

# Polymer foams of ionic liquid polymers as asymmetric membranes for gas separation

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## ABSTRACT

One of the main problems today is climate change caused by the growing amount of greenhouse gases in the atmosphere, namely CO<sub>2</sub>. While developing cleaner processes, it is important to mitigate the effects caused by the processes already in place.

Ionic Liquids (ILs) and Ionic Liquid Polymers (PILs) are materials with enormous versatility at the chemical level, which allows the design of chemical structures for a particular application. It has already been shown in the literature that certain IL families have a high affinity for CO<sub>2</sub> and are therefore materials of choice to be tested in the preparation of membranes for CO<sub>2</sub> separation.

This work focuses on the preparation of asymmetric PIL and PIL+IL membranes for gas separation, using the phase inversion method assisted by supercritical CO<sub>2</sub>, a solvent increasingly used in so-called 'green' processes as an alternative to common solvents.

It was possible to obtain PIL membranes with high permeabilities, but unitary separation efficiencies, being difficult to obtain asymmetric membranes. The following processing parameters stand out: temperature and pressure, pressurization and depressurization speed, processing time and concentration/volume of the PIL and PIL+IL solution.

In terms of gas separation barrier, it was only possible to measure one membrane, in order to obtain its gas permeation properties, presenting very high permeabilities and permeances compared to the two tested gases (CO<sub>2</sub> and N<sub>2</sub>), which translates into a low selectivity, concluding that it was only possible to prepare a porous membrane.

**Keywords:** Separation of CO<sub>2</sub>, Membranes, Ionic Liquids, Ionic Liquid Polymers, Phase Inversion Method, Supercritical CO<sub>2</sub>.

## 1. Introduction

### 1.1. Emissions, Capture and Separation of CO<sub>2</sub>

One of the main concerns of the 21st century is the increase in the amount of greenhouse gases in the Earth's atmosphere, namely CO<sub>2</sub>, whose emissions have been increasing in recent years.

It is imperative to implement environmentally responsible measures and develop alternative energy sources to fossil fuels, such as renewable energies. However, while this transition to more sustainable energies does not occur, CO<sub>2</sub> capture and separation processes are quite attractive. The most expensive step is the capture and compression of CO<sub>2</sub>, accounting for around 75% of the total cost of the process.

Currently, four processes for separating CO<sub>2</sub> from other gases have been developed: absorption, adsorption, cryogenic distillation and membranes.

Membranes have been gaining relevance as an alternative to the processes most used in CO<sub>2</sub> separation, such as absorption and adsorption, due to their great advantages: small equipment, reduced environmental impact, easy implementation in existing processes and low energy/operational costs [1]. In order to compete with existing and implemented processes, mechanical/chemical resistance, selectivity

and permeability still need improvements to be able to be implemented in industrial environments [1].

### 1.2. Ionic Liquids and Ionic Liquid Polymers

Ionic liquids (ILs) are defined as compounds made up entirely of ions whose melting point is below 100°C, mostly made up of organic cations and organic/inorganic anions [1,2]. Generally, they present low volatility and flammability, good thermal stability, high ionic conductivity and a great diversity of particular properties, due to the great variety of cations and anions, designating them as designer solvents. Recently developed, although still with a high cost, it has been quite successful in separating CO<sub>2</sub>, in order to reduce its production cost, since some ILs have a great affinity with CO<sub>2</sub>, justified by the interaction of the quadrupole present in the molecule of CO<sub>2</sub> and the electrical charge present in the ions of the ILs.

Ionic liquid polymers (PILs) are polyelectrolytes whose repeating unit includes a kind of IL and one or more polymerizable units, which can be present in the cation or anion [1,3,4]. They present properties of both classes of compounds, polymers and ILs, being developed in order to amplify the properties of ILs, combining them with the properties of macromolecules,

such as mechanical stability, processability and durability [4].

### 1.3. PIL and PIL+IL Membranes

PIL and PIL+IL membranes emerge as excellent alternatives to the membranes currently used in most CO<sub>2</sub> separation processes. Comparatively, PIL membranes are more mechanically and thermally stable, while PIL+IL membranes have superior permeabilities and diffusivities.

In most PIL membranes, the polymer chain integrates the cation, while the anion acts as a counter-anion. For CO<sub>2</sub> separation, imidazole, thiazole, triazole, pyridinium, pyrrolidinium, ammonium cations and anions with fluorine (NTf<sub>2</sub>, PF<sub>6</sub> and BF<sub>4</sub>) or cyano groups stand out. The presence of fluorine-containing anions in its composition significantly increases the affinity with CO<sub>2</sub>, due to the free volume created by the higher dimension of the fluorine molecule, a volume that will be occupied by CO<sub>2</sub>.

### 1.4. Membrane Preparation through ScCO<sub>2</sub>

An asymmetric membrane has a dense part, with very low thickness, and a porous part, which acts as a support for the dense part, both made of the same material. The existence of these two parts in the membrane leads to the creation of very interesting properties for gas separation. On one hand, the dense part must have a high selectivity through a difference in affinity between the gases to be separated. On the other hand, the porous part must have a high diffusivity. Thus, asymmetric membranes are characterized by high permeability and selectivity gas separation, while being mechanically stable.

The preparation of asymmetric membranes can be carried out in several ways: liquid phase inversion, liquid/dry phase inversion, ScCO<sub>2</sub>-assisted phase inversion and electrospinning [5].

CO<sub>2</sub> has a low critical point, with a critical temperature of 31°C and a critical pressure of 74 bar, has green characteristics, is recyclable, non-toxic and non-flammable, as well as having the viscosity of a gas and the density of a liquid, in addition to reduced costs [6,7]. ScCO<sub>2</sub> is gaining relevance as a replacement for conventional organic solvents.

ScCO<sub>2</sub>-assisted phase inversion consists of processing the solution with ScCO<sub>2</sub> in order to create a solute/solvent/non-solvent system [5]. The introduction of ScCO<sub>2</sub> causes the solvent to dissolve in the ScCO<sub>2</sub>, precipitating the polymer. Polymer precipitation at the upper interface occurs at an accelerated rate, creating a dense zone, whereas in the remaining solution, this precipitation process is slower, creating a porous zone.

### 1.5. Objective

This work aims to study the preparation of asymmetric membranes of PIL and PIL+IL, through the method of phase inversion assisted by ScCO<sub>2</sub>.

The preparation of membranes with ScCO<sub>2</sub> is studied, going through the different methods and processing parameters to be optimized, as well as the microscopic characteristics of the membranes through SEM and the gas permeation properties through an equipment where the time-lag method is implemented.

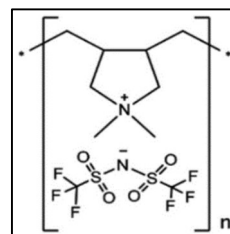
## 2. Methodology

### 2.1. Reagents

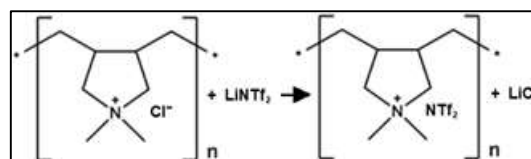
LiNTf<sub>2</sub> with 99% purity was provided by IOLITEC GmbH, Pyr<sub>11</sub>Cl (20% in water) was provided by Sigma-Aldrich, Acetone (C<sub>3</sub>H<sub>6</sub>O) with 99,8% was provided by Fisher Chemical, [C<sub>4</sub>m<sub>pyr</sub>][NTf<sub>2</sub>] with 99,5% was provided by IOLITEC GmbH, [C<sub>2</sub>mim][NTf<sub>2</sub>] with 99% was provided by IOLITEC GmbH and Carbon Dioxide (CO<sub>2</sub>) with 99,998% was provided by Air Liquide.

### 2.2. PIL Synthesis

The PIL used is called Poly[Pyr<sub>11</sub>][NTf<sub>2</sub>] and consists of a repeating unit based on the pyrrolidinium cation and a counter-anion [NTf<sub>2</sub>]<sup>-</sup>. This polymer has the advantages of being easily obtained by ion exchange, from a cheap commercial polyelectrolyte, as well as the presence of fluorine atoms in the counter anion, conferring high affinity with CO<sub>2</sub>, allowing the ScCO<sub>2</sub> to easily dissolve in the solution, dragging a greater amount of solvent and consequently creating greater porosity [8,9].



**Figure 1:** Structure of the Ionic Liquid Polymer Poly[Pyr<sub>11</sub>][NTf<sub>2</sub>].



**Figure 2:** Scheme of the ionic exchange reaction from Poly[Pyr<sub>11</sub>][Cl] to Poly[Pyr<sub>11</sub>][NTf<sub>2</sub>].

To synthesize 10 grams of PIL, 20 grams of the aqueous precursor PIL solution is dissolved in 20 ml of water and 7,5 grams of LiNTf<sub>2</sub> in 20 ml of water, stirring both solutions for 1 hour at room temperature. 60 ml of water is added to the precursor PIL solution, followed by the LiNTf<sub>2</sub> solution, immediately precipitating a white solid, as the final PIL is hydrophobic. Stir vigorously for 10 minutes and the final solution is left under stirring for 24 hours, also at room temperature, in order to maximize yield.

This is followed by the purification step, in which the solution obtained is vacuum filtered with approximately 4 litres of water, continuously stirring the filter cake to promote efficient washing and the removal of all LiCl that may be trapped in the PIL. After filtration, in order to remove all the aqueous phase, the PIL is placed in an oven at 40°C for 72 hours. The PIL is obtained as a white, granular precipitate.

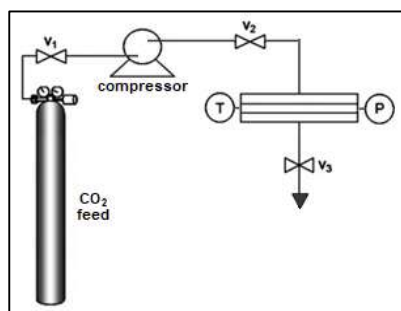
### 2.3. Solvent Selection

ScCO<sub>2</sub> will act as a non-solvent to the polymer, removing the solvent and leading to precipitation of the polymer. With this in mind, the solvent will have to have a wide enough solubility range for the solubilization of the polymer and ScCO<sub>2</sub>. The cost and toxicity of the solvent must also be taken into account.

Acetone was chosen, as it has the necessary characteristics and is a very common solvent, with a relatively low cost and considered safe, without danger of toxicity.

### 2.4. Laboratory Equipment

Two cells were used, consisting of two cylinders of different dimensions (internal diameters of 2,320 mm and 5,455 mm). Both cells have a quartz window, allowing the observation of the interior, as well as two connections to the outside where the ScCO<sub>2</sub> supply and outlet are mounted, as well as a thermocouple and barometer.



**Figure 3:** Scheme of the equipment used for the preparation of membranes through ScCO<sub>2</sub> assisted phase inversion.

## 2.5. Membrane Preparation

### 2.5.1. Discontinuous Method

The discontinuous method consists of introducing and saturating ScCO<sub>2</sub> in the cell at the desired pressure. This method can be carried out with one or several ScCO<sub>2</sub> intakes, according to the volume of solvent introduced into the cell.

The main advantages of the discontinuous method are the use of a smaller amount of ScCO<sub>2</sub> and a lesser movement of ScCO<sub>2</sub> inside the cell, providing more regularity to the membranes, with a more uniform solvent removal by the ScCO<sub>2</sub>.

However, the main disadvantage of the discontinuous method is the main advantage of the

continuous method: the processing time, which is significantly longer in the discontinuous method.

### 2.5.2. Continuous Method

The continuous method consists of introducing and saturating ScCO<sub>2</sub> in the cell at the desired pressure, followed by passing a flow of ScCO<sub>2</sub>, keeping the pressure constant.

The main advantage of the continuous method is the reduced processing time, due to the continuous passage of a constant flow of ScCO<sub>2</sub>, accelerating mass transfer from the solvent to the ScCO<sub>2</sub>.

Although this ScCO<sub>2</sub> flow rate is reduced, the ScCO<sub>2</sub> consumption in the continuous method is remarkably higher than the ScCO<sub>2</sub> consumption in the discontinuous method and brings with it some additional disadvantages.

As the regulation of the inlet and outlet flows is carried out using manual valves, until the desired pressure and temperature value is reached, these vary reasonably inside the cell. Decreasing the temperature leads to a higher heat supply, generating a temperature gradient inside the cell. Another side effect of the continuous ScCO<sub>2</sub> output is its solidification in the outlet pipe, which leads to blockages in the ScCO<sub>2</sub> outlet.

### 2.5.3. Experimental Limitations

In terms of experimental limitations, four stand out: the temperature regulation, the maximum pressure value, the manual regulation of the valves, the position of the ScCO<sub>2</sub> inlet and outlet and the difference in size between the membrane production cells and the time-lag equipment measurement cell.

As the temperature regulation is carried out using a heating plate, for the cell with greater volume, a considerable temperature gradient inside the cell is obtained.

The quartz windows present in the cells have a maximum pressure value of 150 bar, above which there may be rupture, which is why the pressure is limited.

The main experimental limitation is the manual regulation of the inlet and outlet valves, making it impossible to precisely and reproducibly regulate pressure, pressurization and depressurization.

The supply of ScCO<sub>2</sub> is done via a single lateral inlet in the smaller volume cell and a vertical inlet in the larger volume cell, both not centred on the cell. As such, the ScCO<sub>2</sub> feed is not uniform throughout the cell, resulting in noticeable irregularity in the membranes.

Finally, the smaller membranes present a problem, as the time-lag equipment's gas permeation cell has a larger diameter. In order to circumvent this limitation, a gas-sealing aluminium tape was used, creating a crown in order to reduce the active area of the cell, leading to higher errors associated with measurements.

## 2.6. Time-Lag Equipment

The equipment where the time-lag method is implemented consists of a system according to the scheme shown in Figure 4.

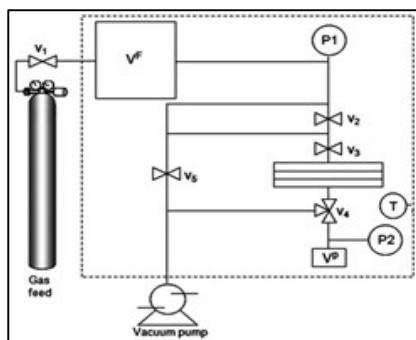


Figure 4: Scheme of the equipment with the time-lag method implemented.

For each membrane to be measured in the equipment, the system is first purged by performing a vacuum for at least 24 hours. The system is then thermostated at the desired temperature.

During measurements, gas is admitted to the cell where the membrane is located, recording the permeate pressure over time, in order to obtain a relation between the two. From this relation, all the parameters necessary for the calculation of permeability, permance, diffusivity and solubility values in regard to the admitted gases are obtained.

## 3. Results

### 3.1. Tests in the Lower Volume Cell

#### 3.1.1. Initial Tests - Solution Volume

Initially, tests were carried out with the objective of obtaining membranes, regardless of their characteristics, in order to test the feasibility of phase inversion assisted by ScCO<sub>2</sub>.

Table 1: Experimental conditions of tests 1 to 5: discontinuous method, temperature of 40°C, pressure of 110 bar, pressurization and depressurization in 1 minute and processing in 45 minutes.

Test	C (% v/v)	V (ml)
1	10	5,0
2	10	4,0
3	10	2,0
4	15	1,0
5	15	0,5

Regarding the first three tests, the polymer is dissolved during depressurization, concluding that the ScCO<sub>2</sub> does not completely remove the solvent.

Thus, in the fourth and fifth trials, the solution volume was reduced, together with an increase in the solution concentration to 15% (v/v). Although polymer redissolution still occurs, there is a greater difficulty for this to occur.

### 3.1.2. Multiple Intakes of CO<sub>2</sub>

In the following tests, it was decided to carry out multiple ScCO<sub>2</sub> intakes to wash out all the solvent.

Table 2: Experimental conditions of tests 6 and 7: discontinuous method, temperature of 40°C, pressure of 110 bar, pressurization and depressurization in 1 minute and processing with intakes of 30/15 minutes.

Test	C (% v/v)	V (ml)	t <sub>proc</sub> (min)
6	15	0,5	30/15
7	15	1,0	30/15/15

With the implementation of several intakes, what can be considered the first PIL membranes were obtained, despite their irregular appearance.

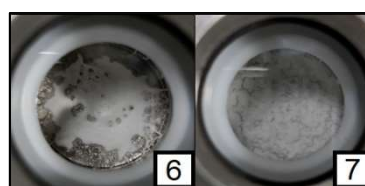


Figure 5: PIL Membranes from tests 6 and 7.

It is concluded that with several ScCO<sub>2</sub> intakes, a greater amount of solvent is removed, as the saturated ScCO<sub>2</sub> is replaced by fresh ScCO<sub>2</sub>.

### 3.1.3. Solution Concentration

The effect of increasing PIL concentration is then studied. At the same time, the effect of increasing the depressurization and pressurization time was also studied, passing to values of 4 minutes.

Table 3: Experimental conditions of tests 8 and 9: discontinuous method, temperature of 40°C, pressure of 110 bar, pressurization and depressurization in 1/4 minutes and processing with intakes of 30/15 minutes.

Test	C (% v/v)	V (ml)	t <sub>pres</sub> (min)	t <sub>depres</sub> (min)
8	20	1,0	1	4
9	20	1,0	4	4

The membranes obtained present much improved macroscopic characteristics, so it can be concluded that the increase in concentration causes an easier removal of all the solvent and a greater amount of polymer for the formation of the membrane. Regarding the pressurization and depressurization times, these greatly affect the regularity of the membranes.

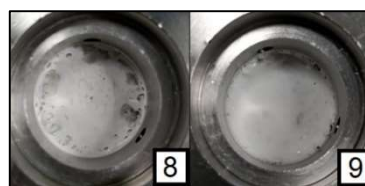


Figure 6: PIL Membranes from tests 8 and 9.

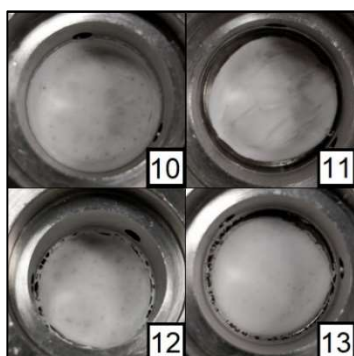
While increasing concentration results in improved exterior characteristics, the interior impact may be the opposite, as solvent removal is directly related to porosity creation and less solvent will result in less porosity. The concentration in the following tests is reverted to values of 10% and 15%.

### 3.1.4. Pressurization Time

To analyse the effect of pressurization time, tests were carried out in which pressurization is progressively slower.

**Table 4:** Experimental conditions of tests 10 to 14: discontinuous method, temperature of 40°C, pressure of 110 bar, pressurization in 4/6/8 minutes, depressurization in 4 minutes and processing with intakes of 30/15 minutes.

Test	C (% v/v)	V (ml)	t <sub>pres</sub> (min)
10	10	1,5	4
11	10	1,5	6
12	10	1,5	8
13	10	1,5	8
14	10	1,0	10

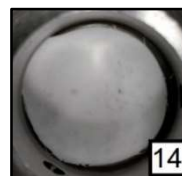


**Figure 7:** PIL Membranes from tests 10 to 13.

Increased pressurization time, as expected, results in greater membrane regularity. This fact can be explained by how the supply of ScCO<sub>2</sub> to the cell is carried out.

ScCO<sub>2</sub> feed is done via an inlet parallel to the base of the cell, which results in marked solvent removal in the ScCO<sub>2</sub> feed zone. Rapid pressurization causes the high flow rate of ScCO<sub>2</sub> to quickly remove the solvent close to the feed, resulting in an uneven membrane surface. Slowly pressurizing, as the ScCO<sub>2</sub> flow rate is reduced, it will be more evenly distributed throughout the cell, and solvent removal is more uniform in the cell, resulting in a more even membrane surface.

Then, a test was carried out in order to test whether the processing time could be considered proportional to the volume of solution used, testing a new increase in pressurization and depressurization times as well.



**Figure 8:** PIL Membrane from test 14.

The result obtained is quite satisfactory, so it is concluded that, for the continuous method, the processing times can be considered proportional to the volume of solution used (keeping the concentration fixed) and that a more uniform membrane is obtained for higher speeds of pressurization/depressurization.

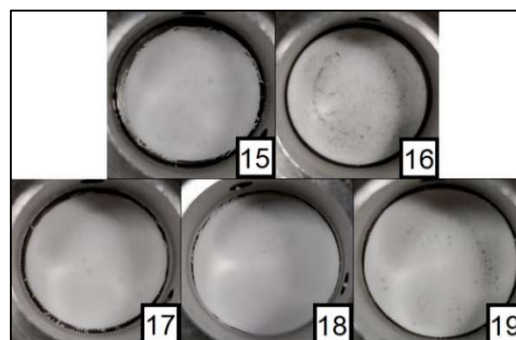
### 3.1.5. Passing to the Continuous Method and Thickness Reduction

For the continuous method, initially, the first discontinuous intake has a fixed duration of 10 minutes and the second continuous intake has a variable duration, according to the volume and concentration of the solution used. In the initial tests, the reduction of membrane thickness is also studied by reducing the volume of solution used.

**Table 5:** Experimental conditions of tests 15 to 19: continuous method, temperature of 40°C, pressure of 110 bar, pressurization in 10 minutes, depressurization in 6 minutes, discontinuous processing in 10 minutes and continuous processing in 20/25/30 minutes.

Test	C (% v/v)	V (ml)	t <sub>proc</sub> (min)
15	15	1,0	10/30
16	15	0,6	10/20
17	10	1,0	10/30
18	10	0,8	10/25
19	10	0,6	10/20

The initial results obtained for the continuous method are quite encouraging, with a notorious surface regularity for membranes whose volume of solution used is greater, and for volumes below 0,6 ml, surface porosity is expected, given the lack of polymer.

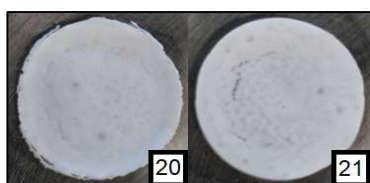


**Figure 9:** PIL Membranes from tests 15 to 19.

In addition, two trials were carried out in which all times were increased and reduced by 50%, relative to trial 19.

**Table 6:** Experimental conditions of tests 20 and 21: continuous method, temperature of 40°C, pressure of 110 bar, pressurization in 5/15 minutes, depressurization in 3/10 minutes, discontinuous processing in 5/15 minutes and continuous processing in 10/30 minutes.

Test	C (% v/v)	V (ml)	t <sub>pres</sub> (min)	t <sub>proc</sub> (min)	t <sub>depres</sub> (min)
20	10	0,6	5	5/10	3
21	10	0,6	15	15/30	10

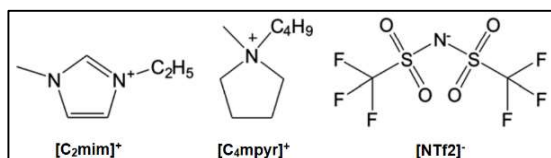


**Figure 10:** PIL Membranes from tests 20 and 21.

Compared with the membrane obtained in test 19, both membranes show greater irregularity. In the membrane obtained with longer times, it is possible to observe even a superficial fracture, with an appearance similar to the membrane in the test 16.

### 3.1.6. Ionic Liquid Introduction

The introduction of IL into the membranes follows. During the tests performed, the PIL/IL mass ratio was fixed at 80/20. The ILs used were [C<sub>4</sub>mpyr][NTf<sub>2</sub>] and [C<sub>2</sub>mim][NTf<sub>2</sub>].



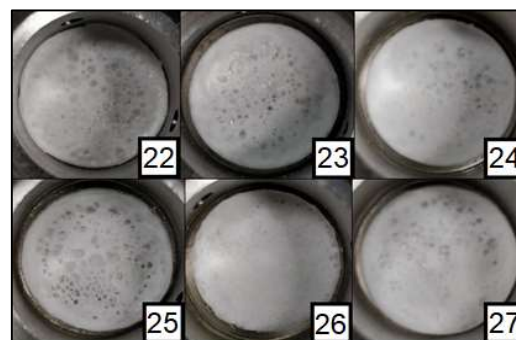
**Figure 11:** Cations and anion of ionic liquids used in the laboratory: [C<sub>4</sub>mpyr]<sup>+</sup>, [C<sub>2</sub>mim]<sup>+</sup> and [NTf<sub>2</sub>]<sup>-</sup>.

Initially, the continuous method was applied in the processing of PIL+IL solutions.

**Table 7:** Experimental conditions of tests 22 to 27: continuous method, temperature of 40°C, pressure of 110 bar, pressurization in 10 minutes, depressurization in 6/10 minutes, discontinuous processing in 15 minutes and continuous processing in 25 minutes.

Test	IL Cation	C (% v/v)	V (ml)	t <sub>depres</sub> (min)
22	[C <sub>4</sub> mpyr]	10	0,75	6
23	[C <sub>4</sub> mpyr]	10	1,0	6
24	[C <sub>4</sub> mpyr]	10	1,0	10
25	[C <sub>2</sub> mim]	10	0,75	6
26	[C <sub>2</sub> mim]	10	1,0	6
27	[C <sub>2</sub> mim]	10	1,0	10

As the first membranes (22 and 25) have a high surface porosity, the volume of solution was increased in order to make up for any lack of polymer. However, the membranes continue to show surface porosity, so depressurization was carried out in 10 minutes. It should be noted that the increase in solution volume was more impactful for the membrane where the IL [C<sub>2</sub>mim][NTf<sub>2</sub>] was introduced.

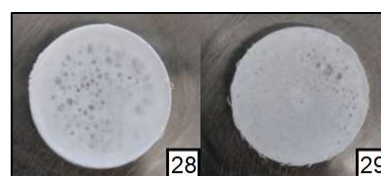


**Figure 12:** PIL+IL Membranes from tests 22 to 27.

Then, two tests were carried out to test the discontinuous method for both ILs and also to test the hypothesis that solvent removal was being carried out too quickly, dragging with it part of the IL introduced.

**Table 8:** Experimental conditions of tests 28 and 29: discontinuous method, temperature of 40°C, pressure of 110 bar, pressurization and depressurization in 10 minutes and processing with three intakes of 20 minutes.

Test	IL Cation	C (% v/v)	V (ml)
28	[C <sub>4</sub> mpyr]	10	1,0
29	[C <sub>2</sub> mim]	10	1,0



**Figure 13:** PIL+IL Membranes from tests 28 and 29.

It is concluded that for the discontinuous method, we obtain PIL+IL membranes identical to those obtained by the continuous method.

## 3.2. Tests in the Greater Volume Cell

### 3.2.1. Initial Tests - Solution Volume

The initial objective is, again, to obtain membranes, regardless of their appearance, but taking into account what was observed and concluded previously. As this upper cell has a greater volume, only the discontinuous method was studied, in order to lower the ScCO<sub>2</sub> consumption.

The area ratio between cells is approximately 5,5, so the volume of solution for the initial trial is fixed at 3,4



ml (about 5,5 times the lower limit value of the smallest cell volume).

**Table 9:** Experimental conditions of tests 30 to 32: discontinuous method, temperature of 40°C, pressure of 110 bar, pressurization in 15/30 minutes, depressurization in 15 minutes and processing in 120/150 minutes.

Test	C (% v/v)	V (ml)	t <sub>pres</sub> (min)	t <sub>proc</sub> (min)
30	10	3,4	15	120
31	10	4,4	30	150
32	10	5,6	30	60/60



**Figure 14:** PIL Membranes from tests 30 to 32.

In the initial membranes, the porosity and surface irregularity are notorious, so the pressurization started to be carried out in 30 minutes. In relation to the volume of solution, this was increased, in order to make up for a possible lack of polymer. In membrane 32, the surface porosity is quite reduced, when compared to previous membranes, so it is concluded that there was a smaller amount of polymer than necessary.

### 3.2.2. Temperature Decrease and Concentration Increase

As the first membranes obtained in the upper cell are unsatisfactory, the possibility that the removal of solvent is being carried out too quickly, carrying out a test at a temperature of 35°C.

**Table 10:** Experimental conditions of test 33: discontinuous method, temperature of 35°C, pressure of 110 bar, pressurization in 10 minutes, depressurization in 15 minutes and processing with two intakes of 20 minutes.

Test	C (% v/v)	V (ml)	T (°C)
33	15	0,4	35



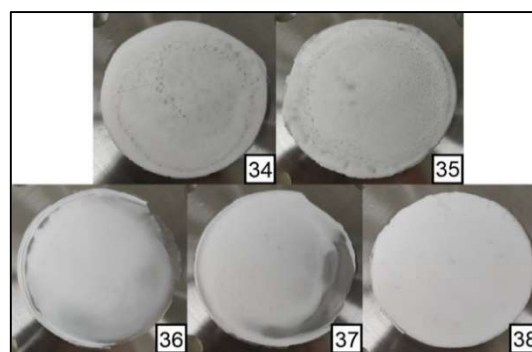
**Figure 15:** PIL Membranes from test 33.

As the membrane obtained has improved macroscopic characteristics, such as greater surface regularity and low porosity on both surfaces, it was decided to carry out the same test in the larger cell, also implementing concentrations of 20% and 30%, in order to also reduce the amount of solvent to be removed.

Pressurization and depressurization times were also increased to ensure a membrane with increased regularity.

**Table 11:** Experimental conditions of tests 34 to 38: discontinuous method, temperature of 35°C, pressure of 110 bar, pressurization in 90 minutes, depressurization in 30 minutes and processing with two intakes of 20/30/40/50 minutes.

Test	C (% v/v)	V (ml)	t <sub>proc</sub> (min)
34	20	4,0	40/40
35	20	5,0	50/50
36	30	2,0	20/20
37	30	2,0	20/20
38	30	3,0	30/30



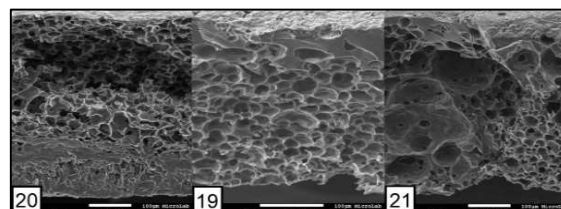
**Figure 16:** PIL Membranes from tests 34 to 38.

With the increase of PIL concentration to 20% and 30%, the membranes present a superior plasticity with the surface regularity also improved. Despite these observations, for tests performed with 2,0 ml at 30%, the membranes do not occupy the entire bottom part of the cell, probably due to the reduced solution volume used and the increased viscosity of the solution. The membrane 38 is, macroscopically, the best membrane obtained, with no observable surface porosity and being regular throughout its surface.

### 3.3. SEM Analysis

#### 3.3.1. PIL Membrane Comparison

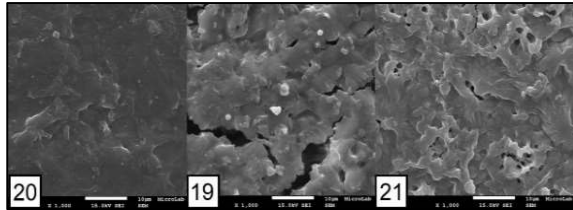
PIL membranes from tests 19, 20 and 21 were selected for SEM analysis.



**Figure 17:** Cross-sections of membranes 19 to 21.

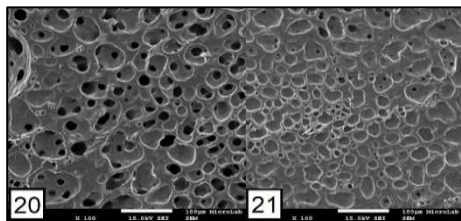
Looking at the cross-section of membranes 19, 20 and 21, it is possible to observe the creation of a thin dense layer near the top in all membranes. According to the order presented in Figure 17, with the increase of

all times, it is observed, from the membrane 20 to 19, an increase in the regularity of the pore size with the elimination of the dense layer in the lower part. Moving from membrane 19 to 21, the lower dense layer does not exist either, but the interior loses the regularity obtained in membrane 20.



**Figure 18:** Upper surfaces of membranes 19 to 21.

Regarding the upper surfaces of the membranes, it is concluded that with the increase of all times, it goes from a completely dense surface to a surface with some porosity and fractures. However, by increasing the times even more, the additional surface regularity reduces the formation of fractures. It can be concluded that the appearance of the upper surface is closely related to pressurization, since this is the zone where the first contact between the solution and the ScCO<sub>2</sub> occurs and where the polymer precipitates first. Very fast pressurization means an equally rapid precipitation of polymer and no porosity. A very slow pressurization means a slower precipitation, however, as the distribution of ScCO<sub>2</sub> inside the cell is more uniform, the surface regularity obtained is much higher, eliminating the formation of superficial fractures.

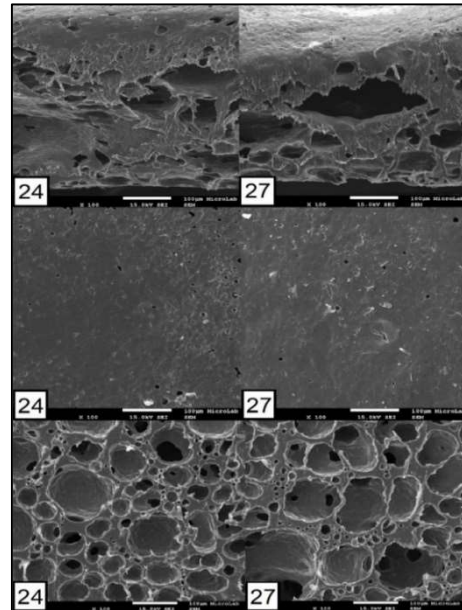


**Figure 19:** Lower surfaces of membranes 20 and 21.

Finally, comparing the lower surfaces of membranes 20 and 21, it can be seen that they are identical in relation to the geometry of the formed pores.

### 3.3.2. PIL+IL Membrane Comparison

The PIL+IL membranes chosen to analyse via SEM correspond to tests 24 and 27, allowing comparison with membrane 19.



**Figure 20:** Cross-sections, upper and lower surfaces of membranes 24 and 27.

In terms of cross-section, both membranes have identical properties. It is notorious the irregularity inside the membranes, observing pores with a great variety of sizes and irregular distribution of the same ones. In the upper zone of the membranes, a dense layer is formed, also irregular, with a very variable thickness.

As for the cross section, the upper and lower surfaces of both membranes are also identical. The upper surfaces are mostly dense, while the lower surfaces are porous and have a uniform pore distribution with a diversity of sizes.

### 3.3.3. PIL and PIL+IL Membrane Comparison

In terms of processing, membrane 19 is closest to membranes 24 and 27.

While membrane 19 has a uniform sponge-like internal porosity, membranes 24 and 27 have irregular internal porosity and the pore size is quite variable. This can be explained by the fact that the ILs introduced into the membranes have a high affinity for ScCO<sub>2</sub>, which means that they are removed in part, creating larger internal pores and giving internal irregularity to the PIL+IL membranes.

The same justification presented above is also valid for the differences observed in the inferior surface of the membranes.

Regarding the upper surface of the membranes, they do not show considerable differences with the introduction of IL.

### 3.4. Time-Lag Equipment Measurements

Among the various membranes obtained, only the membrane related to test 38 was possible to test in the time-lag equipment. All other membranes have pores or fractures, observable with the naked eye, which allow the complete passage of gas.



The test membrane 38 was tested for two gases: N<sub>2</sub> and CO<sub>2</sub>. Three tests were carried out for each gas.

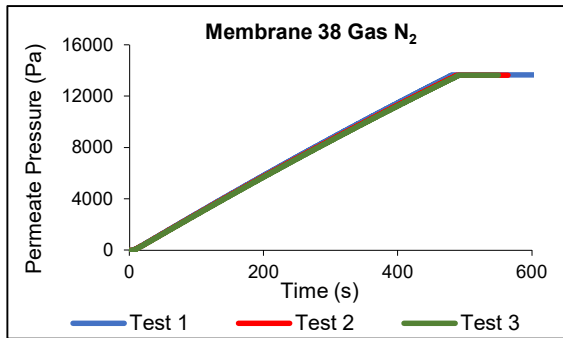


Figure 21: Permeate pressure vs time of measurement of membrane 38 for N<sub>2</sub>.

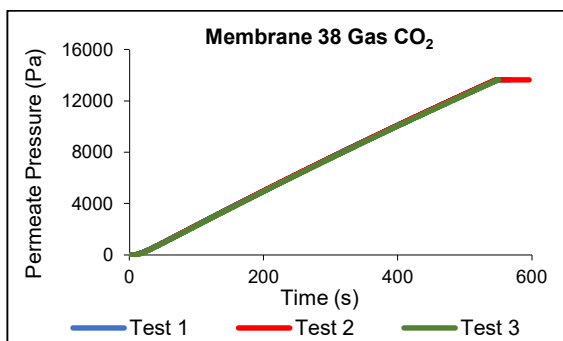


Figure 22: Permeate pressure vs time of measurement of membrane 38 for CO<sub>2</sub>.

Slope values are identical for both gases. However, the ordinate values at the origin are quite different, so the time lag value is also quite different. This means that permeabilities and permeances are expected to be similar, but the diffusivity values of the two gases will be different.

Table 12: Average values of permeability (P), permeance ( $\mathcal{P}$ ) and diffusivity (D) of membrane 38 for N<sub>2</sub> e o CO<sub>2</sub>.

	N <sub>2</sub>	CO <sub>2</sub>
<b>P</b> (m <sup>3</sup> .m.m <sup>2</sup> .s <sup>-1</sup> .Pa)	(80,6±0,4)×10 <sup>-16</sup>	(70,9±0,2)×10 <sup>-16</sup>
<b><math>\mathcal{P}</math></b> (m <sup>3</sup> .m <sup>2</sup> .s <sup>-1</sup> .Pa)	11,94±0,05	10,51±0,03
<b>D</b> (m <sup>2</sup> .s <sup>-1</sup> )	(331±16)×10 <sup>-11</sup>	(16,9±0,2)×10 <sup>-11</sup>

Table 13: Selectivity ( $\alpha$ ) of membrane 38.

$\alpha_{CO_2,N_2}$	0,88
$\alpha_{N_2,CO_2}$	1,14

It is confirmed that the permeability and permeance values of membrane 38 are identical for N<sub>2</sub> and CO<sub>2</sub> and, as such, the selectivity is considerably low. This fact indicates that, although the membrane 38 appears to be dense on the surface, it has some pores of reduced dimensions that do not allow to distinguish between CO<sub>2</sub> and N<sub>2</sub>, due to their similar size.

Regarding the diffusivity of the gases in membrane 38, as expected by the time-lag values, this property differs for both gases. N<sub>2</sub> has a higher diffusivity than CO<sub>2</sub>, which can be explained by the fact that CO<sub>2</sub> has a greater affinity with the PIL than N<sub>2</sub> and, consequently, a lower diffusivity.

#### 4. Conclusions and Future Work

Within the first 10 tests carried out in the laboratory, PIL membranes with very satisfactory macroscopic properties were obtained, therefore the implementation of the ScCO<sub>2</sub> assisted phase inversion method is proven. The same was concluded for PIL+IL membranes for two different ILs within 6 trials.

Within the studied parameters, it is concluded that depressurization is the least relevant step for membrane properties. However, pressurization is the most relevant step, especially with regard to the top surface. For fast and very slow pressurizations, the membranes appear similar on the upper surfaces, microscopically, despite different macroscopic appearances.

As for the processing time of the membranes, it is concluded that this only has to be sufficient to remove all the solvent present in the solution, which is achievable in several ways, such as several ScCO<sub>2</sub> intakes and passing a continuous flow of ScCO<sub>2</sub> in continuous.

Regarding the solution concentration, this is mainly related to the porosity and plasticity of the membranes.

With regard to temperature, it is concluded that for lower temperatures, solvent removal is slower and membranes are more regular at the macroscopic level.

Finally, the membrane measured in the time-lag equipment presents very high and identical permeabilities for the gases studied (CO<sub>2</sub> and N<sub>2</sub>). For CO<sub>2</sub>, permeability is high due to high solubility. As for N<sub>2</sub>, the high permeability is due to a high diffusivity in the membrane.

The only membrane tested serves as proof of concept, proving that it is possible to obtain asymmetric membranes through the phase inversion method using ScCO<sub>2</sub> in order to separate CO<sub>2</sub>, although the dense layer continues to show irregularities and some porosity, bringing it closer to a porous membrane.

For future work, it would be interesting to study some aspects and implement some differences in the equipment used:

- The use of cells that allow high pressures (approximately 300 bar).
- The use of cells with precise temperature and pressure control.
- The use of cells with central inlet and outlet locations and with a uniform ScCO<sub>2</sub> distribution system.
- Computer control of ScCO<sub>2</sub> flows for greater precision in pressurization and depressurization times and to study non-linear pressurizations and depressurizations.

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