Fine Tuning the Molecular Structure of Binaphthalene Polyimides for Gas Separations

Wouter Dujardin^{1,2}, Cédric Van Goethem², Zidan Zhang³, Rhea Verbeke², Marcel Dickmann⁴, Werner Egger⁵, Erik Nies³, Ivo Vankelecom², Guy Koeckelberghs^{1}*

1) Laboratory for Polymer Synthesis, Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001

Heverlee, BELGIUM

2) Centre for Surface Chemistry and Catalysis, Department of Microbial and Molecular Systems, KU

Leuven, Celestijnenlaan 200F, B-3001 Heverlee, BELGIUM

3) Laboratory for Physical Chemistry of Polymer Materials, Department of Chemistry, KU Leuven,

Celestijnenlaan 200F, B-3001 Heverlee, BELGIUM

4) Heinz Maier-Leibnitz Zentrum (MLZ) and Physik Department E21, Technische Universität München,

Lichtenbergstraße 1, 85748 Garching, GERMANY

5) Institut für Angewandte Physik und Messtechnik LRT2, Fakultät für Luft- und Raumfahrttechnik,

Werner-Heisenberg-Weg 39, 85577 Neubiberg

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ABSTRACT

A set of new stiff and contorted polyimides were prepared to systematically link polymer structure with gas separation properties. Seven novel bridged binaphthalene polyimides were synthesized for this purpose using commercial dianhydrides pyromellitic dianhydride (PMDA), biphenyl-tetracarboxylic acid dianhydride (BPDA) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA). From these polyimides, freestanding membranes were prepared and tested on mixed gas CO₂/CH₄ and CO₂/N₂ separation performance. They were further characterized using WAXS and PALS and through the simulation of their free volume elements (FVEs) and gas separation properties. The binaphthalene polyimides had CO₂/CH₄ and CO₂/N₂ mixed gas selectivities of respectively 40 and 29 and mixed gas permeabilities of about 20 barrer for both gas mixtures.

1. INTRODUCTION

Polymer membranes are intensively investigated for gas separation processes, such as biogas and natural gas purification, nitrogen production from air, H₂-recovery and flue gas treatment.[1–4] An often used class of polymers for these applications are aromatic polyimides due to their high selectivity and excellent thermal, chemical and mechanical properties as well as their outstanding film-forming ability.[5–9] Unfortunately, a high selectivity (α) is also typically combined with a rather poor permeability (P) in a trade-off relationship, as famously illustrated by Robeson.[10] Being able to design a polymer membrane that maintains its high selectivity while also realizing a high permeability would be of major interest. In the past two decades, many different polymer classes and strategies have been investigated in search of the ideal polymer membrane, such as polyacetylenes, polybenzimidazoles[11–13], thermally rearranged (TR) polymers[14,15], mixed matrix membranes and polymers with intrinsic microporosity (PIMs)[16–20]. PIM-1 was the first PIM and was a nonnetwork polymer with a rigid and contorted backbone which lead to disrupted chain packing, resulting in high free volume creation. PIM-1 achieved a remarkable combination of a CO₂ permeability of 2300 barrer with a CO₂/CH₄ selectivity of 18.[16] Since then, many PIM derivatives have been developed such as KAUST-PI-1 which introduced bulky ipitycenes[21,22], TPE-PIM which used a comonomer with a slightly less rigid structure, leading to decreased permeability and increased selectivity[23], a mixed matrix PIM to decrease physical aging[24], PIM-SBF-1 which used a spirobifluorene unit with even higher rigidity than found in PIM-1, resulting in similar permeability with greater selectivity[25–27] and PIM-PI-1 which combined PIMs with polyimides[28]. Introducing rigid and contorted structures into polyimides is a powerful idea as it broadens the scope of the ‘PIM concept’ to the already established and extremely varied polyimide chemistry. Recently, DPt-TMPD, a rather rigid polyimide with bulky side groups, achieved high CO₂ permeability but with low selectivities.[29] Even more interestingly, a polyimide with a bulky side chain containing *tert*-butyl groups achieved gas separation performance close to the Robeson upper bound for

CO₂/CH₄. [30] It is therefore opportune to investigate new polyimide structures with contorted or bulky structures. Binaphthalene is a contorted substrate that has found use in fields such as liquid crystals [31–33], circularly polarized luminescence [34], catalyst design [35,36], sensors [37–39] and in nanostructuring [40,41]. Binaphthalene polymers have been briefly explored for gas separation. Ritter et al. used 2,2'-diamino-1,1'-binaphthalene to study the microporosity of the resulting polyimides, but failed to obtain high molar masses and did not test for separation properties. [42,43] Mulunda et al. polymerized binaphthalene monomers using a Sonogashira reaction but could not obtain high molar masses required for reliable membrane formation. [44]

In this article, a new set of well-designed rigid and contorted polyimides is proposed that enables the fine tuning of the molecular structure. The polyimide structure is composed of novel bridged binaphthalene diamines and commercially available dianhydrides. Multiple variations of this polyimide structure are synthesized in terms of variation of the dianhydride, the dihedral angle and the enantiomeric excess of the binaphthalene core. It is hypothesized that each of these variations would result in macromolecular changes, such as FVE, influencing the gas separation properties in terms of selectivity and permeability. Therefore, the mixed gas selectivity and permeability of each polymer structure is measured. In addition, WAXS, PALS and a simulation model are used to understand the subtle differences in crystallinity and FVEs between the binaphthalene polyimides and to gain deeper insight in the observed gas separations.

2. MATERIALS AND METHODS

2.1 Materials

All solvents were purchased from Chem-Labs, VWR or Fisher. All reagents were purchased from Acros Organics, AK Scientific, Sigma-Aldrich, Fischer or J&K Scientific. Matrimid® 5218 was provided by Huntsman (Switzerland) and used after drying at 110 °C. Toluene was dried by a solvent purification system MBRAUN SPS 800. Other solvents and reagents were used as received unless specified

otherwise. NMP was dried on calcium hydride, distilled under reduced pressure and stored with 4A molecular sieves. 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), pyromellitic dianhydride (PMDA) and biphenyl-tetracarboxylic acid dianhydride (BPDA) were sublimated to yield white powders. All reactions using moisture-sensitive reagents were done in oven-dried or flame-dried apparatus under nitrogen or argon atmosphere.

The supplementary information provides more information on the monomer and polymer synthesis.

2.2 Characterization methods

^1H - and ^{13}C -NMR were recorded on a Bruker Avance 300 MHz, a Bruker Ascend 400 MHz or a Bruker Avance II 600 MHz spectrometer. Infrared spectra were recorded on a Bruker Alpha FT-IR-spectrometer equipped with a Platinum ATR single reflection diamond ATR module. A 2 cm^{-1} resolution was used. Gel permeation chromatography (GPC) measurements were carried out on a Shimadzu 10A GPC system. The column was a PLgel 5 μm mixed-D type column which is kept at 35°C . A mixture of DMF/THF (9/1) with 0.05M LiBr, was used at 0.9 ml/min. The detection system consisted of a differential refractometer and a UV-vis spectrophotometer. The GPC system was calibrated toward polystyrene standards purchased from Polymer Laboratories. The polymer samples were dissolved in the same solvent mixture as used for the GPC with a concentration of about 1 mg/ml. Once dissolved, the samples were filtered over a PTFE filter with a pore size of 0.2 μm . CD measurements were performed on a JASCO J-810 circular dichroism spectrometer with quartz cuvettes in chloroform. Optical rotations of the molecules were measured on a Analis Optical Activity Polaar 20 apparatus. The X-ray diffraction patterns were collected in transmission mode on a STOE Stadi P high-throughput powder diffraction apparatus equipped with a $\text{CuK}\alpha$ X-ray tube ($\lambda = 1.5418\text{ \AA}$) and an image plate detector. The T_g of the polymers was recorded using DSC. The measurements were performed with a TA Instruments Q2000-DSC. DSC samples were prepared by weighing 4-7 mg pieces of membrane in Tzero Aluminium Hermetic pans and calibration was done towards an empty pan. A heating rate of $10^\circ/\text{min}$ was employed up to at least 340°C under

nitrogen flow, after which the sample was cooled to 25 °C at the same rate. The thermal degradation temperature and dryness of the membranes were tested by TGA under nitrogen atmosphere. A TA Instruments TGA-Q500 was used with 5 mg polymer membrane samples which were kept isothermal for 5 min at 50 °C after which they were heated at 10 °C/min up to 700 °C. To determine the weight loss, the weight at 65 °C was taken for all membranes as the starting weight. The membrane cross section microstructure was visualized by using a Jeol JSM-6010LV scanning electron microscope operated at 10 kV. The cross-sections were obtained by freeze-fracturing the samples in liquid nitrogen. All samples were sputter coated with Au/Pd for two times 30 seconds by a Jeol JFC-1300 autofine sputter coater in order to minimize sample charging during imaging. Melting points were measured using a Leitz Wetzlar microscope and transformer. Density measurements were performed on a Sartorius YDK01 density determination kit. The membrane thickness was measured by a Mitutoyo Disk micrometer (369-511-30, $\pm 4 \mu\text{m}$).

2.3 Computational details

The simulation method was performed as previously described.[44] To improve accuracy, 10 polymer samples were calculated instead of 5.

2.4 Membrane formation

Free-standing membranes were prepared by dissolving the binaphthalene polyimides in chloroform in a 2.5 wt/v% concentration. The solution was filtered through a PTFE 0.2 μm filter and poured in a Teflon petridish with a diameter of 4.7 cm. The Teflon petridish was covered by a blocked funnel and put in a nitrogen glove bag. The resulting transparent and flexible film was dried at 150 °C under vacuum for 15 h.

The thickness of the membrane coupons were gauged by a micrometre ($\pm 1 \mu\text{m}$) by measuring four different points on the edge of the coupon and one central point (see supplementary information p35).

2.5 Gas separation measurements

The gas separation measurements were performed using high-throughput gas separation equipment.[45] CO₂/N₂ and CO₂/CH₄ measurements were respectively done within 24 and 48 h after membrane drying. The cell temperature was fixed at 35 °C, feed pressure at 5 bar and the permeate side was kept under vacuum. For reproducibility, at least 2 coupons from multiple membranes were measured. Along with the binaphthalene polyimide membranes, a Matrimid-5218® coupon was measured as well to serve as reference. The selectivity and permeability of CO₂/CH₄ and CO₂/N₂ mixtures was measured from 50/50 mixtures. The permeate gas composition was determined by a compact gas chromatograph (Interscience).

The mixed gas selectivity was determined by the following formula with x_i and y_i the mole fractions of gas i in, respectively, the up and downstream:

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j}$$

The mixed gas permeability of the membrane was calculated by recording the increase in gas pressure in a fixed volume cylinder using following equation:

$$P_i = \frac{273 \times 10^6}{760} \frac{y_i V}{AT \left(\frac{76}{14.7} \right) x_i P_2} \frac{dP}{dt}$$

With V the downstream volume in cm³ and dP/dt is the pressure rate. A refers to the membrane area in cm², T is the cell temperature in Kelvin, and P_2 is the feed pressure in Psi.

2.6 PALS

Positron annihilation lifetime spectroscopy (PALS) measures FVEs in polymers and polymeric membranes. The positron thermalizes rapidly after implantation and can form a positronium (Ps) which is a hydrogen-like bound state with an electron. Two variants exist: para-positronium (p -Ps, spin-singlet state) or ortho-positronium (o -Ps, spin-triplet state). The positron of the o -Ps interacts with an electron

of its surroundings and annihilates into two gamma-quanta. These gamma-quanta have an average lifetime, the so called pick-off lifetime, which is measured and correlated to the FVEs present in the material according to the Tao-Eldrup model[46,47]. This model is based on the assumption that the FVEs are spherical in size and have walls with infinite potential. As such it gives a quantum mechanical description of the correlation of free volume radius and *o*-Ps lifetime:

$$\tau_3 = 1/2 \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right]^{-1} ns$$

with τ_3 the *o*-Ps pick-off lifetime, R the radius of the FVE and ΔR the electron layer thickness surrounding the FVE, which is assumed to be 0.166 nm. The intensity of the *o*-Ps is a product of Ps formation probability and the concentration of FVEs. Therefore, it can give an estimation of the relative changes in abundance of FVEs.

PALS measurements were executed at the pulsed low energy positron beam system (PLEPS), which is operated at the neutron induced positron source Munich (NEPOMUC)[48,49]. Measurements were executed under UHV conditions and at an implantation energy of 2 keV, on dried membrane samples, which were soaked in methanol prior to measurement. This is in contrast to the membranes prepared for all the other measurements. However, the methanol soaking is believed to have had little influence on the observed trend because the PALS results are in line with both the gas separation results and the WAXS spectra. For the PALS spectra, 4 million counts were collected with a count rate of about 10 000 cts/s and a time resolution of about 250 ps. All spectra were evaluated with PALSfit3[50]. The resolution function was determined by measuring p-doped SiC, a sample with known lifetimes. The spectra were deconvoluted into four lifetime components (*p*-Ps, free e^+ and two *o*-Ps) leading to overall fit variances from 1.0 to 1.1.

3. RESULTS AND DISCUSSION

3.1 Monomer Synthesis and Characterization

Five new monomers, **3a**, **3a-rac**, **3b**, **3c** and **3d** (Figure 1) were synthesized (Scheme 1). The pathway of **3a-rac** is not shown as it only differs in its use of (*rac*)-1,1'-bi(2-naphthol) instead of (*S*)-1,1'-bi(2-naphthol) as was done for **3a**, **3b**, **3c** and **3d**.

Figure 1. The bridged binaphthalene diamine monomers.

1a was prepared according to literature procedure.[51] Based on this modus quantitative yields were obtained for **1a**, **1a-rac** and high yields for **1c** and **1d**. No high yields could be isolated for **1b**. Next, using a Buchwald-Hartwig reaction, **2a**, **2a-rac**, **2b**, **2c** and **2d** were prepared with yields varying between 40 and 65%. Since the Buchwald-Hartwig reaction requires heating at 80° in toluene for a prolonged time, we investigated whether thermal racemization of the (*S*)-configured **1a**, **1b**, **1c** and **1d** occurred. Therefore the specific rotation $[\alpha]_{\lambda}^T$ was measured before and after heating **1a**, **1b**, **1c** and **1d** during a prolonged time. The specific rotations indicate that heating during multiple days at 80 °C did not racemize the bridged binaphthalenes (see Table S1). The last step involved a catalytic hydrogenation using Pd/C. Since the hydrogenation would not occur in pure ethyl acetate, a mixture of ethyl acetate/ethanol was employed, producing quantitative yields.

Scheme 1. Synthesis of monomers **3a-d**. (i) respective alkylation reagent $\text{Br}(\text{CH}_2)_{1-4}\text{Br}$, K_2CO_3 , NaI; (ii) benzylamine, Pd_2dba_3 , *rac*-BINAP, NaOt-Bu , toluene, 80 °C; (iii) H_2 , Pd/C, EtOAc/EtOH.

3.2 Monomer Selection

Literature suggested that using bridging units of different lengths in binaphthalenes would induce vastly different dihedral angles varying between 45 and 90°.[52,53] To verify this, circular dichroism (CD) spectra of **1a-d** were recorded and shown in Figure 2.

Figure 2. Circular dichroism spectrum of **1a-d** in CHCl_3 .

It is clear that the CD spectrum of **1a** is different from the spectra of **1b-d**. This suggests that the dihedral angles of **1b-d** are fairly similar, while the dihedral angle of **1a** is different because the difference in extinction coefficient is directly related to the ellipticity (θ), as shown in Equation (1) with concentration (c) and path length (l).

$$\Delta\varepsilon = \frac{\theta}{32982 \times c \times l} \quad (1)$$

The concentration and path length was kept the same so the difference in $\Delta\varepsilon$ between **1a** and **1b-d** is related to a difference in θ . This difference in θ is related to the difference in dihedral angle because θ is dependent on (i) the electric and magnetic transition dipole moments of the naphthalene cores and (ii) the dihedral angle between these transition dipole moments. Since the electric and magnetic dipole transition moments of the naphthalene cores are basically the same for **1a-d** because of their almost identical chemical nature, the different $\Delta\varepsilon$ of **1a** and **1b-d** directly indicate different dihedral angles between the naphthalene cores.

This finding is in accordance with the simulation of bridged binaphthalenes recently reported.[44] This simulation calculated a dihedral angle for a methyl bridged binaphthalene of 49.1° on the one hand and dihedral angles of 61.6, 65.6 and 63.1° for a ethyl, propyl and butyl bridged binaphthalene. For this research a new simulation was done for monomers **3a** and **3c**. This simulation calculated the dihedral angle of **3a** and **3c** when incorporated in a polyimide with 6FDA as comonomer, confirming once more that the most abundant dihedral angles of the methyl and propyl bridged repeating units are indeed different: 51.7° and 65.0° respectively (see supplementary information).

Monomers **3a** and **3c** were selected to investigate the influence of the bridge length on the gas separation properties. **3c** was preferred to **3b** because the latter could not be prepared in high yields. Additionally, **3c** was preferred above **3d** because, first of all, the calculated dihedral angle is slightly

larger, increasing the difference with the dihedral angle of **3a** and, secondly, because the overall yield is higher than **3d**.

3.3 Polymer Synthesis

3.3.1 Polymerization method

The selected binaphthalenes were polymerized with dianhydrides in a two-step chemical imidization polymerization, as shown for polymer **P3a** in Scheme 2.

Scheme 2. The two-step polymerization with chemical imidization: (i) NMP; (ii) NMP, Ac₂O, 1,4-diazabicyclo[2.2.2]octane (DABCO), 70 °C

A low-temperature chemical imidization was selected instead of the more commonly used thermal imidization to minimize the chance of racemization of the enantiomeric pure monomers. The recorded CD spectra of **P3a** (methyl bridge) and **P7c** (propyl bridge) (see supplementary information) confirm that the polymers are still CD active after chemical imidization. However this changed after they were heated to 180 °C for 6 hours, a typical temperature and timescale for thermal imidization.[54–56] Polymer **P3a** was completely racemized, evidenced by the absence of a CD signal, while, somewhat surprisingly, **P7c** did not. The conclusion was drawn that a propyl bridge has a better racemization resistance than a methyl bridge.

3.3.2 Rational monomer design

Figure 3 gives an overview of the seven newly prepared polymers where four series can be recognized which each vary in one specific parameter. First of all, polymers **P1a**, **P2a** and **P3a** were prepared with, respectively, PMDA, BPDA and 6FDA. Among the many commercially available dianhydrides, these dianhydrides were chosen because polyimides made with PMDA and BPDA enable the study of the influence of the dianhydride rigidity. Comparing these polyimides with polyimides made with 6FDA would make it possible to measure the influence of fluor groups, well known to substantially increase CO₂ solubility in polymer membranes.[6]

In **P3a**, **P4a** and **P5a**, decreasing amounts of (*S*)-chiral binaphthalene diamine **3a** is used, varying the enantiomeric excess from 100 to 0 %. This was expected to have an influence on polymer stacking and on how the free volumes are formed and connected to each other, influencing the gas separation properties in a step-wise fashion. While both **P5a** and **P6a** have 0% enantiomeric excess, their difference lies within their racemic origin: **P5a** was prepared with **3a-rac**, while **P6a** was prepared in the same way as **P3a** with an added heating step to racemize it.

The last method presented here to influence the gas separation properties is by varying the dihedral angle of the binaphthalene diamine: **P3a** is methyl bridged, while **P7c** is propyl bridged. Since the polymer structure is stiff and contorted, varying the dihedral angle of the bridged binaphthalene unit would influence the magnitude of contortion, fine tuning the stacking and free volume creation.

Figure 3. The bridged binaphthalene polyimides. Enantiomeric excess is abbreviated to e.e.

3.4 Characterization of polymers and polymer membranes

P1a and **P2a**, containing respectively PMDA and BPDA, were not soluble in chloroform. **P1a** was only soluble in NMP and **P2a** in NMP and DMF. In contrast, **P3a**, containing 6FDA, was soluble in NMP, DMF and chloroform, enabling practical work-up and characterization (see Table S 2). Therefore, all other polymers (**P4a-P6a** and **P7c**) were prepared with 6FDA.

Gel permeation chromatography (GPC) showed relatively high weight-average molar masses ($\bar{M}_w$) between 46 and 100 kg mol⁻¹ (Table 1), enabling the production of freestanding membranes. These molar masses were obtained after fractionation during workup, resulting in low to average polymerization yields.

Table 1. Characterization of membrane polymers. GPC data recorded at 268 nm, 35 °C in THF/DMF (9/1) mixture with 0.05 M LiBr. Decomposition temperature was set at 5% mass loss under nitrogen atmosphere.

	$\bar{M}_n$	$\bar{M}_w$	$\bar{D}$	decomposition
	(kg/mol)	(kg/mol)	(kg/mol)	temperature (°C) ^b
P3a	23	61	2.7	462

P4a	21	53	2.5	462
P5a	21	100	4.8	471
P6a	18	46	2.5	460
P7c	17 ^a	47 ^a	2.8 ^a	431

^aGPC values recorded at 330 nm; ^b 20°C/min heating rate

All further characterizations were done on the prepared membranes. Additionally, from commercially available Matrimid[®], a membrane was prepared in exactly the same way as the binaphthalene polyimide membranes to be able to compare the polymer and gas separation characteristics more accurately between this and other publications. This is essential as different membrane production procedures can have a large impact on the gas separation performance.[28] Of course, while Matrimid[®] is often used in membrane research[8,9,57–61], it is hardly a state-of-the-art material. Many other materials have better gas separation performances, but none of them are so freely commercially available as Matrimid[®].

Membranes of all 6FDA polyimides and Matrimid[®] were cast from filtered chloroform solutions and slowly evaporated in a dry nitrogen atmosphere. The resulting flexible membranes were dried in a vacuum oven at 150 °C for 10 h to remove any remaining solvents, yielding membranes as shown in Figure 4. ¹H-NMR, taken in DMSO-*d*₆, showed that only trace amounts of chloroform were left from the membrane preparation (supplementary information p27-29). TGA confirmed the dryness of the membrane and proved temperature stability (Table 1, Figure S36). DSC showed that all binaphthalene polyimides were amorphous since no signs of melting or crystallization were noticed (supplementary information p33-35). Also, no *T*_g up to 340 °C was detected, which evidences the intended rigid structure. A high *T*_g might also explain why not all traces of solvent can be removed as they are trapped in the glassy structure.

Figure 4. Freestanding membranes of 6FDA polyimides and Matrimid®

FT-IR (Figure S35) of the membranes showed a clear presence of imide absorption bands at 1780 and 1722 cm^{-1} . Additionally, there was an absence of amide signals at 1660 cm^{-1} (C=O stretching) and 1550 cm^{-1} (N-H bending). Furthermore, no isoimide signals at 921-943 cm^{-1} were present.

Cross-sections of the membranes were recorded by SEM, showing dense films (Figure 5). Small holes were visible in some of the cross sections. The origin of these holes is unknown but their influence on gas separation properties is assumed to be negligible since they are only sparingly present.

Figure 5. SEM pictures of membrane cross-sections, showing the dense film structure. Different magnifications were used because the cross-sections varied in thickness.

3.5 Gas separations

CO₂/CH₄ and CO₂/N₂ were selected in a 50/50 ratio to study the properties of the membranes for the removal of CO₂ (Figure 6). From the many gas mixtures available, these two mixtures were chosen because polyimides are well known to achieve high selectivity for these gas mixtures.[6]

All binaphthalene polyimides performed better than Matrimid®: the permeability is 3 to almost 5 times higher for both gas mixtures, the $\alpha_{\text{CO}_2/\text{CH}_4}$ is on par and the $\alpha_{\text{CO}_2/\text{N}_2}$ is increased by at least 66%. There is no difference in permeability between CO₂/CH₄ and CO₂/N₂ mixtures, while the CO₂/CH₄ selectivity is higher than for CO₂/N₂. This is explained by the high CO₂-favorable selectivity, making the permeability almost solely dependent on CO₂ permeability. A higher CO₂/CH₄ than CO₂/N₂ selectivity occurs often, as the kinetic diameter of N₂ (3.64 Å) is smaller than that of CH₄ (3.80 Å).[58,62,63] Other specific interactions such as their difference in gas condensability and molecular interactions with the polymers are negligible here because the chemical nature of the studied binaphthalene polyimides are all nearly identical. The racemic binaphthalene polyimides **P5a** and **P6a** perform better than the other binaphthalene polyimides by having an increased permeability while maintaining similar selectivity. However, taking the standard deviation into account, it is clear that there is little difference between the binaphthalene polyimides.

Figure 6. (Left) Mixed gas permeability measured in barrer [$1 \text{ barrer} = 10^{-10} \frac{\text{cm}^3_{STP} \times \text{cm}}{\text{cm}^2 \times \text{s} \times \text{cmHg}}$], both gas pairs measured at 5 bar, 35 °C, 50/50 mixture. (Right) CO₂/CH₄ and CO₂/N₂ selectivity measured under the same circumstances as the permeability.

A Robeson plot was used to put the gas separation performances in perspective to other published data and to the upper bound. However, the gas separations performed here used mixed gases, which is in contrast to the more commonly used single gas measurements, making direct comparison not straightforward as gas mixtures generally lead to lower selectivities. Even so, assuming no interactions between the gas mixture components, it is possible to extract single gas permeabilities from mixed gas permeabilities using the following equation:

$$P_i = \frac{P_{mixed}}{(1 + 1/\alpha_{mixed}) \times x_i} \text{ (Equation 1)}$$

With P_{mixed} the mixed gas permeability (Figure 6 (a)), α_{mixed} mixed gas selectivity (Figure 6 (b)) and x_i the mole fraction of gas i in the upstream.

The Robeson plots (Figure 7) show data for some well-known PIM derivatives and recently published polyimides with bulky side chains. A table with the corresponding structures and data points can be found in the supporting information. It is clear that the binaphthalene polyimides are all closely grouped together, further visualizing the similarity of their gas separation performances. Secondly, while the binaphthalene polyimides are located more to the lower permeability side of the Robeson plots, they have generally a higher selectivity, following the upper bound. This is more outspoken for CO₂/CH₄ than for CO₂/N₂. Finally, compared to Matrimid®, the binaphthalene polyimides achieve higher permeability with maintained or increased selectivity. However, for both Robeson plots, the binaphthalene polyimides are located well under the upper bounds.

Figure 7. The Robeson plots of CO₂/CH₄ (left) and CO₂/N₂ (right). Data taken from [21,23,25,28–30,64–67] Upper bound data was taken from [10].

The gas separation properties showed that the binaphthalene polyimides have, compared to Matrimid®, a high permeability. Unexpectedly, there was little difference measurable between the different polymers prepared here in gas separation properties, even though their molecular design is different. Wide angle X-ray scattering (WAXS), positron annihilation life spectroscopy (PALS) and a detailed simulation model were used to investigate this further.

3.6 WAXS

WAXS measurements on the membranes show that the binaphthalene polyimide membranes are first of all amorphous, evidenced by the broad peaks (Figure 8). Secondly, all binaphthalene polyimides seem to have similar amorphous halos ranging from 9-12.5°, 13-15° and 20-25°. These halos are extremely similar to the halos reported by Ritter *et al.* [43] for their 6FDA containing polyimides. Using Bragg's law, these halos result respectively in *d*-spacings of 9.8-7.1 Å, 6.8-5.9 Å and 4.4-3.6 Å. Smaller *d*-spacings are thought to be correlated to the chain-to-chain distance of efficiently packed polymer chains while the bigger *d*-spacings are correlated to more loosely packed chains.[68–70] Therefore, according to WAXS,

the polymer chain packing of all the studied binaphthalene polyimides is rather similar or at least too similar to differentiate using WAXS. This similarity is confirmed by PALS, as is explained further.

Figure 8. Normalized WAXS spectra of **P3a**, **P4a**, **P5a**, **P6a** and **P7c** membranes.

3.7 PALS

PALS data were collected on **P6a** and **P7c** membranes because these two polymers are, based on their polymeric structure, the most different from each other: a methyl bridged racemic binaphthalene polyimide (**P6a**) and a propyl bridged enantiomeric pure polyimide (**P7c**). By decomposing the lifetime spectra, two *o*-Ps lifetime signals were found (*o*-Ps Short and *o*-Ps Long) in both membranes. Additionally the short and the long lifetime are similar in both membranes and correspond to FVEs with diameters of respectively, ca. 4 Å and ca. 8 Å (Figure 9). These results point to a bimodal pore size distribution and to a similar macromolecular structure of both membranes.

As for the lifetimes of **P6a** and **P7c**, no large differences between the samples for either the intensities of the short or the long *o*-Ps are observed (Figure 9, right). It is concluded that, based on PALS measurements, the difference in polymeric structure of both membranes is not large enough to induce

significant differences in the size and abundance of their FVEs. This further confirms both the similar gas separation performances and WAXS spectra.

Figure 9. PALS diameter (left) and intensity (right) data collected on **P6a** and **P7c** membranes.

3.6 Simulation of structural and gas separation properties

The gas separation performance of the binaphthalene polyimides proved that the molecular design differences such as the varying enantiomeric excess or the varying dihedral angle were not large enough to effectively fine-tune the gas separation properties. From WAXS and PALS, first evidence was collected that the FVE presence and stacking of polymer chains is similar across the studied binaphthalene polyimides. Detailed simulation of the polymers and their properties related to stacking on the one hand, and gas separation properties on the other hand, can further provide evidence for both the PALS data as for the gas separation performances. The employed simulation model has already been described and proven useful for the simulation of gas behavior in glassy polymers.[71,72]

3.6.1 FVE Simulation

The simulated free volume characteristics of **P3a**, **P4a**, **P5a** and **P7c**, which are directly related to the polymer stacking, are very similar (Table 2) even though their molecular structure had subtle differences. The same trend is noticed in the simulated pore size distribution (Figure 10). These results are in agreement with those obtained via PALS.

Table 2. The simulated free volume characteristics of **P3a**, **P4a**, **P5a** and **P7c**: skeletal density (ρ_s), geometric surface area (SA_{geo}), pore volume (V_{pore}) and fractional free volume (f).

	$\rho_{skel} \text{ (g/cm}^3\text{)}^a$	$SA_{geo} \text{ (m}^2\text{g}^{-1}\text{)}$	$V_{pore} \text{ (cm}^3\text{g}^{-1}\text{)}$	f
P3a	1.49 ± 0.01	130 ± 28	0.163 ± 0.011	0.091 ± 0.004
P4a	1.50 ± 0.00	97 ± 16	0.153 ± 0.007	0.100 ± 0.008
P5a	1.49 ± 0.00	96 ± 23	0.148 ± 0.006	0.093 ± 0.006
P7c	1.47 ± 0.01	134 ± 17	0.166 ± 0.007	0.108 ± 0.006

$$^a \rho_{skel} = m / (V_{tot} - V_{pore})$$

Figure 10. The pore size distribution for **P3a**, **P4a**, **P5a** and **P7c**.

3.6.2 Simulation of gas separation properties

While the experimental data were obtained using mixed gases for both the permeability (P) and α , the simulated gas separation data are obtained by first calculating solubility (S) and diffusivity (D) coefficients for CO_2 , CH_4 and N_2 separately (Table S3). Next, P is calculated as the product of S and D ($P = S \times D$). S is mainly dependent on the gas condensability and the chemical nature of the polymer. No large differences in chemical nature exist between the studied binaphthalene polyimides. As such, the S -values reported in Table S3 are almost identical. Even though the binaphthalene polyimides differ in polymeric structure, their simulated D -values are similar. The underlying reason is that D is a function of

f [73], which are all quite comparable (Table 2). Since S - and D -values are all basically the same for the studied polymers, it should not surprise that their products, P , are indistinguishable, as shown for CO_2 in Figure 11 (left). The ratio of P_{CO_2} to P_{CH_4} and P_{N_2} , giving the simulated ideal selectivities for CO_2/CH_4 and CO_2/N_2 (Figure 11, right), confirm the experimental gas separation results: there is no significant difference between the gas separation performance of the binaphthalene polyimides.

A point of interest is why the simulated permeabilities are lower than the experimentally found ones, taking into consideration that experimentally mixed gases were used. Also the selectivity is in the simulation somewhat higher than experimentally found. This points in the direction that the experimental membrane densities would be lower than the simulated densities, indicating that a denser stacking was employed in the simulation. This hypothesis proved to be true since the experimentally measured densities of the membrane coupons (Table S4) were indeed lower than ρ_s (Table 2). Additionally, the experimentally found higher permeabilities and lower selectivities might also be influenced by relaxation and swelling effects during gas separation experiments.[74] These effects are not taken into account during the simulation, which treats the polymer chains as a fixed framework.

Figure 11. (Left) The simulated CO_2 -permeability data. (Right) The simulated ideal selectivity data.

4. CONCLUSIONS

WAXS spectra indicated comparable stacking behavior for all binaphthalene polyimides and PALS pointed to similar size and abundance of free volume elements in the two binaphthalene polyimides that were expected to have the most different polymeric structures. This evidence, in combination with the nearly identical simulated structural properties of the polymers, suggests that even though the polymer structures at molecular scale are different, their macromolecular structure is not different enough to initiate large differences in free volume element creation or stacking behavior. This resulted in similar gas separation performances, both visible in the experimental setup as the simulation model, indicating that if the chemical nature of binaphthalene polyimides are nearly identical, subtle changes in molecular structure will not influence the gas separation performance of the membranes. The gas separation properties put the membranes under the upper bounds for both CO₂/CH₄ and CO₂/N₂, indicating that these new soluble polyimides are suitable for gas separations, but will not deliver the highest performances.

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ASSOCIATED CONTENT

AUTHOR INFORMATION

Corresponding Author

Guy.koeckelberghs@kuleuven.be

Author Contributions

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DECLARATION OF INTEREST

none