

Effects of Pendent Side Chain Length and Spacing on the Mechanical Properties of Hydrated Perfluorosulfonic Acid Polymer Membranes: A Molecular Dynamics Study

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[Abstract] The side chain (SC) length and equivalent weight (EW) of perfluorosulfonic acid (PFSA) have been reported to influence the proton conductivity and mechanical strength of the membranes. In this study, a series of all-atom molecular dynamics simulations was conducted to explore the effect of SC length and spacing on the structural and mechanical properties of the PFSA membrane. Simulation results show that the morphology of the aqueous domain in the shorter SC and lower EW PFSA membranes changes from a channel-network structure to a tortuous layered structure with increasing water content, while water swells the channel-network structure in the longer SC and higher EW PFSA membranes. Furthermore, it is found that the longer SC membranes possessed lower and higher mechanical strengths than shorter SC membranes at lower and higher water contents, respectively, resulting from lower ionic strength and larger polymer domains. These findings will be useful for designing new proton exchange membranes.

[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. Furthermore, the short SC PFSA has been also reported to possess better proton conductivity and mechanical properties than long SC PFSA experimentally. The detail reason has not been well understood yet, though several studies have used MD simulation in attempt to understand the effect of SC length on the structural and dynamics properties at the molecular level. In this study, we conducted a series of AA-MD simulations to explore the effect of SC length on the morphological and mechanical properties of hydrated PFSA membranes at different water contents.

[Methods] Four different PFSA membranes consisting of 200 chains were constructed with six different levels of hydration ($\lambda = 3, 6, 9, 12, 15,$ and 20 , where $\lambda = (\text{H}_2\text{O}, \text{H}_3\text{O}^+)/\text{SO}_3^-$). All the PFSA ionomers had 10 repeat units for which $n = 2$ in the SCs (see Fig. 1). Three of them had 16 ($x = 7, y = 1$) CF_2 groups in the main chain of the repeat units. The EW of the PFSA ionomers were 978 ($m = 0$, SSC), 1144 ($m = 1$, MSC), and 1310 ($m = 2$, LSC), respectively. The other PFSA ionomer (LSCS) had 10 ($x = 4, y = 1$) CF_2 groups in the main chains of the repeat unit for which $m = 2$ in the SC. The EW was 1010. Sulfonic groups in the pendant SCs

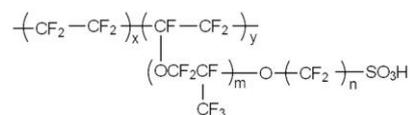


Fig. 1. Chemical structure of PFSA.

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^+). 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 by Mabuchi and Tokumasu [1]. An equilibrating MD run was then conducted at $T = 300$ K and $P = 1$ bar for 300 ns. After the equilibration, uniaxial deformation was applied gradually in the z -direction at a constant rate of 0.1 ns^{-1} (1.2–1.5 m/s depending on water content) up to a strain of 200% at $T = 300$ K.

[Results and Discussion]

The morphology analysis demonstrates that the morphology of the aqueous domain in the shorter SC and lower EW PFSA membrane changes from a channel-network structure to a tortuous layered structure with increasing the water content, while the water swells the channel-network structure rather than forms a water layer in the longer SC and higher EW PFSA membrane (Fig. 2). This is due to the more dynamic nature of the long SC and more hydrophobic region of main chain for high EW PFSA, causing the formation of larger and more heterogeneous aqueous clusters in the longer SC and higher EW PFSA membrane [2-4]. Furthermore, the analysis of the stress-strain curves shows that the LSCS PFSA membrane exhibits the highest yield stress (Fig. 3) but the least crystallinity among the four polymers [4]. This was ascribed to the longer SC and lower EW values, contributing to the larger domain size and stronger ionic strength. In addition, the LSC PFSA membrane was found to possess a comparatively low yield stress at low water contents but a high yield stress at high water contents in comparison with SSC and MSC PFSA membranes. The LSC PFSA membrane possesses a comparatively weak ionic strength and low crystallinity at low water contents, resulting in the low yield stress. However, the differences in the ionic strength and crystallinity between the SSC and LSC become minor with increasing water content. The LSC PFSA membrane with the large polymer aggregate thus shows a comparatively high yield stress at high water contents.

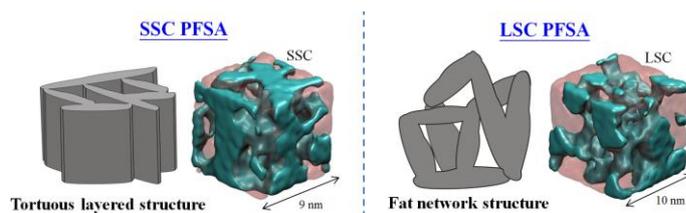


Fig. 2. Schematic illustrating the morphology of the aqueous domains at high water contents.

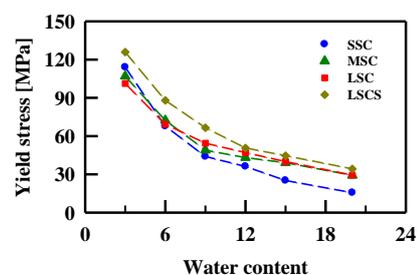


Fig. 3. Yield stresses of PFSA membranes as a function of water content.

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