Gas Permeability and Selectivity in Thermally Modified Poly(oxyindole biphenylylene) Membranes Bearing a tert-Butyl Carbonate Group

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ABSTRACT: The gas permeability and ideal selectivity in poly(oxyindole biphenylylene) polymers that bear a tert-butyl carbonate side group, PN-BOC, have been measured, at 35 °C and 2 bar. It is found that the thermal degradation of the thermo-labile side group, BOC, at moderate temperatures and times, is useful for designing membranes that overcome the typical trade-off between permeability and selectivity. TGA, FTIR-ATR, and DSC analysis reveal that thermal treatments of PN-BOC at 150 °C and short periods of time, 5−60 min, allow the design of membranes with better selectivity−permeability combinations than the pure PN-BOC precursor. For the gas pairs O₂/N₂ and CO₂/N₂, the PN-BOC₅ thermally treated membranes for 5 min show O₂ and CO₂ permeability coefficients higher by a factor of 2.3 with respect to that measured in PN-BOC, while retaining their selectivity. For the gas pairs H₂/CH₄ and CO₂/CH₄, the PN-BOC₆₀ thermally treated membranes for 60 min show a H₂ and CO₂ permeability coefficient higher by a factor of 1.7 and 1.4, respectively, while selectivity increases with respect to that of the PN-BOC precursor by 45% for H₂/CH₄ and 24% for CO₂/CH₄.

1. INTRODUCTION

Membrane technology and polymer science have grown synergistically over the past 30 years. Novel membrane separation processes could not exist without both the sophisticated array of polymers provided by polymer chemistry and the fundamental studies related to the gas separation processes in the polymer solid state provided by researchers from academy and industry.

Recently, a category of solid state thermally rearranged polymers (TR) has drawn interest due to their attractive performance as gas separation membranes and for their excellent chemical and thermal stability. The high values of gas permeability coefficients and gas selectivity characteristics of these polymers are attributed to an unusual microstructure whose cavity size and distribution could be tuned during the thermal rearrangement protocols. TR polymer membranes can be prepared by simple thermal rearrangement after membrane formation with precursor polymers; consequently, the gas permeation properties of those polymers depend upon the degree of thermal conversion.

The breakthroughs in the development of new TR polymers are mainly focused on modifying the chemical backbone structure of precursor polymers followed by thermal treatment protocols, but there are few studies related to the chemical modification of a polymeric unit by thermal decomposition in the solid state, particularly their labile side groups or thermolabile grafted groups, and their effect on the gas transport properties once they are thermally degraded in the solid state. In this direction, Xiao and Chung reported an approach to prepare highly permeable and still highly selective polyimides membranes by thermal treatment of rigid and cross-linkable polyimides grafted with β-cyclodextrin, a thermally labile molecule with large dimensions. In a similar approach but using a polymer containing a short labile group, Martínez-Merced et al. studied the effect on the gas permeability and selectivity of thermally modified poly(oxyindole biphenyl-
... membranes bearing a side carbonyl group, which can be partially or totally eliminated at relatively moderate thermal treatments (160–180 °C) and times (<1 h). The gas permeability and selectivity properties of the thermally modified poly(oxyindole biphenylylene) membranes were higher than the properties measured on the neat polymer containing the thermally labile side group. In a recently published manuscript that describes the syntheses and characterization of poly(phenylquinoline)s grafted with tert-butyl carbonate groups (BOC), it is shown that the thermal degradation of the BOC groups into CO2 and isobutene leads to the formation of a microporous structure1,4 which is highly dependent on the number of BOC units grafted on the polymer repeating unit and on the thermal protocol used to degrade the BOC units. Thus, as continuation on the characterization of the physical and gas transport properties for poly(oxyindole biphenylylene) membranes containing thermally labile side groups, this work reports on the synthesis and gas transport properties of a poly(oxyindole biphenylylene) that bears a BOC unit as a side group, a PN-BOC precursor membrane whose chemical structure is shown in Figure 1 as a reaction product, and which is then thermally modified to degrade the BOC side group to learn if the partial degradation of BOC into CO2 and isobutylene, according to the scheme shown in Figure 2, may guide us to design membrane materials that overcome the typical trade-off between gas permeability and selectivity. The isothermal kinetics BOC decomposition in the solid state membrane is followed quantitatively by TGA and qualitatively by FTIR-ATR and DSC to study in detail the effect of the thermal protocol on the gas separation performance, the specific volume, and the fractional free volume of thermally modified PN-BOC.

2. EXPERIMENTAL SECTION

2.1. Materials and Polymer Synthesis. Materials. All starting materials were obtained from Aldrich Chemical. Di-tert-butyl dicarbonate (BOC) and 4-dimethylaminopyridine were used as received. N-Methyl-2-pyrrolidinone (NMP) was distilled before use.

Figure 1. Chemical reaction to synthesize the pure PN-BOC polymer from the pure PN-H polymer and di-tert-butyl dicarbonate (BOC2O).

Polymer Synthesis. Figure 1 shows schematically the synthesis route to obtain the PN-BOC polymer. It is a chemical modification that uses as a starting material an already synthesized poly(oxyindole biphenylylene) bearing a hydrogen atom, PN-H polymer,2,13 which is then reacted with di-tert-butyl dicarbonate, BOC, to produce the PN-BOC polymer. This route is an alternative to the traditional route that would imply the synthesis of an isatin monomer containing a BOC group that will be further reacted with the biphenylylene monomer. Thus, the chemical modification of PN-H to obtain PN-BOC is described as follows. In a single-necked flask equipped with a magnetic stirrer was added PN-H (0.5 g, 1.76 mmol), and it was dissolved with NMP (3 mL). Afterward, in sequence, were charged di-tert-butyl dicarbonate (0.77g, 3.532 mmol) and a previously prepared solution of 4-dimethylaminopyridine (0.431g, 3.532 mmol) in NMP (2 mL). The mixture was reacted for 24 h at room temperature and was poured into methanol in order to precipitate the polymer. The precipitate, as white fibers, was washed with methanol and acetone in a Soxhlet apparatus to remove completely residual NMP.

2.2. Membrane Formation and Thermal Treatments. Dense polymer films from PN-BOC were solution-cast onto a horizontal surface of cellophane using chloroform solutions containing 3 wt % of polymer. Cast films were dried at room temperature overnight. After solvent evaporation, the membranes were vacuum-dried further at 80 °C for 24 h to eliminate residual solvent. The membrane thicknesses were between 40 and 50 μm. To produce polymeric membranes chemically modified in the solid state from the PN-BOC neat polymer, a thermal treatment protocol was chosen based on the thermogravimetric analysis performed on a TA Instruments Q50 operating at a heating rate of 20 °C/min under a nitrogen flow of 60 mL/min. The thermal modification of membrane samples was studied at 150 °C for 5, 10, 15, and 60 min under vacuum conditions (~1 mmHg) using a Yamato ADP-21 vacuum oven. To establish a standard thermal procedure, the vacuum oven was first set at 150 °C for 1 h before neat PN-BOC membranes were introduced into the vacuum oven. When treatment time was reached, membranes were immediately removed from the thermal treatment and left to cool room temperature.

2.3. Polymer Membrane Characterizations. Attenuated total reflectance Fourier transform infrared spectroscopy, FTIR-ATR, using a Nicolet FTIR-ATR iS10 spectrometer was used to follow the reaction kinetics of the thermo-labile side group, BOC. Normalized IR spectra were performed for PN-BOC, PN-H, and also the thermally treated polymer films using OMNIC 8.0 software to follow qualitatively the conversion degree of PN-BOC into copolymers [(PN-BOC)x−(PN-H)y]n and eventually PN-H. Differential scanning calorimetric analysis was performed on neat PN-BOC and thermally treated PN-
BOC membranes from 25 to 400 °C using a TA Instrument Q20 operating at a heating rate of 10 °C/min under a nitrogen flow of 50 mL/min. Polymer densities of dried films were determined at 30 °C in a density gradient column using well-degassed ZnCl₂ aqueous solutions. The gas permeability coefficients for ultrahigh purity gases H₂, O₂, N₂, CH₄, and CO₂ were measured in that order at 35 °C and 2 bar pressure in a variable pressure-constant volume gas permeation cell according to a procedure reported elsewhere.¹⁴ In order to standardize the measurement protocol, all membranes after their respective thermal treatment were mounted immediately in the permeation cell, and the gas permeation test was carried out 24 h later. The measurements for each gas were determined at least three times within an error less than 4%.

3. RESULTS AND DISCUSSION

3.1. Polymer Synthesis. The ¹H NMR spectrum that confirms the chemical structure for PN-BOC neat polymer is shown in Figure 3. The singlet observed at 1.67 ppm is assigned to protons of the tert-butyl group; the doublets at 7.35 and 7.51 ppm correspond to biphenyl group protons and the other signals described there to the rest of the protons that make up the polymeric repeating unit.

3.2. Thermogravimetric Characterization. Figure 4 shows the TGA results assessed for a recently solvent-cast PN-BOC membrane (curve 1), a PN-BOC vacuum-dried membrane at 80 °C for 24 h (curve 2), and finally for a PN-BOC vacuum-dried membrane that was first vacuum-dried at 80 °C for 24 h and then its temperature increased to 90 °C for an additional 24 h period (curve 3). The expected theoretical weight loss that corresponds to a full thermal decomposition of BOC per polymer repeating unit (Figure 2), a 26.1 wt %, has been included in this figure as a reference line. From the recently solvent-cast membrane, it is possible to observe a 27 wt % mass loss, in a temperature range between 60 and 200 °C, that should correspond mainly to the elimination of residual solvent (chloroform) and thermal degradation of the side BOC group. After vacuum-drying of the recently solvent-cast PN-BOC at 80 °C for a period of 24 h, it is shown that the thermal drying to eliminate the residual solvent lead to a membrane that now reveals a 25 wt % mass loss, suggesting at first sight that the difference of approximately 2 wt % with respect to the recently solvent-cast membrane is due to the elimination of residual solvent. Further vacuum-drying at 90 °C for another 24 h leads to a membrane that now reveals a 22 wt % mass loss, which in turn is lower than the theoretical weight mass loss (26.1 wt %) expected from the thermal decomposition of BOC, but more importantly, lower than the 27 wt % mass loss observed in the solvent-cast PN-BOC. These quantitative results suggest that some BOC mass is being lost under the vacuum-drying treatment when long thermal drying periods are used to eliminate the residual solvent. To standardize a procedure for PN-BOC thermal treatments and avoid an
appreciable amount of BOC mass loss under the vacuum drying process, all membranes used for gas transport properties measurements were first carefully vacuum-dried at 80 °C for 24 h and then subjected to the thermal treatment as described below.

3.3. Reaction Kinetics (Thermal Decomposition of BOC vs Time). To establish an appropriate thermal treatment protocol to follow the decomposition reaction of BOC groups and to study the effect of thermal treatment on gas permeability and selectivity in a suitable time scale, Figure 5 shows the isothermal weight mass loss, at 130, 150, 170, and 200 °C, as a function of time in PN-BOC polymer films. An important observation is related to the time scale of the kinetics reaction which is fast at high temperatures, 170 or 200 °C, and slow at low temperatures, 130 °C; i.e., at a 10 or 15 min constant time practically the total amount of BOC has been eliminated at high temperatures (>170 °C), whereas roughly a 2 to 5 wt % of BOC has been eliminated at 130 °C. From a practical point of view, these results means that PN-BOC will be quickly transformed into PN-H at high temperatures (>170 °C) in short periods of time, whereas long periods of time (>1 h) would be required to convert PN-BOC into PN-H at low temperatures (<130 °C). Thus, a 150 °C temperature is reasonable to thermally treat the PN-BOC membranes if an observer wants to learn about the effect of the thermal treatment on the gas transport properties of these membranes. In effect, at 150 °C, the kinetics reaction is still fast enough to produce a chemical modification of PN-BOC into a [(PN-BOC)_x-(PN-H)_y]_n copolymer that must have different lengths of (PN-BOC)_x or (PN-H)_y, at relatively short periods of time (from 5 to 60 min).

The isothermal decomposition of BOC at any temperature can be followed by the amount of weight loss, as evaluated from TGA studies, against time according to

\[
\text{Conversion} = \left( \frac{W_f(t)}{W_\text{th}} \right) \times 100
\]

where \(W_f(t)\) is the actual mass of BOC lost at time \(t\) when PN-BOC is thermally treated at temperature \(T\), and \(W_\text{th}\) is the theoretical mass loss per polymer repeating unit when all the thermo-labile side group has been lost. Table 1 summarizes the polymer acronym and the isothermal conversion, at 150 °C, when PN-BOC is first partially converted to [(PN-BOC)_x-(PN-H)_y]_n copolymers and then, at infinite time, fully transformed into a neat PN-H polymer according to the mechanism pointed out in Figure 2. At 5 min, there has been a 56% conversion of PN-BOC into a [(PN-BOC)_x-(PN-H)_y]_n copolymer, whereas at 60 min there has been a 96% conversion of BOC units to PN-H. During the BOC thermal conversion in the solid state membrane, it would be expected that these copolymers are packed in a different manner from their initially synthesized and cast PN-BOC packing form, and of course, this ought to be reflected in different combinations of permeability and selectivity with respect to those determined for pure PN-BOC and PN-H membranes.

3.4. Polymer Membrane Characterization. The eventual progress of thermal decomposition of BOC from the thermally treated PN-BOC polymer at 150 °C for different times is also supported by both the FTIR-ATR spectra reported in Figure 6 and DSC scans reported in Figure 7 for PN-BOC membranes isothermally treated at 150 °C for different times. The IR spectra for membranes of neat PN-BOC and neat PN-H have been inserted for comparison purposes. In Figure 6, the chemical progress of reaction can be indirectly followed by a gradual appearance of the signal at 3400 cm\(^{-1}\) corresponding to the N=H bond, as well as the presence of a triplet between 1700 and 1800 cm\(^{-1}\) corresponding to the two carbonyl groups of PN-BOC, which eventually disappears as time increases from 5 to 60 min until it is only observed a single signal corresponding to the carbonyl group of PN-H polymer. In a similar manner, the DSC scans reported in Figure 7 reveal that a chemical reaction with a different conversion of PN-BOC is being carried out when the neat PN-BOC is thermally treated at 150 °C for different times according to the reductions shown by the areas that represent an endothermic reaction between 140 and 240 °C and which practically disappears for PN-BOC_50. These FTIR-ATR and DSC results qualitatively confirm that the chemical reaction is being promoted by

<table>
<thead>
<tr>
<th>polymer acronym</th>
<th>time, min</th>
<th>conversion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PN-BOC</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PN-BOC_5</td>
<td>5</td>
<td>56</td>
</tr>
<tr>
<td>PN-BOC_10</td>
<td>10</td>
<td>79</td>
</tr>
<tr>
<td>PN-BOC_15</td>
<td>15</td>
<td>88</td>
</tr>
<tr>
<td>PN-BOC_60</td>
<td>60</td>
<td>96</td>
</tr>
<tr>
<td>PN-H</td>
<td>∞</td>
<td>100</td>
</tr>
</tbody>
</table>

aConversion percentage, as a measurement of the kinetics reaction, was determined by the ratio of actual mass loss relative to the theoretical mass loss. bConversion percentage calculated according to eq 1.
thermal treatments at 150 °C on the solid state of the PN-BOC glassy polymer.

3.5. Gas Transport Properties. The pure gas transport properties for pure PN-BOC and PN-BOC thermally modified membranes were assessed to learn about the effect of thermal treatment on the permeability coefficients and ideal separation factors. These values, along with the specific volume and their FFV, are summarized in Table 2, where the corresponding values for PN-H have been included for comparison purposes. An important observation is related to the permeability and ideal selectivity measured for pure PN-BOC and pure PN-H membranes and their correlation to FFV since they do not follow the expected typical rules. The PN-BOC membranes possess lower permeability coefficients and also lower ideal selectivity factors than the reported PN-H membranes, even though the FFV of PN-BOC is higher than the corresponding one for PN-H. The thermo-labile BOC group is by far more bulky than a simple –H atom, thus it would be expected that the permeability coefficients in PN-BOC were larger than those values in PN-H. However, this is not the case and a possible explanation may be found in the fact that they were born in different casting solutions. The PN-BOC membranes were born in chloroform, whereas the PN-H membranes were born in NMP. The solvent effects associated with the different thermal histories to remove the low boiling point chloroform compared to the high boiling point NMP could have led to packing efficiencies with different redistributions in the FFV determined for PN-BOC and PN-H membranes. It is out of the scope of this study to determine the FFV redistribution. An additional parameter that could explain the fact that they do not follow the expected typical rules may be found in polymer chain mobility as defined by their glass transition temperature, Tg. However, as it shown in Figure 7, these polymers do not show an appreciable second order transition, or Tg, before they start its decomposition at temperatures higher than 500 °C (Figure 4). Thus, it is not possible to conclude about the effect of the polymer chain mobility imposed by the bulky BOC or the small –H atom on the gas transport properties of these polymers.

As many glassy polymers are not in thermodynamic equilibrium and differences in casting and aging will influence their chain packing efficiency, the explanation given in the last paragraph is also supported by the experimental fact that when the neat PN-BOC membrane is treated at 150 °C for 5 min to

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Table 2. Gas Permeability Coefficients and Ideal Selectivity Factors, Measured at 35°C and 2 bar, as well as the Specific Volume and Fractional Free Volume Determined for Pure PN-BOC and PN-BOC Membranes Isothermally Treated at 150 °C for Different Times

<table>
<thead>
<tr>
<th>polymer acronyn</th>
<th>permeability coefficient, i</th>
<th>ideal selectivity, P(i)/P(j)</th>
<th>V(30 °C)</th>
<th>FFV</th>
</tr>
</thead>
<tbody>
<tr>
<td>PN-BOC90</td>
<td>H2: 39, O2: 5.8, CO2: 38</td>
<td>O2/N2: 4.1, CO2/N2: 1.22, 22</td>
<td>21</td>
<td>0.65</td>
</tr>
<tr>
<td>PN-BOC100</td>
<td>H2: 63, O2: 10.0, CO2: 62</td>
<td>O2/N2: 4.1, CO2/N2: 1.22, 22</td>
<td>21</td>
<td>0.65</td>
</tr>
<tr>
<td>PN-BOC120</td>
<td>H2: 67, O2: 8.7, CO2: 54</td>
<td>O2/N2: 4.1, CO2/N2: 1.22, 22</td>
<td>21</td>
<td>0.65</td>
</tr>
</tbody>
</table>

4Permeability in Barrer (1 Barrer = 1 × 10^-10 cm³ gas STP cm²/s cmHg); 5V(30 °C) is the specific volume determined at 30 °C in density gradient column. 6FFV is the fractional free volume calculated as FFV = [(V(30 °C) – V(0))/V(30 °C)] where V(0) = 1.3 ∑Vₜ is the occupied volume and ∑Vₜ is the van der Waals volume of the repeating unit calculated from group contribution methods developed by Van Krevelen. 7For PN-BOC isothermally treated at 150 °C at different times, V₀ = σΩPN-H + (1 − σ)Ω%d-PN-BOC with σ representing the conversion fraction reported in Table 1. 8Permeability and selectivity values as reported in current literature.
produce the PN-BOC₄ membrane, there is an increase in all the permeability coefficients, and these increases in permeability are accompanied by either a practically constant ideal selectivity for O₂/N₂ and CO₂/N₂ and a decrease in the ideal selectivity for H₂/CH₄ and CO₂/CH₄. If FFV for the PN-BOC₄ membrane is calculated taking into account that at 5 min 56% of the BOC has been transformed into a copolymer [(PN-BOC)ₓ-PN-(H)ᵧ]ₓ, according to eq 1, the calculated FFV is the same as the one estimated for pure PN-BOC, even though the permeability coefficients have increased by a 2.3-fold factor for O₂ and CO₂ and by a 1.9-fold factor for H₂. From these results, it is obvious that different redistributions of the same magnitude of FFV are playing an important role. Moreover, if we compare the permeability coefficients measured for PN-BOC₃ with those determined for PN-H, surprisingly the permeability coefficients of PN-BOC₃ are closer to those values determined for PN-H, a membrane with lower FFV than PN-BOC₄ and PN-BOC.

Thermal treatment at times higher than 5 min lead to membranes with permeability coefficients still higher than pure PN-BOC membranes but lower than those values determined for PN-BOC₅. As time increases from 5 to 60 min, the permeability coefficients for PN-BOC₁₀, PN-BOC₁₅, and PN-BOC₆₀ decrease when it would be expected that they were increasing in the direction of those values determined for pure PN-H membranes. However, this is not the case, but interestingly, what is really increasing are the gas pairs selectivity since the ideal selectivity for O₂/N₂, CO₂/N₂, H₂/CH₄, and CO₂/CH₄ are increasing in the direction of the corresponding selectivity determined for pure PN-H. The reductions in permeability coefficients from 10 to 60 min are in agreement with the reduction in the FFV as calculated from eq 1, but as it was mentioned, they are not in agreement to what would be expected for the permeability coefficients that, in principle, should tend to the values measured for pure PN-H. Since the chemical structural changes promoted by thermal treatments in PN-BOC are partially explaining the expected permeability coefficients in PN-BOC₁₀, PN-BOC₁₅, and PN-BOC₆₀, an alternative explanation could be found on the physical aging or accelerated densification of these glassy membranes that have been subjected to high temperatures for long periods of time. The physical densification promoted at elevated temperatures, a common phenomenon observed when thin glassy polymers are subjected to elevated temperature and that usually decreases the permeability coefficients, is more noticeable in the permeability coefficients for PN-BOC₆₀, a membrane with 96% of BOC transformed into –H, whose permeability coefficients are about 50% lower than in PN-H, even though this membrane practically possesses the same ideal selectivity as the nonphysically aged PN-H polymer.

Figure 8 shows a selectivity–permeability combination for the gas pairs O₂/N₂ and CO₂/N₂ at 35 °C and 2 bar, in pure PN-BOC, pure PN-H, and thermally treated PN-BOC membranes at 150 °C for different times. The Robeson’s upper bounds are included as a reference since they are a representation of the state of the art in the performance of polymers as potential candidates for membrane separation processes. The selectivity–permeability combinations of properties determined for cross-linked β-cyclodextrin-g-polyimide designed as a material for the CO₂ capture, sequestration, or membrane separations are also included as a reference. The selectivity–permeability relationship for all the PN-BOC thermally treated membranes do not follow an additive behavior between the pure PN-BOC and PN-H polymers, the two polymers that are been used “as a model” to explore the potential use of labile side groups to tailor selectivity and permeability combinations that overcome the typical trade-off. A possible explanation could be a quite different packing efficiency of their polymer repeating units that lead to different free volume redistributions arising from the chemical change on one hand, and maybe because of the diffusion of CO₂ and isobutylene, the products of the thermal degradation of BOC side groups could be playing an important role in the redistribution of the free volume elements on the other hand. It is also interesting to observe that the selectivity–permeability relationship presents two well-defined stages. The first one, at 5 min, pushes the selectivity–permeability relationship to the right of that of pure PN-BOC membranes, from PN-BOC to PN-BOC₁₀, and the second one, from 10 to 60 min, pushes the selectivity–permeability properties to the left and above the properties of PN-BOC₁₀ from PN-BOC₁₀ to PN-BOC₆₀. For both gas pairs O₂/N₂ and CO₂/N₂, during the first stage, there is a 2.3-fold increase in the permeability for O₂ and CO₂ without a reduction in the corresponding selectivity, whereas during the second stage there is a decrease in the permeability.
of both gases O₂ and CO₂ which is associated with an increase in their selectivity with respect to N₂. The second stage confirms that the physical aging promoted by long exposure of glassy polymers to high thermal treatments is present during the chemical changes in the solid state studied with these type of polymers; thus, there is another trade-off that needs to be studied between the effect of chemical changes and physical aging on physical properties when tailoring membrane materials for gas separation following the procedure studied in this work. Far away from the fact that physical aging is playing an important role, all membranes thermally treated at 150 °C for 5 and up to 60 min possess better selectivity—permeability combinations than the pure PN-BOC since they possess a combination that is located to the right and above the corresponding properties of pure PN-BOC. That is, the PN-BOC₅ membranes possess a P(O₂) and P(CO₂) of 13.2 and 86 Barrers, and they have the same O₂/N₂ and CO₂/N₂ ideal selectivity of 4.1 and 27, respectively, as those of the PN-BOC precursor membrane. These results that move the gas transport properties in the direction as those recently reported for the thermally treated β-cyclodextrin-g-polyimides PI-g-CD, where it can be seen that the selectivity—permeability properties for the gas pairs O₂/N₂ and CO₂/N₂ moves to the right with respect to the original PI-g-CD200 as the temperature goes up, supports the general hypothesis that the thermal degradation of carefully designed thermo-labile side groups in the polymer repeating units will lead to redistribution of the fractional free volume once they are thermally removed, thus leading to better selectivity—permeability combinations than their precursors. An interesting approach for future work should be (1) to treat the pure PN-BOC membranes at more elevated temperatures (250–400 °C) and for really short periods of time in order to learn if the sudden diffusion of CO₂ formed under the decomposition of BOC lead to the formation of non-interconnected nanopores and (2) to incorporate more than one BOC group per polymer-repeating unit and learn if this will eventually lead to the formation and diffusion of more CO₂ expecting to create a more complex noninterconnected nanoporous structure.

Figure 9 shows the selectivity—permeability combination of properties for the gas pairs H₂/CH₄ and CO₂/CH₄. The selectivity—permeability combination of properties for these gas pairs also moves to the right with respect to the corresponding combination for pure PN-BOC, but only those combinations shown by PN-BOC₁₅ and PN-BOC₆₀ move to the right and above the corresponding pure PN-BOC membranes. The two stages observed for the previous gas pairs are also observed for these gas pairs; however, the typical trade-off between permeability and selectivity is more noticeable in both stages. With respect to pure PN-BOC, the PN-BOC₅ membrane shows a 1.9-fold increase in H₂ permeability and a 2.3-fold increase in CO₂ permeability with an associated decrease in its selectivity for the gas pairs H₂/CH₄ and CO₂/CH₄ in accordance to the typical trade-off lines. After a thermal treatment for more than 5 min has been imposed, the second stage, the opposite behavior is present when the PN-BOC₅ membrane is taken as a reference; i.e. a decrease in permeability is accompanied by an increase in selectivity. From a practical point of view, the PN-BOC thermally treated membranes at 150 °C for 15 and 60 min have better combinations than pure PN-BOC; i.e. the PN-BOC₆₀ membranes possess H₂ and CO₂ permeability coefficients that are 1.7 and 1.4 higher, respectively, than those of pure PN-BOC, and they are more selective for the gas pairs H₂/CH₄ and CO₂/CH₄. Once again this confirms that thermo-labile side groups can lead to membrane materials that overcome the typical trade-off behavior between permeability and selectivity in a particular family of polymers but of course with an appropriate thermal treatment protocol.

4. CONCLUSIONS

A poly(oxyindole biphenylylene) polymer bearing a thermo-labile BOC side group has been successfully synthesized and thermally treated, at different temperatures and times, to learn how the thermal decomposition of PN-BOC to produce [(PN-BOC)ₓ.(PN-H)ₙ]ₙ copolymers, and eventually, at infinite time, PN-H may lead to membranes with selectivity and permeability combinations that overcome the typical trade-off. Systematic studies using TGA, FTIR-ATR, and DSC to follow the progress of thermal modifications show that the decomposition of BOC occurs in a temperature range between 90 and 200 °C. From kinetics studies carried out at constant temperature, it is
concluded that thermal treatment at 150 °C for short periods of time, from 5 to 60 min, are enough to lead to the formation of more permeable and more selective membranes than the original PN-BOC precursor. Nevertheless, care must be taken since the physical aging is accelerated during the chemical transformation in the solid state membrane, at high temperatures for long times, in PN-BOC glassy polymers. For the gas pairs O₂/N₂ and CO₂/N₂, the PN-BOC₉₀ membranes show a 2.3-fold increase in the permeability for O₂ and CO₂ with respect to pure PN-BOC, and they possess practically the same gas pair selectivity. For the gas pairs H₂/CH₄ and CO₂/CH₄, the PN-BOC₉₀ membranes are both more permeable and more selective than pure PN-BOC.

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**Notes**
The authors declare no competing financial interest.

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**REFERENCES**


