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1 Molecular simulation of a reverse osmosis polyamide membrane
2 layer. In silico synthesis using different reactant concentration
3 ratios

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12 **Abstract**

13 We use molecular dynamics simulations at the atomistic level to build a model of aromatic
14 polyamide polymer used in reverse osmosis membranes, from a mixture of *m*-phenylene di-
15 amine (MPD) and trimesoyl chloride monomers (TMC). Our purpose is to use different MPD
16 to TMC ratios to reproduce the compositional depth-dependence observed experimentally
17 during interfacial polymerization. MPD to TMC ratios in the range 1:4 to 5:1 have been
18 employed. Reproducibility of the polymerization algorithm is thoroughly studied through
19 the building of several samples under identical conditions. We notice that simulation time
20 of a few microseconds are necessary in order to reach equilibration. We show that the initial
21 monomer ratio has a strong influence onto the final polymer composition and different chem-
22 ical structures have been created. Large differences are seen concerning cross-linking degree
23 and remaining un-reacted groups. Comparison with available experimental data show that
24 samples built using intermediate values of the MDP to TMC ratio closely resemble aromatic
25 polyamide membranes. We conclude that the simulated samples created under different local
26 concentrations can describe properly the chemical heterogeneities observed experimentally
27 in reverse osmosis membranes.

28 Keywords: Molecular dynamics simulations, reverse osmosis membranes, cross-linked
29 aromatic polyamide, membranes chemical heterogeneities, polymerization algorithm

30 1. Introduction

31 Membrane-based treatments and especially reverse osmosis (RO) are extensively used for pure
32 water production and industrial wastewater treatment, due to advantages such as continuity,
33 easy scaling-up, minimum consumption of chemicals and absence of toxic by-products through
34 this process [1, 2]. As a result, RO occupies more than 50% of seawater desalination market [3].
35 It is also implemented for the treatment of effluents in order to achieve water reuse in various in-
36 dustrial fields, such as plating industry [4], textile industry [5] or sugar and distillery industry [6].
37 Its broad applicability in industrial wastewater treatment includes the removal of trace levels of
38 micro pollutants, such as pharmaceutical compounds [7, 8] and pesticide residuals [9, 10, 11, 12].

39 RO membranes are thin film composite materials and typically consist of a thin layer of
40 cross-linked aromatic polyamide (APA), with a thickness of the order of 150 nm, a microporous
41 polysulfone (PSf) or polyethersulfone (PES) support ($\approx 20\text{-}50 \mu\text{m}$) and a polyester backing
42 fabric ($\approx 100 \mu\text{m}$). The active layer, *e.g.* the separating region of the membrane, is the APA
43 layer. It is obtained using interfacial polymerization between *m*-phenylene diamine (MPD) and
44 trimesoyl chloride (TMC) monomers. In commercial membranes manufacturing, the micropo-
45 rous support [13] is impregnated with an aqueous solution of MPD monomers and placed in
46 contact with an organic TMC solution. Several groups also succeeded in obtaining *free-standing*
47 membranes where polymerization takes place directly at the aqueous/organic solvent interface.
48 In both cases, chemical reactions occur as MPD monomers dissolve into the organic phase. The
49 process is thus controlled by solubility and diffusion of MPD monomers into the latter phase. As
50 polymerization takes place, the medium changes drastically with the formation of the membrane
51 and the process becomes even more complex. As presented in a very recent review by Habib and
52 Weinman [14], many parameters can influence the synthesis process and the final properties of
53 the membrane. The presence and nature of a supporting layer, MPD and TMC concentrations,
54 reaction time, temperature, additives are amongst the most important parameters. Chai and
55 Krantz [15] demonstrated that for very small TMC concentrations, the interfacial polymeriza-
56 tion is controlled by species diffusion in the organic layer, while for higher TMC concentrations
57 appropriate to commercial practice, the process is controlled by MPD diffusion in the interfacial
58 polymerization film layer. Dutta *et al.* [16] noticed that the diffusivity of MPD monomer from

59 the aqueous to the organic phase is the important factor regarding the uniform composition
60 and morphology of the polymer formed. Excess of one of the monomers may lead to an inho-
61 mogeneous concentration of carboxylic group or amine group along the membrane thickness.
62 Khorshidi [17] also demonstrated the importance of the MPD/TMC ratio on the final aspect
63 of the membrane, obtaining thin polyamide layer with nodular structures or looser APA layer
64 with a ridge-and-valley structure. By changing the MPD/TMC ratio, Xu *et al.* [18] were able
65 to optimize both water permeance and sodium chloride rejection. From a fundamental point of
66 view, there is a need for a deeper understanding of the relationship between synthesis protocol
67 and membrane structure and between membrane structure and separation performances. Molec-
68 ular simulation tools have been increasingly employed in recent years to elucidate and quantify
69 atomistic scale mechanisms and processes in functional membrane materials [19, 20]. However,
70 because of time and length scales limitations, molecular simulations must be used with caution
71 to screen the influence of various input parameters. *In silico* synthesis of a realistic active APA
72 layer that can reproduce specific experimental properties is, in itself, a challenging task.

73 Different strategies have been set-up to build APA molecular models. Some groups start with
74 linear chains made from MPD and TMC monomers which are further cross-linked by adding
75 and connecting MPD monomers with free acyl groups [21, 22, 23, 24, 25, 26]. Others directly
76 connect a set of MPD and TMC monomers [27, 28, 29, 30] randomly placed in the simulation
77 box. Some groups also take advantage of a coarse-grained representation of the monomers and
78 of their reaction products to speed up the process and study the kinetics at sight during the
79 membrane formation [31, 32, 33]. In some specific cases, atomic scale membranes can be recre-
80 ated from the final coarse-grained representation [33].

81 The majority of these researches focused on methodological aspects of membrane building
82 through molecular simulation [21, 31, 30], water and salt localizations and diffusion mecha-
83 nisms inside the membrane [21, 22, 27, 23, 26, 34, 28, 35, 36], organic molecules diffusion and
84 foulant model interactions with the APA layer [24, 25, 29, 37, 38, 39, 40]. In most cases, a
85 single molecular simulation box or a few replica are built. The initial conditions are strongly
86 inspired by macroscopic properties given for the FT30 active layer, *i.e.* an hydrated density of
87 1.38 g/cm^3 and a water content of 23 w% [21] corresponding to a dry density of 1.06 g/cm^3 .
88 These data have been discussed by Zhang *et al.* [41]. The authors measured a different water
89 content and consequently a different dry membrane density, around 1.24 g/cm^3 . Also, for most
90 of the contributions presented above, simulation boxes are equilibrated for a few tens of ns.

91 Using large scale molecular simulations, Muscatello *et al.* [33] employed a procedure that mimics
92 experimental interfacial polymerization of TMC and MPD monomers. They studied membrane
93 formation using three different MPD to TMC ratio: 1:1, 3:2 and 3:1. They observed that inter-
94 facial polymerization reaction is self-limited and that simulated membranes display a thickness
95 of 5–10 nm. However, no systematic variations of carboxylic and amine group fractions are
96 observed with the initial monomer concentration ratio. To our knowledge, Suzuki *et al.* [42]
97 realized the first systematic study on APA film heterogeneity. They applied an hybrid Monte
98 Carlo/Molecular Dynamics approach to build four different boxes with MPD/TMC ratios 1:4,
99 1:1, 3:2 and 4:1. Systems with different chemical structures are thus obtained. However, little
100 information is given in terms of structural information or macroscopic properties. In this work,
101 we assume that the compositional depth-dependence observed by several authors [16, 17, 18] is
102 caused by different local MPD/TMC concentrations during the reaction steps. Our purpose is
103 to build several samples starting from different MPD/TMC ratios, to investigate their influence
104 on the chemical structure, local and macroscopic properties and finally relate those data to real
105 systems.

106 The article is organized as follows. In section 2, we present the methodology used, the
107 systems studied and a new set of chemical descriptors to analyze our samples. In section 3, we
108 validate the methodology and give a detailed description of our samples. In section 4, we discuss
109 the relationship between simulated and real systems. Section 5 contains concluding remarks.

110 2. Methodology

111 2.1. Molecular simulation tools

112 The choice of the force field (FF), which describes physical interactions between particles, is
113 crucial if realistic behavior and quantitative data are expected. Many different FF have been
114 used to study APA membranes including CVFF [43], CHARMM [44], AMBER [45], GAFF [46]
115 and OPLS-AA [47] force fields. As mentioned by Ridgway *et al.* [20], similar behaviors have
116 been reported with these different models. To our knowledge, the work by Liyana *et al.* [30] is
117 the only one where different force fields were compared using the same building methodology:
118 for the three force fields studied, TraPPE [48], OPLS-AA, and GAFF, the average hydrated
119 densities of the membranes are in very good agreement.

120 In this work, we used the OPLS-AA force field [47]. The OPLS-AA parameters were opti-

121 mized to fit experimental properties of liquids, such as density and heat of vaporization. Free
122 energy of hydration of organic molecules using the TIP4P model [49, 50] is also an important
123 component of the optimization process. This makes it a good candidate for the study of APA
124 membranes, in presence of water (TIP4P model) and other organic components.

125 Molecular simulations were realized using the Lammmps Molecular Dynamics Simulator (Lammmps,
126 August 2018 version) [51, 52]. Initial box configurations, as well as input files for Lammmps sim-
127 ulations were created using our local molecular dynamics simulation package, Newton [53]. We
128 wrote a set of scripts and codes to control the polymerization steps, based on Lammmps function-
129 alities (see the simulated polymerization section 2.2 for details).

130 During molecular dynamics simulations, a Lorentz-Berthelot combining rule is used for
131 Lennard-Jones interactions between unlike particles with a cut-off distance of 10 Å and tail cor-
132 rections. Long-range electrostatic interactions were calculated with the particle-particle particle-
133 mesh Ewald solver [54], with a 10 Å real space cut-off distance and a reciprocal space relative
134 accuracy of 10^{-4} . The equations of motion are based on Nosé-Hoover style Hamiltonian with
135 a time step of 1 fs [55]. Thermostat and barostat use a damping factor of 0.1 and 1 ps respec-
136 tively. Standard (hydrostatic) and iso-stress NPT simulations were realized using the Lammmps
137 keywords `iso` and `aniso`, respectively. Finally, energy minimization steps used the conjugate
138 gradient algorithm with a stopping tolerance for energy equal to 10^{-4} and a stopping tolerance
139 for forces of 10^{-6} force units.

140 2.2. Simulated polymerization

141 The simulated polymerization strategy implemented in this work is based on the work by Harder
142 *et al.* [27], with minor adjustments presented here. A schematic of the simulated polymerization
143 process is given in Fig. 1. The different steps are commented out below. During step 1, a
144 set of n MPD monomers, m TMC monomers and one dimer (to simplify force field handling in
145 Lammmps) are randomly placed within a simulation box at the target density of 1.38 g/cm^3 so that
146 monomers stay close enough to each other to facilitate amide bond creation. Following several
147 authors [23, 25, 36], the acyl groups of TMC monomers are hydrolyzed, hence no chloride ions
148 are considered; moreover, TMC monomers are modeled in protonated form [56, 57, 20]. Step 2,
149 the initial system is homogenized during a 30 ns molecular dynamics run in the NVT ensemble
150 at 298.15 K. During step 3, a loop including 150 polymerization attempts is started. Our script
151 `paamaker` searches the smallest distance between the carbon atom of a carboxylic group and

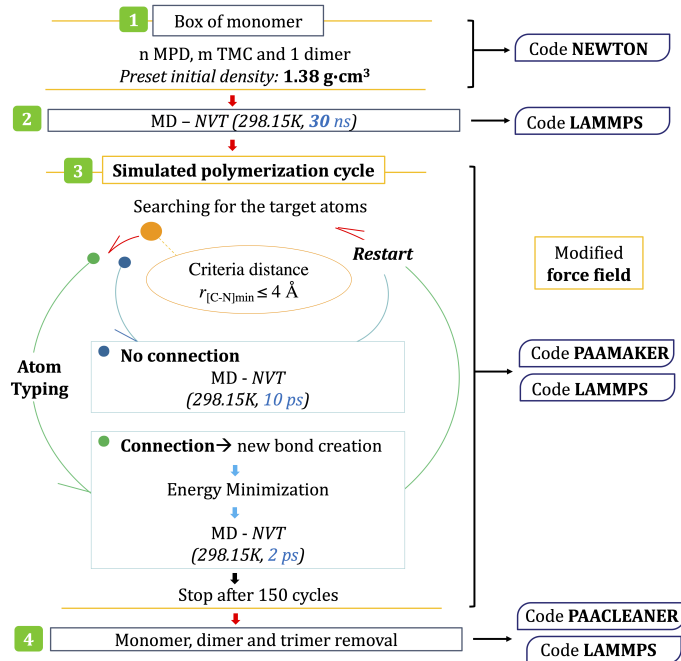


Figure 1: Simulated polymerization algorithm

152 the nitrogen atom of an amine group. If no such pair is found at a distance smaller than 4 Å,
 153 the system is run in the NVT ensemble during 10 ps at 298.15 K. If a pair is found, `paamaker`
 154 creates a command file for the Lammmps code to form an amide bond by changing atom types,
 155 bond, bend, dihedral and improper lists. The amide bond formation is followed by an energy
 156 minimization step and by a 2 ps run in the NVT ensemble at 298.15 K using Lammmps code.
 157 Considering the initial number of MPD and TMC monomers, the amide bond number reaches a
 158 plateau before 125 cycles [58]. Finally, during step 4, remaining monomers, dimers and trimers
 159 are removed from the simulation box. The polymer is then relaxed and equilibrated using
 160 simulations in different statistical ensembles, as described in section 3.1.

161 During the polymerization process, it was necessary to modify the force field associated with
 162 the remaining hydrogen atom on the amide function. OPLS-AA model for this hydrogen atom
 163 type is a single positive partial charge. It happened sometimes during the creation of an amide
 164 bond that a negative partial charge was brought about too close to the hydrogen atom, creating
 165 an infinitely large electrostatic interaction energy, not handled by floating-point arithmetic. To
 166 avoid this, OPLS-AA Lennard-Jones parameters from aromatic hydrogen atom types were used
 167 for these hydrogen atoms. The repulsion term was then strong enough to avoid the collapse of
 168 the partial charges and divergence of the electrostatic energy. Once the polymerization steps
 169 ended, the original OPLS-AA force field was recovered. It is worth mentioning here that simu-

lated polymerization algorithms are a crude approximation of the real ongoing processes during interfacial polymerization. The simulated structures have to be compared with experimental data in order to be validated, as will be done in the following sections.

2.3. Description of the studied systems

Interfacial polymerization is realized using an aqueous solution of MPD and an organic solution of TMC. As TMC monomers have a very low solubility in water, the chemical reactions take place in the organic phase as MPD monomers diffuse into it. Typical MPD concentrations in the aqueous phase range from 0.01 to 20.0 w/v % and for TMC in organic phase (mostly *n*-hexane) from 0.001 to 10 w/v % [18, 59, 14]. Depending on specific experimental conditions, authors report MPD to TMC concentration ratios between 1 and 200 [18, 59]. However, MPD concentration in the organic phase can not be easily defined from the knowledge of its concentration in the aqueous phase. It depends on many other parameters such as the monomer partition coefficient between aqueous and organic phases, the diffusion coefficient of MPD in both phases and at the interface or even the presence of additives like triethylamine (TEA). However, simulated polymerization is done without solvent and the most relevant quantity becomes the MPD/TMC monomer ratio. In our simulations, this ratio is expected to represent the local concentration at the chemical reaction location. The ratio used in this study ranges from 1:4 to 5:1 including 1:1 and 3:2 values. The 1:1 ratio corresponds to the stoichiometry of a fully linear chain, while the ratio 3:2 corresponds to a perfectly reticulated APA network. Extreme cases are accounted for using a large excess of TMC monomers (1:4 ratio) or MPD monomers (5:1). Overall, 15 different ratios are used: 0.25, 0.5, 0.75, 1.0, 1.2, 1.3, 1.5, 1.8, 1.9, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0 with an average number of monomers per simulation box of 170. In order to test the repeatability of the simulated polymerization process for these boxes, we created eleven repetition boxes for MPD/TMC ratio of 0.25, 1.5 and 5.0 (see section 3.2 for analysis). This brings to 46 the total number of simulation boxes studied here.

2.4. Chemical descriptors

In order to quantify the chemical structure of our samples and compare with experimental data, we introduce several chemical descriptors related to APA structure already described in [60].

Due to the presence of a 3-functional monomer (*e.g.* TMC), APA polymer exhibits extensive branching and cross-linking leading to a random amorphous structure. It is often represented

200 as a mixture of two structural units, a linear one and a cross-linked one. These two units are
 201 depicted in Fig. 2. The cross-linked unit X appears from the reaction between a TMC monomer
 202 and 3 MPD monomers. It is the building block of fully reticulated polymers. Its chemical
 203 formula (assuming hydrolyzed and protonated structure) is $C_{18}O_3N_3H_{12}$. The linear unit Y is
 the building block of fully linear polymers. Its chemical formula is $C_{15}O_4N_2H_{10}$. The cross-

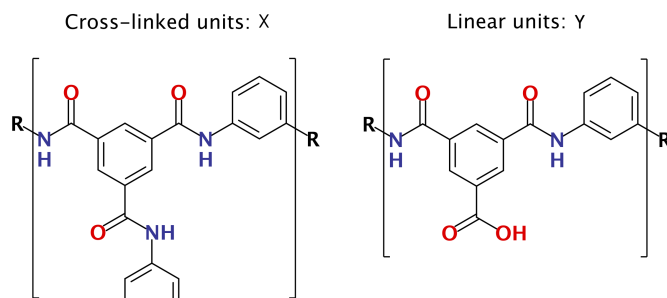


Figure 2: Linear and cross-linked structural units found in APA reticulated polymers.

204

205 linking degree, χ , represents the ratio of cross-linked units to the total number of units. It is
 206 a quantity that can vary between 0 and 1. It can be expressed as a function of the oxygen to
 207 nitrogen ratio, O/N:

$$\chi = \frac{X}{X + Y} = \frac{6}{1 + O/N} - 2. \quad (1)$$

208

For a fully linear structure, the O/N ratio is 2 and the cross-linking degree is zero, whereas
 209 for a fully cross-linked structure, the O/N ratio is 1 and χ goes to 1. Elemental analysis can
 210 thus provide important informations about the chemical structure of the synthesized polymer.
 211 However, this descriptor suffers from several drawbacks. First, it is possible to obtain structures
 212 with identical O/N ratio (hence same cross-linking degree χ) but with different oxygen and
 213 nitrogen atom fractions. Second, it is assumed that real APA is fully described by units X and
 214 Y only. This doesn't account for chain ends as *e.g.* a terminal TMC group with 2 acyl functions
 215 or a MPD group with an amine group, and may not be able to describe quantitatively structures
 216 with a non negligible amount of such units. In such cases, O/N ratio can have values below one
 217 and above two, leading to negative or larger than one cross-linking degree values.

218

This led us to introduce a new set of four different chemical units, shown in Fig. 3. The units
 219 can be seen as *extracted* from a complete APA structure, composed of linear and cross-linked
 220 regions plus unreacted amine and carboxylic groups. Unit a corresponds to a TMC monomer

221 with each carboxylic group replaced by an acyl group. Its chemical formula is $C_9O_3H_3$. Unit b
 222 corresponds to a MPD monomer with each amine group replaced by an NH group. Its chemical
 223 formula is $C_6N_2H_6$. Unit c corresponds to a terminal hydroxyl attached to a TMC unit a forming
 224 one carboxylic group having not reacted. Finally, group d corresponds to terminal hydrogen,
 225 attached to a MPD unit b , forming one amine group having not reacted. The acyl groups of
 226 TMC units a which are not connected with hydroxyl terminals, form an amide bond with a NH
 group of MPD units b .

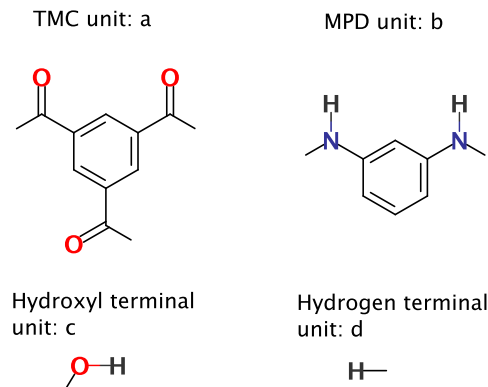


Figure 3: The four chemical units proposed to describe APA polymers.

227

228 The total number of atom types in the system can be expressed as a function of the different
 229 unit number:

$$\begin{aligned}
 C &= 9a + 6b \\
 O &= 3a + c \\
 N &= 2b
 \end{aligned}
 \tag{2}$$

230 The number of hydrogen terminal units is obtained considering that the $C=O$ terminals of
 231 TMC units which are not connected with hydroxyl terminal unit ($3a - c$) form the amide linkage
 232 with NH terminals in MPD units not connected with hydrogen terminal units ($2b - d$):

$$3a - c = 2b - d \tag{3}$$

233 We now define the connection degree of acyl groups, f_{ac} as the fraction of amide groups to the

234 sum of amide groups and remaining carboxylic groups after reaction. Using equations 2 and 3,
 235 this descriptor can be expressed as a function of C, N and O elements:

$$f_{ac} = \frac{n_{\text{CONH}}}{n_{\text{COOH}} + n_{\text{CONH}}} = \frac{3a - c}{3a} = 2 - \frac{3O}{C - 3N} \quad (4)$$

236 This quantity goes to 1 when all acyl groups have reacted to form an amide bond. We proceed
 237 the same way for the connection degree of amine groups, f_{am} :

$$f_{am} = \frac{n_{\text{CONH}}}{n_{\text{NH}_2} + n_{\text{CONH}}} = \frac{2b - d}{2b} = \frac{2C - 3O}{3N} - 2 \quad (5)$$

238 Finally, the ratio of aromatic rings originating from MPD monomers (*i.e.* with up to 2 amide
 239 bonds) to aromatic rings originating from TMC monomers (*i.e.* with up to 3 amide bonds) in
 240 the final structure is simply given by the equation:

$$r_{m:t} = \frac{b}{a} = \frac{9N}{2C - 6N}, \quad (6)$$

241 a quantity called the final MPD/TMC ratio.

242 From molecular simulations, it is a trivial task to obtain elemental composition. We devel-
 243 opped the `paastats` tool to do a topological analysis of our samples in order to identify typical
 244 structures like MPD units connected to one or two TMC units and so on; we obtained this
 245 information from our simulated samples to check the validity of equations 4, 5 and 6.

246 In the following, we will compare simulation with experimental compositions. Because hydro-
 247 gen is not quantifiable by XPS, hydrogen atoms were not accounted for in these computations.
 248 Thus, the nitrogen atom fraction is defined as $x_N = N/(C + O + N)$, the oxygen atom fraction
 249 is $x_O = O/(C + O + N)$ and $x_C = 1 - x_O - x_N$.

250 3. Results

251 3.1. Polymer matrix relaxation and equilibration

252 At the end of the polymerization steps, the simulation boxes are not equilibrated. Although each
 253 amide bond creation was followed by energy minimization and short relaxation using an NVT
 254 run, some residual mechanical constraints remain. For example, the diagonal pressure tensor
 255 elements for the box with an initial MPD/TMC ratio $r_{m:t}^0 = 1.2$ are very different, ranging from

256 -250 to 7200 bars. In order to relax these mechanical constraints, a few cycles involving NVT
 257 followed by NPT simulations are realized. During NVT simulations, the differences between
 258 the pressure tensor elements decrease while the average pressure remains roughly the same.
 259 During NPT simulations, the average pressure converges to the target pressure (1 bar) while
 260 the box volume changes. After such a few cycles (*e.g.* 2 cycles and 250 ns for the system with
 261 $r_{m:t}^0 = 1.2$) small differences still exist between pressure tensor components: $P_{xx} = 215 \pm 50$,
 262 $P_{yy} = -58 \pm 100$, $P_{zz} = -132 \pm 50$. At this stage, a long simulation in the NPT iso-stress
 263 ensemble is realized in order to relax all pressure tensor diagonal elements independently. The
 264 time evolution of the potential energy E_p , the density ρ and box lengths in x , y and z directions,
 265 L_i , for system $r_{m:t}^0 = 1.2$ are shown versus simulation time t in Fig. 4.

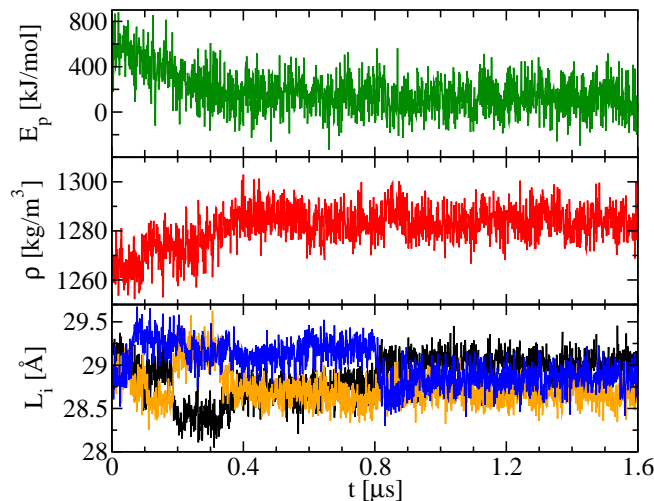


Figure 4: Long time relaxation of the APA box with initial $r_{m:t}^0 = 1.2$. Potential energy E_p , density ρ and box lengths in x , y and z directions, L_i , are shown versus simulation time t . Initial time corresponds to the end of the NVT/NPT cycles. Note that unit of time is in μs .

266 As can be seen in Fig. 4, the complete relaxation of the simulation box requires quite a long
 267 simulation time *after* the end of the NVT/NPT cycles. Over 500 ns are required for the potential
 268 energy and the density to converge. The situation is even worse for box length values where
 269 abrupt changes, accompanying in most cases molecular conformational changes, are observed.
 270 For the system presented here, box length values remain constant after 0.8 μs , although abrupt
 271 box length variations are observed up to 3 μs in some boxes. Therefore, in this study, simulation
 272 boxes were equilibrated for simulation time as long as 5 μs .

273 **3.2. Repeatability analysis**

274 The simulated polymerization used is a random process. Therefore, it is expected that sim-
 275 ulation boxes created under identical conditions will lead to polymers with slightly different
 276 structures. This is worsened by the limited number of monomers used. Before proceeding to
 277 the study of the influence of the initial MPD/TMC ratio, $r_{m:t}^0$, it is important to check that our
 278 polymer construction process gives equivalent samples under identical conditions.

279 We created eleven repetition boxes for each of the following $r_{m:t}^0$ values: 0.25, 1.5, 5.0. Ideally,
 280 several repetition boxes should be done for each set of initial condition. However, large compu-
 281 tation times impose to reduce the number of boxes studied. At the end of the polymerization
 282 process, and after removal of unreacted monomers, dimers and trimers, we did an elemental
 283 analysis of the samples in terms of carbon, oxygen and nitrogen atoms from which different
 284 descriptors can be obtained. Fig. 5 shows the final oxygen to nitrogen ratio, O/N, oxygen atom
 285 concentration, x_O and MPD to TMC ratio, $r_{m:t}$, for the 11 repetition boxes and for each $r_{m:t}^0$.
 286 This set of properties is not fully exhaustive, though we believe it is representative of the chem-
 ical nature of the samples. It is clear from Fig. 5 that simulated polymerization is sensitive

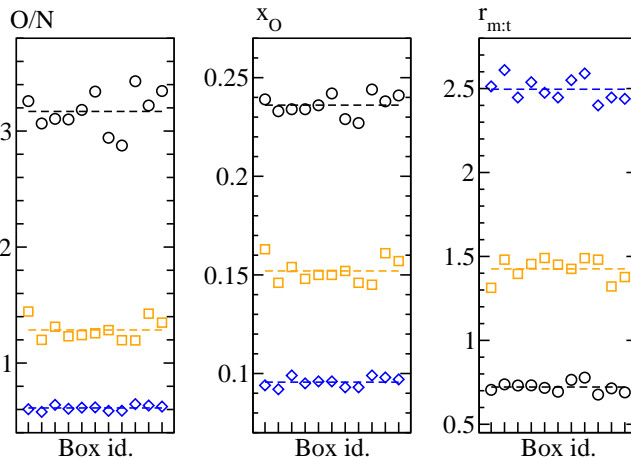


Figure 5: Final oxygen to nitrogen ratio, O/N, oxygen atom concentration, x_O and MPD to TMC ratio, $r_{m:t}$, for the 11 repetition boxes and the different initial MPD/TMC ratio, $r_{m:t}^0 = 0.25$ (circle), 1.5 (square) , 5.0 (diamond). Symbols represent data for each repetition box. Dashed lines are averages over all repetition boxes for a given property and $r_{m:t}^0$.

287
 288 to initial conditions. Boxes obtained with different $r_{m:t}^0$ can be clearly distinguished from each
 289 other using O/N ratio, x_O and $r_{m:t}$. For a given $r_{m:t}^0$, repetition boxes are slightly different and
 290 fluctuations are observed for computed descriptors. However, the standard deviations are small

291 compared with average values and we can assume that each box is representative of the system.

292 3.3. Systems main trends with $r_{m:t}^0$

293 In this section we focus on the main trends observed in our samples for a limited number of
 294 $r_{m:t}^0$ values. Several structural data are given in table 1, averaged over the 11 repetition boxes:
 295 N_{mol} , the number of molecules per box; N_{mono} , the number of monomers per molecule; N_{ce} , the
 296 number of chain ends per molecule, computed from the number of MPD units b with one amine
 297 group plus the number of TMC units a with two carboxylic acid groups; N_{cl} , the number of
 298 TMC cross-linked units per molecule, computed from the number of TMC units a connected to
 299 three MPD units b with no amine group; the molecular size distribution (expressed in number
 of atoms per molecule). It is clear from table 1 that two different trends are observed. Samples

$r_{m:t}^0$	0.25	1.5	5.0
$\langle N_{mol} \rangle_b$	10.9 ± 0.6	5.6 ± 0.6	21.8 ± 0.7
$\langle N_{mono} \rangle_b$	6.0 ± 0.2	25.0 ± 3.0	6.4 ± 0.2
$\langle N_{ce} \rangle_b$	2.05 ± 0.02	6.3 ± 0.8	3.72 ± 0.06
$\langle N_{cl} \rangle_b$	0.07 ± 0.02	1.9 ± 0.4	0.03 ± 0.01
Size distribution (atoms)			
0-200	1	0.62	0.97
200-500	0	0.193	0.03
500-2000	0	0.187	0

Table 1: Structural characteristics of systems built using different initial MPD/TMC ratios, $r_{m:t}^0 = 0.25, 1.5$ and 5.0 . $\langle \rangle_b$ indicates averages over repetition boxes. See text for definition of the different quantities.

300

301 synthesized with extreme $r_{m:t}^0$ values (*i.e.* $r_{m:t}^0 = 0.25$ and $r_{m:t}^0 = 5.0$) are mainly made of small
 302 oligomers. The distribution of molecular sizes is centered below 200 atoms per molecule. The
 303 average number of molecules in the simulation box is large. For $r_{m:t}^0 = 0.25$, the average number
 304 of chain ends per molecule is of the order of 2 with almost no TMC monomer fully connected
 305 to MPD monomers, meaning chains are almost linear oligomers ending with TMC groups. For
 306 $r_{m:t}^0 = 5.0$, the number of chain ends is close to 4 and the total number of monomers is close to 6.
 307 This indicates the creation of short chains with 4 MPD terminal groups. The formation of small
 308 oligomers is also observed for other $r_{m:t}^0$ values. Visual inspection of simulation boxes shows
 309 that for extreme MPD/TMC ratios, some molecules don't span over the entire box. In such

310 cases, the system may not behave like a fully connected membrane, as expected in real systems.
 311 On the other hand, synthesized systems with intermediate value $r_{m:t}^0 = 1.5$ have a different
 312 structure. They contain a smaller number of molecules per box, meaning that polymerization
 313 went further than for $r_{m:t}^0 = 0.25$ and $r_{m:t}^0 = 5.0$. The size distribution spreads up to 2000
 314 atoms per molecule. The number of fully cross-linked sites is larger, indicating a more complex
 315 molecular shape. Synthesized systems with $r_{m:t}^0$ values in the range 1.1-1.9 do contain “infinite
 316 clusters”. This region is roughly indicated on Figs. 6 and 10.

317 3.4. Chemical structure analysis

318 In this section, we study the influence of the initial MPD/TMC ratio on the final chemical
 319 structure of our samples. Chemical data are presented using oxygen *versus* nitrogen atom
 320 plots [61]. Fig. 6 represents such an O/N map obtained from elementary compositions of our
 samples. The region inside the dashed-red line represents all possible APA compositions (see

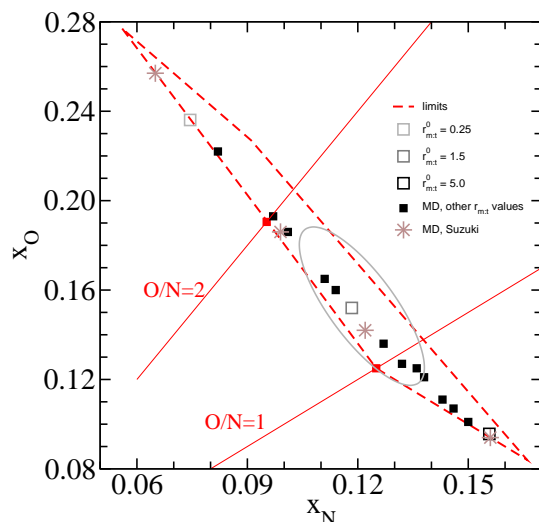


Figure 6: Elemental composition of simulated samples from this work and from Suzuki *et al.* [42]. Data from Suzuki correspond to simulations with $r_{m:t}^0 = 0.25$ (upper left value), 1.0, 1.5 and $r_{m:t}^0 = 4.0$ (lower right value). The region inside the dashed-red lines represents all possible compositions for APA molecules. The region inside the grey ellipse contains simulation boxes with “infinite clusters”. The two red square points indicate the O/N coordinates of a fully linear chain ($x_N \approx 0.095$) and a fully cross-linked APA molecule ($x_N \approx 0.125$). The two thin red lines represent O/N ratio of 1 and 2.

321

322 Supplementary Information section 1 to see how these limits were obtained). Therefore, any
 323 point away from this region may be questionable. The two red square points indicate the O/N
 324 coordinates of a fully linear chain ($x_N \approx 0.095$, O/N=2) and a fully cross-linked APA molecule
 325 ($x_N \approx 0.125$, O/N=1). Both are hypothetical structures that cannot be found in real systems.

326 The two red thin lines are values where O/N ratio are equal to 1 and 2, indicating the region
 327 where the cross-linking degree is defined ($0 < \chi < 1$ thus from equation 1, we have $1 < O/N < 2$).
 328 Obviously, our simulation data fall inside the dashed red line: The algorithm only allows the
 329 formation of APA and the final elemental composition is perfectly known. Statistical error
 330 (SE) was computed from the different repetition boxes for $r_{m:t}^0 = 0.25, 1.5$ and 5.0 . The SE
 331 on composition is smaller than the symbol size (large squares. See Supplementary Information
 332 section 2 for SE data). From the upper left point to the lower right point, simulation points
 333 correspond to boxes with increasing $r_{m:t}^0$ value, from 0.25 to 5.0. Along this line, we observe that
 334 the oxygen content decreases almost linearly with the nitrogen content. Our data are compared
 335 here with the data from Suzuki *et al.* [42]. From upper left to lower right of the graph, their data
 336 correspond to simulations with $r_{m:t}^0 = 0.25, 1.0, 1.5$ and 4.0 . Considering the random nature of
 337 the simulation process, we conclude that the two simulation sets are in good agreement.

338 Fig. 7 shows O/N maps of our samples on which is superimposed as a color map the value of
 339 different descriptors $r_{m:t}$, χ , f_{ac} and f_{am} computed from elemental composition and equations 1,
 4–6. Fig. 7a shows the evolution of the final monomer ratio, $r_{m:t}$. As $r_{m:t}^0$ values increase

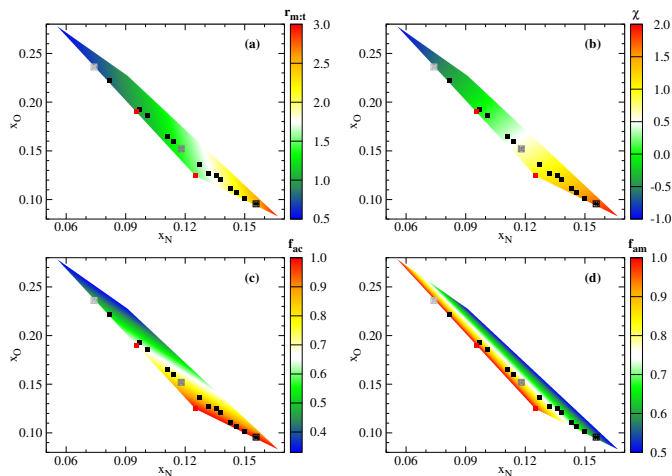


Figure 7: O/N map with chemical structure descriptors $r_{m:t}$, χ , f_{ac} and f_{am} of simulated APA polymers. The color map is plotted for all possible compositions of APA molecules. The two red square points indicate the O/N coordinates of a fully linear chain ($x_N \approx 0.095$) and a fully cross-linked APA molecule ($x_N \approx 0.125$). Open square and black square symbols: see legend Fig. 6.

340

341 from 0.25 to 5.0 with increasing x_N , we can see that final MPD/TMC ratio values can be quite
 342 different from the initial one, ranging from roughly 0.7 to 2.5. When one type of monomer is
 343 present in large excess, many of them do not react leading to a final $r_{m:t}$ different from $r_{m:t}^0$,
 344 whereas for initial MPD/TMC values in the range $1 < r_{m:t}^0 < 2$ (see Supplementary Information

345 section 3 for a plot of $r_{m:t}$ versus $r_{m:t}^0$), the final $r_{m:t}$ is closer to the initial one. Thus a better
346 control of the final monomer ratio can be obtained in this $r_{m:t}^0$ range.

347 These results compare very well with previous simulation studies. Suzuki *et al.* [42] obtained
348 $r_{m:t}$ values in the range 0.6-2.5, very close to what is obtained here. Harder *et al.* [27] obtained
349 a single sample with a $r_{m:t}$ value close to 1. The same group [62] improved their polymerization
350 strategy and obtained a system with a final MPD/TMC ratio equal to 1.1. Wei *et al.* [36] built
351 a large simulation box with a MPD/TMC ratio of 1.32. Globally [27, 23, 63, 25, 26, 34], most
352 authors who prepared a single APA box, obtained membranes with a $r_{m:t}$ in the range 1.0-1.35,
353 as expected from their initial conditions and polymerization algorithm.

354 The cross-linking degree χ is shown in Fig. 7b. As mentioned above, this descriptor assumes
355 that APA chains are composed of linear and cross-linked segments only, neglecting the presence
356 of chain ends. Under such assumption, χ must be a positive quantity smaller than 1.

357 The χ values computed for our systems vary from -0.59 to 1.75 with increasing $r_{m:t}^0$ (or x_N
358 values. See Supplementary Information section 3 for a plot of χ versus $r_{m:t}^0$). Our samples cover
359 the range of systems previously studied [27, 25, 28] with computed cross-linking degree in the
360 range 0.09–0.83. However, the large range of χ values observed here indicates the presence of
361 a large proportion of chain ends, especially at low or high $r_{m:t}^0$ values. It also turns out that
362 χ doesn't give a correct qualitative view of the cross-linking degree of the samples. *E.g.*, for
363 system with $r_{m:t}^0 = 0.75$, we have $\chi = 0$ whereas direct inspection of the molecules shows many
364 cross-linked nodes, *i.e.* TMC monomers fully connected with MPD monomers. On the contrary,
365 for system with $r_{m:t}^0 = 2.5$, we have $\chi = 1.2$ but direct inspection of the molecules shows a
366 very limited number of cross-linked nodes. In face of such inconsistency, we consider that the
367 use of the chemical descriptor χ should be done with caution, at least for systems containing a
368 substantial amount of chain ends.

369 As shown in Fig. 7c and 7d, along with the increase of the initial $r_{m:t}^0$, the fraction of
370 acyl groups that have reacted f_{ac} increases while that of reacted amine f_{am} decreases (see
371 Supplementary Information section 3 for a plot of f_{ac} and f_{am} versus $r_{m:t}^0$). For $r_{m:t}^0 < 1$ (*i.e.*
372 TMC is in excess), the fraction of amine groups that have reacted is close to one. The fraction
373 of acyl groups that have reacted is 0.5 or larger. This indicates the formation of molecules
374 with a large amount of TMC like chain ends, *e.g.* $a + 2c$ structure. For $r_{m:t}^0 > 2$, most acyl
375 groups have reacted ($f_{ac} \rightarrow 1$) while molecules exhibit a large number of unreacted amine groups
376 ($f_{am} \rightarrow 0.6$), corresponding to MPD like chain ends ($b+d$ structure). For $1 < r_{m:t}^0 < 2$, relatively

377 large fractions of acyl and amine have reacted, roughly 80%, indicating a larger efficiency of the
378 polymerization algorithm in this concentration range. For example, the system with $r_{m:t}^0 = 1.8$,
379 which is very close to the fully cross-linked sample on the O/N map, has $r_{m:t} = 0.96$, $f_{ac} = 0.85$
380 and $f_{am} = 0.79$.

381 Finally, a great variability is observed for all descriptors, meaning the initial monomer com-
382 position has a strong influence onto the final composition obtained through simulated polymer-
383 ization and different chemical structures have been created. Some structures built in this study
384 have chemical composition close to a fully cross-linked sample, though this ideal structure is
385 never obtained using the simulated polymerization algorithm as presented section 2.2.

386 3.5. Density

387 In this section, we present and discuss the density values obtained as a function of the final
388 MPD/TMC ratio. As shown in Fig. 8, a slight decrease of ρ , from 1.29 to 1.23 g/cm³, is ob-
389 served with increasing $r_{m:t}$. However, considering the fact that large structural differences exist
390 between our samples, we can say that the density of APA is almost no sensitive to the details
391 of the chemistry. This behavior is partly confirmed by group contribution estimations. Using
392 data found in van Krevelen book [64], we obtain 1.39 and 1.38 g/cm³ for the fully linear and
393 fully cross-linked structures respectively (see Supplementary Information section 4 for details).
394 The above discussion suggests that even APA with large amounts of unreacted groups, as seen
395 with extreme values of $r_{m:t}^0$, have the same density as highly cross-linked systems. This could be
396 attributed to strong hydrogen bonds between hydrogen and oxygen atoms in these free groups
397 to form a structure as dense as a cross-linked network. Short range interactions between aro-
398 matic rings (π - π stacking) has also been reported [36], resulting in a dense, thin two-layer slip
399 structure.

400 Comparison of our data with other simulation results is not easy. Following Kotelyanskii *et*
401 *al.* [21, 22], many authors built a simulation box based on the experimental density 1.38 g/cm³
402 and an estimated water content of the hydrated FT-30 membrane of 23 w% at ambient condi-
403 tions [27, 23, 62, 24, 19, 25, 26, 42]. After a short relaxation time, an hydrated density in the
404 range 1.30–1.39 g/cm³, corresponding to a dry density in the range 1.0–1.1 g/cm³ is obtained.
405 These dry density values must be taken with caution as they were obtained after relaxation times
406 much shorter than the one used here and, most importantly, they correspond to the density of
407 a swollen polymer. Kolev and Freger [28] computed, using molecular simulation, the density of

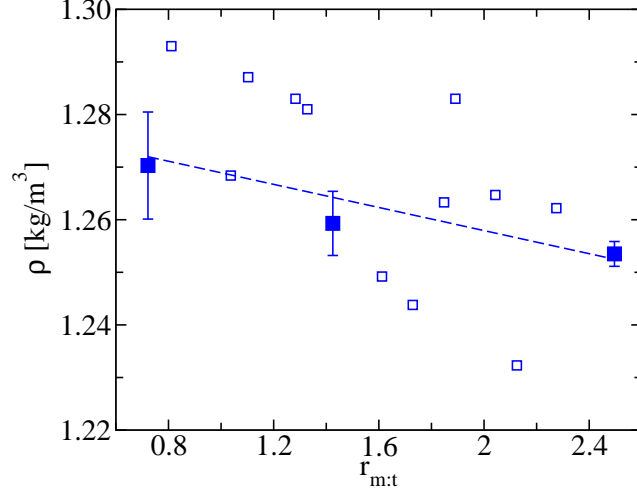


Figure 8: Density versus $r_{m:t}$ for sample equilibrated in the iso-stress ensemble. Large square symbols represent the average density for the 11 repetition boxes at respective $r_{m:t}$. The dashed-line is a linear regression over all data and accounts for the different statistical weight of each data point.

408 the same hydrated (hence swollen) and dry membrane and showed that the calculated density
 409 increases by about 10%. A density value of 1.24 g/cm³ including large voids is proposed while
 410 an average density of the dense region is about 1.3 g/cm³ for the dry polymer. This range is in
 411 full agreement with our set samples. Recent available data for other models of unswollen dry
 412 membrane densities [29, 36, 30, 33] lie in the range 1.17-1.31 g/cm³. Finally we can conclude
 413 that recent molecular simulation values are in good agreement with the average computed from
 414 the 11 repetition boxes at $r_{m:t}^0 = 1.5$ where $\rho = 1.26 \pm 0.02$ g/cm³.

415

416 4. Discussion: simulated versus real membrane properties

417 In this section, we try to relate our simulation results to experimental data on APA RO mem-
 418 brane layer. It is important to keep in mind that molecular simulations, because of time and
 419 length scale limitations, propose a model of the dense region of the APA membrane.

420 The density of the membrane is a typical macroscopic quantity whose knowledge is important
 421 for many transfer and partitioning predictive models. However, the experimental determination
 422 of the dry density of the dense region in the membrane is a difficult task because of the complex
 423 morphology of APA layers. Zhang *et al.* [41] used water adsorption experiments with quartz
 424 microbalance to determine water uptake for the FT30 and LF10 reverse osmosis membranes

425 and obtained values of 11.2 w/w% and 12.8 w/w% respectively. Using the experimental density
426 value of 1.38 g/cm³ given in [21], they deduced a FT30 active layer density of 1.24 g/cm³ and a
427 LF10 active layer density of 1.22 g/cm³. Lin *et al.* [65] measured dry densities of several APA
428 layers from reverse osmosis and nano-filtration membranes. The volumetric density is computed
429 as the areal mass of active layer measured using quartz microbalance divided by the thickness
430 obtained by ellipsometry analyses; it averages to 1.26 ± 0.21 g/cm³ for the uncoated APA active
431 layers. However, these studies do not compute the density of the dense region of the APA active
432 layer but rather an effective dry density including existing voids. Very recently, we measured the
433 density of the APA layer of the reverse osmosis CPA2 commercial membrane [60]. The study was
434 based on the measurement of the effective surface density, the membrane thickness and the void
435 fraction. Density values of 1.18 ± 0.14 g/cm³ and 1.30 ± 0.14 g/cm³ were obtained using AFM
436 and profilometry thickness analysis respectively, leading to an average value of 1.24 g/cm³ for
437 the dense region of CPA2 active layer membrane. Therefore, the good agreement between our
438 simulation results and the experimentally determined density of the dense region [60] validates
439 the force field and the general procedure used here. Moreover, molecular simulations show that
440 the mass density of APA membranes does not depend on the details of their chemistry.

441 The separation performances of active layer of reverse osmosis membranes is controlled by
442 water permeability and solute selectivity. It is widely accepted that free volume holes between
443 cross-linked polymer chains play an important role in small molecules transfer. Positron an-
444 nihilation lifetime spectroscopy (PALS) is an analytical technique using positron annihilation
445 spectroscopy (PAS) which allows for the measurement of the mean size of subnanometre-scale
446 holes (*i.e.* free volume hole-size). This technique has been employed by several authors in the
447 context of reverse osmosis membranes characterization. Henmi *et al.* [66] evaluated boron rejec-
448 tion using similar types of membranes and reported that the rejection of boron decreased with
449 increasing free volume. Chen *et al.* [67] reported that the rejection of four neutral solutes (urea,
450 ethylene, 1-propanol, and 2-propanol) correlated well with the ratio of the molecular volume of
451 solutes to the volume of sphere-shaped free volume holes in the membrane. Fujioka *et al.* [68]
452 reviewed data obtained for RO membranes and suggest to include other techniques *e.g.* molec-
453 ular dynamics simulations to describe the internal structure of APA membranes. We computed
454 the fraction of accessible volume (FAV) defined as the volume occupied by hard-spheres with
455 van der Waals radius divided by the box volume [69] (see Supplementary Information section 5
456 for more details on the methodology employed). Generally speaking, the free volume depends

457 on chain rigidity and the proportion of chain ends (which tends to increase the free volume).
 458 In the case of APA, we believe that the presence of short cross-links between linear segments
 459 leave some empty space that could not be filled by the polymer because of chain rigidity. As can
 460 be seen in Fig. 9, the general trend is that the FAV slightly decreases with $r_{m:t}$ (or $r_{m:t}^0$). It is
 461 accompanied by an increase of the proportion of the chain ends density N_{ce}^t/V (N_{ce}^t is the total
 462 number of chain ends in the simulation box, V is the simulation box volume), mostly seen for
 $r_{m:t}$ larger than one. The increase of the density of cross-linked TMC units N_{cl}^t/V (N_{cl}^t is the

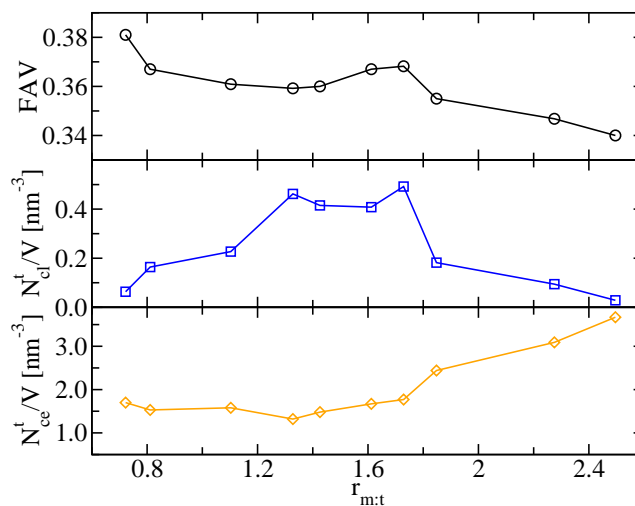


Figure 9: Evolution of the free accessible volume (FAV), the number of cross-linked points per unit volume (N_{cl}^t/V) and the number of chain ends per unit volume (N_{ce}^t/V) with $r_{m:t}$.

463
 464 total number of cross-linked TMC units), seen for $1.3 < r_{m:t} < 1.7$, seems to be associated with
 465 an increase of the FAV. Unfortunately, because of poor statistics, we were not able to establish
 466 a clear link between FAV and the concentration of chain ends and cross-linking point densities
 467 in our samples. Nonetheless, it would be interesting to establish such a correlation in order to
 468 tailor membrane properties from proportion of chain end and cross-linking points.

469 From a microscopic point of view, our simulations reveal that the fraction of reacted amine
 470 and acyl groups varies in a large range. It is clear that most of the systems studied at high
 471 excess of MPD or TMC monomers lead to unrealistic polymers. Meanwhile, boxes with initial
 472 MPD/TMC ratio in the range 1–2 provide systems with composition compatible with almost
 473 fully linear samples and highly cross-linked samples. For these systems, a non negligible amount
 474 of unreacted amine and carboxylic acid groups is found. Signature for these groups have already
 475 been mentioned in the literature. Using tangential streaming ζ -potential measurements [70] it
 476 is possible to determine surface charges at the interface between various reverse osmosis mem-

477 branes and an electrolyte. Due to their composition, uncoated membranes can have a positive
478 charge at acidic pH because of the ionization of the free amine groups at their surface into $-\text{NH}_3^+$.
479 When pH rises, the ζ -potential becomes negative because of the dissociation of free carboxylic
480 groups of TMC into COO^- and the neutralization of NH_3^+ groups.
481 Infrared spectroscopy is extensively used to check presence of coating on commercial membranes.
482 Though, a few studies used IR to reveal the presence of carboxylic and amine groups. Dutta *et*
483 *al.* [16] mention that for membranes synthesized using reacting solutions of 1% TMC and 8%
484 MPD, an excess of amine groups in the sample is observable in FTIR spectra, with an enhance-
485 ment of the band at 1666–1670 cm^{-1} . Identically, for polymers synthesized using 1% TMC and
486 2% MPD concentration solutions, they noticed $-\text{OH}$ stretching frequency bands at 3751 and
487 3856 cm^{-1} . A relatively weak band is also observed by Mi *et al.* [71] at 1450 cm^{-1} correspond-
488 ing to the presence of carboxylic acid groups. Jin *et al.* [72] assigned the vibrational band at
489 1720 cm^{-1} to the $\text{C}=\text{O}$ stretching of carboxylic acid groups for layers synthesized with 4 wt/v%
490 MPD solution and 0.5 to 2 wt/v% TMC solutions. Using spectrum bands deconvolution, they
491 were able to observe the increase in COOH groups with increasing TMC solution concentration.
492 We computed IR spectra from molecular simulation trajectories of our samples to compare with
493 existing data in the literature. Although a clear evolution is seen for several bands indicating
494 concentration changes of amine, carboxylic and amide groups, the results are barely comparable
495 with experiments (see Supplementary Information section 6 and figures therein). Absorption
496 bands specific of amide groups [61] (1660, 1610 and 1540 cm^{-1} corresponding to $\text{C}=\text{O}$ signal
497 *amide I*, aromatic ring breathing and C-N stretching *amide II*) appear at different frequencies
498 than experimental one, due to intramolecular force field and methodological limitations. Group
499 concentrations could be deduced from the computed IR spectra in the high frequency range
500 (3000-4000 cm^{-1}) but unfortunately, this doesn't seem to be applicable to real spectra where
501 the resolution is much lower in this frequency range.

502

503 It is widely accepted that the active layer structure is chemically heterogeneous through-
504 out its depth [73, 74, 75, 76]. Wamser and Gilbert [73] concluded from contact angle titration
505 experiments that carboxylic and amine groups predominate at the APA top-surface (TS) and
506 back-surface (BS) respectively. Freger [75] demonstrated that the polymer charge is distributed
507 across the active polyamide layer in a highly non uniform fashion. The polyamide films ap-
508 pear to be built of a negatively charged outer layer (carboxylic-rich region) sitting on top of an

509 inner layer possessing a small positive charge (amine-rich region). Using X-ray photoelectron
510 spectrometry (XPS) and Rutherford backscattering spectrometry (RBS), Coronell *et al.* [76]
511 extensive analysis of reverse osmosis and nano filtration membranes, support the existence of
512 both depth-homogeneous and depth-heterogeneous active layers. Such studies indicate that in
513 order to improve the current understanding of permeation phenomena during reverse osmosis
514 filtration, there is a need to characterize as a function of depth the physicochemical properties
515 and interactions with contaminants inside active layers.

516 Fig. 10 presents oxygen versus nitrogen atom fraction map and compares chemical composi-
517 tion between our simulation data and conventional reverse osmosis membranes. Six sets of
518 experimental data are presented: Song *et al.* [60] data where the APA layer of the commercial
519 membrane CPA2 has been studied using XPS analysis on top-surface and back-surface (after
520 removal of the support layer); results from Coronell *et al.* [76] on three different reverse osmosis
521 membranes analyzed using XPS (for the top-surface) and RBS to get insights into chemical het-
522 erogeneities along the thickness of the APA layer; data from Park *et al.* [77] using XPS analysis
523 on supported and support-free synthesized APA membranes and where the back-surface (APA
524 membrane surface in contact with the aqueous phase during the polymerization) was analyzed
525 for the support-free polymerized membrane; XPS data from Park *et al.* [78] for APA membranes
526 synthesized on PSf and hybrid metal organic framework/PSf support; a selection of Tang *et*
527 *al.* [61] XPS data for polyamide thin films of 6 commonly used commercial RO membranes; Xu
528 *et al.* [18] XPS analysis of various APA layers prepared by changing the monomer concentrations
529 in a wide range.

530 Experimental data are presented according to three different criteria: top-surface data (TS,
531 upper triangles) and back-surface data (BS, lower triangles), both obtained using XPS measure-
532 ments and data obtained using RBS experiments, giving an average elemental composition of
533 the layer.

534 We first notice that experimental data are rather scattered over the O/N map and many points
535 fall out of the limits imposed by the stoichiometry of APA polymers. This is particularly true
536 for XPS analyses. It may well be that surface contamination by chemicals alter the final com-
537 position. However, this figure demonstrates the influence of the synthesis parameters onto the
538 final composition. One can also notice that top-surfaces (triangle up) generally have smaller
539 nitrogen content than the average composition (square) and the highest nitrogen values corre-
540 spond to data obtained on back-surface (triangle down). This is in agreement with the general

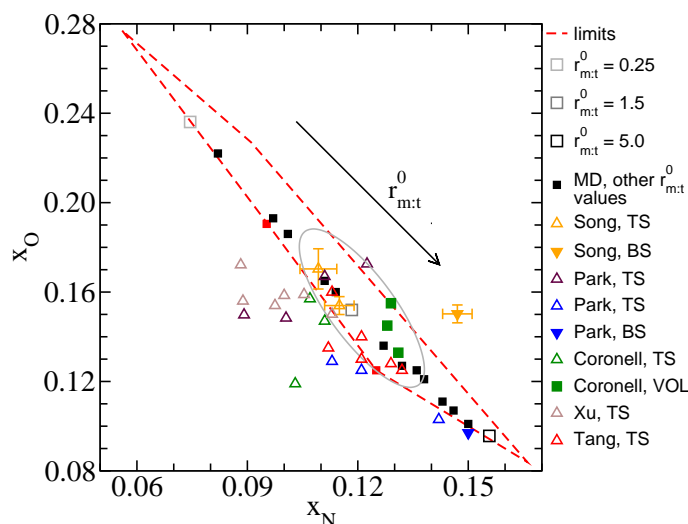


Figure 10: Elemental composition of simulated samples and several commercial and home-made APA reverse osmosis membrane layers. Squares represent data corresponding to an average composition (molecular simulations or RBS experiments). Upper and lower triangles represent XPS data from top-surface (TS) and back-surface (BS) analyses of the membranes, respectively. Colors refer to different works or publications; black: molecular simulations, this work; orange: Song *et al.* [60]; blue: Park *et al.* [77]; maroon: Park *et al.* [78]; green: Coronell *et al.* [76]; brown: Xu *et al.* [18]; red: Tang *et al.* [61]. The region inside the dashed-red lines represents all possible compositions for APA molecules. The region inside the grey ellipse contains simulation boxes with “infinite clusters”.

541 result obtained by Wamser [73] or Freger [75] that carboxylic and amine groups predominate at
 542 the APA top-surface and back-surface respectively, because during membrane synthesis the local
 543 MPD concentration decreases from the aqueous-organic interface to the pure organic phase. The
 544 interesting point is that our simulation data are in agreement with this behavior. As the initial
 545 MPD/TMC ratio is increased, final nitrogen content increases and our samples share charac-
 546 teristics with back-surface region. Inversely, when the initial MPD/TMC ratio decreases, final
 547 nitrogen content decreases and the simulation boxes resemble membrane top-surface region. The
 548 different simulation boxes could thus be used to describe a particular region of the membrane,
 549 from the back-surface, to the top-surface.

550 5. Conclusions

551 Molecular simulation has been used to build APA polymer samples. Our aim was to study how
 552 local monomer composition that appear during interfacial polymerization affect the structure of
 553 a model of APA membrane. We covered a rather large range of initial MPD/TMC monomer
 554 ratios, from 1:4 to 5:1, and did observe many different structures. The polymerization step in

555 itself requires short simulation times but full strains relaxation required up to several microsec-
556 onds.

557 For systems with large excess of TMC or MPD monomers, the behavior is almost “pathological”
558 with the formation a small oligomers with linear structure and few reticulation nodes. The
559 fraction of unreacted acyl and amine groups is high for $r_{m:t}^0 \rightarrow 0.25$ and $r_{m:t}^0 \rightarrow 5.0$ respectively.
560 For $1 < r_{m:t} < 2$, synthesized samples have chemical composition typical of APA membranes
561 ($0.09 < x_N < 0.13$ and $0.12 < x_O < 0.18$). The fraction of acyl and amine groups that have
562 reacted is high although different from 1, indicating that numerous chain ends still exist in these
563 structures. It is likely that during the polymerization steps, amine or acyl groups are trapped in-
564 side the chemical structure and are no longer accessible to other reactants, being large oligomers
565 or even a single monomer.

566 We believe that the simulated samples created under different local concentrations can describe
567 properly the chemical heterogeneities observed experimentally in reverse osmosis membranes.
568 We think that the methodology employed is a tool to produce membranes with slightly differ-
569 ent chemical compositions and to investigate their selectivity performances. As mentioned by
570 Freger and Ramon in a recent review [79], experimentally determined parameters such as density
571 or cross-linking degree may not reflect the film behavior as a selective membrane. This study
572 contributed to the preparation, at the molecular level, of samples with different structural char-
573 acteristics. We believe that further molecular simulation studies to investigate their selectivity
574 performances, could provide better insights into the structure-property relationships.

575 **Funding sources**

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579 **Appendix A. Supplementary information**

580 Detailed information on the definition of compositional limits for APA polymers, statistic errors
581 from repetition boxes, descriptor evolution with $r_{m:t}^0$, density computed using group contribution
582 method, fractional accessible free volume computations and infrared spectrum computation is
583 presented in the supplementary information.

References

- [1] N. M. Al-Bastaki, Performance of advanced methods for treatment of wastewater: UV/TiO₂, RO and UF, *Chem. Eng. Process.: Proc. Intensif.* 43 (7) (2004) 935–940. doi:10.1016/j.cep.2003.08.003.
- [2] A. Sonune, R. Ghate, Developments in wastewater treatment methods, *Desalination* 167 (2004) 55–63. doi:10.1016/j.desal.2004.06.113.
- [3] S. S. Shenvi, A. M. Isloor, A. Ismail, A review on RO membrane technology: Developments and challenges, *Desalination* 368 (2015) 10–26. doi:10.1016/j.desal.2014.12.042.
- [4] I. Frenzel, D. F. Stamatialis, M. Wessling, Water recycling from mixed chromic acid waste effluents by membrane technology, *Sep. Purif. Technol.* 49 (1) (2006) 76–83. doi:10.1016/j.seppur.2005.08.010.
- [5] J. Hoinkis, V. Panten, Wastewater recycling in laundries—from pilot to large-scale plant, *Chem. Eng. Process.: Proc. Intensif.* 47 (7) (2008) 1159–1164. doi:10.1016/j.cep.2007.12.010.
- [6] C. Sagne, C. Fargues, R. Lewandowski, M.-L. Lameloise, M. Gavach, M. Decloux, A pilot scale study of reverse osmosis for the purification of condensate arising from distillery stillage concentration plant, *Chem. Eng. Process.: Proc. Intensif.* 49 (4) (2010) 331–339. doi:10.1016/j.cep.2010.03.002.
- [7] C. Li, Y. Yang, Y. Liu, L.-a. Hou, Removal of PhACs and their impacts on membrane fouling in NF/RO membrane filtration of various matrices, *J. Membr. Sci.* 548 (2018) 439–448. doi:10.1016/j.memsci.2017.11.032.
- [8] K. Licon, L. d. O. Geaquinto, J. Nicolini, N. Figueiredo, S. Chiapetta, A. Habert, L. Yokoyama, Assessing potential of nanofiltration and reverse osmosis for removal of toxic pharmaceuticals from water, *J. Water Proc. Eng.* 25 (2018) 195–204. doi:10.1016/j.jwpe.2018.08.002.
- [9] K. V. Plakas, A. J. Karabelas, Removal of pesticides from water by NF and RO membranes — a review, *Desalination* 287 (2012) 255–265. doi:10.1016/j.desal.2011.08.003.

- 611 [10] H. T. Madsen, E. G. Sogaard, Applicability and modelling of nanofiltration and reverse os-
612 mosis for remediation of groundwater polluted with pesticides and pesticide transformation
613 products, *Sep. Purif. Technol.* 125 (2014) 111–119. doi:10.1016/j.seppur.2014.01.038.
- 614 [11] R. Mehta, H. Brahmhatt, N. Saha, A. Bhattacharya, Removal of substituted phenyl urea
615 pesticides by reverse osmosis membranes: Laboratory scale study for field water application,
616 *Desalination* 358 (2015) 69–75. doi:10.1016/j.desal.2014.12.019.
- 617 [12] M. Nikbakht Fini, H. T. Madsen, J. Muff, The effect of water matrix, feed concentration
618 and recovery on the rejection of pesticides using NF/RO membranes in water treatment,
619 *Sep. Purif. Technol.* 215 (2019) 521–527. doi:10.1016/j.seppur.2019.01.047.
- 620 [13] J. E. Cadotte, R. J. Petersen, R. E. Larson, E. E. Erickson, A new thin-film composite
621 seawater reverse osmosis membrane, *Desalination* 32 (C) (1980) 25–31. doi:10.1016/
622 S0011-9164(00)86003-8.
- 623 [14] S. Habib, S. T. Weinman, A review on the synthesis of fully aromatic polyamide reverse
624 osmosis membranes, *Desalination* 502 (2021) 114939. doi:10.1016/j.desal.2021.114939.
- 625 [15] G.-Y. Chai, W. B. Krantz, Formation and characterization of polyamide membranes
626 via interfacial polymerization, *J. Membr. Sci.* 93 (2) (1994) 175–192. doi:10.1016/
627 0376-7388(94)80006-5.
- 628 [16] D. Dutta, A. Bhattacharyya, B. Ganguly, Microstructural study of aromatic polyamide
629 membrane material, *J. Membr. Sci.* 224 (1-2) (2003) 127–135. doi:10.1016/j.memsci.
630 2003.08.001.
- 631 [17] B. Khorshidi, T. Thundat, B. A. Fleck, M. Sadrzadeh, A novel approach toward fabrication
632 of high performance thin film composite polyamide membranes, *Sci. Rep.* 6 (1) (2016) 22069.
633 doi:10.1038/srep22069.
- 634 [18] J. Xu, H. Yan, Y. Zhang, G. Pan, Y. Liu, The morphology of fully-aromatic polyamide
635 separation layer and its relationship with separation performance of TFC membranes, *J.*
636 *Membr. Sci.* 541 (2017) 174–188. doi:10.1016/j.memsci.2017.06.057.
- 637 [19] H. Ebro, Y. M. Kim, J. H. Kim, Molecular dynamics simulations in membrane-based water
638 treatment processes: A systematic overview, *J. Membr. Sci.* 438 (2013) 112–125. doi:
639 10.1016/j.memsci.2013.03.027.

- 640 [20] H. F. Ridgway, J. Orbell, S. Gray, Molecular simulations of polyamide membrane mate-
641 rials used in desalination and water reuse applications: Recent developments and future
642 prospects, *J. Membr. Sci.* 524 (October 2016) (2017) 436–448. doi:10.1016/j.memsci.
643 2016.11.061.
- 644 [21] M. J. Kotelyanskii, N. J. Wagner, M. E. Paulaitis, Atomistic simulation of water and salt
645 transport in the reverse osmosis membrane FT-30, *J. Membr. Sci.* 139 (1) (1998) 1–16.
646 doi:10.1016/S0376-7388(97)00220-2.
- 647 [22] M. J. Kotelyanskii, N. J. Wagner, M. E. Paulaitis, Molecular dynamics simulation study of
648 the mechanisms of water diffusion in a hydrated, amorphous polyamide, *Comput. Theor.*
649 *Polym. Sci.* 9 (3-4) (1999) 301–306. doi:10.1016/S1089-3156(99)00020-3.
- 650 [23] Z. E. Hughes, J. D. Gale, A computational investigation of the properties of a reverse
651 osmosis membrane, *J. Mater. Chem.* 20 (36) (2010) 7788–7799. doi:10.1039/c0jm01545h.
- 652 [24] Z. E. Hughes, J. D. Gale, Molecular dynamics simulations of the interactions of potential
653 foulant molecules and a reverse osmosis membrane, *J. Mater. Chem.* 22 (1) (2012) 175–184.
654 doi:10.1039/C1JM13230J.
- 655 [25] Y. Xiang, Y. Liu, B. Mi, Y. Leng, Hydrated polyamide membrane and its interaction
656 with alginate: A molecular dynamics study, *Langmuir* 29 (37) (2013) 11600–11608. doi:
657 10.1021/la401442r.
- 658 [26] M. Ding, A. Ghoufi, A. Szymczyk, Molecular simulations of polyamide reverse osmosis
659 membranes, *Desalination* 343 (2014) 48–53. doi:10.1016/j.desal.2013.09.024.
- 660 [27] E. Harder, D. E. Walters, Y. D. Bodnar, R. S. Faibish, B. Roux, Molecular dynamics study
661 of a polymeric reverse osmosis membrane, *J. Phys. Chem. B* 113 (30) (2009) 10177–10182.
662 doi:10.1021/jp902715f.
- 663 [28] V. Kolev, V. Freger, Hydration, porosity and water dynamics in the polyamide layer of
664 reverse osmosis membranes: A molecular dynamics study, *Polymer* 55 (6) (2014) 1420–
665 1426. doi:10.1016/j.polymer.2013.12.045.
- 666 [29] M. Shen, S. Keten, R. M. Lueptow, Dynamics of water and solute transport in polymeric
667 reverse osmosis membranes via molecular dynamics simulations, *J. Membr. Sci.* 506 (2016)
668 95–108. doi:10.1016/j.memsci.2016.01.051.

- 669 [30] T. P. Liyana-Arachchi, J. F. Sturnfield, C. M. Colina, Ultrathin molecular-layer-by-layer
670 polyamide membranes: Insights from atomistic molecular simulations, *J. Phys. Chem. B*
671 120 (35) (2016) 9484–9494. doi:10.1021/acs.jpccb.6b02801.
- 672 [31] R. Nadler, S. Srebnik, Molecular simulation of polyamide synthesis by interfacial polymer-
673 ization, *J. Membr. Sci.* 315 (1-2) (2008) 100–105. doi:10.1016/j.memsci.2008.02.023.
- 674 [32] R. Oizerovich-Honig, V. Raim, S. Srebnik, Simulation of thin film membranes formed by
675 interfacial polymerization, *Langmuir* 26 (1) (2010) 299–306. doi:10.1021/la9024684.
- 676 [33] J. Muscatello, E. Müller, A. Mostofi, A. Sutton, Multiscale molecular simulations of the
677 formation and structure of polyamide membranes created by interfacial polymerization, *J.*
678 *Membr. Sci.* 527 (2017) 180–190. doi:10.1016/j.memsci.2016.11.024.
- 679 [34] M. Ding, A. Szymczyk, F. Goujon, A. Soldera, A. Ghoufi, Structure and dynamics of
680 water confined in a polyamide reverse-osmosis membrane: A molecular-simulation study,
681 *J. Membr. Sci.* 458 (2014) 236–244. doi:10.1016/j.memsci.2014.01.054.
- 682 [35] M. Ding, A. Szymczyk, A. Ghoufi, On the structure and rejection of ions by a polyamide
683 membrane in pressure-driven molecular dynamics simulations, *Desalination* 368 (2015) 76–
684 80. doi:10.1016/j.desal.2015.01.003.
- 685 [36] T. Wei, L. Zhang, H. Zhao, H. Ma, M. S. J. Sajib, H. Jiang, S. Murad, Aromatic polyamide
686 reverse-osmosis membrane: An atomistic molecular dynamics simulation, *J. Phys. Chem.*
687 *B* 120 (39) (2016) 10311–10318. doi:10.1021/acs.jpccb.6b06560.
- 688 [37] A. Ghoufi, E. Dražević, A. Szymczyk, Interactions of organics within hydrated selective
689 layer of reverse osmosis desalination membrane: A combined experimental and compu-
690 tational study, *Environ. Sci. Technol.* 51 (5) (2017) 2714–2719. doi:10.1021/acs.est.
691 6b05153.
- 692 [38] L. Yao, Z. Qin, Q. Chen, M. Zhao, H. Zhao, W. Ahmad, L. Fan, L. Zhao, Insights into the
693 nanofiltration separation mechanism of monosaccharides by molecular dynamics simulation,
694 *Sep. Purif. Technol.* 205 (2018) 48–57. doi:10.1016/j.seppur.2018.04.056.
- 695 [39] Y.-l. Liu, X.-m. Wang, H.-w. Yang, Y. F. Xie, Quantifying the influence of solute-membrane
696 interactions on adsorption and rejection of pharmaceuticals by NF/RO membranes, *J.*
697 *Membr. Sci.* 551 (2018) 37–46. doi:10.1016/j.memsci.2018.01.035.

- 698 [40] Y.-l. Liu, K. Xiao, A.-q. Zhang, X.-m. Wang, H.-w. Yang, X. Huang, Y. F. Xie, Exploring
699 the interactions of organic micropollutants with polyamide nanofiltration membranes: A
700 molecular docking study, *J. Membr. Sci.* 577 (2019) 285–293. doi:10.1016/j.memsci.
701 2019.02.017.
- 702 [41] X. Zhang, D. G. Cahill, O. Coronell, B. J. Mariñas, Absorption of water in the active layer
703 of reverse osmosis membranes, *J. Membr. Sci.* 331 (1-2) (2009) 143–151. doi:10.1016/j.
704 memsci.2009.01.027.
- 705 [42] Y. Suzuki, Y. Koyano, M. Nagaoka, Influence of monomer mixing ratio on membrane
706 nanostructure in interfacial polycondensation: Application of hybrid MC/MD reaction
707 method with minimum bond convention, *J. Phys. Chem. B* 119 (22) (2015) 6776–6785.
708 doi:10.1021/jp512333h.
- 709 [43] P. Dauber-Osguthorpe, V. A. Roberts, D. J. Osguthorpe, J. Wolff, M. Genest, A. T. Ha-
710 gler, Structure and energetics of ligand binding to proteins: escherichia coli dihydrofolate
711 reductase-trimethoprim, a drug-receptor system, *Proteins: Struct., Funct., Genet.* 4 (1)
712 (1988) 31–47. doi:10.1002/prot.340040106.
- 713 [44] A. D. MacKerell, D. Bashford, M. Bellott, R. L. Dunbrack, J. D. Evanseck, M. J.
714 Field, S. Fischer, J. Gao, H. Guo, S. Ha, D. Joseph-McCarthy, L. Kuchnir, K. Kucz-
715 era, F. T. K. Lau, C. Mattos, S. Michnick, T. Ngo, D. T. Nguyen, B. Prodhom, W. E.
716 Reiher, B. Roux, M. Schlenkrich, J. C. Smith, R. Stote, J. Straub, M. Watanabe,
717 J. Wiórkiewicz-Kuczera, D. Yin, M. Karplus, All-atom empirical potential for molecular
718 modeling and dynamics studies of proteins [†], *J. Phys. Chem. B* 102 (18) (1998) 3586–3616.
719 doi:10.1021/jp973084f.
- 720 [45] J. W. Ponder, D. A. Case, Force fields for protein simulations, in: *Advances in Protein*
721 *Chemistry*, Vol. 66, Elsevier, 2003, pp. 27–85. doi:10.1016/S0065-3233(03)66002-X.
- 722 [46] J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman, D. A. Case, Development and testing
723 of a general amber force field, *J. Comput. Chem.* 25 (9) (2004) 1157–1174. doi:10.1002/
724 jcc.20035.
- 725 [47] W. L. Jorgensen, D. S. Maxwell, J. Tirado-Rives, Development and testing of the OPLS
726 all-atom force field on conformational energetics and properties of organic liquids, *J. Am.*
727 *Chem. Soc.* 118 (45) (1996) 11225–11236. doi:10.1021/ja9621760.

- 728 [48] B. L. Eggimann, A. J. Sunnarborg, H. D. Stern, A. P. Bliss, J. I. Siepmann, An online
729 parameter and property database for the TraPPE force field, *Mol. Simul.* 40 (1-3) (2014)
730 101–105. doi:10.1080/08927022.2013.842994.
- 731 [49] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, M. L. Klein, Comparison
732 of simple potential functions for simulating liquid water, *J. Chem. Phys.* 79 (2) (1983)
733 926–935. doi:10.1063/1.445869.
- 734 [50] J. L. F. Abascal, C. Vega, A general purpose model for the condensed phases of water:
735 TIP4P/2005, *J. Chem. Phys.* 123 (23) (2005) 234505. doi:10.1063/1.2121687.
- 736 [51] S. Plimpton, Fast parallel algorithms for short-range molecular dynamics, *J. Comput. Phys.*
737 117 (1) (1995) 1–19. doi:10.1006/jcph.1995.1039.
- 738 [52] LAMMPS molecular dynamics simulator, <http://lammps.sandia.gov>.
- 739 [53] N.-T. Van-Oanh, C. Houriez, B. Rousseau, Viscosity of the 1-ethyl-3-methylimidazolium
740 bis(trifluoromethylsulfonyl)imide ionic liquid from equilibrium and nonequilibrium molec-
741 ular dynamics, *Phys. Chem. Chem. Phys.* 12 (4) (2010) 930–936. doi:10.1039/B918191A.
- 742 [54] R. W. Hockney, J. W. Eastwood, *Computer Simulation Using Particles*, IOP Publishing
743 Ltd, 1988. doi:10.1887/0852743920.
- 744 [55] W. Shinoda, M. Shiga, M. Mikami, Rapid estimation of elastic constants by molecular
745 dynamics simulation under constant stress, *Phys. Rev. B: Condens. Matter Mater. Phys.*
746 69 (13) (2004) 16–18. doi:10.1103/PhysRevB.69.134103.
- 747 [56] O. Coronell, B. J. Mariñas, X. Zhang, D. G. Cahill, Quantification of functional groups and
748 modeling of their ionization behavior in the active layer of FT30 reverse osmosis membrane,
749 *Environ. Sci. Technol.* 42 (14) (2008) 5260–5266. doi:10.1021/es8002712.
- 750 [57] O. Coronell, M. I. González, B. J. Mariñas, D. G. Cahill, Ionization behavior, stoichiometry
751 of association, and accessibility of functional groups in the active layers of reverse osmosis
752 and nanofiltration membranes, *Environ. Sci. Technol.* 44 (17) (2010) 6808–6814. doi:
753 10.1021/es100891r.
- 754 [58] X. Song, Structural characterization and molecular modeling of the active aromatic
755 polyamide layer in reverse-osmosis membranes, Ph.D. thesis, Université Paris Saclay (2020).

- 756 [59] J. M. Dennison, X. Xie, C. J. Murphy, D. G. Cahill, Density, elastic constants, and thermal
757 conductivity of interfacially polymerized polyamide films for reverse osmosis membranes,
758 ACS Appl. Nano Mater. 1 (9) (2018) 5008–5018. doi:10.1021/acsanm.8b01129.
- 759 [60] X. Song, W. Guiga, B. Rousseau, A. Jonquieres, R. Weil, M. Grzelka, J. Waeytens, A. Dazzi,
760 D. Dragoe, C. Fargues, Experimental characterization of commercial and synthesized aro-
761 matic polyamide films for reverse osmosis membranes, Ind. Eng. Chem. Res. 60 (7) (2021)
762 2898–2910. doi:10.1021/acs.iecr.0c05393.
- 763 [61] C. Y. Tang, Y.-N. Kwon, J. O. Leckie, Effect of membrane chemistry and coating layer
764 on physiochemical properties of thin film composite polyamide RO and NF membranes,
765 Desalination 242 (1-3) (2009) 149–167. doi:10.1016/j.desal.2008.04.003.
- 766 [62] Y. Luo, E. Harder, R. S. Faibish, B. Roux, Computer simulations of water flux and salt
767 permeability of the reverse osmosis FT-30 aromatic polyamide membrane, J. Membr. Sci.
768 384 (1-2) (2011) 1–9. doi:10.1016/j.memsci.2011.08.057.
- 769 [63] Y. Luo, B. Roux, Simulation of osmotic pressure in concentrated aqueous salt solutions, J.
770 Phys. Chem. Lett. 1 (1) (2010) 183–189. doi:10.1021/jz900079w.
- 771 [64] D. W. van Krevelen, K. te Nijenhuis, Properties of Polymers: Their Correlation with Chem-
772 ical Structure: Their Numerical Estimation and Prediction from Additive Group Contribu-
773 tions, 4th Edition, Elsevier, Amsterdam, 2009.
- 774 [65] L. Lin, C. Feng, R. Lopez, O. Coronell, Identifying facile and accurate methods to measure
775 the thickness of the active layers of thin-film composite membranes – A comparison of seven
776 characterization techniques, J. Membr. Sci. 498 (2016) 167–179. doi:10.1016/j.memsci.
777 2015.09.059.
- 778 [66] M. Henmi, Y. Fusaoka, H. Tomioka, M. Kurihara, High performance RO membranes for
779 desalination and wastewater reclamation and their operation results, Water Sci. Technol.
780 62 (9) (2010) 2134–2140. doi:10.2166/wst.2010.396.
- 781 [67] Z. Chen, K. Ito, H. Yanagishita, N. Oshima, R. Suzuki, Y. Kobayashi, Correlation study
782 between free-volume holes and molecular separations of composite membranes for reverse
783 osmosis processes by means of variable-energy positron annihilation techniques, J. Phys.
784 Chem. C 115 (37) (2011) 18055–18060. doi:10.1021/jp203888m.

- 785 [68] T. Fujioka, N. Oshima, R. Suzuki, W. E. Price, L. D. Nghiem, Probing the internal structure
786 of reverse osmosis membranes by positron annihilation spectroscopy: Gaining more insight
787 into the transport of water and small solutes, *J. Membr. Sci.* 486 (2015) 106–118. doi:
788 10.1016/j.memsci.2015.02.007.
- 789 [69] D. Hofmann, M. Entrialgo-Castano, A. Lerbret, M. Heuchel, Y. Yampolskii, Molecular
790 modeling investigation of free volume distributions in stiff chain polymers with conventional
791 and ultrahigh free volume: Comparison between molecular modeling and positron lifetime
792 studies, *Macromolecules* 36 (22) (2003) 8528–8538. doi:10.1021/ma0349711.
- 793 [70] C. Fargues, C. Sagne, A. Szymczyk, P. Fievet, M. L. Lameloise, Adsorption of small organic
794 solutes from beet distillery condensates on reverse-osmosis membranes: Consequences on
795 the process performances, *J. Membr. Sci.* 446 (2013) 132–144. doi:10.1016/j.memsci.
796 2013.05.051.
- 797 [71] B. Mi, D. G. Cahill, B. J. Mariñas, Physico-chemical integrity of nanofiltration/reverse
798 osmosis membranes during characterization by rutherford backscattering spectrometry, *J.*
799 *Membr. Sci.* 291 (1-2) (2007) 77–85. doi:10.1016/j.memsci.2006.12.052.
- 800 [72] Y. Jin, Z. Su, Effects of polymerization conditions on hydrophilic groups in aromatic
801 polyamide thin films, *J. Membr. Sci.* 330 (1-2) (2009) 175–179. doi:10.1016/j.memsci.
802 2008.12.055.
- 803 [73] C. C. Wamser, M. I. Gilbert, Detection of surface functional group asymmetry in
804 interfacially-polymerized films by contact angle titrations, *Langmuir* 8 (6) (1992) 1608–
805 1614. doi:10.1021/1a00042a019.
- 806 [74] V. Freger, S. Srebnik, Mathematical model of charge and density distributions in interfacial
807 polymerization of thin films, *J. Appl. Polym. Sci.* 88 (5) (2003) 1162–1169. doi:10.1002/
808 app.11716.
- 809 [75] V. Freger, Nanoscale heterogeneity of polyamide membranes formed by interfacial polymer-
810 ization, *Langmuir* 19 (11) (2003) 4791–4797. doi:10.1021/la020920q.
- 811 [76] O. Coronell, B. J. Mariñas, D. G. Cahill, Depth heterogeneity of fully aromatic polyamide
812 active layers in reverse osmosis and nanofiltration membranes, *Environ. Sci. Technol.* 45 (10)
813 (2011) 4513–4520. doi:10.1021/es200007h.

- 814 [77] S. J. Park, W. Choi, S. E. Nam, S. Hong, J. S. Lee, J. H. Lee, Fabrication of polyamide
815 thin film composite reverse osmosis membranes via support-free interfacial polymerization,
816 J. Membr. Sci. 526 (2017) 52–59. doi:10.1016/j.memsci.2016.12.027.
- 817 [78] H. M. Park, K. Y. Jee, Y. T. Lee, Preparation and characterization of a thin-film com-
818 posite reverse osmosis membrane using a polysulfone membrane including metal-organic
819 frameworks, J. Membr. Sci. 541 (2017) 510–518. doi:10.1016/j.memsci.2017.07.034.
- 820 [79] V. Freger, G. Z. Ramon, Polyamide desalination membranes: Formation, structure, and
821 properties, Prog. Polym. Sci. 122 (2021) 101451. doi:10.1016/j.progpolymsci.2021.
822 101451.