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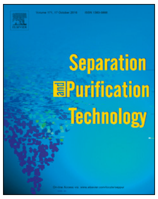

The role of *ortho*-, *meta*- and *para*-substitutions in the main-chain structure of poly(etherimide)s and the effects on CO_2/CH_4 gas separation performance

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ABSTRACT

A homologous series of 12 all-aromatic PEI membranes was investigated with the aim to understand how subtle changes in the PEI main-chain affect the carbon dioxide/methane (CO_2/CH_4) gas separation performance. The 3-ring diamines selected for this study are either *para*-, *meta*- or *ortho*-aryloxy substituted with respect to the central benzene ring, *i.e.* 1,4-bis(4-aminophenoxy)benzene (P1), 1,3-bis(4-aminophenoxy)benzene (M1) and 1,2-bis(4-aminophenoxy)benzene (O1). Doing so changes the backbone geometry from a more linear to a more kinked conformation. In addition, four dianhydrides were selected with the aim to tailor the segmental mobility and hence the free volume of the PEIs, *i.e.* pyromellitic dianhydride (**PMDA**), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (**BPDA**), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (**BTDA**) and 3,3′,4,4′-oxydiphthalic dianhydride (**ODPA**). We have investigated how subtle changes in these prototypical PEIs affect membrane critical performance criteria such as CO_2 permeability, CO_2/CH_4 selectivity and ability to withstand high operating pressures. In ODPA-based membranes the CO_2 permeability decreases in the order P1 > O1 > M1 and remains steady throughout measurements with mixed feed pressures up to 40 bar, however, the selectivity decreases for ODPA-O1 and ODPA-M1. For high-pressure applications, the OPDA-P1 membrane is a good candidate with a selectivity of 48, permeability of CO_2 of 0.74 Barrer and ability to resist plasticization up to 40 bar of total pressure (16 bar of CO_2 partial pressure). Alternatively, for applications up to 10 bar of total mixed feed (5 bar of CO_2 partial pressure), BPDA-O1 is a promising candidate because this membrane displays a high selectivity of 70 and permeability of 1.3 Barrer.

1. Introduction

Membrane-based gas separation is an important unit operation in many industrial processes and is gaining momentum in natural gas upgrading [1], carbon dioxide removal from flue gas [2], biogas purification [3] and landfill gas treatment. Sources of natural gas with higher concentrations of CO_2 are being explored since the sources of low carbon dioxide (CO_2) containing natural gas are limited and all but exhausted. CO_2 reduces the heating value of methane gas streams and causes corrosion in pipelines and equipment [4], so it is important to remove CO_2 from natural gas prior to use. Separation of CO_2 using polymer-based membranes is a competitive alternative with respect to conventional absorption technologies such as amine scrubbing [5] owing to its high energy efficiency, simple design (easy scale-up), and high area-to-volume ratio (compactness) [6]. In order to have the desired robustness and membrane lifetime the polymers used for these membranes need to exhibit high flux and high selectivity, and from the material selection point of view, they need to meet the following requirements: chemical and thermal resistance, good mechanical properties, plasticization resistance and physical aging tolerance [2].

A great deal of research has been done to improve the gas permeability and selectivity for polymer membranes, with the main focus being on the relationship between the polymer backbone structure and the gas separation properties. The gas permeation properties of glassy

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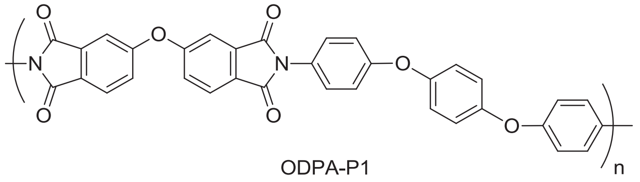
polymers are very sensitive to the chemical structure of the repeating units [7], with their chains having restricted mobility below the glass transition temperature. It has been reported that an increase in backbone rigidity improves selectivity since it helps molecular sieving of gases with similar solubility coefficients [8]. However, this also results in a decrease in permeability. Most of the polymers that have been investigated typically show the general trend that highly permeable polymers possess rather low selectivity and *vice versa*, which is referred to as the permeability/selectivity trade-off relationship [9,10]. The most studied class of polymers for membrane materials for gas separation are polyimides (PIs) and poly(etherimide)s (PEIs) [11]. Both PIs and PEIs are known for their high thermal and mechanical stability.

Commercial PIs for gas separation are known under trade names such as Upilex® and Matrimid®. The later has been extensively studied owing to a combination of properties, for CO_2/CH_4 gas separation at 10 bar, it shows a selectivity of 34 and permeability of CO_2 of 6.5 Barrer [12]. However, with increased CO_2 partial pressure the selectivity coefficient drops, the permeability of the slower gas is enabled by the highly soluble, faster gas. This is attributed to the plasticization effects, caused by the high CO_2 solubility and its interaction with the polyimide membrane. As the membrane is plasticized, the permeability increases significantly, while the selectivity decreases [13–15]. Plasticization is a common problem in polyimide- and polyetherimide-based membranes. If this issue could be resolved, PIs and PEIs could become potential candidates for high-pressure CO_2/CH_4 gas separation applications.

A number of techniques has been reported in literature to improve PI and PEI membranes both in plasticization resistance and in increasing permeability. One such technique is via cross-linking. This has been shown to be an effective method to improve membrane stability, specifically referring to plasticization as well as physical aging, but it comes at cost of low permeability [16,17]. Another method to improve permeability is the introduction of bulky groups on the polymer backbone. They help to disrupt chain packing, which in turn results in an increase in free volume [18] *e.g.* the presence of bulky $-CF_3$ groups in 6FDA-durene leads to very high permeability values (678 Barrer) but low selectivity values of ~20 [19]. When evaluating the available literature, it is clear that a wide variety of PI- and PEI-backbone modifications have been explored. Work of Ayala *et al.* shows that gas permeability typically increases with increasing free volume, and free volume could be related to the chemical composition of the polymer backbone and to the nature of the pendant groups [20]. However, what seems to be missing is a basic understanding of how subtle systematic changes in the PEI main-chain affect the gas separation performance. A start was made by Simons et al. [21] They showed that, under conditions where commercial membranes suffer from plasticization, 3,3′,4,4′-oxydiphthalic dianhydride (ODPA) based PEIs are promising membranes that show increasing CO_2 sorption with increasing T_g. The low extent of swelling for ODPA-based PEIs, between 3 and 4% measured up to 50 bar, as well as high CO_2/CH_4 selectivities (between 40 and 60) at a mixed gas feed pressure of 40 bar, show that these materials are of potential interest for CO_2 removal applications at elevated pressures. ODPA-P1, see Fig. 1, showed a decrease in CH_4 permeability with increasing pressure, which is a desirable property indicating that upon equal CO_2 permeability, the selectivity for separation increased with increasing pressure. Increasing the number of *para*-arylether units in the diamine moiety reduced the CO_2/CH_4 selectivity [21]. This simple prototypical PEI motivated us to investigate how subtle changes in the PEI main-chain affect gas transport properties and CO_2 swelling behavior. The role of the dianhydride structure, *i.e.* rigid versus flexible, were investigated as well as the aryloxy-substitution pattern (*para*, *meta* or *ortho*) of the diamine moiety.



ODPA-P1

Fig. 1. Molecular structure of polyetherimide ODPA-P1 [21].

In order to understand the relationship between the PEI main-chain structure and its membrane gas separation (CO_2/CH_4) performance we have synthesized a systematic series of 12 PEI model compounds. All the diamine moieties are based on either *para*-, *meta*-, or *ortho*-based aryl ether units, which act as “flexible” spacer units between the terminal *para*-phenylamine functionalities (Fig. 2). Three diamines were chosen for this study: 1,4-bis(4-aminophenoxy)benzene (P1), 1,3-bis(4-aminophenoxy)benzene (M1) and 1,2-bis(4-aminophenoxy)benzene (O1). Changing the exocyclic bond angle in this 3-ring diamine changes the PEI main-chain from a more linear to a more bend conformation that significantly affects the chain flexibility. In addition, the (local) electrostatic dipole moment changes as the oxygen atoms move closer to one another when moving from a *para*- to an *ortho*-substitution pattern.

Furthermore, four different dianhydride moieties have been selected with the aim to systematically change the flexibility of the polymer backbone and the non-equilibrium excess free volume of the subsequent PEI membranes. The selected dianhydrides, listed from flexible to rigid, include: 3,3′,4,4′-oxydiphthalic dianhydride (**ODPA**), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (**BTDA**), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (**BPDA**) and pyromellitic dianhydride (**PMDA**). The dianhydrides and their PEI main-chain structures are shown in Fig. 2.

2. Experimental

2.1. Materials

1,2-bis(4-aminophenoxy)benzene (O1) was synthesized according to a standard nucleophilic displacement reaction as shown in Scheme 1 [22]. All other start materials were purchased from commercial sources and used as received unless stated otherwise. Dianhydrides ODPA, BTDA, BPDA and PMDA were purchased from TCI Co. Ltd. and dried prior to use overnight in a vacuum oven at 60 °C. Diamine P1 was purchased from ABCR, diamine M1 from TCI and N-Methyl-2-pyrrolidinone (NMP) was obtained from Acros Organics.

2.2. Characterization

The chemical structure of O1 diamine was confirmed by ^1H NMR (Bruker WM-400, 400 MHz) and ^{13}C NMR (Bruker WM-400, 100 MHz). All samples were dissolved in deuterated chloroform and the recorded spectra were referenced to the solvent ($CDCl_3$: ^1H 7.26 and ^{13}C 77.0 ppm) relative to TMS. For GC/MS analysis of O1, a Shimadzu GCMS-QP2010S gas chromatograph mass spectrometer was used, coupled with the GL Sciences Optic 3 high-performance injector. Separation of the evolved gases was achieved using a 30 m × 0.025 mm SGE forte BPX-5 capillary column operated at a He flow rate of about 1 mL/min. Software ATAS Evolution Workstation (ATAS GL International) controlled heating of the injection port of the GC from 50 °C to 300 °C in 5 min. The GC column oven was programmed from 50 °C, with a heating rate of 20 °C/min, to 300 °C (held for 30 min). LabSolutions data system, GCMSsolutions (Shimadzu) Postrun analysis software was used to integrate the peaks. Melting point of O1 was determined using a Leica DM LM optical microscope equipped with a Linkam TMS94 hot stage; heating rate was 5 °C/min.

Gel permeation chromatography (GPC) measurements of polyamic acids were performed on a Shimadzu Prominence GPC system equipped with two Shodex LF-804 columns. N-Methyl-2-pyrrolidone (NMP) with 5 mM of LiBr was used as eluent at a flow rate of 0.5 mL/min at 60 °C. Data analyses were performed with LabSolutions software using the refractive index detector data. Quantification was made based on