



Partially pyrolyzed gas-separation membranes made from blends of copolyetherimides and polyimides



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ABSTRACT

Herein, a new approach to achieve gas separation materials with improved resistance to plasticization (obtained by partial pyrolysis of new polyimide blends) is presented. Blends of an aromatic polyimide (formally, 6FDA-6FpDA) and aliphatic-aromatic copolyetherimides based on the same polyimide in combination with other aliphatic polyimides, having polyethylene oxide moieties, were obtained. After their synthesis and characterization, a selective elimination of the polyether by thermal treatment was carried and the obtained partially-pyrolyzed materials were tested as gas separation membranes.

For neat blends, permeability was shown to decrease when PEO content increases. This effect is due to polyethylene oxide (PEO) chains encroaching on free volume because phase segregation was minimized. When these blends were subjected to thermal treatment at relatively low temperatures in air or in N₂, it was clearly observed that all the polyether moieties were selectively eliminated from the structure, which gave rise to an increase of permeability. Higher permeabilities were obtained after a thermal treatment at 390 °C in N₂. Degradation of PEO chains after a 290 °C treatment in air produced materials with permeability values lower than those observed under N₂. In both cases, even though PEO was selectively and wholly eliminated, permeability was not totally recovered to give the values observed for neat 6FDA-6FpDA due probably to a combination of shrinkage and crosslinking of the membrane produced during the thermal process. Crosslinking provides the materials with an increased resistance to plasticization. In particular, the best improvement against plasticization proceeded from the thermal treatments of blends at 290 °C in air.

1. Introduction

During the past decades, extensive attention has been devoted to the production of membranes with high permeability and selectivity for separation processes. Robeson in 1991, tested a large number of pairs of experimental data on permeability/selectivity. As a result, he suggested a semi-empirical relationship for polymers [1]. Later, he updated this limit, Robeson upper bond, in 2008 leading to a new and much more demanding empirical relationship [2], so that very few materials are able to overcome this new upper bond. However, the knowledge acquired during recent years in this field has established some basic rules to ensure that the increase of one of these two features (permeability or permselectivity) leads to a low decrease of the other one. After performing multiple studies of different membranes, it was observed that

the best materials are amorphous polymers, with structures that hamper the compact packaging of the chains. This generates a high fraction of free volume and, therefore, an increase in permeability. On the other hand, these materials must be highly rigid to decrease their chain mobility what facilitates their behavior as molecular sieves generating a high selectivity.

Penetrant-induced plasticization of membranes for gas separation has been intensively studied, as far as it is a key factor that downturns the useful life and performance of gas separation membranes. Plasticization facilitates local segmental freedom and mobility of macromolecular chains. This leads to an increase of free volume because local restrictions of the polymer segments are eliminated. This increases permeability with a steeply decrease of selectivity along with an increase of softness, ductility, and a depression of glass transition

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temperature (T_g) [3]. In particular, CO_2 has a strong plasticizing action by causing swelling of the polymer network [4,5]. A classical way of decreasing the plasticization of a material consists in producing cross-linking, by thermal or UV treatments by chemical procedures. However, this crosslinking decreases the fractional free volume, what is translated into a gas separation membrane with lower permeability and higher selectivity.

Polyimides with bulky groups [6,7] exhibit a good balance of permeability and selectivity for various gas pairs, along with high chemical resistance, excellent thermal stability, and good mechanical strength, and thus they have attracted much attention since their first commercial application in separation processes [8]. In another context, Xiao et al. revised the various strategies of molecular tailoring of polyimides in search for better membrane materials. Among them, authors outlined two of the most promising ones: synthesis of new polyimides by designing well-chosen dianhydrides and/or diamines, and use of copolymerization of polyimides with other class of polymers as, for example, those with aliphatic chains [9]. In addition, polymer blends have been used to produce gas separation membranes with excellent properties [10–15].

The objective of this work has consisted in preparing new membrane materials formed through the thermal treatment of polymer blends with the target of achieving materials with good separation features and low tendency to plasticization. Several polyimides [16,17] have been tried as precursors for carbon molecular sieves (CMS) membranes. Polymer blends, including polyethylene oxides (PEO) [18–20] have also been used.

There is no doubt that CMS membranes have been celebrated as very adequate for gas separation, both in terms of separation properties and stability. Our aim is to avoid mechanical damage, by increasing compatibility between the components of the blends, to reduce the pyrolysis temperature and to decrease plasticization. Thus, we will focus here on the preparation of blends of an aromatic polyimide, of high free volume, with block copolymers of aromatic-aliphatic polyimide formed by the same aromatic part but having poly (ethylene oxide) groups in the main chain. The thermal treatment of these blends will produce the selective removal of the PEO, what will produce high thermal stable cross-linked materials.

The aromatic polyimide chosen is 6FDA-6FpDA which shows good gas separation properties for different gas couples, O_2/N_2 and CO_2/CH_4 for example, and has excellent thermal and mechanical features. The resulting membranes have good processability and excellent gas separation performance. However, their plasticization resistance is not very high [21].

The use of block copolymers of 6FDA-6FpDA plus PEO (PEO2000) to be employed in this work, are similar to those extensively developed and studied mostly by Okamoto and other research groups [22–27], and also by our research group [28–32]. It was demonstrated for some of these copolymers that the use of a thermal treatment is able to produce a phase segregation of the aromatic and aliphatic blocks, which leads to materials with excellent capability of separation of acid gases due to the favorable interaction of these gases with the oxygen contained in the polyethylene oxide chain [22,24,28–32]. Also, in these works, it was observed, by thermogravimetric studies, that it was possible to selectively achieve the whole removal of the aliphatic PEO chain by thermal treatment at temperatures well below the aromatic polyimide degradation temperature [28–32]. The 6FDA-6FpDA-PEO copolymer system has the advantage of not presenting phase segregation, as it was observed for other similar structures [29]. Phase segregation, due to the formation of strong charge transfer complexes (CTC), leads to low processability from organic solvents. After thermal treatments, it would lead also to non-homogeneous pore sizes. However, when aromatic diamines having electronic withdrawing moieties or bulky groups are employed, the formation of CTC is hindered and processability is clearly improved. Thus, soluble 6FDA-6FpDA-PEO can be made using the two-step polyimidation method by treatment of the precursor polyamic acid

with a mixture of acetic anhydride and a tertiary base.

Herein, three copolyimides have been made by varying the composition ratio of 6FpDA and PEO 2000 (4/1, 2/1, 1/1 w/w). Afterwards, the blend of (6FDA-6FpDA-bk-6FDA-PEO2000) and 6FDA-6FpDA was obtained in different w/w ratios. These mixtures were made by mixing THF-solutions of their components. After casting, the resulting films were studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and FTIR-ATR, in order to characterize the materials and to figure out the thermal treatment needed to produce the partial pyrolysis of PEO groups. This study was also made for the (6FDA-6FpDA-bk-6FDA-PEO2000) polymers. Finally, the differences, on the final properties, of using thermal treatments under inert or oxidizing atmospheres, were investigated.

As a final point, an exhaustive study of the gas separation properties of the starting materials, along with those of the partially pyrolyzed materials, has been performed. This gas separation study has been extended to the determination of the plasticization resistance for the thermally treated membranes.

2. Experimental

2.1. Chemicals

2,2'-Bis (4-aminophenyl)hexafluoropropane (6FpDA) was obtained from Chriskev (Kansas, USA) and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) was obtained from Apollo Scientific (London, UK). Both monomers were purified by sublimation under high vacuum before use. Bis (2-aminopropyl) poly(ethylene oxide) 2000 (Jeffamine ED 2003, named in this paper for simplicity sake as PEO2000), with a molecular weight of 1942 g/mol was kindly donated by Huntsman (The Netherlands). PEO-2000 was used after vacuum drying in an oven for 5 h at 60 °C.

Anhydrous *N*-methyl-2 pyrrolidone (NMP) and *N,N'*-dimethylacetamide (DMAc) were obtained from Aldrich (Missouri, USA). Anhydrous pyridine (Py), 4-dimethylaminopyridine (DMAP) and high-purity trimethylchlorosilane (TMSCl) were also purchased from Aldrich. Solvents and other commercial reagents such as acetic anhydride and pyridine were obtained from Aldrich and used as received.

2.2. Polymer synthesis

6FDA-6FpDA polyimide was made using the following procedure: In a three-necked flask of 500 mL mechanically stirred under nitrogen atmosphere, 30 mmol (10.03 g) of 6FpDA and 25 mL of anhydrous DMAc were mixed. Once the monomer was dissolved, the solution was introduced into an ice-water bath, and 60 mmol of chlorotrimethylsilane (TMSCl), 60 mmol of pyridine, and (6 mmol) of DMAP were added. Subsequently, 30 mmol (13.33 g) of 6FDA was added. The mixture was allowed to react at room temperature for approximately 12 h. After this time, 120 mmol of acetic anhydride, and 120 mmol of pyridine were added on to produce the cyclo-imidization of the polyamic acid to the final polyimide. This mixture was kept under mechanical stirring at room temperature for 6 h and then at 60 °C during 45 min. Afterwards, the solution was precipitated onto water and washed several times in a water-ethanol (1:1) mixture to remove traces of solvents and reagents. Polymer fibers were dried at 180 °C, overnight under vacuum.

Furthermore, the synthesis of aromatic-aliphatic copolyimides 6FDA-6FpDA-PEO2000, was made by using the same methodology employed for 6FDA-6FpDA in which only the ratio (w/w) of 6FpDA and PEO2000 was varied. Polymerizations were carried out in 3-neck-flasks of 100 mL, equipped with a mechanical stirring, under an inert atmosphere of N_2 . First off, x g, of previously dried PEO2000 (1 g = 0.5149 mmol) was added and dissolved in 5 mL of NMP. When the monomer was completely dissolved, the required amount of the diamine 6FpDA was added. Thus, to obtain the 6FpDA/PEO2000 y/x

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