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Synthesis, cross-linking and carbonization of co-polyimides containing internal acetylene units for gas separation

Youchang Xiao^a, Tai-Shung Chung^{a,*}, Huai Ming Guan^a, Michael D. Guiver^b

^a Department of Chemical & Biomolecular Engineering, National University of Singapore, 10 Kent Ridge Crescent, 119260 Singapore, Singapore

^b Institute for Chemical Process and Environmental Technology, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

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Abstract

Cross-linkable polyimides containing internal acetylene units have been synthesized by random copolymerization of 6FDA dianhydride, 2,3,5,6-tetramethyl-1,4-phenylenediamine (Durene) and 4,4'-diaminodiphenylacetylene (p-intA) diamine as materials for gas separation. Compared with 6FDA-Durene polyimide, 6FDA-Durene/p-intA co-polyimide shows denser polymer chain packing, which is confirmed by wide-angle X-ray diffraction (WAXD). The thermally treated co-polyimides are insoluble in various solvents and show an increase in T_g , indicating the formation of network structures among the polymer chains. Differential scanning calorimetry (DSC) and FT-Raman suggest that cross-linking arises from Diels-Alder cycloaddition between the internally arranged acetylene units along the polymer main chain, resulting in extended conjugated aromatic structures. The thermally cross-linked membranes show enhanced resistance to CO₂ plasticization up to around 5×10^6 Pa (700 psi). The rigidified membrane structure provides increased gas selectivity without severely compromising gas permeability. The gas separation performance of carbonized membranes is remarkably superior to those of neat and cross-linked copolyimides because of a large increase in rigidification in the polymer matrix. A Diels-Alder cycloaddition reaction produces a much more rigid and planar conjugated aromatic structure in the polymer chains and results in a higher degree of graphitization during carbonization, which is confirmed by XPS and WAXD. Carbon membranes derived from co-polyimides with more internal acetylene units show much better gas separation performance than those derived from polyimides without internal acetylene units.

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1. Introduction

Membranes must meet the following performance criteria in order to have broad and successful applicability in various gas separation environments [1–4]: (1) high permeability and high selectivity to minimize capital and operating costs; (2) good chemical resistance to prolong the lifetime of membrane systems; (3) thermal stability and mechanical properties to enable systems to operate at elevated temperatures; and (4) superior plasticization resistance to maintain high separation performance in the presence of highly sorbing penetrants, such as CO₂ and hydrocarbon gases. Among many polymeric materials, aromatic polyimides consisting of rigid chains and containing

bulky and sterically-hindered structures are considered to have great potential as emerging membrane materials [5–7]. Extensive research to tailor polyimide chemical structures for better gas separation performance has been carried out in the last two decades [8–11]. However, structural design attempts to further improve performance have apparently approached a limit as indicated in the trade-off curve describing the relationship between gas permeability and selectivity [12,13]. In addition, no major breakthrough in the improvement of plasticization resistance has been achieved on polyimide membranes through backbone chemical modification or introduction of various side groups in the majority of cases.

Polyimide modification by cross-linking and carbonization has received much attention since it appears to provide a promising approach toward improving selectivity and chemical and plasticization resistance. Cross-linking modifications of polyimides can be induced by several methods, such as ultra-

* Corresponding author. Fax: +65 67791936.

E-mail address: chencts@nus.edu.sg (T.-S. Chung).

violet (UV) irradiation of benzophenone-containing polyimides [14], thermal treatment of polyimides containing acetylene end groups [15,16], or cross-linking polyimide chains by small molecules with multiple reactive groups [17–22]. The cross-linking modification tends to increase chain packing and inhibits the intra-segmental and inter-segmental mobility, resulting in higher gas selectivity. It has been shown that a cross-linked structure would limit material swelling in the presence of plasticizing agents, as well as improve the chemical and thermal stability of membranes.

When transforming polyimide membranes to carbon membranes by high temperature pyrolysis, the gas transport switches from solution-diffusion to a primarily molecular sieving mechanism [23–26]. As a result, the gas separation factor surpasses the upper bound of the trade-off curve for conventional polymer membranes. This phenomenon is especially true for those gas pairs with similar molecular sizes. Moreover, as compared to polymeric materials, carbonized membranes have higher tolerance to harsh environments due to the sluggish chemical reactivity and better thermal resistance. The microstructure of carbon membranes from polyimides is determined by a number of factors including: (1) the different chemical structure of polyimides which induces dissimilar chain packing, thermal stability, molecular flatness and in-plane orientation [27,28]; (2) the pyrolysis conditions such as temperature, atmosphere and heating rate [29,30]; (3) the pre-treatment of polyimide before carbonization using thermostabilization, polymer blending, non-solvent immersion or chemically grafted side groups [31–37]; (4) post-treatment of carbonized membranes by oxidation or chemical vapor deposition [38–40].

In the present work, a combination of cross-linking and carbonization is applied for the first time to fabricate new membrane materials in order to achieve high gas separation performance and better physical/chemical stability simultaneously. It is known that the chemically cross-linked structures of polyimides induced by glycols or amino components are not very thermally stable because the ester or amide linkages are easily cleaved and release small penetrant molecules when the cross-linked polyimides are subjected to high temperature treatments [41]. Therefore, in order to investigate the associated effects of cross-linking and carbonization on the gas transport in polyimide membranes, thermally induced cross-linked carbon precursors are the subject of the present work. Acetylene end-caps are known as excellent cross-linking sites for thermally curing gas separation polyimide membranes [15,16]. However, to our best knowledge, there is no report on the gas transport properties of polyimides containing internal acetylene units as cross-linking sites. Acetylene cross-linking sites situated along the polymer chain should provide a greater degree of rigidification over end-cap sites. Takeichi et al. have studied cross-linking behavior of internally linked acetylene units to the aromatic rings by preparing polyimide from 4,4'-diaminodiphenylacetylene (p-intA) and 2,2'-bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) [42–44]. In order to avoid excessive cross-linking which may result in impractical low gas permeability and poor mechanical properties, a co-polyimide was synthesized that contained 2,3,5,6-tetramethyl-1,4-phenylenediamine (Durene) monomer

to dilute the cross-linking sites. After casting this new co-polyimide (6FDA-Durene/p-intA) into flat dense films, thermal cross-linking behavior was investigated by DSC, WAXD, XPS and FT-Raman. The cross-linked co-polyimide membranes were also carbonized at 800 °C. Based on the gas transport properties of the original polyimides, cross-linked polyimides, and resultant carbonized membranes, the evolution of membrane microstructure and separation performance changes were investigated and discussed.

2. Experimental

2.1. Reagents

2,2'-Bis(3,4'-dicarboxyphenyl) hexafluoropropane dianhydride, supplied from Clariant company, was purified by vacuum sublimation before usage. 2,3,5,6-Tetramethyl-1,4-phenylenediamine (Durene diamine) and 4,4'-diaminodiphenylacetylene supplied from Aldrich company, were recrystallized from methanol. *N*-Methyl-pyrrolidone (NMP) purchased from Merck, was distilled at 42 °C under 1×10^5 mPa (1 mbar) after drying with molecular sieve before use. Other chemicals and solvents such as acetic anhydride, triethylamine and methanol were all reagent grade or better from Aldrich and were used without further purification. The purities of O₂, N₂, CH₄ and CO₂ were 99.99%.

2.2. Co-polyimide synthesis

Chemical imidization was performed during the synthesis of polyimide. A stoichiometric amount of 6FDA was added to a mixture NMP solution consisting of Durene and p-intA diamine at a designated molar ratio in a moisture free flask with stirring and nitrogen inlet at room temperature. After reaction for 24 h, a high molecular weight polyamic acid was formed, and then a mixture of acetic anhydride and triethylamine at 4:1 molar ratio were slowly added to the polyamic acid solution to effect imidization for 24 h. After precipitation in methanol, the polymer was filtered, washed and dried under 150 °C in vacuum for 24 h. The synthetic scheme and chemical structure of co-polyimide are shown in Fig. 1. For simplicity, the polyimide series are designated 6FDA-D, 6FDA-D4A1 and 6FDA-D3A2 according to the different molar ratios of Durene and p-intA diamine, as shown in Table 1.

The preparation of high molecular weight polyimides is crucial for the fabrication of high quality polyimide films. Inherent viscosity of polymer was determined using the Schott Gerate AVS360 Viscometer. The molecular weights of the modified polyimide were determined by gel-permeation chromatography (GPC) measurements, which were carried out on a HP 1100 HPLC system equipped with the HP 1047A RI detector and Agilent 79911GP-MXC columns. Tetrahydrofuran was used as the solvent and the flow rate was controlled at 1.0 ml/min. The polymer was dissolved in tetrahydrofuran at a concentration of 0.005 wt.%. The molecular weights were estimated by comparing the retention times in the column to those of poly(styrene) standards.

Fig. 1. The schemes of co-polyimide synthesis and structure.

The viscosity and GPC results shown in Table 1 confirmed that high molecular weight polyimides were obtained by the present synthetic method. Moreover, all the fluoro-polyimides prepared were soluble in organic solvents such as tetrahydrofuran (THF), NMP and dichloromethane.

2.3. Dense membrane preparation

Before cross-linking and carbonization, polyimides were first prepared as flat dense films. Two percent (w/w) polymer solutions were prepared by dissolving the readily-soluble polyimide powders in dichloromethane. The polymer solutions were then filtered using Whatman's filters (1 μ m) to remove insoluble materials and dust particles. Then the solutions were cast onto silicon wafers at ambient temperature. Dense membranes were formed after most of the solvent was allowed to evaporate slowly over a period of about 5 days. The residual solvent was removed by placing the dense membranes in a vacuum oven at 250 °C. All membranes were cut into circles with a diameter of 38 mm. Only the membranes with a thickness of about 50 ± 5 μ m were used in the following studies.

2.4. Cross-linking and carbonization

The thermal cure and pyrolysis were performed using a Centurion™ Neytech Qex vacuum furnace. During the thermal cure, the temperature was increased to a set point of 400 °C at a rate of 10 °C/min and held there for 1 h. The cross-linked polyimides were thus prepared after natural cooling. Carbonization was achieved by continuously increasing temperature from 400 to 800 °C at a very slow rate of 0.2 °C/min in order to prevent thermal cracking of carbon membranes. Finally, the sample was held isothermally at the final temperature for 2 h. After completing the pyrolysis process, membranes were cooled slowly at 1 °C/min in the vacuum furnace to room temperature and stored in a dry box for further studies. To simplify the sample identification, the cured samples were named as polyimide-temperature, for example 6FDA-D-400 and 6FDA-D-800.

2.5. Characterization

The weight loss of polyimide during post thermal treatment was characterized by thermogravimetric analysis (TGA) with a

Table 1
Preparation of co-polyimides

Sample name	Monomer			Inherent viscosity η_i (dl/g)	GPC		
	Diahydride	Diamine			Mw (g/mol)	Mn (g/mol)	PDI
	6FDA (mmol)	Durene (mmol)	<i>p</i> -IntA (mmol)				
6FDA-D	2.0	2.0	0	1.0	150,000	53,000	2.4
6FDA-D4A1	2.0	1.6	0.4	0.8	130,000	64,000	4.1
6FDA-D3A2	2.0	1.2	0.8	1.2	160,000	33,000	3.9

TGA 2050 Thermogravimetric Analyzer (TA Instruments). The analysis was carried out with a ramp of 10 °C/min in the temperature range from 50 to 900 °C. The purge gas was N₂ and its flow rate was controlled at 50 ml/min. Thermal analyses were measured by a Mettler Toledo Differential scanning calorimetry (DSC) model DSC822. The heating and cooling rates were 10 °C/min. The measurements were conducted in a dry nitrogen environment with a flow rate of 20 ml/min.

The chemical bonds in the polymers were investigated by Fourier Transform Infrared Spectroscopy. The FTIR measurements were performed using an attenuated total reflection mode (FTIR-ATR) with a Perkin-Elmer Spectrum 2000 FTIR spectrometer. FT-Raman spectra were recorded on a Bruker RFS 100 FT-Raman Spectrometer at room temperature with an Nd:YAG laser at an excitation wavelength of 1.064 μm. The detector for collecting radiation scattered at 180° arrangement. The scan frequency was from 3500 to 50 cm⁻¹.

An X-ray photoelectron spectrometer was utilized to monitor the chemical change on the film surface during thermal treatment and pyrolysis. The XPS measurements were carried out on an AXIS HSi spectrometer (Kratos Analytical Ltd., England) using a monochromatic Al Kα X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV. The anode voltage and anode current were 15 kV and 10 mA, respectively. The pressure in the analysis chamber was maintained at around 6.7×10^{-6} Pa (5.0×10^{-8} Torr) or lower during each measurement. All core-level spectra were obtained at a photoelectron take-off angle of 90° with respect to the sample.

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

$$n\lambda = 2d \sin \theta$$

where *d* is the dimension spacing, θ the diffraction angle, λ the X-ray wavelength and *n* is an integral number (1, 2, 3...).

2.6. Gas permeation measurements

Pure gas permeabilities were obtained by a constant volume method at 35 °C and 1.01325×10^6 Pa (10 atm) in the sequence of O₂, N₂, CH₄ and CO₂. A detailed description of the permeation cell design and testing conditions can be found elsewhere [46]. The modified film was mounted onto the permeation cell and vacuumed at 35 °C for more than 24 h before the gas permeation test was carried out. The permeability of each gas was obtained from the average value of at least three tests with a difference smaller than 1%, and each test was carried out at an interval of 6–8 h. The ideal selectivity is defined as follows:

$\alpha_{A/B} = P_A/P_B$, where *P_A* and *P_B* are the permeability of gases A and B, respectively.

3. Results and discussion

3.1. Characterization of co-polyimides containing internal acetylene units

Three kinds of co-polyimides, 6FDA-D, 6FDA-D4A1, and 6FDA-D3A2, prepared from different ratios of diamine monomers were prepared according to Fig. 1 and Table 1. Characteristic absorption bands at 1780, 1720, and 1370 cm⁻¹ arising from the imide structure are clearly observed in the FTIR stacked spectra of the three polyimides as shown in Fig. 2. In addition, the intensity of absorption bands around 1430–1590 cm⁻¹ increases with the p-intA diamine molar ratio content in the polyimides. These bands are attributed to aromatic C=C stretching vibrations that increase in intensity when benzene rings are substituted by conjugated groups such as C=C and C≡C, due to the electronic effects of the substituents. Therefore, the FTIR spectra confirm that the acetylene groups of p-intA diamine have been incorporated into the polyimide structure.

Wide-angle X-ray diffraction patterns of the three polyimides are illustrated in Fig. 3. They are all broad, indicating that they are all amorphous structure. The most prominent WAXD peak in the amorphous glassy polymer spectra is often used to estimate the average interchain spacing distance (*d*-spacing). These values were calculated using the Bragg equation and are notated in Fig. 3. There is an obvious trend of decreasing *d*-spacing with increasing molar fraction of p-intA in the co-polyimide

Fig. 2. FTIR spectra of co-polyimides.

Fig. 3. WAXD spectra of co-polyimides.

backbone. This can readily be explained by a relative structural comparison of the co-polyimide backbone segments derived from Durene and p-intA diamine. Durene has four methyl substituents on a single phenyl ring, which hinder the phenyl rotation around the nitrogen linkage atoms and inhibit interchain packing. On the other hand, the p-intA diamine-derived segment is comprised of two phenyl rings connected by acetylene groups that can rotate freely, resulting in denser chain packing and a decrease in *d*-spacing.

Table 2

The gas permeabilities and permselectivities of the original and modified co-polyimide films

	Permeability (Barrer ^a)				Permselectivity	
	O ₂	N ₂	CH ₄	CO ₂	CO ₂ /CH ₄	O ₂ /N ₂
(a) Polyimide membranes						
6FDA-D	186	55	45	612	14	3.4
6FDA-D4A1	80	21	15	317	21	3.8
6FDA-D3A2	45	11	6.8	180	27	4.3
(b) Cross-linked membranes						
6FDA-D-400	218	67	57	728	13	3.3
6FDA-D4A1-400	52	13	7.5	186	25	4.1
6FDA-D3A2-400	28	5.7	3.9	113	29	4.9
(c) Carbonized membranes						
6FDA-D-800	399	61	44	2700	61	6.5
6FDA-D4A1-800	293	40	35	2430	69	7.3
6FDA-D3A2-800	257	28	16	1200	77	9.0

^a 1 Barrer = 7.5005×10^{-18} m²/s Pa.

Fig. 4. DSC of original and cross-linked co-polyimides.

Table 2 summarizes the permeabilities of pure gases through the co-polyimides. Except for CO₂, the permeability decreases according to O₂ > N₂ > CH₄, which follows the same order of increasing kinetic diameters of the non-condensable penetrants. High CO₂ permeability arises from its condensable nature and its strong interaction with the nitrogen-containing polymer matrix. A comparison of the three different polyimides shows that the gas permeabilities generally decrease with increasing molar content of p-intA for the un-cross-linked co-polyimides. This order is same as the order of *d*-spacing change, indicating the correlation of gas permeability and interchain space. The results are consistent with other reports about 6FDA-Durene copolyimides, which gas permeabilities decrease linearly with a decrease in volume fraction of the Durene component in copolyimides [46–48].

3.2. Thermally cross-linked co-polyimides

TGA was used to study the thermal stability of the polyimides in inert atmosphere. If the thermal degradation temperature is defined as the temperature where 5% weight loss occurs, these co-polyimides exhibit impressive thermal stability and have degradation temperatures greater than 500 °C. Fig. 4 illustrates the DSC thermal analysis of these co-polyimides with over a temperature range from 50 to 480 °C (just before degradation). The polyimide without acetylene units, 6FDA-D, had a *T_g* around 430 °C. The polyimide having internal acetylenes, 6FDA-D4A1, exhibited an exotherm from 370 to 470 °C during the DSC temperature cycle and its *T_g* could not be identified because it was masked by the cross-linking reaction exotherm. After the 6FDA-D4A1 was thermally treated at 400 °C for 2 h, the resulting cross-linked polymer (6FDA-D4A1-400) was insoluble in solvents such as dichloromethane, which could previously be used to dissolve the polymer. The DSC curves of 6FDA-D4A1-400 show that the exotherm almost disappeared and the *T_g* appeared at around 450 °C, indicating that

Fig. 5. FT-Raman spectra of original and cross-linked co-polyimides.

the exotherm in 6FDA-D4A1 originates from the cross-linking reaction induced by the internal acetylene. Compared with reference [44] where the onset temperature of cross-linking reactions was reported to occur at 321–345 °C, the present co-polyimide undergoes cross-linking reactions start at a slightly higher temperature of 370 °C. One of the possible reasons is due to the fact that the present co-polyimides have a lower content of reactive acetylene groups that requires a higher temperature to overcome the energy barrier to initiate the reaction. Another plausible and contributing factor is that the bulky side group of Durene hinders the polymer chain mobility and decreases the possibility of a reaction between polymer chains.

The thermal cross-linking modification has also been monitored by FT-Raman, since $\text{C}\equiv\text{C}$ has a strong characteristic Raman absorption. Fig. 5 shows the FT-Raman stacked spectra of the original and thermally treated co-polyimides. Compared with the FT-Raman of 6FDA-D, 6FDA-D4A1 shows a new peak at 2210 cm^{-1} which can be assigned to the alkyne $\text{C}\equiv\text{C}$ stretching vibration. The band around 1600 cm^{-1} is the result of the enhanced aromatic $\text{C}=\text{C}$ stretching vibration induced by $\text{C}\equiv\text{C}$ conjugation. After thermal treatment of 6FDA-D4A1 at $400\text{ }^{\circ}\text{C}$ for 2 h, the characteristic peak of $\text{C}\equiv\text{C}$ at 2210 cm^{-1} disappears. Additionally, the band around 1600 cm^{-1} becomes wider and the shoulder peak at 1620 cm^{-1} is stronger. This phenomenon indicates that $\text{C}\equiv\text{C}$ is the reactive site during thermal treatment and there are more conjugated aromatic $\text{C}=\text{C}$ in the resultant cross-linked polymer. According to the NMR data previously published [45,49] and the new information from the FT-Raman spectra, we conclude that the most probable cross-linking reaction occurring between the internal acetylene units of polyimide

Fig. 7. XPS of original, cross-linked co-polyimides and carbon membranes.

is the Diels-Alder cycloaddition, as shown in Fig. 6. As a result, naphthalene structure is formed in the polyimide backbone, which may attribute to the strong shoulder peak at 1620 cm^{-1} in the FT-Raman spectra.

XPS experiments were also used to probe the modification process. Fig. 7 shows the respective C 1s core-level spectra of the original polyimide 6FDA-D4A1 and the thermal treated 6FDA-D4A1-400. The C 1s core-level spectrum of the original polyimide membrane has three peak components, bond energy at around 285–286 eV for the C–C, C–H and C–N species, at 288.4 eV for the $\text{N}(\text{C}=\text{O})_2$ (imide) species, and at 293.5 eV for the CF_3 species [52]. After thermal treatment at $400\text{ }^{\circ}\text{C}$, the peaks at 288.4 and 293.5 eV do not show much difference, which provides evidence that the imide structure maintains its stability under such high temperature. However, the peak at around 285–286 eV slightly shifts direction to lower eV, which implies that more C–C or C–H species are produced during the thermal treatment. This result is consistent with Diels-Alder cycloaddition cross-linking occurring.

Wide-angle X-ray diffraction patterns of copolyimides, as shown in Fig. 8, illustrate the subtle decrease in d -spacing after $400\text{ }^{\circ}\text{C}$ thermal treatment. In contrast with other cross-linking methods which markedly decrease d -spacing of the target polymer [14–22], thermal induced cross-linking of acetylene-containing copolyimide maintains comparable d -spacing well. The possible reasons are (1) the steric hindrance from 6FDA and Durene units resists densification by polymer chain packing

Fig. 6. The possible cross-linking and carbonization mechanisms in co-polyimide during thermal treatment.

Fig. 8. WAXD of original, cross-linked co-polyimides and carbon membranes.

during thermal cross-linking; (2) the stiff, rigid planar cross-linking sites fix the chain direction, and prevent large intrachain rotation. In addition, the copolyimide peak becomes sharper after annealing, indicating that redistribution of polymer chain packing occurs under high temperature.

Table 2 lists the gas permeabilities and ideal selectivities of O_2 , N_2 , CO_2 and CH_4 through cross-linked polyimide membranes, obtained by thermal treatment at $400^\circ C$ for 2 h under vacuum. The thermally treated 6FDA-D membranes without the internal acetylene units exhibit a little higher gas permeability as compared to the original polyimide. This phenomenon is consistent with the results reported by Fuhrman et al. [50] and Shao et al. [51] where polyimides thermally treated near T_g resulted in a small increase in gas permeability because of significant increases in chain mobility and configuration adjustment occurring at T_g . However, 6FDA-D4A1 and 6FDA-D3A2 membranes show lower gas permeability after thermal treatment and the effect is greater with increasing molar ratio of cross-linking sites. The decrease in gas permeability is mainly attributed to the effects of cross-linking reactions of the acetylene units along

the polymer main chain, induced by thermal treatment. However, compared with other polyimides with chemically induced cross-linking [14–22], the degree of gas permeability decrease in this study is modest, which is in agreement with the WAXD finding. This is due to the fact that there is relatively a lower fraction of cross-linking sites in the polymer backbone compared with chemically cross-linked polymer, which helps maintain a certain amount of local rotation and chain mobility for the more rigidified cross-linked polymer chains. In addition, the bulky 6FDA and Durene units prevent excess densification of polymer chain packing which could be brought about by the cross-linking. Increasing amounts of cross-linking sites lead to greater chain rigidification, resulting in increasing the gas selectivity.

Fig. 9 illustrates the relationship between gas permeability and ideal permselectivity for O_2/N_2 and CO_2/CH_4 . The gas separation properties of the original and cross-linked co-polyimides follow exactly the trade-off line, which implies that cross-linking modifications induce lower gas permeability and higher selectivity, but cannot surpass the trade-off line. These experimental results agree with the hypothesis of Freeman, which states that

Fig. 9. Permeability and selectivity relationship for original and modified copolyimides.

Fig. 10. Effect of CO₂ feed pressure on the CO₂ permeability through original and cross-linked copolyimides.

the polymer structure does not have much influence on the slope of the upper bound of the tradeoff curves if the mode of gas transport depends only on the diffusion selectivity related to the penetrant size ratio [13]. Based on the solution-diffusion theory, the present experimental data imply that the cross-linking of polyimide is only simply increasing the polymer chain stiffness and decreasing the polymer chain spacing with little change occurring in the solubility selectivity. Although the thermal cross-linking modification cannot improve the gas separation performance, it can significantly enhance the plasticization resistance of polyimides against CO₂ because the resultant polymers have lower chain segmental mobility, as shown in Fig. 10.

3.3. Carbonization of the cross-linked polyimides

Fig. 8 shows the WAXD results for acetylene-containing copolyimides and its derived carbon membranes with different acetylene ratio. When the heating temperature is only 400 °C, the X-ray diffractions show a very broad peak from 15° to 30°, indicating the amorphous structure of copolyimides. However, an obvious new peak at $2\theta = 43^\circ$ is observed in carbon membranes pyrolyzed at 800 °C. This peak could originate from the graphite (1 0 0) plane, which is representative of repeating aromatic rings in a planar graphitic structure. Another peak position is near 25°, which corresponds to a d -spacing of 3.56 Å. Although this value is slightly greater than interlayer spacing, d_{002} , of graphite crystal, it can still be attributed to the average spacing between neighboring two hexagonal layers. This leads us to conclude that monolayer graphitic-type sheets could be formed in carbon membranes during high temperature pyrolysis. Moreover the structure of carbon membranes can be described as turbostratic stacking of hexagonal layers. Comparing WAXD patterns of carbon membranes from copolyimides with different acetylene ratios can also provide some useful information to investigate the effects of the acetylene units during carbon membrane formation. The identical peaks near 25°, which indicate interlayer spacing, d_{002} , of graphite crystal, show that the Diels-Alder cycloaddition between acetylene units will not affect the packing of graphite sheets in carbon membrane. However, the peaks at 43° show some dissimilarity with changing acetylene con-

tent. Increasing the ratio of acetylene units induces narrower peaks at this position. The crystallite size along the a -axis (L_a) of the crystals can be estimated with the Scherrer equation: $L_a = K\lambda/B \cos \theta$, K is a constant (1.84 for the 100 reflection of graphite), λ is the X-ray wavelength, B is the FWHM, and θ is the Bragg angle [53]. Therefore, a conclusion could be drawn that a higher ratio of acetylene units lead to better graphitization along the 1 0 0 planes.

The above conclusions are also supported by XPS analysis, as shown in Fig. 7. The two small peaks attributed to the N(C=O)₂ (imide) and the CF₃ species disappear after pyrolysis at 800 °C. The broad strong peak for the combination of C–H and C–N species, becomes sharper and moves direction to lower binding energy. This means the membranes transform from polyimides to carbon materials. A binding energy of 284.5 eV has been reported for graphite. A similar binding energy of structures formed from polyimide precursors after pyrolysis at 800 °C suggests the formation of some graphite-like carbon [54]. As the ratio of acetylene units is increased in the copolyimides, the peak of the resultant carbon membranes is closer to 284.5 eV, pointing to a more graphitic-type structure.

The gas permeabilities and ideal selectivities of O₂, N₂, CO₂ and CH₄ of the carbon membranes carbonized at 800 °C under vacuum are summarized in Table 2. The carbonized membranes exhibit much higher gas permeability and ideal permselectivity simultaneously as compared to the original and cross-linked polyimides. As a result, the gas separation properties of carbonized membranes surpass the upper limit bond remarkably as shown in Fig. 9. This is due to the fact that the gas transport mechanism through these membranes has been changed after carbonization [23–25]. In polyimide films, gas transport occurs by means of the solution-diffusion mechanism, where thermally activated motions of chain segments generate transient gaps larger than the diffusing gas, thus the diffusive jumps occur. Therefore, the factors determining gas selectivity in polymeric films are related with the d -spacing and flexibility of polymer chains. However, the high gas permeability of carbon membranes is derived from the nature of their highly porous and inflexible structure. Gas transportation in carbon membranes is not regulated by thermally activated transient gaps, but by open channels. When the pore dimension is below 5 Å which is close to the average of gas molecular sizes, the molecular sieving mechanism becomes dominant for the gas transport through the membrane. A higher pyrolysis temperature tends to produce carbon membranes with a smaller pore size, while smaller pore dimensions further restrict the degree of rotational freedom of gas penetrants through the membrane. This is the reason why the increment in gas permselectivity for the CO₂/CH₄ pair, which has bigger size difference, is more distinct than for the O₂/N₂ pair.

When comparing carbonized membrane 6FDA-D-800 (from uncross-linkable polyimide) versus 6FDA-D4A1-800 and 6FDA-D3A2-800 (from cross-linkable polyimides), we find that carbonized membranes from cross-linkable polyimide exhibit relatively lower gas permeability. In addition, an increase in the cross-linking p-intA reaction sites in the co-polyimide, make the resultant carbon membranes have relatively lower

gas permeability. In our previous work, we concluded that the micro-structure of carbonized membranes is related to the chain packing of polyimide precursors [27]. The WAXD study shows that the *d*-spacing decreases when the mole fraction of p-intA is increased in the polymer backbone. It is believed that denser polymer chain packing in the polymer precursors induce lower gas permeability in the resulting carbon membranes. On the other hand, 6FDA-D3A2-800 and 6FDA-D4A1-800 show a greater incremental improvement in permselectivity than 6FDA-D-800. Unlike the polyimide membranes, the increase in ideal gas permselectivity of carbon membranes is more notable compared with the decrease in gas permeability. Consequently, as shown in Fig. 9, the distance of the carbon membrane data above the upper-bound tradeoff lines becomes greater (increased performance) with an increase in the mole fraction of internal acetylene units.

This tendency is also consistent with our previous findings that the degree of graphitization for polyimides is largely responsible for the gas permselectivity of the carbon membranes [27]. Although polymer chain rotation and mobility increase after introducing greater mole fractions of p-intA into the polymer chain backbone, the subsequent thermal cross-linking reaction likely produces naphthalenic structures resulting in more rigid and planar properties of the polymer chains. Thus, the carbon membranes derived from these cross-linked polyimide precursors should have more graphitic structures as hypothesized and shown in Fig. 6, which means more ordered structure and narrow pore dimension distribution. Hence, it is reasonable to explain Fig. 9 such that 6FDA-D3A2-800 and 6FDA-D4A1-800 show increasingly improved gas permselectivity properties over 6FDA-D-800, especially for the O₂/N₂ gas pair. For the CO₂/CH₄ gas pair, increasing the mole fraction of cross-linkable p-intA sites in the polyimide precursor does not necessarily equate to better gas separation performance for the carbon membranes. CO₂ is a more condensable and adsorptive gas and selective surface flow, which is dominated by the pore surface area, is still an important mechanism for CO₂ transport in carbonized membranes [25]. Cross-linking induces more graphitic structure but also decreases the pore structure in carbonized membranes.

To further investigate the influence of cross-linkable units in polyimides structures on the gas separation performance of the resultant carbon membranes, a O₂/N₂ separation trade-off comparison between carbon membranes from crosslinkable polyimide (this work) and those from non-crosslinkable polyimides (literature works) was drawn in Fig. 11. Since the trade-off relationships of the carbon membranes depend significantly on many factors such as pyrolysis conditions and membrane figurations, only flat carbon membranes which were fabricated under the same pyrolysis conditions (800 °C and vacuum) are chosen for comparison. As shown in Fig. 11, carbon membranes from crosslinkable polyimide 6FDA-D3A2 exhibit very competitive O₂/N₂ separation performance.

4. Conclusion

Polyimides containing cross-linkable acetylene sites (p-intA) on the main chain were synthesized by random copolymerization of 6FDA dianhydride, Durene and p-intA diamine. It is found that polyimides containing a greater mole fraction of p-intA in the polymer backbone show denser polymer chain packing in the un-cross-linked polymers. Thermally induced cross-linking occurs through the acetylene groups contained in the p-intA units, which are believed to form naphthalene structures by a Diels-Alder type reaction. Although the cross-linking modification is not able to provide an overall improvement in the gas separation performance, it does significantly enhance the membrane resistance to CO₂ plasticization. The cross-linking modification resulted in improved gas permselectivity with acceptable decreases in gas permeability. Carbonized membranes produced from un-cross-linked and cross-linked polyimide precursors exhibited greatly increased permeabilities and permselectivities, with excellent overall gas separation performance well above the upper-bound performance limit of conventional polymer membranes. The cross-linked polyimide precursors led to relatively higher permselectivities in the carbonized membranes compared with the un-cross-linked precursors, since there was a greater degree of chain packing and rigidification.

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Fig. 11. Permeability and selectivity relationship for carbon membranes.

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