Syndiotactic polypropylene-α-olefin) copolymers with controlled microstructure and desired properties for oxygen enrichment have been synthesized via metallocene catalysts. The controlled incorporation of comonomers as pendant branch mainly improved the oxygen permeability, but the oxygen/nitrogen selectivity dropped around 20%. By controlling the amount and length of the branches in the syndiotactic polypropylene, the permeability of the membrane was enhanced up to 12-fold and it is comparable to typical commercial polymers used for this application. In contrast with conventional commercial polypropylene, copolymers with a large amount of comonomer were soluble in cyclohexane, allowing the manufacture of composite membranes with high permeability.

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Among the polyolefins, isotactic polypropylene (iPP) is widely used in the production of food containers and food packing as a gas barrier film (O₂ permeability from 1.1 to 2.5 Barrer) and many patents and research articles are focused on the study of its behavior on biaxially oriented polypropylene film or nanocomposites made from it. In each of these cases the oxygen permeability need to be decreased [14–17]. In general, polyolefins have established themselves as the ideal material for packaging and other disposables, and they are also finding more applications in automotive, appliances, agriculture, electronic construction, communication, etc. [18].

The synthesis of novel polymers with well-defined structures as "tailored" membrane materials is an important trend to improve polymer membranes [19,20]. In this context, the development of catalytic systems and polymerization processes have allowed the production of syndiotactic polypropylene (sPP) with better and controlled microstructure compared to polypropylene synthesized with traditional catalysts [21]. sPP possesses lower crystallinity than iPP, which is an advantage for membrane materials. The crystallinity decreases further with copolymerization, and thus completely amorphous polymers can be synthesized. These polymers with specific properties are interesting materials and perhaps they can find new applications as membrane materials for gas separation.

The objective of this work is to study how comonomer length and content affect the performance of syndiotactic poly(propylene-α-olefin) copolymer membranes. Oxygen permeability and O₂/N₂ selectivity are studied, and they are correlated with crystallinity, glass transition temperature and fractional free volume. Composite membranes prepared on a polyacrylonitrile microporous support, which showed good performance, are also studied.

2. Experimental part

2.1. Materials

The metallocene catalyst (Ph₂C(Cp)(9-Flu)ZrCl₂) from Boulder Scientific and the cocatalyst (methylaluminoxane, MAO) from Aldrich (10% w/v in toluene) were used as received. Toluene was distilled over sodium under an inert atmosphere, and the propylene was purified by passing it through columns containing BASF catalysts R3-11G and R3-12, and a 4 Å molecular sieve. The liquid 1-hexene and 1-octadecene comonomers were purchased from Aldrich and were dried under inert gas prior to use.

Polyacrylonitrile (PAN) microporous membranes manufactured by GKSS (Germany) were used as support; the PAN membrane had the following characteristics: water flux 140 l/m² h at 1 bar, average pore diameter of about 20 nm, and average thickness of 40 μm. The cyclohexane used for polymer solution preparation was from Aldrich, and was used as received.

2.2. Polymer synthesis and characterization

All manipulations for synthesis were performed in an inert atmosphere in a dry box or using standard Schlenk line techniques. Syndiotactic polypropylene (sPP) and copolymers with 1-hexene and 1-octadecene (CsP-H and CsP-O, respectively) were synthesized in a 1 L Büchi glass reactor. The main polymer properties are shown in Table 1.

Weight-average molecular weights and polydispersity were determined by gel permeation chromatography (GPC) using a Waters Alliance GPC2000 instrument. Tacticity and comonomer content were determined by ¹³C nuclear magnetic resonance spectra (¹³C NMR) recorded on a Varian Inova 300 instrument operating at 75 MHz. Thermal properties were obtained by differential scanning calorimeter (DSC) in a N₂ atmosphere to minimize thermal degradation (Modulated TA Instruments DSC 2920). The crystallinity fraction (Xc) has been estimated using a value of 196.6 J/g (enthalpy of fusion) for a perfect crystallite of sPP [22].

Polymer density (film) was measured according to ASTM D 792. The pycnometric density is based on the difference of between the sample’s weight in air and in a nonsolvent (methanol in our case) of known density. The measurement uncertainty was around ±0.003 g/cm³. The density data were used to evaluate the fractional free volume (FFV), which was calculated using the following relation [23,24]:

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

where \(V = 1/\rho\) is the polymer’s specific volume, \(\rho\) is the polymer’s density, and \(V_w\) is the estimated van der Waals volume calculated by the group contribution method of Bondi [25].

2.3. Membrane preparation

Dense membranes were prepared by melting the polymer in a HP hydraulic press between two hot plates at a temperature 30 °C higher than its melting temperature (for copolymers with high comonomer content a temperature of 100 °C was enough). In order to prepare films without entrapped air bubbles, the load was gradually increased up to 50 bar over a period of 3 min and then maintained at this load for 3 min. The compression-molded film was then cooled to 40 °C in the compression press through the cooling system of the press plates. The thicknesses of the membranes were measured with a digital micrometer (Deltascope MP2C), and they were between 80 and 180 μm. The values used are from at least 30 single measurements within the whole membrane area.
Composite membranes were prepared by dip-coating from polymer solutions (1.5–3 wt% of polymer in cyclohexane) stirred for 24 h at room temperature; the solutions were then filtered through a steel filter. The PAN microporous membrane manufactured by GKSS was dipped into the polymer solution and dried in air at room temperature overnight. In order to coat only one side of the microporous membrane (in laboratory), envelopes (10 cm × 10 cm) sealed on all four sides were prepared using a welding machine. The coated envelopes were then cut to obtain the composite membranes.

2.4. Membrane characterization

Diffusion and permeability of pure gases (O2 and N2) in dense membranes were measured by the time-lag method [26] at 30 °C. Details of the time-lag apparatus are given elsewhere [27]. The feed pressure was 450 mbar for all gases and each measurement was repeated twice for two membrane samples. Diffusion (D) was determined from time-lag and thickness:

\[ D = \frac{P l^2}{609 \theta} \]  

(2)

where \( l \) is the membrane thickness and \( \theta \) is the time lag which corresponds to the intercept on the time axis. The permeability (P) was calculated by determining the rate of steady-state gas transmission. The permeability is given by [20]

\[ P = \frac{V_p (P_2 - P_1)}{A R T \Delta t (P_f - ((P_2 + P_1)/2))} \]  

(3)

where \( V_p \), \( A \), \( R \), \( T \) and \( \Delta t \) are the permeate volume, the effective membrane area, the gas constant, and the absolute temperature, respectively. \( P_1 \) is the time for permeate pressure increase from \( P_1 \) to \( P_2 \), and \( P_f \) is the feed pressure. The permeability is commonly expressed in Barrer units (1 Barrer = 10-10 cm3(STP)·cm/(cm2·s·cmHg)).

The corresponding solubility (S) was calculated from the established definition of

\[ P = D · S \]  

(4)

The permeance values (J) of single gases (O2 and N2) in composite membranes (unknown thickness) were determined by a pressure increase test unit at 30 °C. Three samples were used and the measurements were made twice. For the calculation the following equation was used [28]:

\[ J = \frac{22.414 V_p}{A R T} \ln \left( \frac{P_f - P_1}{P_f - P_2} \right) \]  

(5)

The ideal gas selectivity between two components A and B was calculated by the ratio of permeability or permeance of the membranes:

\[ \alpha_{AB}^P = \frac{P_A}{P_B} \]  

(6)

\[ \alpha_{AB}^J = \frac{J_A}{J_B} \]  

(7)

The standard deviation was not more than 10% of the permeability data, which is acceptable for time-lag apparatus and other experimental errors.

The dense membrane crystallinity was calculated using the heat of fusion (from the first heating scan) obtained by differential scanning calorimetry in a Modulated TA Instrument DSC 2920 calorimeter, carried out under nitrogen at a scan rate of 10 °C/min.

The thickness of the composite membranes was analyzed by scanning electron microscopy (SEM) using a LEO 1550 VP Gemini (ZEISS) microscope. The samples were fractured in liquid nitrogen and coated with Au/Pd prior to observation.

Fig. 1. 13C NMR spectrum: (a) homopolypropylene (sPP), (b) propene/1-hexene copolymer (CsP-H2), and (c) propene/1-octadecene copolymer (CsP-O3).

3. Results and discussion

3.1. Polymer properties

The comonomer content of the copolymer was calculated from the ratio of the backbone carbons of the propylene and α-olefin, and is presented as mole percent (mol%) and weight percent (wt%) in Table 1. An example of 13C NMR spectrum is shown in Fig. 1, and the prominent peaks around 20, 28 and 47 ppm correspond to the methyl, methine and methylene groups of propylene units. The corresponding assignments of the 13C NMR spectra were made taking into account references [29–31].

Table 1 also presents the physical properties of the syndiotactic polypropylene and its copolymers with 1-hexene and 1-octadecene. The weight average molecular weight of the polymers and the narrow polydispersity (characteristic of polymers obtained by metallocene catalysts) are similar, allowing us to study very well the relationship between permeability and polymer properties. By introducing the comonomer as pendant branches on the main chain of sPP, the tacticity is decreased according to the comonomer content and length, and consequently the crystallinity is decreased. The inhibition of crystallization seems to be increased with both molar fraction and comonomer length. The presence of 6.9 mol% of 1-octadecene in the polymer produced completely amorphous polymers and the syndiotacticity decreased by almost 10%. It is therefore expected that these changes in microstructure will strongly affect the properties of sPP membranes.

The glass transition temperatures (\( T_g \)) of all the copolymers were lower than that of the sPP homopolymer and depended not only on the amount but also on the nature of the comonomer [32]. As equal mol% the incorporation of longer chains (1-octadecene) results in lower \( T_g \). The polymer \( T_g \) is associated, among other parameters to the chain motion of the macromolecules, indicating high mobility and high dynamic free volume.

Lower values of experimental density and higher fractional free volume (FFV) were found when comonomer content was high (Table 1). Both the number of branches in the main chain and branch length contributed to the FFV increase. On a mol% basis, 1-octadecene is the more effective comonomer in reducing the density of copolymers, and as such an increase of FFV. Therefore, low crystallinity, low \( T_g \) and high FFV will lead to a increased gas permeability, as discussed in the next section.

3.2. Dense membranes

The dense membranes (films) present lower crystallinity values than that of the raw polymer (Table 2 compared with Table 1). The
Based on copolymers with 1-octadecene (CsP-O) (Fig. 2). On the other hand, the oxygen permeability of copolymer membrane with only 6.9 mol% of 1-octadecene presented the highest oxygen permeability (21.6 Barrer). However, the selectivity dropped from 3.5 to 2.8, which is below the upper bound proposed by Robeson [34]. Membranes prepared from CsP-O5 copolymer (Table 2) might have higher permeability, but the samples were sticky and we could not measure it in the time-lag apparatus.

In analyses based on mol%, membranes prepared from copolymers containing 1-hexene (CsP-H) were less permeable than those based on copolymers with 1-octadecene (CsP-O) (Fig. 2). On the one hand, the oxygen permeability of copolymer membrane with the highest content of 1-hexene (14.1 mol%) increases 8-fold compared to homopolymer sPP, and O2/N2 selectivity is only affected by less than 15%, i.e. it decreased from 3.5 to 3. On the other hand, the copolymer membrane with only 6.9 mol% of 1-octadecene presented the highest oxygen permeability (21.6 Barrer). However, the selectivity dropped from 3.5 to 2.8, which is below the upper bound proposed by Robeson [34]. Membranes prepared from CsP-O5 copolymer (Table 2) might have higher permeability, but the samples were sticky and we could not measure it in the time-lag apparatus.

Since permeability can be expressed as a function of solubility and the diffusivity coefficient (P = D·S), it is important to analyze the effect of comonomer length and content on these properties. In the absence of specific interactions, gas solubility in polymers generally depends on gas condensability and polymer crystallinity. The critical temperature (Tc) of the gas is a measure of condensability [2,35]. As shown in Fig. 2, O2 solubility in the membranes is higher than N2 solubility. The Tc of O2 (154 K) is higher than that of N2 (126 K). Both O2 and N2 solubility were increased with increasing mol% of comonomer, but no relationship with comonomer length (1-hexene and 1-octadecene) was observed. From these results one can conclude that the solubility increased mainly because of crystallinity decrease and FFV increase, since it is known that in semicrystalline polymers the amorphous phase is responsible for gas solubility [33].

Gas diffusion depends on the penetrant size and the nature of the polymer matrix in which the diffusion takes place [36]. Taking the first aspect into account, O2 has a smaller kinetic diameter (3.46 Å) than N2 (3.64 Å), so it is expected that O2 will pass more easily through the membrane than N2. Diffusion also depends on the cooperative polymer chain motion, which is responsible for transient gap formation, i.e. free volume [2]. Hence, gas diffusion through polymeric membranes (rubbery-like) requires high polymer chain motion, high free volume, and high FFV (nature of the polymer).

In these membranes, the diffusivity of gases depends on comonomer length and it increases with its content (mol%), as shown in Fig. 2. Membranes prepared from poly(propylene-co-1-octadecene) presented higher values than poly(propylene-co-1-hexene), and even at lower comonomer concentration the diffusivity values are extremely high compared to that in the copolymer containing 1-hexene and homopolymer. This behavior is related to the greater chain motion and high free volume produced by the octadecene branch. As Tg of copolymers containing 1-octadecene is lower than room temperature, they behave as rubbery-like membranes, showing high flexibility [29,32]. These copolymers therefore present higher gas diffusivity, and conse-

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>C.C. (mol%)</th>
<th>Xcr</th>
<th>FFV</th>
<th>Permeability Barrer</th>
<th>Selectivity O2/N2</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPP</td>
<td>–</td>
<td>0.10</td>
<td>0.168</td>
<td>1.8</td>
<td>0.5</td>
</tr>
<tr>
<td>CsP-H1</td>
<td>1.3</td>
<td>2.6</td>
<td>0.09</td>
<td>0.169</td>
<td>2.5</td>
</tr>
<tr>
<td>CsP-H2</td>
<td>2.6</td>
<td>5.1</td>
<td>0.07</td>
<td>0.170</td>
<td>3.1</td>
</tr>
<tr>
<td>CsP-H3</td>
<td>8.0</td>
<td>14.8</td>
<td>no</td>
<td>0.184</td>
<td>8.1</td>
</tr>
<tr>
<td>CsP-H4</td>
<td>14.1</td>
<td>24.7</td>
<td>no</td>
<td>0.192</td>
<td>14.5</td>
</tr>
<tr>
<td>CsP-O1</td>
<td>0.3</td>
<td>1.8</td>
<td>0.09</td>
<td>0.169</td>
<td>3.5</td>
</tr>
<tr>
<td>CsP-O2</td>
<td>1.6</td>
<td>8.9</td>
<td>0.05</td>
<td>0.170</td>
<td>4.9</td>
</tr>
<tr>
<td>CsP-O3</td>
<td>3.1</td>
<td>16.1</td>
<td>no</td>
<td>0.176</td>
<td>8.7</td>
</tr>
<tr>
<td>CsP-O4</td>
<td>6.9</td>
<td>30.8</td>
<td>no</td>
<td>0.183</td>
<td>21.6</td>
</tr>
<tr>
<td>CsP-O5</td>
<td>10.5</td>
<td>41.3</td>
<td>no</td>
<td>0.193</td>
<td>nd</td>
</tr>
</tbody>
</table>

Xcr = crystalline fraction of dense membrane; FFV = fraction free volume. The standard deviations are not more than 10% of the permeability values.

**Fig. 2.** O2 and N2 transport properties as a function of comonomer content (mol%) and length.
and length.

(CH2)

calculation of FFV using the density measurements (Table 1). The FFV variation was not studied in this work, it is supported by the calculus of FFV using the density measurements (Table 1). The FFV plays an important role in gas diffusion. According to the free volume theory, the diffusion coefficient increases exponentially with FFV [33,36,38]. Because of increased chain motion, the packing of chains was affected more in poly(propylene-co-1-octadecene) than in poly(propylene-co-1-hexene), which resulted in an increased FFV available for gas diffusion, thereby the gas permeability was enhanced 12-fold (Fig. 2).

When the copolymers are compared as a function of wt% the gas transport properties trends are different (compare Figs. 2 and 3). The wt% values are added in Tables 1 and 2, and as expected they are higher than mol%. The 1-octadecene addition results in higher values (wt%) than 1-hexene, which is expected as the molecular weight of 1-octadecene is higher than 1-hexene. In fact, if we compare the copolymers based on wt%, the length of the branches is not considered, only the mass of the comonomer, and thus, the differences between the two monomers disappear. Fig. 3 shows the behavior of permeability, solubility and diffusion of oxygen and nitrogen as a function of wt% comonomer.

Membranes prepared from 1-hexene copolymers had the same permeability trend as those prepared from 1-octadecene copolymers. As we mentioned above, the good correlation observed for these copolymers can be explained by the fact that the pendant groups present the same structure, which can be written as CH3 (CH2)n–, and the gas permeability therefore fall approximately on the same line (considering only as function of comonomer concentration). However the solubility and diffusivity present differences, as observed in Fig. 3.

The solubility values depend on comonomer length, 1-hexene copolymers present higher values than 1-octadecene copolymers. As shown in Table 2, the copolymers with 1-hexene have higher FFV, even when the comonomer content is low. As a result of the higher FFV (higher amorphous phase) the solubility coefficient in these copolymers are higher than those observed for 1-octadecene. On the other hand, the diffusivity coefficient had similar behavior to that reported during analyses taking into account mol%.

From these results, we can conclude that the permeability in both analyses (based on mol% and wt%) mainly depends on diffusivity. Because diffusivity depended on both comonomer content and length, it demonstrates that there is a difference in amorphous region of each copolymer, indicating differences in Tg and FFV.

In order to analyze more deeply the relationship between gas diffusion and Tg for our copolymers, Fig. 4 shows the diffusion values for oxygen and nitrogen versus Tg of copolymers. The diffusion coefficient increases when the Tg decreases, and for both O2 and N2 diffusivity, the data are approximately located on a master line. The ratio between the slopes can be related to the selectivity, so O2/N2 selectivity can be affected mainly by diffusivity selectivity. The results indicate a linear dependence between diffusion and Tg for syndiotactic poly(propene-co-α-olefin)s. As discussed above, the Tg decrease is well related to a free volume increase because of chain motion increase.

3.3. Thin film composite membranes

The copolymers with higher 1-hexene and 1-octadecene content had the most interesting permeability and selectivity values. However, gas fluxes high enough for practical application can only be obtained with the manufacture of thin film composite membranes.

Polypropylenes are insoluble in common organic solvents at room temperature. Their use for making composite membranes on microporous supports has been restricted due to the lack of solvents, which would be convenient for coating without damaging the substrate’s porous structure. This problem has been solved by the synthesis of modified polypropylenes with high comonomer content, which effectively changes their solubility; CsP-H4, CsP-O4 and CsP-O5 are soluble in cyclohexane at room temperature. Their use for making composite membranes on microporous supports has been restricted due to the lack of solvents, which would be convenient for coating without damaging the substrate’s porous structure. This problem has been solved by the synthesis of modified polypropylenes with high comonomer content, which effectively changes their solubility; CsP-H4, CsP-O4 and CsP-O5 are soluble in cyclohexane at room temperature. However, gas fluxes high enough for practical application can only be obtained with the manufacture of thin film composite membranes.

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The performance of these composite membranes was optimized in terms of permeance and selectivity by varying the coating process conditions. The thickness of the coated layer was
Table 3
Gas permeance and O₂/N₂ selectivity for composite membranes prepared from different polymer solutions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration (wt%)</th>
<th>Permeance [GPU]</th>
<th>Selectivity O₂/N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>O₂</td>
<td>N₂</td>
</tr>
<tr>
<td>CsP-H4</td>
<td>1</td>
<td>55.2 ± 5.48</td>
<td>50.9 ± 5.01</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>5.7 ± 0.42</td>
<td>1.5 ± 0.11</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.8 ± 0.40</td>
<td>1.3 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.5 ± 0.23</td>
<td>0.9 ± 0.07</td>
</tr>
<tr>
<td>CsP-O4</td>
<td>1.5</td>
<td>9.6 ± 0.80</td>
<td>2.9 ± 0.25</td>
</tr>
<tr>
<td>CsP-O5</td>
<td>1.5</td>
<td>15.6 ± 1.51</td>
<td>6.3 ± 0.52</td>
</tr>
</tbody>
</table>

1 GPU = 1 × 10⁻⁶ cm³ (STP)/cm² s cmHg.

Fig. 5. SEM micrographs of the cross-section of composite membranes prepared from (a) and (c) CsP-H4 and (b) and (c) CsP-O4.

controlled by changing the polymer concentration in the coating solution.

Initially, polymer solution concentrations of 1, 2 and 3 wt% were studied and the results for CsP-H4 are shown in Table 3. Composite membranes prepared with 1 wt% of polymer concentration presented the highest gas fluxes, but O₂/N₂ selectivity decreased drastically, suggesting that the polymer concentration was not sufficient to produce a defect-free thin layer. Composite membranes prepared from 2 and 3 wt% polymer solutions presented lower fluxes with O₂/N₂ selectivity of 3.8. Lower polymer concentration produced thinner top layer in composite membranes, and consequently they resulted in membranes with higher fluxes. It is important to note that in all cases, the O₂/N₂ selectivities were the same or slightly higher than that of the corresponding dense membranes.

Composite membranes with higher O₂ fluxes (9.6 GPU) and higher O₂/N₂ selectivity (>3) were obtained using CsP-O4 copolymer and a 1.5 wt% polymer solution is apparently sufficient to obtain defect-free thin film composites. The same behavior was observed for CsP-O5 composite membrane, and the values are also reported in Table 3. The CsP-O4 flux value is at least 15-fold higher than those reported for TPX [8], although the selectivity is ≤20% lower.

SEM images of CsP-H4 and CsP-O4 composite membranes are presented in Fig. 5. The coating layer is clearly visible on the PAN support. The thickness of thin layer of the CsP-H4 composite membrane was approximately 1 ± 0.1 μm (Fig. 5c), and for CsP-O4 it was around 1.7 μm (Fig. 5d). The thickness and the numbers of defects in the coating depend on the concentration and viscosity of the solution, the nature of the support membrane (pore size at the surface), and factors during membrane preparation process [39]. In this work it depends only on the viscosity of the polymer solution because the other factors were the same in all cases. CsP-O4 polymer solution probably had higher viscosity, producing a thicker layer. Further evidence of this statement is seen in Fig. 5c, the penetration of polymer solution into the pores of PAN due to the lower viscosity is clearly seen. Slight penetration of polymer solution into the pores can enhance the adhesion between the active layer and the support. However, the mass transfer resistance would increase remarkably and the gas flux through the composite membrane would decrease, which is undesirable.

4. Conclusions

Dense and composite membranes were successfully prepared from syndiotactic poly(propylene-co-α-olefins)s, and showed that
the gas permeability and flux can be well controlled by addition of different comonomers.

The O₂ permeability of syndiotactic polypropylene copolymer membranes increased up to 12-fold by increasing comonomer content, and O₂/N₂ selectivity was decreased around 20%. The permeability increase was mainly attributed to an increase of the diffusion coefficient. The decrease of the glass transition temperature and density and the increase of the fractional free volume were in good agreement with the diffusivity increase.

The copolymer performance for gas separation was explored by manufacturing thin film composite membranes. The composite membranes had a dense thin layer less than 2 μm thick. The O₂ permeance (CSP-04 membrane) has been increased to values comparable to those of commercial composite membranes used for this purpose (TPX membrane). The main advantage of this new membrane material can be its low cost.

Acknowledgments

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