonated Poly(phenylene oxide) Based Composite Membranes for Nanofiltration

Nobuhiro Nogami,[1] Geeta Chowdhury,[2] T. Matsuura[2]

[1]Daito Kasei Kogyo Co., Osaka, Japan
[2]Industrial Membrane Research Institute, Department of Chemical Engineering, University of Ottawa, 161 Louis Pasteur, Ottawa, Ontario K1N 6N5, Canada

ABSTRACT: Sulfonated brominated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPOBr) was synthesized by a sequence of bromination and sulfonation. A thin film of SPPOBr was coated on top of a commercial poly(ether sulfone) membrane. Pure butoxyethanol (BE) solvent or a BE/isopropyl alcohol (IPA) solvent mixture was used to dissolve SPPOBr in the coating process. The thin film composite membranes so prepared were then tested for the separation of carbohydrate and electrolyte solutes. We found that the flux and the carbohydrate separation both increased significantly with increasing IPA content in the solvent mixture. However, the separation of electrolyte solutes did not change significantly. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2624–2628, 2004

Key words: membranes; poly(phenylene oxide); separation techniques

INTRODUCTION

A promising membrane material for reverse osmosis (RO) and nanofiltration applications is sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO).[1] Membranes prepared from SPPO possess a number of advantages compared to other commercially available membranes with electric charges. Since the 1970s, it has been known that SPPO can be cast into thin films with excellent chemical and physical stabilities and good water-flux and solute-rejection characteristics. Asymmetric membranes prepared from SPPO were initially developed for the RO treatment of brackish water by General Electric Co.[2] Their works on the development of SPPO thin film composite (TFC) membranes were summarized by LaConti.[1] In the middle of the 1980s, interest in SPPO material was rekindled when SPPO membranes were studied by a group at the University of Waterloo. They studied the kinetics involved in the sulfonation of poly(phenylene oxide) (PPO),[3] the effect of porous substrate membranes used for the preparation of TFC membranes, and the effect of ion-exchange capacity (IEC) on the performance of TFC membranes.[4] Agarwal and Huang studied the effect of the solvent used for thin-layer coating and the effect of the chemical modification of the surface.[5,6]

Kubota and Yanase observed improved solute separation (f) with 2-butoxyethanol (BE) as a solvent for SPPO coating.[7] Recently, the effects of the substrate membrane and solvent were reinvestigated at the University of Ottawa.[8–10] The effect of the annealing of the TFC membranes on their nanofiltration performance was also investigated.[11] These efforts led to improvements in the performance of SPPO membranes for nanofiltration applications. The optimal results obtained were an NaCl separation of 87.8% with a product permeation flux of 59.8 L/m^2 h at 1034 kPa gauge (150 psig) when the NaCl concentration was 500 ppm. The effect of the ion exchange of SPPO membranes from their hydrogen form was also studied.[12] SPPO membranes were further characterized by their pore sizes and pore size distributions[13] and tested for application in the treatment of wastewater from the pulp and paper industry.[14]

SPPO is also known to be an excellent material for gas separation.[15] In an attempt to improve the permeability and permselectivity of the material, SPPO was brominated to sulfonated brominated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPOBr).[16] TFC hollow-fiber membranes and membrane modules were prepared and tested. In RO and nanofiltration applications, the incorporation of bromine molecules into the polymer backbone led to a flux increase because of the expansion of the polymer networks by bulky bromine molecules. However, unlike an increase in the degree of sulfonation, which also led to polymer network expansion because of a higher degree of swelling by

TABLE I
Ultrafiltration Performance of the HO51 Substrate Membrane

PEG molecular weight	Separation (%)	PWP (L/m² h)	PR (L/m² h)
2,000	54.9	122.1	135.3
4,000	64.4	141.2	138.3
6,000	79.5	141.2	135.3
8,000	90.0	144.2	126.5
10,000	95.2	130.9	117.7

PEG concentration-200 ppm; operating pressure-345 kPa gauge (50 psig).

water molecules, bromination did not make SPPO material unstable in an aqueous environment. Thus, a higher stability of material is expected from SPPOBr compared with SPPO.

The objective of this study was to prepare TFC membranes with SPPOBr and test their performance for nanofiltration applications.

EXPERIMENTAL

Material

The poly(ether sulfone) ultrafiltration membrane was HO51 supplied by Osmonics Co. (Minetonka, MN).

Synthesis of the polymer

SPPO

We carried out the sulfonation of PPO with a weight-average molecular weight (M_w) of 45,000 by following a procedure mentioned elsewhere.[2] A slight modification was made to the sulfonation procedure for the reaction with PPO with M_w's of 310,000 and 370,000. Only a 2.0% (w/v) solution of PPO was reacted with a stoichiometric amount of chlorosulfonic acid instead of 10.0% (w/v) as mentioned in the literature. This procedure was followed to compensate for the high viscosities involved in these solutions and to enhance the uniform sulfonation of the polymer. Nitrogen gas was also purged through the system to facilitate fast removal of HCl vapor, which was formed as a byproduct. The IEC values of sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) in hydrogen form (SPPO-H), as determined by acid–base titration, were 1.99 and 2.3 mequiv/g of dry polymer. We prepared sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) containing Na$^+$ ion (SPPO-Na) by equilibrating SPPO-H in a 1N aqueous sodium hydroxide solution. We removed the excess caustic by thoroughly washing the polymer in distilled water.

SPPOBr

For the preparation of SPPOBr, PPO was first brominated and then sulfonated. We achieved bromination

of the aromatic ring at room temperature by following a general procedure described by White.[17] Modified PPO with a 20% bromine substitution was prepared. The degree of substitution was determined by ^{1}H-NMR analysis. Gel permeation chromatography of PPOBr indicated that there was no decrease in the molecular weight of PPO during the bromination of the polymer. The general procedure for the sulfonation of PPOBr was the same as described previously. The amount of chlorosulfonic acid required for the reaction was based on the amount of unreacted repeat units in the PPOBr molecules. For example, 5 g of PPOBr with a 20% substitution of aromatic rings had 4 g of unbrominated repeat units in the PPOBr molecules. Therefore, the amount of the acid required for the reaction was calculated on the basis of 4 g of polymer. The IEC value was determined by titration, and it was 1.80 mequiv/g of dry polymer.

Preparation of TFC membranes

SPPO or SPPOBr was dissolved in BE solvent or BE/ isopropyl alcohol (IPA) (70/30, 60/40, 50/50, or 40:60) mixtures to the polymer concentration of 0.12 wt %. The skin side of the substrate UF membranes was coated by dip-coating with the dilute SPPO or SPPOBr solutions prepared previously. The membranes were then dried at 60°C for 24 h in an oven.

Determination of pore size distribution

A plot of f (%) versus solute diameter (d_s) on a log-normal probability paper yields a straight line if f correlates with d_s by the log-normal probability function defined by

$$F = erf(z) = \frac{1}{\sqrt{2}} \int_{-\infty}^{Z} e - \frac{u^2}{2} du$$
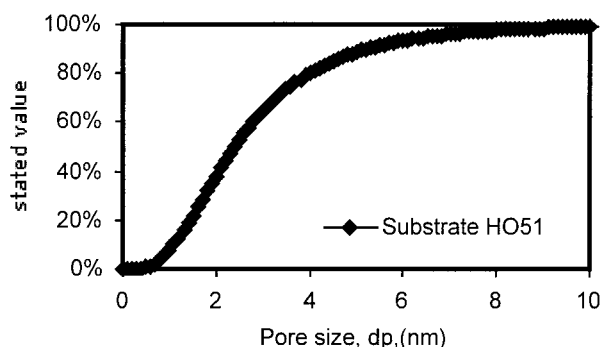
where

Figure 1 Cumulative pore size distribution for the HO51 substrate membrane.

TABLE II
**Characterization of SPPO-Na Composite Membranes Based on SPPO-Na Polymers
with Different IEC Values**

Membrane	Solvent	MWCO (kDa)	Mean pore size (nm)	Standard deviation
IEC value of SPPO-Na-1.99 mequiv/g of polymer				
1	BE	2.0	0.85	2.18
2	BE/IPA (60/40)	2.0	0.80	1.18
IEC value of SPPO-Na-2.3 mequiv/g of polymer				
3	BE	2.0	0.91	2.31
4	BE/IPA (60/40)	6.0	1.50	2.13

$$z = \frac{\ln d_s - \ln \mu_s}{in\ \sigma_g}$$

where μ_s is the diameter of the solute corresponding to $f = 50\%$ on the log-normal plot and is taken as the mean solute diameter and σ_g is the geometric standard deviation about the mean diameter. σ_g can be determined as the ratio of d_s at $f = 84.13$ and 50% on the log-normal plot. If the dependence of f on the steric and hydrodynamic interaction between the solute and the pore is ignored, the mean pore size of the membrane and the geometric standard deviation about the mean pore size can be considered the same as the solute mean size and the solute standard deviation. The cumulative pore size distribution can then be drawn from μ_s and σ_g so obtained.

The Stokes radii of poly(ethylene glycol) (PEG) solutes of known molecular weights were calculated with the following equation:

$$a = 16.73 \times 10^{-10} M^{0.557}$$

The d_s values used in the log-normal plot were based on the Stokes radius.

Ultrafiltration and RO experiments

Ultrafiltration experiments were conducted for the commercial ultrafiltration membranes with laborato-ry-made test cells, each with an effective area of 13.2 cm² and the details of which were described elsewhere.[18] Six cells were connected in a series. All of the experiments were conducted at room temperature and at 345 kPa gauge (50 psig). Each membrane was compacted at 551 kPa gauge (80 psig) for 4 h before any measurement was conducted. The concentration of feed PEG solutes (molecular weight = 1000–10,000) was 200 ppm. PEG concentrations in the feed and in the permeate were measured in terms of total organic carbon (TOC) with a TOC analyzer (DC-190, Folio Instruments).

RO experiments were carried out for the SPPO and SPPOBr composite membranes at an operating pressure of 1034 kPa gauge (150 psig) and at room temperature. The experiments were carried out with feed PEG solutes (concentration = 200 ppm) to characterize the membranes. Also, RO experiments were carried out with the two electrolyte solutes, NaCl and MgSO₄, and several carbohydrates. The solute concentrations were 8.6 and 12.5 mmol/L (500 and 1500 ppm) for NaCl and MgSO₄, respectively, and 100 ppm for carbohydrate solutes. For each experiment, the pure water permeation rate (PWP), product permeation rate (PR), and f, defined as

Solute separation = (feed concentration

− permeate concentration)/(feed concentration)

TABLE III
Results from RO Experiments with Electrolyte Solutes

Membrane	Solvent	PWP (L/m² h)	PR (L/m² h)[a]	f (%) NaCl	f (%) MgSO₄
IEC value of SPPO-Na-1.99 mequiv/g of polymer					
1	BE	26.1	27.2	72.3	58.9
2	BE/IPA (60/40)	57.4	65.9	73.0	59.9
IEC value of SPPO-Na-2.3 mequiv/g of polymer					
3	BE	53.5	64.7	69.2	53.9
4	BE/IPA (60/40)	97.9	116.5	64.2	—

* Solute concentration of NaCl-500 ppm and MgSO₄-1500 ppm; operating pressure-1035 kPa gauge (150 psig).
[a] Average of PR data from the experiments with NaCl and MgSO₄.

TABLE IV
Characterization of TFC Membranes Based on SPPOBr-Na (IEC Value-1.8 mequiv/g) TFC Membranes

Membrane	Solvent	MWCO (kDa)	Mean pore size (nm)	Standard deviation
5	BE	2.0	0.84	1.27
6	BE/IPA (70/30)	2.0	0.91	1.17
7	BE/IPA (60/40)	1.0	0.66	1.53
8	BE/IPA (40/60)	1.0	0.77	1.33

TABLE V
RO Separation of Carbohydrates by the SPPOBr-Na (IEC Value-1.8 mequiv/g) TFC Membranes

Membrane	Solvent	f (%)		
		Glucose	Sucrose	Raffinose
5	BE	35.6	68.1	84.0
6	BE/IPA (70/30)	38.2	65.5	84.8
7	BE/IPA (60/40)	43.3	81.3	97.0
8	BE/IPA (40/60)	61.1	92.3	96.5

Solute concentration-100 ppm; operating pressure-1035 kPa gauge (150 psig).

were obtained. The concentration of the electrolyte was determined conductmetrically.

The concentrations of the carbohydrate solutes were determined by the total carbon analyzer.

RESULTS AND DISCUSSION

Pore size distribution of the substrate membrane

The data from the ultrafiltration experiments with the HO51 substrate membrane are given in Table I. From the data, MWCO was 8000 Da. The cumulative pore size distribution determined by the method described in the theoretical section is given in Figure 1. As shown in Figure 1, the mean pore size (diameter) was 2.4 nm with a standard deviation of 1.83.

Effect of the solvents used for coating thin SPPO-Na films

Some RO data for the composite membranes prepared from SPPO-Na polymer are given in Tables II and III.

Table II indicates that MWCO decreased from 8 kDa for the substrate membrane to 2–6 k Da by the coating of a thin SPPO-Na layer. The mean pore size decreased from 2.4 to 0.8–1.5 nm, accordingly.

When membranes 1 and 2 (IEC value = 1.99 mequiv/g of polymer) in Table III are compared, for almost identical f values (NaCl = 72–73% and MgSO$_4$ ≈ 60%), the membrane flux more than doubled when a solvent mixture BE/IPA (60/40) was used. This indicates the importance of the choice of solvent in membrane coating. Similar results were obtained earlier.[9] The pore size of the substrate membrane, when it was in contact with a solvent, depended on the degree of swelling that was caused by the solvent.[12]

When membranes 3 and 4 (IEC = 2.3 mequiv/g of polymer) are compared, the membrane prepared with the solvent mixture exhibited a flux almost twice as high as that of the membrane prepared with a single solvent, reflecting an increase in the mean pore size from 0.91 to 1.50 nm. The separations for the electrolyte solutes were, however, only slightly lowered. The electrostatic repulsive force working between the ions and the charged membrane surface offset the effect of the increase in the pore size.

In general, TFC membranes made of SPPO-Na of the higher IEC value (membranes 3 and 4) exhibited lower electrolyte separations and higher fluxes than membranes of the lower IEC value (membranes 1 and 2). This was most likely because of the higher degree of swelling for the higher IEC value. Also, NaCl separation was higher than MgSO$_4$ separation. The separation of NaCl relative to that of MgSO$_4$ is known to be dependent on the conditions of membrane preparation and the concentrations of the electrolytes in the feed solution.[19]

Some RO data of the composite SPPOBr-Na membranes are given in Tables IV–VI.

MWCO, mean pore size, and standard deviation for SPPOBr-Na TFC membranes are given in Table IV. MWCO and the mean pore size tended to decrease as the IPA content increased in the solvent mixture. The reduction in the pore size was reflected further in an increase in the separation of carbohydrate solutes such as glucose, sucrose, and raffinose, which do not carry any electric charges (Table V). Thus, the separation of the latter solutes tended to increase with increasing IPA content in the solvent mixture. Hence, the use of solvent mixtures with higher IPA contents was desirable to obtain SPPOBr membranes with a high flux and high separations for carbohydrate solutes. The SPPOBr membranes were tested further for the separation of electrolyte solutes such as NaCl and MgSO$_4$. The results are given in Table VI. Interestingly, PWP increased from 12 to 24% with BE/IPA solvent mix-

TABLE VI
Results from RO Experiments with Electrolyte Solutes

Membrane	Solvent	PWP (L/m^2 h)	PR (L/m^2 h)[a]	f (%)	
				NaCl	MgSO$_4$
5	BE	35.9	48.0	80.6	70.2
6	BE/IPA (70/30)	51.1	60.3	—	66.7
7	BE/IPA (60/40)	44.6	52.8	80.2	68.2
8	BE/IPA (40/60)	45.6	53.9	77.5	69.1

Solute concentrations of NaCl-500 ppm and MgSO$_4$-1500 ppm; operating pressure-1035 kPa gauge (150 psig).
[a] Average of the experiments with NaCl and MgSO$_4$

tures compared with pure BE solvent. It was rather surprising because the pore size decreased with the addition of IPA. The product rates were greater than PWP, as in the case of SPPO-Na membranes. Similar results were obtained earlier[12] and interpreted as the hydration of metal cations in the membrane phase. The separations of both NaCl and MgSO$_4$ solutes tended to decrease, despite the decrease in pore size, with increasing IPA content. However, the change was marginal and within experimental error. This confirms the conclusion obtained earlier that the effect of the pore size on the separation of electrolytes was much less than that on the nonelectrolyte solutes such as poly(ethylene glycol) and carbohydrates.

One can compare TFC membranes based on the SPPO-Na material with those based on the SPPOBr-Na material by comparing the data in Tables II and IV and those in Tables III and VI. Generally, MWCO and pore sizes were in the same range for both SPPO-Na and SPPOBr-Na membranes. However, the electrolyte separations by SPPO-Na membranes were much lower than those obtained by the SPPOBr-Na membranes.

CONCLUSIONS

From the experimental results, we drew the following conclusions:

1. The flux of the SPPO-Na TFC membranes almost doubled with a solvent mixture (BE/IPA) for the coating of a thin layer. The separations for the electrolyte solutes were, however, only slightly lowered.
2. TFC membranes made of SPPO-Na of a higher IEC value exhibited lower electrolyte separations and higher fluxes than membranes of a lower IEC value.
3. As for the SPPOBr-Na membranes, the flux increase was also observed when BE/IPA solvent mixtures were used compared with pure BE solvent. The separations of carbohydrate solutes increased with increasing IPA content in the solvent mixture. However, the separations of the

electrolyte solutes did not change significantly with the change in the IPA content.
4. When the SPPO-Na and SPPOBr-Na TFC membranes were compared, the separations of electrolyte solutes were higher for the latter membranes.

References

1. LaConti, A. B. In Reverse Osmosis and Synthetic Membranes; Sourirajan, S., Ed.; National Research Council of Canada: Ottawa, Canada, 1977; p 211.
2. Plummer, C. W.; Kimura, G.; LaConti, A. B. Development of Sulfonated Polyphenylene Oxide Membrane for Reverse Osmosis; Research and Progress Report No. 551; Office of Saline Water, United States Department of Interior: 1970.
3. Huang, R. Y. M.; Kim, J. J. J Appl Polym Sci 1984, 29, 4017.
4. Huang, R. Y. M.; Kim, J. J. J Appl Polym Sci 1984, 29, 4029.
5. Agarwal, A. K.; Huang, R. Y. M. Angew Makromol Chem 1988, 163, 15.
6. Agarwal, A. K.; Huang, R. Y. M. Angew Makromol Chem 1988, 163, 1.
7. Jpn. Pat. 63-229109.
8. Boucher-Sharma, A. M.S. Thesis, University of Ottawa, 2000.
9. Kim, K.-J.; Chowdhury, G.; Matsuura, T. J Membr Sci 2000, 179, 43.
10. Hamza, A.; Chowdhury, G.; Matsuura, T.; Sourirajan, S. J Membr Sci 1997, 129, 55.
11. Nurlaila, G. M.S. Thesis, University of Ottawa, 1997.
12. Chowdhury, G.; Matsuura, T.; Sourirajan, S. J Appl Polym Sci 1994, 51, 1071.
13. Singh, S.; Khulbe, K. C.; Matsuura, T.; Ramamurthy, P. J Membr Sci 1998, 142, 111.
14. Singh, S.; Matsuura, T.; Ramamurthy, P. Tappi J 1999, 82, 146.
15. Kruczek, B. In Polyphenylene Oxide and Modified Polyphenylene Oxide Membranes: Gas, Vapor and Liquid Separation; Chowdhury, G.; Kruczek, B.; Matsuura, T., Eds.; Kluwer Academic: Boston, 2001.
16. Chowdhury, G. In Polyphenylene Oxide and Modified Polyphenylene Oxide Membranes: Gas, Vapor and Liquid Separation; Chowdhury, G.; Kruczek, B.; Matsuura, T., Eds.; Kluwer Academic: Boston, 2001.
17. White, D. M. Polym Prepr (Am Chem Soc Polym Chem Div) 1974.
18. Sourirajan, S.; Matsuura, T. Reverse Osmosis/Ultrafiltration Process Principles; National Research Council of Canada: Ottawa, Canada, 1985.
19. Matsuura, T. In Polyphenylene Oxide and Modified Polyphenylene Oxide Membranes: Gas, Vapor and Liquid Separation; Chowdhury, G.; Kruczek, B.; Matsuura, T. Eds.; Kluwer Academic: Boston, 2001.