



Tuning of mass transport properties of multi-block copolymers for CO₂ capture applications

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ABSTRACT

Polyether and especially poly(ethylene oxide) (PEO) based segmented block copolymers are very well known for their high CO₂ permeability combined with a high CO₂/light gas selectivity, but most (commercially) available block copolymers have incomplete phase separation between the soft and hard blocks in the polymer leading to reduced performance. Here we present a polyether based segmented block copolymer system with improved phase separation behavior and gas separation performance using poly(ethylene oxide) (PEO) and/or poly(propylene oxide) (PPO) as a soft segment and short monodisperse di-amide (T Φ T) as a hard segment.

In this work we tune the mass transport properties of such multi-block copolymers for CO₂ capture by systematically investigating the effect of the type and length of soft segment in the block copolymer at constant short hard segment. The effect of (1) the length of the PEO soft segment, (2) the type of soft segment (PPO vs. PEO) and (3) the use of a mixture of these two different types of soft segment as a method to tune the gas separation performance and its relation with the thermal–mechanical properties is investigated. The use of such a polyether based segmented block copolymer system as presented here offers a very versatile tool to tailor mass transfer and separation properties of membranes for gas and vapor separation.

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1. Introduction

Block copolymers have been widely investigated for the removal of CO₂ from light gases [1–11]. In general, block copolymers consist of an alternating series of flexible soft segments and crystallizable hard segments [12]. The crystallizable hard segments provide the material its mechanical stability, while the soft segments are the dominant phases for gas permeation. The type of soft and hard segments can be chosen independently, which makes them a versatile instrument to tune the properties of gas separation membranes.

To obtain excellent membrane properties, the microdomain phase separation of the block copolymers is crucial and needs to be controlled. A block copolymer with improved properties for gas permeation should exhibit the following properties: (1) good phase separation of the hard and soft segments; (2) complete crystallization of the hard segment; (3) high PEO content; (4) low glass transition temperature of the soft segment (high chain flexibility);

and (5) no soft phase crystallinity or low soft segment melting temperature.

These properties are not met by today's (commercially) available block copolymers as they often have incomplete phase separation due to non-uniformity of the hard segment, leading to large amounts of non-crystallized hard segments within the soft amorphous phase (properties 1–2). This restricts the amount of PEO that can be used (property 3), it reduces chain flexibility (property 4) and moreover the soft PEO phase often shows semi-crystalline behavior as well (property 5). A schematic representation of the morphology of a typical commercially available block copolymer is shown in Fig. 1a.

To improve the performance of the block copolymers and to allow us to control the microdomain phase separation Husken et al. used monodisperse crystallizable T6T6T hard segments (a tetra-amide) with strongly improved crystallization behavior, resulting in almost complete phase separation and enabling high soft phase concentrations (properties 1–3) (Fig. 1b) [11,13]. Although crystallization of the PEO phase was still present, this could be partially suppressed by extending low molecular weight PEO (600 g/mol) with terephthalic units (property 5) [11,14]. To further improve membrane gas separation properties we propose

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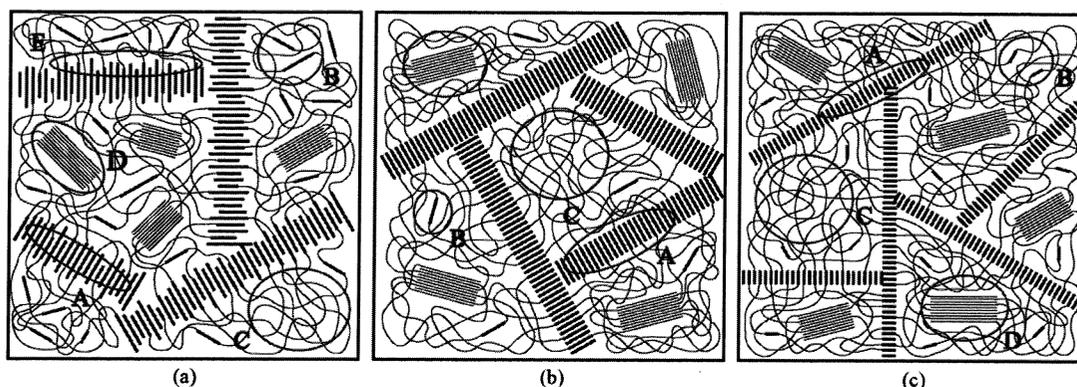


Fig. 1. Schematic representation of the morphology of (a) commercially available block copolymers (e.g. the PEBA[®] family), (b) PEO based block copolymers with monodisperse long T6T6T hard segments as used by Husken et al. [11] and (c) polyether based block copolymers with monodisperse short TΦT hard segments as used in this article. The circled areas are representative for (A) crystalline hard segments, (B) non-crystallized rigid hard segments, (C) continuous amorphous soft phase, (D) crystalline soft phase and (E) intermediate region with mixed crystalline hard segments and non-crystallized soft segments.

the use of a short monodisperse di-amide hard segment (length ~2 nm) instead of the longer tetra-amide hard segment (length ~4.2 nm). The introduction of this type of hard segment will lead to the incorporation of higher amounts of soft segment (property 3). The resulting morphology is shown in Fig. 1c.

Apart from the hard segment, also the type of soft segment can be used as a tool to tune the gas permeation properties of membranes made of such a block copolymer system. By changing the soft segment characteristics, we are able to control the crystallization behavior of the soft segment in the polymer, thus tailoring its gas permeation properties.

In this work we tune the mass transport properties of such multi-block copolymers for CO₂ capture by systematically investigating the effect of the type and length of soft segment in the block copolymer at constant short hard segment. The effect of (1) the length of the PEO soft segment, (2) the type of soft segment (PPO vs. PEO) and (3) a mixture of these two different types of soft segment as a method to tune the gas separation performance and its relation with the thermal–mechanical properties is investigated. The use of PPO soft segments avoids the regular chain packing that is observed in PEO [13]. As a result it suppresses the crystallization of the soft segment and a block copolymer with PPO soft segments is expected to be completely amorphous above its *T_g*. Furthermore, the use of PPO soft segments increases the free volume of the block copolymers, which should result in higher intrinsic gas permeabilities. However, the extra methyl side group decreases the polarity and the CO₂ solubility of the soft segment compared to PEO, thus possibly reducing the CO₂/light gas selectivity.

To investigate the effect of the different aspects mentioned in the previous paragraph on membrane performance, monodisperse di-amide (TΦT) hard segments are used to prepare polyether based block copolymers with PEO, PPO and mixtures of both as soft segments. Their gas permeation properties are systematically studied and related to their thermal–mechanical properties as described in a separate article [15].

2. Gas permeation in macromolecular structures

Gas diffusion in non-porous structures can be described using Fick's first law [16]. Under steady state conditions and expressing concentrations as partial pressures, using Henry's law, the following Eq. (1) can be derived:

$$J_i = \frac{D_i S_i}{l} \Delta p_i \quad (1)$$

where J_i is the gas flux of component i through the membrane ($\text{cm}^3(\text{STP})/(\text{cm}^2 \text{ s})$), D_i is the diffusivity coefficient of component i (cm^2/s), S_i is the solubility coefficient of component i ($\text{cm}^3(\text{STP})/(\text{cm}^3 \text{ cmHg})$), l is the membrane thickness (cm), and Δp_i is the partial pressure difference of component i over the membrane (cmHg). The product of the diffusivity and solubility is the permeability, which is generally expressed in units of Barrer, where 1 Barrer equals $1 \times 10^{-10} \text{ cm}^3(\text{STP}) \text{ cm}/(\text{cm}^2 \text{ s cmHg})$. The ideal selectivity of a membrane for gas A over gas B is given by the ratio of the pure gas permeabilities:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B} \right) \left(\frac{S_A}{S_B} \right) \quad (2)$$

where D_A/D_B is the diffusivity selectivity and S_A/S_B is the solubility selectivity. Gas diffusivity is enhanced by decreasing penetrant size, increasing polymer chain flexibility, increasing polymer fractional free volume (FFV) and decreasing polymer–penetrant interactions [16]. Penetrant solubility is increased by increasing condensability of the penetrant (which increases with increasing critical temperature and boiling point) and increasing polymer–penetrant interactions [16]. In general, polyether based block copolymers exhibit a low *T_g* resulting in high CO₂ diffusivity but low diffusivity selectivity. High CO₂/light gas selectivity is achieved by high CO₂/light gas solubility selectivity, as the quadrupolar CO₂ exhibit favorable interaction with the ether oxygen linkages, favoring the solubility of the polar CO₂ over the non-polar gases like H₂, N₂ and CH₄.

3. Experimental

3.1. Materials

1,1,1,3,3,3-Hexafluoroisopropanol (HFIP), *N*-methyl-2-pyrrolidone (NMP), *p*-phenylenediamine (PPA), phenol, 1,1,2,2-tetrachloroethane and difunctional poly(ethylene glycol)s (M_n of 1000, 1500 and 2000 g/mol) were obtained from Aldrich (The Netherlands). Poly(propylene oxide)s endcapped with 20 wt% ethylene oxide (EO) and a molecular weight of 2200, 4200 and 6300 g/mol were kindly provided by Bayer AG (Germany). Tetra-isopropyl orthotitanate ($\text{Ti}(\text{i-OC}_3\text{H}_7)_4$) was obtained from Aldrich and diluted (0.05 M) in *m*-xylene (Fluka, The Netherlands). Irganox[®] 1330 (1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene) was obtained from CIBA Specialty Chemicals (The Netherlands). Methyl-(4-chlorocarbonyl)benzoate (MCCB) was obtained from Dalian (China). All chemicals were used as received. Pure gases were

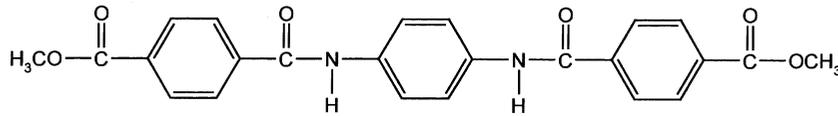


Fig. 2. Chemical structure of TΦT-dimethyl di-amide hard segment.

obtained from Praxair (The Netherlands) and used without further purification.

3.2. Polymer synthesis

3.2.1. Synthesis of TΦT-dimethyl hard segment

TΦT-dimethyl was used as hard segment and synthesized from MCCB and PPA following the procedure described by Niesten et al. (Route II) [17]. The structure of the monodisperse TΦT-dimethyl is shown in Fig. 2.

3.2.2. Synthesis of monodisperse segmented block copolymers

Different monodisperse polyamide block copolymers were synthesized by a polycondensation reaction using PEO, PPO or a mixture of both soft segments and the prepared monodisperse TΦT-dimethyl di-amide hard segments as described elsewhere [15].

3.3. Analysis

3.3.1. Viscometry

Viscometry was used to examine the molecular weight of the synthesized polymers. The polymers were dissolved in a 1:1 (molar ratio) mixture of phenol/1,1,2,2-tetrachloroethane (0.1 g/dL) and the inherent viscosity (η_{inh}) of the solutions was determined at 25 °C using a capillary Ubbelohde type 0B [15].

3.3.2. Differential scanning calorimetry (DSC)

DSC was used to determine the melting and crystallization temperatures and enthalpies of the polyether block copolymers [15]. The melting enthalpies of the soft segment ($\Delta H_{m,s}$) and that of the hard segment ($\Delta H_{m,h}$) were determined from the endothermic peak areas of the second heating scan.

3.3.3. Dynamic mechanical analysis (DMA)

DMA was performed to determine the glass transition temperature (T_g), the flex temperature (T_{flex}) and the flow temperature (T_{flow}) as well as the storage modulus of the block polymers. A detailed description of the procedure can be found elsewhere [15].

3.3.4. Fourier transform infrared (FT-IR)

FT-IR was used to determine the crystallinity of the hard segment. Infrared spectra were obtained with a Biorad FTS-60 spectrometer with a resolution of 4 cm^{-1} . FT-IR spectroscopy was carried out at room temperature on samples prepared by adding a droplet of the block copolymer solution (1 g/L in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP)) on a pressed KBr pellet. Further details relating to the exact determination of hard segment crystallinity can be found elsewhere [15].

3.4. Gas permeation

3.4.1. Film formation

Dense polymer films used for gas permeation experiments were prepared by hot pressing of dry polymer according to the procedure described earlier [11]. The films had a thickness of approximately 100 μm .

3.4.2. Gas permeation

Pure gas permeation properties of the prepared polyether based block copolymers were determined for N_2 , O_2 , He, H_2 , CH_4 and CO_2 subsequently at different temperatures varying from -10 °C to 50 °C. The experiments were performed following the constant volume, variable pressure method described in detail elsewhere [18].

4. Results

4.1. Thermal–mechanical properties

The thermal–mechanical properties (DSC, FT-IR and DMA) of the block copolymer systems studied in this article have been extensively described and discussed in a separate article [15]. For convenience and as a reference for discussions in this work Table 1 gives a summary of these data.

4.2. Effect of PEO soft segment length

4.2.1. Influence of soft segment length on gas permeability and pure gas selectivity

The synthesized PEO_x -TΦT block copolymers are considered to exhibit improved gas separation properties due to the increased crystallinity of the hard segment, improved phase separation and increased PEO contents, as proposed in Fig. 1c. Gas permeation properties of these PEO based block copolymers are investigated in a temperature range from -10 °C to 50 °C and related to their thermal–mechanical properties. Due to the absence of a distinct crystalline hard phase in the block copolymer with a soft segment length of 2000 g/mol, this polymer has no mechanical stability and film formation and subsequent gas permeation analysis was not possible.

Table 2 summarizes the single gas permeabilities and the pure gas selectivities of CO_2 over H_2 , N_2 and CH_4 at 35 °C. At this temperature the soft PEO phase is fully amorphous in all block copolymers.

The CO_2 permeability (and of all other gases as well (not shown)) increases with increasing PEO soft segment length and its relative change increases with increasing kinetic diameter of the gas molecule (He, H_2 , CO_2 , O_2 , N_2 , CH_4). The increase in gas permeability is most likely caused by an increase in soft segment concentration, as the chain flexibility does not change with increasing soft segment chain length (as proven by DMA). Overall, there is no significant effect observed on the pure gas selectivities, and high CO_2 /light gas selectivities are obtained due to the favorable interactions of CO_2 with the ether oxygen linkages in the polymer, resulting in high solubility selectivity.

4.2.2. Influence of temperature on gas permeability

The influence of the temperature on the CO_2 gas permeability of the PEO_x -TΦT block copolymers with a soft segment length of 1000 and 1500 g/mol is shown in Fig. 3 (other gases show similar behavior).

The polymers show an increase in gas permeability with increasing temperature. In both cases two distinct regions can be distinguished due to the occurrence of crystallization of the soft PEO phase at a specific temperature, which results in a significant

Table 1
Thermal-mechanical properties of polyether-T Φ T block copolymers [15].

Polymer	PEO/PPO [mol ratio]	T Φ T [wt%]	Soft segments		η_{inh} [dL/g]	DSC		T Φ T		DMA		FT-IR			
			PEO [wt%]	PEO [mol%]		T_m [°C]	$\Delta H_{m,PEO}$ [J/g]	T_m [°C]	ΔH_m [J/g]	T_g [°C]	T_{flex} [°C]	$T_{m,ref}$ [°C]	G (20°C) [MPa]	G (50°C) [MPa]	$X_{c,ref}$ [%]
PEO ₁₀₀₀	100/0	22.4	77.6	100	1.4	-8	14	120	33	-42	-19	145	29	28	67
PEO ₅₀₀	100/0	16.5	83.5	100	1.5	27	32	na	na	-38	25	100	14	5	41
PEO ₂₀₀₀	100/0	13.1	86.9	100	2.0	35	64	na	na	-41	35	70	79	1	21
PEO ₂₀₀₀ /PPO ₂₀₀	75/25	12.8	69.8	81	1.6	32	64	96	4	-45	35	105	46	6	25
	50/50	12.6	52.4	59	1.7	26	26	111	13	-52	35	115	10	5	33
	25/75	12.4	34.9	40	1.6	-	-	123	28	-60	10	135	9	8	57
PPO ₂₀₀	0/100	12.1	17.6	20	1.0	-	-	135	49	-59	-47	140	9	10	81
PPO ₂₀₀₀	0/100	6.8	18.6	20	1.12	-	-	na	na	-59	-48	100	3	3	59
PPO ₆₃₀₀	0/100	4.7	20.9	20	na	-	-	na	na	-48	-45	75	1.0	1.0	40

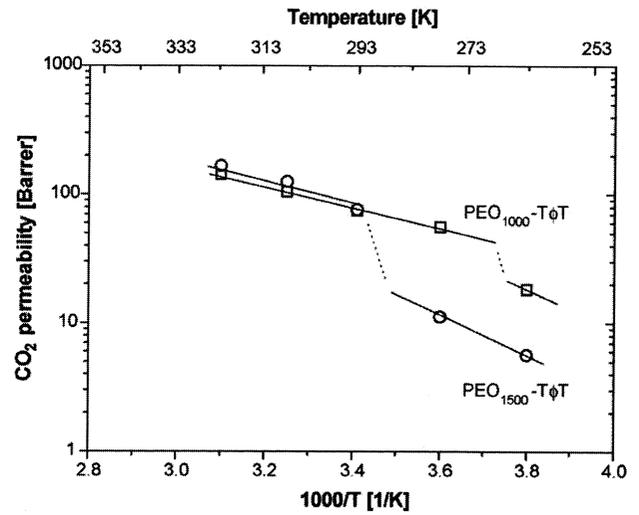


Fig. 3. CO₂ permeability as a function of temperature for (□) PEO₁₀₀₀-T Φ T and (○) PEO₁₅₀₀-T Φ T.

drop in permeability at temperatures below this crystallization temperature. The block copolymer containing PEO₁₅₀₀ as a soft segment shows a steep decrease in permeability below 20°C due to the crystallization of PEO, forming a semi-crystalline PEO phase. This is in good agreement with the melting temperature of the PEO phase as found by DSC (T_m PEO = 27°C). This decrease in permeability is also observed for the PEO₁₀₀₀ containing block copolymer, but at a lower temperature ($T \sim -10^\circ\text{C}$, PEO₁₀₀₀ melting temperature is -8°C as measured by DSC). The effect of PEO crystallization on gas permeability is more pronounced at higher soft segment lengths (stronger decrease) because PEO crystallinity increases with increasing soft segment length as shown by an increase in melting enthalpy (as measured by DSC) of PEO from 14 to 32 J/g for respectively the PEO₁₀₀₀ and PEO₁₅₀₀ block copolymer. In the fully amorphous state (higher temperature) the PEO₁₅₀₀-T Φ T block copolymer has a slightly higher CO₂ permeability than the PEO₁₀₀₀-T Φ T block copolymer as a result of the higher soft segment concentration. In the low temperature region ($\leq 20^\circ\text{C}$) the opposite behavior is observed as the presence of a semi-crystalline PEO (as observed by DSC and DMA) severely restricts gas permeation especially for the PEO₁₅₀₀-T Φ T block copolymer.

4.2.3. Influence of temperature on pure gas selectivity

The effect of the temperature on the pure CO₂/light gas selectivity for H₂, N₂ and CH₄ is shown in Fig. 4.

When the soft PEO phase is in a completely amorphous state (above 20°C, $1/T < 3.4\text{K}^{-1}$), no differences are observed between the two different soft segment lengths, and the pure gas selectivities show a linear decrease with increasing temperature. The presence of a semi-crystalline phase at lower temperatures however reduces the gas permeability and influences the gas selectivity. Both polymers show a decrease in CO₂/H₂ selectivity below their PEO melting temperature ($T_m = 27^\circ\text{C}$ and -8°C). This might be attributed to a more pronounced size-sieving ability of the block copolymer due to the formation of a semi-crystalline PEO phase decreasing diffusivity selectivity. Furthermore, at lower temperatures, also the contribution of the reverse-selective hard segment to the overall permeation behavior increases due to the increased crystallinity of the soft segment, further decreasing CO₂/H₂ selectivity. The selectivity of CO₂ over larger gases (e.g. N₂ and CH₄) shows the opposite behavior and the CO₂/N₂ and CO₂/CH₄ gas selectivity increases in the presence of a semi-crystalline PEO phase as a result of an increase in diffusivity selectivity. This effect can be

Table 2
Pure gas permeabilities and pure gas selectivities at 35 °C for PEO_x-TΦT block copolymers.

Polymer	TΦT [wt%]	PEO [wt%]	Gas permeability [Barrer]				Gas selectivity [–]		
			CO ₂	H ₂	N ₂	CH ₄	CO ₂ /H ₂	CO ₂ /N ₂	CO ₂ /CH ₄
PEO ₁₀₀₀ -TΦT	22.4	77.6	105	14.2	1.9	5.7	7.4	54.5	18.5
PEO ₁₅₀₀ -TΦT	16.5	83.5	126	15.3	2.4	6.9	8.2	53.2	18.2

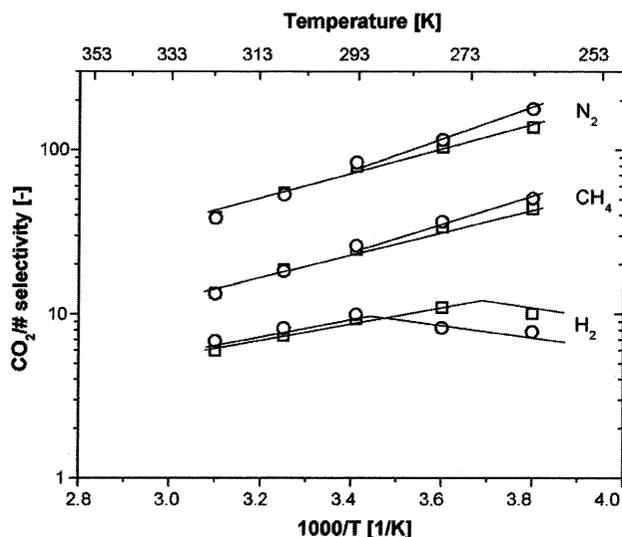


Fig. 4. CO₂/light gas selectivity for H₂, N₂ and CH₄ as a function of temperature for (□) PEO₁₀₀₀-TΦT and (○) PEO₁₅₀₀-TΦT.

clearly seen when the results of the PEO₁₀₀₀-TΦT and PEO₁₅₀₀-TΦT block copolymers below 20 °C are compared.

To evaluate the relation between the CO₂ permeability, CO₂/H₂ selectivity and the temperature, the CO₂/H₂ selectivity is presented as a function of the CO₂ permeability at different temperatures for PEO_x-TΦT block copolymers with a soft segment length of 1000 and 1500 g/mol in Fig. 5.

The graphical representation of the relation between the CO₂ permeability and the CO₂ over H₂ selectivity shows the operating window of the PEO based block copolymer system presented in this work. In the presence of a fully amorphous PEO phase (at higher temperatures) high permeabilities can be obtained and the PEO₁₅₀₀

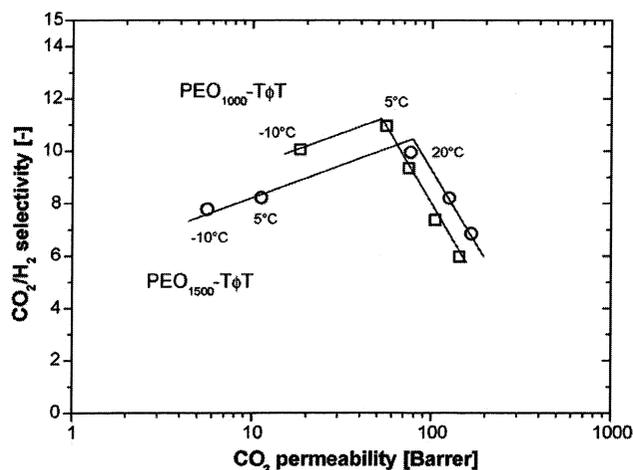


Fig. 5. CO₂/H₂ selectivity as a function of CO₂ permeability and temperature for (□) PEO₁₀₀₀-TΦT and (○) PEO₁₅₀₀-TΦT.

block copolymer shows the highest CO₂ permeability, as discussed earlier. Upon the formation of a semi-crystalline PEO phase at lower temperatures, the CO₂/H₂ separation performance characteristics of the polymers decrease.

4.2.4. Discussion

As described earlier, block copolymers with improved gas permeation properties should exhibit (1) good phase separation of the hard and soft segments; (2) complete crystallization of the hard segment; (3) high PEO content; (4) low glass transition temperature of the soft segment (high chain flexibility); and (5) no soft phase crystallinity or low soft segment melting temperature. The use of the short monodisperse di-amide hard segments as presented in this work enabled us to prepare a block copolymer system with improved membrane gas separation performance characteristics due to the increased PEO content, while maintaining other properties. This resulted in a morphology schematically depicted in Fig. 1c.

We compare the results of our study with the use of the longer tetra-amide hard segment as described by Husken et al. [11] and literature data on PEO based block copolymers [2,6] (Fig. 6). Although a direct quantitative comparison of the gas permeation properties proves to be difficult because many parameters, like soft segment concentration, soft/hard segment crystallinity and glass transition temperature change, a qualitative comparison can be made.

A comparison between PEO₁₀₀₀-T6T6T with the longer hard segment (●) and PEO₁₀₀₀-TΦT with the short hard segment (■) shows an increase in CO₂ permeability from 75 Barrer for the longer hard segment to 105 Barrer for the shorter hard segment. In this case the soft segment concentration changes from 62 wt% (T6T6T, long segment) to 78 wt% (TΦT, short segment) while maintaining reasonable high hard segment crystallinity. This proves that besides chain flexibility (property 4), which is mainly dependent on soft segment length, also the total soft segment concentration (property 3) is of importance. Furthermore, the necessity of good

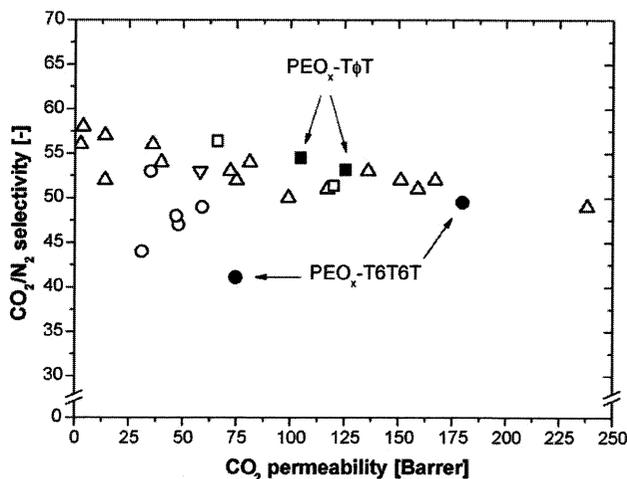


Fig. 6. Comparison of CO₂ permeability vs. CO₂/N₂ selectivity of (■) PEO_x-TΦT, (●) PEO_x-T6T6T [11], (□) PEBAX® block copolymers [2], (○) PEO-PU block copolymers [6], (△) PEO-PI block copolymers [6] and a (▽) PEO-PA block copolymer [6].

Table 3
Pure gas permeabilities and pure gas selectivities at 35 °C for PPO_x-TΦT block copolymers.

Polymer	TΦT [wt%]	PPO [wt%]	Gas permeability [Barrer]				Gas selectivity [–]		
			CO ₂	H ₂	N ₂	CH ₄	CO ₂ /H ₂	CO ₂ /N ₂	CO ₂ /CH ₄
PPO ₂₂₀₀ -TΦT	12.1	70.3	418	68.3	15.8	52.4	6.1	26.5	8.0
PPO ₄₂₀₀ -TΦT	6.8	74.6	520	84.3	20.5	69.5	6.2	25.4	7.5

phase separation and complete crystallization of the hard segment (properties 1 and 2) becomes clear when the CO₂ permeability of PEO₂₀₀₀-T6T6T (180 Barrer) and PEO₁₅₀₀-TΦT (126 Barrer) are compared. Although PEO₁₅₀₀-TΦT has a slightly shorter PEO soft segment length, its CO₂ gas permeability is remarkably lower than the value found for PEO₂₀₀₀-T6T6T, despite a higher total soft segment concentration (84 wt% instead of 76 wt%). This can be explained from the lower hard segment crystallinity and less pronounced phase separation between the hard and soft segments, which results in a morphology where high amounts of non-crystallized hard segment are present in the soft amorphous phase restricting permeation of the gases (Fig. 1a).

A comparison of our PEO_x-TΦT block copolymers with other PEO containing block copolymers is also shown in Fig. 6 [2,6]. Freeman et al. [2] and Okamoto et al. [6] state that the polarity of the hard segment influences the microdomain phase separation and thereby the gas separation performance. Okamoto et al. [6] investigated the thermal–mechanical properties and CO₂ gas separation performance of a series of PEO based block copolymers containing PU, PA and PI hard segments and found that the microdomain phase separation is strongly influenced by the type of hard segment. The degree of phase separation increased from PU < PA << PI due to a decrease in intermolecular interaction (hydrogen bonding) between the hard and soft segments. Our polyamide based PEO_x-TΦT system (■) shows indeed higher CO₂ permeability compared to the PEO-PU based block copolymers (○) (better phase separation) and has a performance which coincides with an average PEO-PI based system (△). Freeman et al. investigated the commercially available PEBAX[®] block copolymers (□) (a PEO-PA) and found a reduction in gas permeability of almost 50% changing the hard segment from PA12 (120 Barrer) to the more polar PA6 (66 Barrer) at comparable soft segment concentration [2]. A PEO-PA block copolymer containing a similar type of hard segment compared to the TΦT di-amide has been reported by Okamoto et al. [6]. Their system (IPA-ODA/PEO3(80)) (▽) had a CO₂ permeability of 58 Barrer at a PEO concentration of 68 wt%, which is approximately half of the maximum CO₂ permeability obtained for our system.

This indicates that although the phase separation behavior for our PEO-PA system is not fully optimal (especially at high soft segment length) due to the highly polar character of the short di-amide hard segment (compared to PA6 and PA12), a distinct improvement in gas separation performance has been achieved. The unique very short and monodisperse nature of the hard segment enabled us to incorporate high concentrations of soft segment resulting in increased CO₂ permeability at comparable selectivity (Fig. 6) with much better defined block copolymer morphology.

4.3. Effect of soft segment type (PPO vs. PEO)

The gas permeation properties of the PPO based block copolymers are investigated in a temperature range from 5 °C to 50 °C and related to their thermal–mechanical properties as discussed and compared to the PEO_x-TΦT block copolymers. Films of the PPO₆₃₀₀ block copolymer could not be prepared due to the low storage modulus, causing too much shrinkage during film formation.

4.3.1. Influence of soft segment length on gas permeability and pure gas selectivity

Table 3 summarizes the single gas permeability and the pure gas selectivities of CO₂ over H₂, N₂ and CH₄ at 35 °C.

The permeability of the PPO based block copolymers is a factor 4–5 higher than the permeability of the PEO based block copolymers. This can be attributed to the extra methyl side group in PPO compared to PEO, which prevents close chain packing (leading to soft phase crystallization), thus increasing the free volume and gas permeability [19]. The permeability of all gases increases with increasing soft segment length (and concentration) and its relative change increases with increasing kinetic diameter as already observed for PEO_x-TΦT block copolymers.

The CO₂/light gas selectivities are found to be independent of the soft segment length. Due to the introduction of PPO as a soft segment the CO₂/light gas selectivity for all investigated gas pairs is lowered compared to the PEO_x-TΦT block copolymers and the relative change in selectivity is different for each gas pair investigated. Due to a reduction in the polarity of the soft phase by replacing PEO with PPO the solubility of the quadrupolar CO₂ in the polymer matrix decreases, while the solubility of non-polar gases is much less influenced. Consequently, the CO₂/light gas solubility selectivity for the PPO based block copolymers is lower than that of the PEO based ones. Secondly, due to the increased free volume, diffusivity selectivity is altered as the diffusivity of larger molecules (like N₂ and CH₄) increases relatively more than the diffusivity of smaller gas molecules (like H₂) [20]. This change has a positive influence on the CO₂/H₂ selectivity, as H₂ is smaller than CO₂, resulting in an increase in diffusivity selectivity partially counterbalancing the decrease in solubility selectivity. However, it has a negative influence on CO₂/N₂ and CO₂/CH₄ selectivity as N₂ and CH₄ are both larger than CO₂ thus decreasing diffusivity selectivity. As a consequence, the relative change in selectivity compared to the PEO_x-TΦT based block copolymers is the lowest for CO₂/H₂ (–21%) followed by CO₂/N₂ (–52%) and the highest for CO₂/CH₄ (–58%).

4.3.2. Influence of temperature on gas permeability

The influence of the temperature on the gas permeation properties of the PPO_x-TΦT block copolymers is shown in Fig. 7. For comparison, the data for the PEO based block copolymers are also shown.

The PPO soft phase remains completely amorphous over the full temperature range investigated, independent of the segment length. Its lower polarity results in higher hard segment crystallinity and improved phase separation. Due to the absence of a semi-crystalline soft phase a linear relation between the CO₂ permeability and temperature is observed over the complete temperature range investigated (5–50 °C). This results in extremely high permeable membranes with a much broader operating window compared to the PEO_x-TΦT block copolymers, due to (1) higher soft segment concentration, (2) increased chain flexibility and (3) increased free volume originating from the methyl side group. The CO₂ permeability for the PPO₄₂₀₀-TΦT block copolymer reaches values as high as 629 Barrer at 50 °C and maintains a high value of 272 Barrer at 5 °C.

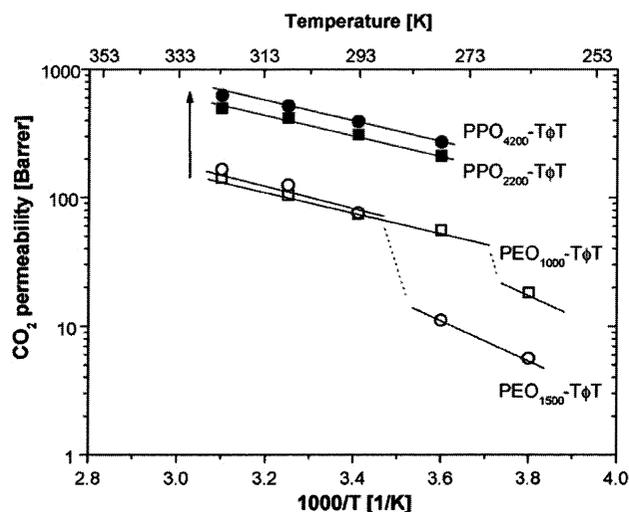


Fig. 7. CO_2 permeability as a function of temperature for (■) $\text{PPO}_{2200}\text{-T}\Phi\text{T}$, (●) $\text{PPO}_{4200}\text{-T}\Phi\text{T}$, (□) $\text{PEO}_{1000}\text{-T}\Phi\text{T}$ and (○) $\text{PEO}_{1500}\text{-T}\Phi\text{T}$.

To conclude, two remarkable differences are observed between the PPO and PEO based membranes. A 4–5-fold increase in CO_2 permeability is observed when using PPO as a soft segment above a temperature of 20 °C in comparison to both PEO based membranes. This increase is mainly attributed to an enhancement of the diffusivity as discussed in the previous paragraph. Second, the drop in gas permeability of the PEO based block copolymers at its melting temperature is absent when PPO based block copolymers are considered. A 20–25-fold difference in CO_2 permeability is visible between the PPO based membranes and the $\text{PEO}_{1500}\text{-T}\Phi\text{T}$ block copolymers at 5 °C. Overall, the use of PPO as a soft segment avoids crystallization, thus improving membrane properties, in particular at lower temperatures.

4.3.3. Influence of temperature on pure gas selectivity

The effect of the temperature on the CO_2 /light gas selectivity for H_2 , N_2 and CH_4 is shown in Fig. 8.

The present PPO based systems exhibit high CO_2 permeability with reasonable high CO_2 /light gas selectivity. The CO_2 /light gas

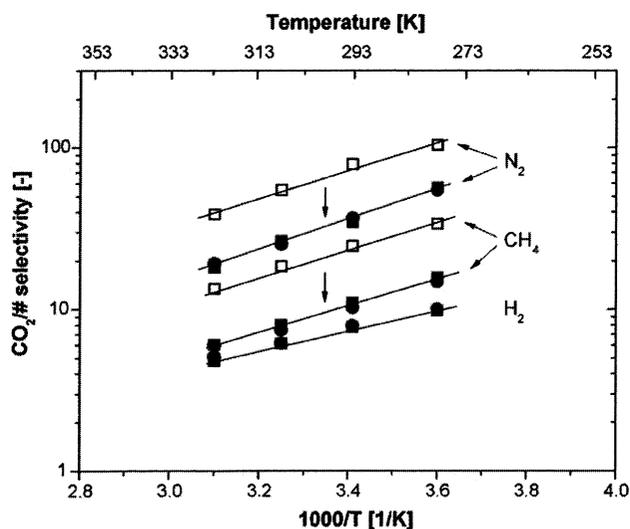


Fig. 8. CO_2 /light gas selectivity as a function of temperature for (■) $\text{PPO}_{2200}\text{-T}\Phi\text{T}$, (●) $\text{PPO}_{4200}\text{-T}\Phi\text{T}$ and (□) $\text{PEO}_{1000}\text{-T}\Phi\text{T}$ (CO_2/H_2 selectivity of $\text{PEO}_{1000}\text{-T}\Phi\text{T}$ is not shown for clarity as it almost overlaps with the $\text{PPO}_x\text{-T}\Phi\text{T}$ block copolymers).

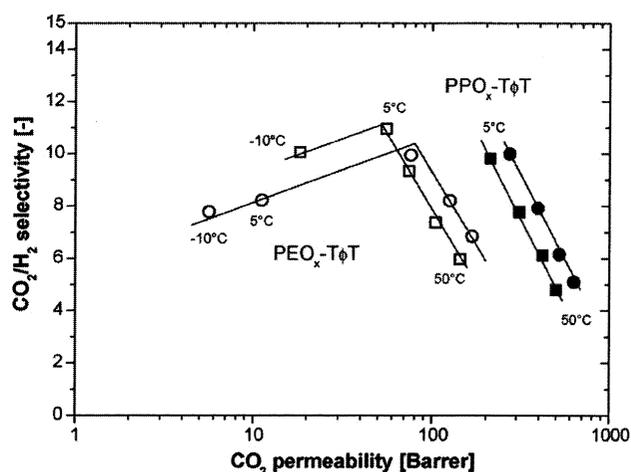


Fig. 9. CO_2/H_2 selectivity as a function of CO_2 permeability for (■) $\text{PPO}_{2200}\text{-T}\Phi\text{T}$, (●) $\text{PPO}_{4200}\text{-T}\Phi\text{T}$, (□) $\text{PEO}_{1000}\text{-T}\Phi\text{T}$ and (○) $\text{PEO}_{1500}\text{-T}\Phi\text{T}$.

selectivity is found to be independent of the soft segment length. More important, the pure gas selectivities show a linear decrease with temperature over the temperature range investigated, as the PPO phase remains completely amorphous.

4.3.4. CO_2/H_2 separation

The applicability of $\text{PPO}_x\text{-T}\Phi\text{T}$ block copolymer membranes can be very promising at low temperatures, where the use of block copolymers with a semi-crystalline PEO soft phase results in reduced gas permeability. This is most evident for CO_2/H_2 separations. In this case the decrease in selectivity in the amorphous state is only 21%, while the increase in CO_2 permeability is around 400%. To demonstrate the applicability of $\text{PPO}_x\text{-T}\Phi\text{T}$ block copolymer membranes for (especially low temperature) CO_2/H_2 separation, the CO_2/H_2 selectivity is presented as a function of the CO_2 permeability and temperature in Fig. 9. For comparison, the results for $\text{PEO}_x\text{-T}\Phi\text{T}$ are also shown.

When the performance of the $\text{PPO}_x\text{-T}\Phi\text{T}$ block copolymers is compared to the $\text{PEO}_x\text{-T}\Phi\text{T}$ block copolymers at temperatures where a fully amorphous PEO soft phase is present (50 °C), the CO_2/H_2 selectivity is only slightly lowered, while a much higher CO_2 permeability is achieved (more than 300% increase). In the temperature region where a semi-crystalline PEO soft phase is present the PPO based block copolymers outperform the PEO based block copolymers on permeability as well as selectivity for CO_2/H_2 separation offering a high potential for future applications.

4.4. Effect of a mixture of PEO_{2000} and PPO_{2200} soft segments

The gas permeation properties of block copolymers based on a mixture of PEO_{2000} and PPO_{2200} soft segments are investigated in a temperature range from –10 °C to 50 °C. The influence of the soft segment composition on the gas permeation properties is investigated and the information obtained by DSC, IR and DMA is used to explain the gas separation performance data. Due to the absence of a distinctive crystalline hard phase, the block copolymer containing 100 mol% PEO_{2000} as a soft phase has insufficient mechanical stability and film formation is not possible as discussed before. Therefore, data from $\text{PEO}_{1500}\text{-T}\Phi\text{T}$ ($M_{w,\text{PEO}} = 1500$ g/mol) are taken as a reference for a 100 mol% PEO soft phase.

4.4.1. Effect of soft segment composition

The influence of the soft segment composition (mol% PEO) is evaluated at a temperature of 35 °C. At that temperature (and at all

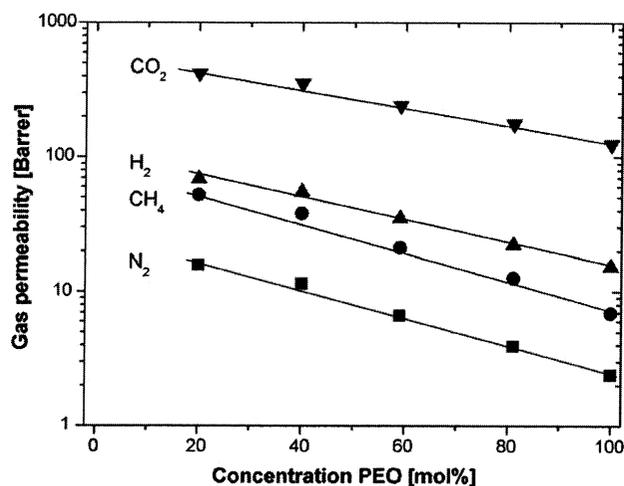


Fig. 10. Gas permeability at 35 °C for (▼) CO₂, (▲) H₂, (■) N₂ and (●) CH₄ as a function of PEO content in the polyether-TPT block copolymers containing a mixture of PEO₂₀₀₀ and PPO₂₂₀₀ soft segments.

temperatures above this value) the PEO phase is fully amorphous in all block copolymer systems. Fig. 10 gives a graphical representation of the N₂, CH₄, H₂ and CO₂ permeability as a function of the PEO content in the mixed PEO/PPO soft phase.

The permeability of all gases in the PEO₂₀₀₀/PPO₂₂₀₀-TPT block copolymers decreases linearly when the PEO content is increased (similar results are obtained at 50 °C but not shown). A similar trend has been observed by Patel et al. [21,22] who investigated the CO₂ transport through crosslinked polyether membranes using a mixture of poly(ethyleneglycol diacrylate) (PEGDA) and poly(propyleneglycol diacrylate) (PPGDA). The decrease in gas permeability with increasing PEO content is most likely caused by a decrease in free volume with increasing PEO content. With increasing PEO content, the relative amount of PPO, which has bulky side groups that can contribute to an increased free volume in the polymer, decreases as well. This hypothesis is supported by Freeman et al., who investigated the relationship between the free volume and the gas permeability in crosslinked networks of PEGDA (polyethylene based) and PPGDA (polypropylene based). They found significantly higher free volume in the PPGDA based networks accompanied by corresponding higher permeability values [19,23,24].

The CO₂/light gas selectivity at 35 °C for H₂, N₂ and CH₄ as a function of the PEO content in the soft phase containing a mixture of PEO₂₀₀₀ and PPO₂₂₀₀ soft segments is presented in Fig. 11.

The selectivity for all the three gas pairs increases linearly with increasing PEO content. The selectivity of these block copolymers is mainly based on solubility selectivity, due to favorable interactions of the polar ether oxygen linkages with the quadrupolar CO₂. Substitution of PPO for the more polar PEO increases the polarity of the soft phase. Consequently, especially the interaction of the polymer with CO₂ increases, resulting in an increase in solubility selectivity, while the diffusivity selectivity is only marginally influenced, because the diffusivity of both CO₂ and the light gases is influenced by an increase in free volume. The CO₂/light gas selectivity thus increases with increasing PEO content. The selectivity of CO₂ over N₂ has the highest value as solubility as well as diffusivity of N₂ is relatively low in comparison to H₂ and CH₄. H₂, which is the smallest molecule of the three, has a much smaller kinetic diameter resulting in more favorable diffusion, while CH₄ has a higher condensability and thus solubility, which reduces the selectivity compared to N₂ [16].

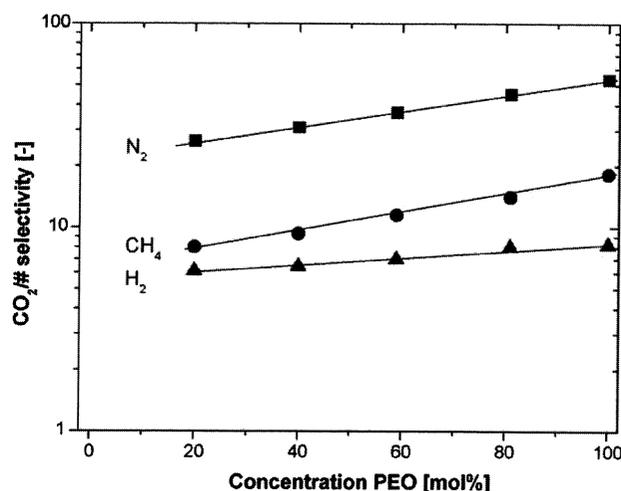


Fig. 11. CO₂/light gas selectivity at 35 °C for (▲) H₂, (■) N₂ and (●) CH₄ as a function of PEO content in the polyether-TPT block copolymers containing a mixture of PEO₂₀₀₀ and PPO₂₂₀₀ soft segments.

4.4.2. Membrane performance as a function of temperature

The influence of the temperature on the CO₂ permeability of the block copolymers with a soft phase consisting of a mixture of PEO₂₀₀₀ and PPO₂₂₀₀ soft segments and TPT as hard segment is shown in Fig. 12.

The block copolymers with ≤40 mol% of PEO soft phase are fully amorphous over the temperature range investigated as shown by DSC and DMA, and show a linear relationship between the CO₂ permeability and the temperature over the full temperature range investigated (no discontinuity is observed). Different behavior is observed for the block copolymers containing 59 and 81 mol% PEO, which do show a discontinuity in CO₂ permeability with increasing PEO content. DSC and DMA indicate low (59 mol% PEO) and significant (81 mol% PEO) amounts of PEO crystallinity at lower temperatures, which is reflected in the temperature dependency of the CO₂ permeability of these polymers as well. As confirmed by DSC and DMA analysis, this discontinuity is in both cases observed at the melting temperature of the soft phase, i.e. at ~26 °C for the

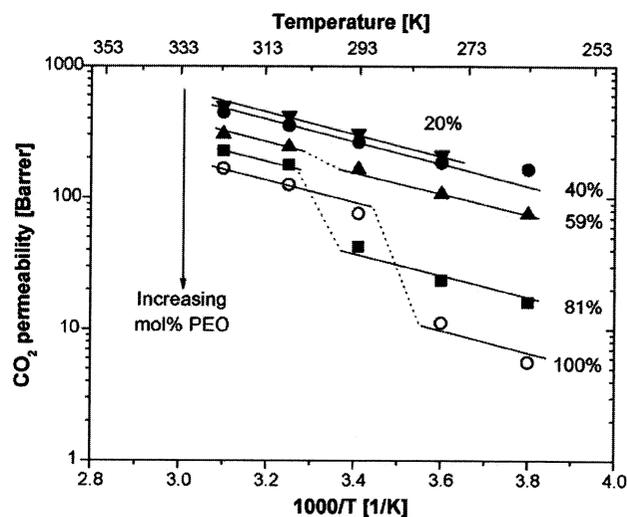


Fig. 12. CO₂ permeability as a function of temperature for block copolymers with a soft phase consisting of a mixture of PEO₂₀₀₀ and PPO₂₂₀₀ soft segments and TPT as a hard segment with (▼) 20 mol%, (●) 40 mol%, (▲) 59 mol% and (■) 81 mol% PEO soft phase. The PEO₁₅₀₀-TPT(○) is given as a reference for a block copolymer containing 100 mol% PEO.

block copolymer containing 59 mol% PEO and at $\sim 32^\circ\text{C}$ for the block copolymer containing 81 mol% PEO. This discontinuity significantly limits the operating window of these PEO/PPO based membranes for application in gas separation. Based on these results, a PPO content of at least 41 mol% of PPO is required to reduce PEO crystallinity in the soft phase sufficiently to maintain gas permeation properties.

The effect of the temperature on the pure gas selectivity of PEO₂₀₀₀/PPO₂₂₀₀-T Φ T block copolymers containing a 100% pure PEO or PPO soft phase is discussed in the previous two sections. The use of a mixture of PEO and PPO results in intermediate pure gas selectivities. The linear relation between the gas selectivity and the composition of the soft phase (as shown for 35°C in Fig. 11) can be expanded to the complete temperature range investigated as long as the soft phase is fully amorphous. A semi-crystalline PEO phase leads to deviation from this linear behavior as demonstrated for PEO_x-T Φ T block copolymers; a decrease in CO₂/H₂ selectivity and an increase in CO₂/N₂ and CO₂/CH₄ selectivity is observed in that case.

To demonstrate the effectiveness of PPO to suppress PEO crystallization and to identify the operating window of the block copolymers based on a mixture of PEO₂₀₀₀ and PPO₂₂₀₀ soft segments used in this study, the CO₂/light gas selectivity as a function of the CO₂ permeability for the different PEO₂₀₀₀/PPO₂₂₀₀-T Φ T block copolymers investigated (40, 59 and 81 mol% PEO) is summarized in Fig. 13. Higher CO₂ permeabilities represent higher temperatures (increasing from -10°C to 50°C in 15°C steps).

The block copolymer containing 40 mol% PEO does not show crystallization in the temperature range investigated and a linear relationship between the CO₂/light gas selectivity and the CO₂ permeability is observed. It combines high CO₂ permeability with high CO₂/light gas selectivity, especially at low temperatures. At a PEO content ≥ 59 mol% PEO, PEO crystallization does play a role. A steep decrease in CO₂ permeability below the PEO melting temperature is observed, which becomes more pronounced at higher PEO/PPO ratios (81 mol% PEO) due to higher PEO crystallinity. The transition between a fully amorphous and a semi-crystalline soft phase is observed as a bend in the graph and occurs at $\sim 20^\circ\text{C}$ and $\sim 35^\circ\text{C}$ for the block copolymer containing respectively 59 and 81 mol% PEO.

The results show the existence of a delicate balance between membrane permeability, selectivity and polymer structure at the microdomain scale. Proper selection and tuning of the polymer on

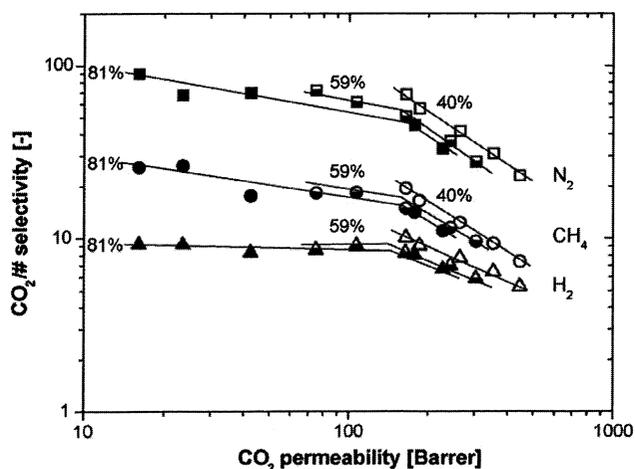


Fig. 13. CO₂/light gas selectivity as a function of CO₂ permeability for H₂ (triangles), CH₄ (circles), and N₂ (squares) for block copolymers with a soft phase consisting of a mixture of PEO₂₀₀₀ and PPO₂₂₀₀ soft segments and T Φ T as a hard segment as a function of the PEO content for 40 mol% PEO (open symbols), 59 mol% (partially filled symbols) and 81 mol% PEO (closed symbols). Higher CO₂ permeability represents higher temperature (increasing from -10°C to 50°C in 15°C steps).

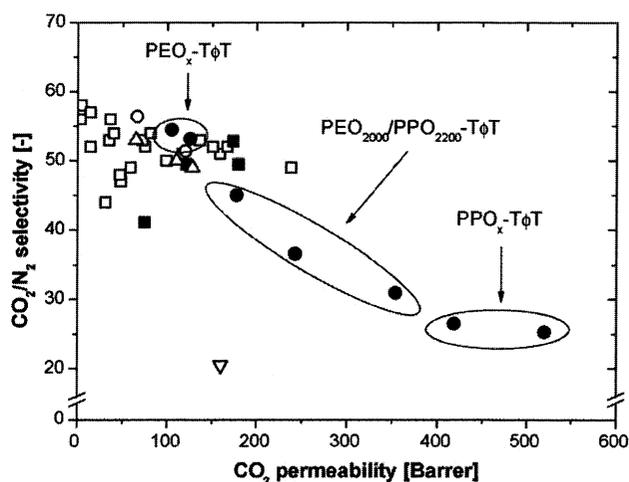


Fig. 14. CO₂/N₂ selectivity as a function of CO₂ permeability at 35°C for (■) PEO based block copolymers with monodisperse long T Φ T hard segments as described by Husken et al. [11] and (●) PEO_x, PPO_x or mixtures of PEO₂₀₀₀ and PPO₂₂₀₀ based block copolymers with monodisperse short hard segment (T Φ T), as used in this article compared with (□) PEO based block copolymers [6], (○) commercially available PEBAX[®] [2], (△) pure PEO di(meth)acrylate crosslinked networks [23–25] and (▽) pure PPO diacrylate networks [19], as described in literature.

the microscale, improves the performance of the membrane at the macro scale. Thus, the composition of the block copolymer needs to be carefully chosen, depending on the operating temperature of the process, to obtain optimal CO₂/light gas separation characteristics. Higher amounts of PPO in the block copolymer are especially beneficial at temperatures below the PEO melting temperature. This not only prevents PEO crystallization but also increases the CO₂ permeability at an only modest decrease in selectivity.

4.4.3. Membrane performance compared to other polyether based systems

In the last section of this article we have combined the benefits of PEO (high selectivity) with those of PPO (high permeability, amorphous) using a mixture of PEO₂₀₀₀ and PPO₂₂₀₀ soft segments in a block copolymer system to tailor the mass transport properties of macromolecular structures. Fig. 14 shows a Robeson trade-off curve of all the polyether based block copolymers described in this article and compares them with similar polyether based (block copolymer) systems described in literature.

The comparison of the PEO_x-T Φ T block copolymers with literature data on PEO based block copolymer systems has been discussed in the corresponding section. Most remarkable is the fact that higher gas permeability has been observed compared to the commercially available PEBAX[®] family at comparable selectivity. Furthermore, if the comparison is expanded and crosslinked, pure networks of poly(ethylene oxide) diacrylates are included as well, the PEO block copolymer systems presented in our work have very similar gas permeability values at comparable selectivity [23–25].

Literature data on PPO or mixed polyether based (block copolymer) systems are scarce. Gas permeation data on block copolymers containing pure PPO as a soft segment have, to the best of our knowledge, not been reported previously. Patel et al. [21,22] studied crosslinked mixed polyether networks based on PEG-diacrylate and PPG-diacrylate, but only reported gas transport properties for CO₂ and H₂. The CO₂ permeability at 35°C ranged from 100 Barrer (100% PEGDA) to 180 Barrer (100% PPGDA), while CO₂/H₂ selectivity ranged from 9 (100% PEGDA) to 4 (100% PPGDA). Freeman et al. studied crosslinked networks of PPGDA and PPG-methyl ether acrylate (PPGMEA) and their system exhibit a CO₂ perme-

ability of 160 Barrer at 100% PPGDA content [19]. In general, the PPO based systems show higher CO₂ permeability at the cost of lower selectivity following the permeability/selectivity trade-off relationship described by Robeson [26]. The maximum CO₂ permeability obtained for pure PPO based systems based on difunctional monomers is less than 200 Barrer as described above. The polyether block copolymer system presented in our work, which is based on monodisperse di-amide hard segments, exceeds this value and CO₂ permeabilities up to 520 Barrer (PPO₄₂₀₀-T Φ T) can be obtained (a 3-fold increase) at comparable selectivity. Moreover, the permeability/selectivity balance can be tuned towards specific applications by clever design of the soft phase using a mixture of PEO and PPO soft segments maintaining the advantage on the previously reported systems due to the very well-defined block copolymer morphology.

5. Conclusions

Polyether based segmented block copolymers with improved gas separation properties were synthesized using poly(ethylene oxide) (PEO) and/or poly(propylene oxide) (PPO) as soft segment and monodisperse di-amide (T Φ T) as hard segment. It allowed us to incorporate higher concentrations of soft segment compared to a system using longer tetra-amide (T6T6T) hard segments, while maintaining sufficient mechanical stability. The influence of the soft segment type and length on the CO₂ permeability and CO₂/light gas selectivity was investigated in relation to their thermal–mechanical properties.

For a PEO based system improved permeation properties were observed at short soft segment lengths (1000 g/mol) due to an increase in total soft segment concentration. Higher soft segment lengths (1500 g/mol) resulted in lower hard segment crystallinity and less efficient phase separation with subsequent lower gas permeability. In addition, the permeability and selectivity of the gases was strongly affected by the presence of a semi-crystalline PEO phase at temperatures below the PEO melting temperature. Below this temperature gas permeability decreased significantly along with the CO₂/H₂ selectivity, while CO₂/N₂ and CO₂/CH₄ selectivity increased. The PPO based system showed higher gas permeability mainly due to an increase in free volume at slightly lower selectivity as a result of the reduced polarity of the soft phase. As the PPO soft phase remains completely amorphous over the entire temperature range investigated a linear correlation between temperature and permeability/selectivity was observed. Gas permeation properties of this block copolymer system could be further tuned using a mixture of PEO and PPO soft segments. Intermediate gas permeabilities and selectivities could be obtained and the PPO has been proven successful in the suppression of PEO crystallization.

Comparison of the gas separation performance with similar systems described in literature showed the advantage of the well-defined block copolymer morphology. The present work clearly shows that the use of polyether based segmented block copolymers using monodisperse hard segments offers a very versatile tool to tailor mass transfer and separation properties of membranes for gas and vapor separations.

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