## Optimization of CO<sub>2</sub>–CH<sub>4</sub> Separation Performance of Integrally Skinned Asymmetric Membranes Prepared from Poly(2,6-dimethyl-1,4-phenylene oxide) by Factorial Design

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ABSTRACT: Integrally skinned asymmetric flat sheet membranes were prepared from poly(2,6-dimethyl 1,4-phenylene oxide)(PPO) for CO<sub>2</sub>–CH<sub>4</sub> separation. Various experiments were carried out to identify PPO membranes, which have good mechanical strength and gas separation abilities. Membrane strength and selectivity depend on the interplay of the rate of precipitation and the rate of crystallization of the PPO. The effects of major variables involved in the membrane formation and performance, including the concentration of the polymer, solvent, and additive, the casting thickness, the evaporation time before gelation, and the temperature of the polymer solution, were investigated. Factorial design experiments were carried out to identify the factor effects. The membrane performance was modelled and optimized to approach preset values for high CO<sub>2</sub> permeance and a high CO<sub>2</sub> : CH<sub>4</sub> permeance ratio. Membranes were prepared based on the optimum conditions identified by the model. Essentially, defect-free membranes were prepared at these conditions, which resulted in a pure gas permeance of 9.2  $\times 10^{-9}$  mol/m<sup>2</sup> s Pa for CO<sub>2</sub> and a permeance ratio of 19.2 for CO<sub>2</sub> : CH<sub>4</sub>. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1601–1610, 1999

Key words: PPO; gas separation; optimisation; factorial design

## INTRODUCTION

Polyphenylene oxide (PPO) is an amorphous polymer proven to be a highly permeable gas separation membrane material. Because of its high glass transition temperature  $(T_g)$  and the presence of the aromatic ring in the main polymer chain, it is expected to give membranes with excellent chemical and thermal stability. The preparation of gas separation membranes from PPO and modified PPO was studied by a number of research groups.

A study of the formation of PPO membranes by Wijmans et al.<sup>1</sup> found that the porosity of the top layer of integrally skinned PPO asymmetric membranes decreased when the PPO concentration increased, and this porous structure was the result of liquid–liquid demixing during membrane formation. For homogeneous PPO membranes, the interplay of the precipitation rate and the crystallization kinetics determines the mechanical stability of the film.

A study<sup>2</sup> of asymmetric hollow fiber membranes prepared from a range of PPO of different intrinsic viscosities found that increasing the intrinsic viscosity of the polymer reduces the minimum skin thickness of the membrane, thus increasing the permeability while selectivity re-

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mained the same. This was attributed to a decrease of the number of imperfections in the skin layer of the membranes prepared from high intrinsic viscosity polymer. A change in the morphology of the sublayer was also identified as a possible cause of the increased permeability.

By a series of plasma-etching experiments, Beuer et al.<sup>3</sup> concluded that the resistance of the sublayer of integrally skinned asymmetric hollow fiber PPO membranes had a significant influence on the overall membrane properties. In addition, it was found that the molecular weight of the PPO has a large effect on the resistance of the sublayer: the higher the molecular weight, the lower the gas resistance of the sublayer would be.

Most of the polymers used for gas separation membranes are glassy polymers. Since the glassy state is not an equilibrium state, *d*-spacing (free volume), orientation, and the crystalline fraction in the membrane can be profoundly influenced by the factors involved in the membrane preparation procedure. The choice and concentration of solvent, nonsolvent, and coagulation bath will affect the kinetics of phase separation and, therefore, the membrane morphology. The concentration of the polymer is also important. The performance of gas separation membranes largely depends on their morphology and, therefore, can be controlled by the membrane-making process.

## **Factorial Designs**

Factorial designs are statistical experimental methods used to study the effect and interaction of several factors on a response. The statistical design of experiments is the process of planning the experiments so that appropriate data will be collected, which may be analyzed by statistical methods, resulting in valid and objective conclusions.<sup>4</sup> In a factorial experiment, several factors are investigated simultaneously, with each factor studied at two or more levels. Levels of the factors may be quantitative, such as temperature, or qualitative, such as the type of polymer. It provides the smallest number of runs while testing all possible combinations of the levels and factors. The factorial design experimental approach has recently been used in the study of asymmetric membrane formation5-7 from polysulfone and polyetherimide.

The objective of this work is to study the effect of various factors involved in membrane preparation on the performance of an integrally skinned asymmetric membrane prepared from PPO. The

parameters studied are the molecular weight of the polymer, the solvents used to prepare the solutions, the concentration of the polymer and additive, the temperature, and the evaporation time before gelation. Further optimization of some of these conditions (concentration of polymer solution, presence of additive, evaporation time before gelation, and the temperature of casting solution) is done using a fractional factorial design. Mathematical models were developed, and the optimum casting conditions to obtain the highest values of  $CO_2$  permeance and  $CO_2 : CH_4$ pure gas permeance ratio were determined from the models. Membranes prepared from the highermolecular-weight PPO were mechanically much stronger than those prepared from lower-molecular-weight PPO. Therefore, the optimum conditions derived from the models were utilized to prepare and test membranes from high-molecular-weight PPO only.

## **EXPERIMENTAL**

## Materials

PPO of intrinsic viscosity 0.46 dL g in chloroform at 25°C (a weight-average molecular weight  $M_w$  of 45,000) was supplied by General Electric (GE) Plastics. Higher-molecular-weight PPO having an intrinsic viscosity of 1.0 dL g in chloroform at 25°C ( $M_w = 176,000$ ) was kindly supplied by A. Ward of GE Plastics, Schenectady, NY. Some of the higher-molecular-weight PPO was synthesized in our laboratory following the method of Hay.<sup>8</sup> The polymers were dried in a vacuum oven or a conventional oven for at least 1 h at 60°C before preparing the solutions. All organic chemicals used in the preparation of the casting solution were of reagent grade purity and were used as received.

## Procedure

Integrally skinned flat sheet asymmetric membranes from PPO were prepared by casting a polymer solution on a clean glass plate to a wet thickness of 152  $\mu$ m at ambient temperature. Various solvents were used to prepare the casting solutions. Earlier work by Smid et al.<sup>2</sup> indicated that defect-free hollow fibers can be prepared from a PPO solution with 2-ethyl-1-hexanol as the additive. The same additive was therefore used for the preparation of the flat sheet membranes from

Membrane	Polymer Concentration (Wt %)	Solvent	Additive Concentration as Wt % of Solvent <sup>a</sup>
L-1	20.0	Chloroform	0
L-2	20.0	Chloroform : 1,1,2-trichloroethene, 70 : 30	0
L-3	20.0	Chloroform : 1,1,2-trichloroethene, 50 : 50	0
L-4	20.0	Chloroform : 1,1,2-trichloroethene, 30 : 70	0
L-5	20.0	1,1,2-Trichloroethene	0
L-5'	20.0	1,1,2-Trichloroethene	0
L-6	20.0	Chlorobenzene	0
L-7	20.0	1,1,2-Trichloroethene	12.5
L-8	20.0	1,1,2-Trichloroethene	14.3
L-9	20.0	1,1,2-Trichloroethene	16.7
L-10	15.0	1,1,2-Trichloroethene	0

Table I Composition of Casting Solution Prepared from PPO([ $\eta$ ] = 0.46 dL g in Chloroform at 25°C)

<sup>a</sup> Additive: 2-ethyl-1-hexanol.

PPO. The casting solution compositions for the lower- and the higher-molecular-weight PPO are given in Tables I and II. Membranes were cast at room temperature unless otherwise specified. The glass plate was then immersed after a predetermined period of evaporation time in a methanol bath for 1 h. The membrane was then dried in a vacuum oven for several days.

## **Membrane Testing**

Pure gas permeation tests were carried out at room temperature and upstream pressures of 414 to 1379 kPa gauge (60–200 psig). The gases studied were CO<sub>2</sub>, CH<sub>4</sub>, O<sub>2</sub>, and N<sub>2</sub>. Volumetric flow rates of the gases through the membrane were measured by a bubble flow meter every hour until a steady state was reached. Pressure-normalized gas fluxes are reported in gas permeation units (GPU) where

#### Table II Composition of Casting Solution Prepared from PPO( $[\eta] = 1.0 \text{ dL g in}$ Chloroform at 25°C)

Membrane	Polymer Concentration (Wt %)	Additive as Wt % of Solvent <sup>a</sup>
H-1	15.0	0
H-2	15.0	0
H-3	15.0	14.0

<sup>a</sup> Solvent, chloroform; additive, 2-ethyl-1-hexanol.

$$\mathrm{GPU} = 1 imes 10^{-6} \ \mathrm{cm^3} \ \mathrm{(STP)/cm^2} \ \mathrm{s} \ \mathrm{cmHg} \quad \mathrm{and}$$

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

The ideal separation factor for the gas pairs was calculated as the ratio of the gas permeation rates through the membrane. A study on the separation of  $CO_2$ -CH<sub>4</sub> gas mixtures was conducted on membranes that showed high permeation rate ratios. In addition to measuring the flow rates, the permeate was analyzed by gas chromatography (GCA) to determine the separation factor. A Varian 3300 gas chromatograph fitted with a molecular sieve 5A column was used. Helium was used as the carrier gas. The separation factor  $\alpha$  was calculated as follows:

 $\alpha = \{(CO_2 \text{ mole fraction}/CH_4 \text{ mole fraction})_{\text{permeate}}/$ 

 $(CO_2 \text{ mole fraction}/CH_4 \text{ mole fraction})_{feed}$ 

## Analysis of Factorial Design Results and Modelling Data

A fractional factorial design experiment was performed to determine the effect of four factors, that is, the polymer concentration, the presence of additive, the evaporation time before gelation, and the temperature of the casting solution on the performance of membranes prepared from the higher-molecular-weight PPO. A linear model was fitted to the results obtained. This model was used to identify the optimum casting conditions to achieve performance data close to the preset values of  $30 \times 10^{-9}$  mol/m<sup>2</sup> s Pa CO<sub>2</sub> permeance and a permeance ratio of 50 for CO<sub>2</sub> : CH<sub>4</sub>.

Two response variables were selected, as follows:  $CO_2$  permeance and  $CO_2$ :  $CH_4$  permeance ratio, at 690 kPa gauge (100 psig) upstream pressure. One-half of the full 2<sup>4</sup> design was performed, based on the assumption that 4-factor and 3-factor interactions are not significant compared to 2-factor interactions and single factor effects. Accordingly, the combined effect AB of polymer concentration A and additive concentration B are confounded with the combined effect of the evaporation time before gelation C and the casting solution temperature D. Similarly, the AC effect is confounded with the BD effect, the AD effect with the BC effect, the single factor effect A is confounded with the BCD interaction, B with ACD and D with ABC. The total effect (1) is confounded with the 4-factor interaction ABCD.

The data were analyzed using SAS<sup>®</sup> statistical software. The response variables of CO<sub>2</sub> permeance and the  $CO_2$ :  $CH_4$  pure gas permeance ratio were analyzed by the half-normal plotting method and modeled using backward stepwise elimination from the most general model using linear regression. Contour plots of the modeled  $CO_2$  permeance and the  $CO_2 : CH_4$  pure gas permeance ratio were plotted, using SAS®, in order to determine the membrane making conditions that would give a membrane having both the preset values for  $CO_2$  permeance and the  $CO_2 : CH_4$ pure gas permeance ratio. By overlaying the two contour plots, it was possible to determine graphically the optimum conditions for the desired membrane.

## **RESULTS AND DISCUSSION**

#### **Effects of Membrane Preparation Conditions**

Preliminary tests of membranes prepared at wet thicknesses of 101.6, 152.4, 203.2, and 254.0  $\mu$ m revealed that a wet thickness of 152.4  $\mu$ m yielded permeable membranes that had enough mechanical strength to withstand operating pressures above 690 kPa gauge (100 psig).

#### **Effect of Solvents for PPO**

The effect of the solvent in the casting solution was studied by using PPO of intrinsic viscosity equal to 0.46 dL g in chloroform at 25°C. PPO

Table III	Effect of Solvent Used in the
Preparation	on of PPO Membranes on CO <sub>2</sub>
Permeanc	e

Membrane	Solvent	$\begin{array}{c} \mathrm{CO_2} \ \mathrm{Permeance} \\ \times \ 10^{10} \\ (\mathrm{mol/m^2} \ \mathrm{s} \ \mathrm{Pa}) \end{array}$
L-1	Chloroform	5.63
L-2	1,1,2-Trichloroethene : chloroform, 70 : 30	5.43
L-3	1,1,2-Trichloroethene : chloroform, 50 : 50	6.79
L-4	1,1,2-Trichloroethene : chloroform, 30 : 70	5.24
L-5	1,1,2-Trichloroethene	6.29
L-6	Chlorobenzene	7.78

Concentration of polymer, 20.0 wt %; upstream pressure, 690 kPa gauge; the membrane number corresponds to the number in Table I.

membranes were prepared from casting solutions, including 20% polymer by weight in the following different solvents: chloroform, 1,1,2-trichloroethene and chlorobenzene. Membranes prepared from solvent mixtures of chloroform and 1,1,2-trichloroethene were also tested. The CO<sub>2</sub> permeance data were of the same order of magnitude for all membranes (Table III). However, the mechanical strength of membranes was different. Most membranes except for those prepared from 1,1,2-trichloroethene, and their mixtures in chloroform were fragile and ruptured while testing. This effect of the solvent on the mechanical strength of the membrane can be attributed to the interplay of the precipitation and crystallization rates of the polymer. For further experiments, only 1,1,2-trichloroethene was used as the solvent. Since different solvents did not affect the permeance of  $CO_2$ , their effect was not taken into account for the factorial design experiment.

#### **Effect of Polymer Solution Concentration**

As previously found by Wijmans et al.,<sup>1</sup> the porosity of the top layer of an integrally skinned asymmetric membrane decreases with increasing polymer concentration. At 15.0% by weight of PPO ( $[\eta] = 0.46$  dL g) in trichloroethene, the membranes were very open, and the pure gas permeation rate ratio for the CO<sub>2</sub> : CH<sub>4</sub> was less than unity, indicating Knudsen flow in pores (Table IV). At 20.0% by weight of PPO in trichloroetylene methane, permeance decreased signifi-

	Polymer	Perme 10 <sup>10</sup> (r H	$\begin{array}{c} \text{Permeance} \times \\ 10^{10} \ (\text{mol/m}^2 \ \text{s} \\ \text{Pa}) \end{array}$		
Membrane	(Wt %)	$\mathrm{CO}_2$	$\mathrm{CH}_4$		
L-10 L-5′	$\begin{array}{c} 15.0\\ 20.0\end{array}$	$\begin{array}{c} 142.0\\ 6.3\end{array}$	$\begin{array}{c} 176.0\\ 0.23\end{array}$		

## Table IVEffect of Polymer Concentration on $CO_2$ and $CH_4$ Permeance

Upstream pressure, 690 kPa gauge; solvent, 1,1,2-trichloroethene; the membrane number corresponds to the numbers in Table I.

cantly showing  $\rm CO_2-CH_4$  separation. The concentration of the polymer in the solution can be used as a factor to control the porosity of the membranes.

## **Effect of Additive Concentration**

The effect of different concentrations of 2-ethyl-1hexanol on the permeance and the permeance ratio of PPO membranes was studied. Membranes prepared from 20.0% by weight of PPO( $[\eta]$ = 0.46 dL g) in 1,1,2-trichloroethene with three different additive concentrations were tested and compared to membranes from solutions without any additive. The results are shown in Table V. There is a significant difference in the performance of the membranes prepared from solutions with and without additive. The presence of additive significantly increases the permeation rate of both  $CO_2$  and  $CH_4$ . For the concentration range studied, the permeation rates do not seem to depend on the concentration of the additive. It is possible that the additive concentrations tested

Table VI	Effect	of Molecular	• Weight	of PPO	on
CO <sub>2</sub> Perm	eance				

Membrane	[η] of PPO in Chloroform at 25°C	${ m CO_2} \ { m Permeance}  imes 10^{10} \ ({ m mol/m^2 \ s \ Pa})$
L-1 H-1	$\begin{array}{c} 0.46 \\ 1.0 \end{array}$	5.63 $8.1$

Upstream pressure,  $690\ \rm kPa$  gauge; the membrane number corresponds to the numbers in Tables I and II.

were too large to see the effect of the concentration of the additive on the membrane performance. The permeation rates for  $CO_2$  and  $CH_4$ may have reached a plateau at the additive concentrations studied. The presence of additive in the polymer solution seems to increase the mechanical strength of the final membranes.

#### Effect of the Molecular Weight of PPO

PPO polymer of intrinsic viscosity equal to 0.46 and 1.0 dL g in chloroform at 25°C were used in this study. Integrally skinned asymmetric membranes were prepared from 20.0 and 15.0 wt % in trichloroethene of the solutions. The results are presented in Table VI. Membranes prepared from the higher-molecular-weight PPO exhibited higher  $CO_2$ . The membranes also possessed greater mechanical strength. Therefore, the higher-molecular-weight PPO was chosen for a thorough study using a fractional factorial design. A study on the gas separation for  $CO_2$ -CH<sub>4</sub> gas mixtures was also carried out with membranes prepared from PPO of lower- and higher-molecular-weight. The data are shown in Table VII. A separation factor

Membrane	Additive Concentration (Wt % of Solvent)	$\begin{array}{c} \mathrm{CO_2} \ \mathrm{Permeance} \\ \times \ 10^{10} \\ (\mathrm{mol/m^2 \ s \ Pa}) \end{array}$	$\begin{array}{c} \text{Permeance} \\ \text{Ratio} \\ (\text{CO}_2:\text{CH}_4) \end{array}$
L-5	0	6.29	_
L-5'	0	6.30	_
L-7	12.5	14.0	6.2
L-8	14.3	21.0	2.7
L-9	16.7	20.0	19.0

 Table V
 Effect of Additive Concentration on the Performance of PPO

 Membranes
 Performance of PPO

Concentration of polymer, 20.0 wt %; upstream pressure, 690 kPa gauge; the membrane number corresponds to the numbers in Table I.

Membrane	49.2% $\mathrm{CO}_2$ in CH	4 Mixture	20.4% $\mathrm{CO}_2$ in $\mathrm{CH}_4$ Mixture		
	$\begin{array}{c} \text{Permeance} \times 10^{10} \\ (\text{mol/m}^2 \text{ s Pa}) \end{array}$	Separation Factor	$\begin{array}{c} \mbox{Permeance} \times 10^{10} \\ \mbox{(mol/m}^2 \mbox{ s Pa}) \end{array}$	Separation Factor	
H-3 H-2 L-1	$25.2 \\ 3.25$	$\begin{array}{c} 10.4 \pm 1.4 \\ 19.4 \pm 0.3 \end{array}$	9.28 1.89 1.20	7.7 20.4 22.4	

Table VIISeparation of CO2-CH4 Gas Mixtures

Upstream pressure, 690 kPa gauge; membrane number corresponds to the numbers in Tables I and II.

as high as 22.4 was achieved for 20.4%  $\rm CO_2$  in the  $\rm CH_4$  mixture.

# EFFECT OF CASTING CONDITIONS ON MEMBRANE PERFORMANCE

A  $2^{4-1}$  factorial design was used to determine the effect of four factors. The variables studied, as well as their respective notations and levels, are shown in Table VIII. The codes -1 and +1 denote the low and high level of factors, respectively. The two levels for each variable were selected empirically based on preliminary experiments. The performance results of the membranes prepared from the eight casting conditions chosen on the basis of the factorial design are shown in Table IX. These results indicate that only membranes

		Levels
Factors	-1	+1
A: Concentration of polymer (% by weight)	10	15
<i>B:</i> Presence of additive	None	6 : 1 Chloroform to 2-ethyl- 1-hexanol by weight
C: Evaporation time before gelation	0	1.5 min
D: Temperature of casting solution	Ambient	60°C

Table VIII	<b>Casting Condi</b>	tions for	Fractional
Factorial D	esign Experime	ents	

prepared from condition 10 had good performance with respect to the targeted values of the  $CO_2$ :  $CH_4$  permeance ratio. The  $CO_2$  permeance was significantly lower than the preset value, but the  $CO_2$ :  $CH_4$  permeance ratio of 50 was contained in the range of the  $CO_2$ :  $CH_4$  permeance ratio obtained for these membranes.

The half-normal plot of all the effects on the  $CO_2$ :  $CH_4$  pure gas permeance ratio indicates that the factor *B*, additive, and *AB* 2-factor interaction effect are distinguishable from the rest. Based on the most general model, the following equations were obtained to show the effect of factors *A*, *B*, *C*, and *D* on the  $CO_2$  permeance and the  $CO_2$ :  $CH_4$  permeance ratio, as follows:

$$CO_2 \text{ Perm., mol/m}^2 \text{s Pa}$$

$$= (15.1 + 2.5A + 15.1B + 2.8C + 14.5D + 14.6(BD + AC) + 2.5(CD + AB) + 2.8(BC + AD)) \times 10^{-6}$$

$$CO_2$$
:  $CH_4$  permeance ratio = 49.1 - 20.5A  
- 47.8B - 21.1D + 20.4(BD + AC)  
+ 20.8(CD + AB)

## **OPTIMIZATION**

With the use of the results obtained from the factorial design experiments, attempts were made to optimize the casting conditions in order to obtain the best values for  $CO_2$  permeance and the  $CO_2$ :  $CH_4$  permeance ratio. Because the intercept of the model for the pure gas permeation rate ratio was 49.1, very close to the preset value of 50, a test with the scaled conditions of A = 0, B

Condition	Polymer Concentration (Wt %)	Additive	Evaporation Time (min)	Temperature of Casting Solution (°C)	${ m CO_2} \ { m Permeance}  imes 10^9 \ ({ m mol/m^2 \ s \ Pa})$	${{ m CO}_2: { m CH}_4}$ Permeance Ratio
1	10	No	0	Room	2.80	_
2	10	No	0	Room	1.38	_
3	15	No	0	60	1.15	3.38
4	15	No	0	60	2.16	1.52
5	10	Yes	0	60	4330.0	0.60
6	10	Yes	0	60	5390.0	0.48
7	15	Yes	0	Room	79.8	2.33
8	15	Yes	0	Room	76.4	2.62
9	15	Yes	0	Room	52.3	2.39
10	10	No	1.5	60	1.09	34.8
11	10	No	1.5	60	1.22	
12	15	No	1.5	Room	0.98	_
13	15	No	1.5	Room	0.98	_
14	10	Yes	1.5	Room	198.0	1.4
15	15	Yes	1.5	60	7600.0	0.68
16	15	Yes	1.5	60	6330.0	0.7

Table IX Results from Fractional Factorial Design Experiments

= 0, and D = 0 was attempted. The scaled value of factor C of -1 was chosen since it was not significant for the permeation rate ratio, but there was less possible error in immersing the membranes immediately than to have a timed solvent evaporation. The membranes prepared under the chosen conditions are coded as FO. Three membrane coupons were tested. The uncoded membrane preparation variables and the membrane performance data are given in Table X.

The membranes obtained under these conditions had good mechanical strength and were  $CO_2$ -selective. Permeance ratio data were slightly higher than the intrinsic value<sup>9</sup> of 16 for homogeneous PPO membranes. They showed, however, a  $CO_2$  permeance significantly higher than the data given in Table VI with a comparable  $CO_2$ -CH<sub>4</sub> selectivity.

Contour plots of the modeled  $CO_2$  permeance and the  $CO_2$ :  $CH_4$  permeance ratio were drawn in order to determine the casting conditions that would give a membrane that would have both the preset  $CO_2$  permeance of  $30.0 \times 10^{-9}$  mol/m<sup>2</sup> s Pa and a  $CO_2$ :  $CH_4$  permeance ratio of 50. (Figs. 1 and 2). In Figure 1, *A* and *C* were fixed to 0 and -1, respectively, and *B* and *D* were varied. It may be observed that permeance ratio decrease from 45:60 to 0:15 along the line corresponding to the  $CO_2$  permeance of  $6.25 \times 10^{-7}$  mol/m<sup>2</sup> s Pa. A set

Table X Results from the Optimization of Membrane Casting Conditions

Membrane	Polymer Concentration (Wt %)	Additive (Wt % of Total Solvent)	Evaporation Time (min)	Temperature of Casting Solution (°C)	$\begin{array}{c} \mathrm{CO_2~Permeance} \times \ 10^9 \\ \mathrm{(mol/m^2~s~Pa)} \end{array}$	$\begin{array}{c} \mathrm{CO}_2 : \mathrm{CH}_4 \\ \mathrm{Permeance} \\ \mathrm{Ratio} \end{array}$
FO	12.5	7.0	0	40	6.81	_
FO	12.5	7.0	0	40	11.9	17.0
FO	12.5	7.0	0	40	6.87	21.1
OP1	12.5	8.75	0	23	9.22	19.2
OP1	12.5	8.75	0	23	16.1	14.4
OP2	10.0	9.8	0	27	554.0	0.7
OP2	10.0	9.8	0	27	422.0	0.7
OP2	10.0	9.8	0	27	634.0	0.7

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0.6	1	+	+	+	/+	-	=	Ħ	=	-	-			,	,	•	•	,	•	•	•	•
0.5	1	0	÷	+	\ +\	÷	=	=	=	22	-		-	-	,	•	,	•		•	•	•
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0.3	+	0	0	0	+	/+	÷	23	=	×	Ħ	-	-	-	-	,	,	,	•	•	•	•
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**Figure 1** Contour plot of the  $CO_2$ :  $CH_4$  pure gas permeance ratio as a function of additive concentration (B) and casting solution temperature (D) with polymer concentration A = 0 and evaporation time C = -1, with the target  $CO_2$  permeance region indicated and a set of optimum casting conditions 1, identified **0**.

of optimum conditions 1(OP1) corresponding to  $\mathbf{0}$  in Figure 1 are as follows: A = 0: 12.5 wt % PPO; B = 0.25: 8.75 wt % 2-ethyl-1-hexanol; C = -1, no evaporation of solvent before gelation; and D = 0.85, casting solution kept at 23.0°C. Another set of optimum conditions 2 (OP2) corresponding

to @ in Figure 2 are as follows: A = 1: 10 wt % PPO; B = 0.4: 9.8 wt % 2-ethyl-1-hexanol; C = -1, no evaporation of solvent before gelation; and D = 0.65, casting solution kept at 27.0°C.

The membranes were prepared under the above sets of conditions and subjected to gas per-

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**Figure 2** Contour plot of the  $CO_2$ :  $CH_4$  pure gas permeance ratio as a function of additive concentration (*B*) and casting solution temperature (*D*) with polymer concentration A = -1 and evaporation time C = -1, with the target  $CO_2$  permeance region indicated and a set of optimum casting conditions 2, identified **2**.

meation experiments. The results are presented in Table X. The best results obtained were from the membrane that gave a selectivity of 19.2 and a  $\rm CO_2$  permeation rate of 9.22  $\times$  10<sup>-9</sup> mol/m<sup>2</sup> s Pa. The second set of conditions gave membranes that were very open and not selective.

These new data points were also used to improve the models for the  $CO_2$  permeance and the  $CO_2$ :  $CH_4$  permeance rate ratio by adding more data points and more degrees of freedom. It was also possible to verify the presence of quadratic terms, for example,  $B^2$ . By backward elimination

from the most general model, the following equations were obtained for  $CO_2$  permeance and the  $CO_2$ :  $CH_4$  permeance ratio.

$${
m CO}_2$$
 permeance, mol/m $^2$  s Pa =  $(0.002 + 1.48B + 1.44D + 1.34BD + 1.49B^2) imes 10^{-6}$ 

 $CO_2: CH_4$  permeance ratio = 44.8 - 51.7B+ 25.5AB + 24.1BD

where the factors A, B, and D are scaled from -1 to +1 as in Table VIII. As expected from the factorial design analysis, factor B, the concentration of additive is very significant for both the CO<sub>2</sub> permeance and the CO<sub>2</sub> : CH<sub>4</sub> permeance ratio. The factor C, evaporation time before gelation, was not significant for the preparation of these PPO membranes in the range studied. All the variables left in the model are significant at the 0.01 level for the CO<sub>2</sub> : CH<sub>4</sub> pure gas permeance rate ratio.

## **CONCLUSIONS**

Based on the experiments performed, it is possible to prepare asymmetric PPO with  $CO_2-CH_4$  separation capabilities. With respect to membrane performance and mechanical strength, the following membrane preparation factors were found to be most significant: membrane wet casting thickness, solvent evaporation, and polymer and additive concentrations. The higher-molecular-weight PPO exhibited both the highest  $CO_2$  permeance and the  $CO_2: CH_4$  permeance ratio, as well as good mechanical strength.

By using a fractional factorial design, it was possible to study the effect and interaction of polymer concentration, the additive concentration, the evaporation time before gelation, and the temperature of the casting solution on the performance of the PPO gas separation membranes. The  $CO_2$  permeance of the membranes made from the higher-molecular-weight PPO was adequately modelled by a straight line; however, a linear model may not be appropriate for modelling the  $CO_2$ :  $CH_4$  permeance ratio. Using these models, it was possible to identify two sets of casting conditions that should have given the preset  $CO_2$ permeance and the  $CO_2$  :  $CH_4$  permeance ratio. When these membranes were prepared and tested, the preset values were not obtained; but improvements in membrane performance were achieved, and a  $\rm CO_2$  permeance of 9.22  $\times$   $10^{-9}$ (mol/m<sup>2</sup> s Pa) and a  $CO_2$  :  $CH_4$  pure gas permeance ratio of 19.2 was obtained.

Further work on optimization of membrane preparation conditions is necessary to improve membrane performance.

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