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Atomistic Simulations of Ionic Aggregation in Sulfonated Polyphenylenes

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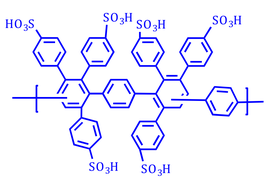
LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Introduction

Alternative energy devices like fuel cells, vanadium flow batteries, and lithium ion batteries employ polymer electrolyte membranes (PEMs) as an ion conducting separator between two electrodes. State-of-the-art PEMs include perfluorosulfonic acid (PFSA) polymers, like Nafion, which have flexible backbones and side chains that readily assemble into distinct hydrophobic and hydrophilic domains. However, they often suffer from high cost, reduced performance at high temperatures and low water contents, and long-term degradation.

Sulfonated Diels-Alder polyphenylene (SDAPP) has been shown to be a promising alternative to Nafion for proton exchange membranes and vanadium flow batteries.[1,2] It has an aromatic backbone with six pendant phenyl groups per repeat unit, which provide up to six sites for post-sulfonation. SDAPP forms thermally and mechanically robust membranes that have high ionic conductivities and low methanol and vanadium crossover.

Chemical structure of SDAPP:

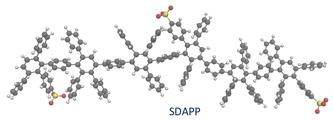


In this work, atomistic molecular dynamics (MD) simulations were performed to study the nanoscale structural properties of SDAPP, focusing on the aggregated ionic domains.

Computational Methods

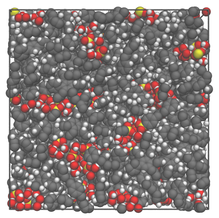
Summary of systems:

- Sulfonation levels (SO_3 per monomer): S = 1, 2, 4
- Hydration levels (H_2O per SO_3): λ = 3, 5, 10
- 5 boxes with random initial configurations
- 70 chains of 3 monomers each
- Box lengths of 66–80 Å, densities of 1.1–1.3 g cm^{-3}



Structure generation:

- Initial structures built via Enhanced Monte Carlo[3]
- Equilibration with MD simulations at high temperatures (up to 2000 K) and high pressures (up to 10,000 atm)
- Production MD simulations for 20 ns



Simulation details:

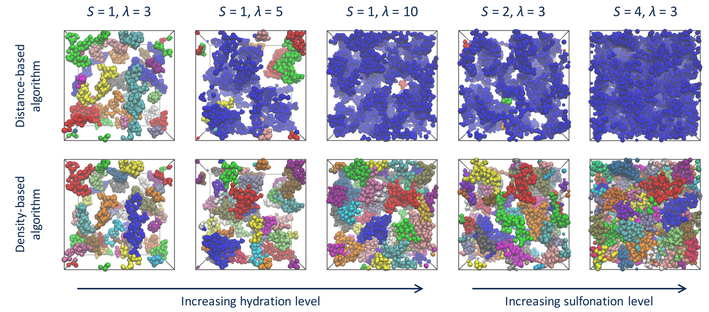
- OPLS-AA force field for polymer interactions
- Rigid TIP4P/2005 water model, flexible 4-site hydronium ion
- MD simulations performed in LAMMPS[4]
- 12 Å short-range cutoff, long-range interactions via PPPM

References

1. CH Fujimoto, MA Hickner, CJ Cornelius, DA Loy, Macromolecules 38, 5010 (2005).
2. Z Tang et al, J Electrochem Soc 161, A1860 (2014).
3. PJ in't Veld, GC Rutledge, Macromolecules 36, 7358 (2003). http://montecarlo.sourceforge.net
4. S Plimpton, J Comput Phys 117, 1 (1995). http://lammps.sandia.gov
5. DS Bolintineanu, MJ Stevens, AL Frischknecht, Macromolecules 46, 5381 (2013).
6. A Rodriguez, A Laio, Science 344, 1492 (2014).

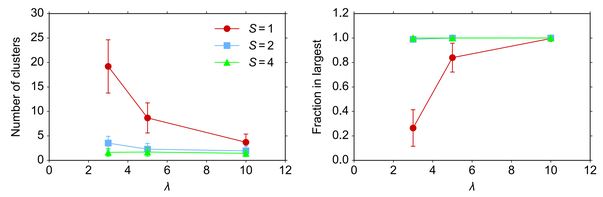
Ionic Aggregates

Two complementary clustering algorithms were used to characterize the ionic domains formed by the sulfonate groups, water molecules, and hydronium ions.



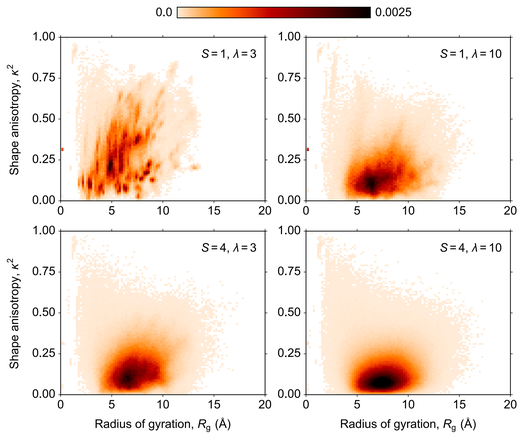
Distance-based algorithm[5]:

- Clusters assigned using cutoff distances between hydrogen bonding O–H and O–O pairs
- Systems became more fully percolated with increasing sulfonation and hydration levels
- Most systems had a large cluster containing nearly all sulfonate groups



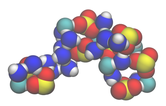
Density-based algorithm[6]:

- Clusters identified by regions of high local density separated by relatively large distances
- Cluster sizes grew only slightly with increasing sulfonation and hydration levels
- Clusters also became less elongated and more spherical in shape

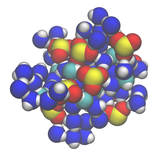


$R_g^2 = \lambda_1 + \lambda_2 + \lambda_3$

$\kappa^2 = 1 - 3(\lambda_1\lambda_2 + \lambda_1\lambda_3 + \lambda_2\lambda_3)/R_g^4$



S = 1, λ = 3: R_g = 7.6 Å, κ^2 = 0.4
N_{SO3} = 8, N_{H3O} = 8, N_{H2O} = 16

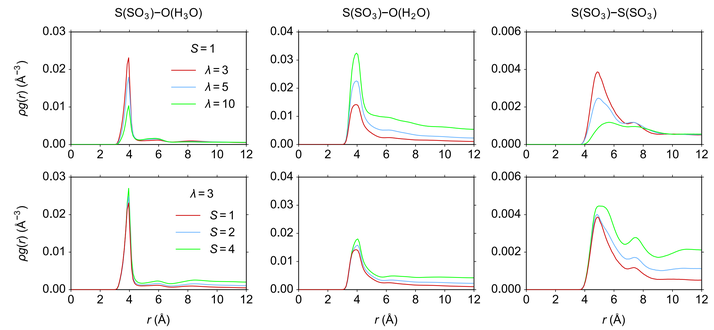


S = 4, λ = 10: R_g = 7.7 Å, κ^2 = 0.05
N_{SO3} = 11, N_{H3O} = 11, N_{H2O} = 60

Local Structure

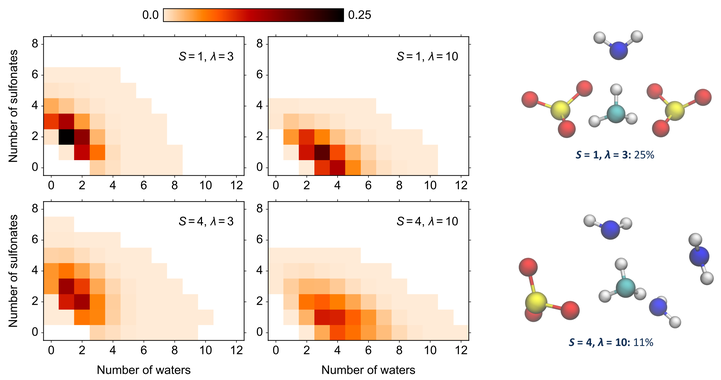
Sulfonate groups:

- More hydrated with increasing sulfonation and hydration levels
- Moved further apart at higher hydration levels, but not at higher sulfonation levels
- More hydronium ions moved from first to second solvation shell at higher water contents



Hydronium ions:

- Often coupled to one or more sulfonate groups at low hydration levels due to strong electrostatics
- Surrounded by more water molecules and fewer sulfonate groups at higher hydration levels



S = 1, λ = 3: 25%

S = 4, λ = 10: 11%

Conclusions

- Distance-based and density-based clustering algorithms provided complementary insight into the nanoscale structure of the ionic domains, including size, shape, and connectivity
- With increasing sulfonation and hydration levels, the ionic clusters became slightly larger and more spherical in shape, and fully percolated ionic domains were formed
- Sulfonate groups and hydronium ions became more hydrated at higher sulfonation and hydration levels, and were therefore less strongly coupled to each other
- Increased size and greater connectivity of the ionic domains, as well as weaker coupling of the ionic groups at higher sulfonation and hydration levels would lead to improved proton transport

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