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A Novel Poly(4-methyl-2-pentyne)/TiO$_2$ Hybrid Nanocomposite Membrane for Natural Gas Conditioning: n-Butane/Methane Separation

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Summary

Poly(4-methyl-2-pentyne)/TiO$_2$ hybrid nanocomposite membranes were investigated for natural gas conditioning. Tailor-made PMP with 35% of cis-content was identified as attractive material to prepare nanocomposite membranes; it presented good stability towards organic vapours and optimal properties for n-butane/methane separation. The PMP/TiO$_2$ hybrid nanocomposite membranes presented an improvement of n-butane permeability and n-butane/methane selectivity. The addition of TiO$_2$ nanoparticles to the PMP enhanced the selectivity more effectively than fumed-Silica and, it is attractively higher than those reported until now in the open literature.

Introduction

Nowadays, natural gas (NG) is a fuel available to operate power generators, compressor stations, offshore platforms, internal-combustion engine driven vehicles, etc. In many cases it contains unacceptable levels of higher hydrocarbons, hydrogen sulphide and carbon dioxide. Use of untreated NG in turbines and engines causes operating problems and leads to increased maintenance cost and downtime. A reliable and proven membrane process for gas conditioning could offer an alternative to upgrade raw natural gas. [1-8] After 1980s, among the polymeric membranes (membranes with rubbery selective layer) for separation of hydrocarbon mixtures as well as organic components removal from permanent gas streams great attention was attracted by disubstituted polyacetylenes, which are glassy polymers having the highest known gas permeability.[7-18] Polyacetylenes such as poly(4-methyl-2-pentyne) (PMP),[7,8,16] poly(1-trimethylsilyl-1-propyne) (PTMSP)[12,13,15] and poly(1-trimethylgermyl-1-propyne) (PTMGP)[17,18] are

more permeable for large organic molecules (condensable gases) than for permanent gases. This property has been attributed to an extremely high fractional free volume resulting from an unusually loose packing of stiff polymer chains containing carbon-carbon double bonds and bulky side-chain groups. [15-20] PTMSP has the highest known permeability and selectivity for separation of organic vapours from permanent gases. [15,20,21] However, practical use of this polymer is limited due to its solubility in higher hydrocarbons present in natural gas. In this work, we present PMP and PMP/TiO$_2$ nanocomposite membranes with enhanced gas permeability. The n-butane/methane selectivity in PMP/TiO$_2$ nanocomposite membrane is attractively higher than those reported until now in the open literature.

PMP is an alternative membrane material for the aforementioned separation process due to its higher resistance towards organic vapours, it can be further improved by adding inorganic filler (e.g. fumed silica) into polymer matrix leading at the same time to enhanced selectivity and permeability.[3,8,20,22,23] These membranes made from organic/inorganic hybrid materials or nanocomposites known as well as mixed matrix membranes (MMM)[24,25] allow overcoming the "upper bound" of the Robeson plot.[26] Thus, in order to develop a membrane material with high hydrocarbon selectivity and good perspective for application in natural gas conditioning, a tailor-made PMP was selected and studied as potential precursor to prepare nanocomposite membrane with TiO$_2$ nanoparticles.

Experimental part

The monomer, 4-methyl-2-pentyne, was synthesized from methyl isobutyl ketone [27]. The purification of the monomer and solvent cyclohexane for polymerization was performed as it was described in [28]. Niobium pentachloride catalysts (99.9%) and cocatalyst Et_3SiH (97%), purchased from 'Fluka', were used as received. A solution of $NbCl_5$ (1.945 g, 7.0 mmol) and Et_3SiH (0.812 g, 7.0 mmol) in cyclohexane (360 ml) was loaded in a glass ellipsoid-shaped reactor in a flow of high-purity argon and rigorously stirred at 25°C for 30 min. Then the mixture was cooled (+3°C) for 5 min and 4-methyl-2-pentyne (28.7 g, 350.0 mmol) was added and the reactor was sealed.

The reactor was kept at +3°C during 6 h. After 24 h, the reactor was unsealed and the reaction mixture was treated with methanol to deactivate the catalyst. The polymer was then dissolved in CCl_4 (1.0 l), precipitated into methanol (5.0 l), filtered, and dried in air over a 24-h period. Then the isolated polymer was redissolved in CCl_4, precipitated into methanol, and vacuum dried for the polymer yield calculation.

The molecular weights were determined by gel permeation chromatography (GPC) using a Waters 600 Powerline GPC system, equipped with 2 mixed-C Pl-gel 5m columns (Polymer Laboratories), a Waters 410 refractive index detector and a Wyatt Dawn Lightscattering detector (temperature at 60°C; flowrate = 1 ml/min; cyclohaxene for polymer solution). The intrinsic viscosity of the polymer solutions in CCl_4 were measured with an Ostwald–Ubbelohde viscometer at 25 °C.

The chemical structure of macromolecules was studied by ^{13}C NMR spectroscopy using 4% PMP solutions in C_6D_{12}. ^{13}C spectra were recorded on a Bruker MSh-300 spectrometer operating at 75.47 MHz (the acquisition number is 12 000). The content of

cis- and *trans*-units in PMP samples was quantified from the ^{13}C NMR spectra using a Bruker 1D WinNMR program for treating poorly resolved spectra.

Dense isotropic membranes were prepared by casting of a polymer solution on a PTFE casting beaker with a flat bottom. In order to prevent the influence of preparation history on membrane properties, all samples were prepared under the same conditions: controlled solvent evaporation for 72 hours at ambient conditions, mechanical membrane removal from PTFE surface and overnight drying in vacuum at 30° C. The polymer solution was prepared in cyclohexane at room temperature (3 %.wt of polymer) by stirring for 24 h.

For nanocomposite membrane, polymer solutions were prepared using cyclohexane/THF mixture (80/20 wt/wt) mixed with TiO_2 sol received from SINTEF ([Ti] = 0,34 mol/L in THF; $D_{Ti\text{-}alcoxo}$= 9,4 ± 3.6 nm) and then, it was stirred for 20 min. Obtained polymer/TiO_2 solution with TiO_2 content of 10 - 40 wt.% (in relation to polymer) was used for membrane formation at conditions as described for pure polymer. Membranes with thickness of 50-120 µm and thickness difference less than 2 µm were obtained and used for gas transport experiments.

Single gas transport properties of CH_4 and n-C_4H_{10} in PMP and nanocomposite dense membranes were determined with a constant-volume/variable-pressure (time-lag) method at 30°C. The feed pressure was 180 mmHg for all gases and the permeate pressure as a function of time was obtained. Permeate pressure did not exceed 10 mmHg. Before each gas permeation experiment, the permeation cell with the polymer membrane under study was evacuated for 12 h. Each measurement was repeated at least 3 times for 3 membrane samples of the same composition and history.

Mixed methane and n-butane permeation experiments were carried out at an experimental facility designed for this purpose. The facility allows studying permeation of binary gas mixtures through flat membranes having wide range of permeances. The gas mixture can be prepared directly in the facility by controlled mixing of individual gases as well as beforehand prepared gas mixtures can be used. The gas flow and pressure of the Feed and Sweep were measured on the entrance to the measurement cell. The compositions of the Feed, Retentate and Permeate side were analyzed by an Agilent 9890N gas chromatograph. Nitrogen was used as a Sweep gas since it has one of the lowest gas permeability coefficients, thus mostly preventing its back diffusion from the permeate side to the feed side of the membrane.

Results and Discussion

Polymer Properties

After an extensive study of 4-methyl-2-pentyne polymerization by different catalyst systems based on Ta, Nb and W, [27,28] PMP samples with different and well-defined microstructures were synthesized. It was demonstrated that by varying synthesis conditions one can control the molecular characteristic (molecular masses and intrinsic viscosity) and microstructure (ratio of *cis/trans-* isomerism) of PMP, and thus, it allows to manipulate polymer properties, stability towards organic solvents and gas permeability.

The $NbCl_5$-based catalysts are the most effective for synthesis of PMP. [27] Polymerization with Nb-containing systems both $NbCl_5$ and $NbCl_5/Et_3SiH$ gives

quantitative yields of polymeric products (90%) with high molecular weight (See Table 1). The use of co-catalyst (Et_3SiH) essentially affected the intrinsic viscosity (from 1.5 to 4.7 dl/g) and polymer microstructure (cis- content from 35 to 50%). These polymers are insoluble in almost all solvents except carbon tetrachloride, cyclohexane and carbon disulfide, and are characterized by good film-forming properties and high gas permeability (P_{O2}= 1000-2000 Barrers and O_2/N_2 selectivity of 2.0 - 2.5). The densities of films prepared from these polymers by solution casting were almost similar (Table 2) what indicates that free-volume in all samples could also be similar.

In this way, "tailor-made" PMP synthesized by $NbCl_5$-based catalysts demonstrated to have unique properties as membrane material, which can be satisfactorily used in separation process of mixtures containing higher hydrocarbons. On basis of these results, polymerization condition was chosen to synthesize PMP with specific properties for gas separation, stability towards organic solvents and big amount to produce membrane at pilot-scale.

Gas permeability

After obtaining PMP samples with well-defined microstructure, methane and n-butane mixed gas (98.4/1.6 mol/mol) permeability of these polymeric membranes were tested. The mixture of methane and n-butane used in this work is a typical natural gas composition. Although methane permeability for all membranes (samples from 35 to 50% of cis- content) was found to be almost constant, n-butane permeabilities for PMP samples with lower cis- content were higher than for the PMP1 sample (Table 2). Because the polymer microstructure is responsible for many properties of a dense

membrane; in di-substituted polyacetylenes, the high permeability and selectivity for large organic vapours is attributed to their high free-volume and free-volume-elements structure, this behaviour is related to the bulky side group (isopropyl) which severely hinders loose packing. [15,16,29] Therefore, alterations in the polymer packing by ordering of the chains would induce changes in the free-volume of the polymer. These changes could be not only in size but also in the distribution of free-volume elements which depends on polymer microstructure, and thus, differences in gas permeability of PMP samples could be mainly attributed to polymer microstructure. [30]

In order to improve the performance of membranes made from PMP for n-butane/methane separation, PMP/TiO$_2$ nanocomposite membranes were prepared. Hybrid organic/inorganic membranes are considered as a promising alternative to conventional polymeric membranes, [8,20,31] the use of inorganic inert or active fillers dispersed into the matrix of the selective polymer can lead to membranes with improved separation properties, stability and durability. The PMP sample demonstrating higher n-butane permeability accompanied with a high n-butane/methane mixed gas selectivity was selected to prepare nanocomposite membranes. This selected polymer can be synthesized in quantities big enough for at least pilot scale production of thin film composite membranes.

Alcohol free sols of TiO$_2$ nanoparticles synthesized by SINTEF were used for the preparation of nanostructured hybrid membranes having increased mixed gas selectivity α(n-C$_4$H$_{10}$/CH$_4$) > 15. TiO$_2$-sol was chosen for membrane preparation because it has a good compatibility with PMP-solutions. In addition, it has been shown that nanoscale TiO$_2$ reinforcement brings new optical, electrical, physicochemical properties attained at

very low TiO_2 content, which makes the polymer TiO_2 nanocomposites as a promising new class of materials. [32,33]

The pure methane permeability for nanocomposite membranes shown in Figure 1A increases when TiO_2 nanofillers are added to the polymer matrix. For example, in PMP membranes containing 33 wt.% of TiO_2, the permeability was approximately 70% higher than for the unfilled PMP membrane. Membrane samples containing 40 wt.% of filler were not used for time-lag (single gas) measurements due to membrane brittleness. As reported before, for high free-volume glassy polymers the Maxwell model is not fulfilled (see Figure 1A), the permeability in this case increases along with the filler content increase. [8,20] However, in our case the inorganic nanoparticles disrupted polymer chain packing leading to higher free volume values and consequently increasing the gas permeability.

The density values obtained by the buoyancy method or from the membrane geometry can be directly related with the free volume of the polymers, as well as the density of a binary polymer/filler system can be calculated by using the additive model. [7] In Figure 1B, the density obtained by the three methods as a function of TiO_2 content is presented. The experimental density increased with filler content increase. Density values obtained by two experimental methods for samples containing 0-20 wt.% of TiO_2 are close to each other and are slightly higher (in the error range) than that calculated by the additive model. For samples with 25-40 wt.% of TiO_2, we observed divergence of experimental data from each other and from theoretical values.

Membranes with high TiO_2 content are significantly less dense than that estimated by the additive model; values obtained from membrane geometry are lower than the ones

obtained by buoyancy method leading us to the conclusion of increased free volume in these membranes. The deviation between two experimental values can be explained by the possibility that the liquid used in the buoyancy method (perfluorinated solvent system 3M Fluorinert^{TM} FC-77) could have been adsorbed into the large free volume voids of the nanocomposite membrane. This behaviour was unexpected since perfluorinated liquids have the biggest known contact angle to all known substances and it was assumed that it would prevent sorption of the solvent molecules into the polymer matrix. As it is seen from density of samples having 0-20 wt.% of filler, the assumption is correct for membranes having "low" (in terms of acetylenic polymers) free volume because membranes with highest free volume have the best gas separation properties. Gas permeability (Figure 1A) is significantly increased compared to membranes with lower TiO_2 content, and thus, membranes with 33 and 40 wt.% of TiO_2 would present higher free-volume.

Single gas measurements give additional support to the aforementioned assumption. For samples with 0-20 wt.% of TiO_2, CH_4 permeability changes insignificantly (Figure 1A), whereas for 25 and 33 wt.% of TiO_2, the permeabilities increases nearly 70% and n-C_4H_{10}/CH_4 single gas selectivity drops to 1.1 what demonstrate that free-volume has been extremely increased. Single gas and mixed gas experiments were carried out at significantly different conditions and results of these experiments can not be compared directly. Nevertheless single gas experiment results support the general idea of changes of the membrane free volume with TiO_2 content.

The challenge of this work was to develop PMP/TiO_2 nanocomposite membrane with simultaneously improved properties of mixed gas permeability and n-C_4H_{10}/CH_4

selectivity for natural gas conditioning. The effect of the TiO_2 filler content on the n-butane (mixed gas) permeability and selectivity at 30° C is shown in Figure 2A. For PMP/TiO_2 sample with 40 wt.% of filler, the n-C_4H_{10}/CH_4 selectivity was approximately 34 and, the permeability increased by 80% relative to PMP pure-polymer membrane (selectivity around 14). As it is known, in size-selective polymer dense membranes, small molecules preferentially permeate relative to larger one. However, in membranes with reverse-selective properties, the larger one preferentially permeates in a gas mixture. The high n-C_4H_{10}/CH_4 selectivity (mixed gas) in polyacetylene membranes has been studied and discussed for many years and this behaviour can be represented either by extended dual-mode mechanism introduced by Koros et al.[34] or by selective surface sorption, where the methane permeability depression is explained by pore blocking due to the capillary condensation of n-butane on the inner surface of microcavities, since the n-butane is more condensable gas and reduces the unoccupied nanospace between chain segments available for methane permeation.

The methane blocking ratio parameter of the nanocomposite membrane defined as a ratio of methane permeability obtained from mixed gas and single gas measurements decreases with increasing of filler content (Figure 2B); it means that methane is blocked by condensable n-butane during the selective separation process. i.e., the n-butane transport increases through the voids of the free volume by the surface flow mechanism, and effectively hindering at the same time permeation of gaseous (or non-condensable) methane. The increase of n-butane permeability in the mixed gas experiment for the sample containing 20 wt.% of TiO_2 leads to a 4 fold decrease of methane flux and significant mixed gas selectivity rise compared to the pure polymer sample. Decreasing

of methane blocking ratio parameter and simultaneously increase of void volume fraction within TiO_2 clusters can be well-correlated (Figure 2B), the void volume fraction were estimated by definition of volume fraction of the filler, i.e., simultaneously solving the next equations [35]:

$$\phi_F^N = \frac{(W_F / \rho_F)}{(W_P / \rho_P + W_F / \rho_F)} \qquad (1)$$

$$\phi_F^T = \frac{\phi_F^N \left[\dfrac{W_P}{\rho_P} + \dfrac{W_F}{\rho_F} \right]}{\left[\dfrac{W_P}{\rho_P} + \dfrac{W_F}{\rho_P} + V_V \right]} = \frac{\left[\dfrac{W_F}{\rho_F} \right]}{\left[\dfrac{1}{\rho_C} \right]} = W_F \frac{\rho_C}{\rho_F} \qquad (2)$$

Where, ϕ_F^N and ϕ_F^N are the nominal and the true filler volume fraction respectively, W_F, W_P, ρ_F and ρ_P, are the weight percents and densities of pure polymer and filler respectively and, ρ_C and V_V are the density of composite and the void volume.

For all TiO_2 containing membranes, it can also be observed that n-butane permeability and n-C_4H_{10}/CH_4 selectivity rise linearly with the filler content until the concentration reaches 25 wt.%, and after this, both parameters jump significantly due to an extreme increase of free volume of the material (Figure 2A). One can speculate that increased free volume has voids and intervoid channels (bottle necks) so big that it allows n-C_4H_{10} to condense effectively in this "pores" and flows according to the surface flow mechanism blocking at the same time permeation of methane. This result (extreme increase of the permeability and selectivity) could also indicate and demonstrate the existence of interstitial nanospace between TiO_2 nanoparticles (within clusters).

It is interesting to compare the results obtained in the current study with the published results on fumed-Silica-PMP system. Figure 3 presents the permeability for PMP/TiO_2 nanocomposite membranes, fumed-Silica/PMP and a variety of polymers reported by

Freeman. [3,7,8] As it can be seen, the addition of TiO_2 nanoparticles to the PMP enhances the permeability and selectivity more effectively than fumed-Silica and, the PMP/TiO_2 system has higher selectivity than the acknowledged leader PTMSP. For comparison purposes the data for a PTMSP membrane prepared in our laboratory are included into the Figure 3 as well (triangle data). This result leads us to conclude that a novel membrane material was developed and, it can be attractively used in NG conditioning. The obtained high values of n-butane/methane selectivity can have at least two explanations. Firstly, as it was reported in the literature, TiO_2 nanoparticles have "neutral" behaviour, so that when they are mixed with PMP polymer, a rather homogeneous distribution of nanoparticles in the polymer matrix and absence of cracks between the nanoparticles agglomerates and surrounding polymer can be expected. Secondly, TiO_2-sol nanoparticles prepared in the used solvent for the membrane formation were never dried, and thus, it allowed to preserve the coordination shells of solvent molecules around the nanoparticles and prevented charging of the nanoparticles.

In order to explore also the stability of these membranes, long-term aging experiments were carried out during four months for a sample with 40 wt.% of TiO_2, it was observed that the permeability of the sample stored in air at room temperature dropped around 40 % relative to the fresh sample, however, the n-C_4H_{10}/CH_4 selectivity was kept and it decreased only by 10% (from 34 to 31). The gas permeability reduction during storage can be related to the physical aging, chemical aging and contamination or a combination of all them. [15,29]

Conclusions

A novel poly(4-methyl-2-pentyne)/TiO$_2$ organic/inorganic hybrid nanocomposite material has been developed for the preparation of membranes, which could be applied in natural gas conditioning. Through controlled catalytic systems tailor-made PMP samples with specific and optimal properties to prepare membranes were synthesized. PMP with 35% of cis-content was identified as a good membrane material, and then it was used to prepare nanocomposites. The PMP/TiO$_2$ hybrid nanocomposite membranes presented a simultaneous improvement of n-butane permeability and n-butane/methane selectivity, what showed an enhancement with respect to other membranes reported until now. Composite membranes on porous support are presently developed and the performance of these membranes is evaluated at large-scale.

Acknowledgment

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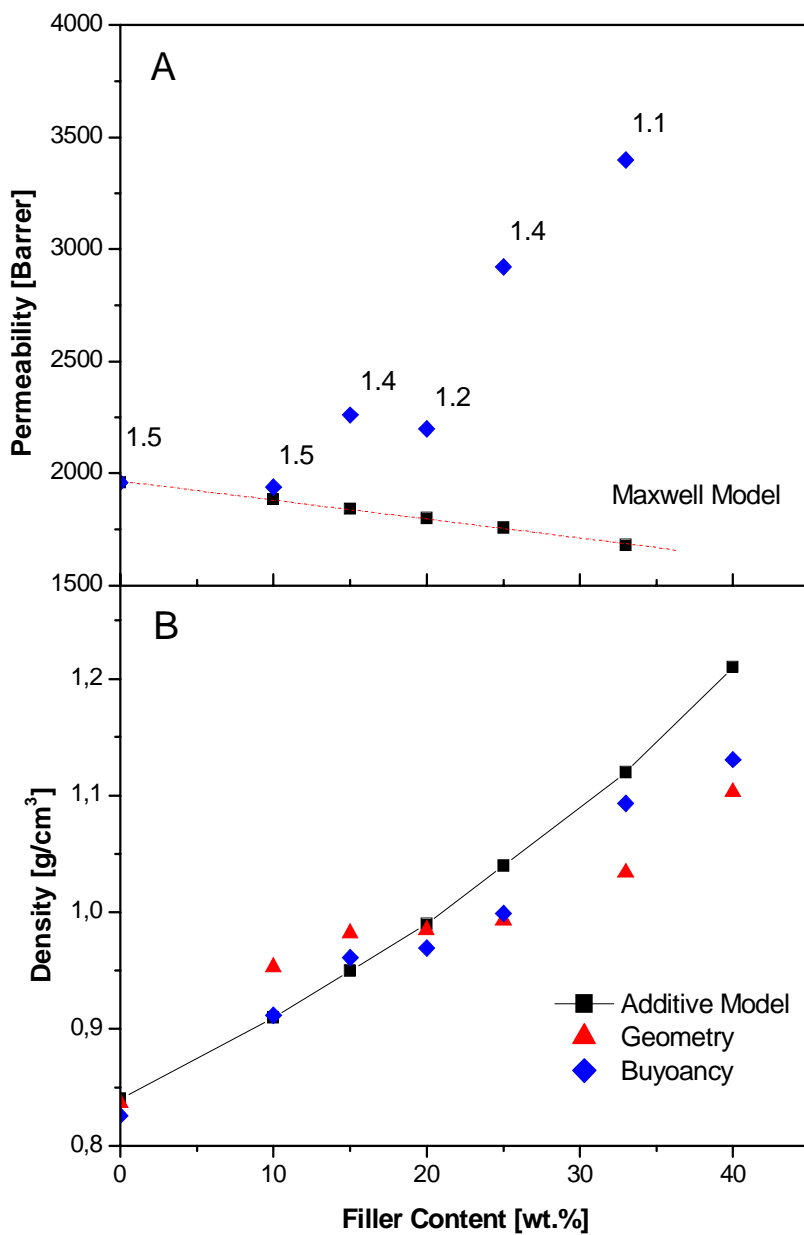
Figure 1 A) Pure methane permeability and n-butane/methane selectivity (numbers next to the experimental points) for PMP and PMP/TiO$_2$ nanocomposite membranes; B) Density of PMP and nanohybrid composite at 25 °C determined by the buoyancy method and from the membrane geometry
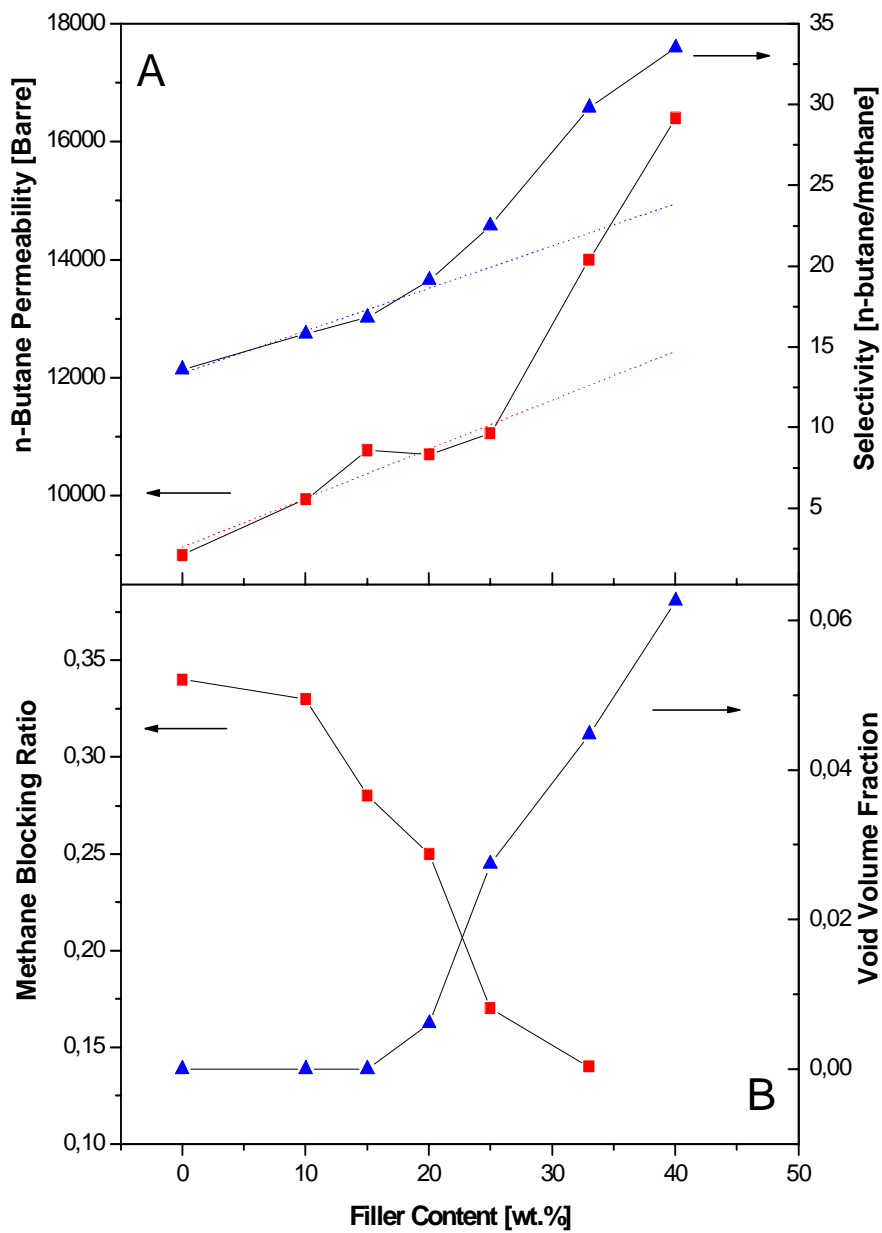
Figure 2 A) Behavior of n-butane permeability and n-butane/methane selectivity; B) Methane blocking ratio and void volume fraction as a function of TiO$_2$ content
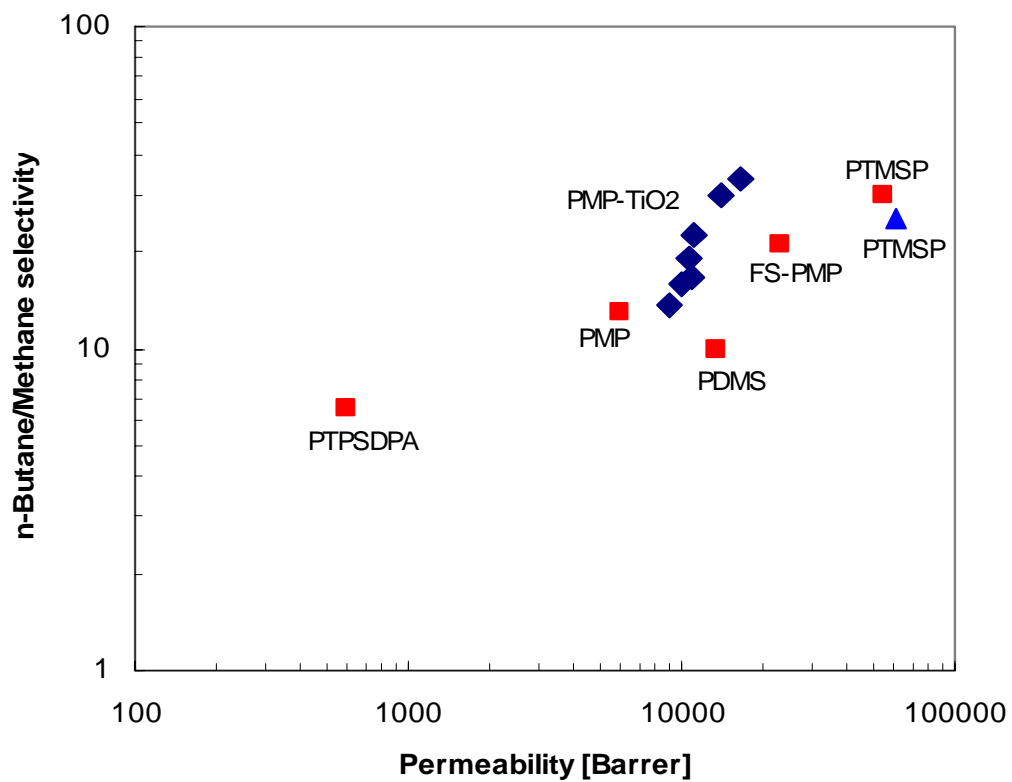
Figure 3 n-butane/methane selectivity as function of butane permeability for PMP and PMP/TiO$_2$ hybrid nanocomposite membranes and other polymers.

Table 1 Catalytic system used in the polymerization and characteristics of PMP samples [a]

Sample	Catalytic system	$[\eta]$ [dl/g]	$M_w \times 10^{-3}$ [g/mol]	M_w/M_n	Cis- content [%]
PMP 1	$NbCl_5$	1.5	525	1.9	50
PMP 2[b]	$NbCl_5/Et_3SiH$	2.0	590	1.8	40
PMP 3[c]	"	2.3	635	1.7	35
PMP 4[d]	"	4.7	-	-	35

[a] Polymerization conditions were: cyclohexane as solvent, [monomer] = 1 mol/l, [monomer]/[catalyst] = 50 , [catalyst]/[co-catalyst] = 1 and 24 h of polymerization. [b] Polymerization at 25°C. [c] and [d] Before the polymerization temperature, the reactor is kept at 3°C and 10°C respectively, for 6h.

Table 2 Some properties of polymers and methane and n-butane mixed gas permeability through PMP membranes at 30°C

Sample	Cis- content [%]	Density [g/cm^3]	l [b] [μm]	Permeability [c] CH$_4$	n-C$_4$H$_{10}$	α[d]
PMP1	55	0.816	54	600	6880	11.5
PMP [a]	35	0.826	60	660	9000	13.6

[a] Either sample PMP3 or PMP4, [b] Thickness, [c] [Barrer]=1x10^{-10} [cm^3(STP)cm/cm^2 s cmHg] and [d] n-C$_4$H$_{10}$/CH$_4$ selectivity

Graphic for the "Table of Contents"

High performance polyacetylene/TiO$_2$ nanocomposite membrane

Polyacetylene membrane

Free-volume

Polymer matrix

CH$_4$

n-C$_4$H$_{10}$

"with nanotechnology key"

Higher permeability
Higher selectivity

TiO$_2$ nanoparticles

Polyacetylene/TiO$_2$ hybrid nanocomposite membrane