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Green Procedure with Ethanol as Solvent for the Preparation of Thin Films of Polybenzimidazole on Flat and Hollow Fiber Supports: Application to Hydrogen Separation

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This work shows the preparation of thin films, with thickness from 70 nm to 1 μm , of polybenzimidazole (m-PBI) on polyimide P84[®] supports. Ethanolic solutions of m-PBI are used to coat flat and hollow fiber supports of asymmetric P84[®] with PBI in a process where the coating and drying is performed at room temperature. A diluted solution of NaOH in EtOH allows the dissolution of the m-PBI powder, providing the perfect coating solution to build thin films of m-PBI without damaging the polymeric support. It also means a green alternative, avoiding the use toxic solvents, such as dimethylacetamide. The resulting membranes have been tested for the separation of H₂ mixtures at high temperature at different setups to allow checking their reproducibility. With 100 nm thickness the membranes showed their best gas separation performance. For flat membranes at 180 °C and 3 bar feed pressure a H₂ permeance of 48.5 GPU was obtained, with respective H₂/CO₂ and H₂/N₂ selectivities of 33.3 of 55.8. Besides, the hollow fibers under a feed pressure of 6 bar and tested at the same temperature showed near 90 GPU of H₂ with a H₂/CO₂ selectivity of 13.5 in the one-fiber module and over 39 GPU of H₂ with a H₂/CO₂ selectivity of 20.2 in the five-fiber module. Finally, the stability of the membranes has been proved for 22 days at 180 °C.

Introduction

Polybenzimidazoles (PBIs) are heterocyclic polymers where the benzimidazole moiety is the repeating unit in the polymer molecular backbone. They were first synthesized in 1961 by Vogel and Marvel^[1] and the best known fully aromatic PBI is poly[2,2-(*m*-phenylene)-5,5-benzimidazole], also known as meta-PBI (*m*-PBI), which is the only PBI commercially available from companies such as Hoechst Celanese Corp., PBI Performance Products Inc. and Fumatech BWT GmbH.

m-PBI is a polymer with high thermal stability, high glass transition temperature (427 °C), good chemical resistance, impressive compression strength and high intrinsic H₂ selectivity over larger gas molecules, such as CO₂, N₂ or CH₄,^[2] being an extraordinary material for the fabrication of membranes for H₂ separation. Nevertheless, its major drawbacks are its low permeability and high brittleness. Membranes of *m*-PBI have been widely prepared as hollow fibers.^[3-7] This membrane configuration has allowed higher permeance gas flows, overcoming the first disadvantage, although the poor mechanical stability of the fibers hampers their handling. The good chemical resistance of this polymer makes *m*-PBI only soluble in *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidone (NMP) or dimethylsulfoxide (DMSO). Not only these solvents are rather problematic owing to their high toxicity, but also because most of them are corrosive, hindering the deposition of films of *m*-PBI solutions on supports for membrane fabrication without destroying them.

Although DMAc, DMF, NMP or DMSO are the most common solvents used for the dissolution of *m*-PBI, ethanol (EtOH) has also been found to be a suitable solvent when it incorporates low amounts of alkali, such as NaOH or KOH. Already in 1998, Litt et. al.^[8] dissolved commercial *m*-PBI in NaOH/EtOH and used the resulting solution to cast flat membranes for fuel cell applications. However, they did not achieve to test the membranes. More recently, Penchev et. al.^[9] prepared solutions of *m*-PBI from mixtures of EtOH with NaOH and KOH and used them for electrospinning. The use of alkali-EtOH mixtures as solvent i) means a green alternative to the traditional solvents, ii) avoids the support destruction during the membrane preparation and ii) allows working at room temperature during the casting and drying steps, saving energy. EtOH has been proved to be an environmentally

friendly solvent, greener in comparison with others,^[10, 11] and even considered as bio-based solvent.^[12] The addition of small amounts of NaOH to it may make it less green, but it still remains being a much less hazardous solvent than DMAc, DMF, NMP or DMSO.

Here we show the preparation of m-PBI supported membranes for hydrogen separation. The membranes consist in thin films of m-PBI prepared from polymeric casting solutions in NaOH/EtOH mixtures and deposited on asymmetric supports (flat and hollow fibers) of polyamide P84[®] by dip-coating and blade-casting. Both procedures performed at room temperature. These membranes have been applied for the separation of hydrogen at high temperature in interesting industrial gas mixtures such as H₂/CO₂ and H₂/N₂.

Results and discussion

Flat membrane characterization

Self-supported membranes of m-PBI have been prepared from DMAc and EtOH casting solutions and they have been characterized to study similarities and differences between them. Figure 1 shows the SEM images of the cross-section of these membranes. It can be seen that, independently of the solvent used to dissolve the polymer, the membranes possess similar morphology, with the characteristic nodular texture of m-PBI. The differences observed in the membranes cross-sections may be related to the fracturing process during the sample preparation or to the beam/surface angle at SEM measurements.

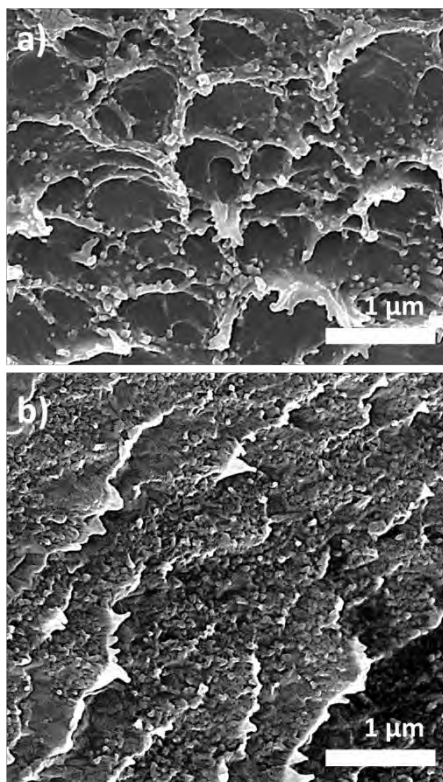


Figure 1. Cross-section of the m-PBI self-supported membranes prepared from casting solutions in DMAc (a) and EtOH (b)

Figure 2a shows the FTIR spectra of the self-supported membranes, where identical patterns indicate the same chemical groups for both membranes. The peak at about 3100 cm^{-1} can be assigned to the self-associated N–H stretching, while that at 1628 cm^{-1} is caused by the C=C and C=N stretching.^[13] The peak at 1277 cm^{-1} corresponds to the imidazole ring breathing mode and that at 793 cm^{-1} is due to the benzimidazole in-plane C–H bending.^[14] Finally, the signal at 1431 cm^{-1} is related to the in-plane ring vibration of 2,6-disubstituted benzimidazole.^[15] As seen in Figure 2b, both self-supported m-PBI membranes also show practically the same thermal stability. The TGA analysis shows an initial weight loss up to $200\text{ }^{\circ}\text{C}$ due to adsorbed water (since m-PBI is a hydrophilic material) and a similar onset temperature for the polymer degradation at around $540\text{ }^{\circ}\text{C}$.

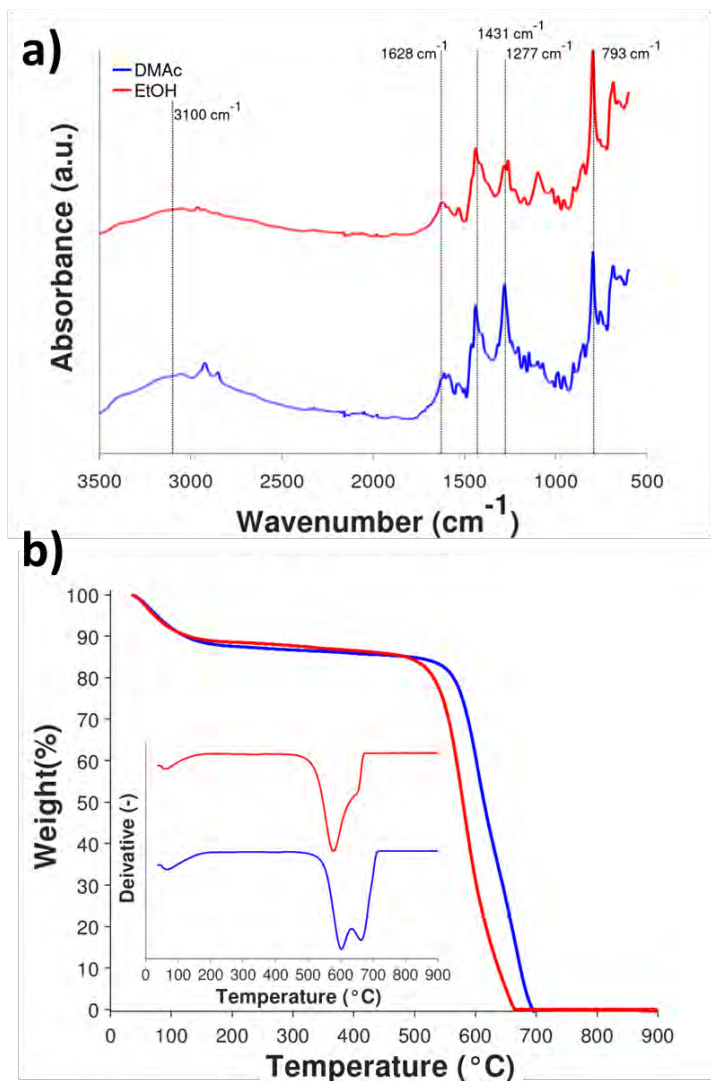


Figure 2. a) FTIR analysis and b) TGA analysis in air and derivative (inset) of the self-supported membranes prepared from solutions of m-PBI in DMAC and EtOH.

m-PBI membranes were also prepared on P84[®] supports coated with PTMSP (poly[1-(trimethylsilyl)-1-propyne]) acting as gutter layer. Doctor blade casting and dip-coating techniques were used for casting films from ethanolic solutions and the cross-section of these membranes can be seen in Figure 3. In all of them the PTMSP gutter layer is 5-7 μm thick. Nevertheless, the thickness of the m-PBI selective layer was different according to the casting procedure. Figure 3a shows that the membrane prepared with doctor blade exhibits a m-PBI thickness of 1 μm (actual measure $1.16 \pm 0.01 \mu\text{m}$). Figures 3b and 3c correspond to the membranes prepared by dip-coating in m-PBI solutions of 1.0 and 0.4 wt%, respectively. This different technique allowed the reduction in the polymer thickness, being of 400 nm (actual measure

395±7 nm) for the highest concentration (Figure 3b) and of 100 nm (actual measure 121±28 nm) for the lowest (Figure 3c). It is worth mentioning that the use of a non-corrosive solvent such as EtOH for the casting solution allowed the successful preparation of m-PBI supported membranes without damaging the polymeric substrate. Moreover, the method involving ethanol as solvent implies important potential energy savings due to the fact that the membrane coating is achieved at room temperature, instead of at 90 °C when working with the typical method with DMAc.^[16, 17] This way, the use of ethanol, a more volatile solvent, reduces the energy requirement for membrane drying.

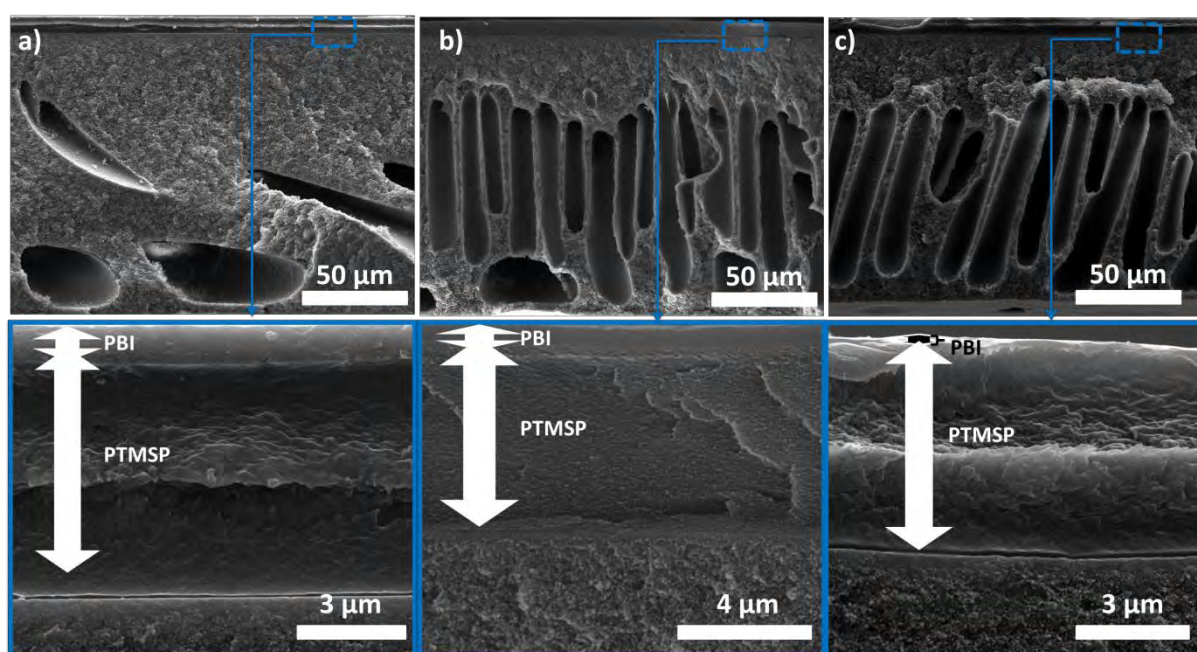


Figure 3. SEM images of the cross-section supported membranes with a m-PBI layer of 1 μm (a), 400 nm (b) and 100 nm (c) prepared with ethanolic m-PBI solutions via doctor blade casting (a) and dip-coating (b, c).

The different layers in the cross-section of these membranes were checked by EDX elemental analysis. Figure 4 shows an example for the supported membrane with 1 μm of m-PBI. The C signal showed maximums at the top layer (m-PBI) and at the bottom layer (P84[®] support). The Si signal showed its highest values in the middle zone, corresponding to the gutter layer of PTMSP.

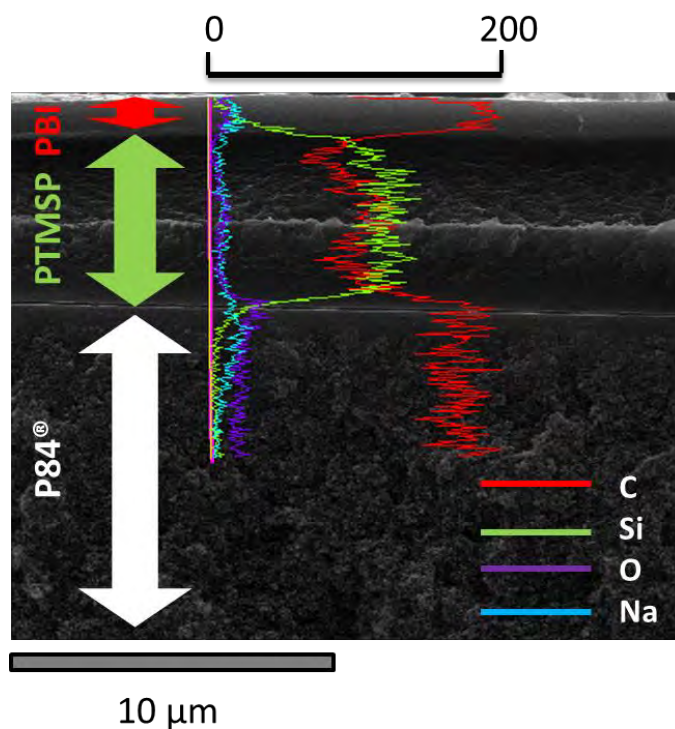


Figure 4. EDX elemental analysis of the m-PBI supported membrane prepared with the doctor Blade (i.e. 1 μm thickness of m-PBI).

Gas separation results with flat membranes

In order to validate the new method developed here to achieve m-PBI membranes, self-supported dense membranes were prepared both with typical DMAc and following the EtOH procedure. The gas separation performance of these self-supported m-PBI membranes was tested for the separation of H_2/CO_2 equimolar mixtures at 150 and 180 $^\circ\text{C}$ and 3 and 6 bar of feed pressure.

Figure 5 shows that the membranes prepared with the DMAc casting solution have slightly superior H_2 permeability and H_2/CO_2 selectivity than those prepared with the ethanolic solution. For example, the membranes prepared with the m-PBI/DMAc solution showed 41.9 ± 1.0 (3 bar feed pressure) and 47.4 ± 2.3 Barrer of H_2 (6 bar feed pressure) at 180 $^\circ\text{C}$, while those prepared with the solution in EtOH had a H_2 permeability of 28.0 ± 0.4 and 32.7 ± 0.6 Barrer at 3 and 6 bar feed pressure, respectively. In terms of selectivity, the m-PBI dissolved in DMAc led to membranes with a H_2/CO_2 selectivity of 6.9 ± 0.5 (3 bar) and 9.9 ± 0.4 (6 bar) at the same temperature. Those prepared in EtOH had a selectivity of 5.8 ± 0.0 and 8.1 ± 0.1 (3 and 6 bar, respectively). The reason for the performance difference according to the solvents used is not obvious. This work, however, intends to create a new methodology with

which demonstrating that it is possible to handle m-PBI for the preparation of membranes with ethanol, a solvent quite different to those traditionally used. There are multiple techniques for improving the gas separation performance of polymeric membranes (crosslinking,^[18,19] blending with other polymers,^[20,21] mixed matrix membranes,^[16, 17, 22-26] etc.) that can be used to enhance that of m-PBI films. They remain as future work once this manuscript has paved the way for handling m-PBI with less hazardous solvents.

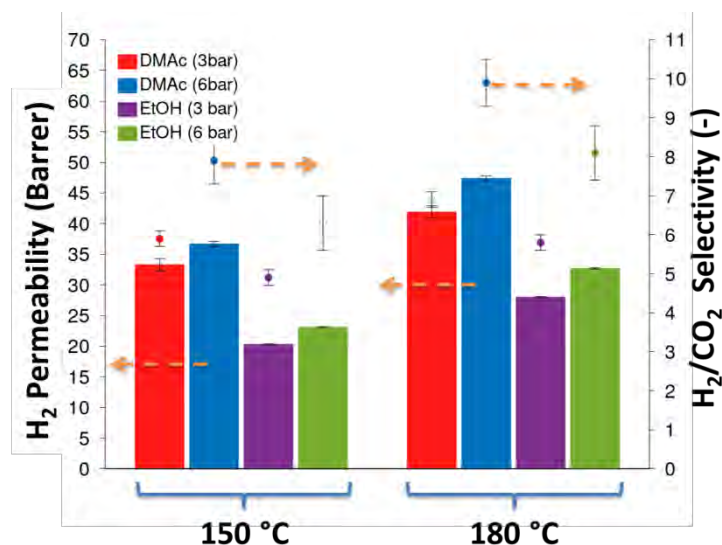


Figure 5. Gas separation performance for the separation of equimolar H₂/CO₂ of the self-supported m-PBI membranes at 150 and 180 °C and feed pressures of 3 and 6 bar. Bars stand for H₂ permeability and scatter circles for the H₂/CO₂ selectivity.

In order to increase the gas permeation flux, supported membranes of m-PBI were prepared on polyimide P84[®] supports coated with a gutter layer of PTMSP. This avoids the penetration of the PBI solution into the support pores. Figure 6a depicts the gas separation performance of these membranes for the H₂/CO₂ mixture at 180 °C. At 3 bar, the thickest supported m-PBI membranes (1 μm) showed a H₂ permeance almost 7-fold higher than the self-supported dense membranes. This increase was even higher when the thickness of the m-PBI film decreased to 400 and 100 nm, rising up to 29.3±2.6 and 40.7±0.3 GPU, respectively. The H₂/CO₂ selectivity also followed the same tendency, rising from 5.8±0.0 (self-supported membranes) to 16.2±0.2, 18.8±9.5 and 26.5±5.2 for 1 μm, 400 nm and 100 nm m-PBI thickness, respectively. At 6 bar feed pressure both permeances and selectivities were slightly superior to those at 3 bar. The values of H₂ permeances and H₂/CO₂ selectivities in Figure 6a have also been fitted by multiple linear regression, providing the mathematical trend shown in

Equation 1 and Equation 2 that describe their dependence with the m-PBI layer thickness and the feed pressure.

$$\text{Log}(P_{H_2}) = 1.62 - 4.39 \cdot 10^{-4} \cdot l \text{ (nm)} + 1.0 \cdot 10^{-2} \cdot P \text{ (bar)}; R^2 > 0.98 \quad (1)$$

$$\text{Log}(\alpha_{H_2/CO_2}) = 1.21 - 1.86 \cdot 10^{-4} \cdot l \text{ (nm)} + 6.2 \cdot 10^{-2} \cdot P \text{ (bar)}; R^2 > 0.90 \quad (2)$$

P84[®] supports coated with PTMSP were also tested at this temperature as reference, providing values of 46.6±1.0 GPU of H₂ with a H₂/CO₂ selectivity of 3.1±0.4 at 3 bar and 49.5 GPU of H₂ with a H₂/CO₂ selectivity of 3.3 at 6 bar. These values allowed the calculation of the thickness of the m-PBI layer considering a model in series. If in a multilayer system the different layers can be treated as analogous to electrical resistors in series and the overall measured permeance of the membrane is given by Equation 3:^[27]

$$\left(\frac{P}{l}\right)_{overall} = \left[\sum_{i=1}^n \left(\frac{P}{L}\right)^{-1}\right]^{-1} \quad (3)$$

where i ranges from 1 to the total number of polymer layers n and P is the gas permeability, L is the layer thickness and P/L the gas permeance. For our case of study, the model would be described by Equation 4:

$$\left(\frac{P}{l}\right)_{overall} = \left[\left(\frac{L}{P}\right)_{P84+PTMSP} + \left(\frac{L}{P}\right)_{m-PBI}\right]^{-1} \quad (4)$$

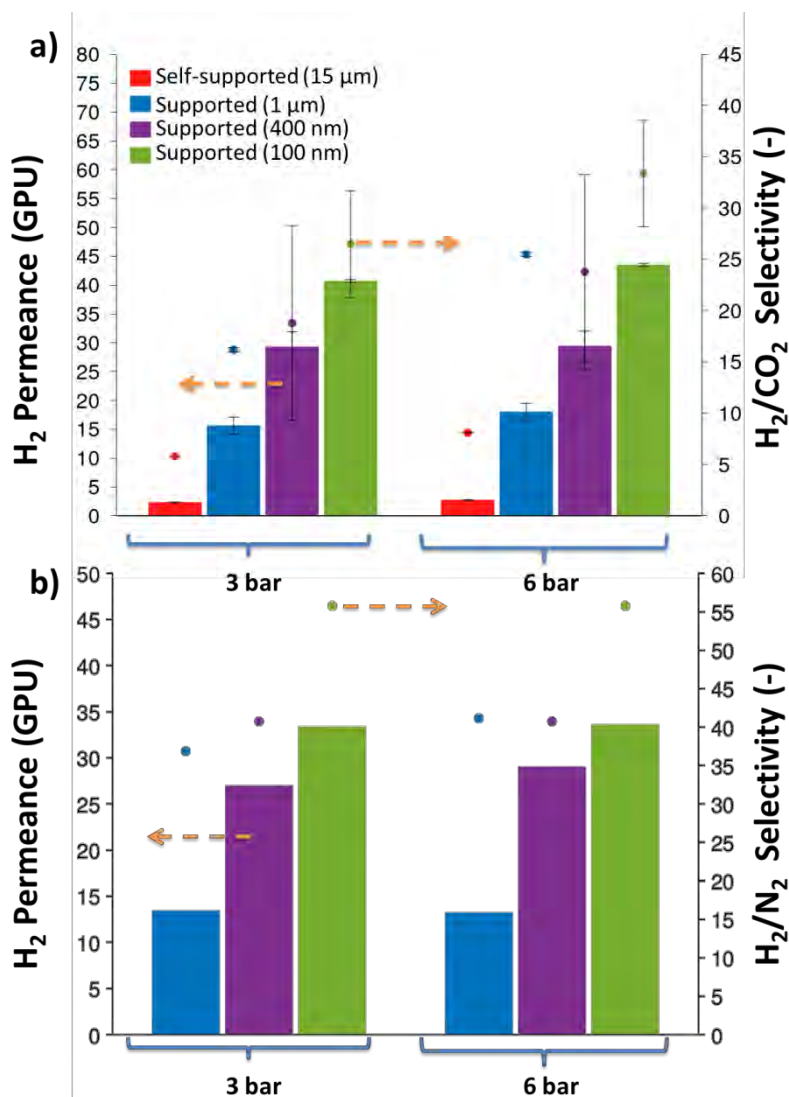


Figure 6. Gas separation performance of the supported m-PBI membranes for H₂/CO₂ (a) and H₂/N₂ (b) equimolar mixtures at 180 °C and 3-6 bar of feed pressure. Bars stand for H₂ permeance and scatter circles for selectivity.

Table 1. Calculation of the thickness of the m-PBI layer from permeation values at 180 °C.

Pressure	Intrinsic m-PBI permeability (P _{m-PBI})	Observed m-PBI layer thickness	P84 [®] +PTMSP H ₂ permeance ((P/L) _{P84+PTMSP})	Overall H ₂ permeance ((P/L) _{overall})	Calculated m-PBI layer thickness (L _{m-PBI})
3	28.0 Barrer	1 μm	46.6 GPU	15.6 GPU	1.19 μm
		400 nm		29.3 GPU	350 nm
		100 nm		40.7 GPU	90 nm
6	32.7 Barrer	1 μm	49.5 GPU	18.0 GPU	1.16 μm
		400 nm		29.4 GPU	450 nm
		100 nm		43.5 GPU	91 nm

Table 1 contains the values regarding the intrinsic permeability of m-PBI (that of the self-supported membranes) and the H_2 permeance of the different supported membranes obtained from Figure 6a. With these values and using the Equation 4, the thickness of the m-PBI layer in the composite was calculated, showing similar values than those obtained by the analysis of SEM images (see Figure 3). This similarity suggests good definition of the selective skin layer thanks to the gutter layer.

The supported m-PBI membranes were also tested for the separation of equimolar H_2/N_2 mixtures at 180 °C (see Figure 6b). This gas separation is typically necessary for the purge gas in ammonia plants. As in the case of the H_2/CO_2 separation, the H_2 permeance increases when the thickness of the m-PBI layer becomes smaller, from almost 13 GPU (thickness of 1 μm) to over 30 GPU (100 nm thick). The H_2/N_2 selectivity followed the same tendency, reaching a value of 55.8 when the m-PBI layer was the thinnest.

The stability of one m-PBI supported membrane (1 μm thick selective layer) was also tested, measuring its H_2/CO_2 gas separation performance during continuous operation at 180 °C for 22 days. It can be seen in Figure 7 that the H_2 permeance remained stable over 14 GPU during all the operation days, while the H_2/CO_2 selectivity mainly oscillated between 17 and 18. The initial augment in selectivity from 16 to near 19 may be related to the conversion of the little remaining NaOH to Na_2CO_3 under the CO_2 flow, since the m-PBI layer was not washed after the membrane preparation.

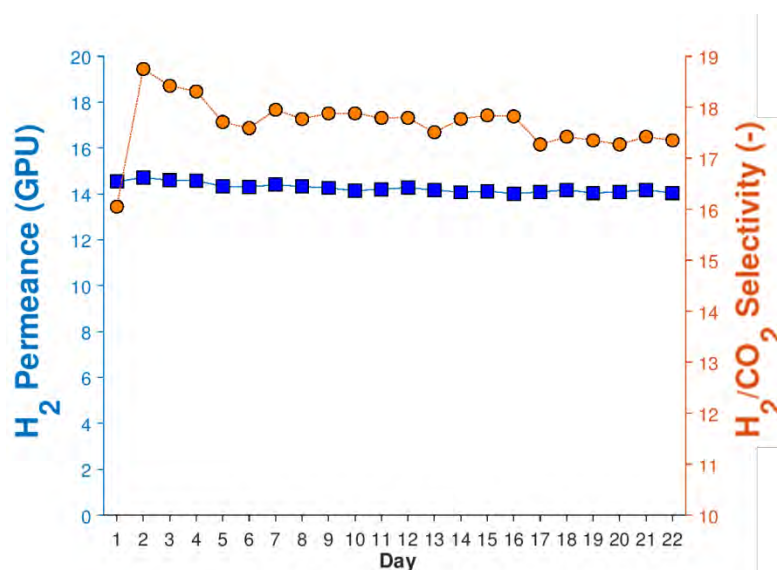


Figure 7. Stability test with a flat m-PBI supported membrane with a 1 μm layer of m-PBI in a gas separation test with a H_2/CO_2 equimolar mixture at 180 °C and 3 bar feed pressure.

m-PBI supported hollow fibers

Figure 8 shows four SEM images of the cross-section of the m-PBI supported membranes in hollow fiber configuration: the first three, a)-c), correspond to different m-PBI film thicknesses, while d) illustrates the application of a PDMS healing coating. All these membranes were prepared on the outer part of the hollow fiber. It can be seen that the P84[®] supports had an outer and inner diameters of ca. 470 and 225 μm , respectively. The gutter layer of PTMSP has a thickness near to 600 nm and the silicon present in the polymer can be distinguished by EDX analysis (blue signal in Figure 8a). The thickness of the outer m-PBI selective layer depended on the concentration of this polymer in the coating solution. When a 2.5 wt% m-PBI solution was used for the dip-coating process, an 800 nm (actual measure 803 ± 20 nm) thick m-PBI layer was generated (see Figure 8a). As Figure 8b shows, using a 0.4 wt% solution to coat the fiber twice resulted in a 130 nm thick layer (actual measure 129 ± 17 nm), while coating the fiber only once produced a 70 nm (actual measure 70 ± 7 nm) selective layer (Figure 8c). Finally, Figure 8d depicts the latter hollow fiber (in Figure 8c) where an outer protective layer of PDMS has been added. It consists therefore in i) P84[®] support, ii) PTMSP gutter layer, iii) m-PBI selective layer and iv) PDMS protective layer. Although this protective layer is so thin that cannot be well distinguished by SEM microscopy, it is certainly present because of the drop in gas permeance that will be explained below, meaning that a new resistance in series has been added to the flux. Besides a more hydrophobic behavior of the membrane surface was noticed when handling it. Since SEM is able to clearly identify layers that are over 50 nm in thickness, it can be deduced that the PDMS layer must be below this limit.

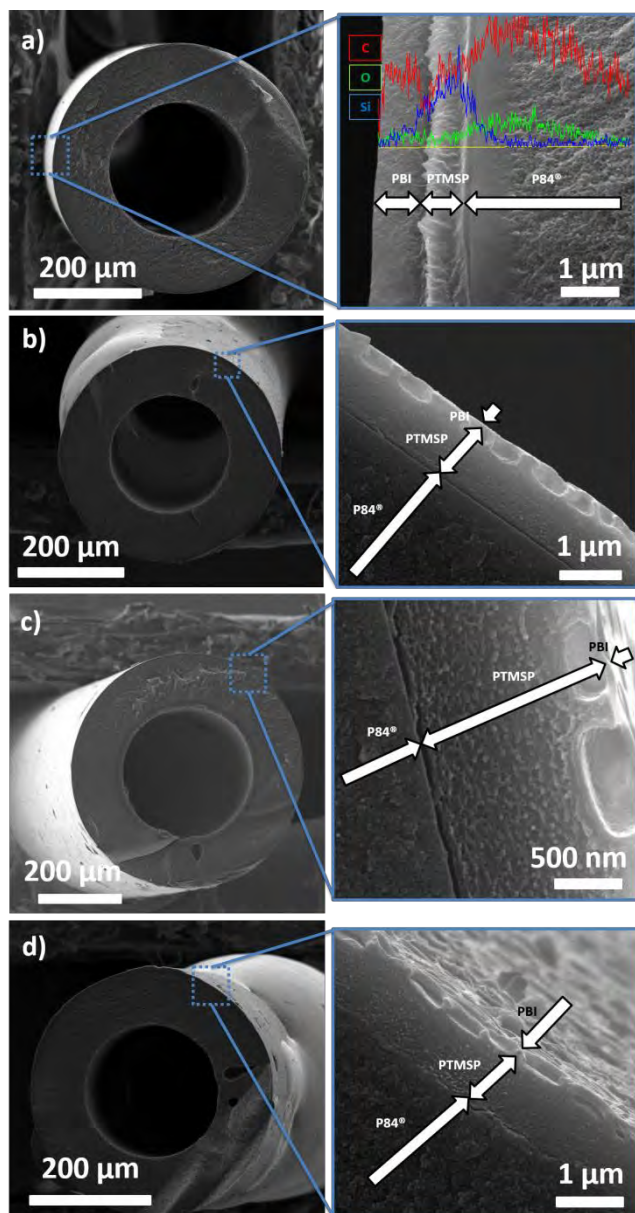


Figure 8. SEM images of the m-PBI supported hollow fibers with different m-PBI selective layer thicknesses: 800 nm (a), 130 nm (b), 70 nm (c) and 70 nm coated with PDMS protective layer (d).

Figure 9 shows the gas separation performance at two different temperatures (150 and 180 °C) of the prepared hollow fibers. The permeate fluxes were so high that no sweep gas was necessary and 6 bar was chosen as feed pressure for the tests, except for the P84® supports, when it was lowered to 3 bar because the flux was too high for the experimental setup. The P84® supports showed a H₂ permeance over 500 GPU at both temperatures with a modest H₂/CO₂ selectivity between 3.0 and 3.5. Adding a m-PBI selective layer decreased the hollow fiber permeances because of the new resistance

added to the composite, but improved the H_2/CO_2 selectivity. At 150 °C, adding a 70 nm selective layer of m-PBI lead to a H_2 permeance of 123 GPU with a H_2/CO_2 selectivity of 10.2. When the thickness of the m-PBI layer doubled (i.e. 130 nm), the H_2 permeance decreased to 51.3 ± 0.7 GPU but the selectivity clearly improved, reaching a value of 15.0 ± 1.0 . This result suggests that with only 70 nm of m-PBI, the selective layer has still some defects that need healing. In consequence, in another set of membranes, a PDMS healing layer was added over the first 70 nm thick m-PBI selective layer. These membranes showed H_2 permeances of 49.1 ± 16.4 GPU and a H_2/CO_2 selectivity of 13.1 ± 0.4 . The raise in the selectivity values proves the necessity of healing in agreement with current publications with conventional m-PBI membranes.^[28] In terms of H_2 permeance, it is equivalent to increase the thickness of the m-PBI layer or adding a PDMS layer onto the first m-PBI selective layer. However, considering the H_2/CO_2 selectivity, the gas separation performance of the membranes becomes better when a second m-PBI layer is added and its total thickness becomes 130 nm, reinforcing the suitability of our ethanolic solution approach.

Although rising the operating temperature does not have special effect on the H_2/CO_2 selectivity, the H_2 permeance of the membranes was clearly enhanced. At 180 °C, the H_2 permeance of the fibers with a 70 nm m-PBI layer raised up to 200 GPU, and that of the membranes with a 130 nm layer of m-PBI or a PDMS healing layer were around 85 GPU.

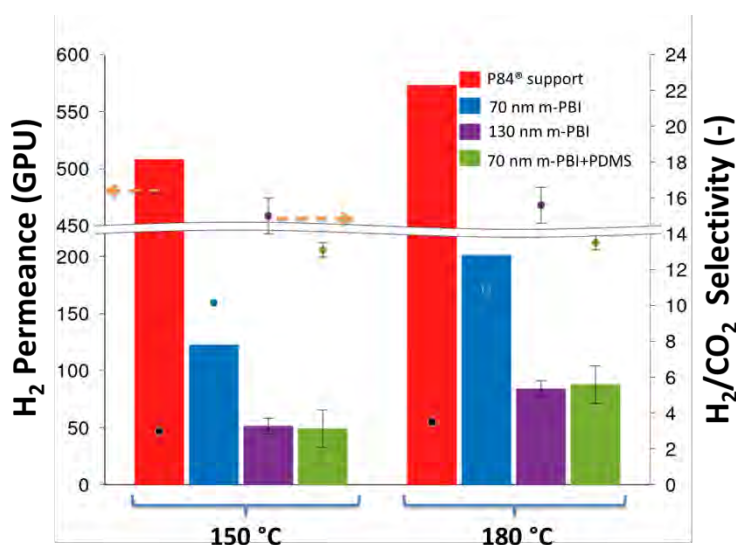


Figure 9. Gas separation performance of the m-PBI supported hollow fibers at 150 and 180 °C. All the measurements were performed under 6 bar feed pressure, except for the polyimide P84® supports that were measured at 3 bar.

Similarly to what was done above for the supported flat membranes, the values of H₂ permeances and H₂/CO₂ selectivities in Figure 9 have been fitted by multiple linear regression, providing the mathematical trend shown in Equation 5 and Equation 6 that describe their dependence with the m-PBI layer thickness and the operating temperature.

$$\text{Log}(P_{H_2}) = 1.92 - 7.7 \cdot 10^{-3} \cdot l \text{ (nm)} + 5.3 \cdot 10^{-3} \cdot T \text{ (}^\circ\text{C)}; R^2 > 0.97 \quad (5)$$

$$\text{Log}(\alpha_{H_2/CO_2}) = 0.28 - 5.9 \cdot 10^{-3} \cdot l \text{ (nm)} + 1.2 \cdot 10^{-3} \cdot T \text{ (}^\circ\text{C)}; R^2 > 0.88 \quad (6)$$

In order to achieve a higher reproducibility in the gas separation results with supported hollow fibers, a new gas separation module was prepared, containing five hollow fibers of the optimum supported membranes (i.e. m-PBI with thickness of 130 nm). This membrane module was tested in Tecnalia's gas separation setup. This way a higher membrane area was used for the tests (in an attempt to set the first step in scaling-up the technology) and experiments at longer times could be collected (up to 31.5 h). Table 2 contains the results of this test. An improvement in the H₂/CO₂ selectivity while the H₂ permeance decreases can be observed when comparing these results with those depicted in Figure 9. Despite these differences, the scale-up of m-PBI supported membranes can be considered partially successful and its complete development remains as future work.

Table 2. Gas separation performance of the five-membrane module with 130 nm m-PBI supported hollow fibers at 150 and 180 °C and 6 bar feed pressure

Membrane	n° fibers	Area cm ²	Testing Temp.	Feed pressure	H ₂ permeance (GPU)	H ₂ /CO ₂ selectivity (-)
130nm m-PBI	5	10.95	150 °C	7 bar	30.4	20.5
			180 °C	7 bar	39.1	20.2

To sum up, a green method to prepare flat and hollow fiber membranes with thin m-PBI coatings has been demonstrated in this work. The procedure is based on the use of environmentally friendly ethanol solutions of m-PBI at room temperature, avoiding typical harmful solvents such as DMAc. The procedure could be easily implemented in current membrane fabrication lines where hollow fibers are coated with polymer on their outer side. Our work did not intend to enhance the gas separation performance of m-PBI, but to set a precedent for a new procedure for the polymer dissolution, the first

step in membrane preparation. Since the polymer used is the same regardless the route selected (m-PBI), its intrinsic separation properties should be similar. Finally, a comparison between the results in our work and those found in the literature following traditional routes for membrane preparation is shown in Table 3.

Table 3. Comparison of the membranes prepared in this work with other currently used m-PBI membranes and methods in H₂/CO₂ gas separation

Year and ref.	Preparation technique for the m-PBI layer	Type of membrane	T (°)	Feed pressure (bar)	H ₂ permeance (GPU)	H ₂ /CO ₂ selectivity (-)
2020 ^[28]	Phase inversion	Hollow fiber	150	7.0	65	17.6
2014 ^[3]	Phase inversion	Hollow fiber	250	-	500	19.0
2012 ^[4]	Phase inversion	Hollow fiber	138-250	1.3-3.4	7.0	47.6-58.0
2012 ^[5]	Phase inversion	Hollow fiber	20	1.0-6.0	26.7-65.1	3.1-4.7
2011 ^[6]	Phase inversion	Hollow fiber	100-400	5.0-8.0	0.3-2.3	7.7-27.3
2010 ^[7]	Phase inversion	Hollow fiber	35	10	29.3-38.7	6.9-11.1
This work	Dip-coating	Hollow fiber	150	6.0-7.0	30.4-51.3	15.0-20.5
This work	Dip-coating	Hollow fiber	180	6.0-7.0	39.1-84.0	15.6-20.2

Conclusions

Thin supported membranes of m-PBI have been prepared in this work for the separation of H₂/CO₂ and H₂/N₂ mixtures at high temperature, where EtOH has been used as green solvent to dissolve the polymer, providing an alternative to the toxic and corrosive traditional DMAc and allowing the membrane processing at room temperature. Self-supported membranes showed similar features and gas separation performance regardless of the solvent used. Blade-casting and dip-coating methods allowed the preparation of supported flat membranes with different m-PBI thicknesses (from 1 μm to 100 nm), without damaging the polymeric support thanks to the use of EtOH as solvent. The thickness of these membranes was also consistent with the permeation results, which improved with increasing feed pressure.

m-PBI supported membranes have also been developed in hollow fiber configuration following the dip-coating technique. Changes in the polymer concentrations of the coating solution allowed the fabrication of membranes with different selective layer thicknesses (from 70 to 800 nm) and the PTMSP gutter layer avoided pore blockage in the P84[®] supports. The minimal m-PBI thickness necessary for a membrane without defects was 130 nm. The hollow fiber configuration allowed superior fluxes than the analogous flat membranes, the latter with demonstrated stability for 22 days at 180 °C. These hollow fibers also set the precedent to fabricate commercial membrane modules

suitable for gas separation in industrial processes. Besides, their reproducibility has been double checked by testing them in two different gas separation setups.

Experimental

Polymer dissolution

Commercial m-PBI was purchased from *Fumatech Bwt GmbH* and two kinds of casting solutions were prepared. Firstly, m-PBI was dissolved in DMAc ($\geq 99.5\%$, Sigma Aldrich) stirring the mixture at $120\text{ }^{\circ}\text{C}$ for 18 h. The resulting solution was centrifuged to remove unsolved particles and had a polymer concentration of 7 wt%. Besides, m-PBI was also dissolved in a basic solution of EtOH (absolute) containing 2 wt% of NaOH ($\geq 98\%$, Scharlau). The mixture was stirred under reflux for 18 h, obtaining a casting solution with 7 wt% of m-PBI that was also centrifuged to remove traces of solid particles.

Flat self-supported membranes

Self-supported membranes are essentially dense thin films prepared from direct solution casting, rather than thin film composite membranes where the support and the selective layer are from the same material formed *via* phase inversion.

Self-supported m-PBI membranes were prepared from the solutions in DMAc (casting at $90\text{ }^{\circ}\text{C}$) and EtOH (casting at room temperature). In both cases, the m-PBI solution was cast onto a glass plate using the Elcometer 4340 Automatic Film Applicator — placed in a fume hood— and evaporated at room temperature for the solution in EtOH and in an oven at $65\text{ }^{\circ}\text{C}$ for the solution in DMAc. Afterwards, the membranes were peeled off and washed with DI water ($90\text{ }^{\circ}\text{C}$, 4 h) and then dried in an oven ($100\text{ }^{\circ}\text{C}$, 24 h). The membranes had an average thickness of around $15\text{ }\mu\text{m}$ (measured with a Digimatic micrometer).

Flat m-PBI supported membranes

For the preparation of thin membranes of m-PBI, films of this polymer were cast at room temperature onto P84[®] flat asymmetric supports. These supports were prepared following the phase inversion method as in our previous works.^[20, 29-31] To avoid the penetration of the polymeric solution into the porous support, a gutter layer of poly(trimethylsilyl)propyne (PTMSP, Gelest) was applied. PTMSP was dissolved firstly at room temperature in n-hexane (extra pure, Scharlau) at 5 wt% concentration.

The polymer solution was cast on the P84[®] support using the Elcometer 4340 Automatic Film Applicator, setting a thickness of 250 μm . Then, the membranes were kept at room temperature for 8 h, and 18 h more in an oven at 100 $^{\circ}\text{C}$, for the complete evaporation of the solvent. The m-PBI solution was then cast on the corresponding support using the same film applicator but with a lower thickness (100 μm). The same drying procedure was applied afterwards and a m-PBI thickness of around 1 μm was achieved.

Supported m-PBI membranes were also prepared following a dip-coating method to reduce the thickness of the m-PBI layer. The original m-PBI solution was diluted with the NaOH/EtOH solution to concentrations of 1.0 and 0.4 wt%. The P84[®] support coated with PTMSP was then immersed in the casting solution and immediately removed. The same drying procedure was followed.

P84[®] hollow fibers

P84[®] (BTDA-TDI/MDI) co-polyimide was supplied by HP Polymer GmbH. The fabrication of P84[®] hollow fiber supports was based on a dry jet followed by wet quench spinning process.^[32, 33] The hollow fiber support preparation procedure has been described in detail elsewhere.^[34] The hollow fiber supports were solvent exchanged in a methanol bath followed by a hexane bath and subsequently dried overnight in a vacuum oven at 100 $^{\circ}\text{C}$ to completely remove residual solvent.

m-PBI supported hollow fibers

m-PBI supported membranes were also developed in hollow fiber configuration using the previously explained P84[®] hollow fibers as supports and following the dip-coating technique. The fibers were firstly coated with a PTMSP solution (3 wt% in n-hexane) to build the intermediate gutter layer. Once dried at room temperature for 8 h, the fibers were immersed at room temperature in a m-PBI solution in NaOH/EtOH with 2.5 or 0.4 wt% concentration and allowed to dry at room temperature overnight. Some of the membranes were also healed with a PDMS protective layer. The coating solution was prepared mixing PDMS polymer base and hardener (SYLGARD[®] 184 kit) with a weight ratio of 10 to 1. The mixture was added to n-hexane to obtain a 2 wt% solution. The fibers were immersed in the coating solution once or twice for a few seconds, and then allowed to evaporate at room temperature for 1 day. The m-PBI supported

membranes were sealed in the permeation module with epoxy resin and heated in an oven at 100 °C for 18 h to remove the remaining traces of solvent.

Membrane characterization

Thermogravimetric analyses (TGA) were carried out using a Mettler Toledo TGA/STDA 851e. Samples (10 mg) placed in 70 μL alumina pans were heated in 40 $\text{cm}^3(\text{STP}) \text{min}^{-1}$ of air flow from 35 to 900 °C at a heating rate of 10 °C min^{-1} . Scanning electron microscopy (SEM) images were obtained using a FEI Inspect F50 model SEM, operated at 20 kV. Cross-sections of the membranes were prepared by freeze-fracturing after immersion in liquid N_2 and subsequently coated with Pd. Fourier transform infrared spectroscopy (FTIR) was performed with a Bruker Vertex 70 FTIR spectrometer equipped with a DTGS detector and a Golden Gate diamond ATR accessory. The spectra were recorded by averaging 40 scans in the 4000-600 cm^{-1} wavenumber range at a resolution of 4 cm^{-1} .

Gas separation analysis

UNIZAR's setup: The flat membranes were placed in a module consisting of two stainless steel pieces and a 316LSS macroporous circular disk support of 2 cm diameter (from Mott Co.) with a 20 μm nominal pore size, and gripped inside with silicon o-rings. The measurements with the m-PBI supported hollow fibers were performed with a different permeation module. It consisted in a tubular stainless-steel container of $\frac{1}{4}$ in diameter, where one fiber of ~ 17 cm active length was inserted and sealed with epoxy resin. The permeation module was placed in a UNE 200 Memmert oven to control the temperature of the experiments. Gas separation measurements were carried out by feeding a H_2/CO_2 and a H_2/N_2 equimolar mixture (25/25 $\text{cm}^3(\text{STP}) \text{min}^{-1}$) at 3-6 bar to the feed side by means of two mass-flow controllers (Alicat Scientific, MC-100CCM-D), while the permeate side of the membrane was swept with a 4.5-10 $\text{cm}^3(\text{STP}) \text{min}^{-1}$ mass-flow controlled stream of Ar at 1 bar (Alicat Scientific, MC-5CCM-D). Sweep gas was only used to test the flat membranes. The hollow fibers were measured without it. Concentrations of H_2 , N_2 and CO_2 in the outgoing streams were analyzed by an Agilent 3000A online gas microchromatograph equipped with a thermal conductivity detector. Permeances were calculated in GPU ($10^{-6} \text{cm}^3(\text{STP}) \text{cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$) once the steady-state of the membrane module exit stream was reached (for at least 3 h), and the separation selectivity was calculated as the ratio of permeances. Permeabilities were also calculated in Barrer ($10^{-10} \text{cm}^3(\text{STP}) \text{cm cm}^{-2} \text{s}^{-1} \text{cmHg}^{-1}$)

¹) for the flat membranes with known thickness. At least 2-3 membrane samples of each type were fabricated and measured to provide the corresponding error estimations.

Tecnalia's setup: In order to achieve a higher reproducibility in the gas separation results, a membrane module containing five fibers was prepared and tested at Tecnalia's facilities. Five fibers of ~17 cm active length was inserted in a tubular stainless-steel container of ¼ in diameter and sealed with epoxy resin. Mixed gas permeation experiments (H₂/CO₂ = 50/50 vol%) were carried out at total feed pressure of 101 psi (7 bar) at 150 and 180 °C. Firstly, the test at 150 °C was performed and the gas permeance was calculated once the steady state was reached in the permeate stream of the membrane (after 4.5 h). The temperature, feed pressure and feed flow were then maintained constant for 19.5 h. Secondly, the operating temperature was risen to 180 °C maintaining these new conditions at 6 bar for 7.5 h. Finally, the gas separation test under 180°C and 6 bar were performed. Feed gas flow and pressure was controlled with a Coriolis mass flowmeters (Bronkhorst). Permeate gas flow was measured using a film flow meter (Horiba). An equimolar H₂/CO₂ gas mixture was fed from the shell side of the fiber and permeate mixture was collected from the lumen side of the fibers in a counter flow configuration. During mixed gas experiments, the stage cut (the ratio between permeate flow rate and feed flow rate) was kept below 1% to avoid concentration polarization phenomena and ensure a constant gas composition at the feed side. This means that maximum permeate flow rate to measure is 100 times lower than the maximum feed flow rate that the permeation system can supply. An online gas chromatograph (Bruker Scion 456-GC) was used to analyze the permeate stream composition over time.

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Conflicts of interests

The authors declare no conflicts of interest.

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Alternative green procedure for the fabrication of supported m-PBI membranes for hydrogen purification. m-PBI is dissolved in ethanol at room temperature aiming membranes with thickness from 70 nm to 1 μm with high separation performance (H_2 permeances up to 90 GPU and H_2/CO_2 selectivity between 13 and 20)

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Green procedure with ethanol as solvent for the preparation of thin films of polybenzimidazole on flat and hollow fiber supports: application to hydrogen separation

