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Design, synthesis, characterization and optimization of PTT-*b*-PEO copolymers: A new membrane material for CO₂ separation

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ABSTRACT

The design and synthesis of polymers with well-defined properties (tailor-made) are important in various fields. In fact, researches in membrane science and technology are seeking highly CO_2-philic materials for CO_2-capture. Here we report the design, the systematic synthesis and the optimization of poly(trimethylene terephthalate)-block-poly(ethylene oxide) (PTT-*b*-PEO) copolymers as CO_2-philic membrane materials. The work focuses on the design of experiments, synthesis and characterization of copolymers, statistical analysis of experimental data, data fitting to mathematical models, as well as the optimization of CO_2 permeability. By these means we synthesized optimal materials with promising CO_2 separation performance (high CO_2 permeability and selectivity); they are also promising because

the synthesis is simple, highly reproducible and scalable for producing on large volumes. Thus, these new and tailored polymers might have potential applications as membrane material for CO_2-capture.

Keywords: Design of polymers, block copolymers, CO_2 separation, PTT-*b*-PEO, polymer membrane

1. Introduction

The design of new polymers with well-defined properties is very important in many chemical, material and pharmaceutical industries. The production on large volumes of such polymers sometime is however difficult and expensive; hence the researchers search alternative polymers. Typical approach is by doing many experiments in the laboratory, which generally require significant skill on synthesis, take a lot of time and they even can become expensive. Other approaches such as theoretical simulation and optimization are also way to design new polymers, but they require data bases, special programs, experts, etc. Actually, different procedures for designing and optimization of new polymers are reported in the literature [1-6].

In membrane science and technology, the design of new polymeric materials with desired properties and at the same time cheap, is crucial for obtaining membranes with good separation performance and potential application. Because of global warming problems, large amount of economic resources and efforts are being invested for developing new materials and membranes, which will direct or indirectly capture the CO_2 from different gas streams [7]. The development of highly CO_2-philic membrane materials therefore are big challenges.

For designing CO_2-selective membranes, polymeric materials containing ether groups were identified as promising [8, 9]. The ether linkage has two electron pairs, which favorable interacts with the poor-electron carbon of CO_2 [10, 11]. Thus, those materials have high CO_2 permeability and selectivity. The polyethers are known and used for many years, but lately more works are focused on them. The copolymers or block copolymers containing polyether segments are interesting, especially those based on polyethylene oxide (PEO); many of them can be found as commercial polymers, which is an

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advantage due to their low cost. However, the commercial grades of these polymers are produced for other applications, and some of them do not present good separation performance; only the modification of those polymers resulted in membranes with improved properties [12-15].

Block copolymers containing polyethylene oxide (PEO) flexible segment were already studied for gas separation membranes [8, 9, 12, 13, 16], the design and synthesis of new polymers with the same characteristics but enhanced properties and cheap are still important for both academic and industrial community. Due to their complex morphological and chemical structure, the multiblock copolymers are more interesting because present good separation performance [12, 17]. They can present up to five microphases into the polymeric matrix, two crystalline and two amorphous phases formed by rigid and flexible segments, and a blend-like around the interface of both amorphous phase [18, 19]. If the molecular weight and the content of segments, as well as the entire molecular weight of copolymers are well-controlled during polymerization, the final properties such as crystallinity, melting and glass transition temperature, flexibility, solubility, hydrophilicity, etc. can also be well-controlled according to the requirements.

For applications as membrane material, the copolymers must be resistant to certain compounds; hence, although the copolymer must be CO_2-philic (increased affinity between CO_2 and polymeric material) it must be somewhat resistant to degradation. This property is adjusted by controlled incorporation of rigid segment. The designed and synthesized block copolymers in this work are segmented poly(trimethylene terephthalate)-*block*-poly(ethylene oxide) (PTT-*b*-PEO), they are thermoplastics with elastomeric behavior which were recently synthesized and characterized in their first series (Figure 1) [18], they are novel and present good mechanical, thermal and processing properties.

This report is the first on design and optimization of these polymers as membrane material, which is potential to be produced on large volumes. The synthesis of these copolymers is simple (transesterification and polycondensation reaction), highly reproducible and might be also cheap. The

interesting of this copolymer is that the exquisite combination of rigid (PTT) and flexible (PEO) segments, allows us manipulating its properties. These copolymers are similar to segmented poly(buthylene terephthalate)-*block*-poly(ethylene oxide) copolymers (PBT-*b*-PEO) known as Polyactive [12], the difference however is that the rigid segment has three methylene units instead of four, thereby this difference resulted in a material with better gas separation properties, as it will be presented later. In contrast to the existing commercial polymers, the PTT-*b*-PEO copolymers are designed following the features of CO_2-philic polymer membrane [20]; thereby they show higher CO_2 separation performance.

It is important to mention that PTT is a known commercial polyester, and due to the number of methylenes in its glycol moiety, it is called odd-numbered polyester, examples of even-numbered polyesters are PBT and poly(ethylene terephthalate) (PET). As reported, PTT has exhibited very good tensile elastic recovery, this property in these polyesters was unexpectedly ranked as PTT>PBT>PET [21]. Recently, PTT became of much interest because the used source for its production is renewable (corn sugar), which significantly lower its cost [22]. Hence, the production of copolymers based on PTT and PEO would also have low costs, they are therefore attractive for production on large volumes as membrane material for CO_2 capture.

The design of PTT-*b*-PEO copolymers as CO_2-philic membrane materials consists in the design of experiments (DoE), synthesis and characterization of copolymers, statistical analysis of the molecular weight and content of PEO segment influence on CO_2 permeability, experimental data fit to mathematical models and its validation for the optimization of membrane properties (i.e. development of tailor-made polymers by using experimental data and mathematical models). The relationship between gas transport properties and physical properties of copolymers are also discussed.

2. Experimental part

2.1. Materials

For the synthesis of block copolymers, dimethyl terephthalate (DMT), 1,3-propanediol (PDO), poly(ethylene glycol) (PEG) with molecular weight of 1000, 2000 and 3000 g/mol and titanium tetrabutoxide (TBT, catalyst) were purchased from Sigma-Aldrich. They were used as received, except PDO, which was distilled before to be used. Irganox 1098 (Ciba-Geigy, Switzerland) was used as thermal stabilizer. Melted PEG was dried under vacuum about 1 hour before introducing to the reaction mixture.

2.2. Synthesis and characterization of copolymers

The new PTT-*b*-PEO copolymers were synthesized by a two-step method involving transesterification and polycondensation reaction of DMT, PDO and PEG in the presence of TBT as catalyst according to the method described elsewhere [18]. Irganox 1098 (a heat stabilizer) was used to protect the polymer chains from thermal degradation during the polycondensation reaction at 250°C.

In order to obtain high-molecular weight copolymers, the time of second step (polycondensation reaction) was varied between 2 and 4 h, depending on the composition of the reaction mixture i.e., increasing with the content and length of introduced PEO segments. The polymerization conditions are well controlled and optimized, what allow us to synthesize polymers with different and controlled PTT/PEO weight ratios and molecular weights. The polymers after synthesis (as pellet) were subjected to extraction for eliminating the presence of soluble low-molecular weight oligomers and no-reacted components. The extraction of polymers was performed by using methanol in a Soxhlet apparatus for 24 h at 5 overflows of extracting liquid per hour; the polymers after that were dried under vacuum at 50 $^\circ$C for about 24 h to constant weight. The yield (for almost all synthesized polymers) after extraction was 96.7-98.6 % depending on the composition.

The real composition (weight fraction) of PEO flexible segment in the copolymer chain was calculated from the relative intensities of the characteristic peaks for the terephthalate residue and for the protons of the PEO in ^{1}H-NMR (nuclear magnetic resonance) spectra [18].

Limiting viscosity values ([η]) were measured at 30 ^{o}C on an Ubbelohde viscometer (capillary Ic; K=0.03294) by using a polymer solution of 0.5 g·dL^{-1} in phenol/tetrachloroethane (60/40 wt/wt).

The number average molecular weight (M_n) and polydispersity (M_w/M_n) were determined by size exclusion chromatography (SEC) by using a Waters GPC instrument equipped with a Shimadzu LC-10AD pump, a WATERS 2414 differential refraction index detector (at 35 ^{o}C) and a MIDAS auto-injector (50 μL injection volume). PSS (2× PFG-lin-XL, 7 μm, 8×300 mm, 40 °C) columns were used. Calibration was performed with PMMA standards. 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was used as eluent with a flow rate of 1.0 mL·min^{-1}. The data acquisition and processing were performed using Viscotek OmniSec 4.0 and Waters Empower 2.0 software.

The density was measured at 23°C on hydrostatic balance (Radwag WPE 600C, Poland), calibrated for standards with known density. Hardness measurements were performed on a Shore D apparatus (Karl Frank GmbH, Type 104) according to the standard DIN 53505.

Thermal properties of the synthesized PTT-*b*-PEO copolymers were investigated by differential scanning calorimetry (DSC) in a TA Instrument Q100 DSC. The DSC curves obtained during the second heating run are from -100 to 250 ^{o}C at 10 ^{o}C/min of heating rate. The degree of crystallinity of PEO and PTT were calculated by the following equation: $x_c = \Delta H_m / \Delta H_m^0$; where ΔH_m is derived from melting peak area on DSC thermograms and ΔH_m^0 is the enthalpy change of melting for a 100% crystalline sample standard. The enthalpy values of 197 J/g [23] and 146 J/g [18] were used for 100% crystalline PEO and PTT, respectively.

2.3. Membrane preparation and characterization

Polymeric solutions (3 wt.%.) were prepared at room temperature in chloroform for at least 12 h by stirring (600 rpm). 3 and 5 wt.% of trifluoroacetic acid was added to the polymer solution for copolymers containing high content of PTT segment. The resulting solutions were filtered through a steel filter with pore size 32 μm (F. Carl Schröter) before membrane preparation. The dense films were

prepared by casting on a Teflon ring mould; the solvent evaporation was controlled by covering it with a glass dish for 24 h at room temperature. The membrane thicknesses were measured by a digital micrometer (Micromaster® Capaμsystem, TESA Technology Swiss made), and they were between 30 and 70 μm.

The permeability of gases was measured at 30 $^{\circ}$C by using a pressure increase time-lag apparatus as reported in Ref [12]. The feed pressure was 300 mbar for all gases, and the permeate pressure did not exceed 15 mbar. Diffusion coefficients were determined by the time lag method. For fast gases like hydrogen, the error of diffusion coefficient is mainly based on the error of the time lag, and its error was determined less than 0.05s. Before performing the experiments, the samples were dried overnight in vacuum conditions. All data are the average of at least two samples (measured twice).

The resulting morphology of membrane surface was analyzed by atomic force microscopy (AFM), which was conducted by a NanoScope IIIa (Digital Instruments) in constant force mode at room temperature with the dried membrane sample.

3. Results and discussion

3.1. Synthesis and properties of PTT-b-PEO copolymers

A series of segmented block copolymers (poly(ether-ester) thermoplastics) based on PTT as rigid segment and PEO as flexible segment were synthesized by a two step bulk polycondensation. The basic properties and composition of all synthesised PTT-*b*-PEO copolymers are summarized in Table 1. Although all copolymers are included in that table, it is important to note that they were systematically synthesized according to the factorial design of experiments (Supplementary data). For better understanding and discussing, the copolymers are called as 1k30, 2k50, 3k70, etc. where 1k for example means 1000 g/mol (molecular weight of PEO segment) and 30 is its content in weight percent. The same rule was followed for the other copolymers. The compositions of the synthesized copolymers were confirmed by ^{1}H-NMR analysis. The weight content of PEO segment and degree of polymerization of

PTT segment (*x*) determined from NMR spectra were similar to the calculated theoretical values (from the reaction mixture composition).

Copolymers having [η] values between 1.18 and 1.98 dl/g were obtained. As observed in Table 1, the [η] is not influenced only by the flexibility of the macromolecular chain (content of PEO segment) but also by the molecular weight, and they are in good agreement. The obtained high values of [η] show that the synthesized copolymers have high molecular weights, which were confirmed by SEC analysis (Table 1).

The PTT-*b*-PEO copolymers, especially those with higher content of PTT segments are not well soluble in common solvents. Hence, the number average molecular weight (M_n) and polydispersity (M_w/M_n) of copolymers were analyzed by using HFIP as solvent. In general, the molecular weights of the copolymers are high and increase with the PEO content and segment length. For instance, when PEO with 2000 and 3000 g/mol are used, higher M_n is obtained.

The physical properties such as density and hardness are dependent on the PTT/PEO ratio and PEO segment length. Both the density and hardness simultaneously decrease with PEO content; the higher the PEO content, the lower the density and hardness values. Although the trend is similar for all samples, the sample 3k80 resulted harder than 3k70. This result is explained by the PEO crystallization (discussed later), it is hence expected that the microphase separation between PEO flexible and PTT rigid segments might produce well crystallized soft (M_w>2000 g/mol) and hard domains.

The copolymer densities decrease with PEO content, what indicates that the fractional and total free volume of the polymer system are increased, the samples 1k70, 2k70 and 3k80 have lower densities than the other samples; thereby they will present high gas permeability. All of these results show us that the copolymer properties can be exquisitely tuned for CO_2 separation membranes (next sections).

3.2. Design of Experiments and effect of PEO molecular weight and content on CO_2 permeability

In previous works [9, 12, 17, 24-26], experimental results have shown that PEO content and its

molecular weight greatly affect the block copolymer membrane performance. Although those reports gave valuable information, studies on optimization of membrane material performance were not carried out; hence the results during the design and synthesis of new polymers can not be the expected.

As typical design and development of new products (in this work new polymers), a factorial design of experiments with two levels and two factors (variable of controls), molecular weight (A) and content (B) of PEO segment was elaborated (supplementary data). The synthesized copolymers were characterized, and the data were then analyzed by effects model and ANOVA (analysis of variance), following the Fischer coefficient (F) with a significance if $P<0.05$. The inferior and superior level of PEO molecular weight (A) were chosen as 1000 and 3000 g/mol, and the PEO content (B) as 30 and 70 wt.%. The arguments to choose these values are the following: molecular weight of PEO segment lower than 1000 g/mol does not present good membrane performance, and molecular weight and PEO content higher than those selected here can induce crystallization [12, 24, 27], thereby the membrane performance can be greatly deteriorated.

As presented in Figure 2, the effect of PEO content on CO_2 permeability is clearly noted, as well as the molecular weight at higher PEO content. The molecular weight at lower PEO content definitely does not affect the CO_2 permeability; they even present extremely low values. As low PEO molecular weight and content result in less number of ethylene oxide (EO) units, these results are expected [11, 12]. Moreover, the PTT rigid phase becomes more crystalline (discussed later). It is worthy to mention that membrane materials with high CO_2 permeability is intended to design, that is why CO_2 permeability is chosen as response variable ($\overline{y_i}$). The polymerization conditions are well optimized what allow us to produce copolymers with controlled and desired properties, as well as the yield.

In Table 2 is summarized the experimental results (samples 1k30, 1k70, 3k30 and 3k70), including the CO_2 selectivity over H_2 CH_4 and N_2. Although higher PEO molecular weight and content result in a little higher selectivity, they are not significant. Nevertheless, we must keep in mind that higher selectivity is also preferred (CO_2-philic). The selectivity values are higher than that reported for

Polyactive [12], making them attractive as membrane materials. For membrane sample containing 3000 g/mol and 30 wt.% of PEO (sample 3k30) the permeability of permanent gases were not reliable, hence the selectivities are not reported in Table 2.

As it will be discussed, higher PEO molecular weight and content mean higher amorphous phase of copolymer system (higher fractional free volume), more ethylene oxide units (increased CO_2 solubility) and high flexibility of the polymeric chains (lower glass transition temperature). Maximize these properties by controlling the PEO molecular weigh and content therefore is the aim of this work. The manipulation of these factors allows having control over thermal properties, crystalline/amorphous phase ratio, self-organization (typical of block copolymers), mechanical properties of copolymers and gas transport properties.

All factors, A (molecular weight of PEO), B (content of PEO) and the interaction AB affect the CO_2 permeability (Table 3), which means that higher PEO molecular weight and content would produce membranes with better performance (as it will be discussed later, it is not true because of PEO crystallization). In the interval of 1000 and 3000 g/mol (PEO molecular weight), the CO_2 permeability is more affected by the PEO content (factor B) than its molecular weight, which is statistically demonstrated in Table 3. According to the "F" values, the ANOVA shows that PEO content at higher molecular weight level is the most influencing factor ($F_{exp} > F_{crit}$).

After this first stage, one can only maximize the PEO content; the CO_2 permeability however is not only dependent of PEO content (factor influencing the CO_2 solubility), but also of another important factor such as crystalline/amorphous ratio (factor controlling the fractional free volume and total free volume), which directly depends from the molecular weight of each block and its microstructure [25]. High PEO molecular weight and content could increase the crystallinity of copolymers (favorable polymer-polymer interaction), resulting in lower CO_2 solubility and diffusivity. The best copolymer for CO_2 selective membranes must be one with low polymer-polymer interaction, high CO_2-polymer interaction, high flexibility (increased polymer chain motion), relative high free volume and high

fractional free volume (completely amorphous polymers are the preferred) [20]. Only copolymers fulfilling these features will result in optimal membrane materials as CO_2-philic. Unlike the CO_2-philic polymer (where the polymer must be dissolved in CO_2) [28, 29], the CO_2-philic polymer membrane must be somewhat resistant, maintaining its integrity. In the synthesized copolymers this property is provided by the PTT rigid segment.

Because PEO content at higher level of molecular weight is the most influencing factor on CO_2 permeability, copolymers with PEO molecular weight of 2000 g/mol and higher PEO content were synthesized (samples 2k50, 2k70). Figure 3 presents the CO_2 permeability as a function of PEO molecular weight and content in the copolymer, it is clearly noted that 70 wt.% of PEO content produced membranes with higher CO_2 permeability. The interesting is that copolymers containing 2000 g/mol of PEO segment enhanced the permeability up to 183 Barrer (average value of 2k70 samples), and together with its CO_2/N_2 selectivity (>50), this copolymer shows the highest separation performance within this group of linear amphiphilic block copolymers. This behavior was predicted for Polyactive membranes, where ~140 Barrer was expected as a maximum of CO_2 permeability [12]. Here we experimentally demonstrate it and the value of CO_2 permeability for PTT-*b*-PEO copolymer is even higher than that for Polyactive.

In order to ensure that 70 wt.% of PEO is enough for the CO_2 permeability enhancement, a copolymer (sample 3k80) containing 80 wt.% and 3000 g/mol of PEO was synthesized (see Figure 3, circle data). As observed, the permeability dropped to lower values (63 Barrer), this result is attributed to the high PEO crystallinity, since higher PEO content and higher molecular weight induce the crystallization (discussed later), the PEO homopolymer even is highly crystalline and presents low gas permeability [27]. Hence, we do not expect that copolymers containing higher PEO content will enhance the CO_2 permeability, unless another copolymer with different rigid segment instead of PTT and PBT is designed.

3.3. Optimization of membrane separation property (CO$_2$ permeability)

Optimize or maximize the separation properties of new copolymers is crucial for large volume production and future applications as membrane material. Having examined the effect of molecular weight and content of PEO on CO$_2$ permeability, the permeability values (experimental data) were fitted to a polynomial mathematical model of second order with two variables of control (PEO molecular weight and content).

For the fit, the PEO molecular weight variable were 1000, 2000 and 3000 g/mol and its content was varied as 30, 50 and 70 wt.%, as presented in supplementary data. The obtained model is shown in Figure 4a) as a response surface, and it was statistically analyzed and validated by ANOVA following the Fischer coefficient (see also supplementary data). Although the results show that the model fit well with a significance if $P<0.05$, this model is only valid within the limits for which was analyzed, i.e. PEO molecular weight 1000-3000 g/mol and its content from 30 to 70 wt.%. The optimization of this response surface will always show higher values of CO$_2$ permeability, what contradicts the experimental results. As previously described, higher PEO molecular weight and content do not present improvement in CO$_2$ permeability, a clear example is that observed for sample 3k80 containing 80 wt.% of PEO (circle data in Figure 3). This result is attributed to the PEO crystallization (discussed later) in the copolymer and its high melting point (42°C), which impede the CO$_2$ permeability enhancement.

The observation that higher PEO content results in lower CO$_2$ permeability leads us to assume that the model or response surface has a maximum, as predicted in a previous report [12]. Thus, a copolymer containing 90 wt.% of PEO and 3000 g/mol was synthesized to validate this hypothesis (sample 3k90). As expected, the CO$_2$ permeability dropped a lot (24 Barrer). The high crystallinity (52%) and higher melting temperature (46°C) of PEO phase were the responsible for that result.

By using the two additional data, the polynomial model changed, and the fit was statistically validated (supplementary data). Figure 4b) shows this result (response surface) including the copolymer containing 3000 g/mol of PEO segment with 80 and 90 wt.% of content (samples 3k80 and 3k90). The

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maximum value of CO_2 permeability can be found in copolymers containing ~70 wt. % of PEO content and 1750-2250 g/mol of molecular weight of PEO segment, this value fit very well with the experimental results, which validates the model (CO_2 permeability >183 barrer). Although the copolymer behavior is not a surprise, the designed and optimized copolymer has a CO_2 separation performance far from similar linear block copolymers (Polyactive), which makes attractive due to its versatility during synthesis, low cost and good thermal and mechanical properties [18]. Nevertheless, the samples containing high content of PEO (80-90 wt. %) could also present good separation performance at higher temperatures.

The CO_2 permeability maximum in these new copolymers is explained by its diffusivity and solubility (solution-diffusion mechanism of gas transport in polymers). As seen in Figure 5a), the H_2 diffusivity increase reaches a maximum at 80 wt.% of PEO content, it is understandable because higher PEO content means higher content of crystalline fraction and bigger crystallite size, which are confirmed by its high crystallinity and high melting temperature (next section). The extremely low amorphous fraction in samples containing 90 wt. % of PEO even hinders the transport of the small H_2 molecule. The trend for N_2 and CO_2 is similar as observed for H_2.

The CO_2 solubility in these copolymers is shown in Figure 5b), as expected it also reaches a maximum (70 wt.% of PEO content). The solubility of other gases (N_2 and H_2) however is continuously decreased, showing that the material is more CO_2-philic, thereby the increase of CO_2 solubility and diffusivity resulted in a highly CO_2 permeable material.

Because the crystalline/amorphous ratio is balanced (optimal) for copolymers containing 70 wt.% of PEO content, the CO_2 diffusivity and solubility coefficient are the optimal for producing membranes with the highest permeability. This is demonstrated in next section for sample 2k70, where the PEO melting temperature even is lower than room temperature (completely amorphous PEO phase), which makes to this sample premising among others.

3.4. Thermal properties and crystallinity of PTT-b-PEO copolymers

The PTT and PEO homopolymers have different properties. At room temperature PTT is rigid, semicrystalline and hydrophobic [21, 30], whereas PEO is flexible and hydrophilic (depending of molecular weight it is also semicrystalline) [27]. These differences provide to the final block copolymer unique set of properties. The variation of rigid and flexible segment content and the molecular weight of the used PEO during the synthesis have had a great effect on the microphase separation of copolymers. All PTT-*b*-PEO copolymers investigated here are semicrystalline with elastomeric behavior at room temperature.

As presented in Table 4, the glass transition temperatures (T_g) of copolymers which is related to the chain flexibility and total free volume, are decreased with content and molecular weight of PEO (expected); this means that the copolymers are more flexible and present increased total free volume, the lower the T_g of copolymers (for rubbery-like), the higher the total free volume. The T_g decrease is a result of increased chain motion of the polymeric chains (increase of PEO flexible segment), hence the total free volume, especially the dynamic free volume which is responsible for gas transport, is greatly enhanced in samples with low T_g [31]. This factor is important for improvement of CO_2 solubility and diffusivity, what improves simultaneously the permeability and selectivity [32].

The melting temperature (T_{m1}) of PEO is mostly affected by its content (see Table 4 and Figure 6). On the one hand, high PEO content produces high T_{m1} which is due to the increased size of crystallites; on the other hand, the T_{m2} of PTT is contrary decreased (expected). The higher the PEO content, the lower the T_{m2} and crystallinity of PTT, the copolymers containing 70 wt. % (samples 1k70, 2k70 and 3k70) however present very well-balanced properties (optimal).

The crystallinity of PEO is increased with its molecular weight (keeping the PEO content), as well as the PTT crystalline phase (see Table 4 and Figure 6). However, each group of copolymers, either with 1000, 2000 or 3000 g/mol of PEO molecular weight show a decrease of PTT crystallinity with PEO content, which is wanted for producing membranes with better performance. Although the PEO

crystallinity is increased in value, it does not mean that the membrane performance is damaged. The PEO crystallites start to melt at temperatures below 10°C (Figure 6), and some of samples are even completely amorphous at room temperature (see Table 4, consider room temperature as 30°C), hence the PEO flexible segments will always be in its molten state or as liquid-like (amorphous), thereby they will exhibit high chain motion, and consequently higher gas separation performance.

The sample 2k70, i.e. copolymer with PEO segment of 2000 g/mol and 70 wt.% of content presents low glass transition temperature (-49°C), low PTT crystallinity (10 %), relative high melting temperature of PTT (178°C) and low melting temperature of PEO (28°C). This copolymer hence has potential application as CO_2 separation membrane material (CO_2 permeability >183 Barrer and CO_2/N_2, CO_2/CH_4 and CO_2/H_2 selectivity of 51, 17 and 10 respectively).

3.5. Surface morphology of PTT-b-PEO membranes

AFM phase images of representative samples (surface morphology) are illustrated in Figure 7. All copolymers are semicrystalline. Due to the incompatibility between flexible and rigid segments, this kind of block copolymers may segregate into separate phases into the solid state, resulting in continuous amorphous phase with dispersed semicrystalline hard domains. Under certain conditions the lamellae of the copolyesters sometimes organize as spherulitc structure or separated crystalline microspheres [33].

The membranes prepared from copolymer containing 1000 g/mol of molecular weight and 70 wt.% of PEO segment (sample 1k70) presented two well-defined structures, i.e. PTT crystalline phase and PEO-rich amorphous phase (Figure 7a and 7b) with crystalline hard domains formed by lamellar crystals that are rather randomly ordered in. Although the crystallites seem to be extremely big, the fraction of amorphous phase was higher than the crystalline; thus it resulted in a membrane with moderate CO_2 permeability (Table 1).

Samples 2k70 and 3k70 (Figure 7c and 7d) exhibited homogeneous morphology at the surface, the hard semicrystalline domains were found to be represented by crystalline lamellae (brighter contrast)

randomly embedded in amorphous phase (dark regions). Differences in hard domains ordering into amorphous PEO-rich phase of sample 2k70 and 3k70 are evident. On the surface of 3k70 samples, thicker crystalline lamellae than in sample 2k70 are observed. At room temperature (AFM experiments), we can expect also the coexistence of PTT and PEO lamellar structures, which is attributed to high molecular weight of PEO segment (3000 g/mol). These results are in good agreement with the melting temperature and crystallinity determined by DCS.

Other two samples (3k30 and 3k90) were also examined by AFM to see the effect of PEO content on surface morphology (Figure 7e and 7f). On the one hand, the sample containing low PEO content (sample 3k30) shows a predominant hard phase (only PTT crystals). On the other hand, the copolymer with the highest PEO content (sample 3k90) exhibited a combination of crystalline and amorphous structure including small lamellae structure (represented by crystalline nano-ribbons/rods) embedded into an amorphous phase (Figure 7f). Here the observed crystalline structures are attributed to PEO segments because PTT sequences are too short to crystallize.

The AFM results are in good agreement with the gas permeability and thermal properties; in general the crystalline fraction and the microphase separation are dependent from molecular weight and content of PEO segment, and consequently the gas permeability vary. However, these images must be carefully analyzed for avoiding misinterpretations related with the AFM technique and sample preparation.

3.6. Separation performance of optimal PTT-b-PEO copolymers

A summary of CO_2 permeability and selectivity over H_2, CH_4, O_2 and N_2 for samples 2k50, 2k70, 2k80, 3k70 and 3k80 is presented in Table 5. The combination of relative high permeability and selectivity shows that the designed PTT-*b*-PEO copolymers have potential application as membrane material. For the optimal copolymer (data in bold), the CO_2 permeability is relatively high and the CO_2/N_2 selectivity is higher than 50. The composite membrane manufacture (development of adequate support and optimization of manufacture process) and the performance (gas separation at different

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operating conditions) of this copolymer will be deeply studied and reported elsewhere. According to the selectivity (Table 5), each block copolymer may have advantage for a specific gas mixture.

First results on composite membrane performance (single gas measurements on membrane samples prepared as in ref. 20) showed that these materials are promising. The CO_2 permeances (flux) are >1.3 m^3 (STP) m^{-2} h^{-1} bar^{-1} for membranes prepared from copolymers called as 2k70 and 2k80 (optimal materials), and the selectivities are the same as in thick film. By simple comparison, these membranes seem to present better performance than those developed from commercially available polymers and those modified by using polyethylene glycols [8, 20, 34, 35]. Therefore, we can say that the developed materials in this work are attractive and potential for CO_2 capture. The interesting is that the membranes presented here are from pristine copolymers. Although the modification of polymers by blending with polyethylene glycols (with low molecular weight) greatly enhances the membrane performance, they were criticized because they might not work under real conditions (i.e. high pressure, high temperature and under humid conditions). These new PTT-*b*-PEO copolymers hence as such are promising.

Conclusions

Tailor-made PTT-*b*-PEO copolymers were designed and systematically synthesized. Their properties were tailored for obtaining optimal CO_2-philic block copolymer membranes. The ratio of rigid (PTT) and flexible (PEO) segment was very well-controlled; thereby the crystalline and amorphous phase as well. The density and glass transition temperature of block copolymers with higher PEO content were decreased to lower values, resulting in copolymers with high fractional free volume and high chain motion (low T_g).

The control of all of these factors allowed designing a polymer membrane material with desired properties, which was synthesized and validated by mathematical analyses and by experimental results. The good gas separation, mechanical and thermal properties make these copolymers attractive for CO_2 separation. Composite membranes (first results) from the tailor-made copolymer (optimal) showed high

separation performance (CO_2 flux >1.3 m^3(STP) m^{-2} $h^{-1}bar^{-1}$).

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List of Tables

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Table 1

Sample	M_w^{PEO}	Theory		NMR		$[\eta]$	M_n x 10^4	M_w/M_n	d	H
		x	w_{PEO}	x	w_{PEO}					
	g/mol	mol	wt %	mol	wt %	dl/g	g/mol		g/cm^3	ShD
1k30	1000	12.8	30	13.1	26.3	1.18	5.58	2.11	1.296	65
1k50	1000	5.4	50	5.6	46.9	1.34	7.38	2.12	1.255	52
1k70	1000	2.4	70	2.6	68.7	1.46	8.89	2.19	1.198	32
2k50	2000	10.3	50	11.4	50.8	1.40	7.69	1.69	1.217	37
2k70	2000	4.4	70	5.1	67.5	1.70	9.64	1.90	1.194	26
2k80	2000	2.6	80	-	-	1.98	10.02	1.66	1.178	28
3k30	3000	35.5	30	37.8	27.8	1.23	5.06	1.89	1.262	55
3k50	3000	15.2	50	16.3	48.2	1.36	8.41	1.68	1.235	38
3k70	3000	6.5	70	6.5	67.0	1.73	11.03	1.65	1.204	32
3k80	3000	3.8	80	4.2	78.3	1.83	10.15	1.55	1.184	44
3k90	3000	1.7	90	1.8	86.9	1.76	9.58	1.69	1.121	-

M_w^{PEO} - average molecular weight of PEO; x - degree of polymerization of PTT segment with reference to 1 mol of PEO segment; w_{PEO}- weight percent of PEO segments theoretical and those determined by NMR; $[\eta]$ - limiting viscosity value, Mn - number average molecular weight; Mw/Mn - polydispersity; d - density; H - hardness.

Table 2

N° Exp.	A [g/mol]	B [wt.%]	$\overline{y_i}$ [Barrer]	α CO$_2$/H$_2$	α CO$_2$/CH$_4$	A CO$_2$/N$_2$
1	1000	30	12	6.3	20	48
2	3000	30	15	-	-	-
3	1000	70	95	10	18	51
4	3000	70	114	11	20	58

$\overline{y_i}$ = CO$_2$ permeability; 1Barrer=1x10^{-10} cm^3(STP)cm cm^{-2} s^{-1} cmHg^{-1}

Table 3

Factor	Effect on $\overline{y_i}$	S.S.	D.F.	M.S.	F_{exp}
A	11	121	1	121	0.28
B	91	8281	1	8281	18.95
AB	8	64	1	64	0.15
Error		1311	3	437	

The values of effect are obtained by effects model, S.S. = sum of square, D.F. = degree of freedom, M.S. = mean square, $F_{crit.}$=10.1 with significance if $P<0.05$.
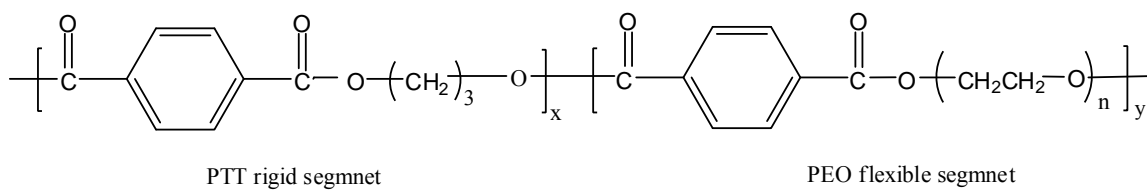
Table 4

Sample	PEO segment				PTT segment			
	T_{g1}	T_{m1}	ΔH_{m1}	x_c^{PEO}	T_{g2}	T_{m2}	ΔH_{m2}	x_c^{PTT}
	[°C]	[°C]	[J/g]	[%]	[°C]	[°C]	[J/g]	[%]
1k30	-34	-	-	-	51	216	38.2	26.2
1k50	-45	-	-	-	49	195	27.4	18.8
1k70	-48	7	6.3	3.2	47	149	13.5	9.2
2k50	-50	15	22.9	11.6	-	212	34.0	23.3
2k70	-49	28	50.9	25.8	-	178	14.6	10.0
2k80	-48	33	64.8	32.9	-	149	5.6	3.8
3k30	-48	15	6.7	3.4	-	226	38.4	26.3
3k50	-48	26	32.5	16.5	-	218	33.9	23.2
3k70	-48	37	68.1	34.6	-	195	19.5	13.3
3k80	-47	42	77.0	39.1	-	172	8.4	5.8
3k90	-47	46	101.8	51.7	-	-	-	-

T_{g1}, T_{g2}, ΔH_{m1}, ΔH_{m2}, T_{m1}, T_{m2}, x_c^{PEO} and x_c^{PTT} are the glass transition temperature, enthalpy of melting, the melting temperature and the crystallinity of PEO and PTT, respectively.

Table 5

Sample	PEO segment [g/mol]	PEO content [wt.%]	CO_2 permeability [Barrer]	α CO_2/H_2	α CO_2/CH_4	α CO_2/O_2	α CO_2/N_2
2k50	2000	50	110	10.8	18	21.7	51.4
2k70	**2000**	**70**	**183**	**10.2**	**17**	**22.0**	**51.2**
2k80	2000	80	129	10.7	17	22.1	57.3
3k70	3000	70	114	11.3	18	23.3	53.1
3k80	3000	80	63	8.6	19	21.6	57.6

PTT rigid segmnet   PEO flexible segmnet

where: x - degree of polymerization of rigid segment and y = 1.

Figure 1
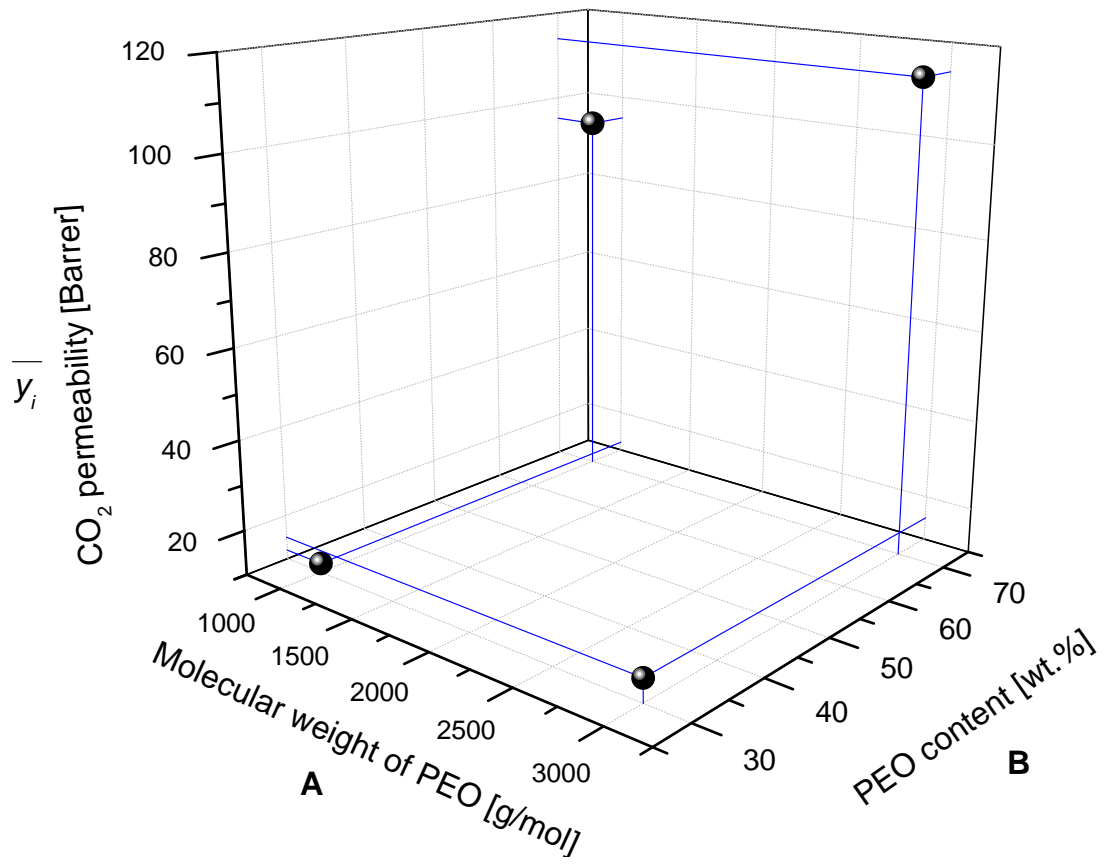
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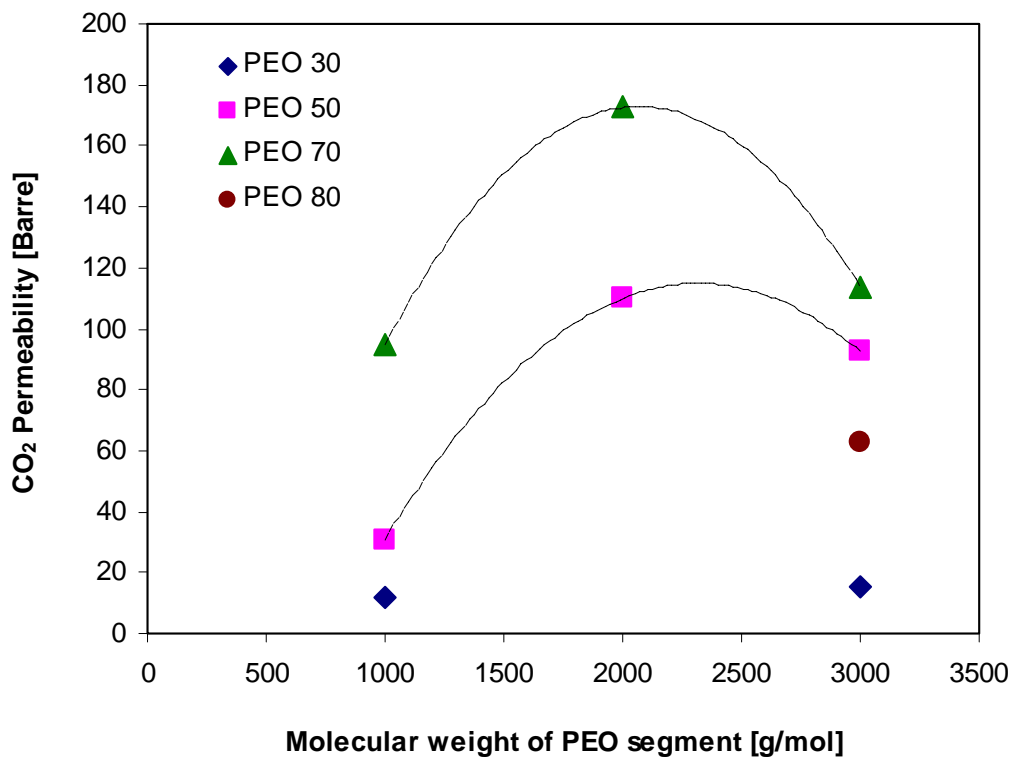
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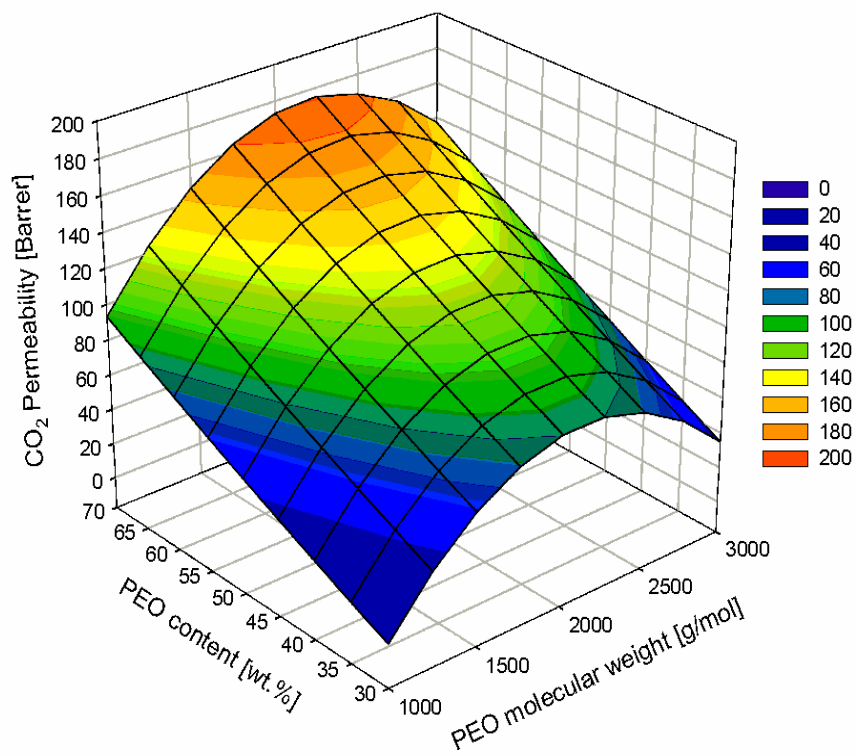
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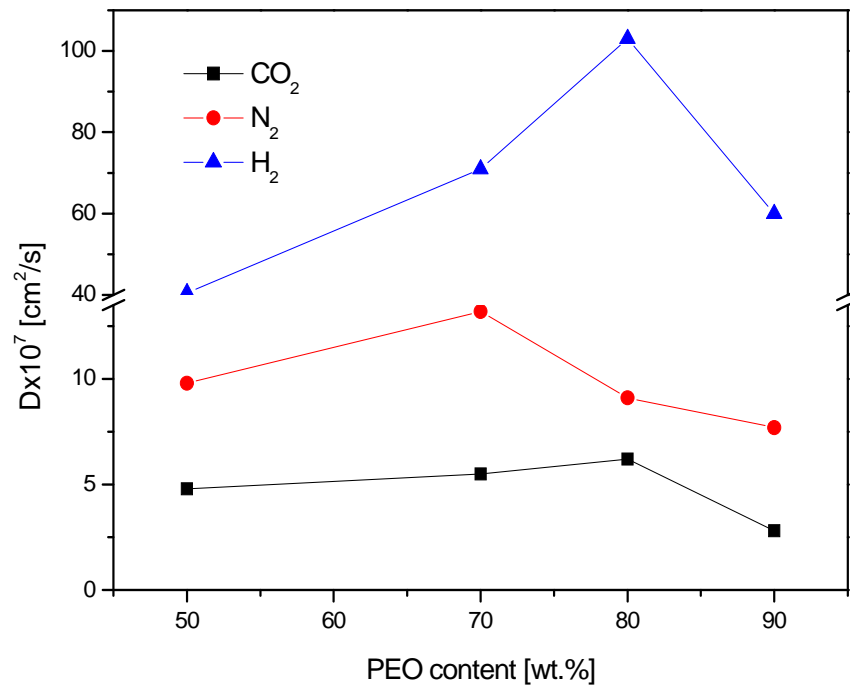
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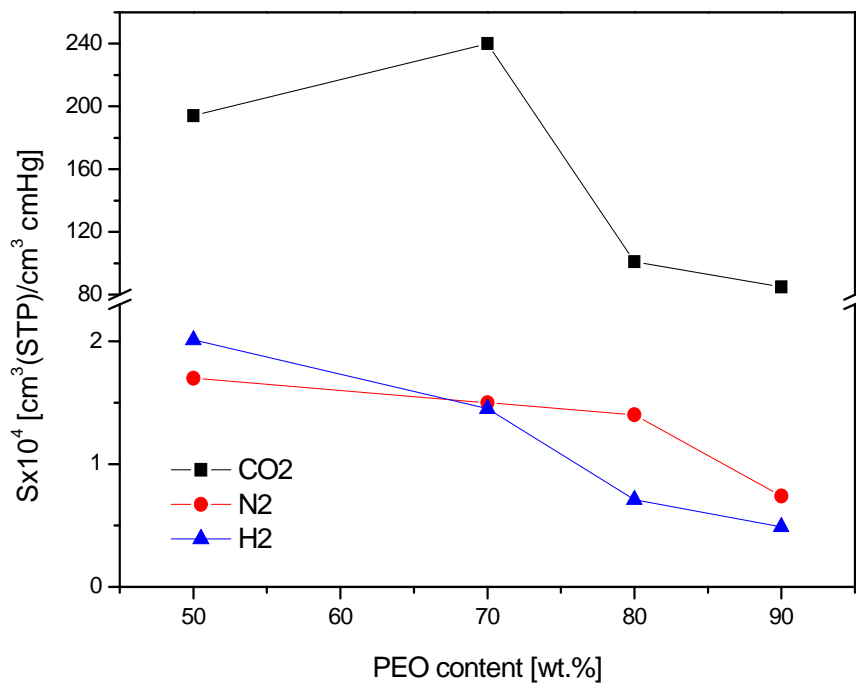
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Figure 5

a)

b)
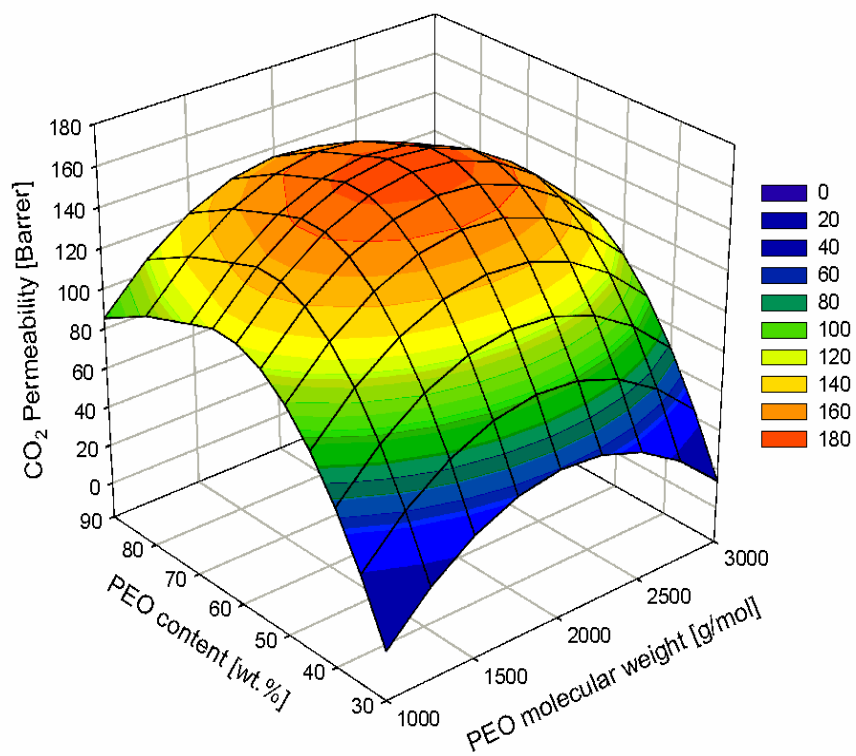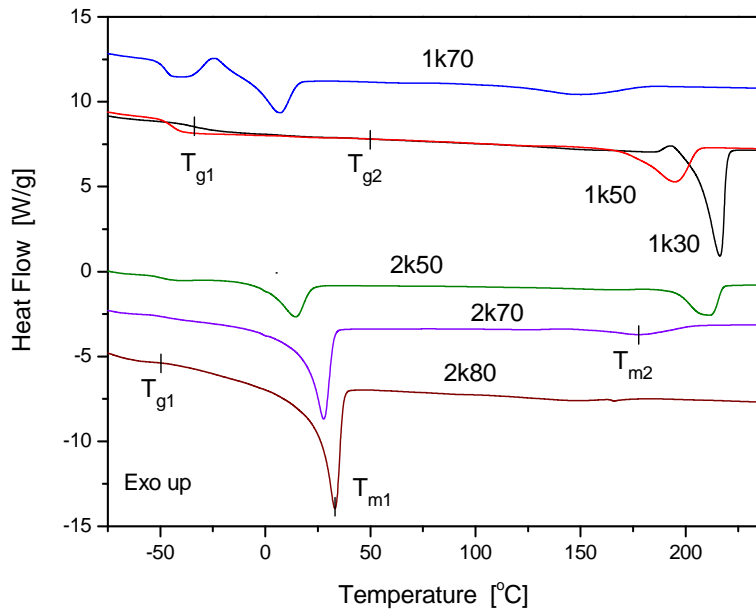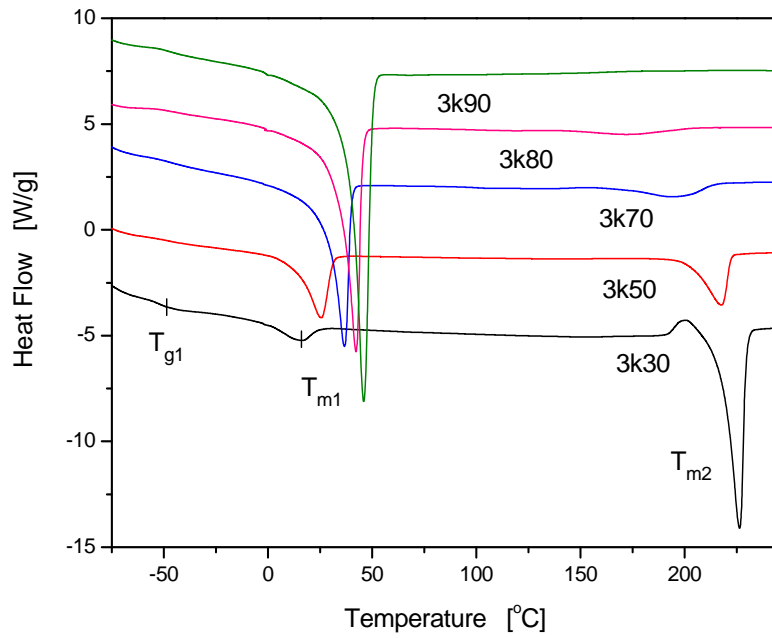
Figure 6

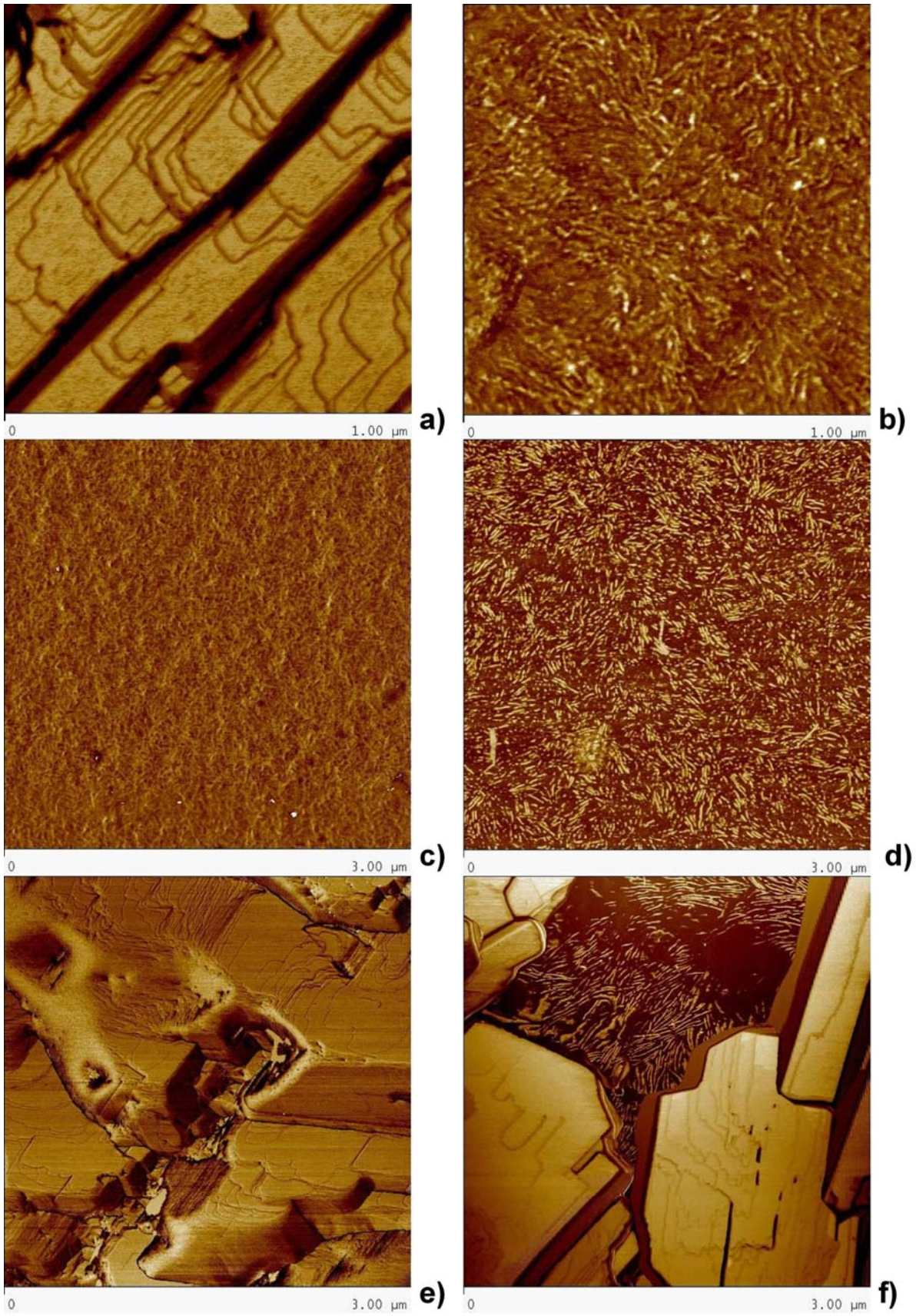**Figure 7**

Experimental design for synthesis of PTT-b-PEO copolymers by DoE (design of experiments)

Table S1. Experiments for designing optimal membrane materials

N° of experiments		Mw of PEO [g/mol]		PEO content [wt.%]	Polymer properties	Gas transport property
1	-1	1000	-1	30		CO$_2$
2	+1	3000	-1	30		P
3	-1	1000	+1	70		E
4	+1	3000	+1	70		R
						M
						E
5	-1	1000	0	50		A
6	+1	3000	0	50		B
						I
						L
7	0	2000	0	50		I
8	0	2000	+1	70		T
						Y

1st step: Experiments from 1 to 4 were carried out in order to study the effect of molecular weight (Mw) and the content of PEO (superior +1 and inferior -1 level, respectively). As the copolymers were designed for CO$_2$ separation membranes, the CO$_2$ permeability was chosen as main response variable. Nevertheless, the physical and thermal properties were also controlled, since they also control the separation performance.

Effects model and ANOVA (analysis of variance), following the Fischer coefficient (F) with a significance if $P<0.05$ were carried out for analyzing the effect of PEO molecular weight (A) content (B) on CO_2 permeability ($\overline{y_i}$).

Table S2. Experimental matrix and experimental data ($\overline{y_i}$ = CO_2 average of permeability)

N° of experiments	A	Mw of PEO [g/mol]	B	PEO content [wt.%]	CO_2 Permeability [Barrer]	$\overline{y_i}$
1	-1	1000	-1	30	12	12
2	+1	3000	-1	30	15	15
3	-1	1000	+1	70	90-100	95
4	+1	3000	+1	70	111-140-90	114

Table S3. Effects model; where the factors A and B are the molecular weight of PEO segment and content in the copolymer, respectively. AB is the interaction between both factors.

	A	B	$\overline{y_i}$	AB	$\overline{y_i}$ A	$\overline{y_i}$ B	$\overline{y_i}$ AB
1	-1	-1	12	+1	-12	-12	12
a	+1	-1	15	-1	15	-15	-15
b	-1	+1	95	-1	-95	95	-95
ab	+1	+1	114	+1	114	114	114
			Σ		22	182	16

$$\text{Effect (factor)} = \frac{1}{2^{k-1}} \sum \left(\overline{y} * factor \right) \qquad (1)$$

Effect (A) = 11

Effect (B) = 91

Effect (AB) = 8

$$\text{Sum of square (S.S.)} = \frac{\left(\overline{y} * factor \right)^2}{2^k} \qquad (2)$$

Table S4. Analysis of variance (ANOVA) for factors A, B and the interaction AB

Factor	$\overline{y}_i$ *factor	S.S.	D.F.	M.S.	F_{exp}
A	22	121	1	121	0.28
B	182	8281	1	8281	18.95
AB	16	64	1	64	0.15
Error		1311	3	437	

The values of effect are obtained by effects model, S.S. = sum of square, D.F. = degree of freedom, M.S. = mean square, S.S. of error = $\sum \sum \left(y_{ij-} \overline{y}_i \right)$, $F_{crit.}$=10.1 with significance if P<0.05.

Mathematical analysis: selection of an appropriate mathematical model, mathematical adjustment of experimental data, statistical analysis, optimization and validation.

2nd step: Samples with 50 wt.% of PEO were synthesized (experiments number 5 and 6 in Table S1) for understanding the behavior of these copolymers at level "0". Then, samples with 2000 g/mol and 50 and 70 wt.% of PEO were also synthesized (experiments number 7 and 8).

CO_2 permeability (average data) of different copolymer membranes were fitted to a polynomial mathematical model of second order:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_1X_2 + b_4X_1^2 + b_5X_2^2 \qquad (3)$$

The fitting of experimental data to this model were done by regression model, this method allows obtaining the covariance matrix of the regression coefficients as:

$$b = (X^TX)^{-1}(X^TY) \qquad (4)$$

Where "b" is the matrix of regression coefficients, X the experimental matrix (factor $A=X_1$ and factor $B=X_2$), X^T the transposed matrix of X and Y the matrix of response.

Table S5. Experimental matrix "X" and response "Y"

	x_1	x_2	x_1x_2	x_1^2	x_2^2	$\overline{y}_i$
1	1000	30	3E-4	1E-6	9E-2	12
1	3000	30	9E-4	9E-6	9E-2	15
1	1000	70	7E-4	1E-6	49E-2	95
1	3000	70	21E-4	9E-6	49E-2	114
1	1000	50	5E-4	1E-6	25E-2	31
1	3000	50	15E-4	9E-6	25E-2	93
1	2000	50	10E-4	4E-6	25E-2	110
1	2000	70	14E-4	4E-6	49E-2	173

By solving the equation 4, we obtain the matrix "b".

Table S6. Matrix of regression coefficients "b"

b_i		b_i
-228.91		b_0
0.24		b_1
1.43		b_2
2E-4	=	b_3
-5.8E-5		b_4
5.3E-3		b_5

Therefore, by replacing the coefficients "b" in equation 3, we obtain:

$$Y = -228.91 + 0.24X_1 + 1.43X_2 + 2E\text{-}4X_1X_2 - 5.8E\text{-}5X_1^2 + 5.3E\text{-}3X_2^2 \qquad (5)$$

This equation was validated by ANOVA

Table S7. Analysis of variance (ANOVA) of the regression and fitting for equation 5

	S.S.	D.F.	M.S.	F_{exp}	F_{crit}
Regression	34331.24	5	6866.25		
fitting	1642.62	2	821.31	3.38	4.39
Error	1455	6	242.5		

Where, S.S. (regression) $= \sum P_i (\hat{y}_i - \overline{y_{oo}})^2 \qquad (6)$

S.S. (fitting) $= \sum P_i (\overline{y_{io}} - \hat{y}_i)^2 \qquad (7)$

S.S. (error) $= \sum \sum (y_{ij} - \overline{y_i})^2 \qquad (8)$

3rd step: Samples with 80 wt.% of PEO were synthesized (PEO molecular weight of 2000 and 3000 g/mol). To ensure that higher PEO content decreases the CO_2 permeability, a sample with 90 wt.% of PEO was also synthesized.

By using the additional data, the mathematical model changed and the data fit very well to the next equation:

$$Y = -416.58 + 0.19X_1 + 12.24X_2 - 4.66E\text{-}5X_1^2 - 0.097X_2^2 \qquad (9)$$

Table S8. Analysis of variance (ANOVA) of the regression and fitting for equation 9

	S.S.	D.F.	M.S.	F_{exp}	F_{crit}
Regression	44220.14	4	11055.03		
fitting	5784.66	3	1928.22	7.27	8.45
Error	1856	7	265		