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# Chemical Cross-Linking Modification of Polyimide/Poly(ether sulfone) Dual-Layer Hollow-Fiber Membranes for Gas Separation

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A novel engineering approach on cross-linking modification of polyimide hollow-fiber membranes is reported. The concept is demonstrated using a dual-layer hollow-fiber membrane structure, where a polyimide {copoly[1,4-durene/1,3-phenylene-2,2-bis(3,4-dicarboxyphenyl)hexafluoropropanediimide] (6FDA-durene/mPDA) (50:50)} is chosen as the outer layer and poly(ether sulfone) (PES) is selected as the inner layer. Chemical cross-linking modification occurs at the outer polyimide layer by immersing the dual-layer hollow fibers in a 5% (w/v) *p*-xylenediamine/methanol solution at ambient temperature for a short period of time. Fourier transform infrared studies show that chemical cross-linking modification takes place by the formation of amide groups through the reactions between *p*-xylenediamine and imide groups. The PES inner layer is found to be immune from the proposed chemical cross-linking modification and remains porous and flexible as a supporting layer. Pure gas tests show that chemical cross-linking modification of dual-layer hollow fibers results in a reduction in permeance but significantly enhances the CO<sub>2</sub>/N<sub>2</sub> and especially CO<sub>2</sub>/CH<sub>4</sub> selectivities. The proposed chemical cross-linking modification also makes the polymer more resistant to plasticization and thus reduces the CO<sub>2</sub>-induced increase in gas permeance.

## Introduction

Polyimides are attractive membrane materials for gas separations because of their good gas separation and physical properties. Extensive works including tailoring the chemical structures<sup>1–5</sup> and performing cross-linking modifications by different methods such as thermal and chemical treatment and UV irradiation<sup>6–16</sup> have been carried out with the aim of obtaining polyimide membranes with better gas separation properties. Among all of the efforts, cross-linking modification is expected to be one of the most promising approaches to improve chemical resistance and resistance to plasticization of polyimide membranes.<sup>17</sup>

Most commercial membranes are in the form of hollow fibers because they offer a higher surface-to-volume ratio. Each hollow-fiber membrane usually has an asymmetric cross-sectional morphology that consists of a thin dense selective layer and a porous supporting substrate. The asymmetric morphology gives the advantage of high flux, which is required for practical applications. However, to our best knowledge, almost all of the reported cross-linking modifications of polyimides have been conducted on thick and flat dense films,<sup>6–16,18</sup> which may have very limited applications for the modification of hollow-fiber membranes. Therefore, it is essential to investigate new and practical cross-linking modification technologies for hollow fibers. Recently, we have reported that chemical cross-linking modification of polyimide dense films can occur through

the reactions between the imide units in polyimide and *p*-xylenediamine.<sup>18</sup> The modification takes place by immersing the polyimide films in a *p*-xylenediamine/methanol solution for a certain period of time at ambient temperature. The easiness of cross-linking makes it potentially extremely suitable for the cross-linking modification of polyimide hollow-fiber membranes. In this paper we intend to apply this novel technology to modify polyimide/poly(ether sulfone) (PES) dual-layer hollow fibers. The dual-layer hollow fibers studied here consist of a copoly[1,4-durene/1,3-phenylene-2,2-bis(3,4-dicarboxyphenyl)hexafluoropropanediimide] [6FDA-durene/mPDA (50:50)] as the thin outer selective layer and a PES as the inner porous supporting layer. The dual-layer hollow-fiber membrane structure is purposely chosen because the inner PES layer is inert to the proposed chemical cross-linking modification, while the outer polyimide layer with a defined thickness can be chemically modified with different degrees of cross-linking. The effects of chemical cross-linking modification on the gas separation performance and antiplasticization properties of dual-layer polyimide/PES hollow fibers will be investigated.

## 2. Experimental Section

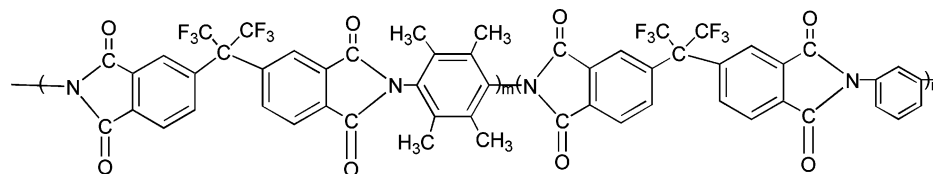
**2.1. Materials.** The chemical structure of 6FDA-durene/mPDA (50:50) is shown in Figure 1. It was synthesized by a similar procedure described elsewhere<sup>18,19</sup> with an inherent viscosity of 1.00 dL/g in *N*-methylpyrrolidone (NMP). This material has N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> permeabilities of 7.09, 35.37, 3.77, and 120 barrer, respectively, with CO<sub>2</sub>/CH<sub>4</sub> selectivity of 31.8 and O<sub>2</sub>/N<sub>2</sub> selectivity of 5 at 35 °C and 10 atm. *p*-Xylenediamine, tetrahydrofuran (THF), dichloromethane,

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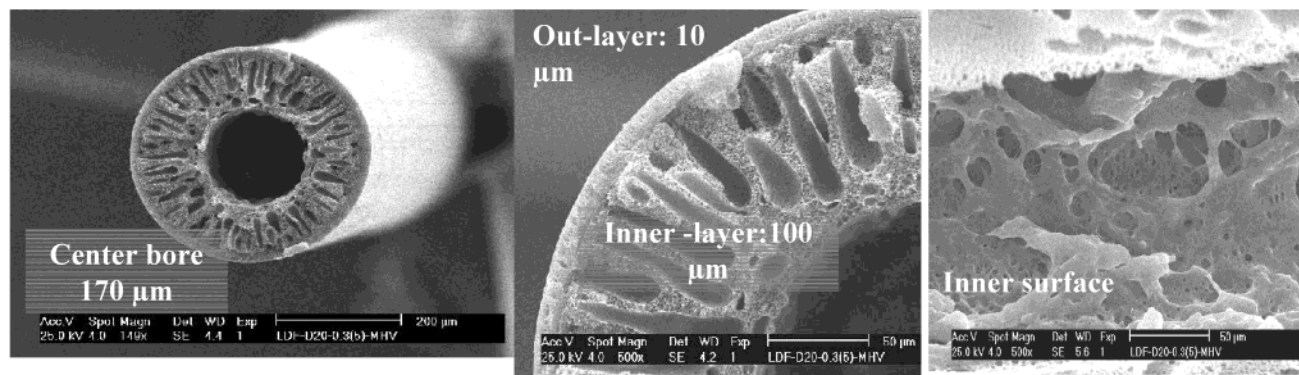
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**Figure 1.** Chemical structure of 6FDA-durene/mPDA (50:50).



**Figure 2.** SEM pictures of polyimide/PES dual-layer hollow fibers (scale bars in the left, middle, and right panels are 200, 50, and 50  $\mu\text{m}$ , respectively).

methanol, and hexane were used as received. PES (Radel A-300P) was purchased from Amoco Polymers Inc., Marietta, OH.

**2.2. Fabrication of Polyimide/PES Dual-Layer Hollow Fibers.** The spinning of dual-layer hollow fibers was carried out in our laboratory, and the details of the spinning process were described elsewhere.<sup>19</sup> A total of 26 wt % 6FDA-durene/mPDA (50:50) in a solvent mixture of NMP/THF (5:3 by weight) was chosen as the dope to yield the outer dense selective layer, whereas 28 wt % PES in a solvent mixture of NMP/H<sub>2</sub>O (10:1 by weight) was selected as the dope to form the inner porous substrate layer. The two dopes were delivered to the spinneret by two metering pumps at a rate of 0.2 mL/min for the outer layer and 0.6 mL/min for the inner layer, respectively. The spinneret temperature was controlled at 60 °C. A 95:5 by weight solvent mixture of NMP/H<sub>2</sub>O was selected as the bore fluid and delivered by an ISCO 500D syringe pump at a rate of 0.2 mL/min. After passing through an air gap of 0.3 cm, the nascent hollow fibers were drawn into a tap water coagulation bath at ambient temperature and collected at a take-up velocity of 40 cm/min. After being stored in water for 3 days at room temperature, the dual-layer hollow fibers were immersed in methanol three times and then in hexane three times for solvent exchange, following the procedure proposed by Prof. Koros' group.<sup>20</sup> Fresh solvents were used in each solvent exchange with a duration of 30 min. Subsequently, thermal treatments of hollow fibers were carried out progressively under vacuum at 35, 45, 55, and 65 °C for 30 min and finally at 75 °C for 1 h.

Modules were prepared by sealing one of the ends of a bundle of 10 dual-layer fibers with a length of 20 cm. The O<sub>2</sub> and CH<sub>4</sub> permeation rates were measured at 200 psi, while N<sub>2</sub> and CO<sub>2</sub> rates were at a pressure range from 50 to 500 psi. All measurements took place at 23 °C. The gas permeance and separation factor were determined using a bubble flowmeter and calculated based on the equation described in our previous papers.<sup>19,21</sup> Five modules were prepared and tested. The as-spun fiber has an initial CO<sub>2</sub> permeance of  $222 \pm 15$

GPU and an O<sub>2</sub> permeance of 28.7 GPU with an average O<sub>2</sub>/N<sub>2</sub> selectivity of  $4.2 \pm 0.2$ .

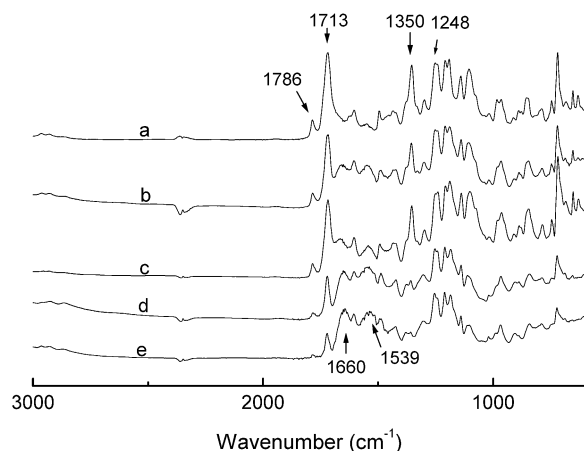
**2.3. Chemical Cross-Linked Modification of Dual-Layer Hollow Fibers.** To remove most of the plasticization effects of CO<sub>2</sub> during and subsequently after the permeance measurements, chemical cross-linking modification of the modules was carried out 5 days later after the CO<sub>2</sub> permeance tests. The modules were immersed in a 5% (w/v) *p*-xylenediamine/methanol solution for a certain period of time, then taken out from the solution, washed with fresh methanol several times, and then dried under ambient temperature for 1 day before tests. Fourier transform infrared (FTIR) spectra of modified polyimide membranes verified that no residual reacting reagents existed.

**2.4. Characterization.** Scanning electron microscopy (SEM) was conducted using a Philips XL30-SEM to investigate the fiber morphology. Attenuated total reflection (ATR)-FTIR measurements were carried out utilizing a Perkin-Elmer FTIR spectrometer on carefully flattened hollow fibers.

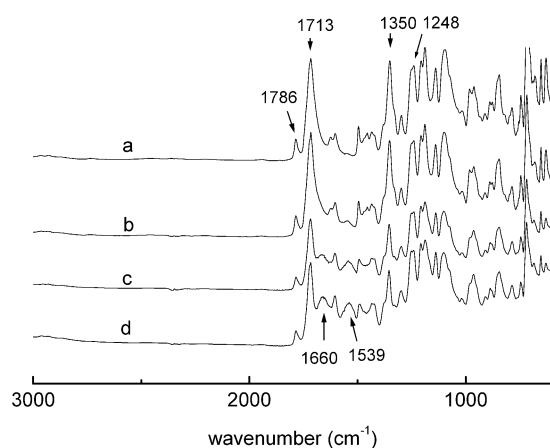
### 3. Results and Discussion

**3.1. Fabrication of Polyimide/PES Dual-Layer Hollow Fibers.** Figure 2 shows SEM photomicrographs of dual-layer asymmetric hollow fibers. The dual fibers have a good concentricity with an inner diameter of 170  $\mu\text{m}$ . The thicknesses of the outer polyimide layer and inner PES porous layer are 10 and 100  $\mu\text{m}$ , respectively. No delamination between the outer layer and inner layer is observed. The inner layer is comprised of macrovoids with interconnected porosities which may significantly minimize the substructure resistance for gas transport. As a result, the outer polyimide layer determines the gas separation properties of dual-layer hollow fibers.

**3.2. FTIR Characterization.** Figure 3 shows a comparison of FTIR spectra of the outer polyimide layer before and after the cross-linking modification. The characteristic peaks of the amide group at 1660  $\text{cm}^{-1}$  (symmetric stretch of C=O in the amide group) and



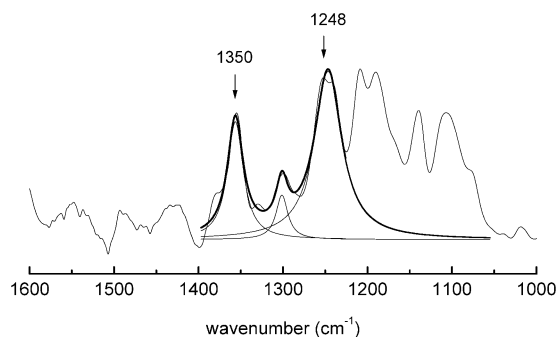
**Figure 3.** FTIR spectra of the outer polyimide layers: (a) unmodified; (b–e) cross-linked dual-layer hollow fibers [obtained by an immersion in a 5% (w/v) *p*-xylenediamine/methanol solution for (b) 5 min, (c) 30 min, (d) 60 min, and (e) 16 h].



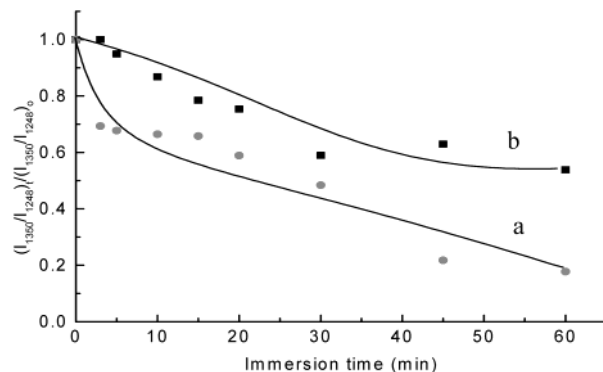
**Figure 4.** FTIR spectra of (a) unmodified and (b–d) cross-linked 6FDA-durene/mPDA (50:50) dense films [obtained by an immersion in a 5% (w/v) *p*-xylenediamine/methanol solution for (b) 5 min, (c) 30 min, and (d) 60 min].

1539  $\text{cm}^{-1}$  (stretch of C–N and bend of N–H in the amide group) appear after the modification as shown in parts b–e of Figure 3. With the progress of chemical modification, the intensities of the characteristic peaks of the imide group at 1786  $\text{cm}^{-1}$  (asymmetric stretch of C=O in the imide group), 1713  $\text{cm}^{-1}$  (symmetric stretch of C=O in the imide group), 1350  $\text{cm}^{-1}$  (stretch of C–N in the imide group), and 850  $\text{cm}^{-1}$  (the deformation of the imide group) decrease with an increase in the immersion time. These phenomena coincide with the cross-linking reaction mechanism previously observed for a 6FDA-durene/polyimide,<sup>18</sup> showing that the reactions between *p*-xylenediamine and imide groups produce amide groups and form the chemical cross-linking.

The difference in cross-linking rate between the outer layer of dual-layer hollow fibers and a thick dense film made of the same material is also compared using an FTIR. Figure 4 illustrates the FTIR spectra of virgin and cross-linked 6FDA-durene/m-PDA (50:50) dense films modified by immersing in the same *p*-xylenediamine/methanol solution. The cross-linking rate may be described by the decrease in the calibrated intensity of the imide characteristic peak at 1350  $\text{cm}^{-1}$  as a function of the immersion time. This is due to the fact that this peak intensity is not affected by the residual anhydride and dichroism effect;<sup>22</sup> thus, it presents the content of



**Figure 5.** Curve-fitting results of the FTIR spectrum of the cross-linked polyimide outer layer [obtained by an immersion in a 5% (w/v) *p*-xylenediamine/methanol solution for 5 min].

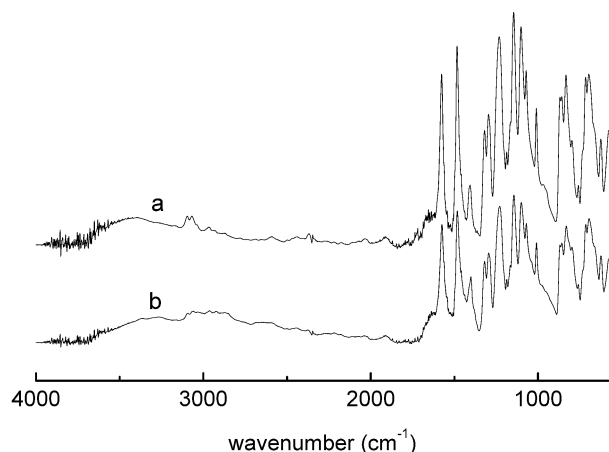


**Figure 6.** Effect of immersion time on the relative values of the calibrated peak intensity at 1350  $\text{cm}^{-1}$ : (a) the outer polyimide surface of a dual-layer hollow fiber; (b) the outer surface of a 40- $\mu\text{m}$ -thick polyimide dense film.

the imide group most accurately. The calibrated peak intensity can be expressed as  $A_{1350}/A_{1248}$ , the area ratio of the peak to the internal standard peak at 1248  $\text{cm}^{-1}$ . Here the peak at 1248  $\text{cm}^{-1}$  is attributed to the C–F stretching mode of the  $\text{CF}_3$  group and is used as an internal reference because its intensity is invariant with the cross-linking modification. The two peaks' areas are determined based on the Lorentzian curve fitting as depicted in Figure 5. The changes in  $(A_{1350}/A_{1248})_t / (A_{1350}/A_{1248})_0$ , the relative values of the calibrated peak intensity of the cross-linked to the unmodified samples, as a function of immersion time ( $t$ ) are shown in Figure 6 for both outer layers of dual-layer hollow fibers and 40- $\mu\text{m}$ -thick flat dense films. Because a faster decrease in  $(A_{1350}/A_{1248})_t / (A_{1350}/A_{1248})_0$  indicates a faster cross-linking rate, Figure 6 suggests that the outer layer of dual-layer hollow fibers has a faster cross-link rate and a higher degree of cross-linking than that of the thick dense film. According to our previous study, membrane swelling by the methanol cross-linking solution is the rate-determining step for the cross-linking process.<sup>18</sup> Because the dual-layer hollow fibers have a thin dense selective outer skin made of nodules and a porous inner substructure, it is much easier for the diffusion of the methanol modification solution into the dual-layer hollow fiber than that into a thick dense film. As a result, the dual-layer hollow fiber has a faster cross-link rate and a higher degree of cross-linking.

Figure 7 shows a comparison of PES's FTIR spectra of unmodified and modified dual-layer hollow fibers after carefully removing the thin polyimide outer layer. No apparent changes in the chemical structure of the PES inner layer can be detected. It clearly indicates the immune property of the PES inner layer to the proposed





**Figure 7.** FTIR spectra of the PES inner layers of (a) unmodified and (b) cross-linked dual-layer hollow fibers [obtained by an immersion in a 5% (w/v) *p*-xylenediamine methanol solution for 16 h].

**Table 1. Gas Permeance of the Reference and Cross-Linked Polyimide/PES Dual-Layer Hollow-Fiber Modules<sup>a</sup> (Pure Gas Tests)**

module no.	immersion time (min)	permeance (GPU) <sup>b</sup>			
		CO <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>
1a	0	70.4	12.9	2.82	1.60
2c	9.5	59.2	8.86	1.97	1.08
3c	1	57.8	7.60	2.41	0.90
4c	3	32.7	3.73	0.82	0.39
5c	5	28.3	3.01	0.69	0.28

<sup>a</sup> Measured at 23 °C with a feed pressure of 200 psi for O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> and 100 psi for CO<sub>2</sub>. <sup>b</sup> 1 GPU = 1 × 10<sup>-6</sup> cm<sup>3</sup> (STP)/cm<sup>2</sup>·s·cmHg.

chemical cross-linking modification. The inert property of the PES inner layer gives us the assurance that there is no significant adversary effect of the chemical cross-linking modification to the inner substrate layer. In the case of mechanical properties, the cross-linked dual-layer hollow fibers obtained by an immersion in a 5% (w/v) *p*-xylenediamine/methanol solution for 16 h remain flexible, while a 1 h immersion makes single-layer asymmetric 6FDA-durene/mPDA (50:50) hollow fibers fragile.

**3.3. Effects of Cross-Linking Modification on Gas Separation Properties.** Five dual-layer fiber modules were prepared under the same conditions as those for the chemical cross-linking modification. Module 1 is used as the reference and modules 2–5 were immersed in a 5% (w/v) *p*-xylenediamine/methanol solution for 0.5, 1, 3, and 5 min, respectively. In comparison with the case of polyimide dense films,<sup>18</sup> the concentration of the *p*-xylenediamine/methanol solution was reduced to half and the immersion time was shortened to obtain suitable degrees of cross-linking because of the faster cross-linking rates occurring in the outer layer of dual-layer hollow fibers as discussed previously.

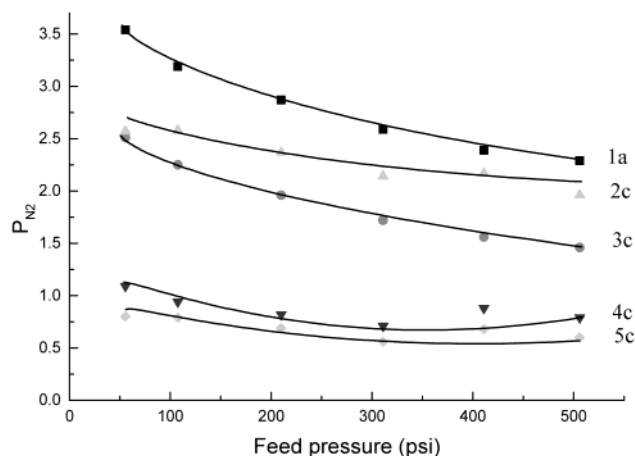
Tables 1 and 2 shows the gas separation properties of the reference module and cross-linking modified modules, which are referred to as modules 1a, 2c, 3c, 4c, and 5c correspondingly.

Clearly, cross-linking modification of dual-layer hollow fibers results in a decrease in the gas permeation rate and an increase in the gas separation factor for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>. In addition, a longer immersion results in a lower gas permeation rate. However, the

**Table 2. Gas Permselectivity of the Reference and Cross-Linked Polyimide/PES Dual-Layer Hollow-Fiber Modules<sup>a</sup> (Pure Gas Tests)**

module no.	immersion time (min)	permselectivity		
		O <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
1a	0	3.6	25	44
2c	0.5	3.5	30	55
3c	1	3.0	24	64
4c	3	3.4	40	84
5c	5	3.8	41	101

<sup>a</sup> Measured at 23 °C with a feed pressure of 200 psi for O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub> and 100 psi for CO<sub>2</sub>.



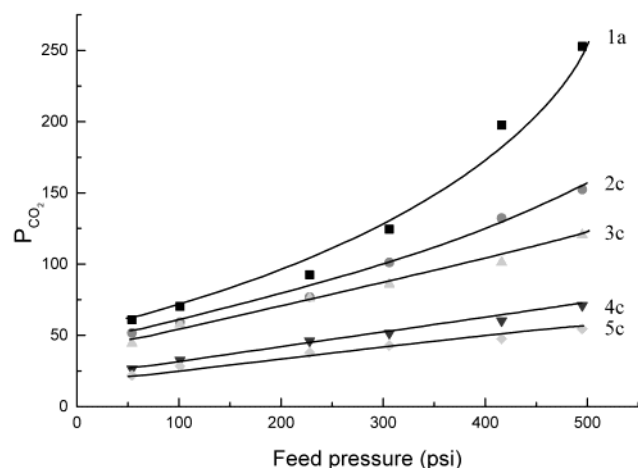
**Figure 8.** Effect of the feed pressure on N<sub>2</sub> permeance of virgin and cross-linked polyimide/PES dual-layer hollow fibers. Modules 1a, 2c, 3c, 4c, and 5c are the same samples as those listed in Table 1.

cross-linking modification shows a much smaller effect on the gas separation factor for O<sub>2</sub>/N<sub>2</sub>. This phenomenon may be due to the fact that kinetic diameters of O<sub>2</sub> (3.46 Å) and N<sub>2</sub> (3.64 Å) are much closer than that between CO<sub>2</sub> (3.3 Å) and N<sub>2</sub> (3.64 Å) or CH<sub>4</sub> (3.80 Å). The cross-linking modification may also tighten the interstitial space among polymeric chains; thus, it results in a much higher diffusion resistance for big gases (O<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>) than for the elongated CO<sub>2</sub> gas molecules. The percentages of permeance drops for various gases calculated from Table 1 support our hypothesis.

Figures 8 and 9 display the gas permeation rates of a relatively uncondensable gas, N<sub>2</sub>, and a relatively condensable gas, CO<sub>2</sub>, measured over a pressure range from 50 to 500 psi at 23 °C. For glassy polymers, their pressure dependence of gas permeance may be expressed by the dual-mode sorption model<sup>1,2,23–25</sup> as follows:

$$P = k_D D_D \left( 1 + \frac{FK}{1 + bp} \right) \quad (1)$$

where  $F = D_H/D_D$ ;  $K = c'_H b/k_D$ ;  $k_D$  is the solubility coefficient of the penetrant gas population dissolved in the polymer matrix by the Henry's law mode;  $c'_H$  is a Langmuir capacity constant, which represents the maximum concentration of the penetrant population dissolved by the Langmuir mode;  $b$  is a Langmuir affinity constant (a kinetic factor); and  $D_D$  and  $D_H$  are the mutual diffusion coefficients for the penetrant gas population dissolved in the polymer by the Henry's law and the Langmuir modes, respectively. The derivation of eq 1 is based on the assumption that the polymer is



**Figure 9.** Effect of the feed pressure on  $CO_2$  permeance of virgin and cross-linked polyimide/PES dual-layer hollow fibers. Modules 1a, 2c, 3c, 4c, and 5c are the same samples as those listed in Table 1.

not significantly plasticized by the penetrant gas, and  $D_D$  and  $D_H$  are constant.

Because polyimide/PES dual-layer hollow fibers cannot be plasticized by the absorption of  $N_2$ , the experimental results shown in Figure 8 indicate that the  $N_2$  permeance of dual-layer hollow fibers decreases with an increase in the feed pressure. This relationship is consistent with the prediction of eq 1 and the partially immobilized dual-sorption model<sup>24</sup> because the Langmuir sites are rapidly saturated and have a much smaller contribution to the overall diffusivity.

In contrast, Figure 9 illustrates that the  $CO_2$  permeance of dual-layer hollow fibers shows an upward relationship with increasing feed pressure in the whole pressure range from 50 to 500 psi. This phenomenon arises from the fact that plasticization induced by the absorption of condensable  $CO_2$  results in increased free volume and polymer chain mobility. The upward inflection in gas permeability when the feed pressure is higher than the plasticization pressure has been extensively investigated on thick polymeric dense films.<sup>25–27</sup> However, the degrees of  $CO_2$  plasticization on thick dense films and dual-layer fibers are different. Figure 9 depicts that the  $CO_2$  permeance of the unmodified dual-layer hollow fibers, module 1a, increases with increasing pressure in the whole measurement range starting from 50 psi and by 4.1 times when the feed pressure reaches 500 psi. The higher permeance increase is due to the fact that the plasticization initiates at a lower feed pressure for the dual-layer hollow fibers, indicating that the thin asymmetric polyimide outer layer is more subjected to plasticization than a thick dense film. A similar phenomenon has been observed by Prof. Koros' research group,<sup>28</sup> who reported that the plasticization of single-layer asymmetric hollow fibers is heavier than that of thick and flat dense films. The easier plasticization for asymmetric hollow fibers probably results from the fact that the thin dense selective layer of hollow fibers consists of loose-packed nodules. Thus, they can be swollen easily with the  $CO_2$  absorption. However, Prof. Freeman and co-workers also provided useful insight on plasticization.<sup>29,30</sup>

Figure 9 also shows that the proposed chemical cross-linking modification is efficient to suppress the plasticization of the dual-layer hollow fibers induced by  $CO_2$ . The cross-linked dual-layer hollow fibers, modules 2c,

3c, 4c, and 5c, obviously have lower permeance increases with an increase in the feed pressure when compared with unmodified module 1a. In addition, a higher degree of cross-linking resulting from a longer immersion time leads to a lower plasticization tendency. The improvements in antiplasticization properties may be attributed to the fact that (1) the proposed cross-linking modification macroscopically tightens and strengthens the polyimide nodules, thus reducing the  $CO_2$  sorption and hindering the nodules from swelling, as well as (2) microscopically stiffens polymer chains which would not allow for increased chain mobility and increased diffusivity. As a result, the integrity of the outer thin dense selective layer and its effective thickness are less susceptible to  $CO_2$  sorption after the chemical modification.

#### 4. Conclusion

We have reported a simple and novel chemical cross-linking method<sup>18</sup> to enhance the resistance to plasticization of polyimide dual-layer hollow-fiber membranes. A dual-layer hollow-fiber structure is purposely chosen for the concept demonstration because the proposed chemical modification can only take place at the outer fluoropolyimide selective layer. The chemical modification of the dual-layer hollow fibers is accomplished just by immersing the dual-layer fibers in a low-concentration *p*-xylenediamine/methanol solution for a very short period of time at ambient temperature. FTIR spectra indicate that the cross-linking reactions take place between the imide groups and *p*-xylenediamine and form amide groups. FTIR spectra show no visible chemical structure changes, indicating that the proposed chemical cross-link modification does not affect the PES inner layer.

The chemical cross-linking modification results in decreases in gas permeation rates for  $CO_2$ ,  $CH_4$ ,  $O_2$ , and  $N_2$ ; however, the separation factors of  $CO_2/N_2$  and  $CO_2/CH_4$  show a significant increase after the modification. The most impressive property of the cross-linked dual-layer hollow fibers is their enhanced resistance to plasticization of polyimide membranes. The  $CO_2$ -induced permeance increase with the feed pressure has been remarkably suppressed.

#### Acknowledgment

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#### Literature Cited

- (1) Koros, W. J.; Fleming, G. K. Membrane-based Gas Separation. *J. Membr. Sci.* **1993**, *83*, 1.
- (2) Stern, S. A. Polymers for the Gas Separation: the Next Decade. *J. Membr. Sci.* **1994**, *94*, 1.
- (3) Liu, Y.; Pan, C. Y.; Ding, M. X.; Xu, J. P. Gas Permeability and Permselectivity of Polyimides Prepared from Phenylendiamines with Methyl Substitution at the Ortho Position. *Polym. Int.* **1999**, *48*, 832.
- (4) Al-Masri, M.; Kricheldorf, H. R.; Fritsch, D. New Polyimides for Gas Separation. 1. Polyimides Derived from Substituted Terphenylenes and 4,4'-(Hexafluoro-isopropylidene)diphthalic Anhydride. *Macromolecules* **1999**, *32*, 7853.
- (5) Fang, J. H.; Kita, H.; Okamoto, K. Hyperbranched Polyimides for Gas Separation Applications. 1. Synthesis and Characterization. *Macromolecules* **2000**, *33*, 4693.

- (6) Hayes, R. A. Polyimide gas separation membranes. U.S. Patent 4,717,393, 1988.
- (7) Hayes, R. A. Amine-modified polyimide membranes. U.S. Patent 4,981,497, 1991.
- (8) Liu, Y.; Pan, C. Y.; Ding, M. X.; Xu, J. P. Gas Permeability and Permselectivity of Photochemically Crosslinked Copolyimides. *J. Appl. Polym. Sci.* **1999**, 73, 521.
- (9) Liu, Y.; Ding, M. X.; Xu, J. P. Gas Permeabilities and Permselectivity of Photochemically Cross-linked Polyimides. *J. Appl. Polym. Sci.* **1995**, 58, 485.
- (10) Staudt-Bickel, C.; Koros, W. J. Improvement of CO<sub>2</sub>/CH<sub>4</sub> Separation Characteristic of Polyimides by Chemical Crosslinking. *J. Membr. Sci.* **1999**, 155, 145.
- (11) Kita, H.; Inada, T.; Tanaka, K.; Okamoto, K. Effect of Photocrosslinking on Permeability and Permselectivity of Gases through Benzophenone-containing Polyimide. *J. Membr. Sci.* **1994**, 87, 139.
- (12) Rezac, M. E.; Schoberl, B. Transport and Thermal Properties of Poly(etherimide)/Acetylene-terminated Monomer Blends. *J. Membr. Sci.* **1999**, 156, 211.
- (13) White, L. S.; Blinka, T. A.; Kloczewski, H. A.; Wang, I. F. Properties of a Polyimide Gas Separation Membranes in Natural Gas Streams. *J. Membr. Sci.* **1995**, 103, 73.
- (14) Bos, A.; Punt, I. G. M.; Wessling, M.; Strathmann, H. Plasticization-resistant Glassy Polyimide Membranes for CO<sub>2</sub>/CH<sub>4</sub> Separations. *Sep. Purif. Technol.* **1998**, 14, 27.
- (15) McCaig, M. S.; Paul, D. R. Effect of UV Cross-linking and Physical Aging on the Gas Permeability of Thin Glassy Polyarylate Films. *Polymer* **1999**, 40, 7209.
- (16) Matui, S.; Ishiguro, T.; Higuchi, A.; Nakagawa, T. Effect of Ultraviolet Light Irradiation on Gas Permeability in Polyimide Membranes. 1. Irradiation with Low Pressure Mercury Lamp on Photosensitive and Nonphotosensitive Membranes. *J. Polym. Sci., Polym. Phys.* **1997**, 35, 2259.
- (17) Koros, W. J.; Mahajan, R. Pushing the Limits on Possibilities for Large Scale Gas Separation: Which Strategies? *J. Membr. Sci.* **2000**, 175, 181.
- (18) Liu, Y.; Wang, R.; Chung, T. S. Chemical Cross-linking Modification of Polyimide Membranes for Gas Separation. *J. Membr. Sci.* **2001**, 189, 231.
- (19) Li, D. F.; Chung, T. S.; Wang, R.; Liu, Y. Fabrication of Fluoropolyimide/Polyethersulfone Dual-Layer Asymmetric Hollow Fiber Membrane for Gas Separation. *J. Membr. Sci.* **2002**, 198, 211.
- (20) Clausi, D. T.; Koros, W. J. Formation of Defect-free Polyimide Hollow Fiber Membranes for Gas Separation. *J. Membr. Sci.* **2000**, 167, 79.
- (21) Shieh, J. J.; Chung, T. S. Cellulose Nitrate-based Multi-layer Composite Membranes for Gas Separation. *J. Membr. Sci.* **2000**, 66, 259.
- (22) Pryde, C. A. FTIR Studies of Polyimides. II. Factors Affecting Quantitative Measurements. *J. Polym. Sci., Polym. Chem.* **1993**, 31, 1045.
- (23) Petropoulos, J. H. Quantitative Analysis of Gaseous Diffusion in Glassy Polymers. *J. Polym. Sci., Part A2* **1970**, 8, 1797.
- (24) Paul, D. R.; Koros, W. J. Effect of Partially Immobilization Sorption on Permeability and the Diffusion Time Lag. *J. Polym. Sci., Polym. Phys.* **1976**, 14, 675.
- (25) Coleman M. R.; Koros, W. J. Conditioning of Fluorine Containing Polyimides. 1. Effect of Exposure to High-Pressure Carbon Dioxide on Permeability. *Macromolecules* **1997**, 30, 6899.
- (26) Ismail, A. F.; Lorna, W. Penetrant-induced Plasticization Phenomenon in Glassy Polymers for Gas Separation Membrane. *Sep. Purif. Technol.* **2002**, 27, 173.
- (27) Thundiyil, M. J.; Jois, Y. H.; Koros, W. J. Effect of Permeate Pressure on the Mixed Gas Permeation of Carbon Dioxide and Methane in a Glassy Polyimides. *J. Membr. Sci.* **1999**, 152, 29.
- (28) Jordan, S. M.; Henson, M. A.; Koros, W. J. The Effect of Carbon Dioxide Conditioning on the Permeation Behavior of Hollow Fiber Asymmetric Membranes. *J. Membr. Sci.* **1990**, 54, 103.
- (29) De Angelis, M. G.; Merkel, T. C.; Bondar, V. I.; Freeman, B. D.; Doghieri, F.; Sarti, G. C. Gas Sorption and Dilation in Poly-(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole-co-tetrafluoroethylene): Comparison of Experimental Data with Predictions of the Non-equilibrium Lattice Fluid Model. *Macromolecules* **2002**, 35, 1276.
- (30) Nagai, K.; Toy, L. G.; Freeman, B. D.; Teraguchi, M.; Masuda, T.; Pinnau, I. Gas Permeability and Hydrocarbon Solubility of Poly[1-phenyl-2-[p-(triisopropylsilyl)phenyl]acetylene]. *J. Polym. Sci., Polym. Phys.* **2000**, 38, 1474.

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