

## Article

## Separation of refrigerant gas mixtures containing R32, R134a and R1234yf through poly(ether-block-amide) membranes

Fernando Pardo, Gabriel Zarca, and Ane Urtiaga

ACS Sustainable Chem. Eng., Just Accepted Manuscript • DOI: 10.1021/acssuschemeng.9b07195 • Publication Date (Web): 24 Jan 2020

Downloaded from pubs.acs.org on January 28, 2020

## Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

1  
2  
3 Separation of refrigerant gas mixtures containing R32, R134a and  
4  
5  
6 R1234yf through poly(ether-block-amide) membranes  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22

23  
24 **Authors:**  
25  
26

27 **Fernando Pardo, Gabriel Zarca\*, Ane Urtiaga**  
28  
29

30 Department of Chemical and Biomolecular Engineering, Universidad de Cantabria,  
31  
32  
33 Av. Los Castros 46, Santander 39005, Spain.  
34  
35

36  
37 \*Corresponding author e-mail address: [zarcag@unican.es](mailto:zarcag@unican.es)  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

**Abstract**

Hydrofluorocarbons (HFCs) are powerful greenhouse gases whose production and consumption must be phased-down in order to reach the reduction goals established by the Kigali Amendment to the Montreal Protocol. However, the share of recycled refrigerant gases remains very low owing to the extremely inefficient separation of refrigerant mixtures by cryogenic distillation. In this sense, the HFCs difluoromethane (R32, GWP = 675) and 1,1,1,2-tetrafluoroethane (R134a, GWP = 1430), together with the hydrofluoroolefin (HFO) 2,3,3,3-tetrafluoropropene (R1234yf, GWP = 4), are among the most common constituents of HFC/HFO refrigerant mixtures currently employed in the refrigeration and air conditioning sector. Therefore, the feasibility of using membrane technology for the selective separation of these compounds is assessed in this work for the first time. A comprehensive study of their gas permeation through several poly(ether-block-amide) (PEBA) membranes that differ on the content and type of backbone segments is performed. Results show that PEBA membranes exhibit superior permeability of R32 (up to 305 barrer) and R134a (up to 230 barrer) coupled with reasonably high selectivity for the gas pairs R32/R1234yf (up to 10) and R134a/R1234yf (up to 8). Moreover, for the blends R32/R1234yf and R32/R134a, the membrane separation performance is not significantly affected under the mixed-gas conditions tested. Thus, results evidence that consideration should be given to membrane technology for the cost-efficient separation of HFCs/HFOs mixtures in order to boost the recycling of these compounds.

**Keywords**

Global warming potential, hydrofluorocarbon, hydrofluoroolefin, membrane separation, refrigerant

## Introduction

Fluorinated gases have been widely used since the early 1930s in aerosols, foams, refrigerants and as solvents due to their outstanding properties, namely, low flammability and toxicity and optimal thermodynamic characteristics. In this context, hydrofluorocarbons (HFCs), the third generation of refrigerants, started to be massively produced and consumed in the refrigeration and air conditioning sector (RAC) as alternative to the ozone depleting substances (ODS), i.e., chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), which were phased-out under the Montreal Protocol.<sup>1-4</sup> Accordingly, the emissions of HFCs to the atmosphere have steadily increased since 1990, 260% in 2017 in Europe,<sup>5</sup> mainly due to fugitive emissions and the lack of recovery protocols from end-of-life equipment. However, HFCs continue to pose severe environmental risks as their global warming potential (GWP) can be up to several orders of magnitude higher than that of CO<sub>2</sub> (GWP = 1), e.g., the GWP of trifluoromethane (R23) is 14800.<sup>6</sup> Therefore, HFCs are among the target greenhouse gases whose emissions must be drastically reduced to mitigate climate change. In this regard, the European Union (EU) promulgated EU regulation No. 517/2014 aimed at scheduling in several periods the phase-down of production and use of HFCs.<sup>7</sup> And more recently, the Kigali Amendment to the Montreal Protocol came into effect in January 2019 aiming at reducing the emissions of HFCs of the signatory parties by 80-85% by 2047.<sup>8</sup>

Although there are not clear alternatives to HFCs that can meet the requirements of both refrigerant and environmental performances for most applications, the commercialization of low GWP refrigerant blends combining HFCs and hydrofluoroolefins (HFOs) is experiencing a rapid development.<sup>9-13</sup> In these mixtures, e.g., R448A, R449A, R450A, R454A, R454C, R455A, R513A, HFCs with low and moderate GWP, namely difluoromethane (R32, GWP = 675) and 1,1,1,2-tetrafluoroethane (R134a, GWP = 1430), are combined with HFOs that exhibit negligible ODP and GWP. In particular, the HFO 2,3,3,3-tetrafluoropropene (R1234yf, GWP = 4) has taken advantage in the market despite being classified as a lower flammability refrigerant (ASHRAE

category A2L).<sup>14,15</sup> Moreover, besides the formulation of new blends, the recovery and reuse of refrigerants is considered a promising approach to increase the refrigerants lifetime while minimizing the amount of new HFCs placed in the market and their release to the atmosphere.

To shift the RAC sector towards a circular economy model, gas separation technologies become a crucial player. Most refrigerants are near-azeotropic blends or exhibit azeotropic behavior, which makes conventional gas separation technologies extremely inefficient for the recovery of the mixture constituents. In this sense, polymer-based membrane separations are growing in importance as a cost-efficient alternative to heat-driven separation processes.<sup>16-19</sup> Indeed, membrane technology has reached a state of maturity for the separation of certain gases of strategic interest such as H<sub>2</sub> separation from ammonia purge gas, syngas ratio adjustment and O<sub>2</sub> enrichment, and can be conceived as a promising candidate for other emerging applications.<sup>20</sup>

However, the available literature is scarce regarding fluorinated gases and only few works report on their gas permeation properties through polymer membranes. In addition, most contributions have focused on the separation of phased-out CFCs and HCFCs from air and the recovery of PFCs, which are valuable gases in the semiconductor industry, using both glassy and rubbery polymers. However, the use of glassy membranes to separate hydrofluorocarbons is not appropriate and results evidence very low permeabilities,<sup>21</sup> except through the exceptionally high free volume PTMSP, which provide very high permeation rates of CFCs and HCFCs at the expense of very low selectivity.<sup>22,23</sup> On the other hand, a predominant solubility controlling behavior is sought using rubbery polymers in which fluorinated gases exhibit enhanced permeability with respect to permanent gases due to their markedly higher condensability. In this sense, Hirayama et al.<sup>24</sup> used crosslinked-membranes of polymetacrylates with poly(ethylene oxide) (PEO) and perfluorononyl moieties to assess the permeation properties of several perfluorinated gases (SF<sub>6</sub>, CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, C<sub>4</sub>F<sub>8</sub>) and CFCs (R11, R12 and R113). The authors highlighted the ability of rubbery PEO segments to provide high permeability towards CFCs ( $P_{R11}$

= 660 and  $P_{R113} = 200$  barrer) and improved gas pair selectivity for the separation of the fluorinated gases from nitrogen ( $\alpha_{R11/N_2} = 194.1$  and  $\alpha_{R113/N_2} = 58.8$ ). Furthermore, Stern et al.<sup>25</sup> studied the effect of pressure on the single gas permeation properties of trifluoromethane (R23) and 1,1-difluoroethylene (R1132a) through rubbery polyethylene membranes and showed that R23 permeability increased remarkably with pressure due its great solubility. Ruan et al.<sup>26</sup> explored the combination of membrane separation using rubbery polydimethylsiloxane (PDMS) with cryogenic distillation for the separation of HFC R23 and HCFC R22.

As evidenced above, there is a research gap of information regarding the gas permeation properties through polymer membranes of the most extensively used commercial refrigerants nowadays (both HFCs and HFOs) and the potential ability of membrane technology to separate them. Thus, this work aims at providing for the first time novel experimental data of the gas permeation properties of three fluorinated gases that are present in most of the HFO/HFC commercial blends that will be employed over the next decades in refrigeration and air conditioning systems: difluoromethane (R32), 1,1,1,2-tetrafluoroethane (R134a) and 2,3,3,3-tetrafluoropropene (R1234yf). Moreover, the permeability of methane ( $CH_4$ ), ethane ( $C_2H_6$ ) and propene ( $C_3H_6$ ), which are the non-fluorinated counterparts of R32, R134a and R1234yf, respectively, are also determined in order to assess the influence of hydrocarbon fluorination on the gas transport properties. In this study, three different commercial grades of poly(ether-block-amide), PEBA, were selected as membrane materials. PEBA is a family of copolymers made of rigid polyamide (PA) segments that provide the mechanical strength to the polymeric film and flexible polyether (PE) blocks, which are the main contributors to the rubbery nature of the polymer and the principal gas transport-controlling phase.<sup>27</sup> The outstanding properties of pure PEBA copolymers and PEBA-based membranes towards the selective separation of condensable gases such as  $CO_2$  and light hydrocarbons from industrial gaseous mixtures have been extensively reported in the literature.<sup>28-36</sup> Moreover, the low-pressure gas solubility and diffusivity are determined for the most selective membrane in order to gain deeper

understanding on the transport behavior of these refrigerant gases. Finally, mixed-gas permeation experiments were performed to assess the membrane separation performance under real conditions.

## Experimental

### Materials

Butan-1-ol (99.9%) from VWR, isopropanol (99.6%) and ethanol (99.9%) from Oppac Química S.A., and ultra-pure grade water (18.2 MΩ cm, Millipore) were used as solvents for PEBA membrane preparation by solvent casting method. Pebax® grades 1074, 1657 and 2533 in pellets were kindly provided by Arkema. R134a (99.8%) and R1234yf (99.9%) were supplied by Carbueros Metálicos (Air Products group) and R32 (99.9%) was supplied by Coproven Climatización (Gas Servei licensed supplier). The physical properties of these fluorinated gases along with those of the analogous hydrocarbons are shown in Table 1. All physical properties, except the dipole moments, were obtained from CoolProp database.

**Table 1. Physical properties of the gases studied in this work.**

Property	R32	R134a	R1234yf	Methane	Ethane	Propene
Molecular formula	CH <sub>2</sub> F <sub>2</sub>	C <sub>2</sub> H <sub>2</sub> F <sub>4</sub>	C <sub>3</sub> H <sub>2</sub> F <sub>4</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>
MW (g mol <sup>-1</sup> )	52.02	102.03	114.04	16.04	30.07	42.08
V <sub>c</sub> (cm <sup>3</sup> mol <sup>-1</sup> )	122.4	200.2	238.6	98.96	146.87	182.93
Normal boiling point (K)	221.5	247.1	243.6	111.65	184.53	225.59
T <sub>c</sub> (K)	351.3	374.2	367.9	190.56	305.41	364.96
P <sub>c</sub> (bar)	57.8	40.6	33.8	46.07	48.80	45.92
Acentric factor	0.277	0.327	0.275	0.011	0.099	0.143
Dipole moment (D) <sup>37</sup>	1.978	2.058	2.240	0	0	0.363
Chung diameter (Å) <sup>38</sup>	4.02	4.73	5.02	3.74	4.27	4.59
GWP 100 years	675	1430	4	25	6	2

Table 2 shows the general chemical structure of Pebax® films and the corresponding properties of each grade used in this work. One of the most significant properties that has a direct

connection with the permeability coefficients of gases through polymers is the so-called fractional free volume (FFV) of the polymer. The FFV can be defined, according to Eq. (1), as the ratio of the free volume to the observed specific volume:

$$FFV = \frac{V_m - V_0}{V} \tag{1}$$

where  $V_m$  is the specific volume of the polymer and  $V_0$  is the specific volume of the polymer at 0 K. An estimate of  $V_0$  was proposed by Bondi et al.<sup>39</sup>, who suggested calculation of the van der Waals volume ( $V_W$ ) occupied by the repeat units of polymers and postulated that:

$$V_0 = 1.3 \cdot V_W \tag{2}$$

In this work, the  $V_W$  of Pebax® polymers were calculated using a group contribution approach,<sup>36,40,41</sup> based on the methodology described by Van Krevelen.<sup>42</sup> The results are shown in Table 2 and compared with available FFV data determined from Positron Annihilation Lifetime Spectroscopy (PALS) experiments,<sup>43</sup> a powerful tool which provides relevant information of the distribution of micro vacancies inside the polymer microstructure.<sup>44,45</sup>

**Table 2. Physical properties of the Pebax® copolymers used in this work.**

Property	Pebax® 1074 SP01	Pebax® 1657 MH	Pebax® 2533 SA01
Chemical structure			
T <sub>g</sub> (°C)	-55 (PEO = -67, PA12 = 40) <sup>a</sup>	-53 (PEO = -67, PA6 = 47) <sup>a</sup>	-77 (PTMO = -86, PA12 = 40) <sup>a</sup>
Block ratio:			
wt%	55% PEO – 45% PA12	60% PEO – 40% PA6	80% PTMO – 20% PA12
mol%	85% PEO – 15% PA12	79% PEO – 21% PA6	92% PEO – 8% PA12
Density (g cm <sup>-3</sup> ) <sup>b</sup>	1.07	1.14	1.00
Melting point (°C) <sup>b</sup>	158 (PEO = 65; PA12 = 180) <sup>a</sup>	204 (PEO = 65, PA6 = 215) <sup>a</sup>	134 (PTMO = 23-28, PA12 = 180) <sup>a</sup>
Fractional free volume:			
Experimental	-	0.125 <sup>43</sup>	-
Estimated	0.153	0.143	0.170 (0.172) <sup>41</sup>

<sup>a</sup> Data of polymer segments.

<sup>b</sup> Technical data provided by the supplier.

*Membrane preparation*



The experimental conditions applied to prepare the polymeric films are summarized in Table S1 as Supporting Information. Around 5 wt% polymer solutions were prepared under magnetic stirring and heating. Afterwards, the polymer solution was poured in a glass Petri dish and solvent evaporation was performed in a vacuum oven under controlled pressure and temperature conditions. The thickness of each membrane was measured with a Mitutoyo digital micrometer MDC-25PX (accuracy  $\pm 1 \mu\text{m}$ ), being the average thickness of all prepared membranes  $80 \pm 5 \mu\text{m}$ . The thermal properties of the films were determined by Differential Scanning Calorimetry (DSC Q100, TA Instruments). Samples of 10-15 mg were encapsulated in hermetic aluminum pans and subjected to a heating/cooling/heating cycle in the range from -80 to 220  $^{\circ}\text{C}$  at a rate of 15  $^{\circ}\text{C min}^{-1}$ . The thermograms, shown in Figure S1 of the Supporting Information, show that the experimental glass transition temperature and melting temperature are in very good agreement with available data (see Table 2). In addition, the surface morphology and cross-section of the PEBA membranes were observed by scanning electron microscopy (SEM, Carl Zeiss EVO MA 15). The samples were prepared by immersing and fracturing the membranes in liquid nitrogen, followed by gold thin film deposition using a sputter coater (Balzers Union SCD040). The SEM images, provided in Figure S2 as Supporting Information, reveal that all membranes were dense homogenous polymeric films without evidence of porosity or formation of differentiated layers.

#### *Gas permeability measurements*

In this work, the permeability of each gas was determined using an experimental setup designed for continuous operation in which the membrane, in flat form, was placed inside a custom-made stainless steel permeation cell. During each permeation experiment, the steady state gas concentration in the permeate side (swept by an Ar stream at 4  $\text{cm}^3_{\text{STP min}^{-1}}$  and 1 bar) was measured by gas chromatography (Agilent 490 micro GC). A channel equipped with a Pora Plot U column and a thermal conductivity detector permitted detection and quantification of all the

fluorinated and hydrocarbon gases studied in this work. Further details regarding the experimental setup and measuring procedure can be found in references.<sup>46-48</sup> In this work, all experiments were performed at 30 °C with pure gases at several feed pressures in the range 1.3–5 bar and mixed gases at 1.3 bar. In addition, mixed gas experiments were performed with R32/R1234yf and R32/R134a mixtures by ranging inlet concentration of each gas between 25 - 75% using individual mass flow controllers (Brooks 5850S, 0-100 cm<sup>3</sup><sub>STP</sub> min<sup>-1</sup>).

Permeability through the membranes was calculated according to Eq. (3):

$$P_i = \frac{Q_i \cdot \delta}{A \cdot (f_{R,i} - f_{P,i})} \quad (3)$$

where  $P_i$  is the permeability of gas  $i$  through the membrane,  $Q_i$  the transmembrane flux of component  $i$ , calculated as the experimental concentration of each gas in the permeate multiplied by the sweep gas flowrate,  $\delta$  is the membrane thickness,  $A$  the membrane area,  $f_{R,i}$  and  $f_{P,i}$  the fugacity of gas  $i$  in the retentate and permeate, respectively.

The fugacity was calculated using Eq. (4):

$$f_i = \phi_i \cdot p_i \quad (4)$$

where  $\phi_i$  and  $p_i$  represent the fugacity coefficient and the partial pressure of component  $i$ , respectively. The Peng-Robinson equation of state (PR-EoS)<sup>49</sup> was used to determine the fugacity coefficients as it has demonstrated to estimate accurately the fugacity of fluorinated gases in the vapor phase.<sup>50</sup>

#### *Low-pressure gas sorption measurements*

According to the solution-diffusion model represented by Eq. (5), the permeability of a gas ( $P$ ) can be described by the product of a diffusion coefficient ( $D$ ) and a solubility coefficient ( $S$ ).

$$P = S \cdot D \quad (5)$$

In this work, the gas solubility coefficients of the fluorinated gases in Pebax® 1657 polymeric films were measured by the pressure decay method<sup>51</sup> with a dual volume sorption cell (gas

reservoir and sorption chamber). Gas sorption measurements were performed at constant temperature and pressure decay was monitored with Gometrics (0-35 bar) and Ruska 7230 (0-35 bar) pressure sensors. A thorough description of the experimental protocol is reported by Tlenkopatchev et al.<sup>52</sup> and Garrido et al.<sup>53</sup>

Gas concentration within the polymer matrix,  $C$ , was calculated according to Eq. (6) as the difference between the gas molecules initially introduced in the sorption chamber and the gas molecules which were not adsorbed after reaching equilibrium conditions:

$$C = \frac{22414 \cdot \rho \cdot V}{R \cdot T \cdot m} \cdot \left( \frac{p_i}{z_i} - \frac{p_e}{z_e} \right) \quad (6)$$

Accordingly,  $m$  and  $\rho$  are the mass and density of the polymer introduced into the sorption chamber, respectively,  $V$  is the unoccupied volume of the sorption chamber,  $R$  and  $T$  are the gas constant and absolute temperature,  $p$  and  $z$  are pressure and compressibility factor of the gas and  $i$  and  $e$  subscripts account for initial and equilibrium conditions, respectively.

At sufficiently low pressures, the Henry's law accurately describes gas solubility in rubbery polymers:

$$C_i = k_{D_i} \cdot f_i \quad (7)$$

where  $k_D$  is the Henry's law solubility coefficient. Eventually, considering that  $S = k_D$  in the low-pressure range assessed, gas diffusivity can be calculated from the experimental permeability and solubility data from Eq. (5).

## Results and discussion

### *Pure gas permeation properties in Pebax®*

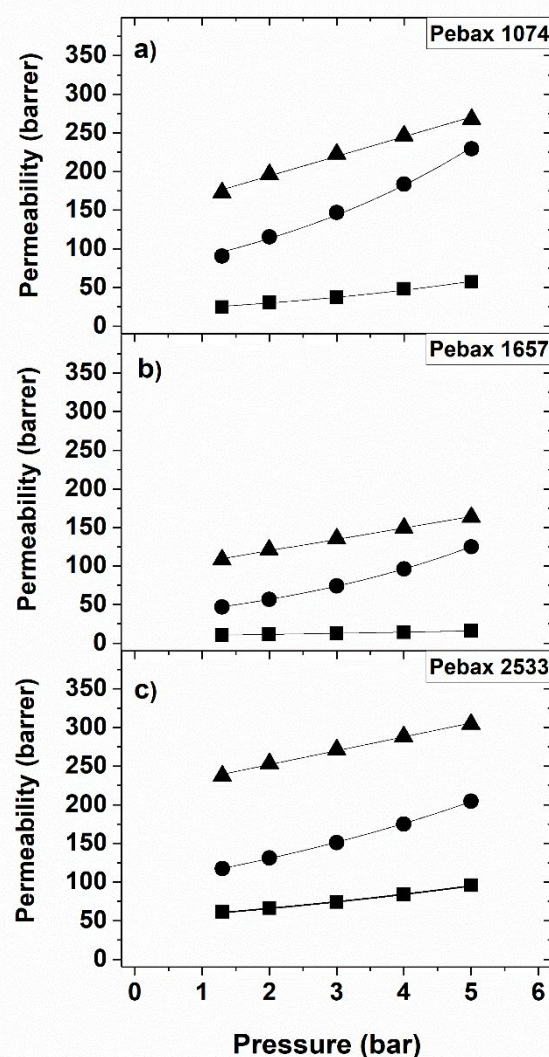
The permeability coefficients of R32, R134a and R1234yf were obtained for the first time through Pebax® membranes (grades 1074, 1657 and 2533). The results are shown in Figure 1 as a function of the partial pressure gradient applied across the membrane. Besides, these results are summarized in Table S2 of the Supporting Information. In addition, the permeability of

nitrogen and hydrofluorocarbon selectivity towards nitrogen are also reported in Table S3 as Supporting Information.

The effect of pressure on the gas permeability behavior through rubbery polymers may comprise different phenomena. Although low-sorbing gases usually exhibit little or no change in permeability, highly soluble penetrants plasticize the polymer with increasing pressure, causing an increase in the chain spacing and mobility, and therefore, enhancing gas diffusivity and permeability. In addition, if solubility increases at high penetrant activity, permeability can markedly increase with increasing pressure. On the other hand, an increase in the upstream pressure may lead to a more compact membrane with reduced fractional free volume and gas diffusivity.<sup>54,55</sup> According to the trends observed in Figure 1, the permeability of each penetrant tested (R32, R134a and R1234yf) is enhanced with increasing feed pressure as a result of an increase in the gas concentration within the polymer chains of the rubbery Pebax® membranes. This pressure effect is particularly significant in the case of R134a, which can be related to its higher solubility as discussed in the following sections. In this sense, the observed permeability behavior is analogue to that of CO<sub>2</sub> and light hydrocarbons such as propane, propene and butane in Pebax® membranes. For instance, Stern et al.<sup>25</sup> observed a mild exponential trend in the permeability of vinyl fluoride through polyethylene membranes and Chen et al.<sup>56</sup> reported a similar effect in the permeation of propene through Pebax® 2533 membranes. Therefore, the observed influence of pressure on the permeability of the fluorinated hydrocarbons suggests strong polymer-penetrant interactions. In fact, the high dipole moment and condensability of the fluorinated gases are two important characteristics that can explain their behavior as strong plasticizers of the PEBA copolymers, which contain polar ether linkages (C-O-C) in the polyether backbone.<sup>30, 34,57</sup>

The fluorinated gases exhibit moderate to high permeability coefficients through the Pebax® membranes. Particularly, R32 is the most permeable fluorinated gas, whose permeability is comparable to that reported by Bernardo et al.<sup>29</sup> for CO<sub>2</sub>, also a condensable gas that exhibits

quadrupolar moment. Moreover, the permeability of the fluorinated hydrocarbons follows the same order in all Pebax<sup>®</sup> grades tested, R32 > R134a > R1234yf, which follows the penetrant activity trend as discussed in detail in the following sections. Regarding the performance of each Pebax<sup>®</sup> grade, the order of permeability is Pebax<sup>®</sup> 2533 > Pebax<sup>®</sup> 1074 > Pebax<sup>®</sup> 1657, which in turn is consistent with the *FFV* of the polymers, i.e.,  $FFV_{\text{Pebax}^{\text{®}}2533}$  (0.169) >  $FFV_{\text{Pebax}^{\text{®}}1074}$  (0.154) >  $FFV_{\text{Pebax}^{\text{®}}1657}$  (0.143), and the content of polyether soft segment (see Table 2). Another feature related to Pebax<sup>®</sup> copolymers is that not only the amount of polyether and polyamide blocks plays an important role in gas permeation, but also the nature of these blocks has an impact on gas permeability. Pebax<sup>®</sup> 1074 and Pebax<sup>®</sup> 1657 have similar composition of rigid polyamide and soft polyether blocks, but they have different types of polyamide segments: PA6 in Pebax<sup>®</sup> 1657 is more polar than PA12 in Pebax<sup>®</sup> 1074, which results in higher cohesive energy density, and hence lower gas diffusion and permeability coefficients through Pebax 1657.<sup>30</sup>



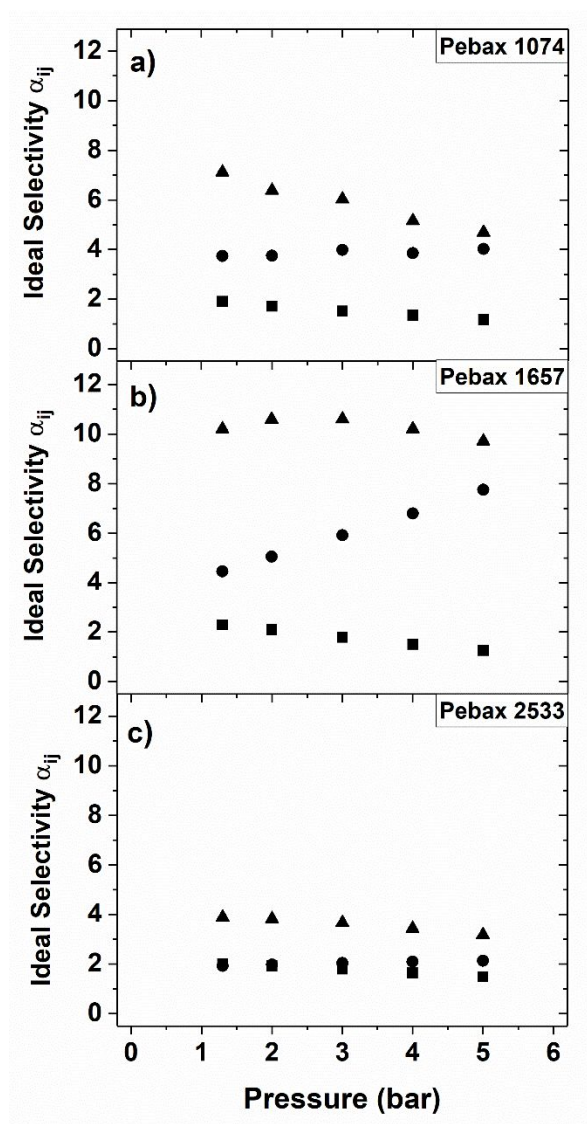
**Figure 1. Permeability of common fluorinated refrigerants R32 (▲), R134a (●) and R1234yf (■) through (a) Pebax® 1074, (b) Pebax® 1657 and (c) Pebax® 2533 at several feed pressures and 30 °C.**

Regarding the membrane separation performance, the ideal gas pair selectivity of fluorinated gases in each Pebax® grade is plotted in Figure 2 and collected in Table S4 as Supporting Information. In all cases, selectivity follows the order  $R32/R1234yf > R134a/R1234yf > R32/R134a$ . Besides, for every gas pair assessed, the different polymer grades present the following selectivity order:  $Pebax® 1657 > Pebax® 1074 > Pebax® 2533$ , which is the opposite trend followed by the *FFV* of these copolymers. These results are consistent with the literature and demonstrate that the polymer composition has a critical influence on the separation performance of Pebax® membranes. In this sense, Pebax® 1657 polymer, which has the highest

1  
2  
3 molar ratio of rigid backbone elements (21 mol% PA6) and the lowest *FFV* (0.143), exhibits the  
4  
5 lowest permeability but the highest gas pair selectivity. These results suggest that, in contrast  
6  
7 to cryogenic distillation, membrane technology can be efficiently employed to separate  
8  
9 azeotropic refrigerant mixtures into their main constituents. This is especially remarkable for  
10  
11 HFC/HFO blends such as R32/R1234yf and R134a/R1234yf.  
12  
13

14 With regards to the influence of pressure on the selectivity, two different trends have been  
15  
16 noticed. For the gas pairs R32/R1234yf and R32/R134a, selectivity slightly decreases with  
17  
18 pressure. This effect, linked to plasticization effects that occur when highly soluble gases  
19  
20 permeate through a rubbery polymer, has already been reported in the literature for gases such  
21  
22 as CO<sub>2</sub>, propane and propene, among others. In other words, the diffusion coefficients increase  
23  
24 and the diffusivity selectivity decreases as the upstream pressure, and therefore, the  
25  
26 concentration of gas inside the polymeric matrix, increases.<sup>58</sup> Conversely, for the gas pair  
27  
28 R134a/R1234yf, the separation slightly improves as pressure increases. Interestingly, this effect  
29  
30 is analogue to that previously observed in the separation of highly soluble gases, like  
31  
32 quadrupolar CO<sub>2</sub>, from nonpolar gases (N<sub>2</sub> and H<sub>2</sub>) through Pebax® membranes.<sup>30,56</sup> Therefore,  
33  
34 these results suggest that for the gas pair R134a/R1234yf the solubility selectivity offsets the  
35  
36 decrease in diffusivity selectivity on increasing the upstream pressure.  
37  
38  
39

40 Finally, regarding the long term membrane stability under the operating conditions, it is worth  
41  
42 mentioning that the membranes were tested over several weeks with various gases and  
43  
44 pressures up to 5 bar without any noticeable loss of performance. This was also confirmed by  
45  
46 periodically measuring N<sub>2</sub> permeability (see Table S3), which was used as reference gas.  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



**Figure 2.** Selectivity of the gas pairs R32/R1234yf (▲), R134a/R1234yf (●) and R32/R134a (■) in (a) Pebax® 1074, (b) Pebax® 1657 and (c) Pebax® 2533 at several feed pressures and 30 °C.

#### *Effect of fluorine substitution*

To gain a deeper understanding of the transport behavior of the fluorinated refrigerant gases through the Pebax® polymers, a comparison is performed in Figure 3 between the permeability of the fluorinated gases (R32, R134a and R1234yf) and their non-fluorinated hydrocarbon analogues (methane, ethane and propene, respectively) in all Pebax® grades (1074, 1657 and 2533). In this regard, the results reveal that, regardless of the Pebax® grade, the permeability coefficients of R32 and R134a are higher than that of methane and ethane, respectively,



whereas the permeability of R1234yf is lower than that of propene. These trends can be ascribed to the differences between fluorinated hydrocarbons and their non-fluorinated analogues. On one hand, the fluorinated gases exhibit much higher electric dipolar moment than the hydrocarbons what leads to higher polymer-penetrant interactions (see Table 1). In addition, the condensability of the fluorinated gases, frequently expressed in terms of the critical temperature or normal boiling point,<sup>34,59</sup> is also greater than that of their non-fluorinated hydrocarbon analogues, except for propene and R1234yf. Therefore, for the case of propene and R1234yf, which exhibit similar critical temperature (see Table 1), the higher permeability of propene can be ascribed to its smaller molecular size, as evidenced by the calculated Chung diameters.<sup>38</sup>

In addition, Figure 4 presents the effect of penetrant size in the permeability of fluorinated hydrocarbons and their non-fluorinated counterparts. Usually, there is a strong relationship between transport properties in both glassy and rubbery polymers and penetrant size or critical volume.<sup>59</sup> Very interestingly, while the permeability of hydrocarbons increases with the number of carbon atoms ( $P_{C_3H_6} > P_{C_2H_6} > P_{CH_4}$ ), the opposite trend is found for the fluorinated hydrocarbons ( $P_{R32} > P_{R134a} > P_{R1234yf}$ ). However, this is not surprising as analogous permeability trends have been reported for perfluorocarbons ( $CF_4$ ,  $C_2F_6$  and  $C_3F_8$ ) and their hydrocarbon counterparts ( $CH_4$ ,  $C_2H_6$  and  $C_3H_8$ ) in high free volume glassy PTMSP.<sup>22,60</sup> This behavior can be ascribed to both solubility and mobility effects in the polymer matrix as discussed in the next section.

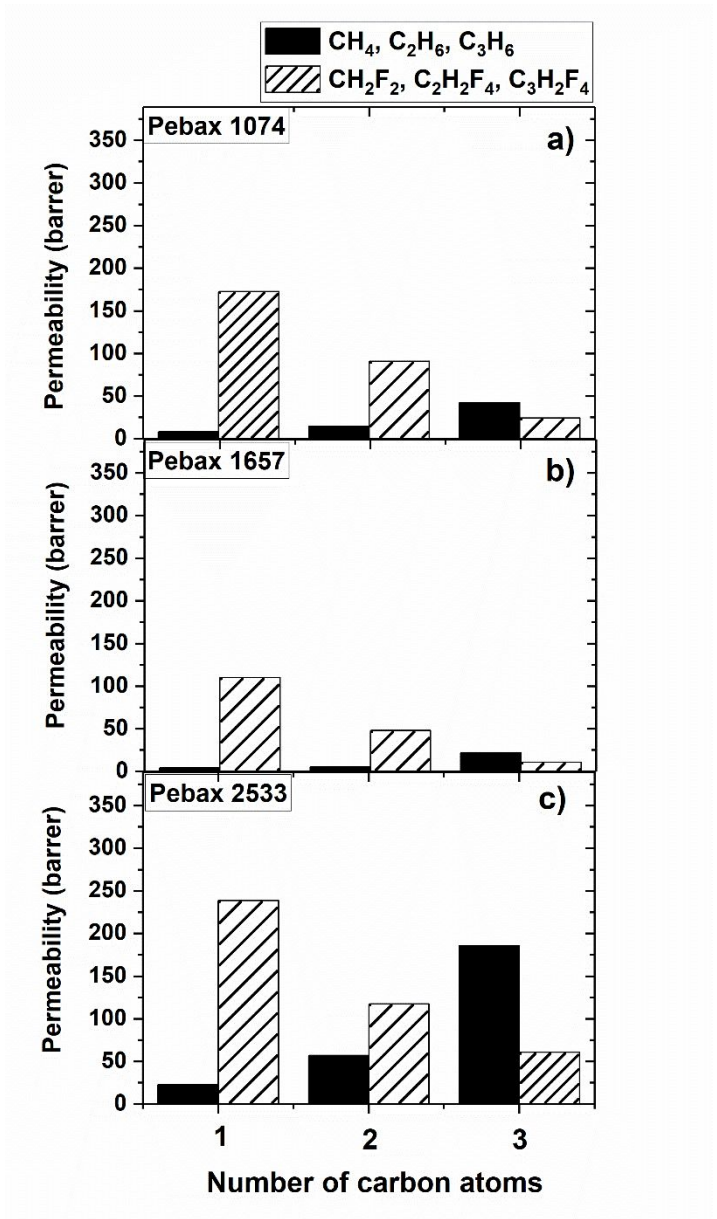
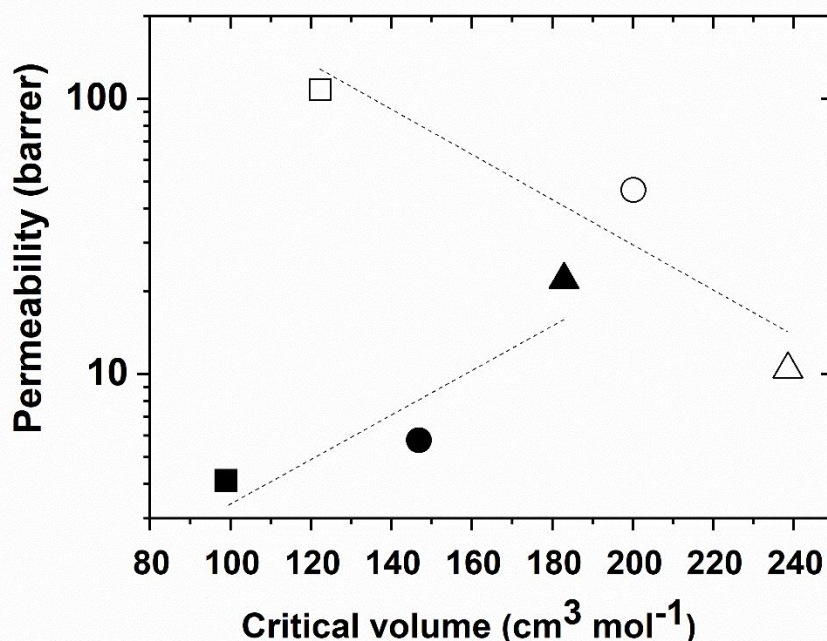


Figure 3. Permeability of hydrofluorocarbons and analogous hydrocarbons in (a) Pebax® 1074, (b) Pebax® 1657 and (c) Pebax® 2533 at 30 °C and 1.3 bar as a function of the number of carbon atoms.

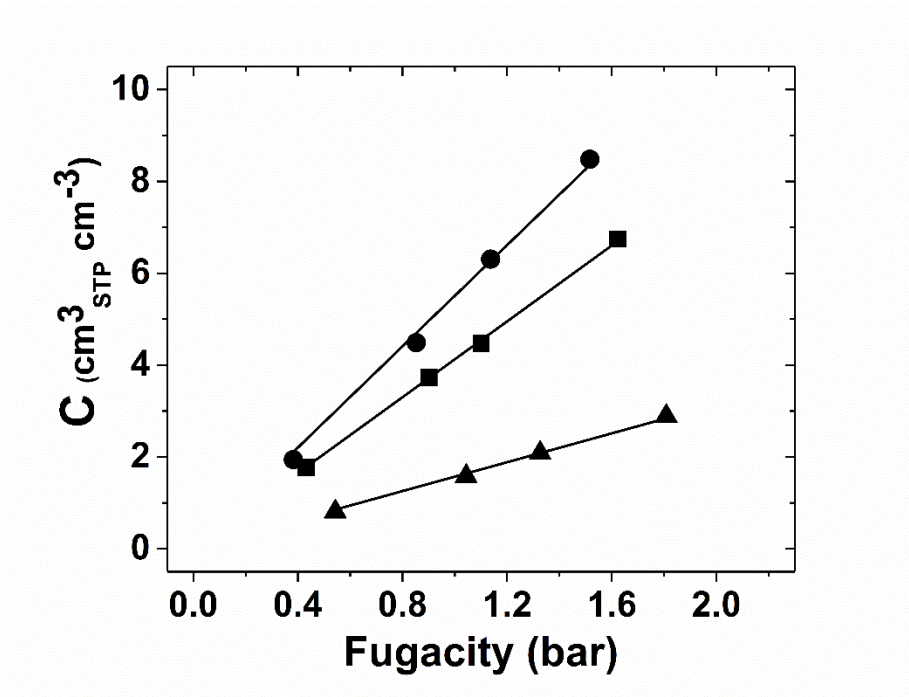


**Figure 4.** Permeability coefficients in Pebax® 1657 of R32 (□), R134a (○) and R1234yf (△) and their non-fluorinated hydrocarbon analogues methane (■), ethane (●) and propene (▲) as a function of critical volume (penetrant size) at 30 °C and 1.3 bar. Dashed lines are a guide to the eye.

#### *Solubility and diffusivity in Pebax® 1657*

To deepen the study of fluorinated gas transport in Pebax® films, the solubility and diffusivity coefficients of the refrigerants were determined in the polymer grade Pebax® 1657, which exhibited the best results in terms of ideal selectivity for all gas pairs. Low-pressure sorption measurements were performed and the equilibrium concentration of each gas within the polymer matrix is presented in Figure 5 as a function of the penetrant fugacity according to Eq. (7). These results are also recorded in Table S5 as Supporting Information. As can be seen, the gas concentrations of the three fluorinated hydrocarbons exhibit a linear trend over the low pressure range examined, thus the Henry's law coefficients,  $k_D$ , were calculated from the slope of the corresponding linear least-squares regressions. Accordingly, the Henry's law constants decrease in the order R134a ( $5.51 \text{ cm}^3_{\text{STP}} \text{ cm}^{-3} \text{ bar}^{-1}$ ) > R32 ( $4.13 \text{ cm}^3_{\text{STP}} \text{ cm}^{-3} \text{ bar}^{-1}$ ) > R1234yf ( $1.57 \text{ cm}^3_{\text{STP}} \text{ cm}^{-3} \text{ bar}^{-1}$ ). These results confirm the trends observed in Figure 1 regarding the influence

of pressure on the permeability coefficients, i.e., the most soluble gas, R134a, underwent the most marked increase in permeability with increasing pressure, followed by R32 and R1234yf.



**Figure 5. Concentration of R32 (■), R134a (●) and R1234yf (▲) in Pebax® 1657 as a function of penetrant fugacity at 30 °C. Solid lines are the linear least-squares regressions.**

Remarkably, it is observed that although R134a is the most condensable and soluble gas, the refrigerant R1234yf, which has similar critical temperature and normal boiling point to R134a, exhibits the lowest Henry's law coefficient. In the absence of refrigerant solubility data in other polymers, it is interesting to compare the solubility behavior of these refrigerants in solvents such as ionic liquids, which have also been explored as entrainers for extractive distillation processes of refrigerant blends.<sup>61</sup> Noteworthy, an analogous sorption behavior has been observed, i.e., the solubility of R32 and R134a in ionic liquids are systematically reported to be 2-4 times greater than that of R1234y.<sup>62-65</sup> Therefore, to further explore the rationale behind these results, the condensability differences among penetrants were normalized by calculating the activity-basis Henry's law solubility in terms of the product  $k_D p_{sat}$ .<sup>22</sup> The results, plotted in Figure S3 of the Supporting Information as a function of gas critical volume, show that the activity-basis Henry's law coefficient decreases with increasing critical volume (a variable related

to penetrant size), which is consistent with the fact that more energy of mixing is required to open larger gaps in the polymer matrix to allocate larger penetrants. These results are analogues to those found for perfluorocarbons by Merkel et al.<sup>22</sup>

Once determined the solubility coefficients, the diffusivity of R32, R134a and R1234yf in Pebax® 1657 was calculated at 30 °C and 1.3 bar using Eq. (5). In this case, the results show that diffusivity decreases, as expected, with the penetrant size as follows R32 ( $20.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) > R134a ( $6.6 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) > R1234yf ( $5.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ). In addition, these results are plotted in Figure S4 together with the diffusion coefficients of several permanent gases reported by Bernardo et al.<sup>29</sup> As expected, a strong correlation between diffusivity and penetrant size is observed. In addition, the comparison reveals that the mobility of R32 is lower than that of its analogue non-fluorinated hydrocarbon CH<sub>4</sub>. Consequently, the much higher permeability of R32 over that of CH<sub>4</sub> (see Figure 3) is mainly ascribed to the superior solubility of R32 in Pebax®, which is two orders of magnitude higher than that of CH<sub>4</sub>.<sup>29</sup>

Finally, Table 3 shows the solubility and diffusivity selectivity contributions to the permselectivity of Pebax® 1657 membranes. Results reveal that for the separation of the gas pairs involving R32 the contribution of the diffusivity selectivity to the overall selectivity is higher than that of the solubility selectivity, nevertheless, solubility selectivity is also significant for the separation R32/R1234yf. This phenomena are in agreement with previous discussion and explains why R32/R1234yf and R32/R134a selectivity decreases with increasing pressure due to plasticization effects. On the other hand, for the gas pair R134a/R2134yf, the solubility selectivity outweighs diffusivity selectivity, thus the decrease in diffusivity selectivity due to plasticization effects is much less pronounced and consequently, the permselectivity increases with pressure.

**Table 3. Permselectivity, solubility selectivity and diffusivity selectivity of the gas pairs R32/R1234yf, R32/R134a and R134a/R1234yf in Pebax® 1657 at 30 °C and 1.3 bar.**

Gas pair	Permeability selectivity	Solubility selectivity	Diffusivity selectivity
R32/R1234yf	10.2	2.7	3.9
R32/R134a	2.3	0.8	3.1
R134a/R1234yf	4.5	3.5	1.3

*Mixed-gas separation of fluorinated refrigerants*

To conclude, we report the mixed-gas permeation data for the gas pairs R32/R1234yf and R32/R134a through the highly selective Pebax®1657 films. Unfortunately, the retention times of R134a and R1234yf in the GC are coincident and therefore, we cannot assess the mixed-gas separation of R134a/R1234yf mixtures. The results are shown in Figure 6 as normalized permeability with respect to pure gas data for several mixture compositions. As can be seen, the permeability of these gases is not significantly affected under mixed-gas conditions, and therefore, both the permeation rate and selectivity remain almost constant in the whole composition range.

These results are very promising and highlight the potential of membrane technology for the selective separation and recovery of hydrofluorocarbon gases from the HFC/HFO refrigerant blends that are penetrating into the refrigeration market nowadays. The industrial application of the membrane separation process requires that the hydrofluorocarbons recovered from end-of-life equipment be stored into large pressurized tanks, which is a usual operation performed in the hydrofluorocarbons waste treatment facilities. These tanks would serve as continuous feedstock for the membrane process that would perform the separation in steady-state conditions.



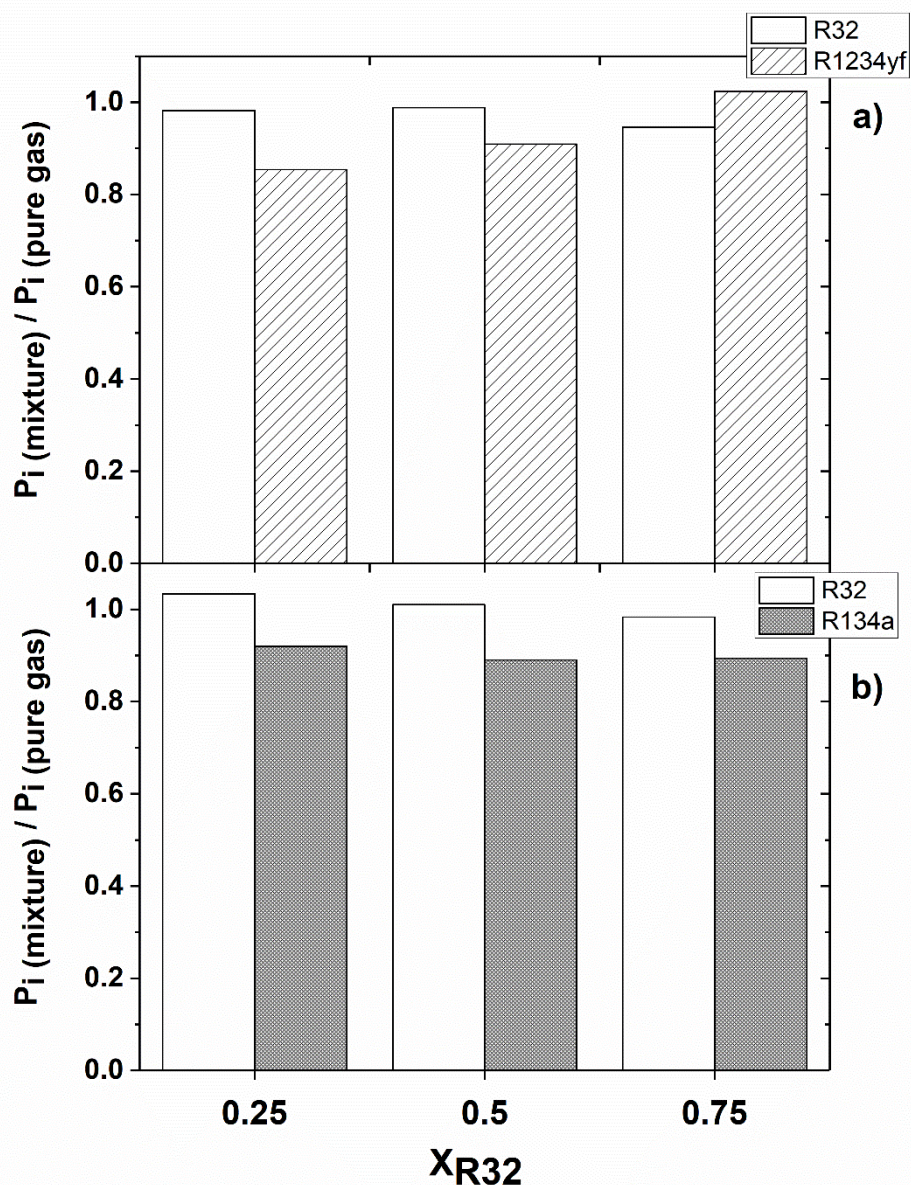


Figure 6. Mixed-gas permeability through Pebax® 1657 at 30 °C and 1.3 bar: a) R32/R1234yf and b) R32/R134a mixtures.

## Conclusions

In this work, we evaluate for the first time the feasibility of using membrane technology for the selective recovery of fluorinated hydrofluorocarbons that are of highest strategic interest for the refrigeration and air conditioning sector. To that end, a comprehensive assessment of the

gas permeation properties of the refrigerants R32 (difluoromethane), R134a (1,1,1,2-tetrafluoroethane) and R1234yf (2,3,3,3-tetrafluoropropene) through several poly(ether-block-amide) membranes is performed. The highest gas permeability and lowest gas pair selectivity were observed in Pebax® grade 2533, which has the highest content in polyether soft segments and highest fractional free volume. In contrast, the lowest permeability and highest gas pair selectivity correspond to Pebax® 1657, which exhibits the lowest fractional free volume of the three grades tested. In any case, pure gas permeabilities are relatively high through these rubbery polymers and followed the order  $R32 > R134a > R1234yf$ . Moreover, this work demonstrates that, in contrast to cryogenic distillation, membrane technology can efficiently separate common HFC/HFO azeotropic blends (e.g., R32/R1234yf and R134a/R1234yf) that are being incorporated into the refrigeration market to comply with the most recent legislation and binding agreements such as the Kigali Amendment. In addition, this work shows that the separation performance remained almost constant under mixed-gas conditions. Accordingly, we believe that membrane technology is worthy of consideration for the separation of HFC/HFO refrigerant blends, thus enabling the recovery of the mixture constituents and minimizing both the release to the environment and the production of high global warming potential HFCs.

### Acknowledgements

This research is supported by Project KET4F-Gas – SOE2/P1/P0823, which is co-financed by the European Regional Development Fund within the framework of Interreg Sudoe Programme. The authors acknowledge the collaboration of Dr. Mar López-González and Dr. Rosario Benavente (Institute of Polymer Science and Technology-CSIC) to perform the sorption and DSC experiments. Dr. Fernando Pardo, acknowledges the post-doctoral fellowship (FJCI-2017-32884, ‘Juan de la Cierva Formación’) from the Spanish Ministry of Science, Innovation and Universities.



## Supporting Information

The Supporting Information is available free of charge at:

Experimental details, DSC thermograms, SEM images, gas permeability, selectivity and solubility data, and solubility and diffusivity trends with penetrant size.

## Nomenclature

$A$  membrane area [ $\text{cm}^2$ ]

$C$  concentration [ $\text{cm}^3_{\text{STP}} \text{cm}^{-3}$ ]

$D$  diffusion coefficient [ $\text{cm}^2 \text{s}^{-1}$ ]

$f$  fugacity [bar]

$FFV$  fractional free volume [-]

$k_D$  Henry's law solubility coefficient [ $\text{cm}^3_{\text{STP}} \text{cm}^{-3} \text{bar}^{-1}$ ]

$m$  mass [g]

$p$  pressure [bar]

$p_{\text{sat}}$  vapor pressure [bar]

$P$  permeability [barrer =  $7.5 \times 10^{-9} \text{cm}^3_{\text{STP}} \text{cm cm}^{-2} \text{s}^{-1} \text{bar}^{-1}$ ]

$Q$  flow rate [ $\text{cm}^3 \text{s}^{-1}$ ]

$R$  gas constant [ $\text{bar cm}^3 \text{K}^{-1} \text{mol}^{-1}$ ]

$S$  solubility coefficient [ $\text{cm}^3_{\text{STP}} \text{cm}^{-3} \text{bar}^{-1}$ ]

$T$  temperature [K]

$V$  volume [ $\text{cm}^3$ ]

$V_m$  specific volume [ $\text{cm}^3 \text{mol}^{-1}$ ]

$V_0$  specific volume at 0 K [ $\text{cm}^3 \text{mol}^{-1}$ ]

$V_W$  van der Waals volume [ $\text{cm}^3 \text{mol}^{-1}$ ]

$z$  compressibility factor [-]

*Greek letter*

$\delta$  thickness [cm]

$\phi$  fugacity coefficient [-]

$\rho$  density [ $\text{g cm}^{-3}$ ]

## References

- (1) United Nations, 1987. Montreal Protocol on Substances that Deplete the Ozone Layer (With Annex). Concluded at Montreal on 16th-September 1987. <https://treaties.un.org/doc/publication/unts/volume%201522/volume-1522-i-26369-english.pdf> (accessed Nov 19, 2019).
- (2) McCulloch, A.; Midgley, P. M.; Ashford, P., Releases of refrigerant gases (CFC-12, HCFC-22 and HFC-134a) to the atmosphere. *Atmos. Environ.* **2003**, 37 (7), 889-902, DOI: 10.1016/S1352-2310(02)00975-5
- (3) Mohanraj, M.; Jayaraj, S.; Muraleedharan, C., Environment friendly alternatives to halogenated refrigerants—A review. *Int. J. Green. Gas Con.* **2009**, 3 (1), 108-119, DOI: 10.1016/j.ijggc.2008.07.003
- (4) Powell, R. L., CFC phase-out: Have we met the challenge? *J. Fluor. Chem.* **2002**, 114 (2), 237-250, DOI: 10.1016/S0022-1139(02)00030-1
- (5) European Environment Information and Observation Network (Eionet), Data viewer on greenhouse gas emissions and removals, sent by countries to UNFCCC and the EU Greenhouse Gas Monitoring Mechanism (EU Member States). <https://www.eea.europa.eu/data-and-maps/data/data-viewers/greenhouse-gases-viewer> (accessed Nov 19, 2019).
- (6) The European Commission, 2015. Information for technicians and users of refrigeration, air conditioning and heat pump equipment containing fluorinated greenhouse gases. [https://ec.europa.eu/clima/sites/clima/files/f-gas/docs/f\\_gas\\_equipment\\_operators\\_en.pdf](https://ec.europa.eu/clima/sites/clima/files/f-gas/docs/f_gas_equipment_operators_en.pdf) (accessed Nov 18, 2019).
- (7) The European Parliament and the Council of the European Union, 2014. Regulation (EU) No 517/2014 of the European Parliament and the Council of 16 April 2014 on fluorinated

- greenhouse gases and repealing Regulation (EC) No 842/2006. *Off. J. Eur. Union* 150, 195–230. <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32014R0517> (accessed Nov 19, 2019).
- (8) United Nations Environment Programme, Ozone Secretariat, 2017. Briefing Note on Ratification of the Kigali Amendment. [http://conf.montreal-protocol.org/meeting/oewg/oewg-39/presession/briefingnotes/ratification\\_kigali.pdf](http://conf.montreal-protocol.org/meeting/oewg/oewg-39/presession/briefingnotes/ratification_kigali.pdf) (accessed Nov 19, 2019).
  - (9) Devecioğlu, A. G.; Oruç, V., Characteristics of Some New Generation Refrigerants with Low GWP. *Energy Procedia* **2015**, 75, 1452-1457, DOI: 10.1016/j.egypro.2015.07.258
  - (10) Flohr, F.; Arimoto, H.; Ohkubo, S. In *Low GWP refrigerant R454A for commercial refrigeration*, Refrigeration Science and Technology, 2018; pp 224-230, DOI: 10.18462/iir.hfo.2018.1134
  - (11) Makhnatch, P.; Khodabandeh, R. In *Evaluation of Cycle performance of R448A and R449A as R404A replacements in supermarket refrigeration systems*, Refrigeration Science and Technology, 2015; pp 437-444, DOI: 10.18462/iir.icr.2015.0563
  - (12) Mota-Babiloni, A.; Haro-Ortuño, J.; Navarro-Esbrí, J.; Barragán-Cervera, Á., Experimental drop-in replacement of R404A for warm countries using the low GWP mixtures R454C and R455A. *Int. J. Refrig.* **2018**, 91, 136-145, DOI: 10.1016/j.ijrefrig.2018.05.018
  - (13) Mota-Babiloni, A.; Navarro-Esbrí, J.; Pascual-Miralles, V.; Barragán-Cervera, Á.; Maiorino, A., Experimental influence of an internal heat exchanger (IHX) using R513A and R134a in a vapor compression system. *Appl. Therm. Eng.* **2019**, 147, 482-491, DOI: 10.1016/j.applthermaleng.2018.10.092
  - (14) Imamura, T.; Kamiya, K.; Sugawa, O., Ignition hazard evaluation on A2L refrigerants in situations of service and maintenance. *J. Loss Prevent. Proc.* **2016**, 36, DOI: 10.1016/j.jlp.2014.12.018
  - (15) Wu, X.; Dang, C.; Xu, S.; Hihara, E., State of the art on the flammability of hydrofluoroolefin (HFO) refrigerants. *Int. J. Refrig.* **2019**, 108, 209-223, DOI: 10.1016/j.ijrefrig.2019.08.025
  - (16) Alqaheem, Y.; Alomair, A.; Vinoba, M.; Pérez, A., Polymeric Gas-Separation Membranes for Petroleum Refining. *Int. J. Polym. Sci.* **2017**, 2017, DOI: 10.1155/2017/4250927
  - (17) Bernardo, P.; Drioli, E.; Golemme, G., Membrane Gas Separation: A Review/State of the Art. *Ind. Eng. Chem. Res.* **2009**, 48 (10), 4638-4663, DOI: 10.1021/ie8019032
  - (18) Koros, W. J.; Mahajan, R., Pushing the limits on possibilities for large scale gas separation: Which strategies? *J. Membrane Sci.* **2000**, 175 (2), 181-196, DOI: 10.1016/S0376-7388(00)00418-X
  - (19) Zarca, G.; Urtiaga, A.; Biegler, L. T.; Ortiz, I., An optimization model for assessment of membrane-based post-combustion gas upcycling into hydrogen or syngas. *J. Membrane Sci.* **2018**, 563, 83-92, DOI: 10.1016/j.memsci.2018.05.038
  - (20) Baker, R. W.; Low, B. T., Gas Separation Membrane Materials: A Perspective. *Macromolecules* **2014**, 47 (20), 6999-7013, DOI: 10.1021/ma501488s
  - (21) Chung, I. J.; Lee, K. R.; Hwang, S. T., Separation of CFC-12 from air by polyimide hollow-fiber membrane module. *J. Membrane Sci.* **1995**, 105 (3), 177-185, DOI: 10.1016/0376-7388(95)00058-K
  - (22) Merkel, T. C.; Bondar, V.; Nagai, K.; Freeman, B. D., Sorption and transport of hydrocarbon and perfluorocarbon gases in poly(1-trimethylsilyl-1-propyne). *J. Polym. Sci. B Pol. Phys.* **2000**, 38 (2), 273-296, DOI: 10.1002/(SICI)1099-0488(20000115)38:2<273::AID-POLB1>3.0.CO;2-X
  - (23) Pinnau, I.; Toy, L. G., Transport of organic vapors through poly(1-trimethylsilyl-1-propyne). *J. Membrane Sci.* **1996**, 116 (2), 199-209, DOI: 10.1016/0376-7388(96)00041-5
  - (24) Hirayama, Y.; Tanihara, N.; Kusuki, Y.; Kase, Y.; Haraya, K.; Okamoto, K. I., Permeation properties to hydrocarbons, perfluorocarbons and chlorofluorocarbons of cross-linked

- membranes of polymethacrylates with poly(ethylene oxide) and perfluorononyl moieties. *J. Membrane Sci.* **1999**, *163* (2), 373-381, DOI: 10.1016/S0376-7388(99)00177-5
- (25) Stern, S. A.; Fang, S.-M.; Frisch, H. L., Effect of pressure on gas permeability coefficients. A new application of "free volume" theory. *J. Polym. Sci. Pol. Phys.* **1972**, *10* (2), 201-219, DOI: 10.1002/pol.1972.160100315
- (26) Ruan, X.; Dai, Y.; Du, L.; Yan, X.; He, G.; Li, B., Further separation of HFC-23 and HCFC-22 by coupling multi-stage PDMS membrane unit to cryogenic distillation. *Sep. Purif. Technol.* **2015**, *156*, 673-682, DOI: 10.1016/j.seppur.2015.10.064
- (27) Car, A.; Yave, W.; Peinemann, K.-V.; Stropnik, C., Tailoring Polymeric Membrane Based on Segmented Block Copolymers for CO<sub>2</sub> Separation. *Membrane Gas Separation* **2010**, 227-253, DOI: 10.1002/9780470665626.ch12
- (28) Azizi, N.; Mohammadi, T.; Mosayebi Behbahani, R., Comparison of permeability performance of PEBAX-1074/TiO<sub>2</sub>, PEBAX-1074/SiO<sub>2</sub> and PEBAX-1074/Al<sub>2</sub>O<sub>3</sub> nanocomposite membranes for CO<sub>2</sub>/CH<sub>4</sub> separation. *Chem. Eng. Res. Des.* **2017**, *117*, 177-189, DOI: 10.1016/j.cherd.2016.10.018
- (29) Bernardo, P.; Jansen, J. C.; Bazzarelli, F.; Tasselli, F.; Fuoco, A.; Friess, K.; Izák, P.; Jarmarová, V.; Kačírková, M.; Clarizia, G., Gas transport properties of Pebax®/room temperature ionic liquid gel membranes. *Sep. Purif. Technol.* **2012**, *97*, 73-82, DOI: 10.1016/j.seppur.2012.02.041
- (30) Bondar, V. I.; Freeman, B. D.; Pinnau, I., Gas transport properties of poly(ether-b-amide) segmented block copolymers. *J. Polym. Sci. B Polym. Phys.* **2000**, *38* (15), 2051-2062, DOI: 10.1002/1099-0488(20000801)38:15<2051::AID-POLB100>3.0.CO;2-D
- (31) Car, A.; Stropnik, C.; Yave, W.; Peinemann, K. V., PEG modified poly(amide-b-ethylene oxide) membranes for CO<sub>2</sub> separation. *J. Membrane Sci.* **2008**, *307* (1), 88-95, DOI: 10.1016/j.memsci.2007.09.023
- (32) Car, A.; Stropnik, C.; Yave, W.; Peinemann, K. V., Pebax®/polyethylene glycol blend thin film composite membranes for CO<sub>2</sub> separation: Performance with mixed gases. *Sep. Purif. Technol.* **2008**, *62* (1), 110-117, DOI: 10.1016/j.seppur.2008.01.001
- (33) Ghasemi Estahbanati, E.; Omidkhah, M.; Ebadi Amooghin, A., Preparation and characterization of novel Ionic liquid/Pebax membranes for efficient CO<sub>2</sub>/light gases separation. *J. Ind. Eng. Chem.* **2017**, *51*, 77-89, DOI: 10.1016/j.jiec.2017.02.017
- (34) Lin, H.; Freeman, B. D., Gas solubility, diffusivity and permeability in poly(ethylene oxide). *J. Membrane Sci.* **2004**, *239* (1), 105-117, DOI: 10.1016/j.memsci.2003.08.031
- (35) Sridhar, S.; Suryamurali, R.; Smitha, B.; Aminabhavi, T. M., Development of crosslinked poly(ether-block-amide) membrane for CO<sub>2</sub>/CH<sub>4</sub> separation. *Colloids Surf. A Physicochem. Eng. Asp.* **2007**, *297* (1-3), 267-274, DOI: 10.1016/j.colsurfa.2006.10.054
- (36) Surya Murali, R.; Sridhar, S.; Sankarshana, T.; Ravikumar, Y. V. L., Gas permeation behavior of pebax-1657 nanocomposite membrane incorporated with multiwalled carbon nanotubes. *Ind. Eng. Chem. Res.* **2010**, *49* (14), 6530-6538, DOI: 10.1021/ie9016495
- (37) Meyer, C. W.; Morrison, G., Dipole Moments of Seven Refrigerants. *J. Chem. Eng. Data* **1991**, *36* (4), 409-413, DOI: 10.1021/je00004a019
- (38) Chung, T. H.; Ajlan, M.; Lee, L. L.; Starling, K. E., Generalized multiparameter correlation for nonpolar and polar fluid transport properties. *Ind. Eng. Chem. Res.* **1988**, *27* (4), 671-679, DOI: 10.1021/ie00076a024
- (39) Bondi, A., van der Waals Volumes and Radii. *J. Phys. Chem.* **1964**, *68* (3), 441-451, DOI: 10.1021/j100785a001
- (40) Fam, W.; Mansouri, J.; Li, H.; Chen, V., Improving CO<sub>2</sub> separation performance of thin film composite hollow fiber with Pebax®1657/ionic liquid gel membranes. *J. Membrane Sci.* **2017**, *537*, 54-68, DOI: 10.1016/j.memsci.2017.05.011
- (41) Rezac, M. E.; John, T., Correlation of penetrant transport with polymer free volume: Additional evidence from block copolymers. *Polymer* **1998**, *39* (3), 599-603, DOI: 10.1016/S0032-3861(97)00302-9

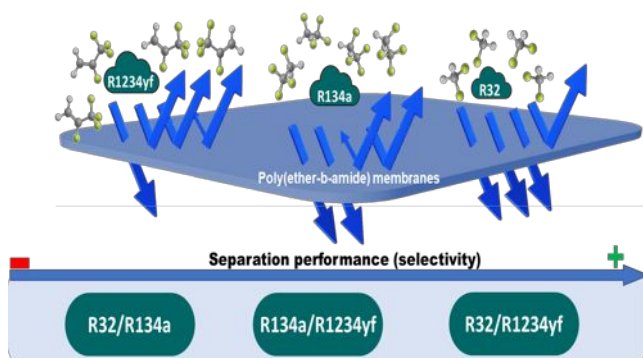
- (42) van Krevelen, D. W.; te Nijenhuis, K., *Properties of Polymers: Their Correlation with Chemical Structure; their Numerical Estimation and Prediction from Additive Group Contributions*. Elsevier Science: 2009.
- (43) Yave, W.; Car, A.; Peinemann, K. V.; Shaikh, M. Q.; Rätzke, K.; Faupel, F., Gas permeability and free volume in poly(amide-b-ethylene oxide)/polyethylene glycol blend membranes. *J. Membrane Sci.* **2009**, 339 (1-2), 177-183, DOI: 10.1016/j.memsci.2009.04.049
- (44) Okamoto, K. I.; Tanaka, K.; Katsube, M.; Kita, H.; Sueoka, O.; Ito, Y., Correlation between positron annihilation and gas diffusion properties of various rubbery polymers. *Polym. J.* **1993**, 25 (3), 275-284, DOI: 10.1295/polymj.25.275
- (45) Schrader, D. M.; Jean, Y. C. Positron and Positronium Chemistry. In *Studies in Physical and Theoretical Chemistry*; Schrader, D. M.; Jean, Y. C., Eds.; Elsevier Science Limited, 1988; vol. 57.
- (46) David, O. C.; Gorri, D.; Urtiaga, A.; Ortiz, I., Mixed gas separation study for the hydrogen recovery from H<sub>2</sub>/CO/N<sub>2</sub>/CO<sub>2</sub> post combustion mixtures using a Matrimid membrane. *J. Membrane Sci.* **2011**, 378 (1-2), 359-368, DOI: 10.1016/j.memsci.2011.05.029
- (47) Zarca, G.; Ortiz, I.; Urtiaga, A., Facilitated-transport supported ionic liquid membranes for the simultaneous recovery of hydrogen and carbon monoxide from nitrogen-enriched gas mixtures. *Chem. Eng. Res. Des.* **2014**, 92, 764-768, DOI: 10.1016/j.cherd.2013.12.021
- (48) Zarca, G.; Ortiz, I.; Urtiaga, A., Copper(I)-containing supported ionic liquid membranes for carbon monoxide/nitrogen separation. *J. Membrane Sci.* **2013**, 438, 38-45, DOI: 10.1016/j.memsci.2013.03.025
- (49) Peng, D. Y.; Robinson, D. B., A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, 15 (1), 59-64, DOI: 10.1021/i160057a011
- (50) Brown, J. S., Predicting performance of refrigerants using the Peng-Robinson Equation of State. *Int. J. Refrig.* **2007**, 30 (8), 1319-1328, DOI: 10.1016/j.ijrefrig.2007.04.006
- (51) Koros, W. J.; Paul, D. R., Design considerations for measurement of gas sorption in polymers by pressure decay. *J. Polym. Sci. Polym. Phys. Ed. Vol.* **1976**, 14 (10), 1903-1907, DOI: 10.1002/pol.1976.180141014
- (52) Tlenkopatchev, M.; Vargas, J.; Almaraz-Girón, M. A.; López-González, M.; Riande, E., Gas sorption in new fluorine containing polynorbornenes with imide side chain groups. *Macromolecules* **2005**, 38 (7), 2696-2703, DOI: 10.1021/ma0480751
- (53) Garrido, L.; García, C.; López-González, M.; Comesaña-Gándara, B.; Lozano, A. E.; Guzmán, J., Determination of Gas Transport Coefficients of Mixed Gases in 6FDA-TMPDA Polyimide by NMR Spectroscopy. *Macromolecules* **2017**, 50 (9), 3590-3597, DOI: 10.1021/acs.macromol.7b00384
- (54) Azizi, N.; Mahdavi, H. R.; Isanejad, M.; Mohammadi, T., Effects of low and high molecular mass PEG incorporation into different types of poly(ether-b-amide) copolymers on the permeation properties of CO<sub>2</sub> and CH<sub>4</sub>. *J Polym. Res.* **2017**, 24 (9), DOI: 10.1007/s10965-017-1297-1
- (55) Mateucci, S.; Yampolskii, Y.; Freeman, B. D.; Pinnau, I., Transport of Gases and Vapors in Glassy and Rubbery Polymers. In *Materials Science of Membranes for Gas and Vapor Separation*, 2006; pp 1-47, DOI: 10.1002/047002903X.ch1
- (56) Chen, J. C.; Feng, X.; Penlidis, A., Gas Permeation Through Poly(Ether-b-amide) (PEBAX 2533) Block Copolymer Membranes. *Sep. Sci. Technol.* **2004**, 39 (1), 149-164, DOI: 10.1081/SS-120027406
- (57) Bondar, V. I.; Freeman, B. D.; Pinnau, I., Gas sorption and characterization of poly(ether-b-amide) segmented block copolymers. *J. Polym. Sci. B Pol. Phys.* **1999**, 37 (17), 2463-2475, DOI: 10.1002/(SICI)1099-0488(19990901)37:17<2463::AID-POLB18>3.0.CO;2-H
- (58) Sanders, D. F.; Smith, Z. P.; Guo, R.; Robeson, L. M.; McGrath, J. E.; Paul, D. R.; Freeman, B. D., Energy-efficient polymeric gas separation membranes for a sustainable future: A review. *Polymer* **2013**, 54 (18), 4729-4761, DOI: 10.1016/j.polymer.2013.05.075

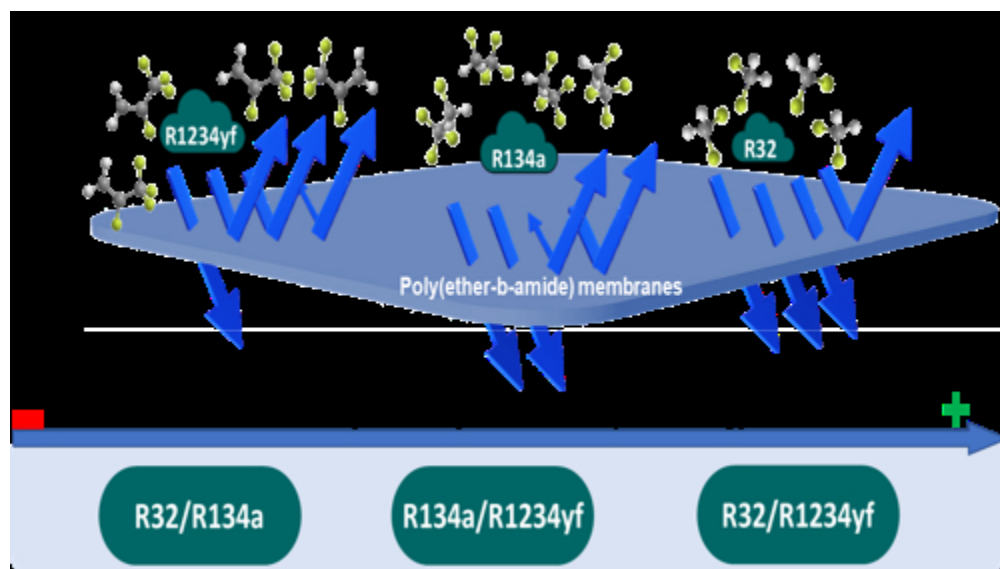
- (59) Zhmakin, V. V.; Teplyakov, V. V., The evaluation of the C1–C4 hydrocarbon permeability parameters in the thin film composite membranes. *Sep. Purif. Technol.* **2017**, *186*, 145-155, DOI: 10.1016/j.seppur.2017.06.004
- (60) Merkel, T. C.; Bondar, V.; Nagai, K.; Freeman, B. D., Hydrocarbon and perfluorocarbon gas sorption in poly(dimethylsiloxane), poly(1-trimethylsilyl-1-propyne), and copolymers of tetrafluoroethylene and 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole. *Macromolecules* **1999**, *32* (2), 370-374, DOI: 10.1021/ma9814402
- (61) Shiflett, M. B.; Yokozeki, A., Separation of difluoromethane and pentafluoroethane by extractive distillation using ionic liquid. *Chim. Oggi* **2006**, *24* (2), 28-30.
- (62) Liu, X.; He, M.; Lv, N.; Qi, X.; Su, C., Vapor–Liquid Equilibrium of Three Hydrofluorocarbons with [HMIM][Tf2N]. *J. Chem. Eng. Data* **2015**, *60* (5), 1354-1361, DOI: 10.1021/je501069b
- (63) Shiflett, M. B.; Yokozeki, A., Solubility and diffusivity of hydrofluorocarbons in room-temperature ionic liquids. *AIChE J.* **2006**, *52* (3), 1205-1219, DOI: 10.1002/aic.10685
- (64) Sun, Y.; Zhang, Y.; Wang, X.; Prausnitz, J. M.; Jin, L., Gaseous absorption of 2,3,3,3-tetrafluoroprop-1-ene in three imidazolium-based ionic liquids. *Fluid Phase Equilib.* **2017**, *450*, 65-74, DOI: 10.1016/j.fluid.2017.07.013
- (65) Zhang, Y.; Yin, J.; Wang, X., Vapor-liquid equilibrium of 2,3,3,3-tetrafluoroprop-1-ene with 1-butyl-3-methylimidazolium hexafluorophosphate, 1-hexyl-3-methyl imidazolium hexafluorophosphate, and 1-octyl-3-methylimidazolium hexafluorophosphate. *J. Mol. Liq.* **2018**, *260*, 203-208, DOI: 10.1016/j.molliq.2018.03.112

## Synopsis

Compact and energy efficient membrane separation processes can be applied to selectively recover value added refrigerants from azeotropic HFC/HFO mixtures used nowadays in the refrigeration sector, thus enabling refrigerant recycling and minimising powerful greenhouse gas emissions.

## TOC graphic - For Table of Contents Use Only





Graphical Abstract

84x47mm (150 x 150 DPI)

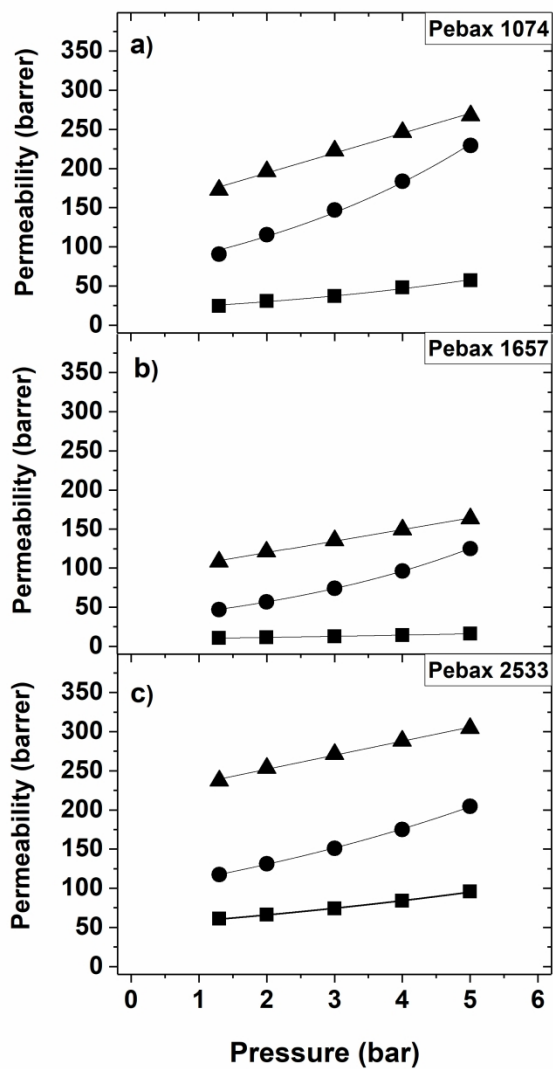


Figure 1

93x164mm (600 x 600 DPI)



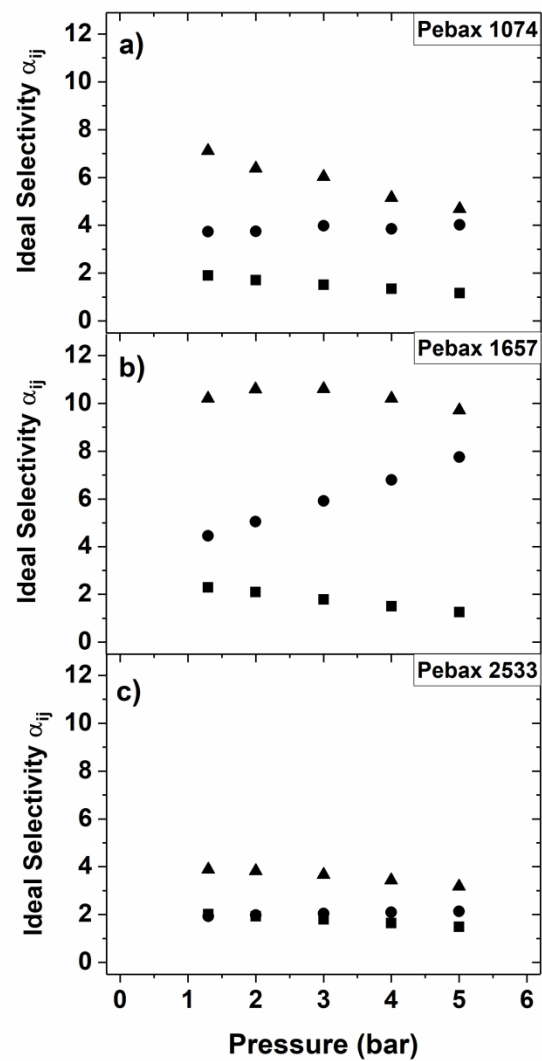


Figure 2

93x164mm (600 x 600 DPI)

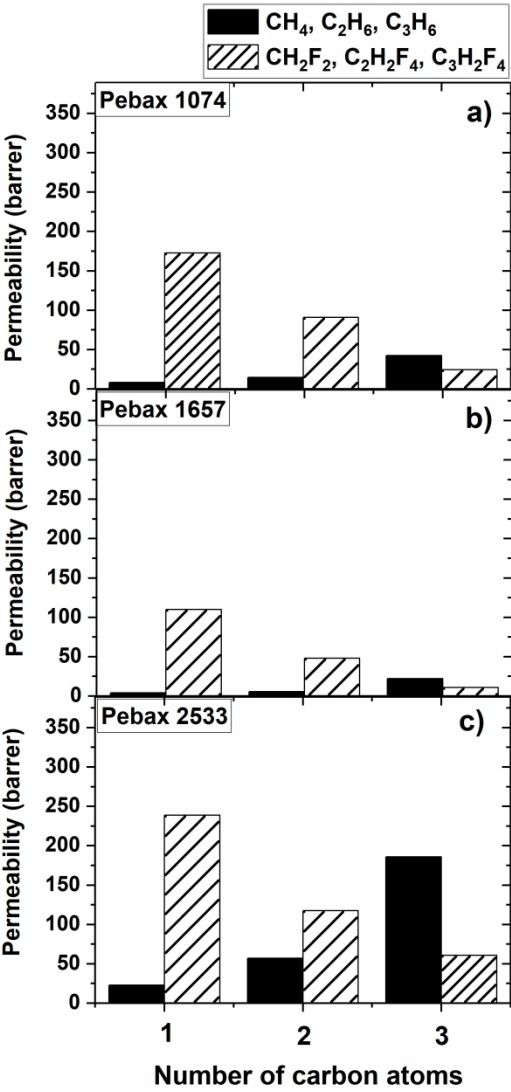


Figure 3

120x172mm (600 x 600 DPI)

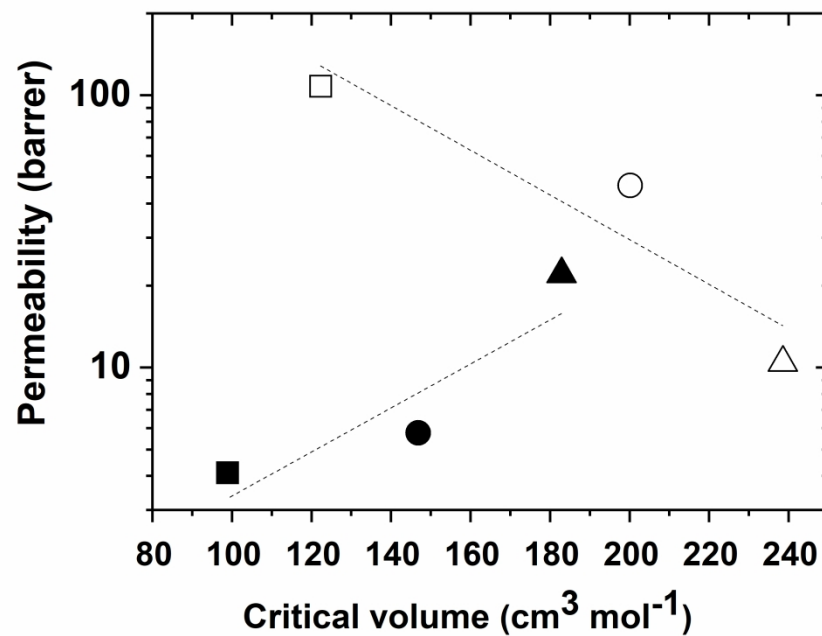


Figure 4

149x109mm (600 x 600 DPI)

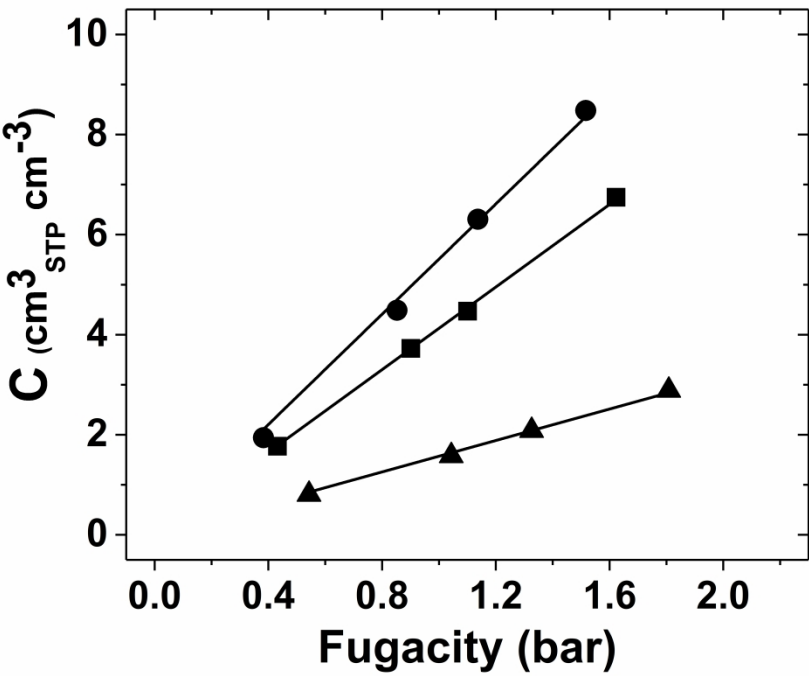


Figure 5

272x208mm (600 x 600 DPI)

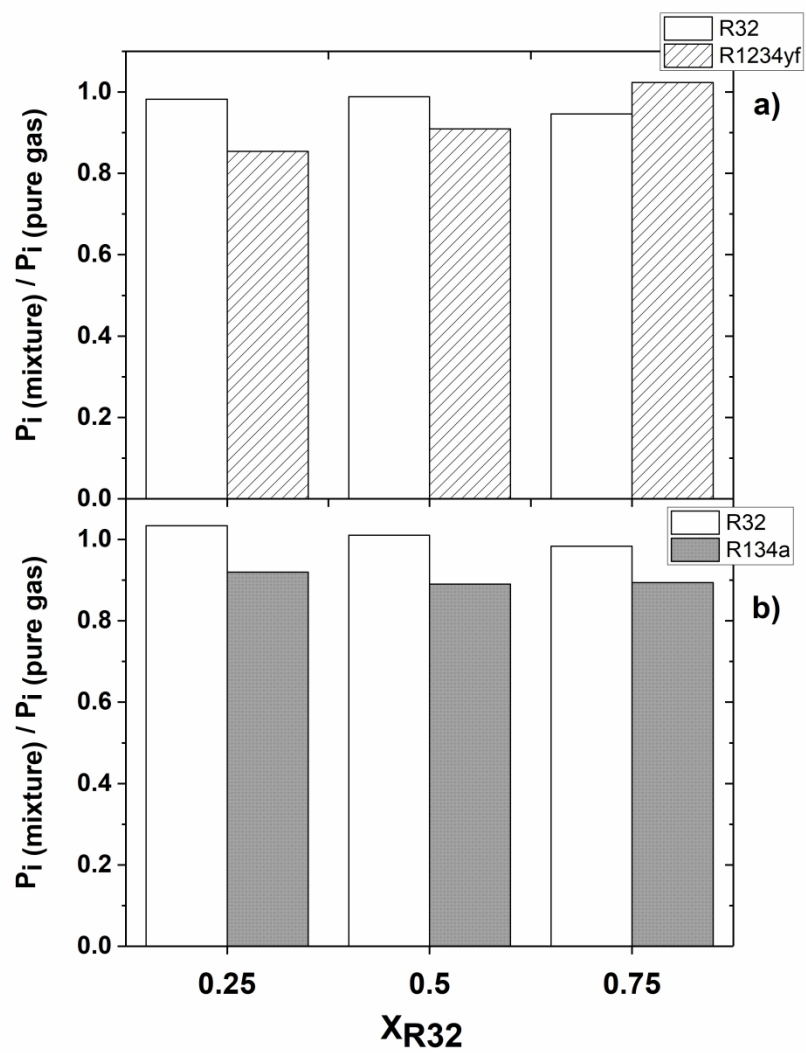


Figure 6

169x202mm (600 x 600 DPI)