

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231372553>

# Advanced Fabrication of Carbon Molecular Sieve Membranes by Nonsolvent Pretreatment of Precursor Polymers

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · AUGUST 2004

Impact Factor: 2.59 · DOI: 10.1021/ie049606c

---

CITATIONS

77

---

READS

77

3 AUTHORS, INCLUDING:



Pei Shi Blyss Tin

Singapore Polytechnic

12 PUBLICATIONS 517 CITATIONS

SEE PROFILE



Tai-Shung Chung

National University of Singapore

726 PUBLICATIONS 19,531 CITATIONS

SEE PROFILE

## SEPARATIONS

## Advanced Fabrication of Carbon Molecular Sieve Membranes by Nonsolvent Pretreatment of Precursor Polymers

Pei Shi Tin,<sup>†</sup> Tai-Shung Chung,<sup>\*,†</sup> and Anita J. Hill<sup>\*,‡,§</sup>

Department of Chemical and Biomolecular Engineering, National University of Singapore, Singapore 119260, Singapore, CSIRO Manufacturing & Infrastructure Technology, Private Bag 33, Clayton South MDC, Victoria 3169, Australia, and School of Chemistry, Monash University, Clayton, Victoria 3800, Australia

We have conducted an extensive study to investigate the effects of nonsolvent (methanol, ethanol, 1-propanol, and 1-butanol) pretreatment of polyimide precursor before carbonization on membrane structure and on the separation performance of carbon molecular sieve membranes (CMSMs). The measured gas separation properties show that carbon membranes prepared with nonsolvent pretreatment have a lower flux and higher selectivity, suggesting a narrower pore size distribution. XRD data show a slightly smaller *d* spacing in pretreated CMSMs. Positron annihilation lifetime spectroscopy results indicate smaller pores in the CMSMs pretreated with nonsolvents. The best separation efficiency is obtained by carbon membranes pyrolyzed from ethanol-treated polymers. The CO<sub>2</sub>/CH<sub>4</sub> selectivity of Matrimid- and P84-derived carbon membrane increases significantly from 61 to 169 and 89 to 139, respectively, after ethanol pretreatment as compared to those carbon membranes when untreated. This study demonstrates for the first time that nonsolvent pretreatment of polyimide precursors can play an essential role in the transport properties of high-performance CMSMs.

## 1. Introduction

Today, large-scale polymeric membrane systems are widely used in different separation processes. However, inorganic membrane technology is rapidly receiving global attention owing to superior separation properties when compared to polymeric membranes. Inorganic membranes, especially molecular sieving materials such as silica, zeolites, and carbon,<sup>1,2</sup> are research-intensive due to their potential in surpassing the upper bound limit of polymeric membranes. Among these materials, carbon molecular sieve membranes (CMSMs) have been recognized as attractive gas separation materials due to their high flux and selectivity.<sup>3–8</sup> Moreover, due to their rigidity, CMSMs are able to retain their stability in aggressive (vapor or solvents, and nonoxidizing acids or bases) and adverse (high temperature and pressure operation) environments that are too harsh for polymeric membranes.<sup>2–4,8–12</sup>

CMSMs are usually fabricated by carbonization of polymeric precursors. Their porous nature has led to high permeability, while their molecular sieving morphology permits effective size and shape separation between gas molecules and restricts the degree of rotational freedom of gas penetrants.<sup>13</sup> In addition, separation properties of CMSMs can be finely adjusted to a specific separation task by tailoring the microstructures

through thermal and chemical treatments. The ability to tailor the structure and properties of carbon membranes holds much promise in application of these materials to gas separation problems.

The main drawback to immediate application of CMSMs is their very high production cost. The cost per unit of membrane area for carbon membranes is between 1 and 3 orders of magnitude greater than polymeric membranes.<sup>12</sup> As a consequence, an immediate challenge faced by membrane scientists is to develop “simple and novel” approaches to control membrane microporous morphology and to fabricate carbon membranes with superior separation performance.

Fabrication of CMSMs is a complicated process that involves several steps, such as precursor selection, polymeric membrane preparation, carbonization, and pre/posttreatment. Optimization of these fabrication parameters is essential to produce high-performance CMSMs.<sup>2,14</sup> Most of the past investigations have focused on the effects of pyrolysis conditions<sup>15</sup> and posttreatment,<sup>9,16–18</sup> examining the impact of conditions such as pyrolysis temperature, carbonization environment, heating rate, and soak time on carbon membrane performance. As shown by our previous work, nonsolvent pretreatment of precursors is also a critical factor in tailoring the microstructure of CMSMs to determine the separation efficiency.<sup>19</sup>

Pretreatment of precursors has been shown to alter the chain packing or chain segmental mobility of the polymer,<sup>20,21</sup> which can have a significant effect on the structural organization of membrane during pyrolysis. Precursor pretreatment stabilizes the structure of the precursors, acts to maintain the molecular structure of

\* To whom correspondence should be addressed. E-mail: chencts@nus.edu.sg (T.-S.C.) and Anita.Hill@csiro.au (A.J.H., contact regarding PALS measurements).

<sup>†</sup> National University of Singapore.

<sup>‡</sup> CSIRO Manufacturing & Infrastructure Technology.

<sup>§</sup> Monash University.

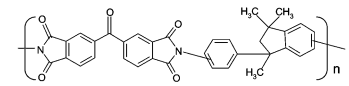
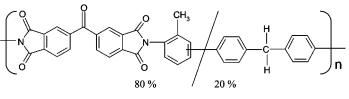
the carbon chains, and/or enhances the uniformity of pore formation during the pyrolysis process. Current pretreatments include oxidation, chemical treatment, and physical methods such as stretching. Oxidation or thermostabilization is the most popular and commonly used method to pretreat the polymeric precursors before pyrolysis. This pretreatment stabilizes the structure of the precursors in order to withstand the high temperatures of pyrolysis. Additionally, thermostabilization can maximize the carbon yields of resultant membranes by preventing excessive volatilization of elemental carbon during carbonization. Oxidation has been carried out by Kusuki et al.,<sup>22</sup> who thermally treated the precursors (polymeric hollow fibers) in atmospheric air at 400 °C for 30 min before pyrolysis. Several researchers, such as Tanihara et al.,<sup>6</sup> Okamoto et al.,<sup>23</sup> and David and Ismail,<sup>24</sup> have also applied thermostabilization in their studies. Schindler and Maier proposed a chemical pretreatment using chemical reagent, where the capillary acrylonitrile membranes were pretreated in aqueous hydrazine solution before carbonization.<sup>25</sup> A concentration of at least 40 wt % hydrazine is suggested in order to solve the problem of tar formation, and the best results were achieved by pretreatment with 80% hydrazine hydrate for 30 min at a solution temperature of 90 °C. Most importantly, Schindler and Maier found that the hydrazine pretreatment improved the dimensional stability of membrane and at the same time prevented tar formation and clogging of pores during the pyrolysis step. Chen and Harrison modified polyacrylonitrile carbon fiber precursors via physical stretching in *N,N*-dimethylformamide (DMF).<sup>26</sup> The postspinning plasticization and stretching process were shown to remove the surface defects of fiber and attenuate the fiber diameter to promote more uniform heat treatment during pyrolysis. Additionally, it was suggested that this process facilitated further molecular orientation by reducing the molecular dipole interactions. The fibers produced were uniformly stabilized fibers with a high degree of graphitic planes, few defects per unit volume, and good mechanical properties. However, it was noted that unstretched or partially stretched membranes are sometimes preferred, because they offer greater dimensional stability and a bigger pore size after carbonization.<sup>25</sup>

Recently, we reported a novel approach in pretreating the polymeric precursor using the nonsolvent methanol before pyrolysis.<sup>19</sup> We emphasized the importance of the swelling effect on the polyimide precursors, where swelling by methanol emerged as an effective modification method in producing CMSMs with excellent separation capability. Therefore, it is worthwhile to expand our previous scope and examine more closely the influence of other nonsolvent pretreatment, such as with ethanol, propanol, and butanol, on the separation performance of resultant carbon membranes. Here we investigate (1) whether these nonsolvents are capable of inducing structural modification in the polymer precursors, (2) whether the nonsolvent pretreatment induces uniform pores, and (3) whether more selective carbon membranes can be produced with tailored pore sizes and narrow pore size distribution after modification.

## 2. Experimental Section

**2.1. Materials and Preparation of Polymer Precursors.** Two commercially available polyimide poly-

**Table 1. Chemical Structure and Properties of Matrimid 5218 and P84**

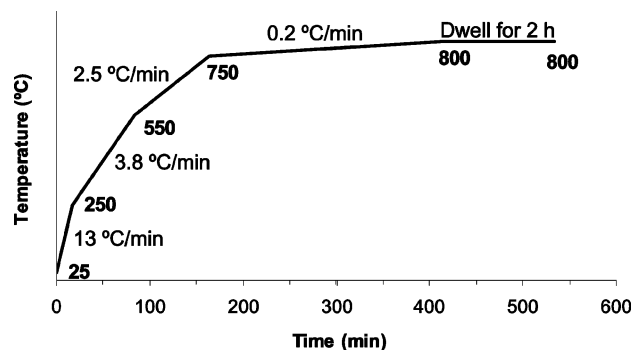
Material	Chemical Structure	$T_g$ (°C)	Density (g/cm <sup>3</sup> )
Matrimid® 5218		323	1.22
P84		315	1.31

mers were used as the precursors in this study, Matrimid 5218 [3,3',4,4'-benzophenone tetracarboxylic dianhydride and 5(6)-amino-1-(4'-aminophenyl)-1,3-trimethylindane] and P84 (copolyimide of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and 80% methylphenylenediamine + 20% methylenediamine). Table 1 shows the chemical structures, glass transition temperatures, and density values for these two materials.

Polymer precursors were first prepared as dense films before pyrolysis. The Matrimid 5218 powder used in this study was purchased from Ciba Polymers (Hawthorne, NY), while the P84 powder was obtained from Lenzing. Dichloromethane and DMF were the solvents for Matrimid 5218 and P84, respectively. The polymers were dried overnight at 120 °C under vacuum prior to use. A solution was prepared by dissolving 2 wt % of the polymer powder in solvent. The solution was then filtered with 1  $\mu$ m filters (Whatman) and cast onto a wafer plate. The casting process for Matrimid was carried out at room temperature. For P84, the film was cast in an oven at 55 °C due to the high boiling point of DMF (153 °C). The polymer films were formed after most of the solvent had evaporated slowly. The nascent films were dried in a vacuum at 250 °C for 48 h to remove the residual solvents. Finally, the membrane films with a thickness of about 50–60  $\mu$ m were ready for pretreatment, pyrolysis, and testing.

**2.2. Nonsolvent Pretreatment of Polymeric Precursor.** The polymeric membranes were subjected to an extremely simple pretreatment before pyrolysis. The swelling agents used in this investigation are methanol (MeOH), ethanol (EtOH), 1-propanol (PpOH), and 1-butanol (BtOH); they are nonsolvents for these two polyimides. However, butanol pretreatment is only conducted for Matrimid polyimide, as it shows no significant effect in modifying P84 precursors. This is due to the fact that the P84 precursor is more tightly packed (with smaller values of  $d$ -space and fractional free volume) and has a larger  $\Delta\delta_{sp}$  with butanol as compared to the Matrimid precursor. The pretreatment was performed by immersing the membrane films into the nonsolvent for 1 day at room temperature, followed by drying naturally for 24 h at room temperature before the carbonization process. The swelling of polyimides by these nonsolvents is confirmed by the weight gained by films after the nonsolvent treatment.

**2.3. Preparation of Carbon Molecular Sieves Membranes.** The pyrolysis was performed using a Centurion Neytech Qex vacuum furnace, where the polymer precursors were placed on wire meshes and carbonized under vacuum. The function of the wire meshes is to create balanced heat and vacuum environments above and below the polymer precursors during pyrolysis. In general, the final pyrolysis temperature



**Figure 1.** Steps involved in the pyrolysis process for a final temperature of 800 °C.

was reached in several steps: the polymer films were heated to 250 °C from room temperature at a rate of 13 °C/min; subsequently, the temperature was raised to 550 and 750 °C with a heating rate from 2.5 to 3.8 °C/min and then the final temperature was reached at a rate of 0.2 °C/min. The final temperature was 800 °C, and the membrane was held at this temperature for 2 h. After completing the heating cycle, membranes were furnace cooled slowly in a vacuum to room temperature. The detailed pyrolysis protocol for 800 °C is shown in Figure 1. The nomenclature of resultant carbon membranes is given in the form "CM-polyimide-nonsolvent-pyrolysis temperature".

**2.4. Measurements of Physical Properties.** Several characterization methods were used to study the CMSMs fabricated with different nonsolvent pretreatment. The weight loss of carbon membranes during pyrolysis was characterized by thermogravimetric analysis (TGA) with a TGA 2050 thermogravimetric analyzer (TA Instruments). The analysis was carried out with a ramp of 10 °C/min in the temperature range from 50 to 900 °C. The purge gas was N<sub>2</sub> and its flow rate was controlled at 50 mL/min.

Wide-angle X-ray diffraction (WAXD) was performed to quantitatively measure the ordered dimensions and interchain spacing of carbon membranes with a Bruker X-ray diffractometer (Bruker D8 advanced diffractometer) at room temperature. The  $d$  spacing values are interpreted as the average chain spacing. The measurement was completed in a scan range of  $2\theta = 2.5$ – $65.4^\circ$  with a step increment of  $0.02^\circ$ . Ni-filtered Cu K $\alpha$  radiation with a wavelength of  $\lambda = 1.5418$  Å was used in the experiments. The average  $d$  spacing was determined on the basis of Bragg's law

$$n\lambda = 2d \sin \theta \quad (1)$$

where  $d$  is the dimension spacing,  $\theta$  is the diffraction angle,  $\lambda$  is the X-ray wavelength, and  $n$  is an integral number (1, 2, 3, ...).

The glass transition temperature ( $T_g$ ) was measured by a Mettler Toledo differential scanning calorimeter (DSC) model DSC822. The heating and cooling rates were 10 °C/min. The measurements were conducted in a dry nitrogen environment with a flow rate of 20 mL/min. The sample was first heated to 400 °C and held for 2 min before cooling to room temperature. These steps were repeated once. The  $T_g$  of polymer was determined from the midpoint of the baseline-shift region. The  $T_g$  value was identified from the first DSC run for all nonsolvent pretreated films, while the second run was adopted for untreated films in the determina-

**Table 2.** Glass Transition Temperatures ( $T_g$ ) of Matrimid and P84 Membranes<sup>a</sup>

polymer	$T_g$ (°C)	polymer	$T_g$ (°C)
Matrimid precursor	323	P84 precursor	315
methanol-treated Matrimid	314	methanol-treated P84	304
ethanol-treated Matrimid	312	ethanol-treated P84	302
propanol-treated Matrimid	314	propanol-treated P84	307
butanol-treated Matrimid	315		

<sup>a</sup> All nonsolvent treatment took place for 1 day.

tion of  $T_g$ . The  $T_g$  for each sample was estimated from the average value of two specimens.

Positron annihilation lifetime spectroscopy (PALS) measurements were made in dry nitrogen at room temperature using an automated EG&G Ortec fast-fast coincidence system. The timing resolution of the system was 240 ps determined using the prompt curve from a <sup>60</sup>Co source with the energy windows set to <sup>22</sup>Na events. Carbon films approximately 15 μm thick were stacked to a total thickness of 1 mm on either side of the 30 μCi <sup>22</sup>Na–Ti foil source. Five spectra for each sample were collected, with each spectrum taking 1 h to collect, and the results are the mean values for these spectra. The standard deviations reported are the population standard deviations for five spectra, and each spectrum consisted of approximately 1 million integrated counts. The spectra were modeled as the sum of two decaying exponentials using the computer program PFPOSFIT. No source correction was used in the analysis on the basis of a fit for pure Al standards of  $169 \pm 2$  ps,  $99.3 \pm 0.3\%$ ; 820 ps, 0.7%.

**2.5. Measurements of Gas Permeation.** Pure gas permeabilities were determined by a constant volume method reported elsewhere.<sup>27</sup> The permeabilities were obtained in the sequence of N<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, and O<sub>2</sub> at 35 °C and 10 atm. The gas permeability  $P$  was determined from the rate of pressure increase ( $dp/dt$ ) obtained when permeation reached steady state using eq 2,

$$P = \frac{273 \times 10^{10}}{760} \frac{VL}{AT \left( \frac{p_0 \times 76}{14.7} \right)} \left( \frac{dp}{dt} \right) \quad (2)$$

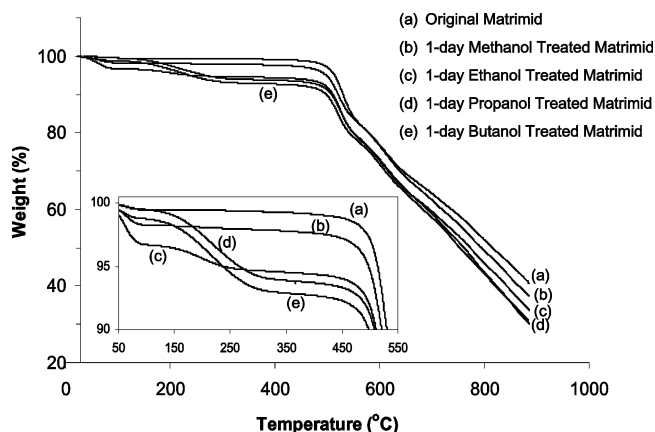
where  $P$  is the permeability of a membrane to a gas in barrer (1 barrer =  $1 \times 10^{-10}$  cm<sup>3</sup> (STP)·cm/cm<sup>2</sup> s cmHg),  $V$  is the volume of the downstream chamber (cm<sup>3</sup>),  $A$  refers to the effective area of membrane (cm<sup>2</sup>),  $L$  is the thickness of membrane (cm),  $T$  is the operating temperature (K),  $dp/dt$  is the rate of pressure measured by the pressure transducer in the downstream stream chamber (mmHg/s), and  $p_0$  is the pressure of feed gas in the upstream chamber in psia. The ideal separation factor of a membrane for gas A to gas B is defined as follows:

$$\alpha_{A/B} = P_A/P_B \quad (3)$$

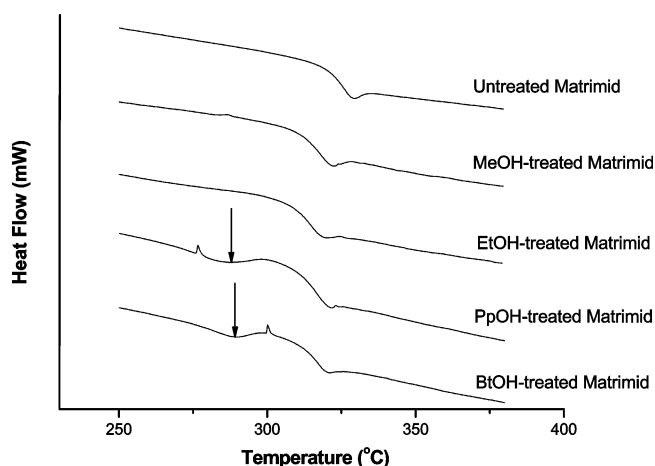
### 3. Results and Discussion

**3.1. Thermal Behavior of Nonsolvent-Treated Matrimid and P84 Precursors.** The nonsolvent pretreatment on polyimides may induce a structural modification that influences the morphology of resultant CMSMs. Accordingly, an investigation of the thermal behavior of nonsolvent-treated polyimides has been carried out. Table 2 compares the glass transition temperatures ( $T_g$ ) of untreated and nonsolvent-treated





**Figure 2.** Thermal degradation of untreated and nonsolvent-treated Matrimid analyzed by TGA.

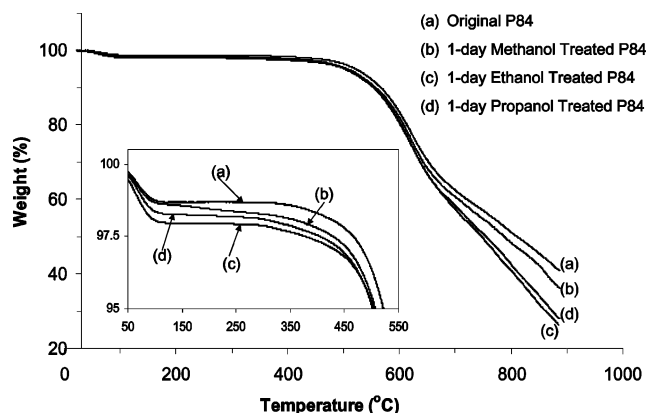


**Figure 3.** DSC thermograms of nonsolvent-treated Matrimid.

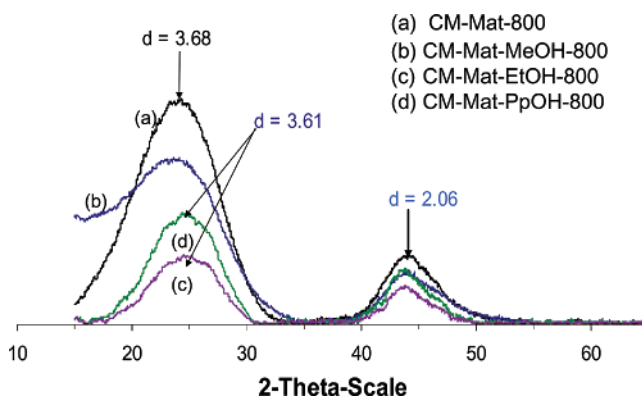
polyimides obtained from DSC experiments. It is clear that the  $T_g$ 's of polyimides vary with the nonsolvent treatment, which reduces the  $T_g$ 's of both Matrimid and P84. The lowest  $T_g$ 's have been measured for ethanol-treated Matrimid and P84. The reduction in  $T_g$  is attributed to the plasticization of polymer precursor by the low molecular weight nonsolvent swelling agents. These nonsolvent molecules weaken and replace the polymer–polymer interactions with polymer–solvent interactions.<sup>28</sup> The  $T_g$  data support the view that nonsolvent pretreatment allows chain swelling and rearrangement that can modify the pore structure of the final CMSMs.

### 3.2. Characterization of Carbon Membranes.

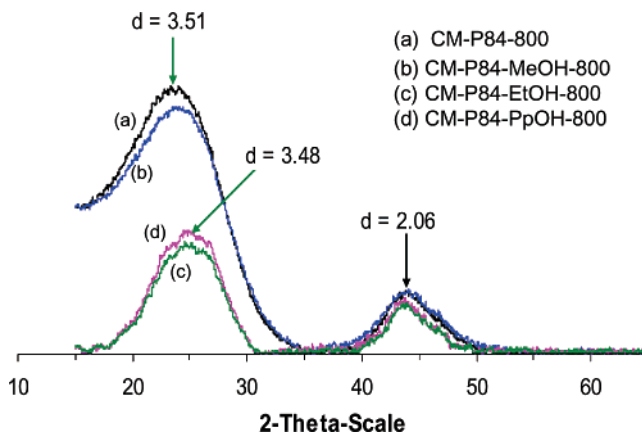
Thermal stability and polymer degradation during the pyrolysis process were investigated using TGA under  $N_2$  inert atmosphere. Figure 2 presents thermogravimetric data for untreated and nonsolvent-treated Matrimid membranes. Untreated Matrimid exhibits the highest thermal resistance and the highest residual weight percent after heating to 900 °C. In the thermograms of methanol- and ethanol-treated membranes, a distinct weight loss can be observed before the main decomposition (at around 500–550 °C), which most likely results from the desorbed water and nonsolvents below 150 °C. However, an additional evolution route is detected below 300 °C for 1-propanol- and 1-butanol-treated Matrimid membranes. This extra thermal transition at ca. 300 °C is further verified by DSC thermograms, as indicated with arrows in Figure 3. As tabulated in Table 3, the molecular sizes and boiling points of



**Figure 4.** Thermal degradation of untreated and nonsolvent-treated P84 analyzed by TGA.



**Figure 5.** WAXD for CMSMs derived from untreated and nonsolvent-treated Matrimid 5218 pyrolyzed at 800 °C.


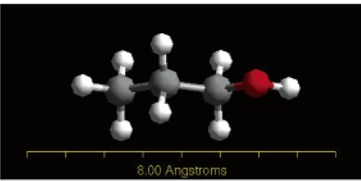
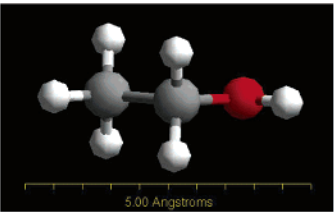
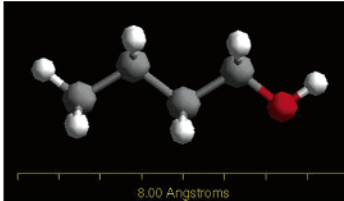


**Figure 6.** WAXD for CMSMs derived from untreated and nonsolvent-treated P84 pyrolyzed at 800 °C.

1-propanol and 1-butanol are higher than those of methanol and ethanol. Presumably, the reduction of weight below 300 °C might be due to the decomposition of residual, strongly bound 1-propanol/1-butanol.

Figure 4 illustrates the TGA results of P84 membranes. Similar to the case of the Matrimid membranes, the final weight loss of nonsolvent-treated P84 membranes is greater than that of the untreated P84. The weight reduction below 150 °C is also caused by the evaporation of water and residual nonsolvents. Nevertheless, it can be seen that the degradation of all P84 films displays a similar trend over a temperature range of 50–550 °C. The similarity indicates that the nonsolvents may be less effective in structural alteration of the P84 precursor than the Matrimid precursor. This

Table 3. Chemical Structures and Properties of Nonsolvents Used for Pretreatment<sup>a</sup>

Solvent	Properties	Solvent	Properties
Methanol 	BP = 64.7 $\rho$ = 0.792 $M_w$ = 32.04 $V_m$ = 40.45	1-Propanol 	BP = 97.8 $\rho$ = 0.804 $M_w$ = 60.09 $V_m$ = 74.74
Ethanol 	BP = 78.4 $\rho$ = 0.789 $M_w$ = 46.07 $V_m$ = 58.39	1-Butanol 	BP = 117 $\rho$ = 0.810 $M_w$ = 74.12 $V_m$ = 91.51

<sup>a</sup> BP = boiling point (°C).  $\rho$  = density at 20 °C (g/cm<sup>3</sup>).  $M_w$  = molecular weight (g/mol).  $V_m$  = molar volume (cm<sup>3</sup>/mol).

Table 4. Solubility Parameters ( $\delta_{sp}$ ) of Polyimides and Nonsolvents

polymer	$\delta_{sp}$ (cal/cm <sup>3</sup> ) <sup>1/2</sup>	solvent	$\delta_{sp}$ (cal/cm <sup>3</sup> ) <sup>1/2</sup>	$\Delta\delta_{sp}$
Matrimid	14.68	methanol	14.5	0.18
		ethanol	12.7	0.98
		1-propanol	11.9	2.78
		1-butanol	11.4	3.28
P84	18.03	methanol	14.5	3.53
		ethanol	12.7	5.33
		1-propanol	11.9	6.13
		1-butanol	11.4	6.63

Table 5. PALS Parameters for Selected CMSMs

sample <sup>a</sup>	$\tau_1$ (ps) ± 6	$I_1$ (%) ± 3	$\tau_2$ (ps) ± 6	$I_2$ (%) ± 3
CM-P84-800	220	30	378	70
CM-MAT-800	220	32	381	68
CM-MAT-MeOH-800	205	19	359	81
CM-MAT-EtOH-800	185	12	352	88
CM-MAT-PpOH-800	197	32	368	68

<sup>a</sup> Membrane ID: CM-polyimide-nonsolvent-pyrolysis temperature.

phenomenon is not surprising, as the P84 precursor is more tightly packed, with substantially higher density and lower fractional free volume than the Matrimid polyimide. The difference in solubility parameter between the polyimides and nonsolvents ( $\Delta\delta_{sp}$ ) is also greater for P84 than Matrimid (Table 4). As generally discussed, the interaction between polymer and nonsolvent becomes more effective when their respective solubility parameters are similar to each other.<sup>29</sup>

WAXD spectra for CMSMs derived from nonsolvent-treated Matrimid and P84 precursors are illustrated in Figures 5 and 6, respectively. There is a slight decrease in  $d$  spacing (from 3.68 to 3.61 Å for Matrimid and from 3.51 to 3.48 Å for P84) for CMSMs derived from nonsolvent-treated polyimides. There is no trend with the varying nonsolvents; all nonsolvents result in similar, very slight decrease in  $d$  spacing.

Table 5 displays the PALS results for selected membranes. Typically PALS analysis of polymeric and organic-inorganic hybrid membranes made from poly-

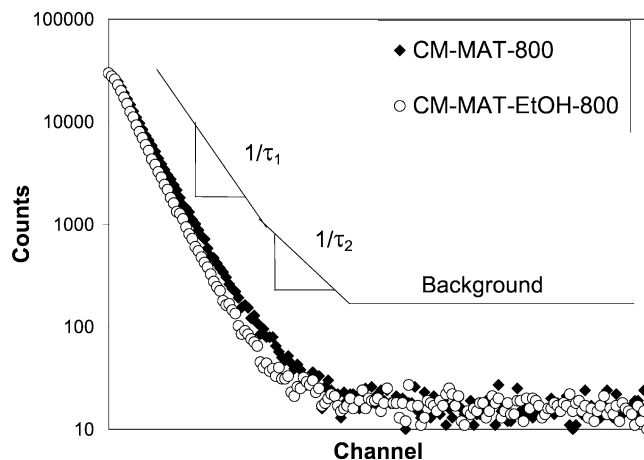


Figure 7. PALS timing histograms for untreated Matrimid and ethanol-pretreated Matrimid CMSMs showing the two-component fit giving positron lifetimes  $\tau_1$  and  $\tau_2$ .

imides<sup>30,31</sup> relies on the formation and detection of ortho-positronium (oPs), a long-lived component ( $\tau_3 > 1$  ns) that gives information on the size of free volume cavities or pores. In the present work, no oPs component was detected, presumably due to the electronic conductivity of the pyrolyzed membranes. Previous PALS work<sup>32</sup> on aromatic polyimide films has shown that even when there is no oPs formation for polyimides such as Kapton and BFDA- and 6FDA-based polyimides, the long lifetime component  $\tau_2$  corresponds to positrons trapped in free volume cavities or pores. This lifetime,  $\tau_2$ , is shorter for smaller pores and this lifetime can be used to indicate the mean size of the pores.<sup>32</sup>

Table 5 shows that the PALS parameters are similar for untreated Matrimid and P84 CMSMs. Nonsolvent pretreatment reduces the positron lifetimes  $\tau_1$  and  $\tau_2$ . The PALS raw data are shown in Figure 7, which compares untreated Matrimid with ethanol-pretreated Matrimid CMSMs. The ethanol pretreatment was the most effective at reducing  $\tau_2$  and hence the mean pore size. The propanol pretreatment was the least effective at reducing the pore size, as indicated by  $\tau_2$ , and this

**Table 6. Gas Permeation Properties of Carbon Membranes Derived from Nonsolvent-Treated Matrimid**

membrane <sup>a</sup>	permeability (barrer)				selectivity		
	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /N <sub>2</sub>
CM-MAT-800	227	30.3	611	10.0	7.5	61	20
CM-MAT-MeOH-800	138	15.8	423	4.8	8.8	88	27
CM-MAT-EtOH-800	75.4	6.3	191	1.1	12	169	30
CM-MAT-PpOH-800	204	24.1	565	6.7	8.5	84	23
CM-MAT-BtOH-800	186	21	547	7.0	8.9	78	26

<sup>a</sup> Membrane ID: CM-polyimide-nonsolvent-pyrolysis temperature.**Table 7. Gas Permeation Properties of Carbon Membranes Derived from Nonsolvent-Treated P84**

membrane	permeability (barrer)				selectivity		
	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /N <sub>2</sub>
CM-P84-800	158	17.8	499	5.6	8.9	89	28
CM-P84-MeOH-800	132	13.6	402	3.7	9.7	109	30
CM-P84-EtOH-800	101	9.0	278	2.0	11.2	139	31
CM-P84-PpOH-800	144	14.6	428	3.9	9.9	110	29

<sup>a</sup> Membrane ID: CM-polyimide-nonsolvent-pyrolysis temperature.**Table 8. Gas Transport Properties of Carbon Membranes Derived from Methanol- and Ethanol-Treated Matrimid at Various Immersion Times**

membrane <sup>a</sup>	permeability (barrer)				selectivity		
	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>	CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	CO <sub>2</sub> /N <sub>2</sub>
CM-MAT-800	227	30.3	611	10.0	7.5	61	20
CM-MAT-2 h-MeOH-800	205	26.6	563	7.6	7.7	74	21
CM-MAT-6 h-MeOH-800	196	22.8	501	6.4	8.6	78	22
CM-MAT-1 day-MeOH-800	138	15.8	423	4.8	8.8	88	27
CM-MAT-2 h-EtOH-800	176	18.7	480	4.7	9.4	102	26
CM-MAT-6 h-EtOH-800	145	14.8	384	3.5	9.8	110	26
CM-MAT-1 day-EtOH-800	75.4	6.3	191	1.1	12	169	30

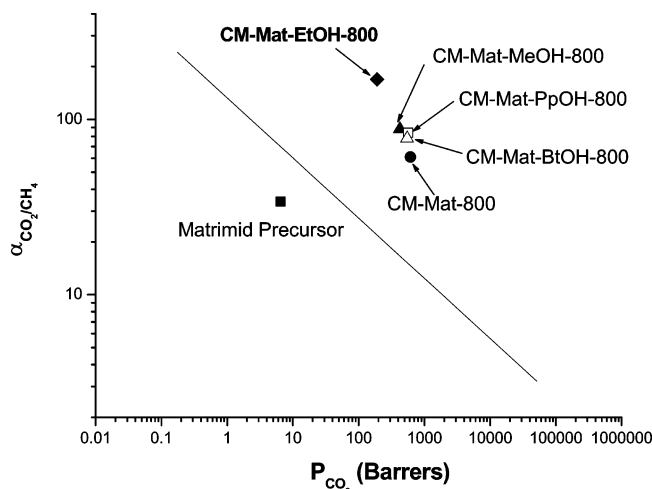
<sup>a</sup> Membrane ID: CM-polyimide-treatment duration-nonsolvent-pyrolysis temperature.

PALS result is supported by the gas transport properties presented in the next section.

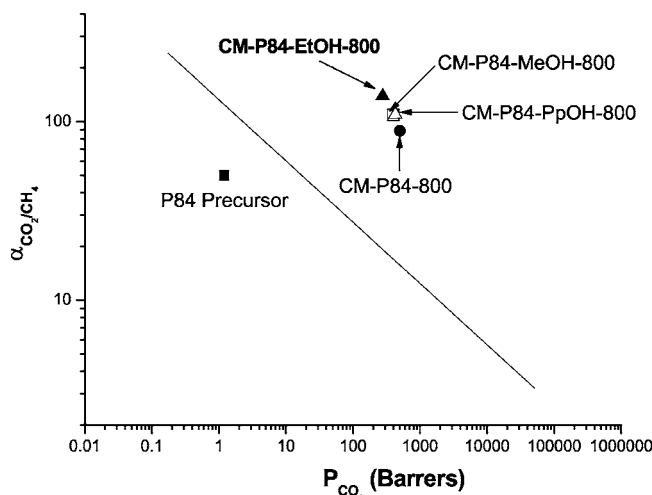
**3.3. Effects of Nonsolvent Pretreatment on the Permeation Properties of Resultant Carbon Membranes.** Polymeric membranes were subjected to nonsolvent pretreatment by methanol, ethanol, 1-propanol, and 1-butanol before undergoing the pyrolysis process, and the nonsolvent effects on the permeation properties of resultant carbon membranes have been examined. In particular it has been investigated whether carbon membranes with superior separation performance can be produced through nonsolvent pretreatment of the polymeric precursors. Tables 6 and 7 list the gas permeation properties of CMSMs derived from nonsolvent-treated Matrimid and P84 precursors, respectively. Tables 6 and 7 clearly show that nonsolvent pretreatment reduces flux but enhances the selectivity of CMSMs. Therefore, an investigation of pretreatment time on Matrimid was conducted by using methanol and ethanol to determine the optimal time for the nonsolvent pretreatment. The data from Table 8 suggest that the selectivity of carbon membranes increases with the pretreatment time. Hence, the 1-day immersion time was selected for this study. The increase in selectivity is most notable for the gas pair of CO<sub>2</sub> and CH<sub>4</sub>, because of the large difference in their molecular sizes. Among all the nonsolvents used in this study, the best (maximum selectivity) is observed for CMSMs derived from 1-day ethanol pretreatment of both Matrimid and P84 precursors. It seems that propanol and butanol are ineffective in enhancing the separation properties of carbon membranes as compared to ethanol. The WAXD spectra did not distinguish an effect of the choice of nonsolvent on chain spacing. However, the PALS data did distinguish the effectiveness of nonsolvent on the

positron lifetime  $\tau_2$  and hence the mean pore size. The PALS data indicate that ethanol pretreatment resulted in the smallest pore size, followed by methanol pretreatment and then by propanol pretreatment. The effectiveness of the pretreatment may depend on factors such as the molecular size of the nonsolvents, the chemical composition of the polymers, the FFV of the polymers, as well as the polarity and difference of solubility parameters between polymers and nonsolvents.

As discussed in the Introduction, the pyrolysis of polymeric precursors produces highly pure carbon membranes with relatively low contaminants. The structure of CMSMs is usually controlled by the chemical composition of carbon precursor, thermal history, and its post/prepyrolysis treatment. The void spaces or pores formed during pyrolysis determine the microporosity and selectivity of a carbon membrane, where the porosity in CMSMs arises as a natural consequence of structural declinations.<sup>33</sup> As confirmed here by DSC analysis, nonsolvent pretreatment weakens the polymeric intermolecular interaction and depresses the  $T_g$ . In addition, TGA experiments also confirm that the polymer degradation for nonsolvent-treated precursors occurs more readily (greater mass depletion) during carbonization as compared to untreated precursors. As a result, it is reasonable to speculate that increased molecular mobility allows the carbon chains extra freedom to become more ordered and closely packed during pyrolysis. By contrast, the lower molecular mobility of untreated rigid polyimide chains results in the formation of larger pore sizes/pore size distribution. The PALS and WAXD data clearly show the decrease in positron lifetime  $\tau_2$  (and hence the mean pore size) and  $d$  spacing, respectively, due to nonsolvent pretreat-



**Figure 8.** Separation properties of CO<sub>2</sub>/CH<sub>4</sub> for Matrimid-derived CMSMs with respect to the upper bound curve.



**Figure 9.** Separation properties of CO<sub>2</sub>/CH<sub>4</sub> for P84-derived CMSMs with respect to the upper bound curve.

ment. We have shown for the first time that the nonsolvent pretreatment alters the separation performance of resultant CMSMs by facilitating reorganization of the carbon chains that leads to smaller selective micropores (CMSMs with higher selectivity but lower permeability).

Finally, as both Matrimid- and P84-derived CMSMs exhibited excellent separation properties for CO<sub>2</sub>/CH<sub>4</sub>, the CO<sub>2</sub>/CH<sub>4</sub> tradeoff lines for both polymer precursors and pyrolyzed membranes are shown in Figures 8 and 9, respectively. It is clear that both permeability and selectivity of membranes are well-above Robeson's upper bound curve<sup>34</sup> after carbonization, especially for those pyrolyzed at an optimum condition, that is, CMSMs derived from the ethanol-treated polymers. Ethanol pretreatment appears to be an extremely attractive and effective method to fabricate high-performance carbon membranes for separation technology.

#### 4. Conclusion

Carbon membranes have been fabricated from the carbonization of Matrimid and P84 precursors. This study investigates the influence of nonsolvent pretreatment in altering the separation performance of resultant CMSMs. The membranes were subjected to methanol, ethanol, 1-propanol, and 1-butanol pretreatment before pyrolysis. Several characterization methods were used

to study the CMSMs fabricated with different nonsolvents pretreatment. TGA and DSC results reveal that the nonsolvent-treated polyimides are less thermally stable and possess reduced  $T_g$ 's. The lowest  $T_g$  has been observed for ethanol-treated Matrimid and P84. XRD and PALS data suggest a tighter chain packing and smaller pore size for the CMSMs fabricated with the nonsolvent pretreatment. The shortest trapped positron lifetime  $\tau_2$ , and hence the smallest pores, were measured for the ethanol-treated Matrimid. The selectivity is increased for CMSMs derived from the nonsolvent-treated polyimides. The maximum selectivity is observed for CMSM derived from polyimide treated with ethanol for 1 day. The function of nonsolvent pretreatment is to weaken the intermolecular interactions, allowing structural reorganization of the carbon chains during pyrolysis, leading to smaller pores. This study has identified the importance of nonsolvent pretreatment, especially ethanol, in enhancing the separation efficiency of carbon membranes.

#### Acknowledgment

The authors express sincere gratitude to A\*Star for funding this research with Grant R-279-000-113-304.

#### Literature Cited

- (1) Centeno, T. A.; Fuertes, A. B. Carbon molecular sieve gas separation membranes based on poly(vinylidene chloride-co-vinyl chloride). *Carbon* **2000**, *38*, 1067.
- (2) Saufi, S. M.; Ismail, A. F. Fabrication of carbon membranes for gas separation-1 review. *Carbon* **2004**, *42*, 241.
- (3) Ismail, A. F.; David, L. I. B. A review on latest development of carbon membranes for gas separation. *J. Membr. Sci.* **2001**, *193*, 1.
- (4) Kishore, N.; Sachan, S.; Rai, K. N.; Kumar, A. Synthesis and characterization of a nanofiltration carbon membrane derived from phenol-formaldehyde resin. *Carbon* **2003**, *41*, 2961.
- (5) Barsema, J. N.; Van der Vegt, N. F. A.; Koops, G. H.; Wessling, M. Carbon molecular sieve membranes prepared from porous fiber precursor. *J. Membr. Sci.* **2002**, *205*, 239.
- (6) Tanihara, N.; Shimazaki, H.; Hirayana, Y.; Nakanishi, S.; Yoshinaga, T.; Kusuki, Y. Gas permeation properties of asymmetric carbon hollow fiber membranes prepared from asymmetric polyimide hollow fiber. *J. Membr. Sci.* **1999**, *160*, 179.
- (7) Fuertes, A. B.; Nevskaya, D. M.; Centeno, T. A. Carbon composite membranes from Matrimid and Kapton polyimides for gas separation. *Microporous Mesoporous Mater.* **1999**, *33*, 115.
- (8) Liang, C.; Sha, G.; Guo, S. Carbon membrane for gas separation derived from coal tar pitch. *Carbon* **1999**, *37*, 1391.
- (9) Kusakabe, K.; Yamamoto, M.; Morooka, S. Gas permeation and micropore structure of carbon molecular sieving membranes modified by oxidation. *J. Membr. Sci.* **1998**, *149*, 59.
- (10) Chen, Y. D.; Yang, R. T. Preparation of carbon molecular sieve membrane and diffusion of binary mixtures in the membrane. *Ind. Eng. Chem. Res.* **1994**, *33*, 3146.
- (11) Itoh, N.; Haraya, K. A carbon membrane reactor. *Catal. Today* **2000**, *56*, 103.
- (12) Koros, W. J.; Mahajan, R. Pushing the limits on possibilities for large scale gas separation: Which strategies? *J. Membr. Sci.* **2000**, *175*, 181.
- (13) Singh, A.; Koros, W. J. Significance of entropic selectivity for advanced gas separation membranes. *Ind. Eng. Chem. Res.* **1996**, *35*, 1231.
- (14) Park, H. B.; Lee, Y. M. Pyrolytic carbon-silica membrane: A promising membrane material for improved gas separation. *J. Membr. Sci.* **2003**, *213*, 263.
- (15) Geiszler, V. C.; Koros, W. J. Effect of polyimide pyrolysis conditions on carbon molecular sieve membrane properties. *Ind. Eng. Chem. Res.* **1996**, *35*, 2999.
- (16) Hayashi, J.; Yamamoto, M.; Kusakabe, K.; Morooka, S. Effect of oxidation on gas permeation of carbon molecular sieving membranes based on BPDA-pp'ODA polyimide. *Ind. Eng. Chem. Res.* **1997**, *36*, 2134.



- (17) Koresh, J. E.; Soffer, A.; Study of molecular sieve carbons Part 1. Pore structure, gradual pore opening and mechanism of molecular sieving. *J. Chem. Soc. Faraday Trans.* **1980**, *76*, 2457.
- (18) Suda, H.; Haraya, K. Alkene/alkane permselectivities of a carbon molecular sieve membrane. *Chem. Commun.* **1997**, 93.
- (19) Tin, P. S.; Chung, T. S.; Kawi, S.; Guiver, M. D. Novel approaches to fabricate carbon molecular sieve membranes based on chemical modified and solvent treated polyimides. *Microporous Mesoporous Mater* **2004**, *73*, 151.
- (20) Fuhrman, C.; Nutt, M.; Vichtovonga, K.; Coleman, M. R. Effect of thermal hysteresis on the Gas Permeation Properties of 6FDA-based polyimides. *J. Polym. Sci.* **2004**, *91*, 1174.
- (21) Ruiz-Trevisano, F. A.; Paul, D. R. Gas permselectivity properties of high free volume polymers modified by a low molecular weight additive. *J. Polym. Sci.* **1998**, *68*, 403.
- (22) Kusuki, Y.; Shimazaki, H.; Tanihara, N.; Nakanishi, S.; Toshinaga, T. Gas permeation properties and characterization of asymmetric carbon membranes prepared by pyrolyzing asymmetric polyimide hollow fiber membrane. *J. Membr. Sci.* **1997**, *134*, 245.
- (23) Okamoto, K.; Kawamura, S.; Yoshino, M.; Kita, H.; Hirayama, Y.; Tanihara, N.; Kusuki, Y. Olefin/paraffin separation through carbonized membranes derived from an asymmetric polyimide hollow fiber membrane. *Ind. Eng. Chem. Res.* **1999**, *38*, 4424.
- (24) David, L. I. B.; Ismail, A. F. Influence of thermostabilization process and soak time during pyrolysis process on the polyacrylonitrile carbon membranes for O<sub>2</sub>/N<sub>2</sub> separation. *J. Membr. Sci.* **2003**, *213*, 285.
- (25) Schindler, E.; Maier, F. Manufacture of porous carbon membranes. U.S. Patent 4,919,860, 1990.
- (26) Chen, J. C.; Harrison, I. R. Modification of polyacrylonitrile (PAN) carbon fiber precursor via post-spinning plasticization and stretching in dimethylformamide (DMF). *Carbon* **2002**, *40*, 25.
- (27) Lin, W. H.; Vora, R. H.; Chung, T. S. Gas Transport Properties of 6FDA-Durene/1,4-phenylenediamine (pPDA) Copolyimides. *J. Polym. Sci.: Part B: Polym. Phys.* **2000**, *38*, 2703.
- (28) Chidambaram, D.; Venkatraj, R.; Manisankar, P. Solvent-induced modifications in polyester yarns. II. Structural and thermal behavior. *J. Appl. Polym. Sci.* **2003**, *89*, 1555.
- (29) Matsuura, T. *Synthetic membranes and membrane separation processes*; CRC Press: Boca Raton, FL, 1994.
- (30) Okamoto, K.; Tanaka, K.; Katsube, M.; Kita, H.; Sueoka, O.; Ito, Y. Correlation between positron-annihilation and gas-diffusion properties of various rubbery polymers. *Polym. J.* **1993**, *25*, 275.
- (31) Marand, E.; Cornelius, C. J.; Meakin, P.; Hill, A. J. Hybrid organic-inorganic membranes. *Polym. Mater. Sci. Eng.* **2001**, *85*, 297.
- (32) Singh, J. J.; Eftekhari, A.; St Clair, T. L. In *A low energy positron flux generator for microstructural characterization of thin polymer films*; Ottewitte, E., Weiss, A. H., Eds.; AIP Conference Proceeding 303; AIP Press: New York, 1994; pp 516–525.
- (33) Foley, H. C. Review. Carbogenic molecular sieves: Synthesis, properties and applications. *Microporous Mater.* **1995**, *4*, 407.
- (34) Robeson, L. M. Correlation of separation factor versus permeability for polymeric membranes. *J. Membr. Sci.* **1991**, *62*, 165.

Received for review May 11, 2004

Revised manuscript received July 3, 2004

Accepted July 22, 2004

IE049606C