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Gas Transport Properties in Cross-Linked and Vacuum Annealed Poly(oxyindole biphenylylene) Membranes

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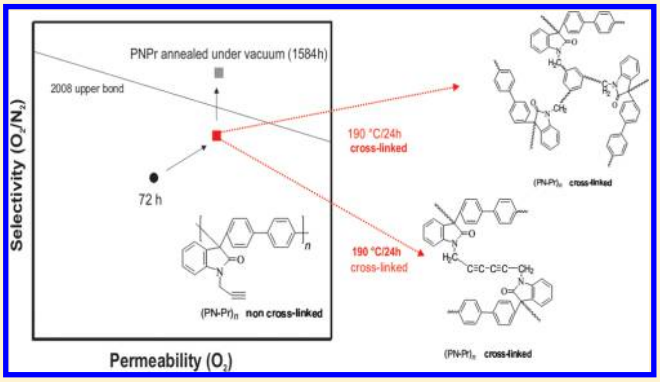
ABSTRACT: This work studies useful routes to produce cross-linked poly(oxyindole biphenylylene) bearing a cross-linkable propargyl group, PNPr. Thus, the effect of cross-linking temperature and time on gas permeability and ideal selectivity for a non-cross-linked PNPr membrane to produce a cross-linked PNPr membrane is studied in detail in order to learn how more productive membranes, in terms of permeability−selectivity combinations, and membranes resistant to solvent swelling and CO_2 plasticization may be produced. Systematic studies on structure/processing/property relationship assessed by Fourier transform infrared attenuated total reflectance (FTIR-ATR), gel content (GC [%]), swelling degree (SD [%]), specific volume, wide-angle X-ray diffraction (WAXD), and gas permeability measurements reveal that PNPr membranes cross-linked under vacuum (1 mmHg) at 190 °C for 24 h, and further vacuum-annealed for 1584 h, at 35 °C and 10^{-3} mmHg, produce membranes that overcome the typical trade-off between permeability and selectivity. In effect, the thermally cross-linked membranes annealed under vacuum for 1584 h, as compared to the non-cross-linked membranes, possess $P(H_2)$ and $P(CO_2)$ that increase by 2.4 and 2.1 factors while selectivity increases from 25 to 45 for the H_2/CH_4 pair and from 25 to 39 for the CO_2/CH_4 pair, whereas $P(O_2)$ increases by a 2.4 factor with an associated increase in selectivity from 4.4 to 9.6 for O_2/N_2 which situates this membrane above Robeson's 2008 upper-bound limit, at least for this pair of gases. The cross-linked membranes are resistant to solvent selling, since their SD [%] in NMP is on the order of 1−3%, and also to CO_2 plasticization since the plasticization pressure was not observed at least up to the 18 bar upstream pressure studied here.



1. INTRODUCTION

Gas polymer membrane separation technology is an attractive alternative since it is based on the relative magnitude of the gas permeability coefficients to be separated, and mainly because it can be carried out at relatively low temperature and pressure as compared to other current separations.[1−4] However, if amorphous polymer membranes want to find generalized application in real situations, they need to be productive in terms of their permeability−selectivity combination,[5−7] in addition to possessing resistance to solvent swelling and CO_2 plasticization. In effect, the current literature presents a great variety of interesting polymers with an attractive permeability−selectivity combination, such as 6FDA-DAM:DABA,[8] Matrimid,[9] HAB-6FDA,[10] KAUST-PI-1,[11] and PIMs;[12] however, their gas transport and separation properties could change due to solvent swelling, aging, or densification, and/or owing to plasticization promoted by high condensable gases such as CO_2.[13−17] It is well-known that all of these changes are associated with changes in free volume due to the amorphous nature of polymer membranes.[18] Thus, an interesting challenge for science and engineering is to learn how changes in free volume, defined as a difference between the amorphous specific volume at given temperature, $V_g(T)$, minus the corresponding specific volume at equilibrium, $V_c(T)$, may be ideally suppressed or at least mitigated.

Thermal treatments and/or cross-linking to change the chemical structure or the solid-state packing of glassy polymers are attractive routes to produce polymer membranes that fulfill all or at least some of the mentioned requirements. Chung[19] et

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al. studied the effect of thermal treatments, between 150 and 320 °C, on the CO_2 plasticization pressure of 6FDA-2,6-DAT hollow fibers, and determined that plasticization can be suppressed up to 14.6 bar upstream pressure, as a consequence of a better chain packing and nodule interaction promoted by annealing at high temperatures. In the direction of cross-linking, Koros and co-workers reported cross-linked polyimide membranes with high resistance to plasticization pressures.[20−22] An alternative approach is also to promote chemical changes, by high temperature treatments, in the polymer structure to increase the rigidity of the polymer chains, while maintaining large interchain spacing, as it has been learned from the so-called thermally rearranged polymers and polymers with intrinsic microporosity (PIMs) that results in a more rigid backbone.[23,24] Moreover, in a previous work Hernández-Martínez[25] et al. showed that a simultaneous thermal cross-linking and decomposition of side groups located strategically in a poly(oxyindole biphenylylene) copolymer may lead to gas separation membranes that are more resistant to physical aging, thus more resistant to changes in their gas transport properties. Particularly in this work, a poly(oxyindole biphenylylene) bearing just a cross-linkable propargyl group (PNPr) membrane is synthesized in order to study the net effect of cross-linking processing variables, such as temperature and time, on the permeability−selectivity combination of the resulting cross-linked membranes. The systematic structure/processing/property relationship is assessed by Fourier transform infrared attenuated total reflectance (FTIR-ATR), gel content (GC), swelling degree (SD), specific volume, wide-angle X-ray diffraction (WAXD), and gas permeability coefficients to learn how to produce a more productive and more resistant cross-linked PNPr membrane.

2. EXPERIMENTAL SECTION

2.1. Materials and Polymer Synthesis. *2.1.1. Materials.* All starting materials were purchased from Aldrich Chemical. Propargyl bromide (BrPr) and potassium carbonate (K_2CO_3) were used as received, whereas *N*-methyl-2-pyrrolidinone (NMP) was distilled before use.

2.1.2. Polymer Synthesis. Figure 1 summarizes the chemical reaction pathway to synthesize a poly(oxyindole biphenylylene) bearing a cross-linkable propargyl group, PNPr (**3**), which will be used as a model to study the effect of temperature and time on the permeability and selectivity properties of the resulting membranes. The chemical reaction that can be carried out at room temperature involves an already synthesized poly(oxyindole biphenylylene) that bears a hydrogen atom, PNH (**1**) polymer, reacted with propargyl bromide (**2**). A typical synthesis is as follows: In a single-necked flask equipped with a magnetic stirrer, fibrous PNH (0.25 g, 0.88 mmol) is dissolved with NMP (2.5 mL). Once dissolution is reached, known amounts of K_2CO_3 (0.6095 g, 4.4 mmol) and BrPr (0.4836 mL, 4.4 mmol) are added, and the mixture is reacted, at room temperature, for 24 h or until a red color, high viscosity solution is formed. Afterward, the polymer is precipitated in methanol, as white fibers, and washed several times in acid water (pH 6) until the residual water becomes pH 7. The polymer is then Soxhlet extracted with methanol/water solutions to remove the residual NMP. For the typical reaction described the yield of PNPr was 0.257 g.

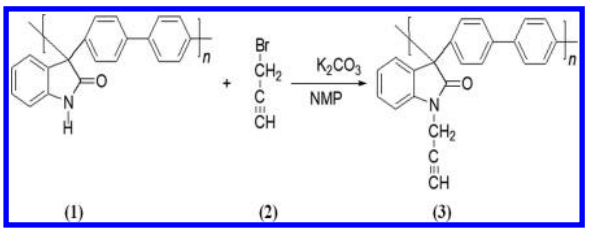

Figure 1. Chemical reaction pathway to synthesize, at room temperature, pure poly(oxyindole biphenylylene) bearing a cross-linkable propargyl group, PNPr (**3**).

2.2. Membrane Formation and Thermal Treatments. Polymer dense films were solution-cast onto a horizontal surface of cellophane using chloroform solutions containing 3 wt % polymer. The cast films were dried overnight and then removed from the cellophane to be further vacuum-dried for an additional 24 h at 80 °C to remove residual solvent. The thicknesses of pure polymer films, the so-called non-cross-linked polymer, were between 20 and 30 μm. To produce the cross-linked polymer as-cast membranes were treated under vacuum (∼1 mmHg) at different temperatures (150, 170, 190, and 210 °C) and maintained at the oven temperature for different times (1 and 24 h), using an standardized thermal protocol that was defined as follows: (1) the vacuum oven, a Yamato ADP 21, was equilibrated (∼20 min) at the desired temperature; (2) the membrane was then introduced for the desired time; (3) the membrane was removed from the vacuum oven and allowed to cool until it reached room temperature.

2.3. Polymer Membrane Characterization. Proton nuclear magnetic resonance (^{1}H NMR) was used to verify the chemical structure of the synthesized poly(oxyindole biphenylylene) that bears a propargyl group (PNPr) in a Bruker Avance spectrometer. The chemical cross-linking reaction throughout the thermolabile propargyl groups was followed indirectly by measuring the gel content, GC [%] = $(M_c/M_0) \times 100$, and the swelling degree in NMP, SD [%] = $(M_s/M_c) \times 100$],[26] where M_c is the weight of an already cross-linked polymer, M_0 is the weight of initially dried membrane, made up a fraction of non-cross-linked and cross-linked polymer, and M_s is the weight of NMP adsorbed at equilibrium in the cross-linked polymer. Similarly, FTIR-ATR, in a Nicolet iS10, was also used to get the corresponding spectra in the non-cross-linked and cross-linked membranes. All spectra were normalized using the software OMNIC 8.0. For all membranes, the specific volumes of dried films, V(30 °C), were measured at 30 °C in a density gradient column using well-degassed $ZnCl_2$ solutions. Wide-angle X-ray diffraction (WAXD) scans were made for non-cross-linked and cross-linked membranes using a Xeuss Xenocs X-ray diffractometer at a Cu K wavelength of 1.54 Å. A corresponding *d*-spacing, as an indicator of the average chain spacing which it is known indirectly correlates with fractional free volume, was calculated from the diffraction peak maxima using the well-known Bragg's equation, $n\lambda = 2d \sin \theta$. Permeability coefficients, $P(i)$, for ultra-high-purity gases H_2, O_2, N_2, CH_4, and CO_2, were measured, at 35 °C and 2 bar, in all membranes after 72 h of any thermal treatment. All $P(i)$ were measured in a variable pressure/constant volume permeation cell following a well-established procedure reported elsewhere.[27] For this work, ideal selectivity for two gas pairs, *i* and *j*, is defined as the ratio of two pure gas permeability coefficients, $P(i)/P(j)$. Specifically, the effect of aging time on the $P(i)$ of an already cross-

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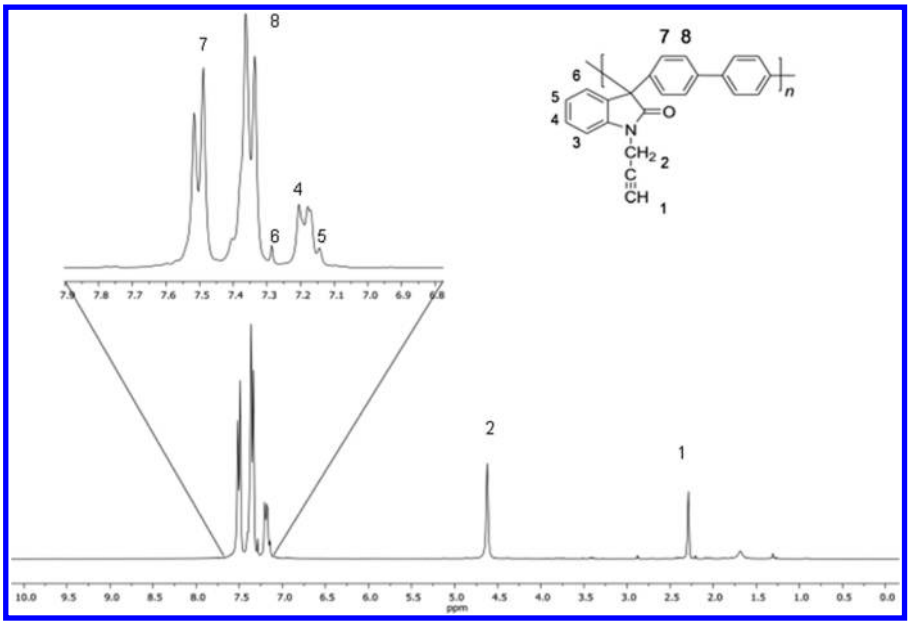

Figure 2. ^{1}H NMR spectrum for synthesized PNPr polymer (solution in $CDCl_3$).

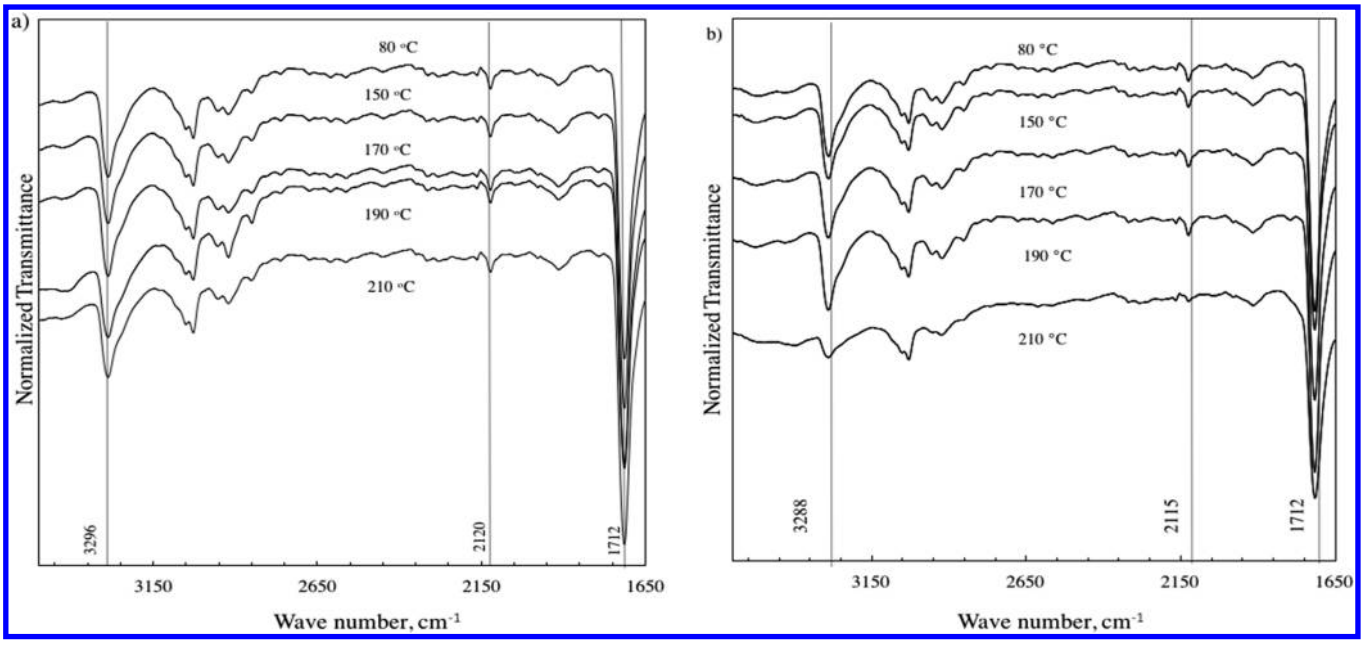

Figure 3. FTIR-ATR spectra for pure PNPr and for PNPr membranes thermally treated at different temperatures for 1 (a) and 24 h (b).

linked membrane was followed for at least 1584 h, maintaining always the membrane at 35 °C under a relatively high vacuum (10^{-3} mmHg).

3. RESULTS AND DISCUSSION

3.1. Polymer Synthesis. Figure 2 shows a characteristic ^{1}H NMR spectrum determined for a poly(oxyindole biphenylylene) bearing a cross-linkable propargyle group synthesized following the reaction scheme described in Figure 1. Signals at 2.25 and 4.65 ppm correspond to propargyl protons, whereas the doublets at 7.35 and 7.51 ppm are representative of biphenyl protons. The remaining signals correspond to the rest of the protons that make up the polymeric repeating unit. The ^{1}H NMR analysis confirms the chemical reaction scheme depicted in Figure 1, where the hydrogen atom of polymer PNH[28] has been completely replaced by the propargyl group to produce a PNPr, a poly(oxyindole biphenylylene) that contains propargyl as a lateral group.

3.2. Membrane Formation and Thermal Treatments. The progress of the cross-linking reaction in PNPr, at different temperatures and times, was followed by FTIR-ATR analysis as described in Figure 3, part a for 1 h and part b for 24 h thermal treatments. Important signals are located at 3296 cm^{-1}, associated with acetylene vibrations, and 2120 cm^{-1}, which corresponds to the C≡C vibrations.[29−32] The area for each signal diminishes as the temperature increases, corroborating the cross-linking reaction between, or among, the propargyl groups. The cross-linking reaction of propargyl groups has been widely studied in air and inert atmospheres at temperatures higher than 200 °C, showing that it can proceed

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under simultaneous complex mechanisms. In this work, the cross-linking reaction, carried out under vacuum (~1 mmHg) at lower temperatures than those reported in air, would be expected to proceed at least with two possible mechanisms: one that implies a simple trimerization reaction among three acetylene end groups to form an aromatic cross-linker as depicted in mechanism a reported in Figure 4, and another one

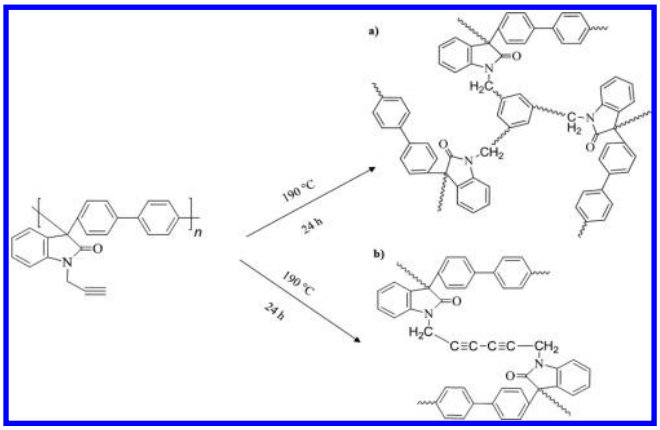

Figure 4. Simultaneous chemical reaction mechanism to produce cross-linked membrane starting from PNPr polymer membrane that has been thermally treated, under vacuum, at 190 °C for 24 h. Part a implies an aromatic cross-linker, whereas part b implies a linear cross-linker.

that implies a complex coupling reaction through the triple bond in the C−C atoms (Strauss coupling, Glaser coupling) to produce a lineal cross-linker as depicted in mechanism b in Figure 4, just as it has been described elsewhere.[32] Table 1 summarizes the weight percent of cross-linked polymer, determined as GC [%], the swelling degree (SD [%]), and a "cross-linking degree" (X_{IR} [%]) determined by FTIR-ATR analysis following the reduction in the area associated with the acetylene vibration (at 3296 cm^{-1}) of a cross-linked PNPr membrane with respect to the area determined for a non-cross-linked one. In Table 1, the GC [%] and X_{IR} increase as the cross-linking temperature and time increase; i.e., at 190 °C, the GC [%] of 96.4% for 1 h increases to 98.5% for 24 h, while at 210 °C, the GC [%] increases from 97.3 to 99%. These results confirm that a high content of a cross-linked polymer, under the vacuum conditions studied here, may be obtained in a 190 and 210 °C temperature range to produce highly resistant cross-linked membranes to solvent plasticization since their SD [%], in an aggressive NMP solvent, is in the range 1−3%, as can be seen in Table 1.

Table 1. Gel Content (GC [%]), Swelling Degree (SD [%]), and Cross-Linking Degree Determined from FTIR-ATR for PNPr and for PNPr Thermally Treated Membranes at Different Temperatures for 1 and 24 h

	cross-linking temp (°C)	GC [%],[a] (NMP)	SD [%][b]	X_{IR} [%][c]
PNPr		0	100	0
PNPr, 1 h	150	14.6	85	22
	170	83.3	17	42
	190	96.4	4	56
	210	97.3	3	90
PNPr, 24 h	150	45.4	55	38
	170	89.5	10	55
	190	98.5	2	80
	210	99.0	1	99

[a]GC [%] = $(M_c/M_0) \times 100$, where M_0 is the initial weight of dried membrane and M_c is the corresponding weight of a cross-linked membrane. [b]SD [%] = $(M_s/M_c) \times 100$, where M_s is the weight of adsorbed solvent (NMP) in a weight of a cross-linked membrane, M_c. [c]X_{IR} [%] = $(A_i/A_0) \times 100$, where A_i and A_0 are the areas under the FTIR-ATR 3296 cm^{-1} signal associated with the acetylene C−H group of PNPr cross-linked membrane at a given temperature and time, A_i, and a PNPr non cross-linked membrane, A_0.

Figure 5 shows the WAXD scans for non-cross-linked and cross-linked PNPr membranes at different temperatures for 1 h (part a) and for 24 h (part b). The results reveal two broad peaks that move to the right or left depending on the temperature and time used to carry out the cross-linking reaction. In general, these membranes are constituted by two types of solid state packing: a fraction of efficient chain-to-chain packing attributed to *d*-spacing between 3.98 and 4.12 Å, a typical range found in glassy polymers, and another fraction loosely packed characterized by *d*-spacing between 7.75 and 8.02 Å, a typical range reported for PIMs. The exact nature of these two well-defined peaks is not known; however, two-well-defined peaks have been reported previously for glassy polymers with pendant phenyl rings such as polystyrene, poly(2,6-diphenyl-1,4-phenylene oxide), glassy polymers with rigid structures such as FBP/tBIA and FBP/IA,[33] and recently for polymers with intrinsic microporosity. In this work, it is assumed that the average *d*-spacing that corresponds to the efficient chain-to-chain packing could correspond to the fraction of cross-linked polymer where a lineal cross-link has been formed, whereas the more loosely packed fraction could correspond to the fraction of cross-linked polymer where an aromatic cross-linker has been formed (see Figure 4). Of course, the fraction distribution is highly dependent on the cross-linking temperature and time conditions.

3.3. Gas Transport Properties. Table 2 summarizes the permeability coefficients and ideal separation factors for several gases, at 35 °C and 2 bar, as well as the specific volume, *V*(30 °C), and two *d*-spacing values for non-cross-linked and cross-linked PNPr membranes at different temperatures and times. For all gases, the net effect of increasing the thermal treatment temperature results in an increase of gas permeability coefficients, with an ideal selectivity that remains practically constant or increases depending on the type of gases being permeated; i.e., the membrane that was cross-linked for 24 h at 190 °C increases permeability coefficients for H_2 and O_2 by 2.24 and 2.50 factors, respectively, whereas H_2/CH_4 increases from 25 to 27 and O_2/N_2 increases from 4.4 to 5.2. It is interesting to note that the permeability coefficients for the cross-linked membranes are higher than the corresponding values for the non-cross-linked membranes, even though the cross-linked membranes possess a lower specific volume (see values in Table 2), as is expected for cross-linked membranes. In order to elucidate the net effect of cross-linking on the increases in permeability coefficients, Table 2 summarizes two *d*-spacing determinations that correspond to the maximum peaks observed in Figure 5. It is assumed in this work that the first *d*-spacing corresponds to a more loosely packed fraction—the one that contains the bulky connector aromatic group (see mechanism a in Figure 4)—whereas the second one corresponds to a fraction of polymer with a more efficient chain-to-chain packing—the one that contains the linear connector group (see mechanism b in Figure 4). It is also

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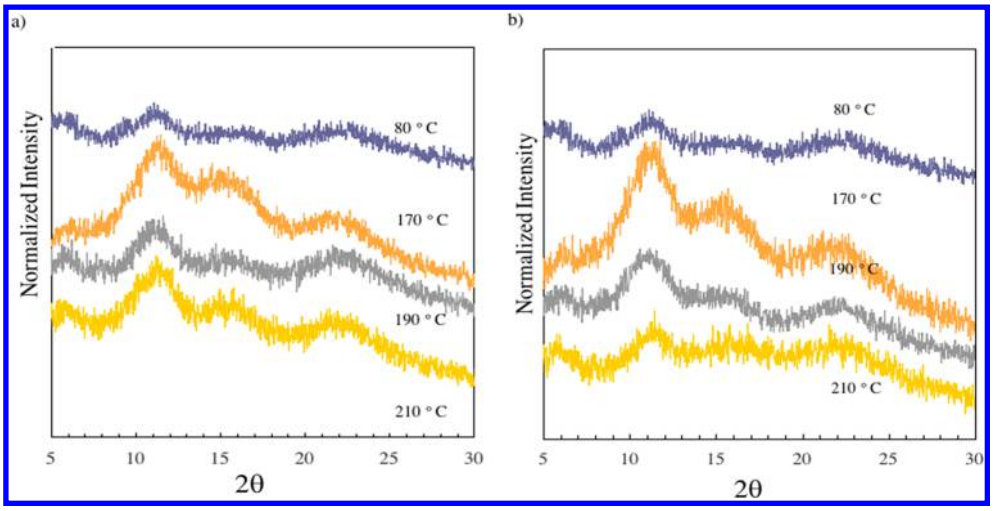

Figure 5. WAXD diffractograms for pure PNPr and for PNPr membranes thermally modified at different temperatures for 1 (a) and 24 h (b).

Table 2. Permeability Coefficients for Pure Gases and Ideal Selectivity, at 35 °C and 2 bar, Specific Volume, V(30 °C), and Two d-Spacing Values Determined for PNPr and for PNPr Membranes Thermally Treated at Different Temperatures for 1 and 24 h

		permeability, $P(i)$[a]					ideal selectivity, $P(i)/P(j)$					
time (h)	cross-linking temp (°C)	H_2	O_2	N_2	CH_4	CO_2	H_2/CH_4	CO_2/CH_4	O_2/N_2	CO_2/N_2	V(30 °C),[b] (cm^3/g)	d-spacing[c] (Å)
		33	4.0	0.9	1.3	32	25	25	4.4	36	0.883	7.94; 4.00
1	170	44	6.0	1.2	1.7	39	26	23	5.0	33	0.885	7.82; 4.12
1	190	47	6.0	1.2	1.6	46	29	29	5.0	38	0.859	7.90; 4.02
1	210	54	8.0	1.7	2.4	53	23	22	4.7	31	0.881	7.79; 4.12
24	170	43	6.0	1.3	1.6	39	27	24	4.6	30	0.861	7.93; 4.11
24	190	74	10	1.9	2.7	67	27	25	5.2	35	0.835	8.02; 3.98
24	210	54	8.0	1.8	2.5	54	21	21	4.4	30	0.852	7.75; 4.08

[a]Permeability in barrer (1 barrer = 1×10^{-10} cm^3 gas STP cm/cm^2s cmHg). [b]Specific volume measured at 30 °C in a density gradient column. [c]d-spacing values determined from WAXD using Bragg equation applied to the corresponding two maximum peaks that appear in Figure 5.

important to note that the cross-linking effect is highly dependent on the size and type of gas being permeated. A careful examination in Table 2 between permeability coefficients and the two d-spacing values reveals that the increases in permeability are associated with the increases in the d-spacing distribution of the more loosely packed polymer chains that increases from 7.93 to 8.02 Å, which is perceptible to H_2, O_2, CO_2, and CH_4, whereas the smaller increase in $P(N_2)$ should be associated with a combination of both an increase in the d-spacing distribution of the more loosely packed polymer chains and a reduction in the d-spacing distribution of the more efficient packing fraction of polymer chains that decreases from 4.11 to 3.98 Å. An additional important observation to be noted in Table 2 is that $P(H_2)$ and $P(CO_2)$ are practically the same independently if PNPr membrane is non-cross-linked or cross-linked. It is well-known that $P(H_2) > P(CO_2)$ for amorphous polymers, while it is common to find that $P(H_2) < P(CO_2)$ for polymers with intrinsic microporosity.[34,35] A more fundamental study is being carried out to learn more about this interesting phenomenon, but a possible explanation could be related to a lower solubility of H_2 in these types of polymers, as compared to typical amorphous polymers.

Figure 6 shows the selectivity−permeability performance for the gas pairs (a) H_2/CH_4, (b) O_2/N_2, (c) CO_2/CH_4, and (d) CO_2/N_2, determined for non-cross-linked PNPr membranes (open squares) and for cross-linked PNPr membranes under vacuum at 190 °C for 1 and 24 h (black squares). Figure 6 reports the effect of aging time (gray squares) at 35 °C and under a relatively high vacuum (10^{-3} mmHg), on the selectivity−permeability performance of the PNPr cross-linked membrane at 190 °C for 24 h. The 2008 upper-bound limit proposed by Robeson[6] has also been incorporated as a reference line. The net effect of increasing the cross-linking time results in an increase in permeability without changes in the ideal selectivity for the pairs of gases shown in Figure 6. For example, for the pair of gases H_2/CH_4, $P(H_2)$ increases by 1.42 and 2.24 factors for thermal treatments of 1 and 24 h, and the selectivity holds practically constant at 25−29. For O_2/N_2, $P(O_2)$ increases by 1.5 and 2.5 factors for 1 and 24 h, and the selectivity increases from 4.4 to 5.2. As mentioned, a possible explanation for the increases in permeability associated with no changes or increases in selectivity could be in the amount of cross-linked polymer, since PNPr membrane cross-linked for 1 h is made up of 96.4% GC, whereas the one cross-linked for 24 h contains 98.5% GC of cross-linked polymer.

Table 2 shows the d-spacing values for these two membranes, the ones cross-linked at 190 °C for 1 and 24 h. Their values reveal that the net effect of increasing time is to increase the d-spacing of the loosely packed PNPr chains from 7.90 to 8.02 Å, while at the same time the d-spacing of the more efficiently packed chains decreases from 4.02 to 3.98 Å. Even though the d-spacing is not a direct measurement of the real free volume fraction available for permeation, in general an

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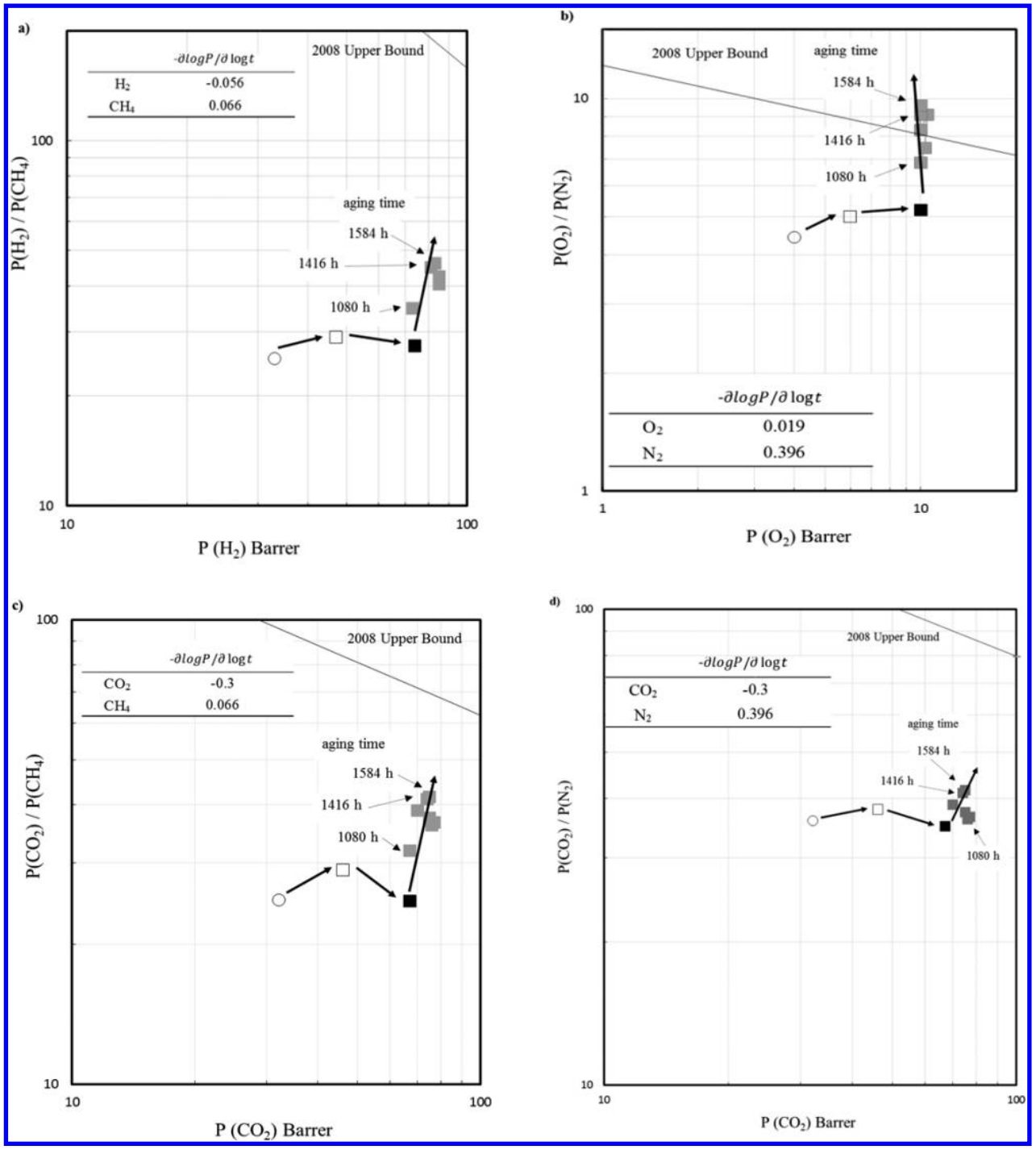

Figure 6. Ideal selectivity−permeability relationship for the gas pairs (a) H_2/CH_4, (b) O_2/N_2, (c) CO_2/CH_4, and (d) CO_2/N_2, at 35 °C and 2 bar, determined for pure PNPr and for PNPr membranes thermally treated at 190 °C for 1 (open squares) and 24 h (black squares). Effect of annealing, at 35 °C under 10^{-3} mmHg vacuum, is also shown for a PNPr cross-linked membrane at 190 °C/24 h (gray squares). Robeson's 2008 upper-bound limit is shown as a reference line.

increase in the largest *d*-spacing, and probably its distribution, seems to favor the permeability of small kinetic diameter gases such as H_2, O_2, and CO_2, whereas the decrease in the smaller *d*-spacing, and probably its distribution, causes smaller increases in the permeability of larger kinetic diameter gases such as N_2 and CH_4 tested here.

Figure 6 shows the effect of aging time, at 35 °C and under vacuum at 10^{-3} mmHg for at least 1584 h, on the selectivity−permeability relationship for a cross-linked PNPr (at 190 °C for 24 h). The effect of aging time under vacuum shows that the permeability coefficients of the fastest gas slightly increase, i.e., $P(H_2)$ and $P(CO_2)$, or remain constant, i.e., $P(O_2)$, during the 1584 h, but interestingly the selectivities for the gas pairs with respect to CH_4 and N_2 show important increases depending on the type of gases. For the gas pairs H_2/CH_4 and CO_2/CH_4, $P(H_2)$ and $P(CO_2)$ increase by 1.11 and 1.04 factors, respectively, and their associated selectivities increase from 24 to 45 for H_2/CH_4 and from 22 to 39 for CO_2/CH_4.

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For O_2/N_2, $P(O_2)$ remains practically constant after aging for 1584 h, and its selectivity increases from 5.2 to 9.6, a selectivity−permeability combination that surpass the 2008 upper-bound limit.[6] This is an interesting result because it indicates that the effect of cross-linking, added to a vacuum-annealing period, leads to membranes that overcome the typical trade-off observed between selectivity and permeability. In effect, these cross-linked membranes annealed at 35 °C and under vacuum for 1584 h show $P(H_2)$ and $P(CO_2)$ increases that are 2.45 and 2.11 times the one found for the non-cross-linked membranes, and they have associated increases in selectivity that almost double from 25 to 45 for H_2/CH_4 and from 25 to 39 for CO_2/CH_4. For the gas pair O_2/N_2, $P(O_2)$ increases by a 2.4 factor and its selectivity increases from 4.4 to 9.6 after cross-linking and annealing under vacuum.

Finally, Figure 7 shows the effect of CO_2 upstream pressure on $P(CO_2)$ measured for PNPr cross-linked membranes at 190 °C for 1 h without annealing, as well as for those membranes that have been cross-linked for 24 h and vacuum-annealed at 35 °C for the 1584 h period. The results shows that the cross-linked membranes also possess a high resistance to CO_2 plasticization at least up to the 18 bar upstream pressure measured in this work.

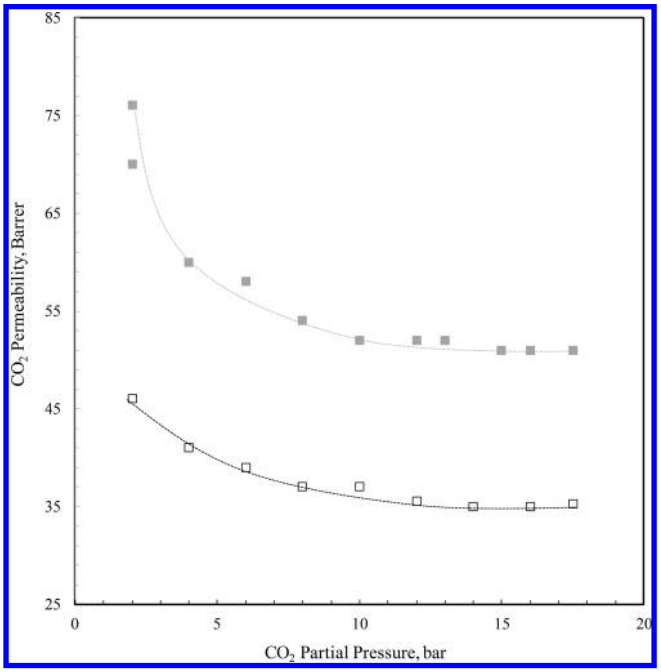

Figure 7. Effect of CO_2 upstream pressure on CO_2 permeability coefficient for PNPr membranes cross-linked at 190 °C for 1 h (open squares) and for 24 h plus an additional annealing period, at 35 °C under 10^{-3} mmHg vacuum, of 1584 h (gray squares).

4. CONCLUSIONS

A poly(oxyindole biphenylylene) containing a cross-linkable propargyl group (PNPr) was successfully synthesized at room temperature. The PNPr was cross-linked, under vacuum (1 mmHg), at temperatures between 190 and 210 °C for periods of time of 1 and 24 h. The cross-linking time increases the GC [%] and the permeability coefficients with practically no changes or increases in selectivity depending on the gas pair to be separated. For cross-linked PNPr membranes at 190 °C, the GC [%] increases from 96.4% in 1 h to 98.5% for 24 h. The gas permeability coefficients increase, with GC [%], by 2.2 and 2.1 factors for $P(H_2)$ and $P(CO_2)$, whereas selectivity remains constant at 25−27 for H_2/CH_4 and CO_2/CH_4. Under the same cross-linking treatment $P(O_2)$ increases by a 2.5 factor with an increase in selectivity that goes from 4.4 to 5.2. The cross-linked PNPr membranes are physically resistant to solvent-swelling since their SD [%], in an aggressive solvent such as NMP, is on the order of 1−3%. This represents a tremendous advantage since the non-cross-linked PNPr, which is soluble in common solvents such as CH_2Cl_2 and NMP, can be processed as a cast film and further cross-linked as a quite resistant membrane to solvent-swelling. Throughout a systematic study of the structure/processing/property relationship supported with FTIR-ATR, specific volume, WAXD, and permeability coefficient determinations, it is concluded that cross-linking followed with an additional 1584 h vacuum-annealing period at 35 °C under a 10^{-3} mmHg vacuum is a useful route to produce cross-linked PNPr membranes that can surpass the typical trade-off observed in the permeability−selectivity relationship. When the PNPr membranes, cross-linked at 190 °C for 24 h and further vacuum-annealed at 35 °C for 1584 h, are compared to the non-cross-linked PNPr membranes, both $P(H_2)$ and $P(CO_2)$ increase by 2.4 and 2.2 factors and selectivity for H_2/CH_4 increases from 25 to 45 and for CO_2/CH_4 increases from 25 to 39. It was also found that $P(O_2)$ increases by a 2.3 factor with a corresponding increase for O_2/N_2 selectivity from 4.4 to 9.6, positioning this membrane above the Robeson's 2008 upper-bound limit[6] at least for this gas pair. Additionally, the cross-linked membranes also possess an acceptable physical resistance to CO_2 plasticization since the plasticization pressure is not detected up to 18 bar upstream pressure.

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Notes

The authors declare no competing financial interest.

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