

Effect of monomeric sequence on nanostructure and water dynamics in Nafion 117

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Abstract

We studied the effect of polar/nonpolar sequences on the structure and water transport of Nafion 117 with 20 wt.% water by molecular dynamics (MD) simulations. Although the systems show clear hydrophilic/hydrophobic segregation in all conditions studied, we observe that increased blockiness leads to better phase segregation, with the anionic moieties unevenly distributed in the interface leaving big hydrophobic patches of polymer/water contact. The vehicular diffusion of water and hydronium was not affected by the blockiness.

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1. Introduction

Nafion is a hydrophobic polyelectrolyte consisting of nonpolar $N=(CF_2-CF_2)$ and polar-ionizable $P=(O-CF_2-CF(CF_3))_2-CF_2-CF_2-SO_3H)$ segments. Hydrated Nafion 117, with an average of 6.5 hydrophobic tetrafluoroethylene units per vinyl ether sulfonate unit, is widely used for membranes in fuel cell operations due to its relatively high proton conductivity and mechanical and electrochemical stability. Although the ratio of hydrophobic to hydrophilic monomers is well known, the monomeric sequence in the Nafion polymer is not well characterized, and its affect has not been included as a design variable to improve fuel cell performance. There is a general consensus supported by experiments [1–7] and simulations [8] that hydrated Nafion has a nanosegregated structure consisting of hydrophobic and hydrophilic domains. Notwithstanding, the details of the segregated morphology remain unclear and highly debated. In this work, we explore, in particular, the effect of monomer sequence on the structure and transport in hydrated Nafion 117 by molecular dynamics (MD) simu-

lations. Our goal is to elucidate the effect of the monomeric sequence of polar (P) and nonpolar (N) units in Nafion on the phase-segregated morphology, the nature of the water-polymer interface, and water/hydronium transport.

2. Simulation methods

To assess the monomeric sequence effect on the properties of our interest, we prepared two model samples of Nafion 117 (equivalent weight 1150) chains.

- One has a $(N_7P)_{10}$ sequence in which the vinyl ether sulfonate unit comes every seven tetrafluoroethylene units. This structure is characterized by a degree of randomness value (DR) of 1.1, and the ionizable monomeric unit is uniformly distributed along the chain.
- The second polymer structure considered is a diblock copolymer with a $N_{70}P_{10}$ sequence, in which the 10 vinyl ether sulfonate units gather at the end of a chain of 70 tetrafluoroethylene units. This latter structure has a DR=0.1. The distance between contiguous sulfonate groups in a fully extended chain is $\sim 22 \text{ \AA}$ for DR=1.1 and $\sim 6 \text{ \AA}$ for DR=0.1.

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The simulation cells consist of four identical ionized Nafion chains of a given DR plus 560 water molecules and 40 hydronium molecules, corresponding to 20 wt.% water content.

MD simulations were performed at two temperatures, 300 and 353 K, relevant for fuel cell operation under isobaric–isothermal conditions using LAMMPS [9,10]. The Dreiding force field was partially modified to handle perfluorocarbon compounds, water, and hydronium [11]. The equations of motion were integrated using the Verlet algorithm with a 1-fs time step, and the PPPM method [12] was used to evaluate the electrostatic interactions. After an equilibration cycle, each system was simulated for additional 2 ns to obtain the equilibrium structural properties and to determine the water and hydronium diffusion.

3. Results and discussion

3.1. Structure: nanophase segregation

We observed water–polymer segregation for both temperatures and monomer sequences (Fig. 1). We found all sulfonate groups to be in the water nanophase, consistent with the experimental observation of complete dissociation for the sulfonic moiety in hydrated Nafion [13,14]. The hydrophilic domain forms a percolated nanophase, and its shape is far from spherical.

We have computed the fraction of water molecules in the first solvation sphere of the hydronium and sulfonate ions. They constitute 49% and 43% of the total for the DR=1.1 and 0.1, respectively, at 353 K. These findings are consistent with the existence of bulk-like water in the IR spectrum of hydrated Nafion with this water content [14]. There are noticeable differences, nevertheless, in the spatial distribution of these bulk waters for the two monomer sequences: While for the DR=1.1, the bulk waters are dispersed all along the hydrophilic nanophase, they are lumped together

in the structures for the blocky polymer of DR=0.1. The structure factor, $S(q)$, at 353 K [15] is in Fig. 2. We observe that, at low q , the intensity of $S(q)$ for the blocky Nafion of DR=0.1 is stronger than that of the DR=1.1, which means that the blocky Nafion of DR=0.1 has better developed phase-segregated structure.

The increased segregation of the sulfonate groups in the polymer chain also has a clear effect on the distribution of the polar and nonpolar groups in the water–polymer interface and on the radial distribution function between sulfonate groups, $g_{ss}(r)$, as shown in Fig. 3. Notice that, although S – S distances in the extended polymer chains are as different as 22 and 6 Å for the alternating and blocky sequences, the sulfonate groups are at comparable distances when the polymer is folded in water. Still, the polymer with DR=0.1 has more S – S neighbors below 8 Å than the DR=1.1 case does. Fig. 3 displays the intrachain contribution to $g_{ss}(r)$, along with the total one. We observe that the most important contribution at low distances to $g_{ss}(r)$ of the blocky, DR=0.1, Nafion comes from S in the same chain, while this is not the case for the alternating, DR=1.1, system.

We define the interface between polymer and water domains as the Connolly surface of water plus hydronium without considering the polymer. For the blocky polymer of DR=0.1, this interface presents patches of hydrophilic and hydrophobic domains that are unevenly distributed, while the sulfonate groups are more “randomly” placed in the interface for the DR=1.1 case. To quantify the differences in surface segregation, we define the hydrophilic portion of the interface as the fraction $f(R)$ of the Connolly surface that is at a distance below a radius R from the S of sulfonate. This $f(R)$ is plotted in Fig. 4 as a function of R . For small R values, the hydrophobic proportion is the same for the two sequences. This indicates the presence of all the sulfonate groups close to the surface but not overlapped. For R values larger than the mean separation between the sulfonate groups, the entire interface is engulfed by the sulfonate

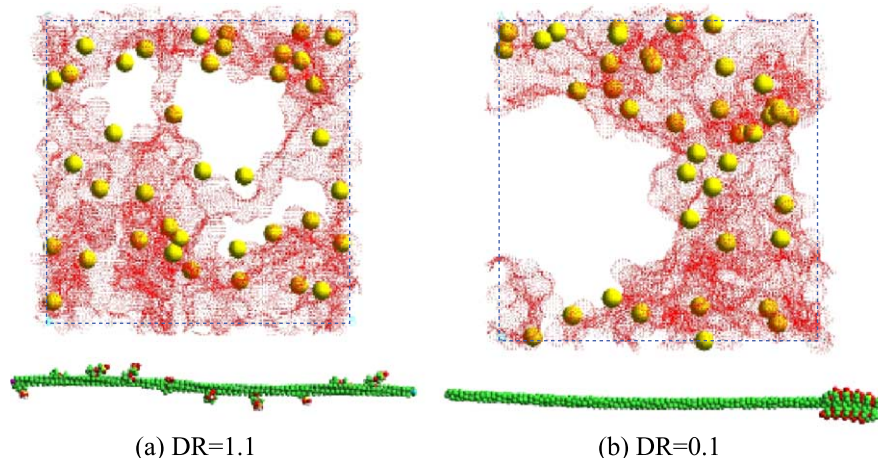


Fig. 1. Nanostructure of hydrated Nafion. White domains are mainly occupied by Nafion backbone. Spheres represent the sulfur atoms. The surface formed by the dense dots is the Nafion/water interface in both figures.

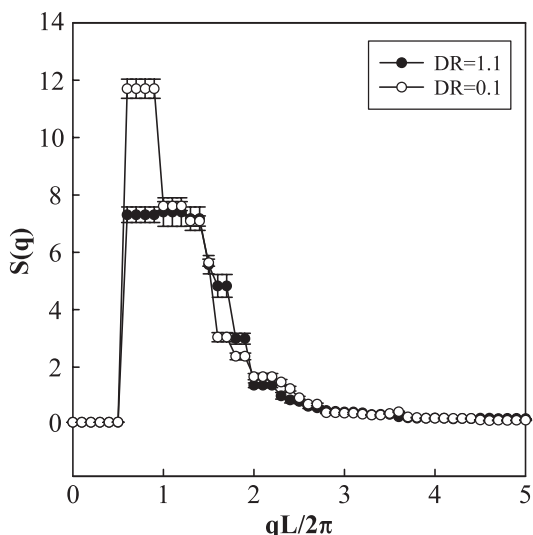


Fig. 2. Structure factor profile for hydrated Nafion with 20 wt.% of water content. $S(q)$ was computed following the method of Ref. [15].

groups. In the intermediate R range, the difference between the spatial distribution of the sulfonate groups becomes evident: The DR=1.1 produces a more dispersed distribution of the sulfonate groups on the interface, and $f(R)$ increases faster with R compared with the segregated surface of the blocky polymer of DR=0.1.

3.2. Diffusion of water and hydronium

The diffusion coefficients for water at 300 K are 0.65×10^{-5} cm²/s for DR=0.1 and 0.67×10^{-5} cm²/s for DR=1.1, and at 353 K, 1.59×10^{-5} cm²/s for DR=0.1 and 1.47×10^{-5} cm²/s for DR=1.1, calculated using the time dependence of mean square displacement. These values

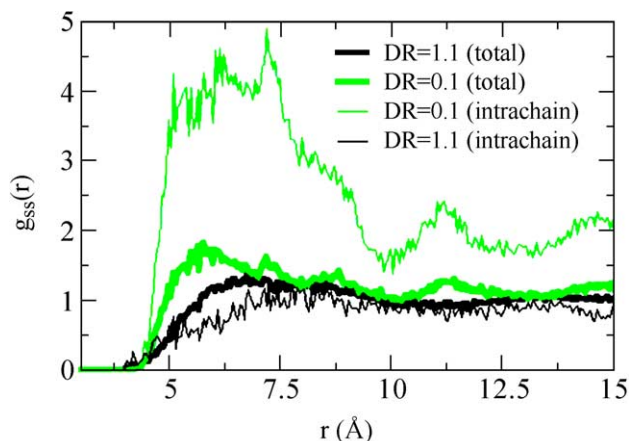


Fig. 3. Sulfur-sulfur radial distribution function ($g(r)$) for hydrated Nafion 117 with 20 wt.% water at 353 K for two sequences of polar/nonpolar monomers. The thick lines show the total $g(r)$, while the thin lines display only the contribution of the distribution of S that belong to the same polymer chain, averaged over the four chains in each cell.

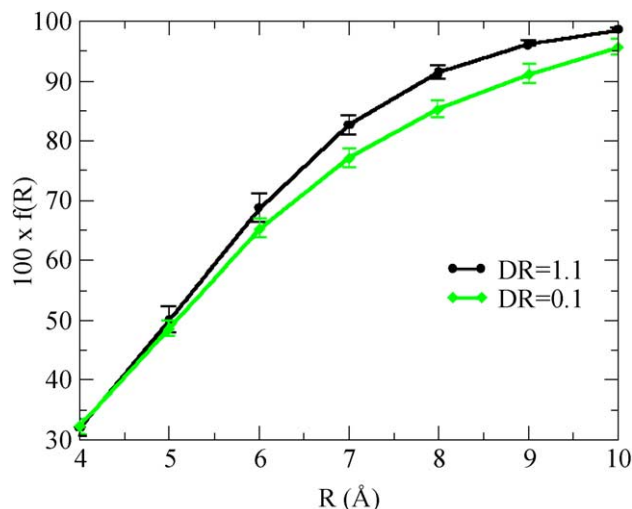


Fig. 4. Hydrophilic portion of water-polymer surface: $f(R)$ quantifies the fraction of the interface that is closer than R from any sulfonate group. The uneven distribution of the anionic moieties in the blocky Nafion (DR=0.1) is evidenced in the slower growth of $f(R)$. The error bars indicate the standard deviation over the 2-ns trajectories.

compare well with the experimental values: 0.5×10^{-5} and 1.25×10^{-5} cm²/s at 300 and 353 K, respectively [16].

The calculated diffusion constants for hydronium ion are 0.3×10^{-5} cm²/s at 353 K for both sequences. The diffusion of hydronium should not be compared with the experiments because we are computing only the vehicular transport of H₃O⁺, and the measured proton transport includes an additional process, namely, the hopping of the bare H⁺ between the water molecules.

4. Conclusions

For both temperatures and sequences, Nafion with 20 wt.% water shows a clearly segregated structure with water and polymer domains. Water domains are far from spherical, indicating that minimization of the interfacial area is not the determining factor, as was assumed in simplified models [1]. The monomer sequence of the polyelectrolyte has an effect on both the extent of segregation and the hydrophilic/hydrophobic patchiness of the interface: The more blocky sequence has better phase segregation, and their anionic moieties are unevenly distributed in the interface forming, leaving big hydrophobic patches of polymer/water contact.

The vehicular transport of water and hydronium is not affected significantly by the monomeric sequence, suggesting that the connectivity of the water domain may be more relevant for the molecular diffusion than the details in the patchiness of the surface and sulfonate distributions. Further investigation on these systems is required to assess whether the different arrangements of the sulfonate groups in the interface for the DR=0.1 and DR=1.1 have an effect on the rate of proton hopping and, hence, the controlling of the overall proton migration.

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