Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23346

146 (2019) 8–21
April

Computational synthesis of highly cross-linked reverse osmosis polyamide membranes with optimization of monomer ratio, initial concentration, and reaction conditions

Aamir Alaud Din[a], Young Mi Kim[b,*], Ho Sik Park[b], Seung Eun Nam[b], You In Park[b], Joon Ha Kim[b,c]

[a]*Department of Chemical Engineering, Khwaja Fareed University of Engineering and Information Technology, Abu Dhabi Road, Rahim Yar Khan, UAE*
[b]*Membrane Research Center, Advanced Materials Division, Korea Research Institute of Chemical Technology, Daejoen 34114, Korea, Tel. +82 42 860 7527; Fax: +82 42 860 7283; email: youngmi@krict.re.kr (Y.M. Kim)*
[c]*School of Earth Sciences and Environmental Engineering, Gwangju Institute of Science and Technology, Gwangju 61005, Korea*

Received 27 August 2018; Accepted 21 October 2018

ABSTRACT

In this study, 98%–100% of cross-linked polyamide (PA) membranes were synthesized by interfacial polymerization between trimesoyl chloride (TMC) and *m*-phenylenediamine (MPD), using molecular dynamics (MD) simulations. Previous studies have not been able to synthesize such highly cross-linked membranes, due to a lack of monomer diffusion near the unreacted sites inside the complex three-dimensional PA matrix. This barrier was removed by raising the temperature of the reaction mixture to 1,000 K for 0.02 ns, which increases the monomer diffusion inside the PA matrix for cross-linking. In this study, an automatic, fully generalized, and self-contained Python module was developed to synthesize PA membranes using MD simulations, employing a new algorithm that mimics the physicochemical synthesis of the membranes. Initial amounts of 100, 200, 300, and 400 TMC molecules with varying ratios (TMC:MPD) of 1:0.5, 1:1, 1:1.5, 1:2, 1:2.5, and 1:3 were used. The reaction progress was investigated based on the number of amide bonds formed, which showed an exponentially decreasing trend. The effect of the TMC to MPD ratio on membrane size and degree of cross-linking (DOCL) revealed that a 1:2 (TMC:MPD) ratio was optimal for maximum membrane growth, with approximately 90% TMC consumption and 90% cross-links. The observed DOCL in the membranes synthesized with TMC:MPD < 1:2 was around 99%, and in a few cases 100% cross-linked membranes were obtained. The cross-sectional examination of membranes showed two distinct pore sizes of approximately 5.32 Å ± 0.66 and less than 5.17 Å ± 0.74, for the membranes synthesized with TMC:MPD = 1:1 and <1:1, respectively. These results will be achieved with the ability to synthesize membranes of various DOCLs, by simply changing the ratio between the monomers. The module is available free of charge, and any efficacious suggestions for the improvement of this module will be fully acknowledged.

Keywords: Polyamide; Membrane; Polymerization; Cross-linking; Molecular dynamics simulation

* Corresponding author.

1. Introduction

Water crisis has become an increasing global issue, due to the gap between potable water supply and demand. By 2025, water withdrawal is expected to increase by 50% in developing countries and 18% in developed countries. This will lead to absolute water scarcity for 1.8 billion people and water-stressed conditions for two-thirds of the world's population [1]. Desalination is one of the most economical and leading technologies available; for the past several decades, it has been playing a role to supply potable water in developing and developed countries [2]. Reverse osmosis (RO) is a well-developed and widely used desalination technology to meet water demand, and the membrane is the most important component of the RO process. The membranes for desalination in an RO process are composed of three layers: (1) an ultra thin polyamide (PA) membrane layer (0.1–0.3 μm), (2) a mesoporous polysulfone layer (30–50 μm), and (3) a polyester layer (100–200 μm). The ultra thin layer (PA membrane), also known as the active layer, controls the separation phenomena and is responsible for membrane performance [3]. However, the membrane performance in an RO process decreases due to membrane fouling, which leads to a decline in permeate flux, higher applied pressure, and increased energy consumption. In the case of organic foulants, the permeate flux declines during the initial stages of the RO process, and this has been confirmed with a time series image analysis of the membrane surface [4,5]. Despite decades of research, the physical phenomena that govern the separation process, as well as the membrane fouling, in PA membranes are not fully understood, particularly at the atomic scale because the phenomena occur at a sub-nanometer length scale [6,7].

Given the success of molecular dynamics (MD) methods in gaining insight into the transport behavior of water and ions across boron nitride nanotubes, carbon nanotubes, and graphene, it is a suitable approach to investigate separation and fouling phenomena in PA membranes [8–13]. Unfortunately, over the last several decades, there has been a little progress in understanding the phenomena of salt and water transport, and membrane fouling on an atomistic scale, using MD simulations. This slow progress is a consequence of the complexities involved in the synthesis of a cross-linked three-dimensional PA matrix using MD simulations. The major challenge in synthesizing a PA membrane using atomistic simulations is achieving a high degree of cross-linking (DOCL). In the pioneering works studying water and salt transport across PA membranes using MD simulations, uncross-linked PA chains and PA membranes with only six cross-links were used [14,15]. Due to the complex synthesis process of PA membranes using MD simulations, other methods of synthesizing PA membranes were developed by other researchers [16–19]. However, the DOCL achieved in these studies was still quite low. Experimental studies of PA membrane characterization using X-ray photoelectron spectroscopy and Rutherford backscattering spectroscopy showed that the DOCL in PA membranes is in the range of 60%–100% [20–24]. Recently, developed methods of PA membrane synthesis using MD simulations involve the formation of linear PA chains, as well as the insertion of free monomers at the reaction sites among linear chains, for cross-linking [6,7,25–27]. Using this approach, PA membranes with a DOCL value of 80% have been synthesized.

In this study, a new, improved, and unique method of synthesizing PA membranes using MD simulations was developed (Fig. 1). To synthesize a highly cross-linked PA membrane, a fully automatic, generalized, and self-contained polyamide synthesis toolbox (PAST) using Python version 2.7.10 was developed. PAST is available as a free module under the terms and conditions of the GNU General Public License v 3.0 and can be downloaded free of cost from https://esel.gist.ac.kr [28]. The salient features of PAST that make this study's results prominent are described as follows. Using PAST, an initial system of virgin monomers can be built with any desired concentration and ratio of trimesoyl chloride (TMC) to *m*-phenylenediamine (MPD). Unlike the initial systems consisting of linear PA chains and free monomers, described in previous studies [6,7,14–19,25–27], PAST can start a reaction among free monomers that confirms the random three-dimensional structure of the resulting PA membrane. Membrane synthesis using PAST is an iterative process, and after each iteration the largest PA molecule formed can be separated from other small PA molecules and unreacted monomers present in the reaction mixture and then investigated. Through every stage of synthesis, there is no need to insert extra monomers into the reaction mixture, to increase either the size of the membrane or the DOCL value. Rather, the optimized initial concentration ratio between the monomers (TMC:MPD) gives a sufficiently large PA membrane with an extremely high DOCL. After each iteration, the formation of PA links, as well as the deletion of unwanted bonds and atoms, is controlled by PAST. Bonded terms (bond, angle, dihedrals, and improper

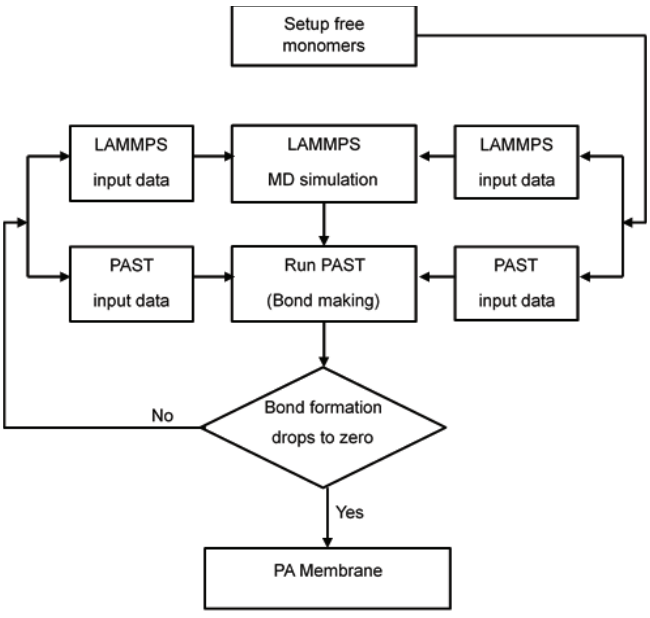

Fig. 1. Flowchart representing the PA membrane synthesis protocol using MD simulation. The algorithm is iterative, starts with free monomers, fully automatic, and operates without the addition of an intermolecular potential or a bias force at any stage to make amide bonds.

terms) to the relevant generalized amber force field (GAFF) parameters, non-bonded terms, and partial charges for the newly formed molecules are all assigned automatically. Similarly, for the unwanted atoms, bonded and non-bonded terms are deleted automatically. The membrane size, number of atoms, number of TMCs and MPDs, and DOCL in the PA membrane can be investigated after each iteration. Using PAST, PA membranes with varying DOCL values (60%–100%) can be synthesized and can be used to study microfiltration (MF), nanofiltration (NF), ultrafiltration (UF), and RO processes. PAST makes it possible to cut the PA membrane into cross sections of any desired thickness in order to visualize and analyze pore size in the membrane. Moreover, the synthesis of 24 membranes in this study revealed the optimized TMC:MPD required to achieve high DOCL and membrane size. A step-by-step tutorial on using PAST to synthesize a PA membrane from virgin monomers is given in Appendix A.

2. Computational details

2.1. Monomer and dimer models

The monomers, TMC and MPD, required to synthesize the PA membranes were obtained from the built-in Cambridge Crystallographic Data Center library in the software package Conquest v1.6. The quantum mechanical calculations of molecular geometry optimization for both monomers were carried out using density functional theory at B3LYP level employing the 6-311++G** basis set, using the quantum chemistry software Jaguar v 6.0 [29,30]. The antechamber program in the AmberTools software package for MD was used to compute Gasteiger partial charges on all of the atoms of both of the monomers [31–34]. The topology and GAFF parameters were generated with the moltemplate package. The intermolecular repulsion and dispersion forces, represented by non-bonded potential energy (Coulombic interactions and Lennard-Jones potential), were also generated using moltemplate [35]. An oligomer of a single repeat unit (one TMC and one MPD) was also modeled with Gasteiger charges and GAFF parameters to determine the addition and removal of bonded terms, non-bonded terms, and partial atomic charges for any amide link formed during the reaction. As the oligomer was used to update charges, bonded, and non-bonded terms, there was no need to optimize the dimer. The optimized monomers and a non-optimized dimer with Gasteiger charges are shown in Fig. 2.

2.2. Membrane synthesis protocol

In this study, we synthesized 24 PA membranes, each starting with different initial concentrations and ratios (TMC:MPD), as shown in Table 1. The initial system setups to synthesize all the 24 PA membranes were built using PAST. The flowchart in Fig. 1 summarizes the membrane synthesis protocol used in this study, which is different from previous studies [6,7,14–19,25–27,36]. From Fig. 1, it is clear that this membrane synthesis is an iterative process, starting with the setup of a system of free monomers with any desired concentrations and ratio between the monomers. All of the simulations were run in Large-scale Atomic/Molecular

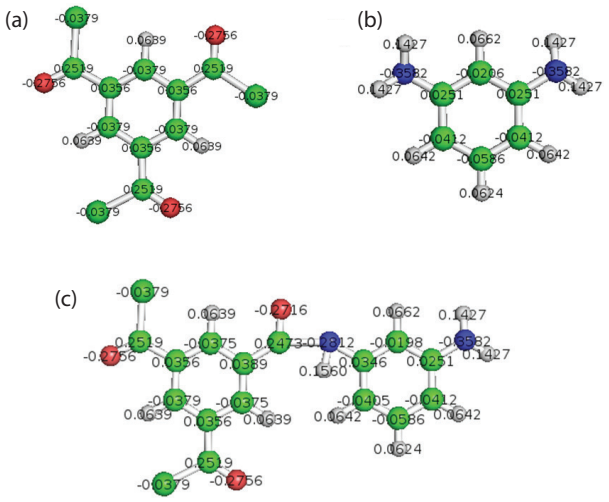

Fig. 2. Optimized structures of (a) TMC, (b) MPD, and (c) dimer with Gasteiger partial charges.

Table 1
Effect of concentration ratio (TMC:MPD) and initial concentration on average pore size and degree of cross-linking in the membrane

TMC:MPD	TMCs	MPDs	Average pore size (Å)	Degree of cross-linking (%)
1:0.5	100	500	–	66.67
	200	100	–	66.67
	300	150	–	66.67
	400	200	–	62.75
1:1	100	100	5.38 ± 0.88	77.08
	200	200	5.32 ± 0.66	77.78
	300	300	5.35 ± 0.98	75.93
	400	400	5.33 ± 0.74	79.62
1:1.5	100	150	5.16 ± 0.89	90.21
	200	300	5.17 ± 0.74	88.61
	300	450	5.02 ± 0.83	89.42
	400	600	5.04 ± 0.70	90.36
1:2	100	200	4.94 ± 0.76	98.86
	200	400	5.11 ± 0.59	97.55
	300	600	5.03 ± 0.76	98.61
	400	800	5.08 ± 0.85	98.76
1:2.5	100	250	5.17 ± 0.86	99.35
	200	500	4.90 ± 1.03	99.81
	300	750	4.96 ± 0.63	99.63
	400	1,000	5.00 ± 0.70	100.0
1:3	100	300	4.94 ± 0.62	100.0
	200	600	5.06 ± 0.57	99.67
	300	900	4.94 ± 0.87	99.68
	400	1,200	5.01 ± 0.85	100.00

Massively Parallel Simulator (LAMMPS) [37]. The input script and all of the data needed by LAMMPS to run MD simulations, and the data required by PAST to initiate the reaction among monomers, were written by PAST itself. The monomers were equilibrated (thermally and mechanically), and random positions without steric clashes were acquired after a 1 ns MD simulation. PAST was then run on the equilibrated system of monomers, which makes amide links between carbonyl carbons of free acyl groups and amine nitrogens of free amine groups, which were found within a cutoff distance of 5 Å (user defined). After the formation of each amide link, the irrelevant chlorine and hydrogen atoms and the bonded and non-bonded terms for the newly formed oligomer were deleted from the system. The system was updated by applying partial charges, and bonded and non-bonded terms with GAFF parameters, for the new amide bonds formed within the system. After the completion of bond formation and a system update, the input script and data required by LAMMPS and PAST for the next iteration were generated by PAST itself again. During the synthesis of each of the 24 membranes, the bond formation dropped to critically low values of two to three bonds after the last iteration. At this stage, the membrane was separated from small PA molecules and unreacted monomers using PAST, and the membrane was equilibrated by running a 1 ns MD simulation. All of the commands to set up the system of monomers, to run the MD simulation and PAST, to visualize the simulation, to separate the membrane, and to analyze the membrane properties are given and explained in Appendix A.

2.3. Simulation and polymerization details

All MD simulations in this study were performed in the program LAMMPS using the Verlet algorithm and periodic boundary conditions in all three dimensions [38]. The initial size of the simulation box was determined based on the distance between the monomers, and the separation of the system from the faces of the periodic box. The particle-particle-particle-mesh method, with a cutoff distance of 10.0 Å, was used to compute non-bonded interactions via long-range Coulombic and Lennard-Jones potential, while GAFF was used to evaluate bonded interactions in all of the N-body simulations [39–41]. The system of monomers was optimized following a 0.02 ns MD simulation with Langevin dynamics at 1,000 K, and a microcanonical (NVE) ensemble was used to perform Brownian dynamics to achieve random molecular positions [42]. A 0.08 ns simulation was run under an isenthalpic (NPH) ensemble to perform time integration of the system with Nose–Hoover style and the system was cooled to a temperature of 298 K. Finally, a 1 ns simulation under an isothermal-isobaric ensemble was run at 1 atm and 298 K for system equilibration. The final molecular positions were utilized by PAST to determine the cutoff distance of 5.0 Å between carbonyl carbons of free acyl groups and nitrogens of free amine groups, for amide link formation. The membrane polymerization was accomplished in nine steps, each utilizing a 1 ns MD simulation. The membrane was separated from small PA molecules and unreacted monomers using PAST, following a final 1 ns MD simulation to optimize and equilibrate the membrane. Therefore, each membrane was synthesized on an MD time scale of 10 ns. The details of amide link formation have already been explained in Section 2.2.

3. Results and discussion

3.1. Membrane polymerization

Synthesizing a PA membrane using MD simulations, while respecting molecular constraints offered by molecular topology, as well as experimental studies, is a challenging task. In this study, the experimental conditions were followed by using free virgin monomers and ambient conditions in the MD simulations of PA membrane synthesis. While synthesizing the PA membrane using MD simulations, the reaction was carried out starting with virgin monomers at 1 atm and 25°C. It should be noted that the real timescale of membrane synthesis is over minutes, which is difficult to meet in the MD simulation timescale. However, compared with previous studies of membrane synthesis using MD simulations, the time constraint has been improved by introducing an iterative process (nine iterations each of 1 ns duration) of membrane synthesis [16,17]. After the first stage (1 ns) of polymerization, a number of small PA clusters were formed at random locations in the reaction mixture. This resulted in a decrease of the reaction rate due to a decrease in the number of bond-making TMC MPD pairs that fell under the cutoff distance criterion of 5.0 Å for bond formation. The cluster formation also resulted in a decrease of the diffusion potential of the monomers at the reaction sites of small PA molecules formed, especially at the later stages of the reaction. However, after each bond formation stage, the system was randomized by employing an NVE ensemble at 1,000 K via the Langevin thermostat algorithm. At this elevated temperature, the small PA clusters and unreacted monomers were separated without adding a bias force to acquire random positions. In the next stage, the system was cooled to 25°C at 1 atm, under an NPH ensemble. The use of the two ensembles, one after the other, not only brings bond-making TMC MPD pairs under the cutoff distance of 5.0 Å, but also solves the problem of diffusion drop of monomers among the PA clusters. In previous studies, the diffusion problem was resolved by introducing a weak bias force or an intermolecular potential and increasing the cutoff distance to facilitate bond formation among unreacted monomers that are more than 5 Å apart. Another strategy was the addition and deletion of monomers adjacent to the unreacted and reacted sites of monomers and PA clusters, respectively [6,16,18]. However, in this study, the reaction was carried out without any addition of external intermolecular potential. The cutoff distance was kept constant (5.0 Å) and without the addition or removal of monomers in the system. A snapshot of a membrane, synthesized by implementing the algorithm shown in Fig. 1, is shown in Fig. 3.

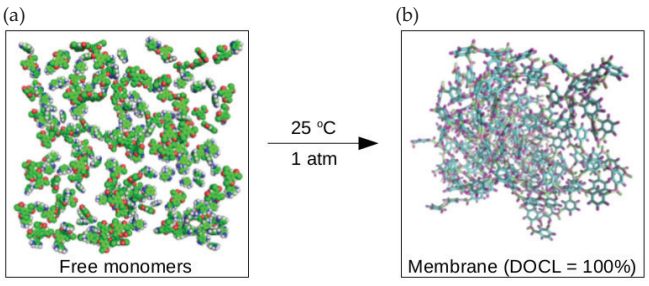

Fig. 3. (a) Initial configuration of monomers (reactants) and (b) PA membrane synthesized (product) at 1 atm and 25°C.

The reaction progress of PA membrane synthesis was investigated in terms of the number of amide bonds formed after each stage of the 1 ns MD simulation (Fig. 4). All six plots in Fig. 4 show an exponentially decreasing trend in the number of bonds formed over the entire timescale of the MD simulations. The MD simulation timescale is different from the real timescale of membrane synthesis; however, the exponential decrease shown in all plots of Fig. 4 represents the behavior of a general chemical reaction. From Fig. 4(A) through (F), it is clear that after 1 ns (first stage of simulation) the number of amide bonds formed increase with decreasing TMC:MPD (from TMC:MPD = 1:0.5 [Fig. 4(A)] to TMC:MPD = 1:0.66 [Fig. 4(F)]). This increase in the number of amide bonds formed with decreasing TMC:MPD is also observed after 2 ns (second stage of simulation) and 3 ns (third stage of simulation). The decrease in the initial concentration ratio (TMC:MPD) is a result of an increase in the initial concentration of MPD. Due to an increase in the initial concentration of MPD (low concentration of TMC), the probability of reaction between TMC and MPD increases because each TMC molecule is surrounded by several MPD molecules. However, the availability of TMC molecules to react with MPD molecules decreases because of the low initial concentration of TMC, and this results in the formation of small PA clusters formed at various locations of the reaction mixture. Therefore, an increase in amide bond formation was observed with decreasing monomers ratios (TMC:MPD). From the fourth stage of simulation and onwards, first the number of bonds formed increased with a decrease in the monomer ratio from 1:0.5 = 2 to 1:2.0 = 0.5 (Figs. 4(A)–(D)), and then decreased with a further decrease in the monomer ratio from 1:2.5 = 0.4 to 1:3 = 0.33 (Figs. 4(E)–(F)). This surprising result can be explained by the ratio of free acyl to amine (AC:AM) groups in the system. With a decrease in the monomer ratio from 1:0.5 to 1:2.0 (Figs. 4(A)–(D)), the ratio of acyl to amine groups (AC:AM) decreases from 3:1 (three acyl groups for one amine group) to 3:4 (three acyl groups for four amine groups).

Although the ideal ratio of acyl to amine groups (AC:AM) is 1:1 (one acyl group for one amine group), a larger membrane size was obtained with a slight decrease in AC:AM (<1.0). As the TMC:MPD was decreased further from 1:2.5 and 1:3.0, the ratio AC:AM decreases from 3:5 (three acyl groups for 5 amine groups) to 1:2 (one acyl group for two amine groups), resulting in overcrowding of amine groups. As AC:AM decreases, MPD becomes the limiting reactant and the membrane size reduces. The ratio between the monomers used to synthesize a PA membrane is important, as it determines the membrane properties, such as membrane thickness, water flux, and ion rejection [43].

3.2. Effect of the initial concentration and monomer ratio on membrane size and DOCL

In this study, initial concentrations and the ratio (TMC:MPD) between the monomers to synthesize PA membranes of large size and high DOCL were optimized. Optimization of the initial concentrations and the monomer

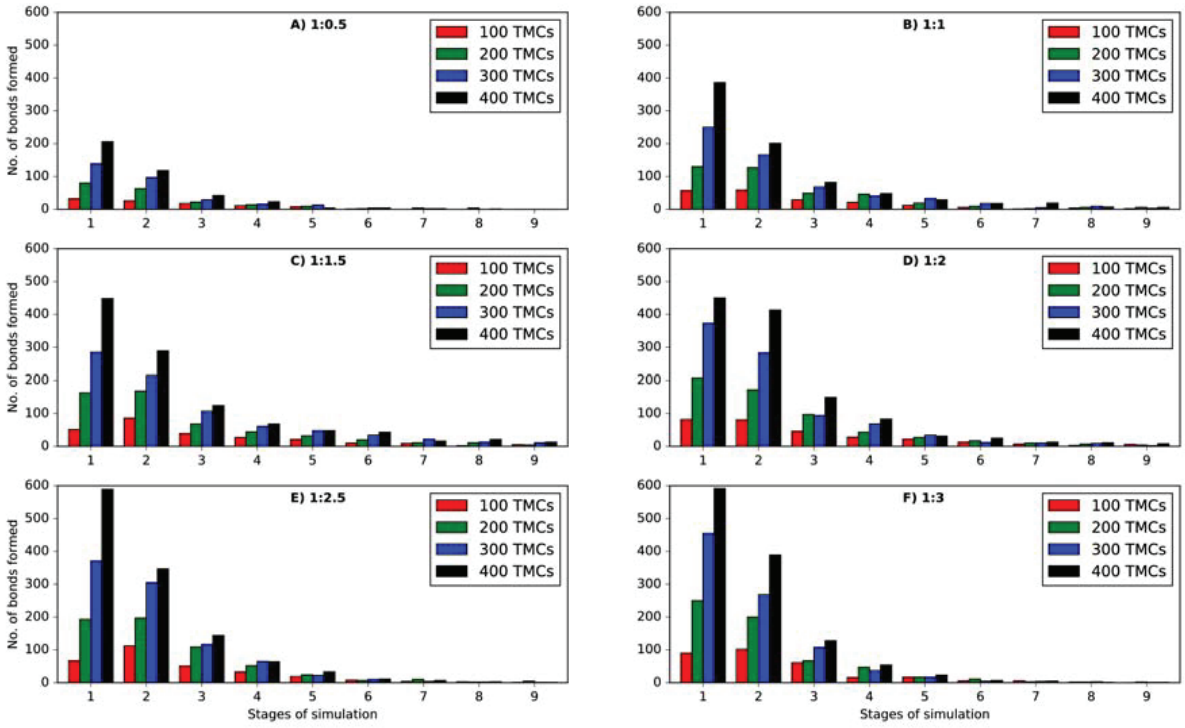

Fig. 4. Effect of monomer ratio (TMC:MPD) on the number of bonds formed after each1 ns stage of simulation (A) 1:0.5, B) 1:1, (C) 1:1.5, (D) 1:2, (E) 1:2.5, and (F) 1:3. Horizontal and vertical axes represent the stages of simulation and number of bonds formed after each stage of simulation. Red, green, blue, and black color bars represent 100, 200, 300, and 400 TMCs in the system, respectively. The number of MPDs can be found using the monomer ratio labeled on each plot.

ratio to obtain larger membrane size is important because of the high computational cost of MD simulations. On the other hand, a high DOCL is important as it determines the membrane properties that affect membrane performance in an RO process [6,7]. Because several PA molecules (clusters) are formed during MD-simulated synthesis of a PA membrane. The percentage of TMC consumption in the largest PA molecule formed after each stage of the MD simulation was used as an indicator of the membrane size and the corresponding DOCL, as shown in Fig. 5. This figure has two panels: (1) the left panel represents the percentage of TMC consumption, and (2) the right panel shows the DOCL in the largest PA molecule formed after each stage of the simulation. The vertical and horizontal axes in both panels represent the initial

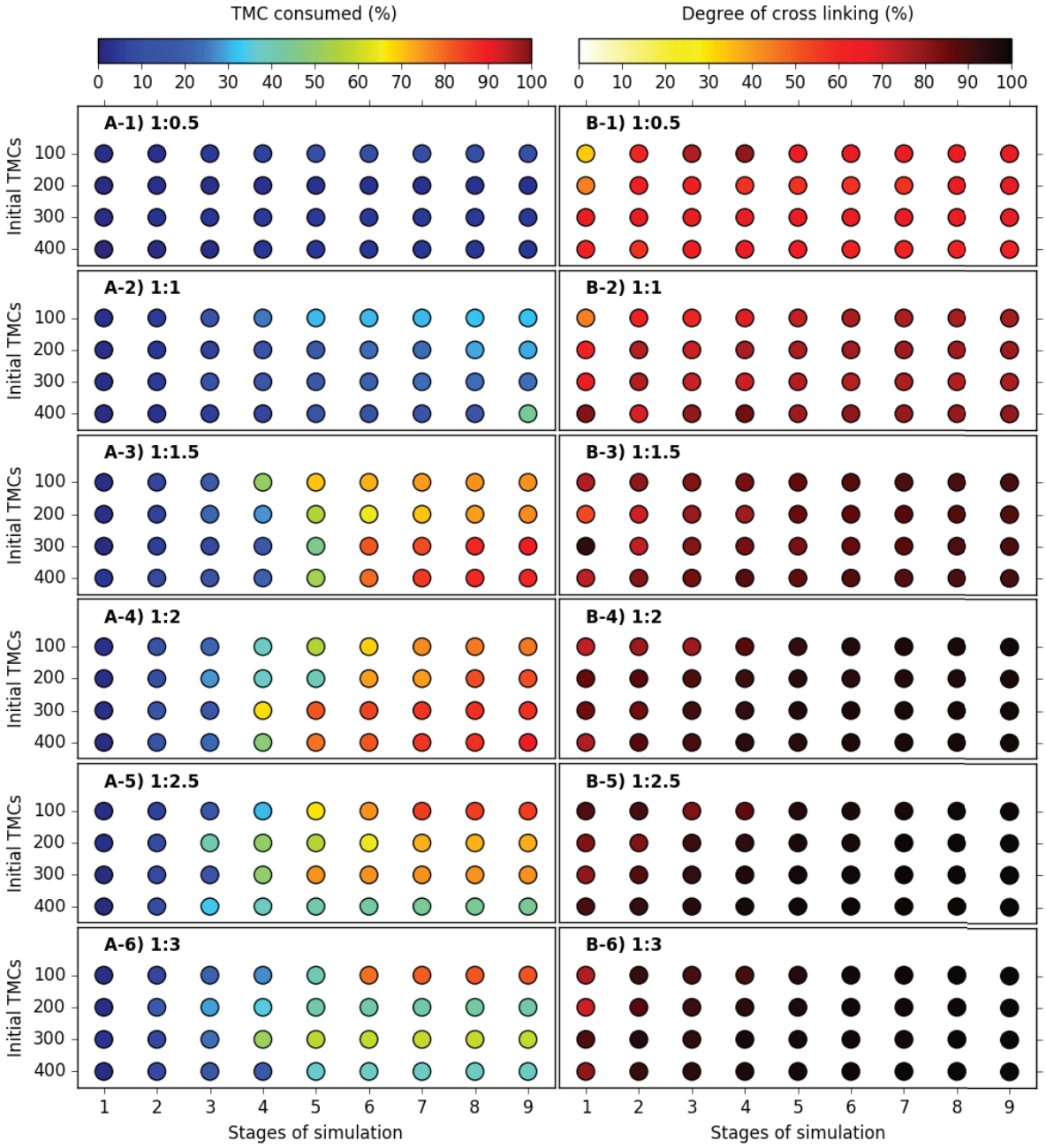

Fig. 5. Effect of initial concentrations and ratio between monomers on (A) membrane size (left panel plots from (A-1) through (A-6)) and (B) degree of cross-linking (right panel plots from (B-1) through (B-6)). The horizontal and vertical axes in all 12 plots represent stages of simulation (the ninth stage is the finalized membrane) and initial concentration of TMC, respectively. The colors of the circles in the left and right panels show the percentage of TMC consumption and degree of cross-linking in the largest PA molecule formed (and in the membrane at the ninth stage). The color of the circle can be read from the color bar shown at the top of the respective panels.

concentration of TMC and the stages of simulation, respectively. Each panel has six plots, which represent descending ratios (TMC:MPD) between the monomers. The color of each circle in the left and right panels represents the percentage of TMC consumption and the DOCL, respectively. The numerical values of the colors can be read from their respective color bars, shown at the top of each panel.

From the left panel in Fig. 5, it is clear that the percentage of TMC consumption increases with a decrease in the monomer ratio from 1:0.5 to 1:2, and then it starts decreasing with a further decrease in the ratio from 1:2.5 to 1:3. However, the right panel shows that the DOCL increases as TMC:MPD decreases from 1:0.5 to 1:2, and then it remains same with further decreases of TMC:MPD. For TMC:MPD = 1:0.5, at any stage of the simulation, the percentage of TMC consumption does not exceed 10%, while the DOCL is approximately 60% (except stages 3 and 4, with 100 TMCs). It is also observed that the DOCL is greater than 80% at the fourth stage of the simulation (plot B-1 with 100 TMCs), which then decreases. This result shows that the biggest PA molecule formed at the fourth stage of the simulation has a high DOCL (80%). At the fifth stage, this molecule with a high DOCL (80%) reacts with another PA cluster with an extremely low DOCL, resulting in the formation of a PA molecule with an intermediate DOCL (approximately 60%). Another possibility at the fifth stage is the formation of the largest PA molecule with an intermediate DOCL, by a reaction between two PA molecules with comparable DOCL. Therefore, the ratio TMC:MPD = 1:0.5 is not suitable for RO membrane synthesis because the resulting membrane has small size and a low DOCL. In plots A-2 and B-2 (TMC:MPD = 1:1), it can be seen that the percentage of TMC consumption is approximately 40%, except in the PA cluster formed with 400 TMCs where the percentage is approximately 50% (plot A-2 with 400 TMCs). The DOCL value is approximately 80% with TMC:MPD = 1:1 (plot B-2). In the case of TMC:MPD = 1:1.5, the percentage of TMC consumption is approximately 70% for 100 and 200 TMC molecules, and 80% for 300 and 400 TMC molecules (plot A-3) with a DOCL of approximately 90% (plot B-3). For TMC:MPD = 1:2, the percentage of TMC consumption is approximately 70% with 100 TMCs, 80% with 200 TMCs, and 90% with 300 and 400 TMCs (plot A-4) and the DOCL is approximately 98%. It is also observed that the percentage of TMC consumption increases from 70% to 80% as TMC molecules increase from 100 to 400 (plot A-3), and from 70% to 90% (plot A-4) with an increased initial concentration of TMC. These results show that the ratio of acyl to amine groups in the system is crucial for determining the membrane size and DOCL. The ideal ratio of acyl to amine groups to synthesize a PA membrane with larger size and a high DOCL is 1:1. However, a slight decrease in the ratio of acyl to amine groups gives a membrane with a maximum size and a higher DOCL. This is because a system with a slightly smaller ratio of acyl to amine groups has more amine groups that can react with acyl groups (responsible for cross-linking), which produces the maximum size and a higher DOCL.

In the system with a TMC to MPD ratio of 1:2.5, the membrane size reduces (85% TMC consumption for 100 TMCs, and less than 65% for 200, 300, and 400 TMCs), but the DOCL surpasses 99%. In this study, a membrane with a 100% DOCL was obtained with 400 TMCs using MD simulations that has not yet been studied based on a literature survey [6,7,14–19,25–27,44]. Finally, in the case of TMC:MPD = 1:3, the percentage of TMC consumption is less than 60% with 200, 300, and 400 TMCs, and approximately 80% with 100 TMCs, while the DOCL is 100%. For these systems (1:2.5 and 1:3), the decrease in membrane size is a result of TMC molecules being crowded by MPD molecules, and various clusters of PA molecules are formed. As TMC is responsible for cross-linking, and each TMC is crowded by several MPD molecules, the PA clusters have an extremely high DOCL. The cases with TMC:MPD = 1:2.5 and 1:3 are opposite to those with ratios of 1:1.5 and 1:2 with reference to membrane size. This is a consequence of the low diffusion potential of TMCs in MPDs and PA clusters owing to a low concentration of TMC.

3.3. Membrane properties analysis

3.3.1. Analysis of membrane size and DOCL

In Section 3.2, an increase in the membrane size and DOCL during the course of the reaction was shown. The PA membrane is obtained after the ninth stage of the simulation and the final membrane size in terms of the percentage of TMC consumption and the corresponding DOCL are shown in Fig. 6. The horizontal axes represent the TMC to MPD ratio, while the vertical axes represent the percentage of TMC consumption and DOCL in the lower and upper plots of Fig. 6, respectively. The lower plot of this figure shows that the membrane size increases with decreasing TMC to MPD ratios up to 1:2, in a sigmoidal manner, and then starts decreasing with further decreases in the TMC to MPD ratio. It is clear that 1:1.5 is the ideal ratio of monomers theoretically (with an equal number of free acyl and amine groups), in which case the membrane growth should be ideal. However, a ratio of 1:2 proves to be optimum to synthesize a PA membrane with a larger size. This result indicates that a slight increase in the initial concentration of MPD increases the membrane size. In the case of the ideal ratio between the monomers (1:1.5), it is

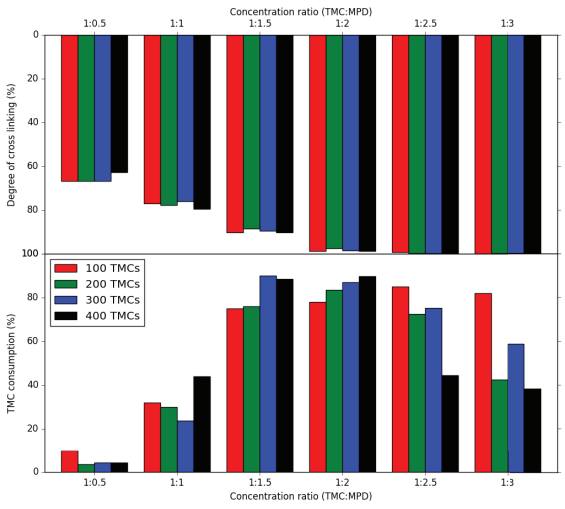

Fig. 6. Percentage of TMC consumption and degree of cross-linking against monomer ratio (TMC:MPD) in the lower and upper plots, respectively.

obvious that every PA cluster formed would be fully cross-linked, and two fully cross-linked clusters have no reaction sites available to react with, hindering the reaction between the clusters. Also, increasing the initial concentration of TMC (1:2.5 and 1:3) decreases the membrane size, with 40% TMCs obtained in the final membrane (black bars). This reduction in membrane size with an increase in initial concentration of TMC is due to the low diffusion potential of MPDs inside PA clusters, as has already been explained.

As far as the DOCL is concerned, it continues to increase as the TMC to MPD ratio decreases. The membranes synthesized with TMC to MPD ratios of 1:2.5 and 1:3 are almost fully cross-linked, but with a compromise in membrane size. The membranes synthesized with a high initial concentration of TMC (400 TMCs in the cases of 1:2.5 and 1:3) have approximately 40% of the initial concentration of TMC in the membrane. As there will also be other highly cross-linked clusters (with no reaction site), the clusters will not join, giving a membrane of small size. Also, starting with a TMC to MPD ratio of 1:3, a finished membrane containing 300 TMCs would require an initial concentration of 750 TMCs and 2,250 MPDs, which requires heavy computational resources. In contrast, in the case of a ratio of 1:2, an initial system size of 330 TMCs and 990 MPDs is sufficient to synthesize a PA membrane containing 300 TMCs with a 98% DOCL. These results indicate that a slight excess concentration of MPD (1:2) over the theoretical ideal can synthesize a PA membrane with 90% TMC consumption and an approximately 99% DOCL. Membranes with varying DOCL values affect water flux and ion rejection in an RO process, and PAST can be helpful to synthesize membranes with varying specific properties [45,46]. Moreover, PAST can also be used to synthesize membranes to study a variety of processes such as MF, NF, UF, and RO.

3.3.2. Pore size

Membrane pore size is an important property in PA membranes and plays a vital role in water molecule diffusion in the membrane. In this study, the average pore size was analyzed in the membranes by cutting them into cross sections (along the *yz* plane) using PAST. In the membranes synthesized with TMC:MPD = 1:0.5, the membrane size was extremely small, comprising only a few TMC and MPD monomers, and therefore the pore size for these membranes was not investigated. The average pore sizes for all of the membranes are shown in Table 1. The average pore size in the membranes synthesized with TMC:MPD = 1:1 were 5.38 Å ± 0.88, 5.32 Å ± 0.66, 5.35 Å ± 0.98, and 5.33 Å ± 0.74, corresponding to membranes synthesized with initial concentrations of 100, 200, 300, and 400 TMCs, respectively. The average pore size declines insignificantly (maximum pore size of 5.17 Å ± 0.86) for other membranes with TMC to MPD ratios lower than 1:1 (1:1.5–1:3). From these results (Table 1), it is shown that the average pore size decreased in the membranes with a high DOCL. With a high DOCL, almost all of the acyl groups are bonded to amine groups, which increases the packing density of the membrane and reduces the average pore size. The average pore size found in this study is in close agreement with published values of PA membrane pore sizes obtained experimentally using a positron annihilation spectroscopic analysis [47]. The average pore size found in this study is slightly larger than that found elsewhere experimentally, but it matches well with pore sizes in membranes synthesized by an MD simulation [16]. A snapshot of a cross-sectional view of the membrane, with a cross-section width of 5 Å, is shown in Fig. 7, and the pores in the membrane are marked with black circles.

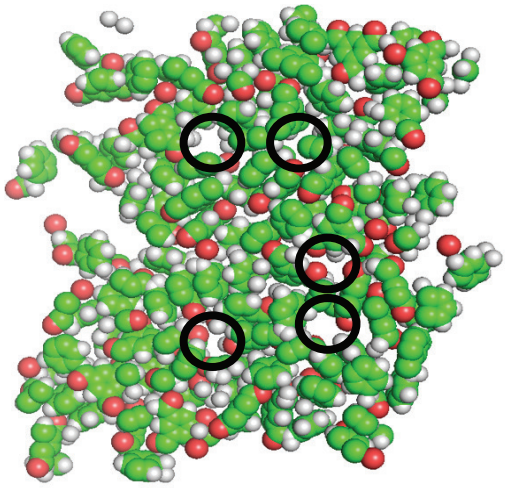

Fig. 7. A cross-sectional view of PA membrane showing pores encircled with black circles.

4. Concluding remarks

This study provides an optimized synthesis of RO PA membranes using MD simulations. It provides a new algorithm that breaks the artificial barriers to the synthesis procedures of PA membranes using MD simulations. In order to implement the new algorithm, a generalized and free Python module was developed, with capabilities ranging from setting up a system of monomers to membrane synthesis and investigation of membrane properties. The synthesis of PA membranes was presented, and the reaction behavior and analyses of membrane properties such as the DOCL, percentage of TMC consumption, and pore size were investigated. The major conclusions drawn from this study are as follows:

1. The synthesis of all of the PA membranes carried out in this study showed an exponentially decreasing trend in the number of amide bonds formed, representing reaction progress. This exponential trend of reaction progress showed two levels of decay that were explained on the basis of the TMC:MPD ratio and the free acyl groups to amine groups ratio.
2. This study presented optimal initial concentrations of TMC and MPD as well as the optimal TMC:MPD to synthesize highly cross-linked PA membranes with maximum membrane size.
3. One of the biggest challenges in PA membrane synthesis is achieving a high DOCL with maximum membrane size, which is hindered by the diffusion of monomers inside the PA clusters formed during the reaction. This diffusion barrier is removed by incorporating an NVE

ensemble with Langevin dynamics at 1,000 K for 0.02 ns that randomizes the reaction mixture to overcome the problem of monomer diffusion inside the PA matrix. This approach removed the artificial ways of overcoming diffusion problems to achieve a high DOCL.

The implementation of a new algorithm and a Python module to synthesize PA membranes described in this study can be used to synthesize highly cross-linked PA membranes. Membranes with varying DOCL can be used to study fouling mechanisms, which is a notable open challenge faced by RO processes. By changing the initial concentrations and the TMC to MPD ratios between monomers, this method can synthesize specific membranes for MF, NF, UF, and RO. It can also assist in studying the arrangement of membrane elements in an RO pressure vessel.

Acknowledgment

This research has been performed as a project no. KK1802-B60 (development of key membranes for high efficiency seawater desalination) and supported by the Korea Research Institute of Chemical Technology.

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Appendix A

In this appendix, we shall describe the complete and step-by-step procedure in the form of a tutorial to synthesize PA membrane using PAST. The tutorial is organized in such a way that the file and folder names appear in red and blue color Courier New font, respectively, with full path in quotes because same files and folder names exist in the working folder as we shall see. Commands of Linux operating system, LAMMPS, VMD, and PAST used in this tutorial to synthesize PA membrane appear in green, black, red, and blue color bold Courier New font, respectively. The commands are explained in such a way that the actions taken by the command are explained followed by the command output. If you are using PAST the first time, we recommend following this tutorial exactly with the same file and folder names and the commands as described in the tutorial.

Step 1. Setting up the system (computer) for membrane synthesis

In order to synthesize PA membrane using molecular dynamics simulation, the required software and packages are Moltemplate, LAMMPS, VMD, PAST, and a molecular system visualization software [35,37,48]. In order to install these software and packages without any compilation effort, we have prepared two installers (1) packages_ubuntu.tar.gz and (2) packages_debian.tar.gz for Ubuntu and Debian OS, respectively, and most of their derived Linux distributions. The installers and the complete tutorial have been tested in house on Debian, Ubuntu, and Linux Mint OS. Download the installer that is more appropriate to your operating system to some suitable location (suppose `'~/Downloads'`). Open the terminal (press Ctrl+Alt+T for Ubuntu) and navigate to the folder where you downloaded the installer (suppose `'cd ~/Downloads'`) and enter the following commands.

OS command 1: `mkdir -p ~/research/past`

OS command 2: `tar zxvf packages_ubuntu.tar.gz -C ~/research/past/`

OS command 3: `cd ~/research/past`

OS command 4: `sh setup.sh`

These commands will create the folder `'~/research/past'`, extract the compressed installer (`packages_ubuntu.tar.gz`) to `'~/research/past'`, and will install all the required software and packages required to synthesize PA membrane using this tutorial. The installer will also add these software and packages to your path and any of them can be called from any folder without using full path to the software or package.

For Linux distros, where the installer does not work, install Moltemplate, VMD, LAMMPS, and a molecular visualization software according to the instructions given in the respective distributions. After successful installation of these packages, use OS commands 1 and 2 and then OS commands 4.1 and 4.2 as shown as follows.

OS command 4.1: `cd ~/research/past/past`

OS command 4.2: `sh setup.sh`

These commands will navigate you to the folder `'~/research/past/past'` and install PAST on your box and the rest of the tutorial (steps 2 through 4) described in the following will remain same.

Step 2. Preparing assembly of monomers for membrane synthesis

In order to prepare an assembly of monomers, PAST has ability to build the system of monomers with any concentration ratio of the monomers (TMC:MPD). In this tutorial we shall synthesize PA membrane starting with 100 TMCs and TMC:MPD = 1:2 (obviously 200 MPDs). To set up this system of monomers, enter the following commands:

OS command 5: `mkdir -p ~/research/membrane/stage_1`

OS command 6: `cd ~/research/membrane/stage_1`

PAST command 1: `python -m setupsys -r 1 2 -m 6 6 -n 5 4 5 -d 6 6 12 -f 6 6 6`

The OS commands 5 and 6 will make a folder `'~/research/membrane/stage_1'` and navigate you to this folder. The PAST command 1 calls Moltemplate and prepares a system of monomers with TMC:MPD = 1:2 (switch `-r 1 2` in PAST command 1) with a distance of 6 Å in x and y directions (switch `-m 6 6`) between TMCs and MPDs of a repeat unit (Fig. (A-1)). The repeat unit is replicated 5, 4, and 5 times in x, y, and z directions (switch `-n 5 4 5`), respectively, and a system of 100 TMCs and 200 MPDs is set up (Fig. (A-2)).

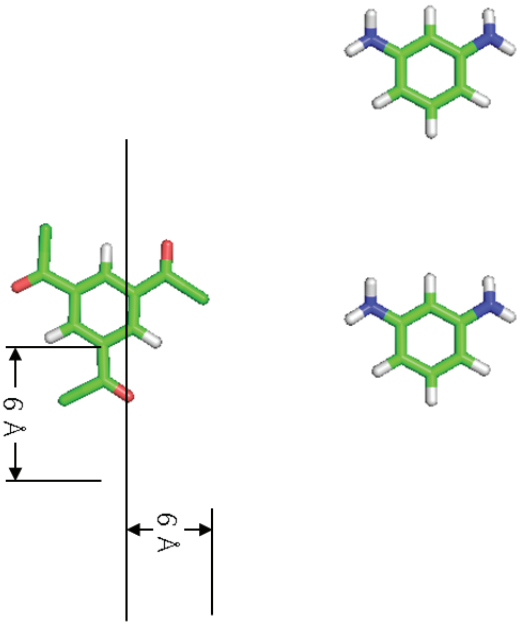

Fig. A-1. A repeat unit of one TMC and two MPDs (TMC:MPD = 1:2) separated 6 Å in x and y directions. The repeat unit is replicated in x, y, and z directions to build system of monomers.

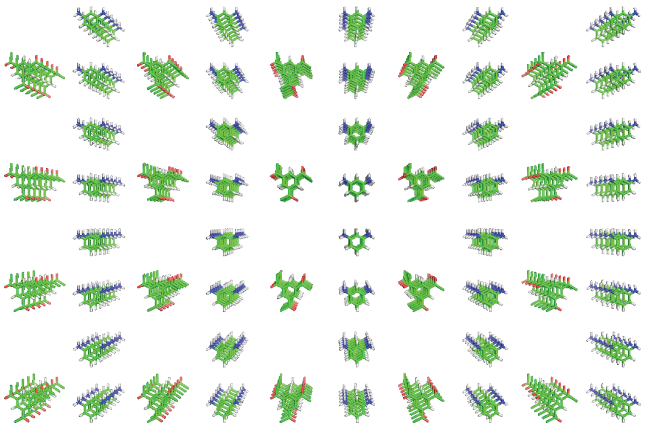

Fig. A-2. System of monomers with 100 TMCs and 200 MPDs. The repeat units are 6 Å apart in x and y directions and 12 Å in z direction. The system is 6 Å apart from periodic box (not shown).

The repeat units are separated by 6 Å in x and y directions, 12 Å in z direction (switch `-d 6 6 12`), and the system of monomers is 6 Å apart (switch `-f 6 6 6`) from each face of the periodic box (periodic box not shown in Fig. (A-2)). The PAST command also opens VMD Main and Display windows. In VMD Main window, open Extensions menu and click TkConsole which will open VMD TkConsole window. In VMD TkConsole window, enter the following VMD commands.

VMD command 1: `topo readlammpsdata system.data full`

VMD command 2: `pbc box`

VMD command 3: `animate write psf system.psf`

VMD command 4: `exit`

These commands will display the system of monomers with periodic boundary around the monomers in VMD Display window, write a psf file (`'~/research/membrane/stage_1/lammps_data/system.psf'`) that helps in proper visualization of simulation video, and exit VMD. The PAST command 1 creates three folders `'bonding'`, `'lammps_data'`, and `'moltemplate_data'` in `'~/research/membrane/stage_1'` and the contents of these folders are described as follows. The folder `'~/research/membrane/stage_1/bonding'` contains six data files (PAST data files) which are used by PAST itself to make amide bonds between carbonyl carbon atoms of TMC and amine nitrogen atoms of MPD. PAST also deletes bonds between carbonyl carbon and chlorine atoms of TMC and one of the two hydrogen atoms and amine nitrogen atoms of MPD using PAST data files. PAST also deletes the chlorine and hydrogen atoms broken from carbonyl carbon and amine nitrogen atoms of TMC and MPD molecules, respectively, after making an amide link between TMC and MPD. Finally, PAST updates (1) partial charges on all the atoms, (2) all the bonded and non-bonded terms, and (3) record of amine nitrogen and carbonyl carbon atoms that have already made an amide bond. The folder `'~/research/membrane/stage_1/lammps_data'` contains LAMMPS input data and script to run LAMMPS simulation. Though these files are written as a result of the call to Moltemplate by PAST, these files are modified by PAST to run LAMMPS simulation smoothly without errors and bugs. The third folder `'~/research/membrane/stage_1/moltemplate_data'` contains Moltemplate data files that are used by Moltemplate to build the system of monomers and will no longer be required in next stages of simulation. Once all the files and folders are created and are at their proper location, we can move to next step of this tutorial, the LAMMPS simulation.

Step 3. Running LAMMPS simulation

Once the system of monomers is ready, use OS command 7 to navigate to `'~/research/membrane/stage_1/lammps_data'` and LAMMPS command 1 to run LAMMPS simulation.

OS command 7: `cd ~/research/membrane/stage_1/lammps_data`

LAMMPS command 1: `mpirun -np x lmp_esel < system.in`

In LAMMPS command 1, x is the number of cores of CPU(s) that can be found using OS command 8 shown as follows.

OS command 8: `lscpu`

Sometimes, LAMMPS simulation may break at any time with an error message of "*Bond atoms x y missing on proc z at step n*", where x, y, z, and n are integers [49]. This error can be overcome by increasing the distance of the system from all the six faces of periodic box, and it can be achieved by entering the PAST command 2 and OS commands 9 and 10 given as follows.

PAST command 2: `python -m bring_inbox -dat system.data -d 25 25 25`

OS command 9: `rm ~/research/membrane/stage_1/lammps_data/system.data`

OS command 10: `mv ~/research/membrane/stage_1/lammps_data/sysinbox.data ~/research/membrane/stage_1/lammps_data/system.data`

PAST command 2 rewrites the already existing system (`'system.data'`) in such a way that the new system (`'sysinbox.data'`) is 25 Å apart from each face of the periodic box. OS commands 9 and 10 delete the old system file (`'system.data'`) and rename `'sysinbox.data'` to `'system.data'` which is default system name in LAMMPS input script. Now, run the LAMMPS simulation again by using LAMMPS command 1 which will make two files `'log.lammps'` and `'dumpfile.lammpstrj'` containing screen output of LAMMPS simulation and atomic trajectory, respectively.

Step 4. Making amide links

After successful completion of LAMMPS simulation, bond formation can be initiated. PAST has the facility of going through the bond formation process either by a single PAST command or by a series of OS, VMD, and PAST commands. First, we show the bond formation process using the single PAST command 3 given as follows.

PAST command 3: `python -m bond_process dumpfile.lammpstrj system.data 2`

This command copies `'dumpfile.lammptrj'` and `'system.data'` files from `'~/research/membrane/stage_1/lammps_data'` to `'~/research/membrane/stage_1/bonding'`. The integer number 2 in the command creates a folder `'~/research/membrane/stage_2'` with two subfolders `'lammps_data'` and `'bonding'` to contain necessary data files to run LAMMPS simulation and bond formation for the next stage (Stage 2). The bonds are formed between carbonyl carbon atoms of TMCs and amine nitrogens atoms of MPDs if they are 5 Å apart or less (default cutoff distance) and the progress of bond formation is displayed. The details of bond formed, deleted, and system update have already been described in Step 2 of the tutorial. The updated system for LAMMPS simulation and PAST data for next stage of simulation and bond formation is written in `'~/research/membrane/stage_1/bonding/New System'`. In addition, a Sybyl mol2 file (`'out.mol2'`) is also written in `'~/research/membrane/stage_1/bonding/New System'` for quick visualization of the system after bond formation. Finally, VMD Main and Display windows pop up, and VMD commands 1 through 4 will write system.psf file in `'~/research/membrane/stage_2/lammps_data'` as has been described already (Step 2 of tutorial). Navigate to `'~/research/membrane/stage_1/bonding/New System'`, right clicking on `'out.mol2'` and then clicking 'Open With' and then 'Other Application...' buttons will pop up application selection window. Click 'Show Other Applications', navigating and clicking 'PyMol Molecular Graphics System' and then 'Select' button will open the `'out.mol2'` in PyMol. In the PyMol Viewer window, click and hold the left mouse button and then move the mouse to rotate and visualize the molecular system. Clicking and holding right mouse button and moving mouse up and down will zoom in and zoom out the molecular system. Now, navigate to `'~/research/membrane/stage_2/ lammps_data'` by entering the OS command 11 and extract the biggest polyamide molecule synthesized by entering PAST command 4.

OS command 11: `cd ~/research/membrane/stage_2/lammps_data`

PAST command 4: `python -m wash system.data`

PAST command 4 will display the total number of atoms, number of TMCs and MPDs in the polyamide molecule, membrane size, and degree of cross-linking. PAST deletes all unreacted monomers and small molecules, hydrates the membrane, and writes moltemplate files 'membrane.lt' and 'system.lt'. If the degree of cross-linking is low, repeat steps 3 and 4 and replace the integer number 2 in PAST command 3 with number 3 (for third stage of simulation and bond formation). Similarly in all folder trees the folders `'stage_1'` and `'stage_2'` in any command (of steps 3 and 4 for this tutorial) must also be replaced with `'stage_2'` and `'stage_3'`, respectively. When the degree of cross-linking is high enough, use PAST command 5 which writes data for LAMMPS simulation. Run LAMMPS simulation finally which optimizes and relaxes membrane geometry that can be used for further research, for example, water treatment after successful completion of LAMMPS simulation.

PAST command 5: `python -m hydrated`

This command will overwrite `'system.data'` file with the hydrated synthesized membrane so this command should be used if the desired degree of cross-linking or user selected specification of membrane is achieved.

Step 4 can also be accomplished with a bunch of OS, VMD, and PAST commands as shown as follows.

OS command 12: `cp system.data dumpfile.lammpstrj ../bonding/`

OS command 13: `cd ../bonding/`

OS commands 12 and 13 copy `'system.data'` and `'dumpfile.lammpstrj'` from `'~/research/membrane/stage_1/lammps_data'` to `'~/research/membrane/stage_1/bonding'`.

PAST command 6: `python2 -m bome -cutoff 5.0 -trj dumpfile.lammpstrj -dat system.data`

This command makes polyamide bonds between carbonyl carbon atoms of TMCs and amine nitrogen atoms of MPDs provided they are apart by 5 Å or less (switch `-cutoff 5.0`). The details of making and deleting the bonds, deleting atoms, and updating bonded terms and the system have already been described in detail.

OS command 14: `cd New\ System`

PAST command 7: `python2 -m mol2`

PAST command 8: `python2 -m bring_inbox`

The OS command 14 navigates you to `'~/research/membrane/stage_1/bonding/New System'`. PAST commands 5 and 6 invoke python modules mol2 and bring_inbox to write a Sybyl Mol2 and LAMMPS input data files, respectively, for the atomic system obtained after completion of bond formation step (obtained as a result of PAST command 4).

OS command 15: `mkdir -p ../../../stage_3/lammps_data`

OS command 16: `cd ../../lammps_data`

OS command 17: `cp system.in system.in.init system.in.settings ../../stage_3/lammps_data`

OS command 18: `cp ../bonding/New\ System sysinbox.data ../../stage_3/lammps_data/system.data`

OS command 19: `cd ../../stage_3/lammps_data`

OS command 20: `mkdir -p ../bonding`

OS command 21: `cd ../../stage_2/bonding/New\ System/`

OS command 22: `cp addindices.txt chargeindices.txt charges.txt constants.txt deleteindices.txt nonsaturated.txt ../../../stage_3/bonding`

OS command 23: `cd ../../../stage_3/lammps_data`

OS command 24: `vmd`

OS commands 15 through 24 make '~/research/membrane/stage_2/ lammps_data' and ~/research/membrane/stage_2/bonding' and copy files needed for next stage (Stage 2) of LAMMPS simulation following bond formation at proper locations. VMD windows pop up and VMD commands 1 through 4 described in Step 2 of the tutorial should be used at this stage. Finally, run LAMMPS simulation as described in Step 3 of the tutorial. Once the desired degree of cross-linking is achieved, use PAST commands 4 and 5 to get the membrane as has already been described.