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Structure – promoted high performance properties of triphenylmethane - containing polyimides and copolyimides

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ABSTRACT

Novel triphenylmethane-based polyimides and copolyimides were synthesized by polycondensation reaction of 4,4′-(4,4′-isopropylidenediphenoxy)bis(phthalic anhydride) with a triphenylmethane-based diamine, or an equimolar mixture of 4,4′-oxydianiline and triphenylmethane-based diamine, via conventional two-step procedure. Three novel diamines were developed as well, being obtained from *ortho*-toluidine and one of the following aldehydes: benzaldehyde, 4-bromobenzaldehyde or 4-fluorobenzaldehyde. The relationship between the macromolecular structural motif and physical properties of the synthesized polymers was investigated in detail, with emphasis on thermal transitions and stability, dielectric behavior, molecular disorder, mechanical toughness and gas separation performance. The amorphous, free-standing, tough and defectless films prepared from these polymers showed excellent thermal stability, their decomposition starting above 425 °C. For all polymer films which were subjected to dielectric properties measurements, the variation of the real and imaginary parts of the dielectric permittivity with frequency and temperature was measured and discussed. The values of the dielectric constant and dielectric loss were measured at room temperature and in the frequency domain from 1 Hz to 1 MHz, and the obtained results proved the beneficial effect of fluoro and bromo graphting on the dielectric constant reduction. The dielectric spectroscopy data showed distinct γ and β subglass transitions at lower activation energies for copolyimides compared to polyimides, suggesting that the incorporation of the comonomer diamino-diphenyl ether allows faster motions of the small molecules, but hinders the mobility of charge carriers. The permeability of several gases through these membrane-forming materials were measured and discussed with respect to the structural variations in the polymer repeating unit.

1. Introduction

Aromatic polyimides have aquired growing importance as high performance materials, due to their high thermal stability, ability to maintain dielectric, physical and mechanical properties over a wide temperature range, low thermal expansion, accessibility and easy proccesing to final products [1]. Commercial and synthesized dianhydrides and diamines of diverse chemical structures have been used as condensation monomers to develop novel aromatic polyimides. As a result, versatile soluble and processable polyimides have been reported and evaluated as materials useful in applications related to advanced technologies [2–4]. Although the unique properties of polyimides make them attractive in many areas, there is still a need for better understanding of structure-properties relationships to improve their characteristics and to advance their application in new commercial fields. The extensive studies on structure-property correlations have already indicated few fundamental rules for design of polyimides with improved properties. It has been established that incorporation of ether or isopropyl groups into the main polyimide chains generally leads to lower glass transition temperatures (T_g), as well as to significant improvement of solubility and thermoplasticity of the polymers [4]. Additionally, introduction of bulky groups into the polymer main chains or attachment of bulky pendant groups can impart significant increase in T_g by restricting the segmental mobility, while providing a good solubility due to the decreased degree of packing and lower crystallization. Taking into account those facts, possibility to obtain materials with desired properties is closely related to the use of an appropriate molecular design. In case of polyimides, implementation of design results can be carried out by chemical structure modulation of diamine and dianhydride monomers.

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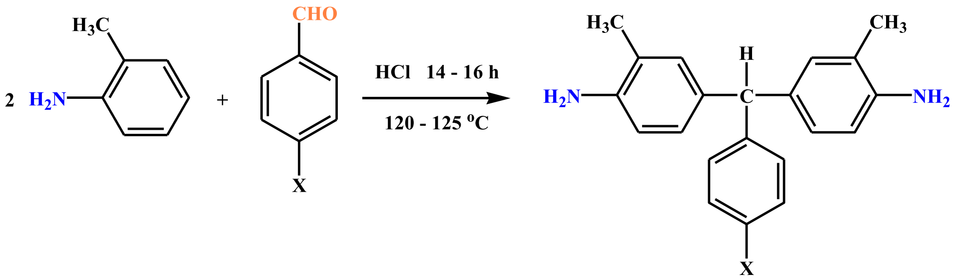

AMPM: X = H ; AMPM-F: X = F ; AMPM-Br: X = Br

Scheme 1. Synthetic procedure to diamine monomers.

It has been generally known that penetration of small molecules is restricted through polymer matrices with strong interchain attraction forces and high degree of molecular packing, as it is the case of wholly aromatic classical polyimides. Thus, the main approach used to improve gas permeability is to disrupt chain packing, whereas that used to enhance selectivity is based on reducing chain mobility. Unfortunately, polymers with good selectivity exhibit low permeability and vice versa [5,6]. To minimize the trade-off between permeabilty and selectivity as well as that between processability and improved physical propeties, a specific tailoring of the polyimide molecular structure has to be carried out. Selection of adequate chemical structure to achieve the most favourable balance of transport properties can be considered a challenge for researchers. The majority of the chemical modification attempts have been directed to enhance diffusivity through an increment of the fractional free volume (FFV). From this point of view, fluorine-containing polyimides, mainly those containing the hexafluoroisopropylidene core, have received special importance as they provide a favourable balance of permeability and selectivity [7,8].

Another way to increase FFV and to improve gas separation properties of a polymer material is to introduce bulky groups and to increase at the same time the rigidity of the main chain, because the use of structures with high rigidity results in a strong size sieving ability [9]. The monomers containing bulky pendant groups, aromatic diamines or dianhydrides, could lead to aromatic polyimides with good solubility, preserving their thermal stability and mechanical properties [4]. The introduction of pendant phenyl ring in the structure of an aromatic diamine is an accesible way for the synthesis of processable polymers. Among various bulky diamines used in the synthesis of aromatic polyimides those containing 4,4′- triphenylmethane (TPM) core were rarely used. The pendant phenyl ring induces a free internal rotation of the triphenylmethane bridging group and makes these diamine excellent candidate for synthesis of processable polymers [10]. The literature mentions the existence of a wide variety of diamines derived from TPM using different substituted anilines and benzaldehydes [11], but only several aromatic polyimides have been reported to date [10,12–15]. Thus, the approach followed in this work consisted of using diamines with bulky side groups, such as phenyl or Br- / F-substituted phenyl units, conveniently placed to produce an increase in both FFV and rigidity, thus improving the gas permeation properties, beside others. Graphting a bromo substituent on the phenylene ring would make the polymer more bulky in nature, leading to lower interchain interactions and preventing the polymer chains from packing into tight structures. Furthermore, by virtue of restricted rotation about the bond joining the aromatic ring system, the Br-substituted polymers should have higher glass transition temperatures with respect to analogues polymers without this substituent [16]. On the other hand, the substitution of C-H bonds in polymers by C-F bonds generally endows polyimides with unique properties, such as reduction of dielectric constants, refractive indices or water absorption and increases of solubility, free volume, thermal stability, transparency, or gas permeability, among others [17].

As part of our continuing efforts in developing easy processable, highly thermostable polymers for use as advanced materials, it appeared chalenging to us to synthesize novel aromatic polyimides and copolyimides containing halogen-substituted/unsubstituted triphenylmethane core and flexible isopropylidene units in the main chain. Our work surveys the correlations between the structural features and polymer characteristics, with a special concern on the effect of chemical structure on thermal transitions and stability, dielectric behavior, molecular disorder, mechanical toughness and gas separation performance. By studying those effects, additional insight into structure-properties relationship is expected to be obtained, which may develop strategies to better control polyimide properties as well as to improve predictions of their performance as advanced materials.

2. Experimental

2.1. Starting materials

Benzaldehyde (≥99.5%), 4-fluorobenzaldehyde (98%), 4-bromobenzaldehyde (ReagentPlus®, 99%), *o*-toluidine (≥99%), 4,4′-(4,4′-isopropylidenediphenoxy)bis(phthalic anhydride), (6HDA, 97%), 4,4′-oxydianiline (97%), sodium hydroxide (granulated EMPLURA®), hydrochloric acid (37%, AR grade), 1-methyl-2-pyrrolidinone (HPLC grade; NMP), chloroform (anhydrous, 99%) and ethanol (analytical standard) were purchased from Sigma–Aldrich.

2.2. Monomers

The synthetic pathway to triphenylmethane-based diamines, namely αα-bis(4-amino-3-methylphenyl)phenylmethane (**AMPM**), α,α-bis(4-amino-3-methylphenyl)-4′-fluorophenylmethane **(AMPM-F)** and α,α-bis(4-amino-3-methylphenyl)-4′-bromophenylmethane **(AMPM-Br)** is outlined in Scheme 1 and the details are described as follows.

2.2.1. α,α-Bis(4-amino-3-methylphenyl)phenylmethane (AMPM)

The synthesis of **AMPM** was carried out by a slightly modified procedure reported for related diamines [13]. Shortly, *o*-toluidine (21.4 g, 0.2 mol) was heated at 120 °C in nitrogen, then benzaldehyde (10.6 g, 0.1 mol) dissolved in 15 mL (12 N) of hydrochloric acid was added dropwise over a period of 1.5 hrs. The reaction mixture was continously refluxed at ca. 120–124 °C for another 12–14 hrs. After cooled to room temperature, 7.92g of 20% aqueous solution of sodium hydroxide was added to yield a pale blue suspension, which was separated by filtration. The purification of the crude diamine involved the dissolution in chloroform and washing with acid water (pH = 1), when diamine chlorohydrate is formed and passed into water phase. The organic phase was removed and the water phase was washed three times with chloroform to eliminate the impurities. Then the pH was ajusted to 9, and the diamine was extracted with chloroform. The organic residue was concentrated under reduced presure, redissolved in small quantity of methanol, followed by pouring into alcaline solution