Thermal degradation of crosslinked copolyimide membranes to obtain productive gas separation membranes

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Abstract

Partially pyrolyzed membranes (**PPMs**) prepared by removing at 430ºC anhydride groups from cross-linked copolyimide membranes were investigated and related to the content of labile groups and also to the chemical composition of the copolyimide backbone. The spaces occupied by the linking anhydride groups prevailed as micropores, what greatly improved the gas transport properties.

The release of the labile groups was confirmed by TGA and FT-IR spectroscopy which permitted to establish that polymer main chains did not suffer any substantial change during the pyrolytic treatment. During the heating step new cross-linking points are created and no Tg below 450ºC could be observed and the process prevents the collapse of micropores.

The **PPM** attained from the precursor with the lowest content of anhydride groups showed the highest permeability values: 101, 25, 17 and 446 barrers to O_2, N_2, CH_4 and CO_2 respectively, and a selectivity to CO_2/CH_4 of 26 which are good enough to place this membrane close to Robeson's new upper bound (2008), while the cross-linked precursor membrane fell below Robeson's old upper bound (1991).

Keywords

Copolyimides–Anhydride groups- Membranes-Pyrolysis-Gas permeation

1. Introduction

Partial degradation of polyimides to remove labile side groups affords interesting materials for gas separations because the spaces occupied by these groups remain as micropores after the degradation, which helps for an increase of permeability. In the case of polyimides containing side carboxylic groups, the removal of the side groups occurs at temperatures between 375 and 475ºC while the polyimide backbone is not altered in a significant extent.

Islam et al. reported the first work on this subject, which involved the preparation of toughness and flexible pyrolytic membranes from sulfonated polyimides by removing the sulfonic acid pendant groups at 450ºC. The partially degraded membranes had better gas separation performance than that of the sulfonated precursors, as they showed high gas permeability and reasonably high selectivity, comparable to carbon sieve membranes (CMS). In this study they observed also that the gain in gas permeability was larger for the polyimides with higher sulfonic acid content [1]. Recently, Xiao et al. have published a work based on this approach applying a thermal treatment at 425ºC to copolyimides containing carboxylic acid groups with grafted cyclodextrine moieties. The cavities formed by the decomposition of cyclodextrine groups prevailed as micro-pores in the polymer matrix resulting in high permeability values. Besides, the high temperature produced cross-linking reactions by decarboxylation processes that rigidized the polymer matrix increasing the gas selectivity.

Despite the partial degradation, these membranes have acceptable mechanical properties and high thermal stability, and they could replace the carbon molecular sieve separation membranes (CMS) because although the latter display the best known gas separation properties [4-6] its practical application is very limited due to inherent brittleness.

In the case of polyimides having carboxylic acid pendant groups, the release of acid groups takes place beyond 420ºC while the decomposition of the polyimide backbone proceeds at higher temperature (>500ºC) [7]. In this regard, it has been demonstrate that carboxylic acid pendant groups can be removed at higher temperatures (up to 475ºC) without any substantial effect on the structure of the polyimide backbone [6]. After removing the carboxylic acid groups the membranes showed significantly higher permeability (gas flux) than the starting polyimide, between 6.5 and 25 times higher, depending on the gas tested and the final temperature [7]. The free carboxylic acid groups of these copolyimides have been commonly incorporated using 3,5-diamino benzoic acid as comononer [2, 8-16] and, in some cases, the free –COOH groups were made to react with diamines or diols to get cross-linked copolyimides for pervaporation experiments or to suppress plasticization. [8-11, 13, 15] Another way to get cross-linked membranes is by the formation of new covalent bonds between benzene rings due to decarboxylation process that occurs by heating the membrane at a temperature 15° higher than the glass transition temperature [3]. Recently, we have demonstrated the formation of anhydrides by direct condensation between the free carboxylic acid groups of copolyimides upon heating the membranes at 400ºC for some minutes [17]. This study revealed also that the membranes with the smallest amount of interchain anhydride linkages exhibited the lowest densities and the best gas transport properties [17]. The formation of anhydride has been also recently supported by Askari et al. who have proposed this cross-linked structure when membranes containing carboxylic acid groups grafted with cyclodextrine groups were thermally treated below 350ºC [3]. The anhydride groups can be considered as labile moieties since their degradation can occur at similar temperatures as carboxylic acid groups [7]. Based on these antecedents, we report in this work the effect that the loss of anhydride groups have on the gas permeation properties of cross-linked membranes prepared from copolyimides containing –COOH free groups.

Figure 1 shows a schematic representation of this evolution up to the partially pryrolyzed membranes (**PPMs**) which showed also a cross-linked structure due to the decarboxylation process [3,16]. The gas separation properties of these **PPMs** have been investigated in this work and compared with those previously obtained for the precursor membranes.

To endorse the role of the labile groups removal on the gas permeation properties two copolyimides without side groups have been synthesized and included in this study.

Figure 1

2. Materials and methods

2.1. Materials

2.2.1 Monomers

2,2-Bis(3,4-dicarboxyphenyl) hexafluoropropanedianhydride (**6FDA**), m-phenylenediamine (**mPD**) and 2,4,6-trimethyl-1,3-phenylenediamine (**A**) were provided by Aldrich and were purified by sublimation.

bis(4-Amino-3-isopropyl-5-methylphenyl)methane (**B**) was supplied by Across and was recrystallized three times from hexane [18].

2.2.2.Polymers

Copolyimides containing –COOH side groups and the corresponding cross-linked dense membranes (**ADABA-75**, **ADABA-50**, **ADABA-25**, **BDABA-75**, **DBADA-50** and

BDABA-25, Figure 2) were prepared as previously reported [17].

Reference copolyimides without labile side groups, **AmPD-25** and **BmPD-25** (Figure 6) were synthesized following a general method reported elsewhere [6].

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. Preparation of Partially Pyrolyzed Membranes

The partially pyrolyzed membranes (**PPMs**) were obtained in a Carbolite CTF 1200 furnace. Membrane disks (2.5 cm in diameter) were placed approx. in the middle of the furnace tube, where they were subjected to the heating protocol depicted in Figure 3 under a nitrogen flow of 0.3 L/min.

2.3. Measurements

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.

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:

$$\rho_{sample} = \rho_{liquid} \left((w_{air}-w_{liquid})/w_{air} \right)$$

The gas permeation properties were determined for single gas feeds using a constant volume/variable pressure apparatus at 30ºC.The initial downstream pressure was kept below 10^{-2} mbar, while the upstream pressure was maintained at 3 atm. For the permeation experiments, high purity 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:

$$P= K (BxL)/P_0 \tag{1}$$

where K is an apparatus constant that includes parameters such as temperature, cell permeation area and volume of the system, B is the slope of downstream pressure versus time, L is the film thickness and P_0 is the upstream pressure.

The diffusion coefficients (D) were estimated from time-lag data (θ), using the relation:

$$D=L^2/6\theta \tag{2}$$

where θ is the permeation time-lag. Once P and D were calculated, the apparent solubility coefficients (S) were evaluated by means of the following expression:

$$S= P/D \tag{3}$$

The ideal separation factors were calculated from the ratio of permeability coefficients:

$$\alpha_{A/B} = P_A/P_B \tag{4}$$

where P_A and P_B refer to the permeability coefficients of pure gases A and B, respectively. By substituting Eq.(2) into Eq.(4), the ideal separation factor can be split into two parts:

$$\alpha_{A/B} = \left(\frac{D_A}{D_B}\right)\left(\frac{S_A}{S_B}\right) \tag{5}$$

where D_A/D_B is the diffusivity selectivity and S_A/S_B is the solubility selectivity.

To ensure reproducibility of results, each membrane was measured at least twice.

3. Results and Discussion

*3.1. Preparation and characterization of partially pyrolyzed membranes(**PPMs**)*

The partially pyrolyzed membranes (**PPMs**) of this work were obtained by removing the anhydride groups of two series of cross-linked copolyimide membranes prepared from copolyimides containing –COOH free groups [17]. So, anhydride groups are located as cross-linking sites between polyimide chains. The series A encloses 2,4,6-trimethyl-1,3-phenylenediamine (**A**) and the series B has a more flexible diamine, bis(4-amino-3-isopropyl-5-methylphenyl)methane (**B**), so that the **PPMs** prepared were designed as **PPM-A-X** or **PPM-B-X** depending on the starting copolyimide membrane used, and X refers to carboxylic acid content of the copolyimide precursors (Figure 2).

Figure 2

The temperature protocol applied to remove the anhydride groups has been depicted in Figure 3. It consisted of six successive heating stages, maintaining the membrane 10 min at the final temperature of each step. Thus, the polymer films were first heated from room temperature to 100ºC at a rate of 10ºC/min. Then the temperature was raised to 150ºC with at a heating rate of 5ºC/min and to 200ºC at a rate of 3ºC/min. After that, the temperature rose to 250ºC at a rate of 1ºC/min and to 375ºC at a rate of 0.5ºC/min, and finally to 430ºC at a heating rate of 0.1ºC/min. Once the pyrolysis was completed, the furnace was turned off and allowed to reach room temperature.

Figure 3

The removal of anhydride groups was checked using thermogravimetrical analysis (TGA). Figure 4 shows the TGA thermograms of a precursor copolyimide membrane (**ADABA-25**) and the corresponding **PPM**. Thermal degradation of the starting copolyimide membrane occurred in two steps, the first one took place above 440ºC and was associated with the loss of the anhydride groups, and the second one occurred at a higher temperature (over 520-520ºC) and it was associated with the generalized aromatic polyimide decomposition [17]. Consistently, the **PPM** exhibited a thermogram curve with a one-step decomposition pattern, which indicated the complete release of the anhydride groups at the end of the thermal treatment.

Figure 4

PPM of series A (Table 1, Figure 5 up) showed an initial decomposition temperature (T_d) between 520-525ºC and **PPMs** of series B (Table 1, Figure 5 down) between 510-525ºC. In both series the values are closed to those of the corresponding starting cross-linked copolyimide membrane. This indicated that partial pyrolysis yielded also very thermally stable membranes, and it is in agreement with data reported for other partially pyrolyzed membranes [2,6].

Table 1 and Figure 5

In both series, the char yield at 800ºC increased slightly when the amount of removed anhydride groups increased, which can be associated with a higher amount of cross-linking. This fact was in agreement with Kratochvil et al. who reported that decarboxylation process of polyimides containing carboxylic acids groups induce cross-linking reactions [16].

If cross-linking through recombination of radicals, which could have been formed by the removal and splitting of anhydride groups, did not reach significant extent, the chemical structure of the copolyimides of **PPMs** after removing the labile groups should be similar to the structures depicted in Figure 6. Thus, for comparative purposes the reference copolyimides without labile groups**,** **AmPD-25** and **BmPD-25** were synthesized and included in this work.

Figure 6

To check if partial pyrolysis affected the polyimide main chain, TGA curves and FTIR spectra of **PPM-A-25** and **PPM-B-25** were compared with the corresponding reference copolyimides, **AmPD-25** and **BmPD-25** respectively.

The TGA thermograms of Figure 7 shows that both pyrolyzed membranes have the same degradation pattern with identical decomposition temperature and quite similar char yield that their counterpair reference copolyimides.

Figure 7

Both partially pyrolyzed membranes showed also virtually identical FT-IR spectra as the corresponding reference copolyimides, which indicated that the aromatic polyimide structures prevailed after the partial pyrolysis. FT-IR spectra of polyimides tend to change when they are subjected to extreme thermal treatments. Thus, the absorption intensity of specific groups decrease and a widening of bands can be observed upon heating, due to the progressive conversion of the polymer into a carbon structure [19]. However, in our case the pyrolyzed membranes exhibited the characteristic bands of polyimides at 1780, 1725 and 720 cm^{-1}, the C-N asymmetric stretching vibration at 1360 cm^{-1} and the peaks corresponding to the aromatic C-O-C stretching between 1240 and 1100 cm^{-1}. Reference copolyimides showed all these characteristic bands too, which confirmed the statement that **PPMs** of this work essentially hold their chemical architecture after the severe thermal treatment applied for removing anhydride cross-linking bridges.

Kratochvil et al. have proposed that cross-linking sites are actually produced by the formation of aryl radicals during release of side groups [16]. These authors have also reported that these cross-linking points do not alter significantly the FT-IR spectra, so one cannot confirm the existence of crossover points with only this technique.

As an example, Figure 8 shows the FT-IR spectra of **PPM-B-25** and **BmPD-25,** where a great similarity between both structures can be seen.

Figure 8

To further investigate the actual chemical morphology of **PPMs**, evidences were sought using DSC and comparing the results of solubility in organic solvents. DSC curves of the pyrolyzed membranes showed no Tg inflection below 450ºC, and this can be attributed to this cross-linking induced by the thermal treatment that greatly affected the polymer segmental mobility.

As it was reported for the cross-linked membrane with anhydride groups [17], all **PPMs** were also completely insoluble in any solvent which confirmed the presence of cross-linking after the elimination of the anhydrides groups.

3.2. Gas separation properties

Although pyrolysis provides a cross-linked structure that theoretically hinders the collapse of pores [2], all membranes were measured after 1000 h to ensure the permanence of micropores.

3.2.1. PPM-B series

All pyrolyzed membranes derived from series B were suitable to be evaluated as gas separation membranes as they exhibited good mechanical resistance, yet the severe heating treatment turned the films black. Data of permeability coefficients (P), diffusivity (D), solubility (S) and ideal selectivity for O_2, N_2 ,CH_4 and CO_2 have been listed on Table 2 together with those of their precursors [17]. For a better comparison of the data, permeability coefficients have been graphically represented in Figure 9.

All **PPMs** exhibited higher P than that of the corresponding copolyimide membrane precursors, between 2.5 and 7.7 times higher, depending on the gas tested. It can be seen that the greater the number of available anhydride groups the greater the gain in permeability, which confirmed the positive effect of removing labile groups on gas separation properties. On the other hand, the starting copolyimide with the lowest labile groups content yielded the membrane with the highest permeability of this series [17]. As happened with its precursor membrane, **PPM-B-25** was the most permeable membrane of this series with P(O_2) and P(CO_2) around 100 and 450 Barrers respectively, whereas **PPM-B-75** and **PPM-B-50** exhibited similar permeability coefficients.

Table 2 and Figure 9

Consistently with the improvements observed in permeability, the density values found for pyrolyzed membranes (Table 2) were lower than those of the corresponding precursors. When **PPM-B-25** was compared with its reference copolyimide (**BmPD-25**) (see Table 2) a great difference in permeability was noticed, the pyrolyzed one showing much higher permeability coefficients, between 5 and 6.5 times higher. This result confirmed also the positive effect of removing labile groups from polymer membranes; as a matter of fact **PPM-B-25** has the same chemical structure as its homologous **BmPD-25** but is much more permeable and it has a lower density.

On analyzing the diffusion coefficients (D) and solubility coefficients (S), it is to notice that all **PPM-B** not only showed higher D than the corresponding membrane precursors due to the high free volume generated after the thermal treatment, but they showed also higher S. Islam et al observed also that pyrolytic membranes had higher S than the polyimide precursors and attributed this behavior to the larger amount of microvoids generated after the thermal process [1]. Thus, the increment of P in the pyrolyzed membranes was endorsed to the increase of diffusivity and solubility.

In order to wholly characterize the performance of these membranes they were evaluated in terms of the permeability-selectivity balance because polymeric membranes undergo a trade–off limitation between permeability and selectivity: as selectivity increases, permeability decreases, and vice versa. In 1991, Robeson collected for the first time the gas permeation data of a lot of polymeric membranes and established that an empirical upper limit existed in a permeability-selectivity diagram [20]. Figure 10 illustrates the relationship between gas permeability and permselectivity for CO_2/CH_4 separation of membranes of B series. As a general rule, the permselectivity to the pair O_2/N_2 of pyrolyzed membranes was similar to those of the membrane precursors but the selectivity to CO_2/CH_4 was slightly higher in the new materials.

All precursor cross-linked membranes containing anhydride groups fell below Robeson's old upper bound (1991) whereas all pyrolyzed ones exceeded it, moreover **PPM-B-25** and **PPM-B-75** are close to Robeson's newest upper bound (2008) [21]. This result indicated that **PPMs** of series B have promising CO_2/CH_4 separation properties.

Figure 10

3.2.2. PPM-A series

Among the pyrolyzed membranes of series A, only the membrane prepared from the copolyimide with the lowest anhydride content (**PPM-A-25**) was flexible and tough enough to be tested as gas transport material. Unfortunately, **PPM-A-75** and **PPM-A-50** gave brittle films and they could not be evaluated. The reference copolyimide membrane without labile groups (**AmPD-25**) did not present also suitable mechanical properties to be studied. This fact could be attributed to the high rigidity of these polymers imparted by diamine A [17]. However, the gas separation parameters of **AmPD-25** were previously reported [22] and we have used them for comparison.

PPM-A-25 exhibited higher permeability coefficient (P) than its precursor and reference membranes (Table 3 and Figure 11). This confirmed again the helpful effect of removing the anhydride groups at high temperature. As it was expected, **PPM-A-25** showed also the lowest density of this group of membranes (Table 3) following the same trend than the gain of free volume after the thermal treatment.

The gas selectivity of **PPM-A-25** to the pair O_2/N_2 was lower than that of the precursor, and lower also than that of the reference membrane, and only the selectivity to CO_2/CH_4 was slightly higher.

Table 3 and Figure 11

The performance of **PPM-A-25** for CO_2/CH_4 separations is depicted in Figure 12. The pyrolyzed membrane lies above the Robeson's old upper bound (1991) whereas its precursor membrane remained below it. However, the reference membrane **AmPD-25** exhibited the best gas separation properties since it was between the two limits. This result indicated that for series A the direct synthesis of the copolyimide without side groups would be preferable to its preparation by controlled pyrolysis.

Figure 12

3.2.Comparison between PPM-B-25 and PPM-A-25

When permeability coefficients of both pyrolyzed membranes were compared together with the reference membranes (**BmPD-25** and **AmPB-25**) (Figure 13), two remarkable facts were observed: first, **AmPD-25** showed higher permeability coefficients than **BmPD-25** whereas the pyrolyzed membranes showed the opposite trend; second, the increase of permeability coefficients observed for **PPM-B-25** respect to **BmPD-25** was much greater than the increase achieved by **PPM-A-25** respect to its reference membrane. These results could be attributed to differences in the flexibility of polymer backbones. The copolyimide chains of **PPM-B-25** should have more flexibility, imparted by comonomer B, which is longer than comonomer A and has a linking CH_2

group between the two benzene rings; therefore they are easier to move during the pyrolysis process and are more prone to create a much more open structure, with an easier access for gas molecules. As a consequence, this pyrolyzed membrane was more permeable than **PPM-A-25**. In general terms, the difference between the densities of both pyrolyzed membranes was consistent with the observed permeability differences. Thus, it can be established that not only the removal of anhydride groups plays a beneficial role but also the flexibility of the polymer chain may positively contribute to improve the permeability coefficient.

Figure 13

Conclusions

The present work shows that partial pyrolysis at 430ºC of copolyimide membranes having anhydride groups as cross-linking bonds can afford partially pyrolyzed membranes (**PPMs**) whose properties depend on the anhydride groups content of the starting membrane and also on the chemical structure of the polymer main chain. In the course of this research it could be demonstrated that those copolyimides containing anhydride linking groups and the co-monomer bis(4-amino-3-isopropyl-5-methylphenyl)methane (series **B**) yielded **PPMs** with better mechanical properties than **PPMs** derived from copolyimide membranes containing co-monomer 2,4,6-trimethyl-1,3-phenylenediamine (series **A**).

During the thermal treatment new cross-linking points are formed that helps to prevent the collapse of the micropores created after anhydride removal.

PPM from series B exhibited higher permeability coefficients and slightly higher

CO_2/CH_4 selectivity than the cross-linked precursor membranes. The **PPM** prepared from the copolyimide with the lowest anhydride content, **PPM-B-25**, showed the highest permeability coefficients of this series with values to O_2, N_2, CH_4 and CO_2 of 101, 25, 17 and 446 barrers respectively. Thus, this pyrolyzed membrane was positioned near the Robeson's new upper bound (2008) for the pair CO_2/CH_4 while its precursor membrane kept below Robeson's old upper bound (1991).

On comparing the permeation properties of two pyrolyzed membranes, **PPM-A-25** and **PPM-B-25**, and the homologous lineal copolyimides without labile groups, **AmPD-25** and **BmPD-25,** it could be realized that pyrolysis yielded more permeable membranes and that the chemical composition played also an important role, particularly the flexibility of the polymer chain. Thus, **PPM-B-25** exhibited greater permeability coefficients than those of **PPM-A-25** and much greater than that of **BmPD-25**.

As a final conclusion it can be stated that controlled pyrolysis of polyimides and copolyimides can render polymer membranes with a real potential for gas separation.

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Table 1.Thermal properties of PPMs compared with the corresponding precursor membranes.

Membrane	Td(1st step)	Td(2nd step)	Residue (800ºC)
ADABA-75(1)	445	525	51
ADABA-50(1)	440	520	49
ADABA-25(1)	430	520	53
PPM-A-75	525		59
PPM-A-50	535		57
PPM-A-25	525		56
BDABA-75(1)	440	520	47
BDABA-50(1)	430	500	57
BDABA-25(1)	440	510	57
PPM-B-75	525		64
PPM-B-50	515		62
PPM-B-25	510		58

(1) Data taken from reference [17]

Table 2. Permeability (P, Barrers*), diffusion coefficient (D x 10^8 cm^2/s), solubility coefficient (S x 10^3 cm^3/STP/cm^{3}cmHg, selectivity at 3 atm and density values of PPMs of series B, precursor membranes and reference copolyimide .

Polyimides (NMP films)		O_2	N_2	CH_4	CO_2	O_2/N_2	CO_2/CH_4	Density(g/mL)
BDABA-75	P(1)	7.96	1.65	0.91	27.91	4.82	30.67	1.393(1)
	D(1)	5.55	1.47	0.33	1.56	3.77	4.72	
	S(1)	14.3	11.2	27.5	179	1.2	6.5	
PPM-B-75	P	41.86	8.82	4.99	187.27	4.74	37.52	1.346
	D	12.68	3.38	0.61	5.13	3.75	8.40	
	S	33.01	26.09	81.80	365.04	1.26	4.46	
BDABA-50	P(1)	16.34	3.65	2.54	51.30	4.47	20.19	1.325(1)
	D(1)	7.11	3.88	0.63	2.91	1.83	4.61	
	S(1)	22.9	9.4	40.3	176	2.4	4.3	
PPM-B-50	P	40.20	9.03	6.34	175.92	4.45	27.74	1.296
	D	19.48	5.45	1.08	8.08	3.57	7.48	
	S	20.63	16.56	58.70	217.72	1.24	3.70	
BDABA-25	P(1)	30.18	8.36	6.19	123.67	3.61	19.97	1.257(1)
	D(1)	20.37	7.65	2.46	7.92	2.66	3.21	
	S(1)	14.8	10.9	25.1	156	1.3	6.2	
PPM-B-25	P	101.30	25.26	17.10	446.43	4.01	26.10	1.226
	D	37.58	9.36	2.03	14.33	4.01	7.06	
	S	26.95	26.98	84.23	311.53	0.99	3.69	
BmPD-25	P	20.25	4.79	2.59	90.23	4.22	34.83	1.256
	D	12.91	5.53	0.71	4.43	2.33	6.24	
	S	15.68	8.66	36.47	203.67	1.81	5.58	

(1) Data taken from reference [17]

*1 Barrer = 10^{-10}cm^3(STP)cm/cm^3 s cmHg

Table 3. Permeability (P, Barrers*), diffusion coefficient (D x 10^8 cm^2/s), solubility coefficient (S x 10^3 cm^3/STP/cm^{3}cmHg), selectivity at 3 atm and density values of **PPM-A-25**, **ADABA-25** and **AmPD-25** membranes .

Polyimides (NMP films)		O_2	N_2	CH_4	CO_2	O_2/N_2	CO_2/CH_4	Density(g/mL)
ADABA-25	P(1)	39.58	9.49	6.49	145.28	4.17	22.38	1.355(1)
	D(1)	21.64	6.58	1.25	6.92	3.28	5.54	
	S(1)	18.2	14.4	51.9	209	1.2	4.03	
PPM-A-25	P	64.49	17.73	9.70	240.96	3.64	24.84	1.322
	D	22.71	13.88	1.76	9.66	1.63	5.48	
	S	28.39	12.77	55.11	249.44	2.22	4.52	
AmPD-25	P(2)	38.87	8.86	5.79	195.16	4.39	33.70	1.372(2)
	D(2)	17.41	4.80	0.98	6.31	3.62	6.43	
	S(2)	22.32	18.45	59.08	309.28	1.20	5.23	

(1) Data taken from reference [17] (2)Data taken from reference [22]

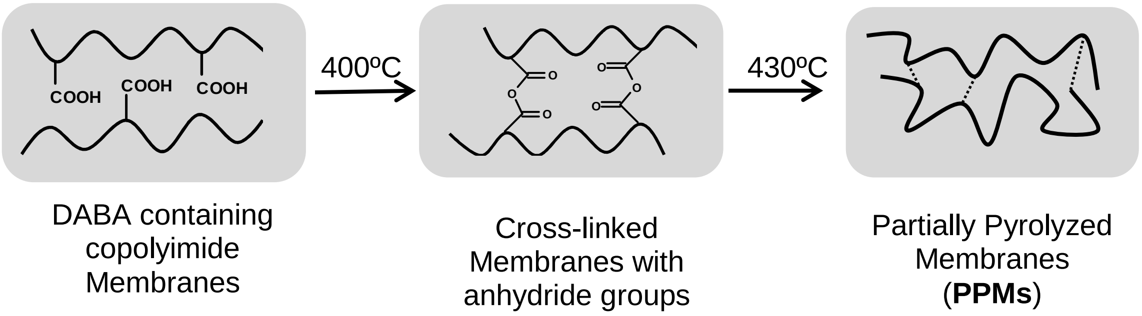


Figure 1. Schematic representation of the evolution of DABA-containing copolyimide Membranes to Partially Pyrolyzed Membranes (**PPMs**)

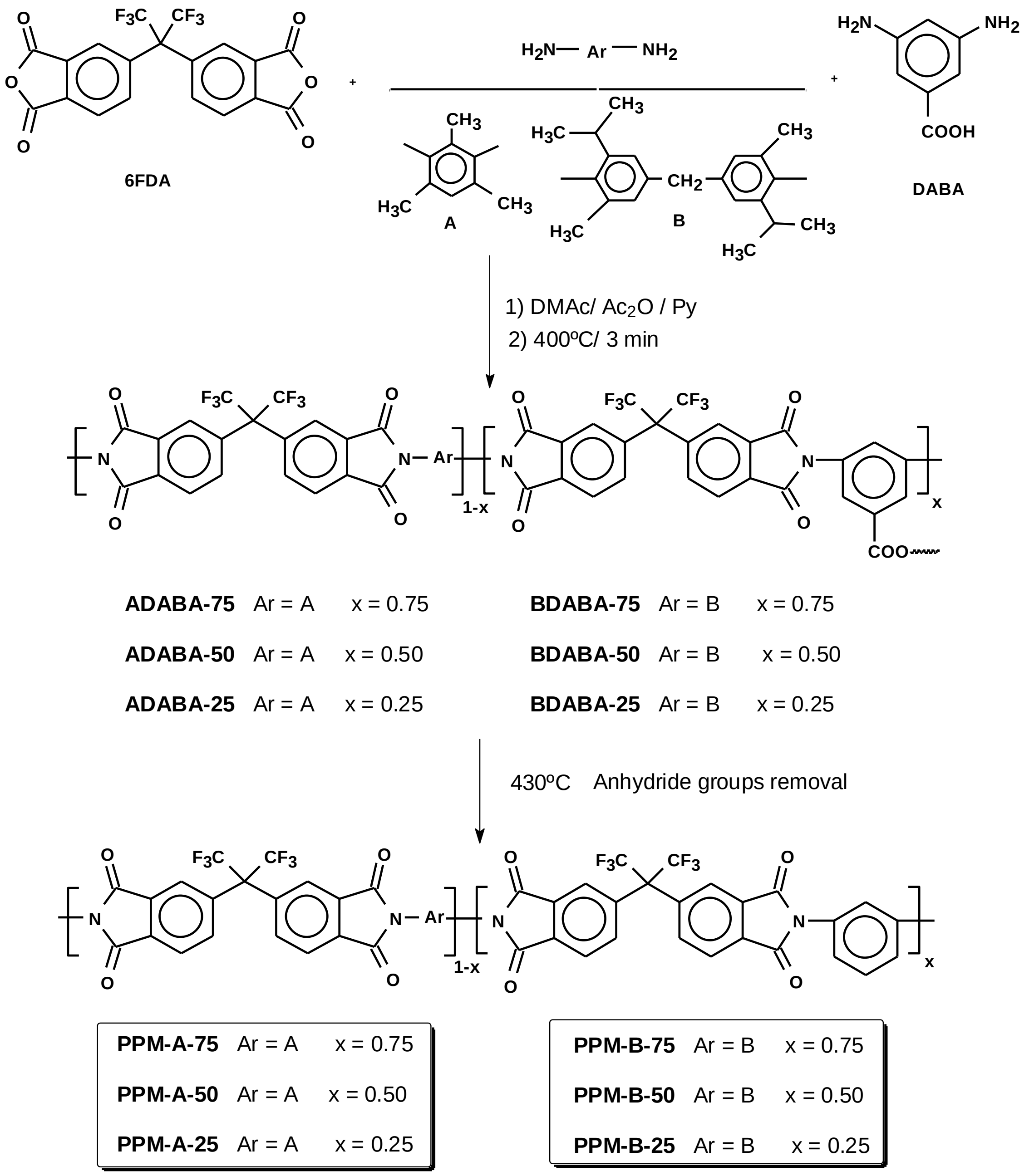


Figure 2. Structure and designation of cross-linked copolyimide membranes and partially pyrolyzed membranes (**PPMs**)

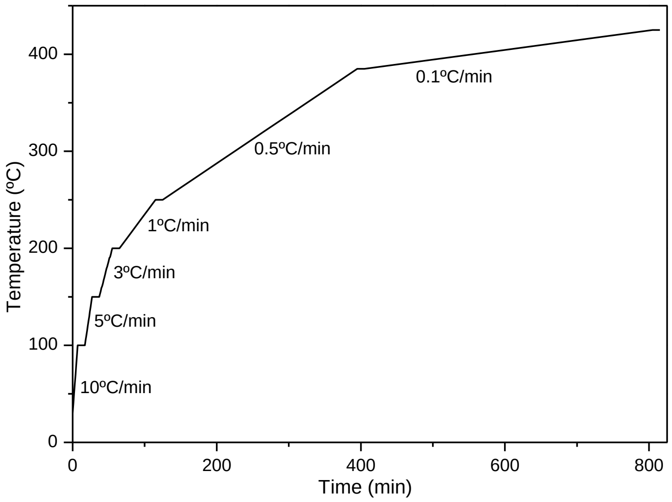


Figure 3. Pyrolysis Protocol for **PPMs**

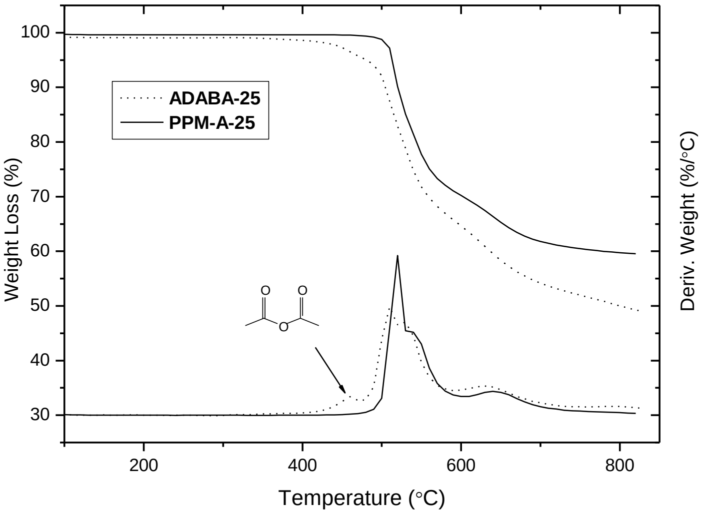
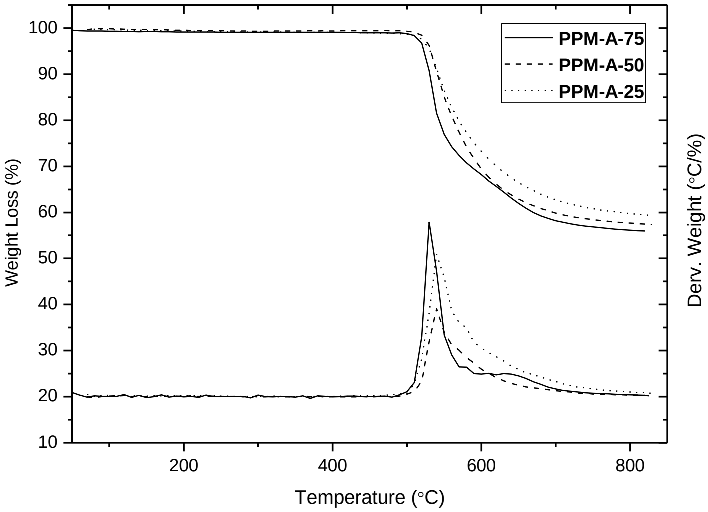


Figure 4. Thermogram of a partially pyrolyzed membrane (**PPM-A-25**) compared with the starting copolyimide membrane (**ADABA-25**).



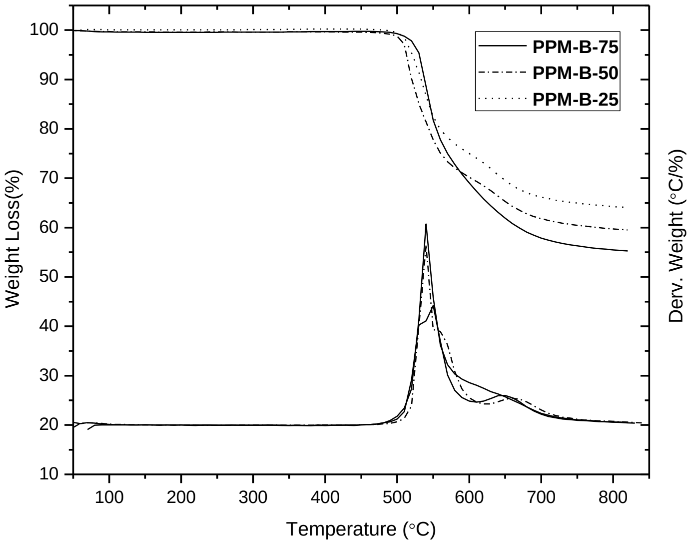
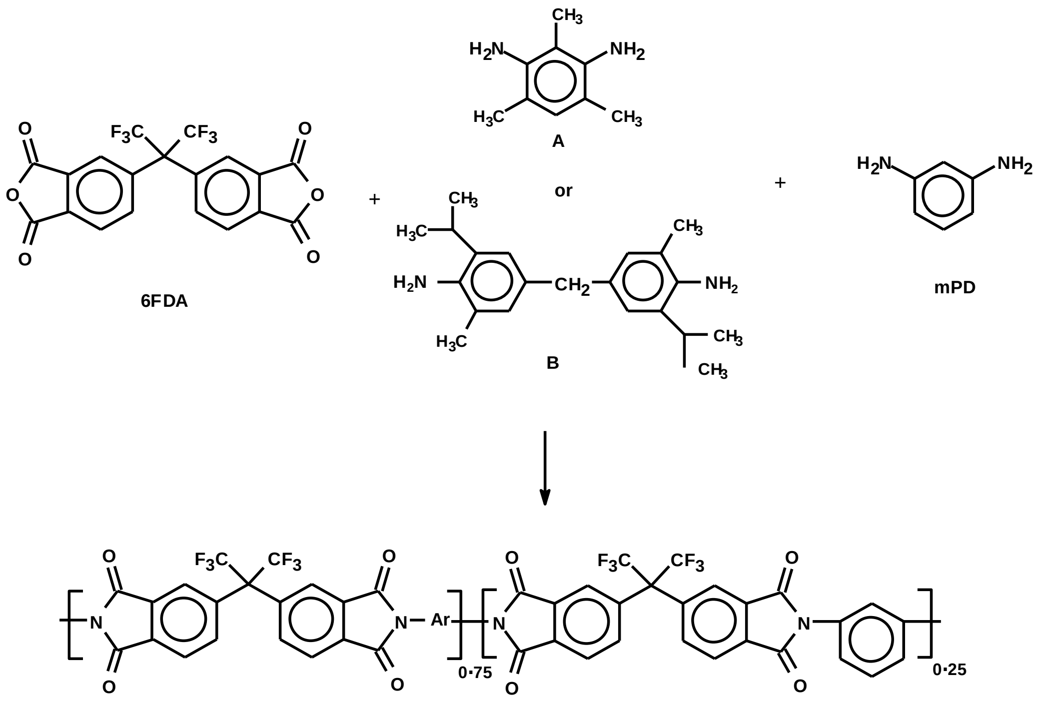


Figure 5.Themorgrams of **PPM-A** series (up) and **PPM-B** series (down)



AmPD-25 Ar = A

BmPD-25 Ar = B

Figure 6.Structure and designation of reference copolyimides without labile side groups

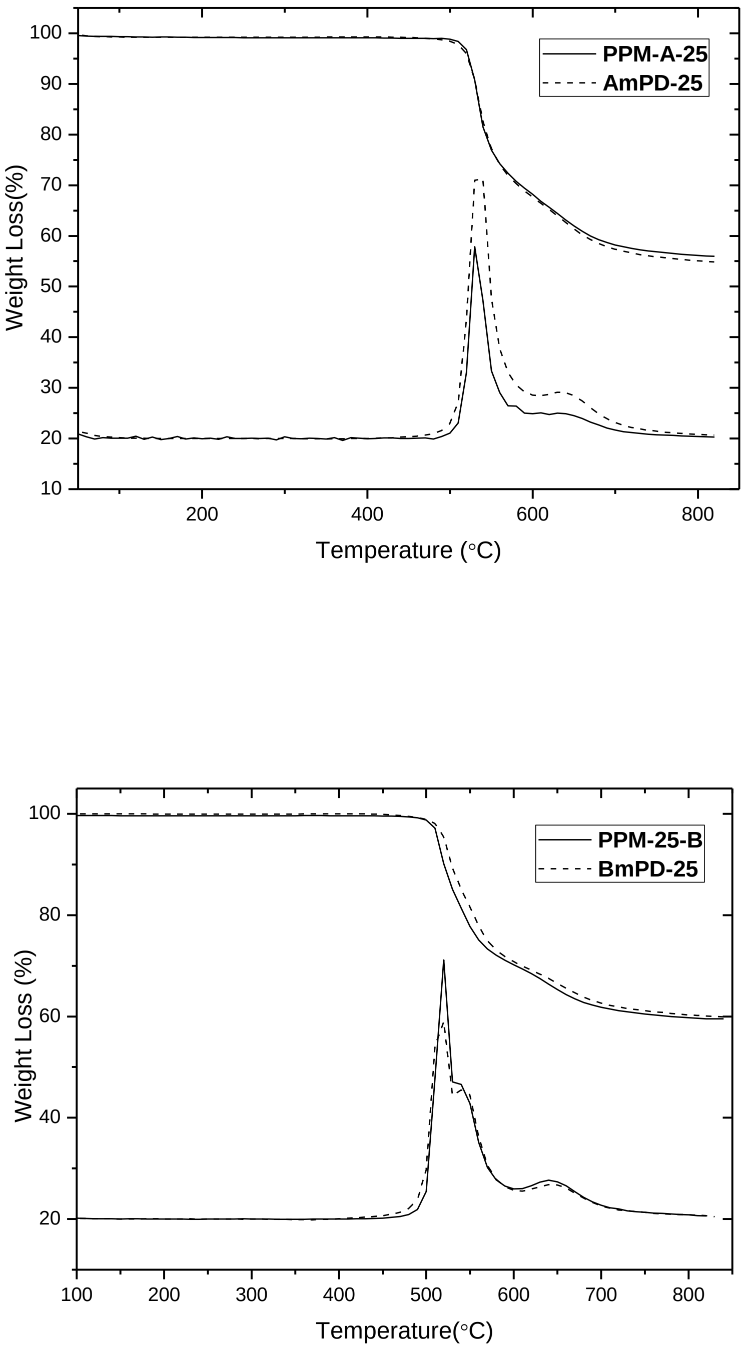


Figure 7. TGA curves (up) **PPM-A-25** compared with the reference copolyimide membrane **AmPD-25**and (down) **PPM-B-25** compared with the reference copolyimide membrane **BmPD-25**

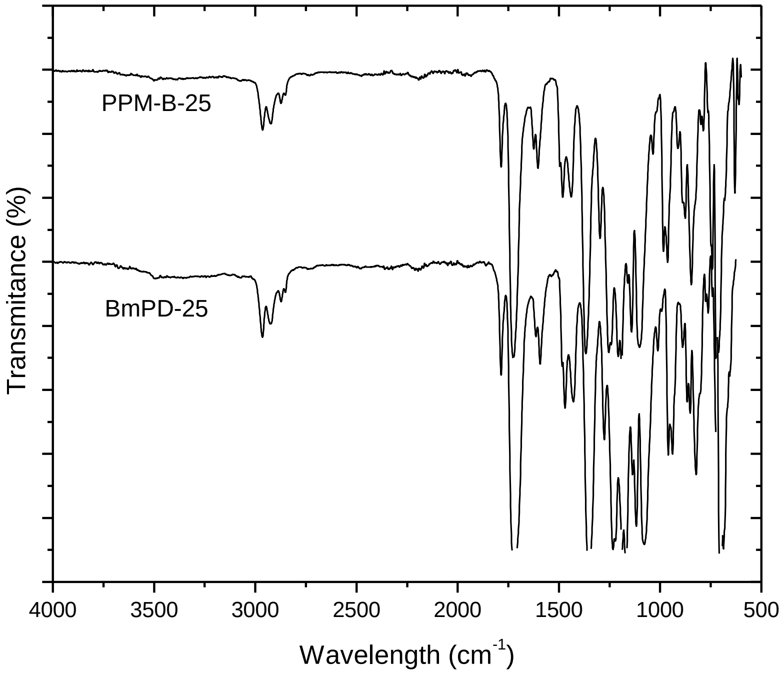


Figure 8. FT-IR spectra of **PPM-B-25** compared with the reference copolyimide membrane **BmPD-25**

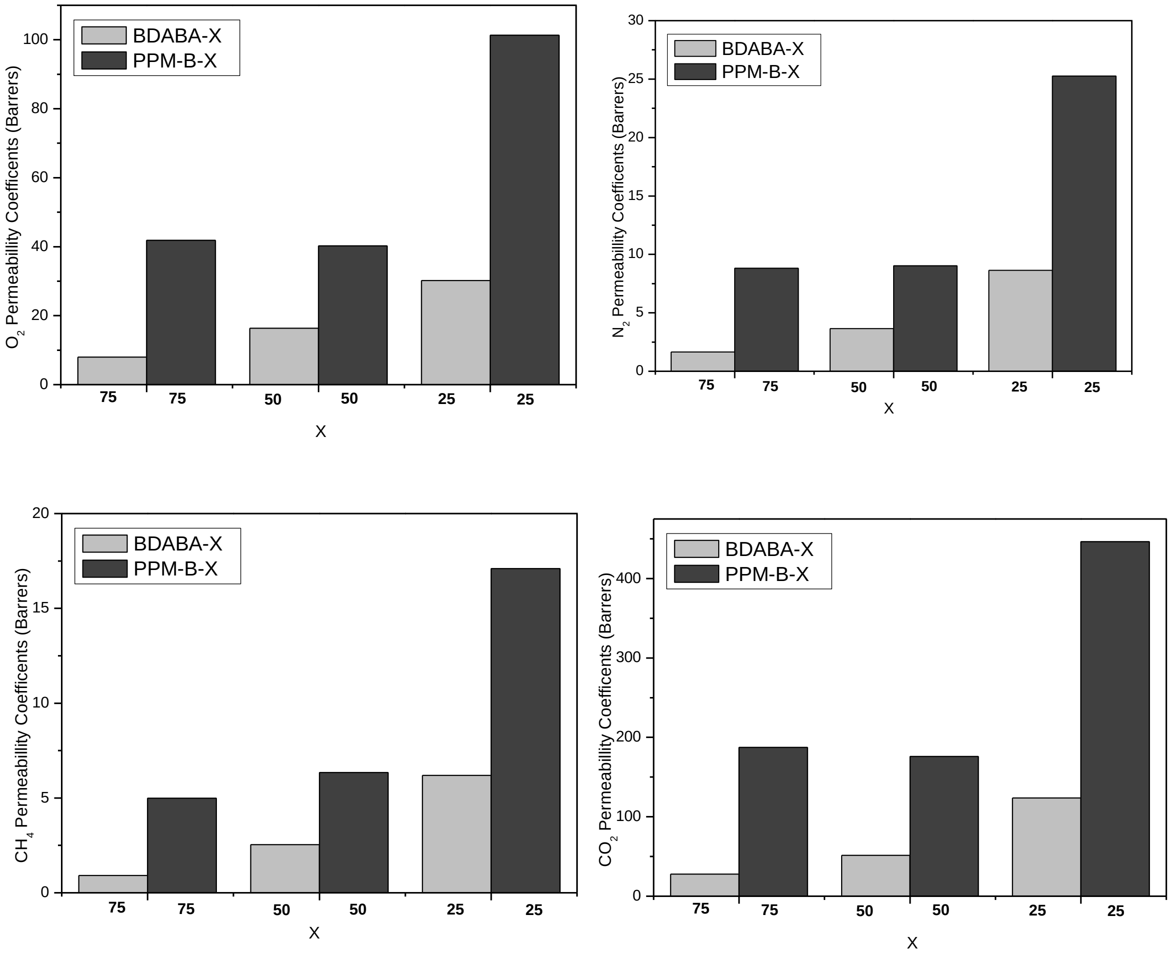


Figure 9. Permeability coefficients of starting copolyimide membranes and **PPMs** of B series

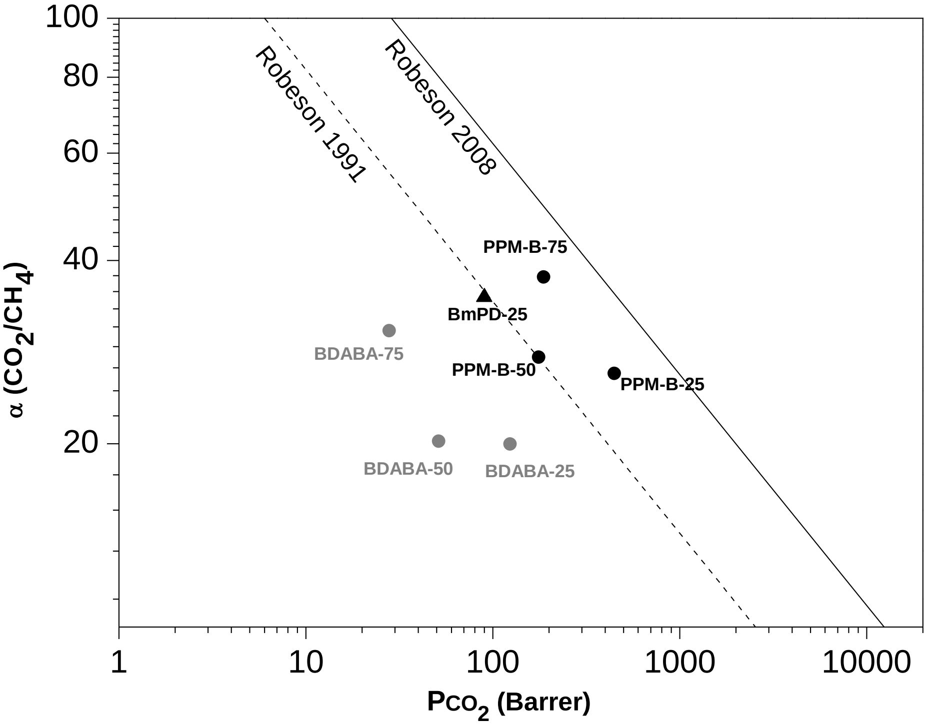


Figure 10. Performance of precursor cross-linked copolyimide membranes (**BDABA-25**, **BDABA-50** and **BDABA-75**), the corresponding pyrolyzed membranes (**PPM-B-25**, **PPM-B-50** and **PPM-B-75**) and the reference copolyimide without pendant groups **BmPD-25** for CO_2/CH_4 separations.

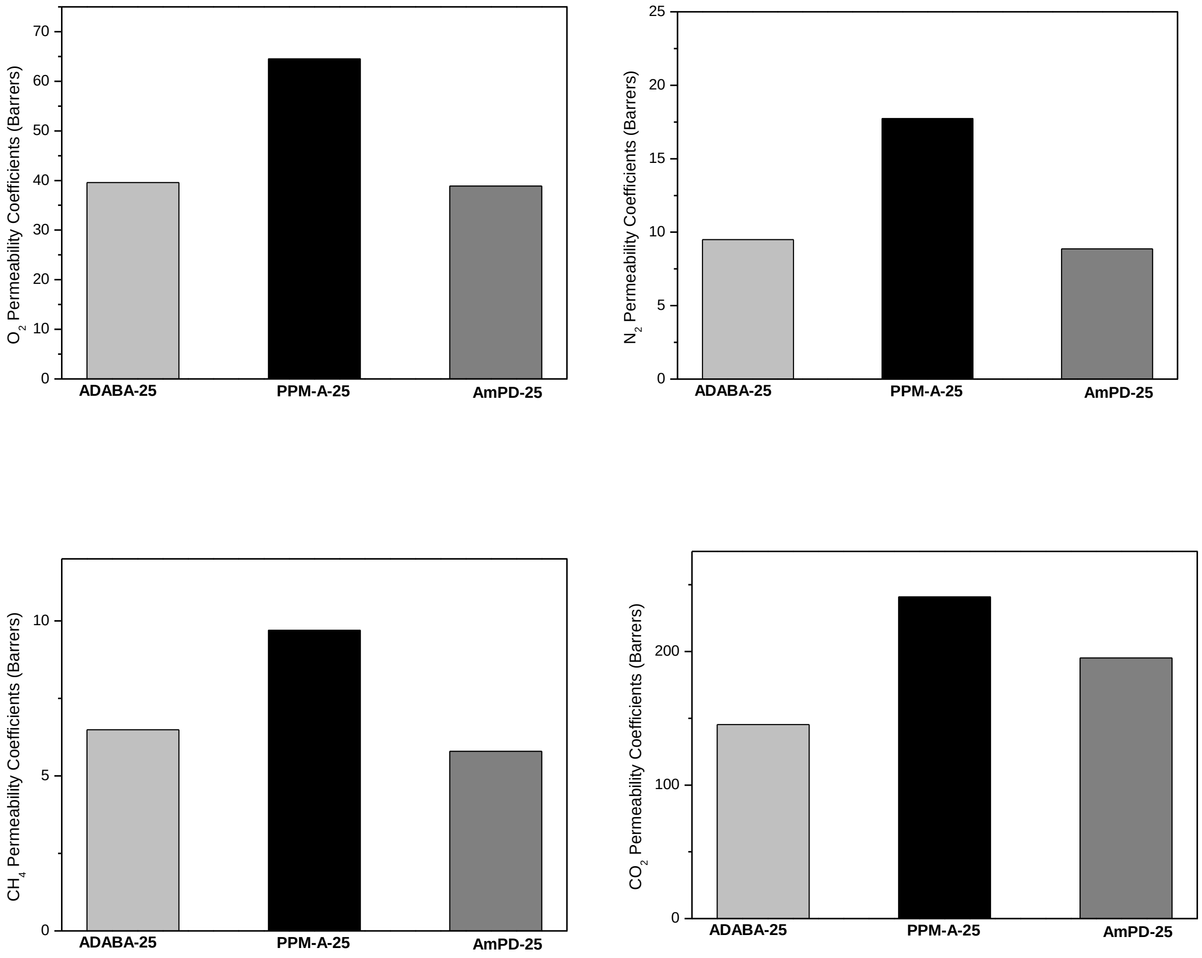


Figure 11. Permeability coefficients of **ADABA-25**, **PPM-A-25** and**AmPD-25**

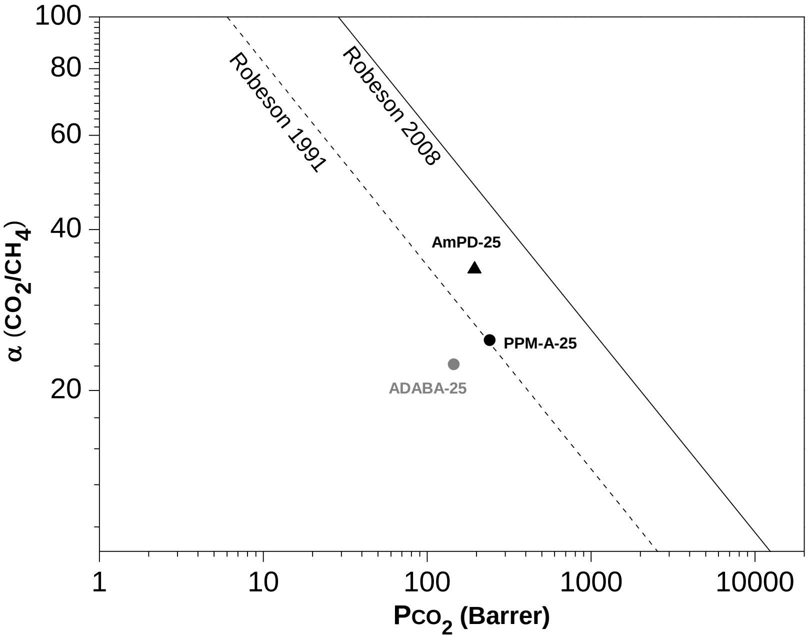


Figure 12. Performance of precursor cross-linked copolyimide membrane **ADABA-25**, the corresponding pyrolyzed membrane (**PPM-A-25**) and the reference copolyimide without pendant groups **AmPD-25** for CO_2/CH_4 separations.

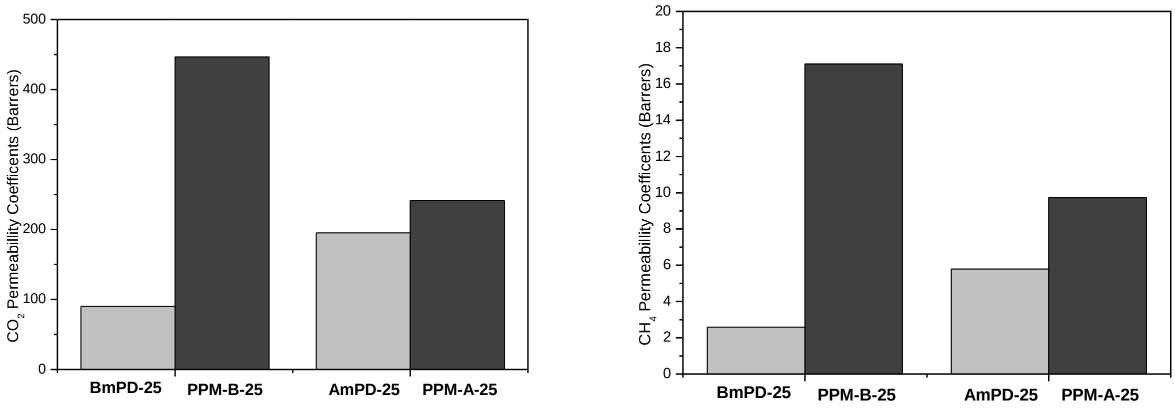


Figure 13.CO$_2$ and CH$_4$permeability coefficients of the pyrolyzed membranes **PPM-B-25** and **PPM-A-25** compared with the reference copolyimides**BmPD-25** and **AmPD-25.**