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Thermally rearranged polybenzoxazoles membranes with biphenyl moieties: Monomer isomeric effect

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ABSTRACT

A nucleophilic monomer (3,3′-diamino-4,4′-dihydroxybiphenyl, *m*HAB), isomer of the commercial 3,3′-dihydroxybenzidine (*p*HAB), has been synthesized in good yield and high purity by a two-step synthesis. This monomer was polymerized with 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride(6FDA) to form a new *ortho*-hydroxy polyimide (*m*HAB-6FDA) followed by thermal rearrangement to polybenzoxazole in solid state. *m*HAB-6FDA polyimide film showed excellent film-forming ability and good mechanical properties, which were similar to those found for the isomeric polymer *p*HAB-6FDA. A detailed thermal study was carried out for both polymers (*m*HAB-6FDA and *p*HAB-6FDA) to discover the relationship between the thermal treatment employed and the degree of conversion to polybenzoxazole (PBO). Thermal rearrangement (TR) to PBO for the polymer derived from *m*HAB started from a lower temperature than for the polymer pHAB-6FDA. Final TR conversion was higher for *p*HAB-6FDA when the employed temperature and residence time were high enough; also, for any treatment temperature, fractional free volume (FFV) was higher for the polymer derived from *m*HAB. Gas separation properties were measured and it was found that gas permeability (and particularly CO_2 permeability) was much better for the material made from *m*HAB. The high gas permeability along with good selectivity qualifies *m*HAB-6FDA as a good candidate in carbon capture applications.

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1. Introduction

Significant advances have been made in recent years in the chemistry of polymer membranes for gas separation [1–5]. Considering that polymer chemical structure directly affects the performance of polymeric gas separation membranes, particularly due to the existence of a trade-off relationship between gas permeability (flux) and gas selectivity (separation factor of a mixture of gases), efforts have been mainly targeted to improve fractional free volume (FFV) and to increase molecular rigidity in order to achieve high permeability and better selectivity [6,7]. Following these simple rules, a great number of polymers, especially glassy polymers, have been developed and evaluated as gas separation membranes [6,8–10]. Among them, aromatic polyimides have been favored and developed for gas separation membranes [11–14]. One modern example of polyimides or related structures that have deserved the attention of many groups working in the field of gas separation is that of the thermally rearranged polymers (TR polymers) [15]. It has been discovered that a carefully controlled thermal treatment of *ortho*-OH aromatic polyimides in solid state leads to a chemical rearrangement to convert the *ortho*-OH imide moiety into a benzoxazole one [15–18]. This thermally-driven interconversion produces a new generation of materials having outstanding properties, particularly those related to the separation of condensable gases [3,19–22]. Aromatic polyimides containing *ortho*-OH groups can be synthesized by reaction of dianhydrides and bis-*ortho*-dihydroxy aromatic diamines applying conventional synthetic methods. The chemical transposition involves the release of a CO_2 molecule per imide group at a temperature exceeding 350 °C, and more commonly around 450 °C, where this temperature depends on the T_g of the starting *ortho*-OH polyimide [23]. Although there is some controversy on the mechanism and nature of conversion, it seems sufficiently proved that the final chemical composition actually corresponds to a polybenzoxazole, and that this rearrangement (from polyimide to polybenzoxazole) is responsible for the extreme increase in gas permeability observed in these materials [24–26]. Also, an additional

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advantage, derived from the high temperatures employed, is the appearance of crosslinking, with a consequent decrease in the plasticization and physical aging. Following the trade-off between permeability and selectivity, a small loss of perm selectivity has been detected for TR membranes in respect to the corresponding *ortho*-OH polyimide precursors [26,27]. Probably the major drawback of TR membranes is the high temperature necessary to pass from polyimide to polybenzoxazole, which challenges the thermal resistance of many structures and that can lead to an incipient decomposition as the temperature is close to that of material decomposition. Indeed, it has been postulated that a supplementary partial pyrolysis can take place, although it should be virtually negligible as spectroscopic characteristics of the final polymers are in a fairly good agreement with the postulated polybenzoxazoles [24]. There exists a great concern because it has been observed that the properties depend to a great degree on the conversion imide-benzoxazole, and that only by reaching a full conversion among moieties, the membrane achieves outstanding gas permeation properties [28]. Preferred examples of these systems are polyimides prepared from the dianhydride hexafluoroisopropylidene diphthalic anhydride (6FDA). 6FDA is known to provide soluble polyimides, which is a very valuable property as TR membranes should be processed from solution of the OH-polyimide precursors. Among aromatic dihydroxydiamines, a small number of them have been tested until now as monomers in this topic. Two of them have deserved much attention so far: 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (APAF) and 3,3′-dihydroxybenzidine (*p*HAB). The latter is much cheaper and endows to the final material with a comparatively better thermal resistance. On the other hand, APAF is preferred in terms of solubility and handling on fabricating dense and porous membranes; and furthermore, its lower glass transition temperature helps for a thermal rearrangement at a slightly lower temperature [23]. However, APAF is much more expensive and it has a low reactivity what makes it difficult to obtain high molecular weight precursors.

In the present paper, 3,3′-diamino-4,4′-dihydroxybiphenyl (*m*HAB) has been prepared as a novel condensation monomer to react with 6FDA as a precursor polymer (*m*HAB-6FDA) for TR gas separation membranes. This monomer, relatively easy to be made, is an isomer of the commercial *p*HAB monomer, and it has been employed for the preparation of OH-polyimides by polycondensation with the dianhydride 6FDA, which have been used as precursors of polybenzoxazoles (PBO) obtained after thermal rearrangement. The aim of this work has been to explore the potential of this novel polymer in TR gas separation materials, as well as to study the effect of isomers of precursor polymers on the physical and gas separation properties of their corresponding TR-PBO membranes. The properties of *m*HAB-6FDA have been compared with those of the polymer made from 6FDA and *p*HAB (*p*HAB-6FDA).

The preparation of *m*HAB was optimized to the grade of condensation monomer. Also, the polycondensation reaction was refined, combining the in situ silylation of the aromatic diamines [29] with azeotropic cycloimidization, in order to obtain high molecular weight polymers with good film-forming properties. A systematic characterization has been performed for the precursor OH-polyimides and for the final polybenzoxazoles. Finally, a study of their gas separation properties has been accomplished.

2. Experimental section

2.1. Materials

Solvents and reactants *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), Celite®, concentrated nitric acid (65%), glacial acetic acid, methanol (MeOH), diethylether, were of reagent-grade quality and used without further purification unless otherwise noted. 4,4′-Dihydroxybiphenyl (97%), hydrazine monohydrate, palladium 10 wt% on activated carbon, chlorotrimethyl silane (CTMS), pyridine (Py), *N*,*N*-dimethylaminopyridine (DMAP), *o*-xylene and anhydrous *N*-methyl-2-pyrrolidinone (NMP) were all purchased from Aldrich and used as received. 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was provided by Cymit Química (Barcelona) and sublimed just before use. 3,3′-Dihydroxybenzidine (*p*HAB) (TCI Europe) was dried at 120 °C under vacuum prior to be used.

2.2. Synthesis of 3,3′-dinitro-4,4′-dihydroxybiphenyl

Concentrated nitric acid (12.2 mL) was added dropwise over 1 h to a stirred solution of toluene (60 mL), 4,4′-dihydroxybiphenyl (10.0 g, 0.0537 mol) and glacial acetic acid (40 mL) maintained at 0–5 °C. After stirring for an additional 1 h, the mixture was allowed to warm up to room temperature. The dinitro compound was then separated as a solid by filtration, which was thoroughly washed with cold water, methanol and diethyl ether. The collected solid was finally recrystallized from toluene/DMF to give a yellow product. Yield: 95%. m.p. 284 °C (DSC). *Anal. Calcd*. for $C_{12}H_8N_2O_6$:C, 52.18; H, 2.92; N, 10.14%. *Found*: C, 52.95; H, 3.04; N, 10.68%. ^{1}H-NMR (DMSO-d_6, 300 MHz):11.13 (s, 2H, OH),8.14 (d, 2H, $J=2.4$ Hz),7.86 (dd, 2H, $J=8.6$ Hz, $J=2.4$ Hz), 7.20 (d, 2H, $J=8.6$ Hz). ^{13}C NMR (DMSO-d_6, 75 MHz): δ151.38, 137.37, 132.80, 129.16, 122.49, 119.71.

2.3. Synthesis of 3,3′-diamino-4,4′-dihydroxybiphenyl (mHAB)

A three-necked flask was charged with 3,3′-dinitro-4,4′-dihydroxybiphenyl intermediate (3000 g, 0.0138 mol), 100 mL of ethanol and 0.300 g of 10% palladium on carbon (Pd/C). Hydrazine monohydrate (12 mL) was added dropwise to the mixture over a period of 30 min at 85 °C. When the addition was complete, the solution was heated and maintained at reflux for 24 h. Afterwards, DMAc was then slowly added to the reaction suspension until the precipitate was completely dissolved. The final hot solution was filtered through Celite® to remove the Pd/C catalyst, and partially evaporated in a rotary evaporator before pouring into cold distilled water. The crude product precipitated as a white solid, which was filtered, washed carefully with water, dried and purified by sublimation at 270 °C under reduced pressure. Yield: 92%. m.p. 329 °C (DSC). *Anal. Calcd*. for $C_{12}H_{12}N_2O_2$:C, 66.65; H, 5.59; N, 12.96%. *Found*: C, 66.73; H, 5.48; N, 13.11%. ^{1}H-NMR (DMSO-d_6, 300 MHz): 8.92 (*s*, 2H, OH), 6.75 (*d*, 2H, $J=2.2$ Hz), 6.63 (*d*, 2H, $J=8.1$ Hz), 6.53 (dd, 2H, $J=8.1$ Hz, $J=2.2$ Hz), 4.51 (*s*, 4H, NH_2). ^{13}C NMR (DMSO-d$_6$, 75 MHz): δ 144.26, 134.92, 129.83, 116.81, 114.78, 111.89.

2.4. Synthesis of poly(o-hydroxyimide)s (HPIs)

A three-necked flask, equipped with a mechanical stirrer and gas inlet and outlet, was charged with 10.0 mmol of diamine (*p*HAB or *m*HAB), and 10.0 mL of NMP. The mixture was stirred at room temperature under nitrogen atmosphere until the solid was entirely dissolved. Then, the solution was cooled to 0 °C and the required amount of CTMS (1 mol/mol reactive group) was added to the experiment, followed by pyridine (1 mol/mol reactive group) and small amounts of DMAP (0.1 mol/mol pyridine). The temperature was raised to room temperature, and the solution was stirred for 15 min to ensure the formation of the silylated diamine. After this time, the solution was additionally cooled to 0 °C, and 6FDA (10.0 mmol) was rapidly added followed by 10 mL of NMP. The reaction mixture was stirred for 15 min at 0 °C and then the temperature was raised up to room temperature and left overnight to form the poly(amic acid) solution. The viscosity of the solution greatly increased during this period. *o*-Xylene (20 mL) as an

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