Insight from molecular modelling: Does the polymer side chain length matter for transport properties of perfluorosulfonic acid membranes?

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Electronic Supplementary Information

Details of the force field

The force fields used in this work were originally developed by the Goddard group[1,2] and the Daggett group.[3] The parameters have been published previously.[1-3] For the sake of completeness, we have provided below the parameters of the force field including the partial charges. In addition to the electrostatic interaction, the total potential energy includes bond stretching (E_b), angle bending (E_a), torsion (E_t), and van der Waals (E_{VDW}) terms, which are given by the following expressions.

$$E_b(R) = \frac{1}{2} K_b \left(R - R_0\right)^2$$

$$E_a(\theta) = \frac{1}{2} K_\theta \left(\theta - \theta_0\right)^2$$

$$E_t(\phi) = \sum_n \frac{1}{2} V_n \left[1 - d_n \cos(n\phi)\right]$$

$$E_{VDW}(R) = D_0 \left[\left(\frac{R_1}{R}\right)^{12} - 2\left(\frac{R_1}{R}\right)^{6} \right].$$

Tables I and II list the parameters of the interactions and Figure S1 presents the partial charges.

References

1 S. L. Mayo, B. D. Olafson and W. A. Goddard, *J. Phys. Chem.*, 1990, **94**, 8897-8909.
2 S. S. Jang, V. Molinero, T. Cagin, and W. A. Goddard III, *J. Phys. Chem. B*, 2004, **108**, 3149-3157.
3 M. Levitt, M. Hirshberg, R. Sharon, K. E. Laidig and V. Daggett, *J. Phys. Chem. B*, 1997, **25**, 5051-5061.

Table I. Bonded interaction parameters.

Bond	K_b	R_0	Angle	K_θ	θ_0	Torsion	Parameters
S-O	700.0	1.48	O-S-O	350.0	115.50	X-C-C-X	$V_3(d_3)$: 2.0000 (-1)
S-C^2	700.0	1.80	O-S-C^2	350.0	109.47	C^1-C^1-C^1-C^1	$V_3(d_3)$: 6.4342 (1)
C^1-C^1	429.320	1.4982	S-C^2-F	100.0	109.47	F-C^1-C^1-C^1	$V_3(d_3)$: 8.2444 (1)
C^1-C^2	700.0	1.53	X-C-X	100.0	109.47	F-C^1-C^1-F	$V_3(d_3)$: 8.0848 (-1)
C^2-C^2	700.0	1.53	C-C-C	106.27	122.55	X-C-O-X	$V_3(d_3)$: 2.0000 (-1)
C-F	605.259	1.336	C-C-F	100.34	118.32	X-C-S-X	$V_3(d_3)$: 2.0000 (-1)
C^2-O	700.0	1.42	F-C-F	108.24	121.50		
H^h-O^h	1085.96	0.982	H^h-O^h-H^h	79.03	113.40		
H^w-O^w	500.0	1.00	H^w-O^w-H^w	120.0	109.47		

C^1 and C^2 are carbon atoms (see Figure S4). C refers to C^1 or C^2. X represents any atom type. H^w and O^w represent H and O of H_2O, respectively. H^h and O^h are H and O of H_3O^+, respectively. K_b is in kcal/mol/Å^2, R_0 in Å, K_θ in kcal/mol/rad^2, θ_0 in degree, and V_n in kcal/mol.

Table II. van der Waals interaction parameters.

Atom type	D_0 (kcal/mol)	R_1 (Å)
S	0.344	4.03
O (membrane)	0.0957	3.4046
C^1	0.0844	3.8837
C^2	0.0951	3.8983
F	0.0496	3.3953
O^h, O^w	0.1848	3.5532
H^h, H^w	0.01	0.90

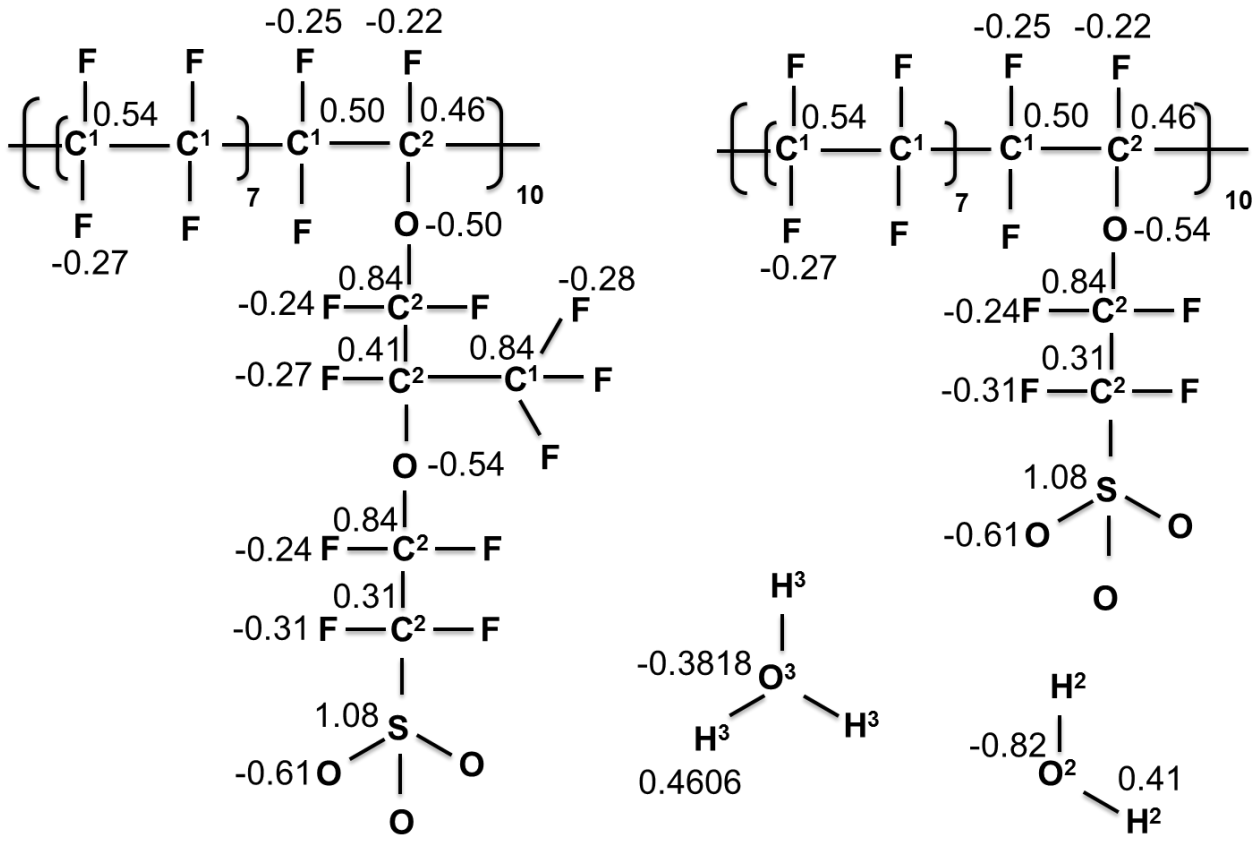

Figure S1. Partial charges for Nafion, short-side chain membrane, H_3O^+ and H_2O.

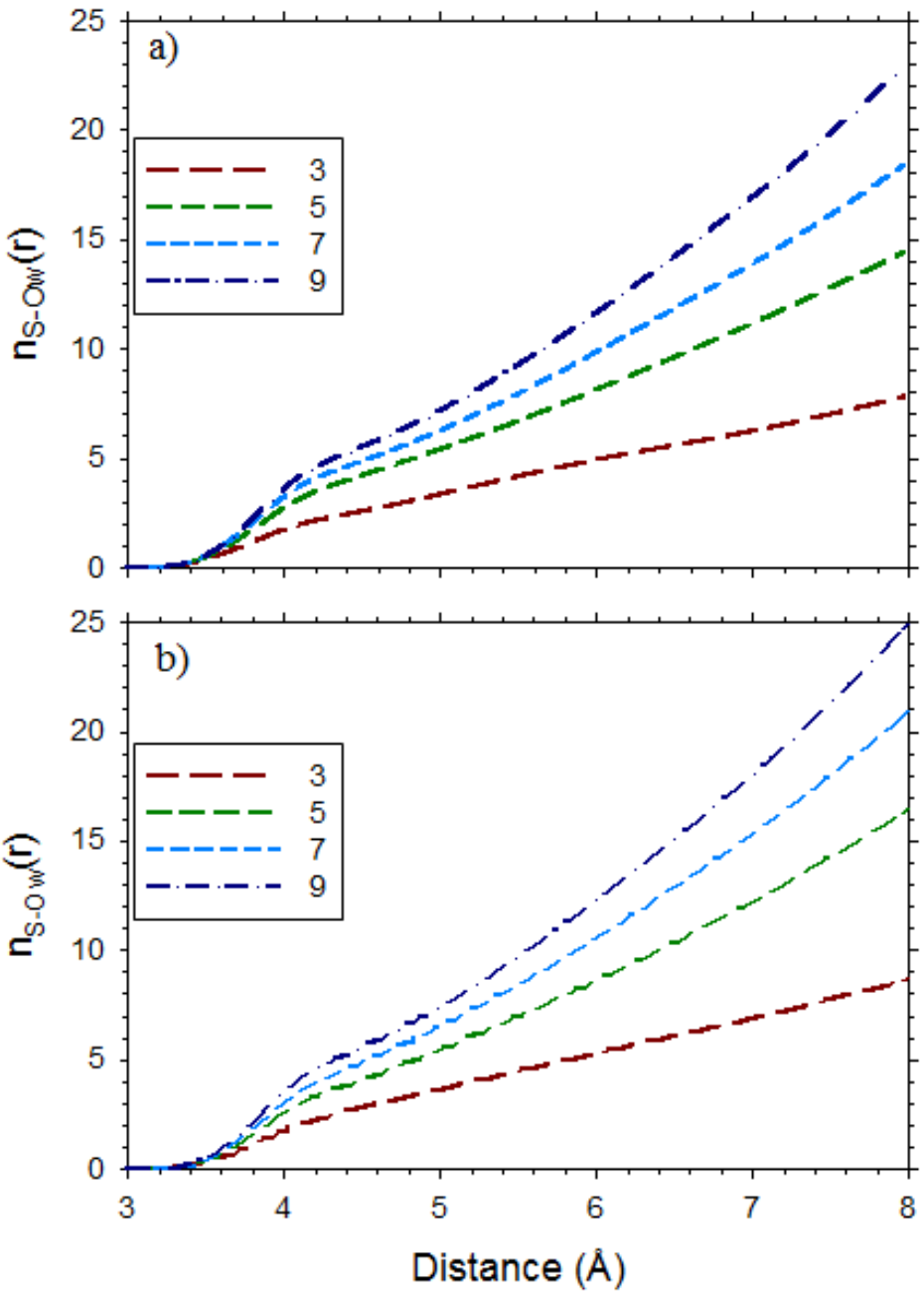

Figure S2. The number of water oxygen atoms near sulfur atoms as a function of the sulfur-water oxygen distance at several hydration levels for a) Nafion (EW 1148) and b) SSC membrane (EW 982) at 300 K.

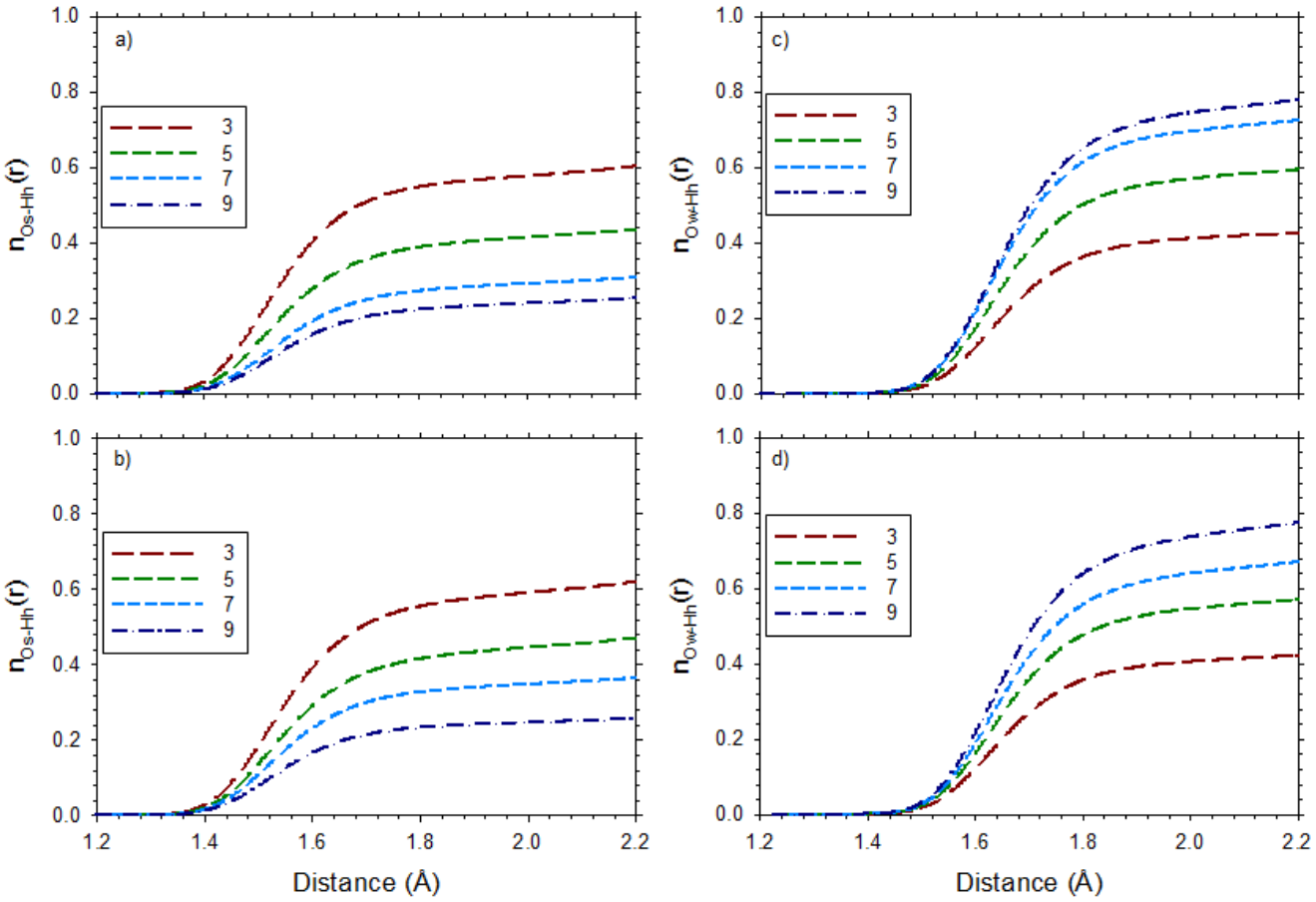

Figure S3. Coordination numbers for a) sulfonate oxygen-hydronium hydrogen in Nafion; b) sulfonate oxygen-hydronium hydrogen in SSC membrane; c) water oxygen-hydronium hydrogen in Nafion; d) water oxygen-hydronium hydrogen in SSC membrane. The temperature is 300 K.

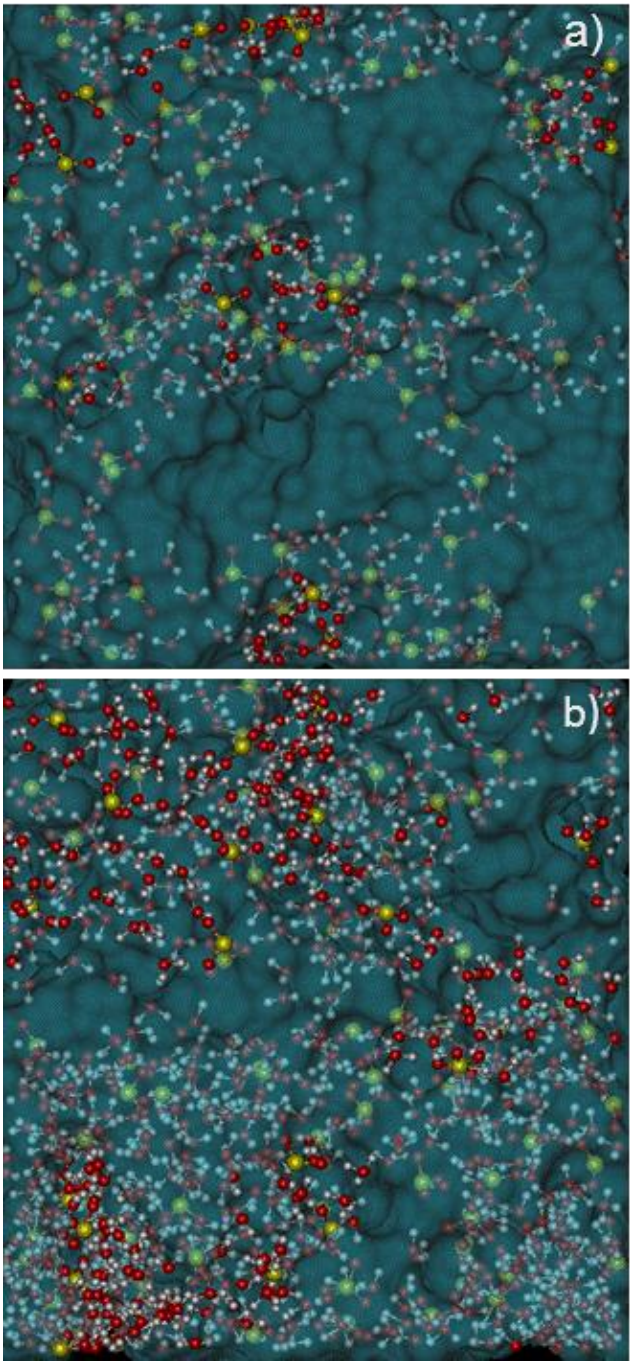

Figure S4. Orthographic projection of atoms in hydrated SSC membrane at 300 K for a) $\lambda = 3$ and b) $\lambda = 9$. S, O and H are shown as yellow, red and white spheres, respectively, in ball and stick representation. The rest of the membrane is shown as a translucent surface.