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Local chain mobility dependence on molecular structure in polyimides with bulky side groups: Correlation with gas separation properties

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ABSTRACT

The effect of bulky side groups on the molecular mobility and chain packing of three polyimides derived from dianhydrides with *m*-terphenyl moieties and 2,4,6-trimethyl-*m*-phenylenediamine has been studied. Moreover, structure–properties relationships in terms of gas transport have been established. One of the polyimides has no side groups, while the other two have a *t*-butyl group in 5′ (*meta*) position on the central ring of the *m*-terphenyl moiety and one of them has also a pivaloylimino group placed in the 2′ (*ortho*) position. The changes in chain packing of the membranes were evidenced by wide angle X-ray diffraction (WAXS), whilst the molecular mobility was evaluated from the dielectric sub-ambient secondary relaxation, γ relaxation. The WAXS pattern of the polyimide containing both *t*-butyl and pivaloylimino side groups evidenced a greater degree of packing regularity than in the other two polyimides. Moreover, the additional pivaloylimino group strongly restricted the local molecular mobility associated with the phenylene-imide ring flips. On the other hand, the gas permeability of the polyimides strongly increased with the introduction of side groups. This increase was mainly related to the increase in the gas diffusivity, which could not be explained by an increase in fractional free volume (FFV). The results presented in this work indicate that the difference in gas diffusivity of the substituted polyimides is consistent with a difference in size distribution of free volume elements.

1. Introduction

Glassy aromatic polyimides are among the most attractive and promising gas-separation materials because of their high gas selectivity (separation efficiency), excellent thermal stability, high chemical resistance and good mechanical properties [1]. However, in many instances the high degree of packing and low mobility of molecular chains greatly limits the diffusion of small molecules through the polymer matrix, and consequently aromatic polyimide membranes commonly have low to moderate permeability (gas flux). The introduction of packing-disrupting units into the backbone has been the most effective way of reducing the molecular packing in order to enhance diffusivity through an increment of the fractional free volume (FFV). However, this gain in gas diffusivity is usually accompanied by a substantial loss in selectivity, owing to a rather general trade-off between permeability of polymer materials and their selectivity, which was quantified by Robeson for several gas pairs, using a large number of existing polymers permeability data [2].

The gas diffusion through a glassy polymer matrix is considered to proceed by a jumping mechanism whereby molecules located inside holes (or free volume elements) move to neighbour holes through channels, which are occasionally opened by thermal fluctuations of the matrix. In this model, the distribution of free volume elements changes at each instant and the gas molecules can jump through any transient channel equal to or larger than their effective size. Local to short scale cooperative segmental motions, like chain bending, bond rotation or phenyl ring flips, have been assumed to be responsible for the opening of these channels in the glassy state. Consequently, the molecular mobility of polymer chains can be considered as another key factor that has a direct impact on gas diffusion. Besides, Freeman's theory [3] to explain Robeson's upper bound for amorphous polymers has indicated that the usual approach of improving the behaviour of membranes by simultaneously increasing interchain separation (i.e., FFV increase) and chain rigidity (i.e., molecular mobility restriction), will not be effective if the size of the free volume elements is significantly larger than the size of the penetrant molecules. In this case, the gas diffusion would not necessarily be controlled by the polymer chain motions.

It is well known that molecular motions below glass transition temperature, T_g, are manifested in sub-T_g relaxation processes, as measured by relaxation techniques such as dynamic mechanical analysis and dielectric spectroscopy. The study of mechanical sub-T_g relaxations in gas separation membranes has paid particular attention to the influence of systematic changes of polymer

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intrasegmental mobility and chain packing efficiency in permeability and selectivity. Polymers such as polycarbonates [4–6], polyphenylene ethers [7], polysulfones [4,8–11] or polyimides [12–14] have been investigated for that purpose.

With regard to aromatic polyimides, three relaxation processes are usually observed in order of decreasing temperature: the α relaxation, related to the glass transition and two sub-T_g relaxations designed as β and γ [15–18]. Typically, β and γ relaxations are detected in the temperature range from 50 to 250 °C and from -140 to 50 °C, respectively. Owing to the local, non-cooperative character of the sub-T_g relaxations, their time-temperature relations can be described by a constant activation energy, according to the Arrhenius equation. The apparent activation energy (E_a) for the β relaxation is approximately 130–160 kJ mol^{-1} and for the γ relaxation, E_a=30–60 kJ mol^{-1}. The lower activation energy indicates that the γ relaxation is due to more local motions of the chain than those involved in the β relaxation. Nonetheless, the molecular mechanisms responsible for both relaxations are still open to question. For γ relaxation, in particular, some studies have indicated that there is a direct correlation between absorbed water and the intensity of the relaxation [15], while others have shown that local motions such as phenyl ring flips are involved in the relaxation process as well [16]. Irrespective of the mechanisms implicated, the γ relaxation appears to be strongly sensitive to changes in FFV or chain rigidity. In this respect, T_γ has been recently shown as a suitable microstructural probe in order to predict the gas permeability and selectivity of polyimides [19]. But, this interesting topic has been scarcely explored so far. It seems thus appropriate to explore the γ relaxation behavior of novel polyimides in order to establish reliable correlations among chemical structure, chain packing and molecular mobility. This work aims to gain a better understanding of how the balance of these factors controls the performance of polyimides as gas separation membranes.

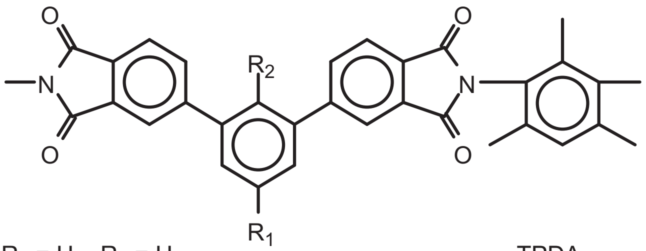
In recent works our approach to prepare polymer membranes with an improved selectivity/permeability balance has consisted of using monomers, diamines or dianhydrides, with bulky side groups conveniently placed to increase in a synergistic way chain rigidity and FFV [20–22]. In particular, polyimides based on monomers derived from *m*-terphenyl dianhydride and 2,4,6-trimethyl-*m*-phenylenediamine or 2,2-bis(4-aminophenyl)hexafluoropropane have offered a good balance of permeability and selectivity with values close to the 1991 Robeson upper bound, especially for O_2/N_2 [20,21]. It will thus be desirable to understand how the incorporation of very bulky side groups, in particular *t*-butyl and pivaloylimino (or pivalamide: $C(CH_3)_3CONH$–), affects either the gas diffusivity or the selectivity of those polyimides.

In this work we have explored the molecular mobility in the glassy state of the polyimides derived from diamine 2,4,6-trimethyl-*m*-phenylenediamine (see Fig. 1) by using dielectric spectroscopy. Moreover, the effect of the side groups on chain packing and FFV has been analyzed by wide-angle X-ray scattering (WAXS) and density measurements. Combination of the results from both techniques usually allows for a description of chain packing in polymers. Finally, the gas transport coefficients of these polyimides have been evaluated in terms of both chain packing and molecular mobility.

2. Experimental part

2.1. Materials

Starting reactants and commercially available solvents were used as-received unless otherwise indicated.



R_1 = H, R_2 = H	TPDA
R_1 = *t*−butyl, R_2= H	BTPDA
R_1 = *t*−butyl, R_2= $NHCOC(CH_3)_3$	PBTPDA

Fig. 1. Repeating units of the aromatic polyimides studied.

2,4,6-Trimethyl-*m*-phenylenediamine was sublimated just before polycondensation. The synthesis of 5′-*t*-butyl-2′-pivaloylimino-3,4,3″,4″-*m*-terphenyltetracarboxylic dianhydride (PBTPDA) has been previously outlined by the authors [21]. 3,4,3″,4″-*m*-Terphenyltetracarboxylic dianhydride (TPDA) and 3,4,3″,4″-(5′-*t*-butyl-*m*-terphenyl)tetracarboxylic dianhydride (BTPDA) were synthesized through a multi-step synthetic route described elsewhere [23]. In particular, this route has greatly enhanced the reaction yield of dianhydride TPDA in comparison with the route reported before [24].

TPDA: yield 98%; m.p.: 303 °C,
^{1}H-NMR (DMSO-d$_6$, ppm): δ=8.62 (s broad, 2H); 8.50 (dd, 2H); 8.34 (s broad, 1H); 8.18 (d, 2H); 8.00 (dd, 2H); 7.72 (t, 1H).
^{13}C-NMR (DMSO-d$_6$, ppm): δ=162.5, 162.3, 146.6, 137.7, 134.0, 131.6, 129.4, 129.2, 127.5, 125.9, 125.0, 122.9.
$C_{22}H_{10}O_6$ (4 1 4): Calcd. C 71.36%; H 2.72%; Found C 71.08%; H 2.98%.
BTPDA: yield 96%, m.p.: 305 °C,
^{1}H-NMR (DMSO-d$_6$, ppm): δ=8.62 (d, 2H); 8.48 (d, 2H); 8.16 (d, 2H); 8.09 (t. 1H), 7.92 (d, 2H).
^{13}C-NMR (DMSO-d$_6$, ppm): δ=163.15, 163.01, 153.01, 147.88, 138.43, 135.04, 132.20, 129.86, 125.78, 125.23, 124.02.
$C_{26}H_{18}O_6$ (4 2 6): Calcd. C 73.23%, H 4.25, Found: C 73.03%, H 4.30.

2.2. Polymers syntheses and membrane preparation

Polyimides were obtained according to the following procedure: 5.0 mmol of diamine were dissolved in 20 mL of *m*-cresol in a 100 mL three-necked flask. 5.0 mmol of dianhydride were added and the mixture was warmed to 80 °C, under a dry nitrogen atmosphere, until total solution and then pyridine (0.3 mL) was added. The solution was maintained at that temperature for 2 h and then benzoic acid (1 mmol) was added. The solution was heated to 190 °C for 6 h. After cooling, the very viscous solution was poured slowly into a mixture 1:2 (v/v) of water/ethanol, forming a white, fibrous polymer precipitate that was filtered off, washed thoroughly with the same mixture, extracted with ethanol in a Soxhlet apparatus, and dried in a vacuum oven at 100 °C overnight. Yields were nearly quantitative.

The films were made by casting a 10% (w/v) filtered solution of polyimide in *m*-cresol onto a leveled glass plate and heating at 80 °C for 12 h and at 180 °C under vacuum overnight. Subsequently, the temperature was risen to a temperature slightly above the T_g of the polyimide under a nitrogen atmosphere and then the films were slowly cooled down to room temperature. No traces of solvent were detected by thermal gravimetric analysis.

Prior to perform dielectric spectroscopy measurements, the films were dried at 120 °C for 24 h over P_2O_5 and kept in a closed desiccator to prevent moisture absorption.