

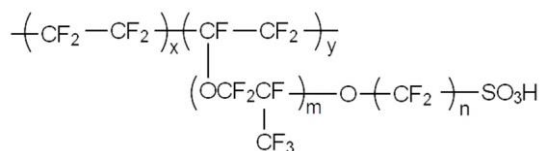
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Molecular dynamics study on the morphology of hydrated perfluorosulfonic acid membranes

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[Introduction]

The perfluorosulfonic acid (PFSA) ionomers composed of a hydrophobic polytetrafluoroethylene backbone with pendant side chains terminated by a sulfonic acid (Fig. 1) are widely used as proton exchange membranes. Since the phase-segregated morphology of the hydrated



PFSA membrane is supposed to directly influence the proton conductance, many morphological models, such as cluster-network model, fibrillar structure model, parallel cylinder model, and film-like model, have been proposed to describe the water swelling behavior and proton transport mechanism through the experimental studies. However, the ongoing structural debate has not been completely resolved yet.

To provide the details of the membrane structure and function, a number of computer simulations of model PFSA systems have been studied. However, less atomistic simulation studies focused on the morphology of the membranes. We here conducted a series of molecular dynamics simulations of the hydrated PFSA membrane to probe the phase-segregated morphology of the membrane. The quantitative characteristics of the geometry, such as Euler characteristic and surface-to-volume ratio, were calculated to evaluate the morphological change at different water contents (λ ; the number of water molecules per sulfonic group).

[Simulation method]

We examined two different equivalent weight (EW = 844 and 1144 g/equiv) PFSA ionomers consisting of 10 monomers. The monomers are composed of 10 (EW 844) and 16 (EW 1166) CF_2 groups in the main chain with $m = 1$, $n = 2$ (See Fig. 1). Sulfonic groups in the pendant side chains are assumed to be fully ionized to H^+ and SO_3^- at all hydration levels and all protons exist in water as hydronium ions (H_3O^+). Simulation systems consisted of 200 polymer chains, 2000 hydronium ions, and water molecules. Six different water contents ($\lambda = 3, 6, 9, 12, 15, \text{ and } 20$) were considered. The modified DREIDING force field by Mabuchi and Tokumasu [1] for PFSA together with the F3C water model and classical hydronium model were adopted. All-atom MD simulations were carried out by using the Gromacs package version 5.04. Each system has been thermalized by the annealing procedure proposed

Figure 1. Chemical structure of perfluorosulfonic ionomers.

by Mabuchi and Tokumasu [1]. After the annealing process, a production MD run was conducted in the NPT ensemble at $T = 300$ K and $P = 1$ bar for 300 ns.

[Results and Discussion]

The snapshot of the water region in the PFSA membrane (Fig. 2) showed that the water molecules and sulfonic groups of polymer tend to form the random water channels in the membrane at $\lambda = 3$. The water region gradually grows up and forms a large water cluster with increasing water content. We calculated the Euler characteristic and surface-to-volume ratio and found that a connected network structure of the aqueous domain is formed at $\lambda = 3$ and gradually turned into a layered structure to separate the hydrophobic region with increasing water content to $\lambda = 9$. Through the analysis of structure factor, we found that the cluster spacing in sulfonic groups is smaller than that in water molecules at the high water content. This provides an evidence for the layered structure of the aqueous domain. The morphological behavior observed in this study is similar to the film-like model [2]. However, the irregular continuum water cluster was observed in the snapshot of the membrane, reflecting that the water cluster forms a tortuous layered structure instead of a film-like structure. Thus, we concluded that the morphology change of the hydrated PFSA membrane with increasing water content is from a channel-network structure at $\lambda = 3$ to a tortuous layered structure at $\lambda = 9$. The tortuous water layer then increases its thickness with further increasing water content. Furthermore, a comparison between the EW 844 and EW 1144 PFSA membranes showed that water molecules in the higher EW PFSA membranes prefer to form a local aggregated water cluster. This demonstrated the strongly aggregated behavior of the aqueous domain in the higher EW PFSA membranes.

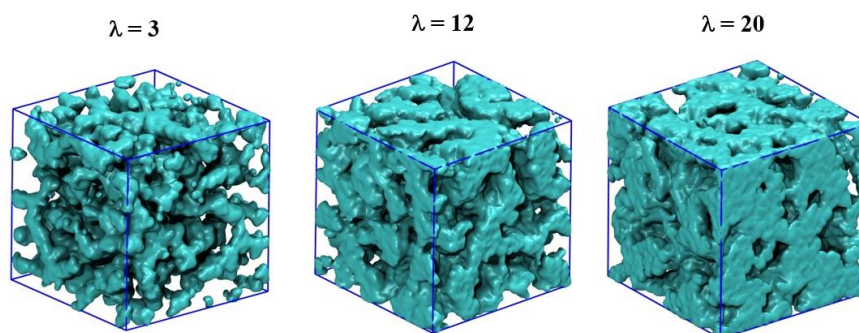


Figure 2. Isosurface representations of water regions including sulfonic group in the EW 844 PFSA membranes.

[Acknowledgement]

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[References]

- [1] T. Mabuchi and T. Tokumasu, *J. Chem. Phys.*, **141**, 104904 (2014).
- [2] K.-D. Kreuer and G. Portale, *Adv. Funct. Mater.*, **23**, 5390 (2013).