Influence of Polyvinylidene Fluoride Polymorphs in Membrane-Assisted Crystallization: NaCl Crystals Nucleation and Growth

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Abstract Membrane-assisted crystallization is a new unit operation for separation and/or promotion of pure crystals formation, where microporous hydrophobic membranes are used not as selective barriers but to promote water vapor transfer between phases inducing supersaturation in solution. Polyvinylidene fluoride (PVDF) is one of the most utilized polymers due to its excellent combination of properties and processability and has been used in a wide plethora of applications in membrane technology including membrane crystallization. PVDF has different polymorphs and this property is important in membrane technology because different phases might significantly affect the final membrane properties and performances, e.g., on membrane fouling and membrane wetting. A clear correlation between the dominating crystalline phases in PVDF and the performance in membrane contactor applications, and in particular in membrane crystallization is still missing and necessary. In this work, molecular dynamics simulation was utilized to analyze the relationship and influence of different polymorphs of PVDF membranes on crystals formation via membrane crystallization process. Atomistic simulations were used to study the crystal nucleation and growth of sodium chloride in contact with amorphous, α and β PVDF hydrophobic polymer surfaces at a supersaturated concentration of salt. Predictions about the ability of α and β polymorphs to influence the nucleation and growth of salts were obtained. The results specified the crystals (as cluster) size distributions, the size of critical nuclei, and the nucleation rate. The amorphous PVDF led to the formation of smaller but more regular clusters in reference to the other samples; α PVDF produced much more inhomogeneous crystals and of small dimensions; β PVDF produces crystals of larger dimensions than α PVDF.

Keywords molecular simulation, membrane assisted crystallization, crystal growth, nucleation, NaCl

Introduction

In membrane technology, polyvinylidene fluoride (PVDF) is one of the most utilized polymers due to its excellent combination of properties and processability.^[1] It is available in a wide range of molecular weights as powders and pellets to fulfil typical fabrication requirements. PVDF is a semi-crystalline thermoplastic polymer with excellent chemical resistance and easy processability.^[1]

PVDF has five different polymorphs (α (phase II), β (phase I), γ (phase III), δ and ϵ) determined by its thermal mechanical history.^[2] The α and ϵ -phases are non-polar, the other three are polar. The most common polymorphs in PVDF membranes are α and β phases. The β form is the most thermodynamically stable polar form, whilst α form of PVDF is a kinetically favourable non-polar crystalline form. The specific polymorphs in membranes can be obtained according to the membrane preparation technique and solvent used.^[3–5] Polymorphism is important in membrane technology, because different phases might significantly affect the final membrane properties and performances in terms of membrane fouling and membrane wetting.^[6,7]

PVDF, owing to its good properties such as inertia to various solvents, oils, and acids, has been used in a wide plethora of applications of membrane technology, including ultrafiltration (UF)/microfiltration (MF), membrane distillation (MD), pervaporation (PV) and in membrane contactors such as membrane distillation, membrane crystallization, membrane condensers and membrane emulsifiers.^[8,9]

Membrane-assisted crystallization is a new unit operation for separation and/or formation of solid pure crystals. Microporous hydrophobic membranes are used to promote the water vapor transfer between phases inducing supersaturation in solution, leading to precipitation of solute and formation of crystals.^[9,10] Some important advantages make this methodology of growing interest: well-controlled nucleation and growth kinetics, fast crystallization rates and reduced induction time (the induction time can be defined as the time when the first NaCl crystals pictures are observed and crystals start to be characterized), membrane surface promoting heterogeneous nucleation, fine modulation of the level and rate of supersaturation and selection of polymorphic forms.^[9]

Membrane crystallization is strongly affected by the mem-

brane and by its chemical-physical properties.^[10] In a membrane crystallizer, microporous hydrophobic membranes are used to create and sustain a controlled supersaturated environment, in which crystals can nucleate and grow. Owing to hydrophobic character of used membranes, only the volatile components can permeate through the membrane, non-volatiles do not permeate. Furthermore, the crystallizing solution is in direct contact with the membrane surface, so there is a solution-membrane interaction influenced by the fluid dynamics. The effects can be due to both structural and chemical properties of membrane surface that might operate as a physical substrate for heterogeneous nucleation, by inducing a reduction in the free energy barrier.^[11] For example, PVDF membranes reduce induction time of crystals compared to conventional crystallization without the presence of a membrane as a physical barrier supporting the vapor-liquid interface;^[12] moreover, the addition of nanoparticles in membranes has an amplifying effect that reduces the nucleation rate of crystals more and more. For instance, the addition of graphene platelets in PVDF membranes induced faster supersaturation and faster nucleation when compared to the pristine PVDF.^[13,14]

Nevertheless, a clear correlation between the dominating crystalline phases in PVDF and the performance in membrane contactor applications, and in particular in membrane crystallization is still missing and necessary. Today, molecular simulations can help to gain detailed comprehension of involved mechanisms of crystal nucleation and growth.^[15–33] However, there are not many computational studies on mechanisms of crystals nucleation and growth applied to membrane-assisted crystallization.^[13,14] To our knowledge, only the influence of a hydrophobic polymeric membrane of polypropylene (PP) and PVDF was observed computationally to reduce nucleation times in comparison with NaCl crystallization in simple bulk solution.^[12] No study is available if polymer matrices have polymorphs.

The innovation of the present work is to utilize molecular dynamics simulation to investigate the ability of the two main investigated polymorphs of PVDF (*i.e.*, α and β) to induce changing in Na^+Cl^- crystals formation and growth, in comparison with the amorphous phase during membrane crystallization process (MCR).

In particular, the aim of the work was to compare the behaviour of crystallization process of NaCl solution approaching the α and β PVDF and the amorphous phase. We have compared the results obtained in this work with that of crystallization of NaCl simulated in bulk solution and with amorphous PVDF^[12,14] and validated the theoretical data with the experimental ones available. In this paper, we show the prepared new amorphous models, assuming that the membranes were without any polymorphism. In analogy, fully α and fully β membrane models were prepared, too. The real membranes exist only with a certain fraction of α or β phase and/or with mixture of both phases, according to several parameters used to fabricate membranes, such as solvent, temperature, addition of nanoparticles and/or salts, *etc.*^[5,6,34]

In our atomistic simulation, we made some assumptions: (1) The membranes are dense because the dimensions of our models are in the range of a few nanometers; a larger size that could consider also micropores will require such high computational power as to be out of scale. (2) The distillation stage of the crystallization process implying the removal of water in the form of vapor from a liquid stream was not considered. (3) The crystallization process was analysed with the solution already in supersaturation condition.

The goal was to analyse the influence of the membrane material on the crystallization of NaCl. For this reason, the

behaviour of dense surfaces can be considered analogous to that of experimental microporous membranes. Despite these limitations, the predictive results that could be obtained will deliver useful insights on the materials structure-properties relationship and, in particular, on how different PVDF membranes can be responsible for nucleation times and crystallization phenomena also different salt solutions.

Changes in polymorphs, allowed the evaluation of significant difference in water sequestration by the membranes. This aspect allowed to achieve reduced induction times for all PVDF membrane systems with respect to crystallization without membrane (bulk crystallization). The nucleation rate was determined as well as critical nucleus size for each system and computational induction time. The crystal growth was analysed investigating the averaged cluster size in the solution. The results indicated that the presence of amorphous PVDF increases the nucleation rate and promotes the simultaneous growth of a large number of clusters. On the other hand, α and β PVDF leads to a regular growth of only a small number of clusters. In addition, α PVDF produces much more inhomogeneous crystals and of small dimensions; β PVDF produces crystals of larger dimensions than α PVDF. These computational results provide interesting suggestions about the ability of α and β polymorphs to influence the nucleation and growth of salts.

Materials and Membranes

Models construction

Unbiased molecular dynamics simulations using all the atoms were performed for the investigation of feasibility of growing NaCl crystals. The Material Studio package (version 7.0) of BIOVIA^[35] was used to build the models of amorphous α and β PVDF, with COMPASS force field (Condensed phase Optimized Molecular Potentials for Atomistic Simulation Studies)^[36] that is an ab-initio force field parameterized and validated using various empirical data and condensed phase properties for molecules in isolation.

The amorphous template chain consisted of 100 monomers (602 atoms). Amorphous polymer packings were constructed with periodic boundary conditions using the Theodorou/Suter method^[37] as implemented in the Amorphous-Cell module. The amorphous PVDF models contained 13 polymer chains, with a total of 7826 atoms. For equilibrating the models, they were energy-minimized and then molecular dynamics (MD) simulations were performed until final densities, at the values of the experimentally measured, were reached with a time step of 1.0 fs. The nonbond interactions (electrostatic and van der Waals) were calculated using the Ewald summation method^[38] with an accuracy of $0.001 \text{ kcal mol}^{-1}$. Temperature and pressure were controlled by using the Berendsen algorithm with a decay constant of 0.1 ps.^[39] The amorphous membrane models were prepared according to the procedure detailed in Tocci *et al.*^[40,41] The initial densities were set to 0.8 g cm^{-3} . The models were equilibrated using the following procedure: (1) constant particle number, volume, and temperature (NVT) MD simulation at 308 K for 50 ps, (2) constant particle number, pressure, and temperature (NPT) MD simulation at 308 K and 0.005 GPa (50 bar) for 50 ps, (3) constant particle number, volume, and temperature (NVT) MD simulation at 600 K for 30 ps, (4) NVT MD simulation at 400 K for 30 ps, (5) NVT MD simulation at 300 K for 20 ps, (6) NPT MD simulation at 308 K and 0.0001 GPa (1 bar) for 50 ps, (7) NPT MD simulation at 298 K and 1 GPa for 50 ps, (8) NPT MD simulation at 298 K and 1 GPa for 300 ps. Steps 3–7 were repeated until the simulated densities were stabilized then Step 8 was performed. The final density of $1.7 \pm 0.015 \text{ g/cm}^3$ for pristine PVDF was obtained and agrees with the value

of 1.68 g/cm³ of the PVDF polymer experimentally used (SOLEF 60/20; Solvay Specialty polymers, IT) and as in reference.^[42] The final box sizes have dimensions size of (5.632 × 5.626 × 2.559) and (5.418 × 5.418 × 2.462) nm³.

For α and β PVDF membrane models, a different procedure was used owing to their crystalline structures. A single cell was built using BIOVIA software with X, Y and Z axes size of (0.496 × 0.964 × 0.462) nm³ for α PVDF and of (0.866 × 0.493 × 0.258) nm³ and for β PVDF. Then two supercells of the crystal structures were grown with a size of (2.480 × 5.784 × 6.006) nm³ for α PVDF and of (2.598 × 5.916 × 5.934) nm³ for β PVDF, respectively. A final density of 1.925 g/cm³ and of 1.931 g/cm³ was reached for α and β PVDF.

Then, the GROMACS software version 5.1.4^[43–45] was used for subsequent calculation of crystallization process with the VMD, version 1.9.3^[46] software package used to visualize the structures. The equilibration of the models was checked: steps 3–8 were performed also with GROMACS until the simulated densities of polymeric PVDF were stabilized.

The box size of membrane models was extended along the Z-axis in order to put the water/salt solution into contact with the polymeric surface reaching a final size of (5.63 × 5.63 × 11.38) and (5.418 × 5.418 × 10.951) nm³ for amorphous PVDF, of (10.416 × 5.784 × 6.006) nm³ for α PVDF and (10.916 × 5.916 × 5.934) nm³ for β PVDF. Owing to small changes in the density of the amorphous PVDF models, small differences were found with a final volume of 350.23 ± 4.23% nm³. A total volume of 361.84 nm³ for α PVDF and of 383.23 nm³ for β PVDF was obtained. Then, the boxes were filled with 7405, 7246 and 7768 water molecules, respectively. The NaCl molar concentration of about 6 M was prepared for the three systems. This value is above the supersaturated conditions of 5.4 mol/L at 303 K. In particular, a molar concentration of 6.016 ± 0.100 mol/L, 5.974 ± 0.049 mol/L and 5.969 ± 0.082 mol/L was reached for amorphous, α and β PVDF, respectively. At about 769–832 pairs of Na⁺ and Cl[−] ions were added in order to simulate the condition near a membrane surface during crystallization experiments.

The supersaturation ratio, *S*, is calculated as the ratio $S = c/c^*$, where *c* and *c*^{*} are solution concentration and equilibrium saturation value, respectively (crystallization of NaCl to occur at sodium chloride concentrations larger than 5.4 mol/L^[47]). If *S* is 1.0, it means that the solution is saturated; if the value is below 1.0, the solution is undersaturated, whilst values above 1.0 denote supersaturated conditions. The metastable limit for NaCl, i.e., the supersaturation ratio limit for spontaneous crystal formation (primary nucleation) is $S = 1.0025$.^[48] All the molecular details of the models realised are reported in Table 1.

Table 1 Computational details of models produced

PVDF	# NaCl	# H ₂ O	NaCl initial concentration/ (mol/L)	<i>S</i> (−)
PVDF	793.5 ± 4.4%	7404.5 ± 4.4%	6.016 ± 0.100%	1.114
α	776 ± 0%	7246 ± 0%	5.974 ± 0.049%	1.106
β	832 ± 0%	7768 ± 0%	5.969 ± 0.082%	1.105

The SPC/E model^[49] was used for water; the ion parameters were those of the OPLS force field,^[50,51] the force field parameters of the PVDF polymer developed by Bytner and Smith^[52] were utilized with all pair interactions consisted of Lennard-Jones (LJ) (Table 2) and Coulombic terms. The LJ cross-interactions were obtained using the usual Lorentz-Berthelot combining rules. Coulombic interactions were treated employing the particle mesh Ewald (PME) summation method.^[53] All membrane/solution systems were equilibrated for 2 ns (both NVT and NPT ensembles), and then two production

Table 2 Nonbonded force field parameters and charges of Lennard-Jones potential for water, ion and PVDF^a

Atom Type	$\sigma/\text{\AA}$	$\epsilon/(\text{kJ/mol})$	Charge/e
O _w	3.166	0.6501	−0.8476
H _w	0.000	0.000	+0.4238
Na ⁺	3.330	0.0116	+1
Cl [−]	4.417	0.4928	−1
C _{PVDF,H}	3.500	0.2763	−0.6502
C _{PVDF,F}	3.500	0.2763	+0.7650
H _{PVDF}	2.500	0.1256	+0.2258
F _{PVDF}	2.983	0.2512	−0.2832

^a The O_w and H_w parameters are for water and are taken from Ref. [51], the Na⁺ and Cl[−] parameters are from Refs. [51] and [50], respectively. The parameters of C_{PVDF,H}, C_{PVDF,F}, H_{PVDF}, and F_{PVDF} are for PVDF and from Ref. [52].

runs of 100 and 200 ns were carried out for each system, respectively. The simulations were carried out in the NPT ensemble at 300 K and with a pressure of 1 atm with a time step of 1 fs, using a velocity rescaling algorithm^[54] ($\tau_t = 0.1$ ps), to control the temperature and the Berendsen barostat^[39] ($\tau_p = 0.1$ ps) for the pressure.

Molecular structures of models produced are represented in Figure 1.

Figure 1 Molecular structures of models produced. (a) Chain used for amorphous PVDF; (b) and (c) unit cells used for α and β PVDF, respectively. (a'), (b') and (c') final boxes of amorphous, α and β PVDF, respectively. (a'') Amorphous PVDF, (b'') α PVDF and (c'') β PVDF boxes filled with NaCl and water molecules.

Radial distribution function $g(r)$

The $g(r)$ indicates the local probability density of finding type B atoms at a distance *r* from type A atoms, averaged over the equilibrium density.^[55] It is defined by the following equation:

$$g(r) = \frac{n_B / 4\pi r^2 dr}{N_B / V} \quad (1)$$

where N_B is the total number of type B atoms, *V* is the total volume, n_B is the number of type B atoms lying at a distance *r* from atom A, considering a shell of thickness *dr*.

Coordination number

The coordination number (CN) counts the number of ions within a predefined distance r_θ from a selected ion *i*. The coordination numbers were computed by using standard radial distribution functions $g(r)$ and then counting the average num-

ber of ions or water within the first hydration shell of the counterions (or integrating the $g(r)$ up to the location of the first minimum).

The first coordination number can be described from the following equation:

$$n_1 = 4\pi \int_0^1 r^2 g(r) \rho \, dr \quad (2)$$

where 0 is the rightmost position starting from $r = 0$ whereon $g(r)$ is approximately zero, $r = 1$ is the first maximum. Therefore, it is the area under the first peak of $g(r)$. The ρ was calculated:^[56]

$$\rho = \frac{n^\circ \text{ of Na atoms} + n^\circ \text{ of Cl atoms}}{V \text{ (}\text{\AA}^3\text{)}} \quad (3)$$

for the CN calculation of $\text{Na}^+ \text{Cl}^-$ interactions, while:

$$\rho = \frac{n^\circ \text{ of Na atoms} + n^\circ \text{ of H}_2\text{O atoms}}{V \text{ (}\text{\AA}^3\text{)}} \quad (4)$$

for CN calculation of Na^+ element O (from water molecule) interactions.

Diffusion coefficient

The diffusion coefficients (D) of ions is calculated using the Einstein equation:^[38]

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle (r_i(t) - r_i(0))^2 \rangle \quad (5)$$

where D is diffusion coefficient and $\langle (r_i(t) - r_i(0))^2 \rangle$ is mean square displacement of the penetrants.

Nucleation rates

We have used the Yasuoka-Matsumoto method^[15] analysing the time change of clusters with time. The number of nuclei that are larger than the critical size nucleus generated per unit volume per unit time, are counted and plotted against time. A growth-decay evolution curve is produced^[21,57] and schematically indicated in Figure 2.

Figure 2 Sketch of the Yasuoka-Matsumoto method indicating the change over time for the number of nuclei (N) larger than a threshold size.

Here domain I indicates the induction time where no nuclei larger than the critical ones appear. Domain II indicates the time interval where nuclei with a size above the critical one appear. Domain III specifies the stopping of formation of new nuclei and in parallel the balancing of collision processes such as agglomeration and coalescence, with the results that the number of clusters above in this domain remains nearly constant. Domain IV is the enlargement regime. The nucleation rate was determined from a slope of the curve in domain II (which does

not change if the size of a cluster reached a critical value) divided by the volume of the simulation box. The nucleation rate is indicated in the number of nuclei per cubic meter per second.

Crystals (cluster) detection

The Density-Based Spatial Clustering of Applications with Noise (DBSCAN) algorithm,^[58,59] was adopted in order to detect NaCl crystals organized in clusters, as proposed by G. Lanaro and G. Patey.^[60] A “cluster” is here a group of mutually connected ions, following the DBSCAN definition. The main idea of the DBSCAN algorithm is to locate regions characterized by a high density of ions separated from others by low density regions, considering two parameters: the number of ions η and the distance ε , the radius of search of each iteration. The parameter ε is the minimum distance, for which two ions are considered to be part of the same cluster. The calibration of this distance is fundamental in order to identify independent clusters that are close to each other or to connect ions that are effectively part of the aggregate. On the other hand, parameter η is a threshold for the size of the aggregate. Clusters with a number of elements lower than η are extremely short-lived and are excluded from the clusters analysis and considered as noise. The parameter set (ε) is the length between ions and is equal to 0.3 nm, i.e., approximately the NaCl bond length. The nuclei sizes consisting of at least six atoms were counted during the MD simulation to obtain statistics.

The DBSCAN algorithm can be summarized as follow: (a) an ion is selected randomly and the number of neighbour ions within the distance ε is counted; (b) if the number of neighbours is greater than or equal to the threshold η , the ion chosen is identified as a core ion and its neighbours as border ions, otherwise if the number of neighbours is lower than the threshold η the ion chosen is identified as a noise ion (Figure 3); (c) steps (a) and (b) are repeated starting from an ion from the border. If it is a new core ion, new border ions around it are identified and the procedure is repeated. Otherwise, if it is an actual edge of the cluster, all the ions are labelled as part of the same cluster; (d) the procedure is repeated choosing another random ion not previously analysed until all the ions are considered.

Figure 3 Core and Border Points in a Database with the red data point considered as Noise.

Results and Discussion

The kinetics of formation of NaCl particles and their growth, from random ion arrangements, was studied at 303 K and at a supersaturated condition of about $S = 1.1$ for NaCl approaching amorphous, α and β PVDF. A face-centered cubic lattice crystal of NaCl was observed, with lattice parameter of $a = 5.66 \text{ \AA}$ in agreement with the experimental value of $5.64 \text{ \AA}$ determined on synthetic NaCl powders.^[61] Initial and final configurations of the system are shown in Figure 4, where water molecules are omitted for clarity.

Figure 4 Snapshots of MD simulations for (a) at the beginning of the simulations, (b) amorphous PVDF at 200 ns, (c) α PVDF at 200 ns and (d) β PVDF at 200 ns.

At 0 ns, there is a disordered distribution of ions whilst at 200 ns. When crystals formation is well established for all three systems, multiple irregularly structured crystals can be seen: a much more compact structure in the amorphous PVDF, more fragmented for both α and β phases. Moreover, a larger number of free ions are visible for α and β PVDF polymers in comparison with the amorphous phase.

The global crystals formation during the simulation time can be visualized by analysing the $\text{Na}^+ \text{Cl}^-$ coordination number (Figure 5). The average number of ions within the first hydration

Figure 5 Coordination Number (CN) estimated from radial distribution function between Na^+ and Cl^- ions.

shell of the counterions was easily obtained by simply integrating the ion-ion radial distribution function up to the location of the first minimum in the radial distribution function. The $\text{Na}^+ \text{Cl}^-$ coordination number increased with time up to a value of about $n^+ = 5.0$ for amorphous PVDF and of about 4 for α PVDF, β PVDF and bulk solution. All these values are different from those of a perfect cubic crystal, *i.e.*, $n^+ = 6$, owing to the remaining ions in solution and the irregularity of the crystal structures; for such high concentrations, these results were expected. The ion aggregation is much more massive for amorphous PVDF with respect to the α and β PVDF models.

The contribution of water molecules to the formation of crystals, is reflected by the $\text{Na}^+ \text{O} (\text{H}_2\text{O})$ coordination number (Figure 6), which drops from the value of $n^+ = 5.4$ (lower than $n^+ = 5.9$ at infinite dilution solution – that is the value of water molecules in the first coordination sphere, because of such high concentrations of salts) as the cation-anion coordination number surges.

Figure 6 Coordination Number (CN) of Na^+ ion and element O. Here O denotes the oxygen atom of the water molecule.

The average number of waters within the first hydration shell of the counterions remains higher for β and α PVDF until ≈ 20 ns with respect to amorphous PVDF, where the $\text{Na}^+ \text{O}$ coordination number decreases rapidly after a few nanoseconds of simulation. This is a clear indication about the more rapid nucleation and, in particular, the faster stabilization of crystals formation, which happens for the amorphous PVDF model.

Nucleation rate

The formation of a crystal from solution is a process composed of two stages: an initial nucleation followed by subsequent growth of the crystal to macroscopic size. The nucleation stage, which is particularly difficult to understand, is generally the rate determining step. In the classical theory of nucleation (CNT),^[24] the major assumption is that the arrangement of molecules/ions in a crystal nucleus are identical to that of the stable bulk crystalline phase. In other words, the surface free energy of the nuclei is equivalent to that of the crystal interface. The free energy change associated with the formation of a nucleus is determined by competition between two terms: an unfavourable surface-energy term and a favourable bulk. At a certain size, the favourable term dominates, and then the nucleus becomes stable and continues to grow into a bulk term. However, the CNT model proposed by Gibbs^[62] of free energy minimization is too simple, depending only on the one-dimensional structure of the nucleus (radius r) and on the fastest nucleation pathway.

In reality, there are multiple pathways for molecules between the initial solvent state to the final crystal structure. Local fluctuations appear in the bulk metastable phase that are similar to an intermediate phase distinct from the stable phase. Then, this intermediate fluctuation undergoes a transition, in which the stable – crystalline phase emerges.^[25,26,63–65] In detail, Na^+ and Cl^- ions during the simulation time organize themselves in regions of highly concentrated disordered ions and then the initial formation of ordered clusters and growth can be detected.

The formation of unstable nuclei before the nucleation as well as the first stable nuclei was all identified with the method of Yasuoka and Matsumoto.^[15] The nucleation rate is strongly related to the supersaturation ratio and to the critical size of the nuclei. The role of temperature is dual: nucleation is generally promoted by low temperatures (which slow down ions from drifting away from new nuclei), but lower ions diffusion, limiting the growth of the nuclei.

From the curves of the number of clusters as a function of time, the induction times with no nuclei larger than the critical ones are of few nanoseconds for all systems. The domains II are in the range of 30 ns for the amorphous PVDF, ~ 40 ns for α and β PVDF. It indicates the time interval where nuclei with a size above the critical one, where a critical nucleus size is defined as the minimum size required for continuous growth of a crystalline nucleus.

The slope of the curves in domain II has been calculated and divided by the volume of the box, leading to the nucleation rate. The nucleation rate is defined as the number of nuclei (larger than the critical size nucleus) per unit volume per unit time.

In order to span the different possibilities, we defined several thresholds of clusters size dimension, *i.e.*, $N > 6$, $N > 8$, $N > 10$, $N > 12$ and $N > 14$ for the three systems (Figure 7). In the three PVDF systems, the slope slowly decreases until the cluster sizes exceed the value of 12. Above these values the slopes were constant and therefore the nucleation rate was calculated for $N > 12$ (Table 3).

Moreover, the observation of the number of clusters indicated that after nucleation they were reaching the plateau (domain III), where the number of clusters remains nearly constant with the two opposite processes of coalescence and dissolution. The small decrease observed at about 200 ns of simulation is not enough to indicate that domain IV is reached (indicating that a longer simulation would be needed to observe the enlargement of the crystals formed).

(a) α PVDF

(b) β PVDF

(c) amorphous PVDF

Figure 7 Number of clusters larger than the critical nucleus at the given sizes of $N > 6$ (solid line), $N > 8$ (dashed line), $N > 10$ (dotted line), $N > 12$ (red dot dash line) and $N > 14$ (dot dash line), along the simulation time, (a) for α , (b) for β and (c) for amorphous PVDF. In a) the three domains are indicated: the induction time with no nuclei larger than a threshold size (I), the growth (II) and the constancy of number of clusters.

Table 3 Nucleation rate and critical nucleus size details of models produced

PVDF	Critical nucleus N^* atoms	Computational Induction time in ns	Nucleation rate $J (\times 10^{33} \text{ m}^{-3} \text{ s}^{-1})$
Amorphous	~13–14	0	2.26 ± 0.15
α	19	3–4	1.20 ± 0.18
β	13–19	5.5–8	1.10 ± 0.03

*Critical size producing constant nucleation rate.

The β PVDF showed the lowest nucleation rate (although close to the value of α), whilst the amorphous membrane showed the highest one. As we expect, there is a significant difference in the surface properties of the amorphous PVDF compared to the α and β crystalline forms. Moreover, the nucleation rates calculated for the three systems are in the same range of values of computed NaCl nucleation as other authors.^[57] Today, with state-of-the-art measurements, nucleation has also been observed at the molecular scale,^[66,67] however, it is difficult to access these steps experimentally, so these results can give useful insights into the mechanisms.

Amorphous membranes form quickly stable nuclei, in fact, since the beginning of the simulation. No evidence of unstable

nuclei was seen for this sample. This could be explained by the ability of amorphous PVDF to increase the supersaturation in less time with respect to α and β PVDF.

This feature was confirmed by the largest variations in [NaCl] molar concentration along the several stages of the simulated crystallization process (Table 4) owing to the higher water uptake (Table 5). The values in Table 4 confirmed the tendency to shorten nuclei formation due to augmented water subtraction from NaCl solutions through the membranes.

Table 4 [NaCl] molar concentration at several stage of simulated MCr process

PVDF	[NaCl] initial [mol/L]	[NaCl] nucleation time* [mol/L]	[NaCl] stabilization of crystals formation** [mol/L]	[NaCl] final at 200 ns [mol/L]
Amorphous	6.016 ± 0.004	6.016 ± 0.004	6.142 ± 0.009	6.158
α	5.974 ± 0.003	6.026 ± 0.013	6.082 ± 0.001	6.103
β	5.969 ± 0.003	6.012 ± 0.017	6.043 ± 0.008	6.083

*[NaCl] molar concentration at each simulated induction times for the different PVDF models. **[NaCl] molar concentration after the stabilization in crystals growth, at 10 ns for amorphous PVDF and at 20 ns for α and β PVDF.

Table 5 Water uptake at simulated induction time and after the stabilization of crystals growth

System	Water uptake [%] (nucleation time)*	Water uptake [%] (10 ns)**	Water uptake [%] (20 ns)**
Amorphous PVDF	1.09±0.01	2.55±0.55	n.a.
α PVDF	0.87±0.23	1.14±0.16	1.81 ± 0.04
β PVDF	0.72±3.13	1.05±0.33	1.25 ± 0.09

*Water uptake [%] at each simulated induction time of the models realized. ** Water uptake [%] at different times after stabilization of crystals, i.e., at 10 ns for amorphous PVDF, at 20 ns for α and β PVDF.

The water uptake percentage throughout the membranes [%] (Table 5) was calculated at each simulated induction time, after the stabilization of crystals by measuring the difference between the amount of water molecules in the polymer matrix at each time and that at the beginning of the simulations.

The results indicated that the percentage of water was the highest within the amorphous PVDF model inducing quicker supersaturation, and thus, crystallization. This is due to the fact that some water molecules can move thorough the three membrane systems: in a relatively higher number in the free volume of amorphous polymer chains, in a lesser number through the crystalline α and β PVDF due, as expected, to their rigid and ordered structure. The free volume, that is the space existing inside the polymer chains created by the gaps left between them, can be indicated in terms of fractional free volume (i.e., the ratio of the free volume of a polymer (cm³/g) and the specific volume, defined as reciprocal density). The fractional free volume of amorphous of PVDF is 16.54%. The interspace between chains in α is of 2.3 Å and in β (slightly lower) of 2.2 Å. Moreover, the densities of α and β PVDF are higher than that of the amorphous phases (about 1.7 g/cm³), indicating that α and β are more packed (with less free spaces inside – with densities of about 1.9 g/cm³).

In amorphous PVDF, supersaturation occurred earliest due to a faster passage of water molecules from their initial position towards the polymer matrix, in the instants, in which the nucle-

ation takes place confirmed also by an increase of the diffusion coefficients of water with the mass fraction of Graphene platelets, in particular, in the range between 0 and 1 ns of simulation.

Moreover, the analysis of the diffusion coefficients of ions in the solution approaching the different membrane systems, calculated through the mean squared displacements of ions from the beginning of the simulation and the simulated induction time) and not crossing the membranes, give an indication of different mobility of ions. A nucleation event can take place in solution if the dissolved ions come into contact to form clusters. The diffusion coefficients were higher in the amorphous phase than in α and β . The averaged diffusion coefficient values were $0.53 + 0.04 \times 10^{-9}$ m²/s for PVDF, $0.24 + 0.014 \times 10^{-9}$ m²/s for α PVDF and $0.22 + 0.03 \times 10^{-9}$ m²/s for β PVDF, respectively.

These values are in same order of magnitude as the measure diffusion of NaCl (at 25 °C).^[68] This is also an interesting indication of the difference in the behaviour of the three systems, considering that the rate-controlling step for growth can also be the diffusion of ions through the solution (so the rate of the surface reaction).

Coming back to Table 3, the critical sizes of the nuclei, from which nucleation starts were calculated to be about 13–14 for amorphous PVDF, and 19 for α and β (the last is in the range 13–19). The critical sizes of nuclei are defined if they grow spontaneously to macroscopic sizes instead of going toward smaller clusters. These values are in the same range as that reported by Nahtigal *et al.*^[57] being in the range between 14–24 ions for systems at similar concentrations. These small differences can also be clarified in term of the computational induction time (that is the time when the first nuclei appear). In Figure 8 are compared the simulated induction times of all membrane-based systems. Figure 8 also indicates the experimental data available for the amorphous PVDF^[14] and NaCl bulk solution.^[69]

Figure 8 Experimental (in min) and computational (in ns) induction time for NaCl crystals. The experimental data for the amorphous PVDF are kept from Ref. [14] and for NaCl bulk solution from Ref. [69]

It has to be noticed that the experimental induction time can be defined as the time when the first NaCl crystals pictures (SEM micrographs) are observed. Nucleation is not normally observable at macroscopic level. Moreover, the experiments start with a lower concentration of the solutions and the supersaturation happens after water is removed via a distillation process. Despite different time scales, both the theoretical and experimental trends are in good agreement. The tendency observed indicates a reduced time to detect crystals in the presence of the membrane surface approaching the solutions than in the bulk solutions.

The crystal growth can be observed from the analysis of the

Figure 9 Averaged number of ions of the centres of nucleation for β PVDF along the simulation time.

averaged cluster size in the system along the simulation time, as shown in Figure 9 for the β PVDF during the first 20 ns of the simulation.

In the domain III of the Yasuoka-Matsumoto method, when the number of clusters remains nearly constant, the averaged cluster size, *i.e.*, the number of ions, follows the progression $\beta > \alpha > \text{amorphous}$; as well the dispersion of the size values following the same trend.

The different images of NaCl particles show a random ion arrangement at the beginning. The crystalline state starts to be observed for the evolving NaCl at nucleation stage (the yellow rectangle), where the regular NaCl structure is surrounded by disordered ions. After this transitional period the number of ions gradually grows, finally leading to the formation of a well-ordered stable nucleus at 20 ns. This phenomenon was also observed for the other systems. The investigation of the largest cluster size, in Figure 10, indicated that the nuclei of NaCl increased gradually during simulation, which means that the generated nuclei merged partially with each other.

The scrutiny of the largest clusters (among all those formed) states that: 1) up to nucleation, there is a large oscillation in the amorphous system as well in α but not in β PVDF; 2) at the end of the simulation, α PVDF make smaller clusters, while β and amorphous PVDF produce clusters of larger dimensions (then that of α PVDF). Moreover, at the stage of nucleation, the largest cluster size does not vary much because small clusters collide with most of the free ions. The oscillation in values is made when large clusters were in contact and the maximum cluster size starts to fluctuate along the crystal growth due to interaction with large clusters. Additionally, also considering 200 ns of simulations, it was not possible to observe the phenomenon called Ostwald ripening, *i.e.*, when large crystal grow occurs at the expense of the smaller ones, indicating that longer simulation time are needed to have a complete thermodynamic description of the crystallization process, although in principle it does not happen often because simultaneous nucleation of several small crystal, reduces the level of supersaturation disfavoring the growth of large crystals.

In Figure 11, the relation between simulation time, cluster size and the number of clusters for each sample is shown. The surface plots are made counting the number of clusters present in 25 classes of the same dimension, 10 ions wide each, where the first one goes from 0 to 9 ions. The first observation is that the sample with amorphous PVDF shows a higher number of clusters in the lowest sections of the plots, for each time step. As already mentioned, the amorphous PVDF leads to a quicker nucleation. The differences between amorphous and crystalline PVDF in the time region between 0 and 20 ns are remarkable.

Figure 10 Largest cluster size along the simulation time, (a) for α , (b) for β and (c) for amorphous PVDF.

Figure 11 Relation between simulation time, cluster size and the number of clusters for a) amorphous PVDF; b) α PVDF and; c) β PVDF.

Crystals formed when the solution is in contact with α and β PVDF are more inhomogeneous in size than that produced with morphous PVDF. Furthermore, α PVDF produces crystals even more inhomogeneous in size than β PVDF, as can be seen from the distribution of cluster size, which is not continuous in the same time step even in the region between 0–80 ions, where the other samples show a regular behaviour. It can be speculated that the inhomogeneous cluster size distribution in that sample could be due to the continuous formation and disaggregation of medium-size clusters since the beginning of domain II. As a consequence, no large clusters were observed in this sample compared to samples with β and amorphous PVDF. Summarizing, the amorphous PVDF leads to the formation of smaller but more regular clusters with reference to the

other samples; α PVDF produces much more inhomogeneous and of small dimensions crystals; β PVDF produces crystals of larger dimensions than α PVDF. These results related to the growth kinetics of the crystals, might be of particular interest in the design of membrane crystallizers. Larger samples, describing amorphous PVDF combined with α or β phase, different concentrations and temperatures are necessary in order to provide a direct comparison and prediction with experimental data. Computational studies will be developed on the influence of specific polymorphs α and β for the kinetics of the crystal growth.

Conclusion

Molecular dynamics simulations were used to investigate crystal nucleation and growth of NaCl in membrane-assisted crystallization. In this work, the ability of α and β polymorphs of PVDF membranes to impact on Na^+Cl^- crystals formation and growth was successfully predicted and compared with that of the amorphous PVDF phase.

Important change in water sequestration by the membranes was observed with changes in polymorphs, reducing the induction times for all PVDF membrane systems with respect to crystallization without membrane (bulk crystallization).

The crystals (cluster) size distributions, the size of critical nuclei and the nucleation rate are reported. The clusters consisting of approximately 13–19 ions appear critical for their growth. The investigation of the largest cluster size indicated that the nuclei of NaCl increased gradually during simulation, merging partially with each other. Probing the cluster size along the simulation time, the results were that the amorphous PVDF leads to the formation of smaller but more regular clusters with reference to the other samples; α PVDF produced much more inhomogeneous crystals and of small dimensions; β PVDF produces crystals of larger dimensions than α PVDF.

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Conflict of Interest

The authors declare no conflict of interest.

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