On the Way to Transport Controlled Membranes: Solvent Effects on Structured Ionic Polymers

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Abstract

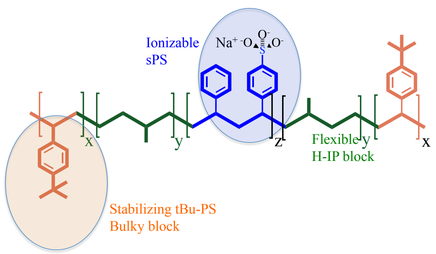
Complex ion containing polymers are in the core of numerous current and potential applications including clean energy, water purification membranes, piezoelectric materials and sensors. The ability to facilitate ions and electrons transport is a key to their function and is controlled by their structure. Moving from a laboratory concept to devices requires processing means in which well controlled structures are formed on a large scale. As these polymers are often processed from solvents, one effective path to gain structural control is tuning their conformation by solvent interactions. These polymers often consist of transport facilitating blocks tethered to mechanical stabilizing ones. Here we present results of molecular dynamics simulations of the effects of solvents on the conformation of one complex macromolecule of the shape of ABCBA symmetric ionic pentablock copolymer. The center block C is a randomly sulfonated polystyrene that can facilitate transport, tethered to a flexible block, B, and t-butyl polystyrene A, that provide mechanical stability. The effects of two solvents, a cyclohexane and n-heptane mixture, a commercially viable solvent, which is a good solvent for nonpolar blocks, and propanol which is a preferential solvent for the center block will be presented. We find that while in cyclohexane:n-heptane the ionic block is fully collapsed, the propanol tunes the conformation of the ionic block. Understanding solvent effects to enable prediction of the conformation of the polymers offers a design tool for structured polymeric membranes.

Introduction

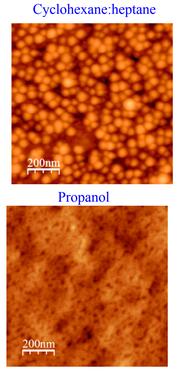
Structured ionic polymers:

- Ionic block copolymers which have incompatible blocks, are segregated into nanoscale structures in solutions and condensed phases
- Tunable nanoscale segregations of ionic block copolymers are critical to use them as transport membranes in different applications

Structured pentablock ionomer



Effect of solvents on film morphology



Goal

- Understand the effect of solvent on the conformation of structured ionic polymers that contain incompatible blocks

Methodology

System

Polymer

- MW: ~ 50, 000 g/mol
- Number of atoms: ~ 12,000
- Sulfonation levels *f*: 0. 0.15, 0.55

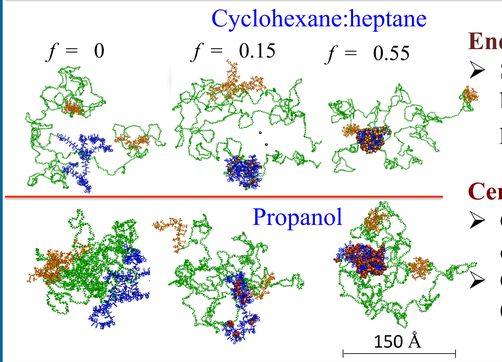
Solvents

- Cyclohexane:n-heptane (1:1)(cyh/hep) and 1-Propanol
- Number of atoms: ~ 80,000

- ❑ Molecules built with Material Studio, Accelrys Inc.
- ❑ Force fields OPLS-AA[2]
- ❑ Molecular dynamics simulation code-LAMMPS[1]
- ❑ Time step 1 fs
- ❑ RESPA[3]
- ❑ Computational time ~40-80ns

Results

Single chains in polar and non polar solvents



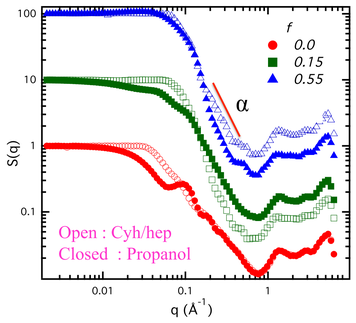
End and flexible blocks

- Swollen in both solvents but slightly extended in propanol

Center block

- Collapsed in cyh/hep and open in propanol
- Opening is dominant in $f = 0.15$ than $f = 0.55$

Static structure factor of single chain

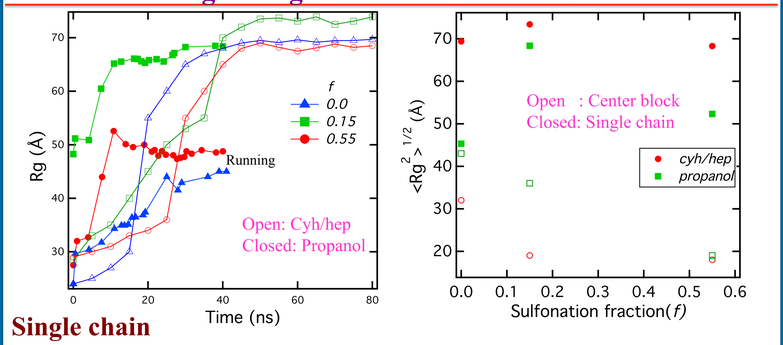


Porod law: $S(q) \alpha q^{-\alpha}$

f	α	
	cyh/hep	propanol
0.0	1.5	1.5
0.15	3.0	2.6
0.55	2.3	3.0

- $f = 0$: forms extended confirmation in both solvents
- Increasing sulfonation results in localized internal structures

Rg of single chain and center block



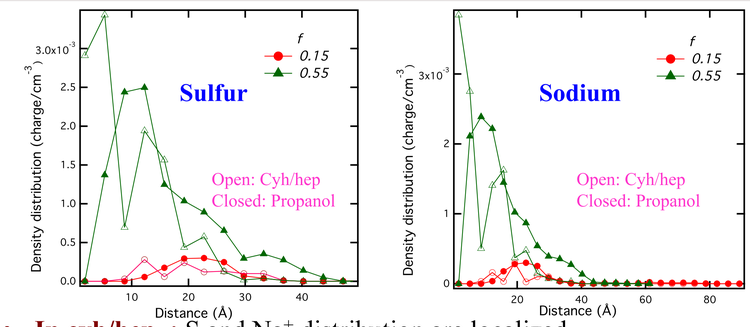
Single chain

- Rg is higher in cyh/hep than in propanol for all sulfonation levels

Center block

- Rg is higher in propanol than cyh/hep for all sulfonation levels

Distribution of ionic groups in single chain



- **In cyh/hep :** S and Na^+ distribution are localized
- **In propanol:** S and Na^+ distribution are dispersed

Summary

In cyclohexane:n-heptane:

- Flexible and end blocks are swollen
- Center block is collapsed

In 1-propanol:

- Flexible and end blocks are comparatively less swollen
- sPS block is fully swollen at lower sulfonation levels
- sPS block is collapsed at sulfonation levels higher than 0.55

Outlook

Apply to understand the behavior of pentablock ionomer in different solvents and the stratification of different blocks in thin films

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