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Organic-Inorganic CO_2 Selective Membranes Prepared by the Sol-Gel Process

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Abstract: Composite membranes prepared from mixtures of 3-glycidoxypropyl trimethoxysilane (GPTMS) and different diamines containing polyether segments were synthesized by the sol-gel process. The membranes were obtained by coating asymmetric porous polyacrylonitrile (PAN) supports with the silane solutions. The composite membranes were characterized by single and mixed gas permeation and by atomic force microscopy. The selectivity increased by increasing the molecular weight of the poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol)bis(2-aminopropyl ether) (PAPE), and also with the addition of poly(ethylene glycol) (PEG) to the coating solution. The CO_2/N_2 selectivity values up to 75 and the CO_2/CH_4 selectivity values up to 20 were measured. High gas selectivity was also confirmed by measurements with mixed gas feed, although slightly lower than in the measurements with single gases.

Keywords: CO_2/N_2 separation, epoxy silane, gas separation, organic-inorganic membranes, sol-gel

INTRODUCTION

Atmospheric concentrations of several greenhouse gases (CO_2, CH_4, nitrous oxide) have increased by about 2 percent collectively since the

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industrial revolution began in the middle 19th century. In particular, anthropogenic CO_2 emission has increased dramatically due largely to the burning of fossil fuels, such as coal or natural gas for the production of electricity and petroleum or diesel for transportation. Increasing concentration of greenhouse gases is likely accelerating the rate of climate change. Unless significant controls are implemented, a continued rise in the atmospheric concentration of CO_2 is projected in the foreseeable future, due to increased consumption of fossil fuels. Several options exist to reduce CO_2 emission resulting from fossil fuel combustion, including increasing the efficiency of fossil fuel combustion systems, or replacing fossil fuels with renewable energy sources.

One important possibility which is currently under consideration is the modernization of power plants introducing effective membrane processes to drastically reduce the CO_2 emission. The potential of membrane technology for CO_2 recovery from post combustion processes has been recently reviewed by Favre (1). Membranes potentially compete with absorption in terms of energy requirement as soon as the CO_2 content in the feed exceeds 20%, which is relevant for many industrial plants. Membrane units to be used in post-combustion application have also the advantage of reduced size. Furthermore, membrane processes can be integrated in power plants in pre-combustion and oxyfuel processes in power plants.

A big challenge is to develop membranes able to effectively perform the aimed separation tasks. Although many processes require high temperature operation, which could only be provided by inorganic membranes, there are important tasks for polymeric membranes working at reasonably low temperatures (e.g., CO_2/N_2 separation around 60°C in post-combustion processes of coal power plants). Polymeric membranes have the advantage to be more easily up scaled and manufactured into modules. Carbon dioxide is quite soluble in many polymers. Polymeric membranes, which transport by the solution-diffusion mechanism, are usually preferentially permeable for CO_2. The CO_2 solubility is even larger in membranes containing ethylene oxide segments (2–5). Membranes containing amino groups are usually referred as separating by facilitated transport and have been also reported with large selectivity values (6,7).

In other words the CO_2 affinity to many polymers has a positive effect on CO_2 permeability. However, high solubility usually leads to high swelling, altering also the permeability of other gases through the membrane and leading to a decrease of selectivity when the measurements are performed with a mixed gas feed. It is therefore very important to develop strategies to keep high CO_2 solubility and minimize swelling which is not an easy task. An approach used by our group years ago was based on organic-inorganic networks containing ethylene oxide segments to improve solubility and hard inorganic segments to control swelling (8). At that time only preliminary characterization with single gases was performed. This approach was further developed in this paper with a much more complete characterization using mixed gases.

Additional advantages are known to be obtained when combining organic and inorganic materials. A review on organic-inorganic membranes for gas separation has been recently published (9). Organic components contribute to the formation of defect-free inorganic membranes and make it less brittle. On the other hand organic membranes can have their separation ability as well as chemical and temperature stability improved by the incorporation of an inorganic phase. It is a very common procedure to improve mechanical properties and thermal stability of polymeric (organic) materials by the incorporation of inorganic materials. Besides the addition of well-distributed fillers (aerosil, zeolites, layered silicates) to organic polymer matrices forming mixed-matrix membranes with tailored permeability properties, the preparation of hybrid organic-inorganic materials using the sol-gel process has been a subject of growing interest. Using the sol-gel process it is possible to grow the organic phase into an organic polymer matrix, with a very fine dispersion of the inorganic phase even at the molecular level.

EXPERIMENTAL

Materials

3-Glycidoxypropyltrimethoxysilane (GPTMS) was purchased from Gelest and used without further purification. The diamines poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol)bis(2-aminopropyl ether) PAPE (MW = 600 g/mol and 2000 g/mol), tetraethoxysilane (TEOS) and poly(ethylene glycol) (PEG) with molecular weight 600 and 1000 g/mol were supplied by Aldrich and used as received. Tetrahydrofuran (THF) was purchased from Merck and used as received.

Preparation of Composite Membranes

PAPE/GPTMS Membranes

The amine and epoxy functionalized silanes (GPTMS and PAPE) were mixed for 24 hours at room temperature in THF before coating. In some of the membranes PEG with molecular weight 600 or 1000 g/mol was added to the mixture to prepare membranes. The solutions were then used to coat asymmetric porous supports of polyacrylonitrile (PAN), forming composite membranes with thin selective layers.

PAPE/GPTMS/TEOS Membranes

The amine and epoxy functionalized silanes were mixed for 24 hours at room temperature in THF as mentioned before, but in this case TEOS and HCl 0,15 M were added in stoichiometric amounts and mixed for 24 hours more at ambient temperature, followed by drying for 2 hours at 80°C. The solution was cast on the asymmetric porous PAN supports.

In all the cases before preparing the composite membranes with organic-inorganic layers, the asymmetric porous PAN supports were previously coated with a 0.3 wt% PEBAX 4011 solution in n-butanol. This layer of PEBAX 4011 had only the purpose of partially closing the pores of the PAN support, avoiding that the organic-inorganic solution flows into the pores. After preparation of the composite membranes, they were dried for 2 h, and further coated using 1 wt.% PDMS solution in isooctane. This additional layer had the function of closing eventual pin-holes. The membranes were then dried in a vacuum oven at 60°C for 24 h. Membranes with a final selective layer thickness of 170–500 nm were in this way obtained.

Gas Permeability and Selectivity Measurements

The composite membranes were first characterized by single gas permeability measurements using the equipment based on a constant volume variable pressure method. A schematic representation of the system used is illustrated in Fig. 1.

The permeate flux through the membrane, J; was calculated using Eq. 1:

$$J = \frac{V \cdot 22.4}{R \cdot T \cdot A \cdot t} \cdot \ln\left(\frac{p_F - p_0}{p_F - p_{p(t)}}\right) \qquad (1)$$

where V is the permeate volume, R the ideal gas constant, T the temperature, A the membrane area, and t the measurement time; p_F is the feed pressure and p_0 and $p_{p(t)}$ are the pressures at the permeate side at the beginning and at the end of the measurement. The ratio between fluxes

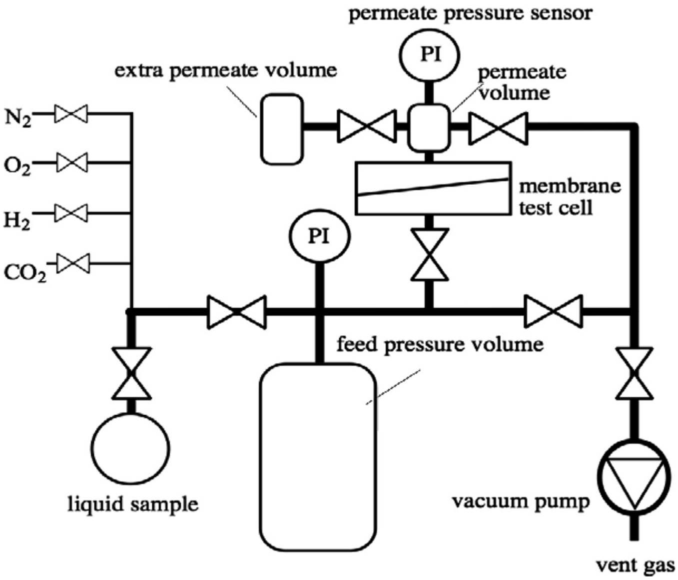


Figure 1. Scheme of the pressure increase measurement system.

of different gases A and B is the single gas selectivity (α), as calculated by Eq. 2:

$$\alpha_{AB} = \frac{J_A}{J_B} \tag{2}$$

The equipment allows setting a sequence of tests for up to 8 gases carried out at different temperatures (10–80°C), feed (0–2 bar) and permeate (0–100 mbar) pressures. In the current study membranes were tested at 30°C in the range of feed pressures 0.3–2 bar using a measurement cell with active membrane area of 34.2 cm^2.

The gas fluxes through the membranes were later measured using a feed gas mixture containing 25% vol. CO_2 and 75% N_2; 40% vol CO_2 and 60% vol CH_4 at 20°C at different feed pressures and standard permeate pressure 1.1 bar using the apparatus schematically shown in Fig. 2. The mixed gas measurement system equipped with the counter-flow gas permeation cell, flow, and pressure sensors and gas chromatograph (GC) for gas streams analysis allowed straightforward determination of gas fluxes, according to Eq. 3:

$$J = \frac{V\underline{p}}{A \cdot (f_R - f_P)} \tag{3}$$

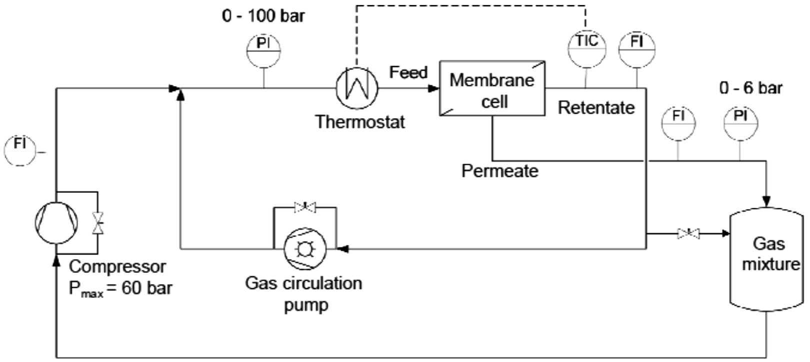


Figure 2. Scheme of the mixed gas permeation apparatus: PI – Pressure sensor, FI – Flow sensor, TIC – Temperature controller.

where V_P is the permeate volume flow rate, A is the membrane area, f_R and f_P are the fugacities of the retentate and permeate. The fugacity for a gas A was calculated using Eq. (4):

$$f_A = \Phi_A \cdot X_A \cdot P \tag{4}$$

where the fugacity coefficient Φ_A was determined by the Redlich-Kwong-Soave equation (10), using Aspen Plus, x_A is the molar fraction of gas A, and P is the total pressure. The selectivity was calculated by Eq. 2.

The GC used was a MTI Refinery Gas Analyser. Before permeation testing the GC was calibrated by one set of Messer gas mixture of CO_2 and N_2 or CO_2 and CH_4 with known composition to obtain the GC peak area as a function of the gas mole fraction. The membranes to be tested were conditioned under vacuum to extract any residual water from the selective layer material and thus to avoid a possible change of membrane properties during experiment.

Morphological Investigation by Atomic Force Microscopy

The structure of the membrane surfaces was observed using the tapping mode of the VEECO NANOSCOPE 4 Atomic Force Microscope. Measurements were carried out in the topographic and phase contrast mode with a phosphorus (n) doped Si probes (VEECO) having a natural oscilating frequency of 300 kHz. The samples were analyzed without any previous treatment or coating.

RESULTS AND DISCUSSION

PAN supports covered coated with 0.3% butanol/PEBAX 4011 solutions were used as substrate for the preparation of all membranes dicussed in this paper. The thin layer of PEBAX avoided that the casting solution, which would give rise to the selective organic-inorganic layer, would enter the pores of the PAN structure. The PEBAX coated PAN substrate were characterized. The CO_2 and N_2 fluxes of this supports were 0.7 and 0.06 m3 $m^{-2} h^{-1} bar^{-1}$, respectively. The average CO_2/N_2 selectivity was 14, which is much lower than the values obtained for the organic-inorganic membranes reported in this paper.

Single Gas Permeation Results

As mentioned before the membranes prepared in this paper aim to use the advantage of polyether segments for the preferential CO2 transport and at the same time control the swelling of the membrane by incorporating inorganic segments due to the addition and hydrolysis of TEOS in the coating solution. Preliminary results obtained with analogous systems (8) have already indicated that the gas transport properties of membranes prepared with PAPE having different molecular weight can widely change. The results presented in Fig. 3 confirm that the molecular weight

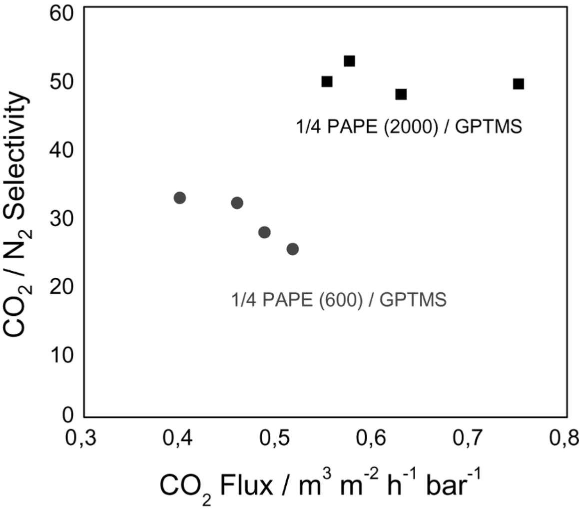
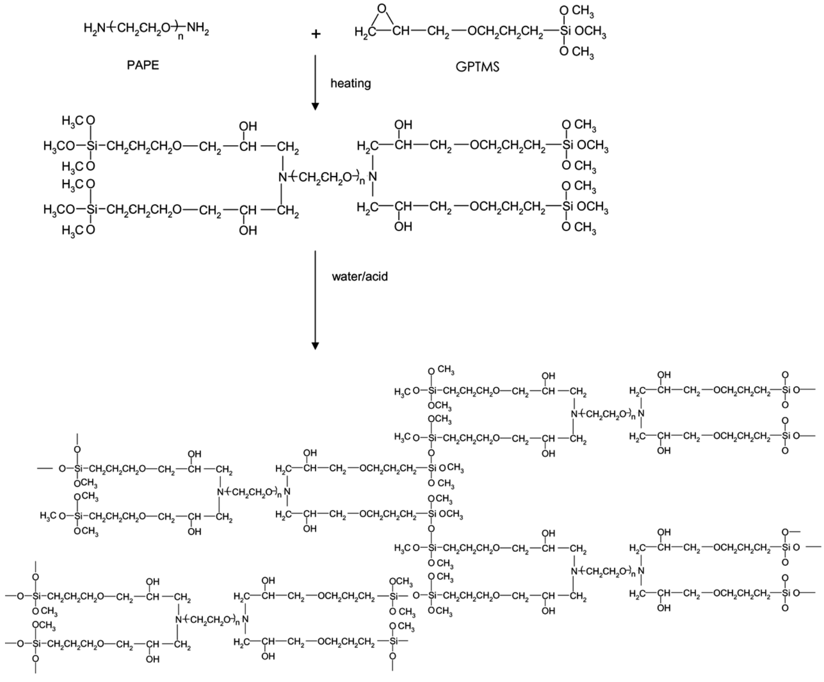


Figure 3. Effect of molecular weight on selectivity on the CO_2/N_2 selectivity and CO_2 flux of the prepared PAPE/GPMTS membranes.

of PAPE used for the membrane preparation have a significant influence on the gas permeation properties. It was observed that CO_2/N_2 selectivity increased with increasing molecular weight. It has been previously reported (8) for analogous membranes, prepared with PAPE 900 and PAPE 2000, that the crystillanity is higher when using PAPE with longer polyether segments. Therefore it is expected that membranes prepared with PAPE 2000 in this paper are also more crystalline than membranes prepared with PAPE 600. This higher crystallinity contributes to a lower permeability to H_2, N_2, O_2, and CH_4. The higher polyether content favors the CO_2 solubility in the membrane and makes it much more selective to CO_2/N_2 or CO_2/CH_4.

The CO_2 flux is clearly higher at lower GPTMS contents. PAPE is a difunctional linear molecule. The epoxy groups of GPTMS react with the amine terminal groups of PAPE, as shown in Scheme 1, and a further crosslinking is possible by the hydrolysis of the silane groups of GPTMS. Larger GPTMS contents lead to higher crosslinking degree, decreasing the free volume and the membrane permeability. The CO_2/ N_2 selectivity



Scheme 1. Reaction between GPTMS and PAPE and further hydrolysis and condensation of silane moieties, forming the organic-inorganic hybrid.

slightly increases by increasing the GPTMS content for both of the membranes prepared with PAPE 600 and 2000, as shown in Figs. 4 and 5. Different membranes with practically the same composition are plotted to give an idea of the measurement data dispersion. The membranes were prepared from different batches in different days. Factors which might lead to the observed dispersion are slight changes in the room temperature during membrane solution preparation and casting, leading to different extension of hydrolysis/condensation, environment humidity during casting and membrane characterization, small differences in coating thickness, use of porous supports from different batches, etc.

The unique interaction between polar ether oxygen atoms and CO_2 has attracted much interest, increasing solubility and membrane permeability. Generally, polar groups in a polymer matrix might improve also polymer chain packing efficiency and promote chain crystallization with direct consequences for the diffusivity and permeability. Considering now the CO_2 solubility, lone electron pairs on oxygen (ether group) in the polymer led to strong Lewis acid-Lewis base interactions to the C atom of CO_2 (11). The interaction stimulates the solubility and increases the CO_2 permeability. This is clearly the case of poly (ethylene oxide) or poly (ethylene glycol). The CO_2 transport for these materials follow a solution-diffusion mechanism, which is highly influenced by the content

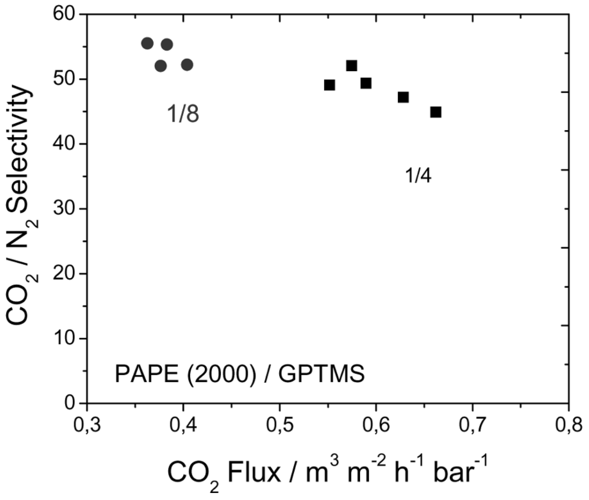


Figure 4. Effect of the GPTMS content in the coating solution on the CO_2/N_2 selectivity and CO_2 flux of the prepared membranes (PAPE/GPMTS membranes were prepared with PAPE 2000).

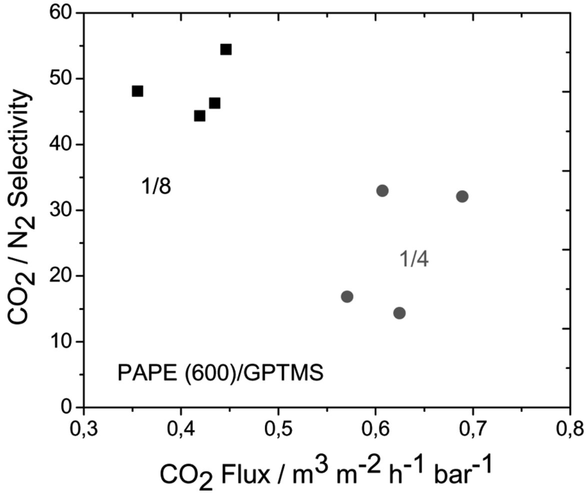


Figure 5. Effect of the GPTMS content in the coating solution on the CO_2/N_2 selectivity and CO_2 flux of the prepared membranes (PAPE/GPMTS membranes were prepared with PAPE 600).

of interactive groups able to increase solubility and by the interchain distance, crystallinity, and the interphase space (in case of phase segregation), which directly affect the diffusivity. We can see from Fig. 6 that

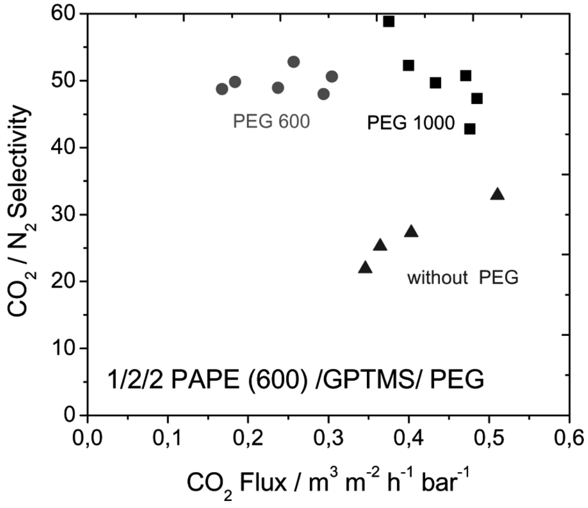


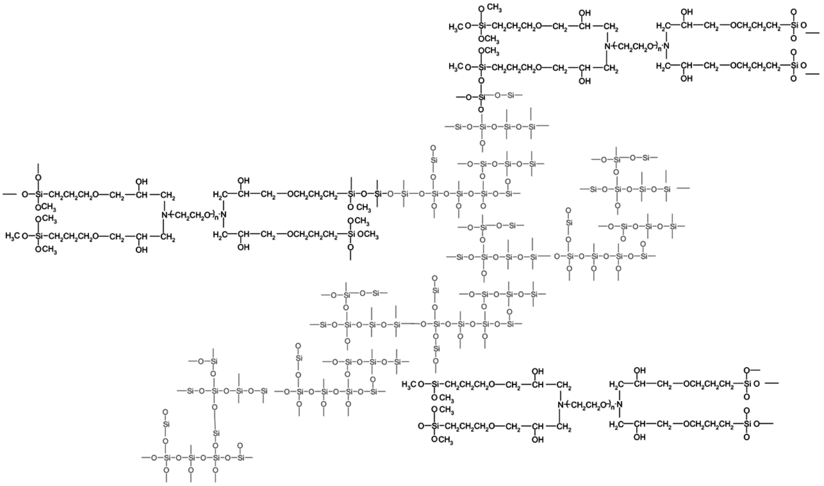
Figure 6. Effect of PEG content on the CO_2/N_2 selectivity of PAPE (600)/GPMTS/PEG membranes.

the selectivity for CO_2/N_2 increases when PEG is added to the coating solution. Additional factors that seem to have an effect on the permeabilities are the PEG segment length, the amount of rigid segment that is dissolved and the morphology of the rigid segments (12). The CO_2/N_2 selectivity values shown in Fig. 6 are quite good when compared to values reported in the literature for other polymeric materials (2). The presence of polyether segments in the organic-inorganic network made the membranes particularly permeable for CO_2. Higher PEG molecular weight led to higher flux, since the longer segments promote a higher content of ether groups in the membrane.

Beside the ether groups, tertiary amines and hydroxyl groups are known to contribute to the membrane permeability to CO_2. However, opposite to the ether groups, amine and hydroxyl support the facilitated transport of CO_2 molecules. Hydroxy groups "react" with CO_2 forming bicarbonate ions like in the case of polyvinylalcohol (13). Tertiary amines (14) becomes reactive with CO_2 only in the presence of water, forming then HCO_3^-. Adding more PAPE than the expected stechiometric ratio would favor the presence of non-reacted primary amine groups. In this case the contribution of facilitated transport would be promoted. By increasing the PAPE content not only the amine groups are increased, but also the ether groups, contributing for high CO_2 solubility both due to facilitated transport and solution-diffusion mechanism. On the other hand, by increasing the GPTMS the solubility can only increase due to the OH groups, which are formed when the epoxy group is opened.

Now taking into account the TEOS content in the membrane, TEOS will contribute to the formation of the network by adding more Si-O-Si segments, as shown in Scheme 2. These silica-rich segments might be embedded in the PAPE/GPTMS network being covalently bonded to it or might also polycondensate apart from the network, segregating and forming separated domains, as shown below by atomic force micrographs in Figs. 11 and 13. TEOS seems to decrease the available free volume for diffusion in the organic-inorganic polymer matrix with immediate consequences to the permeability (Fig. 7). The gas fluxes decrease and at the same time the selectivity becomes higher.

In order to be competitive not only high selectivity values must be reached, but high fluxs are decisive. Membranes based on blends of copolymers and PEG with considerably quite high permeability values (ca. 190 Barrer) and $CO_2/N_2 = 47$ have been recently reported by Car et al. (4). If those membranes would be manufactured with selective layers of thickness up to 500 nm, as reported in this work, the CO_2 fluxes would be around $1\,m^3\,m^{-2}\,h^{-1}\,bar^{-1}$. PAPE (2000)/GPTMS membranes shown in Fig. 7 have CO_2/N_2 selectivity ca. 50 and CO_2 fluxes around



Scheme 2. Organic-inorganic hybrid obtained from the reaction between GPTMS, PAPE, and TEOS, followed by hydrolysis and condensation.

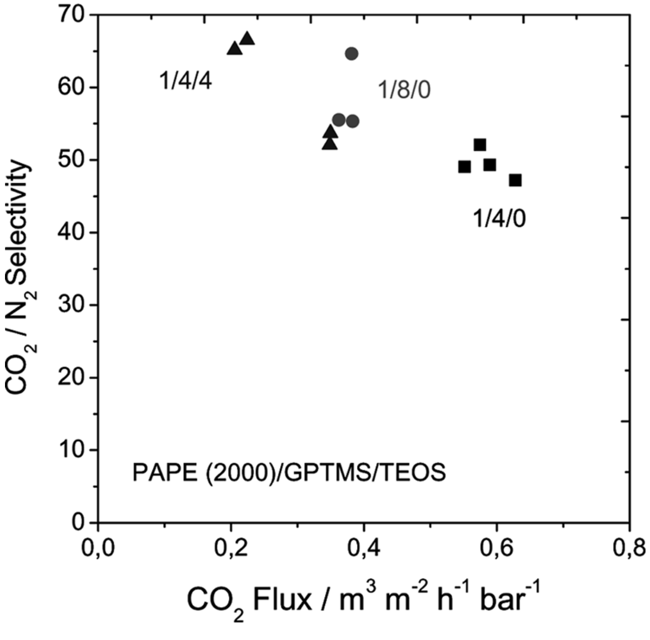


Figure 7. Effect of GPMTS and TEOS contents on the CO_2/N_2 selectivity of PAPE (2000)/GPMTS/TEOS membranes.

$0.6\,m^3\,m^{-2}\,h^{-1}\,bar^{-1}$, which is more or less the same range of good membranes reported in the literature. With fluxes around $0.4\,m^3\,m^{-2}\,h^{-1}\,bar^{-1}$, CO_2/N_2 selectivity higher than 60 could be obtained by increasing the GPTMS content.

Mixed Gas Permeation Results

The variation of the permeability between the pure gas and mixed gas has always been observed because the transport of a component in the mixture of gases is significantly affected by presence of other components (15–17). This discrepancy is believed to arise from the effect of penetrants competition, gas phase non-ideality, plasticization phenomena, and gas polarization (11–13). For these reasons, mixed gas permeation measurements were conducted additionally to single gas permeation tests for CO_2, N_2 and CH_4. Measurements with mixed gas (Fig. 8) indeed showed a slight decrease of selectivity, but the values are still quite high. The results of the membranes prepared from solutions with TEOS were unexpected. While in experiments with single gases, the membranes with TEOS had the highest CO_2/N_2 selectivity values, in experiments with mixed gas feed the selectivity was more or less the same as that of membranes with similar PAPE/GPTMS without TEOS. Much more decisive with mixed gas feed was the GPTMS content. Probably the silica-rich

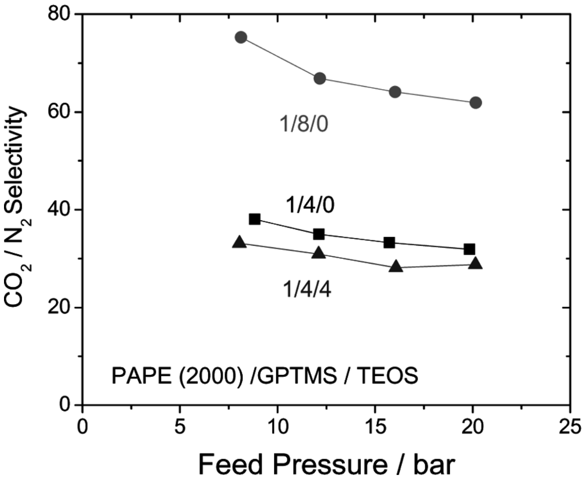


Figure 8. Characterization of PAPE (2000)/GPMTS/TEOS membranes using a 25/75 CO_2/N_2 mixed feed gas.

Table 1. A comparison of gas selectivity values measured with single gases and with mixed gas feed (mixture with 25% CO_2 and 75% N_2)

	Mixed gas (25% CO_2 75% N_2)		Single gas	
Membrane	Pressure(bar)	$\alpha CO_2/N_2$	Pressure(bar)	$\alpha CO_2/N_2$
1/4 PAPE(2000)/ GPTMS	8	38	0.3–2	52
1/4/4 PAPE(2000)/ GPTMS/TEOS	8	33	0.3–2	67
1/2/2 PAPE(600)/ GPTMS/PEG(600)	8	59	0.3–2	53

segments originated by the introduction of TEOS segregate and are not so effective in controlling swelling. The GPTMS on the other side increases much more the crosslinking degree and reduces swelling when the feed contains CO_2.

Surprisingly, as shown in Table 1, the selectivity CO_2/N_2 obtained in the mixed gas tests for the samples prepared with PEG was greater than those of single gas tests and the values were higher than for membranes with TEOS and without TEOS and PEG. PEG600 might be conveniently packed between the network polyether segments, which are of the same size. As a consequence the chains mobility was reduced with the membrane becoming less susceptible to swelling.

Table 2 shows the characterization of PAPE/GPTMS membranes containing PEG1000, in this case using a gas mixture feed of CO_2 and CH_4. For membranes prepared with PAPE 2000 there was practically no difference between the selectivity measured with single gases and with

Table 2. A comparison of gas selectivity values measured with single gases and with mixed gas feed (mixture with 40% CO_2 and 60% CH_4)

	Mixed gas (40% CO_2 60% CH_4)		Single gas	
Membrane	Pressure(bar)	$\alpha CO_2/CH_4$	Pressure(bar)	$\alpha CO_2/CH_4$
1/2/2PAPE(2000)/ GPTMS/PEG(1000)	8	17	0.3–2	17
1/2/2PAPE(600)/ GPTMS/PEG(1000)	8	15	0.3–2	18

gas mixture. Membranes prepared from PAPE 2000 are more crystalline (8) than analogous membranes prepared from lower molecular weight PAPE, as shown in a previous paper. The higher crystallinity avoids the swelling of the membrane by CO_2 and a consequent increase in diffusivity of other gases. For membranes prepared with PAPE 600 the

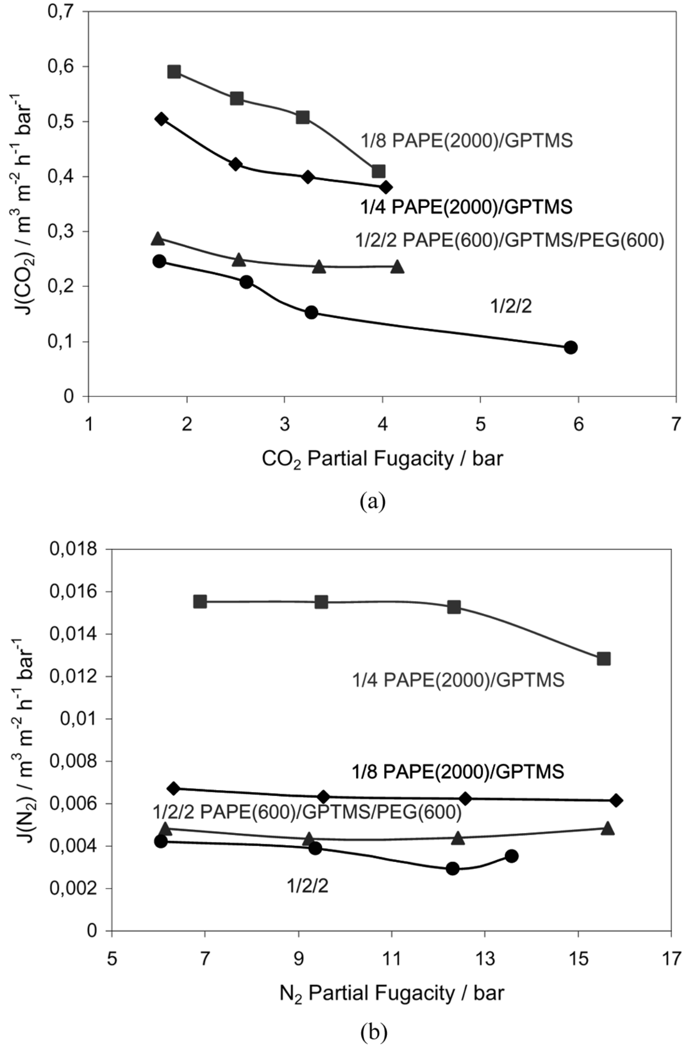


Figure 9. Flux of (a) CO_2 and (b) N_2 as a function of their fugacity in the feed for membranes with different compositions.

selectivity with gas mixture was lower. These membranes are rather amorphous and more susceptible to swelling by CO_2, which then led to an increase of diffusivity of other gases and lower selectivity. Furthermore, there might be an influence of compatibility and incorporation of the PEG molecules into the organic-inorganic matrix. Probably when the PEG molecule is larger than the polyether segment in the organic-inorganic network, packing is not effective and it rather segregates. An AFM micrograph depicted in Fig. 13 indicates phase segregation for 1/2/2 PAPE 600/GPTMS/ PEG 1000 membranes.

Figure 9 shows how the flux of CO_2 and N_2 is affected by the fugacity of these gases, which is directly related to their partial pressure (Eq. 4). The flux of N_2 practically does not change with pressure. Only for 1/4 PAPE (2000)/GPTMS membranes above 12 bar a slight flux decrease (ca $0.003\,m^3\,m^{-2}\,h^{-1}\,bar^{-1}$) is observed. This might be due to a membrane compaction by pressure. No decrease is observed for analogous membranes with much more GPTMS, confirming that a higher degree of crosslinking makes the membrane not only less susceptible to swelling, but also more mechanically stable and less susceptible to compaction under pressure. No flux change was observed also with membranes containing PEG. In contrast to the results obtained for nitrogen, the CO_2 flux decreases up to 30% by increasing the fugacity from ca. 1.5 to 4 bar.

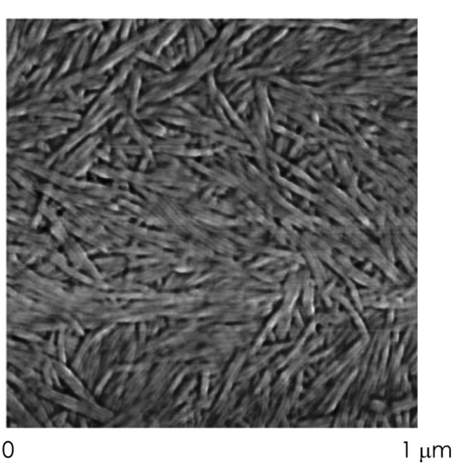


Figure 10. AFM micrographs (phase contrast) of 1/4 PAPE(2000)/GPTMS membranes.

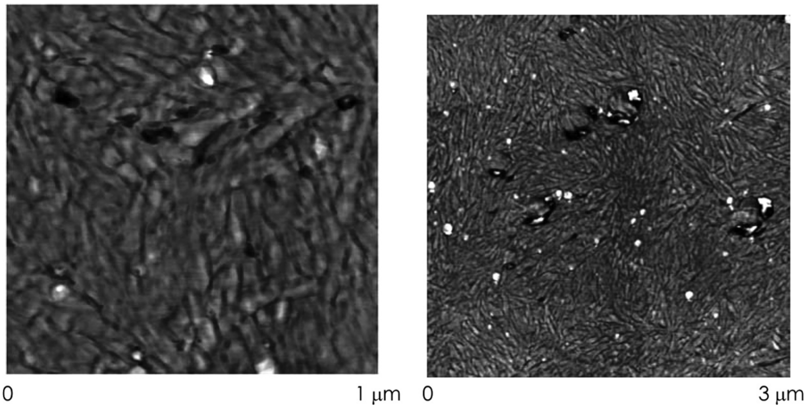


Figure 11. AFM micrographs (phase contrast) of 1/4/4 PAPE(2000)/GPTMS/TEOS membranes.

Membrane Morphology

Figures 10 to 12 show the AFM micrographs of PAPE/GPTMS/TEOS membranes. A lamellar structure can be seen for all membranes. The morphology of the membrane prepared without TEOS is very regular, reflecting separated lamellae formed due to the presence of the long polyether segments, which are part of the organic-inorganic network. As the TEOS content is increased, the regularity is slightly decreased and the lamellae become broader due to the incorporation of silica segments

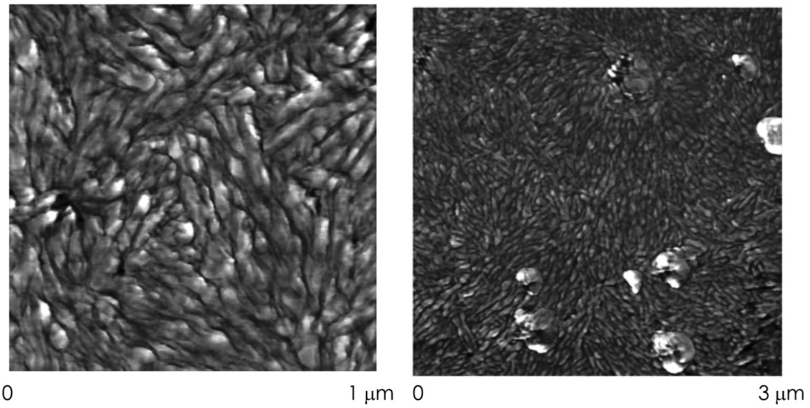


Figure 12. AFM micrographs (phase contrast) of 1/4/8 PAPE(2000)/GPTMS/TEOS membranes.

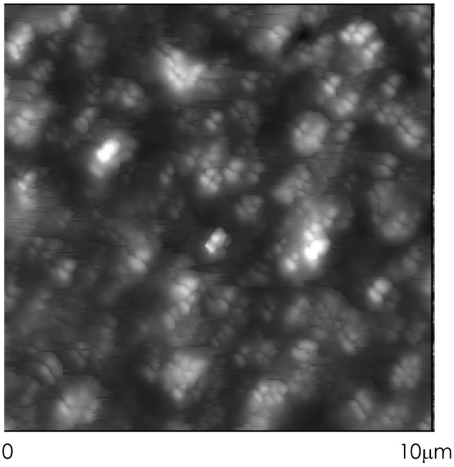


Figure 13. AFM micrographs (topographic contrast) of 1/2/2 PAPE 600/GPTMS/ PEG 1000 membranes.

coming from the hydrolyzed TEOS. Some more microscopic phase separation with segregation of silica-rich domains can be also seen with increasing TEOS contents.

Figure 13 for 1/2/2 PAPE 600/GPTMS/PEG 1000 membranes shows that the addition of PEG to the coating solution leads to a segregation in a larger scale, with PEG rich phases demixing from the organic-inorganic matrix.

CONCLUSION

The organic-inorganic hybrid membranes prepared from GPTMS and PAPE were especially interesting for gas separation. Due to the presence of polyether segments, amine and hydroxyl groups the transport of CO_2 was prevailing compared to other permanent gases. In experiments with single gases, the hybrid membranes prepared with coating solutions containing TEOS and therefore leading to higher inorganic content exhibited higher CO_2/N_2 selectivities than those of membranes prepared just from GPTMS/PAPE. For mixed gases much more decisive was the content of GPTMS. Additionally the selectivity increased when PEG was added to the coating solution for membrane preparation. CO_2/N_2 selectivity values up to 75 and CO_2/CH_4 selectivity values up to 20 were measured. Measurements with mixed gas feeds containing CO_2 are important since CO_2 might swell the membrane and thus affect the selectivity and the permeability. Measurements with mixed gas showed indeed a slight decrease of selectivity with the increase of feed pressure, but the obtained values are still high compared to the other available membranes.

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