Effect of substituents on the permeation properties of polyamide membranes

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Abstract

Aromatic polyamides, designed for evaluation as gas separation membranes, were processed into dense films, whose properties were measured with special emphasis on their mechanical and thermal properties. The polymers had been synthesized from monomers bearing side substituents, such as methyl, iso-propyl or tert-butyl, and various hinge-like connecting linkages of p-phenylene moieties, which yielded amorphous aromatic polyamides, with improved solubility, high glass transition temperatures (over 250 °C) and excellent mechanical properties (tensile strength about 100 MPa, and moduli about 2.0 GPa). The permeability of the polymer films were investigated using helium, oxygen, nitrogen, carbon dioxide and methane. Gas permeability typically increased with increasing free volume, and, in general, free volume could be related to the chemical structure. The analysis of the transport parameters (permeability, diffusivity and solubility coefficients) as a function of the chemical structure, confirmed the predominant role of the side substituents and of the linking groups connecting phenylene units on the permeation properties. Besides, a molecular modelling study carried out via computational chemistry, made it clear that an acceptable theoretical explanation can be given of how the nature of hinge groups between aromatic rings can affect torsional mobility and gas diffusion of aromatic polyamides.

The experimental aromatic polyamides of this report, as a whole, showed a favourable combination of permeability–selectivity, better than that of conventional polyamides and that of most engineering thermoplastics, confirming the hypothesis that the incorporation of side bulky substituents is a convenient approach to hinder the inherently efficient chain packing of polyamides.

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1. Introduction

Research on polymeric materials for gas separation has focused in last decades in aromatic, glassy polymers, and particularly on relatively rigid, high \( T_g \) polymers, such as polysulfones, polycarbonates, polyimides, etc. [1–5]. Technical aromatic polyamides have achieved significant importance as high performance materials, thanks to their excellent balance of mechanical and thermal properties [6–8]. However, they have not deserved special attention as membrane-forming materials, so that rather few studies have been reported on the permeation properties of aromatic polyamides (APAs), either in scientific journals [9–11] or in the patents literature [12–14]. On the other hand, commercial APAs are very difficult to process, as they do not melt, and they are insoluble or very poorly soluble in highly polar organic solvents. There are inherent structural elements of APAs which are responsible of these drawbacks, for instance their high degree of chain rigidity, provided by the presence of aromatic rings, and the strong interchain forces, particularly hydrogen bonding, which account for an elevated cohesive energy density and molecular packing.

Regards gas permeability, penetration of small molecules is severely restricted through polymer matrices which have strong interchain attraction forces and high degree of molecular packing, as it is the case of wholly aromatic, classical polyamides. This is especially true for commercial APAs, for instance polyterephthalamides and polyisophthalamides [15]. As a matter of fact, the permeability of technical gases, like oxygen or nitrogen, is rather low in comparison with other glassy polymers such as polysulfones [16], polysulfones [17,18] or polyamides [19,20]. On the other hand, polyamides are taken as not suitable for gas permeation if only diffusion coefficients are consid-
ered, but when attending to the other factor which contributes to permeation, that is solubility, one can see that the solubility coefficient of gases towards APAs is comparatively high [14,21]. Therefore, it is the low diffusivity which actually determines their unusual resistance to gas permeation, and the challenge at this respect is to conveniently manipulate the APAs structure to achieve the most favourable permeability–selectivity balance of transport properties.

Thus, it is to presume that there is still room to improve the permeation properties of APAs, for instance by means of convenient modification of their primary chemical structure, as it has been the case for other aromatic polymers, such as polyimides, which have undergone a great deal of chemical modifications looking for better permeation properties [22–27]. Moreover, the chemistry of APAs is related to that of polyimides, and their physical properties are comparable in many aspects. Polyimides generally have an element of better thermal stability than polyamides, while the latter, particularly those para-oriented, usually show superior mechanical resistance, especially in the form of high-modulus, high-resistance fibers. Advantages for polyamides are that they can be synthesized easier by well-established high yield methods and that they offer a great versatility for chemical composition, in such a way that, thanks to the great number of available commercial and experimental monomers, they virtually offer an unlimited number of possible combinations. On the contrary, the number of available dihydrides for aromatic polyimides is comparatively low, and they are more expensive that diacids or diacid chlorides used as condensation monomers to prepare APAs. Furthermore, the synthesis of polyimides is generally more complicated, because it is carried out by a two-step method, which involves a final step of imidation of polyamic-acids to polyimides, either by thermal or chemical means [28]. Thus, it seems interesting to investigate the capabilities of novel APAs especially designed to be tested as membranes for gas separation.

Taking into consideration these antecedents and having in mind the very high density of cohesive energy of APAs, one major objective of the present work has been to introduce appropriate substituents providing chains separation and hindering hydrogen bonding, in other words, leading to an enhancement of the fractional free volume. The design of monomers has been done to achieve this goal in maximal extent, without loss of the positive characteristics of APAs, particularly without significant lowering of the gases selectivity and transition temperatures. Thus, monomers have been selected with voluminous side substituents to promote chains separation, amorphous character and high free volume.

Apart from the experimental work, which has consisted of the preparation of novel polymer films and their evaluation as dense membranes for gas permeation, a theoretical study has been carried out by means of computational chemistry methods to calculate properties directly related to permeability, such as torsional mobility and rotational energy barriers.

2. Experimental

Polymers were prepared by combination of experimental and technical diamines with a non-technical diacid, by the synthetic routes earlier reported [29]. They were characterized spectroscopically and by their inherent viscosities (ηinh).

Polymer films were fabricated at laboratory scale by casting polymer solutions (7–8%, w/v) in N,N-dimethylacetamide (DMA) on glass plates at room temperature, with the aid of a casting blade. Solvent elimination was carried out in every case by the following protocol: first a free standing film was formed by heating at 70 °C for 24 h; next the film was stripped off by deepening the glass plate in deionized water; then the film was dried at 120 °C/1 mmHg for 48 h; finally the film was extracted with ethanol in a Soxhlet apparatus for 24 h, and dried again at 100 °C/1 mmHg for 24 h. Creasable, transparent films were attained in every case. It was verified that extraction with ethanol was necessary to entirely remove DMA. Otherwise DMA rests could not be totally removed, as it was checked by thermogravimetric analysis (TGA). All films were between 40 and 60 μm thick.

Mechanical properties of films were investigated by their tensile strength, elongation to break and modulus. Strips 5 mm wide and 30 mm long were cut from polymer films and tested on a MTS Sinergie 2000 universal testing machine at 25 °C. An extension rate of 5 mm/min was applied; with a gauge length of 10 mm. Data listed in Table 1 are average values of at least six measurements.

Wide angle X-ray diffraction (WAXD) patterns were obtained for polymer films at room temperature by using a Philips Geiger X-ray diffractometer, operating in the 2θ range between 5 and 35° and using Ni-filtered Cu Kα radiation.

Polymer density was measured on films by a flotation method in a solution of calcium nitrate in water at 25.0 ± 0.1 °C. The density of the solution was determined by picnometry. The density data were used to evaluate chain packing by calculating the fractional free volume (FFV), which was calculated using the following

Table 1 Properties of aromatic polymides

<table>
<thead>
<tr>
<th>Key</th>
<th>φ (g/mL)</th>
<th>ηinh (dL/g)</th>
<th>θ (°C)</th>
<th>Tensile strength (MPa)</th>
<th>Modulus (GPa)</th>
<th>ρ (g/cm³)</th>
<th>ηinh</th>
<th>FFV</th>
</tr>
</thead>
<tbody>
<tr>
<td>APA1</td>
<td>1.03</td>
<td>254</td>
<td>105</td>
<td>2.10</td>
<td>1.112</td>
<td>642</td>
<td>0.142</td>
<td></td>
</tr>
<tr>
<td>APA2</td>
<td>0.81</td>
<td>275</td>
<td>97</td>
<td>2.09</td>
<td>1.098</td>
<td>672</td>
<td>0.151</td>
<td></td>
</tr>
<tr>
<td>APA3</td>
<td>1.21</td>
<td>295</td>
<td>97</td>
<td>2.15</td>
<td>1.073</td>
<td>702</td>
<td>0.168</td>
<td></td>
</tr>
<tr>
<td>APA4</td>
<td>1.30</td>
<td>260</td>
<td>110</td>
<td>2.15</td>
<td>1.063</td>
<td>738</td>
<td>0.166</td>
<td></td>
</tr>
<tr>
<td>APA5</td>
<td>0.51</td>
<td>268</td>
<td>88</td>
<td>2.23</td>
<td>1.200</td>
<td>658</td>
<td>0.187</td>
<td></td>
</tr>
</tbody>
</table>
relation:

\[ FFV = \frac{(V - 1.3V_w)}{V} \]  

where \( V \) is the polymer specific volume and \( V_w \) is the specific van der Waals volume. The van der Waals volume was estimated by several approximations, including the traditional method of Bondi [30] and the Hyperchem computer program, version 7.0 [31]. Hyperchem employs a grid method based on the work of Bodor et al. [32], using the atomic radii supplied by Gavezotti [33]. Moreover, the computer-based method can estimate van der Waals volume for structural units not included in the tables typically used by the Bondi method [34].

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, for all gases, at 3 bar. For the permeation experiments, carbon dioxide, nitrogen, oxygen, methane and helium were used. The purity of these gases was greater than 99.5% for CH4 and O2 and greater than 99.99% for the other gases.

Permeability values were determined from the slope of a downstream pressure versus time plot once steady state had been attained. Gas diffusivities were estimated from time-lag data (9), using the relation:

\[ D = \frac{l^2}{6\theta} \]  

where \( l \) is the film thickness and \( \theta \) is the time-lag.

As permeability is a product of \( D \) and a thermodynamic parameter \( S \) (solubility coefficient), \( S \) could be obtained from the expression:

\[ S = \frac{P}{D} \]  

The selectivity \( \alpha \) of a membrane for a pair of gases A and B is the ratio of the corresponding permeabilities and can be calculated as follows:

\[ \alpha_{A/B} = \frac{P_A}{P_B} \]  

Permeation data listed in Table 3 are average values of three measurements made in the same conditions and using samples cut from the same polymer film.

3. Results and discussion

The chemical structure of APAs used in this study is depicted in Fig. 1. A distinguishing characteristic of current polyamides is the presence of side substituents. The various substituents could be incorporated by selecting the monomers used in their preparation [29]. The diacid monomer bore two tert-butyl bulky substituents, which should bring about chain separation and opening of molecular packing. As a matter of fact, previous results have been reported on the beneficial effect of tert-butyl groups on enhancing fractional free volume (FFV) and permeability [27,35–38]. Moreover, ether linkages were incorporated to the monomer with the purpose of assuring a certain level of chain mobility and good solubility (processability). The diamines consisted of bis-(p-aminophenyl) monomers, and they were designed with the same purposes, so that they exhibit symmetrical replacement of hydrogens on the phenyl rings by aliphatic substituents of different size. All the polyamides chosen for this work were soluble in polar organic solvents; in some instances even in common solvents such as tetrahydrofuran or chloroform. Thus, polymer films could be fabricated in every case by usual methods of casting and solvent evaporation.

Physical properties of polymers and films are listed in Table 1. Molecular weights (inherent viscosities) were high enough for the polymers to develop good thermal and mechanical properties. Glass transition temperatures, in the range 250–295°C, compared well with those of other APAs and with engineering thermoplastics, such as polysulfones or polyimides, which are being used as gas membrane materials. The polyamide films were also characterized by wide angle X-ray diffraction, showing only an amorphous halo and no indication of crystallinity [29].

Polymer films showed excellent mechanical properties, with tensile strength about 100 MPa and modulus in the range 2.00–2.22 GPa. Thus, the combination of thermal and mechanical properties exhibited by current polymers fitted well the requirements of thermal and mechanical resistance of polymer membranes to meet the demands of separation processes.

The presence of a variable number of side substituents in the set of APAs, offered the opportunity for counting on a range of chemical compositions that could be related to the properties shown by any individual polymer. As it can be seen in Table 1,

![Fig. 1. Chemical structure of aromatic polyamides.](image)
there was a direct correlation between the proportion and size of substituents, introduced through the diamine monomers, and specific properties directly affecting gas transport, such as density, van der Waals volume and fractional free volume. At this regard, it was confirmed that the greater the number of methyl and isopropyl side groups in the repeating unit, the lower the experimental density and the bigger the van der Waals volume and FFV. The introduction of the hexafluoroisopropylidene group greatly enhanced both the density and the FFV. This result was not anomalous at all as diamine 6F is known to provide high density and high free volume, just by the presence of fluorine atoms and by the particular spatial characteristics of the bulky hexafluoroisopropylidene group [39].

4. Transport properties

Table 1 provides a summary of properties directly related with transport of gases through APAs dense membranes. The density data were used to characterize chain packing by estimating the fractional free volume FFV with Eq. (1). As described in the experimental section, the FFV can be calculated from density data and estimations of the van der Waals volume by a group contribution method. Polymers APA3 and APA4 have higher FFV than APA1 and APA2, what is very consistent with the notion that side substituents disrupt chain packing. Polymer APA5, although having unsubstituted phenylene in the diamine moiety, has a great value of FFV thanks to the presence of the hexafluoroisopropylidene linkage.

A conventional barometric method was used to perform permeation experiments for the polymer films. Permeabilities measured for pure gases at 30°C and 3 atm. are presented in Table 2. The following technical gases were tested: helium, oxygen, nitrogen, carbon dioxide and methane. Time-lag for helium were too short to allow accurate determination of its diffusion coefficients. The trend of permeability values observed was: \( P(\text{He}) > P(\text{CO}_{2}) > P(\text{O}_{2}) > P(\text{N}_{2}) = P(\text{CH}_{4}) \), and this trend was virtually the same for all the five APAs studied in this work. This behaviour is the same for most glassy polymer membranes and it indicates the existence of a relationship between the permeability and the kinetic diameter of the tested gases. In fact, this trend followed the same tendency as the reverse order of kinetic diameter of the assayed gases (He, 2.60 Å; CO\(_2\), 3.30 Å; O\(_2\), 3.46 Å; N\(_2\), 3.64 Å; CH\(_4\), 3.80 Å) [40], as it could be expected.

Polymers APA1 through APA3 showed increasing values of permeability to all penetrants tested; consistently, the number of side methyl substituents increased from two to six from APA1 to APA3, with a good correlation between permeability and FFV. Polymer APA4, however, showed a disruption of this tendency on exhibiting much less permeability than APA3 in spite of having a similar value of FFV. APA4 repeat unit bears two bulky side isopropyl groups, which should provide chain separation in a greater extent than the methyl groups of APA3, but APA4 has CH\(_3\) instead of C(CH\(_3\))\(_2\) as linking group between the two \( p \)-phenylene rings of the diamine moiety. Two phenylene rings linked by a methylene unit have more rotational freedom than that of two phenylene rings joined by isopropylidene, and the restricted torsional mobility of the latter is responsible for macroscopic effects such as higher \( T_g \), and also higher chain rigidity. This should be accompanied by a decrease of permeability, however, APA3 showed higher permeability than APA4. So, the presence of the voluminous isopropylidene group in the main chain of APA3 can prevent a dense packing of the polymer chains due to increasing the steric repulsion or due to lowering the density of cohesive energy. The effect became still more evident for APA5, with a hexafluoroisopropylidene unit between the two \( p \)-phenylene rings. In this case, the large volume of the fluorine atoms relative to the hydrogen atoms gave both a high FFV and a low rotational mobility. The global, observable effect was higher gas permeability for APA5 compared to that of polymer APA3.

To provide some insight into this behaviour in terms of torsional mobility, quantum semipirical calculations were performed on the model compounds diphenylmethane, isopropylidene diphenyl and hexafluoroisopropylidene diphenyl by the AM1 method [41]. Fig. 2 presents energy barriers calculated by rotating the dihedral angle \( \phi \) in 15° increments for X=CH\(_2\), C(CH\(_3\))\(_2\) and C(CF\(_3\))\(_2\), respectively. The maximum value of the rotational barrier was approximately 1.11 kcal/mol for C(CF\(_3\))\(_2\), while the phenylene rings of APA4 can rotate on the CH\(_3\) linkage almost freely, surpassing a barrier of hardly 0.06 kcal/mol.
and the rotational barrier for C(CH₃)₂ was about 0.6 kcal/mol. In principle, a lower rotational barrier should allow for a more efficient chains packing, what means lower FFV and lower permeability. Thus, while in polymers APA1 through APA4, the side methyl and isopropyl groups appear to disrupt chain packing and increase gas permeability, the high FFV and permeability in polymer APA5, which does not bear side substituents on its diamine moiety, should be attributed to the bulky hexafluoroisopropylidene linkage within the main chain.

The permeability values were in the opposite order with selectivity, which is consistent with the commonly observed trade-off between permeability and selectivity for gases with polymer membranes. Yet, it seems that the incorporation of substituents on the diamine moiety of the current APAS, increases FFV and permeability without largely increasing non-discriminant backbone molecular mobility commonly understood to reduce selectivity. Moreover, polymers APA4 and APA5 offer a very favourable combination of permeability–selectivity for CO₂ and CH₄ as they permit the gases to pass through with higher flux and higher selectivity than polymers APA1, APA2 and APA3. Selectivities followed fairly well the permeability–selectivity trade-off for polymers APA1 through APA4, but for polymer APA5, having mobility restrictive hexafluoroisopropylidene linkages, the selectivity is considerably higher than expected: FFV of polymer APA5 was the highest of the series and, consequently, their permeabilities to the different gases were also high, always comparable to those of APA3, but its CO₂/CH₄ selectivity was about 30% higher than that of APA3. This may be explained by the presence of hexafluoroisopropylidene linkages in APA5, which provided higher chain rigidity than the isopropylidene linkages of APA3. From Table 3, for the oxygen/nitrogen gas pair, the less-substituted APA1 was the most selective polymer, followed by APA4, and APA3 exhibited the lowest selectivity.

To more thoroughly understand the relation between chemical composition and transport properties, the solubility and diffusivity components of each polymer were also studied (Table 3). Diffusion coefficients were estimated from the time-lag at 3 atm. and solution coefficients were calculated by means of Eq. (3). Substantial differences can be observed for diffusion coefficients in Table 3. Polymers APA3 and APA5 have diffusion coefficients 2–3 times higher than those of the less permeable APA1. These results further confirm that, for the set of APA membranes reported here, the incorporation of side methyl and isopropyl side groups or perfluorinated units actually brought about a considerable increase in FFV and diffusivity. The nature of the hinged linkages between the p-phenylene units of the diamine moiety had the same influence on diffusivity as that discussed above for permeability.

It should be pointed out that the solubility coefficients were not very different from one polymer of this series to the others. In fact, for each pure gas, solubilities lied within a range of values ±30% from the average, with gas solubility slightly increasing with increasing free volume. This indicated that the solubility coefficients were influenced mainly by the polar character of the amide groups, with the other structural chemical elements playing a secondary role. For this same reason, solubility selectivities for the gas pairs O₂/N₂ and CO₂/CH₄ were very similar for all the polymers: S_{O₂}/S_{N₂} ≈ 1.4–1.5 and S_{CO₂}/S_{CH₄} = 3.6–3.9. From the data in Table 3, gas solubility changes in the following order: S_{O₂} > S_{CH₄} > S_{N₂} > S_{CO₂}. This trend is consistent with the decreasing condensability of the gases, which can be associated to the gas critical temperature, in such a way that, generally, a decreasing of the solubility coefficient can be observed on decreasing the critical temperature. Furthermore, a relationship can be found between the critical temperature of gases and their solubility in polymer matrices. Fig. 3 presents log S as a function of the critical temperature of the gases for polymer APA2. The linear dependence found between log S and the critical temperature for polymer APA2 was also found for the other polymers of this work.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>S_{O₂}</th>
<th>S_{CH₄}</th>
<th>S_{N₂}</th>
<th>S_{CO₂}</th>
<th>S_{O₂}/S_{N₂}</th>
<th>S_{CO₂}/S_{CH₄}</th>
<th>D_{O₂}</th>
<th>D_{CH₄}</th>
<th>D_{N₂}</th>
<th>D_{O₂}/D_{N₂}</th>
<th>D_{CO₂}/D_{CH₄}</th>
</tr>
</thead>
<tbody>
<tr>
<td>APA1</td>
<td>98</td>
<td>11.0</td>
<td>7.6</td>
<td>28.0</td>
<td>1.18</td>
<td>4.4</td>
<td>3.11</td>
<td>0.70</td>
<td>0.18</td>
<td>4.4</td>
<td>6.6</td>
</tr>
<tr>
<td>APA2</td>
<td>109</td>
<td>10.0</td>
<td>6.9</td>
<td>31.1</td>
<td>1.90</td>
<td>4.50</td>
<td>4.50</td>
<td>1.18</td>
<td>0.29</td>
<td>3.8</td>
<td>6.5</td>
</tr>
<tr>
<td>APA3</td>
<td>119</td>
<td>11.3</td>
<td>7.6</td>
<td>34.0</td>
<td>3.60</td>
<td>8.30</td>
<td>3.00</td>
<td>0.44</td>
<td>0.09</td>
<td>3.6</td>
<td>5.6</td>
</tr>
<tr>
<td>APA4</td>
<td>98</td>
<td>10.4</td>
<td>7.2</td>
<td>27.5</td>
<td>2.61</td>
<td>6.21</td>
<td>2.61</td>
<td>1.64</td>
<td>0.44</td>
<td>3.8</td>
<td>5.9</td>
</tr>
<tr>
<td>APA5</td>
<td>109</td>
<td>11.0</td>
<td>7.4</td>
<td>28.0</td>
<td>3.33</td>
<td>7.14</td>
<td>7.14</td>
<td>2.04</td>
<td>0.50</td>
<td>3.5</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Fig. 3: Log S vs. gas critical temperature of gases for APA2.
Most of the polymers in the glassy state present the same trend for permeability and for diffusivity as the diffusion coefficient controls in great extent permeability; however, for the current APAs selectivities and diffusivities did not follow exactly the same trend. The relative order of diffusivities experimentally measured was: \( D(O_2) > D(CO_2) > D(N_2) > D(CH_4) \). This indicated that the dependence between diffusivity and kinetic diameter was not the expected for the case of CO\(_2\) as O\(_2\) has a larger diameter than CO\(_2\). CO\(_2\) diffusion coefficients generally decrease as polymer polarity increases and, at sufficiently high matrix polymer polarity, it is not uncommon to observe CO\(_2\) diffusion coefficients that are lower than O\(_2\) [11,27]. Thus, the good correlation experimentally found for permeability vs. kinetic diameter should be associated to the high CO\(_2\) solubility coefficient exhibited by the APAs of the class here reported.

For comparison, the commercial polyamide poly(2,2-dimethyl-4-methyl-hexamethyleneterephthalamide) (Trogamid(TM)) was measured in the same conditions as the current APAs. Asymmetric alkyl segments of Trogamid(TM) account for the good solubility and amorphous character of this technical polyamide, which, to the best of our knowledge, is the technical polyamide that shows the highest permeability to the gases tested in this work. However, as it can be seen in Table 2, it showed permeabilities which were one or two orders of magnitude lower than those measured for the current APAs. Gas permeability for other technical APAs as poly(4-phenyleneisophthalamide) (Nomex(TM)), which are wholly aromatic and have a regular chemical structure and very high density of cohesive energy, show even less permeability to gases than Trogamid(TM) [15].

The performance of these APAs for the pair O\(_2\)/N\(_2\) is compared with the performance of several commercial gas separation materials in Fig. 4, and the upper bound defined by Robeson [42]. Here again, the comparison is favourable to the APAs studied in this report, which lie closer to the upper bound than polysulfones, polycarbonates or polyether-imides. Moreover, the preparation of competitive gas separation membranes depends on factors such as mechanical properties, high service temperatures, and ability to process the polymer into either asymmetric flat sheets or hollow fibers. In this regard, the current APAs exhibit excellent mechanical and thermal properties and are amenable to processing from solutions, a common route in the formation of membranes for gas separation.

5. Conclusions

Chemical modifications of APAs primary structure, performed by using novel monomers bearing symmetrically-located bulky side groups, allow for the attainment of novel APAs which exhibit favourable characteristics, in terms of solubility, mechanical properties, thermal stability and molecular packing, for their use as gas separation membranes. The novel polyamides reported here have a more advantageous balance between permeability and selectivity than any engineering polyamide; and virtually any other polyamide reported so far. Their performance as separation membranes is also comparable or better than that of classical, commercial membrane-forming polymers, such as polysulfones, polyimides, or polyether-imides.

The improvements achieved in permeability in comparison with other aromatic glassy polymers are related to an increase in free volume, brought about by the presence of bulky side groups, while maintaining a significant degree of chain rigidity. This improvement appears not to greatly affect the gas selectivity of APAs as the selectivities found compare fairly well with those of technical and experimental gas membranes.

The experimental aromatic polyamides of this report, as a whole, showed a favourable combination of permeability—selectivity, confirming the hypothesis that the incorporation of bulky side substituents is a convenient approach to hinder the inherently efficient chain packing of polyamides, and to improve permeability without a significant loss of the selectivity exhibited by conventional APAs.

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