Driven by mutual segregation, block copolymers exhibit a fascinating ability to self-assemble into a variety of ordered mesoscopic structures. Incorporating an ionizable block enhances incompatibility that together with tailoring blocks for specific functions presents an immense step towards engineering controlled transport systems. Here the interplay between the interactions of solvents with the specific blocks of a pentablock with a randomly sulfonated polystyrene center, tailored for transport, tethered to flexible poly (ethylene-r-propylene) blocks end-capped with poly (t-butyl styrene) is studied by fully atomistic molecular dynamics simulations. The assembly of macromolecules in water results in a spherical, tightly packed aggregate in which the ionizable blocks dominate the water interface. Transferred to a cyclohexane and heptane mixture, the hydrophobic blocks migrate to the interface. Surprisingly the ionics blocks form a nano-network rather than as a core. Further, this network also develops when assembled from hydrophobic solvents, where now the hydrophobic blocks dominate the interface. This network only slightly contracts or expands as the solvent is changed while concurrently the hydrophobic blocks migrate towards or away from the solvent interface.

**Abstract**

**Goals**

- Follow formation pathways, resolve the structure, and elucidate the factors that govern shape and stability of aggregates

**Methodology**

<table>
<thead>
<tr>
<th>Polymer:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single chain - Total MW ~50,000 g/mol</td>
</tr>
<tr>
<td>Sulfonation fraction ( f = 0.30 &amp; 0.55 )</td>
</tr>
</tbody>
</table>

**Solvent:**

- Cyclohexane/heptane (1:1) and Water

**Results**

**Self-assembly in Cyclohexane/heptane**

- Molecules were built using Material Studio, Accelrys Inc.
- Force fields OPLS-AA
- TIP4P/2005 water model
- Molecular dynamics simulation code-LAMMPS
- Time step 1 fs
- Constant pressure or constant volume

**Summary**

- Structure of aggregate is sensitive to solvent quality
- In cyclohexane/heptane: ellipsoidal aggregates are formed with collapsed center blocks and swollen flexible blocks with intermixing of a random distribution of end blocks
- In water: the center blocks increasingly segregate from the hydrophobic regions of the aggregates
- Nano-organisms are observed in both solvents

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**References**