

Development of Microporous Polymer Membranes for Energy Efficient Gas Separations

Investigators

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Abstract

Polymer membrane based gas separation is an important technology to significantly reduce the energy consumption and minimize the greenhouse gas generation of globally important gas separation processes. Development of high performance membrane materials is the key for the success of this technology. Current commercial membranes have low permeability and moderate selectivity. We developed a new family of microporous ladder polymers that exhibit >100 higher permeability and comparable or higher selectivity as compared to the commercial membranes. These polymers also exhibit excellent thermal and chemical stability, good mechanical properties, and can be synthesized easily from readily available building blocks. With new synthetic capability to access diverse microporous polymer structures and fundamental understanding of their structure-performance relationships, we aim to develop a new membrane platform, “game changer” membranes, with tunable gas transport properties and rationally designed polymers for various gas separation applications.

Introduction

Energy-efficient gas separations are essential for reducing the carbon footprint of chemical and power industry and capturing generated greenhouse gases to mitigate their emission. Today, the primary processes used for gas separations are thermo-based and energy-intensive. Considering two major gas separations, natural gas purification (3.1 trillion cubic meters per year worldwide) and CO₂ capture from flue gas, amine absorption (scrubbing) is the dominant technology. While it is effective at removing or capturing CO₂, it consumes 30% or more of the energy generated at a power plant. Furthermore, the aqueous sorbent is highly corrosive and decompose over time, yielding toxic wastes that are environmentally harmful. Solid sorbents have been actively investigated, but still require an energy-intensive activation step to remove the captured CO₂ and enormous volumes of sorbents are needed to capture CO₂ released from a power plant. Energy-efficient and environmentally friendly gas separation technologies are critical for a sustainable future. A promising alternative technology is polymer membrane gas separation, because of its high energy efficiency (no regeneration needed), minimal environmental impact, continuous operation, simple installation, and low maintenance cost.¹ The success of membrane-based gas separation technology relies on the development of high-performance and robust polymer membranes. Polymer membrane-based gas separation is growing rapidly for several important industrial separations of gases, including air separation (O₂/N₂ separation), natural gas purification (removing acidic and condensable gases such as CO₂, H₂S, and C₃+ hydrocarbons), hydrogen recovery, and carbon capture (separating CO₂ from flue gas at power plants). The membrane gas separation market is estimated to exceed \$1 billion/year in 2020.

Permeability and selectivity are two of the most important parameters for membrane performance. Permeability defines the membrane productivity and selectivity sets the purity of recovered gas. However, there is a well-known trade-off between permeability and selectivity, thus creating an “upper bound” in the separation performance.² Current commercial membranes for gas separations are predominantly based on cellulose acetate, polyimides, and polysulfones that are not specifically developed for these gas separation applications. These membranes generally exhibit low permeability and moderate selectivity, because of their dense chain packing and non-porous structures. So large membrane areas are required to compensate for the small permeance. More recently, a few types of microporous polymers have been developed to give very high permeability but often low or moderate selectivity.³⁻⁵ Highly permeable membranes also lose their permeance very quickly during “aging”.⁶ Physical aging is a phenomenon observed in highly glassy polymers whose specific volume and other bulk properties are out of equilibrium. In the physical aging process, the specific volume of the polymer glass slowly approaches equilibrium. In the context of gas separation membranes, the decrease in fractional free volume during aging leads to decrease in permeability. Ideal membranes would exhibit relatively stable performance over time with minimized aging. Therefore, polymer membranes with moderately high permeability but high selectivity, slow aging, and long-term stability are highly desired for gas separation applications. The performance of membranes would strongly depend on the gas mixtures to separate, and there is not a single optimal membrane for all gas separations. Therefore, for the development of “game changer” membranes, it is critical to establish a membrane platform with tunable gas transport properties and rational understanding of how polymer structures affect many performance parameters.

Background

Rigid contorted ladder polymers with high surface areas have recently garnered intense interest as the next generation of materials for membrane gas separation due to their ultrahigh permeability,³⁻⁵ but the structural diversity of such polymers is very limited and their synthesis requires complex specialty monomers. Aging of such polymers is usually significant, quickly losing the original performance. Our research aims to establish a new platform of high performance gas separation membranes based on microporous ladder polymers that are synthesized from a broad range of readily available building blocks via catalytic arene-norbornene annulation (CANAL) polymerization that the Xia lab at Stanford has developed.⁷⁻⁹ The CANAL polymers exhibit a variety of kinks and conformations, depending on the monomer structures, which are largely fixed once they are synthesized, regardless of the physical state or environmental conditions. Such rigid and kinked conformations result in high surface areas in these polymers (BET surface areas 300-800 m²/g) with abundant ultra-micropores (pore width < 1 nm), resulting from the molecular scale voids between kinked polymer segments. The presence of ultra-micropores is most important to create the sieving effect for selective separation of gas molecules with similar sizes and dimensions. In contrast to many crosslinked or framework insoluble microporous materials, which are commonly used for gas separation and storage in an *adsorption/desorption* process, these microporous polymers are soluble in organic solvents and can be cast into membranes via slow solvent evaporation. The solubility or processability and mechanical integrity are critical for fabrication of robust membranes. In

addition, these polymers have excellent thermal stability up to 400 °C with no observable glass transition and excellent chemical resistance to strong acids and bases, which are required for membranes designed for separations of corrosive gas mixtures and under harsh conditions.

We aim to generate a library of CANAL ladder polymer membranes with varied structures and finely tuned microporosity to establish systematic understanding on how the macromolecular structures affect gas transport properties and aging process. To develop high performance membranes, we targeted the versatility to tune the transport properties through molecular design, high selectivity, high permeability (~100 times higher than commercial membranes) but not necessarily ultra-high permeability (otherwise, aging is significant), slow aging or stable permeation performance over a long period of time, and robust mechanical properties. We have developed several types of polymers using CANAL chemistry to meet these challenging targets. Continued research on these unique materials and the fundamental structure-performance relationship knowledge will allow rational design of a new generation of high performance membrane materials that can be custom-designed to minimize impacts of hydrocarbon extraction/use and enhance the energy efficiency of industrially and globally important gas separations.

Results

Synthesis of microporous ladder or pseudo-ladder polymers

To expand the variety of microporous ladder or pseudo-ladder polymers, we used CANAL chemistry to synthesize a series of ladder-shaped diamines from readily available bromo-anilines and norbornadiene in high yields (Figure 1). These ladder-shaped diamines were then used to synthesize ladder-containing polyimides (PIs) and ladder polymers with Tröger's base (TB) linkage (Figure 2). We then formed homogenous, transparent, and mechanically robust membranes by casting their chloroform solutions in circular and flat Petri dishes. The film thickness was controlled to be 40-55 μm . The films showed excellent mechanical performance with high Young's modulus around 1 GPa and tensile strength tens of MPa and were highly flexible to allow for easy processing. We next report the gas permeation performance of these two series of polymers separately.

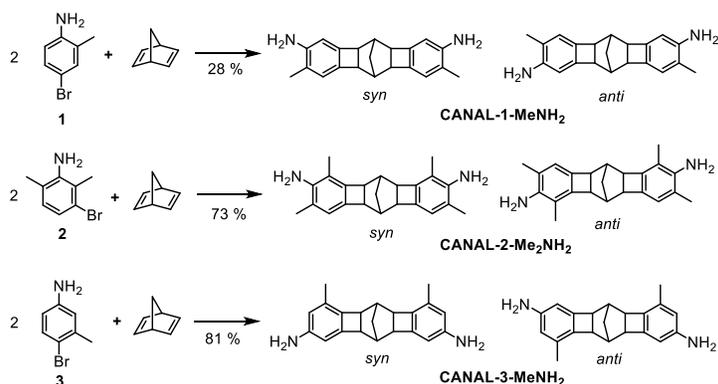
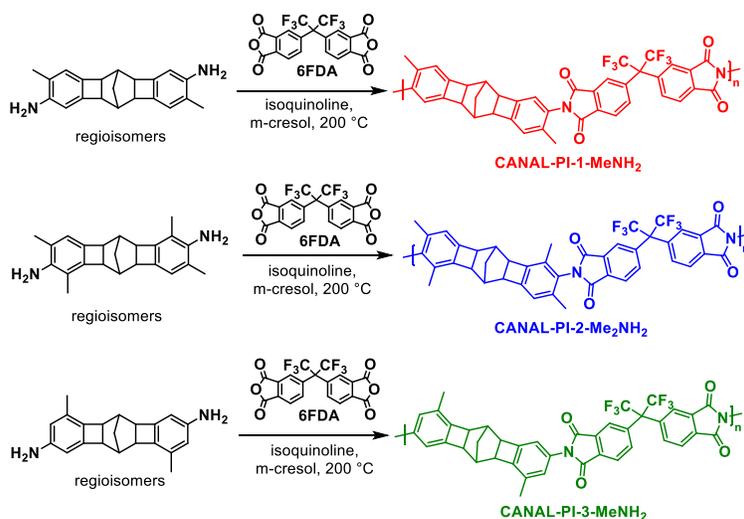


Figure 1. Synthesis of CANAL diamines. Reaction conditions: 1 equiv. bromoaniline, 0.5 equiv. norbornadiene, 1 mol% Pd(OAc)₂, 2 mol% PPh₃, 1 equiv. Cs₂CO₃, 1,4-dioxane, 150 °C.

(a) CANAL-Polyimides



(a) CANAL-TB Polymers

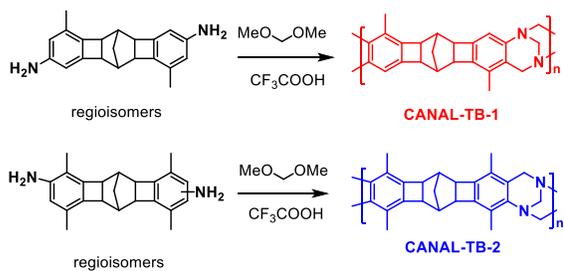


Figure 2. Synthesis of CANAL-polyimides (PIs) and CANAL-Tröger's base (TB) polymers. Photo shows the flexibility of formed polymer membrane.

Micropore and Gas Permeation Properties of CANAL-PIs

CANAL-PIs exhibited Brunauer-Emmett-Teller (BET) surface areas of 200-530 m²/g, based on N₂ sorption isotherms at 77 K. *Ortho* substitution on the aryl imide is expected to restrict the C-N bond rotation in the backbones of PIs, thus leading to higher intrachain rigidity and more frustrated chain packing. Therefore, CANAL-PI-2-Me₂NH₂, which has two methyl substituents *ortho* to the imide linkage, had a much higher BET surface area (533 m²/g) than the other two PIs with only one or no methyl substituent *ortho* to the imide linkage (both ~ 200 m²/g).

We measured the permeability of light gases, including H₂, N₂, O₂, CH₄, and CO₂. The permeability qualitatively followed the same trend as the BET surface areas in this series of CANAL-PIs. In general, the polymers displayed high permeability with moderate gas-pair selectivity (Table 1). For example, the O₂ permeability values of CANAL-PI-1-MeNH₂, CANAL-PI-2-Me₂NH₂ and CANAL-PI-3-MeNH₂ were 81, 319, and 33 barrer, respectively (1 barrer = 10⁻¹⁰ cm³ cm cm⁻² s⁻¹ cmHg⁻¹). The presence of methyl groups *ortho* to the imide linkage significantly increased permeability but lowered permselectivity. Permselectivity consists of diffusivity selectivity and solubility selectivity. To better understand the observed permselectivity, we calculated diffusion coefficients of different gases for CANAL-PIs using the time lag equation and determined the solubility

coefficients by assuming the solution diffusion model $P = DS$. Both the solution and diffusion coefficients of CANAL-PIs are one to two orders of magnitude higher than those of “nonporous” PIs.¹⁰⁻¹¹ Concomitant with the increase in permeability for CANAL-PIs is the increase in diffusion coefficient with simultaneous decrease in diffusivity selectivity. The order of permeability for gases in CANAL-PI-1-MeNH₂ and CANAL-PI-3-MeNH₂ followed the same trend as the kinetic diameters of gases ($P_{H_2} > P_{CO_2} > P_{O_2} > P_{N_2} > P_{CH_4}$). Interestingly, CANAL-PI-2-Me₂NH₂ exhibited reverse selectivity for gas pairs H₂/CO₂ and N₂/CH₄, leading to the following order of gas permeability: $P_{CO_2} > P_{H_2} > P_{O_2} > P_{CH_4} > P_{N_2}$. Reverse selectivity for the gas pairs of H₂/CO₂ and N₂/CH₄ can be attributed to the higher condensability of the larger gases. Notably, CANAL-PI-3-MeNH₂ has similar ideal CO₂/CH₄ permselectivity as commercial polymers such as Matrimid, but is almost two

Table 1. Gas Permeability and Permselectivity of CANAL-PIs (T=35 °C; 2 bar)

Polymer	Permeability (Barrer)					Ideal selectivity ($\alpha_{X/Y}$)			
	H ₂	N ₂	O ₂	CH ₄	CO ₂	H ₂ /N ₂	H ₂ /CH ₄	O ₂ /N ₂	CO ₂ /CH ₄
CANAL-PI-1-MeNH ₂ , 44 μ m									
Freshly prepared	462	20.7	81	16.3	419	22	28	3.9	26
Aged 73 d	425	16.6	71	13.7	365	25	31	4.2	27
Aged 115 d	417	16.7	69	12.9	353	25	32	4.1	27
CANAL-PI-2-Me ₂ NH ₂ , 51 μ m									
Freshly prepared	1154	91	319	108	1691	13	11	3.5	15
Aged 54 d	1120	79	274	89	1330	14	13	3.5	15
Aged 101 d	1060	67	244	72	1237	16	15	3.7	17
CANAL-PI-3-MeNH ₂ , 45 μ m									
Freshly prepared	282	7.0	33	4.8	157	40	59	4.7	33
Aged 65 d	259	5.53	25	3.6	122	41	64	4.7	34

^a Measured using the constant-volume/variable-pressure method at 2 bar and 35 °C. ^b Calculated from $\alpha_{X/Y} = P_X/P_Y$.

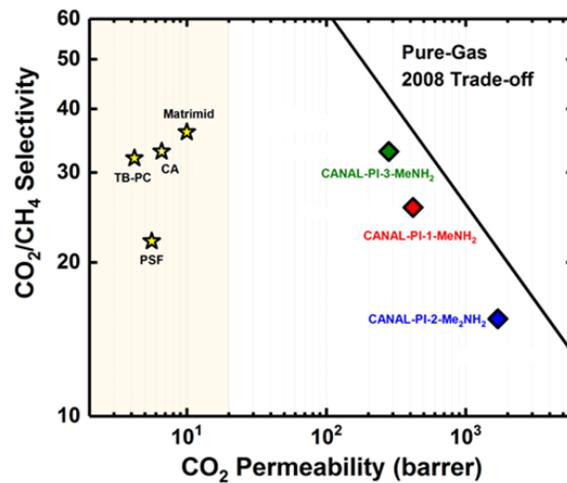


Figure 3. CO₂/CH₄ separation performance of CANAL-PIs and commercial polymers (TB-PC, Matrimid, cellulose acetate (CA), polysulfone (PSF)) relative to the 2008 CO₂/CH₄ permeability/selectivity upper bound.

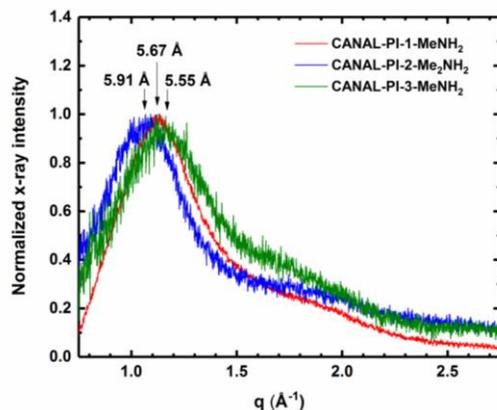


Figure 4. Wide-angle X-ray scattering data (WAXS) of CANAL-PI films.

orders of magnitude more permeable (Figure 3). This makes the CANAL motif a promising building block for the development of polymeric membrane materials for gas separation.

To better understand and rationalize the gas transport properties of CANAL-PIs, we conducted wide-angle X-ray scattering (WAXS). All CANAL-PIs were amorphous and exhibited a broad scattering feature that peaks around $q = 1-1.2 \text{ \AA}^{-1}$ in the WAXS patterns, corresponding to intersegmental distances of 5-6 \AA (Figure 4). The scattering peak of CANAL-PI-2-Me₂NH₂ slightly shifted to lower q corresponding to a larger intersegmental distance at 5.9 \AA , as compared to CANAL-PI-1-MeNH₂ and CANAL-PI-3-MeNH₂, which showed intersegmental distances at 5.5-5.7 \AA .

The aging process of the CANAL-PI membranes was tracked by their gas permeability over time. Thin polymer films and polymers with extremely high fresh permeability are known to age relatively fast.¹²⁻¹³ These CANAL-PI membranes were found to have slow aging, exhibiting only moderate reduction in permeability, the O₂ permeability of CANAL-PI-1-MeNH₂ decreased by only 15 % after 115 days.

Micropore and Gas Permeation Properties of CANAL-TBs

CANAL-TB-1 and CANAL-TB-2 showed very high BET surface areas of 881 and 987 $\text{m}^2 \text{ g}^{-1}$ and pore volumes of 0.61 and 0.66 cm^3/g , respectively. Presumably, CANAL-TB-2 with tetramethyl substitution resulted in more frustrated packing. These surface areas are among the highest for soluble microporous polymers reported in literature.

WAXS of CANAL-TBs again gave a broad scattering feature, corresponding to intersegmental distances of 6-8 \AA . The scattering of CANAL-TB-1 peaked at 7.6 \AA , while that of CANAL-TB-2 peaked at 6.3 \AA . The difference in their average intersegmental spacing again reflects the effect of even subtle substitutions on chain packing.

Table 2. Gas Permeability and Ideal Selectivity of CANAL-TB-1 and CANAL-TB-2 (T = 35 °C; p = 2 bar).

Polymer	Permeability (barrer)					Ideal selectivity ($\alpha_{X/Y}$)			
	H ₂	N ₂	O ₂	CH ₄	CO ₂	H ₂ /N ₂	H ₂ /CH ₄	O ₂ /N ₂	CO ₂ /CH ₄
CANAL-TB-1 ^a	3981	205	897	280	3420	19.4	14.2	4.4	12.2
CANAL-TB-1 ^b	2760	97	463	121	1678	28.5	22.8	4.8	13.9
CANAL-TB-2 ^c	5046	263	1170	324	3935	19.2	15.6	4.5	12.1
CANAL-TB-2 ^d	3608	162	747	205	2520	22.3	17.6	4.6	12.3

^a thickness of 92 μm , soaked in MeOH and air-dried for 3 days. ^b thickness of 39 μm , soaked in MeOH and then dried at 120 °C under vacuum for 24 h. ^c thickness of 86 μm , soaked in MeOH and air-dried for 3 days. ^d thickness of 39 μm , soaked in MeOH and then dried at 120 °C under vacuum for 24 h.

Both CANAL-TB polymers exhibited high gas permeability. The sequence of the gas permeabilities followed $P_{\text{H}_2} > P_{\text{CO}_2} > P_{\text{O}_2} > P_{\text{CH}_4} > P_{\text{N}_2}$. Thicker (~90 μm), fresh air-dried films gave much higher permeabilities but lower selectivities than the corresponding thinner (~39 μm) films that were dried at 120 °C. The fresh air-dried CANAL-TB-1 film exhibited an O₂ permeability of 897 barrer and O₂/N₂ selectivity of 4.4, whereas the 120 °C treated film showed an O₂ permeability of 463 barrer and an O₂/N₂ selectivity of 4.8. Such high selectivity and still much higher (~100 x) permeability than commercial membranes make these polymers attractive materials for air separation. We have filed a provisional patent on these polymers. We are currently investigating their aging and preliminary results showed similarly slow aging to CANAL-PIs.

Conclusions

Within the past year of GCEP funding, we have synthesized two series of (pseudo)ladder polymers easily from readily available starting materials. These polymers exhibited excellent thermal stability and high BET surface areas. We showed that even small changes in simple substituents can modulate the surface area, microporosity, and thus the gas transport properties of the ladder polymers. These polymers exhibited high permeabilities and selectivities of industrially important gases and also experienced relatively slow aging. Facile synthesis, mechanically robust membranes, and good gas transport properties of these microporous polymers make them promising materials for membrane gas separations. We are expanding to a much broader range of ladder-shaped microporous polymers with varied structures with systematic investigation of their micropore structures and gas transport properties. These data will allow us to establish the impact of this research will be both fundamental and applied: generating new materials and new insights for developing future membranes for gas separations, which are important growing industrial processes. Higher performance membranes would lead to significant energy saving and minimal environmental impacts as compared to other thermally based separation technologies, thus reducing greenhouse gas emissions during these global scale gas separation processes.

Publications and Presentations

Publications

1. Abdulhamid, M. A.; Lai, H. W. H.; Wang, Y.; Jin, Z.; Teo, Y. C.; Ma, X.; Pinnau, I.; Xia, Y. [Microporous Polyimides from Ladder Diamines Synthesized by Facile Catalytic Arene-Norbornene Annulation as High-Performance Membranes for Gas Separation](#), *Chemistry of Materials* **2019**, *31*, 1767.
2. Provisional Patent Application: "Arene-Norbornene-Tröger's base-Derived Ladder Polymers and Membranes Made Thereof" Ma, X.; Lai, H. W. H.; Pinnau, I.; Xia, Y.

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1. Lai, H. W. H.; Xia, Y. Microporous CANAL polymers for membrane gas separation. North American Membrane Society Annual Meeting, Pittsburgh, May 2019.

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