

# Investigation of New Polymeric Membranes with Controlled Architecture for CO2 Capture

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# Preface

This specialization project and master thesis were held in the Chemical Engineering Department (IKP) of the Norwegian University of Science and Technology (NTNU) in Trondheim, Norway, between the 22<sup>nd</sup> of August and the 9<sup>th</sup> of December, 2011, for the project and the 16<sup>th</sup> of January and the 11<sup>th</sup> of June, 2012, for the master thesis.

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# Abstract

The capture of CO<sub>2</sub> is of high interest in a society concerned by climate change and consequently by greenhouse gas emissions. If the amine absorption or hot potassium scrubbing are widely used, several membrane processes are also employed. Many studies are realized to develop new polymers in order to increase the selectivity and permeability of membranes. Polyether based copolymers are particularly studied because of the high flexibility of the polyether chain which enables good gas diffusion properties and favorable polar interactions between the oxygen atoms of ether and the carbon dioxide. Moreover, the mechanical and thermal properties can be tailored using different hard segments, different chain lengths or compositions for the soft segment which affect the crystallinity of both phases. Fixed sites carrier membranes are also studied because facilitated transport enables to get membranes with both high selectivity and permeability.

In this study, polyether based copolymers containing poly(ethylene oxide) or poly(propylene oxide) soft segments are considered. The hard segments are aldehyde groups for one series and aldehyde and histamine groups for a second series, based on the same soft segments. The permeation properties for pure  $N_2$ ,  $CH_4$  and  $CO_2$  have been tested using a time lag permeation rig at 5 bars. Mixed gases experiments have also been performed using a gas mixture of  $10\% CO_2 - 90\% N_2$  at 1.2 and 5 bars feed pressure, in dry and humidified conditions, in order to identify the presence of a possible facilitated transport. The sorption of carbon dioxide has been studied by gravimetric method using a Rubotherm magnetic suspension balance. The membranes materials have been characterized by Differential Scanning Calorimetry and by Fourier Transformed Infrared spectroscopy and some of them with Atomic Force Microscopy. Water vapor swelling experiments have been performed in order to characterize the amount of water sorbed in each membrane and its influence on membrane properties. The gas permeability and gas sorption results were correlated with the chemical polymers structure.

Twelve membranes have been studied, half of them containing histamine groups. Infrared Spectroscopy showed that all the membranes have the same functional groups but in different relative proportions which is consistent with the structures of the membranes. Differential Scanning Calorimetry gave the characteristic temperatures of the polymers, the most interesting one being the glass transition temperature. All the soft membranes had a negative Tg whereas the glassy ones had a Tg greater than 35°C. The membranes from the series "without histamine" were softer than the other membranes. Histamine membranes, due to their additional amine groups which can react with water, were able to uptake a bigger amount of water per volume of polymer.

 $CO_2$  sorption in polymers followed different mechanisms depending on the membranes: Henry's law for rubbery membranes – all "without histamine" series and T3 and T6; dual sorption model for the other membranes.

The membranes without histamine showed higher  $CO_2$  permeability for both pure and mixed gases experiments. This is expected and correlated with their rubbery structure which enables bigger free volume. The  $CO_2/N_2$  selectivity was generally higher for the membranes without histamine. For all the membranes,  $CO_2/N_2$  selectivity was higher in wet conditions than in dry conditions, proving that facilitated transport was occurring in a certain degree for all membranes. However, it is not possible to conclude that histamine groups enhance this facilitated transport. Robeson type of graphs, selectivity versus permeability, provides a good tool to identify the most interesting membranes for different applications:

• Ideal separation of carbon dioxide and nitrogen at 5 bars

Ideal  $CO_2/CH_4$  separation at 5 bars

Ideal CO2/ N2 Selectivity vs CO2 permeability at 5 bars



Figure 1 Robeson type graph for ideal CO<sub>2</sub>/N<sub>2</sub> separation at 5 bars

T6 without histamine (red circle) is the best membrane but if selectivity is preferred, T1 without histamine and T5 without histamine (green circle) show good properties. T2, T3 and T2 without histamine (blue circle) show high permeability with lower but still interesting selectivity.



Figure 2 Robeson type graph for ideal  $CO_2/CH_4$  separation at 5 bars

T6 without histamine show the best separation properties but other membranes can be chosen with higher selectivity and lower permeability and vice versa.

• *Mixed gas experiments:* The best results were obtained for 1.2 bars wet.



Selectivity vs CO2 permeability at 1.2 bar wet

Figure 3 Robeson graph for 1,2 bars wet

T3 without histamine and T6 without histamine present the best tradeoff between selectivity and permeability and T2 without histamine and T5 show also good separation properties.

Therefore, they are the membranes which could be further developed in order to be used in industry.

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# List of symbols

# **Abreviations**

AFM	Atomic Force Microscopy
DSC	Differential Scanning Calorimetry
EO	Ethylene Oxide
FTIR	Fourier transform infrared spectroscopy
IPCC	Intergovernmental Panel on Climate Change
MSB	Magnetic Suspension Balance
PEO	Poly(ethylene oxide)
PEG	Poly(ethylene glycol): PEO with M<20 000 g/mol
РО	Propylene Oxide
РРО	Poly(propylene oxide)
UNFCC	United Nations Framework Convention against Climate Change
SRK	Soave-Redlich-Kwong

# <u>Symbols</u>

A	Area	m <sup>2</sup>
a, b	SRK model parameters	cm <sup>6</sup> .mol <sup>-2</sup> , cm <sup>3</sup> .mol <sup>-1</sup>
D	Diffusion coefficient	$m^{2}.h^{-1}, cm^{2}.s^{-1}$
D <sub>k</sub>	Knudsen diffusion constant	$m^{2}.h^{-1}, cm^{2}.s^{-1}$
J	Flux through the membrane	m <sup>3</sup> <sub>STP</sub> .m <sup>2</sup> .h <sup>-1</sup>
К	Koseny-Carman constant	-
I	Membrane thickness	m
Μ	Molar mass	g.mol <sup>-1</sup>
n	Molar quantity	mol
Р	Permeability	Barrer $(10^{-10} \text{ cm}^3_{\text{STP}}.\text{cm}.\text{cm}^{-2}.\text{s}^{-1}.\text{cmHg}^{-1})$
р	Pressure	bar, cmHg
R	Ideal gas constant	82.057 atm.cm <sup>-3</sup> .mol <sup>-1</sup> .K <sup>-1</sup>
S	Solubility	cm <sup>3</sup> <sub>STP</sub> .cm <sup>-3</sup> . cmHg <sup>-1</sup>
S	Internal surface area	m <sup>2</sup>
Т	Temperature	к, °С
V	Volume	m <sup>3</sup>
V	Molar volume	cm <sup>3</sup> .mol <sup>-1</sup>
Z	Compressibility factor	-

# Greek letters

ır
I.S
cm⁻³

## **1. Introduction**

#### **1.1 Background: Interest of CO<sub>2</sub> capture**

Global warming and greenhouse gas effect are topics currently of high interest in our societies concerned with climate change and its negative effects. Numerous international meetings have been held to tackle this challenge. Related to climate change, in 1992 was held the United Nations Framework Convention against Climate Change (UNFCC) where the UN countries recognized that *"the climate system is a shared resource whose stability can be affected by industrial and other emissions of carbon dioxide and other greenhouse gases"*[1]. And then, in 1997, they decided to take commitments in order to reduce the greenhouse gas emissions through the Kyoto Protocol. This Protocol and the different meetings related to its application have been and are still highlighted by most of the media in the world, and thus the public is fully aware about the problem of global warming. The global warming is the increase in temperatures noticed everywhere in the world. This could be seen from the diagrams published by the Intergovernmental Panel on Climate Change (IPCC) in their Fourth Assessment Report: Climate Change 2007[2].



Figure 4 Evolution of temperatures compared to the average during the period 1961-1990 (top) and patterns of linear global temperature trends from 1979 to 2005 (bottom) [2]

This phenomenon is linked with the increase of greenhouse gas emissions due to human activities. Amongst the greenhouse gases, carbon dioxide represents the main part of the emissions. The main sources of  $CO_2$  are the power generation by combustion of fossil fuels, cement industry, refineries and transportation. With the industrialization of the world, the proportion of  $CO_2$  has dramatically increased during the last years and it can be related to the increase of temperature. [3]



Figure 5 Evolution of global temperature and CO<sub>2</sub> concentration since 1880 [3]

So it appears really important to be able to reduce the emissions of such greenhouse gases and particularly carbon dioxide. An efficient strategy is to develop the capture of  $CO_2$  when and where it is formed and before it is released in the atmosphere; but the development of storage capacities and methods is also necessary. The capture of  $CO_2$  in fossil fuel power plants has been intensively studied and three paths exist with different issues, advantages and disadvantages[4] :

- <u>Post-combustion capture</u>: it concerns flue gas, meaning that the separation is mainly between nitrogen and carbon dioxide. The partial pressure of CO<sub>2</sub> is low but the process can be easily adapted to existing plants.
- <u>Pre-combustion capture:</u> after gasification of the feed gas, a gas rich in hydrogen and carbon dioxide is obtained. The separation occurs between H<sub>2</sub> and CO<sub>2</sub> and then hydrogen is burned. The driving force is high as the partial pressure is high.
- <u>Oxy-</u>combustion capture: The combustion occurs using an oxygen rich gas so the exhaust gas obtained is rich in carbon dioxide. Once again the driving force is good but it is energy consuming to produce oxygen rich feed gas.

For the storage, two main ways are investigated: geological and maritime storage.

Another place where carbon dioxide capture is required is the production of liquefied natural gas (LNG) from natural gas. The natural gas is mainly composed of methane with many other gases such as  $CO_2$ ,  $SO_2$  and other alkanes. Those impurities can freeze at the storage and transport conditions of methane (-162 °C and 0.1 bar) and thus need to be removed before liquefaction. This separation involves then methane and carbon dioxide.

## **1.2 CO<sub>2</sub> capture processes**

There are two main processes used to remove CO<sub>2</sub> from a gas mixture:

- Absorption process: the gas goes counter current with a chemical or physical solvent and one
  of the components has better affinity for the solvent (or can react with the chemical solvent)
  and so is removed. This process needs a step of regeneration of the solvent, step often
  expensive or energy consuming, which is a real disadvantage.
- Membrane process: Membranes can be made from organic, inorganic or mixed materials. Once again, one component has better affinity for the membrane and is able to go through more easily than the others. This technology requires a lot less energy than absorption and does not need the use of chemicals. However, the challenge is to use a membrane with the desired properties to realize the wanted separation.

The properties of a membrane needed to obtain the desired separation are the selectivity of the membrane and the permeance of the desired gas. Unfortunately, it is difficult to obtain both high selectivity and high permeance. It was proven and expressed by Robeson as the upper-bound [5]. This limit can be seen in such graphs:



Figure 6 Upper Bound according to Robeson showing the trade-off between selectivity and permeance for CO<sub>2</sub> and N<sub>2</sub> separation [5]

The structure and the different functional groups of the polymer constituting the membrane have an influence on the performances of the membrane and many studies are made to find new materials with better separation properties.

# 1.3 Aim of the project

The aim of this project is to study copolymeric membranes synthesized by the Supramolecular Nanosystems Group, Institut Européen des Membranes adaptives, University of Montpellier. The membranes studied are all polyether based copolymers with hard group coming from a trialdehyde. For half of the investigated samples having the same soft segments, the hard groups contain also an imidazole moiety. This group had been added in order to increase the facilitated transport of carbon dioxide in presence of water. The performances of the membranes are determined through gas permeation (for single and mixed gases, in dry and wet conditions) and sorption experiments whereas the structure and properties of the materials can be highlighted by Atomic Force Microscopy (AFM), Infrared spectrometry (FTIR) and Differential Scanning Calorimetry (DSC). A literature review was made to improve the understanding of the links between structure and performance and the challenges of the use of membranes for the capture of CO<sub>2</sub>.

# 2. Literature review

# a. Separation CO<sub>2</sub>/light gases (CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub>)

The main separations including CO<sub>2</sub> are the following:

- Capture of CO<sub>2</sub> from natural gas or natural gas sweetening: it is a separation between CO<sub>2</sub> and CH<sub>4</sub>. Sridhar et al. [6] made an exhaustive review of all the membranes and membrane processes which can be used for this separation
- Capture of CO<sub>2</sub> from flue gas: the main components are nitrogen and carbon dioxide. It often happens in post-combustion stages where gas is at atmospheric pressure, the content of CO<sub>2</sub> is average (10-20 % of the volume) and at around 50°C [4].
- Pre-combustion capture of CO<sub>2</sub>: the separation happens between CO<sub>2</sub> and H<sub>2</sub>. The feed pressure is much higher (70 bar) as well as CO<sub>2</sub> content (45%) and the temperature (300°C) [4]. A review to help choosing one membrane or one process has been published by Scholes et al. [7].

The separation of  $CO_2$  and  $H_2$  can be made based on the size of the molecules (kinetic diameter of 2.6Å for  $H_2$  and 3.3Å for  $CO_2$ ): it happens by diffusion. It is the same type of separation for the capture of  $CO_2$  from natural gas because  $CO_2$  is smaller than  $CH_4$  (d=3.8Å) and then its diffusivity through the polymer is higher. To help this separation, it is necessary to develop rigid polymers, which present high glass transition temperatures, to increase the diffusivity separation without losing  $CO_2$  permeability [8].

As the nitrogen and carbon dioxide sizes are very similar, the separation happens mainly by differences of solubilities. To increase the solubility of  $CO_2$  in a polymer it is important to choose a material with a close polarity to the one of  $CO_2$  [6]. The Debye moment of the C=O link is about 2.5 and so, for example, imine bond, which has also a Debye moment of 2.5, will develop favorable interactions with  $CO_2$ . This amine/  $CO_2$  affinity has been reported by Ghosal et al.[9]. The affinity of  $CO_2$  with ether groups is reported in many other studies [4, 8, 10-25]. Lin and Freeman, in their Materials selection guidelines for membranes that remove  $CO_2$  from gas mixture,[8], present several polar groups which can help to increase the solubility selectivity:

- Carbonyl, carbonates and amides are used to improve barrier properties by increasing chain rigidity. The carbonyl groups help increasing the solubility. However, if the chain rigidity increases, the diffusivity will be lowered [26].
- Ether oxygens improve CO<sub>2</sub> sorption and solubility selectivity. If concentration increases (polybutadiene to polyethylene oxide passing by poly(tetramethylene oxide)) the solubility increases monotonically from 0.89 to 1.4 cm<sup>3</sup><sub>STP</sub>/(cm<sup>3</sup>.atm) [10, 13].
- Nitrile groups, for example in polyacrylonitrile, present the same behavior: an increasing CO<sub>2</sub> permeability and solubility selectivity with an increasing acrylonitrile concentration.

The introduction of polar groups should be made with precaution because it decreases the free volume and so increases the chain rigidity. Then diffusivity is lowered and often a trade off is necessary.

# b. Interest of block copolymers for gas separation and especially polyether copolymers

A block copolymer is made from at least two monomers. Its properties can be tailored by the choice of different monomers which have different properties. For example, for gas separation, the permeability is high through a rubbery polymer but usually those polymers have low mechanical and thermal resistance. It could be useful to make a copolymer with permeable soft segments and with hard parts in order to provide resistance.

Lin and Freeman [8], showed that the ether oxygens provided a good balance between CO<sub>2</sub> solubility and permeation properties and it has been used in various studies [4, 8, 10-25]. Indeed, ether oxygen atoms provide flexibility to the polymeric chains and enable a high diffusivity. They also are polar groups which favor interactions with CO<sub>2</sub> providing high solubility of carbon dioxide [4]. The most used polymer made of ether oxygens is the poly(ethylene oxide) (PEO). Lin and Freeman, [13], studied gas solubility, diffusivity and permeability in PEO and showed that the permeability of permanent gases such as He, H<sub>2</sub>,O<sub>2</sub> and N<sub>2</sub> was independent of the pressure whereas for CO<sub>2</sub> and hydrocarbons it increases with the pressure. The selectivity was proved to decrease with temperature decrease. One of the main disadvantages of PEO is that, in pure state or at high concentrations, it crystallizes easily. The crystallites prevent good permeation of gases through the polymer. Lin and Freeman propose different methods to decrease the crystallinity of PEO:

- To use poly(ethylene glycol) (PEG) which is a liquid over 17-22 °C. It can be made by liquid membranes or by blends with solid membranes like PDMS or PTMSP.
- To design phase separated block copolymers with too short ethylene oxide (EO) segment to crystallize at room temperature. For example: polyamides (PEBAX) or polyimides.
- To obtain highly branched, crosslinked networks with high concentration of PEO. The ideal would be to get molecular weight between crosslinks under 1500. The crosslinking can be made with acrylates. Highest permeabilities are obtained using this configuration.

Reijerkerk [16], summarizes favorable properties of a polyether based block copolymer used for CO<sub>2</sub> separation:

- 1. Good phase separation of the hard and soft segments
- 2. Complete crystallization of the hard segment
- 3. High PEO content
- 4. Low glass transition temperature of the soft segment (high chain flexibility)
- 5. No soft phase crystallinity or low soft segment melting temperature.

The gas permeation properties are good if there are large areas of soft amorphous membrane so if the soft part does not crystallize and if the hard part avoids mixing with the soft part and is well crystallized. This has been notably proved by Barbi et al., [25], studying polyether-block-polyamide copolymer membranes with time-lag method and small angle X-ray scattering (SAXS): the samples with poor phase separation show decreased gas permeability and diffusivity. The poly(propylene oxide) (PPO) is also a polymer extensively used for the same purpose as PEO. The extra methyl side groups (compared to PEO) hinder PEO crystallization [27] because regular chain packing is avoided. The polymer has a low glass transition temperature providing amorphous phase and good properties even at low temperatures. This increases the free volume [16] and consequently CO<sub>2</sub> permeability but it decreases the polarity of the polymer and consequently the CO<sub>2</sub> solubility and membrane selectivity. That's why it is often used, not alone, but in addition to PEO to enhance its properties.

Several polyether based copolymers have been studied and it was always observed that the selectivity increased with an increase of the soft segment length and that the main contribution to the high selectivity was the solubility selectivity.

- Arun et al. [27], studied (PEO/PPO)- aramide copolymers. PEO and PPO length and concentration were varied. They also studied the hydrophilic and hydrophobic properties of respectively PEO and PPO and then the resulting property for the copolymer. They found that the PEO crystallinity and melting temperature increased when the PEO segment length increased.
- Simons et al.,[11], studied ODPA-based polyetherimide films. The polymers were notably characterized by AFM, DSC, sorption and permeation. They observed that, for their glassy polymers, the CO<sub>2</sub> sorption was higher if the glass transition temperature was higher. And they deduced that it came from the fact that the non-equilibrium excess free volume was higher.
- Reijerkerk, studied different combinations of PEO and PPO [4, 15-21]: pure PEO [15, 16], pure PPO [16], block copolymer PEO/PPO [16] and randomly distributed PPO in PEO segments[15-18, 20]. The hard part was a short monodisperse diamide [16] or tetra-amine based segment [15, 17, 18, 20].
  - He first studied different copolymers made of the same hard segment (TΦT, a diamide) and different soft segments (PEO, PPO, or a mixture of the two)[16]. He showed that the permeability was up to five times higher for the propylene oxide than for ethylene oxide but the selectivity is lower because of the lower CO<sub>2</sub> solubility. The effect of the length of the soft segment was also studied: the permeability increased with the length but the selectivity was almost constant. The main difference between PEO and PPO soft segments is the effect of temperature: there is a clear transition for PEO whereas the selectivity and the permeability decrease linearly for a PPO soft segment because it stays amorphous and the phase separation is better. Finally, he studied a mixture of PEO and PPO. If the content of PEO is lower than 40%, the copolymer is amorphous and the permeation properties are good. The permeability decreases with an increase of PEO content because of a decrease of the free volume whereas the selectivity increases because of the increasing polarity.

- He studied then another copolymer with T6T6T (a tetra-amide) as hard segment and a soft segment made of a random distribution of PPO in a PEO segment with a content of 25% of PPO [15, 17, 18, 20]. This type of hard segments was able to provide a very pure soft amorphous phase (and then the glass transition temperature of this phase was really low). The random distribution of PPO enables to decrease the crystallinity of PEO as well as the melting temperature of the soft segment [15]. He showed that the mass transport was happening through the soft segment but influenced by the microdomain morphology [15]. After, he studied the permeabilities were much higher than through other copolymers especially at low temperature whereas the selectivity was only slightly lowered. Increasing the length of the soft segment using terephtalic units was made but the flexibility of the chain was decreased and the properties lowered.
- The plasticization phenomenon was then studied for CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/H<sub>2</sub> separations [20]. Plasticization is observed when the permeability of methane or hydrogen in a mix of gases with carbon dioxide is higher than the permeability measured for pure gases. The selectivity for mixed gases is lower than the one for pure gas and related to the concentration of CO<sub>2</sub> in the polymer, which is a function of the temperature and of the fugacity of CO<sub>2</sub>. This phenomenon enhances CO<sub>2</sub>/H<sub>2</sub> separation performances because it enhances the diffusion of the biggest gas. That is also why CO<sub>2</sub>/CH<sub>4</sub> separation performances are lowered when plasticization happens. The phenomenon was studied through sorption and permeation experiments. As the amount sorbed and the permeability of CO2 was the same for pure or mixed gases, the sorption and the permeability of CO2 is considered independent of the other components.
- The same membranes (PEO-ran-PPO + T6T6T) were also studied for simultaneous CO2 capture and dehydration of flue gas [18]. It was shown that although the water sorption was strong, especially for water activity higher than 0.6, no plasticization phenomena was observed. The selectivity for  $CO_2/N_2$  separation was slightly increased. The strong sorption of water leads to the swelling of the membrane: Flory-Huggins behavior should be taken into account as well as the change of thickness to calculate the correct diffusivity. The amount of sorbed water increases if the length of soft segment increases mainly because the decrease of physical crosslink density enables a higher swelling but also because of the increase of the concentration of hydrophilic domains. The membranes are attractive for post combustion  $CO_2$  capture due to the high vapor and  $CO_2$  permeabilities and the reasonable  $CO_2/N_2$  selectivity.
- Reijerkerk studied also another strategy to obtain highly permeable membranes for CO<sub>2</sub> capture by blending a PEO based copolymer with different additives [19]. The PEO copolymer used was PEBAX (polyether block amide) for its high CO<sub>2</sub> selectivity and the additive was PDMS-PEG (polydimethylsiloxane polyethylene glycol) at a ratio 20-80 % in moles, for its high permeability. For 50% of additive, the

permeability and the solubility of  $CO_2$  were highly increased and the selectivity of  $CO_2/H_2$  separation was enhanced. A competition between plasticization effects and hydrostatic pressure was observed when the fugacity of CO2 was increased: indeed, the plasticization at high activity of carbon dioxide enhances the diffusion of the other gases whereas the pressure applied compresses the membrane and reduces the free volume. The selectivity of  $CO_2/CH_4$  separation was lowered.

- Hirayama et al., [12], studied films containing crosslinked polyether oxide. High PEO content films have been obtained by photo polymerization from mono and dimethylacrylates containing PEO. High CO<sub>2</sub> permeability and high CO<sub>2</sub>/N<sub>2</sub> selectivity have been observed, due to high solubility selectivity, thanks to the affinity of CO<sub>2</sub> for PEO segments. Crystallization occurred when the length of the PEO segments was increased and this more easily in the side chains than in the crosslinked chains. The free volume effect was also studied: increasing the length of PEO segments in crosslinked chains or in side chains leads to an increase in permeability, in solubility and in diffusivity. Finally, the introduction of phenylene rings was studied: as the affinity of PEO to CO<sub>2</sub> and the segmental motion were decreased, all the separation properties were decreased.
- Bondar, Freeman and Pinnau, [10, 23], studied poly(ether-b-amide) segmented block copolymers from the PEBAX family. The soft parts were made of polyethylene oxide or of poly(tetramethylene oxide) (PTMEO) whereas the hard segments were polyamides 6 or 12 (PA6 or PA12). The solubility selectivities for CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/H<sub>2</sub> separations are high due to high CO<sub>2</sub> solubility. Solubilities and permeabilities are higher in membranes made of less polar units (PTMEO or PA12 instead of PEO or PA6) but the selectivities are higher when the concentration of polar units is higher. The competition between plasticization effects and hydrostatic pressure has also been noticed.
- Husken et al., [22], studied poly(ether oxide) based copolymers with monodisperse amide segments as hard parts to ensure a well phase separated morphology because they have a high crystallinity and only a low amount of hard segments is dissolved in the amorphous phase.
- Yoshino et al., [24], studied the effects of the hard segments of PEO segmented copolymers on CO<sub>2</sub>/N<sub>2</sub> separation. The hard segments studied were polyurethane, polyamide and polyimide. The best performances were found for polyimide. Indeed, hydrogen bondings between the oxygens of PEO and the hydrogen of urethane or amide lead to an increase of the amount of hard segments dissolved in the soft parts and to decreased diffusivity, selectivity, permeability and selectivity. Polyetherimide/ PEO membranes present however decreased performances with time and difficulties to be prepared.

The interest of block copolymers for membrane preparation is to fine tailor their separation properties. Functional groups can be added in order to increase the permeability or the solubility of a given species. For example, Ghosal et al., [9] studied the effect of basic substituents such as amines and phtalimides on gas transport properties for polysulfone. Indeed, as CO<sub>2</sub> and H<sub>2</sub>S are acidic gases their solubility is expected to be increased by the presence of basic substituents. They showed that for strong base as benzylamine (pKa=9.33) CO2 solubility is indeed increased but that the decrease of free volume leaded also to a decrease of the diffusion coefficient. This tuning has been considered not interesting enough to separate carbon dioxide from methane.

#### c. Facilitated transport membranes

Facilitated transport membranes for CO<sub>2</sub> capture are one particular subject of research in our group, mostly for fixed-site carrier polyvinylamine membranes and several articles and thesis have been published on this subject [28-31]. Beside the explanation of the mechanisms, most of those works aim to test different supports and polymers in order to get good permeation properties, good selectivity and good durability. Both flat membranes and hollow fibers are studied.

Modification of polymers to add amine groups has also been studied. Matsuyama et al., [32], studied polyethylene membranes grafted with 2-(N,N-dimethyl)aminoethyl methacrylate (DAMA) by plasma polymerization. They studied dry and water containing membranes for  $CO_2/N_2$  separation. Water containing membranes achieved much higher selectivity and  $CO_2$  flux than dry membranes. For both types of membranes, both selectivity and  $CO_2$  flux decreased with increasing  $CO_2$  partial pressure showing that carrier transport was happening for both cases, with, however, difference in the mechanism. For dry membrane, weak acid base interaction between the amine moiety and  $CO_2$  enables  $CO_2$  transport: it is a fixed carrier membrane. For wet membrane, the mechanism differs. As it is a tertiary amine, there is no carbamate formed; the amine acts as a weak base catalysis for  $CO_2$  hydration reaction. The transport happening is the one of  $HCO_3^-$ , the membrane is called "fixed reaction site membrane" or "catalysis membrane".

Yu et al., [33], studied also tertiary amino containing membrane based on the same catalysis mechanism explained earlier. They chose tertiary amines due to their better stability in presence of air than primary or secondary amines whose protons can react. Tertiary amines are also less crystalline than primary amines. Interfacial polymerization was used with 3,3'-diamino-N-methyldipropylamine(DNMDAm) and trimesoyl chloride (TMC) and a polysulfone support membrane. They proved that transport was happening thanks to hydration of  $CO_2$  to form  $HCO_3^-$  and also observed a decrease of selectivity and flux with increased feed pressure, strong decrease at first and then only slight due to carriers saturation.

# d. Some points about characterization methods and theories

- Dual sorption theory:
  - $\circ$  Koros [34], studied the sorption and transport of CO<sub>2</sub> in polycarbonate which is a glassy polymer. He proved that the dual sorption theory corresponds to a model where the gas adsorbed by Langmuir type is partially immobilized in the polymer. He showed also that the permeability and the time lag decreased when the feed gas pressure was increased.
- Hysteresis in desorption:
  - Simons et al. [11], studied the sorption and the desorption of gases into the membranes to study possible non-equilibrium hysteresis. They concluded that the hysteresis seen was the result of the induction of new free volume sites during the sorption. The collapse of these new sites happening in longer scale time than desorption of CO<sub>2</sub>, a higher free volume exists during desorption and a hysteresis can be seen.
  - Fleming and Koros, [35],compared the dilation of silicone rubber and polycarbonate (glassy polymer) by sorption of carbon dioxide at elevated pressures. They showed that sorption in rubber has low dependence on pressure whereas for glassy polymers, the partial specific volume of CO<sub>2</sub> was smaller, strongly dependent on gas pressure and then a large hysteresis was observable. They proved that Henry's law was valid for rubber until 21 bar and the swelling of the polymer fitted with Flory-Huggins model. For glassy polymers, there is one fraction of the gas uptake done in dissolved state (Henry's law) and another into microvoids due to the non equilibrium state of glassy polymers (Langmuir). The hysteresis phenomenon in glassy polymer has been particularly studied. They explained that this phenomenon was due to two semi-permanent states which can exist at the same external CO<sub>2</sub> pressure because the presence of CO<sub>2</sub> increased the Langmuir capacity, the amount of un-relaxed volume. The presence of CO<sub>2</sub> during depressurization retards relaxation of the polymer to its former thermodynamic state which has been observed during pressurization.
  - Hysteresis in sorption/ desorption in polymers has also been studied by Kamiya, [36], for low density polyethylene(LDPE), polysulfone(pSf) and polycarbonate(PC). For LDPE, a rubbery polymer, no hysteresis has been noticed and both sorption and desorption data were fitted with Henry's law. For pSf and PC, a conditioning effect and a hysteresis have been highlighted. The conditioning effect comes from the fact that after the exposition of a glassy polymer to high pressure CO<sub>2</sub>, the sorption capacity is increased due to a structural relaxation of the polymer. The conditioning effect is long term relaxation, due to the plasticizing effect of sorbed gas. Hysteresis is a short term relaxation and a time dependent phenomenon. They noticed that the width of the hysteresis loop was reduced with an increase in temperature.
  - Atomic Force Microscopy: Reijerkerk [4], studied his copolymers with AFM and observed that, as it was proposed by Cella [37], there were long ribbons formed by crystallized lamellae. This is the common morphology of segmented block copolymers. Yu et al., [33], proved the existence of the tertiary amino containing layer for their composite membrane using AFM.

• Differential Scanning Calorimetry: Reijerkerk [4], studied his copolymers with DSC. The following figure is representative for the thermal behavior of block copolymers made of soft and hard segments:



Figure 7 DSC results obtained by Reijerkerk [4]

Four different transitions can be seen:

- 1. A second order endothermic transition which corresponds to the glass transition temperature Tg
- 2. A first order exothermic transition which can be called "dynamic state of copolymer"
- 3. A first order endothermic transition which corresponds to the soft phase melting
- 4. A first order endothermic transition which corresponds to the <u>hard phase</u> melting. This is observable only if the soft group length is smaller than 5000g/mol.

DSC is often used to characterize polymers, with however different cycles. Hirayama, [12], increased temperature from -120°C to 150°C at the rate of 5°C/min. Lin and Freeman, [13], chose an increase from 0°C to 120 °C at 20°C/min. Bondar, [10], studied a larger domain of temperature (-150 to 250°C) with a rate of 20°C/min and using the results from the second scan. Husken, [22], used samples of 5 to 10 mg. A first heating was done between -50 and 250°C at 20°C/min followed by a cooling and a second scan. The melting temperature and enthalpy of melting  $\Delta$ Hm were obtained from the second scan peaks. Yoshino, [24], obtained the melting and glass transition temperatures from a first heating cycle run at 10°C/min whereas Ghosal, [9], used the second heating scan and a rate of 20°C/min.

# 3. Theory

## 3.1. Membranes

#### 3.1.1 Definition of a membrane

A membrane is able to separate different molecules and is defined as a selective barrier between two phases. This means that if a mix of different molecules is given at the feed side, one component will be transported through the membrane more easily than the others. This selectivity is due to chemical or physical properties of the component and of the material of the membrane. For example, the separation can occur based on the size of the molecules or because one molecule has better affinity for the membrane material. A driving force is needed in order to perform the separation[38]. Different driving forces exist but the most common are the pressure difference or the concentration difference. The figure 8 below presents the principle of the membrane separation.



Driving force ( $\Delta P$ ,  $\Delta c$ ,  $\Delta T$ ,  $\Delta E$ )

Figure 8 Schematic representation of a membrane separation [38]

#### **3.1.2 Membrane performance**

Two parameters are used to evaluate the performance of a membrane: its selectivity and the flow going through. The flow, also called permeation rate, is expressed as the gas volume passing through the membrane per unit area and time. The selectivity is often expressed as the retention R or the selectivity factor  $\alpha$ .

$$R = \frac{c_f - c_p}{c_f} = 1 - \frac{c_p}{c_f}$$
 where c refers to concentration and the subscripts f and p, respectively to

feed and permeate sides.

$$\alpha_{\underline{A}} = \frac{\underline{y_A}}{\underline{x_A}}$$

 $x_B$  where y and x are the concentration respectively in the permeate and feed side. Usually, this selectivity is chosen in order to be greater than 1. It expresses the fact that the component A goes more easily through the membrane than the component B.

A good membrane enables a very high purity of the product (a good selectivity) and with a sufficient rate (flow). This is quite difficult to obtain simultaneously and most of the researches nowadays are focused on increasing both selectivity and flow to overcome the Robeson's upper bound [5].

Another important point about membranes is their chemical and physical resistance. Indeed, they can be subjected to hard conditions, for example acidic gases as  $SO_2$ ,  $NO_{x_2}$  high pressure, humidity or high temperature.

#### **3.1.3 Classification of membranes**

- Membranes can be divided into two categories: biological or synthetic. In this work, as in most of the current researches, only the synthetic membranes will be investigated. However, the biological ones are in use in medicine and biomedicine fields. The synthetic membranes can again be divided into two: organic and inorganic. Inorganic membranes are made of ceramic materials or metal, whereas organic ones, which are those of interest here, are either polymeric or liquid.
- Another division can be made based on the structure of the membrane. They can be symmetric, with only one layer, or asymmetric, if they are made of different layers with different properties.
   Each layer (or the symmetric membrane), can be *porous* or *dense* (also called non-porous or homogeneous). On the figure 9 below, the different configurations possible are presented.





The separation principle is not the same in porous or dense membranes. In porous membranes, which are characterized by a voided structure, there are many pores. Those membranes differ one from another by the size of the pores and by the pores size distribution. The separation is based on difference in molecular sizes of the different components. Non porous membranes are made of dense films and separation occurs because of different relative transport rate of the components through the membrane. The difference comes from differences in the solubility and diffusivity of the components in the membrane. A separation of same size molecules having various solubilities is then possible.

The interest of asymmetric membranes comes from the fact that the permeation rate increases when the thickness of the membrane decreases. The porous sublayer gives mechanical stability to the thin dense and selective toplayer which can then have both high selectivity and high permeance. If the two layers come from different polymeric materials, the membrane is called *composite* and both layers can be optimized separately.

The membranes studied in this work are expected to be dense homogeneous membranes.

# 3.2 Polymeric membranes

#### 3.2.1 Definitions and important notions

#### Polymer definition

A polymer is a macromolecule whose long chain is made of a lot of small unities, called monomers. A polymer is characterized by a high molecular weight. The different properties of a polymer come from the chemical nature of the repetitive units but also from their average molecular weight or from the configuration of the chain.

#### Structure of a polymer

If all the repetitive units are the same, the polymer is called **homopolymer.** If not, it is called **copolymer** and it is usually made of 2 or 3 different monomers. Depending on the way the various unities are linked, the properties of the polymer will differ. If the polymer is made of A and B units without any order, it is a *random polymer*. A *block copolymer* is made of several chains of A linked with chains of B in a linear way. If the main chain is made of A monomers and some side chains of B are linked to the first one, the polymer is *grafted*.

<u>Homopolymer:</u> ААААААААААААААААААААААААААААААААААА								
Copolymers:								
Random polymer: ABBABABABABABAAABABABABBABABABABABAB								
Block copolymer: AAAAAABBBBBBBBBBBBBBBBBBBBBBBAAAAAAAAA								
Graft copolymer: AAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAAA								
В	В							
В	В							
	В							

Figure 10 Different structures of a polymer [38]

It is also possible to classify polymers on the overall structure: they can be linear, branched or crosslinked.



Figure 11 Overall structures of polymers [38]

The crosslinking has a great influence on the physical, mechanical and thermal properties of a polymer: it can become insoluble and so chemical resistant. Chemical or physical crosslinking can be used.

#### State of a polymer

A polymer contains generally two different phases: one is **amorphous** and the second one is **crystalline**. Such a polymer is then characterized by the degree of crystallinity and called **semi-crystalline** polymer. It is possible to produce only amorphous polymer but seldom to find a complete crystalline polymer. The amorphous phase is characterized by lack of order at the molecular level. If the polymer is very regular, with a symmetrical structure, the chains can order themselves and so the structure becomes crystalline.

The state of the polymer is mainly determined by the glass transition temperature Tg (except for crystalline polymers for which the melting temperature Tm is more important). This temperature marks the boundary between two different states of the polymer: **glassy** for T<Tg and **rubbery** for T>Tg. This transition can be noticed by following different properties, as for example tensile modulus E, when increasing the temperature. The tensile modulus is the force applied to a given area to obtain a given deformation and it is obtain from stress-strain curves, see Fig. 12 below.



Figure 12 Glass transition temperature for an amorphous polymer [38]

For a semi-crystalline polymer, this transition is observed for the amorphous parts whereas the crystalline parts melt for T>Tm. The curve obtained is then the following one:



Figure 13 Glass transition temperature and melting temperature for a semi-crystalline polymer

The glass transition temperature can be increased by increasing the size of the side groups, by a loss of rotation freedom or by an increase of the number or the proportion of polar groups.

#### 3.2.2 Effect of the polymer properties on the membrane performances

The performances wanted are high selectivity, high permeance (so a big flow) and also good chemical and thermal stability.

- Chemical stability:
  - Glassy polymers, with high Tg, show better resistance than elastomers.
  - The chemical stability is improved if the degree of crystallinity increases.

#### Permeability:

- Usually, high permeability is obtained through elastomers, with low Tg, whereas permeability in glassy polymers is low.
- Crystalline polymers are not suitable for membranes because the permeability is lowered down.

#### • <u>Mechanical resistance:</u>

 Elastomers show poor mechanical properties whereas glassy and crosslinked polymers have better resistance.

The state of the polymer is very important because it plays an important role on gas transport properties through the membrane. The polymer free volume is a good example to show how the polymer structure affects the gas transport. The free volume variation with temperature is shown on the following figure:



Figure 14 Variation of the free volume with the temperature

The free volume is the volume not occupied by the macromolecules. To obtain a good gas solubility, it is important to have a large polymer free volume. Consequently, the elastomers demonstrate better permeability properties than glassy polymers. On the other hand, as there is more space, the selectivity is decreased for elastomers. This shows once again the trade-off between selectivity and permeability.

### 3.3 Transport in membranes

#### 3.3.1 Transport in porous membranes

Different models can be used depending on the shape and size of the pores.

For cylindrical pores, Hagen-Poiseuille's law is used:

$$J = \frac{\varepsilon r^2}{8\eta\tau} \frac{\Delta P}{\Delta x}$$

where  $\varepsilon$  is the porosity,  $\eta$  is the viscosity,  $\tau$  is the tortuosity.  $\Delta P$  is the pressure difference which is the driving force and  $\Delta x$  is the thickness of the membrane.

For closed packed spheres, the flux is given by Kozeny-Carman's law:

$$J = \frac{\varepsilon^3}{K\eta s^2 (1-\varepsilon)^2} \frac{\Delta P}{\Delta x}$$

where K is the Koseny-Carman constant, depending on the shape of the pores and on the tortuosity, and S is the internal surface.

When the pores are smaller (20nm to 0.2  $\mu$ m), it is the Knudsen diffusion which is the most important.

$$J = \frac{\pi n r^2 D_k \Delta p}{R T \tau \ell}$$

where D<sub>k</sub> the Knudsen diffusion constant is :  $D_k = 0.66r \sqrt{\frac{8RT}{\pi M_w}}$ .

#### 3.3.2 Transport in non-porous membranes

Non-porous membranes are used for the separation of molecules having similar sizes. To achieve the separation, it is necessary that some pores exist but only at molecular level. It is most common to speak of free volume instead of pores for a non-porous membrane.

The transport of gases through such membranes follows a solution-diffusion mechanism [39]. This mechanism, firstly proposed by Sir Thomas Graham, is a three-step process:

- 1. The gas dissolves into the membrane on the feed side layer, which is the high pressure or high chemical potential face of the membrane. All the components dissolve in different proportions, it is a first step to separation. The amount of gas dissolved is characterized by the *solubility* S of this gas into the polymer.
- 2. The dissolved gas diffuses through the membrane. This is the slowest part of the mechanism so it is the rate-limiting step in mass transport through membranes. The ability of the gas to diffuse is expressed by the *diffusivity* D.
- 3. The gas desorbs at the other face of the membrane, to the permeate side.

The permeability of the gas through the membrane is expressed as the product of solubility and diffusivity:

#### P=S\*D.

The transport of gases through membranes can be described by Fick's first law:

$$J = -D\frac{dc}{dx}$$

where D is the diffusion coefficient  $(cm^2/s)$  and dc/dx is the concentration gradient through the membrane. If the diffusion coefficient is constant, which is often assumed for gases, Fick's second law can also be used:

$$\frac{\partial c}{\partial t} = -D \frac{\partial^2 c}{\partial^2}.$$

The diffusion coefficient is dependent on the size of the molecule: if the size increases diffusion will decrease. This is usually valid for non-interactive gases. Indeed, for interactive gases, swelling of the material will occur and the effect of diffusion separation will be less visible.

#### 3.3.2.1 Transport mechanism for ideal systems

Ideal systems usually consist of elastomeric membrane and non-interactive gases. In this case, both solubility and diffusivity are constant and Henry's law can be applied. Henry's law state that the concentration on the membrane is linearly linked to the partial pressure:

$$c=S*p.$$

The Fick's law can then be expressed as:

$$J = \frac{SD}{\ell} (p_1 - p_2) = \frac{P}{\ell} (p_1 - p_2)$$

where 1 refers to feed side and 2 to permeate side.

The solubility of a gas in an elastomer is generally low but it increases if the molecular size increases because then the critical temperature increases and solubility is linked with the ease of condensation.

The permeability is dependent on two opposed parameters. Then, helium and hydrogen, which are small molecules, present high permeability because of high diffusivity whereas larger molecules like carbon dioxide demonstrate high permeability by the mean of high solubility.

#### 3.3.2.2 Transport mechanism for interactive systems

Those systems, also called concentration dependent systems, are usually met when glassy polymers are used and when swelling occurs. In this case, the concentration is no longer anymore linked linearly to the pressure but follow the Langmuir type sorption:

$$c = \frac{c'_h bp}{1+bp}$$
 where  $c'_h$  is the saturation constant and b the hole affinity constant. [38]

In reality, such systems follow the dual sorption theory which means that both Henry's law and Langmuir's law are contributing to the sorption.

The dual sorption theory is defined by:



Figure 15 Henry's law and Langmuir sorption contribute both to the dual sorption[38]

The diffusion coefficient is not constant anymore. The permeability can be studied with free volume theory and Flory-Huggins thermodynamics. As the solubility increases with the size of molecules, and the free volume increases with solubility, permeability increases with increasing size of molecule.

#### 3.3.3 Facilitated transport membranes

To increase the transport of one species through the membrane, facilitated transport membranes can be used. They contain a carrier (C) which specifically reacts with one of the components (A) and enhances its flux because the complex AC also diffuses through the membrane. The reaction should be reversible so the component can be released at the other side of the membrane. The free carrier diffuses back afterwards. The other components do not react with the carrier and only follow the solution diffusion model. The principle of facilitated transport compared to passive transport is schematically represented in the Figure 16, below.



Figure 16 Schematic representations of passive and facilitated transport [38]

Facilitated transport can be coupled if a component from the permeate (B) makes also a complex with the carrier and diffuses through the membrane in the opposite direction of the complex AC. This coupled transport enables to move species against its concentration gradient.

With facilitated transport, which is the combination of solution diffusion mechanism and reversible chemical reaction specifically for A, the flux of A is not proportional anymore to the driving force. High fluxes can still be obtained at low feed concentration.

Facilitated transport is easily understandable for liquid membranes but they suffer from practical disadvantages as degradation due to the wash out or evaporation of the carrier solution over time [29]. Some polymers with fixed site carriers have then been developed. Two mechanisms of transport have been developed: Cussler [40] proposed the hopping mechanism whereas Noble [41, 42] described a dual solution-diffusion mechanism.

- <u>Hopping mechanism</u>: as polymer chains show a certain mobility, Cussler assumed that if the distance between two chained carriers is smaller than the mobility distance, the two carriers can come close enough for the solute to hop from one to the other (like *"Tarzan swinging from one vine to the next"*). The transport happens by intramolecular diffusion. This model implies that if the distance between two chained carriers if bigger than the mobility, no transport happens, so there is no flux. A minimal concentration of chained carriers is needed.
- <u>Dual solution-diffusion model</u>: The mechanism proposed by Noble is based on the dual sorption model which considers that gas solubility in a membrane happens both by Henry's law and Langmuir sorption models in distinct regions but with equilibration between them. Noble used also the analysis of dual-mode transport developed by Barrer [43] which defines four diffusion coefficients for transport through each region and exchange between regions. The diffusion coefficients correspond to the diffusion of A through the polymer matrix, the diffusion of A from the polymer matrix to a hole (or free volume) in the Langmuir region, diffusion of A between two holes and diffusion of A from a hole to the polymer matrix. This model is able to predict facilitated transport even in absence of diffusion or mobility of the carrier. The effective diffusion coefficient of the solute depends on the morphology of the membrane between two sites.

#### Facilitated transport of carbon dioxide:

Carbon dioxide is an acidic gas and can react with bases. This reactivity is used for the absorption processes to capture  $CO_2$ , mainly using amines as solvent. In aqueous solution, they react with  $CO_2$  to form carbamates and this reaction is reversible. The mechanism for this reaction has been proposed by Caplow [44] and consists of two steps : the formation of a switterion complex and the removal of a proton by a base. The mechanism is described for a secondary amine by the following equation:

$$\begin{array}{c} R_2NH + CO_2 \rightleftharpoons R_2N^+HCO_2^- \rightleftharpoons R_2NCO_2^- + H_3O^+ \\ \\ H_2O \end{array}$$

Bao et al., [45], showed that the reaction of primary amine with  $CO_2$  is fast but the desorption is difficult, the reaction of tertiary amines is slow. Reaction with secondary average has an average rate but is easily reversible and that is why there are more often used.

The principle of facilitated transport of  $CO_2$  is explained in the following figure, which represents transport through a composite membrane made of poly-vinylamine.



Figure 17 Facilitated transport principle for CO<sub>2</sub> through a polyvinylamine membrane.[30]

# 4. Experimental

## 4.1 Synthesis of the membranes

The membranes were synthesized by Thomas Macron from the Supramolecular Nanosystems Group, Institut Européen des Membranes adaptives, University of Montpellier, in September 2010, in January 2012 and in April 2012 The membranes studied during this project are from two different series : one with histamine groups (CAS 51-45-6), and another one, without histamine groups, but with the same other monomers. All are block copolymers made from trialdehyde (CAS 3163-76-6) and polyether chains ending by amine groups as presented below:





Figure 19 The different polyetheramines used for the sythesis

All the membranes were synthesized by reflux with methanol at 80-85°C during 12 to 18 hours. Now the final polymers will be presented as well as the aspect of the membranes.

#### 4.1.1 Histamine serie



Figure 20 Membrane T1: made with polyTHF-350

T1 is a dark orange, quite brown, and quite glassy polymer. It is really translucent. This is a PEO based copolymer.



This membrane is yellow and translucent and is a rubbery polymer. It has the same structure than T1 but with longer polyether chain. It is also a PEO based copolymer.



Figure 22 Membrane T3 made with triamine star shape

This membrane is a light yellow rubbery polymer and it is quite opaque. It is a PPO based copolymer.

# 4.1.1.3 Membrane T3

#### 4.1.1.4 Membrane T4



Figure 23 Membrane T4 made with polyPeG-Me star shape

This membrane is a yellow glassy polymer quite translucent and really brittle. It has the same structure as T3 with much shorter polyether chains. It is also a PPO based copolymer.



Figure 24 Membrane T5 made with D400

This membrane is a yellow, glassy one. The main structure is the same than for T3 and T4 but with linear chain opposed to star shape. It is also a PPO based copolymer.

#### 4.1.1.6 Membrane T6



Figure 25 Membrane T6 made with D2000

T6 is a yellow quite rubbery polymer. It has the same structure than T5 with a longer polyether chain. It is also a PPO based copolymer.



Figure 26 Membrane T8 made with polyPeG

T8 is a dark orange membrane really glassy. It has the same structure than T6 without the methyl groups in the polyether chain: it is a PEO based copolymer with extra methyl at both ends of the soft segment.
#### 4.1.2 Membranes without histamine.

Those membranes were synthesized only by using the poly ethers and the trialdehyde.



Figure 27 Membrane T1 without histamine

This membrane is dark yellow, translucent and soft. It is the same polymer than T1 but without the histamine groups.



Figure 28 Membrane T2 without histamine

This membrane has a light color, is translucent and soft. This is the equivalent to the membrane T2 without the histamine groups.

#### 4.1.2.3 Membrane T3 without histamine



Figure 29 Membrane T3 without histamine

This membrane is light yellow, translucent and soft. Some bubbles are visible at the surface. This is the equivalent to the membrane T3 without the histamine groups.



#### 4.1.2.4 Membrane T4 without histamine

Figure 30 Membrane T4 without histamine

This membrane is light yellow, a bit translucent and not really soft (but not brittle neither). This is the equivalent of the membrane T4 without the histamine groups.

#### 4.1.2.5 Membrane T5 without histamine



This membrane is yellow, translucent and rubbery. It is the same membrane than T5 but without histamine. It is a PPO based copolymer.

### 4.1.2.6 Membrane T6 without histamine



Figure 31 Membrane T6 without histamine

This membrane is light yellow, transparent and soft. This membrane is equivalent to the membrane T6 without the histamine groups.



#### Figure 32 Membrane T8 without histamine

This membrane is yellowish, opaque and solid. Despite the fact that it is thick, some small cracks are visible on the surface. This membrane is the equivalent of the membrane T8 but without the histamine groups.

## 4.2 Characterization of the membranes

### 4.2.1 Atomic Force Microscopy (AFM)

The AFM is used to characterize the surface of a membrane. It is based on London-Van der Walls interactions between the polymer and a sharp tip of very small diameter (less than 100 Å). There is an attractive force when the tip is far from the surface and a repulsive force when they are close.



Probe Distance from Sample (z distance)



The tip is located at the end of a cantilever and a laser is reflecting on the back of this cantilever. The reflection beam is detected by a photodiode detector. The tip is scanning across the surface with a constant force. The modification of the force by the interactions makes the cantilever move and so the laser reflection beam is moving. This movement is then converted into differences in topography. This gives the profile of the surface. The pore size and the porosity can then be determined as well as the roughness of the surface. No pretreatment is needed and the experiment is made under atmospheric conditions[27, 38].

The AFM characterizations were made with a Veeco Multimode V in tapping mode with a J-scanner.

## 4.1.2 Differential Scanning Calorimetry (DSC)

It is used to find the transition temperatures for a polymer as glass transition temperature (Tg), melting temperature (Tm) or even degradation temperature (Td). It is also possible to determine crystallization temperature (Tc). The sample temperature is compared with the temperature of a reference. The energy necessary to counteract the difference between those two temperatures is what is determined from a DSC analysis. [38] In Figure 34, a DSC curve for a semi-crystalline polymer is given. The area of the peaks (for melting and crystallization) can be proportionally related to the enthalpy change which is related to the degree of crystallinity of the polymer.



Figure 34 Example of a DSC curve of a semi-cristalline polymer

The analyses were made with a Q1000 Differential Scanning Calorimeter of TA Instruments. Several cycles of heating/cooling were made with increasing temperatures.

### 4.1.3 Fourier Transform Infra Red spectroscopy (FTIR)

This method consists of a light beam directed towards the sample. When the wavelength of the light, which corresponds to the energy of the beam, is close to the vibrational energy of one chemical bind of the molecule, light will be absorbed and then the intensity transmitted will decrease. The light beam wavelength is between 2.5 and 25  $\mu$ m which is the infrared area.

The specificity of Fourier Transform IR spectroscopy is the use of a Michelson interferometer and then a computer use of Fourier Transform to obtain an infrared spectrum from the interferogram. Thus, all the absorption results for all the wavelengths can be recorded in one short cycle whereas for common spectroscopy the measure is made for one given wavelength which needs to be changed afterwards. Several cycles can be made in a short time which enables to increase the resolution of the spectrum. The results obtained are a graph plotting the absorbance versus the wave number defined as the inverse of the wavelength. Usually, a spectrum is plotted between 4000 and 400 cm<sup>-1</sup>.

This characterization method enables to find the functional groups of one molecule because the vibration at a certain wave number is characteristic of one type of binding. Tables of characteristic absorption peaks related to functional groups are used to interpret the spectra.

The spectrometer used was a Nexus FTIR of ThermoNicolet working with the mode Smart Endurance Diamond ATR.

### 4.1.4 Swelling experiments

Membranes are intended to be used for CO2 capture from flue gas, natural gas, biogas. For all these applications, the gas is fully humidified. In addition, water plays an important role in material durability, as membranes can swell and get degraded, and in gas transport properties especially for facilitated transport membranes. Indeed, water interacts with basic atoms and solves more easily acidic gases as carbon dioxide. It can therefore be useful to know to which extent the polymer is able to uptake water.

In order to measure the amount of water absorbed by the membranes, swelling experiments have been performed. The membranes have been dried for 90 hours in a vacuum oven at 50°C and dried weight was measured and recorded. The membranes were installed in a "humidity box" together with an open recipient filled with water. The box was covered with aluminum foil in order to guarantee a 100% humidity atmosphere.



Figure 35 Schematic representation of the material used for swelling experiments

The membranes were weighted again after 2, 4, 6, 24, 28, 96 and 168 hours. For each point, 3 weight measurements have been taken and an average value has been used for graphs plotting and calculations.

## 4.3 Gas permeation experiments

### 4.3.1 Preparation of the membrane

The membranes investigated are pure copolymer films and so can be fragile to handle. The risk is that they break during the experiment leading to false results as the gas will find an easy way to go from the feed to the permeate side. To avoid this problem, it is important to set one support: one disc of filter paper for example because it is porous enough to prevent any limitation in the flow of gas but strong enough to increase the mechanical resistance of the membrane.

The membranes with filter paper were mounted in a sandwich mode, between two discs of aluminum tape. For the really soft membranes, which easily form a bell when tight in the cell, smaller areas were chosen and the cell was closed carefully, screwing in star shape instead of diagonal. For all the membranes, the diameter of the hole in aluminum was at least 4 mm smaller than the membrane diameter. This "sandwich" was not glued to the cell. The cell is made of a metallic sinter and leakage is avoided thanks to one rubber O-ring.



### 4.3.2 Single gas permeation experiments

### 4.3.2.1 Principle of the measurement

In Figure 36 below, the apparatus used is presented. The feed gas comes from the left and a pressure sensor enables to control and check the pressure applied. Vacuum is applied on the permeate side of the membrane thanks to a vacuum pump.



Figure 36 Gas permeation system: flowsheet

#### 4.3.2.2 Protocol

After placing the cell in the gas permeation setup, a sufficient evacuation time was needed to be sure that all the gases adsorbed on the membrane and on the tubes of the apparatus were desorbed. For this, all the valves were opened and the vacuum pump was functioning. An overnight evacuation was performed, at the installation of the cell.

A leakage test has been performed for the permeate side: after evacuation, all the valves were closed and the pressure in the permeate side was followed. Then, the slope of the curve "pressure versus time" is the permeate side leakage rate.

Each membrane was tested at 5 bars with different gases. The gases used were nitrogen  $(N_2)$ , methane  $(CH_4)$ , and carbon dioxide  $(CO_2)$ , in this order, to avoid modifications of the membrane due to the strongest adsorbing gases [47]. The pressure was set in the feed side using the first pressure sensor (between V1 and V3) and the valve V6 was opened after that, valves V10, V11 and V12 have been closed. The second pressure sensor (in the permeate side before V11) enabled to follow the increasing pressure. Between two gases, the whole system was evacuated, for at least twice the time of exposition to gas.

#### 4.3.2.3 Calculations

This experiment gives us the permeate side pressure as a function of the time. When the steady state is attained, this evolution is linear and the slope of the line is dp/dt and allows calculating the permeability.

$$P_i = \frac{dp}{dt} * \frac{T^0}{P^0} * \frac{V_p}{T_p} * \frac{l}{P_f} * \frac{1}{A_m}$$

Where  $T^0(K)$  and  $P^0(atm)$  are the standard temperature and pressure,  $V_p(cm^3)$  and  $T_p(K)$  are the volume and the temperature of the permeate side, I (cm) is the thickness of the membrane,  $P_f(K)$  is the pressure of the feed side and  $A_m(cm^2)$  is the area of the membrane.

It is more common to express the results in terms of permeance, P/I, which enables to compare membranes of different thicknesses.

It is also possible to calculate the diffusion coefficient of one gas using these data and the time-lag method.[48] During the permeation experiment, there is usually a transient state before steady-state. The permeation curve is then initially curved before getting linear. The steady state straight line is extended until the time axis as it is shown on the following figure and this intersection is defined as the time lag. This time, noted  $\theta$  is related to the diffusion coefficient by the following equation:



Figure 37 Principle of time lag determination [38]

#### 4.3.3 Mixed gases permeation experiments

#### 4.3.3.1 Principle of the measurement

A schematic representation of the set-up used is presented in the figure 38 below. A pressure indicator enables to measure the feed pressure. The retentate flow is read thanks to a bubble flow meter. The sweep pressure is set but the flow can be changed and read thanks to a flow meter or a flow controller. The permeate is regularly sent to a gas chromatograph in order to analyze its composition.

Two different configurations are possible: with dry gas or with wet gas. In case of wet gas, both feed and sweep gases follow different pipes and bubble in a metallic cylinder filled with water. The gases are humid.



Figure 38 Schematic drawing of the mixed gas experiment set-up

#### 4.3.3.2 Protocol

The membranes used were the same membranes used for the single gas experiments –except when they had been broken. Each membrane was tested with a 10%-90% in volume mix of carbon dioxide and nitrogen at 1.2 and 5 bars in both dry and wet conditions. The dry experiments were run first and then an exposure to wet gases was done overnight before taking measurements. The sweep used was pure methane or pure helium at a flow of 5.6 mL/min and a pressure of 1.02 bars. A leakage test for each condition was run with pure  $CO_2$  or  $CH_4$  to measure the nitrogen amount leaking into the set-up during the experiments. The permeate gas was sent to the chromatograph and the permeate composition was recorded at steady state.

#### 4.3.3.3 Calculations

From the experiments, the amounts of nitrogen and carbon dioxide in the permeate flow are obtained. From those values and knowing the feed pressure and feed composition, it is possible to calculate the  $CO_2$  and  $N_2$  flows as well as the selectivities.

The selectivity can be obtained from the composition of the permeate compared to the composition

$$\alpha_{\underline{co_2}} = \frac{\left[\frac{x_{\underline{co_2}}}{x_{N_2}}\right]^{permeate}}{\left[\frac{x_{\underline{co_2}}}{x_{N_2}}\right]^{feed}}$$

The flux of CO<sub>2</sub> –and the flux of N<sub>2</sub> by the same way- can be calculated with the following equation:

$$CO_2 flux = \frac{Permeate flow * x_{CO_2}^{permeate}}{Area * \left(P_{feed} * x_{CO_2}^{feed} - P_{sweep} * x_{CO_2}^{permeate}\right)}$$

The selectivity can also be calculated from the fluxes:  $\alpha_{\frac{CO_2}{N_2}} = \frac{CO_2 flux}{N_2 flux}$ 

## 4.4 Sorption experiments

### 4.4.1 Principle of the measure

A gravimetric method was used to characterize the sorption of the different gases in the membranes. The experiments were conducted using a Rubotherm magnetic suspension balance (MSB). The specificity of this instrument is that the sample and the holder are not directly linked to the balance and so very hard conditions of pressure and temperature can be applied. The holder is maintained suspended by a permanent magnet. The system is presented in the figure 39 below:



Figure 39 Magnetic suspension balance: schema of the system

The system enables to measure the variation of weight of the holder and the sample under different conditions of pressure and/or temperature. This variation can be related to the specific gas uptake. The plot of specific gas uptake at one given temperature versus pressure is called sorption isotherm of the gas in the membrane. To avoid the perturbations due to non ideality, it is better to take into account the fugacity instead of the pressure.

#### 4.4.2 Experimental protocol

Before all experiments, it is necessary to know the weight of the holder and the volume of the holder. A "blank" measurement is then necessary: different pressures of helium, which is considered as a non-adsorbent gas, are applied to the holder only – no sample. The plot of the weight obtained versus the density of the gas gives a straight line whose slope gives the volume of the holder and the intercept the weight. The density is calculated using the ideal gas law:

$$\rho = \frac{p * M}{R * T}$$

where  $\rho$  is the density, p the pressure, M the molar mass of Helium, R the ideal gas constant and T the temperature.

It is also necessary to know the weight and the volume of the sample. The sample is placed in the holder and the whole is subjected to different pressures of Helium. The weight of the holder and the sample is obtained. Again, the plot of weight against density gives the volume and the weight. From the first blank measurement and this one, it is possible to determine the weight and the volume of the sample.

Before the sorption experiment, it is necessary to evacuate the system at least overnight to be sure that a complete desorption of gas from the sample and from all the instrument piping walls has been made.

#### 4.4.3 Calculations

The weight of the sample and the holder is what is obtained from the experiment. This weight has to be corrected due to the buoyancy effect. The buoyancy is determined from the density of the gas (obtained from the pressure and the ideal gas law) and the volume of the sample and the holder  $(V_{sc+s})$ :

$$B = V_{sc+s} * \rho$$

This buoyancy can be added to the weight given by the apparatus to obtain the corrected weight. If the initial weight of the sample with the holder is then subtracted, the weight of adsorbed gas is determined. The specific uptake is defined as the mass of adsorbed gas per gram of membrane:

specific uptake = 
$$\frac{m_{gas \ ads}}{m_s}$$
 expressed in  $\left[\frac{g_{gas \ ads}}{g_{membrane}}\right]$ 

This specific uptake can then be plotted against the pressure. But the gases studied are non ideal gases and so deviations from ideality can occur. To take these deviations into consideration, fugacity was used.

The fugacity was calculated from the Soave-Redlich-Kwong (SRK) equation of state, following the method described elsewhere[49], [50].

The SRK equation is the following one:

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)}$$

Where v is the molar volume, a and b are the model parameters. These parameters are characteristic for a component and are calculated from the following equations:

$$m = 0,48 + 1,574\omega - 0,176\omega^{2}$$

$$a = \frac{0,42747R^{2}T_{c}^{2}}{p_{c}} \left[ 1 + m\left(1 - T_{r}^{\frac{1}{2}}\right) \right]^{2}$$

$$b = \frac{0,08664RT_{c}}{p_{c}}$$

 $T_r$  is the reduced temperature ( $T_r=T/T_c$ ) and  $T_c$  and  $P_c$  are the critical temperature and pressure. w is the acentric factor of the component.

This equation is a cubic equation of v which means that the molar volume is the solution of a third degree equation:

$$pv^{3} - RTv^{2} + (RTb + a - pb^{2})v - ab = 0$$

By solving this equation, the molar volume is obtained. This volume enables to calculate Z, the compressibility factor:

$$Z = \frac{pv}{RT} = \frac{v}{v-b} - \frac{a}{RT(v+b)}.$$

The fugacity can then be calculated:

$$\ln\left(\frac{f}{p}\right) = -\ln\left(\frac{v-b}{v}\right) - \frac{a}{bRT}\ln\left(\frac{v+b}{v}\right) + Z - 1 - \ln Z$$

# 5. Results and discussion

## **5.1 Summary of the experiments**

Two series of seven membranes were tested. Several characterization methods were used: gas permeation, gas sorption, Differential Scanning Calorimetry (DSC), Fourier Transform Infra Red spectroscopy (FTIR), Atomic Force Microscopy (AFM). A summary of the experiments made is presented in Table 1.

	Gas		DCC			<b>2</b>
Name	permeation	Sorption	DSC	FIIR	AFIVI	Comments
T1	Yes	Yes	Yes	Yes	Yes	
Т2	Yes	Yes	Yes	Yes	-	
Т3	Yes	From before	Yes	Yes	Yes	
Т4	-	-	Yes	Yes	-	Membrane too brittle: broken during experiment
T5	Yes	Yes	Yes	Yes	-	
Т6	Yes	yes	Yes	Yes	-	
Т8	From before	From before	Yes	Yes	-	Membrane dissolved during wet mixed gas experiment.
T1 without histamine	Yes	Yes	Yes	Yes	-	
T2 without histamine	Yes	Yes	Yes	Yes	-	
T3 without histamine	Yes	Yes	Yes	Yes	-	
T4 without histamine	Yes	-	Yes	Yes	-	Sorption experiment missing
T5 without histamine	Yes	Yes	Yes	Yes	Yes	
T6 without histamine	Yes	-	Yes	Yes	-	Sorption experiment missing
T8 without histamine	-	Yes	-	-	-	Membrane too brittle: broken during experiment

Table 1 Summary of the experiments

## 5.2 Characterizations of the polymers

### 5.2.1 Atomic Force Microscopy

Three membranes have been studied by Atomic Force Microscopy: T1 with histamine whose soft segments are linear and made of 4 ethylene oxide groups and whose hard segments contain histamine groups; T3 with histamine whose soft segments have a star shape form with each branch made of 17 propylene oxide groups and whose hard segments contain histamine groups; T5 without histamine whose soft segments are linear and made of 6 propylene oxide groups and whose hard segments do not contain histamine groups. Areas of  $10\mu m^2$  and  $1\mu m^2$  have been studied by tapping mode.

### a. T1 with histamine:



Figure 40 AFM pictures of T1 with histamine. a) Area of 10µm<sup>2</sup> b) Area of 1µm<sup>2</sup>

The relief of the surface can be seen thanks to the colours used: from the deepest to the highest the colors go from the darkest to the lighest.

It can be noticed that both surfaces are not flat and many irregularities can be seen in the  $10\mu m^2$  picture. The parallel lines which can be seen on the  $10\mu m^2$  picture seem to be artefacts from the AFM machine or from the software but the lines on the  $1\mu m^2$  picture could show some order of the chains of the polymer. Indeed the lines seem to follow the relief. However, contrary to Reijerkerk observations [15], it is not possible to distinguish the soft parts from the hard segments.

### b. T3 with histamine:



Figure 41 AFM pictures of T3 with histamine. a) Area of 10µm<sup>2</sup> b) Area of 1µm<sup>2</sup>

The surface of T3 with histamine show a different aspect than T1 one: some bubbles and cracks seem visible on the  $10\mu m^2$  picture. The bubbles might be places where there is more material, maybe because of the hard segments or of the crosslinking due to the star shape form of the polyether parts. On the  $1\mu m^2$  picture, some structural organization can be seen with the curves at the bottom of the picture. If the main parallel lines are due to some artefact, the grain can be due to the structure of the polymer.



c. <u>T5 without histamine:</u>

Figure 42 AFM pictures of T5 without histamine. a) Area of 10µm<sup>2</sup> b) Area of 1µm<sup>2</sup>

Once again, the surface is not uniform. The picture of  $1\mu m^2$  shows a high roughness. The grain can also show the polymer chains and therefore a linear organization.

The AFM pictures show clearly that the membranes have different structure. However, it is not possible to state on the macromolecular organization nor to see the hard of soft parts of the copolymers.

## 5.2.1 Analysis by Fourier Transform Infra Red spectrometry

All the membranes studied are made of the same functional groups we can then find on the spectra obtained: [51, 52]

- C=C ring (benzene): usually between 1450 and 1600 cm<sup>-1</sup> but, here, additional conjugation with C=N so slightly shifted towards lower wave numbers.
- ✤ C=N: 1640-1690 cm<sup>-1</sup>
- ✤ C-O-C: between 1070 and 1150 cm<sup>-1</sup>
- ✤ C-H alkanes : \*bending : 1350-1480 cm<sup>-1</sup>

\*stretch: 2850-3000 cm<sup>-1</sup>:

♦ C-N: \*aryl: 1250-1360 cm<sup>-1</sup>
 \*alkyl: 1025-1200 cm<sup>-1</sup>

As those groups are present in all the membranes, those peaks should be found in all the spectra. The spectra and the different membranes can be compared by looking to the relative size of the peaks taking for reference the peak for C=C aromatic, for example.

The first spectrum is completely interpreted and then only comparisons will be made.

### i. Interpretation of one spectrum : T2 (with histamine)

## ii. Interpretation and comparison of the other spectra

The spectra obtained for the other membranes can be seen in ANNEX I.

	Wave	Peak intensity (% transmittance)												
Peak	number								T1	T2	Т3	Т4	T5	Т6
	(cm)	T1	T2	Т3	T4	T5	Т6	Т8	without	without	without	without	without	without
									hista	hista	hista	hista	hista	hista
C-H strech 1	~2900	81,1	84,2	85,1	88,2	86,2	86,4	-	85,0	83,8	89,4	87,0	87,4	87,149
C-H strech 2	~2850	72,8	74,0	83,7	87,0	83,1	85,2	92,9	75,9	73,9	88,3	83,6	84,8	86,352
C=N	~1650	79,0	93,1	89,5	85,5	79,6	-	98,5	79,9	91,4	98,0	78,4	82,0	94,702
C=C aryl	~1450	82,1	90,7	85,8	85,6	84,4	89,6	93,0	89,2	89,4	93,0	84,5	87,6	89,911
C-H	~1350	78,1	83,9	76,2	85,8	78,0	77,6	87,7	82,7	82,1	92,7	80,6	78,8	90,471
C-O-C	~1100	39,6	41,8	38,5	64,6	44,2	36,3	68,0	40,4	36,6	41,1	43,4	42,2	41,067

The intensities of the main peaks were taken and the results are presented in Table 2:

#### Table 2 Intensities of the main peaks

The characteristic peak of the benzene around 1450 cm<sup>-1</sup> was taken as reference because it is present in all the polymers and because only the length and the nature of the chains between are changing.

The comparison of the membranes can then be made from the following table:

	Wave		Peak relative intensity compared to C=C aryl intensity											
Poak	number								T1	T2	Т3	T4	T5	Т6
FEak	(cm <sup>-1</sup> )	T1	T2	Т3	Т4	Т5	Т6	Т8	without	without	without	without	without	without
	(cm)								hista	hista	hista	hista	hista	hista
C-H strech 1	~2900	1,06	1,70	1,05	0,82	0,89	1,31	-	1,21	1,53	1,51	0,84	1,02	1,27
C-H strech 2	~2850	1,53	2,79	1,15	0,90	1,08	1,43	1,02	1,94	2,45	1,67	1,06	1,23	1,35
C=N	~1650	1,18	0,74	0,74	1,00	1,31	-	0,22	1,62	0,81	0,29	1,40	1,45	0,53
C=C aryl	~1450	1,00	1,00	1,00	1,00	1,00	1,00	1,00	0,87	1,00	1,00	1,00	1,00	1,00
C-H bending	~1350	1,22	1,73	1,68	0,98	1,41	2,16	1,75	1,39	1,68	1,04	1,25	1,71	0,94
C-O-C	~1100	3,39	6,25	4,34	2,46	3,58	6,14	4,56	4,81	5,96	8,39	3,65	4,66	5,84

Table 3 Comparison of the membranes based on aryl groups as reference

#### • T1 and T2 (with histamine):





From the Table 3, it can be seen that T2 has around twice more -C -O - C- groups than T1 and more C -H groups. This is coherent with the formula of the molecules: T2 is made from polyTHF 1100 (six  $-O - C_4 H_{8^-}$  groups) whereas T1 is made from polyTHF 350 (three  $-O - C_4 H_{8^-}$  groups). However, the difference for imine groups can be noticed. From the spectra, we can see that the peaks correspond quite well to each other. It can be noticed on T1 spectra that the baseline is not really straight. However, it seems that there is a broad peak over 3000 cm<sup>-1</sup> (circled). This peak might be related to some impurities or to water adsorbed on the polymer.



### • T3 and T4 (with histamine):

Figure 44 Comparison of T3 (top) and T4 spectra (bottom)

The two polymers T3 and T4 have the same structure but once again, it is only the length of the ether chain which is modified: there are 17 groups in each branch of T3 whereas only 2 for each branch of T4. Once again, the difference can be seen from the relative intensities of ether and C-H links even if it is not quantitative. On the spectra the same phenomenon as for T1 and T2 can be noticed. The fact that the baseline is not flat comes from the fact that it is hard to get a good contact between the sample and the diamond tip of IR instrument when samples are glassy polymers.



### • T5 and T6 (with histamine):

Figure 45 Comparison of T5 and T6 spectra

The relative intensity of -C-O-C- bonds around 1450 cm<sup>-1</sup> is almost twice higher for T6 than for T5. The T6 ether chain is made of 32 groups whereas T5 is made of 5 groups. Once again, T5, a glassy polymer, has a bad baseline.

• T8 (with histamine) :



Figure 46 Comparison of T8 (top), T6 (middle) and T2 (bottom) spectra

The ether chain of T8 is as long as T6 ones but without the methyl groups. The intensities of C-H peaks around 2900 and 2850 cm<sup>-1</sup> are effectively smaller for T8 than for T6 but the –C-O-C- intensities around 1100 cm<sup>-1</sup> cannot be compared. T8 could also be compared with T2 - longer ether chain and 2 extra methyl groups than T2. It can be noticed that the peaks of C-H stretch at 2900 and 2850 cm<sup>-1</sup> are reduced to one single peak for T8. It seems also that, if T8 is taken as a reference, T6 and T2 spectra are shifted to the left, towards lower wave numbers. This is often seen when conjugation or favorable interactions exist. This can be explained looking to the polymers states: T8 is a glassy membrane, T2 and T6 quite rubbery ones. The free movement of chains is higher in rubbery polymer, the chains are more flexible and then favorable interactions happen more easily. The DSC experiments, presented in 5.2.2, show that T2 is a more rubbery polymer than T6. So the fact that T2 spectra is more shifted than T6 ones is logical.

• The same differences of structures exist between the membranes <u>without histamine</u>. They will not be commented as detailed as for the first series. However, it can be noted that the comparison between T3 without histamine (17 groups in the polyether chains) and T4 without histamine (2 groups in the polyether chains) is particularly clear: T3 without histamine shows much more of the groups present in the polyether chain, as C-O-C or C-H, but much less C=N, which are specific of the hard group. This is logical as the polyether chain is much longer for this membrane (so there are more groups specific of it) and so the concentration of hard groups is lowered. The same phenomenon can be observed for the other couples of membranes (T1/T2, T5/T6) but with a less important difference in the ether content.

• The membranes <u>with</u> and <u>without</u> histamine can be compared too. Unfortunately, no peak can be related only to histamine groups. To facilitate the interpretation, a comparison related to the ether peak (which should be the same between the membranes with and without histamine) has been made. The results are presented in the following table:

	Wave		Peak relative intensity compared to C-O-C intensity											
Book	number								T1	T2	Т3	T4	T5	Т6
FEak	(1)	T1	T2	Т3	T4	T5	Т6	Т8	without	without	without	without	without	without
	(cm <sup>-</sup> )								hista	hista	hista	hista	hista	hista
C-H strech 1	~2900	0,31	0,27	0,24	0,33	0,25	0,21	-	0,25	0,26	0,18	0,23	0,22	0,22
C-H strech 2	~2850	0,45	0,45	0,26	0,37	0,30	0,23	0,22	0,40	0,41	0,20	0,29	0,26	0,23
C=N	~1650	0,35	0,12	0,17	0,41	0,37	1	0,05	0,34	0,14	0,03	0,38	0,31	0,09
C=C aryl	~1450	0,30	0,16	0,23	0,41	0,28	0,16	0,22	0,18	0,17	0,12	0,27	0,21	0,17
C-H bending	~1350	0,36	0,28	0,39	0,40	0,39	0,35	0,38	0,29	0,28	0,12	0,34	0,37	0,16
C-O-C	~1100	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00	1,00

Figure 47 Comparison of the membranes based on ether groups as reference

It can be seen that, usually, for a same amount of ether groups, there are more other groups in the membranes with histamine, which is logical. However, no big difference can be noticed considering the imine groups. There is only one extra imine group in histamine group, that's why the influence is not very marked.

A comparison of two membranes will now be done.

#### • T5 and T5 without histamine:



Figure 48 Comparison on T5 without histamine (top) and T5 (bottom)

From the spectra, it is difficult to see any difference, except the baseline problem for T5 (glassy) and a little peak supplementary around 1700 cm<sup>-1</sup> for T5 without histamine (circled). This peak appears also in T2 in a smaller extent but it seems difficult to explain. The two spectra are compared below with ether peak as reference.

Peak	Wave number	Peak relative intensity compared to C-O-C intensity			
	(cm)	Т5	T5 without		
C-H strech 1	~2900	0,25	0,22		
C-H strech 2	~2850	0,30	0,26		
C=N	~1650	0,37	0,31		
C=C aryl	~1450	0,28	0,21		
C-H bending	~1350	0,39	0,37		
C-O-C	~1100	1,00	1,00		

Table 4 Comparison of T5 and T5 without histamine with ether groups as reference

It can be seen than imine links around 1650 cm<sup>-1</sup> are more frequent for T5 than for T5 without histamine (there is one imine group by histamine function) and also more C-H bonds. This seems coherent with what was expected.

An overall view of the spectra for both series can be made:



Series "with histamine": spectra





Figure 50 Comparison of the spectra for all membranes of the series "without histamine"

Looking to those spectra, it appears clearly that the polymers are all made of the same chemical groups. The length of the ether peak is the more different point between the membranes even if the other peaks vary also.

The analysis of infrared spectra enabled us to confirm the different compositions and structures of the membranes.

## 5.2.2 Analysis by Differential Scanning Calorimetry

The analyses were made with different cycles of heating and cooling:

- Heating from -70°C to 120 °C and cooling again until -70°C
- If appropriated, cycle around one interesting temperature (Tg, Tm)
- Heating from -70°C to 250°C and cooling again until -70°C
- Heating from -70°C to 400 °C and cooling again until -70°C

There are different types of peaks:

- First order peak: the corresponding characteristic temperature is the temperature at the top of the peak.
  - o melting: endothermic peak in heating curve
  - o crystallization: exothermic peak in heating or cooling curves
- Second order peak: the characteristic temperature is the temperature of the inflexion point
  - o glass transition: exothermic transition in heating and in cooling curves

In Table 5 below are shown the summary of DSC measurements:

Membrane	Tg (°C)	Tc (°C)	Tm (°C)	Td (°C)	Room temperature aspect
T1					quite glassy
T2		-34	1,8		rubbery
Т3	-53			337	Rubbery, soft
Т4	66				Glassy, really brittle
Т5	-4		354		glassy
Т6	-56			352	rubbery
Т8		4,17	64		Glassy, brittle
T1 without histamine	-37		375		rubbery
T2 without histamine		-25	1	372	rubbery
T3 without histamine	-55			357	rubbery
T4 without histamine	38				glassy
T5 without histamine	-14		348		Rubbery, soft
T6 without histamine	-59			321	Rubbery, soft

Table 5 Results obtained by DSC



Figure 51 DSC curve of T1

T1 is a glassy polymer and the fact that no characteristic temperatures can be found by DSC shows that it is a crystalline polymer. Consequently, no Tg is found and if the melting temperature is very high (higher than 400°C) it cannot be seen. The ether chain in T1 is not very long so the benzene and histamine groups which are stiff are often repeated. Then the polymer is rigid and this fits well with the observation of a glassy polymer. The possible crystallinity of the polymer could come from the nature of the ether chain: PEO is a crystalline polymer (the melting temperature is about 27°C for pure PEO)[4]. However, the chain is short (3 groups) and the side groups are relatively big so the packing should not be that easy.





Figure 52 DSC curve for T2 (first cycle)



Figure 53 DSC curve for T2 (cycle 2)

T2 has the appearance of a rubbery polymer. The DSC results show that no glass transition appears (maybe it is below -70°C) and a melting peak is seen at 1.8°C. This could correspond to the melting of the crystallites of the soft segment of the copolymer (the PEO part). According to Reijerkerk [4], the exothermic peak around -35°C in the heating curve is related to the dynamic state of the copolymer. On the cooling part, the crystallization of PEO happens around -37°C. On the second cycle, the melting temperature is a little higher.





Figure 54 DSC curve for T3

T3 is a rubbery polymer and the glass transition temperature found by DSC, -52°C, seems coherent with the fact that at room temperature the polymer is completely in the rubbery domain. This can also been deduced from the structure: T3 has a structure which prevents tight chain packing with very long flexible chains made of 17 ether groups. Those groups are propylene oxide groups and those polymers are known to be amorphous at room temperature. This means that, despite its star shape, it is a flexible polymer and consequently a rubbery one. The free volume of this polymer is then really high and the diffusivity is expected to be high also.

### ✤ T4:

T4 has the same star shape structure than T3 but with very shorter ethyl chains (only 2 groups). The flexibility is lowered and the chain becomes more rigid due to benzene and histamine groups: the polymer becomes glassy. This can also be deduced from the DSC analysis: T4 has a high glass transition temperature of 66°C and at room temperature it is still in the glassy state.

(DSC curves in ANNEX II.a)

✤ T5:

From the DSC results we could infer that T5 is a rubbery polymer because of its low Tg (-6°C) whereas the visual observation leads to think it is quite glassy. The structure of T5, having 5 ether groups chain with extra methyl groups compared to the previous ethyl chains, could lead also to the interpretation of a quite glassy polymer. The methyl groups reduce rotation and freedom and the short chain gives more frequent stiff groups (benzene and histamine cycles).

#### (DSC curves in ANNEX II.b)





The very low Tg obtained by DSC (-55°C) is coherent with the observation of a rubbery polymer. This is also quite obvious from the chemical structure, with the 32 propylene oxide groups of the chain of T6.







T8 is also made of a 32 ether groups chain but they are ethylene oxide groups opposed to propylene oxide groups for T5 and T6. So it can be expected that the freedom is increased and then that the polymer becomes more rubbery. Instead of this, it seems that the polymer is a glassy one. This long chain is easily packed with other chains and the polymer becomes crystalline. This is what can teach the DSC results with a melting and a crystallization peaks. T8 is a semi crystalline polymer and that explains why a glass transition temperature is not seen. Those deductions are coherent with the known fact that PEO is a crystalline polymer [4]. That's why it is important to find effective copolymers to keep particularly good solubility and permeability properties of PEO avoiding those crystallites which hinder good diffusivity.

#### Series without histamine groups :

Most of those polymers are rubbery and this can be explained because, without the histamine groups, the size of the side groups is reduced and the chain rotation is possible more easily.

#### T1 without histamine:

The low Tg (-37°C) is coherent with the rubbery state of the membrane at room temperature. Therefore, the absence of histamine groups has a strong influence because no glass transition temperature was visible for T1.

(DSC curves in ANNEX II.d)

### T2 without histamine:

As for T2, no glass transition temperature is seen although the polymer is rubbery, it might be under -70°C. There are also strong exothermic and endothermic peaks: a first exothermic peak at -25 °C, a melting peak around 1°C and, on the cooling curve, a crystallization peak around -39°C. T2 without histamine and T2 seem much closer than T1 and T1 without histamine. As the polyether chains are much longer for T2 that for T1, the effect of the histamine group can be diluted, less important.

(DSC curves in ANNEX II.e)

## T3 without histamine:

The low Tg (-55°C) is in accordance with the aspect at room temperature and close the Tg observed for the membrane containing histamine. Once again, the long polyether chain might reduce the effect of histamine groups on the packing and consequently on the characteristic temperatures. As for T3 with histamine, the polymer is degraded but at a higher temperature (357°C instead of 337 °C).

(DSC curves in ANNEX II.f)

## T4 without histamine:

This polymer is the only one from the without histamine series which is glassy at room temperature and this is confirmed by DSC experiments: the glass transition temperature (38°C) is higher than room temperature. However this temperature is lower than the one of T4 with histamine (66°C). The polyether chains are short and the density of histamine groups is therefore important. Their effect on the properties of the polymers is important.

(DSC curves in ANNEX II.g)

## T5 without histamine:

This rubbery polymer has a low Tg (-14 $^{\circ}$ C), lower than the same polymer with histamine groups (-6 $^{\circ}$ C). The polyether chain length (5 units) is average between the shortest (for T4: 2 units) and the longest (for T6: 32 units) and the effects of the histamine groups are then marked but not excessively.

(DSC curves in ANNEX II.h)

## T6 without histamine:

T6 membranes have also long chains (32 units) and the effect of histamine groups is not very important on the glass transition temperatures (-57°C (without histamine) versus -56°C (with histamine) or degradation temperatures (321°C versus 352°C). The membrane is rubbery what is coherent with the temperatures.

(DSC curves in ANNEX II.i)

### 5.2.3 Swelling experiments

From the weight measurement in time, it was possible to draw graphs presenting the evolution of weight of the membranes with the time spent in humid atmosphere. Here is only presented the graph obtained for the membrane T1 with histamine to illustrate the trend. The other graphs are presented in APPENDIX III.



Figure 57 Evolution of the uptake of water in T1 with histamine with the time spent in humidified atmosphere

From all graphs, several observations can be made.

- The overall evolution of weight change in time follows a logarithmic increase trend with a strong increase at first followed by a plateau. This plateau represents the maximal amount of water absorbed by the material: it corresponds to the saturation of the membrane with water.
- It can be noticed that usually the plateau is reached after a relatively long period (more than 50 hours) and earlier for the membranes without histamine than for the one containing histamine (around 60 hours compared to around 100 hours).

This observation was expected. Indeed, the amines groups of histamine function can form hydrogen bonds with water and the membranes containing histamine functions are expected to absorb more water. That's why more time is needed to completely swell the membranes.

The results should be taken in account when experiments in humid conditions are performed: a steady-state should be attained before starting the measurement. However, for our gas permeation experiments, performed by using humidified gas feed, the membranes were stored in atmospheric conditions (around 60% of humidity) prior to experiments so they already contain a big fraction of the saturation quantity of water. In addition, the membranes were conditioned overnight before experiments by using humidified feed and sweep gases. The feed-permeate pressure difference applied induces also an active water transport through membranes enabling the membranes to reach saturation much faster than in static measurement.

Two membranes show a strange evolution with a strong decrease for the last point (after one week in humid conditions) compared to the previous points: T6 and T8.
 The aspect of the surface of T3 has changed during the drying in the oven: it became uneven, the part in the middle seems thicker than the edges of the membrane.

The swelling is not apparent by visual observation on most of the membranes. However, T8 seems to have been completely dissolved in the presence of water. This result was coherent with the mixed gases permeation experiments made with humid gases: the membrane completely dissolved during the experiments and no results were recorded. T6 without histamine has not dissolved completely but the membrane was considerably deformed: part of the membrane has flowed down and the polymer accumulated to one edge of membrane due to gravity (vertical storage position).

• For almost all the membranes, the weight measurement point at 28 hours seems out of the trend (smaller weight than expected). It might be because the aluminum had not been put back correctly after the 24 hours measurement and the atmosphere inside was not 100% humidity anymore. It can also come from the time spent in normal atmosphere for the 24 hours measurement. It is more likely due to an error related to difference in atmospheric conditions (humidity, temperature) of the room where the scale is.

The weight increase related to the volume of the polymer has also been calculated to compare the swelling of the membranes.

$$weight\ increase = \frac{Weight_{saturation} - Weight_{dry}}{Volume}$$

where the volume of the membrane is calculated from the area and the thickness of the membrane.

The results are presented in the following table:

Membrane	Amount of water sorbed (g) per volume of polymer (cm <sup>3</sup> )	Uptake of water (cm <sup>3</sup> <sub>water</sub> / cm <sup>3</sup> <sub>polymer</sub> )	
T1 histamine	0,76	0,95	
T2 histamine	0,37	0,46	
T3 histamine	0,45	0,56	
T5 histamine	0,45	0,56	
T6 histamine	0,25	0,31	
T8 histamine	3,97	4,94	
T1 without histamine	0,20	0,25	
T2 without histamine	0,18	0,22	
T3 without histamine	0,10	0,12	
T4 without histamine	0,14	0,17	
T5 without histamine	0,16	0,20	
T6 without histamine	0,07	0,08	

Table 6 Weight increase for the different membranes

• The increases are different from membrane to membrane but are substantially smaller for the membranes without histamine. Once again this result is the one expected due to the presence of extra amine groups in the histamine series. T8 histamine, which has been dissolved, shows the biggest increase.

To conclude, those swelling experiments have shown that the time to reach the permanent state is quite long (over 80 hours) and this should be taken into account in experimental protocols. As expected, the membranes containing histamine absorb more water and need more time to reach the permanent state that the membranes without histamine.

## 5.3 Single gas permeation experiments

### 5.3.1 Several remarks about the experimental protocol

- Two series of 7 membranes were to test. Two of them (T4 with histamine and T8 without histamine) were too brittle and broke when the cell was closed and consequently have not been tested, neither for single nor mixed gases.
- In order to avoid any damage to the membrane, the mounting of the "sandwiches" and the closing of the cell were done really carefully as well as the application of pressure to avoid chocks.
- After an overnight evacuation, 5 bars of nitrogen were applied during approximately two hours. After four hours of evacuation, 5 bars of methane were applied, again followed by four hours evacuation before the application of 5 bars of carbon dioxide.
- One membrane, T5 with histamine, seems to have been plasticized during the experiment. A new test with nitrogen showed a much higher flux after the exposure to CO<sub>2</sub> than before. A new test has also been carried for a membrane without histamine and the results were the same than before the exposure to CO<sub>2</sub>.

#### 5.3.2 Results obtained

The results obtained are presented in the two following tables:

Manaharana	Permeab	ility (Barrer)	Selectivity
wembrane	N2	CO2	(CO2/N2)
T1	0,09	2,34	26
T2	7	196	30
Т3	15	424	28
Т5	13	34	2,5
Т6	108	517	4,8
Т8	0,01	0,26	19
T1 without histamine	1	59	42,5
T2 without histamine	8	250	31
T3 without histamine	43	711	17
T4 without histamine	107	119	1,1
T5 without histamine	0,81	34	42
T6 without histamine	27	895	33

Table 7 Permeation results for nitrogen and carbon dioxide

Mombrono	Permeabil	ity (Barrer)	Selectivity
wemprane	CH4	CO2	(CO2/CH4)
T1	0,17	2,34	14
T2	22	196	9
Т3	50	424	8,5
T5	15	34	2,3
Т6	194	517	2,7
Т8	0,01	0,26	18
T1 without histamine	4	59	14
T2 without histamine	27	250	9
T3 without histamine	126	711	6
T4 without histamine	123	119	0,97
T5 without histamine	2,24	34	15
T6 without histamine	104	895	9

Table 8 Permeation results for methane and carbon dioxide

#### **\*** Overall interpretation:

From the tables 7 and 8 presented above, several remarks can be done:

- $\circ$  The selectivity is higher for CO<sub>2</sub> /N<sub>2</sub> than for CO<sub>2</sub>/CH<sub>4</sub>.
- For all the membranes, the CO<sub>2</sub> permeability is higher for the membrane without histamine that for the membrane with histamine, or equal (for T5). Most of the membranes from "without histamine" series are softer than their equivalent in the histamine series. A soft membrane present higher free volume than a glassy one. The membranes from the series "without histamine" have then a higher free volume, which means a higher sorption capacity. Usually, this bigger amount of free volume has the same effect on CO2 than on the other gases and so the selectivity is lowered.
- $\circ$  But, here, except for T3, the CO<sub>2</sub> /N<sub>2</sub> selectivity is higher for the membrane without histamine that for the membrane with histamine. However, this difference can be really small (only 1 for T2) or more important (40 for T5).
- $\circ$  There is no particular trend about the N<sub>2</sub> permeability comparing the two series.
- There is no particular trend neither for selectivity or permeability inside one series: the values can be really different (1.1 to 42.5 for the selectivity, 0.26 to 895 for CO<sub>2</sub> permeability).

The results can also be interpreted and compared if they are presented in a Robeson type of graph.





Figure 58 Comparison of the CO<sub>2</sub>/N<sub>2</sub> selectivity and permeability of the different membranes

## Ideal CO2/ CH4 Selectivity vs CO2 permeability at 5 bars



Figure 59 Comparison of the CO<sub>2</sub>/ CH<sub>4</sub> selectivity and permeability of the different membranes

These graphs highlight different trends:

- The membranes of commercial interest are those with high selectivity and high permeability, which means those situated in the right hand corner of those types of graphs. Here, we can conclude than **T6 without histamine** can be preferred for the separation of CO<sub>2</sub> and N<sub>2</sub> because it presents the best compromise selectivity/flux. *T1 without histamine and T5 without histamine* have also good selectivity properties with a lower permeability. *T2, T3 and T2 without histamine* show a high permeability with a lower selectivity but are still of interest.
- For the separation of methane and carbon dioxide, no so obvious conclusions can be made. *T6* without histamine shows a higher permeability than the other membranes with a not too bad selectivity whereas *T5 without histamine* show a higher selectivity but a less good permeability. The membranes tested enable to choose into a large range of applications from medium selectivity with small flux until low selectivity with high flux.
- However, those results should be taken with precaution: the measurements were made with pure gases and results can be modified in mixed gases conditions.
- $\circ$  T2 and T1 have the same structure but T2 has longer polyether chains. It is the same for T4 and T3, and for T5 and T6. If the length of the polyether chain increases, the CO2 permeability increases for both series, the CO<sub>2</sub> /N<sub>2</sub> selectivity increases for histamine series and decreases for "without histamine" series. The results for N<sub>2</sub> and CH<sub>4</sub> permeabilities show almost always the same trend. Increasing the length can seem a useful mean to increase the permeabilities but this should be done carefully as the membranes start to crystallise with too long chains, as it is the case for T8 or T8 without histamine.

### 5.3.3 Effect of pressure

Some membranes have been tested at several pressures: 3, 5, 8 and 10 bars for each gas. This study can bring interesting results.



• <u>T1:</u>

Figure 60 Gas permeability versus pressure for T1
The  $CO_2$  permeability and the selectivity of this membrane both toward methane and nitrogen are medium. We can see a slight increase of the permeability with the pressure but not so much variation. T1 is a glassy polymer consequently the effect of pressure should not be really important because the chains cannot move freely. The free volume should be low and constant and then the diffusivity is low. Moreover, solubility of gases in polymers is usually low. That's why permeability in glassy polymer is low.







Unfortunately, for T3 only one pressure has been measured for the carbon dioxide due to a damage appeared after testing with 3 bar  $CO_2$  feed. For this pressure, the selectivity  $CO_2/N_2$  is good (33) whereas it is really low for  $CO_2/CH_4$  (9). The flux of  $CO_2$  is high also (500 Barrer). So this membrane appears to be a good compromise. This high permeability can be explained by the rubbery state of the polymer. Indeed, theoretically, in a rubbery polymer, the free volume is high and then the diffusivity is high. The solubility of condensable gases (as  $CO_2$ ) is high whereas the solubility of quite ideal gases such as  $N_2$  or  $CH_4$  remains low. The permeability, which is equal to the product solubility and diffusivity, is then higher for  $CO_2$  than for  $CH_4$  and  $N_2$ .



T5 without histamine:



T5 without histamine seems also to be an interesting membrane because of its high selectivity for  $CO_2$  against  $N_2$  (between 41 and 55) and the high  $CO_2$  permeability (around 300 Barrer). This high permeability, as its increase with pressure can be explained by the rubbery state of the polymer and then its evolving free volume.

It was possible to apply the time lag method at 5 bars for this membrane because a clear transient state was observed (blue points on the Figure 62). The slope utilized for the permeability calculations above was only the slope of the steady state points (red points on the Figure 62). The intersection of this straight line with the axe of abscises is called  $\theta$  and it is a time. This time is related to the diffusion coefficient by:  $\theta = \frac{l^2}{6D}$ 

Here,  $\theta$ =3.73 min so **D=3.77.10<sup>-7</sup> cm<sup>2</sup>/s.** 









Figure 64 Gas permeabilities in T8 versus pressure

For this membrane, the permeability is low (around 0.25 Barrer for  $CO_2$ ) and the selectivity is in the same range as for T1 (around 20 for nitrogen and the same for methane). It seems then a not so interesting membrane. One interesting trend is the decrease of permeability with the pressure. This might be explained by the fact that the free volume of a glassy polymer is constant and then the polymer has a higher capacity at low feed pressures (the time to "fill" this free volume) and then a decreasing capacity and finally a constant flux. We can also notice that the selectivity  $CO_2/N_2$  is quite high (30) at high pressure.

### Conclusion from permeation experiments

Those experiments enabled to get the permeabilities and ideal selectivities for  $CO_2/N_2$  and  $CO_2/CH_4$  separations for different membranes. The <u>membranes without histamine</u> present higher selectivities and permeabilities than the membranes containing histamine. If the permeabilities increase with the length of the polyether chain, the  $CO_2/N_2$  selectivity increase only for the membranes containing histamine. The membranes *T3 without histamine*, *T6 without histamine* and *T6* show a very high permeability (over 500 Barrer) but only **T6 without histamine** shows also a good selectivity towards nitrogen (33). *T1 without histamine* and *T5 without histamine* have the highest selectivity (42) but low  $CO_2$  permeabilities (59 and 34).

T2 T3 T5 T6 • Ideal CO2/N2 Selectivity vs CO2 permeability at 5 bars Т8 T1 without T2 without 1000 T3 without T4 without T5 without T6 without T1 100 PE at 10 atm and 35°C (Lin, Freeman) \*^ CO2/N2 selectivity PEO at 10 atm and 35°C (Lin, Freeman) PSF-NH2 (38%) (Ghosal) DM14/MM9(90/10) (Hirayama) 1 bar \* 10 Poly(ether-imide) (Okamoto) + DB30/MM9 (30/70) (Hirayama) 1 bar \* BDPA-PEO3/ODA (75/25) polyimide (Suzuki) PE01000-T6T6T 4 bars 35°C (Husken) \* ☆ PEO2000-T6T6T 4 bars 35°C (Husken) 1 (PE0 600/T)2500-T6T6T 4 bars 35°C (Husken) ☆ ☆ (PE0 600/T)5000-T6T6T 4 bars 35°C (Husken ) BDPA-ODA/DABA/PEO2(70) 35°C 2 atm (Yoshino ) \* ☆ PDMA-pDDS/PEO4(80) 35°C 2 atm (Yoshino ) 쇼 80PTMEO/PA12 10 atm 35°C (Bondar) 0,1 ☆ 57PEO/PA6 10 atm 35°C (Bondar) 100 1000 10000 0,1 1 10 PEO1000- TphiT 35°C (Reijerkerk) \* PP0220-TphiT 35°C (Reijerkerk) CO2 permeability (Barrer) PEO-ran-PPO1000-T6T6T 35°C 4 bar (Reijerkerk) ╈ PPO4200-T6T6T 35°C 4 bars (Reijerkerk) ☆ PEBAX 10 wt.% PDMS-PEG blend 35°C 4 bar (Reijerkerk) ☆ PEBAX 10 wt.% PEG200 blend 35°C 4 bar (Reijerkerk)

The results obtained can be compared with other results found in literature.

Figure 65 Robeson type of graph comparing experimental data with literature data

The literature data come from Lin [13], Ghosal [9], Hirayama [12], Okamoto [53], Suzuki [14], Husken [22], Yoshino [24], Bondar [23] and Reijerkerk [16, 17, 19]. It can be seen that the membranes studied in this work show as good properties as other membranes reported in literature. The membrane **T6 without histamine** (circled) shows even better trade off than the other membranes. If all those results come from single gas experiments, the experimental conditions are often different (pressure, temperature). A global idea can nevertheless be drawn.

The selectivities obtained are ideals: the experiments were made separately, with pure gases, in ideal conditions. Interesting results to conclude about a real industrial interest can be obtained with mixed gases experiments. Moreover, those membranes have been synthesized with the goal to enhance facilitated transport thanks to histamine groups. Experiments in wet conditions should also be made.

## 5.4 Mixed gases permeation experiments

## 5.4.1 Several remarks about the experimental protocol

- Only carbon dioxide/ nitrogen separation has been studied using 10 vol% CO<sub>2</sub>/90vol%N<sub>2</sub> feed gas mixture, a mixture close to the real flue gas composition. Two feed pressures were used: a low pressure of 1.2 bar close to atmospheric conditions and to flue gas pressure and 5 bars as a comparison point to single gas permeation data. The presence or absence of CO<sub>2</sub> facilitated transport mechanism was investigated by using the same pressures with humidified gas, due to the fact that facilitated transport should be enhanced by the presence of water.
- Only the membranes tested for single gas have been tested for mixed gas: that represents 12 membranes.
- One membrane, T8, has been completely dissolved in presence of water and only the dry experiments have been performed.
- The flux through the membrane T1 was extremely small and no carbon dioxide was detected by the gas chromatograph
- The experimental data were collected and reported only when a steady state was obtained when the CO<sub>2</sub>/N<sub>2</sub> selectivity and CO<sub>2</sub> permeance were constant.
- Only one leakage test for each condition has been made and the results were used for all the membranes. For some membranes the amount of nitrogen permeating is about the same as the amount of nitrogen leaking from the air into the set-up. This can lead to errors on CO<sub>2</sub>/N<sub>2</sub> selectivity calculations. It would have been more precise to make a leakage test before each measurement –for each membrane in each conditions- but this would have taken twice the same amount of time.

## 5.4.2 Discussion about selectivity results.

Mambuana	Selectivity				
wemprane	1,2 bar dry	5 bar dry	1,2 bar wet	5 bar wet	
T1	-	-	0,43	3	
Т2	1	5	9	24	
Т3	5	15	5	17	
Т5	11	16	94	104	
Т6	9	7	10	13	
Т8	9	5	-	-	
T1 without histamine	2	6	2	8	
T2 without histamine	15	50	60	63	
T3 without histamine	46	46	62	55	
T4 without histamine	21	6	20	27	
T5 without histamine	13	23	47	71	
T6 without histamine	31	39	68	54	

The  $CO_2/N_2$  selectivities obtained are presented in the following table:

Table 9 Mixed gas CO<sub>2</sub>/N<sub>2</sub> selectivities

Several observations can be made:

#### • For dry experiments:

- The <u>selectivities</u> are higher for the membranes without histamine than for the membranes with histamine. The selectivities are low for the membranes with histamine whereas the values are higher for the membranes without histamine. The membranes <u>without histamine</u> are more rubbery than the membranes <u>with histamine</u>, and the diffusion should be similar for both gases. The higher selectivity recorded for membranes without histamine should be related to a higher CO<sub>2</sub> solubility the membranes <u>without histamine</u>. The histamine groups are big and by a steric hindrance CO<sub>2</sub> can be prevented to interact with the ether groups of the main chain, a favorable interaction for CO<sub>2</sub> transport as mentioned in the theory part.
- <u>Effect of pressure</u>: No general trend can be observed. For some membranes, increasing the pressure change change very little the selectivity (T6 or T3 without histamine). For some others, a small increase of selectivity is observed (T2, T5, T1 without histamine, T6 without histamine) whereas some bigger increases are also noticed (T3, T2 without histamine, T5 without histamine). Finally some membranes show a decrease of selectivity (T8 and T4 without histamine) by increasing the feed pressure. When the feed pressure increases, the partial pressures of CO<sub>2</sub> and N<sub>2</sub> increase too and the solubility is expected to increase. For the feed pressure range investigated (1.2 to 5 bar), the CO<sub>2</sub> partial pressure remains in the range where solubility increases considerably with pressure this can be understood from the sorption experiments. From the single gas experiments, the selectivities were expected to increase with pressure. However, they were ideal selectivities. For mixed gas experiments, both gases are applied at the same time and a competitive transport exists between the CO<sub>2</sub> and N<sub>2</sub>.

CO2/N2 selectivity in dry histamine membranes



CO2 partial pressure (bar) CO2/N2 selectivity in dry " without histamine" membranes



CO2 partial pressure (bar)

Figure 66 Evolution of selectivity in dry membranes with pressure

#### o <u>Comparison between single and mixed gas experiments.</u>

	CO <sub>2</sub> /N <sub>2</sub> Selectivity			
Membrane	5 bar (single gas)	5 bar (mixed gases)		
T1	26	-		
Т2	30	5		
Т3	28	15		
Т5	2,5	16		
Т6	4,8	7		
Т8	19	5		
T1 without histamine	42,5	6		
T2 without histamine	31	50		
T3 without histamine	17	46		
T4 without histamine	1,1	6		
T5 without histamine	42	23		
T6 without histamine	33	39		

The results obtained by each type of experiments are displayed in the following table:

Usually, the  $CO_2/N_2$  selectivities are expected to be higher in single gas experiments, which corresponds to ideal conditions, when the solution-diffusion mechanism predominates and no competitive transport occurs. Indeed, in mixed gas conditions, a competition between the two species can appear as well as some concentration polarization which reduces the flux through the membrane. Decreased selectivity using mixed gas is observed for T2, T3, T8, T1 without histamine and T5 without histamine. There is no particular link between the structure of the membrane and the behavior. This decrease of selectivity is however linked with an increase in  $N_2$  permeability.

	N2 Permeability (Barrer)			
Membrane	5 bar single	5 bar dry mix		
T1	0,09	5		
T2	7	23		
Т3	15	19		
T5	13	7		
Т6	108	55		
Т8	0,01	0,59		
T1 without histamine	1	8		
T2 without histamine	8	5		
T3 without histamine	43	24		
T4 without histamine	107	2,2		
T5 without histamine	0,81	1,6		
T6 without histamine	27	23		

Table 11 Comparison of N<sub>2</sub> permeability for single and mixed gas experiments

Table 10 Comparison of CO<sub>2</sub>/N<sub>2</sub> selectivities obtained by single and mixed gases experiments

This could be related to the plasticization phenomena: the sorption of  $CO_2$  enhances the diffusion of  $N_2$  because of a change in the structure of the membrane. However, this phenomenon is often reported for higher pressures (over 12 bars) and the enhancement of  $N_2$  permeability should go along with an almost constant permeability of  $CO_2$ , which is not exactly observed in the experimental data, presented in the following table, except for T5 without histamine.

	Permeability (Barrer)			
Membrane	5 bar single	5 bar dry mix		
T1	2,34	-		
T2	196	174		
Т3	424	295		
Т5	34	108		
Т6	517	389		
Т8	0,26	3		
T1 without histamine	59	44		
T2 without histamine	250	272		
T3 without histamine	711	1128		
T4 without histamine	119	14		
T5 without histamine	34	32		
T6 without histamine	895	898		

Table 12 Comparison of CO<sub>2</sub> permeability for single and mixed gas experiments

For the other membranes (T5, T6, T2 without histamine, T3 without histamine, T4 without histamine), an increase of selectivity is observed when the experiments are made using mixed gases, as well as a decrease of  $N_2$  permeability. This could be related to an increased solubility of  $CO_2$  without important modification of the polymer structure which would have enhanced nitrogen diffusion. However, for a membrane like T6 or T4 without histamine, both permeabilities are strongly decreased by the application of mixed gas, but the ratio (the selectivity) is higher in this case.

To conclude about this comparison, it can be noticed that making the mixed gas experiments was worth it because the results cannot be predicted from the single gas experiments. Some membranes show higher selectivity and higher permeabilities. The results from mixed gas experiments are the most interesting because they are obtained under experimental conditions similar to the industrial ones.

#### • For wet experiments:

For most of the membranes, the <u>selectivities</u> are higher when there are no histamine groups. This
is not the case for T5 which shows the best selectivities (around 100) and much higher
selectivities than T5 without histamine. T5 is a polypropylene based copolymer with a short chain
length (6 groups). The membrane is quite glassy (glass transition temperature of -4°C).

#### o Effect of pressure:

CO2/N2 selectivity in wet histamine membranes



CO2 partial pressure (bar) CO2/N2 selectivity in wet " without histamine" membranes



CO2 partial pressure (bar)

Figure 67 Evolution of selectivity in wet membranes with pressure

For most of the membranes, the selectivity is higher at 5 bars than at 1.2 bars – except for T3 without histamine and T6 without histamine. Most of the time, the difference is not really important (around 10). Usually, for thin layer supported membranes with facilitated transport, the contrary phenomenon is observed. Indeed, with facilitated transport, N<sub>2</sub> permeability is constant but  $CO_2$  permeability can reach a plateau when carriers are saturated. This saturation occurs often around 0.5 bars of  $CO_2$  partial pressure. When the pressure increases, as N<sub>2</sub> permeability remains constant and  $CO_2$  permeability decreases, selectivity decreases.

### • Comparison between dry and wet experiments in terms of selectivity:

- The results are presented earlier in Table 9.
- For all the membranes, the selectivity in wet conditions is higher than in dry conditions. That would mean that for all the membranes, facilitated transport occurs. This is possible as carbon dioxide can interact thanks to hydrogen bonds to the oxygens of the ether chain or to the nitrogens of the hard groups. There can also be an acid-base reaction with the secondary amine of the histamine group.
- For some membranes, T5, T2 without histamine, T5 without histamine and T6 without histamine, the difference between dry and wet conditions is particularly marked whereas for the others, the difference is small or even inexistent. It would mean that for the membranes previously cited, facilitated transport is particularly efficient. There is, unfortunately, no real effect of histamine group on this efficiency of facilitated transport, contrary to what was expected, even if the biggest increase of solubility is for a membrane containing histamine (T5).
- For histamine membranes, the increase of selectivity is higher at 5 bars whereas for the membranes without histamine it also happens at 1.2 bars.
- To conclude about selectivity results, it can be said that both series of membranes show an increase in selectivity in presence of water proving that facilitated transport occurs. In most of the cases, selectivity is smaller for the membranes containing histamine groups. The selectivities are often higher at higher pressures. In dry conditions, T3 without histamine and T6 without histamine, as well as T2 without histamine (but only at 5 bars) show high, interesting selectivity. In wet conditions, the same membranes show also good properties as well as T5 without histamine and T5 which is the best membrane.

## 5.4.3 Discussion about permeability results:

Mombrano	CO <sub>2</sub> Permeability (Barrer)				
Weilibralle	1,2 bar dry	5 bar dry	1,2 bar wet	5 bar wet	
T1	-	- 10		13	
T2	159	174	115	125	
Т3	282	295	268	267	
T5	68	108	157	130	
Т6	302	389	318	294	
Т8	20	3	-	-	
T1 without histamine	50	44	55	53	
T2 without histamine	372	272	418	408	
T3 without histamine	786	1128	741	726	
T4 without histamine	55	14	50	49	
T5 without histamine	59	32	59	40	
T6 without histamine	e 1086 898 876		658		

The permeabilities are displayed in the Table 13 and Table 14 shown below:

Table 13 CO<sub>2</sub> permeability results

Membrane	N <sub>2</sub> Permeability (Barrer)				
Membrane	1,2 bar dry	5 bar dry 1,2 bar wet		5 bar wet	
T1	23	5	24	5	
Т2	95	23	21	7	
Т3	53	19	50	15	
T5	6	7	2	1	
Т6	35	55	33	22	
Т8	2	1	-	-	
T1 without histamine	31	8	32	7	
T2 without histamine	25	5	5	6	
T3 without histamine	5	24	12	13	
T4 without histamine	3	2	3	2	
T5 without histamine	5	2	1 1		
T6 without histamine	36	23	13	14	

Table 14 N<sub>2</sub> permeability results

- In dry conditions:
- As already commented, the nitrogen permeabilities follow the same trend as the selectivities when single and mixed gases experiments are compared.
- $\circ$  For most of the membranes, the CO<sub>2</sub> permeability is higher through "without histamine" membranes. As they are more rubbery than histamine membranes, it can be deduced than diffusivity is higher.

#### • Effect of pressure:

CO2 permeability in dry histamine membranes



CO2 partial pressure (bar)

Figure 68 Evolution of CO<sub>2</sub> permeability in dry histamine membranes

For histamine membranes –except T5 and T8 –  $CO_2$  permeability is higher at 5 bars than at 1.2 bars. This can be understood by the fact that, when the pressure increased, the partial pressure of  $CO_2$  increases also. As this partial pressure is still small (0.12 and 0.5 bars respectively), it is in the first part of sorption curves, in Henry's law domains. From the sorption experiments presented in 5.5, it can be seen that for this domain, a small increase of pressure gives a big increase in solubility. As the solubility increases, the permeability, which is the product of solubility by diffusivity, increases also.



CO2 permeability in " without histamine" membranes

CO2 partial pressure (bar)

Figure 69 Evolution of CO<sub>2</sub> permeability in dry "without histamine" membranes

However, the opposite trend, a decrease of  $CO_2$  permeability with pressure, can be observed for the membranes without histamine – except for T3 without histamine. As the membranes are more rubbery, it is possible that the pressure compresses the membranes and reduces the free volume and consequently both solubility and diffusivity would be reduced.

Those hypotheses are confirmed by  $N_2$  permeability: it is, most of the time, higher at low pressure, for both series. For histamine series, only  $CO_2$  solubility increases with feed pressure whereas for "without histamine" series, diffusivity for both gases is decreased by increasing the feed pressure. (The graphs are presented in ANNEX IV).

## • In wet conditions:

- $\circ$  The same observation than in dry conditions can be made towards the comparison of CO<sub>2</sub> permeability in the two series of membranes: for histamine series an increase and for "without histamine" a decrease.
- Concerning the <u>effect of pressure</u>, it can be noticed that  $N_2$  permeability is higher at lower pressure for histamine membranes, whereas it is almost constant for "without histamine" membranes. This is coherent to a solution-diffusion transport mechanism for  $N_2$ , a relatively inert and non-reactive gas.  $CO_2$  permeability is higher for lower pressure for "without histamine" membranes but no trend can be given for the membranes with histamine. These observations seem consistent with usual observations for facilitated transport: almost constant permeability of  $N_2$  and decreasing  $CO_2$  permeability with increasing pressure. The membranes without histamine seem to show a more characteristic facilitated transport behavior.

## • Comparison of dry and wet membranes:

- For most of the membranes, the change of conditions does not change significantly the <u> $N_2$ </u> <u>permeability</u>. The presence of water has no influence on the transport of nitrogen. This is consistent with facilitated transport theory only the reactive species transport is enhanced.
- Concerning <u>CO<sub>2</sub> permeability</u>, more changes can be observed but in both directions: some membranes show higher permeability in dry conditions and the others in wet conditions. T5 and T2 without histamine show a big increase in permeability by going to wet conditions. As the selectivity is the ratio of N<sub>2</sub> permeability and CO<sub>2</sub> permeability, it is the relative change which matters. In addition, the behavior can be different depending on the dominant transport mechanism. For some membranes, solution diffusion is dominant compared to facilitated transport and water can have a negative influence for very glassy polymers. Indeed, water can compete for sorption sites with CO<sub>2</sub>. For membranes where facilitated transport dominates water should have a positive effect.

To conclude about permeability results, most of the membranes show high CO<sub>2</sub> permeabilities, increasing with increasing pressure for histamine membranes, decreasing with increasing pressure for "without histamine" membranes. In dry conditions as well as in wet ones, **T3**, **T6**, **T2** without histamine, **T3** without histamine and **T6** without histamine show high CO<sub>2</sub> permeabilities and can therefore be interesting for an industrial use.

### 5.4.4 Discussion about the Robeson graphs obtained:

The Robeson type of graphs obtained for the different conditions are presented in the following figures:



Selectivity vs CO2 permeability at 1.2 bar dry

Figure 70 Robeson graph for 1,2 bars dry

From this graph, it can be said that **T3 without histamine** and **T6 without histamine** are the most interesting membranes to get together a high  $CO_2/N_2$  selectivity of respectively 46 and 31 and a high  $CO_2$  permeability of respectively 786 Barrer and 1086 Barrer for a mix of 10% vol  $CO_2/90\%$  N<sub>2</sub> dry at 1.2 bars.



#### Selectivity vs CO2 permeability at 5 bar dry



From this graph, it can be pointed again that **T3 without histamine** and **T6 without histamine** are the most interesting membranes to get together a high  $CO_2/N_2$  selectivity of respectively 46 and 39 Barrer and a high  $CO_2$  permeability of respectively 1128 Barrer and 898 Barrer for a mixture of 10% vol  $CO_2/90\%$  N<sub>2</sub> dry at 5 bars but **T2 without histamine** shows also good properties (selectivity of 50 and permeability of 272 Barrer). T8 shows bad properties (small selectivity and small permeability).



Selectivity vs CO2 permeability at 1.2 bar wet

Figure 72 Robeson graph for 1,2 bars wet

From this graph, it can be said that **T3 without histamine, T6 without histamine** and **T2 without histamine** are the most interesting membranes to get together a high  $CO_2/N_2$  selectivity, of respectively 62, 68 and 60, and a high  $CO_2$  permeability of respectively 741, 876 and 418 Barrer for a mix of 10% vol  $CO_2/90\%$  N<sub>2</sub> wet at 1.2 bars. **T5** shows also good properties, with even higher selectivity (94) but a smaller permeability (157 Barrer). T1 shows bad properties (small selectivity of 0.43 and small permeability of 10 Barrer). The results obtained by Matsuyama [32] (blue star) for his poly(2-(N,N-dimethyl)aminoethyl methacrylate) membrane are better with almost the same permeability than T6 without histamine but with higher selectivity. The  $CO_2$  partial pressure was 0,047 atm which is lower than the value we used. The results obtained by Sandru [31] (red star) with a polyvinylamine membrane are even better, but they were obtained at 0.2bars of  $CO_2$  partial pressure and the membrane is composite. Indeed, it is a thin layer of PVAm supported by a polysulfone support.



#### Selectivity vs CO2 permeability at 5 bar wet



From this graph, it can be said that **T3 without histamine, T6 without histamine** and **T2 without histamine** are the most interesting membranes to get together a high  $CO_2/N_2$  selectivity of respectively 55, 54 and 63 and a high  $CO_2$  permeability of respectively 726, 658 and 408 Barrer for a mix of 10% vol  $CO_2/90\%$  N<sub>2</sub> wet at 5 bars. **T5** shows also good properties, with even higher selectivity (104) but a smaller permeability (130 Barrer). T1 shows bad properties (small selectivity (3) and small permeability of 13 Barrer).

To conclude about mixed gas experiments:

- Those experiments were needed to conclude about the real industrial interest of the membranes even if further development stages are need to attain a membrane which can be used in industry. Indeed, the results in mixed gas are different than with pure gases.
- The experiments with wet gases showed that facilitated transport was happening in every membrane and not more in membranes containing histamine.
- Contrary to what was expected, histamine membranes do not show better properties. Regardless of experimental are the conditions, <u>T3 without histamine</u> and <u>T6 without</u> <u>histamine</u> show the best tradeoff between selectivity and CO<sub>2</sub> permeability. *T2 without histamine* and *T5* show also good tradeoff and can be further developed.

The best properties are obtained in **wet conditions at 1.2 bars**.

## 5.5 Sorption experiments

### 5.5.1 Some remarks about the experiments and the exploitation of results

- During this project, the sorption of CO<sub>2</sub> in eight membranes has been studied. The data recorded in 2011 by student Mohammad Mashkur for T3 and T8 have also been re-calculated, analyzed and used for this project.
- Concerning the experimental protocol, the volume measurement was always conducted following the same procedure: 17h of evacuation at 60°C, 20h of evacuation at 25°C and then 10 segments at different pressures (0.5, 1, 1.5, 3, 5, 7, 10, 12, 15 and 20 bars). This volume measurement was followed by the study of carbon dioxide sorption: 17h of evacuation at 60°C, 20h of evacuation at 25°C and then 8 segments at different pressures (0.5, 1, 1.5, 3, 5, 7, 10, 12, 15 and 20 bars). This volume 20 bars). Desorption was then studied: the pressure was decrease with the same steps. Each segment was made of 3 hours of exposure to gas. The values used in calculation are an average of the 60 last points from the static measurement, to be sure to be in equilibrium state.
- After each segment, a static measurement was performed. All the valves of the instrument were closed during 30 minutes. The sorption calculations were investigated both in the flow mode and static mode. It was concluded that the results were more easily exploited in static mode measurement. The values used in calculation are an average of the 60 last data points from the static measurement, to be sure to be in equilibrium state.

## 5.5.2 Experimental results and interpretation

## 5.5.2.1 Overall remarks:

- For most of the membranes, both series altogether, the behavior is quite clear until 10 or 15 bars and the last point (or two last points) is lower than expected. This can be explained by the competition between sorption of the gas and hydrostatic pressure [19, 23]. Indeed, at high pressures (like 15 or 20 bars) the membrane is compressed and the free volume decreases. Consequently, less gas than forecasted by the theory can be sorbed. In this case, the characteristic coefficients will be determined excluding those points but it should be kept in memory than they are valid on a restricted domain of pressure. However, the decrease seems higher than what is usually observed and might also come from an incertitude in the volume measurement, inherent to the set-up.
- Almost all the membranes without histamine do not show a hysteresis phenomenon and sorption – as desorption- follows Henry's law. This is consistent with the fact that the membranes are rubbery. And this is confirmed by looking at T8 without histamine, which is the glassiest membrane of this series, and the only membrane showing some hysteresis at low pressures.

- For histamine membranes, which are glassy or glassier that "without histamine" series, except for T3, dual mode sorption model has been used to fit experimental data. For most of them, a hysteresis was observed, with different loop widths: for T4, which is really glassy, the hysteresis is strong, whereas it is only a small difference for the quite rubbery T6. T3 which is a rubbery membrane, show a Henry's law behavior towards CO<sub>2</sub> sorption.
- It can be noted that the solubilities obtained through Henry's law are much higher than those obtained with dual sorption model: between 0.9 and 1.6 cm<sup>3</sup><sub>STP</sub> / (cm<sup>3</sup> <sub>membrane</sub>.atm) for the first ones versus 0.18 and 0.64 cm<sup>3</sup><sub>STP</sub> / (cm<sup>3</sup> <sub>membrane</sub>.atm) for the second ones.
- Some fitting problems were experienced. Even if the experimental data seem to show the coherent behavior, some solubility coefficients were really small or negative, which is physically not acceptable. As the physical validity predominates on the mathematical model, the results obtained are not considered as reflecting the real phenomenon.

## 5.5.2.2 Results membrane by membrane:

## o <u>T1 with histamine</u>

The sorption and desorption isotherm of  $CO_2$  in T1 in presented in the following graph. The specific uptake has been plotted as a function of the fugacity to take into account the non-ideality of carbon dioxide.

It can be seen from the curve shape that the  $CO_2$  sorption for this membrane is not following Henry's law. This is in correlation with the DSC measurements which enabled to show that T1 is a glassy membrane. Consequently, the dual sorption theory is to be considered. As a reminder, the dual sorption theory is defined by the following equation:

$$c = S * p + \frac{c'_h b p}{1 + b p}$$

It means that the  $CO_2$  dissolves into the polymer but exists also in the non-equilibrium excess free volume.

This equation was used to fit the sorption part of the curve. The coefficients obtained are:

```
S=0.636 \text{ cm}^{3}_{STP} / (\text{cm}^{3}_{membrane}.atm)
```

## b=0.6808 atm<sup>-1</sup> $c'_{h}$ =14.5236 cm<sup>3</sup><sub>STP</sub> / cm<sup>3</sup><sub>membrane</sub>

with a correlation coefficient of 0.9911.



Figure 74 Sorption isotherm at 25°C for CO<sub>2</sub> and T1

It can be said that T1 is following the dual sorption model because the data fit well with the model.

The diffusion coefficient can be calculated from the permeability obtained by permeation experiments and the solubility coefficient. Indeed, P = S \* D so  $D = \frac{P}{s}$ .

Then D<sub>T1</sub>(5 bars)=2.8\*10<sup>-8</sup> cm<sup>2</sup>/s.

Usually, gas diffusion coefficients are between  $10^{-15}$  and  $10^{-5}$  cm<sup>2</sup>/s, the last value being obtained for diffusion in liquids. The diffusion coefficient of T1 is of average value and the permeability is low. This is characteristic of a glassy membrane.

The solubility coefficient for this membrane is the highest of those obtained by dual mode sorption. As the soft segments are made of polyethylene oxide, the oxygen groups are easy to reach and can interact with the carbon dioxide to increase its solubility.  $c'_h$  is the smallest: the contribution of Langmuir sorption might be smaller for this membrane than for the others.

### o <u>T2 with histamine:</u>





Figure 75 Sorption isotherm at 25°C for CO<sub>2</sub> and T2

From the adsorption-desorption isotherm presented above, a fitting with dual sorption theory was made giving the following parameters:

S= 0.0214 cm<sup>3</sup><sub>STP</sub> / (cm<sup>3</sup> membrane.atm)

**b=0.1123** atm<sup>-1</sup>  $c'_{h}$ =17.6269 cm<sup>3</sup><sub>STP</sub> / cm<sup>3</sup><sub>membrane</sub> with a correlation coefficient of 0.9968.

## Then D<sub>T2</sub>(5 bars)= 6,97.10<sup>-5</sup> cm<sup>2</sup>/s

The solubility coefficient is really low, almost ten times smaller than the usual values. As a consequence, the diffusion coefficient is very high, in the same range than diffusion in liquids. The membrane is rubbery but does not show degradation or complete dissolution in presence of carbon dioxide. It is therefore difficult to accept such a high diffusion coefficient. The fitting might be not trustable, even if the experimental data seem to be coherent. However, the curvature of the curve prevents a fitting with Henry's law. The results obtained are to be used carefully.

A fitting of the results with a linearized Langmuir equation has been done:



Figure 76 CO2 sorption in T2: Langmuir linearisation

The Langmuir linearized equation is:

$$\frac{1}{c} = \frac{1}{c'_h} + \frac{1}{c'_h b} * \frac{1}{f}$$

The fitting done gives the following coefficients:

## **b=0.121** atm<sup>-1</sup> $c'_{h}=0.031 \text{ cm}^{3}_{STP} / \text{cm}^{3}_{membrane}$

If b is in the expected order of magnitude,  $c'_h$  is very low. In addition, the fact to reduce the sorption to only Langmuir contribution has to be discussed. Indeed, it would mean than the gas is sorbed in the membrane only in the free volume and no solubility selectivity will occur. This assumption is not consistent with all the theories which state solution-diffusion, following Henry's law, as basis mechanism which is, for some membranes, accompanied by Langmuir contribution. It might be explained by the fact that the free volume is so high that the solubility contribution is negligible in front of Langmuir contribution.

#### o T3 with histamine:



T3: Specific uptake for CO2 vs fugacity



The sorption isotherm and the fitting with dual sorption theory are shown above. The following parameters can be deduced:

 $S= 0.1864 \text{ cm}^3_{STP} / (\text{cm}^3_{membrane} \text{.atm})$ 

**b=0.0392** atm<sup>-1</sup>  $c'_{h}$ =44.1787 cm<sup>3</sup><sub>STP</sub> / cm<sup>3</sup><sub>membrane</sub> with a correlation coefficient of 0.9999.

Then D<sub>T3</sub>(5 bars)=1.73\*10<sup>-5</sup> cm<sup>2</sup>/s

Even if T3 is a rubbery membrane, the dual sorption model seems to fit the experimental data. However, by looking to the too high diffusion coefficient value and the values of Langmuir coefficients (b is really low and  $c'_h$  is very high) it seems that it is not the good model to use. If the data are fitted with Henry's law, which is expected for rubbery membranes, the following results are obtained:



Figure 78 Sorption isotherm for T3 fitted by Henry's law

## k<sub>d</sub>=1.4099 cm<sup>3</sup><sub>STP</sub>/(cm<sup>3</sup>.atm)

The corresponding diffusion coefficient is:  $D_{T3}(5bars)=2.29*10^{-6} \text{ cm}^2/\text{s}$ .

This value is high but in a coherent range. The high value is understandable: the permeation is fast and it is logical when a rubbery polymer is considered. The star shape form of the polymer with long branches gives a high free volume and big diffusion ability. The solubility is also very high and this comes from favorable interactions between the ether groups and the polar molecule of  $CO_2$ .

o <u>T4 with histamine:</u>



T4: Specific uptake of CO2 vs fugacity

Figure 79 Sorption isotherm at 25°C for CO<sub>2</sub> and T4

The fitting with dual sorption model has been made only between 0.5 and 15 bar and the results obtained are:

S= -0,0926 cm $^{3}$ <sub>STP</sub> / (cm $^{3}$  membrane.atm)

**b=0,19 atm**<sup>-1</sup>  $c'_{h}$ =**13,5016 cm**<sup>3</sup><sub>STP</sub> / cm<sup>3</sup><sub>membrane</sub> with a correlation coefficient of 0.9997.

As no permeation experiment has been done, it is not possible to obtain the value of the diffusion coefficient.

If the values of Langmuir coefficients (b and  $c'_h$ ) are in a correct range, the negative solubility coefficient is physically impossible to exist and explain. The mathematical fitting of the curve is not able to represent to real phenomenon. Several attempts have been made to obtain a better fitting excluding some of the experimental points but the values reported are the best ones. The difference between this membrane and the previous one is the smaller specific uptake (around 7.5 at the saturation plateau, whereas it is higher than 12 for the other membranes).

Another characteristic point about this membrane is the large hysteresis. This could be explained by the fact that hysteresis is the result of structural rearrangement of the polymer matrix by the absorption of penetrant [54]. As T4 is a really glassy polymer (highest glass transition temperature of the series, 66°C), the structural change has been extensive and the relaxation time is very high. Therefore, the width of the hysteresis loop is large.

o T5 with histamine:

T5: Specific uptake for CO2 vs fugacity



Figure 80 Sorption isotherm at 25°C for CO<sub>2</sub> and T5

The sorption-desorption isotherm has been plotted and is shown above. The sorption part has been fitted with dual sorption model and the results are:

 $S=0.2739 \text{ cm}^3_{STP} / (\text{cm}^3_{membrane}, \text{atm})$ 

b=0.4330 atm<sup>-1</sup> c'<sub>h</sub>=12.4411 cm<sup>3</sup><sub>STP</sub> / cm<sup>3</sup><sub>membrane</sub>

with a correlation coefficient of 0.9968.

```
and D<sub>T5</sub>(5 bars)=9.47*10<sup>-7</sup> cm<sup>2</sup>/s
```

All the coefficient determined are in the correct order of magnitude. However, this polymer shows the smallest solubility and average  $c'_{h}$ . The diffusion coefficient is low, but this is in accordance with the quite glassy nature of the polymer. Hysteresis is observable, with a small width.

#### • <u>T6 with histamine:</u>



#### T6: Specific uptake of CO2 vs fugacity



S= -2.5978 cm<sup>3</sup><sub>STP</sub> / (cm<sup>3</sup> membrane-atm) b=0.0186 atm<sup>-1</sup> c'<sub>h</sub>= 249,9078 cm<sup>3</sup><sub>STP</sub> / cm<sup>3</sup> membrane with a correlation coefficient of 0.9988.

### and D<sub>T6</sub>(5 bars)=-1.51\*10<sup>-6</sup> cm<sup>2</sup>/s

Once again, the fitting with dual sorption model is problematic as the solubility coefficient is negative and both Langmuir coefficients are out of the range expected (too small b and really too high  $c'_h$ ). The diffusion coefficient deduced from the solubility coefficient and the permeability measured is therefore also without physical meaning. However, the experimental data follow the expected behavior, in the correct order of magnitude (the saturation plateau is around 16 cm<sup>3</sup><sub>STP</sub> /cm<sup>3</sup><sub>membrane</sub>). Hysteresis phenomenon is hardly existent which is coherent with the fact that T6 is rubbery.

A fitting with Henry's law for the first points has been made:





 $k_d=1.4445 \text{ cm}^3_{\text{STP}}/(\text{cm}^3.\text{atm})$  The corresponding diffusion coefficient is:  $D_{T6}(\text{5bars})=2,72.10^{-06} \text{ cm}^2/\text{s}.$ 

Both Henry's coefficient and diffusion coefficient are in the expected order of magnitude. The diffusion coefficient is high, in accordance with the rubbery nature of the polymer.

o <u>T8 with histamine:</u>

As before, the sorption isotherm has been plotted and fitted with dual sorption model.

S=0.3054 cm<sup>3</sup><sub>STP</sub> / (cm<sup>3</sup> membrane.atm) b=0.1809 atm<sup>-1</sup> c'<sub>h</sub>=21.2568 cm<sup>3</sup><sub>STP</sub> / cm<sup>3</sup> membrane with a correlation coefficient of 0.9975. D<sub>T8</sub>(5 bars)=6.39\*10<sup>-9</sup> cm<sup>2</sup>/s

T8 is a glassy polymer and the low diffusivity obtained, due to a really low permeability, is expected but it should be noted that it remains really low. The other coefficients are in the correct range with a quite high solubility and  $c'_{h}$ .



T8: Specific uptake for CO2 vs fugacity

Figure 83 Sorption isotherm at 25°C for CO<sub>2</sub> and T8

• <u>T1 without histamine:</u>



Figure 84 Sorption isotherm for T1 without histamine fitted by Henry's law

 $k_d=0.9066 \text{ cm}^3_{\text{STP}}/(\text{cm}^3.\text{atm})$  The corresponding diffusion coefficient is:  $D_{T1 \text{ without}}=4.97*10^{-7} \text{ cm}^2/\text{s}$ .

For this membrane, which does not contain histamine groups, no hysteresis is observable: the relaxation of the polymer with desorption is complete and fast. The fitting with Henry's law is possible at low pressures (under 10 bars). The Henry's coefficient is lower than the coefficients obtained for the rubbery membranes of the histamine series. The diffusion coefficient is average.



• <u>T2 without histamine</u>:

Figure 85 Sorption isotherm for T2 without histamine fitted by Henry's law

 $k_d$ =1.1008 cm<sup>3</sup><sub>STP</sub>/(cm<sup>3</sup>.atm) The corresponding diffusion coefficient is:  $D_{T2 \text{ without}}$ =1.72\*10<sup>-6</sup> cm<sup>2</sup>/s.

For this membrane, once again, no hysteresis phenomenon occurs and Henry's law fits very well the experimental results. Henry's coefficient is higher than for T1 without histamine as the diffusion coefficient but they are still in coherent orders of magnitude.

## • T3 without histamine:



Figure 86 Sorption isotherm for T3 without histamine fitted by Henry's law

k<sub>d</sub>=1.2837 cm<sup>3</sup><sub>STP</sub>/(cm<sup>3</sup>.atm) The corresponding diffusion coefficient is: D<sub>T3 without</sub>=4.21\*10<sup>-6</sup> cm<sup>2</sup>/s.

T3 without histamine shows the same behavior than the two previous membranes: Henry's law behavior, no hysteresis, higher Henry's coefficient and diffusivity. This is in accordance with the thermal properties of the membranes, determined by DSC: T3 without has the lowest glass transition temperature. Consequently, it is the most rubbery membrane, and has the best diffusion properties.



• T5 without histamine:

Figure 87 Sorption isotherm for T5 without histamine fitted by Henry's law

k<sub>d</sub>=0.9508 cm<sup>3</sup><sub>STP</sub>/(cm<sup>3</sup>.atm) The corresponding diffusion coefficient is: D<sub>T5 without</sub>=2.73\*10<sup>-7</sup> cm<sup>2</sup>/s

T5 without histamine is still a rubbery membrane but less than the previous ones (glass transition temperature of -14°C versus -39°C for T1 without histamine). The non hysteretic behavior, and the Henry's law fitting with low Henry's coefficient and diffusion coefficient are therefore expected.

o <u>T8 without histamine:</u>



Figure 88 Sorption isotherm for T8 without histamine fitted by Henry's law

## k<sub>d</sub>=1.5728 cm<sup>3</sup><sub>STP</sub>/(cm<sup>3</sup>.atm)

The corresponding diffusion coefficient cannot be calculated as no permeation experiment has been possible to make.

The Henry's coefficient is higher than all of those for "without histamine" series but still in a coherent order of magnitude.

The results, however, seem strange as the desorption curve is under the sorption curve, which would mean that free volume collapsed faster than it was filled. This is not a usual result and no logical explanation can be found.

## 5.5.2.3 Overall results

Membrane	Solubility (cm <sup>3</sup> <sub>STP</sub> /(cm <sup>3</sup> * atm))	D (cm²/s)	<b>C'h</b> (cm <sup>3</sup> <sub>STP</sub> /cm <sup>3</sup> )	<b>b</b> (1/atm)	Domain of validity (bar)	Comments
T1	0,636	2,80E-08	10,5876	0,68	0,5-15	Dual sorption
т2	0,0214	6,97E-05	17,63	0,11	0,5-15	Dual sorption
	-	-	0,031	0,12	0,5-20	Langmuir
тз	0,1864	1,73E-05	44,18	0,04	0,5-15	Dual sorption
	1,4099	2,29E-06	-	-	0,5-15	Henry's law
Т4	-0,0926	-	13,5	0,19	0,5-10	Dual sorption
Т5	0,2739	9,47E-07	12,44	0,43	0,5-15	Dual sorption
т6	-2,5978	-1,51E-06	249,9	0,02	0,5-20	Dual sorption
	1,4445	2,72E-06	-	-	0,5-10	Henry's law
Т8	0,3054	6,39E-09	21,26	0,18	0,5-20	Dual sorption
T1 without hista	0,9066	4,97E-07	-	-	0,5-10	Henry's law
T2 without hista	1,1008	1,72E-06	-	-	0,5-15	Henry's law
T3 without hista	1,2837	4,21E-06	-	-	0,5-20	Henry's law
T5 without	0,9508	2,73E-07	-	-	0,5-20	Henry's law
Ilista	-	3.77E-7	-	-	-	Time lag
T8 without hista	1,5728	-			0,5-10	Henry's law
ODPA-P1 [11]	32	-	0,44	0,23		Dual sorption
PSF-NH2 (16%) [9]	0,4	-	21	0,26		Dual sorption
80PTMEO/PA 12 [10]	0,96	1,74E-06	-	-		
57PEO/PA6 [10]	0,88	5,70E-07	-	-		

Table 15 Comparison of sorption models

The table above presents the results obtained by fitting, and when it was possible, by other means. The last lines present the results obtained in other studies. Some results have been obtained by Simons [11] with thick films of ODPA based copolymers with one para-aryloxy substitution on the diamine moieties. The polymers are also made of ether chains but with numerous benzyl groups. The values they obtained are in the same range of order than the values obtained from our experiments. A large solubility is observed by K.Simons but it is still lower than the solubility of T1. They also explained the hysteresis between sorption and desorption curve, hysteresis that can be observed for the most of histamine membranes (T1, T2, T4, T5, T6).The hysteresis is the result of the induction of new free volume sites during the sorption. The collapse of these new sites happening in longer scale time than desorption of  $CO_2$ , a higher free volume exists during desorption and hysteresis can be observed. The results obtained by Ghosal [9] for a polysulfone membrane with extra amine moieties are close to those obtain for T8 with histamine. The solubility coefficients found by Bondar [10] are close to the values obtained for some of the membranes of this work as well as the diffusion coefficient.

It can be noticed that time lag method and sorption experiment give similar values of diffusivity for T5 without histamine, the results can be trusted.

The sorption experiments enabled us to relate the transport phenomena with the structure of the membrane and to obtain the diffusion coefficient of carbon dioxide in the different membranes.

# 6. Conclusion

As it is highlighted in numerous publications and the current study, the polyether based copolymers are interesting materials because they can be tuned in different ways in order to get some particular permeability or selectivity properties for membranes. The polyether based copolymers studied during this project where made of soft segments of polyethylene oxide (PEO) or polypropylene oxide (PPO) and hard segments made of trialdehyde and, for some of them, imidazole groups. Consequently, the main chemical functions were the same for all the copolymers. The differences came from the chain length, the spatial structure (linear or star shape chains) and composition of the soft segments. This was clearly highlighted by Fourier Transform Infra Red spectroscopy. Different structures were obtained, from really glassy to rubbery, which were further characterized by Differential Scanning Calorimetry analyses.

The separation properties of the membranes were investigated by two types of experiments: gas permeation experiments to determine their gas permeability and sorption experiments to understand the transport mechanism and to determine the solubility coefficient. Using both results, it was possible to calculate the diffusion coefficient. Those experiments were made with CO<sub>2</sub> for sorption and two types of permeation experiments were made: single gas experiments with pure N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>; mixed gases experiment with a 10vol% CO<sub>2</sub>-90vol% N<sub>2</sub> feed mixture in dry and humidified conditions. The membranes were expected to behave as facilitated transport membranes in presence of water due to the large amount of oxygen and nitrogen atoms. Swelling experiments using water vapors have also been performed in order to characterize the amount of water sorbed in each membrane.

Mixed gas experiments proved that facilitated transport was occurring because both  $CO_2/N_2$  selectivity and  $CO_2$  permeability were increased in presence of water. The best separation properties were obtained in wet conditions at 1.2 bars. The most interesting membrane studied in this work, regardless of testing conditions , was <u>T6 without histamine</u>, a rubbery and long linear PPO based copolymer, showing both high selectivity (up to 68 at 1.2 bars humidified) and permeability (up to 1086 Barrer at 1.2 bar dry). However, other membranes show good properties:

- T5, which is a a rubbery and short linear PPO based copolymer, shows the highest CO<sub>2</sub>/N<sub>2</sub> selectivities (up to 104) for lower but still acceptable permeabilities (up to 157 Barrers), especially at 1.2 bar wet for mixed gases and 5 bars for pure gases.
- T2, T3 and T2 without histamine showed good properties for ideal CO<sub>2</sub>/N<sub>2</sub> separation at 5 bars, with high CO<sub>2</sub> permeability. T2 and T2 without histamine are rubbery and long linear PEO based copolymers. T3 is a rubbery polymer, with star shape structure made of long PPO chains.
- **T5 without histamin**e has good properties for ideal CO<sub>2</sub>/CH<sub>4</sub> separation at 5 bars.
- **T3 without histamin**e has similar properties than T6 without histamine for CO<sub>2</sub>/N<sub>2</sub> separation with mixed gases.

If T6 without histamine showed really interesting separation properties, water vapor swelling experiments have also proven that the membrane was easily solved by water and so it should be handed carefully and long-term experiments should be done to be sure that the properties will remain.

Further development should be done if the membranes are to be used in industry, the main one being to develop a thin layer membrane in form of composite membranes.

The strategy used to conceive and synthesis a membrane with interesting properties can be used again from the results obtained: rubbery membranes show better properties; a smaller hard group containing more secondary amine could be an interesting subject of research. Indeed, if the hard segment is small it will not increase too much the crystallinity and the increased number of reacting sites could enhance  $CO_2$  facilitated transport.

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# ANNEX I Infrared Spectrometry analysis: spectra obtained

a. T1



























## h. T1 without histamine



## i. T2 without histamine



j. T3 without histamine



## k. T4 without histamine



## I. T5 without histamine



#### m. T6 without histamine





# **ANNEX II Differential Scanning Calorimetry: Curves obtained**

a. T4







## c. T8 Cycle 2



d. T1 without histamine



#### e. T2 without histamine



f. T3 without histamine





g. T4 without histamine



## h. T5 without hista



### i. T6 without histamine





## **ANNEX III : Swelling experiments graphs**

Graphs representing the increase of weight versus the time spent in humid conditions.























## **ANNEX IV Mixed gas experiments**

N2 permeability in histamine membranes



N2 partial pressure (bar)

N2 permeability in "without histamine" membranes



N2 partial pressure (bar)

# ANNEX V Risk evaluation

NTNU								Risikovurdering	Nummer	Dato	
		Hazardous activity id	entification	nrocess				HMS-avd.	HMSRV2601		
	·		entinoation	Godkjent av	Side Erstatter		$\langle \langle \rangle$				
HMS		Ì	1			1	1			ļ	
Unit:				Kiemisk n	rosesstekn	ologi	Date:	16/01/2012			
Line mana	ger:		Øyvind Gregersen								
Participant	ts in the identification process (incl	uding their function):		Marie Pra	che (Studen	t) Marius S	Sandru an	d May-Britt I	Hägg (Supe	rvisors)	
						r		1			1
Short desc	ription of the main activity/main pr	rocess:	-								
ID no.	ID no. Activity/process Responsible person			tions etc.	Existing documentation		Existing safety measures		Comment		
1	Pressure (High pressure sorption rig, Permeation rig)	Marius Sandru May-Britt Hägg Rooms: -Sorption: Idda Noddeland - Permeation: Vajiheh Nafisi	AMO	2	Operating manuals		Use of safety goggles				
2	Temperature (High pressure sorption rig)	AMO	MC Operating manuals								
3	Condensation of CO2 in pipes (High pressure sorption rig)	AMO	AMC Operating m			Maxima CO2 u	l pressure of sed: 25 bar				
4	Power failure (High pressure sorption rig, Permeation rig)	Marius Sandru May-Britt Hägg Rooms: -Sorption: Idda Noddeland - Permeation: Vajiheh Nafisi	AMO	АМС		Operating manuals		Ventilation of the room			
5	Leakage (permeation rig)	Marius Sandru May-Britt Hägg Rooms: -Sorption: Idda Noddeland - Permeation: Vajiheh Nafisi	AMO	2	Operating manuals		Ventilation of the room				
6	Marius Sandru May-Britt Hägg Jse of glue (Araldite 2012, 2028) Rooms: - Sorption: Idda Noddeland - Permeation: Vajiheh Nafisi		AMO	2			Use of s and	afety goggles 1 gloves			

Likelihood, e.g.:	Consequence, e.g.:							
1. Minimal	A. Safe	Risk value (each one to be estimated senarately):						
2. Low	B. Relatively safe	Human = Likelihood x Human Consequence						
3. Medium	C. Dangerous	Environmental = Likelihood x Environmental consequence						
4. High	D. Critical	Financia/material = Likelinood X Consequence for Economy/materiel						
5. Very high	E. Very critical							

NTNU										Utarbeidet av	Nummer	Dato		
				Risk assessment						HMS-avd.	HMSRV2603	04/02/2011		
	1									Godkjent av	Side	Erstatter		
HMS /KS		1		1	1	1		r						
l Init.						Vi and also		] :	Data	16/01/2012				
Line mana	ine manager:					Kjemisk prosessieknologi			Date:	10/01/2012				
Participants in the identification process (includin			ncluding their fun	ction):	Marie Prac	che (Stud	ent) Marius	Sandru an	d May-Britt H	ägg (Super	visors)			
Signature	s:													
ID	ID no. Activity from the identification process form		Potential undesirable		Likelihood:	Likelihood: Consequence			·	Risk value	Comm Suggeste	ents/status ed measures		
ID no.			ess form	incident/strain		Likelihood (1-5)	Human (A-E)	Environmen t (A-E)	Economy/ material (A-E)	Reputation (A-E)	Human			
1	Pressure (High pressure sorption rig, Permeation rig)			Malfunction of pressure bu	valves, ildup	2	В	А	В	В	B2	The pressure is contained inside the rig and will be vented as long as necessary		
2	Temperature (High pressure sorption rig)			Malfunction temperature re	n of gulator	2	В	A	В	В	B2	Insulated jackets around the pipes. Be careful in case of oil leak.Check the temperature controller before feeding		
3	Condensation of CO2 in pipes (High pressure sorption rig)			Formation of damages on ma controlle	water, ass flow rs	3	A	A	В	А	A3	Flush the p No pressur for	bipes with He. e over 25 bars CO2	
4	Power failure (High pressure sorption rig, Permeation rig)			No pressure/ten controllers, no ve no vacuum p	nperature entilation, umps	2	В	В	A	А	B2	Power sup be manually failure. Op windows to	ply will have to reset after the ben doors and b help eventing	
5	Leakage (permeation rig)		Release of flamm (CH4), or inert g N2, CO2	nable gas ases (He, 2)	3	В	В	A	А	B2	A gas detector can be used. Check that vacuur pumps and ventilation ar working			
6	Use of glue (Araldite 2012, 2028)			Skin problem problems if c	s, eyes ontact	2	А	А	A	А	A2	Wear safe	ty goggles and loves	

Potential undesira	able incident/strain											
Identify possible inc	cidents and conditions that may lea	ad to situations that p	oose a hazar	d to people,	the environm	ent and	d any r	materiel/equi	ipment involv	/ed.		
Criteria for the as	ssessment of likelihood and con	sequence in relatio	n to fieldwo	ork								
Each activity is ass	sessed according to a worst-case s	scenario. Likelihood a	and conseque	ence are to b	e assessed	separat	tely fo	r each poten	tial undesira	ble incident.		
Before starting on t	the quantification, the participants	should agree what the	ey understan	d by the ass	essment crit	eria:	-					
Likelihood Minimal		Low	Low				High				Very high	
	Once every 50 years or less	Once every 10 year	rs or less	Once a year or less			Once a month or less			Once a we	ek	
	Grading	Huma	n	E	nvironment		Financial/material					
Consequence	E Verv critical	May produce fatalit	May produce fatality/ies		Very prolonged, non-reversible			tdown of work	>1 year.	T		
	D Critical	Permanent injury, r serious serious hea damage/sickness	Permanent injury, may produce serious serious health damage/sickness		Prolonged damage. Long recovery time.			Shutdown of work 0.5-1 year.				
	C	Serious personal in	jury	Minor damage. Long recovery time Minor damage. Short recovery time Insignificant damage. Short recovery time		overy	Shu	hutdown of work < 1 month				
	B Relatively safe	Injury that requires treatment	medical			Shutdown of work < 1week						
	A Safe	Injury that requires	first aid			ort	Shutdown of work		< 1day			
The unit makes its	own decision as to whether opting	to fill in or not conse	quences for	economy/ma	teriel, for exa	ample if	f the u	nit is going t	o use partic	ularly valuabl	e equipment.	
It is up to the individ	dual unit to choose the assessmer	nt criteria for this colu	ımn.									
Risk = Likelihood	x Consequence											
Please calculate the risk value for "Human", "Environment" and, if chosen, "Economy/materiel", separately.												
About the column	n "Comments/status, suggested	preventative and co	orrective me	easures": M	easures can	impact	on bo	oth likelihood	and concec	quences. Pric	ritise measu	res
that can prevent the	e incident from occurring; in other v	words, likelihood-redu	cing measur	es are to be	prioritised at	oove gre	eater e	mergency p	reparedness	,		
i.e. voncequence-r	reducing measures.											