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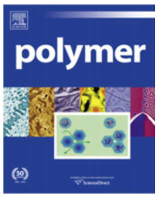

CO_2 sorption and transport behavior of ODPA-based polyetherimide polymer films

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ABSTRACT

Plasticization phenomena can significantly reduce the performance of polymeric membranes in high-pressure applications. Polyetherimides (PEIs) are a promising group of membrane materials that combine relatively high CO_2/CH_4 selectivities with high chemical and thermal stability. In this work sorption, swelling, and mixed gas separation performance of 3,3′,4,4′-oxydiphthalic dianhydride (ODPA)-based PEI polymers, with 1, 2 or 3 *para*-aryloxy substitutions in the diamine moeiety, is investigated under conditions where commercial membranes suffer from plasticization. Particular focus is on the influence of the amount of *para*-aryloxy substitutions and the film thickness. Results are compared with those of commercially available polymeric membrane materials (sulphonated PEEK, a segmented block-co-polymer PEBAX and the polyimide Matrimid).

The glassy polymers display increasing CO_2 sorption with increasing T_g. The larger extent of sorption results from a larger non-equilibrium excess free volume. Swelling of the polymers is induced by sorption of CO_2 molecules in the non-equilibrium free volume as well as from molecules dissolved in the matrix. Dilation of the polymer is similar for each molecule sorbed. Correspondingly, the partial molar volume of CO_2 is similar for molecules present in both regions.

Mixed gas separation experiments with a 50/50% CO_2/CH_4 feed gas mixture showed high CO_2/CH_4 selectivities for the ODPA PEI films at elevated pressure. This shows that these materials could potentially be interesting for high-pressure gas separation applications, although additional gas permeation experiments using different feed gas compositions and thin films are required.

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1. Introduction

The separation of CO_2 from CH_4 is an important industrial application. Common examples are Enhanced Oil Recovery (EOR), natural gas sweetening and CO_2 recovery from landfill gas [1]. Next to its environmental impact, CO_2 reduces the heating value of the CH_4 gas streams in power plants and it causes corrosion in pipes and equipment [2]. Currently, CO_2 is removed from gas mixtures mainly by absorption technology (such as amine or hot potassium scrubbing) and pressure swing adsorption [3], but, membrane technology, using glassy or rubbery polymer membranes, is frequently applied for this high-pressure separation [4] due to its reduced energy requirements, abdication of amine solutions, flexible design, and compactness [5].

Rubbery polymer membranes typically have higher permeabilities than glassy polymers, because of the increased segmental mobility of the polymer chains in the rubbery state, whereas in the glassy state, the mobility of the polymeric chains is restricted [6]. Due to their rigid structure, glassy polymers usually exhibit higher selectivities [7], but frequently suffer from severe plasticization, reducing the selectivity. According to Baker [4], the competitive position of membranes for the separation of CO_2 and CH_4 would strengthen, if plasticization resistance membranes, with a selectivity of 40 during operation, would become available.

Most of the industrial processes to separate CO_2 from CH_4 are high-pressure applications with total feed pressures up to 100 bar [4], depending on the fraction of CO_2 in these feeds resulting in CO_2 partial pressures of approximately 10–50 bar. Most gas separation membranes are based on polysulfone, cellulose acetate or polyimide [4]. Especially these higher pressures of highly sorbing gases (e.g., CO_2) can induce severe plasticization phenomena in glassy polymer membranes [8–10]. Due to the presence of the plasticizing gas, relaxational phenomena and swelling stresses on the polymer network may occur, resulting in an increase in free volume and segmental mobility of the polymer network, causing a rise in permeability for all components [11]. As the permeability of the low

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permeable component is usually more affected, plasticization results in a decrease in selectivity [12–14]. Next to the properties of the specific polymer, plasticization phenomena are especially dependent on the CO_2 concentration in the polymer network, which is directly related to the CO_2 partial pressure and the temperature [9]. Methods to increase the resistance against plasticization and swelling of glassy polymer membranes include physical and chemical crosslinking [5,15,16], thermal treatments [12,16,17] and polymer blending [18].

A way to increase the CO_2 flux through the membrane is the preparation of the material into ultrathin layers. Changes in film thickness however can generate changes in membrane performances [9]. CO_2 sorption and plasticization phenomena in thin films can be distinctively different from sorption in bulk materials [9,19]. Kim et al. [20] showed for glassy 6FDA-based polyimide films that the aging rate is greatly accelerated for thin films compared to thick bulk films and that a correlation of aging rate to free volume is expected. Plasticization in thin films usually occurs at lower feed pressures when compared to bulk materials [9,21].

Polyetherimides are an attractive class of polymers as they posses relatively high CO_2/CH_4 selectivities, high chemical and thermal stability and the potential to prepare asymmetric fibers as high flux membranes [22]. In this work a specific group of poly(etherimide)s, i.e. 3,3′,4,4′-oxydiphthalic dianhydride (ODPA)-based PEIs, as membrane material for CO_2 separation is evaluated. High CO_2 affinity is expected due to two imide groups in the main chain of the polymer. The number of *para*-arylether moieties in the polymer chain is used as a tool to tailor the segmental mobility and the non-equilibrium excess free volume of the polymer, expressed in the glass transition temperature of the polymer. CO_2 sorption and swelling behavior in thin and bulk polymer films is evaluated and the CO_2 partial molar volume in the polymer films is calculated. The results are related to the gas permeation performance of the films. As a reference, the transport behavior of three other polymeric membrane materials is evaluated: the glassy polymer SPEEK, the glassy polymer Matrimid®, which is known for the occurrence of strong plasticization in the presence of CO_2 [10] and the rubbery polymer PEBAX®.

2. Theory

2.1. Sorption

Ideal polymers are considered to be in a hypothetical thermodynamic equilibrium liquid state. For such systems solubility is independent of concentration and the concentration of gas in the polymer can be described by Henry's law [23–25]:

$$C = k_D \times p \tag{1}$$

In Equation (1) C (cm^3 gas (STP)/cm^3 polymer) is the concentration of the sorbed component in the polymer, k_D (cm^3 gas (STP)/(cm^3 polymer bar)) is the Henry's law constant, and p (bar) is the partial pressure of the gaseous component in the environment surrounding the polymer sample in equilibrium with the concentration of the component in the sample. This linear relationship between pressure and concentration is generally observed for sorption of gases in rubbery polymers [26]. For glassy polymers, sorption can usually be described by the dual mode sorption model. In this model the glassy polymer is considered to consist of a homogeneous dense polymer matrix in which microcavities are embedded [24,25,27]. The dense polymer matrix is considered to be in the ideal hypothetical equilibrium liquid state, and Henry's law can be used to describe sorption of gases in this matrix. The microcavities correspond to the non-equilibrium excess free volume and are considered to be fixed, independent sorption sites. Sorption in the microcavities can be described as Langmuir sorption [24,25].

Following the dual mode sorption model, the total concentration of a gas in a polymer below its glass transition temperature in equilibrium with the surrounding pressure consequently follows from [23–25]:

$$C = k_D p + \frac{C'_H bp}{1 + bp} \tag{2}$$

In Equation (2) the constant C'_H (cm^3 gas (STP)/cm^3 polymer) is the Langmuir capacity and describes the sorption capacity of the non-equilibrium excess free volume related to the glassy state of the polymer. The parameter b (1/bar), the Langmuir affinity, is an equilibrium constant that includes the affinity of the penetrant molecules for Langmuir sorption sites in the polymer.

2.1.1. Ellipsometry

Spectroscopic ellipsometry is a non-destructive optical technique in which a sample is illuminated with a polarized light beam. A detector analyzes the polarization state of the reflecting light beam. Subsequent fitting of the experimental data with an optical model allows quantification of the thickness and refractive index of thin films. For more details the reader is referred to, for instance, Tompkins [28].

For a single, thin, polymer film on a glass substrate, this optical model contains the wavelength dependent refractive index (referred to as dispersion) of the substrate, the dispersion of the thin film, and the thickness of the film as fitting parameters. Both the glass substrate and thin film are dielectric materials and their dispersion can be described by the Cauchy relation [21,29]:

$$n = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4} \tag{3}$$

In Equation (3) n (−) is the refractive index, λ (nm) is the wavelength of the light, and a, b and c are constants.

The change in refractive index of the film upon sorption of a gaseous component (here CO_2) can be directly related to the concentration of this component in the film. The mass based concentration of the sorbed gas in the polymer ($\mathbf{C_{CO2}}$ in g/cm^3) required to construct the sorption isotherm, can be calculated using the Clausius–Mosotti Equation as described by Sirard et al. [30]:

$$\frac{\left\langle n_f \right\rangle^2 - 1}{\left\langle n_f \right\rangle^2 + 2} = q_{CO_2} C_{CO_2} + q_{\text{polymer}} C_{\text{polymer}} \tag{4}$$

In Equation (4) $\langle n_f \rangle$ (−) is the effective refractive index of the swollen film, as determined with the Cauchy relation (Equation (3)) from the experimental results, C_{CO2} and C_{polymer} (g/cm^3) are the mass based concentration of the sorbed gas or the polymer respectively, and q_{CO2} and q_{polymer} (cm^3/g) are characteristic constants for the gas or the polymer respectively that can be determined from pure component data [30]:

$$\frac{\langle n_j \rangle^2 - 1}{\langle n_j \rangle^2 + 2} = q_j \rho_j \tag{5}$$

where $\langle n_f \rangle$ (−) is the refractive index of the pure component (gas or polymer) and ρ_j is the density of the pure component. The densities of the gas and the polymer and the refractive index of pure CO_2 can be obtained from literature [30], whereas the refractive index of the pure polymer can be experimentally determined from an ellipsometry experiment at zero pressure (vacuum).

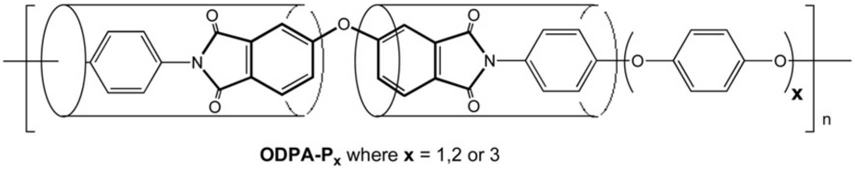


Fig. 1. Structure of the ODPA-based poly(ether imide)s with an increasing *para*-arylether content ($X = 1$, 2 or 3).

2.1.2. The mass based concentration of the swollen polymer ($C_{polymer}$) is calculated from

$$C_{\text{polymer}} = \rho_{\text{polymer}}\frac{h_0}{h} \quad (6)$$

In Equation (6) ρ_{polymer} (g/cm^3) is the density of the non-swollen polymer film, h_0 is the initial thickness of the non-swollen polymer film (cm) and h is the thickness of the swollen film (cm), which is determined from the fitting parameters of the experimental ellipsometry data. The volume based CO_2 concentration in the polymer in cm^3 (STP)/cm^3 polymer required for the sorption isotherm can subsequently be recalculated from the mass based concentration (C_{polymer} in g/cm^3) using the molar volume at standard conditions and the molecular weight of the gas.

3. Experimental part

3.1. Materials

3.1.1. ODPA pei

Fig. 1 shows the general structure of the 3,3′,4,4′-oxydiphthalic dianhydride (ODPA)-based polyetherimide (PEI) series.

Poly(ether imide)s with different numbers of *para*-arylether substitutions ($X = 1$, 2 or 3) were used and subsequently denoted as ODPA-P1, -P2 and -P3. The monomer syntheses were performed at Delft University of Technology, The Netherlands according to the procedure described elsewhere [31]. 1-Methyl-2-pyrrolidinone (NMP) was used as the solvent for film preparation, and was obtained from Acros (The Netherlands). 3,3′,4,4′-Oxydiphthalic dianhydride (ODPA) was purchased from Sigma–Aldrich and used as received.

3.1.2. Speek

S-PEEK (Fig. 2) with a sulfonation degree of 70% ($y = 0.7$; $x = 0.3$), was obtained from the sulfonation of PEEK, as described by Komkova et al. [32]. SPEEK was recently identified as membrane material for the dehydration of (flue) gas streams with extremely high water vapor permeabilities combined with very high water vapor over N_2 and CO_2 selectivities [33,34].

PEEK was purchased from Victrex (United Kingdom) and sulfuric acid (95–98 wt%) was obtained from Merck, Germany. Methanol was used as solvent for film preparation and was obtained from Merck, Germany.

3.1.3. Matrimid® 5218

Matrimid® 5218 (Fig. 3) is a commercially available polyimide (3,3′,4,4′-benzophenonetetracarboxylic dianhydrid and diamino-phenylindane), frequently studied and used for membranes for gas separation [10,16,35].

Matrimid® was obtained from Huntsman and THF (Tetrahydrofuran) and NMP (1-methyl-2-pyrrolidinone) were used as solvent and obtained from Merck, Germany and from Acros, the Netherlands, respectively.

3.1.4. Pebax® 2533

Poly(amide-6-b-ethylene oxide) (PEBAX® 2533) is a hydrophilic, commercially available block copolymer consisting of a soft polyether (PTMEO poly(tetramethyleneoxide)) block and a hard polyamide (PA 12 (nylon-12)) block. Permeation of gases preferentially occurs through the soft, amorphous polyether blocks whereas permeation through the soft, semicrystaline PE segments and the hard polyamide blocks is limited. The hard PA blocks provide the mechanical stability. Polyether based block copolymers offer an attractive material for high permeance CO_2 separation membranes [36]. Fig. 4 shows the chemical structure of PEBAX®.

The polymer used for this work was PEBAX® 2533, which contains 20 wt% hard segment. The PE constituents' glass transition temperature is −77 °C. 1-butanol and 1-propanol were used as solvent for film preparation and obtained from Merck, Germany.

3.2. Preparation of freestanding films

ODPA PEI flat films were prepared by reacting ODPA with an equimolar amount of the appropriate diamine, i.e. P1, P2 or P3, in 1-methyl-2-pyrrolidinone (NMP) at room temperature (25 wt.% solids) and casting the resulting polyamic acid solution with a 0.25 mm casting knife on a glass plate. The solvent was evaporated in a nitrogen box for 24 h. After that the films were heat treated (imidization) in an oven under nitrogen atmosphere according to the temperature program 100 °C, 200 °C and 300 °C, each temperature for 1 h. After that the films were placed in a water bath, released from the glass plate and subsequently dried in an oven at 30 °C for 24 h. Finally, the freestanding films were placed in an oven at 260 °C for 1 h. To avoid crystallization the films were immediately cooled down in air when removed from the oven. Freestanding films with a thickness of 17–27 μm were obtained.

3.3. Thin film preparation

Supported thin films were prepared as described below. Films were supported by a glass plate.

3.3.1. ODPA pei (P1, P2 and P3)

Solutions containing 25 wt.% of the appropriate polyamic acid in NMP were prepared. An excess amount of solution was dropped on

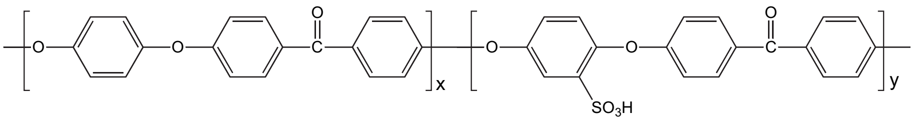


Fig. 2. Chemical structure of SPEEK.

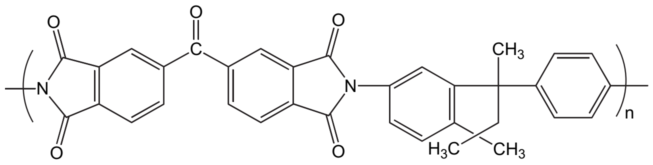


Fig. 3. Chemical structure of Matrimid® 5218.

the glass substrate and a spin coater (WS-400B-6NPP/LITE) rotating at 3000 rpm for 1 min was used to prepare a thin polymer layer. The solvent was evaporated in a nitrogen box for 24 h. After that the films were heat treated (imidization) in an oven under nitrogen atmosphere according to the temperature program 100 °C, 200 °C and 300 °C, each temperature for 1 h. To avoid crystallization the films were immediately cooled down in air when removed from the oven. Films with a thickness in the range of 0.5–3.8 μm were obtained.

3.3.2. *Speek*

A 3 wt.% SPEEK in methanol solution was prepared. The solution was dropped directly on a glass plate and dried under nitrogen atmosphere at room temperature for 3 days. Films with a thickness of approximately 1 μm were obtained.

3.3.3. *Matrimid® 5218*

A mixture of 30 wt% THF and 70 wt% NMP was used as solvent for the preparation of thin supported Matrimid® films. Matrimid® (3 wt%) was mixed with the solvent and the solution was spread on a glass plate. The film was placed in a nitrogen atmosphere for 3 days and afterward in a vacuum oven at 150 °C for approx. 1 week to allow evaporation of the solvent. Films with a thickness of approximately 2 μm were obtained.

3.3.4. *Pebax® 2533*

A mixture of 25 wt.% 1-butanol and 75 wt.% 1-propanol was used as solvent for the preparation of thin PEBAX® films. PEBAX® (3 wt%) was dissolved in the solvent mixture and the solution was spread on a glass plate. To evaporate the solvent, the film was placed in a nitrogen atmosphere for 3 days. Films with a thickness of approximately 2.5 μm were obtained.

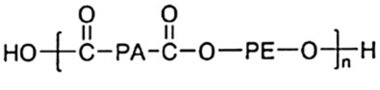
3.4. *Gas sorption*

Single gas sorption of CO_2 and CH_4 in freestanding thick, bulk polymer films was investigated using a gravimetric sorption balance (Rubotherm) as described elsewhere [37]. The measured weight (w_t in g) was corrected for buoyancy according to the Archimedes principle by subtracting the weight at zero sorption at a certain pressure from the initial weight of the sample (w_0 in g). The mass increase of the polymer sample upon sorption (m_t in g) was calculated according to Equation (7) [37]:

$$m_t = w_t - \left(w_0 - V_t\rho_{gas}\right) \tag{7}$$

where V_t is the sample volume in m^3 and ρ_{gas} is the density of the surrounding gas in g/m^3 (which is determined using the van der Waals Equation). The density of the polymer sample was determined with a Micromeritics AccuPyc 1330 pycnometer at room temperature. The concentration of gas in the polymer (in cm^3 (STP)/cm^3 polymer) was subsequently calculated from this corrected mass increase, the volume of the polymer sample, the molar volume at standard conditions and the molecular weight of the gas.

Before each experiment, the sample with an approximate weight of 0.06 g, was degassed in the sample chamber for at least 12 h. The gas sorption, monitored as the weight increase of the sample in time was then determined for different pressures (2, 4, 5, 10, 20, 30 and 35 or 40 bar) at a constant temperature of 35 °C. For CO_2, after the pressure increase run, the pressure was reduced step wise again to study possible non-equilibrium hysteresis. All experiments were performed until equilibrium was reached and the mass remained constant in time.



$$HO\left[\overset{O}{\overset{\|}{C}}-PA-\overset{O}{\overset{\|}{C}}-O-PE-O\right]_n H$$

Fig. 4. Chemical structure of PEBAX®.

3.5. *Ellipsometry*

An Alpha-SE™ Spectroscopic Ellipsometer (SE) system was used to study the sorption behavior of the thin polymeric films. Samples were placed in a home-built test-cell with two windows perpendicular to the ellipsometric beam and the measurements were performed with an angle of incidence of 70° in the wavelength range from 370 to 900 nm.

The measurement procedure for all polymers was equal. For each sample, helium, N_2 and CO_2 were applied, consecutively. Before each measurement, the sample was degassed under vacuum for at least 1 h. The temperature was kept constant at a value of 35 °C. The pressure was increased step wise from 1 to 51 bars (pressures: 1, 2, 4, 6, 11, 21, 31, 41, 51 bar). In order to study possible non-equilibrium hysteresis for CO_2, the pressure increase run was followed by a pressure decrease run.

For helium and N_2 the refractive index of the gaseous ambient was assumed to be unity and independent of the applied pressure and temperature. The pressure dependent refractive index of the CO_2 atmosphere was taken from literature [38].

The CO_2 sorption in the thin polymer films was determined as described in the theoretical section. The swelling of the thin polymeric films was determined from the change in film thickness:

$$Swelling = \frac{(h - h_0)}{h_0}\cdot 100\% \tag{8}$$

where h (cm) is the thickness of the swollen film and h_0 (cm) is the initial thickness of the polymer film.

3.6. *Gas permeation*

The CO_2/CH_4 gas separation performance of the ODPA PEI membranes was investigated with a temperature-controlled high-pressure gas permeation setup using a constant volume-variable pressure method as described elsewhere [39]. A constant feed pressure was applied and the permeate side was kept under vacuum. The gas permeability through the membrane was calculated from the steady state pressure increase in time in a calibrated volume at the permeate side. The permeability values are expressed in Barrer, where 1 Barrer = 10^{-10} cm^3 (STP)·cm/(cm^2·s·cmHg) (= $7.5\cdot10^{-18}$ m^3 (STP)·m/(m^2·s·Pa)). In the case of mixed gas permeation experiments the feed and permeate compositions were analyzed with a Varian gas chromatograph. The selectivity α (CO_2/CH_4) is calculated as:

$$\alpha = \frac{Y_{CO_2} / Y_{CH_4}}{X_{CO_2} / X_{CH_4}} \tag{9}$$

where Y_i is the concentration of component i in the permeate stream and X_i is the concentration of component i in the feed.

Table 1
Glass transition temperature values of bulk films of ODPA-P1, -P2 and -P3 [31], SPEEK [41], Matrimid® [42] and of the soft segment of PEBAX® [35].

Material	T_g (°C)
ODPA-P1	243
ODPA-P2	214
ODPA-P3	206
SPEEK	208
Matrimid	338
PEBAX	−77

Table 2
CH_4 Henry's law sorption parameter k_D in thick ODPA PEI (-P1, -P2 and -P3) films at 35 °C.

Polymer	k_D cm^3 (STP)/$cm^3 \cdot$bar
ODPA-P1	0.44
ODPA-P2	0.36
ODPA-P3	0.37

The permeability and separation performance of the membranes using mixed gases (CO_2/CH_4 (50/50vol.%)) was determined at different feed pressures (10, 20, 30, 35 bar) at 35 °C and all experiments were performed in duplo.

4. Results and discussion

4.1. Glass transition temperature

The glass transition temperature, T_g, of a polymer is an important property of the polymer and is related to the rigidity and excess free volume of that polymer [40]. For structurally related polymers, like a series of polyether imides, lower molecular motion and higher rigidity can be expected for polymers with higher T_g. Table 1 shows the T_g values of bulk films of the materials investigated.

The glass transition temperature values show that all investigated ODPA PEI materials are in their glassy state at the experimental temperature used. The T_g decreases with increasing amount of *para*-arylether substitutions (going from ODPA-P1 to ODPA-P3). This suggests a higher flexibility for the arylether group compared to the remainder of the main chain and an increase in chain mobility for the polymer with the higher number of *para*-arylether units in the main chain.

4.2. Gas sorption in thick films

Fig. 5 shows the CO_2 and CH_4 concentration in thick ODPA-P1, -P2 and -P3 polymer films as a function of the pure gas pressure. All measurements have been performed with at least two different films and the experimental error was always below 4% (except for the 2 bar sorption experiments where the experimental error was 10%).

For all three polymers the sorption of CH_4 linearly increases with pressure as described by Henry's law. The linear relation between concentration and pressure suggests that sorption of CH_4 predominantly occurs in the homogeneous dense matrix of the ODPA PEI materials. Table 2 shows the Henry's law constant for CH_4 sorption in the thick ODPA PEI films.

The value of the Henry's law constant (k_D) for CH_4 of the thick ODPA PEI polymer films stays relatively constant with increasing amount of *para*-arylether groups. This suggests a similar affinity of CH_4 for the arylether moieties as compared to the imide groups.

Sorption of CO_2 shows different behavior. Fig. 5 shows that at all feed pressures and for all three polymers the concentration of CO_2 in the polymer films is higher than the CH_4 concentration. In contrast to CH_4, sorption of CO_2 in the ODPA PEI polymer films does not follow Henry's law. Sorption of CO_2 can be described by the dual mode sorption model, indicating that CO_2 molecules do not only dissolve in the dense polymer matrix, but can also be present in the non-equilibrium excess free volume. For all three materials hysteresis is observed as the CO_2 sorption (closed symbols) and desorption (open symbols) isotherms do not coincide. Desorption values are higher for all polymers. In their pioneering work, Kamiya [43,44] and Koros and Fleming [45,46] were the first who observed the occurrence of time-dependent hysteresis in polymers upon CO_2 sorption/desorption. Berens et al. [47] and Wessling et al. [9] interpret this hysteresis as the induction of new free volume sites and subsequent filling of this additional free volume during sorption, whereas during desorption, the collapse of the free volume occurs on longer time scales than the desorption of CO_2. Consequently a higher amount of free volume is available during desorption, resulting in higher CO_2 concentrations.

Table 3 lists the data for the different parameters of the dual mode sorption model for CO_2 as obtained from the experimental results.

The results in Table 3 show that the Henry's law constant (k_D) and the Langmuir affinity parameter b are only slightly influenced by the number of *para*-arylether moieties in the polymer. When compared to the values obtained for the Henry's law constants for CH_4, similar values for CO_2 were obtained. A more pronounced decrease of C'_H with increasing number of *para*-arylether groups is

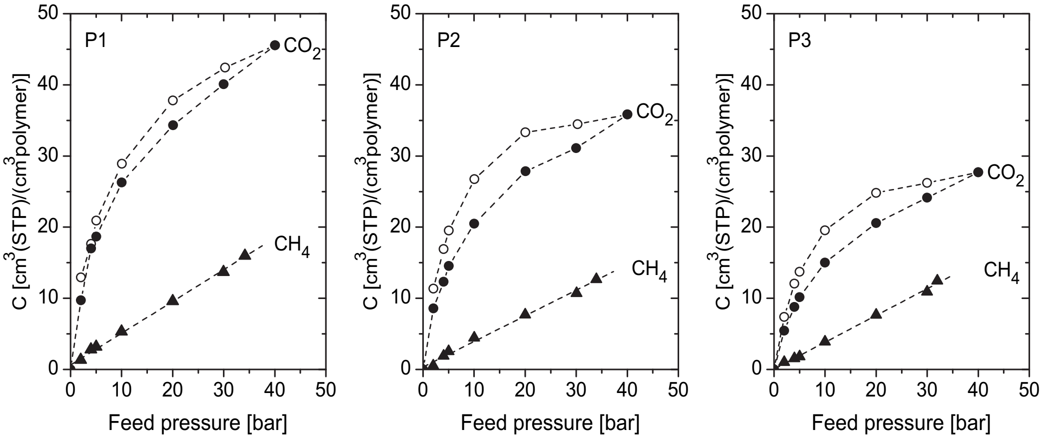


Fig. 5. CO_2 sorption (●) and desorption (○) and CH_4 (▲) sorption as a function of the gas pressure for thick ODPA-P1, -P2 and -P3 films at 35 °C.

Table 3
CO_2 dual mode sorption parameters in thick ODPA PEI (-P1, -P2 and -P3) films at 35 °C.

Polymer	C'$_H$ [cm^3 (STP)/cm^3]	k_D [cm^3 (STP)/cm^3·bar]	b [1/bar]
ODPA-P1	32	0.43	0.23
ODPA-P2	25	0.35	0.22
ODPA-P3	18	0.29	0.19

Table 4
CO_2 sorption parameters in thin ODPA PEI (-P1, -P2 and -P3) films at 35 °C.

Polymer	C'$_H$ [cm^3 (STP)/cm^3]	k_D [cm^3 (STP)/cm^3·bar]	b [1/bar]
ODPA-P1	21	0.40	0.25
ODPA-P2	17	0.35	0.23
ODPA-P3	15	0.30	0.22

observed. This is in accordance with the differences in glass transition temperature of the three polymers. The addition of *para*-arylether to the polymer chain results in enhanced macromolecular dynamics, and hence less pronounced non-equilibrium characteristics. With an increasing number of *para*-arylether moieties, the glass transition temperature and consequently the excess of non-equilibrium free volume decrease. Consequently, the parameter C'_H, which is related to the non-equilibrium excess free volume decreases as well, with decreasing T_g.

4.3. Gas sorption behavior in thin films

Fig. 6 shows the CO_2 concentration in the thin ODPA PEI films as determined by ellipsometry using thin supported films. We determined the degree of swelling of ODPA-P2 as a function of its thickness and did not observe any difference in swelling degree for the thicknesses investigated (0.5–3.8 μm). The thickness of the ODPA-P1 films was 0.9 μm, the ODPA-P2 films had a thickness of 0.5 and 3.8 μm and the thickness of the ODPA-P3 films was 1.26 μm. All measurements have been performed with at least two different films and the experimental error in the swelling values was always below 4%.

The sorption isotherms obtained for the thin films are in general in very good agreement with the isotherms obtained for the thick films (compare Figs. 5 and 6). In agreement with the observations for the thick polymer films, CO_2 sorption in all three materials follows the dual mode sorption model. As was the case for the thick films, hysteresis is also observed for the thin films. As hysteresis is a time-related effect [44] and due to the difference in time scales of desorption of the gas and the collapse of the free volume, hysteresis in especially the ODPA-P2 and -P3 thin films is less pronounced than for the freestanding thick films.

The experimental results allow extracting the Henry's law and Langmuir sorption parameters and the results are summarized in Table 4. The same trends as obtained for the thick films are observed for the thin films (a decrease in all sorption parameters with increasing number of *para*-arylether moieties).

Fig. 7 compares the sorption parameters of the thin and the bulk ODPA PEI films as a function of the amount of *para*-arylether rings in the polymer. The thickness of the thin films ranged from 0.9 μm for the ODPA-P1, to 0.5 and 3.8 μm for the ODPA-P2 and to 1.26 μm for the ODPA-P3 films. The bulk films had a thickness of 17–27 μm.

Fig. 7 clearly shows that the values obtained for the Henry's law constant (k_D) and the Langmuir affinity parameter b for both the thick and the thin films coincide. This indicates that the affinity of CO_2 for the polymer materials is determined predominantly by the inherent chemical characteristics of these materials, and not by how the film is formed and whether it is attached to a substrate and the history of the film [49]. In contrast, the values obtained for the Langmuir capacity (C'_H) show distinctively lower values for the thin supported films as compared to the thick films, which can be attributed to differences in the amount of non-equilibrium excess free volume between the thin and the thick films, which may well originate from restrictions imposed by the glass substrate on the polymer conformation close to the glass–polymer interface, and faster evaporation of the solvent from thinner films during film synthesis. Others also found a smaller non-equilibrium excess free volume of the thin films as compared to that of bulk materials. Wind et al. [21] observed a reduced value for C'_H for very thin polyimide films (around 0.1 μm), which they correlated to differences in aging of films of different thicknesses. The enhanced rate of aging of thin films can be associated with the thickness dependence of the rate of diffusion of free volume toward the outer surface of the polymer film. For thinner films the rate of diffusion of this free volume is faster [48]. Although aging definitely influences the non-equilibrium free volume and consequently the Langmuir capacity, this effect is not considered to be the dominant effect in our work as all films are freshly prepared.

The results obtained for the sorption of CO_2 in thin ODPA PEI films were compared to the sorption behavior of CO_2 in two other

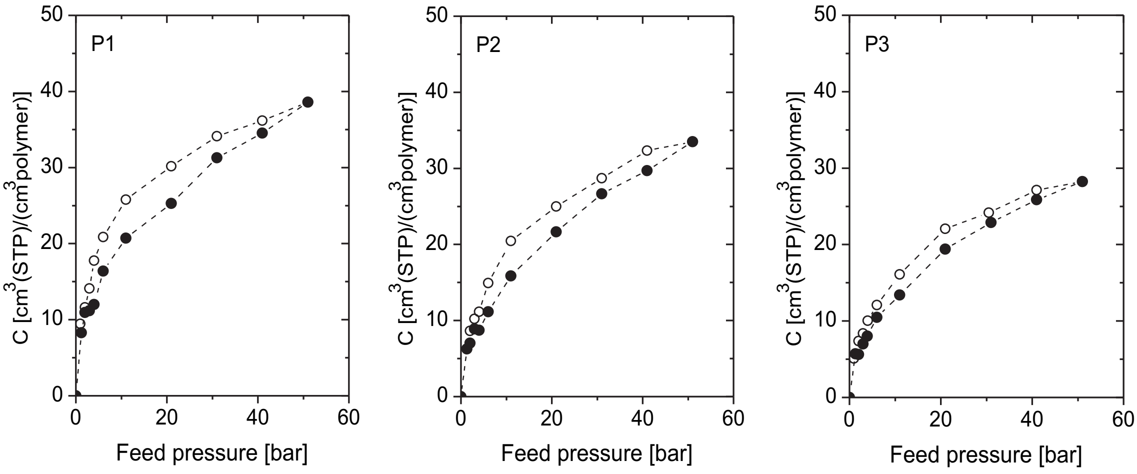


Fig. 6. CO_2 sorption (●) and desorption (○) as a function of the CO_2 pressure for thin ODPA-P1, -P2 and -P3 films at 35 °C.

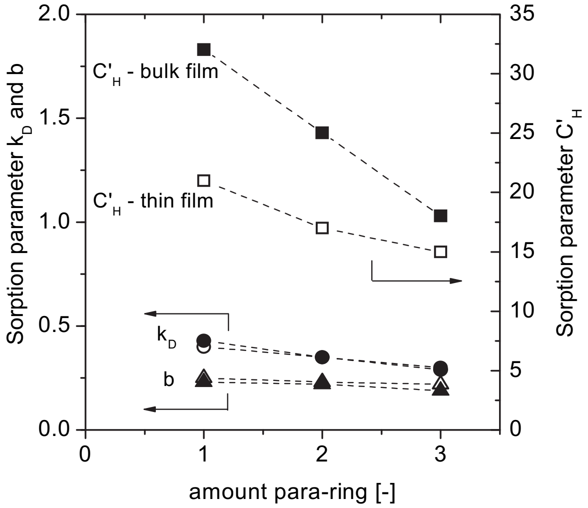


Fig. 7. Gas sorption parameters in thin (open symbols) and thick, bulk (closed symbols) ODPA PEI (-P1, -P2 and -P3) films at 35 °C k_D (● and ○) expressed in (cm^3 (STP)/(cm^3 polymer·bar)), C'$_H$ (■ and □) expressed in (cm^3 (STP)/cm^3 polymer) and b (▲ and △) expressed in (1/bar).

glassy polymers (SPEEK and Matrimid®) and the rubbery polymer PEBAX®. Especially Matrimid® [10] and PEBAX® [36] are well known materials for CO_2 separation, whereas SPEEK has been considered for gas dehydration purposes [33,34]. The sorption isotherms for thin films of these materials are presented in Fig. 8. The offset in the concentration of CO_2 in PEBAX® is directly related to the experimental method and the extraction of the data from the experimental values. The CO_2 concentration is extremely sensitive to only small changes in the refractive index. At low pressures, small changes in the *fourth* digit of the refractive index directly introduce a significant change in the CO_2 concentration in the polymer, which is directly visible in the data and consequently in Fig. 9. At higher pressures, these variations are less pronounced. As the swelling and the thickness of the films are not dependant on the refractive index, this effect is not visible in the film thickness nor swelling.

Fig. 8 shows that the two glassy polymers Matrimid® and SPEEK both follow the dual mode sorption model as well and that for both glassy materials hysteresis is also observed (as is the case for the ODPA PEI polymers). Especially Matrimid®, which has a very high glass transition temperature when compared to the other polymers (Table 1) and is known for its low plasticization resistance [10], shows strong hysteresis.

PEBAX® shows the behavior typically observed for rubbery polymers, and only sorption according to Henry's law occurs. As non-equilibrium excess free volume is absent in rubbery polymers, hysteresis phenomena are not observed.

4.4. Swelling

Sorption induced changes in polymer film thickness of ODPA PEI, Matrimid®, SPEEK and PEBAX® films are studied with spectroscopic ellipsometry. The change in thickness upon sorption with respect to the initial film thickness in the absence of the pressurized gas is referred to as swelling.

4.4.1. Swelling of ODPA PEI (-P1, -P2 and -P3) films

Fig. 9 shows the relative swelling of the thin ODPA PEI (-P1, -P2 and -P3) films as a function of the CO_2 or N_2 pressure. Safety reasons prohibited experiments with pressurized CH_4 in our ellipsometry setup.

Fig. 9 shows that swelling induced by N_2 increases linearly with pressure and is comparable for the three ODPA PEI materials. Similar to CH_4, N_2 molecules are not expected to have specific interactions with the ether and imide groups, and dissolve only in the polymer matrix (sorption according to Henry's law). The linear relation between pressure and swelling indicates that the extent of dilation of the polymer matrix is equal for each additional dissolved N_2 molecule. No pronounced effect of the number of *para*-arylether groups on the overall dilation is observed, as extent of swelling is comparable for the three materials. An explanation for the absence of an overall effect of ODPA group substitution on dilation is that the anticipated reduction in dilation for the more rigid polymers may be compensated by a larger extent of sorption for these materials. This will be discussed in more detail for CO_2 sorption induced swelling.

For CO_2 a non-linear dependence of swelling on pressure is observed, and the shapes of the graphs are similar as compared to the CO_2 sorption isotherms. The non-linear behavior implies that dilation of the polymer results from CO_2 molecules present in the polymer matrix (Henry sorption) as well as in the non-equilibrium excess free volume (Langmuir sorption). The extent of swelling for

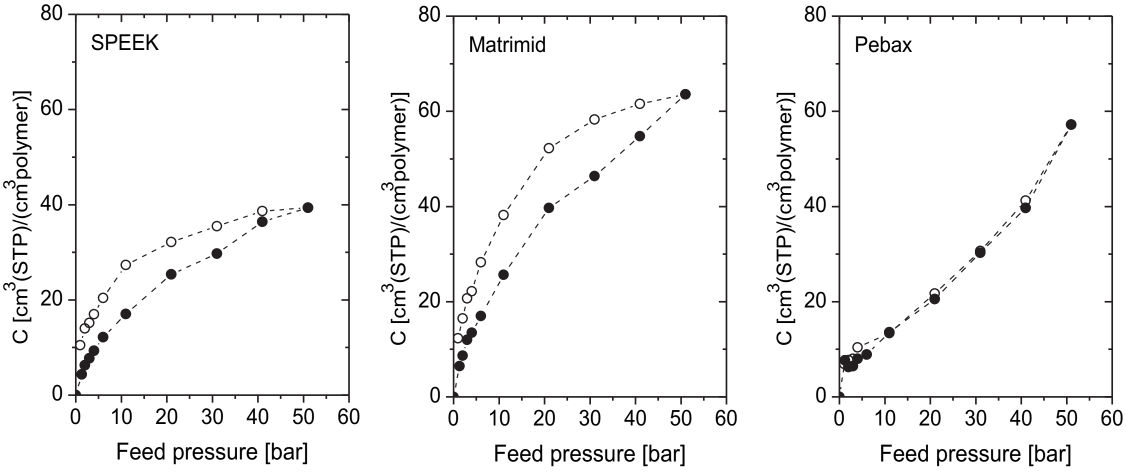


Fig. 8. CO_2 sorption (●) and desorption (○) as a function of the CO_2 pressure for thin SPEEK, Matrimid® and PEBAX® films at 35 °C (note the difference in Y-axis scale when compared to the values obtained for the ODPA PEI polymers).

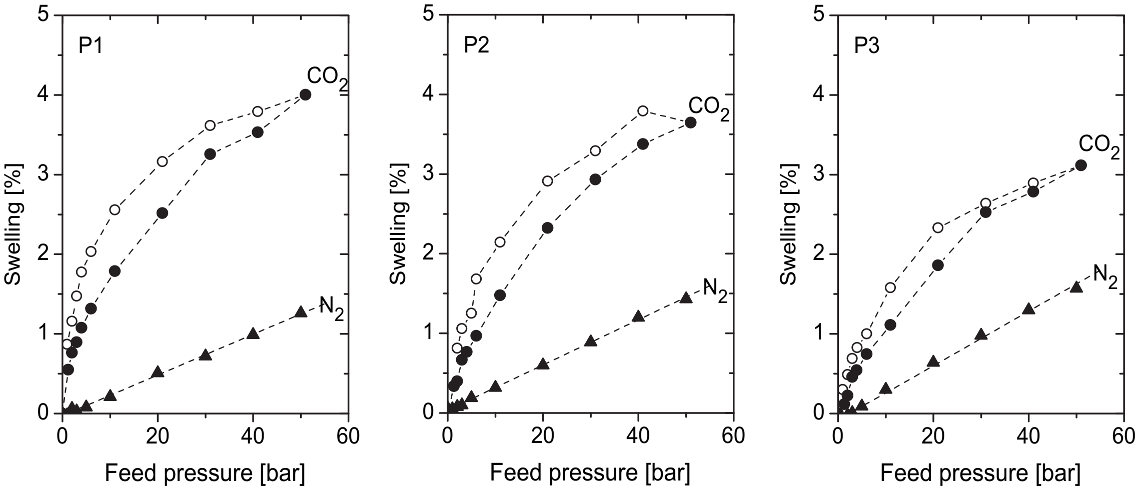


Fig. 9. Swelling of the thin ODPA PEI films for CO_2 (● pressurized and ○ depressurized) and N_2 (▲) as a function of the pressure at 35 °C.

polymers studied here decreases in the order: ODPA-P1 > ODPA-P2 > ODPA-P3. This order is opposite as compared to the order of polymer rigidity, or T_g. The larger dilation of the more rigid materials results from the increase in excess free volume of these materials, and a corresponding larger concentration of penetrant molecules in the polymer. Concurring with the enhanced T_g, for ODPA-P1 and ODPA-P2, hysteresis effects are more pronounced as compared to ODPA-P3. Hysteresis implies that the dynamics of relaxation of the macromolecular structure upon desorption is insufficient to allow the materials to return to their initial states.

4.4.2. Swelling of SPEEK, Matrimid®, and PEBAX® films

For comparison, the swelling behavior of the three other polymers (Matrimid® and SPEEK, which are both glassy polymers and PEBAX®, which is a rubbery polymer) was studied as well (Fig. 10).

Fig. 10 shows CO_2 induced swelling of SPEEK, Matrimid®, and PEBAX® films. SPEEK and Matrimid® are glassy polymers. Their CO_2 induced swelling behavior is analog to that of the ODPA PEI films: dilation increases less than linear with pressure and hysteresis is observed upon desorption. The extent of swelling of SPEEK is in the same range as that of the ODPA PEI films. Matrimid® shows a larger degree of sorption induced swelling, due to the large excess free volume of this high T_g material (338 °C) and the corresponding high concentration of sorbed CO_2. As compared to the ODPA PEI films, hysteresis is more distinct for SPEEK. For Matrimid hysteresis is even more pronounced. In contrast to the glassy polymers, PEBAX® shows a more than linear dependence of swelling on pressure with no significant hysteresis. The absence of hysteresis and the increasing slope of swelling versus pressure are due to the rubbery character of PEBAX®.

We attribute the enhanced swelling of the more rigid materials to the larger non-equilibrium excess free volume in these materials, and the corresponding higher concentration of sorbed CO_2 molecules in that volume. In the next section focus will be on comparing the extent of dilation induced by molecules sorbed in either the non-equilibrium or equilibrium regions of the polymers.

4.5. CO_2 partial molar volume

Sorption of CO_2 into the polymer causes an increase in thin film thickness. This change in film thickness can be used to calculate partial molar volume of sorbed CO_2 molecules in the polymer film.

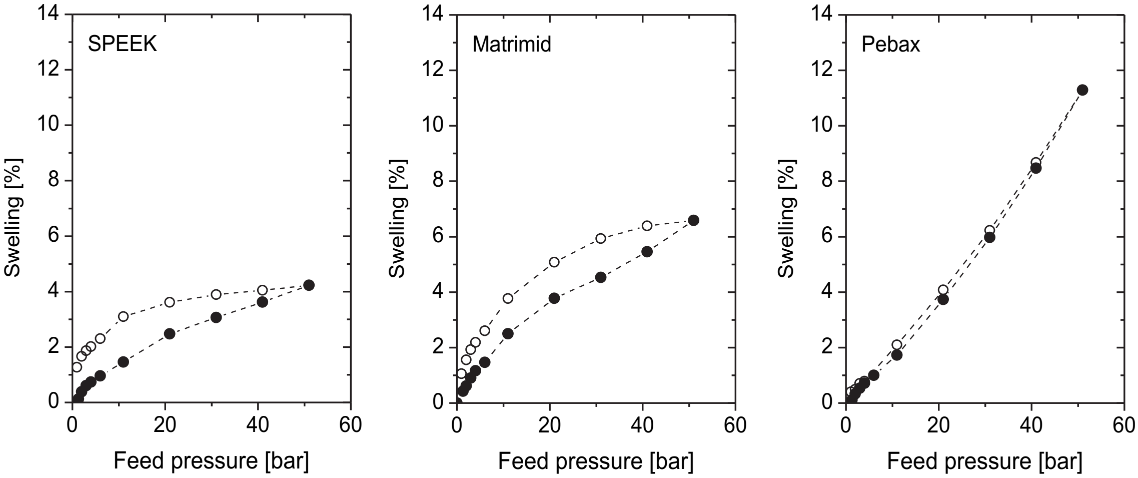


Fig. 10. Swelling for CO_2 (● pressurized and ○ depressurized) as a function of pressure for thin SPEEK, Matrimid® and PEBAX® films at 35 °C (note the difference in *Y*-axis scale when compared to the values obtained for the ODPA PEI polymers).

For a thin film that shows sorption induced dilation in a single direction only, the partial molar volume of CO_2 in the polymer can be calculated from [21,50]:

$$v_{CO_2} = 22400 \cdot \frac{\partial \frac{\Delta h}{h_0}}{\partial C} \tag{10}$$

Where Δh is the change in film thickness due to gas sorption (cm), h_0 is the initial thickness of the polymer film (cm) and C is the CO_2 concentration in the polymer film (cm^3(STP)/cm^3). The slope of a plot of the concentration versus the swelling ($\Delta(h/h_0)$) (Fig. 11) represents the partial molar volume of CO_2 in the corresponding polymer material.

For all films studied, the data in Fig. 11 fit well to a linear relation with a small offset in the low-pressure range. The offset is most likely an artifact of our technique. The linear relation between swelling and concentration implies that the molar volume of CO_2 in the polymer is independent of concentration. For the glassy polymers in the low concentration range, changes in concentration arise predominantly from molecules entering the non-equilibrium excess free volume. At higher concentration this free volume has become more or less saturated and changes in concentration arise predominantly from molecules dissolving in the polymer matrix. The independence of molar volume on concentration suggests that CO_2 molecules in the non-equilibrium and equilibrium regions of the polymer have a similar partial molar volume. Wessling observed similar effects [50] and Wijmans puts the role of partial molar volume into a perspective for the solution-diffusion model [51].

Hirose [44] determined the partial molar volume of CO_2 in the rubbery material PDMS and found a value of 44.5 cm^3/mol for a temperature range of 25–55 °C. Koros and Fleming [45] reported a value of 46.2 cm^3/mol for the same material. For the glassy polymer polycarbonate, they observed a significantly lower partial molar volume. The differences in partial molar volume of CO_2, as determined in our work, in especially the glassy polymers are small and there is no distinct correlation between the glass transition temperature and the corresponding partial molar volume of CO_2 in the polymer. In general, less stiff polymer matrices can dilate more easily than stiff matrices [50]. The partial molar volume of CO_2 in the different glassy polymers (as obtained from the slopes of Fig. 11) has an average value of 25.3 cm^3/mol. In comparison to the glassy polymers, the partial molar volume of CO_2 in PEBAX®, which has a T_g of the soft, amorphous PE phase of −77 °C, is 49.1 cm^3/mol. This value is comparable to the molar volume found for liquid CO_2.

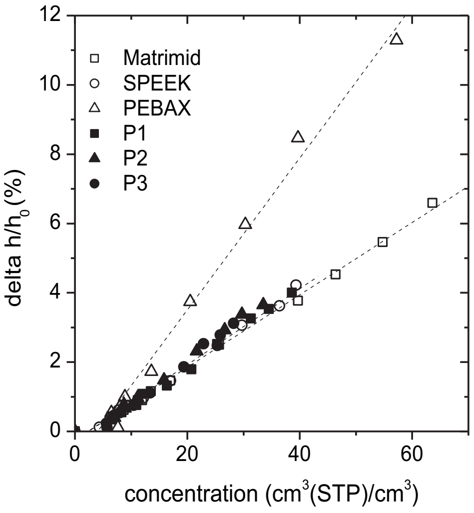


Fig. 11. Swelling ($\Delta(h/h_0)$) of the thin ODPA-P1, -P2 and -P3 films and thin Matrimid®, SPEEK and PEBAX® films as a function of the CO_2 concentration at 35 °C. The slope of the plots represent the partial molar volume of CO_2 in the corresponding polymer material.

4.6. *Gas permeation*

Fig. 12 shows the CO_2 and CH_4 permeability through the three thick ODPA PEI polymer films as a function of the gas partial pressure at 35 °C.

The three materials all show a decrease in CO_2 permeability with increasing feed pressure. When the pressure is increased, the absolute amount of CO_2 molecules absorbed in the polymer still increases, but the relative increase in this amount with pressure decreases as increasingly less Langmuir sorption sites for CO_2 sorption are available.

Permeation of gases through dense polymeric membranes is generally described by the solution-diffusion model ($P = D \cdot S$) [52] and both the solubility and the diffusivity determine the overall permeability of a gas. An increase in T_g generally gives rise to two counteracting phenomena: a reduction in mobility of the CO_2 molecules (diffusivity) and an increase in the extent of their sorption (solubility). There are no general rules as to which of these two phenomena dominates and attempts to find a general correlation between T_g and permeability have failed [53]. For the ODPA PEI materials investigated, the enhanced sorption with increasing T_g seems to overcompensate the reduced mobility of CO_2 molecules, and as compared to ODPA-P1 and ODPA-P2, polymer ODPA-P3 has the lowest T_g (206 °C) and shows the lowest permeability. Considering the significant differences in T_g (P1: 243 °C and P2: 214 °C) and sorption for ODPA-P1 and ODPA-P2, the small difference in permeability between these two polymers implies a significant reduction in CO_2 mobility for ODPA-P1.

For P1 the permeability of CH_4 shows a decrease with pressure. The mutual presence of both species in the equilibrium regions seems to reduce the transport of CH_4. This might be, to a small extent, due to competition for the Langmuir sorption sites by CH_4 and CO_2 [37]. Although the sorption results indicate that sorption of CH_4 occurs predominantly in the polymer matrix, a small amount could absorb in the Langmuir sorption sides. For P2 the decrease in permeability with pressure is far less pronounced. For P3 an increase in permeability versus pressure is observed. Fig. 13 shows the CO_2/CH_4 selectivity as a function of CO_2 partial pressure.

The different ODPA materials display a similar selectivity (around 50) at a CO_2 partial pressure of 5 bar. With increasing pressure, differences in selectivity are observed. ODPA-P3 shows a slight reduction in selectivity, the selectivity of ODPA-P2 remains relatively constant up to 15 bars and shows a subsequent decrease and the selectivity of ODPA-P1 increases with increasing CO_2 partial pressure. The decrease in selectivity can indicate weak plasticization behavior of the polymer. Plasticization effects appear more evident for polymer ODPA-P3 than for the other two polymers. This can be related to the relatively low T_g and large molar volume of CO_2 in the case of ODPA-P3. The large partial molar volume of CO_2 in this polymer corresponds to a larger dilation per sorbed CO_2 molecule, and hence more pronounced plasticization is anticipated.

Despite the reduction in selectivity for ODPA-P2 and -P3, these materials still have a selectivity of approximately 40 at a CO_2 partial pressure of 17.5 bar (total feed pressure of 35 bar). This selectivity is much higher than the selectivity of the commercially available polymer Matrimid®. Bos et al. observed a CO_2/CH_4 selectivity for Matrimid® (55/45 mol% feed mixture at 35 °C) of approximately 30 at 35 bar [18]. For the rubbery polymer PEBAX®, even much lower ideal selectivities (16.2) by Sridhar et al. [54] are observed, although

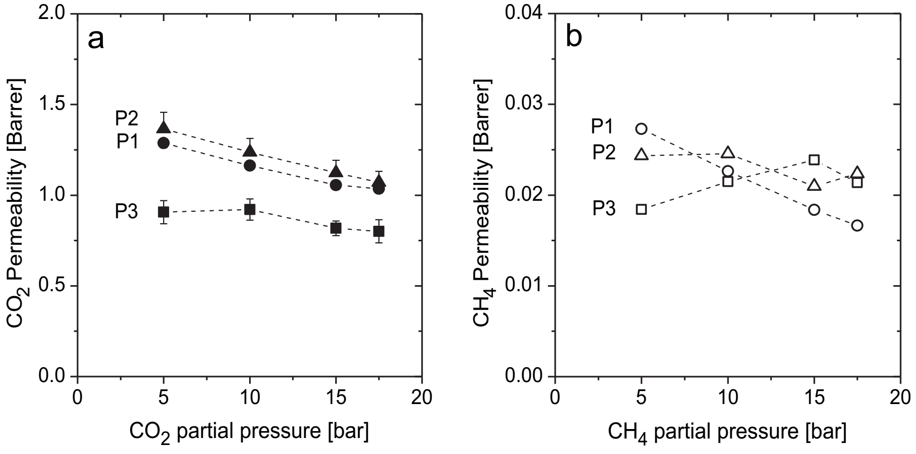


Fig. 12. CO_2 (a) and CH_4 (b) permeability as a function of gas partial pressure for thick ODPA-P1, -P2 and -P3 films at 35 °C. Feed mixed gas: CO_2/CH_4 (50/50 vol.%).

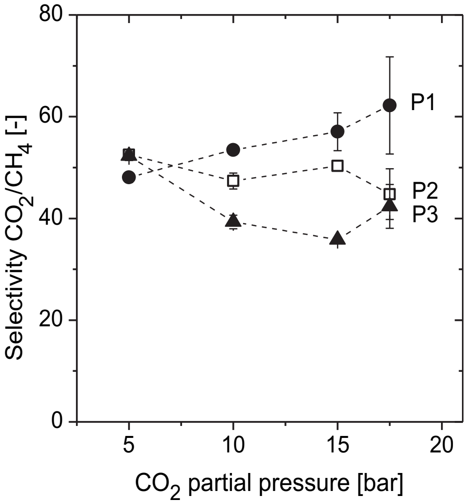


Fig. 13. CO_2/CH_4 selectivity as a function of CO_2 partial pressure for thick ODPA-P1,-P2 and -P3 films at 35 °C. Feed gas mixture: CO_2/CH_4 (50/50 vol.%).

permeability is significantly higher (5.5 Barrer at 19.6 bar). The high selectivities of the ODPA PEI films at high CO_2 partial pressure show the potential of this material for the effective separation of CO_2 from light gases.

5. Conclusions

Many CO_2/CH_4 gas separations involve high-pressure CO_2 applications, for which membranes are an attractive separation technology. Plasticization phenomena can significantly reduce the performance of polymeric membranes. In this work sorption, swelling, and mixed gas separation performance of ODPA PEI polymers, with 1, 2 or 3 *para*-arylether substitutions, is investigated under conditions where commercial membranes suffer from plasticization. Particular focus is on the influence of the amount of *para*-arylether substitutions and the film thickness. Results are compared with those of three commercially available polymeric membrane materials, the glassy polymers SPEEK and Matrimid®, and the rubbery polymer PEBAX®.

The glassy polymers displayed increasing CO_2 sorption with increasing T_g. The larger extent of sorption results from a larger non-equilibrium excess free volume. Swelling of the polymers is induced by sorption of CO_2 molecules in the non-equilibrium free volume as well as from molecules dissolved in the matrix. Dilation of the polymer is similar for each molecule sorbed, irrespective of the fact that the molecule enters the non-equilibrium or equilibrium region. Correspondingly, the partial molar volume of CO_2 is similar for molecules present in both regions. The smallest molar volume is found for the material with the highest T_g, Matrimid®. For the rubbery polymer Pebax® the partial molar volume of CO_2 resembles that of pure liquid CO_2.

Sorption of CO_2 in thin films only differs from that in bulk materials, regarding the Langmuir capacity (C'_H), while the values obtained for the Henry's law constant (k_D) and the Langmuir affinity parameter b coincide. This indicates that the overall affinity of CO_2 for the polymer materials is determined predominantly by the inherent chemical characteristics of the material, rather than by the consolidation of the polymer from solution during film synthesis.

The extent of swelling of the ODPA PEI films is very low, which potentially can be beneficial for CO_2 removal at elevated pressures. Mixed gas separation experiments with a 50/50% CO_2/CH_4 feed gas mixture showed high CO_2/CH_4 selectivities for the ODPA PEI films at elevated pressure. This shows that these materials could potentially be interesting for high-pressure gas separation applications, although additional gas permeation experiments using different feed gas compositions and thin films are required.

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