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Structure and dynamics of water confined in a polyamide reverse-osmosis membrane: A molecular-simulation study

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ABSTRACT

Molecular dynamics simulations were carried out to investigate both the structural and dynamical properties of water trapped inside a highly cross-linked polyamide RO membrane. The heterogeneous structure of the membrane was characterized through local water density and cavity size distributions. Interactions between water molecules and the polyamide membrane were investigated. Water structure and dynamics were explored and correlated with the heterogeneous distribution of the free volumes inside the membrane.

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1. Introduction

The availability of potable water has become nowadays a global problem due to the continuous growth in water demand not balanced by an adequate recharge. The United Nations predict that by 2025, two-third of the world's population will live in areas of significant water stress, lacking sufficient safe water for drinking, industry or agriculture [1]. Some methods to increase water supply beyond what is available from the hydrological cycle are desalination and water reuse [2]. Membrane separation processes are recognized worldwide as promising tools for addressing the growing concern about water availability in a process intensification strategy, i.e. by developing methods aiming at decreasing raw materials utilization, energy consumption, equipment size, and waste generation [3]. Reverse osmosis (RO) process is particularly well suited for desalination and it is now the leading desalination technique used worldwide. This pressure-driven process makes use of thin film composite membranes made up of three layers: an ultra thin (100–300 nm) and relatively dense polyamide active layer that controls the separation performances of the membrane, an intermediate mesoporous polysulfone layer (30–50 μm) and a polyester backing material (100–200 μm) providing mechanical

strength to the membrane [4]. Currently, the active layer of most RO membranes used for desalination purposes is made from interfacial polymerization between meta-phenylene diamine (MPD) (Fig. 1a) and trimesoyl chloride (TMC) (Fig. 1b), which leads to the formation of a very thin and dense layer of fully aromatic polyamide (Fig. 1c) [4–6]. Despite years of intense research on the transport of water and solutes through RO membranes, the physical phenomena that control transport through the active layer are not yet fully understood, particularly at the atomistic level. The molecular dynamics (MD) technique is a potential method for gaining insights into the polymeric membrane characteristics, including the polymer configuration, free volume, and transport phenomena at a microscopic scale [7–10]. This powerful tool has already been applied extensively to investigate water and ion transport through model porous systems such as e.g. carbon nanotubes [11] or mesoporous and microporous silica [12–15]. However, the limited information about the three-dimensional molecular structure of RO polyamide membranes makes the use of this computational method much more challenging. Indeed, a prerequisite for MD simulations is to have a complete three-dimensional atomic model of the polyamide active layer. That is challenging because the cross-linking of the MPD and TMC monomers is random and the resulting polymer matrix is highly disordered [16]. Consequently, the identification and understanding at a microscopic level of the underlying mechanisms of water and ion transport through RO membranes is proceeding very

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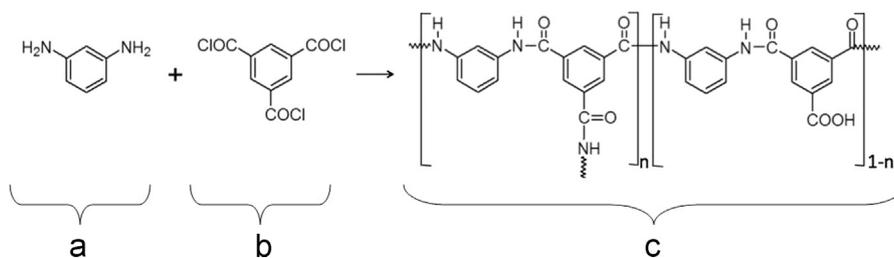


Fig. 1. Illustration of the polymerization of meta-phenyldiamine and benzene-1,3,5-tricarboxylic acid chloride to produce polyamide: (a) component: meta-phenyldiamine (MPD) molecule; (b) component: benzene-1,3,5-tricarboxylic acid chloride (TMC) molecule; (c) product: polyamide with degree of cross-linking n (n has value in between 0 and 1, $n=1$ for fully cross-linked polyamide and $n=0$ for fully linear one).

slowly and only few studies reported on the attempt of building full atomistic models of RO polyamide membranes [16–20]. In the pioneer work of Kotelyanskii et al. [17,18], a single chain with 62 repeat units was generated and further cross-linked artificially by connecting some TMC and MPD fragments. A decade later, Hughes and Gale [20] succeeded in building a fully aromatic linear polyamide composed of 24 chains of 23 repeat units each. Once equilibrated, the un-crosslinked polymer was cross-linked according to the procedure followed by Kotelyanskii et al. In both cases the degree of cross-linking achieved was less than 20%. Harder et al. [19] and Luo et al. [16] used a different methodology, starting from TMC and MPD monomers which were polymerized during the course of the simulation on the basis of a distance criterion between the nitrogen of a free amine group and the carbonyl carbon of a free acyl chloride group. This procedure resulted in a ratio of cross-linked to linear segments of 37:63 [19]. The cross-linking degrees obtained in the above-mentioned computational studies appear, however, quite low with respect to those of actual RO polyamide membranes. Indeed, recent experimental results obtained from either X-ray photoelectron spectrometry (XPS) [6,21–23] or Rutherford backscattering spectrometry (RBS) [24,22] suggest that the percentage of cross-linked repeat units is in the range 60–100%.

In this work we used a previously developed approach [25] to build realistic all-atom models of highly cross-linked RO membranes. In our previous work we discussed on the overall translation dynamics, the hydrogen bonds per water molecule, the water–water interactions and the dielectric permittivity of water [25]. In this work, we accurately investigate the interactions between water molecules and the polyamide membrane, the structure of confined water and the mechanism of water transport.

2. Computational details

2.1. Polyamide membrane construction

As mentioned previously, most current reverse osmosis membranes used for desalination purposes are synthesized from polymerization between TMC and MPD monomers (see Fig. 1). In the first stage of our construction protocol several linear chains of polyamide are packed into a simulation box according to a well-established method combining Monte Carlo (MC) and molecular dynamics (MD) simulations and yielding a fairly relaxed linear (i.e. un-crosslinked) polymer [26]. An additional MD simulation is then performed by randomly adding a given number of MPD monomers inside the free volumes of the un-crosslinked network. At the end of this simulation the polymer chains are cross-linked artificially by bridging free carboxylic acid groups on the polymer chains and some of the added MPD monomers on the basis of a heuristic distance criterion. Proceeding this way the degree of cross-linking can be easily controlled by tuning the number of additional MPD monomers inserted in the simulation. Thus our cross-linking

method is based on two stages (i) construction of a linear polyamide and (ii) cross-linking of the linear structure.

Studying fluid transport across the membrane involves a consideration of the explicit polyamide/water interface. Therefore we began to build a 2D periodic linear polyamide membrane by removing the periodic boundary conditions (PBCs) along the z direction during the construction. The generation of the un-crosslinked polymer was made from the Amorphous Cell package of Material Studio software [27]. The model building uses a modified Markov process with biased conformational probabilities chosen to account for both intramolecular and intermolecular non-bonded interactions [26]. Thus, an orthorhombic cell containing five polymer chains of 50 monomer units each was constructed under 2D periodic boundary conditions. Afterwards, a standard minimization protocol was used to minimize the energy structure via a Polak–Ribiere algorithm. Kotelyanskii reported that the experimental density of a commercial polyamide membrane (FT30) made from MPD and TMC monomers was 1.38 g/cm^3 in the hydrated state with 23 wt% water content at ambient conditions [17]. In our simulations the target density of the un-crosslinked membrane was set at 1.0 g/cm^3 . This lower initial density allows increasing the insertion probability of MPD monomers during the subsequent cross-linking process. The initial configuration was built with two water reservoirs surrounding the polyamide membrane. Details of the MD procedure will be discussed in the computational procedure section (Section 2.4). Fig. S1 of the supporting information (SI) shows the initial configuration of the atomistic model of the un-crosslinked polyamide network confined along the z -axis. It contains 5 identical chains containing 50 repeat units each. The final dimensions of the orthorhombic cell were $L_x=L_y=38.3 \text{ \AA}$ and $L_z=80 \text{ \AA}$.

As shown in Fig. S2 of the SI the construction of the cross-linked polyamide is based on a random insertion of 250 MPD molecules into the un-crosslinked polyamide network. In order to model explicitly the water/polyamide interface we surrounded the un-crosslinked polyamide network by two water reservoirs along the normal z -direction of the interface (Fig. S2). Since water molecules can diffuse into the polymeric matrix and are likely to modify the interactions between MPD monomers and the polyamide chains, we checked that the chemical nature of the molecules inside the external reservoirs did not impact the cross-linking process. That was done by performing another simulation in which the external reservoirs were filled with MPD monomers instead of water molecules. No impact of the chemical nature of the reservoir-filling molecules was observed (actually, only a very small amount of these molecules diffuse into the polyamide network during the cross-linking process). Molecular dynamics simulation of 2 ns was performed in NpT ensemble at $T=300 \text{ K}$ (both the force field and the computational procedure are described below). Afterwards, the Carbon–Nitrogen (C–N) radial distribution function (RDF) was estimated between nitrogen atoms of the added MPD molecules and the carbon atoms of the pending carboxylic acid groups on the polyamide chains. From

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