Molecular-Sieving Energy-Efficient Gas Separation Membranes Enabled by Multi-covalent-crosslinking of Microporous Polymer Blends

Nanwen Li (✉ linanwen@sxicc.ac.cn)

Institute of Coal Chemistry, Chinese Academy of Sciences

Xiuling Chen

Hubei University of Science and Technology

Yanfang Fan

China University of Petroleum

Linzhou Zhang

China University of Petroleum

Dong Guan

China University of Petroleum

Canghai Ma

Dalian University of Technology

Article

Keywords: highly permeable membranes, selective membranes

Posted Date: January 18th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-140525/v1>

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Version of Record: A version of this preprint was published at Nature Communications on October 22nd, 2021. See the published version at <https://doi.org/10.1038/s41467-021-26379-5>.

Abstract

Highly permeable and selective membranes that exceed the conventional permeability-selectivity upper bound are attractive for energy-efficient gas separations. In the context microporous polymers have gained increasing attention owing to their high porosity and exceptional permeability. However, the moderate selectivity of microporous polymers caused by inherent broad distribution of cavities leads to a loss of valuable gas products, making them unfavorable for separating similarly sized gas mixtures. Here we report a new approach to designing polymeric molecular sieve membranes via multi-covalent-crosslinking of miscible blends of Polymer of Intrinsic Microporosity, i.e. bromomethyl (PIM-BM) and Tröger's Base (TB), enabling simultaneously high permeability and selectivity. Selective gas permeation is achieved via adjusting reaction temperature, reaction time and the oxygen concentration with occurrences of polymer chain scissor, rearrangement and thermal oxidative crosslinking reaction simultaneously. Upon a thermal treatment at 300 °C for 5h, membranes exhibit an O₂/N₂, CO₂/CH₄ and H₂/CH₄ selectivity as high as 11.1, 155.7 and 814.1, respectively, with an O₂, H₂ and CO₂ permeability of 18.2, 358.2 and 67.6 Barrer, respectively, transcending the state-of-art upper bounds. The design strategy represents a generalizable approach to creating molecular-sieving polymer membranes with enormous potentials for energy-efficient separation processes.

Introduction

The energy cost associated with the separation and purification of industrial gases, fine chemicals and water, currently accounts for 10-15% of national total energy consumption¹. By 2050 such number is projected to triple²⁻³. Global energy scarcity along with climate change and rapid growth of population stimulate the exploration of energy-efficient technologies for gas separations, water purification and energy generation⁴⁻⁶. Owing to the advantages of low-energy consumption, small footprint, and easy operation⁷⁻⁹, membrane-based separation technologies hold great promise to address the need of energy-efficient separation processes. Currently, gas separations with membranes mostly rely on synthetic polymeric membranes with customizable gas transport properties. Ultra-permeable and selective polymeric membranes have become the critical factors to achieve the most desirable recovery and purity of gas products in the practical industrial applications.

To enhance the performance of polymeric membranes, various material synthesis and design strategies have been proposed and extensively studied, including adjusting the rigidity of polymers through grafting bulky groups¹⁰⁻¹³, construction of hybrid membranes via integrating molecular sieving fillers into polymers¹⁴⁻¹⁶ and external stimulus (e.g. heat, light, and oxygen) induced polymer structural modification at microscopic levels¹⁷⁻¹⁹. For example, the rigid polymers with high free volume such as Polymer Intrinsic of Microporosity (PIMs)²⁰, Tröger's base polymers (TB) and bulky groups containing polyimides²¹ have demonstrated appealing gas permeability with several orders of magnitude higher than commercial polymer membranes, such as Matrimid²². The poor polymer chain packing in these rigid polymers results in the formation of microcavities in the solid state, allowing the fast diffusion of gases

without significantly losing selectivity. Additionally, the polymer matrices incorporated with inorganic or organic molecular sieves such as covalent organic frameworks, metal organic frameworks and graphene oxides provide alternative options to obtain membranes with a wide range of gas separation performance²³⁻²⁴. Subsequently, crosslinking or re-arrangement of aforementioned polymer systems induced by chemical, light or heat treatment provide further approaches to tailor polymer structures at microscopic levels¹⁷⁻¹⁹. While all of these systems demonstrate reasonable properties as membranes and established the feasibility for gas separation, microstructural engineering of polymeric membranes to narrow the free volume size distribution and enhance molecular sieving properties has remained a crucial challenge for energy-efficient gas separations.

Herein, we developed a novel methodology for fabricating multi-covalent cross-linked microporous membranes, exhibiting advantages of moderate heating temperature with low energy consumption (<300 °C) as well as excellent molecular sieving properties. Unlike the above-mentioned studies on crosslinked polymers through external stimulus, which deal only with the intramolecular crosslinking reaction and could hardly finely tune the polymer microstructure, we establish the strategies of oxygen-induced chain scissor, polymer segment rearrangement alongside *in-situ* intra/inter polymer chain crosslinking to construct hyper-crosslinked networks in a microporous polymer system under a moderate temperature.

In this work, we judiciously selected the highly compatible polymer blends of bromomethylated PIM-1 (PIM-BM) and Tröger's base polymers (TB) as a prototype of microporous polymer system to simultaneously provide inter- and intra-crosslinking reaction sites (Fig. 1). The resultant membranes exhibit ultrahigh selectivities with respect to technically important gas pairs such as H₂/CH₄, CO₂/CH₄ and O₂/N₂. Compared to single crosslinked PIM-1¹⁸ and oxidative crosslinked PIM-1¹⁷ as previously reported in literatures, our membranes demonstrate the highest CO₂/CH₄ selectivity up to 144.8 with a CO₂ gas permeability of 67.6 Barrer. Moreover, the membranes display a H₂/CH₄ selectivity as high as 814.1 with a H₂ permeability of 358.2 Barrer. In comparison with intra-crosslinked PIM-BM, crosslinked PIM-BM/TB (denoted as XPIM-BM/TB) manifest unprecedented gas separation properties and perform far beyond current permeability-selectivity upper bounds for multiple gas pairs (e.g. CO₂/CH₄, H₂/CH₄, H₂/N₂, O₂/N₂). We attribute such high separation performance to finely tuned free volume distribution in cross-linked membranes through integrated multi-covalent crosslinking reactions including self-crosslinking within PIM-BM and inter/intramolecular crosslinking (PIM-BM and TB) of polymer blends. In any case, the membranes demonstrate unparallel gas separation performance enabling ultra-selective separation of industrially relevant gas pairs as discussed in this work.

Results

Materials synthesis and characterizations

The N atom in the Tröger's base moieties could interact with -CN groups in PIMs, considerably improving the miscibility of PIMs and Tröger's base polymer. The bromomethylated PIMs were prepared through

converting methylated PIM-1 to PIMs with bromomethyl groups by using *N*-bromosuccinimide as bromomethylating agent (represented by PIM-BM-*x*, *x* is the degree of bromomethylation and *x*=70, Fig S1-3)²⁵. Then the blends of PIM-BM-70 with rigid TB polymers (Fig S4-5) with excellent mechanical properties (PIM-BM/TB) (Fig S21 and Table S3) were selected as the framework to develop cross-linked microporous membranes.

Physically blended PIM-BM-70 and TB polymers with excellent miscibility were readily fabricated into transparent membranes by dissolution in chloroform and cast on a glass plate. The resultant PIM-BM/TB membrane could be simply cross-linked when thermally processed in a temperature window of 120 °C-300 °C over varied periods in nitrogen with ppm level of oxygen. The cross-sectional morphology of membranes was characterized by Scanning Electron Microscopy (SEM). As the SEM images show in Fig. 1a-f, all membranes regardless of thermal cross-linking temperatures display a smooth, macrovoid-free surface. With the increase of thermal processing temperature from 120 °C to 300 °C, the membrane color changed from originally yellow, to brown yellow and then black as observed in Fig. 1g. PIM-BM/TB treated at 200 °C over 20 h is partially insoluble in common organic solvents such as chloroform and NMP (Fig. S10) which can easily dissolve the pristine PIM-BM/TB. Upon treated at much higher temperatures between 250 °C - 300 °C, PIM-BM/TB became completely insoluble as seen in Fig. 1g.

We proposed three types of chemical cross-linking mechanisms likely occurring during the heating process, i.e. reactions of tertiary amine with bromomethyl groups with the formation of quaternary ammonium salts, alkylation reactions and oxidative crosslinking reactions within PIM-BM/TB membranes as schematically shown in Fig. 2 and Fig S7-9.

In the first scenario, we found the critical role of reactive sites of CH₂Br groups of PIM-BM and tertiary amino groups of TB in PIM-BM/TB blends. One or two -CH₂Br groups per repeat units of PIM-BM reacts with tertiary amino groups in TB polymers or phenyl groups in PIM or/and TB. X-ray photoelectron spectrometer (XPS) results (Fig. 3a-e) confirm that the covalent C-Br bonds in fresh PIM-BM/TB membranes are gradually transformed to the Br-containing salt via nucleophilic coupling reactions of tertiary amine with bromomethyl groups during the initial thermal treatment. This reaction occurs at a low temperature from 120 °C to 300 °C. The extent of nucleophilic coupling reactions between C-Br bonds and tertiary amine quantified by XPS results was found to increase from 12% to 40% with reaction temperature increasing from 120 °C to 300 °C (Table S2). Thus, the primary reaction mechanism is proposed that partial tertiary amino groups in TB polymers with bromomethyl groups in PIM-BM (bromomethylated PIMs) were converted to quaternary ammonium salts [N⁺(R)₃]CH₂RBr⁻ through coupling reactions (Fig S7). The cross-linking degree regarding to such reaction for XPIM-BM/TB-250 °C-10 h and 300 °C-5 h estimated from XPS results were 25%, and 40%, respectively.

With respect to the second reaction mechanism, the membranes were subjected to inert gas with ppm level of O₂ in the temperature range of 250-300 °C. In this case, we proposed a possible thermal cross-linking of C-Br bonds and benzene rings via alkylation reaction route, generating HBr as gaseous product,

besides the aforementioned coupling reaction. As evidenced by the ion current corresponding to HBr from TGA/Mass Spectrometry (Fig S15), HBr was released from 230 °C to 300 °C for pristine PIM-BM/TB, corroborating the crosslinking mechanism through alkylation reaction. In contrast, the amount of HBr released during alkylation reaction reduced significantly for the case of crosslinked XPIM-BM/TB-250 °C-10 h, since most of CH₂Br groups had participated in the crosslinking reaction with benzene rings, TGA-MS did not detect HBr signal for XPIM-BM/TB-300 °C-5 h (the trace amount of HBr was difficult to detect), suggesting consumption of the majority of C-Br groups as reactions proceeding within polymer blends. The consumption of C-Br groups was also verified by XPS results where Br 3d core signal ratio of C-Br (70.3 eV) to Br⁻ (68.3 eV) in XPS spectra significantly decreased for the membrane thermally treated at 300 °C for 5 h (Fig. 3e). The cross-linking degree regarding to alkylation reaction for XPIM-BM/TB-250 °C-10 h and XPIM-BM/TB-300 °C-5 h estimated from XPS results were 22%, and 40%, respectively. Moreover, as depicted by Fourier transform infrared spectra (FTIR) of the membranes (Fig. 3f), the characteristic peak of C-Br near 660 cm⁻¹ for XPIM-BM/TB membranes treated at high temperatures ≥250 °C become less intense comparing with the original PIM-BM/TB.

In the third stage, we proposed an oxidative induced crosslinking mechanism that PIM-BM/TB membranes experience a thermal-oxidative reaction during heating treatment in a temperature of 250-300 °C in the presence of ppm-level oxygen. Such phenomena was also observed in the temperature range of 300-450 °C for pure PIM-1.^[17] The oxygen plays a key role to partially decompose polymer chain into polymer fragments. The scissor of spiro linkage of PIM-1 and methylene groups linked to N atoms of TB is likely the dominant decomposition step. Partial backbones were oxidized and led to the formation of COOH groups.^[17] Afterwards, fragmented polymer chains are hypothetically thermally rearranged to an energy favorable state. Simultaneously, the chemical reaction took place among reactive groups including the oxidative induced free radicals, CH₂Br and N containing groups in the polymer chain, causing extensive covalent crosslinking (Fig 2). The degree of oxidative polymer chain scissor is tunable via changing the O₂ concentration in the purge gas as discussed later.

As discussed above, despite the different trends observed in PIM-BM/TB membrane characterizations under various temperatures, the three possible crosslinking mechanisms are inherently coupled, all of which could contribute to the crosslinked network formed within the membranes. Decoupling the crosslinking reaction mechanisms in PIM-BM/TB membranes merits further study to clarify effects of each individual reaction on membrane structures and properties.

Membrane characterizations

The physicochemical properties of membranes were further characterized using a wide range of techniques. As TGA profiles show, the dependence of weight loss on crosslinking temperatures demonstrated that crosslinked membranes had improved thermal stability over uncrosslinked PIM-BM/TB blends (Fig. 4a and Fig S11). In fact, the XPIM-BM/TB-300 °C-5 h membranes start to decompose at a temperature of ~400 °C, significantly higher than the case of untreated PIM-BM/TB membranes or treated at 200 °C with

a decomposition temperature of ~ 300 °C. XRD spectra of PIM-BM/TB before and after thermal crosslinking revealed all polymers were amorphous (Fig. 4b). Referring to XRD profiles of pristine membranes, the peak at the angle of 11.9° (d-space values of $7.43 \text{ \AA}$) is attributed to loosely packed polymer chains²⁶⁻²⁷. With increasing crosslinking extent, the broad peaks at 11.9° slightly shifted to a higher angle (i.e. a smaller d-space value), implying crosslinking reactions tighten the chain spacing and potentially enhance molecular sieving properties of membranes. A molecular modelling comparison PIM-BM/TB and XPIM-BM/TB shows reduced free volume fractions with increasing crosslinking degree, which is consistent with PALS results (Table S1).

A typical plot of stress-strain curve of membranes (Fig. 4c) shows a reduction in elongation and tensile strength at break with increasing cross-linking degree, suggesting that the XPIM-BM/TB polymer films became less ductile compared with untreated PIM-BM/TB. For example, pristine membranes have an ultimate yield stress of 43 MPa at 8.8% strain whereas the membranes treated at 200 °C for 20 h have a tensile stress of 19 MPa at 1.9% strain at break. When treating membranes above 250 °C, the films became rigid and beyond the testing capability of our experimental apparatus.

Pore structure characterization

As evidenced by the above XRD testing, the formation of covalent crosslinking bonds tends to tighten the polymer chains, leading to a reduced d-spacing in polymer matrix. To further gain insights of microstructures, the pore size distribution of membranes was characterized using combined simulated and experimental approaches based on the MELT program and PALS results. As visualized by molecular simulation in Fig. 5a, the rigid polymer chains in PIM-BM/TB was poorly packed, leading to the formation of irregularly shaped free volume. Molecular modelling comparison of pristine PIM-BM/TB with crosslinked PIM-BM/TB shows the occurrence of efficient packing after cross-linking (Fig. 5a,b). This crosslinking induced tightening effect was consistent with the fractional free volume (FFV) simulation (supplementary Table S1). For instance, with H_2 gas for the structure probe, the calculated FFV reduced from 0.228 to 0.187 for the uncrosslinked and crosslinked membranes, respectively.

Fig. 5c reveals the free volume distributions generated from MELT program based on PALS results. The average free volume radii shifted to a lower value upon crosslinking. As a result, crosslinked membranes exhibited a smaller fractional free volume than the pure polymers, as described in Supplemental Table S1. Moreover, a thermal treatment at the temperature of 250 °C and 300 °C results in much narrow pore size distribution over untreated membranes, indicating the more restricted chain motion and smaller cavities in the crosslinked format of membranes²⁸. Indeed, crosslinking not only tightens the inner pores of membranes but also tailors the width of ultramicropores connecting neighboring cavities, potentially allowing selective diffusion of smaller gases such as H_2 and CO_2 while excluding larger gas molecules like N_2 , and CH_4 , which will be discussed the section below.

Gas transport properties

To explore the gas transport properties in the membranes, single gas permeation was first conducted on pristine polymer membranes and thermally cross-linked membranes using gas molecules including H₂ (2.89 Å), CO₂ (3.3 Å), O₂ (3.46 Å) N₂ (3.64 Å) and CH₄ (3.8 Å) at 35 °C under a feed pressure of 50 psia. Gas permeabilities and ideal selectivities of the membranes are described in Table 1. The pristine PIM-BM/TB membranes exhibit high permeability with moderate gas selectivities, consistent with reported PIMs family membranes. As expected, the crosslinking reaction results in a drastic decrease in gas permeability for XPIM-BM/TB due to pore structure shrinkage as discussed above. Particularly, gas permeability of large gas molecules (CH₄, N₂) reduced much more significantly over smaller gas molecules like O₂, H₂, CO₂ as shown in Fig. 6a. Nevertheless, the gas selectivity increases remarkably upon thermal crosslinking. Moreover, the sequence of gas permeability follows the order of H₂>CO₂>O₂>N₂>CH₄ in XPIM-BM/TB regardless of crosslinking temperatures. Such trend is in accordance with the order of gas kinetic diameters, suggesting the molecule sieving property of these membranes. Indeed, the crosslinked membranes with efficiently packed chain geometry display substantially enhanced molecular sieving ability. For instance, the H₂/CH₄ selectivity of representative XPIM-TM/TB membranes prepared upon heating at 250 °C for 10 h increased from 17.2 to 118.6 and CO₂/CH₄ selectivity increased from 18.0 to 54.1.

Table 1 Gas permeabilities and selectivities of uncrosslinked PIM-BM/TB and crosslinked XPIM-BM/TB.

Polymer	P (Barrer) ^{a)}					Selectivity ^{b)}			
	H ₂	CO ₂	O ₂	N ₂	CH ₄	H ₂ /CH ₄	CO ₂ /CH ₄	O ₂ /N ₂	CO ₂ /N ₂
PIM-BM/TB	1925.2	2007.2	422.5	109.	111.	17.2	18.0	3.8	18.2
				9	8				
80 °C-20 h	1392.1	987.4	215.8	44.2	46.8	29.7	21.1	4.8	22.3
120 °C-20 h	839.2	617.5	149.5	32.5	31.2	26.9	19.8	4.6	19.0
200 °C-20 h	720.9	391.3	87.8	17.6	12.4	58.5	31.7	5.0	22.4
250 °C-5 h	582.4	430.7	103.7	25.2	15.7	37.1	27.5	4.2	17.1
250 °C-10 h	427.1	197.0	46.8	9.1	3.6	118.6	54.1	5.3	21.9
250 °C-20 h	355.8	148.5	33.0	4.4	1.8	197.7	79.9	7.5	33.7
300 °C-2 h	455.1	218.4	58.8	9.4	4.0	132.0	63.4	6.3	23.2
300 °C-5 h	358.2	67.6	18.2	1.6	0.44	814.1	155.7	11.1	42.8

^{a)}Permeability coefficients measured at 35 °C and 50 psi feed pressure. 1 barrer = 10⁻¹⁰ [cm³ (STP) cm]/(cm²

s cmHg); ^{b)}Ideal selectivity $\alpha = (P_a)/(P_b)$

The CO₂/CH₄ and H₂/CH₄ separation data are plotted with current upper bounds and compared with literatures. Fig. 6b and c show the overall trends of remarkable enhancement of selectivity with moderate reduction in gas permeabilities over other existing PIM based membranes. In comparison to industrially used polymeric gas separation membranes (e.g. polysulfone, PSF), the XPIM-BM/TB membranes have apparently higher selectivities while maintaining orders-of-magnitude higher permeability, well exceeding present upper bounds²⁹⁻³¹. Notably, the H₂/CH₄ selectivity of XPIM-BM/TB membranes treated at temperature of 300 °C for 5 h is as high as 814.1, increased by 47-fold over un-crosslinked PIM-BM/TB, which is one of the highest values reported for other comparable polymeric membranes. Owing to rigid structures with closely packed chains in these membranes, a significantly high H₂/CH₄ permselectivity is achieved due to the large difference in kinetic diameters for H₂ and CH₄ molecules. The substantial reduction of CH₄ permeability after thermal treatment indicates the narrow pore structure of XPIM-BM/TB and large reduction of cavities sizes preferentially permeating H₂ over CH₄.

Other notable gas pairs including O_2/N_2 , and H_2/N_2 are described in Supplementary Fig. S19-20. Similar to H_2/CH_4 , all these gas pairs achieve highest selectivity for crosslinked PIM-BM/TB treated at 300 °C and substantially exceed the gas separation limits of conventional polymeric membranes. The separation process of O_2/N_2 is much more difficult as compared to H_2/CH_4 and CO_2/CH_4 as O_2 and N_2 have similar kinetic diameters with only Ångstrom-level differences. Nonetheless, the crosslinked membranes exhibit great promise for O_2/N_2 separation as the separation performance is located well above the Robeson upper bound. With increasing reaction temperature, O_2/N_2 selectivities remarkably increased from 3.8 to 11.1 with a reduction of O_2 permeability from 422.5 Barrer to 18.2 Barrer. This impressive gas separation performance is similar to that of carbon molecular sieve and other molecular sieving membranes³²⁻³³, further confirming the enhanced molecular sieving effects within these cross-linked membranes.

Tunable gas transport properties

One of the important advantages of PIM-BM/TB polymer membranes is the versatility in tailoring the microporous structure and gas separation performance. The gas transport properties intimately correlated with pore structures of membranes could be precisely tuned by controlling cross-linking reaction temperature, reaction time and the atmosphere. Fig. 7 shows the effects of reaction temperature, reaction time and oxygen concentration in the purging gas on gas permeability and selectivities in crosslinked PIM-BM/TB. Evidently, as the cross-linking temperature increased from 80 °C to 300 °C, gas permeability gradually decreased while gas selectivity increased significantly (Fig. 7a-b). In fact, the cross-linked membranes demonstrated the most substantial drop in gas permeability of largest gases of CH_4 and the least reduction in H_2 permeability depending on reaction temperature (Fig. 7b). Correspondingly, the H_2/CH_4 gas pair with the largest kinetic diameter difference is most sensitive to reaction temperatures. In addition to the reaction temperature, the gas separation performance can be readily tailored by changing crosslinking time. For the membranes reacted with identical reaction temperature of 250 °C, increasing cross-linking time from 5 h to 20 h leads to the increase of gas selectivities along with a reduction in gas permeability. For example, CO_2 permeabilities reduce from 430.7 Barres to 148.5 Barres and CO_2/CH_4 selectivity increase from 27.5 to 79.7 (Table S6). We further investigated the effects of O_2 concentration on the gas separation performance of crosslinked membranes at a temperature of 250 °C with a reaction duration of 10 h as shown in Fig 7e-7f. For example, the CO_2 gas permeability reduced when increasing O_2 concentration from inert gas to a level of 21000 ppm. The gas selectivity of CO_2/CH_4 reached the maximum of 56 at 200 ppm O_2 . The oxygen concentration plays a critical role during thermally oxidative crosslinking reaction. Therefore, adjusting the cross-linking temperature, time and oxygen concentration can simply generate polymeric membranes with commercially attractive gas separation performance. To further improve the membrane performance, blending ratio of PIM-BM/TB and degree of bromomethylation are other potential tunable factors to improve the gas transport properties, which is currently being explored in our lab.

Effects of high feed pressures and ageing behavior

To explore the practical applicability of membranes under aggressive feed conditions, the membranes were subjected to high CO₂ pressures. In the case of un-cross-linked PIM-BM/TB membranes, exposure of membranes under high pressure pure CO₂ leads to reduced gas permeability owing to the non-ideality under high pressures (Fig. 8a) which is commonly observed in highly porous PIMs³⁴. The CO₂/CH₄ selectivity reduced with increasing pressure to 500 psia. On the other hand, the cross-linked membranes exhibit much less permeability decline over pristine membranes, indicating considerably stabilized structure in the membranes. The mixed gas permeation tests were performed using CO₂/CH₄ 1:1 gas mixture for PIM-BM/TB-250 °C-10 h (Fig. 8c-d). Mixed gas separation properties were comparable to pure gas permeation results.

With the consideration of long-term stability of membranes, physical aging over a period of 12 months for XPIM-BM/TB treated at 250 °C for 10 h were investigated. Gas permeability of XPIM-BM/TB gradually reduced and gas selectivities increased during aging. As shown in the Robeson plot (Fig. 6b-c), the aged XPIM-BM/TB membranes still demonstrate outstanding gas separation performance well above the upper bound.

Discussion

In this work, we describe a novel principle of designing microporous polymer blend membranes through multi-covalent-crosslinking of PIM-BM/TB. We propose three possible cross-linking mechanisms within PIM-BM/TB membranes dependent of crosslinking temperatures: a) the formation of quaternary ammonium salts through reactions of tertiary amine with bromomethyl groups; b) alkylation reactions at elevated temperatures; and c) thermally oxidative crosslinking reactions after the polymer chain scissor and rearrangements. The complex intra and inter-cross-linking reaction simultaneously occur between PIM-BM and TB.

The crosslinked PIM-BM/TB molecular sieving membranes with tailorable porosity exhibit desired gas separation performance for industrially important gas pairs. The membranes display unprecedented H₂/CH₄ selectivity of 814.1 in crosslinked XPIM-BM/TB at 300 °C for 5 h while maintaining high H₂ permeability of 358.2 Barrer. More importantly, the crosslinked membranes substantially exceed present upper bound limits of conventional polymeric membranes for multiple gas pairs, including H₂/CH₄, CO₂/CH₄, H₂/N₂, and O₂/N₂.

In the future, the physical and gas separation properties of microporous polymeric membranes developed in this work can be further tailored by controlling degree of bromomethylation and optimizing the blending ratio of PIM-BM to TB during polymer synthesis. Overall, the strategy in this work provides a new route of designing and fabricating promising molecular sieving membranes for energy-efficient separations.

Methods

Preparation of membrane. Dense membranes were prepared by solution casting of filtered equimolar PIM-BM and Tröger's Base (TB) in chloroform on clean glass substrate, with solvent slowly evaporated in 2 days, the dry free-standing membranes were obtained and exposed to methanol soaking for overnight and further dried in a vacuum oven at 70 °C for 24 h. The thickness of the PIM-BM/TB membrane was about 50 µm (± 10 µm).

Thermal analyses. Thermal analyses of PIM-BM/TB fresh and thermally treated membranes were performed in a TGA to study the thermal degradation in nitrogen atmosphere. Polymer membranes were dynamically heated from room temperature to 100 °C at 5 °C/min and held for 30 min then to 800 °C at 5 °C/min in nitrogen atmosphere. TG-MS were performed in TGA Q50 V20.10 Build 36 in nitrogen atmosphere.

Thermal Cross-Linking Treatments. The membrane of PIM-BM/TB was performed using a CenturionNeytechQex vacuum furnace under 200 ppm O₂ balanced with nitrogen. The vacuum furnace was swept for 60 min, then the temperature was raised to between 80 and 300 °C at a rate of 3 °C/min and held for a period of 5 to 20 h. After the thermal cross-linking treatment process, the membranes were cooled at a rate of 3 °C/min in the furnace to room temperature for further studies. The membrane was labeled as "XPIM-BM/TB-temperature (h)", for example, XPIM-BM/TB-80 °C-20 h.

Characterization. X-ray diffraction (XRD) was intended to study the change of d-spacing. The results were recorded on a Bruker AXS GADDS apparatus using Cu radiation with wavelength of 1.54 Å (voltage: 40 kV, current: 30 mA). d-spacing was computed following Bragg's law ($d = \lambda / 2 \sin \theta$). An X-ray photoelectron spectrometer (XPS) was utilized to monitor the chemical changes of PIM-BM/TB-fresh and thermally cross-linked PIM-BM/TB membranes. They were recorded on HSi spectrometer (Thermo Fisher ESCALAB 250 xi., England) using a monochromatic Al K α X-ray source (1486.6 eV photons) at a constant dwell time of 100 ms and a pass energy of 40 eV under full vacuum. The anode voltage and anode current were 15 kV and 10 mA, respectively. All core-level spectra were obtained at a photoelectron takeoff angle of 90 ° with respect to the sample. To compensate for surface charging effects, all binding energies (BE's) were referenced to the C1s hydrocarbon peak at 284.8 eV. Surface elemental stoichiometries were determined from the peak area ratios and were accurate to within $\pm 5\%$.

SEM analysis of membranes was performed using a Hitachi S5500 microscope. The polymer films were fractured and coated with a thin layer of gold. Determination of polymer molecular weights were accomplished using gel permeation chromatography (GPC, Shimadzu LC-20A) with Ultrastayragel columns and tetrahydrofuran (THF) as the eluent flowing at a rate of 1 mL/min. The FTIR measurements were performed using an attenuated total reflection mode (FTIR-ATR), with a Perkin-Elmer Spectrum 2000 FTIR spectrometer. Each sample was scanned 32 times. Wide-angle X-ray scattering was performed with a DX-2700 machine operated at 30 mA and 40 kV using Cu K α radiation with a step of 0.03 per second. Tensile tests of polymer films were carried out at Instron-1211 (Instron Co., USA) mechanical testing instrument at a cross head speed of 1 mm·min⁻¹. Polymer films were cut into thin slices with an effective length of 10 cm and a width of 1 cm, with the accurate value determined from high-resolution photos and

calibrations from known length. The average value of Young's modulus was derived from the initial slope. The tensile strength at break and elongation at break were also measured. The positron annihilation experiments were conducted by using a fast-fast coincidence PALS. A ^{22}Na source was used as positron source. The activity of the ^{22}Na source is about 10 mCi. Kapton film is used to encapsulate dry ^{22}Na source. The PALS measurements were performed at various relative humidities ranging from $\sim 0\% \text{RH}$ to $\sim 100\% \text{RH}$. The membranes were cut into 1 cm x 1 cm slice, the thickness test slice was around 1.5 mm. Two slices of the same sample sandwiched a 20 μCi positron source (^{22}Na), which was sealed with two thin Kapton membranes of 7 μm . The positron lifetime spectrum of single-crystal Ni was used as a reference in order to subtract the source components of positron annihilation in Kapton membranes and ^{22}Na . The energy of positron annihilation is 1.28 MeV and the time difference of annihilation γ ray is about 0.5118 MeV accompanied by γ ray and the positron annihilation lifetime was obtained.

Gas permeation

Pure gas permeation tests were carried out at temperature of 35 °C and 50 psi except for PIM-BM-TM-300 °C-5 h (100psi, 35 °C), using a constant-volume pressure-increase apparatus. The mixed gas permeation properties were measured in the same membrane cell using the same constant-volume pressure-increase apparatus. The membrane was exposed to certified gas mixtures of CO_2/CH_4 (50/50 vol%) with feed pressures up to 50 psi-150psi at 35 °C. The gas compositions were analyzed by a gas chromatograph (GC-7820A, Agilent).

Molecular simulation

The Molecular Dynamics (MD) simulation was constructed by the Forcite module in Materials Studio software package (Accelrys Inc., CA, USA). In one cubic simulation box, four polymer chains (2 PIM-BM-70% polymer chains and 2 TB polymer chains) with 10 repeating units were constructed. The initial density is 0.5 g/cm^3 and the target densities is 1.177 g/cm^3 before crosslinking. The force field was PCFF. The Berendsen algorithm with a decay constant of 0.1 ps was used to control the temperature and pressure of each box. The specific procedures before crosslinking are as follows: (1) energy minimization; (2) 50ps NVT-MD simulation at 600 K; (3) 100ps NPT-MD simulation at 600 K at 1 GPa; (4) 100ps NPT-MD simulation at 298.15 K at 1 GPa; (5) 100ps NPT-MD simulation at 298.15 K at 0.1 MPa; (6) 50ps NVT-MD at 298.15K. The Ewald summation method was used to calculate the non-bond interactions with an accuracy of 0.001 $\text{kcal}\cdot\text{mol}^{-1}$.

After this, the final equilibrium structure was used to crosslink Br with N or C atoms, and the cubic simulation box with crosslinked polymers was used as the initial structure for molecular dynamics simulation. The specific procedures after crosslinking are as follows: (1) 100 ps NPT-MD simulation at 298.15 K at 2 GPa; (2) 100 ps NPT-MD simulation at 298.15 K at 0.1 MPa; (3) 50 ps NVT-MD simulation at 298.15 K. The force field and other parameters are the same as before crosslinking.

Declarations

Acknowledgments

Financial support from the National Natural Science Foundation of China (Nos. U1510123, 21603068, Grant No.21978321), the Hundred Talents Program of Shanxi Province and the Fundamental Research Funds for the Central Universities”(DUT20RC(3)023)

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Figures

Figure 1

SEM images and photos of polymer membranes after thermal crosslinking at varied temperatures. (a) (c) (e) Cross-sectional image of PIM-BM/TB, PIM-BM/TB-250 oC-10 h and PIM-BM/TB-300 oC-5 h. (b) (d) (f) Surface image of PIM-BM/TB, PIM-BM/TB-250 oC-10 h and PIM-BM/TB-300 oC-5 h. (g) photos of PIM-BM/TB treated at different temperatures

Figure 2

Schematic of cross-linking reactions between PIM-BM and TB. (a) chemical structure of PIM-BM and TB. (b) proposed crosslinking mechanisms between PIM-BM and TB.

Figure 3

Structures characterization of fresh and thermally cross-linked PIM-BM/TB. (a) XPS spectrum of Br 3d of fresh PIM-BM/TB. (b) XPS spectrum of Br 3d of PIM-BM/TB-120 °C-20 h. (c) XPS spectrum of Br 3d of PIM-BM/TB-200 °C-20 h. (d) XPS spectrum of Br 3d of PIM-BM/TB-250 °C-10 h. (e) XPS spectrum of Br 3d of PIM-BM/TB-300 °C-5 h. (f) FTIR spectra of fresh and thermally cross-linked PIM-BM/TB.

Figure 4

Properties of crosslinked microporous membranes. (a) thermal stability of PIM-BM/TB and crosslinked PIM-BM/TB; (b) XRD profiles; (c) mechanical properties of polymer membranes

Figure 5

Characterization of PIM-BM/TB and XPIM-BM/TB membranes physical structures. (a) representative chain conformations in crosslinked PIM-BM/TB from computer modelling results; (b) 3-D view of crosslinked PIM-BM/TB modelling structure in an amorphous cell (79% crosslinking degree). (cell size: 30*30*30 Å; density of ~ 1.X g/cm³ grey: Van der Waals surface; dark grey: Connolly surface with pore radius of 1.45 Å); (c) pore size distribution from PALS.

Figure 6

Gas transport properties. (a) Gas permeabilities as a function of kinetic diameters; (b) CO₂/CH₄ separation with Robeson upper bound; (c) H₂/CH₄ separation with upper bounds.

Figure 7

Gas transport properties of membranes prepared under various conditions. (a). gas permeability and (b). gas selectivity as a function of reaction temperature. All samples were thermally treated at set-point temperature for 10-20 h under 200 ppm of O₂, except that the sample at 300 oC was annealed for 5 h; (c). gas permeability and (d). gas selectivity as a function of reaction time treated at 250 oC of crosslinked membranes; (e). gas permeability and (f) .gas selectivity as a function of oxygen concentrations for membranes treated at 250 oC of 10 h.

Figure 8

Effects of high pressures and physical aging of membranes. (a). CO₂ permeability versus feed pressure; (b). CO₂/CH₄ selectivity versus feed pressure; (c). CO₂ permeability versus the fugacity of CO₂ for separation of gas mixtures (CO₂/CH₄ : 50/50 vol%). (d). CO₂/CH₄ selectivity versus the fugacity of CO₂ for separation of gas mixtures (CO₂/CH₄: 50/50 vol%); (e). Pure gas permeability versus aging time of 250 °C-10 h; (f). gas selectivity versus aging time.

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