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The effect of structural isomerism on carbon dioxide sorption and plasticization at the interface of a glassy polymer membrane

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ABSTRACT

Changing a glassy polyimide dianhydride–diamine bond location from *para* to *meta* has been shown experimentally to lead to significant decreases in gas permeabilities. This work is aimed at comparing a fully-atomistic molecular model of a *meta*-linked 6FDA-6FmDA polyimide membrane to its *para*-linked 6FDA-6FpDA isomer using large-scale molecular dynamics simulations (MD). The effects of structural isomerism on the early stages of CO_2 sorption and matrix plasticization are also assessed. Both isomers are close in densities, but the *meta*-chains are more coiled than the *para*-chains, their void-space is slightly smaller and their mobility is lower. The higher resistance of the *meta*-matrix to localized chain motions leads to a better conservation of its cohesion and a reduced volume dilation upon CO_2 entry into the membranes. In agreement with its larger dilating capacity, the gas uptake is always higher in the *para* isomer. The concave behavior of the sorption curves compares favorably with experimental data, except for the highest-pressure system which exhibits a quasi-supercritical behavior for CO_2. However, in all cases, swelling is associated to local relaxations of the matrices rather than to large changes in the structures, while glassy chain mobility remains fairly restricted. Gas mobility is directly correlated to the underlying mobility of the matrices and, as such, is slower in the *meta* than in the *para* isomer.

1. Introduction

Fluorinated polyimides based on the 4,4′-(hexafluoroisopropylidene)diphtalic (6FDA) dianhydride have long been considered for gas separation applications because of their good mechanical, chemical and thermal properties combined with relatively high permeabilities and permselectivities [1,2]. In such glassy dense polymer membranes, small gas transport is described by the sorption–diffusion mechanism [2–4], with gas molecules in an upstream compartment entering the polymer matrix, diffusing across it and desorbing onto a downstream gas compartment. Permeability P_{gas} is then expressed as the product of the average gas solubility coefficient S_{gas} and the average gas diffusion coefficient D_{gas}.

The effect of isomerism on the physical and gas separation properties of such polymers is particularly puzzling. Indeed, the mere fact of changing the dianhydride–diamine bond location from *para* to *meta* is known to significantly decrease P_{gas}, S_{gas} and D_{gas} [5–15]. The *meta*-linked systems consistently have a slightly higher density and a lower fractional free volume (FFV), but also a lower glass-transition temperature T_g than the corresponding *para*-linked materials. As far as CO_2 is concerned, permeabilities are usually ~3–4 times smaller and diffusivities ~2–3 times smaller in the *meta* isomers [5,11–13]. In the specific case of the *meta* 6FDA-6FmDA polyimide (Fig. 1), P_{CO_2} at 10 atm has been reported as being lower by an unusual factor of ~12 at 308 K with respect to its *para* 6FDA-6FpDA isomer, when measured in films cast from methylene chloride and used directly after solvent removal [6,10]. This is mainly due to the *meta* D_{CO_2} being lower by a factor of ~7.5, but it is difficult to explain by simple structural considerations, since the differences are very small between both isomer densities (only about 1%), intersegmental packings and FFV [6,10]. It is well known that such transport parameters can be quite dependent on the processing conditions. Indeed, when the films are quenched from 15 °C above T_g into an ice bath, the difference between both P_{CO_2} falls from a factor of ~12 to ~8 [16]. Providing that the solubilities are close to those of the aforementioned studies, that would amount to a factor of ~5 difference between both D_{CO_2}. The *para*-isomer P_{CO_2} is also affected by the quench temperature, by aging, and by the solvent from which the membranes are cast [16,17], although, to our knowledge, no comparative data are available for the *meta*-isomer. However, once again, these various factors only appear to result in small variations of the densities and FFV [16]. On the other hand, both isomers are known to differ notably in T_g and sub-T_g temperatures,

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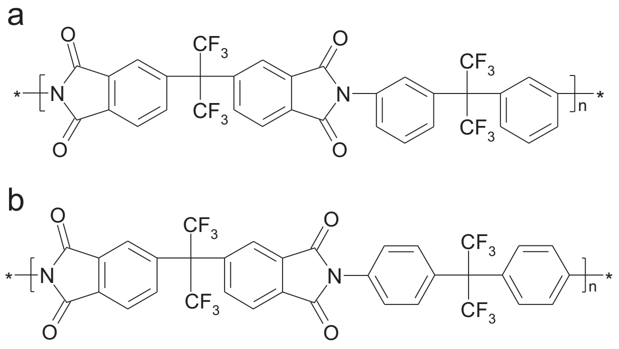

Fig. 1. (a) meta: the 6FDA-6FmDA and (b) para: the 6FDA-6FpDA isomers.

and hence in dynamic properties [10,18]. In particular, 6FDA-6FpDA, which has a T_g at ~593 K, is the only one to display a sub-T_g transition at ~392 K with a marked change in the slope of CO_2 permeability *vs* T curve. In 6FDA-6FmDA, the T_g is at 527 K, with a sub-T_g transition at 422 K which is difficult to distinguish as it appears as a shoulder to the T_g. It has been suggested that sub-T_g transitions are representative of the local chain motions necessary for diffusion, and as such, that the *para* transition at 392 K is associated with enhanced gas transport. It has also been reported that this transition could be separated in two relaxation processes, one at lower T associated with the local motion of the diamine and one at higher T with that of the dianhydride [19]. This could explain the fact that the sub-T_g transitions of both isomers appear to overlap more at higher T [10]. In 6FDA-6FmDA, the asymmetric *meta*-diamine is generally thought to lead to a more restricted local mobility with greater steric resistance to internal rotations. Despite this, experimental evidence suggests that a more efficient packing is obtained [10,14,16,18]. This agrees with the accessible volume and cavity sizes being smaller in the *meta*-isomer [20,21].

Exposure of such glassy matrices to medium or high CO_2 activities leads to penetrant-induced plasticization phenomena including volume-swelling, higher gas permeabilities and hysteretic changes of the matrix, both in experimental studies [14,15,22–29] and in molecular dynamics (MD) simulations [30–35]. The latter include extensive CO_2 sorption and desorption simulations in bulk 6FDA-6FpDA and 6FDA-6FmDA matrices [30,31,36]. Despite the limited time scale available to MD simulations, such bulk models were able to reproduce the plasticization phenomena and the sorption–desorption hysteresis, while the self-diffusion D_{CO_2} coefficients compared very well to experimental evidence for 6FDA-6FpDA [31,36]. The 6FDA-6FmDA model D_{CO_2} was slightly higher than the only experimental value available [6,10], but its activation energy for diffusion was in close agreement with experiment [18].

Bulk molecular models, which are periodic in three dimensions, can only be considered as representative of the membrane cores [30,31,36]. In order to assess the uptake mechanisms at the gas/polymer interface, larger membrane models with explicit surfaces and gas reservoirs have to be used. Based on former work [37–41], we have recently created a ~50,000-atom 6FDA-6FpDA membrane with dimensions of $\sim 95 \times 85 \times 85$ Å^3 [32]. Different CO_2 concentrations were then placed in 100 Å-wide reservoirs on each side of the membrane and the early stages of CO_2 sorption and plasticization were followed over a time scale of up to 20,000 ps. The present work reports similar glassy membrane simulations, but which have been carried out for the *meta* 6FDA-6FmDA isomer. The model setup and the generation procedure are identical to those used earlier [32] and, as such, the only difference is the bond location of the dianhydride (6FDA)–diamine (6FpDA or 6FmDA) basic unit (Fig. 1). Results for the *meta*-isomer membrane are compared here both to those of the corresponding bulk models [30,31,36] and to those of the *para* membrane model [32], in order to address the effects of structural isomerism on early CO_2 sorption and glassy matrix plasticization.

The 6FDA-6FmDA membrane preparation procedure and a discussion about the sizes of such fully-atomistic models are given in Section 2, along with a comparison of both *meta* and *para* isomers. The insertion procedure for the gas and CO_2 sorption, diffusion and induced-plasticization in the *meta*-isomer are discussed in Section 3. All calculations were performed using the *gmq* package [42] in its parallel form on the French GENCI supercomputing centers as well as on the MUST Linux server at the University of Savoie.

2. The 6FDA-6FmDA polyimide model membrane

2.1. Preparation procedure

The 6FDA-6FmDA membrane contained 15 molecules of length 50 monomers (3302 atoms), *i.e.* a total of 49,530 atoms. The forcefields and simulation parameters have already been described in detail elsewhere [21,30–32,36]. Consequently, only the main features will be summarized here.

The polyimide macromolecules were described by a combination of angle-bending, torsional, out-of-plane, excluded-volume Lennard-Jones LJ 12-6 and electrostatic potentials [42]. The last two potentials were applied to all atom pairs separated by more than two bonds on the same chain or belonging to different chains. The bonds were kept rigid [43] in order to use a timestep of 10^{-15} s in the integration algorithm. CO_2 was modeled as a rigid three-site molecule [44] with each atom carrying a partial charge and LJ 12-6 parameters [45]. Lorentz-Berthelot combination rules [46] were used for all unlike-atom LJ interactions, while electrostatic interactions were evaluated using the Ewald summation method [47,48]. Long-range corrections to the van der Waals contributions to the energy and the pressure were added [46]. The temperature T was maintained at 308 K in the production runs by loose-coupling to a heat bath [49] with a constant equal to 0.1 ps. The pressure P was also maintained by loose-coupling with a constant equal to 5 ps [50].

In experimental studies, such nonequilibrium glassy systems depend on the way the membrane is made, and each step of the experimental processing and post-processing procedure is likely to affect the film properties [17,51–61]. For the systems under study here, this is illustrated by the differences between the *para* and *meta* P_{CO_2} being reported as either ~12 or ~8, depending on the processing conditions [6,10,16]. In fully-atomistic molecular models, the most "natural" approach is to remove bulk periodicity in one direction in order to eliminate interactions of the parent chains with their images in that direction and subsequently allow for the membrane to relax naturally [62–66]. Unfortunately, this is only valid for small and flexible chains which have enough mobility to relax on their own from bulk to surface-like chains within the limited MD time scale of 10^{-8}–10^{-9} s. This approach cannot be used here, as it is just simply impossible for glassy high molecular-weight polymers to relax on their own under the MD time scale. Another possibility is to use multiscale approaches with coarse-grained models [65,67–71], but they require intricate parametrization and complicated reverse mapping procedures. It is not expected either to be straightforward as an attempt on BPDA-based polyimide bulks led to surprisingly low densities [72]. The method used here is one of many possible atomistic-scale strategies, which was initially developed [37–41] to loosely mimick the experimental solvent-casting process used by experimentalists, in which a concentrated polymer solution is placed on a flat surface and the solvent is slowly removed *via* evaporation to obtain a polymer film.