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Title: Partially pyrolyzed membranes (PPMs) derived from copolyimides having carboxylic acid groups. Preparation and gas transport properties.

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Abstract: A series of partially pyrolyzed membranes (PPMs) was prepared from a copolyimide having carboxylic acid pendant groups (PIA). The effect of the final pyrolysis temperature (425, 450 and 475°C) on the gas separation properties was investigated and compared with those of PIA. The thermal treatments caused a progressive removal of the carboxylic acid pendant groups of PIA and a simultaneous increase of the fractional free volume of the PPMs. Thus, it was found that the permeability coefficients of PPMs were higher than that of PIA, between 6.5 and 25 times higher, depending on the gas tested and the final pyrolysis temperature, while the selectivity slightly decreased.

All PPMs were attractive materials to separate CO₂ from CH₄ since were inside the commercially interesting region and are close to the present Robeson trade-off limit line. The pyrolysis at 475°C yielded the PPM with the best performance: CO₂/CH₄ selectivity of 47 and CO₂ permeability close to 95 barrers.

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Please find enclosed the manuscript "Partially pyrolyzed membranes (PPMs) derived from copolyimides having carboxylic acid groups. Preparation and gas transport properties" which we are requesting to your consideration to be published in Journal of Membrane Science.

If there is any additional information needed, I will be pleased to comply and may be contacted at the numbers or addresses below.

Best Regards

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7 **Partially pyrolyzed membranes (PPMs) derived from copolyimides having**
8 **carboxylic acid groups. Preparation and gas transport properties.**
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5 **Abstract**
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9 A series of partially pyrolyzed membranes (PPMs) was prepared from a copolyimide
10 having carboxylic acid pendant groups (PIA). The effect of the final pyrolysis
11 temperature (425, 450 and 475°C) on the gas separation properties was investigated and
12 compared with those of PIA. The thermal treatments caused a progressive removal of
13 the carboxylic acid pendant groups of PIA and a simultaneous increase of the fractional
14 free volume of the PPMs. Thus, it was found that the permeability coefficients of PPMs
15 were higher than that of PIA, between 6.5 and 25 times higher, depending on the gas
16 tested and the final pyrolysis temperature, while the selectivity slightly decreased.
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19 All PPMs were attractive materials to separate CO₂ from CH₄ since were inside the
20 commercially interesting region and are close to the present Robeson trade-off limit
21 line. The pyrolysis at 475°C yielded the PPM with the best performance: CO₂/CH₄
22 selectivity of 47 and CO₂ permeability close to 95 barrers.
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45 **Keywords**
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48 Copolyimides, membranes, gas separation, pyrolysis, carboxylic acid groups.
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Introduction

Aromatic polyimides have been extensively used as gas separation membranes due to their excellent permeability-selectivity balance besides their high glass transition temperatures, thermal stability and good mechanical properties [1].

For these reasons, aromatic polyimides have been investigated as polymeric precursors for the preparation of carbon molecular sieve (CMS) membranes. CMS membranes have been fabricated from polyimide membranes by heating them up to very high temperatures (700-900°C), which causes the polyimide chain degradation to form a graphite-like structure. The pyrolysis conditions, such as temperature [2], time of pyrolysis and heating rate [1] have a considerable effect on the gas separation properties of the resulting CMS membranes. Moreover, the chemical structure and physical properties of the starting polyimide play also an important role in the final CMS membrane performance. Thus, the presence of bridging groups in the polymer chain such as $-\text{C}(\text{CF}_3)_2$ [3] or $-\text{CO}-$ [2] greatly affects the pore formation. Kim et al. have recently investigated the behaviour of CMS membranes derived from polyimides with pendant groups, such as carboxylic acid or sulfonic acid groups, and have confirmed that the removal of the pendant groups during the pyrolysis greatly increase their permeabilities [4,5].

Despite the proved advantages of the polyimide CMS membranes on gas separation, the polymer structure is not maintained after the pyrolysis and the mechanical properties of the carbonized membranes greatly drop by the high temperatures applied.

The use of polyimides that contain labile groups, suitable to be removed at relatively

1 low pyrolysis temperature, can afford interesting materials for gas separation since the
2 spaces occupied by the labile groups might be kept as microvoids after the pyrolysis
3 while the polyimide backbone prevails. To our knowledge, only one example of this
4 subject has been reported, where polyimides with different content of sulfonic acid
5 pendant groups (15-28 wt.%) have been pyrolyzed at 450°C. The gas transport
6 properties of these membranes were controlled by the -SO₃H content, which caused
7 microvoids when removed, increasing the gas permeability [6,7].
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17 In the case of polymeric membranes having carboxylic acid pendant groups, the
18 pyrolysis at relatively low temperature has not been yet studied. The side carboxylic
19 acid groups of polyimides can be removed at relatively low temperature (beyond 420°C)
20 whereas the decomposition of the polyimide backbone takes rise at higher temperature
21 (>500°C) [4,8,9]. Moreover, carboxylic groups behave in a different manner when
22 compared with other side groups because of their great tendency to form hydrogen
23 bonds, which generally enhances the polymer packing density [10]. In fact, carboxylic
24 acid groups have been extensively introduced in polyimides for several purposes such
25 as to get cross-linkable copolyimides membranes for gas separation [11], to modify the
26 physical aging rate [12] or more recently to get conductive copolyimide films [13].
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41 Thus, functionalized polyimides with the acid groups are interesting targets to explore
42 their gas separation properties after removing the carboxylic acid groups at relatively
43 low pyrolysis temperature.
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48 On the other hand, it has been well established for CMS that the final temperature of
49 pyrolysis has a great effect on the gas separation properties. It has been repeatedly
50 reported that an increase in the pyrolysis temperature does induce a significant decrease
51 in permeability with a simultaneous increase in selectivity due to the higher packing
52 degree of the CMS membranes [14-17]. At the light of this observation, it was also of
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interest to study the effect of increasing the treatment temperature of the polyimides to cause, besides the splitting off of the pendant carboxylic groups, changes in chain conformation and membrane topology that will affect the gas transport behaviour.

Thus, the main objective of this work has been to investigate the effect of the final pyrolysis temperature on the gas separation properties of copolyimides that contain labile groups. The study has focussed on the influence of three pyrolysis temperatures (425°C, 450°C and 475°C) on the gas transport properties of a copolyimide with carboxylic acid pendant groups (**PIA**, Scheme 1).

To confirm the role of the labile group's degradation on the gas permeation properties, the homologous copolyimide without carboxylic acid groups (**PIH**, Scheme 1) has been synthesized and included in this study.

2. Experimental Part

2.1. Materials

2,2-Bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (DA6F), 4,4'-oxydianiline (ODA) and *m*-phenylenediamine (MPD) were provided by Aldrich and sublimed before use. 3,5-Diaminobenzoic acid (DABA) was recrystallized twice from water.

Anhydrous N,N-dimethylacetamide (DMAc) (99.8%) was purchased from Aldrich and used as received.

Other solvents and reagents were used without further purification.

The purity of the gases employed for permeation measurements was greater than 99.5% for oxygen and methane and greater than 99% for the others.

2.2. Polymers syntheses

1 A mixture of ODA (5 mmol) and DABA or MPD (15 mmol) was dissolved in
2 anhydrous DMAc (40 mL) in a 100 mL three-necked flask under nitrogen atmosphere.
3
4 The solution was cooled to 0°C and then DA6F (20 mmol) was added portionwise for 5
5 min. The mixture was stirred for 12 h at room temperature and a very viscous clear
6 solution of polyamic acid was obtained in every case. Then, a mixture of acetic
7 anhydride (60 mmol) and pyridine (60 mmol), was added and the solution was stirred
8 for 6 h at room temperature and a further 45 min at 60°C. The viscous polyimide
9 solution was poured onto water and the precipitate formed was washed several times
10 with water and with boiling ethanol for 6 h in a Soxhlet. Copolyimide **PIA** was
11 redissolved in THF and poured onto ethanol for further purification. Then copolyimides
12 were dried in a vacuum oven at 120°C overnight, 30 min at 250°C and 5 min at 300°C.

26 **PIA:** κ_{inh} (dL/g) = 0.85; ¹H-NMR (DMSO_{d6}) (see Scheme 1): 7.24 (d, 1H, H_e), 7.50 (d,
27 1H, H_d), 7.79 (d, 2H, H_b), 7.86 (m, 0.75H, H_f), 7.97 (d, 2H, H_a), 8.16-8.22 ppm (m,
28 3.5H, H_c y H_g).

34 FT-IR: 3250-3500 (OH), 1790 (C=O st as) and 1722 (C=O st), 1358 (C-N st), 1242,
35 1185, 1142 and 1082 (C-O-C), 715 (OC-N-CO) cm⁻¹.

39 **PIH:** κ_{inh} = 0.40; ¹H-NMR (DMSO_{d6}) (see Scheme 1): 7.24 (d, 1H, H_e), 7.50 (d, 1H,
40 H_d), 7.56 and 7.58 (2xm, 2.25H, H_g y H_h), 7.71 (d, 2H, H_b), 7.78 (s, 0.75H, H_f), 7.96 (d,
41 2H, H_a), 8.19 ppm (d, 2H, H_c).

46 FT-IR: 1782 (C=O st as) and 1722 (C=O st), 1363 (C-N st), 1243, 1188, 1145 and 1103
47 (C-O-C), 715 (OC-N-CO) cm⁻¹.

54 2.3. Measurements

56 ¹H-NMR spectra were recorded on a Varian Gemini spectrometer at 300 MHz.

59 FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer

using polymer films.

Thermogravimetric analysis (TGA) were recorded on a TA Q-500 analyzer, using 5 mg of sample under a nitrogen atmosphere, by means of the Hi-Res Dynamic method where the heating rate is adjusted in response to changes in the rate of weight loss, which results in improved resolution.

Differential scanning calorimetry (DSC) data were obtained on a Perkin-Elmer DSC 7 analyzer from 5 mg samples heating at a 20°C/min between 50 and 450°C under a nitrogen atmosphere.

Densities were measured in a density balance by weighting the samples in air and then in a liquid of known density (isooctane in this case). The density of the sample was calculated from the expression:

$$\rho_{\text{sample}} = \rho_{\text{liquid}} \left(\frac{W_{\text{air}} - W_{\text{liquid}}}{W_{\text{air}}} \right)$$

The density data were used to evaluate chain packing by calculating the fractional free volume (FFV), which was estimated using the following relation:

$$\text{FFV} = (V_e - 1.3V_w) / V_e$$

Where V_e is the polymer specific volume and V_w is the van der Waals volume, which was given by the Hyperchem computer program, version 7.0 [18]

A barometric permeation method was used to determine steady state pure gas permeability at 30°C. The downstream pressure was kept below 10^{-2} mbar, while the upstream pressure was maintained at 3 atm. For the permeation experiments, helium, oxygen, nitrogen, methane and carbon dioxide were used.

Permeability values (P) were determined from the slope of downstream pressure versus time plotted once steady state had been achieved, according to the expression:

$$P = K (B \times L) / P_0$$

where K is an apparatus constant that joined some parameters such as temperature, cell

1 permeation area and volume of the system, B is the slope of downstream pressure
2 versus time, L is the film thickness and P_0 is the upstream pressure.
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4 Gas diffusivities (D) were estimated from time-lag data (θ), using the relation:
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$$6 \quad D=L^2/6\theta$$

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9 Apparent solubility coefficients, S, were estimated using the relation:
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$$11 \quad S= P/D$$

12 13 14 15 16 17 *2.4. Membrane preparation*

18 Copolyimide membranes were prepared by casting 10% (w/v) filtered NMP solutions of
19 polymers onto a glass plate for copolyimide **PIH**, and onto a Teflon plate for **PIA**
20 because of the polarity caused by introducing -COOH in the polymer chains. In every
21 case, most of the solvent was evaporated at 60°C overnight. Self supported films could
22 then be stripped off and were dried in a vacuum oven following the next protocol:
23 120°C/12h, 160°C/12h and 180°C/2h. The absence of residual solvent was confirmed by
24 TGA. Films thicknesses were 55-80µm.
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41 *2.5. Partially pyrolyzed membranes (PPMs)*

42 The partially pyrolyzed membranes (PPMs) were obtained in a Carbolite CTF 1200
43 furnace. Membrane disks (2.5 cm of diameter) were placed approx. in the middle of the
44 furnace tube, where they were subjected to a heating protocole under a nitrogen flow of
45 0.3 L/min.
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51 Figure 1 shows the temperature protocol for the three heating programs applied in this
52 work. In the first instance, the pyrolysis temperature of 425°C was reached by several
53 steps: the polymer films were heated from room temperature to 200°C at a rate of
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10°C/min, and the membranes were maintained at that temperature for 10 min; subsequently the temperature was raised to 300°C with at a heating rate of 5°C/min, and after 10 min at 300°C, the temperature was raised to 350°C at a rate of 3°C/min, and maintained for 10 min; then, the temperature was increased to 375°C at a rate of 1°C/min and maintained at that temperature for 10 min; finally the temperature was raised to 425°C at a heating rate of 0.5°C/min and was kept for 10 min.

The pyrolysis at 450°C was done following the same time-temperature program, but additionally the temperature was raised at 450°C at a heating rate of 0.5°C/min and was kept at that final temperature for 10 min.

The pyrolysis at 475°C was done following the above procedure but after 10 min at 450°C the temperature was raised at 475°C at a heating rate of 0.5°C/min and was kept at that final temperature for 10 min.

The cooling protocol consisted on shutting off the power of the apparatus and allowing the furnace to reach room temperature.

The partially pyrolyzed membranes (PPMs) obtained from the membrane containing carboxylic acid groups (**PIA**) were designed as **PPM-X** where X was the final pyrolysis temperature applied.

PIH membrane undergone the same pyrolysis treatments but the membranes obtained were brittle and their gas permeation measurement could not be tested.

Figure 1

3. Results and Discussion

3.1. Synthesis and characterization of copolyimides **PIA** and **PIH**

Both copolyimides were prepared by a standard two-step procedure (Scheme 1) in

1 which diamines ODA and DABA or MPD in 1:3 molar ratio were combined with an
2 equimolecular amount of dianhydride DA6F to polymerize at room temperature in
3 solution of DMAc. The intermediate poly (amic acid)s attained in this way were then
4 chemically imidized by dehydration with a mixture of acetic anhydride and pyridine.
5 Same procedure was previously reported by us for the synthesis of a copolyimide
6 containing dianhydride DA6F and diamines ODA and DABA in 1:1 molar ratio [8].
7 Xiao et al. have reported similar copolyimides with lower DABA content using *m*-
8 cresol as polymerization solvent [9].
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22 Scheme 1

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26 The novel copolymers were characterized by ¹H-NMR and FT-IR. The ¹H-NMR spectra
27 of both copolyimides showed all signals corresponding to the aromatic protons. The ¹H-
28 NMR spectrum of **PIA** did not show the peak corresponding to the -COOH groups, very
29 probably due to the interaction between the carboxylic acid groups, which can form
30 hydrogen bonds as has been earlier reported for other polyimides containing carboxylic
31 acid groups [8].
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41 The FT-IR spectra of both copolymers showed the characteristic bands of polyimides:
42 the stretching vibration band of C=O (1780 and 1725cm⁻¹), the asymmetric stretching
43 vibration of C-N (1360 cm⁻¹), the bands corresponding to the aromatic C-O-C stretching
44 (1240-1100 cm⁻¹) and the deformation of the imide ring band (720 cm⁻¹). The **PIA**
45 spectrum showed a very weak O-H vibrational band, at about 3500-3250 cm⁻¹, which
46 confirmed the association of the carboxylic acid groups. The carbonyl stretching of the
47 acid group was partially overlapped by the absorption of the imidic carbonyl.
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1 Thermal stabilities of all copolyimides were determined by thermogravimetric analysis
2 (TGA). Thermograms of **PIA** and **PIH** are shown in Figure 2. Thermal degradation of
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4 **PIA** occurred in two steps, at around 440°C and at very high temperature (520°C). The
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6 first one was attributed to the removal of the carboxylic acid groups and the weight loss
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8 was fairly coincident with the theoretical content of carboxylic acid groups in the
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10 polymer. This behaviour had been observed before for other polyimides containing
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12 carboxylic pendant groups [4,8,9]. The second step was associated with the polyimide
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14 decomposition. As it was expected copolyimide **PIH** showed only a degradation step
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16 with an initial decomposition temperature around 540°C.
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24 Figure 2

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29 Glass transition temperatures were determined by DSC (Table 1). The presence of acid
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31 groups greatly affected the Tg, and so, copolyimide **PIA** showed higher Tg than **PIH**.
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33 This was due to the strong interchain association through hydrogen bonds and dipolar
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35 attraction that brought about an increase of the polyimide rigidity.
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41 Table 1

42 3.2. Preparation and characterization of partially pyrolyzed membranes (PPMs)

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46 In this study, the same protocol was maintained for all processes, except the final
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48 pyrolysis temperature as the role of the final temperature was the subject of our interest.
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50 Thus, films from **PIA** and **PIH** were pyrolyzed at final temperatures of 425, 450 and
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52 475°C, following the procedure depicted in Figure 1. The pyrolysis was carried out in
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54 five steps, the two first steps were done at 10°C and 5°C /min heating rates respectively,
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1 up to 300°C. The following heating rates were lower, at 3°C and 1°C/min up to 375°C,
2 and the last heating rate was very slow, at 0.5 °C/min to reach the final temperature of
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4 425°C. At the end of each step, the temperature was maintained for 10 min. Above
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6 425°C, slow heating rates were also applied, 0.5 °C/min to achieve the final
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8 temperatures of 450 and 475°C.
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11 Pyrolyzed membranes from **PIA**, that is, **PPM-425**, **PPM-450** and **PPM-475**, were
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13 flexible and tough enough to be tested for gas permeation measurements. However **PIH**
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15 gave brittle films in all cases, so that they could not be evaluated as gas separation
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17 membranes. These results seemed to point out that the toughness of the pyrolyzed
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19 membranes was caused by the removal of the carboxylic acid groups. As it has been
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21 reported by Kratochvil and Koros [19], heating of acid containing polyimides can cause,
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23 first the formation of inter-chain anhydride linkages and eventually cross-linking
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25 through decarboxylations at high temperature.
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33 The thermal resistance of pyrolyzed membranes was investigated by TGA (Table 1 and
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35 Figure 3). Except for **PPM-425**, all pyrolyzed membranes showed a one-step pattern
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37 with decomposition onset at 550°C which confirmed the complete removal of the
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39 carboxylic acid groups after the thermal treatment. The degradation temperatures of the
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41 pyrolyzed membranes were some higher than for the corresponding precursor (**PIA**),
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43 which indicated that partial pyrolysis yielded more thermally stable membranes thanks
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45 to molecular packing and cross-linking. **PPM-425** showed two degradation steps. The
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47 first one corresponded to the loss of residual carboxylic acid groups that were not
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49 wholly removed during the thermal treatment.
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55 The char residue at 800°C increased slightly when the treatment temperature increased,
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57 which can be again associated to the higher amount of cross-linking. The thermal
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1 treatment and eventual cross-linking greatly affected the polymer segmental mobility,
2 thus, DSC curves of the pyrolyzed membranes showed no Tg inflection below 400°C.
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7 Figure 3
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11 To investigate how the pyrolysis could have affected the chemical composition of
12 copolyimides and to know whether chain degradation had occurred, FT-IR spectra of all
13 **PPMs** were recorded. Generally, when a polymer is thermally treated, the FT-IR spectra
14 change with the intensity of the treatments. Thus, the absorption intensity of specific
15 groups decrease and a widening of bands are produced upon heating, due to the
16 conversion of the polymer to a carbon structure [20]. However, in our case, all partially
17 pyrolyzed membranes showed identical FT-IR spectra with similar absorption
18 intensities and band wideness when compared to **PIA**.
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31 As an example Figure 4 shows the spectra of **PPM-475** and **PIA**. They exhibited the
32 characteristic bands of polyimides at 1780, 1725 and 720 cm^{-1} , the C-N asymmetric
33 stretching vibration at 1360 cm^{-1} and the four peaks corresponding to the aromatic C-O-
34 C stretch between 1240 and 1100 cm^{-1} . Thus, it could be stated that the **PPMs**
35 essentially maintained their aromatic polyimide structure after the pyrolysis.
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51 Figure 4
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55 3.3. Gas separation properties

56 3.3.1 Gas permeability

57 The gas permeabilities (P) of pure O₂, N₂, CH₄ and CO₂ through partially pyrolyzed
58 membranes and precursor membranes, **PIA** and **PIH**, are listed in Table 2. It can be
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1 observed that the permeability of **PPMs** was significantly higher than those of the
2 precursor membrane **PIA** and the reference membrane **PIH**, and (P) increased with the
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10 The increments of (P) of the pyrolyzed membranes, compared with **PIA** and **PIH**, are
11 depicted in Figure 5. The pyrolysis at 425°C roughly increased (P) between 6.5 and 9
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The increments of (P) of the pyrolyzed membranes, compared with **PIA** and **PIH**, are depicted in Figure 5. The pyrolysis at 425°C roughly increased (P) between 6.5 and 9 times, when compared with **PIA** (Figure 5a), depending on the gas tested. At 450°C the increases of (P) were greater, between 7.5 and 11.5 times, and finally after the pyrolysis at 475°C, (P) increased between 14 and 25 times. When **PPMs** were compared with **PIH** (Figure 5b), it could be noticed that **PPM-425** showed higher (P) coefficients (between 4 and 6.5 times), **PPM-450** exhibited (P) increments between 5 and 9 times and finally, **PPM-475** yielded the highest (P) increments, between 11 and 16 times. This result indicated that, through the removal of the carboxylic acid groups of copolyimide **PIA**, it was possible to achieve copolyimides with the same chemical structure than **PIH** but with higher permeability.

On analyzing the behaviour of the membranes against each gas, it could be noticed that O_2 and CO_2 were the most permeable and showed similar permeability increments after each thermal treatment. N_2 and CH_4 , which showed the smallest permeability coefficients, yielded the highest (P) increases, when the pyrolysis temperature was raised. Along with these positive results in permeability, a small decrease on permselectivity was observed for all the samples.

Table 2 and Figure 5

To understand the gas transport process it is helpful to split the permeability coefficient

1 into its kinetic parameter, diffusion coefficient (D), and its thermodynamic parameter,
2 solubility coefficient (S) (Table 3). D and S seemed to increase after each thermal
3 treatment, so that the P improvement was due to a simultaneous increase of both
4 parameters.
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11 Table 3
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16 Diffusion coefficients grew between 2.3 and 13.5 times (depending on the gas tested
17 and final pyrolysis temperature), whereas S improved only between 1.2 and 3.5 times,
18 indicating that the increase of diffusivity is the determining factor in the improvement
19 of gas permeability.
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25 The pyrolysis at 425°C increased D between 3.8 and 7.5 times, when compared with
26 **PIA**. At 450°C the increases of D were greater, between 4 and 9 times, and finally after
27 the pyrolysis at 475°C, D augmented between 6 and 13.5 times. When **PPMs** were
28 compared with **PIH**, it could be noticed that **PPM-425** showed higher D coefficients
29 (between 2.3 and 3.7 times), **PPM-450** exhibited D rises between 2.5 and 4.5 times and
30 finally, **PPM-475** yielded the highest D increments, between 3.5 and 6.7 times. As it
31 happened for P increments, the D growths were higher when **PPMs** were compared
32 with **PIA** than with **PIH**.
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46 The increases of D suggested that the removal of the carboxylic acid groups of **PIA**
47 improved the fractional free fraction volume (FFV) in the pyrolyzed membranes with a
48 growing effect on increasing the temperature. In order to confirm this assumption, the
49 FFVs of all pyrolyzed membranes and their precursors were estimated (Table 1).
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54 The FFV followed the same trend than permeability and diffusion coefficients, that is:
55 $FFV(\mathbf{PPM-475}) > FFV(\mathbf{PPM-450}) > FFV(\mathbf{PPM-425}) > FFV(\mathbf{PIH}) > FFV(\mathbf{PIA})$ which is in
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1 agreement with the statement that the removal of the carboxylic acid groups of **PIA**
2 gave rise to an increase of FFV and to an enhancement of the gas diffusion. Moreover,
3
4 the increase of the final temperature of pyrolysis seemed to cause not only the complete
5 removal of the pendant groups, but also changes in the FFV distribution, probably due
6
7 to the uncontrolled evolution of gases produced during the pyrolysis.
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11 **PIA** showed the lowest FFV because their chain packing was favoured by interaction
12 between the –COOH groups, which leads to a higher density and therefore to a lowest
13 fractional free volume, as it has been previously reported for other polyimides having
14 carboxylic acid groups [4, 11, 21]. Consistently, **PIA** exhibited the lowest permeability
15 and diffusion coefficients of the series.
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26 *3.3.2. Gas selectivity*

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28 The ideal separation factors of O₂/N₂ and CO₂/CH₄ pairs are listed in Tables 2 and 3.

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30 **PIA** and **PIH** were the most and least selective membranes respectively.

31
32 **PPM-425** and **PPM-450** showed similar O₂/N₂ and CO₂/CH₄ permselectivity values,
33
34 1.3 and 1.1 times lower than **PIA**. When pyrolysis was made at 475°C, the selectivity
35 drop was greater, 1.5 times for O₂/N₂ and 1.8 times for CO₂/CH₄. Thus, the thermal
36 treatment produced less selective membranes compared to the untreated one. This
37 behaviour is in agreement with that reported for sulfonated polyimide membranes which
38 had undergone partial pyrolysis at 450°C [6]. However this behaviour seems to be the
39 opposite of that observed for CMS membranes, where selectivity improves after
40 pyrolysis at high temperatures [2, 14-17]. Shigh-Ghosal et al., studying the effect of the
41 thermal treatment on the gas separation properties of CMS membranes, observed that
42 the use of relatively low temperatures, around 500°C, brought about an important
43 increase of permeability with slight gain of selectivity. They concluded that when the
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1 temperature is raised, permselectivity undergoes a sudden increase because
2 graphitization is favoured [3].
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4 Despite this small selectivity drop, **PPMs** exhibited excellent CO₂/CH₄ selectivities,
5 between 47 and 60, similar or higher than copolyimides recently reported [22-26].
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7 Nevertheless, these values are lower than those reported for carbon sieve membranes
8 derived from polyimides [1,15,16, 27-29]
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12 When **PPMs** were compared with **PIH**, no loose was observed as all membranes
13 showed similar selectivities for O₂/N₂ separation, between 5.3 and 6. Moreover, for
14 CO₂/CH₄ separation, all pyrolyzed membranes were more selective than **PIH** (between
15 1.3 and 1.7 times better).
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26 *3.3.3. Permeability-selectivity balance*

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28 In order to wholly characterize the performance of the membranes they were evaluated
29 in terms of the permeability-selectivity trade-off [30]. Thus, Figure 6 illustrates the
30 relationship between gas permeability and permselectivity for O₂/N₂ and CO₂/CH₄
31 separations. In both cases, when permeation properties of **PPMs** were compared with
32 **PIA** it could be established that the pyrolysis induced higher gas permeability and lower
33 selectivity.
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43 For O₂/N₂ separations only **PPMs** were located in the former Robeson upper bound [31]
44 and in the limit of the commercially interesting region.
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47 For CO₂/CH₄ separations, all membranes lied within the commercial region of interest.
48 Specifically, only **PPMs** were between the two trade-off lines [31, 32], which clearly
49 indicated that the pyrolysis process yields competitive membranes for this separation.
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58 Figure 6
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5 **Conclusions**
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7 The present study shows that the pyrolysis processes made at relatively low temperature
8 (from 425 to 475 °C) of a polyimide having carboxylic acid pendant groups (**PIA**), yield
9 tough membranes (**PPMs**) with better thermal stability than untreated **PIA**. **PPMs**
10 showed higher permeability coefficients and slightly lower selectivity than the
11 precursor, **PIA**, and were more permeable and selective than **PIH** (a copolyimide which
12 was taken as reference because it has the same chemical structure than **PPMs**).
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21 The permeability coefficients (P) increased with the final temperature of the pyrolysis.
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23 The increases in P were due to increments of both, diffusion (D) and solubility (S)
24 coefficients, being the gain in the diffusion coefficient the determining factor. The
25 increases of D were due to an increase of fractional free volume (FFV) which become
26 higher with the temperature.
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34 **PPMs** are attractive materials to separate CO₂ from CH₄ (all of these pyrolyzed
35 materials fall inside the commercially interesting region and are close to the present
36 empirical upper bound). **PPM-475** is of especial interest, displaying CO₂/CH₄
37 selectivity of 47 and CO₂ permeability close to 95 barrers.
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46 **Acknowledgements**
47

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49 (project MAT-2007-62392) is gratefully acknowledged.
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Table 1. Thermal and physical properties of starting copolyimides and partially pyrolyzed membranes (PPMs)

Copolyimide	Thermal Properties			Physical Properties			
	Tg(°C)	Td (°C)	Char yield (800°C, %)	ρ (g/cm ³)	V _e (cm ³ /g)	V _w (Å ³)	FFV
PIH	300	540	57.1	1.4526	0.6884	391.45	0.175
PIA	335	440 / 520	49.7	1.4801	0.6755	409.42	0.171
PPM-425	nd	430 / 550	52.9	1.4504	0.6894	404.32	0.178
PPM-450	nd	550	54.2	1.4331	0.6977	391.45	0.186
PPM-475	nd	550	56.1	1.4204	0.7040	391.45	0.193

nd = not detected

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Table 2. Gas permeabilities and selectivities of PIA, PIH and PPMs measured at 30°C and 3 atm.

Membrane	Permeability (Barrer)*				Permselectivities	
	P(O ₂)	P(N ₂)	P(CH ₄)	P(CO ₂)	P(O ₂)/ P(N ₂)	P(CO ₂)/ P(CH ₄)
PIH	1.95	0.36	0.17	5.98	5.4	35
PIA	1.61	0.20	0.06	5.22	8.0	87
PPM-425	10.45	1.74	0.65	39.1	6.0	60
PPM-450	12.79	2.21	0.87	52.0	5.8	59
PPM-475	22.17	4.21	2.02	94.8	5.3	47

*1 Barrer = 10⁻¹⁰ cm³(STP)cm/cm³ s cmHg

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Table 3. Diffusion ($D \times 10^8 \text{ cm}^2/\text{s}$), solubility coefficients ($S \times 10^3 \text{ cm}^3/\text{STP}/\text{cm}^3$ cmHg), and selectivities of PIH, PIA and PPMs at 30°C and 3 atm.

Membrane		O ₂	N ₂	CH ₄	CO ₂	O ₂ /N ₂	CO ₂ /CH ₄
PIH	D	1.60	0.54	0.04	0.40	2.96	10.00
	S	12.2	6.70	42.5	149	1.82	3.50
PIA	D	1.32	0.26	0.02	0.30	5.07	15.00
	S	12.2	7.70	30.0	174	1.58	5.80
PPM-425	D	5.14	1.29	0.15	1.32	3.98	8.80
	S	20.3	13.5	43.3	296	1.50	6.83
PPM-450	D	5.30	1.34	0.18	1.75	3.95	9.72
	S	24.1	16.5	48.3	297	1.46	6.14
PPM-475	D	8.03	1.91	0.27	2.44	4.20	9.03
	S	27.6	22.0	74.8	388	1.25	5.18

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Captions

Scheme 1. Synthesis of polyimides PIA and PIH

Figure 1. Pyrolysis protocole for PPMs

Figure 2. Thermogravimetical analyses of PIA and PIH

Figure 3. Thermogravimetical analyses of PPMs

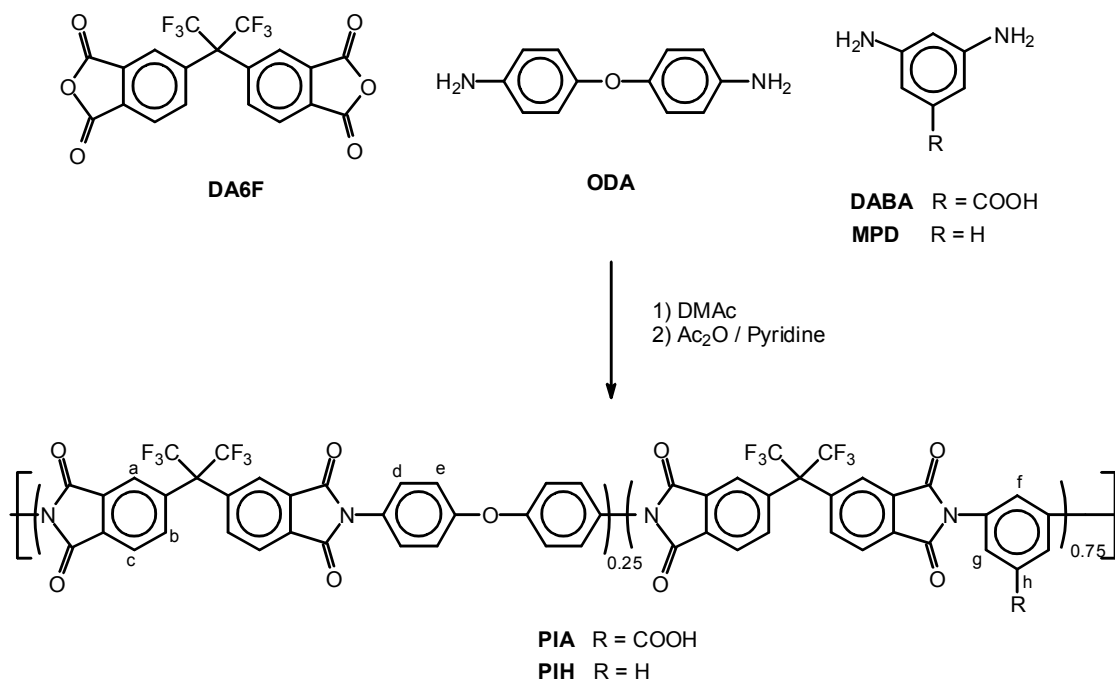
Figure 4. FT-IR spectra of PIA and PPM-475

Figure 5. Permeability increments of PPMs compared with PIA (a) and PIH (b)

Figure 6. Performance of PIA, PIH and PPMs for O₂/N₂ and CO₂/CH₄ separations

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Scheme1



Scheme 1

Figure1

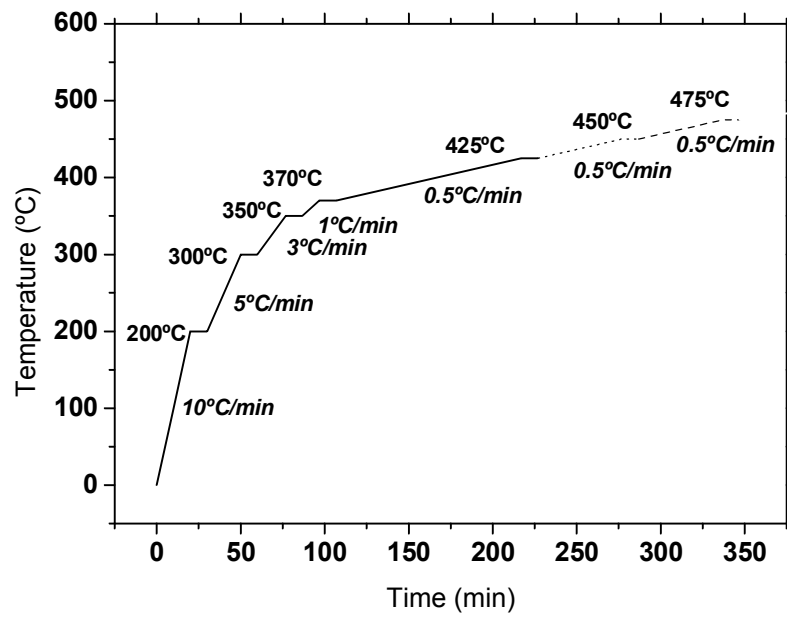


Figure 1

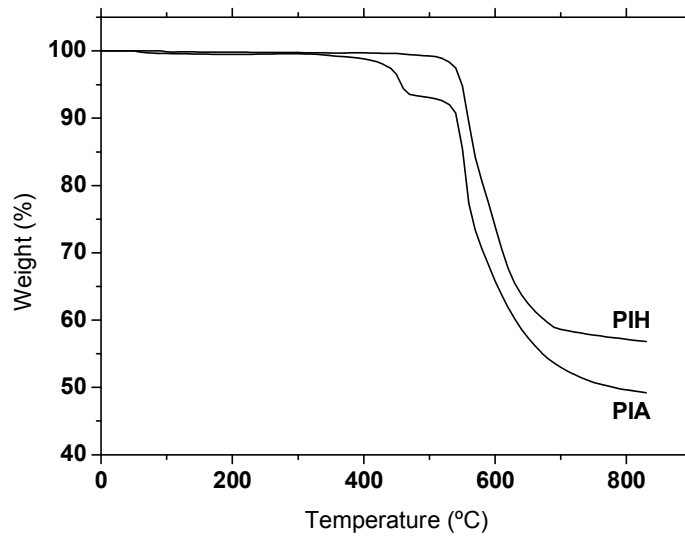


Figure 2

Figure3

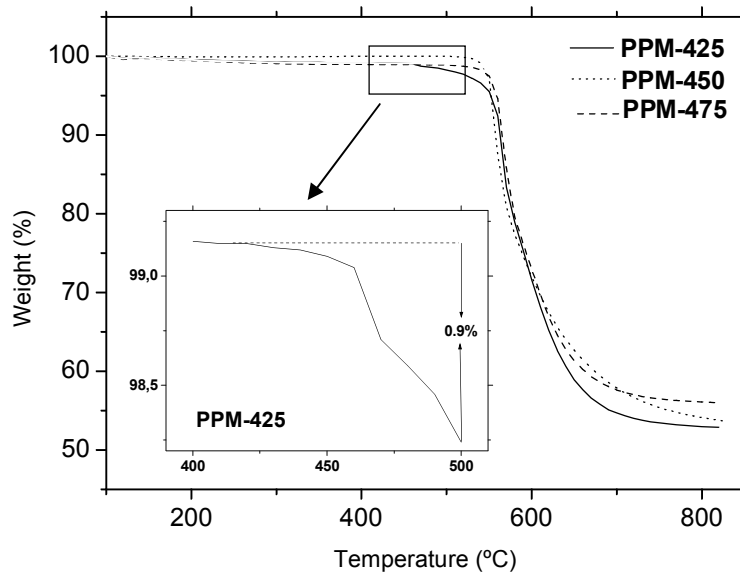


Figure 3

Figure4

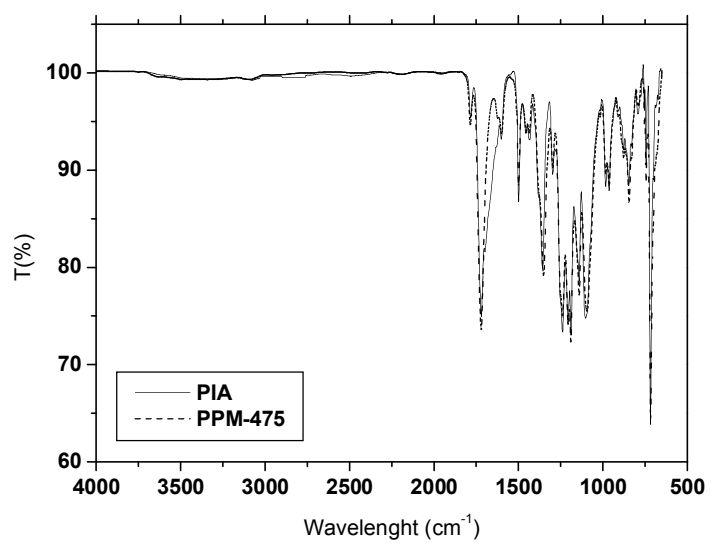


Figure 4

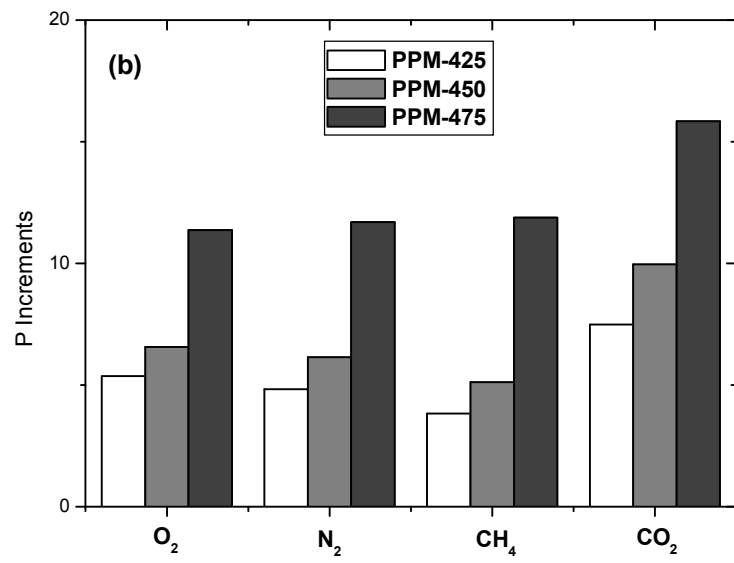
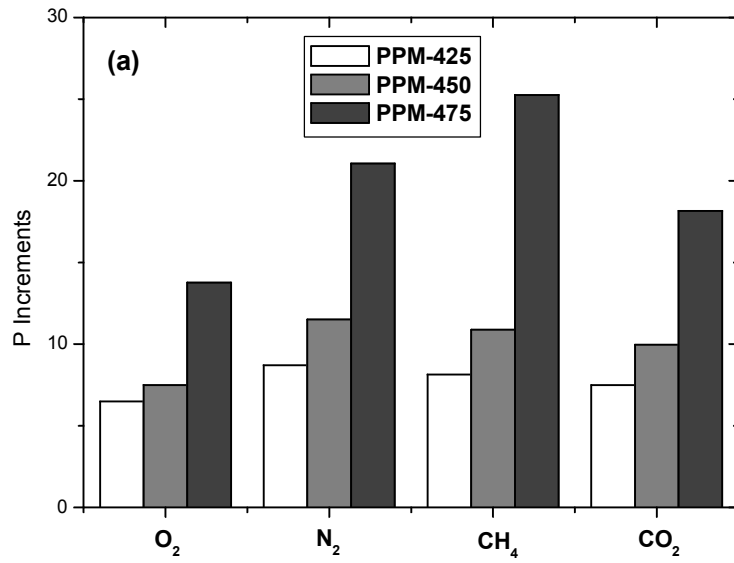


Figure 5

Figure6

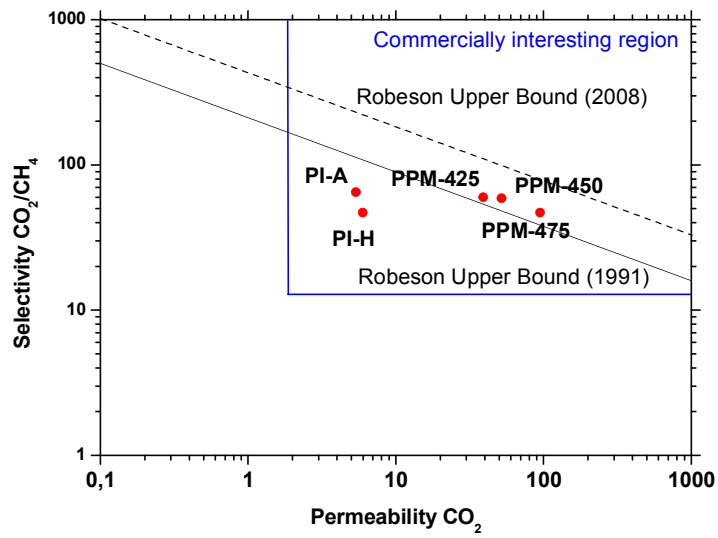
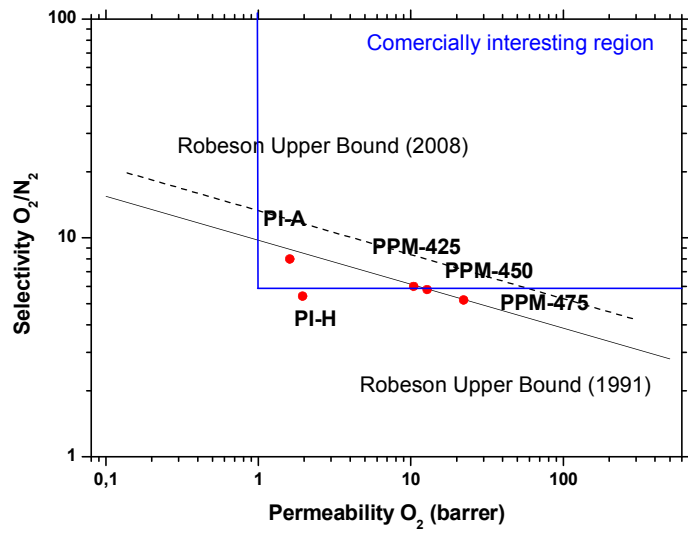


Figure 6