



Novel sulfonated and fluorinated PEEK membranes for CO₂ separation



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ABSTRACT

Polymeric membranes containing sulfonated and fluorinated poly (ether ether ketone) were prepared by solution casting method. The monomers were pre-sulfonated before the polymerization to avoid the side-effects of polymer post-sulfonation, like low degree of sulfonation and poor mechanical and thermal properties. The degree of sulfonation was varied from 20% to 40% to study its influence on the membrane performance. Pure and mixed gas permeation experiments were performed to evaluate the potential of this novel polymer in separation of CO₂ from mixtures containing CH₄ and N₂. Increasing degree of sulfonation improved the CO₂ permeability and selectivity for both gas pairs. The incorporation of fluorinated groups further enhanced the performance of membranes by simultaneous increase in gas permeability and selectivity. Diffusion and solubility measurements were also performed in order to get further insight into the role of sulfonic and fluorinated groups in membrane performance. The comparison of results with literature revealed the promising characteristics of the polymer in industrially relevant gas separations.

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1. Introduction

The excessive use of fossil fuels such as coal and petroleum products is one of the primary sources of CO₂ emissions. CO₂ thus emitted is a major contributor to the greenhouse effect of earth, resulting in increase in global warming [1]. Apart from the environmental concerns, the presence of CO₂ in natural gas and biogas reduces its calorific value. Therefore, from an energy perspective, the removal of CO₂ from such mixtures is also necessary. Membrane technology is an attractive choice to perform this task due to its many advantages over other separation techniques such as being environmentally friendly, cheap and energy efficient [2].

Among the materials available for the synthesis of CO₂ separation membranes, polymers have shown promising potential due to their low cost, easy commercial availability and film forming abilities. Several efforts have been made to introduce task-specific functional groups in the polymers, such as sulfonation, carboxylation, acylation, bromination [3–5]. Polymer sulfonation is an effective way to improve the membrane separation performance. The solubility of CO₂ is considerably increased by the introduction of –SO₃ polar groups in the polymeric chain due to extra interactions

with the CO₂ quadrupole [6,7]. Studies have been reported on sulfonation of different polymers, like poly (ether ether ketone), poly (aryleneethersulfone), poly (styrene-*b*-butadiene-*b*-styrene), poly (phenylene oxide) and polyethersulfone [8–12]. Sulfonation of polystyrene and PES showed that the polymer sulfonation lowered the gas permeability but increased selectivity [13,14]. In our previous study, the gas transport properties of sulfonated poly ether ketone were investigated. The sulfonation of monomers was carried out before the polymerization to avoid the side-effects of polymer post-sulfonation, like low degree of sulfonation and poor mechanical and thermal properties. The results showed that the CO₂ solubility increased with increased degree of sulfonation leading to a simultaneous increase in gas permeability and selectivity [8].

The introduction of CO₂ philic groups that can lead to simultaneous increase in gas permeability and selectivity is one of the promising techniques to overcome the permeability-selectivity trade-off. The polymer diffusivity can be improved by increasing its fractional free volume (FFV) [15]. To achieve high permeability, the polymers containing fluorinated groups have received tremendous attention [16,17]. The presence of fluorinated groups improves the FFV by the inhibiting of chain packing. These groups also restrict the torsional motion of the polymeric chains and simultaneously increase the rigidity of polymer to enhance size sieving [13,18]. Calle et al. studied different polyimides containing

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different fluorinated groups, and reported that the hexafluoro-diamine (6FDA) based polyimides showed the highest FFV, and a slight increase in FFV resulted in a drastic increase in permeability [19]. Ayala et al. showed that the incorporation of a hexafluoroisopropylidene linkage in the polymer chain improved the gas permeability [20]. Matsumoto and Xu studied the gas permeation properties of polyimides with different structures and reported that polyimides with $C(CF_3)_2$ groups showed significantly high permeation properties [21]. Along with the increase in FFV, fluorinated groups are also known as CO_2 philic groups due to the presence of slight intermolecular interactions between CO_2 and Fluorine atoms [22,23].

Both sulfonation and fluorination of polymers have thus proved to be effective ways for improving the gas permeabilities and selectivities. In order to take advantage of their superior properties, sulfonated and fluorinated groups were for the first time introduced here in a single polymer used for the synthesis of membranes for gas separation. In analogy with our earlier work on CO_2 separation, the monomers were pre-sulfonated before polymerization.

2. Experimental

2.1. Synthesis of fluorinated and sulfonated PEEK (F-SPEEK)

The F-SPEEKs with different degree of sulfonation (Fig. 1) were prepared via nucleophilic substitution [24]. The procedure includes two steps: sulfonated monomer preparation and polymer synthesis. The degree of sulfonation was controlled by varying the different amounts of reacting monomers.

2.1.1. Monomer synthesis

In a typical monomer synthesis, 0.1 mol of 4,4'-difluorobenzophenone was dissolved in 30% fuming sulfuric acid (50 ml). The excess acid was neutralized with NaOH, and the sulfonated monomer was precipitated with sodium chloride. The product was re-crystallized using a mixture of methanol and water.

2.1.2. Polymerization

The synthesis of F-SPEEK polymers was carried out via nucleophilic substitution of monomers: 4,4'-difluorobenzophenone (m mol), sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate) (n) and 4,4'-difluorobenzophenone (DFBP) (m + nmol). The monomers were mixed in a DMSO/toluene solvent system (Fig. 1). The temperature was first kept at 140 °C for 4 h and then increased to

170 °C for 6 h using anhydrous potassium carbonate as catalyst. The resulting products were precipitated using a methanol/water mixture. The degree of sulfonation in this reaction was controlled by varying the amounts of the monomers used, as listed in Table 1.

2.2. F-SPEEK membrane preparation

F-SPEEK was dried overnight at 110 °C to remove the absorbed water. After drying, calculated amounts of F-SPEEK and DMA (dimethyl acetamide) were added in a vial and were continuously stirred overnight to form a homogeneous mixture. The resulting solution was cast onto a flat bottom glass petri dish, covered with an inverted funnel to make evaporation more controlled, and placed in the oven for drying. The solution was first heated for 4 h at 90 °C. The temperature was increased to 160 °C at a rate of 5 °C/h. Similar procedure was used for the fabrication of the membranes with 20%, 30% and 40% degree of sulfonation.

2.3. Fractional free volume (FFV) of membranes

Density measurement was performed using a gas pycnometer typically at 30 °C, which uses helium gas to displace the sample of known mass.

The fractional free volumes (FFV) of these polymeric membranes were calculated using the group contribution method [25]. Fractional free volume has been defined as

$$FFV = (V - 1.3V_w)/V$$

where V is the specific volume of polymer, obtained from the experimental measurements of their densities and V_w is the van der Waals volume determined by the sum of atomic and bond contributions [26].

2.4. Characterization

A PhilipsXL 30 FED SEM, a semi-in-lens type SEM with a cold field-emission electron source, was used to acquire the SEM images of membrane's cross-section. Membranes were cryogenically broken in liquid nitrogen and the samples were then sputter-coated with gold using a Cressington HR208 (UK) high-resolution sputter coater.

A TA instruments DSCQ1000, at a heating rate of 10 °C min⁻¹, was used to determine the glass transition temperature (T_g). For

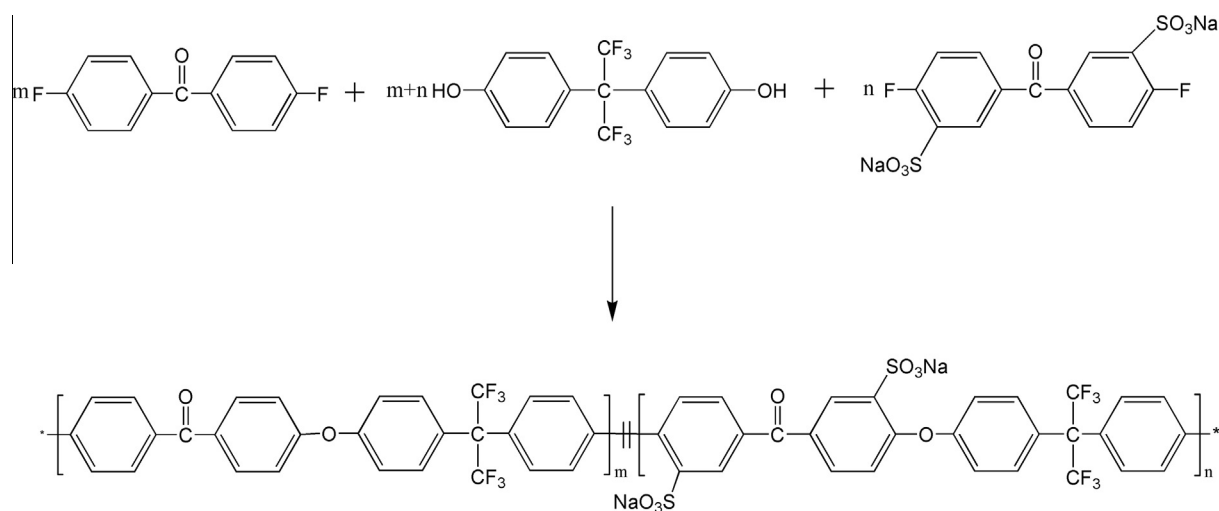


Fig. 1. Scheme of F-SPEEK synthesis.

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