

Development of Thin-Film Composite Hollow-Fiber Membranes from Modified Polyphenylene Oxide for Gas Separation Applications

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ABSTRACT: The effect of sulfonation and bromination-sulfonation on the gas transport properties of polyphenylene oxide has been investigated. These high-performance modified polymers have been studied in the form of TFC membranes by solution coating on the skin side of polyetherimide hollow fibers. TFC membrane modules prepared from sulfonated-brominated polyphenylene oxide as the active layer coated on polyetherimide hollow fibers. Stability of the TFC membranes was greatly improved when a wet feed stream was used instead of a dry one. Water vapor in the feed stream most likely prevented the active layer from stress cracking on drying. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 275–282, 2001

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INTRODUCTION

Thin-film composite (TFC) membranes capable of effectively separating one component of a gas or vapor mixture from the others are well known. Typically, these membranes are produced by depositing a thin layer of the selective material on a porous support. For practical purposes, such membranes should be durable, free of defects, and must be capable of achieving a good level of selectivity along with high permeance for the more rapidly permeable component of the gas or vapor mixture being treated. The most attractive aspect of TFC structures is their potential for minimizing cost because only small quantities of the high-

performance polymer is utilized for its formation. Basically, one has to choose a low-cost, solvent-resistant support, and the selective layer can be selected for specific application. The flux through the membrane may be optimized by reducing the effective thickness of the selective layer.

A number of separation layer materials, support structures, and membrane manufacturing methods are known for producing composite membranes.^{1–5} In such composite membranes, the separation layer may comprise a single membrane material or a blend of several materials. Some authors have reported methods of preparing a two-part composite structure that is formed simultaneously with the precipitation of the membrane.^{6,7}

The most widely used method of TFC membrane preparation is dipcoating. Even these single-layer TFC membranes, generally prepared by

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applying a dilute coating solution to a microporous support requires addressing a number of practical issues. Development of imperfections as a result of stress buildup during the drying step of the coated layer, especially in the case of glassy polymer, is one of the problems. The effect of the pores and the pore size distribution of the microporous support on the final performance of the TFC membranes has been mentioned in the literature.^{8,9} Some authors⁹ have addressed the problem of pore penetration (which results in a large effective thickness) by impregnating the support with a nonsolvent so as to achieve a thin, defect-free skin layer of a glassy polymer. They have also shown a high molecular weight polymer along with a good solvent give maximum hydrodynamic dimensions, reducing the extent of pore penetration resulting in a thin top layer.

In this work, TFC membranes were prepared by coating the skin side of polyetherimide (PEI) hollow fibers with highly selective modified polyphenylene oxide (PPO). PPO was chosen as the parent material due to its excellent film-forming characteristics and high gas permeability.¹⁰ The literature has described methods of overcoming the low selectivity of this material by chemically modifying the polymer. Thus, Bikson and Nelson⁵ have reported an O₂/N₂ separation factor of about 7.1 by using a composite membrane having separation layer comprising of sulfonated PPO (SPPO) in the lithium form. Polotskaya et al.¹¹ have reported improved selectivity of SPPO compared to PPO. In their work, selectivity of SPPO for CO₂/N₂ was 86 compared to 15 for PPO. The permeability of SPPO for CO₂ was, however, as low as 13.8 Barrer compared to 91.0 Barrer obtained for PPO. This loss of permeability of the highly selective SPPO material has been overcome in the present work by introducing a bulky bromine group to the phenyl ring of the PPO backbone. The bromine group primarily increases the inter-chain spacing while the presence of ionic sulfonic group enhances crosslinking within the polymer matrix.

The aim of this work was to study the effect of sulfonation and bromination-sulfonation on the gas transport of PPO. For this purpose PPO was sulfonated by reacting with chlorosulfonic acid to form SPPO. Ring bromination of PPO was also conducted to give brominated PPO (PPOBr). PPOBr was then sulfonated to produce SPPOBr. Excellent gas transport properties of SPPO and SPPOBr used as dense films have been reported earlier by the present authors.¹² These high-per-

formance polymers have now been studied in the form of TFC membranes by solution coating on the skin layer of PEI hollow fibers. The target was to achieve high permeances for the TFC membranes thus prepared. Permeance of the resulting composite membrane would depend on the thickness of the coated film. A minimum film thickness is, however, necessary to obtain the intrinsic selectivity of the coating material.

The effect of the following parameters on the properties of the TFC membranes were studied: (a) effect of the PEI substrate; (b) effect of SPPO as the coated layer; (c) effect of SPPOBr as the coated layer.

Membrane stability with time was also studied, and methods to improve on it was investigated.

EXPERIMENTAL

Materials

A sample of PPO of $[\eta]$ equal to 1.73 dL/g was generously supplied by General Electric Company, Selkirk, NY. Polyetherimide was purchased from General Electric Company, and is marked under the trade name, Ultem[®] 1000. All other chemicals used in the experiments were reagent grade, and were used without any further purification.

Chemical Modification of PPO

Sulfonation and bromination followed by sulfonation of brominated PPO was carried out using the methods described earlier.¹² The ion exchange capacity (I.E.C.) of SPPO was 2.0 mEq/g of dry polymer. The degree of bromination for the SPPOBr samples, studied by ¹H-NMR analysis, was 20.0%. It may be noted that under our experimental conditions only ring bromination took place. The I.E.C. of SPPOBr was 1.8 mEq/g of dry polymer.

Preparation of PEI Hollow Fibers

A dry-wet spinning technique was applied to spin integrally skinned asymmetric hollow fiber membranes from PEI. Two different polymer solution compositions were utilized for this study. In the first case, a 22.5 wt % solution of PEI in dimethylacetamide (DMAc) or *N*-methylpyrrolidone (NMP), containing 1.0–1.5 wt % of lithium nitrate

was used following the method similar to that described by Deng and others.¹³

In the second case, a spinning procedure described by Kneifel and Peinemann¹⁴ was adopted. Here, NMP was used as the solvent, and γ -butyrolactone (GBL) was used as the nonsolvent. Distilled water was used as the bore liquid. The temperature of the polymer solution and the bore liquid was 20–22°C. The solution constituted of 25.0 wt % PEI in 55.0 wt % of NMP and 20.0 wt % of GBL. This was spun at a solution pressure of 1.0 psig. The bore liquid flow rate was 2.0 mL/min. The air gap was maintained at 90.0 cm. After leaving the spinneret, the hollow fiber was coagulated in a water bath at room temperature. Spinning was carried out at ambient temperature. The solidified membranes were subjected to posttreatment by heating in water at 92.0°C for different periods of time. They were then solvent exchanged in ethanol for 24 h and dried overnight. The fibers had an outer diameter of 0.93 mm and an inner diameter of 0.65 mm.

Preparation of TFC Membranes

TFC membranes from the fibers prepared from PEI/DMAC/LiNO₃ solution were coated on the shell side by a method similar to the dip-coating method. The hollow fibers were wiped with ethanol or acetone before being coated with the selective layer. The coating solution used was dilute solutions of high-performance modified PPO, namely SPPO and SPPOBr. The concentration of SPPO was varied from 0.1–1.0 wt % in a mixture of methanol and ethanol. SPPOBr thin film composite membranes were prepared by coating the shell side of the fibers with a 0.5 wt % solution in a chloroform–methanol mixture. Some fibers were then coated with a thin layer of polydimethylsiloxane (PDMS) in *n*-pentane. The coated layer of PDMS was cured in an oven at 60°C for 75 min. In some cases, a layer of RTV rubber (RTV sealant 734 from Dow Corning) in *n*-hexane was deposited on top of the PEI fibers before coating them with SPPOBr. The TFC membranes were thoroughly dried under ambient conditions.

To determine membrane permeation properties testing a module for shell side feed was designed. The hollow fibers, which can be varied in length, were suspended inside the tube. The module was made of 3/8 in. stainless steel tubing, 35 cm in length, with a side arm of 1/4 in. stainless steel welded 5 cm from one end. A 3/8 in. stainless steel male Swagelok connection was welded to

each end. Two to four fibers were potted at one end in a 3/8 inch polyethylene tube using epoxy resin (Revcon 5 minute Epoxy from Mastercraft). A nylon ferrule around this tube was used to provide a tight seal when the fibers were lowered into the module and the stainless steel Swagelok net at the top of the module is screwed in place. The other ends of the fibers were sealed with epoxy resin.

PEI hollow fibers prepared from a PEI/NMP/GBL solution were inspected under a high-resolution optical microscope. These fibers had an integral skin layer on the lumen side as a result of which testing modules were designed for lumen side feed. It may be noted that only these fibers were used to prepare SPPOBr TFC membranes. The testing module consisted of a stainless steel tube similar to that mentioned above. A bundle of two to four fibers were potted on both ends using epoxy resin and then fitted into steel tube using Swagelok fittings. The fibers were open at both ends. The bore side of the fibers were coated one to three times with a 2.0 wt % solution of SPPOBr in methanol. This was done by pumping the polymer solution through the fiber lumen by means of a syringe pump. The solution was allowed to reside within the fibers for 10–15 min, after which excess of the solution was drained out. The coated layer was dried by slowly blowing dry air through the bore side for 15 h. The coating procedure was repeated. The residing period of the solution within the lumen was however reduced to 1–2 min. The membranes were dried by the method similar to that described above. The total membrane area was 14–28 cm². After the initial testing of these membrane modules larger modules were constructed by using about 80–100 PEI hollow fibers of a 35-cm length. These fibers were potted at both ends using epoxy resin into 1-1/4 inches diameter steel tube having an outlet on the side. The module was sealed at both ends by means of steel end caps fitted with O-rings. Fiber lumens were open at both ends. The total membrane area per module was in the range of 800–850 cm².

TFC Membrane Testing

The fluxes of the pure gases, namely CO₂, CH₄, O₂, and N₂ were measured at different pressure gradients from the bore side to the shell side or vice versa, depending on which side the fibers were coated. Volumetric flow rates of the gases through the membrane were measured by a bub-

Table I Gas Separation Characteristics of SPPO-Coated TFC Hollow Fiber Membranes

| Module No. | Concentration of SPPO, wt % | Solvent Mixture Composition, wt/wt % | | Nos. of Coating Layers | Permeance, GPU | | Permeance Ratio, CO ₂ /CH ₄ |
|------------|-----------------------------|--------------------------------------|---------|------------------------|-----------------|-----------------|---|
| | | Methanol | Ethanol | | CO ₂ | CH ₄ | |
| SPPO1 | 0.1 | 96 | 4 | 2 | 6.8 | 0.3 | 19.4 |
| SPPO2 | 0.3 | 88 | 12 | 2 | 5.5 | 0.2 | 23.3 |
| SPPO3 | 0.5 | 60 | 40 | 1 | 16.2 | 0.7 | 24.7 |
| SPPO4 | 0.8 | 60 | 40 | 1 | 19.1 | 0.8 | 23.3 |
| SPPO5 | 1.0 | 60 | 40 | 1 | 6.5 | 0.3 | 19.5 |

Intrinsic permeability of SPPO film was 50.¹²

SPPO coated on PEI hollow fibers prepared from PEI (22.5 wt %)/DMAc (76.0 wt %)/LiNO₃ (1.5 wt %) solution.

I.E.C. of SPPO = 2.0 mEq/g of dry polymer.

Transmembrane pressure difference: 100 psig.

ble flow meter every hour until steady state was reached. Pressure-normalized gas fluxes were reported in gas permeation units, GPU, where:

$$\text{GPU} = 1 \times 10^{-6} \frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^2 \text{ s cmHg}} \quad \text{and}$$

$$= 3.349 \times 10^{-10} \frac{\text{mol}}{\text{m}^2 \text{ s Pa}}$$

The ideal separation factor for the gas pairs CO₂/CH₄ and O₂/N₂ was calculated as the ratio of the gas permeances through the membrane. A study on the separation of CO₂/CH₄ gas mixtures was conducted on membranes that showed high-permeance ratios. In addition to measuring the flow rates, the permeate was analyzed by gas chromatography to determine the separation factor. A Varian 3300 gas chromatograph fitted with a molecular sieve 5 Å column was used. Helium was used as the carrier gas. The separation factor, α , was calculated as:

$$\alpha = \frac{\{(\text{CO}_2 \text{ mol fraction}/\text{CH}_4 \text{ mol fraction})_{\text{permeate}}\}}{\{(\text{CO}_2 \text{ mol fraction}/\text{CH}_4 \text{ mol fraction})_{\text{feed}}\}}$$

Permselectivity was calculated as:

$$\beta = \frac{\{(\text{CO}_2 \text{ permeation rate}/\text{crossmembrane CO}_2 \text{ partial pressure difference})/\{(\text{CH}_4 \text{ permeation rate}/\text{crossmembrane CH}_4 \text{ partial pressure difference})\}}{\{(\text{CH}_4 \text{ permeation rate}/\text{crossmembrane CH}_4 \text{ partial pressure difference})\}}$$

RESULTS AND DISCUSSIONS

Tables I and II show the performance data of SPPO and SPPOBr-coated TFC membranes, respectively. PEI hollow fibers spun from PEI/NMP/LiNO₃ solution were used as the substrates for these membranes. The fibers were coated on the shell side. Initial observation showed that when

Table II Gas Separation Characteristics of SPPOBr-Coated TFC Membranes

| Module # | Solvent Mixture Composition, wt/wt % | | Nos. of Coating Layer | Permeance, GPU | | Permeance Ratio, CO ₂ /CH ₄ |
|----------|--------------------------------------|----------|-----------------------|-----------------|-----------------|---|
| | Chloroform | Methanol | | CO ₂ | CH ₄ | |
| SPPOBr1 | 20 | 80 | 1 | 14.2 | 0.7 | 19.0 |
| SPPOBr2 | 40 | 60 | 2 | 7.7 | 0.2 | 34.2 |
| SPPOBr3 | 40 | 60 | 3 | 7.1 | 0.2 | 40.4 |

Intrinsic permeability of SPPOBr films was 59.¹²

SPPOBr coated on PEI hollow fibers prepared from PEI (22.5 wt %)/DMAc (76.0 wt %)/LiNO₃ (1.5 wt %) solution.

Transmembrane pressure drop: 100 psig.

Table III Performance Characteristics of SPPOBr-PEI TFC Membranes

| Module No. | Concentration of SPPOBr in Methanol, wt % | | | | Permeance, GPU | | Permeance Ratio, CO ₂ /CH ₄ |
|------------|---|-----------|-----------|-----------|-----------------|-----------------|---|
| | 1st Layer | 2nd Layer | 3rd Layer | 4th Layer | CO ₂ | CH ₄ | |
| SPPOBr4 | 1.5 | 1.8 | 1.8 | 1.8 | 72.2 | 1.1 | 66.8 |
| SPPOBr5 | 2.0 | 2.0 | 2.0 | — | 77.4 | 1.5 | 51.9 |
| SPPOBr6 | 2.0 | 2.0 | — | — | 93.0 | 2.1 | 43.5 |

Transmembrane pressure: 100 psig.

PEI hollow fibers spun from PEI (25 wt %)/GBL (20 wt %)/NMP (55 wt %) dope solution.

lower concentrations of SPPO solutions (0.1–0.3 wt %) were used to coat the fibers, the gas fluxes were very large, and the TFC membranes showed no selectivity towards CO₂/CH₄ gas pair. When the substrate fibers were coated two times CO₂ permeance was low (5.5–6.8 GPU). Table I also indicates that an increase in concentration of SPPO to 1.0 wt % caused a significant decrease in CO₂ permeance. This effect could be due to an increase in the effective layer thickness. The permeance ratios of CO₂/CH₄ gas pairs were, however, much lower than the intrinsic permeability ratio of 50 for SPPO films.¹²

When similar PEI substrates were coated with SPPOBr solutions, the permeance ratio for CO₂/CH₄ showed much improvements (Table II) compared to PEI-SPPO composite membranes. CO₂ permeance was, however, very low. At this point it was believed that the shell side of the fibers were microporous, leading to the penetration of the coating solutions into the pores, thus increasing the effective thickness of the coated layer. This effect brought about a large decrease in the membrane permeance without any significant improvement to the selectivity of the TFC membranes.

Coating of the substrates was then carried out with PEI hollow fibers prepared by the second method described in the Experimental section. These fibers were coated on the lumen side, which constituted the skin layer of the fiber. It may be noted that only SPPOBr was used to prepare the TFC membranes.

Experiments were conducted to find out the optimum coating conditions. The data shown in Table III describes the effect of concentration of SPPOBr solutions and the number of layers of coating on CO₂—CH₄ permeances and permeance ratios. Use of more dilute solutions and more numbers of layer of coating gave TFC membranes of high CO₂/CH₄ permeance ratio with reasonable CO₂ permeance. Coatings from more concentrated solutions did not improve the CO₂/CH₄ permeance ratio. Membranes with high separation factor along with reasonable permeances could be achieved by coating the substrate membranes three times with a 2.0 wt % solution of SPPOBr in methanol. Therefore, more of these modules consisting of two to four fibers were made and tested for CO₂/CH₄ as well as O₂/N₂ gas pairs. Some of these membrane modules were tested later for CO₂—CH₄ (20–80) gas mixtures. The test results

Table IV Single Gas Permeation Data of PEI-SPPOBr TFC Hollow-Fiber Membrane Modules (Small Modules)

| Module No. | Surface Area, cm ² | Permeance, GPU | | | | Permeance Ratio | |
|------------|-------------------------------|-----------------|-----------------|----------------|----------------|----------------------------------|--------------------------------|
| | | CO ₂ | CH ₄ | O ₂ | N ₂ | CO ₂ /CH ₄ | O ₂ /N ₂ |
| SPPOBr7 | 27.4 | 38.3 | 0.6 | — | — | 58.5 | — |
| SPPOBr8 | 13.8 | 79.2 | 1.4 | 8.3 | 1.1 | 55.0 | 7.4 |
| SPPOBr9 | 15.2 | 108.5 | 2.5 | 13.6 | 2.1 | 43.4 | 8.1 |

Feed pressure: 100 psig.

All fibers were coated three times with a 2 wt % solution of SPPOBr in methanol.

Table V Separation of CO₂/CH₄ Gas Mixture by PEI-SPPOBr TFC Hollow-Fiber Membrane Modules (Small Modules)

| Module No. | Surface Area, cm ² | Permeance Ratio, CO ₂ /CH ₄ (Pure Gas) | CO ₂ Mol Fraction | | Selectivity | |
|------------|-------------------------------|--|------------------------------|-----------------------------|-----------------------------|--------------------------|
| | | | CO ₂ in Feed | CO ₂ in Permeate | Separation Factor, α | Permselectivity, β |
| SPPOBr7 | 27.4 | 58.5 | 20.30 | 83.26 | 19.5 | 40.8 |
| SPPOBr8 | 13.8 | 55.0 | 20.30 | 81.89 | 17.7 | 36.4 |
| SPPOBr9 | 15.2 | 43.4 | 20.30 | 77.95 | 13.9 | 26.8 |

Feed pressure—100 psig.

$$\alpha = \{(\text{CO}_2 \text{ mol fraction/CH}_4 \text{ mol fraction})_{\text{permeate}} / (\text{CO}_2 \text{ mol fraction/CH}_4 \text{ mol fraction})_{\text{feed}}\}$$

$\beta = \{(\text{CO}_2 \text{ permeation rate/crossmembrane CO}_2 \text{ partial pressure diff.}) / (\text{CH}_4 \text{ permeation rate/crossmembrane CH}_4 \text{ partial pressure diff.})\}$.

for single gas experiments are shown in Table IV. The membranes tested here showed a very high permeance ratio for the O₂/N₂ gas pair. The permeance for O₂ was on an average of 10.5 GPU. The permeance ratio for the CO₂/CH₄ gas pair in these cases was also high, and close to the intrinsic permeability ratio of 59 in most of the membranes tested.

Results on the separation of CO₂/CH₄ gas mixture by the TFC membranes described above are shown in Table V. For some of the membrane modules permselectivity of 40.8 for a CO₂/CH₄ was achieved.

As mentioned above PEI hollow fibers coated with SPPOBr polymer demonstrated excellent performance for the separation of CO₂ and CH₄. However, deterioration of the performance was observed with an increasing operating period. It was suspected that the performance decay was due to formation of cracks on the coated layer when the later was dry. Hence, it was attempted to test the performance of the hollow fibers in the presence of water vapor in the feed gas stream. This would keep the surface of the membrane moist, and thus prevent stress cracking.

A saturator consisting of a water-filled stainless steel cylinder was, therefore, connected to the feed stream line. The cylinder was immersed in a temperature-controlled water bath. The feed gas was bubbled through the water layer to pick up the moisture. The vapor content in the feed stream was controlled by regulating the temperature of the bath. The feed and the permeate streams were subjected to gas chromatographic analysis.

Table VI summarizes the water content in the feed CH₄ and CO₂ gases along with the feed CO₂/CH₄ gas mixture with a CO₂ content of 25%. The

table also includes the data for the water content in the permeate stream. Considering that the saturated gas stream at 25°C should contain 0.71, 0.4, and 3.1 mol% of water vapor when the gas stream is at 50, 100 psig, and atmospheric pressure, respectively, it can be concluded that both feed and permeate gas streams are significantly under saturated.

Table VII shows the performance data of two hollow fiber modules tested at 50 and 100 psig. There were two sets of experiments conducted with these modules. The first set of experiments were conducted on freshly prepared modules in the following sequence: CH₄ permeance was measured at 50 psig and then at 100 psig. The modules were then left at 30 psig in a CO₂ atmosphere for 3 days after which CO₂ permeances both at 50 and 100 psig were measured. The whole proce-

Table VI Water Content (%) in Feed and Permeate Gas Stream

| Permeating Gas | Water Content in Feed | | Water Content in Permeate ^b | |
|---|-----------------------|----------|--|----------|
| | Feed Gas Pressure | | Feed Gas Pressure | |
| | 50 psig | 100 psig | 50 psig | 100 psig |
| CH ₄ | 0.4 | — | 1.7 | 1.8–2.3 |
| CO ₂ | 0.3 | 0.1 | 0.7–1.5 | 0.3–0.5 |
| CO ₂ /CH ₄ mixture ^a | 0.5 | 0.2 | 0.1–0.5 | 0.2–0.4 |

^a CO₂ content, 25%.

^b Permeate gas pressure is 1 atmospheric pressure.

Table VII Effect of Water Vapor in the Feed on Membrane Stability^a

| Module No. | Test No. | Feed Pressure, 50 psig | | | Feed Pressure, 100 psig | | |
|------------|----------|------------------------|-----------------|-----------------|-------------------------|-----------------|-----------------|
| | | Permeance, GPU | | Permeance Ratio | Permeance, GPU | | Permeance Ratio |
| | | CO ₂ | CH ₄ | | CO ₂ | CH ₄ | |
| 1 | 1st test | 43.5 | 1.2 | 35.1 | 47.6 | 1.2 | 39.87 |
| | 2nd test | 35.7 | 0.9 | 41.5 | 38.1 | 0.9 | 42.90 |
| 2 | 1st test | 48.0 | 1.1 | 41.0 | 55.9 | 1.5 | 38.04 |
| | 2nd test | 42.0 | 0.9 | 38.3 | 44.3 | 1.2 | 35.81 |

^a Experiments with single gases.

ture took 5–7 days to complete. Membrane modules were then left in an atmosphere of CH₄ at 30 psig for 1 week after which the second set of tests were conducted. It was observed that the membrane permeance decreased to about 80% of the first series, but the permeance ratio remained unchanged. Our initial study in the absence of water vapor in the feed stream had indicated a decrease in selectivity between 10–80%. Therefore, improvement in the stability of the membrane selectivity with a wet feed stream is undeniable.

After single gas experiments were completed within a period of 20 days, the same modules were used to conduct gas mixture experiments. Prior to separation of gas mixtures the membranes were exposed to CH₄ at 30 psig for 10 days, then to CO₂/CH₄ mixture at 30 psig for 3 days. The results on CO₂/CH₄ gas mixture separation are shown in Table VIII. As can be seen from the table, the permselectivity was as high as 33.4 even after a month of running experiments using the same membranes.

Larger membrane modules having surface area about 700–800 cm² were also prepared and tested. Separation and permeance data for CO₂/CH₄ gas pair is shown in Table IX. The tests were conducted without introducing any water vapor in the feed stream. The performance data of these modules were not as high as the smaller modules tested earlier. For the smaller modules we had achieved permselectivity, β as high as 40.8 in some cases, whereas permselectivity as high as 27.61 only was obtained for the larger modules (Tables V and IX). Experiments were conducted to verify if the coated SPPOBr layer went through any chemical degradation under our testing conditions. To do so, XPS analysis was conducted on flat sheet thin-film composite membranes coated

with SPPOBr. The membranes were analyzed before and after they were exposed to our experimental conditions for 10 days. The results of the analysis is shown in Table X. It is obvious from this table that the ratio of carbon, oxygen, sulfur, and bromine has not changed in the used membranes. Therefore, the low values of permeance ratio and separation factor could be the result of leaks through the membrane modules.

CONCLUSIONS

From our initial experiments with PEI-modified PPO TFC hollow fiber membranes it may be con-

Table VIII Separation of CO₂/CH₄ Gas Mixtures in the Presence of Water Vapor in Feed Stream^a

| | Feed Gas Pressure | | | |
|-----------------------------|-------------------|-----------------|-----------------|-----------------|
| | 50 psig | | 100 psig | |
| | Membrane Module | Membrane Module | Membrane Module | Membrane Module |
| | 1 | 2 | 1 | 2 |
| Feed composition | | | | |
| CH ₄ (mol %) | 74.2 | 74.2 | 74.36 | 74.36 |
| CO ₂ (mol %) | 25.3 | 25.3 | 25.42 | 25.42 |
| Permeate composition | | | | |
| CH ₄ (mol %) | 21.6 | 22.0 | 13.59 | 13.56 |
| CO ₂ (mol %) | 78.3 | 77.7 | 86.21 | 86.09 |
| Permeance | | | | |
| CH ₄ (GPU) | 0.69 | 0.90 | 0.81 | 0.94 |
| CO ₂ (GPU) | 22.9 | 29.7 | 25.85 | 30.22 |
| Permselectivity (β) | 33.37 | 31.8 | 32.03 | 32.04 |

^a Experiments with feed gas mixtures.

Table IX Separation of CO₂/CH₄ Gas Mixture by PEI-SPPOBr TFC Hollow-Fiber Membrane Modules (Large Modules)

| Module No. | Surface Area, cm ² | Mixed Gas Experiments | | | | | | |
|------------|-------------------------------|--------------------------------|---|-------------------------------|----------|-----------|-----------------------------|--------------------------|
| | | Single Gas Experiments | | CO ₂ Mole Fraction | | | Selectivity | |
| | | CO ₂ Permeance, GPU | Permeance Ratio, CO ₂ /CH ₄ | Feed | Permeate | Retentate | Separation Factor, α | Permselectivity, β |
| SPPOBr10 | 830.4 | 28.64 | 28.50 | 0.215 | 0.667 | 0.197 | 7.30 | 27.61 |
| SPPOBr11 | 419.7 | 32.65 | 34.62 | 0.212 | 0.636 | 0.208 | 6.49 | 19.49 |
| SPPOBr12 | 719.6 | 38.20 | 41.75 | 0.257 | 0.731 | 0.255 | 7.84 | 20.50 |

Feed pressure 50 psig.

$\alpha = \{(\text{CO}_2 \text{ mol fraction}/\text{CH}_4 \text{ mol fraction})_{\text{permeate}}/(\text{CO}_2 \text{ mol fraction}/\text{CH}_4 \text{ mol fraction})_{\text{feed}}\}$.

$\beta = \{(\text{CO}_2 \text{ permeation rate}/\text{crossmembrane CO}_2 \text{ partial pressure diff.})/(\text{CH}_4 \text{ permeation rate}/\text{crossmembrane CH}_4 \text{ partial pressure diff.})\}$.

cluded that better separation characteristics for SPPOBr was attained compared to that for SPPO for similar gas permeances. It was also important to chose an appropriate substrate to coat the active polymer material onto. Hence, TFC membrane modules prepared with SPPOBr as the active layer coated on PEI hollow fibers spun from a PEI/NMP/GBL solution showed superior performances compared to those prepared from PEI/DMAc/LiNO₃ solutions. Coating on the lumen side of the fibers gave better performance than coating on the shell side. This could be due to the fact that the skin layer of the fibers was formed on the bore side.

Stability of the coated layer was greatly improved when a wet feed stream used instead of a dry feed stream. Water vapor in the feed stream most likely prevented the active layer from stress cracking on drying.

Table X XPS Analysis: Composition in Atomic %

| Sample | Fresh | Used |
|--------------|-------|------|
| Total carbon | 76.0 | 74.0 |
| Total oxygen | 19.7 | 20.0 |
| Sulfur | 2.2 | 2.1 |
| Bromine | 1.6 | 1.5 |
| Nitrogen | — | 1.9 |

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