Supporting Information for

Cross-Linked Polysaccharide Assemblies in Marine Gels − an Atomistic Simulation

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Parameterization of protonated α-D-glucuronic acid

The geometry of protonated α-D-glucuronic acid was optimized by Hartree-Fock (HF) calculations employing the 6-31G* basis set[1] as implemented in the Gaussian 09 program.[2] At the optimized geometry, electrostatic potential (ESP) was calculated at the HF/6-31G* level of theory according to the Merz−Singh−Kollman scheme.[3] Partial atomic charges for subsequent molecular dynamics simulations were derived on the basis of the restrained electrostatic potential (RESP).[4]

Based on the derived partial atomic charges, one protonated α-D-glucuronic acid molecule was solvated by 888 TIP3P water molecules in a simulation box with dimension of 29.8 × 29.8 × 29.8 $Å^3$ and simulated under constant-*NpT* ensemble (T = 298 K and p = 1 atm) for 50 ns. From the last 40 ns trajectory, 80 snapshots were extracted with equal interval. The structure of protonated α-D-glucuronic acid in each snapshot was subject to a partial optimization with rotatable exocyclic dihedral angles fixed and a subsequent RESP calculation for atomic charges. The charges derived from the 80 snapshots were averaged to give the final set of charges for protonated α-D-glucuronic acid. Bonded parameters for the atoms in the −OH group of −COOH were adopted from the general Amber force field.[5]

Supplementary figures

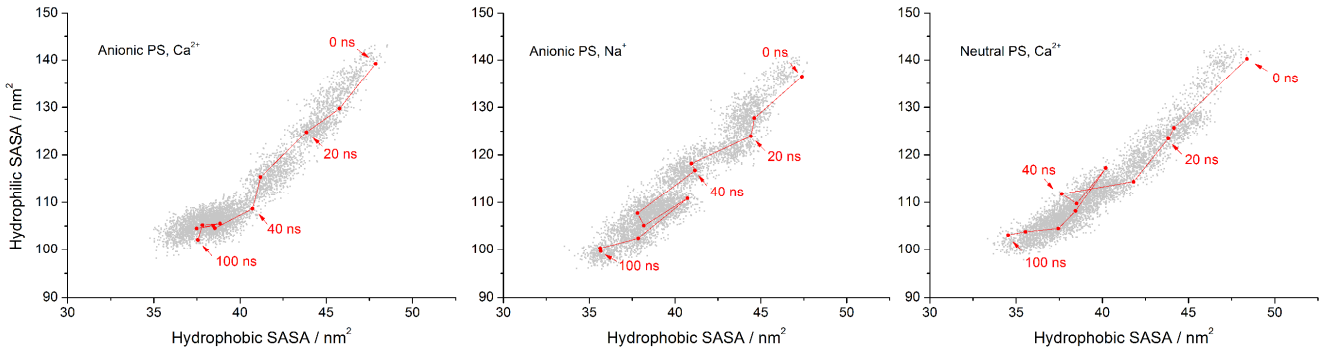

Figure S1. Hydrophobic and hydrophilic contributions to solvent accessible surface area in polysaccharide assemblies. Red dots highlight instantaneous values at 0, 20, 40 and 100 ns, and the red lines are shown only to guide the eyes.

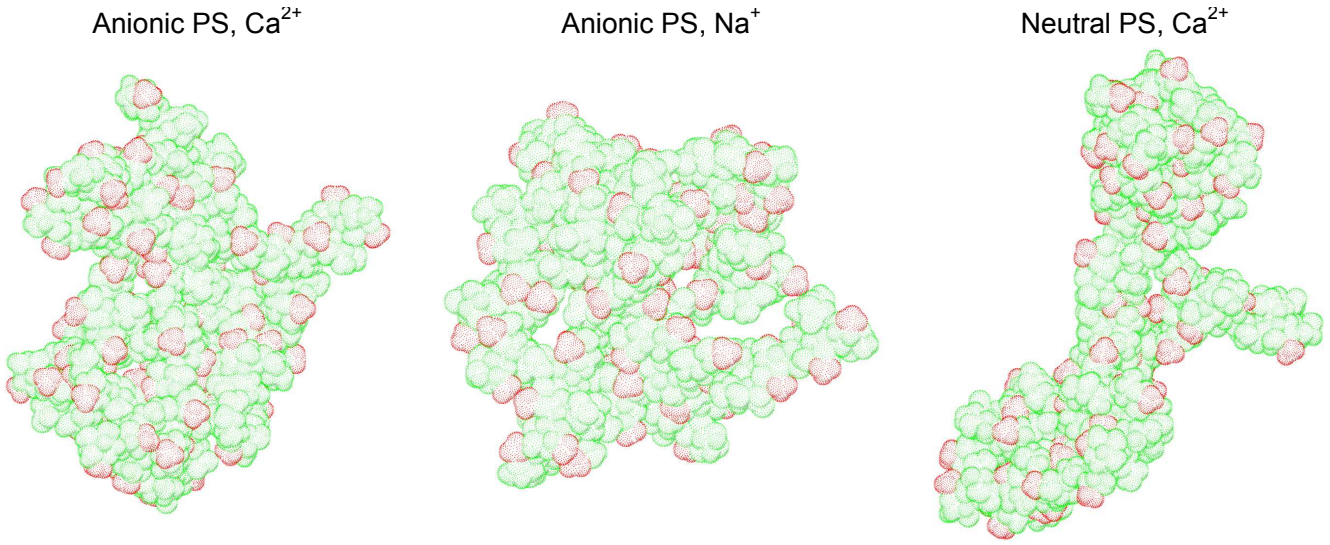

Figure S2. Surface plots of the assemblies consisting of ten polysaccharide chains at 100 ns. Red surfaces correspond to methyl groups of fucose, and green surfaces represent contributions from the rest of polysaccharide atoms. Metal ions are not shown.

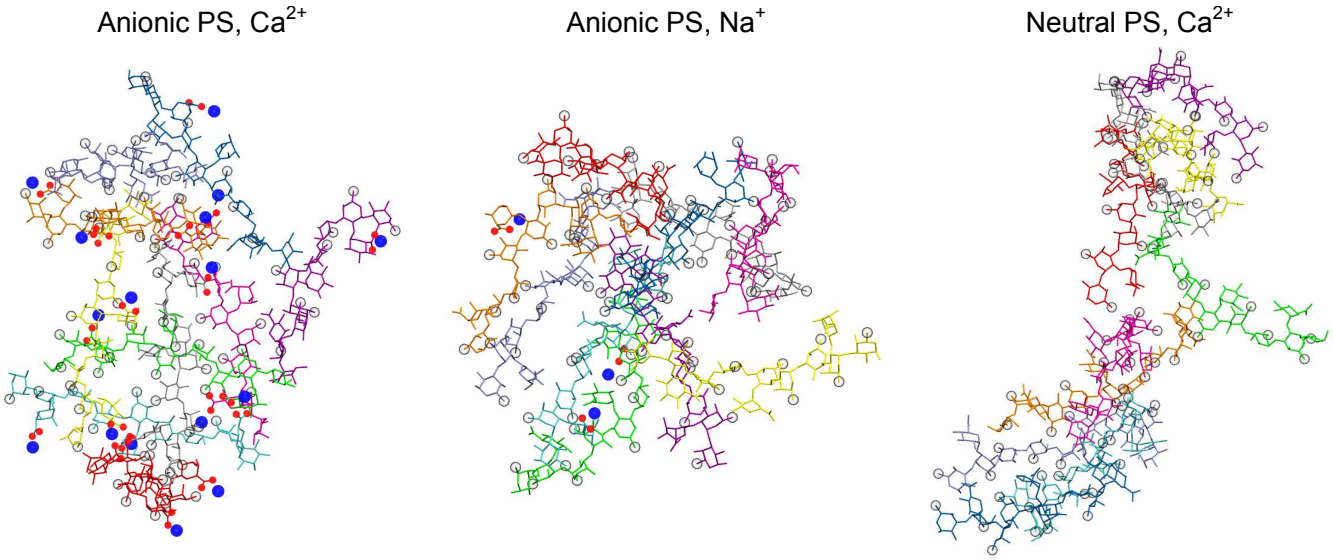

Figure S3. Snapshots of the assemblies consisting of ten polysaccharide chains at 100 ns. Each polysaccharide chain is shown in different color. Blue, red and transparent spheres represent metal ions, carboxylic oxygen atoms and methyl groups of fucose, respectively.

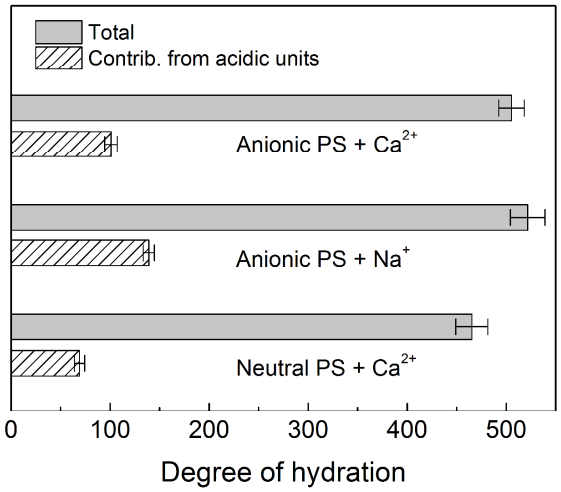

Figure S4. Degree of hydration of the three polysaccharide assemblies, defined as the number of water molecules involved in forming H-bonds with the polysaccharides. Both the total degree of hydration and contribution from the acidic units (COO^{-} or COOH) are shown as an average over the last 50 ns of simulation trajectory together with standard deviation.

References

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