

Subambient Temperature CO₂ and Light Gas Permeation Through Segmented Block Copolymers with Tailored Soft Phase

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ABSTRACT The permeation properties of a series of block copolymers based on poly(ethylene oxide)-*ran*-poly(propylene oxide) (PEO-*ran*-PPO) soft segments and monodisperse tetra-amide (T6T6T) hard segments have been studied. The polyether soft segment used in the current study differs from the commonly used pure poly(ethylene oxide) (PEO) soft segment by the fact that it contains 25 wt % randomly distributed poly(propylene oxide) (PPO). The presence of the methyl group of PPO suppresses crystallization of the soft segment and strongly improves the permeability of these materials, especially at subambient temperatures. In addition, the unique monodisperse character of the hard segment ensures a very well phase-separated morphology, resulting in a very pure soft phase. The soft segment length of these block copolymers was varied between 1000 and 10000 g/mol (62–89 wt %). High soft segment concentrations and flexibility were obtained resulting in high CO₂ permeabilities (up to 570 Barrer at 50 °C). Due to the random distribution of PPO in the predominantly PEO based soft segment crystallization of PEO was not observed at temperatures as low as –10 °C. CO₂ permeabilities exceeding 200 Barrer could be obtained at this low temperature. The CO₂/light gas selectivity in these materials is governed by the solubility selectivity and consequently only slightly lowered because of the introduction of PPO in the soft segment. Comparison with literature revealed that this block copolymer system has exceptionally high CO₂ permeabilities combined with reasonable CO₂/light gas selectivities. It is very interesting in CO₂ separation processes where subambient conditions are present (e.g., separation of CO₂ from natural gas), as at these low temperatures, one can take maximum advantage of the increased separation ability of the polymer materials while maintaining excellent transport characteristics.

KEYWORDS: carbon dioxide • segmented block copolymer • morphology • gas separation • poly(ethylene oxide)-*ran*-poly(propylene oxide)

1. INTRODUCTION

The removal of carbon dioxide (CO₂) from mixtures with light gases such as hydrogen (H₂), nitrogen (N₂), and methane (CH₄) is an increasingly important application in industry. CO₂/H₂ and CO₂/CH₄ separation are relevant separation processes in the synthesis gas and natural gas production, whereas CO₂/N₂ separation (e.g. flue gases) has the potential to become a large-scale application in order to reduce the antropogenic CO₂ emissions (1).

Currently, CO₂ is mainly removed by chemical or physical absorption or pressure swing adsorption (PSA), but membrane technology (especially for CO₂/CH₄ separation) also plays an important role. The use of membrane technology has inherent advantages, such as small footprint, mechanical simplicity (no rotating equipment), and a high energy ef-

iciency (2). The large scale of these separation processes requires large membrane areas and/or highly permeable membranes with sufficiently high CO₂/light gas selectivities to remove the CO₂.

Recently Freeman et al. (3) have reported extensive material selection guidelines that provide an overview of desirable membrane characteristics to achieve a combination of high CO₂ permeability and high CO₂/light gas selectivity. They identified (and also generally accepted and demonstrated in other literature on membranes for gas separation) that polar groups, in particular ethylene oxide (EO) units, are a versatile building block to prepare highly permeable and sufficiently selective membranes for CO₂ separation. The polar ether oxygen linkages favor the solubility of the quadrupolar CO₂. As the nonpolar gases (like H₂, N₂, and CH₄) do not possess these favorable interactions, their solubility is significantly lower, resulting in high CO₂/light gas solubility selectivities. Furthermore, the flexible EO linkages permit high CO₂ diffusivity (high permeability). Specifically, they developed chemically crosslinked networks using acrylates based on poly(ethylene oxide). The use of 30 wt % poly(ethyleneglycol diacrylate) (PEGDA) and 70 wt % poly(ethyleneglycol monoethylacrylate) (PEGMEA) (PEGDA/PEGMEA 30/70) ensured a fully amorphous PEO phase (as low

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as the T_g) and subsequently a high CO_2 permeability ($P_{\text{CO}_2} = 320$ Barrer at $35\text{ }^\circ\text{C}$) (4–6).

As an alternative route, segmented block copolymers containing poly(ethylene oxide) (PEO) are of specific interest as they can be easily processed (in the melt or by dissolving them in a suitable solvent) and their specific properties can be easily tuned by smart selection of the individual building blocks in the copolymer. In general, multi-block copolymers consist of an alternating series of flexible soft segments and crystallizable hard segments. The flexible soft segments usually have a low glass-transition temperature and provide the material its flexibility and gas permeability, whereas the rigid hard segments give the material its mechanical and heat stability (7).

The block copolymers studied in the literature differ in amount of poly(ethylene oxide) (PEO) and type of hard segment used. Typical examples described in literature contain hard segments such as polyamides (8–16), polyimides (17), polyurethanes (12), and polyesters (18, 19). Commercially available PEO-based block copolymers are, for instance, produced by Arkema under the trade name PEBAX. A typical example is PEBAX 1074, a block copolymer containing 55 wt % PEO and 45 wt % polyamide, which shows a reasonable CO_2 permeability of 120 Barrer at 10 atm (9). However, the low crystallinity of the PEBAX amide phase leads to the dissolution of hard segment in the soft PEO phase deteriorating gas transport characteristics (9, 11). Another commercially available PEO block copolymer family having poly(butylene terephthalate) (PBT) as a hard segment (Polyactive produced by Isotis B.V.) was studied by Metz et al. (18). They systematically studied the relationship between polymer composition and morphology on the gas separation performance of these block copolymers and demonstrated that dissolution of the PBT hard segment into the permeable soft phase reduced the CO_2 permeability.

Studies on noncommercial block copolymers (12, 15–17) also indicate that the degree of phase separation and soft segment flexibility highly influence the gas transport properties of the materials. These studies suggest that the incorporation of a second dispersed phase, e.g., the hard segment of a block copolymer, in the continuous soft domains reduces the chain flexibility of the PEO soft segments, thereby lowering the gas permeability of the material. A similar effect has been observed as a result of the formation of PEO crystalline domains (15, 16, 18). These domains, which are formed below the PEO melting temperature, reduce the content of soft amorphous PEO phase available for gas permeation and at the same time decrease the flexible soft segment length between the crystallized hard segments. Consequently the gas permeability is reduced. As an illustration of this effect, pure high molecular weight PEO ($M_w = 1\,000\,000$ g/mol, $T_m = 68\text{ }^\circ\text{C}$), which has a high crystallinity of 71 vol %, has a CO_2 permeability of only 12 Barrer at $35\text{ }^\circ\text{C}$ (20).

Overall, the gas permeation properties of PEO based block copolymers are a complex function of amorphous phase content, dispersed impermeable phase content and

soft segment flexibility. The ideal morphology of a block copolymer system desired for gas separation membranes would 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.

Researchers attempt to obtain this ideal morphology and, for instance, Husken et al. (15) studied PEO based block copolymers with monodisperse tetra-amide (T6T6T) hard segments. These block copolymers, denoted as PEO-T6T6T, showed very high hard segment crystallinity ($\sim 85\%$), which resulted in improved mass transport characteristics. The CO_2 permeability of a PEO_{2000} -T6T6T block copolymer ($M_{w,\text{PEO}} = 2000$ g/mol) was 180 Barrer (an almost 50% increase compared to PEBAX 1074). Nonetheless, these block copolymers still contained large PEO crystalline domains below ambient temperature, thus restricting their applicability (15). A method to suppress this crystallization is the use of poly(propylene oxide) (PPO) as a soft segment (21). The presence of the methyl side group in PPO restricts regular chain packing of the soft phase and suppresses crystallization. This leads to highly permeable membranes due to an increase in soft segment flexibility and a larger fractional free volume as compared to PEO. Furthermore, as PPO is fully amorphous, the permeability remains high at temperatures as low as $-10\text{ }^\circ\text{C}$ (16). Unfortunately, the selectivity of PPO-based block copolymers is lower compared to PEO-based block copolymers because of the lower size sieving ability as well as the lower CO_2 solubility (16). A combination of the beneficial properties of both types of soft segment (the high selectivity of PEO and the amorphous character of PPO) would be ideal.

Following this idea, we synthesized a block copolymer system based on predominantly PEO-based soft segments (75 wt % PEO) containing a random distribution of 25 wt % PPO (20 mol %) (PEO-*ran*-PPO) and monodisperse tetra-amide (T6T6T) hard segments. These block copolymers, denoted as PEO-*ran*-PPO-T6T6T, have a very low PEO melting temperature ($< 0\text{ }^\circ\text{C}$), as the methyl group present in PPO restricts crystallization of the PEO, combined with an extremely pure soft phase due to the very high hard segment crystallinity. Hence, these block copolymers approach the ideal morphology as described above and are therefore exceptionally interesting as a membrane material for CO_2 separation, especially at sub-ambient temperatures (e.g., the separation of CO_2 from natural gas). We recently reported the synthesis, morphology, and thermomechanical properties of this block copolymer system (22).

The present article investigates the pure gas separation properties of these PEO-*ran*-PPO-T6T6T block copolymers in a temperature range from -10 to $50\text{ }^\circ\text{C}$ and highlights the advantage of the new soft segment by comparing the results with other PEO-based block copolymers reported and in particular with the PEO-T6T6T block copolymers reported by Husken et al. (15).

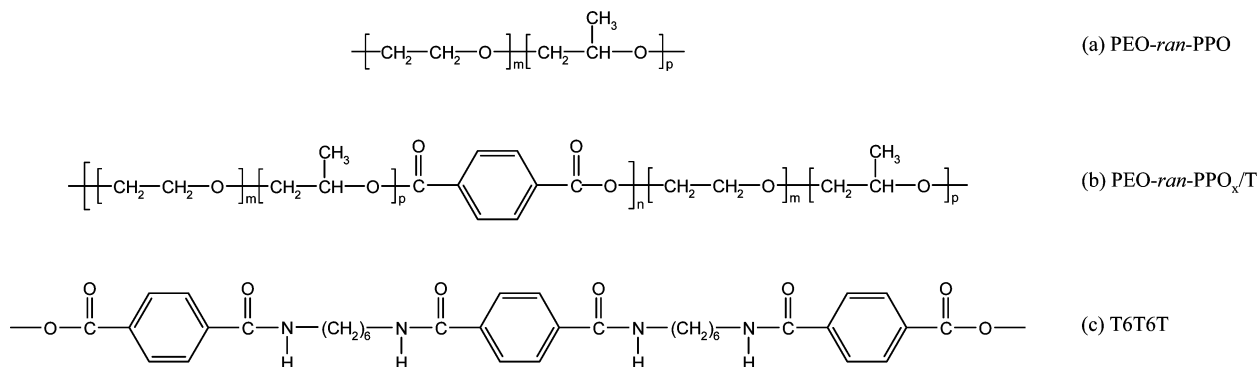


FIGURE 1. Chemical structure of (a) the PEO-*ran*-PPO soft segment, (b) the terephthalic extended PEO-*ran*-PPO soft segment, and (c) the monodisperse tetra-amide (T6T6T) hard segment used.

2. THEORY

Mass transport in nonporous polymeric structures following the solution-diffusion model has been well-documented in the literature (23–25). The steady state gas permeability coefficient of a dense polymeric membrane is given by eq 1

$$P_i = \frac{N_i l}{f_{2,i} - f_{1,i}} \quad (1)$$

where P_i is the gas permeability coefficient (cm^3 (STP) $\text{cm}/(\text{cm}^2 \text{ s cmHg})$), N_i is the steady state flux of the component through the membrane (cm^3 (STP)/($\text{cm}^2 \cdot \text{s}$)), l the membrane thickness (cm) and $f_{2,i}$ and $f_{1,i}$ are respectively the upstream and downstream fugacity (cmHg). The permeability coefficient is usually expressed in units of Barrer, where 1 Barrer equals 1×10^{-10} (cm^3 (STP) $\text{cm}/(\text{cm}^2 \text{ s cmHg})$) or 7.5×10^{-18} (m^3 (STP) $\text{m}/(\text{m}^2 \text{ s Pa})$). The fugacity can be replaced by (partial) pressure if gas phase nonideality is neglected.

When diffusion can be described using Fick's first law and the upstream pressure is significantly higher than the downstream pressure, the permeability coefficient can be expressed by eq 2

$$P_i = D_i S_i \quad (2)$$

where D_i is the average effective diffusion coefficient (cm^2/s) and S_i is the solubility coefficient (cm^3 (STP)/(cm^3 cmHg)). The ideal selectivity of a membrane for gas A over gas B is given by the ratio of the pure gas permeability coefficients according to eq 3

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B} \right) \left(\frac{S_A}{S_B} \right) \quad (3)$$

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 (often characterized by a decrease in glass transition temperature), increasing polymer fractional free volume (FFV) and de-

creasing polymer-penetrant interactions (25). Penetrant solubility is increased by increasing condensability of the penetrant (which increases with increasing critical temperature and boiling point) and increasing polymer-penetrant interactions (25). In general, polyether-based block copolymers exhibit a low T_g , resulting in high CO_2 diffusivity but lower diffusivity selectivity. In this case, CO_2 /light gas selectivity is mainly achieved by high CO_2 /light gas solubility selectivity, as the quadrupolar CO_2 exhibits favorable interaction with the ether oxygen linkages, favoring the solubility of the polar CO_2 over the nonpolar gases like H_2 , N_2 , and CH_4 (3).

3. EXPERIMENTAL SECTION

3.1. Polymer Synthesis. Two series of polyether-based segmented block copolymers using a soft segment containing a random distribution of PEO and PPO (weight ratio 3:1), denoted PEO-*ran*-PPO_x-T6T6T and (PEO-*ran*-PPO₂₅₀₀/T)_y-T6T6T, were used (Figure 1a,b). In the first series, the polyether soft phase was varied by changing the polyether molecular weight (x) up to a maximum of 2500 g/mol (Figure 1a). Segmented block copolymers with longer soft segments (>4600 g/mol for PEO_x-T6T6T (26)) often experience liquid-liquid demixing during synthesis, resulting in a low-molecular-weight material, which should be avoided. This problem can be overcome by extending short polyether soft segments with terephthalic groups (27). Hence, in the second series, short PEO-*ran*-PPO₂₅₀₀ soft segments were extended with terephthalate groups up to a total segment length (y) of 10000 g/mol (Figure 1b). No liquid-liquid demixing was observed in this series and block copolymers with sufficient molecular weight were obtained. As such, by changing x and/or y , the total length of the soft segment was varied from 1000 to 10,000 g/mol. The crystallizable hard segment used is a monodisperse tetra-amide (T6T6T) (Figure 1c). The actual synthesis and the thermomechanical properties of these segmented block copolymers are described in a separate article (22).

PEO-*ran*-PPO_x-T6T6T Block Copolymers. The PEO-*ran*-PPO_x-T6T6T copolymers were synthesized by a polycondensation reaction using PEO-*ran*-PPO_x soft segments with a molecular weight (x) of 1000 and 2500 g/mol and T6T6T hard segments (22).

(PEO-*ran*-PPO₂₅₀₀/T)_y-T6T6T Block Copolymers. The (PEO-*ran*-PPO₂₅₀₀/T)_y-T6T6T copolymers were synthesized by a polycondensation reaction using PEO-*ran*-PPO₂₅₀₀ soft segments, which are extended with terephthalic units (T), and T6T6T hard segments (22). The total molecular weight of the soft segment (y) was varied from 3750 to 10000 g/mol.

The polymerization of PEO-*ran*-PPO₂₅₀₀-T6T6T is given as an example. The reaction is carried out in a 250 mL stainless steel reactor equipped with mechanical stirrer and nitrogen inlet. The vessel contained T6T6T-diphenyl (6.48 g, 8 mmol), PEO-*ran*-PPO₂₅₀₀ (20 g, 8 mmol), Irganox 1330 (0.20 g), catalyst solution (0.8 mL of 0.05 M Ti-*(i*-OC₃H₇)₄ in *m*-xylene) and 50 mL NMP. The reaction mixture was heated in an oil bath to 180 °C under a nitrogen flow. After 30 min, the temperature was increased to 250 °C in 1.5 h. After 2 h at 250 °C, the pressure was slowly reduced ($P < 21$ mbar) to remove all NMP. The pressure was then further reduced ($P < 1$ mbar) to allow melt polycondensation for 1 h. The polymer was cooled to room temperature while maintaining the vacuum. Before use, the polymer was dried overnight in a vacuum oven at 80 °C.

3.2. Membrane Preparation. Films of approximately 100 μm in thickness were prepared from vacuum-dried (50 °C) block copolymers using a Lauffer OPS 40 press. The temperature of the mold was set at approximately 30 °C above the melting temperature (T_m) of the block copolymer as determined by DSC. Air was removed from the polymer in the mold by quickly pressurizing/depressurizing the samples. This pressurization/depressurization cycle was repeated three times before pressing the films 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 plates of the press, glass-fiber reinforced PTFE sheets were used as an intermediate layer between the polymer film and the metal plates (Benetech type B105).

3.3. Gas Permeation Properties of the Prepared Films. The pure gas permeation properties of the prepared films were determined for subsequently N₂, O₂, He, H₂, CH₄, and CO₂ at different temperatures varying from -10 to 50 °C. Pure 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 (28), at an upstream pressure of 4 bar. The feed pressure instead of fugacity has been used in eq 1 to evaluate the gas permeability due to the low feed pressure used and consequential assumed nearly ideal behavior. Ideal gas selectivity values were calculated from the ratio of pure gas permeability values.

4. RESULTS & DISCUSSION

4.1. Introduction. In this article, the effect of the block copolymer composition and the soft segment flexibility on the mass transport characteristics of the synthesized PEO-*ran*-PPO-based block copolymers are studied in a temperature range from -10 to 50 °C. In particular, the effect of the random distribution of 25 wt % PPO in the predominantly PEO (75 wt %) based soft segment will be discussed. Hence, the gas separation performance of these new block copolymers will be primarily compared to the properties of a block copolymer system based on pure PEO (without PPO) with the same type of hard segment, denoted as PEO-T6T6T (15), and a block copolymer system with a slightly different hard segment (a di-amide denoted as T Φ T) in which a mixture of PEO and PPO soft segments is used at an equal (3:1) weight ratio. This polymer is denoted as PEO₂₀₀₀/PPO₂₂₀₀-T Φ T (75/25) (16). The thermomechanical and gas transport properties of these reference block copolymers are reported elsewhere (15, 16, 21, 26, 27).

4.2. Effect of Block Copolymer Composition on Gas Permeability. The primary focus of this paper is the CO₂ separation performance of the developed materials. Figure 2 shows the CO₂ permeability at 35 °C as a function

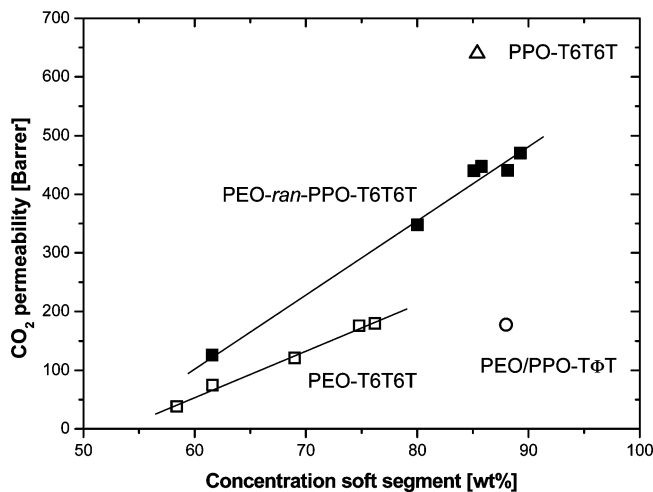


FIGURE 2. CO₂ permeability as a function of the soft segment concentration at 35 °C for (■) PEO-*ran*-PPO-T6T6T, (□) PEO-T6T6T (15), (○) PEO₂₀₀₀/PPO₂₂₀₀-T Φ T (75/25) (16), and (△) PPO₄₂₀₀-T6T6T block copolymers.

of the soft segment concentration in the PEO-*ran*-PPO block copolymers synthesized and compares its values with the results obtained for the two other block copolymer systems reported previously (PEO-T6T6T (15) and PEO₂₀₀₀/PPO₂₂₀₀-T Φ T (16)). Yoshino et al. (12) and Freeman et al. (9) showed that the degree of phase separation between the flexible soft segments and the crystallizable hard segments of the block copolymer has a profound effect on the CO₂ permeability: A decrease in phase separation efficiency led to a significant decrease in CO₂ permeability. However, in our work the degree of phase separation of the block copolymer systems based on a monodisperse tetra-amide hard segment (T6T6T) is high ($\sim 85\%$) and comparable for all block copolymers (22, 26, 27). This allows direct comparison of their gas separation properties on the basis of soft segment concentration. Pure gas permeability values of the prepared PEO-*ran*-PPO-T6T6T block copolymers for all the six different gases studied are, for completeness, summarized in Table S1 (see the Supporting Information).

The CO₂ permeability of the PEO-*ran*-PPO-based block copolymers increases strongly with increasing soft segment concentration in the block copolymer. The permeability values of the other gases show a similar trend (see Table S1 in the Supporting Information). The same has been observed for other PEO based block copolymer systems (9, 12, 15, 17, 18). As will be shown later, the CO₂/light gas selectivity is almost independent of the soft segment concentration, which suggests that gas permeation predominantly occurs through the soft polyether domains, whereas the crystallized hard domains act as impermeable filler, providing the material its mechanical and dimensional stability (9, 12, 15, 17, 18).

The CO₂ permeability of the PEO-*ran*-PPO based block copolymers increased by a factor of approximately two over the entire soft segment concentration range compared to their pure PEO-based counterparts (PEO-T6T6T). This shows the strong benefit of the random replacement of 25 wt % of PEO for PPO in the soft segment (compare □ with ■) as

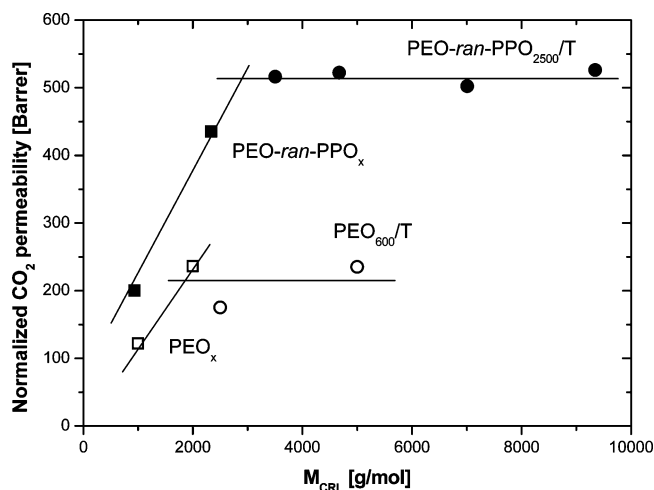


FIGURE 3. Normalized CO_2 permeability ($n\text{-}P_{\text{CO}_2}$) as a function of the molecular weight between physical crosslinks (M_{CRL}) at 35 °C for (■) $\text{PEO-ran-PPO}_x\text{-T6T6T}$, (●) $(\text{PEO-ran-PPO}_{2500}/\text{T})_y\text{-T6T6T}$, (□) $\text{PEO}_x\text{-T6T6T}$ (15), and (○) $(\text{PEO}_{600}/\text{T})_y\text{-T6T6T}$ (15).

it significantly enhances the gas permeability of the polyether based block copolymers. This increase can be attributed to a significant increase in soft segment flexibility (which is visible when the respective T_g 's of both polymers are compared (see Table S1 in the Supporting Information) enhancing gas diffusivity (3, 22)), combined with, most likely, an increase in fractional free volume (FFV) as the FFV in PPO-based materials is generally higher than in PEO-based materials because of the presence of the methyl group in PPO (29). The observed increase in permeability for PEO-ran-PPO is more than what would be expected based on simple mixing rules, which is most probably due to the random distribution of PPO, which also influences the packing of the PEO chains.

The prerequisite of a random distribution of the PEO and PPO moieties in a single soft segment is evident when the results are compared with the $\text{PEO}_{2000}/\text{PPO}_{2200}\text{-T}\Phi\text{T}$ (75/25) block copolymer where the two soft segments are only physically mixed. Although this block copolymer has a rather low hard segment crystallinity (25 %) because of the highly polar nature of the short monodisperse $\text{T}\Phi\text{T}$ di-amide hard segment, it shows that simple mixing of PEO and PPO soft segments does not enhance CO_2 permeability (nor does it reduce PEO crystallinity (21)).

4.3. Effect of the Soft Segment Flexibility on CO_2 Permeability. Although the soft segment concentration is an important parameter to tune the gas permeation characteristics in block copolymers, it is not considered to be the only one. Yoshino et al. (12), Okamoto et al. (17), and Metz et al. (18) state that also the soft segment flexibility (typically characterized by changes in glass transition temperature) influences the gas separation performance of these block copolymer systems.

This effect becomes evident when the CO_2 permeability is normalized for the soft segment concentration (denoted as $n\text{-}P_{\text{CO}_2}$ ($= P_{\text{CO}_2}/\text{wt} \%$ soft segment) in Table S1 in the Supporting Information) and plotted versus the molecular weight between physical cross-links (M_{CRL}) (Figure 3). This

molecular weight between physical cross-links (the crystallized hard segments) is defined as the actual soft segment length (methyl side groups of PPO are not taken into account).

The sharp increase of the normalized CO_2 permeability as a function of M_{CRL} for the $\text{PEO-ran-PPO}_x\text{-T6T6T}$ (■) block copolymer series with a soft segment length up to 2500 g/mol (and the reference $\text{PEO}_x\text{-T6T6T}$ (□) block copolymer series with a soft segment length up to 2000 g/mol) shows that the mass transport properties of these polymer systems not only depend on the soft segment concentration but also strongly depend on the soft segment length and consequently the soft segment flexibility. An increase in the soft segment length and thus flexibility (as proven by a decrease in T_g , see Table S1 in the Supporting Information) significantly increases the CO_2 permeability, which was also observed by other researchers (12, 17, 18). This suggests that high soft segment lengths are beneficial for the mass transport properties.

In our work, we prepared block copolymers containing higher soft segment lengths (> 2500 g/mol) and thus higher anticipated soft segment flexibility by extending the PEO-ran-PPO soft segment ($M_w = 2500$ g/mol) with terephthalic units (●, $(\text{PEO-ran-PPO}_{2500}/\text{T})_y\text{-T6T6T}$ (22)). These terephthalic units do not crystallize and belong to the amorphous soft phase. As a consequence, the soft phase concentration is increased. However, the use of these terephthalic units limits the rotational freedom of the soft segment near this terephthalic unit (27). This results in an increase in glass transition temperature of the $(\text{PEO-ran-PPO}_{2500}/\text{T})_y\text{-T6T6T}$ block copolymers (the extended ones) compared to the $\text{PEO-ran-PPO}_{2500}\text{-T6T6T}$ block copolymer (unextended) (see Table S1 in the Supporting Information), which indicates that the soft segment flexibility of the $(\text{PEO-ran-PPO}_{2500}/\text{T})_y\text{-T6T6T}$ block copolymers is reduced compared to the $\text{PEO-ran-PPO}_{2500}\text{-T6T6T}$ block copolymer, although a higher total soft segment length is obtained. This is clearly visualized in Figure 3, where the soft segment concentration normalized CO_2 permeability ($n\text{-}P_{\text{CO}_2}$) of the terephthalic extended PEO-ran-PPO block copolymers (●) reaches a plateau value, as the soft segment flexibility within this series is constant ($T_g \approx -60$ °C) due to the presence of these terephthalic extender which limits the flexibility. This effect is also observed for the PEO based block copolymer systems studied by Husken et al. (15), in which terephthalic units were used to extend low molecular PEO of 600 g/mol (○).

These results indicate that besides the soft segment concentration, the soft segment flexibility (represented by the T_g of the soft segment of the polymer) is also a crucial parameter that determines the mass transport properties as shown in Figure 4.

Lin et al. (3) showed this relation to be generally applicable to all PEO based materials (pure PEO, PEO-based block copolymers, and cross-linked PEO structures). For block copolymer systems this implies that the microdomain morphology is of great influence on the macroscopic gas permeation properties. One desires a very pure soft amor-

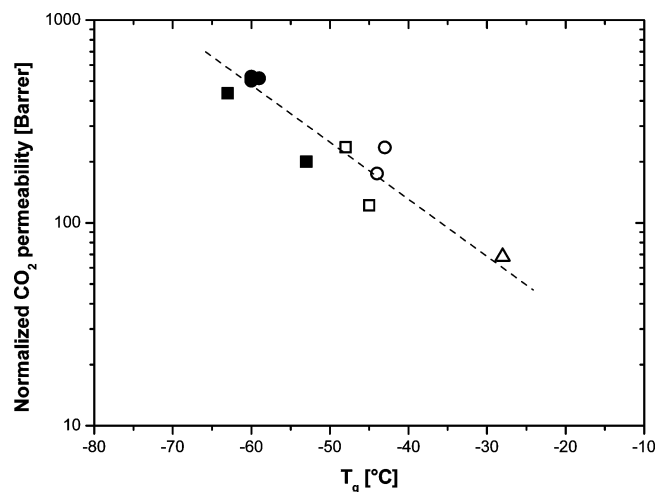


FIGURE 4. Normalized CO₂ permeability at 35 °C as a function of the glass transition temperature for (■) PEO-*ran*-PPO_{*x*}-T6T6T, (●) (PEO-*ran*-PPO₂₅₀₀/T)_{*y*}-T6T6T, (□) PEO_{*x*}-T6T6T (15), (○) (PEO₆₀₀/T)_{*y*}-T6T6T (15), and (Δ) (PEO₃₀₀/T)₂₅₀₀-T6T6T (15).

phous phase (to obtain an as low as possible T_g) and this is achieved in the current work by the use of the monodisperse tetra-amide hard segments.

The CO₂ permeability of the PEO-*ran*-PPO based block copolymer system could probably be even higher if a soft segment length above 2500 g/mol can be achieved without the use of terephthalic units. Unfortunately, the only other PEO-*ran*-PPO soft segment commercially available has a molecular weight of 12,000 g/mol, which proved to be unsuitable for block copolymer synthesis due to liquid–liquid demixing (22). Husken et al. (26), who prepared PEO_{*x*}-T6T6T based block copolymers, could successfully prepare block copolymers with a soft segment length of up to 4600 g/mol. Because of the reduced polarity of the soft segment, PPO_{*x*}-T6T6T based block copolymers could successfully be prepared up to a soft segment length of 6200 g/mol. Therefore, we think that PEO-*ran*-PPO based block copolymers with a maximum soft segment length of approximately 5000–6000 g/mol (a total soft segment concentration between 89–91 wt. %), which would exhibit even better performance, could be prepared.

4.4. Effect of Block Copolymer Composition on CO₂/Light Gas Selectivity. Table 1 summarizes the CO₂/light gas selectivity at 35 °C for a selection of the investigated PEO-*ran*-PPO based block copolymers and compares them with polyether based block copolymers reported in literature (15, 16). The CO₂/light gas selectivity is practically independent of the soft segment length and only the CO₂/H₂ selectivity seems to decrease at short soft segment length ($x = 1000$ g/mol). This behavior is also observed by Husken et al. (15) and Metz et al. (18).

In rubbery materials, like the polyether block copolymer systems studied in this work, the diffusion coefficient is not a strong function of penetrant size and the overall selectivity is primarily the result of a high solubility selectivity due to the favorable interactions between CO₂ and the polar ether oxygen linkages (3). Because the composition of the soft segment, and in particular the concentration of ether oxygen

linkages in the soft segment, is not changed significantly by the random substitution of 25 wt % PEO for PPO, it is expected that the solubility selectivity and thus the overall CO₂/light gas selectivity is not significantly affected. This is indeed visible in Table 1.

To illustrate this, we compare the gas separation performance of the different polymers at relative similar soft segment length (~2000–2500 g/mol). The PEO-*ran*-PPO₂₅₀₀-T6T6T block copolymer ($M_{w,PEO-ran-PPO} = 2500$ g/mol) has a CO₂ permeability of 348 Barrer, which is double the permeability of the PEO₂₀₀₀-T6T6T block copolymer (180 Barrer), which has a soft segment length of 2000 g/mol. At this specific soft segment length, the CO₂/H₂ selectivity is similar for both polymers (~10) as the small decrease in solubility selectivity (due to a decrease in polarity of the soft phase by the introduction of the less polar PPO) is offset by an small increase in diffusivity selectivity (as the diffusivity of the larger CO₂ is increased more as compared to the diffusivity of the smaller H₂). Furthermore, CO₂/N₂ (~45) and CO₂/CH₄ (~13) selectivity values have decreased only slightly compared to the PEO₂₀₀₀-T6T6T based block copolymer, which has CO₂/N₂ and CO₂/CH₄ selectivities of 49 and 16, respectively. This is due to a combination of a small decrease in solubility selectivity combined with a small decrease in diffusivity selectivity. A block copolymer containing a pure PPO soft segment (PPO₄₂₀₀-T6T6T) has much lower CO₂/light gas selectivities (CO₂/H₂ = 6, CO₂/N₂ = 24, and CO₂/CH₄ = 7), essentially caused by a much more pronounced decrease in solubility selectivity. As such, the currently studied PEO-*ran*-PPO-based block copolymers combine an increase in soft segment flexibility and corresponding large increase in gas permeability (compared to pure PEO based block copolymers) with a high selectivity attributable to the high fraction of PEO in the soft phase.

4.5. CO₂ Permeability and CO₂/Light Gas Selectivity As a Function of Temperature. The molecular organization of the block copolymer and especially the presence of crystalline polyether domains within the soft phase, which formation strongly depends on the temperature, has a major influence on the permeability (15, 16, 18). In general, polyether crystallization limits the amount of permeable amorphous soft phase and moreover it restricts the soft segment flexibility resulting in strongly reduced gas permeabilities. Therefore, crystallization of the polyether soft phase should be prevented at the temperatures of interest.

The influence of the temperature on the CO₂ permeability of the PEO-*ran*-PPO based block copolymers is shown in Figure 5 (filled symbols). The temperature dependence of the CO₂ permeability of a pure PEO based block copolymer (PEO₂₀₀₀-T6T6T) (15) and a block copolymer containing a mixture of PEO₂₀₀₀ and PPO₂₂₀₀ soft segments in an equal weight ratio (PEO₂₀₀₀/PPO₂₂₀₀-T Φ T (75/25)) (16) are both shown as well (open symbols, dashed line).

As a result of the remarkably low PEO melting temperature and low crystallinity in the PEO-*ran*-PPO-based block copolymers (22), these materials show a linear increase in

Table 1. CO₂/Light Gas Selectivity for H₂, N₂ and CH₄ for a Selection of PEO-*ran*-PPO-T6T6T Block Copolymers and Several Other Block Copolymers used as a Reference at 35 °C

sample	CO ₂ permeability (Barrer)	selectivity		
		CO ₂ /H ₂	CO ₂ /N ₂	CO ₂ /CH ₄
PEO- <i>ran</i> -PPO ₁₀₀₀ -T6T6T	123	7	46	13
PEO- <i>ran</i> -PPO ₂₅₀₀ -T6T6T	348	10	45	13
(PEO- <i>ran</i> -PPO ₂₅₀₀ /T) ₁₀₀₀₀ -T6T6T	470	10	43	13
PEO ₁₀₀₀ -T6T6T (15)	75	7	41	14
PEO ₂₀₀₀ -T6T6T (15)	180	10	49	16
(PEO ₆₀₀ /T) ₂₅₀₀ -T6T6T (15)	121	8	50	17
(PEO ₆₀₀ /T) ₅₀₀₀ -T6T6T (15)	174	9	53	17
PPO ₄₂₀₀ -T6T6T	640	6	24	7

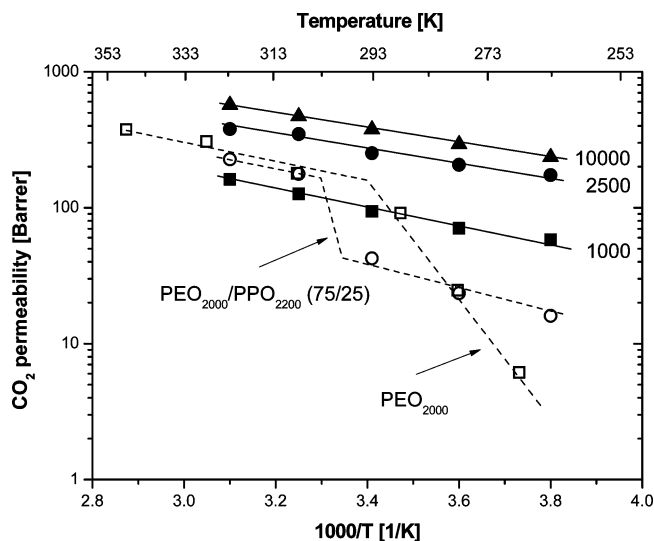


FIGURE 5. CO₂ permeability as a function of the temperature for the (■) PEO-*ran*-PPO₁₀₀₀-T6T6T, (●) PEO-*ran*-PPO₂₅₀₀-T6T6T, (▲) (PEO-*ran*-PPO₂₅₀₀/T)₁₀₀₀₀-T6T6T, (□) PEO₂₀₀₀-T6T6T (15), and (○) PEO₂₀₀₀/PPO₂₂₀₀-T Φ T (75/25) (16) block copolymers.

CO₂ permeability over the entire temperature range investigated (−10 to 50 °C). The block copolymer with the highest soft segment length ((PEO-*ran*-PPO₂₅₀₀/T)₁₀₀₀₀-T6T6T) has a CO₂ permeability as high as 570 Barrer at 50 °C. Furthermore, the CO₂ permeability at −10 °C remained also high at a value of 235 Barrer. This high permeability at lower temperatures is especially interesting, as CO₂/light gas selectivity is significantly increased at these low temperatures, as will be described below. This gives the opportunity to apply these PEO based block copolymers in CO₂/light gas separations in a much broader temperature window as compared to currently available commercially materials like PEBA (8–11) or Polyactive (13, 18), as these commercially available materials have a semicrystalline PEO soft phase at these low temperatures, which significantly reduces the gas permeability. The decrease in performance when crystallization occurs is also evident for the noncommercial reference block copolymers shown in Figure 5 (open symbols). The PEO₂₀₀₀-T6T6T block copolymer (15) shows a linear increase in CO₂ permeability between 35 and 75 °C as the PEO phase is completely amorphous at these temperatures. However, below 25 °C, a steep decrease in CO₂ permeability is observed because of the formation of crystalline PEO domains ($T_{m,PEO} = 21$ °C (26)), which decreases

the amount of PEO accessible for gas transport and reduces the soft segment flexibility, thus decreasing diffusivity (15). At −5 °C, this block copolymer has a CO₂ permeability of only 6 Barrer, which is almost two orders of magnitude lower than values obtained for the PEO-*ran*-PPO-based block copolymers presented in this work. Moreover, the necessity of a random distribution of the PPO within the PEO soft segment is evident when the results of the PEO-*ran*-PPO block copolymers are compared with those of the PEO₂₀₀₀/PPO₂₂₀₀-T Φ T (75/25) block copolymer in which the two types of soft segment (PEO and PPO) are simply mixed (Figure 5) (containing an equal PEO/PPO ratio compared to the PEO-*ran*-PPO based block copolymers) (16). The use of a mixture of both soft segments did not successfully suppress PEO crystallinity ($T_{m,PEO} = 32$ °C (21)), and consequently results in a significant decrease in gas permeability below this melting temperature. As an illustration of this, the CO₂ permeability obtained with the PEO-*ran*-PPO soft segment (at a similar length of 2500 g/mol), in the temperature range where the PEO₂₀₀₀/PPO₂₂₀₀-T Φ T (75/25) block copolymer has a semicrystalline soft phase (≤ 20 °C), is approximately 1 order of magnitude higher.

These two comparative examples signify the importance of a random distribution of PPO within the PEO soft segment and demonstrate the benefits of this novel type of soft segment at temperatures where block copolymers containing pure PEO soft segments contain a semicrystalline soft phase. Especially if a soft segment length above 2500 g/mol could be used (without the use of the terephthalic unit as an extender), as in general the PEO melting temperature increases with soft segment length (26). For instance, a PEO₄₆₀₀-T6T6T block copolymer ($M_{w,PEO} = 4600$ g/mol) has a PEO melting temperature of 53 °C (26), severely limiting its applicability in gas separation applications below this temperature. The PEO-*ran*-PPO soft segment overcomes this disadvantage and combines a low PEO melting temperature with the ability to use high soft segment lengths. Hence, high soft segment flexibility and thus highly permeable membranes over a wide temperature range could be obtained.

The CO₂/light gas selectivity as a function of the temperature for the PEO-*ran*-PPO₂₅₀₀-T6T6T block copolymer is shown in Figure 6 (filled symbols). The block copolymers with other soft segment lengths exhibit similar dependency of the CO₂/light gas selectivity on the temperature, but are

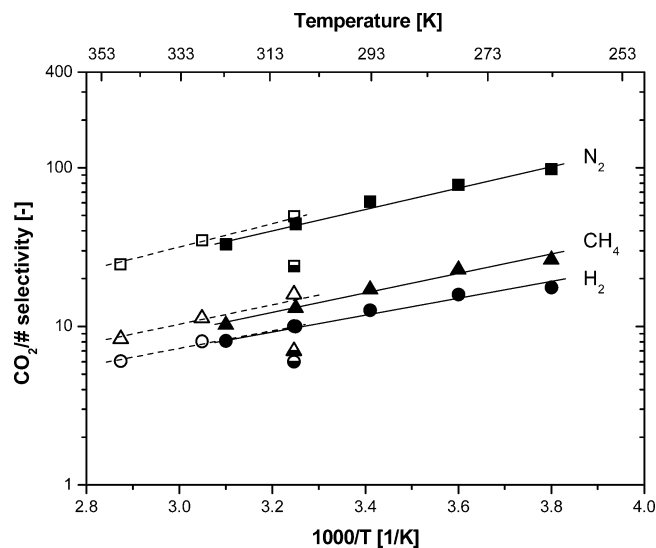


FIGURE 6. CO_2 /light gas selectivity as a function of the temperature for CO_2/H_2 (circles), CO_2/CH_4 (triangles) and CO_2/N_2 (squares) for PEO-*ran*-PPO₂₅₀₀-T6T6T (closed symbols), PEO₂₀₀₀-T6T6T (open symbols) and PPO₄₂₀₀-T6T6T (partially filled symbols).

for clarity not shown here. For comparison, the CO_2 /light gas selectivity of a PEO₂₀₀₀-T6T6T block copolymer (open symbols) (for $T \geq 35$ °C as the PEO phase is completely amorphous at these temperatures and crystallizes at lower temperatures) has been added.

The ideal selectivity of the PEO-*ran*-PPO-based block copolymers for CO_2/N_2 , CO_2/CH_4 , and CO_2/H_2 increases with decreasing temperature (Figure 6) and a linear behavior is observed over the complete temperature range investigated, as the soft phase is fully amorphous at all temperatures. Despite the addition of 25 wt % PPO to the soft PEO phase, the selectivity of this polymer is only very slightly decreased compared to the PEO₂₀₀₀-T6T6T block copolymer (open symbols). This is due to the only minor difference in chemical composition of the soft segment, as discussed before. The CO_2 /light gas selectivity of a pure PPO-based block copolymer (PPO₄₂₀₀-T6T6T, Figure 6 and Table S1 in the Supporting Information) at 35 °C is shown for comparison as well (partially filled symbols). Although this block copolymer has a CO_2 permeability of 640 Barrer, which is likely to be achieved with a PEO-*ran*-PPO soft segment of similar length, its selectivity is only half the value found for the PEO-*ran*-PPO-based block copolymers. The PEO-*ran*-PPO-based block copolymers thus combine a high permeability with a high CO_2 /light gas selectivity. This is especially important at temperatures below ambient, where other PEO-based block copolymers exhibit inferior mass transport properties as a result of a semicrystalline soft phase. This class of materials is as such very interesting in CO_2 separation processes where subambient conditions are present, as at these low temperatures one can take advantage of the increased separation ability of the polymer materials while maintaining excellent transport characteristics. An example of such a process is the separation of CO_2 from natural gas (to meet pipeline specifications). The fields that are being commissioned at the moment contain increasingly higher levels of CO_2 . In the separation of CO_2 from these natural gas streams containing

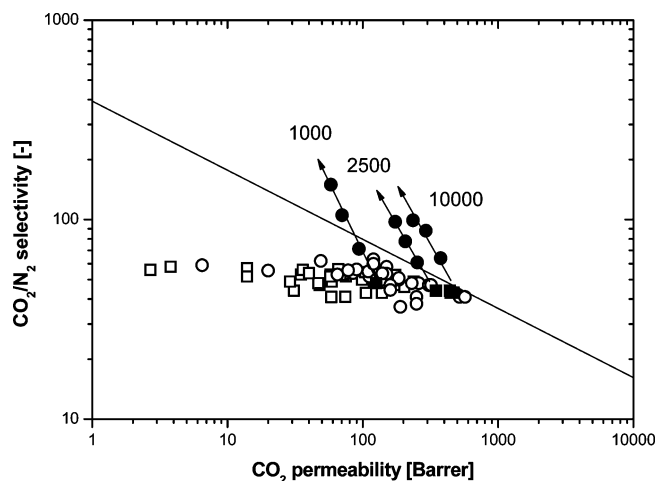


FIGURE 7. Robeson upper bound relationship between the CO_2/N_2 selectivity and the CO_2 permeability at 35 °C. The PEO-*ran*-PPO block copolymers studied in this article are represented by the filled symbols (■). CO_2/N_2 permeability/selectivity data at reduced temperature (< 35 °C) of the PEO-*ran*-PPO based block copolymers with a total soft segment length of 1000, 2500, and 10,000 g/mol are also shown (●). Lower permeability represents lower temperature decreasing from 20 °C to −10 °C with steps of 15 °C. Data obtained from literature on (□) pure PEO-based block copolymers (9, 12, 15, 16, 18) and (○) PEO based crosslinked networks (4, 34, 35) have been added for comparison. The upper bound line has been drawn with data from (33).

high levels of carbon dioxide, the Joule–Thompson effect lowers the temperature of the gas as it expands from the high-pressure feed side to the low-pressure permeate side. This can even cool the membrane in the membrane module by 30–40 °C (30). Thus, even feed gas that starts out at temperatures above ambient often will be cooled inside the module to subambient temperatures. The understanding of the membrane performance characteristics at these low temperatures is thus highly relevant for practical operation.

4.6. CO_2/N_2 Upper Bound Relationship. Figure 7 presents a CO_2/N_2 permeability/selectivity trade-off curve in which the PEO-*ran*-PPO-based block copolymers investigated in our work as well as relevant literature data on PEO-based polymeric materials are summarized. The existence of a relationship between the permeability and selectivity of polymer membranes, the so called upper bound or trade-off relationship, has been first described by Robeson (31) and later theoretically predicted by Freeman (32). Recently, Robeson (33) revisited his original 1991 paper and included the latest literature data and several new gas pairs including CO_2/N_2 . This CO_2/N_2 gas pair has been chosen here to assess our PEO-*ran*-PPO-based block copolymer membranes, as it is the most widely documented gas pair regarding PEO-based membranes.

The CO_2/N_2 selectivity at 35 °C for all studied polymers is rather constant at a level of ~50, which reflects the fact that the soft PEO phase is the continuous domain for gas transport. The CO_2 permeability varies roughly from 1 to 500 Barrer because of differences in the microdomain morphology of the polymers (3). The maximum CO_2 permeability at 35 °C reported in the literature for PEO-based block copolymers only (□) is around 200 Barrer using polyimide hard segments (12). The very high permeability of the PEO-*ran*-

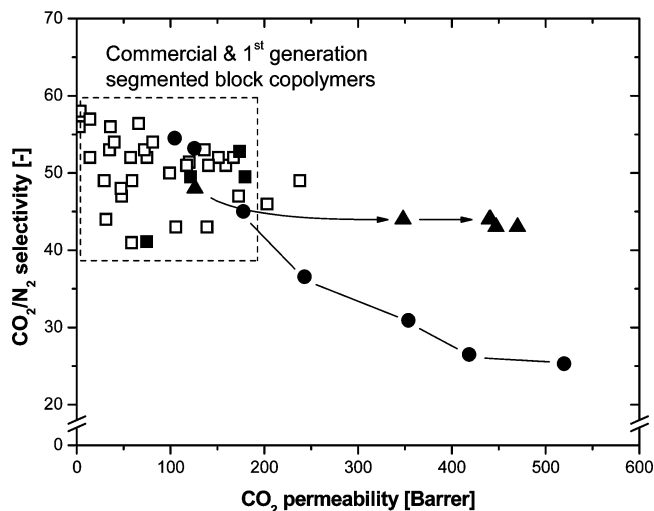


FIGURE 8. Robeson CO_2/N_2 upper bound relationship at 35 °C. The filled symbols show the progress in our work on polyether based block copolymers systems for CO_2 separation using monodisperse hard segments, which are (■) PEO-T6T6T (15), (●) polyether-T Φ T (16), and (▲) the current work on PEO-*ran*-PPO-T6T6T. Relevant literature data have been added (□) (9, 12, 18).

PPO-based block copolymers studied in our work approaches the upper bound illustrated by Robeson.

These PEO-*ran*-PPO block copolymers exhibit similar mass transport properties compared to the cross-linked PEO structures described by Freeman et al. (4–6), which reached a CO_2 permeability as high as 320 Barrer for a PEGDA/PEGMEA ratio of 30/70. Their PEGDA/PEGMEA networks containing more than 70% of PEGMEA reached higher permeability values (up to 570 Barrer); however, these networks developed PEO crystalline domains below 0 °C because of the highly flexible nature of the monofunctional PEGMEA chains, resulting in a distinct decrease in CO_2 permeability.

Because the block copolymers we studied keep high permeabilities (as no soft phase crystallization occurs) at temperatures as low as –10 °C, the temperature dependency of the CO_2/N_2 permeability/selectivity has been presented in Figure 7 as well (●). The figure clearly shows that a decrease in temperature (below 35 °C) moves the CO_2/N_2 separation performance significantly above the upper bound at all soft segment lengths. This highlights the advantage of these PEO-*ran*-PPO-based block copolymers; a high CO_2 permeability combined with a good CO_2/N_2 selectivity even at temperatures as low as –10 °C could be reached. This is especially important at temperatures below ambient, where other PEO-based block copolymers exhibit inferior mass transport properties as a result of a semi-crystalline soft phase (12). This class of materials is as such very interesting in CO_2 separation processes where subambient conditions are present (e.g., separation of CO_2 from natural gas), as at these low temperatures one can take maximum advantage of the increased separation ability of the polymer materials while maintaining excellent transport characteristics.

The literature data presented in Figure 7 and that have been used to create the upper bound line are generally obtained at a temperature of 25–35 °C. Nevertheless, it is

assumed (as also shown in our work) that the upper bound lines are a function of temperature; though no model exists that predicts this dependence and limited literature data at other temperatures are available. Yet, the current set of data as well as data on CO_2/H_2 and CO_2/CH_4 separation at subambient temperatures using cross-linked PEO structures by Freeman et al. (5, 6) suggest that the upper bound lines move up when the measurement temperature decreases (if no changes in microdomain morphology occur). Nevertheless, more data are needed to further investigate the temperature dependence of the Robeson upper bound to allow more accurate prediction of the effect of temperature on the behavior of upper bound lines.

To summarize, Figure 8 presents the progress made in our work on polyether based block copolymer systems for CO_2 separation using monodisperse hard segments. First, Husken et al. (15) prepared PEO based block copolymers using monodisperse tetra-amide hard (T6T6T) segments. PEO crystallization in these block copolymers, which is an issue, was partially suppressed by extending short PEO soft segments ($M_w = 600$ g/mol) with terephthalic units. Second, we prepared block copolymers based on a mixture of PEO₂₀₀₀ and PPO₂₂₀₀ soft segments and monodisperse diamide (T Φ T) hard segments (●) (16). PEO crystallization could be successfully suppressed if at least 41 mol % of PPO was incorporated. Although the incorporation of PPO also resulted in an increase in permeability there has been made a significant sacrifice in selectivity (as shown by the downward slope of the data). In the current work (▲) we have shown that high CO_2 permeability and high CO_2/N_2 (and other light gas) selectivity can be achieved simultaneously by using long PEO-based soft segments containing a random distribution of 25 wt % PPO. As such, we overcome the usual trade-off dilemma (an increase in permeability gives a decrease in selectivity) by a smart design of the block copolymer system.

5. CONCLUSIONS

The mass transport properties of two block copolymer series based on poly(ethylene oxide)-*ran*-poly(propylene oxide) (PEO-*ran*-PPO) soft segments and monodisperse tetra-amide (T6T6T) hard segments have been studied. A commercially available polyether, which contains a random distribution of 75 wt % PEO and 25 wt % PPO, has been used as a soft segment and its length has been varied between 1000 and 10000 g/mol. The CO_2 permeability strongly increased as the soft segment length increased. High soft segment lengths (> 2500 g/mol) were obtained by extending the soft segment with a molecular weight of 2500 g/mol with terephthalic units. However, this terephthalic unit restricted the soft segment flexibility and thus influenced the mass transport properties. Overall, very high CO_2 permeabilities (up to 470 Barrer at 35 °C) were obtained without any significant decrease in CO_2 /light gas selectivity, when compared to commercially available and previously investigated PEO based polymers.

The temperature dependency of the mass transport properties between –10 and 50 °C was investigated and a

linear relationship between the logarithm of the gas permeability (and thus gas selectivity) as a function of inverse temperature was observed. Because of the random presence of the methyl group of PPO, crystallization of the soft phase was restricted and the soft phase remained fully amorphous until temperatures as low as $-10\text{ }^{\circ}\text{C}$. This is a major advantage of these polymers when compared to PEO-based block copolymer systems reported earlier, as these usually have a semi-crystalline PEO phase at or below ambient temperatures, which severely restricts gas permeation. In the current system, the CO_2 permeability at $-10\text{ }^{\circ}\text{C}$ remained surprisingly high (> 200 Barrer), whereas CO_2 /light gas selectivity increased to 19, 99, and 31 for CO_2/H_2 , CO_2/N_2 , and CO_2/CH_4 , respectively. This class of materials is as such very interesting in CO_2 separation processes where subambient conditions are present (e.g. the separation of CO_2 from natural gas) as at these low temperatures one can take advantage of the increased separation ability of the polymer materials while maintaining excellent transport characteristics.

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Supporting Information Available: Pure gas permeation properties of PEO-*ran*-PPO-T6T6T block copolymers and several other block copolymers used as a reference at $35\text{ }^{\circ}\text{C}$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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