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Designing Aromatic Polyamides and Polyimides for Gas Separation Membranes

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Summary: Aromatic polyamides and polyimides with improved gas permselectivity, can be designed and prepared by systematically changing structural elements that affect these properties. Indeed, a conscientious choosing of the chemical changes may still provide a promising approach to get better and better polymers for selective filtration of gases.

The results of this work, in which novel monomers have been used, have confirmed that gas permeability through aromatic polyamides and polyimides much higher than that of conventional polyamides and polyimides can be achieved. It has been done by introducing bulky side groups, using non-planar monomers, and combining these elements on both monomers: diamines and dianhydrides or diamines and diacids. A theoretical study has also been made to explain the behaviour of some individual polymers, comparing experimental and calculated values of density and free volume.

Keywords: aromatic polyimides, gas separation, theoretical calculations

Introduction

Aromatic condensation polymers have got special importance in advanced technologies, mainly because of their excellent balance of mechanical, electrical and thermal properties. Thus, aromatic polyamides and polyimides have achieved particular importance for applications in a number of industrial fields such as electrical and electronic industry, aerospace industry and automotive industry.[1-3] For these applications, thermal resistance has been a crucial factor, but new applications, such as selective filtration through semipermeable membranes, are imposing other requirements, that are dependent to a great extent on chemical composition. For these

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applications, polymers have to be designed with a favourable balance of properties such as solubility, crystallinity, glass transition temperature, density or free volume.

Many efforts have been done at this respect on engineering thermoplastics so far, for instance on polysulfones, polycarbonates, or cellulose derivatives, and more recently on thermoplastic polyimides specially designed for these applications.[4-6] A characteristic of all these polymer materials is that they are amorphous and show relatively high glass transition temperatures (Tg), so that they behave as actual glassy materials at room temperature. Although significant advances have helped for the application of these materials in separation technologies, involving operation such as dialysis, in particular hemodialysis, ultrafiltration, or reverse osmosis, gas separation and purification are operations where polymers have not yet achieved the degree of performance and disposal enough to be competitive against conventional technologies, like chemical absorption or cryogenic distillation.[7-9]

At this respect, it is worthy remarking that there is a growing demand for novel polymers to be used as permselective membranes in the separation of gas and vapour mixtures in refineries and in the petrochemical industry in general, and also for the separation of carbon dioxide and water from natural gas, the separation of nitrogen oxides and sulphur oxides from industrial gas streams and polluted atmospheres, the enrichment of synthesis gas, the recuperation of hydrogen from ammonia synthesis, the separation of nitrogen and oxygen from air, etc. Pairs of gases that are intensively studied at present are: O_2/N_2, H_2/CH_4, CO_2/CH_4, CO_2/N_2, He_2/N_2, H_2O/CH_4 and C_2H_2/ C_2H_4 and in general the mixtures olefin/paraffin.

This paper deals with the preparation and evaluation of novel aromatic polyamides and polyimides, especially designed and developed to be tested as barrier materials for the separation of gases. A study has been done of their general properties, particularly thermal transitions and solubility (processability), and a comparative evaluation of their properties as membranes has been carried out based on permeation measurements and theoretical calculations of macroscopic properties, such as density and fractional free volume.

Experimental

The synthesis of monomers and the preparation of polymers by conventional polycondensation methods have been previously reported.[10-12]

Glass transition temperatures (Tg) were determined by differential scanning calorimetry (DSC), using a Perkin-Elmer DSC-7 device, in nitrogen atmosphere, on approx. 10mg samples, at a heating rate of 20°/min from 50 to 400°C.

Solubilities were investigated by mixing 20 mg polymer with 1 mL solvent at room temperature for 24 h, shaking the mixture from time to time. Samples that did not dissolve in 24 h were heated up to the boiling temperature of the solvent if needed to get a clear solution.

The permeability to pure gases was studied on polymer films, made by casting of polymer solutions from appropriate solvents. A barometric method was used, applying a constant feed pressure of 3 bars, and an initial pressure in the expansion chamber less than 0.01 mbar.

Simulations of the amorphous structures of the polymers were performed using the computer program Cerius2, version 4.2[13] on a Silicon Graphics Octane workstation. A combination of molecular mechanics and molecular dynamics was used to obtain low energy structures. For these computations, 10 bulk amorphous chains of each polymer were built using the amorphous builder incorporated in the Cerius2 package. The bulk amorphous state was simulated using periodic boundary conditions. The amorphous polymer chains were generated using a random method without any rotational restriction.

The potential energy of each bulk polymer chain was minimized using the Dreiding [14] force field, version 2.21. Partial atomic charges, computed by the Rappé-Goddard method [15] , were included in the non-bonded energy calculations. An external stress of 0.0001 GPa (1 atm) was applied to the cell. Ewald summation[16] was used to determine the Van der Waals and Coulomb energy terms, using a non-bond list with a 2.000 Å buffer in both cases.

Molecular dynamics simulations were performed to relax the minimized structures (annealing cycles at constant pressure P (1 atm) and moles N, starting and ending at 300 K, mid-cycle temperature of 1000 K). The structures obtained after each cycle were minimized again as described previously. Successive cycles of molecular mechanics and molecular dynamics were performed until energy and density convergence was achieved.

Results and Discussion

A major goal of this investigation was to achieve aromatic polyamides and polyimides with a number of specific properties, more precisely: good solubility in organic solvents, absence of crystallinity, high glass transition temperatures that assure glassy state at temperatures below 100°C, good mechanical properties and high fractional free volume, and film-forming properties.

Considering the poor permeability of conventional wholly aromatic polyimides and polyamides, monomers were designed and synthesized following empirical rules concerning chemical modification oriented to the development of processable aromatic polymers. Thus, dianhydrides, diamines and diacids were prepared that incorporate some of the following elements:

Bulky side substituents (pendent groups)
Combination of *meta/para* substitution
Enlarged monomers
Non planar chemical structures

Polyimides were prepared by conventional condensation methods, particularly by low temperature solution polycondensation and chemical imidation. Polyamides were prepared by direct polyamidation from diamines and diacids using the method of Yamazaki-Higashi (phosphorylation) at about 100°C. All polymers were soluble in organic media, showed high molecular weight, and exhibited good film-forming properties.

Polyimides

The polyimides of this work were prepared from dianhydrides containing three benzene rings. The general formula for them has been depicted in Fig 1. The substituent R may be H, phenyl, nitrophenyl or *tert*-butyl, and the benzene rings are directly joined in a *m*-terphenyl fashion or they are joined through carbonyl bonds, corresponding to an isophthaloyldiphthalic moiety. Most of them are original polymers, prepared from the novel dianhydrides and selected aromatic diamines.

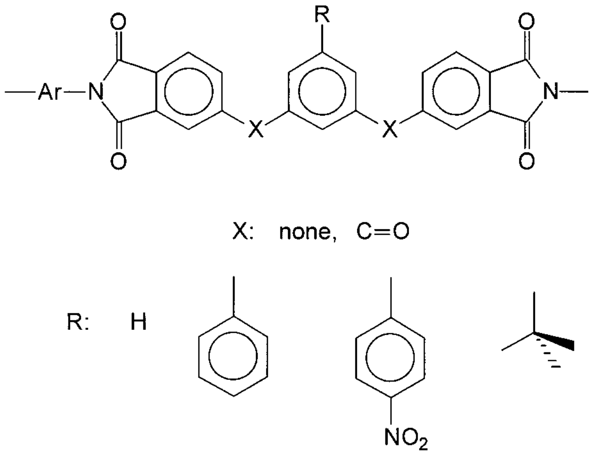


Fig. 1. Chemical structure of novel polyimides.

Polyimides of this family showed glass transition temperatures around 300° C, and fairly good solubility in organic solvents. The good solubility of polyimides from isophthaloyldiphthalic anhydrides is to be mainly attributed to the torsional mobility provided by the carbonyl groups. For the polymers containing *m*-terphenyl moieties, the good solubility should be attributed to the non-planar structure of the anhydride. The presence of pendent groups in both series greatly helps for an improvement of the solubility and free volume.

In dense membranes, the transport of gases is conveniently described by the solution-diffusion mechanism, which involves three steps: 1) solution of the permeant in the polymer, 2) diffusion through the polymer matrix and 3) desorption. Thus, the permeability P of a solid polymer is defined by the product of a diffusion coefficient D and a solubility coefficient S. Hence, the permeate flux J can be correlated with the permeability by

$$J = P\frac{\Delta p}{l}$$

where Δp is the pressure difference and l is the membrane thickness.

The ideal separation factor α, which is an index of the overall selectivity of the polymer, can be expressed in the following terms:

$$\alpha_{A/B} = \frac{P_A}{P_B}$$

Where P_A and P_B are the permeabilities for gases A and B. In Table 1 are listed the gas permeation properties for these polyimides

Furthermore, the diffusion of gases through dense polymer membranes directly depends on the free volume (FV), as it has been established by Fujita[17] and Cohen and Turnbull.[18] The FV can be calculated by using additive contributions combined with experimental measurements of the polymer specific weight, and more recently by methods of computational chemistry. A comparison of the results obtained by both methods for a set of polyimides is presented in Fig. 2.

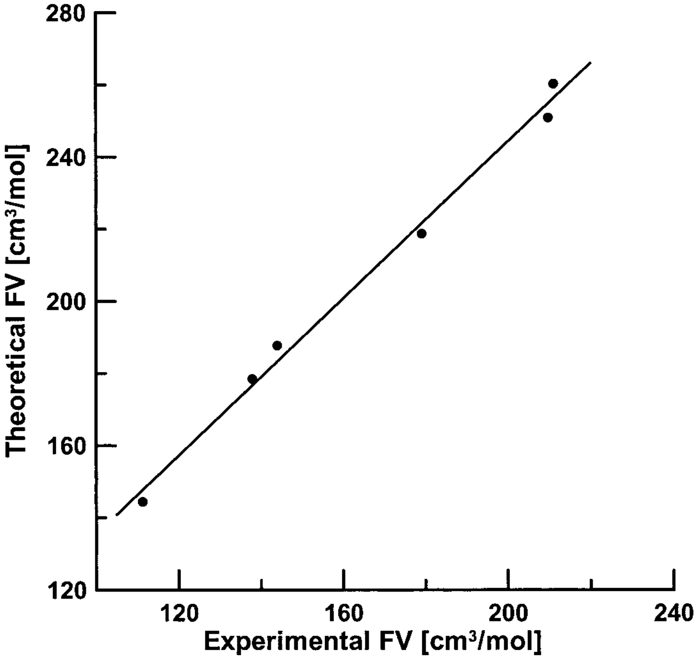


Fig. 2. Plot of experimental FV vs. calculated FV for novel polyimides.

The good correlation observed permits a theoretical treatment of molecular structures, and an *a priori* estimation of some macroscopic properties of condensation polymers specially designed for specific applications. In our case, they were foreseen to be useful barrier materials for gas separation, so that calculations were made of the density of the foreseen polyimides structures by a combination of molecular mechanics and molecular dynamics. The procedure implies the generation of chain conformations by a Monte Carlo method, and the minimization of energy states by iterative calculations that lead to average minimum energy conformations. Polymer chains containing not more than eleven repeating units are visualized as confined in a box of defined size, as it is shown in Fig. 3. for one polyimide containing *tert*-butyl pendent groups.

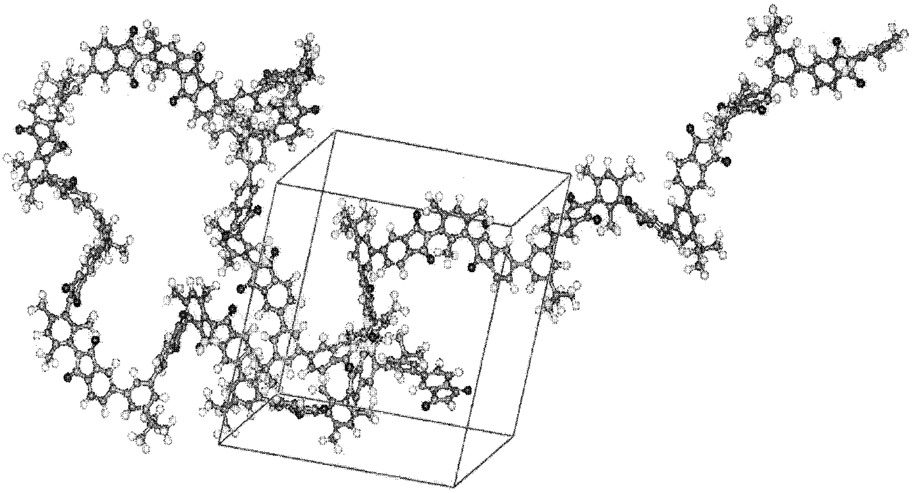


Fig. 3. Periodic cell of a chain of polyimide from TMMPD (trimethyl-*m*-phenylenediamine).

Hence, the theoretical density can be calculated with reasonably acceptable accuracy (s. Fig. 4), even for polymers with a complex structure and strong intermolecular attractive forces as polyimides. At this respect, it is worthy mentioning that, apart from density, extreme-extreme distance or mean square radius can also be calculated, what gives additional information on polymer flexibility.

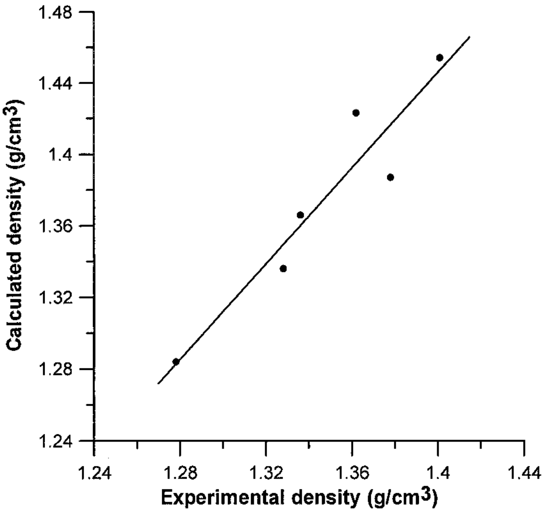


Fig. 4. Plot of measured density vs. calculated density of polyimides.

The theoretical permeabilities agreed fairly well with the experimental permeation measurements, and both coincide on the good permeation properties that could be achieved by using monomers that hinder molecular packing and three dimensional order, and improve solubility and free volume (s Table 1). As a matter of fact, upon comparing the permeability to pure oxygen and nitrogen of some of these novel polyimides with conventional aromatic

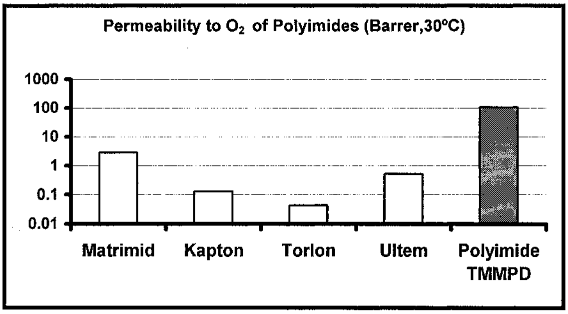
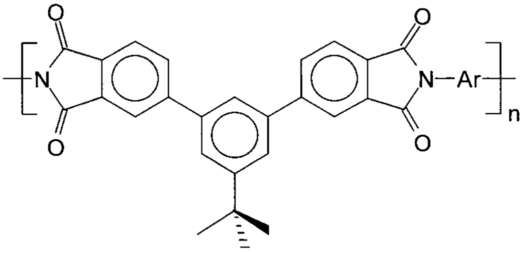


Fig. 5. Comparison of permeability to O_2 for technical polyimides and the experimental polyimide containing TMMPD.

polyimides like Kapton®, or even with thermoplastic polyimides like Ultem® or Matrimid®, a great gain of permeability can be observed, and that without a significant loss of selectivity (s. Fig. 5).

Table 1. Permeation properties of novel polyimides.



	Permeability (Barrer)					Ideal separation factor		
Ar	**He**	**CO_2**	**O_2**	**N_2**	**CH_4**	**He/CH_4**	**CO_2/CH_4**	**O_2/N_2**
6F	115	114	24.2	5.8	5.0	23.0	22.9	4.2
TMMPD	270	600	130	35.1	47.6	5.7	12.6	3.7
IMDDM	130	196	43.1	10.8	14.7	8.8	13.4	4.0
ODA	33	25	5.1	0.97	0.96	34.0	25.6	5.3

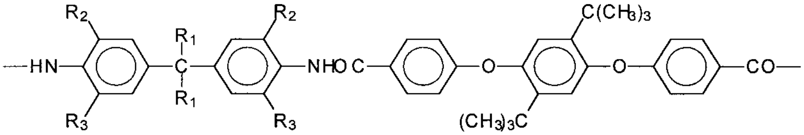
6F: Hexafluoroisopropylidene dianiline.
TMMP: Trimethyl *m*-phenylene diamine.
IMDDM : Methylene bis(3-isopropyl-5-methyl-4-aminobenzene).
ODA: Oxydianiline.

Polyamides

The same strategy was applied to aromatic polyamides. Traditionally, aromatic polyamides have been considered as very efficient barrier materials, with a high selectivity for gas separation, however, the high packing density of conventional wholly aromatic polyamides, such as poly-p-phenylene terephthalamide (PPTA) or poly-m-phenylene isophthalamide (PMIA), provides very small values of gas permeability. Rigid, rod-like polyamides are among the less permeable polymers, showing permeability to oxygen some orders of magnitude lower than that of common glassy polymers. The high density of cohesive energy of polyamides is caused by the strong associative forces through hydrogen bonds, so that most of the chemical modifications outlined to improve the solubility (processability) of aromatic polyamides, are directed to effectively prevent interchain hydrogen bonds, for instance by introducing bulky pendent groups.[19-22]

Chemical modification of the primary structure can provide, also in this case, a considerable improvement of free volume and permeability. For instance, the family of polyamides derived from a monomer specially designed for this application, that is shown in Table 2, exhibited an outstanding permeability to gases, comparable or even higher than that of glassy, engineering thermoplastics, and with an acceptable selectivity to such pairs of technical gases as O_2/N_2, H_2/CH_4 or CO_2/CH_4.

Table 2. Permeation properties of polyamides.



Key	R_1	R_2	R_3	$P(O_2)$	$P(N_2)$	$P(CO_2)$	$P(CH_4)$	$\alpha(O_2/N_2)$	$\alpha(CO_2/CH_4)$
PA1	CH_3	H	H	4.59	0.83	21.52	0.91	5.53	23.64
PA2	CH_3	CH_3	H	2.85	0.48	11.78	0.48	5.93	24.54
PA3	CH_3	CH_3	CH_3	9.32	1.83	43.00	2.04	5.09	21.07
PA4	H	CH_3	$CH(CH_3)_2$	6.25	1.10	25.21	1.20	5.68	21.00
PA5	CF_3	H	H	7.52	1.46	33.58	1.33	5.15	25.24

Theoretical calculations corroborated that the chemical modification can actually help for an efficient improvement of the conformational freedom and free volume. The results are consistent with a gain of permeability that agrees fairly well with experimental measurements. In Fig. 6, the permeability/selectivity relationships of one of them are compared with that of a technical, amorphous polyamide. As it can be observed, gases permeate much faster through polyamides of the family shown in Table 2 than through Trogamid®, which is probably the commercial polyamide that offers higher permeability to gases.

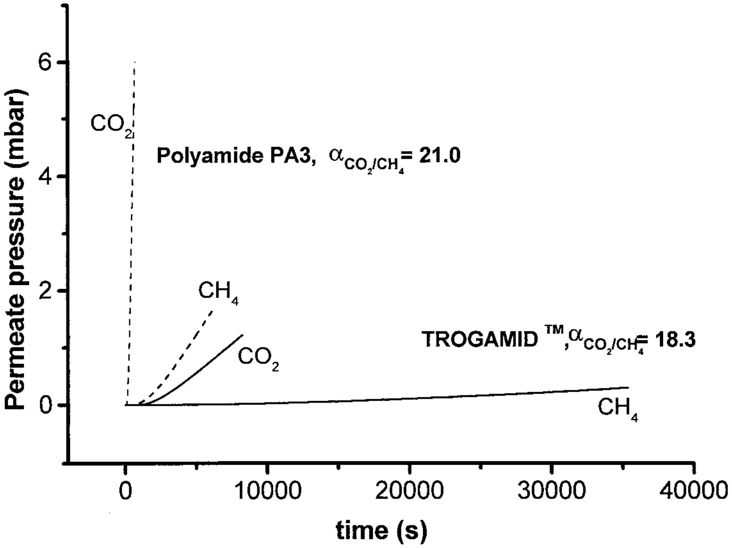


Fig. 6. Permeation curves of Trogamid® and polyamide PA4 for O_2, N_2, CO_2 and CH_4.

Here again, a good agreement between theoretical calculations and experimental measurements of permeability could be observed. (Fig. 7), is quite illustrative at this respect. It was confirmed that there is a direct relationship between calculated FV and experimental values of permeability through aromatic polyamide dense membranes, and that the presence of a growing number and growing size of substituents may substantially improve the FV and the permeability. An additional advantage of these polyamides is their unusually good solubility in organic solvents, so that they could be fabricated into defect-free films, of excellent mechanical properties, by casting from solutions of common solvents, such as chloroform or tetrahydrofuran.

As a conclusion, it can be stated that methods of computational chemistry and molecular modelling, have revealed exceptional potential as a tool to investigate novel chemical compositions for aromatic polymers, more precisely aromatic polyamides and polyimides, that may offer better and better performances as barrier materials for gas separation and purification.

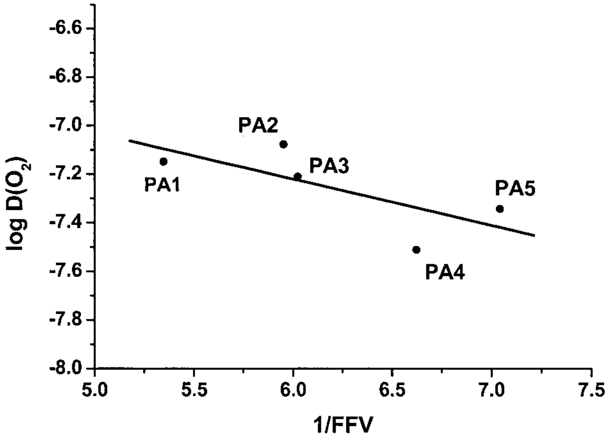


Fig. 7. Plot of diffusion coefficient vs. calculated FFV for polyamides.

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