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Synthesis, characterization and studies of properties of six polyimides derived from two new aromatic diamines containing a central silicon atom

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ABSTRACT

Two series of novel aromatic polyimides (**PIs**) containing three polymers each one were prepared using two new aromatic silylated-diamine monomers. These monomeric diamines contain biphenylsilane units and biphenyl moieties in their structures. All **PIs** were obtained in high yield and the inherent viscosities were in the range of 0.44 to 0.82 dL/g. Polyimides showed excellent solubility in a wide variety of aprotic polar solvents, including THF and chloroform and were thermally stable with thermal decomposition temperature ($TDT_{10\%}$) over 500 °C and high glass transition temperatures (Tg) between 230 and 270 °C. Additionally, two films were prepared and gas transport properties were determined. These films offered a reasonably acceptable balance of permeability and selectivity with values close to a commercial polyimide (Matrimid), in particular for the CO_2/N_2 gases pair. Experimental density of the films was measured and the fractional free volume was calculated.

1. Introduction

Aromatic polyimides constitute a special group of engineering organic materials and are classified as high performance polymers because they have excellent thermal, mechanical and chemical properties [1–4]. Membranes based on aromatic polyimides have been used in gas separation field, even some of them are commercially available [5].

Glassy aromatic polyimides are preferred for gas separation because they provide high fractional free volume and molecular stiffness [6–10]. However, entirely aromatic polyimides show very poor solubility in common organic solvents, which limit their processing and therefore their utilization in this field [11–13].

The inclusion of bulky groups in polymeric chains increases membrane permeability, since they act as molecular spacers, reducing packing forces by the increase of free volume [14]. These groups generate high structural stiffness, and yet these modifications allow access to solvents through polymer chains, resulting in the dissolution of the material. Methyl (CH_3) and other alkyl groups (both linear and branched, as isopropyl or *tert*-butyl groups), the CF_3 group, halogen atoms and silylated substituents, are examples of groups that could be incorporated as substituents in the main polymer chain, in order to increase the fractional free volume [15–22].

A high fractional free volume increases solubility and permeability but also decreases the selectivity of the material. The key challenge for many research groups is to obtain polymers exhibiting at the same time, high permeability and selectivity. Stern et al.,

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in 1990, measured the permeability of polyimide membranes containing silicon atoms using gases such as hydrogen, oxygen, nitrogen, carbon dioxide and methane. The permeability was substantially higher in these polymers than with other similar membrane based on carbon atoms, probably due to the larger size of the silicon atom incorporated to the main chain, favoring in this way the increment of the free volume of the polymer [23].

Since then, the use of other silicon-containing polymers with silarylene moieties [$-$Ar$-$Si(R_1R_2)$-$Ar$-$] has not been reported in the gas separation field. In accordance with the above information, the present research is based on the synthesis and characterization of new aromatic polyimides containing one or two silicon atoms on the repeating unit. Solubility, thermal behaviour and gas separation ability are also investigated and discussed.

2. Experimental

2.1. Materials

Anhydrous *N,N*-dimethylacetamide (DMAc), anhydrous pyridine, acetic anhydride, 3-nitrophenylboronic acid, hydrazine monohydrate (80%), Pd/C (10% w/w), bis(triphenylphosphine)palladium (II) dichloride, 1,4-dibromobenzene, *n*-butyllithium (*n*-BuLi) 2 M in cyclohexane, dichlorodimethylsilane, dichlorodiphenylsilane, 4,4′-hexafluoroisopropylidene diphthalic anhydride (**6FDA**) and 4,4′-oxydiphthalic anhydride (**ODPA**) were obtained from Aldrich Chemical (Milwaukee, WI). **6FDA** and **ODPA** were sublimated before used. Bis-(4-bromophenyl)dimethylsilane (**1**), bis-(4-bromophenyl)diphenylsilane (**2**) and 4,4′-(dimethylsilanediyl) diphthalic anhydride (**SiDA**) were synthesized following a procedure already reported in the literature [24–27]. For the permeation experiments, helium, oxygen, nitrogen and carbon dioxide were used. The purity of the gases was greater than 99.5% for O_2 and greater than 99.99% for the other ones. All other reagents and solvents were purchased commercially as analytical grade and used without further purification.

2.2. Instrumentation and measurements

FT-IR spectra (KBr pellets) were recorded on a Perkin-Elmer (Fremont CA) 1310 spectrophotometer over the range of 4000–450 cm^{-1}. Melting points (uncorrected) were obtained on a SMP3 Stuart Scientific melting point apparatus. ^{1}H, ^{13}C and ^{29}Si NMR spectra were carried out on a 400 MHz instrument (Bruker AC-200) using DMSO-d_6 or $CDCl_3$ as solvent and TMS as internal standard. Viscosimetric measurements were made in a Desreux-Bischof type dilution viscosimeter at 25 °C (c = 0.5 g/dL). Size exclusion chromatography (SEC) measurements were carried out at 25 °C using a system composed of three PLgel 5 μm Mixed-C columns placed in series, refractive index (Optilab DSP) and light-scattering (EA-02 Dawn Eos Enhanced Optical System) detectors and Knauer pump model 14163. THF was used as eluent with a flow rate of 0.3 mL/min. The glass transition temperature (Tg) values were obtained with a Mettler-Toledo (Greifensee, Switzerland) DSC 821 calorimetric system (10 °C/min under N_2 flow) and taken in the second thermal scan. Thermogravimetric analyses were carried out in a Mettler (Switzerland) TA-3000 calorimetric system equipped with a TC-10A processor, and a TG-50 thermobalance with a Mettler MT5 microbalance (temperature range between 25 °C and 800 °C at 10 °C/min under N_2 flow). Elemental analyses were carried out on a Fisons EA 1108-CHNS-O equipment. The density (ρ) of the films was determined from the Archimedes' principle using a top loading electronic XS105 Dual Range Mettler Toledo balance and density kit. The samples were sequentially weighted in air and in high purity isooctane at 25 °C. The Fractional Free Volume (FFV) was calculated from density by using the following equation [28]:

$$\mathrm{FFV} = \frac{(\mathrm{V}-1.3\mathrm{V_w})}{\mathrm{V}} \tag{1}$$

where V = (1/ρ) is the polymer specific volume and V_w is the van der Waals volume, which was estimated using the Hyperchem computer program (version 7.0). A barometric method was used to determine steady-state pure gas permeability of the polymeric films at 30 °C. For all gases, the downstream pressure was maintained at less than 10^{-2} mbar (1 Pa), and the upstream pressure was maintained at 3.0 bar (0.3 MPa). The permeability coefficients, P, were calculated from the slope of the downstream pressure versus time in the stationary state by using the following equation [29]:

$$\mathrm{P}=\frac{273}{76}\frac{Vl}{\mathrm{AT}p_o}\frac{dp(t)}{dt} \tag{2}$$

where A, V and l are the effective area, the downstream volume and the thickness of the membrane, respectively, T denotes the temperature of the measurement in Kelvin, p_0 refers to the pressure of the feed gas in the upstream compartment and (*dp(t)/dt*) is the rate of the pressure rise at steady state.

2.3. Membrane preparation

Dense membranes were prepared using a solution-casting method. The casting of the polyimide was done from a 5% (w/v) solution in DMAc. The solution was filtered through a 3.1 μm fiberglass Synta® syringe filter to remove dust and other non-soluble impurities. Then, it was poured onto a glass ring placed on a levelled glass plate and maintained at 60 °C overnight to remove most of the solvent. The membrane was peeled off the glass and placed into a vacuum oven at 150 °C for 12 h and 200 °C for 3 h. The thickness of the membranes ranged from 40 to 60 μm.