Macromolecules **2008,** *41,* 1297−1309

Simultaneous Occurrence of Chemical Grafting, Cross-Linking, and Etching on the Surface of Polyimide Membranes and Their Impact on H_2/CO_2 Separation

Bee Ting Low,[†] Youchang Xiao,[†] Tai Shung Chung,*,[†] and Ye Liu[‡]

Department of Chemical and Biomolecular Engineering, National University of Singapore,
10 Kent Ridge Crescent, Singapore 117602, and Institute of Materials Research & Engineering,
3 Research Link, Singapore 117602

Received October 24, 2007; Revised Manuscript Received December 27, 2007

ABSTRACT: Surface modifications of copoly(4,4′-diphenylene oxide/1,5-naphthalene-2,2′-bis(3,4-dicarboxylphenyl)hexafluoropropanediimide (6FDA−ODA/NDA) dense membranes were performed using ethylenediamine (EDA), 1,3-diaminopropane (PDA), and 1,4-diaminobutane (BuDA). Chemical grafting, cross-linking, and etching on the film surface have been verified by ATR−FTIR, UV−vis, AFM, and gel content analyses. The varying extent of the above-mentioned types of surface modification is dependent on the nucleophilicity and molecular dimensions of the diamines, which were computed using molecular simulation. Highly severe chemical etching occurred with EDA modification due to its small molecular dimensions and high nucelophilicity. The greatest degree of cross-linking was provided by PDA modification due to its favorable kinetic property and appropriate nucleophilicity. The ideal H_2/CO_2 permselectivity escalated from a polymer intrinsic permselectivity of 2.3 to a remarkable value of 64 after PDA modification for 90 min. This promising result was reconfirmed by the binary gas tests showing a H_2/CO_2 permselectivity of 45 at 35 °C. To the best of our knowledge, this mixed gas permselectivity emerged as the highest ever reported for glassy polymers in the literature. However, because of the inherent nature of the diamines modified films, direct comparison of the gas separation performances reported in this work with the Robeson upper bound cannot be established. In short, appropriate selections of diamino reagent and modification duration are required to cross-link the polymeric chains substantially while maintaining the main-chain rigidity, thereby giving the desired gas separation performance of the membrane.

1. Introduction

The gradual emergence of a hydrogen-based economy for a future sustainable environment, together with the demand for hydrogen as a chemical feedstock from the industries, navigates the continuous push and emphasis on hydrogen separation with outstanding efficiency.[1−4] Membrane technology competes with other conventional separation techniques including absorption, pressure swing adsorption, and cryogenic distillation in hydrogen purification.[1,2] Nevertheless, because of the inherent advantages of membrane technology, there is no doubt to its major role in hydrogen separation.[1−7]

Currently, hydrogen enrichment using membranes makes up a significant portion of the overall membrane market for gas/vapor related separations and is expected to increase over the next few decades.[4] In the year 2000, the separation of nitrogen from air contributed almost 50% of the total membrane market (US $155 million) while CO_2/CH_4 and H_2 separations amount to US $30 million and US $25 million, respectively.[4] As a forecast, the membrane market for hydrogen separation is expected to manifest a 6-fold increment to US $150 million in the year 2020.[4] The future prospects of membrane technology in hydrogen separation are evident.[6]

The separation of hydrogen from methane, nitrogen, and argon in ammonia purge-gas streams has long been commercialized, and the challenge awaiting membrane researchers is the separation of H_2 from plasticizing gases such as CO_2.[4] To date, steam re-forming of methane serves as the economically favored route for the industrial production of hydrogen as compared to alternative methods including partial oxidation of methane and autothermal re-forming.[1,2] To improve H_2 purity (decrease CO concentration), a water gas shift reactor (WGSR) is required downstream which operates under high- or low-temperature modes.[1,2] The main composition of the product stream from the WGSR is 75 mol % H_2 and 19 mol % CO_2.[1,2]

Membranes that are hydrogen-rejective allow CO_2 to permeate preferentially. Freeman and co-workers identified that the ether oxygen in ethylene oxide units among other functional groups provides a good balance between high CO_2 permeability and CO_2/H_2 permselectivity.[8−10] Lin et al. reported highly permeable, CO_2-selective membranes comprising of a copolymer network of poly(ethylene glycol) diacrylate and poly(ethylene glycol) methyl ether acrylate whose performance heightens with CO_2 plasticization.[11] Excellent gas separation performance can be realized, especially under low-temperature conditions. Lin et al. reported a mixed-gas CO_2/H_2 selectivity of 31 at an operating temperature of −20 °C.[11] Other polymeric membranes that allow the preferential transport of more condensable gases (CO_2) have been reported by Merkel and Toy.[12,13]

For hydrogen-selective membranes, palladium membranes are capable of producing H_2 of high purity, but the flux is rather inferior.[1] The transport of H_2 across Pd membranes occurs in seven consecutive steps: (i) movement of H_2 molecules to the membrane surface facing the feed, (ii) dissociation of H_2 into H^+ and electrons, (iii) adsorption of H^+ in the membrane, (iv) diffusion of H^+ across the membrane, (v) desorption of H^+ from the membrane, (vi) reassociation of H^+ and electrons to form H_2, and (vii) diffusion of H_2 from the permeate side of the membrane.[1] Thin Pd membranes are necessary for higher flux.

---

* Corresponding author: e-mail chencts@nus.edu.sg, Fax (65)-67791936.
[†] National University of Singapore.
[‡] Institute of Materials Research & Engineering.

10.1021/ma702360p CCC: $40.75

Therefore, attempts have been made by Athayde et al.[14] and Mercea et al.[15] to fabricate a "sandwich membrane", whereby the metals are deposited on one or both sides of a polymeric support. However, because of the brittleness of Pd membranes and the considerable cost of precious Pd metal, they are not commercially attractive.[1,2] In addition, it is difficult or almost impossible to fabricate defect-free Pd hollow fiber membranes, which possess a larger surface-to-volume ratio due its poor processability.

A novel approach that attempts to combine the high selectivity of Pd with the good processability of polymers in the form of metal−polymeric nanocomposite membranes was introduced. However, the improvement in the gas separation performance of metal−polymeric nanocomposite membranes remains uncertain. Fritsch and Peinemann incorporated 15 wt % Pd within a poly(amide−imide) matrix, and a slight enhancement in H_2/CO_2 selectivity was achieved at the expense of H_2 permeability.[16] Compton et al. fabricated hybrid Pd−polyimide membranes (5 wt % Pd loading), and there was no enhancement in H_2/CO_2 permselectivity while H_2 permeability decreased as compared to the neat polyimide films.[17] The decrease in H_2 permeability is due to the presence of Pd nanoclusters which increases the tortuosity and hence siginifcantly decreases H_2 diffusivity.[16,17] The different effects of Pd on H_2/CO_2 selectivity may be due to the variation in Pd loading in the polymeric nanocomposite membranes.[16,17] A high Pd loading is necessary to enhance the solubility selectivity significantly in order to compensate the decrease in diffusivity selectivity.

Polymeric membranes that are selective for H_2 can be employed for refinery streams at low temperatures and tail stream from PSA units.[1] Despite the processability of polymeric materials along with significantly lower cost, H_2-selective polymeric membranes are far from commercialization. Most polymers exhibit low intrinsic H_2/CO_2 selectivity in the range 0.5−5.[7] The high diffusivity of H_2 coupled with the high solubility of CO_2 makes the separation of this gas pair via the solution diffusion mechanism through polymeric membranes intricate. Among the various classes of polymers, polyimides are widely studied for use in gas separation due to its inherent advantages.[18−20] Studies involving the modification of polyimide membranes and carbonization of polyimide precursors for gas separation have been investigated extensively. However, the use of carbonized polyimide membranes for H_2/CO_2 separation has not been reported.[21−23] Polyimides, especially those containing (2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride) (6FDA) moiety are good materials for gas separation membranes because the $-C(CF_3)_2$ group is expected to account for both high gas permeability and gas pair permselectivity.[24−27] In addition to the favorable gas transport properties, fluorine-containing polyimides also possess excellent thermal and mechanical characteristics.[28−30] However, 6FDA-based polyimides too suffer from poor intrinsic H_2/CO_2 selectivity, and the gas separation performance may deteriorate in the presence of plasticizing gases. Therefore, in order to enhance the physiochemical properties of the 6FDA-based polyimides and to maintain the performance of the polymeric membrane even in harsh chemical environment, one promising approach is the modification of polyimides by chemical methods.

Chung and co-workers have developed a simple diamino modification technique applied to polyimides. This solid-state modification is carried out as a posttreatment step following membrane fabrication and is performed at room temperature. This method has been applied to both dense and hollow fiber membranes. Liu et al. discussed the mechanism for the cross-linking process and proposed that polymer swelling by methanol is a prerequisite to reaction.[24] During the chemical modification, the amine group reacts favorably with the imide ring, resulting in the cleavage of the ring and the resultant formation of two amide groups.[24−26,30−37] Amine-containing compounds of various configurations have been explored by Chung's group, including aromatics (e.g., *p*-xylenediamine),[24−26,30] linear aliphatics (e.g., ethylenediamine),[31] cyclics (e.g., 1,3-cyclohexanebis(methylamine)),[33] network structure with plentiful supply of NH_2 groups (e.g., polyamidoamine dendrimers),[34−37] etc. Most of the works related to diamino cross-linking of the polyimides were focused on carbon dioxide removal from natural gas.[24−26,30−37]

The robustness of this chemical modification approach motivates one to engage the same method for H_2/CO_2 separation. In a recent work reported by Chung et al., 6FDA−durene membranes were cross-linked using aliphatic diamines.[7] Surprisingly, the ideal H_2/CO_2 permselecitivity of 1,3-diaminopropane cross-linked film increased by 100 times after an immersion duration of 10 min.[7] All the cross-linked films exhibit gas separation performance above the trade-off line.[7]

In view of the present state of art for H_2/CO_2 separation using polymeric-based membranes, the objective of this work is to investigate the diamino modification of a copolyimide, 6FDA−ODA/NDA, on the gas separation performance for H_2/CO_2 gas pair. This polymer was chosen on the basis of the consideration of its lower material cost as compared to 6FDA−durene.[26] In addition, there are limited studies reported in the literature which employed 6FDA−ODA/NDA copolyimide as the working polymer, and this polymer has not been used for H_2/CO_2 separation.

In the present work, three aliphatic diamines, namely ethylenediamine, 1,3-diaminopropane, and 1,4-diaminobutane, were used. The effects of different immersion times on the gas transport parameters were investigated. In addition, the occurrence of polymeric backbone scission during the chemical modification, which has not been formally reported in previous works, is proposed here. A comparison between the gas separation performance of diamine-modified 6FDA−ODA/NDA and 6FDA−durene dense membranes is presented. Lastly, the effectiveness of the modification approach which is dependent on the nature of the polyimides and the diamines will be discussed.

2. Experimental Section

2.1. Materials. The working polymer, copoly(4,4′-diphenylene oxide/1,5-naphthalene-2,2′-bis(3,4-dicarboxylphenyl)hexafluoropropanediimide) (6FDA−ODA/NDA), was synthesized in our laboratory via the chemical imidization approach. The monomers 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA), 4,4′-oxydianiline (ODA), and 1,5-naphthalenediamine (NDA) were sublimated under vacuum prior to use. *N*-Methyl-2-pyrrolidone (NMP) from Merck was further purified via distillation before use. Equimolar amounts of dianhydride and diamines (ODA:NDA = 50:50) were dissolved in NMP under a nitrogen atmosphere to form a viscous solution of poly(amic acid). Subsequently, triethylamine and acetic anhydride (molar ratio of 1:4) which served as the reaction catalyst and dehydrating agent respectively were added to form the copolyimide. The polyimide solution was precipitated in methanol and dried before use. Detailed description of the polymer synthesis can be found elsewhere.[38,39] Dimethylformamide (DMF) and methanol from Merck were used without further purification. Ethylenediamine (EDA), 1,3-diaminopropane (PDA), and 1,4-diaminobutane (BuDA) from Fluka were used as received.

2.2. Dense Membrane Fabrication and Modification. A 2% (w/w) of polymer solution was prepared by dissolving 6FDA−

ODA/NDA in DMF. The solution was stirred overnight and subsequently filtered using 1.0 μm PTFE membrane before ring casting onto a wafer plate at 55 °C to allow slow evaporation of the solvent. After approximately 1 week, most of the solvent has been removed and the nascent film was further dried under vacuum following the heating protocol: (1) hold at 60 °C for 24 h, (2) increase temperature to 250 °C at 12 °C/20 min, (3) hold at 250 °C overnight followed by (4) natural cooling.

1.65 M of diamine in methanol solution was prepared for the chemical modification. The films were immersed in the respective solutions for a stipulated time. A fresh solution was used for each film. After which, the modified films were washed with methanol for 5 min to remove residual unreacted diamines and dried at 70 °C under vacuum for 24 h.

2.3. Characterization. The changes in the chemical structure of the polymeric membranes before and after chemical modification were monitored by the attenuated total reflectance (ATR) mode using Bio-Rad FTIR FTS 135 over the range 650−2000 cm^{-1}. The number of scans for each sample was 32. To determine the gel content of the dense films after modification with the respective diamines (immersion time of 60 min), DMF was added to the modified films for 24 h. The remaining insoluble portions of the membranes were dried under vacuum at 100 °C for 24 h to remove residual solvent before weighing. The gel content was calculated using eq 1

$$\%\ \text{gel content} = M_1/M_0 \tag{1}$$

where M_1 and M_0 are the mass of the insoluble fraction and the original mass of the cross-linked films, respectively.

An attempt to determine the approximate thickness of the modified layer was conducted. For this purpose, only one surface of the polyimide membrane was modified with PDA for 90 min. This step was taken in order to ensure a more complete dissolution of the unmodified polyimide. A total of four one-side modified membranes were prepared. The modified membranes were washed in methanol for 5 min, followed by drying under vacuum at 70 °C. The initial masses and thickness of the modified films were obtained before immersing them in DMF for 24 h. The residues (cross-linked portion) remaining after dissolution were dried at 100 °C under vacuum for a day. The masses of the residues were determined, and the mean value obtained was used for subsequent calculations. Since the density of the original polyimide film can be obtained using the buoyancy method, the thickness of the unreacted film can be estimated.

After modification, the spent diamines in methanol solutions were investigated in quartz cuvettes using Shimadzu UV-1601 UV−vis spectrophotometer in the wavelength ranging from 200 to 800 nm. UV−vis analysis was conducted to track the presence of additional chemical species in the solution after reaction.

The surface topology of the dense membranes modified with the respective diamines for immersion time of 60 min was examined using a Nanoscope IIIa atomic force microscope (AFM) from Digital Instruments Inc. For each modified film, an area of 5 μm × 5 μm was scanned at a rate of ∼1 Hz using the tapping mode of the AFM. To examine the hydrophobic/hydrophilic nature of the membrane surfaces, the original dense film and the membranes modified with the respective diamines for an immersion time of 60 min were tested for their contact angles with water using a Ramé-Hart goniometer.

To determine the weight loss of the membranes upon thermal decomposition, thermogravimetric analysis (TGA) was conducted using a Perkin-Elmer TGA 7 at a constant heating rate of 5 °C/min from room temperature to 800 °C in a nitrogen environment. In addition, the unmodified and PDA-modified (immersion time of 90 min) membranes were soaked in deionized water for a week, following which the surfaces of the H_2O-sorbed films were blotted between tissue papers to remove the excess water. The weight loss profiles as a function of temperature for these H_2O-sorbed membranes were similarly determined using TGA.

The tensile properties of the films (pure and PDA modified for 90 min) with and without water sorption were determined using an Instron 5542 Universal tensile tester. The analysis was carried out at ambient temperature. The grip separation was set at 50 mm, and a testing speed of 5 mm/min was used. The width of the thin films analyzed was 4.5 ± 0.5 mm, and the membrane thickness was 0.050 ± 0.005 mm.

The changes in intersegmental properties of the polymeric membranes were investigated using X-ray diffractor (XRD) Bruker, D8 series, GADDS (General Area Detector Diffraction system). The modified films were immersed in DMF, and the insoluble (cross-linked) portions were used for carrying out the analysis. Cu X-ray source of wavelength 1.54 Å was used. Average *d*-spacing was determined based on the Bragg's law as shown in eq 2

$$n\lambda = 2d \sin \theta \tag{2}$$

where n is an integral number (1, 2, 3, ...), λ denotes the X-ray wavelength, d represents the intersegmental spacing between two polymer chains, and θ indicates the diffraction angle.

2.4. Molecular Simulation. Fukui function indices are reliable intramolecular site reactivity descriptors.[40,41] Hence, to determine the nucleophilicities of the aliphatic diamines used in this study, the Fukui function indices for electrophilic attacks were computed using the Materials Studio software by Accerlys. Geometry optimization of the respective diamines was done by the DMol3 module followed by the calculation of Fukui function for electrophilic attacks.

As the modification of the polyimide films using the diamines were carried out in methanol, the COSMO function was used whereby methanol was chosen as the solvent for the diamines. The resultant Fukui function indices based on the N atoms for the three aliphatic diamines were compared and the molecular models of the diamines were shown to provide visualization of the electron density distribution surrounding the active sites. The scale for the electron density used for all three diamines were standardized, and the same isovalue was used. The isosurface generated (based on the isovalue) shows the surface whereby the electron density is uniform.

2.5. Measurements of Gas Transport Properties. All the dense films with and without chemical modification were tested for their pure gas permeation properties. Pure gas measurements were done using a variable-pressure constant-volume gas permeation cell. A detailed description of the permeation cell setup can be obtained elsewhere.[39] The gas permeation of H_2 was tested followed by CO_2. The upstream pressure was 3.5 atm, and the temperature was 35 °C. The rate of pressure increase (dp/dt) at steady state was used for the calculation of gas permeability according to eq 3

$$P = \frac{273 \times 10^{10}}{760} \frac{VL}{AT(p_2 \times 76/14.7)} \left(\frac{\mathrm{d}p}{\mathrm{d}t}\right) \tag{3}$$

where P is the gas permeability of a membrane in barrer (1 barrer = 1 × 10^{-10} cm^3 (STP) cm/(cm^2 s cmHg)), V is the volume of the downstream chamber (cm^3), A refers to the effective membrane area (cm^2), l is the membrane thickness (cm), T is the operating temperature (K), and the pressure of the upstream pressure is given by p_2 (psia).

The ideal permselectivity of a membrane for H_2 to CO_2, α, was evaluated as follows

$$\alpha = \frac{P_{H_2}}{P_{CO_2}} \tag{4}$$

where P_{H_2} and P_{CO_2} are the gas permeabilities for H_2 and CO_2, respectively.

Mixed gas permeation tests were conducted for the modified membrane which exhibited the best ideal H_2/CO_2 permselectivity. A binary gas mixture containing 50% H_2 and 50% CO_2 was used as the feed mixture, and the measurements were performed at 35 °C

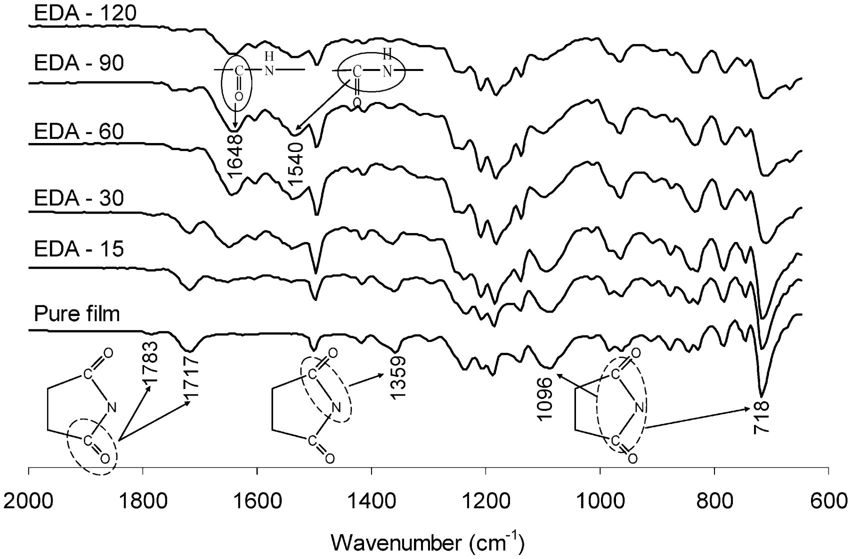

Figure 1. FTIR spectra of EDA modified films at different immersion times.

and 7 atm. A detailed description of the facility used for mixed gas permeation tests has been previously reported.[31] The gas permeability was determined using eqs 5 and 6 as follows

$$P_{CO_2} = \frac{273 \times 10^{10}}{760} \frac{y_{CO_2}VL}{AT(76/14.7)(x_{CO_2}p_2)}\left(\frac{dp}{dt}\right) \quad (5)$$

$$P_{H_2} = \frac{273 \times 10^{10}}{760} \frac{y_{H_2}VL}{AT(76/14.7)(x_{H_2}p_2)}\left(\frac{dp}{dt}\right) \quad (6)$$

where P_{CO_2} and P_{H_2} are the permeabilities (barrer) of CO_2 and H_2, respectively. p_2 is the upstream feed gas pressure (psia), and p_1 represents the downstream permeate gas pressure (psia). x and y refer to the gas molar fraction in the feed and the permeate, respectively (%). Subsequently, the mixed gas selectivity can be simplified into the calculating equation as described in eq 2 due to the negligible downstream pressure.

2.6. Measurements of Gas Sorption. Carbon dioxide sorption tests were conducted using a Cahn D200 microbalance sorption cell at 35 °C over a pressure range of 0−250 psi (0−17.24 bar) for the membranes before and after PDA modification (immersion time of 60 min). A detailed description of the dual volume sorption cell was reported elsewhere.[42] For each run, films with thickness of 50 ± 5 μm, diameter of 1 cm, and total mass of approximately 80−100 mg were placed on the sample pan. The system was evacuated for 24 h prior to testing. The gas at a specific pressure was fed into the system. The mass of gas sorbed by the membranes at equilibrium was recorded. Subsequent sorption experiments were done by further increment of the gas pressure. The equilibrium sorption value obtained was corrected by the buoyancy force.

3. Results and Discussion

3.1. Characterization of the Modified Films. The dense membranes before and after chemical modification were studied using ATR−FTIR. With reference to Figure 1, the pure 6FDA−ODA/NDA film exhibits a characteristic doublet near 1717 and 1783 cm^{-1} which is attributed to the carbonyl group of the imide ring, the former resulting from the asymmetric stretch of C═O and the latter is brought about by the symmetric stretch of the carbonyl group. The characteristic peak at 1359 cm^{-1} is due to the C−N stretch of the imide group while the peak at 1096 cm^{-1} is indicative of the transverse stretch of C−N−C in the imide group. The peak at 718 cm^{-1} is due to the out-of-plane bending of C−N−C in the imide group.

Upon modifying the pure polymeric film with EDA, distinct peaks representative of the amide groups are clearly visible. Referring to Figure 1, the characteristic peaks at 1648 and 1540 cm^{-1} are attributed to C═O stretch and C−N stretch of the amide group, respectively. This supports the reaction mechanism proposed by Liu et al.[24] As the immersion time is increased, the characteristic peaks of the amide groups become more prominent while the peaks representative of the imide groups become less intense. The trends observed for PDA and BuDA modified membranes for different immersion times are similar to EDA modified films (data not shown).

The different diamines react with the polyimide membrane to varying extent. Figure 2 shows the FTIR spectra of the unmodified film together with EDA, PDA, and BuDA modified films for immersion duration of 60 min. The characteristic peak representing C−F at 1242 cm^{-1} is used as the reference peak since the $C(CF_3)_2$ group is unaffected by the modification. Apparently, for the EDA modified film, the amide peaks at 1648 and 1540 cm^{-1} are relatively sharper, reflecting the higher concentration of amide groups present. For PDA and BuDA modified films, the characteristic peaks of the amide group are less intense. The peak representative of the C═O group in the imide ring at 1717 cm^{-1} is almost imperceptible for the EDA modified film but remains visible for BuDA modified film. This shows that EDA modification results in the greatest proportion of amide groups in the amide−imide polymeric network which is due to its highest reactivity.

The diamines in methanol solutions may react with the dense polyimide film in various ways. The initiation step involves the reaction of one of the amine groups constituting the diamine molecule with an imide group. Subsequently, if the other amine group from the same molecule remains free, the diamine is attached to the polymer chain via chemical grafting, as shown in Figure 3b. On the other hand, cross-linking of two polyimide chains via the reaction of each amine group with neighboring imide groups may occur (Figure 3b). The reaction between the amine group and the imide ring breaks the ring structure, creating two amide groups. Recall that amide groups are electrophilic by nature and hence are susceptible to nucelophilic attacks. In fact, amide groups readily exchange with amine groups.[43]

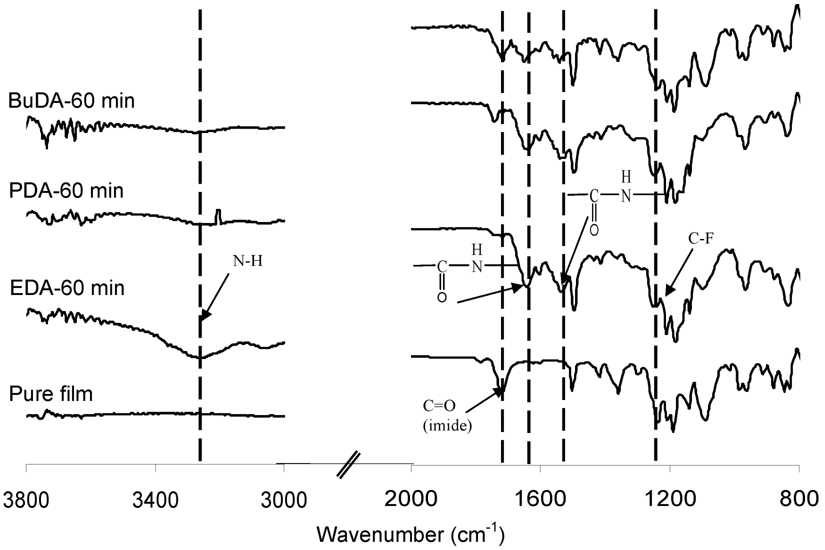

Figure 2. FTIR spectra of diamine modified films with immersion time of 60 min.

Since the diamine is in excess, there exists the possibility of reaction between another diamine molecule and the amide group in the main chain, causing scission of the polymeric skeleton (Figure 3c).

The degrees of chemical grafting and cross-linking by different modification reagents differ. With reference to Figure 2, a broad peak at 3250 cm^{-1} that is representative of the N−H bond in amine group is observed only for the EDA modified film which implies the presence of a considerable number of free amine groups. Hence, this suggests that although the high reactivity of EDA results in the significant conversion of imide to amide groups, the majority of the conversion is due to grafting instead of cross-linking. The presence of free amine groups on the surface of EDA modified membrane also alters the hydrophobic/hydrophilic nature of the membrane. The contact angle of the original polyimide film is 93°, which indicates that the surface is slightly hydrophobic. However, the contact angle of EDA modified film for immersion time of 60 min is 83°. Hence, the modification of the polyimide membrane with EDA increases the hydrophilicity of the surface. The contact angles of PDA and BuDA modified film are 92° and 88°, respectively, which are comparable to that of the original polyimide membrane.

A good indication of the extent of chemical cross-linking by the respective modification reagents is provided by the gel content of the modified films. The gel content of EDA, PDA, and BuDA modified membranes (immersion time of 60 min) are 15%, 30%, and 9%, respectively. PDA modified membrane gave the highest gel content which shows that it the most effective cross-linking agent for this type of 6FDA−polyimide. The results from the gel content analysis reinforce the suggestion that the bulk of the amide groups formed by EDA modification is due to chemical grafting. If majority of the conversion is due to chemical cross-linking, the gel content of EDA modified films should be the highest, which is not so. The gel content of BuDA modified film is smaller than EDA modified film. This is due to the larger molecular dimensions of BuDA molecule which inhibits its penetration into the polymeric matrix. Hence, the majority of the chemical modification by BuDA occurs at the surface.

A closer look at the resultant diamine/methanol solutions after reaction supports the existence of polymeric main chain scission. For long immersion times, the resultant solutions (EDA and PDA) turn slightly orange (this is the color of the polyimide). Hence, the resultant solutions after modification were analyzed using UV−vis spectroscopy. Figure 4a−c shows the UV−vis spectra of the various modification solutions. The peak intensity and peak area increases with increasing modification time. The trend is obvious for EDA and PDA in methanol solution. However, for BuDA in methanol solutions, the change in the spectra with immersion time is negligible. No peaks are detected in the UV−vis spectra of the diamine/methanol solutions before modification. This shows that neither the diamines nor methanol absorbs radiation in the UV−vis range. Therefore, the existence of peaks in the spectra of the resultant diamine/methanol solutions after long immersion times is attributed to the presence of polyimide fragments which absorb in the UV−vis range.

To investigate the topology of the modified films, AFM analysis was performed. Figure 5a−c show the 3-dimensional plots of the surfaces of the diamine modified polyimide films. EDA modified film represented by Figure 5a shows a highly rugged terrain while BuDA modified film represented by Figure 5c shows an almost smooth surface. This visual evidence further supports the proposed chain scission mechanism which occurs during the chemical modification process. The mean roughness of the EDA, PDA, and BuDA modified films are 6.777, 0.831, and 0.783 nm, respectively. The degree of chemical etching by EDA is much more severe than PDA and BuDA, thereby giving rise to a rougher surface. The increased roughness of EDA modified film also intensifies the surface hydrophilicity. The mean roughness values of PDA and BuDA modified films are comparable.

The differences in the UV−vis peak intensities and mean roughness of the membranes can be explained using the nucleophilicities and molecular dimensions of the respective diamines. Molecular simulation using Accelrys Materials Studio software gives the Fukui function for electrophilic attacks at the active sites (N atoms) of the diamines in methanol. Figure 6 shows the simulated PDA molecule while Table 1 summarizes the results computed by the software. The pK_a values of the diamines are also included in Table 1.[44] The smaller the pK_a value for the amine group, the more basic is the amino compound which indicates greater reactivity. The Fukui function indices increase in the order of BuDA < PDA < EDA, while the pK_a values increase in the order of BuDA > PDA > EDA. Both the Fukui function indices and the pK_a values indicate that EDA is the most nucleophilic among the diamines used. EDA has the smallest molecular length of 5.32 Å, and hence,

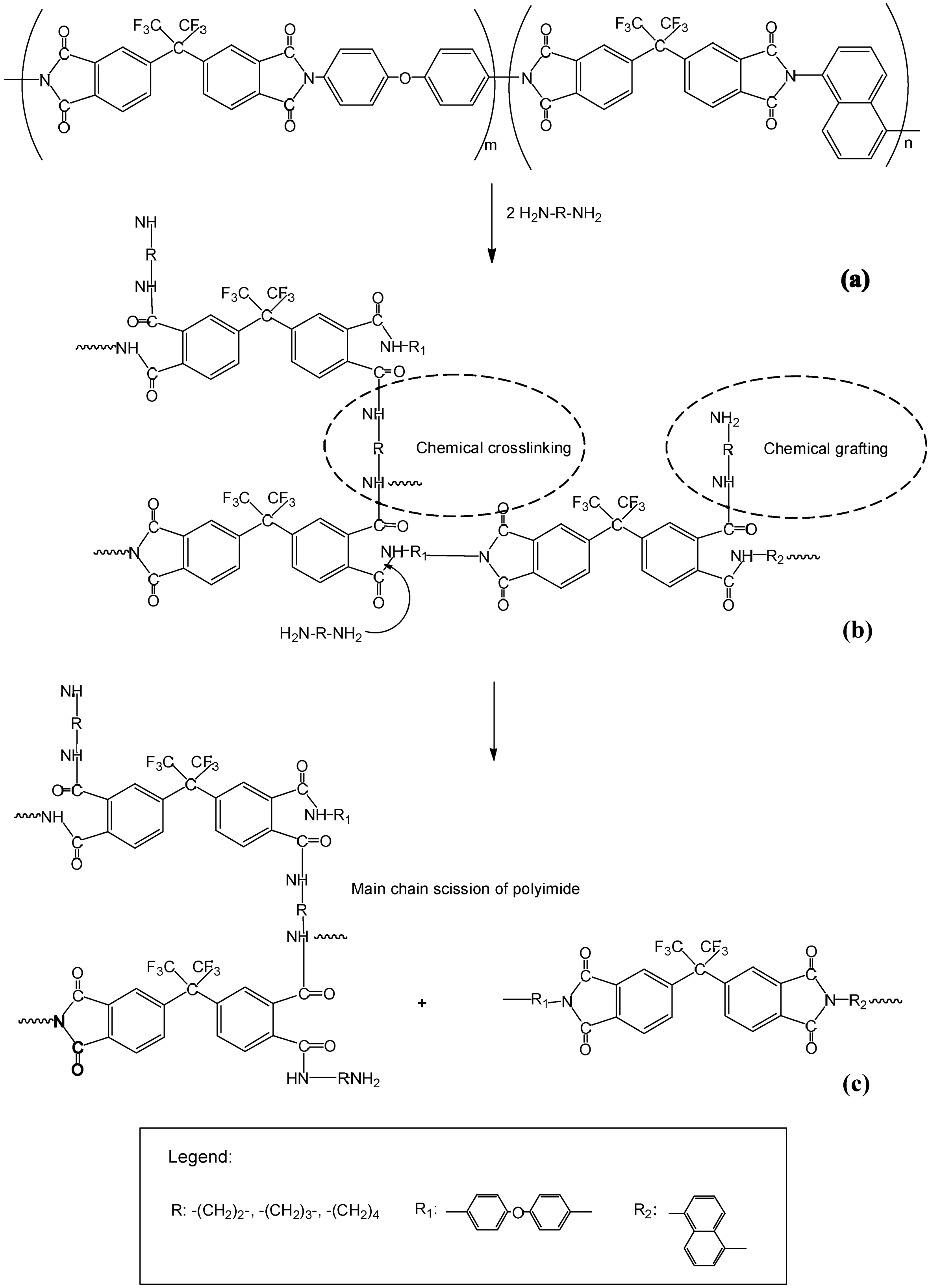

Figure 3. Reaction mechanism between diamines and polyimide.

it is able to penetrate deeper into the dense polymeric matrix. Both the high nucleophilicity and small molecular dimension of EDA facilitate the reaction, causing more severe main-chain scission. The polymeric fragments formed as a result of the chain scission diffuse into the solution, thereby increasing the peak area and intensity. Hence, the peaks obtained from the UV−vis analysis are the most prominent for EDA/methanol solutions. The greater penetration and reactivity of EDA also account for the considerably larger mean roughness for the EDA modified film.

Thermal gravimetric analyses of the polymeric films before and after modification were conducted (results not shown). All the modified films exhibit dual transitions while the unmodified film shows a single transition. The original copolyimide is stable

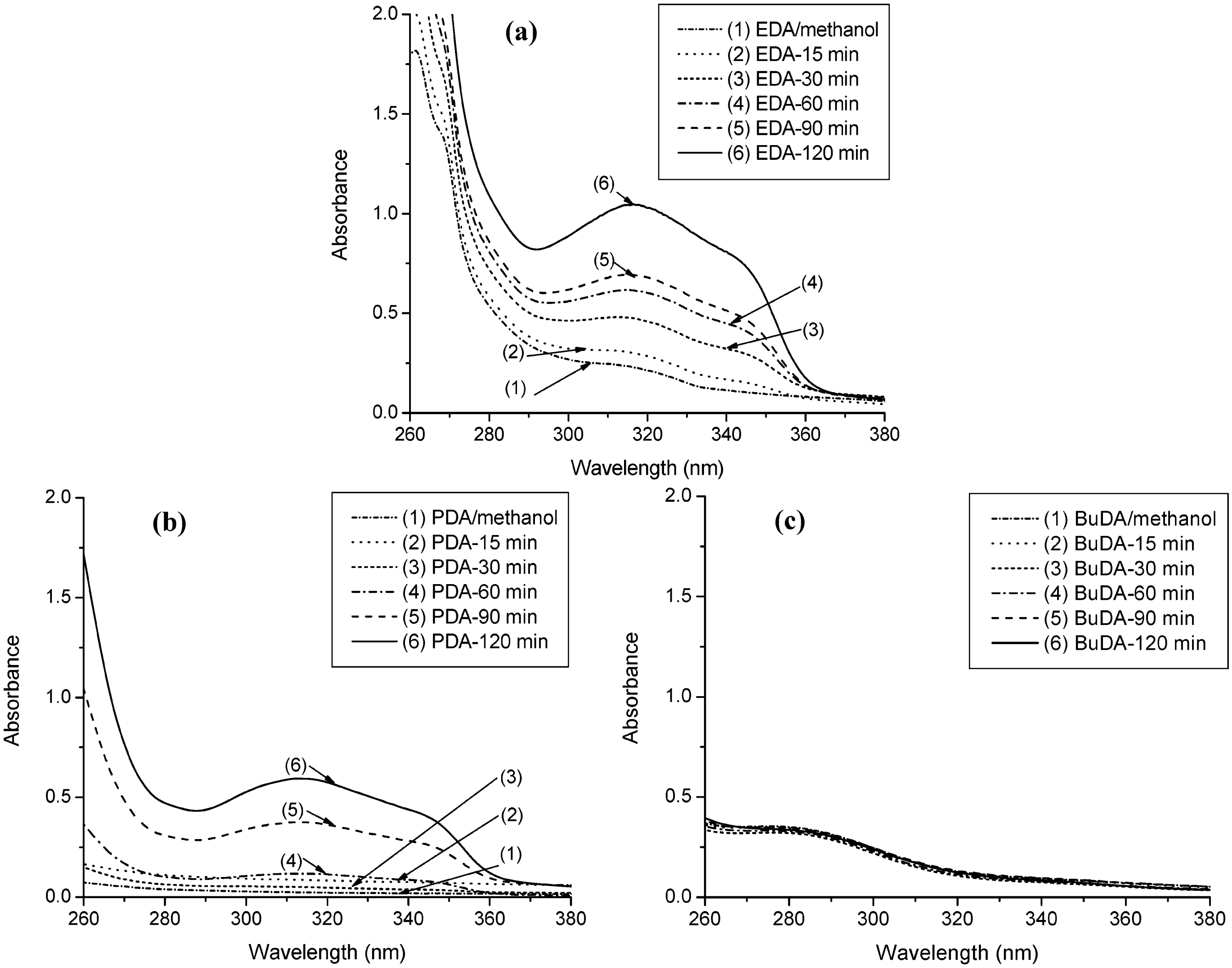

Figure 4. UV−vis spectra of (a) EDA, (b) PDA, and (c) BuDA in methanol solutions after modification.

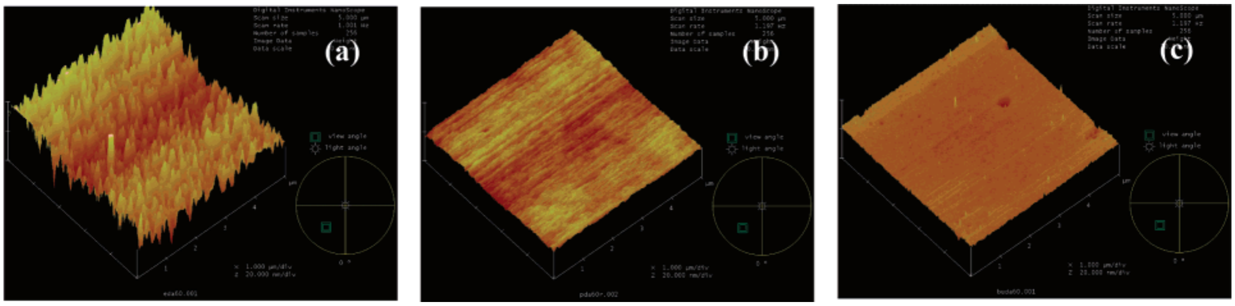

Figure 5. AFM images of showing the topology of 6FDA−ODA/NDA dense films modified using (a) EDA, (b) PDA, and (c) BuDA for an immersion time of 60 min.

up to 500 °C, whereas the modified films exhibit the onset of degradation at approximately 150−200 °C. With increasing immersion time, the weight loss of the polymeric films was greater for the same temperature increment. Hence, chemical modification decreases the thermal stability of the polyimide films. In addition, as majority of the H_2/CO_2 mixtures that require separation normally contains H_2O as a contaminant, the thermal stability of the neat polyimide film and the 90 min PDA cross-linked membrane before and after water sorption were determined. The results obtained showed that there is negligible change in the thermal stability of the films after water sorption (data not shown). Hence, the thermal stability of the modified membranes can be maintained even in the presence of water.

The thermal stability of the chemically modified polyimide films with amino compounds and the reversible reaction between the imide rings and amine groups have been studied in detail by Shao et al. and Powell et al.[31,33,45] Shao et al. proposed the elimination of the diamine molecules upon the reversible formation of the amide groups back to the imide rings after thermal annealing.[31] Powell et al. explored the phenomenon further and suggested that, in addition to the elimination of the diamines, main chain scission of the polymeric backbone also occurs.[45] Gel permeation chromatography was carried out for the unmodified film, and the modified film after thermal treatment and a decline in the molecular weight of the latter was reported.[45] The combined ideas from Shao et al. and Powell

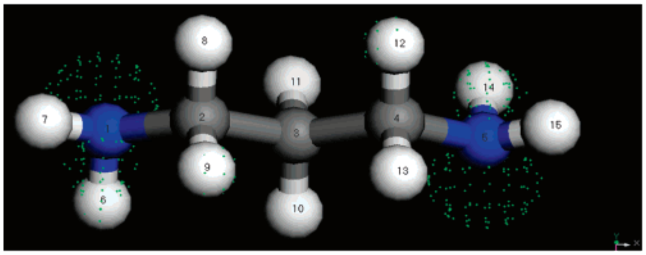

Figure 6. Molecular simulation showing the electron density surrounding the nucleophilic sites of a PDA molecule.

Table 1. Fukui Indices, Dimensions, and pK_a Values of the Aliphatic Diamines

		Fukui index (based on N atom)		
diamine	length (Å)	Mulliken	Hirshfeld	pK_a
EDA	5.32	0.196	0.216	9.92
PDA	6.58	0.184	0.197	10.55
BuDA	7.83	0.180	0.191	10.82

et al. suggest that main-chain scission and release of diamines occur during the thermal treatment of the modified membranes.

However, in our study, we showed that main-chain scission occurred during the chemical modification process. This implies that the decrease in polymer molecular weight after thermal treatment may not be fully attributed to main-chain scission arising from the heat treatment. Polymeric backbone breakage which occurs during chemical modification too brings about a decline in the molecular weight after the elimination of the diamines. Not all the polymeric fragments formed as a result of chain scission end up in solution after modification since the polymeric chains that form the membrane are twined and tangled to each other. Those fragments in the solution probably have shorter chain lengths and are nearer to the membrane surface, thereby facilitating their diffusion into the solution. Therefore, we propose a modified scheme which suggests that main-chain scission occurs with long immersion time, and further backbone breakage and the release of diamines occur during thermal treatment.

The mechanical properties of the neat 6FDA−ODA/NDA films and the membranes modified with PDA for 90 min were analyzed. With reference to Table 2, the elongation at break of the PDA modified membrane decreases by ∼15% as compared to the pure polyimide film. This decrease is possibly due to the existence of weak points within the membrane resulting from the effect of chemical etching (main chain breakage) caused by the reactive diamines. Similarly, the unmodified and modified membranes were immersed in water before undergoing the mechanical analysis. The results are shown in Table 2, and a quick comparison reveals that the extensions at break for the membranes with or without water sorption are comparable. This shows that the mechanical integrity of the diamine modified membranes can be maintained even when employed for aggressive feed streams that contains water as the contaminant.

To study the changes in the interstitial space of the polyimide films after chemical modification, XRD analysis was performed. The *d*-spaces of the unmodified and modified 6FDA−ODA/NDA dense membranes remain in the range 5.77 ± 0.15 Å, regardless of the diamines used. This observation is consistent with the work by Ren et al. where 6FDA−ODA/NDA hollow fibers were modified with *p*-xylenediamine, and negligible change in *d*-space was observed.[26] In another work by Cao et al., 6FDA−2,6-DAT (2,6-diaminotoluene) hollow fibers were cross-linked by aromatic diamines, and no change in *d*-space was observed after modification.[30] The *d*-space of the pure 6FDA−2,6-DAT membrane is 5.69 Å.[30] Previous works by Chung and co-workers employing 6FDA−durene as the working polymer for diamines modification showed decline in *d*-space with increasing immersion time. For instance, the modification of 6FDA−durene with PDA for an immersion time of 10 min changes the *d*-space from 6.40 to 5.86 Å.[7]

Considering these three 6FDA-based polyimides, a generalization for the effect of diamino modification on the *d*-space of these polyimide membranes can be drawn. Referring to Figure 7, for polyimide membranes with a smaller *d*-space (proportional to free volume) to begin with, diamino modification does not bring about chain tightening effects, regardless of the type of diamines used. Since the *d*-spaces of 6FDA−ODA/NDA and 6FDA−2,6-DAT are comparable and are relatively smaller than 6FDA−durene, both do not exhibit significant changes in *d*-space after chemical modification. On the other hand, as the original 6FDA−durene has a larger *d*-space, the diamino modification results in noticeable decline in *d*-space. Another interesting phenomenon is the similarity in the average *d*-space of 6FDA−durene after considerable extent of modification with the *d*-spaces of 6FDA−ODA/NDA and 6FDA−2,6-DAT membranes.

3.2. Gas Separation Properties of Modified Copolyimide Films. The permeability (P) of a gas through a polymeric membrane is dependent on the diffusivity (D) and solubility (S) of the gas as shown in eq 7. Both the gas diffusivity and solubility are in turn dependent on the available free volume present within the polymeric matrix.

$$P = SD \tag{7}$$

The ideal permselectivity of a membrane for a particular gas pair depends on the interplay between the diffusivity selectivity and the solubility selectivity

$$\alpha_{H_2/CO_2} = \frac{D_{H_2}}{D_{CO_2}} \frac{S_{H_2}}{S_{CO_2}} \tag{8}$$

where D_{H_2} and D_{CO_2} represent the diffusivity of H_2 and CO_2, respectively; S_{H_2} and S_{CO_2} are the solubility of H_2 and CO_2, respectively.

Generally, the chemical modification of polyimide membranes with diamines results in three scenarios. First, the cross-linking reaction may tighten the polymeric chains (decrease *d*-space), thereby resulting in lower free volume. On the other hand, diamine molecules grafted or cross-linked to the polymer chains introduces additional organic moiety to the polymeric matrix which too reduces the available free volume and hence acts as

Table 2. Mechanical Properties of the Membranes with and without Water Sorption

sample	max load (N)	extension at break (%)	load at break (N)	modulus (GPa)
without water sorption				
6FDA−ODA/NDA pure film	22.09 ± 3.51	5.73 ± 0.05	21.95 ± 3.49	2.92 ± 0.12
PDA cross-linked for 90 min	19.61 ± 0.46	4.85 ± 1.50	19.31 ± 0.45	3.02 ± 0.06
with water sorption				
6FDA−ODA/NDA pure film	24.65 ± 0.43	5.74 ± 0.88	24.54 ± 0.41	3.11 ± 0.10
PDA cross-linked for 90 min	20.91 ± 1.43	5.07 ± 0.17	20.46 ± 1.55	2.84 ± 0.10

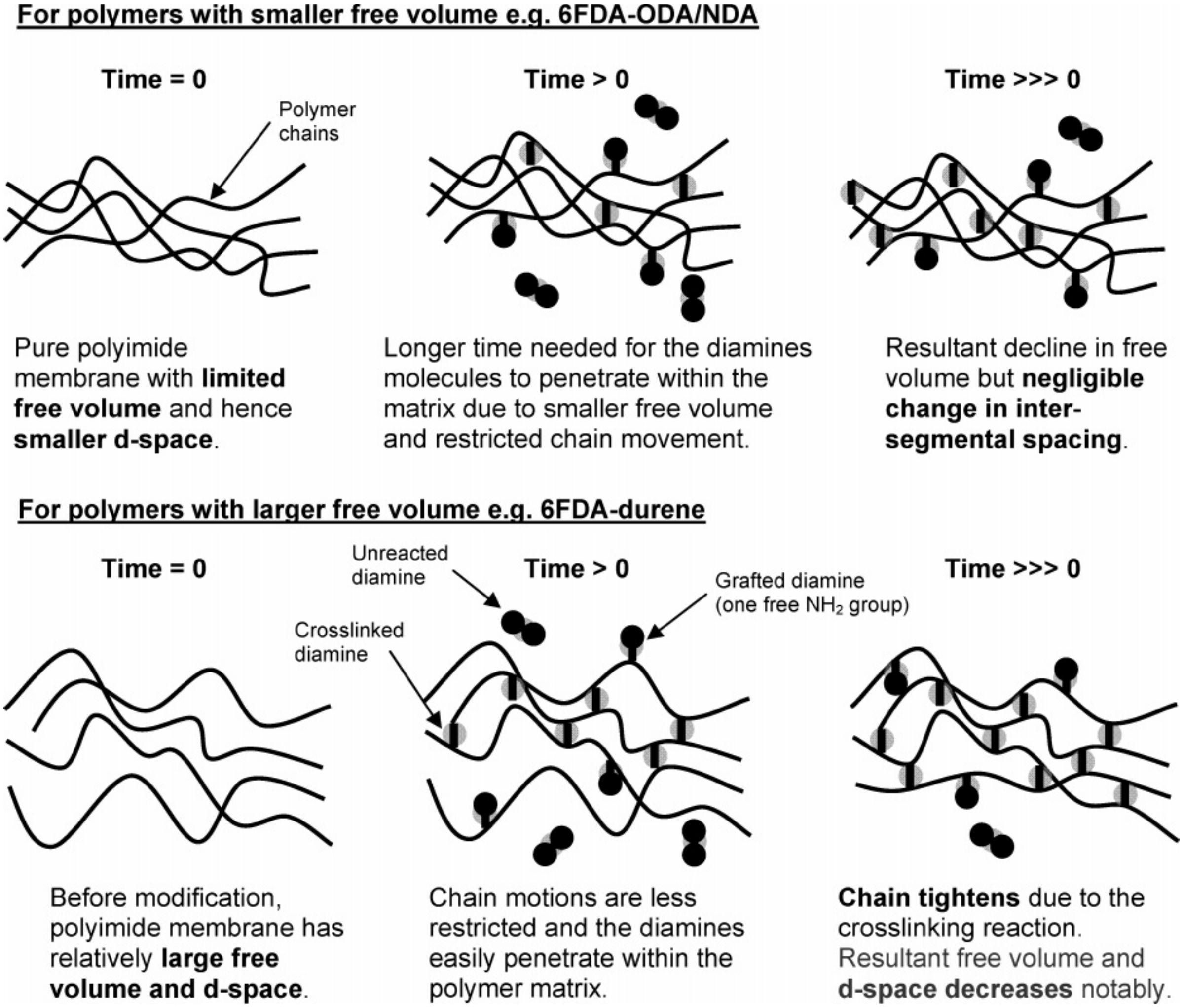

Figure 7. Effects of modification on intersegmental spacing of polyimide membranes.

a hindrance for the transport of gas molecules. Last, the amide groups formed as a result of the reaction between the imide and amine groups, and the unreacted free amine groups affect polymer−polymer and polymer−penetrant interactions.

The gas permeabilities of H_2 and CO_2 through the 6FDA−ODA/NDA films modified using EDA, PDA, and BuDA as a function of immersion duration are shown in Table 3. The decrease in gas permeability with increasing immersion time is due to the reduction of free volume resulting from the presence of additional diamines moieties since XRD analysis indicates negligible change in *d*-space after modification. The difference in the reactivity and diffusivity of the diamines within the membrane accounts for the difference in the relative declines in the gas permeabilities. As previously mentioned, EDA being the smallest and most nucleophilic diamine is able to modify (includes both grafting and cross-linking) the polyimide membrane by the largest extent within a short immersion time. For an immersion duration of 15 min, H_2 permeability decreases by ∼25% for EDA modified film which is larger than the corresponding decrease for PDA modified film (∼10%). For BuDA modified film, H_2 permeability increases by about 5%. This increment is due to the effect of methanol swelling. As BuDA is a larger molecule with lower nucleophilicity, it takes time for the diamine to penetrate and react with the imide group. Hence, at a short modification time of 15 min, the limited degree of cross-linking does not offset the effects of methanol swelling for small gases like H_2.

Table 3. Gas Permeation Properties of 6FDA−ODA/NDA Membranes at 35 °C and 3.5 atm

	permeability (barrer)[a]		selectivity
samples	H_2	CO_2	H_2/CO_2
6FDA−ODA/NDA pure film	69.78	29.01	2.3
EDA modified for			
15 min	51.50	9.47	5.4
30 min	36.84	2.08	17.7
60 min	26.72	0.98	27.1
90 min	22.70	0.76	29.7
120 min	16.55	0.71	23.4
PDA modified for			
15 min	60.14	9.06	6.6
30 min	36.55	1.58	23.2
60 min	23.34	0.60	39.2
90 min	16.48	0.26	64.1
120 min	13.90	0.23	60.0
BuDA modified for			
15 min	70.74	14.18	5.0
30 min	63.04	13.33	4.7
60 min	55.11	6.24	8.8
90 min	45.82	3.98	11.5
120 min	38.55	1.84	20.9

[a] 1 barrer = 1×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg) = 7.5005×10^{-18} m^2 s^{-1} Pa^{-1}.

The diamino modification of polyimide membranes alters both the diffusivity selectivity and the solubility selectivity. Sorption tests were conducted for the original polyimide membrane and the membrane modified with PDA for

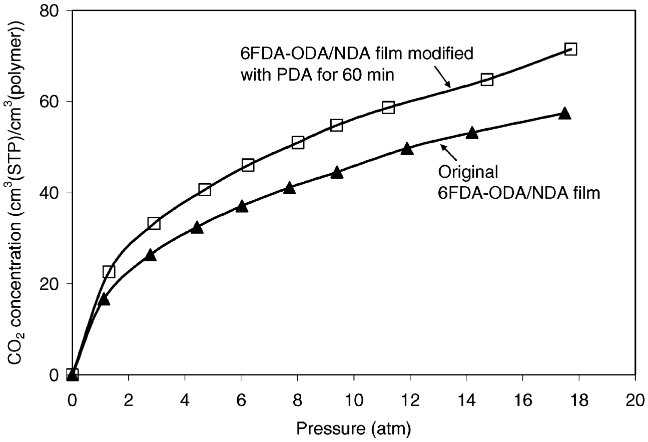

Figure 8. CO_2 sorption isotherms of unmodified and modified dense films.

immersion duration of 60 min. Figure 8 shows the CO_2 sorption isotherms for the unmodified and modified polyimide films. CO_2 sorption increases after PDA modification. The increase in gas sorption may be due to the increase in available sorption sites within the polymer matrix or enhanced polymer−penetrant interactions. Since the diamino modification decreases the available free volume, the increase in gas sorption is hence attributed to the increase in polymer−penetrant interactions. Therefore, PDA modification decreases the solubility selectivity for H_2/CO_2. This in turn implies that the enhancement in diffusivity selectivity after diamino modification more than compensate for the decline in solubility selectivity. Hence, the H_2/CO_2 permselectivity increases after modification.

Figure 9 shows the gas separation performance of the diamino modified 6FDA−ODA/NDA dense films in comparison to the Robeson trade-off line.[46] However, one important point to ponder is that the Robeson upper bound is only valid for homogeneous membranes.[46] Robeson et al. suggested that for laminated films like the diamines modified membranes in this work the gas separation performance of the modified layer may be in close proximity to the upper limit.[46] Based on a simplified resistance model for our diamines modified membranes (Figure 10), the relationships between the modified layer thickness (L_1) and the permeability of the modified layer (P_1) are shown by eqs 9−11.

The assumptions made in the development of the simplified model includes (1) homogeneous modified layer, (2) negligible modification of the circular piece of membrane from the radial direction, and (3) equal thickness of the top and bottom modified layers.

$$\frac{L_T}{P_T A_T} = \frac{2L_1}{P_1 A_1} + \frac{L_2}{P_2 A_2} \tag{9}$$

$$\frac{L_T}{P_T} = \frac{2L_1}{P_1} + \frac{L_T - 2L_1}{P_2} \tag{10}$$

$$P_1 = \frac{2L_1}{\left[\frac{L_T}{P_T} - \frac{L_T - 2L_1}{P_2}\right]} \tag{11}$$

P refers to the permeability, L refers to the thickness, and A represents the surface area. The subscripts 1 and 2 refer to the modified and unmodified layers, respectively, while T represents the total or overall property.

Equation 11 cannot be solved explicitly due to the dependence of P_1 and L_1. Therefore, an approximate thickness of the modified layer is required before a rough value of P_1 can be determined. From the dissolution of the one-sided PDA modified (90 min) membranes, the thickness of the dissolved portions can be determined, given the density of the neat polyimide film as 1.4 g/cm^3 (determined from the buoyancy method) and the diameter of the modified film as 1.5 cm. The rough thickness of the dissolved portion subtracted from the initial thickness of the membrane provides an estimate of the thickness of the modified layer. The mean approximate thickness of the modified layer is 4.87 ± 0.67 μm. With this rough value of L_1, the permeabilities of H_2 and CO_2 through the diamine modified layer (determined from eq 11) are 3.37 and 0.043 barrer, respectively, and the corresponding ideal H_2/CO_2 selectivity is 78. When this point is plotted against the Robeson plot, its position still falls above the upper bound as shown in Figure 11.

The rough thickness of the modified layer obtained as such may be an underestimate or overestimate of the true value. The immersion of the modified membrane in DMF not only dissolves the unmodified polymeric matrix but also the portions that are grafted by the diamines and the regions which have smaller degree of cross-linking. The grafting of diamines also changes the gas separation performance of the membrane and therefore should be considered in the determination of the modified layer thickness. Hence, the approximate thickness which we have determined may be an underestimate of the true value of the modified layer. If this is the case, the actual position indicating the gas separation performance of the modified layer alone probably falls further away from the upper bound. Hence, this provides preliminary justification for the claim that the PDA modified 6FDA−ODA/NDA membranes exhibit better performance than conventional polymers.

On the other hand, the counterargument is that the diamine modified layer is certainly not homogeneous as assumed in the simplified resistance model. The outermost surface is modified to a larger extent, and the degree of modification decreases with increasing membrane depth from the axial direction. This implies the existence of a stratified structure within the diamine modified layer. The highly modified outermost layer may be the determining factor for the enhancement in H_2/CO_2 permselectivity while the remaining modified portions may only exert a marginal effect on the overall gas separation performance. In this case, the rough thickness may be overestimated. Therefore, further studies are required to provide a closer estimate for the true value of the modified layer which significantly contributes to the enhancement in H_2/CO_2 permselectivity. Although the gas separation performances of the diamine modified membranes reported in this work cannot be compared directly with the Robeson trade-off line, the results obtained nevertheless suggest the potential use of these membranes for H_2 purification.

The ideal H_2/CO_2 permselectivity of 6FDA−ODA/NDA films modified using EDA, PDA, and BuDA are shown in Table 3. A comparison of the gas separation performance of the three diamines modified films shows that PDA modification brings about greater enhancement in H_2/CO_2 permselectivity as compared to EDA and BuDA modification. For instance, immersing the dense films in the EDA, PDA, and BuDA in methanol solutions for 90 min increases the H_2/CO_2 selectivity by 13, 27, and 5 times, respectively. The polymer intrinsic H_2/CO_2 selectivity is 2.3, and after modifying the original film with PDA for 90 min, an ideal H_2/CO_2 selectivity of 64 was achieved in the present work. The corresponding H_2 permeability was 17 barrer. In view of the promising result obtained from

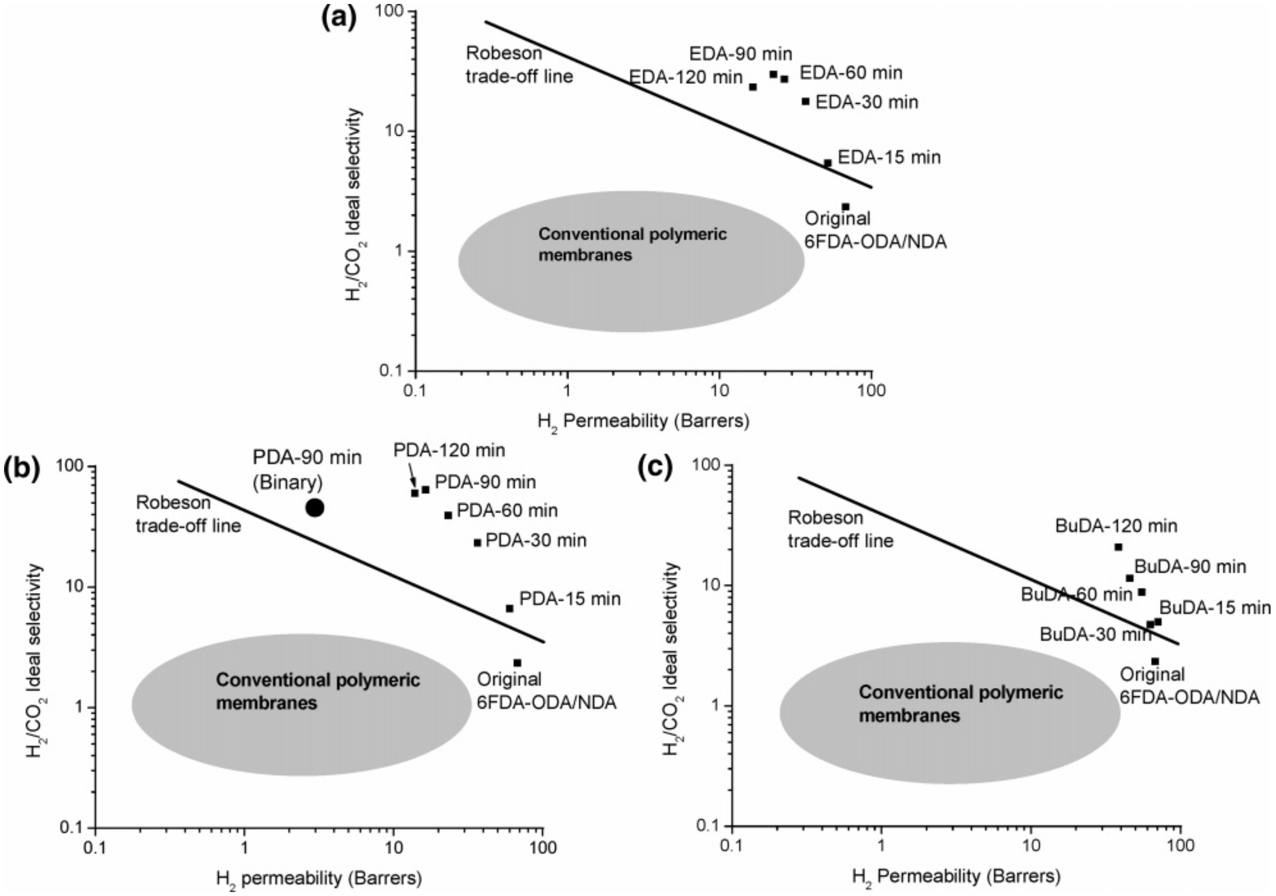

Figure 9. H_2/CO_2 separation performance of (a) EDA, (b) PDA, and (c) BuDA modified 6FDA−ODA/NDA films compared to the Robeson trade-off line.

the pure gas tests, the dense membrane modified with PDA for immersion time of 90 min was used for mixed gas tests. The H_2/CO_2 selectivity obtained from mixed gas tests was 45, and the H_2 permeability was 3 barrer. The decreases in H_2/CO_2 selectivity and H_2 permeability in mixed gas tests were due to the effects of competitive sorption between the two gases. Nevertheless, the gas separation performance of the PDA modified 6FDA−ODA/NDA dense film (immersion time of 90 min) in a binary system is still impressive despite the presence of undesirable competitive sorption between H_2 and CO_2.

In order to enhance H_2/CO_2 selectivity, the diamine used for modification has to be able to reduce polymeric chain mobility. The effectiveness of the modification reaction is thus dependent on the nucleophilicities and molecular dimensions of the diamines. BuDA is the least nucleophilic, and it has the largest molecular dimensions. Hence, it is harder for BuDA molecules to penetrate within the polymeric matrix which is a prerequisite for the reaction to take place. Hence, the majority of the modification occurs at the surface, and an overall smaller percentage of the polymeric matrix is affected. Furthermore, as the length of BuDA molecule is longer, the molecule backbone is more flexible. Hence, the chains are still mobile to certain extent even after chemical cross-linking. On the other hand, EDA too does not inhibit chain-to-chain movement effectively due to the presence of significant chemical grafting and severe chemical etching. Therefore, both BuDA and EDA are not effective cross-linking reagents for the enhancement of H_2/CO_2 permselectivity of these polyimide dense films.

For the effective modification of polyimide membranes with diamino compounds, the balance between the interplay of chemical cross-linking and chemical etching must be established. Moreover, the diamine needs to have the potential to cross-link neighboring polyimide chains since pure grafting of diamine on the polyimide does not restrict interchain movements which are necessary for significant improvement in H_2/CO_2 permselectivity. PDA has the appropriate molecular dimension and reactivity. Therefore, PDA is the most effective reagent for the diamino modification of polyimide membranes to enhance qjH_2/CO_2 selectivity.

Generally, diamine modification of 6FDA−ODA/NDA films using EDA, PDA, and BuDA increases H_2/CO_2 selectivity with increasing immersion duration. However, for EDA and PDA modified films, the H_2/CO_2 selectivity exhibits a peak at an immersion time of 90 min and beyond which the gas pair selectivity starts to decline (Table 3). This trend can be explained from the molecular aspect of the effects of modification on chain packing and rigidity. Recall that the diamino modification of polyimide membranes causes the imide rings to open, forming two amide groups. The destruction of the ring structure in the polymeric main chain decreases the polymeric backbone rigidity.[33]

At short immersion time, the interchain movements are restricted after cross-linking while the backbone rigidity is maintained since majority of the imide rings are intact, providing the mechanical integrity of the polymeric chains forming the network. However, with long modification time, most of the imide rings have opened, forming the amide groups. As such, although the chain to chain movement is inhibited effectively, the backbone rigidity is greatly reduced. Hence, for long modification duration, the mobility of the polymeric chains increases and this accounts for the decrease in H_2/CO_2 selectivity.

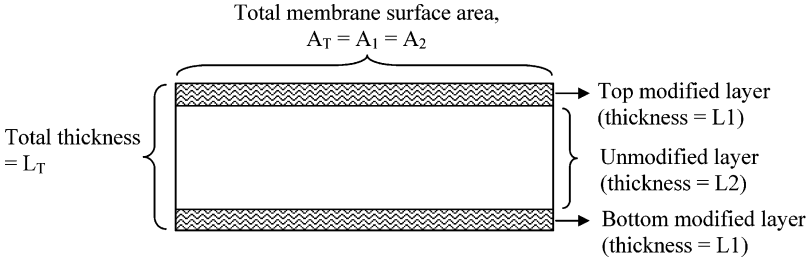

Figure 10. Schematic of the diamine modified polyimide films (simplified).

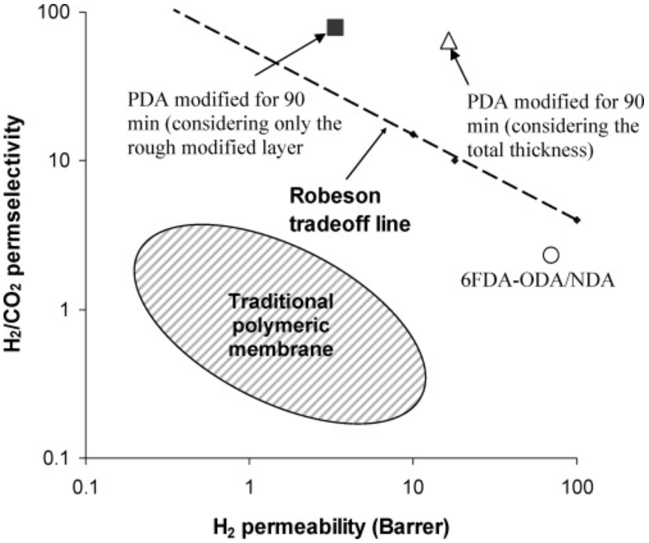

Figure 11. Gas separation performance of 90 min PDA cross-linked membranes.

Table 4. H_2/CO_2 Separation Performance of PDA Modified 6FDA−Durene and 6FDA−ODA/NDA Dense Membranes at 35 °C and 3.5 atm

6FDA−durene (ref 7)[a]			6FDA−ODA/NDA (current work)		
modification time (min)	$P_{\mathrm{H}}2$ (barrer)	α_{H_2/CO_2}	modification time (min)	P_{H_2} (barrer)	α_{H_2/CO_2}
0	600	1	0	68	2.3
1	200	4	30	37	23
5	15	38.5	60	23	39
10	10	101	90	17	64

[a] Permeability and ideal permselectivity values are approximated from plots.

Table 4 compares the H_2/CO_2 gas separation performance of 6FDA−durene and 6FDA−ODA/NDA. For 6FDA−durene membranes, relatively shorter immersion times were required and modification with PDA for 10 min gave H_2/CO_2 selectivity of 101, which is 100 times greater than the intrinsic selectivity. However, the H_2 permeability decreases by 60 times. This tradeoff between permeability and selectivity is often a problem encountered by membrane scientists. In the present work, longer immersion times are required before substantial cross-linking effects are experienced. This is because of the smaller free volume of 6FDA−ODA/NDA and the lesser swelling effect by methanol. For 6FDA−ODA/NDA, the highest H_2/CO_2 selectivity achieved was 64 (30 times increment), but the decrease in H_2 permeability is not as drastic as 6FDA−durene. For PDA modified 6FDA−ODA/NDA membranes (immersion time of 90 min), H_2 permeability only decreases by 4 times. The selectivity of 6FDA−ODA/NDA membranes modified with PDA peaks at 90 min and fails to increase with further modification. This is due to the effects of chemical etching from prolonged immersion times. Nonetheless, 6FDA−ODA/NDA modified membrane provides a better compromise between good H_2/CO_2 selectivity and H_2 permeability and also lower material cost as compared to 6FDA−durene.

4. Conclusions

6FDA−ODA/NDA polyimide dense films were modified successfully, forming a poly(amide−imide) network which was verified by ATR−FTIR analysis. UV−vis analysis of the resultant modification solutions and AFM analysis of the topology of the modified films supported the occurrence of chemical etching during the modification process. ATR−FTIR and gel content analysis verified the presence of considerable chemical grafting for EDA modification. Among the three aliphatic diamines, EDA is the most nucleophilic and has the smallest molecular dimensions. Hence, main-chain scissions for EDA modified films were more severe. TGA analysis showed a reduction in the thermal stability of the membranes after diamino modification. On the basis of the XRD results, there was no significant change in the *d*-spacing. One observation is the diamino modification of polyimide membranes results in chain tightening effects only for polyimides with larger free volume. In general, the diamino modification of 6FDA−ODA/NDA membranes increases the ideal H_2/CO_2 permselectivity. PDA was identified as the most effective modification reagent for enhancing the H_2/CO_2 permselectivity of 6FDA−ODA/NDA films. An ideal H_2/CO_2 permselectivity of 64, which is 30 times larger than the polymer intrinsic permselectivity, was obtained with PDA modification for 90 min and mixed gas tests returned a selectivity of 45. In conclusion, H_2/CO_2 separation performance can be tailored via the appropriate selections of diamine and immersion duration.

Acknowledgment. The authors thank Dr. Yi Li, Ms. Natalia Widjojo, and Mr. Sina Bonyadi for giving valuable suggestions to this work. Special thanks to Dr. Abhijit Chatterjee from Acceryls for assisting in the molecular simulations of the diamines using Materials Studio software. Ms. Low thanks the Singapore National Research Foundation (NRF) (NRF-G-CRP 2007-06) grant for supporting this work. In addition, the additional financial support through the leftover grants from UOP, Merck, and Mitsui via grant N-279-000-010-001 is greatly appreciated.

References and Notes

(1) Ockwig, N. W.; Nonoff, T. M. *Chem. Rev.* **2007**, *107*, 4078−4110.
(2) Ritter, J. A.; Ebner, A. D. *Sep. Sci. Technol.* **2007**, *42*, 1123−1193.
(3) Perry, J. D.; Nagai, K.; Koros, W. J. *MRS Bull.* **2006**, *31*, 745−749.
(4) Baker, R. *Membr. Technol.* **2001**, *138*, 5−10.
(5) Merkel, T. C.; Freeman, B. D.; Spontak, R. J.; He, Z.; Pinnau, I.; Meakin, P.; Hill, A. J. *Science* **2002**, *296*, 519−522.
(6) Baker, R. W. *Ind. Eng. Chem. Res.* **2002**, *41*, 1393−1411.
(7) Chung, T. S.; Shao, L.; Tin, P. S. *Macromol. Rapid Commun.* **2006**, *27*, 998−1002.
(8) Lin, H.; Freeman, B. D. *J. Mol. Struct.* **2005**, *739*, 57−74.

(9) Lin, H.; Van Wager, E.; Swinnea, J. S.; Freeman, B. D.; Pas, J. S.; Hill, A. J.; Kalakkunnath, S.; Kalika, D. S. *J. Membr. Sci.* **2006**, *276*, 145−161.

(10) Raharjo, R. D.; Lin, H.; Sanders, D. F.; Freeman, B. D.; Kalakkunnath, S.; Kalika, D. S. *J. Membr. Sci.* **2006**, *283*, 253−265.

(11) Lin, H.; Van Wager, E.; Freeman, B. D.; Toy, L. G.; Gupta, R. P. Gupta *Science* **2006**, *311*, 639−642.

(12) Merkel, T. C.; Toy, L. G. *Macromolecules* **2006**, *39*, 7591−7600.

(13) Toy, L. G.; Nagai, K.; Freeman, B. D.; Pinnau, I.; He, Z.; Masuda, T.; Teraguchi, M.; Yampolskii, Yu. P. *Macromolecules* **2000**, *33*, 2516−2524.

(14) Athayde, A. L.; Baker, R. W.; Nguyen, P. *J. Membr. Sci.* **1994**, *94*, 299−311.

(15) Mercea, P.; Muresan, L.; Mecea, V. *J. Membr. Sci.* **1985**, *24*, 297−307.

(16) Fritsch, D.; Peinemann, K.-V. *J. Membr. Sci.* **1995**, *99*, 29−38.

(17) Compton, J.; Thompson, D.; Kranbuehl, D.; Ohl, S.; Gain, O.; David, L.; Espuche, E. *Polymer* **2006**, *47*, 5303−5313.

(18) Dai, Y.; Guiver, M. D.; Robertson, G. P.; Kang, Y. S. *Macromolecules* **2005**, *38*, 9670−9678.

(19) Guiver, M. D.; Robertson, G. P.; Dai, Y.; Bilodeau, F.; Kang, Y. S.; Lee, K. J.; Jho, J. Y.; Won, J. O. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4193−4204.

(20) Ayala, D.; Lozano, A. E.; de Abajo, J.; Garćia-Perez, C.; de la Campaa, J. G.; Peinemann, K.-V.; Freeman, B. D.; Prabhakar, R. *J. Membr. Sci.* **2003**, *215*, 61−73.

(21) Kim, Y. K.; Lee, J. M.; Park, H. B.; Lee, Y. M. *J. Membr. Sci.* **2004**, *235*, 139−146.

(22) Kim, Y. K.; Park, H. B.; Lee, Y. M. *J. Membr. Sci.* **2005**, *255*, 265−273.

(23) Xiao, Y.; Dai, Y.; Chung, T. S.; Guiver, M. D. *Macromolecules* **2005**, *38*, 10042−10049.

(24) Liu, Y.; Wang, R.; Chung, T. S. *J. Membr. Sci.* **2001**, *189*, 231−239.

(25) Liu, Y.; Chung, T. S.; Wang, R.; Li, D. F.; Chng, M. L. *Ind. Eng. Chem. Res.* **2003**, *42*, 1190−1195.

(26) Ren, J.; Wang, R.; Chung, T. S.; Li, D. F.; Liu, Y. *J. Membr. Sci.* **2003**, *222*, 133−147.

(27) Coleman, M. R.; Koros, W. J. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 1915−1929.

(28) Stern, S. A.; Mi, Y.; Yamamoto, H.; St. Clair, A. K. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 1887−1909.

(29) Coleman, M. R.; Koros, W. J. *Macromolecules* **1999**, *32*, 3106−3113.

(30) Cao, C.; Chung, T. S.; Liu, Y.; Wang, R.; Pramoda, K. P. *J. Membr. Sci.* **2003**, *216*, 257−268.

(31) Shao, L.; Chung, T. S.; Goh, S. H.; Pramoda, K. P. *J. Membr. Sci.* **2005**, *256*, 46−56.

(32) Liu, Y.; Chng, M. L.; Chung, T. S.; Wang, R. *J. Membr. Sci.* **2003**, *214*, 83−92.

(33) Shao, L.; Chung, T. S.; Goh, S. H.; Pramoda, K. P. *J. Membr. Sci.* **2005**, *267*, 78−89.

(34) Xiao, Y.; Chung, T. S.; Chng, M. L. *Langmuir* **2004**, *20*, 8230−8238.

(35) Xiao, Y.; Shao, L.; Chung, T. S.; Schiraldi, D. A. *Ind. Eng. Chem. Res.* **2005**, *44*, 3059−3067.

(36) Chung, T. S.; Chng, M. L.; Pramoda, K. P.; Xiao, Y. *Langmuir* **2004**, *20*, 2966−2969.

(37) Shao, L.; Chung, T. S.; Goh, S. H.; Pramoda, K. P. *J. Membr. Sci.* **2004**, *238*, 153−163.

(38) Cao, C.; Wang, R.; Chung, T. S.; Liu, Y. *J. Membr. Sci.* **2002**, *209*, 309−319.

(39) Lin, W. H.; Vora, R. H.; Chung, T. S. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 2703−2713.

(40) Yang, W.; Mortier, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 5708−5711.

(41) Kolandaivel, P.; Praveena, G.; Selvarengan, P. *J. Chem. Sci.* **2005**, *117*, 591−598.

(42) Wang, R.; Cao, C.; Chung, T. S. *J. Membr. Sci.* **2002**, *198*, 259−271.

(43) Shonaike, G. O., Simon, G. P., Eds. *Polymer Blends and Alloys*; Marcel Dekker: New York, 1999.

(44) Lide, D. R., Ed. *CRC Handbook of Physics and Chemistry*; CRC Press: Cleveland, OH, 2006.

(45) Powell, C. E.; Duthie, X. J.; Kentish, S. E.; Qiao, G. G.; Stevens, G. W. *J. Membr. Sci.* **2007**, *291*, 199−209.

(46) Robeson, L. M.; Burgoyne, W. F.; Langsam, M.; Savoca, A. C.; Tien, C. F. *Polymer* **1994**, *35*, 4970−4978.

MA702360P