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. The effects of two solvents, a preferential solvent for the center block will be presented. We find that cyclohexane:n-heptane, which is a good solvent for nonpolar blocks, and propanol which is a solvent for 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 solutions in condensed phases
- Tunable nanoscale segregations of ionic block copolymers are critical to use them as transport membranes in different applications

Methodology

Polymer
- MW ~ 50,000 g/mol
- Number of atoms: 12,000
- Sulfonation levels: f = 0.15, 0.55
- Cyclohexane-n-heptane (1:1) and 1-Propanol
- Number of atoms: 80,000
- Molecules built with Material Studio, Accelrys Inc.
- Force fields OPLS-AA
- Molecular dynamics simulation code-LAMMPS
- Time step 1 fs
- RESPA
- Computational time ~40-80ns

Goal

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

Results

Single chains in polar and non polar solvents

Cyclohexane:heptane
- f = 0: forms extended confirmation
- f = 0.15: slightly extended in propanol
- f = 0.55: collapsed in cyh/hep and open in propanol
- Center block: collapsed in cyh/hep and open in propanol
- Opening is dominant in f = 0.15 than f = 0.55

Propanol
- Flexible and end blocks are comparatively less swollen

Static structure factor of single chain

Porod law: S(q) ~ q^n
- f = 0: forms extended confirmation in both solvents
- Increasing sulfonation results in localized internal structures

Solvents

- Cyclohexane-n-heptane and 1-Propanol

Rg of single chain and center block

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