CO$_2$ permeation properties of poly(ethylene oxide)-based segmented block copolymers

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ABSTRACT

This paper discusses the gas permeation properties of poly(ethylene oxide) (PEO)-based segmented block copolymers containing monodisperse amide segments. These monodisperse segments give rise to a well phase-separated morphology, comprising a continuous PEO phase with dispersed crystallised amide segments. The influence of the polyether phase composition and of the temperature on the permeation properties of various gases (i.e., CO$_2$, N$_2$, He, CH$_4$, O$_2$ and H$_2$) as well as on the pure gas selectivities were studied in the temperature range of $-5\,^\circ$C to $75\,^\circ$C. The CO$_2$ permeability increased strongly with PEO concentration, and this effect could partly be explained by the dispersed hard segment concentration and partly by the changing chain flexibility. By decreasing the PEO melting temperature the low temperature permeabilities were improved. The gas transport values were dependant on both the dispersed hard segment concentration and the polyether segment length (length between crosslinks). The gas selectivities were dependant on the polyether segment length and thus the chain flexibility.

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1. Introduction

The removal of CO$_2$ from gas mixtures containing light gases such as CH$_4$, O$_2$, N$_2$ and H$_2$ is increasingly relevant. Possible industrial applications are the CO$_2$ recovery from natural-, flue- or synthesis gas and in the food packaging industry. For these processes dense polymer films (membranes) can be used and particular copolymers based on poly(ethylene oxide) (PEO) are interesting membrane materials for this due to a specific high transport of carbon dioxide [1,2]. The transport of gases through non-porous polymers is well described in literature [2–5]. The permeability (P) of a material is the product of the molecular mobility of the penetrant molecule (diffusion coefficient, D) and the affinity of the penetrant with the polymer (solubility, S) ($P = D \times S$).

Segmented block copolymers are of specific interest as they are linear polymers that are melt- and solvent processable. These materials, contain soft segments of PEO and hard segments of either polyamide [1,6–10], polyimide [11], polyurethane [12–14] or polyester [15]. The crystallized hard segment provides the copolymer with a solvent, mechanical and heat stability. If the hard segments are monodisperse in length than their crystallinity is high and the amount of hard segment dissolved in the amorphous

polyether phase is low [16–20]. The hard segments have a ribbon like morphology with a high aspect ration and dispersed in the continuous soft segment phase (Fig. 1a).

The dissolved non-crystallised hard segment reduce the flexibility of the soft phase, which results in an increased glass transition temperature and a reduced gas permeability [2,6,12,15]. Often, interphases are also present, and these influence the molecular transport properties too.

As the PEO has a regular structure it can crystallize too and the PEO crystalline melting temperature increase with PEO segment chain length. If PEO crystals are present the amount of dispersed phase is increased and the length of the amorphous PEO segment between crystallites is decreased (Fig. 1b). The presence of a crystalline PEO reduces the gas permeation values strongly; so has a high molecular weight PEO a high crystallinity (71 vol%) and as a result of this a very low CO$_2$ permeability, i.e., 1.2×10^{-9} cm^3 (STP) cm/cm^2 s cmHg (12 Barrer) at $35\,^\circ$C [2,21]. The useful temperature range of the PEO copolymers starts at the PEO melting temperature.

The gas permeation properties are a function of the chain flexibility of the continous phase, the amount of dispersed impermeable phase and special interactions between the gas and the continuous phase (gas solubility) [1–3,6,12–15]. The permeability (P) of the PEO phase was found to be directly related to the glass transition temperature (T_g) of that phase and was explained by the free volume in the material [2]. Increasing the PEO segment length led to a decrease in the network density and decreased the T_g of the PEO phase [2,16]. The influence of the amount of dispersed phase
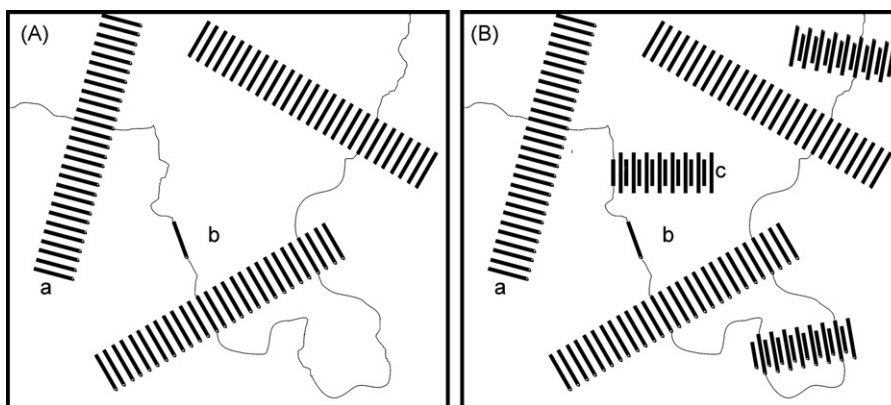
Fig. 1. Cartoon of a PEO containing segmented block copolymer with crystallized hard segments of monodisperse length and PEO segments are either fully amorphous (A) or semi-crystalline (B). (a) Crystalline hard segment; (b) amorphous PEO phase with non-crystallized hard segment; (c) crystalline PEO.

on the gas permeability of filled polymers has been described by Nielsen [22] and Maxwell [3]. However, these particle filled models did not display a good fit with the data of semi-crystalline polymers [2,15]. The solubility of CO_2 in the PEO phase is high due to a strong dipole–dipole interaction and as a result high CO_2 permeability (P_{CO_2}) and high CO_2 selectivity over other gasses (P_{CO_2}/P_x) are obtained.

Permeabilities of segmented block copolymers are most often reported at a temperature of 35 °C and the highest CO_2 permeability at 35 °C has been found to be approximately 1.2×10^{-8} cm^3 (STP) cm/cm^2 s cmHg (120 Barrer) [1,6,15]. Upon decreasing the measuring temperature, the gas permeation values have been observed to drop. This drop in gas permeation values was very strong if the PEO segments started to crystallize. Copolymers containing PEO$_x$ with a segmental molecular weight x of 1000 or 2000 g/mol have been shown to have PEO melting temperatures of −5 and 20 °C, respectively, whereas copolymers with a segmental molecular weight of 600 g/mol have been seen to be fully amorphous [16]. A practical lower limit temperature for use of the block copolymers in gas separation is the PEO melting temperature, and this rules out the use of long PEO segments, which have high melting temperatures.

Upon chemical crosslinking of copolymers the CO_2 permeability (P_{CO_2}) strongly decreased, however, the CO_2/CH_4 selectivity increased [9]. Moreover, the CO_2 permeability of membranes of crosslinked poly(ethylene glycol diacrylate) at 35 °C was also reported to be 1.2×10^{-8} cm^3 (STP) cm/cm^2 s cmHg (120 Barrer), and for a partly crosslinked polyacrylate with PEO side chains, this value increased strongly with the PEO side chain content up to a value of 6×10^{-8} cm^3 (STP) cm/cm^2 s cmHg (600 Barrer) [2].

In segmented block copolymers the amount of crystallised and dissolved hard segments in the soft phase can be reduced by using short monodisperse hard segments that crystallise fully [16–20]. An interesting monodisperse segment is the tetra-amide T6T6T based on nylon 6,T (Fig. 2).

The T6T6T segments are 4 nm long, and have a nano-ribbon like crystallite structure with a high aspect ratio (Fig. 1) [19,23]. The thickness and the width of these ribbons are both about 4 nm. The effect of the nano-ribbons on the gas transport values is expected to be similar to a particle filled system as the width and the thickness of these ribbons have about the same value [24]. The T6T6T the crystallinity was very high (∼85%) and, high PEO concentrations (up to 76 wt%) can be reached while still obtaining a good thermal mechanical properties of the copolymers [16].

It is desirable to have high gas permeabilities, but high selectivities might be even more attractive. The selectivity of CO_2 over other gases (CO_2/X) has been studied and particular the CO_2/N_2 selectivity at 35 °C is an often given value. For segmented block copolymers containing PEO a value of about 50 has been reported [1,2,15]. With regard to the heavier gases (O_2, N_2, CH_4), the selectivities changed very little with the PEO-copolymer composition, whereas for CO_2/H_2 and CO_2/He, the selectivities varied with the composition [1,12,15]. The selectivities increased strongly with decreasing temperature, however, at the same time the gas permeabilities decreased and this particular when the PEO segments are crystallizing [8,15]. A way of suppressing the PEO crystallinity at long segmental length is by disturbing the PEO structure regularity and incorporation of terephthalic units (T) in the PEO chain has this effect (Fig. 2b) [23]. Such copolymers have been prepared and were denoted (PEO$_{600}$/T)$_y$-T6T6T.

The present article reports on gas permeability of PEO$_x$-T6T6T and (PEO$_{600}$/T)$_y$-T6T6T segmented block copolymers. The permeability of the gases He, H_2, CO_2, O_2, N_2, and CH_4 was determined as a function of temperature on melt pressed PEO$_x$-T6T6T films over a temperature range of −5 to 75 °C.
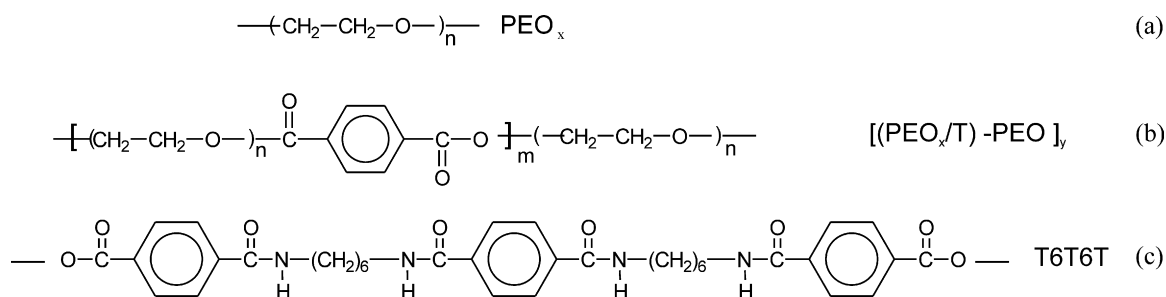

Fig. 2. The chemical structures of PEO$_x$ (a) and (PEO$_x$/T)$_y$ (b) and T6T6T (c), wherein x and y are the segmental molecular weights.

Table 1
Thermal properties of PEO$_x$-T6T6T and (PEO$_{600}$/T)$_y$-T6T6T copolymers.

Copolymer	Soft segment length [g/mol]	Conc. hard segment [wt%]	Conc. PEO [wt%]	Conc. T [wt%]	T_g^a [°C]	T_m PEO [°C]	ΔH_m PEO [J/g PEO]	X_c^b PEO [%]	T_m hard segment [°C]
PEO$_{1000}$-T6T6T	1000	38.4	61.6	0	−45	−2	20	10	195
PEO$_{2000}$-T6T6T	2000	23.8	76.2	0	−48	21	49	25	167
(PEO$_{600}$/T)$_{2500}$-T6T6T	2500	20.0	69.0	11.0	−44	−6	5	3	187
(PEO$_{600}$/T)$_{5000}$-T6T6T	5000	11.1	74.8	14.1	−43	−3	6	3	171

[a] Determined by DMA [16,23].
[b] The PEO crystallinity (X_c) was calculated by using a PEO melting enthalpy of 197 J/g for 100% crystalline PEO [26].

2. Experimental

2.1. Materials

2.1.1. PEO$_x$-T6T6T block copolymers

PEO$_x$-T6T6T copolymers were synthesised by a polycondensation reaction using T6T6T and PEO$_x$ segments with a molecular weight (x) of 1000 and 2000 g/mol [16].

2.1.2. (PEO$_{600}$/T)$_y$-T6T6T block copolymers

(PEO$_{600}$/T)$_y$-T6T6T copolymers were synthesised by a polycondensation reaction using T6T6T and PEO$_{600}$ segments extended with terephthalic units (T) [23]. The total molecular weight of the soft segment (y) was 2500 and 5000 g/mol.

2.2. Film preparation

Melt pressed films, approximately 100 μm thick, were prepared from the dried copolymers using a Lauffer 40 press. The temperature was set approximately 40 °C above the melting temperature of the respective copolymers. In a first step, air was removed from the polymer in the mould by quickly pressurising and depressurising the samples. This procedure was repeated three times before actually pressing the samples at ∼8.5 MPa for 5 min. Subsequently, the samples were cooled to room temperature while maintaining the pressure. To prevent sticking of the polymer onto the metal mould, glass-fibre reinforced PTFE sheets were used (Benetech type B105).

2.3. Differential scanning calorimetry (DSC)

DSC spectra were recorded on a Perkin Elmer DSC7 apparatus, equipped with a PE7700 computer and TAS-7 software. Dry polymer samples (5–10 mg) were heated from −50 to 250 °C at a rate of 20 °C/min. Subsequently, a cooling scan from 250 to −50 °C at a rate of 20 °C/min, followed by a second heating scan under the same conditions as the first heating were performed. The melting temperature (T_m) and enthalpy (ΔH_m) were determined from the endothermic peak in the second heating scan.

2.4. Dynamic mechanical analysis (DMA)

The mechanical behaviour of the materials was measured using a Myrenne ATM3 torsion pendulum at a frequency of 1 Hz and 0.1% strain. Before use, samples (70 mm × 9 mm × 2 mm) were dried in a vacuum oven at 50 °C overnight. During the tests, the samples were cooled to −100 °C and then heated at a rate of 1 °C/min. The glass transition temperature (T_g) was defined as the temperature location of the maximum of the loss modulus peak. The transition temperatures had a measuring error of 3 °C.

2.5. Gas permeation

The single gas permeation properties of the PEO-T6T6T block copolymer were determined with N$_2$, CH$_4$, O$_2$, He, H$_2$ and CO$_2$ in a temperature range of −5 to 75 °C. Single gas permeability values were calculated from the steady-state pressure increase in time in a calibrated volume at the permeate side, following the constant volume variable pressure method as described in detail elsewhere [25]. The measurements were conducted at a gas pressure of 4 bar. Pure gas selectivity values were calculated from the ratios of single gas permeability values. The experimental error was <15% which fell within the systematic error limits for the characterisation equipment used.

3. Results and discussion

The gas permeation properties of two PEO-based segmented block copolymer series, i.e., PEO_x and $(PEO_{600}/T)_y$ will be discussed. The soft phase composition of the copolymers was varied by changing the soft molecular weight (x and y) (Table 1). The hard segment was in all cases the tetra-amide T6T6T (Fig. 2c). The influence of the PEO phase concentration and soft segment length on the gas permeation properties was studied.

3.1. Thermal properties of PEO_x- and $(PEO_{600}/T)_y$-based copolymers

Table 1 summarises the thermal properties of the PEO_x-T6T6T and $(PEO_{600}/T)_y$-T6T6T copolymers, as determined by DSC and DMA measurements [16,23]. The glass transition temperature (T_g) depended on two opposing effects: soft segment length and the amount of dissolved hard segments. The soft segment length is also to the distance between network points and is inversely related to the crosslink density. An increase in the soft segment length led to a decrease in the network density and a decrease in T_g [16]. The dissolved hard segments were amorphous T6T6T and the terephthalic extender units. The terephthalic units (11–14 wt%) did not crystallise and thus belonged to the amorphous phase and thereby restricted the mobility of the soft segment phase a bit [18,23,27]. The monodisperse T6T6T segments, had a very high crystallinity (~85%), indicating that approximately 15% of the hard segment concentration had not crystallised and was present in the polyether phase [16,23]. Thus, PEO_{1000}-T6T6T and PEO_{2000}-T6T6T contained approximately 5.8 and 3.6 wt% non-crystallised T6T6T in their respective PEO phases. As these concentrations were rather low and little varied, the effect on the T_g of the soft phase was expected to be rather small. Due to these effects, at similar soft segment molecular weights, were the T_g values of the $(PEO_{600}/T)_y$ copolymers slightly higher (~5 °C) than for of PEO_x (Table 1) [23].

The PEO melting temperature and crystallinity were found to increase with the PEO_x length (Table 1). The PEO_{2000} in the block copolymer had a soft segment melting temperature of 21 °C, whereas the PEO_{1000} in the copolymer had a significant lower melting temperature and crystallinity. The PEO in the PEO_{600}-T6T6T copolymer was fully amorphous [23].

By extending the short PEO_{600} segments with terephthalic units (($PEO_{600}/T)_{2500–5000}$), a certain crystallisation of the extended polyether segments took place. Interestingly, the longer soft segment $(PEO_{600}/T)_{5000}$ in the copolymer displayed a significantly lower melting temperatures and crystallinities as compared to the PEO_{2000} materials. However, the T_g was not lowered.

The T6T6T melting temperature in the copolymers was high, well above the gas transport test temperatures.

3.2. Effect of the polymer composition on the gas permeabilities at 35 °C

A standard temperature for evaluating the gas permeabilities of polymers is 35 °C. At this temperature, the PEO phase of the studied copolymers was in all the studied copolymers amorphous (Table 1). The permeabilities of various gases in the PEO_x-T6T6T and $(PEO_{600}/T)_y$-T6T6T copolymers are presented in Table 2.

For PEO-based copolymers, the CO_2 permeabilities (P_{CO_2}) are high due to their specific interactions [1,2,6–15]. In the present study, the P_{CO_2} values of the copolymers were all high 0.75–1.8 × 10^{-8} cm^3 (STP) cm/cm^2 s cmHg (75–180 Barrer). The transport values are expected to be dependant on the PEO concentration (dispersed hard segment concentration) and the PEO phase chain flexibility. CO_2 permeability of the copolymers as function of PEO concentration is given in Fig. 3a.

Table 2
Gas permeabilities and selectivities at 35 °C.

Copolymer	SS^a length (g/mol)	[PEO] (wt%)	HS cryst.[b] (wt %)	Permeability [10^{-10} cm^3 (STP) cm/cm^2 s cmHg]						Selectivity		
				CO_2	He	H_2	O_2	N_2	CH_4	CO_2/H_2	CO_2/O_2	CO_2/N_2
PEO_{1000}-T6T6T	1000	61.6	33	75	6.3	10.4	4.7	1.8	5.5	7.2	16	41
PEO_{2000}-T6T6T	2000	76.2	20	180	10.9	17.9	8.8	3.6	11.3	10	21	49
$(PEO_{600}/T)_{2500}$-T6T6T	2500	69.0	17	121	9.4	14.6	6.2	2.5	7.1	8.3	20	49
$(PEO_{600}/T)_{5000}$-T6T6T	5000	74.8	9.4	176	12.2	19.6	8.7	3.3	10.2	9.0	20	53

[a] Soft segment length.
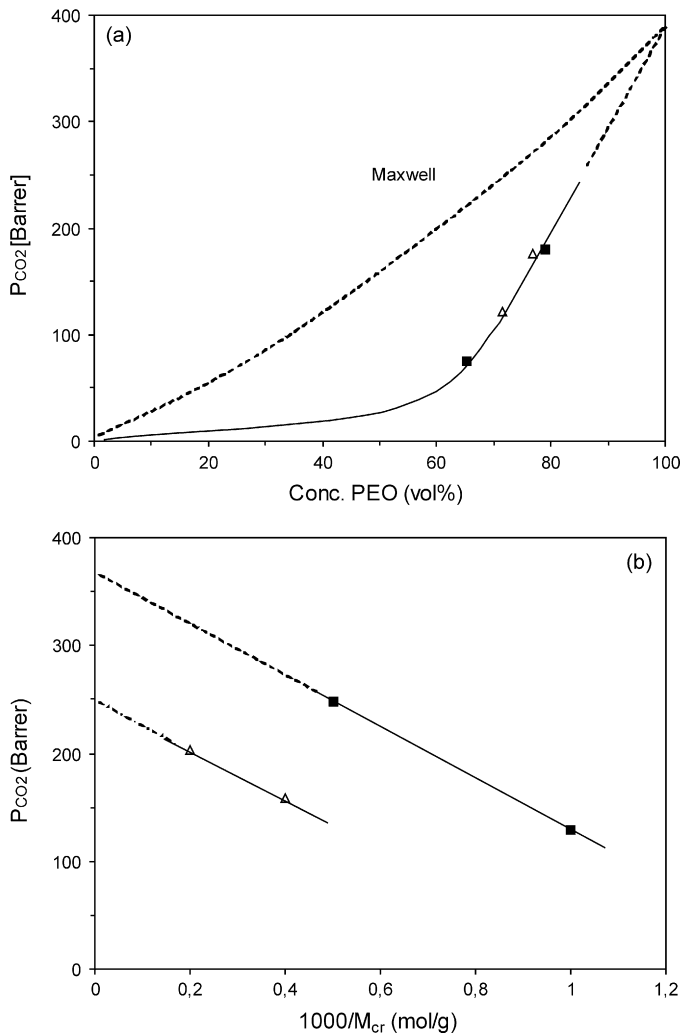[b] Hard segment crystalline concentration (HS concentration × crystallinity).

Fig. 3. The CO_2 permeability (35 °C) as a function of PEO concentration (a) and the CO_2 permeability corrected for the crystallized hard segment as function of the reciprocal soft segment length (M_{cr}) (b): (■) PEO_x-T6T6T; (△) $(PEO_{600}/T)_y$-T6T6T. The dashed line in (a) is according to the Maxwell model (Eq. (1)).

The CO_2 permeability increased strongly with PEO concentration and all the data seem to fall on one line. Extrapolating this line to 100% PEO (at very long soft segment length) a $P°_{CO_2}$ of $\sim 3.9 \times 10^{-8}$ cm³ (STP) cm/cm² s cmHg (390 Barrer) was obtained. For $(PEO_{600}/T)_y$-T6T6T copolymers with zero T6T6T content is the PEO_x concentration in $(PEO_{600}/T)_y$ is 84% and is due to the presence of the terephthalic groups. At this 84% PEO concentration the P_{CO_2} for $(PEO_{600}-T)_y$ was 2.4×10^{-8} cm³ (STP) cm/cm² s cmHg (240 Barrer). The T6T6T segments were mainly present as dispersed crystalline phases and crystallites have very low permeabilities [2]. By knowing the $P°_{CO_2}$ value the effect of the impermeable dispersed phase on the permeabilities can be calculated with the Maxwell model (Eq. (1)) [2,15,28].

$$P_b = P_c \left(\frac{1 - \Phi_d}{1 + \Phi_d/2} \right) \quad (1)$$

where Φ_d is the volume fraction of the impermeable dispersed phase, the P_b and P_c are the gas permeability in the composite and the continuous phase ($P°_{CO_2}$). In this relationship it was assumed that the properties of the polyether phase did not change with composition. The P_{CO_2} as function of the PEO concentration was calculated with this relationship assuming that the $P°_{CO_2}$ was 3.9×10^{-8} cm³ (STP) cm/cm² s cmHg (390 Barrer) (Fig. 3a, dashed line). The Maxwell model did not fit the experimental data and the

measured values were much lower than expected from the model. This discrepency suggests that not only the amount of impermeable phase changed but also the properties of the PEO phase were changed and with decreasing PEO segment length the deviation was stronger. By decreasing the soft segment molecular weight, the crosslink density and the PEO T_g increased. In crosslinked polymers, the chain flexibility is inversely related to the chain length between the network points ($1/M_{cr}$) [29]. The effect of the crosslink density on the gas permeation properties was studied by plotting the P_{CO_2} as function of $1/M_{cr}$ of the soft segment. The M_{cr} is taken the length of the soft segments (x or y) which is the number average molecular weight. However, first the P_{CO_2} values were corrected for the presence of impermeable crystalline fraction of T6T6T ($P_{CO_2,Maxwell}$) using the relationship of Maxwell (Eq. (1)). The crystalline fraction of T6T6T, being the product of the concentration of T6T6T multiplied by the crystallinity (85%). By plotting the $P_{CO_2,Maxwell}$ as function of reciprocal molecular weight, the effect of the network density and the influence of the dissolved terephthalic units in the PEO phase on the CO_2 permeability is demonstrated (Fig. 3b).

The $P_{CO_2,Maxwell}$ increased with decreasing $1/M_{cr}$ (increasing soft segment length). For a given soft segment length values the $P_{CO_2,Maxwell}$ for PEO_x were higher than for $(PEO_{600}/T)_y$. This can be explained by a reduced chain flexibility due to the terephthalic units in $(PEO_{600}/T)_y$ which were dissolved in the PEO phase, as suggested by the higher T_g values. The $P°_{CO_2}$ values at the intercept with the y-axis is the $P°_{CO_2}$ at infinite soft segment molecular weight. The $P°_{CO_2}$ value for PEO_x series was 3.7×10^{-8} cm³ (STP) cm/cm² s cmHg (370 Barrer) and for $(PEO_{600}/T)_y$ series 2.5×10^{-8} cm³ (STP) cm/cm² s cmHg (250 Barrer). The $P°_{CO_2}$ for PEO_x and $(PEO_{600}/T)_y$ as determined by the PEO concentration and the crosslink density (Fig. 3a and b) corresponded well (Fig. 3a and b). However, both the PEO_{2000}-T6T6T and the $(PEO_{600}/T)_{5000}$-T6T6T materials had high P_{CO_2} values ($\sim 1.8 \times 10^{-8}$ cm³ (STP) cm/cm² s cmHg (180 Barrer)) at 35 °C. The P_{CO_2} values were dependant on the amount of crystallized hard segment, the soft segment length and the amount of hard segment dissolved in the PEO phase.

The gas permeabilities are related to the free volume in the polymer and the free volume is related to the glass transition [2]. This suggests that the gas permeabilities and the T_g are directly related. However these relationships only hold as long as the chemical structure of the soft segment is not changed. The PEO_{2000}-T6T6T and the $(PEO_{600}/T)_{5000}$-T6T6T have a similar P_{CO_2} values at 35 °C but the T_g for $(PEO_{600}/T)_{5000}$-T6T6T was a 5 °C lower than that of PEO_{2000}-T6T6T. This discrepency can be explained by the change in the chemical composition of the soft segment phase and as a result of this changed the gas permeabilities/T_g relationships.

3.3. Effect of the polymer composition on the gas selectivity at 35 °C

Polymers containing polar PEO segments have a strong interaction with CO_2 and thus an enhanced solubility. Due to this are the gas selectivity in PEO copolymers of CO_2 over other gases (P_{CO_2}/P_x) mainly influenced by the gas solubility selectivity and not by the size-sieving ability. As P_{CO_2}/P_x is dominated by the special interaction of CO_2 with the PEO phase it is expected the crystallinity has little effect on the selectivity. However, increasing the PEO segment length is expected to improve the P_{CO_2}/P_x values. Table 2 lists various selectivities at 35 °C and at this temperature the PEO phase of the copolymers was amorphous. Two trends seem to be apparent: the P_{CO_2}/P_x selectivities increased with increasing size of the second gas and the selectivities increased with the soft segment molecular weight (M_{cr}). The effect of the size of the second gas is probably due to a size sieving effect, although the gas with the smallest kinetic diameter (He) did not have did not have the high-
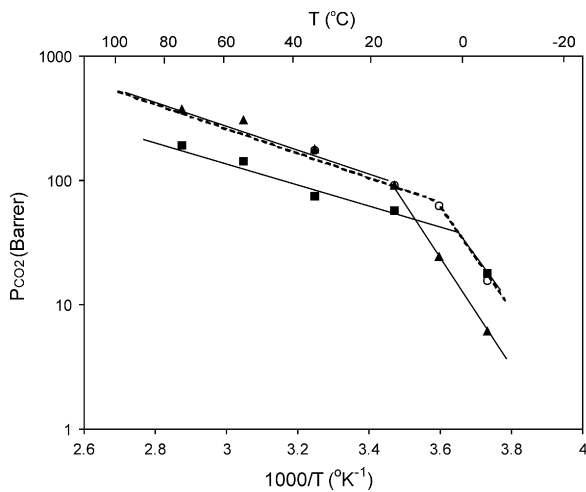
Fig. 4. The CO_2 permeability (P_{CO_2}) as a function of the temperature: (■) PEO_{2000}-T6T6T; (●) PEO_{1000}-T6T6T; (▲) $(PEO_{600}/T)_{5000}$-T6T6T.

Fig. 5. The gas permeability as a function of the temperature for PEO_{2000}-T6T6T: (▲) P_{CO_2}; (■) P_{H_2}; (□) P_{CH_4}; (+) P_{O_2}; (○) P_{He}; (●) P_{N_2}.

est permeability value and the gas with the largest kinetic diameter CH_4 not the lowest permeability values. Similar tends were earlier observed [15]. Thus suggest that PEO had also interactions with of some the other gasses. For the PEO_{2000}-T6T6T block copolymer the CO_2/H_2, CO_2/O_2 and CO_2/N_2 values were comparable to the selectivity values found on other PEO block copolymers [2].

3.4. Effect of the temperature on P_{CO_2}

The CO_2 permeabilities of the PEO_{1000}-T6T6T, PEO_{2000}-T6T6T and $(PEO_{600}/T)_{5000}$-T6T6T copolymers were studied over the temperature range −5 to 75 °C (Fig. 4).

At temperatures above room temperature the (log) P_{CO_2} decreased linearly with increasing inverse temperature (decreasing temperature). At lower temperatures a transition is apparent accompanied with a very strong decrease in P_{CO_2} with decreasing temperature. The temperature of these transitions correspond well with the melting temperature of the PEO phases (Table 1), cf. 21 °C for PEO_{2000} and −2 °C for PEO_{1000}. As a consequence of the lower melting temperature of PEO_{1000}, were at temperatures <10 °C the P_{CO_2} values higher, despite the fact that the PEO_{2000} had higher P_{CO_2} values above room temperature. At the transition PEO is crystallizing and the crystalline PEO phase not only increased the amount of crystallites in the system but also decreased the length of the remaining amorphous segments (Fig. 1b). The practical lower limit use temperature is the PEO melting temperature.

The $(PEO_{600}/T)_{5000}$-T6T6T block copolymer combines long soft segments with a low PEO melting temperature and crystallinity [23]. The $(PEO_{600}/T)_{5000}$-T6T6T block copolymer had at 35 °C similar P_{CO_2} values as PEO_{2000}-T6T6T, however, the transition in gas permeability now took place at approximately 0 °C ($T_{m,PEO}$ = −3 °C). As a result of the low PEO melting temperature in $(PEO_{600}/T)_{5000}$-T6T6T, the P_{CO_2} values were relatively high down to 0 °C, and also higher than for PEO_{1000}. Summarizing the $(PEO_{600}/T)_{5000}$-T6T6T copolymer had superior gas permeabilities as compared to either

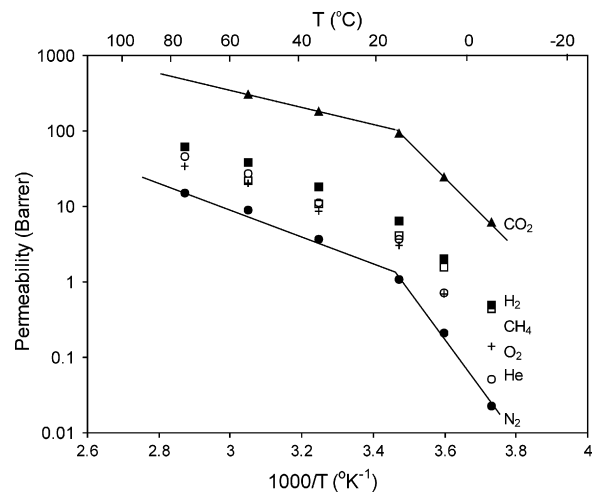the PEO_{1000} and PEO_{2000} copolymers over the complete temperature range investigated. It was thus possible to create PEO-based segmented block copolymers with relatively high CO_2 permeabilities even at lower temperatures by suppressing the PEO melting temperatures.

3.5. Effect of the temperature on the transport of other gases

The influence of the temperature on the permeation properties of a variety of gases was studied on the PEO_{2000}-T6T6T copolymers (Fig. 5).

All gases showed a linear decrease in their (log) permeability with increasing inverse temperature (decreasing temperature) in the region from 75 to 30 °C and all gasses has a transition point at the PEO melting temperature (∼20 °C). The PEO crystallinity had a strong effect on all the studied gas permeabilities. The strong decrease in permeation values below the PEO melting temperature is due to the combination of two effects: the increase in impermeable PEO crystalline phase and the decreasing length of amorphous PEO chains between crystallites (network points). As we have seen above, the gas permeabilities could not just be explained by the gas sieving effect as a result of the kinetic diameter.

For each gas, the activation energy for permeation (E_p) was determined in the PEO-T6T6T copolymers in the temperature range of 30–75 °C (Table 3), and this value is depend on the activation energy for diffusion as well as on the heat of solution [4].

The E_p values for H_2 and He are lower than those for O_2, N_2 and CH_4 since the activation energies for diffusion are lower for smaller gases. However, the lowest E_p values were found for CO_2 as a result of the difference in sorption enthalpies between the gases. The E_p values for PEO_{2000}-T6T6T was slightly lower than for PEO_{1000}-T6T6T block copolymers, and thus either the hard segment concentration or the PEO molecular weight had some effect. The E_p values for small gases like H_2 and He, were between 27 and 29 kJ/g, while larger gases had Ep values between 30 and 32 kJ/mol.

Table 3
Activation energies for permeation (E_p in kJ/mol) of various gases through the PEO_x-T6T6T and $(PEO_{600}/T)_y$-T6T6T copolymers (the kinetic diameter of each gas is given between brackets).

Polymer	CO_2 (3.30 Å)	He (2.60 Å)	H_2 (2.89 Å)	O_2 (3.46 Å)	N_2 (3.64 Å)	CH_4 (3.80 Å)
PEO_{1000}-T6T6T	21	29	28	30	32	31
PEO_{2000}-T6T6T	17	27	28	30	32	31
$(PEO_{600}/T)_{2500}$-T6T6T	23	32	34	41	45	41
$(PEO_{600}/T)_{5000}$-T6T6T	24	33	35	40	44	43
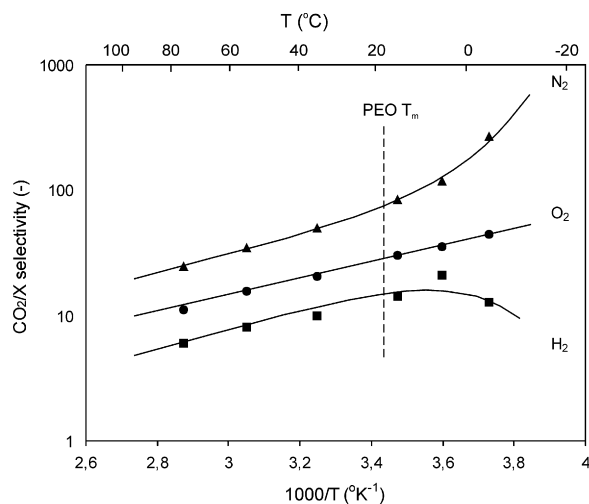
Fig. 6. Gas selectivities as functions of temperature for PEO$_{2000}$-T6T6T: (■) CO$_2$/H$_2$; (●) CO$_2$/O$_2$; (▲) CO$_2$/N$_2$.

The activation energies of permeation for the (PEO$_{600}$/T)$_{2500}$-T6T6T and (PEO$_{600}$/T)$_{5000}$-T6T6T copolymers were also comparable, and the E_p values of the copolymers containing PEO segments extended with terephthalic units were higher than those of the PEO$_x$-T6T6T copolymers and particular the larger gases had higher activation energies (Table 3).

3.6. Effect of the temperature on gas selectivity

As the activation energy for P_{CO_2} was lower than for all the other gasses (Table 3), the P_{CO_2}/P_x selectivities increased with decreasing temperatures. The results for PEO$_{2000}$-T6T6T are given here which is representative for all the studied copolymers (Fig. 6).

The (log) P_{CO_2}/P_x selectivities increased with decreasing temperature down to 20 °C. However, below the PEO melting temperature, the CO$_2$/H$_2$ selectivity was a little lowered, however, at the same time the P_{CO_2}/P_{N_2} was extra increased. This decrease in P_{CO_2}/P_{H_2} and increase in P_{CO_2}/P_{N_2} at low temperatures can be explained by a more pronounced size-sieving effect when crystalline PEO domains are present. This size-sieving effect is caused by a more tortuous pathway, which influences the larger molecules more than the smaller ones, as well as a reduction in chain flexibility. Both phenomena influence the diffusion selectivity. As the kinetic diameter of O$_2$ is similar to CO$_2$ the extra size sieving effect for P_{CO_2}/P_{O_2} on PEO crystallization was minimal. Consequently the CO$_2$/N$_2$ and CO$_2$/CH$_4$ selectivities increased remarkably when a semi-crystalline PEO phase was present.

4. Conclusions

PEO-based segmented block copolymers are interesting membrane materials for gas separation applications since they have high CO$_2$ permeability and high CO$_2$/light gas selectivity values. The gas transport behaviour was studied on well-defined segmented block copolymers. By using a short monodisperse hard segment the concentration in the copolymer was low and most segments had crystallized. As a result of this only very small amounts of non-crystallised hard segments were dissolved in the PEO phase.

The P_{CO_2} values changed stronger with changing PEO concentration than could be expected from the Maxwell model. The second effect that was important was the PEO segment length. Increasing the soft segment length increased the soft segment flexibility and with that the gas transport properties. The chain flexibility is inversely related to the segment length between network points

and the gas transport increased with $1/M_{cr}$ of the PEO segments. Extrapolating the P_{CO_2} values to long PEO chains a theoretical P_{CO_2} value at 35 °C of 3.7–3.9 × 10^{-8} cm^3 (STP) cm/cm^2 s cmHg (370–390 Barrer) was calculated.

Increasing the polyether segment length by extending PEO$_{600}$ with terephthalic groups resulted in higher P_{CO_2} values but the theoretical attained P_{CO_2} was lower as the dissolved terephthalic groups disturbed the chain flexibility of the PEO phase somewhat.

The gas transport selectivities P_{CO_2}/P_x at 35 °C were relatively high due to the special interaction of CO$_2$ and PEO (high solubility) and increased with the size of the light gas. The gas selectivities also increased with the PEO segment length. For PEO$_{2000}$-T6T6T, the CO$_2$/H$_2$, CO$_2$/O$_2$ and CO$_2$/N$_2$, values at 35 °C were 10, 21 and 49 respectively.

The gas permeability values decreased with decreasing temperature and a transition in the gas permeability values was observed at the melting temperature of the PEO segments. On crystallisation of PEO, the concentration of the impermeable objects increased and at the same time the length of the PEO segments between network points decreased with as a result strongly decreased gas transport values. The low temperature gas permeation properties could be improved by suppressing the PEO melting temperature. A way to create long PEO segments with a low PEO melting temperature was by extending a PEO$_{600}$ with terephthalic units.

The pure gas CO$_2$/X selectivities increased with decreasing temperatures, this as the activation energy for P_{CO_2} was lower. At low temperatures below the melting temperature of PEO the selectivities for the small gases (H$_2$ and He) did not decrease any more while for the larger gases (N$_2$ and CH$_4$) the selectivities increased. In presence of a PEO crystalline phase a stronger size sieving effect was taking place.

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