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Pushing the limits of block copolymer membranes for CO_2 separation

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ABSTRACT

The current work describes the synthesis and mass transport properties of a series of blend membranes based on a highly permeable polyether based segmented block copolymer and a poly(ethylene glycol) based additive. This series of polymers integrates the knowledge of molecular design and molecular blending and presents CO_2 permeabilities currently unknown to any polyether based block copolymer (system) known in literature. The concept presented is not limited to this specific case and hence opens a window of opportunity for further development of highly permeable block copolymer systems for CO_2 separation and in particular for use in post-combustion CO_2 capture.

1. Introduction

The capture and subsequent storage of carbon dioxide (CO_2), commonly known as CCS, from large point sources such as coal-fired power plants attracts a significant amount of attention [1]. Especially membrane technology has been recognized to have significant opportunities as a so-called ‘post-combustion’ capture method as it offers an energy-efficient and low-cost CO_2 capture option [2]. In a post-combustion membrane process, CO_2 is separated from light gases, mainly N_2, present in the flue gas.

Merkel et al. [2] state that due to constraints imposed by practical operating conditions, costs and energy considerations a membrane material for post-combustion CO_2 capture should posses a high permeance rather than a high selectivity. In particular they state that increasing the CO_2/N_2 selectivity to values higher than ∼30 has little benefit. Poly(ethylene oxide) (PEO) based block copolymers are well recognized for their desired CO_2/N_2 selectivity (40–50 at 30–35 °C). Although such PEO based materials are commercially available, like PEBAX® [3,4] and PolyActive® [5], their relatively low permeability remains an issue.

Here we present an integrated concept of our recent work on the design strategies for PEO based block copolymers as a method to increase the CO_2 permeability while maintaining the CO_2/N_2 selectivity. We combine the enhancing effect on the permeability of tailoring the molecular design of the block copolymers with that of molecular blending in order to control mass transfer through membranes for CO_2 capture. As such we obtain high CO_2 permeabilities previously unknown, combined with reasonable CO_2/N_2 selectivities.

1.1. Design strategies

The low permeability of the commercially available block copolymers is mainly related to their complex microdomain morphology (in particular the crystallinity of the soft phase) counteracting high permeation rates [4,5]. Also studies on non-commercial block copolymers [6–9] indicate that the degree of phase separation and soft segment flexibility highly influences the gas transport properties of the materials as gas transport preferentially occurs through the amorphous soft phase of the block copolymer (while on the other hand the hard segments provide the block copolymer with mechanical and dimensional stability). Tuning of the microdomain morphology by smart design of the molecular structure of the block copolymer truly improves its permeation characteristics [8–11].

In particular, we recently reported a block copolymer system based on soft segments containing a random distribution of 75 wt.% PEO and 25 wt.% PPO and uniform tetra-amide (T6T6T) hard segments, denoted as PEO-*ran*-PPO-T6T6T [12]. This block copolymer system reached CO_2 permeabilities as high as 470 Barrer (3.5×10^{-15} m^3 (STP) m/(m^3 s Pa)) (see Fig. 1,) while selectivity is maintained above 40 [10].

Besides the tuning of the microdomain morphology, molecular blending of polymers has proven to be a successful tool to increase the gas permeability of commercially available block copolymers. Examples are, for instance, a blend of PEBAX® 1657 with low molec-

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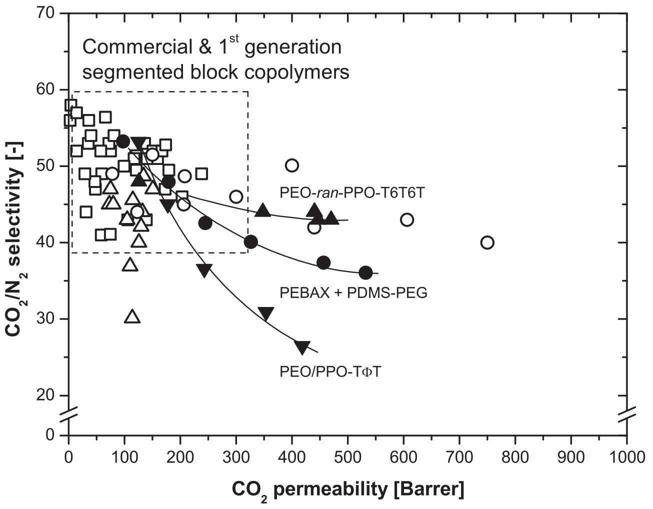

Fig. 1. Robeson CO_2/N_2 upper bound relationship at 35 °C. The figure displays the progress made in our recent work on pure PEO-*ran*-PPO-T6T6T block copolymer membranes (▲) [10] and PEBAX®1657/PDMS-PEG blend membranes (●) [17]. Recent data obtained by Car et al. (△) [13,15] and Yave et al. (○) [14,16] on poly(ethylene glycol) based blend membranes have been added for comparison. Furthermore data from our recent work on polyether based block copolymers using short monodisperse TΦT hard segments (▼) [9] and on 1st generation segmented block copolymers (□) [4,5,7,8] are incorporated. All measurements depicted by a closed symbol are performed at an upstream pressure of 4 bar.

ular weight PEG (Mw = 200 g/mol) [13] or its derivatives [14]. Similar results have been obtained by the blending of these components with PolyActive® [15,16].

We recently showed a 5 times increase in CO_2 permeability upon mixing the commercially available PEO based block copolymer PEBAX®1657 with a poly(dimethyl siloxane) (PDMS) based oligomer grafted with low molecular weight PEG [17]. Although the CO_2/N_2 selectivity decreased somewhat upon the increase in CO_2 permeability (and thus additive content) its selectivity remained reasonably high. As such, we managed to combine the high selectivity of poly(ethylene oxide) with the high permeability of PDMS (see Fig. 1, ●). Similar results have been very recently obtained by Freeman et al. who incorporated siloxane monomers within a crosslinked poly(ethylene oxide) network [18,19].

We believe that these concepts are generally applicable, as we will show here. We expect that starting from block copolymers with significantly higher initial CO_2 permeabilities as compared to PEBAX® or PolyActive® (e.g. the polymers designed in our recent paper) the addition of the PDMS-PEG oligomer would result in an even further increase in membrane performance.

2. Theory

Mass transport in non-porous, dense, polymeric structures follows the solution-diffusion mechanism and has been well documented in literature [20–22]. The steady state gas permeability coefficient of component *i* through a dense polymeric membrane is given by Eq. (1):

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

where P_i is the gas permeability coefficient ($\mathrm{cm^3\,(STP)\,cm/(cm^2\,s\,cmHg)}$), N_i is the steady state flux of the component through the membrane ($\mathrm{cm^3\,(STP)/(cm^2\,s)}$), l the membrane thickness (cm) and $f_{2,i}$ and $f_{1,i}$ respectively are the upstream and downstream fugacity (cmHg). The permeability coefficient is usually expressed in units of Barrer, where 1 Barrer equals $1 \times 10^{-10}\,\mathrm{(cm^3\,(STP)\,cm/(cm^2\,s\,cmHg)}$ or $7.5 \times 10^{-18}\,\mathrm{(m^3\,(STP)\,m/(m^3\,s\,Pa))}$. If gas phase non-ideality is not significant, fugacities can be replaced by partial pressures.

The permeability may be described using Fick's first law, resulting in the permeability coefficient as expressed by Eq. (2):

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

In Eq. (2) D_i is the average effective diffusion coefficient ($\mathrm{cm^2/s}$) and S_i is the solubility coefficient ($\mathrm{cm^3\,(STP)/(cm^3\,cmHg)}$) of component *i* respectively. In the most ideal case of mass transport *P*, *D* and *S* are independent of feed and permeate pressure.

The selectivity of a polymer membrane for gas A over gas B is given by the ratio of the gas permeability coefficients according to Eq. (3) and consequently this selectivity is the product of diffusivity and solubility selectivity:

$$\alpha = \frac{P_A}{P_B} = \frac{D_A}{D_B}\frac{S_A}{S_B} \qquad (3)$$

where D_A/D_B is the diffusivity selectivity and S_A/S_B is the solubility selectivity. Gas diffusivity is generally enhanced by decreasing penetrant size, increasing polymer chain flexibility (often characterized by a decrease in glass transition temperature), increasing polymer fractional free volume and decreasing polymer–penetrant interactions [22]. Penetrant solubility is increased by increasing condensability of the penetrant (which increases with increasing critical temperature of the gas) and increasing polymer–penetrant interactions [22]. In general, polyether based block copolymers exhibit a low T_g resulting in high CO_2 diffusivity. The size sieving ability (diffusivity selectivity) however is low and high overall CO_2/light gas selectivity is mainly achieved by high CO_2/light gas solubility selectivity [3,4,23].

3. Experimental

3.1. Materials

The PEO-*ran*-PPO_{5000}-T6T6T block copolymer was synthesized according to the procedure described earlier [12]. The chemical structure of the PEO-*ran*-PPO polyether soft segment (a) and the T6T6T polyamide hard segment (b) are depicted in Fig. 2. The value of *n* (Fig. 2a) equals to 1. The additive poly[dimethylsiloxane-co-methyl(3-hydroxypropyl)siloxane]-graft-poly(ethylene glycol) methyl ether (PDMS-PEG) was obtained from Aldrich (The Netherlands). The PDMS oligomer (Fig. 2c) is grafted with low molecular weight PEG (80 wt.%). According to the supplier, the PDMS-PEG has a molecular weight of approximately 3800 g/mol, however the exact values of *m*, *n* and *p* are not provided. Ethanol (purity ≥ 99.9%) is obtained from Merck (The Netherlands). All chemicals were used as received. Pure gases were obtained from Praxair (The Netherlands).

3.2. Membrane preparation

Ethanol was used as a solvent to prepare the polymer solution (5 wt.%). The PEO-*ran*-PPO_{5000}-T6T6T block copolymer was dissolved under reflux and continuous stirring at 80 °C for ~2 h. After complete dissolution of the polymer, the solution was cooled to room temperature and a homogeneous solution was obtained (no gelation). PEO-*ran*-PPO_{5000}-T6T6T blend membranes were prepared by the addition of different amounts of the additive to this solution ranging from 10 to 50 wt.% relative to the amount of PEO-*ran*-PPO_{5000}-T6T6T. After addition of the additive, the solution was stirred again for at least another hour. Membrane films were prepared by pouring the obtained solution in a Petri dish. Subsequently, the membranes were placed under a nitrogen atmosphere at room temperature for at least 3 days to evaporate the solvent. After removal from the Petri dish, the films were dried in a vacuum