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Thermally rearranged polybenzoxazoles made from poly(*ortho*-hydroxyamide)s. Characterization and evaluation as gas separation membranes

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ABSTRACT

Two series of aromatic poly(*ortho*-hydroxyamide)s (poly(*o*-hydroxyamide)s, HPAs) were prepared by reaction of two diamines, 2,2-bis(3-amino-4-hydroxyphenyl) propane (APA) and 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (APAF), with four aromatic diacid chlorides; terephthaloyl dichloride (TPC), isophthaloyl dichloride (IPC), 2,2-bis[4-chlorocarbonylphenyl)hexafluoropropane (6FC) and 4,4′-sulfonyldibenzoyl dichloride (DBSC). Amorphous HPAs with high molecular weights (inherent viscosities higher than 0.5 dL/g) and relatively high glass transition temperatures (220–280 °C) were obtained. Dense membranes of HPAs were able to undergo a thermal rearrangement (TR) process to polybenzoxazoles (β-TR-PBOs) heating at moderate temperatures (between 250 and 375 °C), and their complete conversion was reached at a temperature below 375 °C, depending on the *o*-hydroxy diamine moiety, APA and APAF. The β-TR-PBOs films derived from APAF showed a higher thermal stability and higher Tg than those from APA. Gas separation properties of TR-PBOs membranes were superior to those of their poly(*o*-hydroxyamide) precursors, particularly for the following gas pairs: O_2/N_2, CO_2/CH_4, He/CH_4 and He/CO_2.

1. Introduction

Gas separation applications by employing membranes are a field demanded by the industry [1–3]. For these applications, the use of amorphous glassy polymers with high glass transition temperatures is widely sought [4–6]. Aromatic polyimides, PIs, are among the best materials due to the right combination of their properties. However, their synthesis is energy-intensive, the cost of monomers uses to be high and thus its industrial use in common applications is scarce [7]. In contrast, aromatic polyamides, PAs, show also a convenient balance of properties; high thermal resistance, good mechanical and chemical stability and easier processability than aromatic polyimides when their precursor monomers are well chosen [8]. However, their gas separation properties, except for some structures, are not very good, in particular when gas permeability is the main factor to be considered [9,10]. There have been many attempts to improve the gas separation performance of aromatic polyamide membranes by introducing bulky moieties [10,11], contorted structures [12] or, more usually, by introducing hexafluoropropane moieties in the macromolecular chain [13]. Nevertheless, even after these modifications, gas separation properties of PAs, when compared with other aromatic structures, are not excellent.

In the last decade, two new generations of gas separation materials, polymers of intrinsic microporosity, PIMs [14–16], and thermally rearranged, TR, polymers [17–20], with outstanding properties have been developed. These materials offer an excellent combination of permeability and permselectivity, what places many of them well above the 2008 Robeson limit [1,17,21]. TR materials (α-TR-PBOs) are usually obtained by thermal treatment of poly(*o*-hydroxyimide)s, poly(*o*-acylimide)s or poly(*o*-alkoxyimide)s at temperatures above 350–400 °C [17,18,22]. By this thermal treatment, a chemical rearrangement of the

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o-substituted imide moiety to benzoxazole happens by losing CO_2 or other entities, depending of the employed precursor. This thermal rearrangement is additionally complemented by a process of crosslinking that produces a material with superb resistance to plasticization and reduced physical aging [23]. Moreover, a huge excess of controlled fractional free volume (FFV) is attained. Thus, outstanding gas separation properties with permeability values above 1000 barrer are observed along with a satisfactory permeselectivity [17]. In addition, the final structure, polybenzoxazole (TR-PBO), is a chemically stable structure, what permits its use in harsher conditions (high temperature, presence of water or acidic molecules) than most of classical polymeric structures.

Aromatic polybenzoxazoles are directly made from aromatic *o*-dihydroxydiamines and aromatic diacids (or their corresponding diacid chlorides) by reaction in polyphosphoric acid or Eaton's reagent (a mixture of phosphorous pentoxide and methanesulfonic acid) at temperatures around 200 °C [24]. Another convenient and neat way of making PBOs consists of the reaction of aromatic *o*-dihydroxydiamines and aromatic diacid chlorides in a polar aprotic solvent at room temperature to form poly(*o*-hydroxyamide)s, HPAs [25]. Afterwards, the purified HPA is cast as a film and thermally treated at temperatures around 300–375 °C [26,27]. This process produces materials with PBO conversion above 95–98%.

Gas separation properties of membranes formed by casting PBO solutions are not good, because the formation of charge transfer complexes between the aromatic rings produces materials with high cohesive energy and consequently with low fractional free volume, and in addition they are not easy to process [28]. However, when the membrane is formed by thermal treatment of as-cast poly(*o*-hydroxyamide), better properties are observed whether the thermal procedure is well optimized [29]. These thermally obtained PBOs from HPAs, are named as β-TR-PBOs in the field of gas separation. These materials have lower FFV than common α-TR-PBO materials but they have excellent mechanical properties, superlative thermal stability, very high chemical stability, and they can be processed from soluble HPAs. Several researchers demonstrated that β-TR-PBOs are valid materials for precombustion applications because it is possible to modulate the size cavity of the FFV units to tailor-made a membrane able to separate hydrogen from other gases at temperatures around 200 °C without suffering any degradation of the macromolecular structure at these operation conditions [29–31].

In this study, two nucleophilic monomers (*o*-hydroxyamines) were reacted with four acid chlorides in order to get insight on the TR process of poly(*o*-hydroxyamides). Both monomers are quite similar but the hinge of the two aromatic rings is, for one of them, an electron-withdrawing hexafluoroisopropylidene group (APAF) whilst for the other monomer it is an electron-donating isopropylidene moiety (APA). In order to find new materials with tailor-made properties, some properties have been related with the electronic properties of monomers. Throughout the paper, for clarity sake, the acronym TR-PBO will be used instead of β-TR-PBO.

In addition, the combination of techniques, such as Fourier transform infrared, thermogravimetric analysis and differential calorimetry scan, has allowed establishing the temperature range where the TR-process occurs. Finally, the performances of these materials as gas separation membranes for several gas pairs (O_2/N_2, CO_2/CH_4, He/CH_4 and He/CO_2) have been tested.

2. Experimental

2.1. Materials

2,2-Bis(3-amino-4-hydroxyphenyl)hexafluoropropane (APAF) was purchased from Apollo Scientific and purified by sublimation at 220–225 °C before use. 2,2-Bis-(4-hydroxyphenyl)propane (bisphenol A) was purchased from Sigma-Aldrich and purified by recrystallization from toluene. Terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were purchased from Sigma-Aldrich and purified by recrystallization from hexane and sublimated at 70 °C and 60 °C, respectively, prior to use. 2,2-Bis[4-carboxyphenyl)hexafluoropropane and 4,4′-sulfonyldibenzoic acid were purchased from TCI and Sigma Aldrich, respectively. Thionyl chloride was purchased from Scharlau and distilled under reduced pressure before use. All solvents were obtained from Sigma-Aldrich.

2.1.1. Synthesis of acid dichlorides

The two acid dichlorides with SO_2 and $C(CF_3)_3$ as hinge groups were synthesized by reaction of their corresponding diacids, 4,4′-sulfonyldibenzoic acid and 2,2-bis(4-carboxyphenyl)hexafluoropropane with thionyl chloride (3-fold $SOCl_2$ mol/acid mol) in the presence of some drops of *N*,*N*-dimethylformamide (DMF), which was used as catalyst, at 60 °C for 6 h. The excess of thionyl chloride was distilled off at reduced pressure and the remaining solid was then purified. Thus, 4,4′-sulfonyldibenzoyl dichloride (DBSC) was recrystallized from toluene and sublimated at 160–170 °C [32,33], whereas 2,2-bis(4-chlorocarbonylphenyl)hexafluoropropane (6FC) was recrystallized from pentane and sublimated at 80–90 °C [34,35].

2.2. Synthesis of 2,2-bis(3-amino-4-hydroxyphenyl) propane (APA)

The monomer was synthesized from 2,2-bis(4-hydroxyphenyl) propane **(1)** following the two step methodology depicted in Fig. 1.

Synthesis of 2,2-bis(3-nitro-4-hydroxyphenyl) propane **(2)**: Concentrated nitric acid (15 mL) was added dropwise over 1 h to a stirred solution of toluene (75 mL), 2,2-bis(4-hydroxyphenyl) propane **(1)** (15.0 g, 0.066 mol) and glacial acetic acid (50 mL) at 0–5 °C. After stirring for 1 h more at that temperature, the mixture was allowed to warm up to room temperature and then stirred for 2 h. The solid was then filtered, washed with cold water and dried at 90 °C for 12 h under vacuum. The dinitro compound was obtained as a yellow powder: yield 94%; mp. 284 °C (DSC); ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 10.80 (s, 1H, *OH*), 7.72 (d, $J = 8.8$ Hz, 1H, H_{ar}), 7.33 (dd, $J = 8.8$ Hz, 2.5 Hz, 1H, H_{ar}), 7.04 (d, $J = 2.5$ Hz, 1H, H_{ar}), 4.3 (s, 2H, NH), 1.63 (s, 3H, CH_3).

Synthesis of 2,2-bis(3-amino-4-hydroxyphenyl) propane **(3)**: The dinitro compound **(2)** (10,000 g, 0.0314 mol) was heated to reflux in absolute ethanol (100 mL) in the presence of wet 10% Pd/C catalyst (0.650 g). Hydrazine monohydrate (20 mL) was then added dropwise over a period of 30 min, and the reaction was maintained at reflux for 24 h. The hot solution was filtered through Celite® to eliminate the catalyst and partially concentrated under reduced pressure. Afterwards, the concentrate was poured into cold distilled water. The crude product was filtered, washed with water, dried under vacuum and recrystallized twice from methanol to give **(3)**. The diamino compound was obtained as a white powder: yield: 88%; mp. 263 °C (DSC); Analysis: Calculated for $C_{15}H_{18}N_2O_2$: C, 69.74%; H, 7.02%; N, 10.84%. Found: C, 69.35%; H, 7.15%; N, 11.02%. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm); 8.57 (s, 1H, OH), 6.43 (d, $J = 8.1$ Hz, 1H, H_{ar}), 6.34 (d, $J = 1.8$ Hz, 1H, H_{ar}), 6.21 (dd, $J = 8.1$ Hz, 1.8 Hz, 1H, H_{ar}), 4.23 (s, 2H, NH) 1.37 (s, 3H, $CH_{3\,f}$). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 142.4, 141.4, 135.4, 114.4, 113.5, 113.4, 40.8, 30.9.

2.3. Synthesis of polymers (HPAs)

A general procedure was carried out as follows: 5.0 mmol of diamine were dissolved in 5 mL of 1-methyl-2-pyrrolidinone (NMP) at room temperature in a 50 mL three-necked flask, equipped with mechanical stirrer and nitrogen inlet and outlet. The solution was cooled down to 0 °C, and then 11 mmol of trimethylsylil chloride and 11 mmol of pyridine (1.1 mol/mol of amine group) were slowly added. Afterwards, the reaction temperature was allowed to rise to room temperature and 5.0 mmol of the acid dichloride and 5 mL of NMP were

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