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Denis Roizard, Y. Kiryukhina, A. Masalev, V. Khotimskiy, V. Teplyakov, et al.. Development of vinylic and acetylenic functionalized structures based on high permeable glassy polymers as membrane materials for gas mixtures separation. NAMES10: NEW ACHIEVEMENTS IN MATERIALS AND ENVIRONMENTAL SCIENCES, Oct 2010, Nancy, France. Journal of Physics Conference Series, 416, 2013, NAMES10: NEW ACHIEVEMENTS IN MATERIALS AND ENVIRONMENTAL SCIENCES. <10.1088/1742-6596/416/1/012012>. <hal-01292156>

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2013 J. Phys.: Conf. Ser. 416 012012

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# Development of vinylic and acetylenic functionalized structures based on high permeable glassy polymers as membrane materials for gas mixtures separation

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**Abstract.** There are several challenging separation problems in industries which can be solved with the help of membrane technologies. It is the case for instance of the purification of gas energy carriers (i.e. H<sub>2</sub>, CH<sub>4</sub>) from CO<sub>2</sub> as well as the CO<sub>2</sub> recovery from flue gas. Glassy polymers containing trimethylsilyl residues like poly(1-trimethylsilyl-1-propyne) [PTMSP] and polyvinyltrimethylsilane [PVTMS] are known to exhibit good membrane properties for gas separation. This paper reports two ways of improving their performances based on the controlled introduction of selective groups – alkyl imidazolium salts (C<sub>4</sub>I) and polyethyleneglycol (M-PEG)- able to enhance CO<sub>2</sub> selectivity. CO<sub>2</sub> Isotherm sorption data and permeability measurements have shown that the membrane performances could be significantly improved when C<sub>4</sub>I and M-PEG were introduced as residues covalently bounded to the main polymer chain. Moreover the introduced bromine reactive centres could also be used to induce chemical crosslinking giving rise to more resistant and stable membranes to organic vapours. With the C<sub>4</sub>I groups, the CO<sub>2</sub> sorption could be enhanced by a factor 4.4.

## 1. Introduction

Polymeric membranes have attracted the attention of many scientists since more than 30 years in the field of gas separation because membranes are able to induce the molecular separation of species having relatively similar physical properties under rather simple conditions compared to conventional methods. For instance, the separation of the two major constituents of air can be achieved by cryogenic distillation; but applying a simple pressure difference between the two sides of a well chosen membrane can also lead to the production of nitrogen of high purity [1] as commercialized by Mosanto in the 80s with the Prism gas module. The separation principle through dense membranes is explained by the solution-diffusion mechanism early evidenced by Graham in 1861 [2] and Long [3]: in the 1<sup>st</sup> step, the molecules are sorbed into the polymer network according to their affinity with the polymer structure, i.e. it corresponds to a thermodynamic equilibrium; in the 2<sup>nd</sup> step these molecules,

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called permeant, diffuse through the membrane with respect to their activity gradient maintained between the two sides of the membrane: this is the kinetic step which is also the limiting one.

In the field of gas permeation, the interactions of the molecules with glassy polymers such as PVTMS or PTMSP are generally small with gas having a low critical temperature like H<sub>2</sub>, O<sub>2</sub>, ... Therefore the membrane selectivity is ruled by a size sieving effect, the smallest molecules being the fastest permeating ones. For a given gas **i**, the driving force of the permeation through a membrane is its pressure difference between the two sides; under steady state conditions, the mass transfer is known to follow the first Fick law [4]:

$$J_i = -D_i \frac{dC_i}{dx} \quad (1)$$

with **D<sub>i</sub>**, the diffusion coefficient of the gas **i**, and **dC<sub>i</sub>/dx** the thermodynamic gradient of **i** within the membrane thickness. For a gas under low pressure, the concentration **C<sub>i</sub>** can be related to the fugacity **f<sub>i</sub>** as:

$$C_i = S_i \cdot f_i \approx S_i \cdot P_i \quad (\text{Nm}^3/\text{m}^3 \cdot \text{Pa}) \quad (2)$$

where **S<sub>i</sub>** is the sorption coefficient of the gas **i** for the considered membrane, and **P<sub>i</sub>** is the gas partial pressure.

Therefore the mass transfer **J<sub>i</sub>** can be written as:

$$J_i = D_i \cdot S_i \frac{\Delta P_i}{x} = P_i \frac{\Delta P_i}{x} \quad (\text{Nm}^3/\text{m}^3 \cdot \text{s}) \quad (3)$$

where **P<sub>i</sub> = D<sub>i</sub> · S<sub>i</sub>** is the permeability coefficient, and **x** the membrane thickness.

Hence for a binary mixture, the selectivity **α<sub>i/j</sub>** is equals to the ratio of the permeability coefficients:

$$\alpha_{i/j} = \frac{P_i}{P_j} \quad \text{i.e.} \quad \alpha_{i/j} = \frac{D_i}{D_j} \cdot \frac{S_i}{S_j} = \alpha_{D_{i/j}} \cdot \alpha_{S_{i/j}} \quad (4)$$

The usual **P<sub>i</sub>** unit is the Barrer: 1 Barrer = 10<sup>-10</sup> cm<sup>3</sup>(STP).cm/cm<sup>2</sup>.s.cm(Hg), i.e. 0.75.10<sup>-15</sup> m<sup>3</sup>.m/m<sup>2</sup>.s.Pa.

PVTMS [5] and PTMSP [6-7] can lead to very interesting gas separation membranes for H<sub>2</sub> and CH<sub>4</sub> purification because they are endowed with very high permeation fluxes; but these membranes are too sensitive to hydrocarbons vapours and lack also of selectivity for CO<sub>2</sub> [8-9]. This paper reports two ways of improving the membrane performances by the controlled introduction of selective groups in the polymer structure able to enhance the membrane stability and the CO<sub>2</sub> selectivity.

## 2. Materials and methods

*Bromination of polymers.* The halogenation was carried out with Br<sub>2</sub> or N-bromosuccimide (NBS) on polymer membranes, but it was shown that the substitution degree was better controlled with NBS. The substitution was confirmed by FTIR and quantified by elemental analysis. In the case of PTMSP the maximum Br content in the modified polymer was 27% wt., but only 60% wt. in the case of PVTMS [10].

*Membrane crosslinking.* 1,12-diaminododecane was used to react with the bromine-containing films to generate crosslinks through the polymer network. Thickness of films: 50-200 μm, T = 60 °C, [diamine] / [Methanol] = 0.5 mol/L, Duration of treatment: 60 min.

*Introduction of CO<sub>2</sub> selective groups in PTMSP.* The Bromine was used as reactive center to incorporate polyethyleneglycol groups (M-PEG) and ionic-liquid-like groups (imidazolium C<sub>4</sub>I).

*Introduction of ethylenoxide groups into polymer structure of PTMSP.* Reaction of bromine-containing polymer with low molecular poly(ethyleneglycol) monomethyl ether was carried out in presence of sodium under argon atmosphere at 25°C; THF was chosen as reaction solvent and the reaction duration was 24 h. According to elemental analysis data, it was established that the yield reached 90% of the brominated centers. Taking into account the degree of bromination (maximum 27% wt. for PTMSP) it was possible to introduce up to 60% wt. of PEG in the polymer structure.

*Introduction of ionic liquid like groups.* The modification of the brominated polymers required two steps. The first one was the quaternization of the bromine-containing polymers (PTMSP and PVTMS) with N-butylimidazol. Reaction was carried out under argon atmosphere at 25°C, CCl<sub>4</sub> was chosen as solvent with reaction duration of 48 h. The maximum reaction yield reached was about 40% in the case of PVTMS and 30% in the case of PTMSP, that are respectively 28% wt. and 21.5% wt. of N-butylimidazolium bromide.

The second stage is anion-exchange reaction with KPF<sub>6</sub>. The reaction was carried out under argon atmosphere at 25°C, in a THF-acetone solvent mixture (ratio 4:1) with reaction duration of 48 h. The reaction yield was almost quantitative according to the elemental analysis data.

Preparation of blends of PTMSP and PVTMS with low molecular model compounds. Two low molecular model compounds, i.e. M-PEG and C<sub>4</sub>I, were synthesized from chloromethyl trimethylsilane (CMTMS) to get molecular models analogous to the PTMSP and PVTMS structures in order to induce better compatibility when blending with polymers.

The schemes of synthesis of models M-PEG is represented on Figure 1. Reaction was carried out under argon atmosphere at 25°C in THF with reaction duration 24h. The reaction yield was up to 90% (as calculated using elemental analysis data).

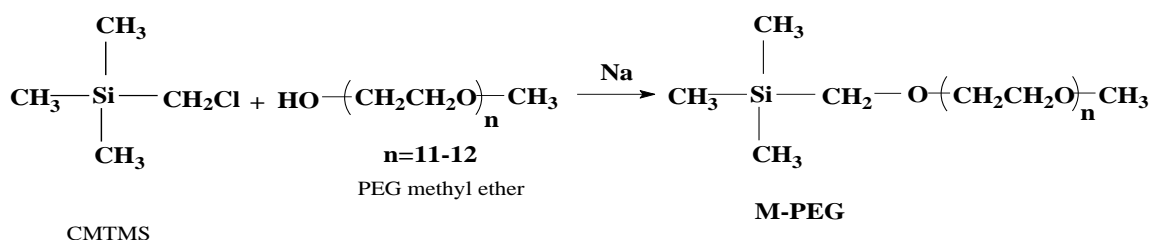


Figure 1. Scheme of synthesis of the model compound M-PEG used to prepare polymer blends

The scheme of synthesis of models C<sub>4</sub>I is represented on Figure 2. The first step of reaction was carried out under argon atmosphere and at 45°C in THF with a reaction duration of 12h; the yield of the halogen substitution was about 90% (elemental analysis). In the second step at 25°C, acetone was chosen as a solvent with reaction duration of 48h; the yield of second stage was almost quantitative.

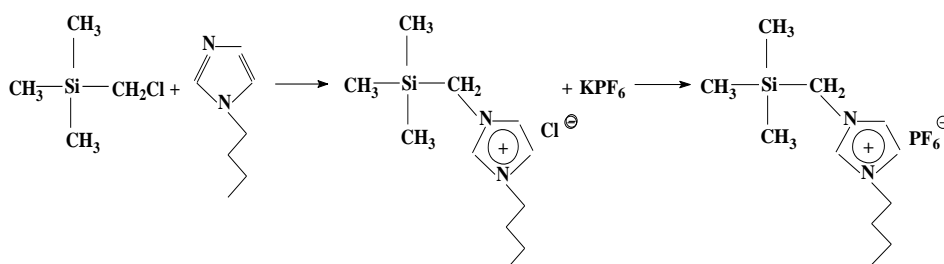


Figure 2. Scheme of the two steps synthesis of the imidazolium model C<sub>4</sub>I used for polymer blend

*Blend films.* They were prepared from mechanical stirring of polymer solutions with various weight amounts of the low-molecular models. The films were then obtained by casting from chlorobenzene or CCl<sub>4</sub> polymers solutions.

*Gas permeation experiments.* The well-known barometric time lag method was used to determine the permeability coefficients of O<sub>2</sub> and N<sub>2</sub> as reported elsewhere [11].

*CO<sub>2</sub> sorption measurements.* They were carried out with a magnetic suspension microbalance (Rubotherm, precision 0.1 µg) at 35°C, in a pressure range of 3 to 10 bar.

### 3. Results and discussion

Creation of the reaction centres is necessary on PVTMS and PTMSP (Fig. 3) for the introduction of groups which may provide high separation selectivity of CO<sub>2</sub>-containing gas mixtures and also to improve polymer stability towards hydrocarbons by chemical crosslinking. Bromine atoms can be one of such reactive centres. It was established earlier that bromination of PTMSP and PVTMS takes place at one of the silicon methyl groups, with formation of the following structure (CH<sub>3</sub>)<sub>2</sub>-Si-CH<sub>x</sub>-Br<sub>x</sub>, where x=1-3. The introduced bromine atoms were further used to induce polymer crosslinks to improve membrane chemical stability and to generate CO<sub>2</sub> selective groups.



Figure 3. Chemical structure of PVTMS (left hand side) and of PTMSP (right hand side)

#### 3.1. Crosslinking of bromine containing PVTMS

Polymer cross-linking is one of methods which can be used to obtain more stable membranes; the substitution of bromine with a di-functional reagent generates indeed covalent bonding between the polymer chains and thus reduces the swelling ability of the network towards chemical solvent. After reaction with the  $\alpha,\omega$ -diamino alkyl reagent, the modified polymers were found to be insoluble in organic solvents. Density of the cross-linking was regulated by bromine content in initial polymer; higher bromine content led to higher crosslinking density.

Data on gas permeability for cross-linked PVTMS films are given in table 1. As one can see, permeability coefficients decrease as cross-linking density increasing whereas ideal selectivity does not change (e.g.,  $\alpha_{PO_2/N_2}$ ). Obtained crosslinked PVTMS samples combine high gas separation selectivity parameters with the resistance to organic solvents of different types.

Table 1. Gas permeability of Br-containing PVTMS upon treatment by 1,12-diaminododecane.

Br content in polymer, % wt	P <sub>N<sub>2</sub></sub> , barrer		P <sub>H<sub>2</sub></sub> , barrer		P <sub>O<sub>2</sub></sub> , barrer		P <sub>CO<sub>2</sub></sub> , barrer		Selectivity $\alpha_{PO_2/P_{N_2}}$	
	before	after	before	after	before	after	Before	after	before	after
0	10	10	193	193	40	40	160	160	4	4
4	9	17	180	216	36	44	144	145	4	3
17	4.2	6	61	149	15.3	26	50	99	2.5	4
44	2	0,3	44	14	6	1,3	25	4	2.3	4
61	0.4	-	12	-	0.7	-	5.9	-	2.6	-

#### 3.2. Introduction CO<sub>2</sub> selective groups.

Two different groups were used to enhance PVTMS and PTMSP CO<sub>2</sub> affinity: ethylene oxide groups [12] and ionic liquids like groups [13], on the basis of quaternized N-butylimidazol. In order to

establish the influence of the nature and quantity of functional groups needed, as well as the best method of introduction of these groups to get reversible interaction with CO<sub>2</sub>, two ways of membrane materials preparation were investigated: a) the chemical modification of brominated PTMSP and PVTMS with CO<sub>2</sub> selective groups; b) the preparation of blends of PTMSP and PVTMS, with the low molecular compounds having structures close to chemically modified polymers.

### 3.3. Investigation of CO<sub>2</sub> sorption

Sorption was studied on the two types of PVTMS and PTMSP modified films, i.e. grafted and blend ones; the recorded measurements are presented on Figures 4-5 and compared to the initial PVTMS and PTMSP sorption data. The data shown correspond to measurements recorded at 35°C under increasing pressure of CO<sub>2</sub> up to 10 bar.

The difference of sorption capacity between the two initial polymers can be explained by the differences between the available free volumes of the two polymer networks; indeed it is well-known that PTMSP has a much higher free volume than PVTMS which induces in turn a much higher sorption capacity for gas [14]. With CO<sub>2</sub>, the recorded data indicate that the sorption capacity is at least two times the PVTMS capacity under the set experimental conditions used.

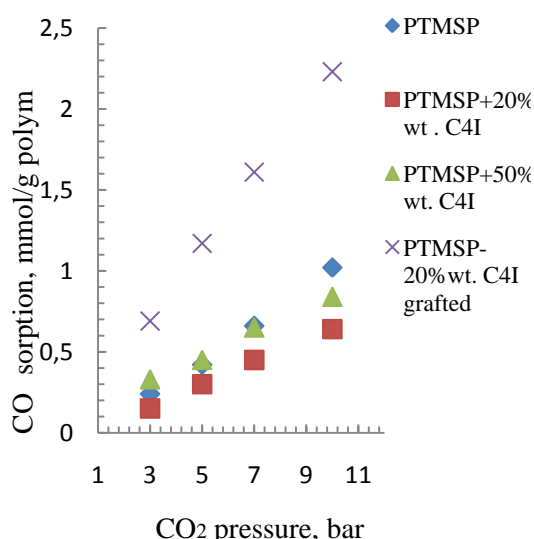


Figure 4. CO<sub>2</sub> sorption in PTMSP with ionic liquid-like groups (grafted polymers and blends) at T=35 C

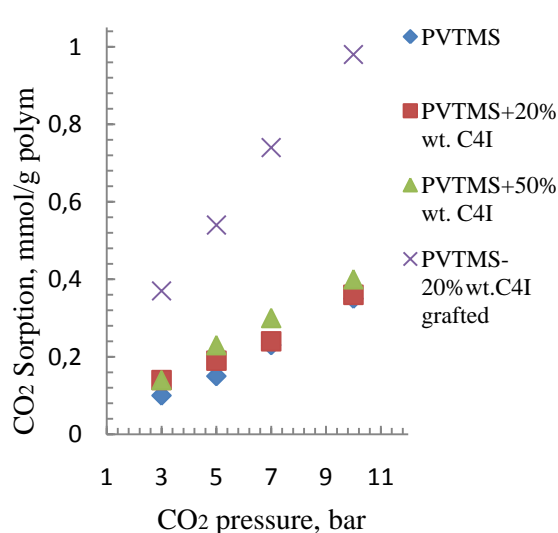


Figure 5. CO<sub>2</sub> sorption in PVTMS with ionic liquid-like groups (grafted polymers and blends) at T=35 C

For blends systems, either with PVTMS or with PTMSP, the sorption capacity was increased with the CO<sub>2</sub> pressure like with the native polymers, as expected. The blends having the higher amount of additive (here C<sub>4</sub>I in the Figures) led to the higher sorption values either PVTMS or PTMSP, but C<sub>4</sub>I gave slightly higher values than M-PEG. However, surprisingly, the CO<sub>2</sub> sorption was not increased at all. The same trend was also obtained with M-PEG blends (data not shown here).

For grafted polymers, the sorption levels obtained with the two C<sub>4</sub>I grafted polymer series were higher than the ones reached with M-PEG grafted polymers (data not given here). C<sub>4</sub>I grafted polymer exhibited a very different trend than blends; indeed, CO<sub>2</sub> sorption was markedly increased compared to the initial polymers, both with PVTMS and with PTMSP: in each case, the sorption was multiplied by a factor 2.5 to 3. Nevertheless, like for the case of native polymers, the C<sub>4</sub>I grafted PTMSP gave better results than C<sub>4</sub>I grafted PVTMS.

This last set of results seems to indicate that the high free volume characteristic of the PTMSP network was also saved in the grafted PTMSP structure. Obviously, the lower sorption values recorded

with the blend series indicate that it was not the case with the addition of low molecular weight models in PTMSP.

## Conclusion

It was shown that adequate modifications of PVTMS and PTMSP could give gas membranes more stable to organic vapors. With the two polymer series, CO<sub>2</sub> selective groups were successfully grafted on the trimethylsilyl substituent of the polymer backbone.

It was established that the level of sorption of the modified materials essentially depends on the method used for the introducing of the CO<sub>2</sub> selective moieties. Indeed the data showed that the CO<sub>2</sub> sorption in chemically modified polymers was higher than that in the blends having similar mass composition in the CO<sub>2</sub> selective moieties, i.e. either polyethyleneoxide groups or n-butylimidazolium groups.

Moreover with the grafted PVTMS and PTMSP polymers, it was possible to surpass the initial level of CO<sub>2</sub> sorption of the native polymer. For each type of grafted polymers, ionic liquids-like groups induced a much greater influence on CO<sub>2</sub> sorption properties than polyethylene oxide groups.

Therefore the two grafted polymer series can be considered as promising new materials for the purification of permanent gas from CO<sub>2</sub> rich mixtures.

**Acknowledgments.** The authors are grateful to the financial supports granted by the French Embassy of Moscow, ARCUS-Région Lorraine, LIA "Plate" CNRS and Russian Foundation for Basic Research (project 08-03-92497-НЦНИЛ\_a).

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