

***Final Draft***  
**of the original manuscript:**

Car, A.; Stropnik, C.; Yave, W.; Peinemann, K.-V.:  
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In: Advanced Functional Materials (2008) Wiley

DOI: 10.1002/adfm.200800436

## **Tailor made polymeric membrane based on segmented block copolymer for CO<sub>2</sub> separation**

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**Abstract**

This paper reports the design of a tailor made polymeric membrane by using PEO-PBT poly(ethylene(oxide)-poly(butylene terephthalate) multi-block copolymers. Their properties are controlled by the fraction of the PEO phase and its molecular weight. To explain the effect of structural changes in copolymer membranes, transport properties of four gases (CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>) are discussed. After characterization, the two best copolymers were selected in order to prepare tailor made blends by adding polyethylene glycol (PEG). The best selected copolymer containing 55 wt. % of PEO and 4000 g/mol of PEO segment produced a blend with high CO<sub>2</sub> permeability (~190 barrer), which was two fold with regard to the pristine copolymer membrane. At the same time, an enhancement of CO<sub>2</sub>/H<sub>2</sub> selectivity was observed (~13). These results suggest that the morphology of PEO-PBT could be well controlled by addition of low molecular PEG, and consequently the gas transport properties can be tuned.

Keywords: Polyactive, PEO-PBT, block copolymer, tailor made blend, CO<sub>2</sub> separation.

## **1. Introduction**

A number of technologies exist for capturing carbon dioxide from large volume streams, and membrane technology is one of them offering some advantages [1], including simple design, lower energy requirements and exceptional reliability. These advantages have allowed the membranes to make significant commercial advances in CO<sub>2</sub> removal application, especially in fuel gas streams [2].

The design and synthesis of new polymers are essential for membrane technology [3]. Block copolymers composed of two or more different polymers offer the possibility to

manipulate their structure, and consequently allow to obtain products with desired properties [4, 5]. The combination of two incompatible polymers by chemical link limits phase separation to the microscopic scale, and the nanostructure might be considerably varied by modifying the type of blocks, composition of each block, their length and their processing [6].

Membranes prepared from commercial block copolymers exhibit often an improved performance, when they are compared with homopolymers [7,8]. Copolymers based on PEO have been identified as promising membrane materials for CO<sub>2</sub> separation [9-12], and therefore, a detailed study of the relationship between structure of block copolymers and physical properties are important for tailoring a membrane with improved performance for a specific application.

Poly(ethylene oxide)-poly(butylene terephthalate) (PEO-PBT) multi-block copolymers are known under the trade name Polyactive, and they are considered as semicrystalline polymers [13]. In these copolymers, the PEO block is the permeable amorphous phase and the PBT is the rigid crystalline phase, considered as impermeable for gas transport. A study of these copolymers with different molecular weight and fraction of the PEO block has been carried out in order to develop a new membrane material for gas separation [14]. The CO<sub>2</sub> permeability strongly varied with the PEO segment length, and the chain flexibility decreased with increasing amounts of PBT. The permeability was also affected by degree of crystallinity and melting temperature of PEO phase. Thus, an increase of the PEO segment length till certain molecular weight (Mw) at the same ratio of PEO-PBT resulted in higher gas permeabilities. Therefore, by tailoring this multi-block copolymer it should be possible to produce membranes with improved properties for CO<sub>2</sub> separation.

One way to obtain a tailor made polymeric membrane for CO<sub>2</sub> separation is to design a polymer with defined content and molecular weight of PEO. Thus, the synthesis of PEO-PBT [15] allows to attain a superior block copolymer for gas separation, but the amounts of the PEO

phase and its Mw have to be tuned in order to control the performance of the membrane. An additional method to tailor membrane properties is to blend the polymer with polyethyleneglycol (PEG) [16]. The last method is much simpler and cheaper than the synthesis of new polymers. However, during the design of a tailor made polymer system, used for membrane in gas separation, many important parameters (e.g. the diffusivity and solubility selectivity, permeability, thermal stability, solubility in conventional solvents, and its cost) must be taken into account [17-20].

In this work, membranes from different PEO-PBT multi-block copolymers were prepared and characterized in order to design a polymer with specific gas transport properties. Blend membranes with PEG were tailored for obtaining an optimised CO<sub>2</sub> separation membrane. This group of polymers was already explored for water vapour transport [21-24], but there is not much work in the field of membranes for gas separation [14].

## **2. Experimental part**

### *2.1 Materials and membrane preparation*

Different grades of PEO-PBT multi-block block copolymers were kindly supplied by IsoTis OrthoBiologics (USA) and they were used without further purification. Chloroform (Merck) was used as a solvent to prepare polymer solutions (3 wt. % of PEO-PBT); it was stirred for 12h at room temperature. Only in the case of polymer 4000PEO55PBT45 trifluoroacetic acid (2. wt. % according to chloroform) (Merck) was added to the chloroform in order to obtain a homogeneous solution. The solutions were filtered through a steel filter and poured into a Teflon mould. Two multi-block copolymers were chosen as polymers with the best performance to prepare blends by adding PEG 200 g/mol (Aldrich). After addition of different amounts of PEG 200 the solutions were stirred for 3h at room temperature. The solvent evaporation was controlled by covering the

membrane with a glass dish for 24 h at 30 °C. The membranes were stored in a vacuum oven overnight at 30 °C to remove residual solvent.

## 2.2 Membrane characterization

Thermal properties of samples were characterized in the temperature range from -100 to 250 °C by using a Netzsch (Differential Scanning Calorimetry) DSC 204 calorimeter.

Measurements, including baseline determinations were performed at the scan rate of 10K/min, and the experiments were conducted by using a nitrogen purge gas stream. Melting and glass transition temperature values were obtained from second scan thermograms. The degree of crystallinity of the PEO and PBT phases within the PEO-PBT multi-block copolymer was calculated using the heat of fusion for a 100% crystalline PEO (166.4 J/g) [25] and PBT (213.4 J/g) [26]. In addition, TGA (Thermal gravimetric analyses) were performed under argon with a Netzsch 209 instrument at a heating rate 10 K/min.

Swelling experiments were performed on polymer films with Millipore water at room temperature during 2 weeks in order to reach equilibrium. The excess of water was removed with filter paper and then samples were weight immediately. Water absorption was determined by equation (1):

$$\%WA = \frac{(m_w - m_d)}{m_d} \cdot 100\% \quad (1)$$

where  $m_w$  and  $m_d$  are the mass of wet and dry sample. The weight measurements were done using a Sartorius balance (LE623P, AG Germany) and the results are the average of three samples.

Experimental values of membrane density were determined by the buoyancy method in a perfluorinated liquid (3M Fluorinert™ FC-77) with known density (1.766 g/cm<sup>3</sup>) by using equation (2):

$$\rho = \frac{M_A}{M_A - M_L} \cdot \rho_0 \quad (2)$$

where  $\rho$  and  $\rho_0$  are the densities of copolymer and perfluorinated liquid, and  $M_A$  and  $M_L$  are the membrane weight in the air and in the liquid, respectively.

Permeabilities of pure gases were measured by a pressure increase time-lag apparatus at 30 °C. The feed pressure was 300 mbar for all gases and the permeate pressure did not exceed 15 mbar. Membrane thickness measured by a digital micrometer (Deltascope® MP2C) varied from 60 to 80  $\mu\text{m}$ .

### 3. Results and discussion

#### 3.1 PEO-PBT block copolymer properties

Figure 1 presents chemical structure of PEO-PBT block copolymer, where x and y represents weight percent of each block and n gives information about the molecular weight (g/mol) of PEO. The PBT hard segment gives strength to the material, it is able to crystallize and show behaviour of glassy polymers ( $T_g$  above room temperature). The rubbery PEO blocks (glass transition below room temperature) provide to the system flexibility and hydrophilicity. As reported by Fakirov et al. [26, 27], the morphology of PEO-PBT multi-block copolymers is very complex. These can comprise up to five different phases: amorphous and crystalline phase in both blocks, and interphase between them. Hence, the variation of both segments and molecular

weight of PEO lead to materials with different properties. An increased molecular weight of blocks favours micro-phase separation [28].

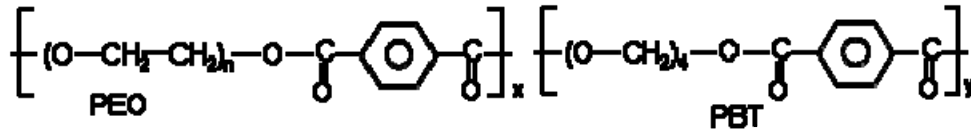


Figure 1: Schematic presentation of chemical structure of PEO-PBT multi-block copolymer.

In Table 1 typical basic properties of the copolymers are shown. These are the ratios of PEO-PBT blocks (composition for each block, e.g.: 600PEO77PBT23 sample means 600 g/mol and 77 wt. % of PEO, and 23 wt. % of PBT ), the density of membranes obtained by buoyancy method and equation 2 (see Table 1), which are between the values for PEO (~1.13 g/ mol) and PBT homo-polymer (~1.31 g/mol) (technical data), and the swelling of dense membranes performed in Millipore water during 14 days.

In samples, where the molecular weight of PEO block increased (at the same PEO content) the density slightly decreased (Table 1). The highest equilibrium sorption was observed in samples with high molecular weight of PEO (1500 and 4000 g/mol). The hydrophilic PEO block produces PEO-PBT copolymers with a high water sorption, which is due to the EO units, either by molecular weight or by PEO content increase. Sample with the lowest Mw of PEO and high PBT fraction (hydrophobic) does not show strong tendency to swell (300PEO55PBT45 sample).

Table 1: Physical properties of Poly(ethylene oxide)-Poly(butylene oxide terephthalate) multi-block copolymers



<b>Polymer</b>	<b>Ratio_PEO:PBT</b>	<b>Density</b>	<b>Swelling</b>
	<b>[wt. %]</b>	<b>[g/cm<sup>3</sup>]</b>	<b>[%]</b>
600PEO77PBT23	77:23	1,202	45
1000PEO80PBT20	80:20	1,191	96
1500PEO77PBT23	77:23	1,188	109
300PEO55PBT45	55:45	1,278	6
4000PEO55PBT45	55:45	1,228	126

Table 2 shows thermal properties (obtained from second heating) of different PEO-PBT copolymers. Since the PEO content varies between 55 and 80 wt. % and its Mw is in the range of 300 to 4000 g/mol, different glass transition temperatures (T<sub>g</sub>) are expected for each sample. T<sub>g</sub> corresponding to the PEO phase was possible to observe in all samples, while melting temperatures (T<sub>m</sub>) were not clearly depicted. The T<sub>g</sub> of PBT blocks were impossible to detect with DSC method; according to literature it should be located around 60 °C [26]. T<sub>g</sub> in block copolymers with 77-80 wt. % of PEO content decreases according to the PEO Mw increase, whereas T<sub>m</sub> and degree of crystallinity (X<sub>c</sub>) increase with length of PEO segment. Interpretation of T<sub>g</sub> and T<sub>m</sub> is consistent for copolymers containing 55 wt. % of PEO phase as well, meanwhile T<sub>m</sub> and X<sub>c</sub> for PEO in sample 300PEO55PBT45 were not observed. For the PBT phase is difficult to discuss T<sub>m</sub> and X<sub>c</sub> comparing block copolymers with the same fraction of blocks, because some data were impossible to determine. However, it seems that an increase of PBT fraction leads to higher values of T<sub>m</sub> and X<sub>c</sub>. T<sub>m</sub> for crystalline PBT is in the range of 110 and 213 °C, which is in accordance with literature data [15]. Due to the unknown PBT lengths (Mw), their influence on the thermal properties can not be discussed very well. Therefore, taking into

account these results, block copolymers with high Mw and fraction of PEO could exhibit desired properties for gas transport; since likely low T<sub>g</sub> and lower X<sub>c</sub> mostly affect gas transport properties.

Table 2: Thermal properties of Poly(ethylene oxide)-Poly(butylene oxide terephthalate) multi-block copolymer

Polymer	PEO			PBT	
	T <sub>g</sub>	T <sub>m</sub>	X <sub>c</sub>	T <sub>m</sub>	X <sub>c</sub>
	[°C]	[°C]	[%]	[°C]	[%]
600PEO77PBT23	-42	-	-	110	3
1000PEO80PBT20	-45	19.6	16	-	-
1500PEO77PBT23	-49	27.0	24	-	-
300PEO55PBT45	-20	-	-	152	6
4000PEO55PBT45	-49	40.5	19	213	9

Figure 2 illustrates results of thermogravimetric examination performed under argon. Tested samples start to degrade approximately at 330 °C, except copolymer 300PEO55PBT45, which shows no mass loss up to 380 °C. There is no significant difference in temperature of degradation between different copolymers, but it is still possible to observe that samples with high PEO content start to degrade at lower temperatures. However, all samples show good thermal stability, and they can be considered as potential material for membranes which can be used in gas separation at moderate high temperature (~100 °C).

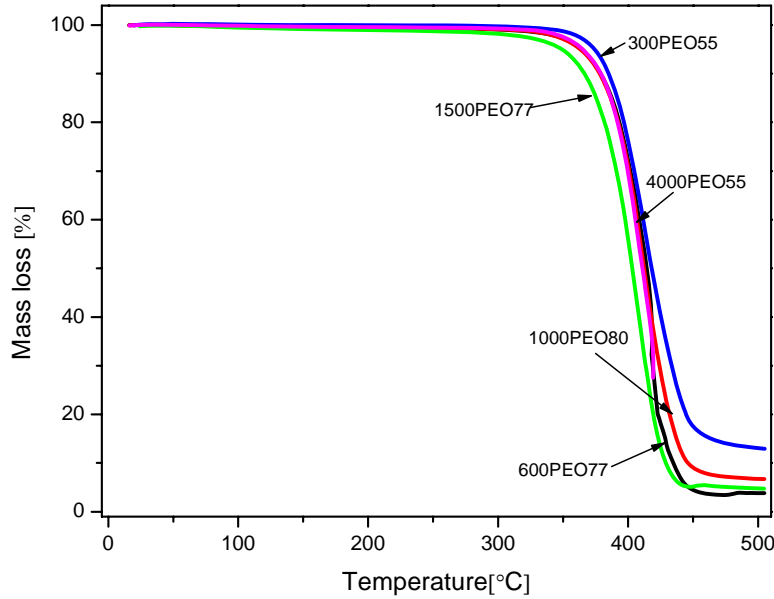


Figure 2: Thermal gravimetric analyses of PEO-PBT multi-block copolymer.

### 3.2 Gas permeation of PEO-PBT membranes

The gas permeability measurements were carried out by the time-lag method and the permeability (P), diffusivity (D), solubility (S) and selectivity ( $\alpha$ ) for gases A and B were determined under steady state by the following equations: [29].

$$P = D \cdot S = \frac{V_p \cdot l \cdot (p_{p_2} - p_{p_1})}{A \cdot R \cdot T \cdot \Delta t \cdot (p_f - \frac{p_{p_2} + p_{p_1}}{2})} \quad (3)$$

$$D = \frac{l^2}{6 \cdot \theta} \quad (4)$$

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A \cdot S_A}{D_B \cdot S_B} \quad (5)$$

where  $V_p$  [m<sup>3</sup>] is the constant permeate volume,  $R$  [Pa·l·mol<sup>-1</sup>·K<sup>-1</sup>] is the gas constant,  $l$  [m] is the film thickness,  $A$  [m<sup>2</sup>] is the effective area of membrane,  $\Delta t$  [s] is the time for permeate pressure increase from  $p_{p1}$  to  $p_{p2}$ ,  $p_f$  [Pa] is the feed pressure, and  $\theta$  is called time-lag [s].

The solution-diffusion transport model [30] was applied for discussing the gas transport properties of dense membranes. Figure 3 shows the permeability of CO<sub>2</sub> for PEO-PBT block copolymers with different Mw and different PEO content (we are using the well established barrer unit for permeability, where 1 barrer corresponds to 7.5005 m<sup>2</sup> s<sup>-1</sup> Pa<sup>-1</sup>, SI units). Permeabilities increase proportionally to the molecular weight and fraction of PEO (the lines are only shown in order to identify each group of samples). The interaction of CO<sub>2</sub> with EO units in the polymer is very well known from literature and was discussed in many publications [16-18, 31-37]. Therefore, these results were expected. The block copolymer with approximately 77 wt. % of PEO (copolymer with 1500 g/mol of PEO) presented the highest measured permeability 115 barrer (862.6 m<sup>2</sup> s<sup>-1</sup> Pa<sup>-1</sup>), while the copolymer with 4000 g/mol of PEO and 55 wt. % of PEO exhibited 96 barrer (720 m<sup>2</sup> s<sup>-1</sup> Pa<sup>-1</sup>). Considering that samples with 77 wt. % and 80 wt. % of PEO content are the same, one can suppose that higher molecular weight of PEO would result in higher permeability. However, this assumption is only a speculation (it will be discussed below). Although the permeability is lower in a copolymer with 55 wt. % of PEO content, it seems that the Mw of PEO has a stronger effect on gas transport than the fraction of PEO.

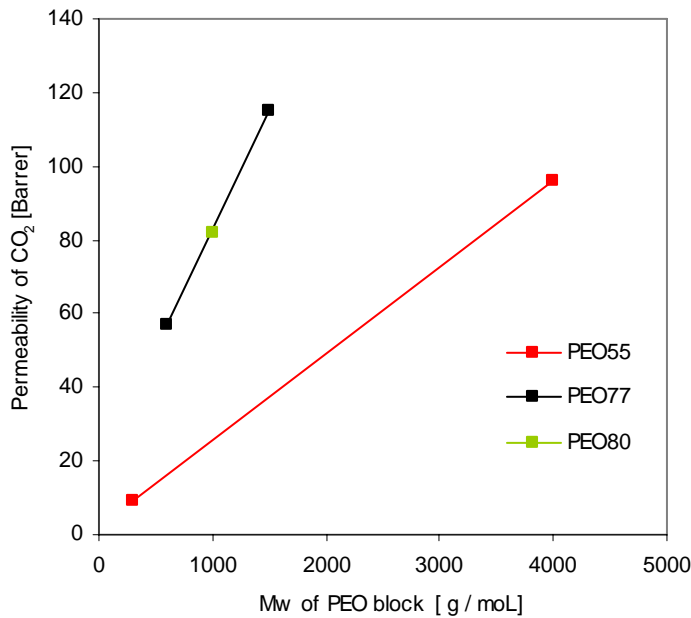


Figure 3: Permeability of CO<sub>2</sub> as a function of Mw of PEO.

Efficient membranes for CO<sub>2</sub> separation must exhibit enhanced solubility selectivity [32] and a weak size sieving ability approaching diffusivity selectivity ( $D_A/D_B$ ) close to 1. Figure 4 presents the trend of both selectivities as a function of Mw of PEO. Diffusivity selectivity is favoured in 4000PEO55PBT45 sample. It indicates higher diffusivity selectivity in copolymers with 77 or 80 wt. % of PEO content and higher molecular weight (>1500 g/mol). Solubility selectivity is evidently higher in copolymers with high fraction of PEO. Nevertheless, there is a deviation of solubility selectivity in 1000PEO80PBT20 sample; this deviation could be due to the slightly higher content of PEO. Therefore, an increase of Mw of PEO at higher PEO content would produce a membrane with improved performance.

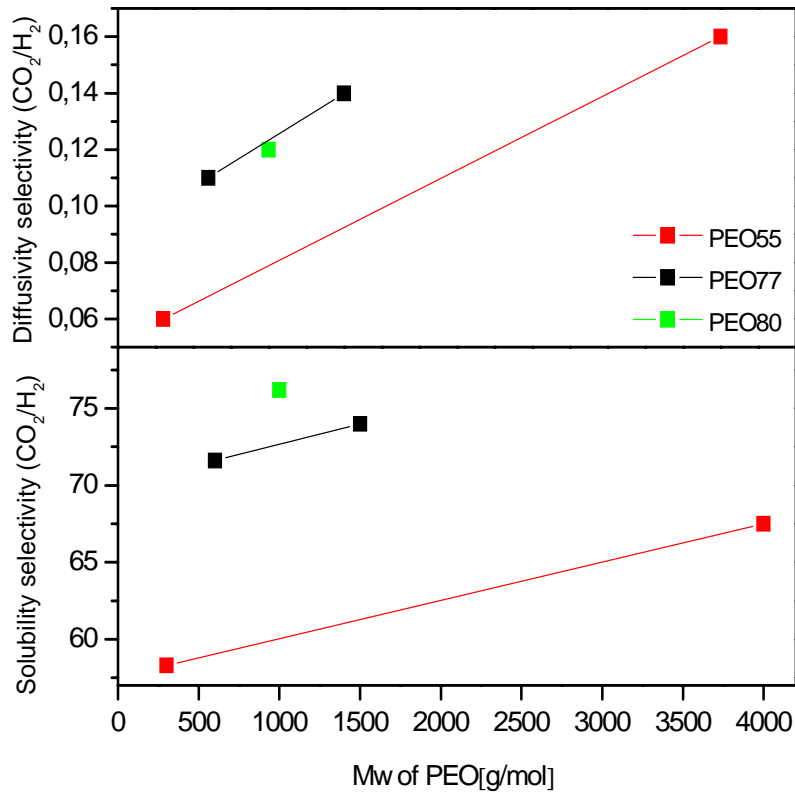


Figure 4: Diffusivity and solubility selectivity of CO<sub>2</sub>/H<sub>2</sub> as a function of fraction of PEO.

Table 3 shows permselectivity of CO<sub>2</sub> over H<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub>. Selectivity of CO<sub>2</sub>/H<sub>2</sub> is strongly influenced by Mw of PEO blocks, and this is clearly observed in samples with 55 wt. % of PEO content, where it is increased from 3.7 to 10.9. On the other hand, CO<sub>2</sub>/N<sub>2</sub> seems to be influenced by both PEO content and its Mw. No significant change is observed in CO<sub>2</sub>/CH<sub>4</sub> selectivity, what could be attributed to the molecule size similarity between CO<sub>2</sub> and CH<sub>4</sub>.

Although all these results show that the tuning of PEO content and molecular weight of PEO segment leads to membranes with higher performance, other factors such as crystallization

of both blocks, microphase separation (morphology) and solubility in common solvents play important role to optimize a carbon dioxide selective membrane.

Table 3: Selectivities of different Poly(ethylene oxide)-Poly(butylene oxide terephthalate) multi-block copolymers.

Polymer	Permselectivity		
	CO <sub>2</sub> /H <sub>2</sub>	CO <sub>2</sub> /N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>
600PEO77PBT23 (A)	7.8	46	18
1000PEO80PBT20 (B)	8.9	44	18
1500PEO77PBT23 (C)	10.2	50	17
300PEO55PBT45	3.7	21	20
4000PEO55PBT45 (D)	10.9	44	17

### 3.3 PEO-PBT tailor made membranes

The CO<sub>2</sub> permeabilities of the polymers A, B, C, D (Table 3) are plotted versus the molecular weight of the PEO block in Figure 5. These experimental data are fitted using a polynomial mathematical equation, which is used for estimation of CO<sub>2</sub> permeability (triangle data).

$$P(\text{CO}_2) = -2.2746 + 0.1081(M_w) - 2 * 10^{-5} (M_w)^2 \quad (6)$$

From these points one may conclude that the CO<sub>2</sub> permeability could have a maximum value for a copolymer containing PEO with a molecular weight between 2000 and 3500 g/mol. However, the commercially available polymer (D) did not differ only in the PEO molecular weight but also in the PEO weight fraction (55 instead of 77 wt. % PEO). Therefore, in order to validate this

value, the polymer 4000PEO77PBT23 was ordered and synthesized at PolyVation (Netherlands). The permeability of synthesized polymer (point E in Figure 5) was lower than expected.

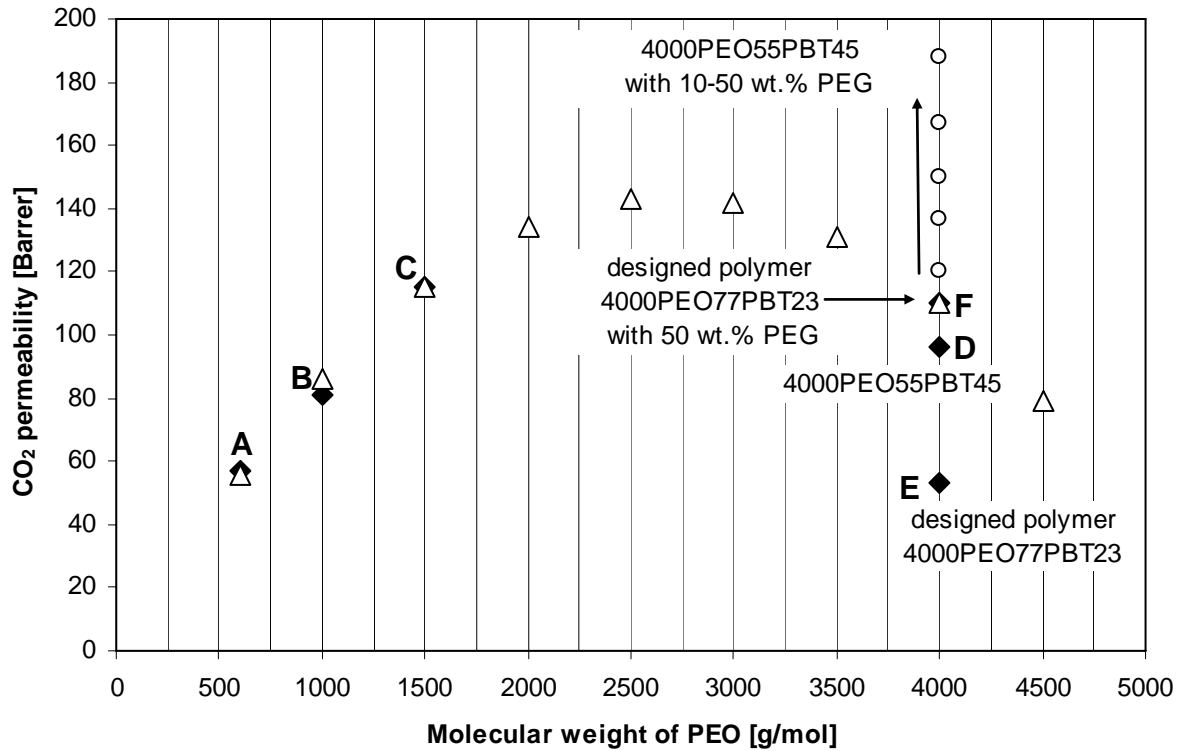


Figure 5: Experimental and predicted data of CO<sub>2</sub> permeability as a function of molecular weight of PEO block.

The reason for lower permeability can be attributed to an increased crystallinity in the PEO phase, since the  $T_m$  was 45°C and  $X_c = 0.42$ , which are higher than those observed in Table 2. Thus, besides the PEO content in the polymer system, the ratio amorphous to crystalline phase is also very important for improving the CO<sub>2</sub> permeability, where an increase of the crystalline phase leads to a strong decrease of solubility and diffusivity [18], consequently the permeability is dropped. One way to increase the gas permeability is destroying the crystalline phase, which will improve the solubility as well as diffusivity (amorphous phase increase). Addition of 50 wt.



% of PEG (200 g/mol) destroyed/reduced the crystallinity of the PEO phase ( $T_m = 38\text{ }^\circ\text{C}$ ,  $X_c = 0.23$  and  $T_g = -79\text{ }^\circ\text{C}$ ) in the polymer system, thus a membrane with a higher permeability resulted (point F in Figure 5). Therefore, a simple and effective method to improve the performance of these multi-block copolymers is to add PEG with low molecular weight, which at the same time destroys the crystalline phase and increases the content of EO units.

The two most promising copolymers, i.e. 1500PEO77PBT23 (C) and 4000PEO55PBT45 (D) were chosen for the preparation of blends with PEG in order to tailor a blend membrane with improved gas transport properties. Blend membranes prepared from both selected copolymers showed excellent miscibility with PEG200 up to 50 wt. % and, transparent films were obtained. In Table 4 the permeabilities of different gases and selectivities for 1500PEO77PBT23/PEG200 blends are shown.  $\text{CO}_2$  permeability slightly increases from 115 barrer (pristine copolymer) to 134 barrer (blend with 30 wt. % of PEG), then it decreased to 110 barrer. As it is seen, all gases behave similar, i.e. first the permeability increases at lower content of PEG (< 30 wt. %), and then at higher PEG content it decreases to values close to the pristine 1500PEO77PBT23 sample. This behaviour can be related to a crystallinity increase (or chain ordering); since during thermal characterization a new melting point was observed between 50 and 150  $^\circ\text{C}$  (it will be discussed later). The selectivities were almost constant  $\text{CO}_2/\text{H}_2 \sim 10.5$ ,  $\text{CO}_2/\text{N}_2 \sim 40$  and  $\text{CO}_2/\text{CH}_4 \sim 15$ , respectively.

Table 4: Permeability and selectivity of PEG200 blend membranes with polymer 1500PEO77PBT23.

<b>Permeability</b>						
PEG [wt. %]	0	10	20	30	40	50
H <sub>2</sub>	11,3	11,8	11,5	12,1	10,8	10,1
N <sub>2</sub>	2,52	3,1	3,2	2,8	3,8	3
CH <sub>4</sub>	6,76	7,63	8,3	8,9	7,6	7,5
CO <sub>2</sub>	115	130	126	134	114	110
<b>Permselectivity</b>						
CO <sub>2</sub> /H <sub>2</sub>	10,2	11,0	11,0	11,1	10,6	10,9
CO <sub>2</sub> /N <sub>2</sub>	45,6	42,1	40,0	48,7	30,1	36,9
CO <sub>2</sub> /CH <sub>4</sub>	17,0	17,0	15,2	15,1	15,0	14,7

The diffusivity of gases through the blends was plotted as a function of PEG content (Figure 7). The diffusivity of H<sub>2</sub> in blends with 50 wt. % of PEG decreased almost 100 % compared to pristine 1500PEO77PBT23. The diffusivity of other gases has a similar trend; therefore, it can be concluded that the amorphous phase decreased in the blends with higher PEG content. Blend membranes were optically homogeneous, since all samples were completely transparent. Thus, no phase separation is expected. Usually, the homogeneity is discussed by the glass transition temperature (T<sub>g</sub>) behaviour, where single T<sub>g</sub> represents a homogenous system. But it was not possible to determine the T<sub>g</sub> of the blend membranes (see Figure 8).

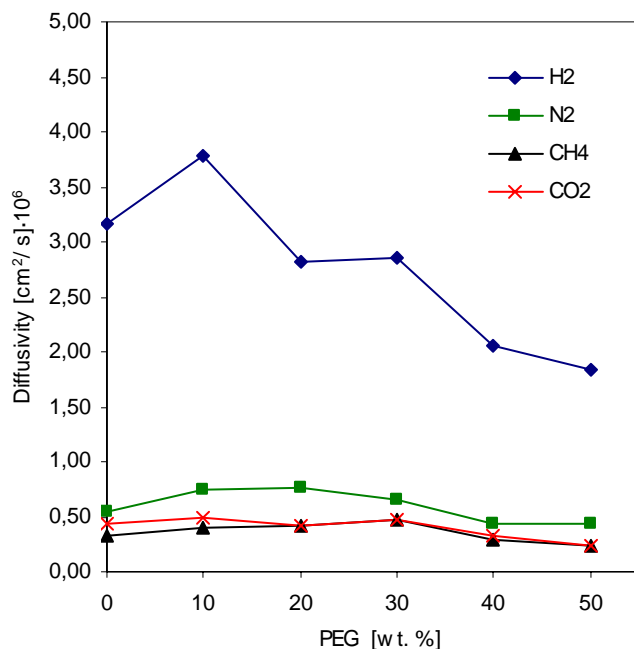


Figure 7: Diffusivity of different gases (H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>) in copolymer 1500PEO77.

In Figure 8 the thermograms of copolymer 1500PEO77PBT23 and its blends with PEG (first and second heating) are presented. In the first (fill line) and second heating (dash line) the melting temperatures of the PEO phase (10-35 °C) are clearly observed, although for second heating the peaks are shifted to higher values. The observed peaks around 140 °C in the first heating disappear when the second heating was done. These results show us that an ordered phase was present in the membrane samples (presence of endothermic peak), since after first heating the thermal history of samples is completely different compared to the second heating, where no ordering is observed (no endothermic peak).

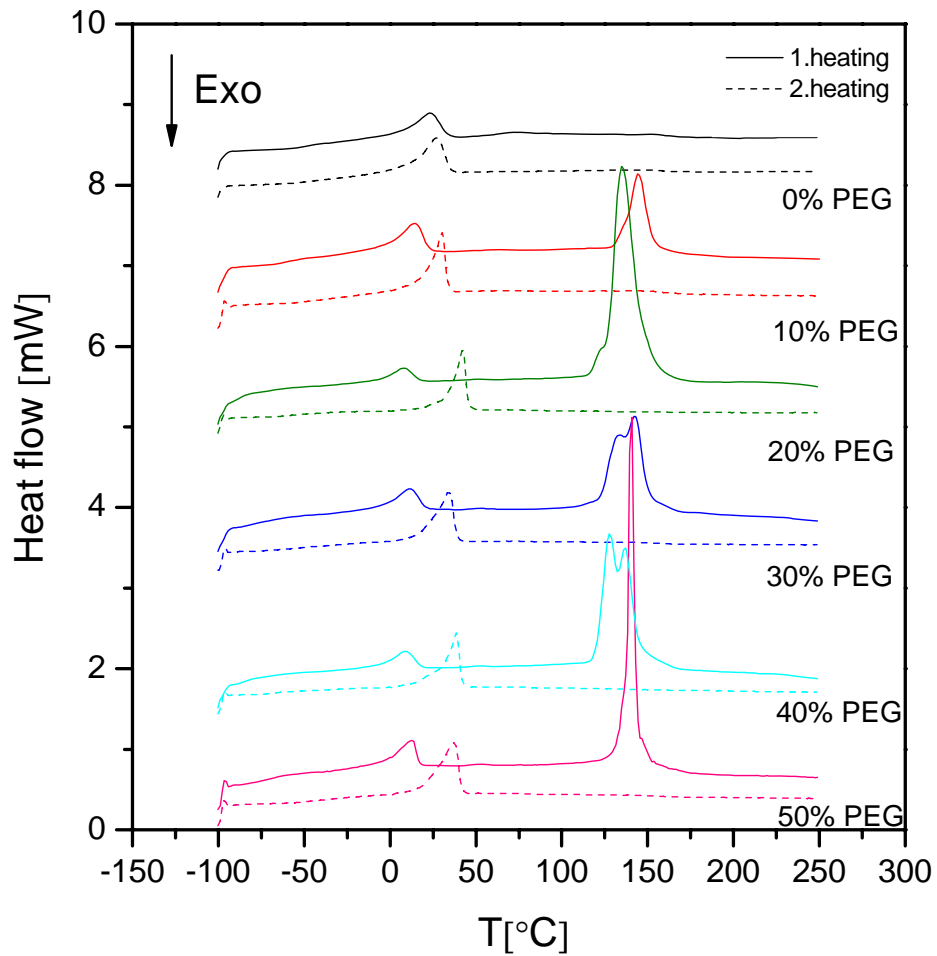


Figure 8: DSC thermogram of copolymer 1500PEO77PBT23 and its blends with PEG200. The thermograms have been displaced vertically for easier viewing.

Therefore, the observed low permeability in blend membranes with higher PEG content can be explained by the presence of this ordered phase in the film. Since after 20 wt. % of PEG, the CO<sub>2</sub> diffusivity dropped to lower values, and thus, the permeability decrease fits with formation of a ordered phase in the blends (possible crystalline phase). This observed peak could correspond to melting temperature of PBT, since T<sub>m</sub> of this phase varies between 110 °C and

213 °C according to composition in different copolymers (Table2). The formation of this ordered phase can be mainly attributed to the membrane formation process and presence of PEG. Low molecular PEG could induce better microphase separation and crystallization of PBT phase, which could be related to the compositional heterogeneity of complex morphology between interphases [26].

The 4000PEO55PBT45 sample and its blend with PEG behave completely different compared to the above mentioned system. Here the addition of PEG shows strong impact in improvement of gas transport properties. To explain the differences, the thermal behaviour and crystallinity of copolymer and its blends are presented in Table 5.

Table 5: Thermal properties and crystallinity of 4000PEO55PBT45 and PEG blends

Polymer PEG blends	PEO			PBT	
	$T_g$	$T_m$	$X_c$	$T_m$	$X_c$
	[°C]	[°C]	[%]	[°C]	[%]
4000PEO55PBT45	-49	40.5	19	213	10
4000PEO55PBT45+10%PEG	-	46.7	20	-	-
4000PEO55PBT45+20%PEG	-	47.7	21	-	-
4000PEO55PBT45+30%PEG	-	47.0	21	-	-
4000PEO55PBT45+40%PEG	-	50.1	25	-	-
4000PEO55PBT45+50%PEG	-	51.8	24	-	-

In pristine 4000PEO55PBT45 polymer, two characteristic  $T_m$  were clearly observed, what is consistent with the microphase separated structure in block copolymers [38]. For blend samples  $T_m$  for the PEO (Table 5 and Figure 9 a) crystalline phase is shifted to higher values when PEG is added into the polymer matrix. These results are contradictory to those observed in Pebax/PEG system reported recently [16]. High PEG content slightly increases the crystallinity from 19 % (pristine polymer) to 24 % (blend with 50 % of PEG). These results can be attributed to the presence of low molecular weight PEG and longer segment of PEO in 4000PEO55PBT45 sample.

$T_m$  values of PBT in blend samples are not well defined (Figure 9 b), they are shifted to lower values with PEG content, and high PEG content presents only amorphous phase. Decrease of crystallinity in PBT phase greatly led to improved diffusivity for all gases (Figure 10), especially for  $H_2$  and  $CO_2$ . Thus, thermal properties which give information about crystallinity are in a good agreement with permeability values, the higher the amorphous phase, the higher the gas transport.

The observed peak ( $\sim 140$  °C) in previous blend based on 1500PEO77PBT23 copolymer was not detected in the present blend (4000PEO55PBT45/PEG). Therefore, the lower permeability obtained in 1500PEO77PBT23/PEG blends can be mainly attributed to that ordered phase found by DSC analysis. Although this ordered phase is not thermally stable, its presence in fresh films could have affected to the gas permeability.

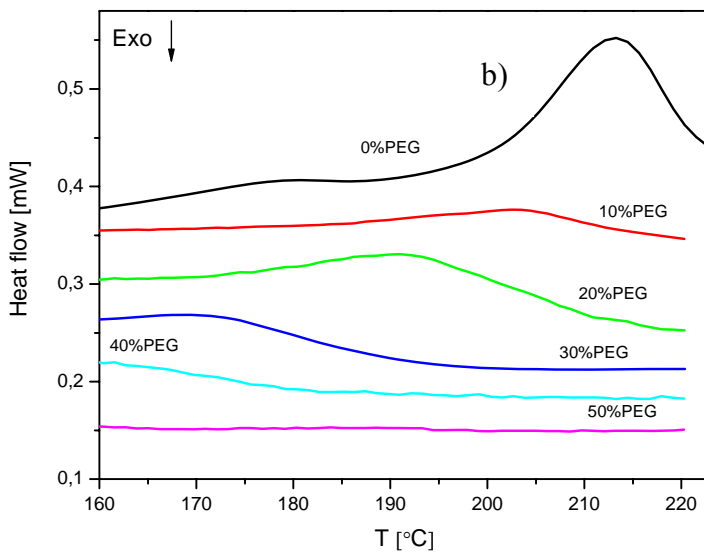
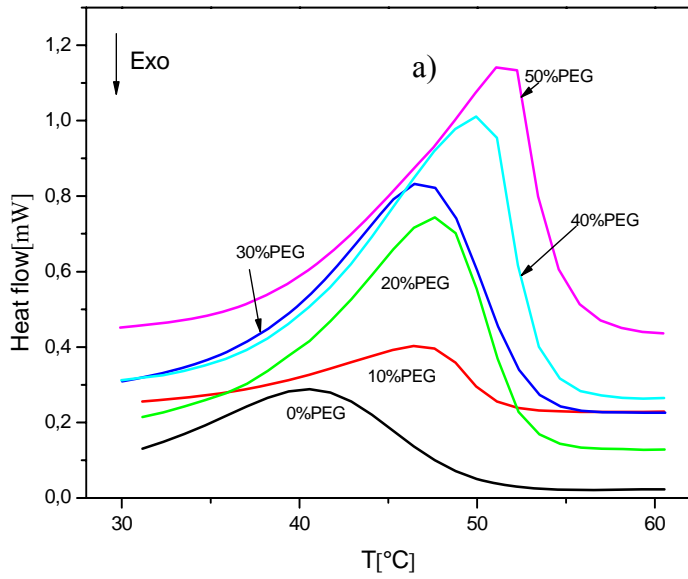


Figure 9a) and b): DSC thermograms for PEO and PBT blocks in copolymer 4000PEO55PBT45.

The permeabilities for 4000PEO55PBT45/PEG blend membranes are shown in Figure 10 as a function of total PEO, whereas the PEO content was recalculated by equation 6 according to total amount of PEO ( $w.\%_{PEO_{total}}$ ) in the blend system:

$$wt.\%_{PEO_{total}} = 0.55 \cdot m_{copolymer} + m_{PEG200} \quad (6)$$

where 0.55 represents the weight fraction of PEO in the copolymer,  $m_{copolymer}$  and  $m_{PEG200}$  are the weight of copolymer and PEG in 100 g of blend, respectively. Recalculation has been done in order to calculate the total fraction of PEO, which leads to easier comparison between tailor made blends and designed polymer.

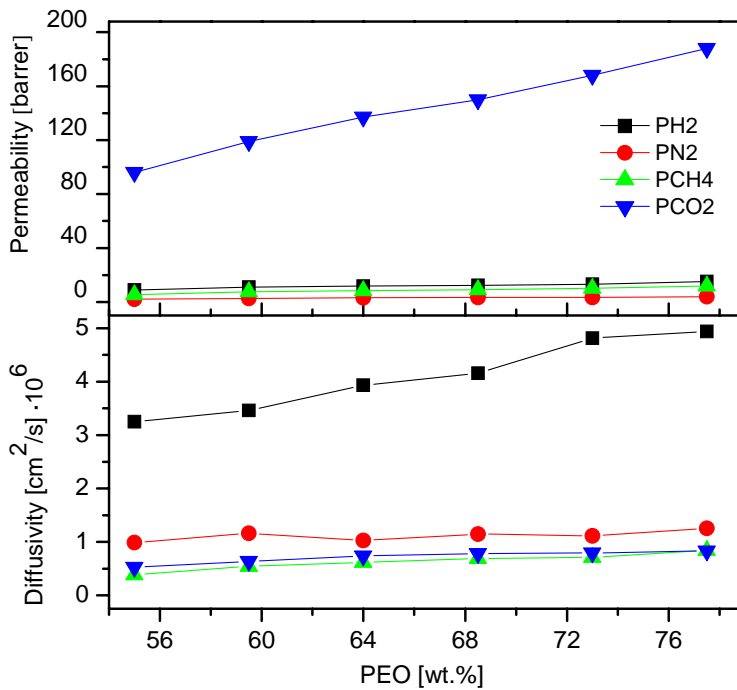


Figure 10: Permeability and diffusivity of 4000PEO55PBT45 blends with PEG as function of total PEO.



Measured permeability for pristine copolymer 4000PEO55PBT45 is 96 barrer ( $720 \text{ m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$ ) and it is increased two fold ( $\sim 190$  barrer,  $1425 \text{ m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$ ) by addition of 50 wt. % of PEG (after recalculation, this blend contains 77.5 wt. % of PEO phase). Therefore, incorporation of EO units as PEG into the 4000PEO55PBT45 polymer matrix clearly led to a material with improved gas transport properties (see Figure 5, circle data). This fact can be assigned to structural (increase of EO units) and morphological (decrease of crystallinity) changes in the membrane matrix. Evident effect of structural changes reflects in increased  $\text{CO}_2$  solubility (Figure 11) obtained by increase of PEG content in the system, this enhancement is approximately 25 % in copolymer 4000PEO55PBT45 at highest content of PEG.

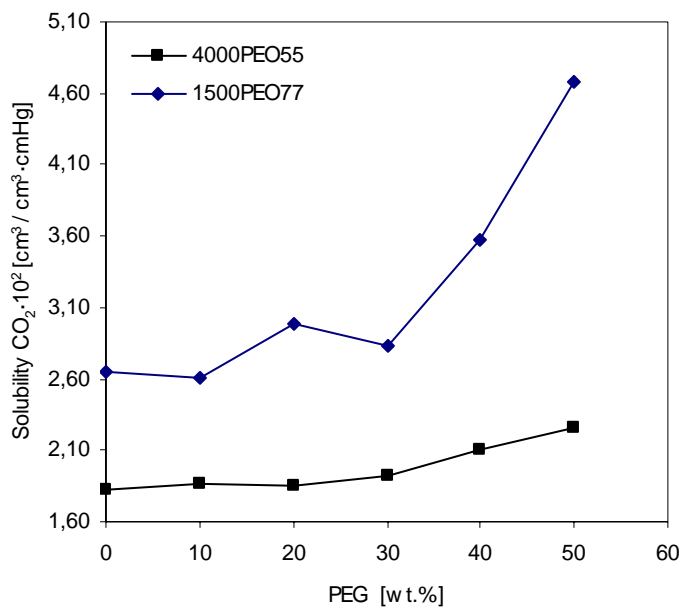


Figure 11: Solubilities of  $\text{CO}_2$  in copolymer 1500PEO77PBT23 and 4000PEO55PBT45 as a function of PEG200 content.

To discuss the enhancement of permselectivity of the membranes, a detailed overview of their solubility selectivity and diffusivity selectivity is presented in Table 6. The successful  $\text{CO}_2$

separation by using a membrane prepared from a rubbery polymer is based on high solubility selectivity, while diffusivity selectivity should be maintained or increased.

Table 6: Perm-, solubility- and diffusivity selectivity of PEG200 blend membranes with polymer 4000PEO55PBT45.

<b>Permselectivity</b>						
<b>PEO [wt.%]</b>	<b>55.0</b>	<b>59.5</b>	<b>64.0</b>	<b>68.5</b>	<b>73.0</b>	<b>77.5</b>
CO <sub>2</sub> /H <sub>2</sub>	10.8	10.6	11.7	12.3	12.4	13.2
CO <sub>2</sub> /N <sub>2</sub>	43.5	46.8	44.9	45.4	49.1	47.3
CO <sub>2</sub> /CH <sub>4</sub>	17.1	15.8	16.4	16.4	16.4	15.9
<b>Solubility selectivity</b>						
CO <sub>2</sub> /H <sub>2</sub>	67.5	58.8	61.7	64.9	72.9	77.8
CO <sub>2</sub> /N <sub>2</sub>	82.1	85.0	62.3	66.7	68.2	71.7
CO <sub>2</sub> /CH <sub>4</sub>	12.6	13.5	13.8	14.5	14.5	16.1
<b>Diffusivity selectivity</b>						
CO <sub>2</sub> /H <sub>2</sub>	0.16	0.18	0.19	0.19	0.17	0.17
CO <sub>2</sub> /N <sub>2</sub>	0.53	0.55	0.72	0.68	0.72	0.66
CO <sub>2</sub> /CH <sub>4</sub>	1.36	1.17	1.19	1.13	1.13	0.99

An increased CO<sub>2</sub>/H<sub>2</sub> permselectivity is observed when PEO content is increased, which is a consequent of solubility selectivity increase. In this type of separation the strategy of increasing the solubility plays an important role, because of the unfavourable diffusivity selectivity. Incorporation of PEG pushes the permselectivity of CO<sub>2</sub>/H<sub>2</sub> close to 13. However, the

CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> permselectivity are maintained almost constant due to the similar penetrants size. Thus, rivalries between both D and S factors keep permeability nearly constant.

## **Conclusions**

Different PEO-PBT multi-block copolymers were used to prepare carbon dioxide selective membranes. The influence of PEO block length and weight fraction was studied. The CO<sub>2</sub> permeability runs through a maximum when plotted versus the molecular weight of the PEO block (constant weight fraction of PEO block). According to the estimated values (tailor made polymer), a molecular weight of 2000 or 2500 g/mol of PEO in the PEO-PBT multi-block copolymer could present the highest CO<sub>2</sub> permeability.

Low molecular weight PEG was added to increase EO units in the system. The incorporation of EO units did not necessarily lead to increased permeability, since in blends of 1500PEO77PBT23, the permeability decreased due to the PEO and PBT crystallization. Thermal properties were used to correlate morphological and structural changes in the copolymer system.

The newly designed copolymer 4000PEO77PBT23 showed a different behavior and its blend with 50 wt. % of PEG presented higher permeability. However, a two fold improvement in CO<sub>2</sub> permeability was achieved for 4000PEO55PBT45/PEG blend membrane, and the CO<sub>2</sub>/H<sub>2</sub> selectivity was increased up to 13 at room temperature. The combination of CO<sub>2</sub> permeability and CO<sub>2</sub>/H<sub>2</sub> selectivity is among the best ones published up to now.

## **Acknowledgments**

The authors thank Dr. Jeroen Pieper for providing polymers (IsoTis OrthoBiologics, USA) and S. Nowak for DSC measurements. A. Car thanks the Ministry of Higher Education, Science and Technology, Slovenia and the Deutscher Akademischer Austauschdienst (DAAD) fund for grant.

Part of the work was supported by the Helmholtz-Alliance MemBrain (Gas Separation Membranes for Zero-Emission Fossil Power Plants).

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