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Decarboxylation-Induced Cross-Linking of Polymers of Intrinsic Microporosity (PIMs) for Membrane Gas Separation[†]Naiying Du,[‡] Mauro M. Dal-Cin,[‡] Gilles P. Robertson,[‡] and Michael D. Guiver^{*,‡,§}[‡]National Research Council Canada, Ottawa, Ontario K1A 0R6, Canada[§]WCU Department of Energy Engineering, Hanyang University, 17 Haengdang-dong, Seongdong-gu, Seoul 133-791, South Korea

S Supporting Information

ABSTRACT: Cross-linked membranes for gas separation have been prepared by thermal treatment of carboxylated polymers of intrinsic microporosity (C-PIMs). The optimal cross-linking temperature was investigated and possible cross-linking pathways involving aryl radical-induced thermal decarboxylation are provided, while several other possible mechanisms are ruled out. Carboxylated PIMs are accessible by controlled hydrolysis of the nitrile-containing parent polymer. The resulting cross-linked PIMs were insoluble in typical solvents and were characterized by Fourier transform infrared spectroscopy (FTIR), TGA-MS, TGA-FTIR, and gel content analysis. The decarboxylated PIM (DC-PIM) membranes showed higher selectivities for the O₂/N₂, CO₂/N₂, and CO₂/CH₄ gas pairs, with evidence of suppression of swelling-induced densification under high CO₂ pressure.

INTRODUCTION

In the past two decades, CO₂ separation and capture has become ever more important because of progressively increasing CO₂ emissions associated with fossil fuel combustion, biomass energy facilities, or natural gas processing. For example, in the natural gas industry, gas compositions and pressures vary widely by geographical location, and some fields contain as much as 70% CO₂ at pressures up to 5000 psia. In order to meet natural gas pipeline specifications and to minimize corrosion, CO₂ contaminant is typically required to be present at less than 2%.¹ The conventional process to remove CO₂ from natural gas is amine scrubbing, but membrane separation processes provide an attractive alternative technology, which has a relatively lower capital cost and is less energy intensive, while being more environmentally benign.^{2–4} Gas transport through a membrane is defined by the “solution-diffusion” mechanism. Under a driving force, determined by the partial pressure (fugacity) difference of each gas component, a penetrant from a feed stream sorbs at the surface of the upstream side of the membrane and then diffuses through the membrane film to the downstream surface where it desorbs into the permeate stream. However, in real-life membrane gas separation applications, exposure of membranes to CO₂ and other condensable gases affects CO₂/N₂ and CO₂/CH₄ separation performance, especially at high pressure, due to swelling-induced plasticization. Plasticization increases local segmental mobility, resulting in an increase in permeability and a decrease in separation efficiency of the membrane. In our previous work,^{5a} it was observed that PIMs did not appear to suffer serious plasticization, although they did show that the microporous structures were affected by sorbed CO₂, resulting in

a decrease in permeability with increasing CO₂ pressure. It was assumed that the rigid polymer chain matrix was swelled by sorbed CO₂, which led to a slight increase in segmental mobility. With progressively higher CO₂ pressures, the intrinsically microporous structure began to collapse, due to the initially large free volume and increased overall chain movement, though no rotational chain mobility is possible in ladder-type polymers. Although the observed phenomenon is similar to plasticization for typical glassy polymers, it could be more accurately defined as “swelling-induced densification” in the case of PIMs. Traditional methods for stabilizing polymeric membranes are either annealing or cross-linking. Recently, Koros and co-workers reported cross-linked polyimide membranes, which were found to be stable at significantly higher CO₂ pressures, i.e., membranes having high plasticization pressures.^{1,6,7} The new cross-linking approach was reported to occur through a thermally activated decarboxylation mechanism for carboxylic acid-containing copolyimides, creating free radical sites capable of cross-linking.^{8–10} Compared to propanediol monoester cross-linked polyimide, the polyimide cross-linked by decarboxylation had reasonable gas transport properties, while avoiding the potential hydrolysis of ester linkages in aggressive acid gas feed streams, which would reverse the effects of cross-linking and lead to a reduction in membrane efficiency.^{4,8}

In the present work, polymers of intrinsic microporosity containing carboxylic acid groups (C-PIMs), derived from controlled hydrolysis of the nitrile group of PIM-1,^{11,12} are used as the membrane materials to study the mechanism of the

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cross-linking reaction, with the goal of controlling swelling-induced densification. PIMs are a novel class of polymers which were first reported by Budd and McKeown in 2004.^{13–16} Their structural characteristics comprise rigid quasi-planar ladder-type chains connected with contorted or kinked centers, which prevent efficient space packing. The resulting intrinsically microporous structures exhibit very high gas permeabilities. In addition, PIMs have good processability and are soluble in common solvents, allowing membrane preparation.^{17–21} PIMs have characteristically very high permeability combined with moderate to good selectivity for a number of gas pairs, such as O₂/N₂, CO₂/N₂, and CO₂/CH₄.^{22–24} PIMs are typically thermally stable because of their rigid mostly aromatic ladder chain structure. The best-known polymer PIM-1 exhibits an initial decomposition at around 460 °C, with no observable *T_g* occurring before the decomposition temperature, because of the absence of rotational chain mobility. Despite their attractive intrinsic properties, their susceptibility to membrane densification has a negative impact on process economics and reliability. Different from traditional glassy polymer membranes, PIMs are intrinsically microporous, with very high surface areas (~800 m²/g). At high pressures, sorbed CO₂ tends to swell the polymer chain matrix, leading to compaction and a change in cavity shape or size. Hence, instead of increasing permeability as observed in typical plasticization behavior, a significant decrease in CO₂ permeability was observed for PIM membrane.^{5a} Plasticization behavior is known to be thickness dependent.²⁵ Thinly skinned membranes, such as asymmetric or thin-film composites used in commercial modules, show less resistance to CO₂ swelling.²⁶ Thus, the gas transport characteristics of thinly skinned PIM membranes (skin layers of 0.1–10 μm) could be affected more seriously by swelling-induced densification. In the present study, we focus on (1) investigating a reasonable mechanism for the cross-linking reaction of carboxyl-modified PIM-1, (2) a method of preparing cross-linked PIM membranes by decarboxylation (DC-PIMs), and (3) gas transport of the cross-linked membranes, which exhibit considerably suppressed swelling-induced densification under high CO₂ pressure.

EXPERIMENTAL SECTION

Preparation of C-PIM. The PIM used in this work is carboxylated PIM-1 (referred to as “C-PIM”), which was prepared by controlled base hydrolysis of the nitrile group of PIM-1 according to the procedure previously reported.^{11,12} C-PIMs were prepared by boiling PIM-1 membranes (*M_n* = 60 000 Da, PDI in the range of 2–3, membranes thickness in the range of 70–90 μm) in 20 wt % sodium hydroxide solution (H₂O/ethanol = 1:1) for 1–5 h, which are referred to as “C-PIM1-5”, where the numerical suffix denotes the hydrolysis treatment time in hours. The degree of hydrolysis of C-PIM1 was ~22%, C-PIM2-41%, C-PIM3-62%, C-PIM4-85%, and C-PIM5-100%, which corresponds to the percent conversion of –CN groups in the starting polymer (PIM-1) to –COOH groups. After neutralizing and washing the membranes in acidified water (2 < pH < 4) for 1 h, the membranes were soaked in methanol for 1 h and then allowed to dry at ambient temperature.

Cross-Linking of C-PIM. As with PIM-1, no *T_g* was observed for C-PIM due to the absence of rotational freedom in the polymer chain. The cross-linking reaction temperature was investigated and optimized using thermogravimetric analysis (TGA, TA Instruments, model Q-5000IR). The thermal cross-linking procedures were conducted under a controlled environment in a tube furnace, which was fitted with an internal thermocouple for temperature control and an argon purge to create an inert environment. The furnace was purged with at least 10 times its tube volume prior to the thermal decarboxylation cross-linking reaction, and the argon purge was maintained at a flow rate of ~50 mL/min during the cross-linking process. All membranes (PIM-1 and C-PIM1-5) were placed in a ceramic boat. The procedure involved a

drying step at 200 °C for 0.5 h to remove any residual solvent, followed by a 5 °C/min ramp to 375 °C, and then holding at 375 °C for 40 min. At the 40 min mark, the PIM-1 (annealed-PIM-1, PIM-1^A) and DC-PIM films (decarboxylated cross-linked C-PIM1-5, 3 films for each sample) were rapidly cooled to room temperature by removal from the furnace.

RESULTS AND DISCUSSION

Possible Pathways for the Formation of Cross-Linked Structures. A previous investigation of the decarboxylation of 6FDA-based copolyimides ruled out several possible cross-linking pathways or intermediates, such as charge transfer complexing, oligomer cross-linking, decomposition, and dianhydride formation.⁸ In the present work, after thermal treatment, the DC-PIM samples showed insolubility in NMP to different degrees. Since C-PIMs and 6FDA-based copolyimides have entirely different main-chain structures, it is possible that one of the pathways ruled out in the study on polyimides could be responsible for the cross-linking of DC-PIMs.

Polyimides are capable of forming charge transfer complexes, which have been shown to stabilize polymer chains²⁷ and lead to greater insolubility. From a thermodynamic point of view, when polyimides are in the rubbery region during the annealing process, enhanced chain mobility will allow alignment of the necessary components to form these complexes.⁸ However, no *T_g* was observed for PIM-1 and C-PIM because it has a ladder-like structure with no degrees of rotational freedom in the main chain. Thus, charge transfer complexes may be difficult to form in PIMs due to their special rigid chain structures. Additional evidence for the formation of charge transfer complexes in polymers is seen by an increase in fluorescence because charge transfer complexes lead to a more favorable lower energy state. In the present work, no evidence of charge transfer complex formation was observed because the fluorescence spectra for DC-PIM5 membranes showed a slight decrease in intensity (the emission peak at 515 nm) compared to the precursor C-PIM5. Solubility tests showed that DC-PIM5 was insoluble in common solvents such as chloroform, THF, and NMP, even at high temperatures or acid conditions, which was in contrast with PIM-1^A subjected to the same thermal treatment. This also indicates the formation of cross-linked structures and the absence of charge transfer complexes in DC-PIM5, since polymers with charge transfer complexes become more soluble at high temperature.

The possibility of a cross-linking pathway involving –OH or –F end groups on oligomers was also excluded by thermally treating oligomer-free C-PIMs. Oligomers were removed from high molecular weight PIM-1 (*M_n* = 60 000, PDI in the range of 2–3) by reprecipitation from chloroform solution. The C-PIM5 membranes were prepared from the oligomer-free PIM-1 membranes. Under the same thermal cross-linking conditions mentioned previously (375 °C for 40 min, under Ar), the DC-PIM5 was also insoluble, indicating that oligomers are not responsible for cross-linking.

To gain further insight into the cross-linking process, TGA measurements coupled with MS and FTIR of the evolved gases were conducted on the C-PIM5. Figure 1 shows the TGA mass loss analysis for C-PIM5 subjected to a thermal ramp up to 600 °C at a rate of 5 °C/min in a helium purge. The initial mass loss occurring at 140–220 °C and amounting to 5–10% is attributed to desorption of small amounts of absorbed CO₂ and residual NMP, since a similar desorption also occurs for PIM-1^A. The significant second mass loss between 330 and 375 °C is discussed in the next section. Considerable mass loss associated with the decomposition of the polymer main chain begins at 410 °C.

Figure 1. Comparative TGA-FTIR spectra of PIM-1 and C-PIM5 membranes. The inset shows FTIR spectra of gaseous decomposition products corresponding to mass losses of C-PIM5 at different temperatures.

Analysis of gaseous decomposition products by FTIR spectra (in Figure 1, at 503 °C) shows a band at $>3500\text{ cm}^{-1}$ associated with

H_2O , a band at 3000 cm^{-1} corresponding to CH_4 , a band around 2260 cm^{-1} corresponding to CO_2 , and a band around 2100 cm^{-1} corresponding to CO . Since the cross-linking reaction temperature occurs at or below 375 °C, carbon evolution from polymer main chain decomposition (beginning at 410 °C) does not appear to be responsible for the observed insolubility.

Anhydride formation, which is another plausible pathway for the thermal cross-linking in C-PIM5, was not evident based on an investigation of hydrolysis. C-PIM5 membranes, which had been preheated at 375 °C for 40 min, were placed in boiling water (pH = 6) in order to hydrolyze any possible anhydride cross-links that may have formed. After boiling in water for 8 h, the resulting DC-PIM5 membranes remained insoluble in common solvents, which indicates that anhydride formation does not play a role in the observed insolubility effects.

Recently, Xiao et al. reported a thermally-induced nitrile cross-linking reaction for PIM-1, which required from 0.5 day to 2 days at 300 °C.^{5b} We previously explored this cross-linking approach at a temperature of 375 °C and 45 min, but did not observe any cross-linking, most likely due to the insufficient annealing time.

Decarboxylation-Induced Cross-Linking. Thermal decarboxylation in polymers has been previously reported.^{28,29} For

Scheme 1. Structures of PIM-1, C-PIM, and Possible Cross-Linking Sites on the C-PIM (1) through the Methyl, (2) Biphenyl Cross-Link, and (3) at the Cleaved CH_3 Site

example, the decarboxylation of aromatic carboxylic acids occurs through anhydride formation and subsequent decomposition to form aryl radicals.^{8–10,30–32} After ruling out several possible cross-linking pathways for the thermal cross-linking in C-PIM5, it is reasonable to conclude that the cross-linking mechanism of C-PIMs is similar to the decarboxylation of aromatic carboxylic acids in those polymers reported before, although the C-PIM structures are dissimilar. In the present work, TGA-FTIR data confirmed that a mass loss of $\sim 16.5\%$ between 330 and 375 °C in C-PIM5 is attributed to CO₂ (Figure 1). This value is close to the theoretical amount corresponding to complete removal of –COOH groups in C-PIM5 and to the formation of cross-linked membrane. It was assumed that DC-PIM followed a known decarboxylation mechanism: a carboxylic acid anhydride formed on the main chain of C-PIMs, and then decomposed to form aryl radicals, which may combine with each other to form a biphenyl cross-link. Scheme 1 shows the sites where cross-linking is proposed to occur on the backbone. The methyl group hydrogen has the lowest bond dissociation energy and is therefore most likely to be abstracted first, creating a methyl radical as a possible cross-linking site (site 1).⁸ In addition, the bond forming biphenyl cross-linking could also form through combination of two aromatic radicals (site 2). A further possible site exists for potential cross-linking. At 330–375 °C, a TGA-MS signal for m/e 15 increased, peaked, and then decreased, which likely arose from –CH₃ loss, leaving sterically hindered radical sites available for cross-linking (site 3). The three proposed cross-linking sites in DC-PIM should not significantly alter the FTIR signatures of C-PIM and DC-PIM. The only substantial differences between the spectra of C-PIM5 and DC-PIM5 (Figure 2) are

Figure 2. Comparative FTIR spectra of C-PIM5 and DC-PIM5 membranes.

the disappearance of the broad band at 3700–3100 cm^{−1} (typically associated with OH stretching vibrations) in DC-PIM5 and a diminished absorption at 1650 cm^{−1} in DC-PIM5, indicating the removal of the –COOH groups from the polymer. During the thermal decarboxylation investigated by TGA-FTIR, the band detected at 2260 cm^{−1} corresponds to gaseous CO₂ evolution. In the decarboxylation temperature range, no obvious H₂O evolution was detected by FTIR. During the same period of time, the strong MS signals for m/e 44 increased, peaked, and then decreased, indicating that CO₂ evolved from decarboxylation of the polymer. In comparison with the TGA curve of C-PIM5, PIM-1 had no decomposition mass loss up to 460 °C.

Gas Transport Properties of DC-PIMs. Free-standing films of C-PIM1-5 with different ratios of –COOH groups were heated at 375 °C for 40 min under an argon atmosphere. The gas transport properties of the resulting DC-PIM1-5 membranes were compared with PIM-1^A membranes, which were subjected to the same thermal treatment. Single-gas permeability coefficients (P) for O₂, N₂, CH₄, and CO₂ were determined at 25 °C for dense, isotropic films, and a summary of these P values and ideal selectivities for three gas pairs is shown in Table 1 and Figure 3.

The DC-PIM membranes having higher initial COOH contents (higher degree of hydrolysis) had the lowest permeability after thermal decarboxylation. In comparison with PIM-1^A, the DC-PIM membranes exhibited higher selectivities coupled with expected reductions in gas permeabilities. Selectivities for O₂/N₂ and CO₂/N₂ were in the range of 3.4–4.6 and 12.2–24.6, respectively. These results agree with the trade-off tendency for selectivity–gas permeability for polymeric membranes; i.e., higher O₂ and CO₂ permeability is gained at the cost of lower selectivity and vice versa. Compared to PIM-1 reported previously,¹¹ the permeability values of the thermally pretreated PIM-1^A were almost half, but coupled with correspondingly higher selectivities.

C-PIM1 and C-PIM2 were selected for preparing DC-PIM1 and DC-PIM2 because of their sufficiently high permeability necessary for pressure-dependent gas permeability measurements. It is reported³³ that at low pressures the permeability of typical glassy polymers, such as polyimides, decreases with increasing pressure due to the filling of Langmuir sorption sites, while at higher pressures, the contribution of the Langmuir region to the overall permeability diminishes and gas permeability approaches a constant value associated with simple dissolution (Henry's law) transport. However, for more strongly sorbing and interacting penetrants like CO₂ or condensable gases, glassy polymers eventually exhibit an upswing in the permeation isotherm due to swelling-induced plasticization. In contrast with the majority of glassy polymers, PIMs have no discernible T_g and they behave like amorphous materials with high free volume. Although

Table 1. Pure Gas Permeabilities and Ideal Selectivities of Cross-Linked DC-PIM1-5 Compared with PIM-1^A

polymers	P^a (barrers)				α^b		
	O ₂	N ₂	CH ₄	CO ₂	O ₂ /N ₂	CO ₂ /N ₂	CO ₂ /CH ₄
DC-PIM1	554	161	192	2345	3.4	14.6	12.2
DC-PIM2	411	118	157	1987	3.5	16.9	12.6
DC-PIM3	375	103	116	1996	3.6	19.4	15.0
DC-PIM4	238	57.6	86.4	1536	4.1	25.9	17.8
DC-PIM5	231	49.9	52.6	1291	4.6	28.8	24.6
PIM-1 ^{A c}	1017	342	555	5093	3.0	14.9	9.2

^aPermeability coefficients measured at 25 °C; feed pressure: 3.4 atm (50 psig); permeate at atmospheric pressure: 1.0 atm (0 psig). 1 barrer = 10^{−10} cm³ (STP) cm/(cm² s cmHg). ^bSelectivity $\alpha = (P_a)/(P_b)$. ^cPIM-1^A was PIM-1 annealed at 375 °C for 40 min under an argon atmosphere.

Figure 3. Relationship between pressure and pure gas normalized permeability for CO₂ (A) and N₂ (B).

PIM-1 does not exhibit typical glassy polymer “plasticization” as shown by an upswing in the permeation under high pressure, permeability is nevertheless seriously affected by highly sorbing CO₂. In comparison with DC-PIM1 and DC-PIM2 (Figure 3), the CO₂ permeability of PIM-1^A declined by almost 60% at 54.4 atm (800 psig) and showed a continually declining trend, while the N₂ permeability of PIM-1^A, DC-PIM1, and DC-PIM2 declined by only 5–10% at the same pressure. A significant loss in gas permeability shows the microporous structure is appreciably affected at high CO₂ pressure, but the behavior of PIM-1^A is unlike typical glassy polymers. Compared to PIM-1^A, the permeability decline of DC-PIM1 and DC-PIM2 membranes at high CO₂ pressure was less. A similar phenomenon was observed during mixed gas CO₂/N₂ testing. Figure 4 shows the mixed gas selectivity data for feeds of 90/10% CO₂/N₂. A 90% CO₂ concentration was used because it was a more rigorous test for the plasticization resistance or swelling-induced densification of the materials. The membranes maintained modest permeability and exhibited a substantial increase in pure and mixed-gas selectivity, indicating swelling-induced densification was suppressed. Figure 4 is given in fugacity, rather than pressure, because at high pressures condensable gases such as CO₂ have a fugacity/pressure ratio, or fugacity coefficient, that can deviate significantly from unity; at low pressure or for non-

Figure 4. Mixed gas normalized selectivity for CO₂/N₂ for cross-linked DC-PIM1, DC-PIM2, and PIM-1^A.

condensable gases, the fugacity and pressure are virtually the same. When the mixed gas selectivity is calculated, fugacity is the more accurate means of calculating the effective driving force across the membrane for permeation.

CONCLUSIONS

Cross-linked membranes were prepared by thermal decarboxylation using membranes prepared from carboxylated polymers with intrinsic microporosity (C-PIM)s. An investigation of the cross-linking by a combination of techniques including TGA, TGA-MS, TGA-FTIR, and FTIR suggested a mechanism involving aryl radicals was likely, while some other possible mechanisms did not appear to occur. The gas transport properties of the cross-linked membranes (DC-PIM1-5) were dependent on the amount of carboxylic acid cross-linkable sites present in the precursors. In comparison with PIM-1^A, DC-PIM1-5 prepared under optimized reaction conditions exhibited higher O₂/N₂, CO₂/N₂, and CO₂/CH₄ selectivities coupled with expected reductions in pure gas permeabilities. The results of pure gas CO₂ and N₂ permeability and mixed gas CO₂/N₂ normalized selectivity under the higher pressure indicate that DC-PIMs exhibit a reduction of swelling-induced densification for CO₂.

ASSOCIATED CONTENT

Supporting Information

Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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