Engineering Controlled Nano Systems: Understanding Aggregation of Structured Ionic Copolymers

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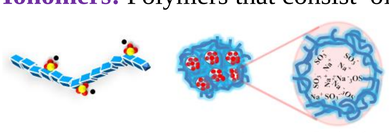
Abstract

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 ionic blocks form a nano-network rather than 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.

Introduction

Ionomers: Polymers that consist of ionizable groups



Bulk polymer Ionic cluster

Applications: Selective Transport

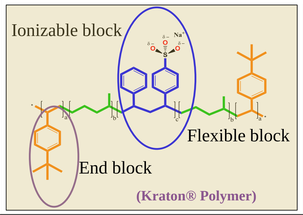
- ❑ Separation membranes
- ❑ Ion sensor
- ❑ Fuel cell

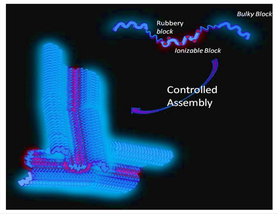
Industrial Challenge: Under the conditions that ionic transport is optimized, the mechanical and chemical stability of membranes are compromised

Ionic Block Copolymers: consist of at least one block containing ionizable groups such as sulfide

- Interest arises mainly from the extreme incompatibility between the hydrophilic and hydrophobic blocks
- Local phase segregation into ionic and non-ionic domains controls both the internal structure of the polymer and the formation of transport pathways.

Ionic Pentablock Copolymer





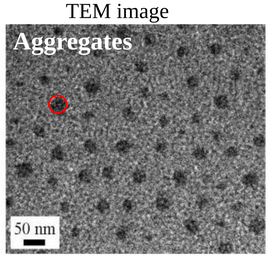
Formation of Aggregates depend on:

- Compatible of blocks
- Relative solubility of the blocks in the solvent
- Temperature

Challenge: Controlling the structure of complex copolymers

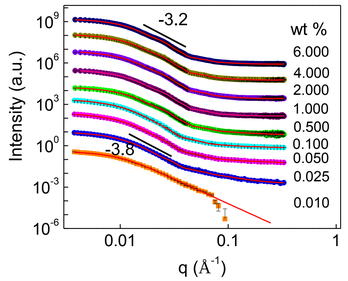
What is Experimentally Known

TEM image



Dry: Spherical aggregates[1]

Small Angle Neutron Scattering (SANS)



Cyclohexane/heptane: Spherical aggregates with swollen hydrophobic blocks and collapsed ionic blocks[2]

Goals

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

Methodology

Polymer:

- Single chain – Total MW ~50,000 g/mol
- Sulfonation fraction (f) = 0.30 & 0.55

Solvent:

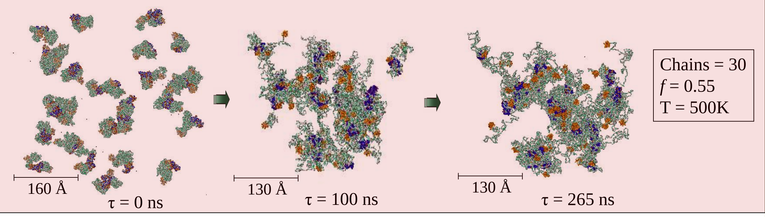
- Cyclohexane/heptane (1:1)
- Water

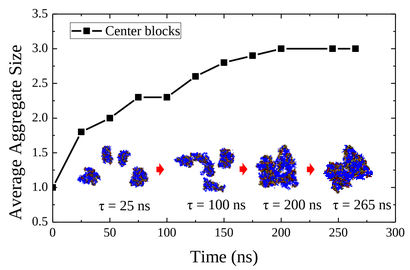
Total number of atoms: ~4 millions

- Molecules were built using Material Studio, Accelrys Inc.
- Force fields OPLS-AA[3]
- TIP4P/2005 water model[4]
- Molecular dynamics simulation code-LAMMPS[5]
- Constant pressure or constant volume
- Time step 1 fs
- RESPA[6]

Results

Self-assembly in Cyclohexane/heptane

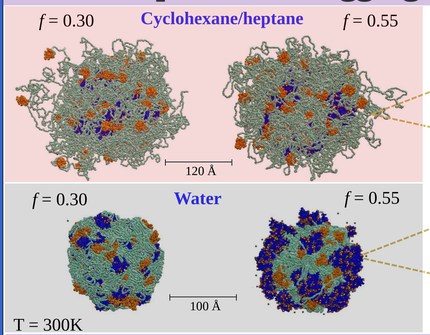




- Self-assembly into ionic domains and hydrocarbon domains
- Size of ionic aggregates increases as time process and remains stable after 200 ns

Computational trick: Form aggregates by compressing all molecules and follow their arrangement in solvents.

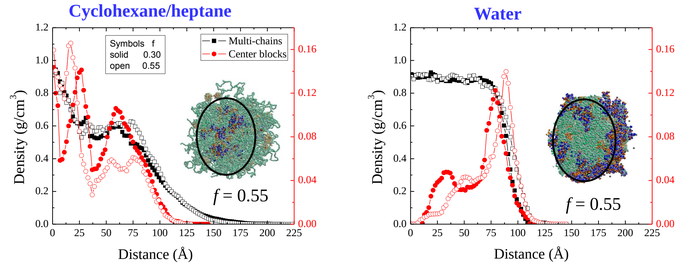
Equilibrated Aggregates in Solutions



- Collapsed center blocks in core form ionic network
- Swollen flexible blocks intermixed with end blocks

- Compact structure
- Center blocks are more segregated from hydrophobic regions as f increases

Density Distribution

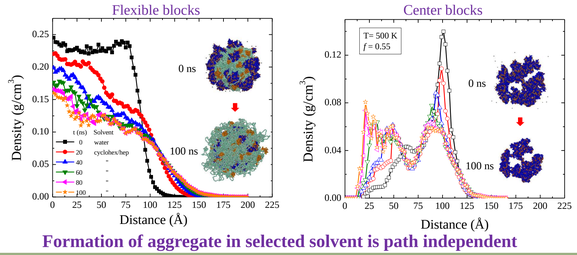


- Radius of aggregate is ~150 Å
- Center blocks are closer to center

- Radius of aggregate is ~95 Å
- With increasing f more center blocks migrate to the interface

Solvent Inversion: Polar to non-Polar

- Exploring how the aggregate reorganizes



- Upon transferring to cyclohexane/heptane, the flexible blocks migrate to the interface
- Collapsed center blocks remain in core
- Ionic blocks form a network

Formation of aggregate in selected solvent is path independent

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 as f increases
- ❑ Nano aggregations are observed in both solvents

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