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

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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

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