



Thermally rearranged polybenzoxazoles and poly(benzoxazole-co-imide)s from ortho-hydroxyamine monomers for high performance gas separation membranes

Bibiana Comesaña-Gándara^{a,b,c,d}, Antonio Hernández^c, Jose G. de la Campa^a, Javier de Abajo^{a,c}, Angel E. Lozano^{a,c,d,*}, Young Moo Lee^{b,*}

^a Department of Macromolecular Chemistry, Institute of Polymer Science and Technology, ICTP-CSIC, 28006 Madrid, Spain

^b Department of Energy Engineering, Hanyang University, Seoul 133-791, Republic of Korea

^c Group of Porous Materials and Surfaces, SMAP, UVa-CSIC Research Unit, 47011 Valladolid, Spain

^d CINQUIMA, College of Sciences, University of Valladolid, 47011 Valladolid, Spain

ARTICLE INFO

Article history:

Received 9 February 2015

Received in revised form

13 May 2015

Accepted 28 May 2015

Available online 26 June 2015

Keywords:

Aromatic ortho-hydroxypolyimides
Thermally rearranged (TR) polymers
Gas separation membranes
Polybenzoxazoles
Fractional free volume

ABSTRACT

Ortho-hydroxypolyimides (HPIs) undergo thermal rearrangement processes in a solid state at high temperatures to produce thermally rearranged polybenzoxazoles (TR-PBOs), which are promising materials for gas separation membranes due to their exceptional permeability-selectivity performance. The strong dependence between the structure of HPIs and the final properties of the TR-PBOs and the high cost of the HPI precursors are considered excellent reasons for their continued study. In this work, a set of low-cost HPIs were synthesized via the reaction of 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) with 2,4-diaminophenol dihydrochloride (DAP-Cl) and 4,6-diaminoresorcinol dihydrochloride (DAR-Cl). The polyimide made from 6FDA and *m*-phenylene diamine (MPD) was also obtained for comparison purposes. The polyimide precursors and the corresponding TR-PBOs, which were tested as films, were thoroughly characterized. The glass transition temperature of these precursor polyimides was shown to be a function of the number of hydroxyl groups such that the lowest value corresponded to the polyimide from MPD and the highest value corresponded to that derived from DAR. The conversion rate of HPIs to PBO at different processing temperatures was determined, and the highest conversion rate matched the DAP derived polyimide. With respect to their gas separation properties after thermal treatment at 450 °C, these HPIs gave rise to TR-PBOs with very high permeability and satisfactory permselectivity values for several gas pairs.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

In recent decades significant research efforts have been made to identify novel polymer materials with an adequate balance of productivity and permselectivity to be considered as candidates for competitive gas separation membranes. Importantly, these materials are useful for a variety of industrial operations, such as stripping of carbon dioxide from natural gas, nitrogen and oxygen enrichment, hydrogen recovery from petrochemical recycling, purging of gas streams, water vapor removal from air, and recovering volatile organic compounds and monomers [1–4]. Membrane separation technologies are more energy efficient, simple, and lower in cost than classical methods for gas separation and purification.

Commercial applications rely primarily on solution-diffusion membranes due to their ability to facilitate transportation of gas molecules. The specific mechanism of this type of membrane involves molecular scale interactions between the permeating gas and the membrane polymer. Thus, permeability can be expressed in terms of the gas transport and sorption coefficients [5]. A common way of expressing this relationship is as follows:

$$P = D \cdot S$$

In this relationship, the quantity *S* represents the solubility coefficient, which is thermodynamic in nature, and is affected by polymer–penetrant interactions. Conversely, the average diffusion coefficient *D* is kinetic in nature and is determined primarily by the penetrant molecular size and polymer–penetrant dynamics. The paramount importance of the diffusion coefficient determines the gas separation behavior and defines the existence of a trade-off between gas permeability and gas selectivity [6,7].

The chemical structure of a polymer greatly affects its

* Corresponding authors.

E-mail addresses: lozano@ictp.cisc.es (A.E. Lozano), ymlee@hanyang.ac.kr (Y.M. Lee).

properties and behavior as a gas separation membrane. Thus, research on this topic has been targeted at developing polymers with a high fractional free volume (FFV) to improve permeability and high molecular rigidity to attain high selectivity [8,9]. Indeed, these are the goals of numerous new polymers that have been synthesized in recent years, especially glassy aromatic polymers [10–12]. In this regard, aromatic polyimides have achieved major importance as they offer affordable synthesis routes and balanced properties that are especially well suited for gas separation, namely, they are thermally stable, consist of glassy materials with a high molecular stiffness and glass transition temperatures commonly over 300 °C, and can be solubilized by organic solvents, thereby simplifying the fabrication of dense membranes by classical casting techniques [13].

One successful example of polyimides with enhanced gas separation properties is thermally rearranged polymers (TR polymers), which are derived from thermal structural conversion of precursor aromatic polyimides with hydroxyl groups in the *ortho* position to the imide ring [14,15]. This thermally driven rearrangement, produced in the solid state at high temperature, leads to dramatic changes in the composition and molecular conformation of *ortho*-hydroxy-containing polyimides, resulting in polybenzoxazoles (TR-PBOs) with an unusual microporous structure that translates into a substantial improvement in gas permeability, with minimal loss of selectivity [16,17].

Dianhydride hexafluoroisopropylidene diphthalic (6FDA) is the preferred dianhydride monomer to prepare these special polyimides, as it is a strong electrophile that affords soluble polyimides. Aromatic dihydroxydiamines (2HDA), 2,2'-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (APAF), 3,3'-dihydroxybenzidine (*p*HAB), and its isomer 3,3'-diamino-4,4'-dihydroxybiphenyl (*m*HAB) have been used for these purposes [16–20]. APAF is quite expensive; much more so than *p*HAB, while *m*HAB is a non-commercial reagent that was recently reported to be a suitable raw material for TR polymers [20]. All three 2HDAs have proven to be good nucleophiles and present a reasonably high reactivity against the dianhydride 6FDA, although the diamine APAF is comparatively less reactive because of the electron withdrawing effect of its hexafluoroisopropylidene group. The combination of lower reactivity and significant price makes the diamine APAF less recommendable. Furthermore, *m*HAB and *p*HAB endow the final materials with a better thermal stability.

Within the framework of the continuous research effort on this topic, we introduced in the present study two commercial *ortho*-hydroxydiamines (HDAs) as HPI monomers. The class of molecules known as *ortho*-aminophenols is sensitive to both air and light, and can spontaneously evolve to oxidized side products. These oxidized chemicals are inactive with respect to polycondensation, and that is the reason why HDAs are not traditionally used for the synthesis of aromatic polymers, unless they contain an electron acceptor group such as trifluoromethyl or hexafluoroisopropylidene [21]. However, it is possible to achieve high molecular weight polyamides and polyimides by using trimethylsilyl or hydrochloride derivatives [22,23]. In the present study, we used the latter approach wherein the preparation of HPIs from 2,4-diaminophenol dihydrochloride (DAP-Cl) and 4,6-diaminoresorcinol dihydrochloride (DAR-Cl) was optimized to obtain high molecular weight polymers. TR poly(benzoxazole-co-imide) membranes have been previously reported by Jung et al. [24]; however, these authors did not use HDA as monomers, but rather mixtures of aromatic diamines and 2HDA in combination with dianhydrides to prepare HPIs that were eventually converted into poly(benzoxazole-co-imides) (TR-PBOI) by thermal rearrangement.

In the present study, the polycondensation reaction was refined by using chlorotrimethylsilane as a polyimidization promoter and by thoroughly purifying DAP-Cl, DAR-Cl, and the dianhydride 6FDA. In this way, high molecular weight HPIs with good film-

forming capability could be attained. For comparison purposes, a pristine polyimide was also prepared from 6FDA and *meta*-phenylenediamine, which allowed for the creation of three chemically related polymers with final compositions corresponding to polyimide (PI), poly(benzoxazole-co-imide) (PBOI) and polybenzoxazole (PBO).

All of the precursor polyimide films and final TR polymer films were systematically characterized by spectroscopic methods. Special emphasis was given to monitoring the thermal rearrangement process, which was followed by thermogravimetry, X-ray diffraction, and free volume analysis. In addition, the gas permeation properties of the final membranes were evaluated by measuring single gas permeability properties and ideal selectivity.

2. Experimental

2.1. Materials

Chlorotrimethylsilane (CTMS), pyridine (Py), 4-dimethylaminopyridine (DMAP), *o*-xylene, acetic anhydride, anhydrous *N,N*-dimethylacetamide (DMAc) and anhydrous *N*-methyl-2-pyrrolidone (NMP) were 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. Diamines including 2,4-diaminophenol dihydrochloride (DAP), 4,6-diaminoresorcinol dihydrochloride (DAR) and *m*-phenylenediamine (MPD) were supplied by Aldrich. DAP was dried at 100 °C under vacuum, DAR was recrystallized in SnCl₂ dissolved in HCl 3.5 M, and MPD was sublimed prior to be used.

2.2. Synthesis of polyimides

2.2.1. Polyimide from MPD and 6FDA (PI-MPD)

A total of 10.0 mmol of MPD was dissolved in 10 mL of anhydrous DMAc in a three-necked flask equipped with a mechanical stirrer under a nitrogen atmosphere. The solution was cooled to 0 °C and 20 mmol of CTMS were mixed into the reaction vessel, followed by addition of 20 mmol Py and 2 mmol DMAP. The temperature was raised to room temperature and the solution was stirred for 15 min to ensure formation of the silylated diamine. Next, the solution was cooled to 0 °C and 6FDA (10.0 mmol) was added. The mixture was then stirred for 12 h at room temperature upon which a very viscous clear solution of polyamic acid formed. To this solution a mixture of acetic anhydride (80 mmol) and pyridine (80 mmol) was added followed by stirring for 6 h at room temperature and an additional 45 min at 60 °C. The viscous polyimide solution was poured onto water and the resulting precipitate was washed several times with water and finally dried in a vacuum oven at 130 °C overnight. The synthesized polyimide was designated as **PI-MPD**. ¹H NMR (DMSO-*d*₆, 300 MHz): 8.18 (d, 2H, *J*=7.9 Hz), 7.95 (d, 2H, *J*=7.9 Hz), 7.76 (s, 2H), 7.69 (m, 1H), 6.62 (s, 1H), 7.57 (s, 2H), 7.54 (s, 1H). FT-IR (film): imide ν (C=O) at 1785 and 1716 cm⁻¹, imide ν (C-N) at 1353 cm⁻¹. η_{inh} (dL/g)=0.56.

2.2.2. *Ortho*-hydroxypolyimides (HPIs)

A three-necked flask equipped with a mechanical stirrer and gas inlet and outlet was charged with 10.0 mmol of diamine dihydrochloride, DAP, or DAR and 10 mL of NMP. The mixture was then cooled to 0 °C and the required amount of CTMS (1 mol/mol reactive group) was added, followed by pyridine (1 mol/mol reactive group) and DMAP (0.1 mol/mol pyridine). The salt protection of the amino groups of the unstable DAP and DAR was not removed prior to synthesis, and thus an extra amount of pyridine (10 mmol/ mmol of diamine) was required to remove the HCl that formed during the synthesis. The solution was allowed to warm to

Download English Version:

<https://daneshyari.com/en/article/7021040>

Download Persian Version:

<https://daneshyari.com/article/7021040>

[Daneshyari.com](https://daneshyari.com)