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Phase Behavior of a Single Structured Ionomer Chain in Solution

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Notes

The authors declare no competing financial interest.

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Structured polymers offer a means to tailor transport pathways within mechanically stable manifolds. Here we examine the building block of such a membrane, namely a single large pentablock co-polymer that consist of a center block of a randomly sulfonated polystyrene, designed for transport, tethered to poly-ethylene-r-propylene and end-capped by poly-t-butyl styrene, for mechanical stability,using molecular dynamics simulations. The polymer structure in a cyclohexane-heptane mixture, a technologically viable solvent, and in water, a poor solvent for all segments and a ubiquitous substance is extracted. In all solvents the pentablock collapsed into nearly spherical aggregates where the ionic block is segregated. In hydrophobic solvents, the ionic block resides in the center, surrounded by swollen intermix of flexible and end blocks. In water all blocks are collapsed with the sulfonated block residing on the surface. Our results demonstrate that solvents drive different local nano-segregation, providing a gateway to assemble membranes with controlled topology.

1.Introduction

Structured ionic polymers are in the core of innovative technologies where controlled transport is desired. Examples include clean energy production,[1,2] and storage[3, 4] as well as actuators[5, 6] and drug delivery.[7, 8] Enhancing molecular complexity of the polymers, via incorporating function enabling segments while controlling their phase behavior presents an immense step towards designing controlled transport systems. Incorporating highly incompatible groups, such as ionic blocks into a hydrophobic polymer, however, results in a new set of challenges to control miscibility and long range correlations that offer mechanical stability. The ionic segments often enhance the glass transition temperature of the polymers, making solvent casting the method of choice for membrane preparation. In contrast to neutral, van der Waals polymers, the ionic blocks tend to associate posing kinetic barriers to formation of equilibrium structured membranes. Controlling the structure and dynamics of the individual polymer molecule in solution becomes imperative to controlling assembly into membranes. Here we probe the conformation of a single molecule of structured co-polymer that consists of a centered ionic group tethered to an aliphatic block and terminated by bulky group, in solutions of four solvents, using atomistic molecular dynamics (MD) simulations. We show that the nature of the polymer results in phase segregation within one large molecule of molecular weight of 50,050 g/mol hold a key to understanding the association of molecules into membranes.

The realization that topology affects polymer properties is of particular significant in presence of ionizable groups has driven significant efforts, revealing a rich manifold of control factors. In contrast to semi flexible and flexible polymer solutions, there is hardly any insight into solution structure of ionic structures polymers.[9,10] Most studies have focused on membranes showing that the topology of the polymers impact the formation of transport pathways, however impact the stability of the membranes. Among the most significant

factors for homopolymers have been the degree and distribution of ionizable groups. Zhang et al.[11] for example have carefully mapped the degree and distribution of ionic groups along the backbone of sulfonated polystyrene. Qiao and Weiss[12] have shown that this distribution affects the rheology of the polymers. Further complexity has been introduced via crosslinking of the polymers as demonstrated by Kim et al.[1] Tailoring polymers with multiple blocks has been one of the most promising pathways to form mechanically stable transporting systems. In this frame, block copolymers that contain ionizable or ion transporting blocks are of particular interest since the incompatibility between individual blocks drives the formation of structured materials with domains that facilitate transport and hydrocarbon domains that enhance mechanical stability. Recent studies [13-16] have demonstrated the potential of ionic co-polymers for energy storage and correlated morphology with transport. Wang et al.[14] measured the ionic conductivity and degree of hydration of model membranes composed of polystyrene sulfonate-b polymethybutylene copolymers and their imidazolium salts, demonstrating morphology-hydration-transport correlations.

Despite an immense effort, one significant challenge remains that under the conditions in which ionic transport is optimized, the mechanical and chemical stability of polymers are often compromised. With the rational of tailoring highly transporting blocks with segments that control mechanical stability, a number of co-polymers have been designed. As the complexity of the copolymer increases, the ability to tailor properties is enhanced, though extracting the correlations between the chemical structures of the polymers, their phase structure, and their characteristics becomes a challenge.[17]

The current study probes the fundamental building block of structured ionic polymer membranes, namely the molecular structure of the structured polymers in solution, using MD simulations. Specifically we probe a pentablock, A-B-C-B-A, co-polymer that consists of an A block of poly(t-butyl-styrene), a B block of ethylene-r-propylene and a C block of a randomly sulfonated styrene, shown in Supporting Information Figure S1 in a variety of

solvents. The end poly(t-butyl-styrene) blocks, free of sulfonation, are designed to enhance mechanical strength. The flexible ethylene-r-propylene blocks provide additional means to prevent brittleness in dry condition, while the sulfonated styrene facilitates ion transport. As ionic polymers exhibit high glass transition temperatures, solution casting is often the pathway to formation of functional membranes. The interactions within the co-polymer and the interactions of each of the blocks with the surrounding solvent determine the conformation of the polymer and hence impact their assembly into membranes. Here we resolve for the first time the structure of a single co-polymer in solution. We demonstrate that its overall conformation is dictated by the ionic segment segregation.

Previous studies of this pentablock using small angle X-ray scattering and transmission electron microscopy,[18-20] concluded that for all sulfonation levels, spherical micelles are formed in 11 Wt% cyclohexane/heptane mixtures, with a core of the sulfonated styrene and a corona of solvated flexible and end blocks. Recent water transport studies have shown that water sorption and absorption increase with increasing sulfonation levels as expected.[21] As the industrial process to form such membranes is solvent casting, and the three different blocks are of different nature with different T_g's and verification temperatures, controlling the structure in solution is a key element in understanding formation of a membrane.

2. Model and Methodology

Using fully atomistic MD simulation we probe the conformation of the pentablock A-B-C-B-A of total molecular weight of 50,050 g/mol containing randomly sulfonated atatic polystyrene in the center block (C) tethered to polyethylene with randomly substituted 1.1% propylene (B) and end-capped by atatic poly-t-butyl styrene (A) as shown in Figure S1. The total wt% of the center sulfonated block is ~40% with a random sulfonation fraction f=0.30, while each of the randomly substituted polyethylene blocks is ~20% and each of poly-t-butyl

styrene blocks is ~10%. The counterion in all the simulations was Na+. Details regarding simulation code [22] and force fields [22, 24] are presented in Supporting Information. The results show that a unimolecular aggregates with well-defined hydrophilic and hydrophobic regions are formed where the interplay of solvent-polymer interactions and polymer-polymer interactions control the phase behavior and conformation of the individual blocks.

A mixture of cyclohexane and heptane, which is used industrially to cast films and water, among most ubiquitous substances, are studied. While water is a poor solvent for this polymer, similar to Nafion™,[25] membranes take up significant amounts of water and under high-pressure, high temperature conditions are dissolved in water-alcohol to form colloidal solutions. The polymer is initially equilibrated in implicit solvents, i. e. a solvent modeled by an interaction parameter and a dielectric constant and then transferred to explicit solvents, cycling the temperature in a closed system, above the glass transition temperature of the polymer to equilibrate the chains. Results of simulations in cyclohexane heptane mixture and in water are compared to those in an implicit poor solvent with dielectric constant ε=1.0 and 77.73. ε =1.0 is the value for a vacuum where no screening occurs and ε= 77.73 is chosen to match the dielectric constant of water.

Here we utilize an atomistic description of the solvents which is computationally expensive, coupled with implicit solvents. While implicit solvents do not carry the chemical details of the solvents, they adequately describe most properties and allow tunability of the interaction of the polymer and solvent in a manner that is not accessible experimentally. Requiring less computational resources implicit solvents allow longer simulations, expending the range of conditions that can be realistically probed. Most importantly, a large temperature range is accessed and universal guide lines for the range of dielectric constants necessary to drive desired structures are attained.

High pressure-temperature conditions or extremely long dissolution times of weeks are required to experimentally dissolve this polymer in water. Here preparation follows the experimental temperature cycling in a closed system. To address one of the most critical aspects of polymers in both experiments and simulations, attaining equilibrium, the pentablock was heated to 500k and cooled back to 300K, resulting in a significantly more compact structure than collapsing the chains directly at 300K. We consider these more compact systems, obtained from heating to higher temperature and cooling back to 300K, closer to equilibrium and then the structure obtained by directly collapsing at 300K. All results in this paper were obtained in this manner for both explicit and implicit solvents.

3. Results and Discussion

Snapshots of the pentablock, the center block and a sulfonated PS chain identical to the center block in water are shown in Figure 1 at T = 300 and 500K. At all temperatures, the polymer collapses into a unimolecular aggregate with a spherical symmetry with a clear segregation into hydrophilic and hydrophobic regions with no solvent in the core. This phase segregation to ionic blocks and the rest of the polymer provides the first insight into internal phase segregation. Additionally, we found that the connectivity of polymer impacts the conformation of the ionic blocks. The structure of the ionizable segment is compared with a randomly sulfonated polystyrene (PSS) chain identical to that of the center block in Figure 1-c and 1-d. Surprisingly the ionic block is significantly more extended in comparison with that of the non-tethered polystyrene. A similar set of snapshots for the two implicit poor solvents with ε =77.73 and 1.0 are shown in Supporting Information.

In water and in the two implicit solvents all three blocks are collapsed as shown in Figure 2. The overall density of the core is uniform as shown in Figure S4. In water the ionic groups reside almost completely on the outer surface. The conformation of the pentablock and a sulfonated PS chain in water similar to that in the implicit poor solvent with ε = 77.73 where the ionic groups also reside on the outer surface. These results are in good agreement with

those of Carrillo and Dobrynin [9] who reported that sulfonated PS chains in water and in the implicit poor solvent for ε = 77.73 form a globule-like conformation with all sulfonated groups located on the outer surface and the benzene rings of the styrene forming the inner surface.

Upon heating the system, the pentablock in water as well as for the two implicit solvents expands with most of the increase in size coming from expansion of the outer and middle blocks. The center block and sulfonated PS are much less temperature sensitive. At all temperatures, phase segregation of the hydrophobic and ionic blocks is observed, where the open structures at higher temperatures point towards a state where interpenetration of the hydrophobic parts to form a steady network is more likely. The effects of temperature on the mean square radius of gyration $\langle R_g^2 \rangle^{1/2}$ of the pentablock, the center sulfonated block and the PSS chain are shown in Figure S5 for both the two implicit solvents in comparison with water. The polymer in cyclohexane/heptane follows similar trends however it is highly swollen and is discussed separately.

For both values of ε, $\langle R_g^2 \rangle^{1/2}$ of the entire pentablock increases with increasing temperature. Similarly, $\langle R_g^2 \rangle^{1/2}$ of the center block and PSS chains of the same length, increases monotonically as the temperature increases for ε=77.73. These solutions behave as expected for ionic polymers in polar solvents such as water. However for ε = 1.0, $\langle R_g^2 \rangle^{1/2}$ of the entire pentablock, the center block of the pentablock and PSS, depends only weakly on the temperature.

A comparison between the dimensions of the homopolymer PSS solution and that of the center block show that the homopolymer is smaller than the center block bound in the pentablock, independent on ε. It is also significantly less sensitive to temperature variation. This dimension difference is attributed to the impact of the hydrophobic blocks that are strongly affected by temperature and essentially are pulling on the ionic segment.

To further understand the impact of the interactions with solvents, the pentablock was immersed in a 1:1 mixture of cyclohexane and heptane which is a good solvent for the flexible and end blocks. In this case, as seen in Figure 2b both the flexible and end blocks are extended while the center ionic block is collapsed. As a function of temperature, $<R_g^2>^{1/2}$ for the entire pentablock is 18% larger at T=500K compared to 300K while the center block and PSS chain by less than 2%. Note that in all four solvents the ionic block remains collapsed where the distribution and conformation of the center and end blocks vary offering different topological building blocks for membrane assembly.

The distribution of the sulfur and sodium atoms from the center of mass of the entire pentablock is shown in Figure 3. The majority of the sulfur atoms reside on the outer surface of the collapsed pentablock for both water and implicit poor solvent with $\varepsilon = 77.73$, as shown in Figure 3-a, though the segregation to the surface is significantly larger in water. For $\varepsilon = 1.0$ most of sulfur atoms are distributed closer to center of mass. This result is consistent with the conformations shown in Figure 2 in which most of the sulfur atoms are on the outer surface in water and implicit poor solvent with $\varepsilon = 77.73$. This result also shows that most of the sulfur groups are on outer surface. Figure 3b shows the distribution for the sodium counterions for the three solvents. For water and poor solvent with $\varepsilon = 77.73$, the sodium atoms are more widely dispersed compared to the case with $\varepsilon = 1.0$ as one would expect since the former two cases the Coulomb interactions are screened. At 300K, in water only 10% of the Na^+ counterions are condensed on a SO_3^- sulfonated group. For the two implicit solvents the fraction increases to 25 and 100% for $\varepsilon = 77.73$ and 1.0 respectively.

This computational study resolved for the first time the structure of molecular aggregate of a structured ionic polymer. These structures have been proven to be complex to the extent that scattering experiments are limited in resolving the internal structure of the aggregates, and in solutions sufficiently dilute at the detection limit of scattering. This dilute limit is essential for avoiding aggregation. Here we calculate the static structure factor S(q),

where q is the momentum transfer vector. To study the size and shape of polymer chains, we calculated radius of gyration and structure factor S(q). Structure factor is calculated using $S(q)= |\sum_i b_i \exp(i\mathbf{q}\bullet\mathbf{r}_i)|^2$, where b_i and $\mathbf{r}_i$ are the scattering length and position vector of atom i, respectively. All results for S(q) are averaged over 500 configurations with 500 different random **q** vectors for each q.

S(q) of the pentablock in different solvents is shown in Figure 4a and b. The structure factors exhibit a characteristic slope at intermediate q region (shown by an ellipse in Figure 4a and become structured at high q. The general shape of the scattered object is determined from this intermediate q range where the slope of S(q) provides a first indication of the shape. We find that magnitude of the slopes increase from 3.5 to 3.7 as ε of the implicit solvent increase from 1.0 to 77.73. These slopes indicate that the pentablock collapsed into a slightly aspherical object which becomes more spherical as ε increases. In water and 1:1 mixture of cyclohexane and heptane, the slopes decrease to 3.0 and 2.7 respectively. The changes in presence of water are attributed to the structure inversion i.e. hydrophilic ionic block exposed to water while hydrophobic blocks are shielded. In the presence of mutually good solvent for flexible block and end blocks, the center block is collapsed while flexible blocks float around the matrix. These behaviors are further supported by the snapshots of pentablock as shown in Figure 2.

Further, insights of the structure are observed by fitting the data to an ellipsoid core-shell form factor[26] which captured the characteristics of asymmetric and highly interacting blocks in solvents. This form factor is capable of capturing the overall symmetry. In an ideal core-shell model where the core surface is smooth and well defined and the shell is homogenously distributed around the core, this ellipsoid presents an excellent description of the system. In here however, with the presence of multiple intertwined blocks, the visualization offered by computations in imperative to in depth understanding of the structure as shown in Figure 4b, where the partial structure factors, fits for elliptical models and

visualization are presented for implicit poor solvent with ε = 1.0. The ionic block is collapsed to a slightly asymmetric shape captured by an elliptical form factor, where the roughness is described by the shell. The end blocks and aliphatic chains are interwoven and segregate from the ionic block. With increasing complexity of the polymers, and diversion from highly symmetric shapes, the visualization obtained from computations is essential to resolve the structure.

4. Conclusions

A single chain of pentablock and sulfonated PS of the same molecular weight as that of the center block has been studied as a function of solvent quality. All blocks of pentablock are collapsed nearly spherical shape in water and in both implicit poor solvents with ε =1.0 and ε =77.73. Pentablock in water is very close to that in the implicit poor solvent for ε =77.73 where the ionic groups are on outer surface. The three different blocks of pentablock segregate from each other in the 1:1 mixture of cyclohexane and heptane. Both the flexible and end blocks in the 1:1 mixture of cyclohexane and heptane are swollent while the center block is collasped. Comparing $<R_g^2>^{1/2}$ of the sulfonated PS with that of the center block of the pentablock, $<R_g^2>^{1/2}$ of center block is slightly higher than that of sulfonated PS. In both water and ε =77.73, center block of pentablock and sulfonated PS chains are a globule-like conformation with all sulfonated groups located on the outer surface and the benzene rings of the styrene forming the inner surface. Similarly, the sodium counterions are more widely dispersed whereas for ε =1.0 the counterions are largely condensed. The distribution of the sulfur atoms and sodium atoms from the center of mass of the entire pentablock revealed that the majority of the sulfur atoms are on the outer surface of the collapsed pentablock and sodium atoms are more widely dispersed in both water and ε =77.73.

This study shows for the first time that the blocks of a single pentablock chain locally phase separate into distinct regions depending on the solvent. By varying the solvent and temperature, the local morphology of membranes formed from by solvent processing of these

pentablocks can be varied depending on how readily the different blocks can associate. Future studies are on underway to explore membranes and micelles made from these pentablock molecules.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the authors.

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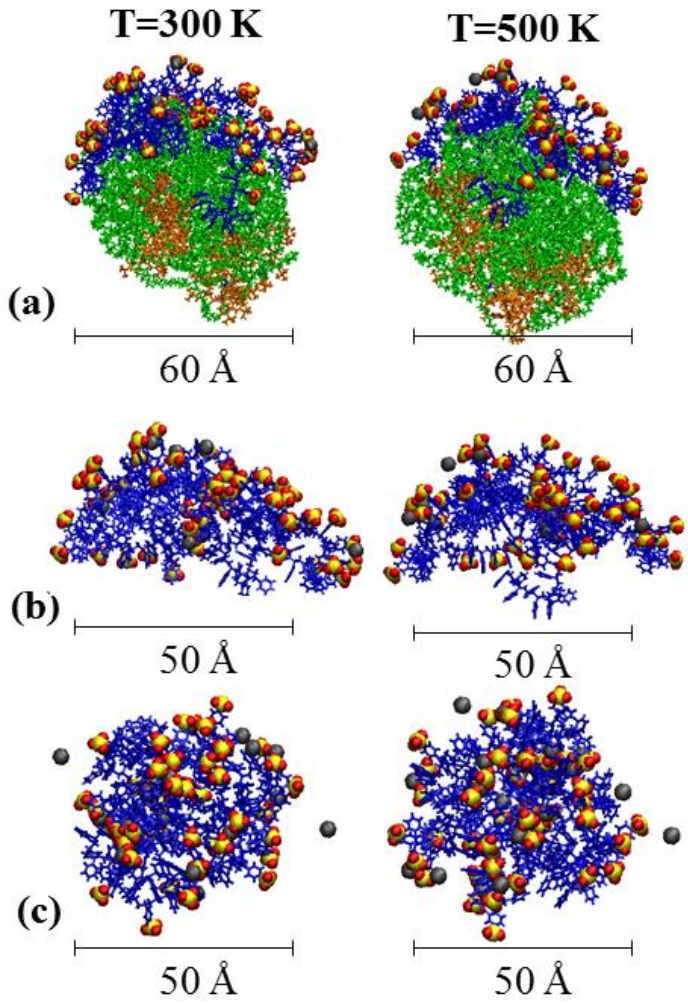

Figure 1. Snapshots of (a) pentablock, (b) center block of pentablock, and (c) sulfonated PS for f = 0.30 in water at T=300 and 500K. The end block is shown in orange, flexible block in green, middle block in blue, oxygen atoms in red, sulfur atoms in yellow and sodium atoms in gray.

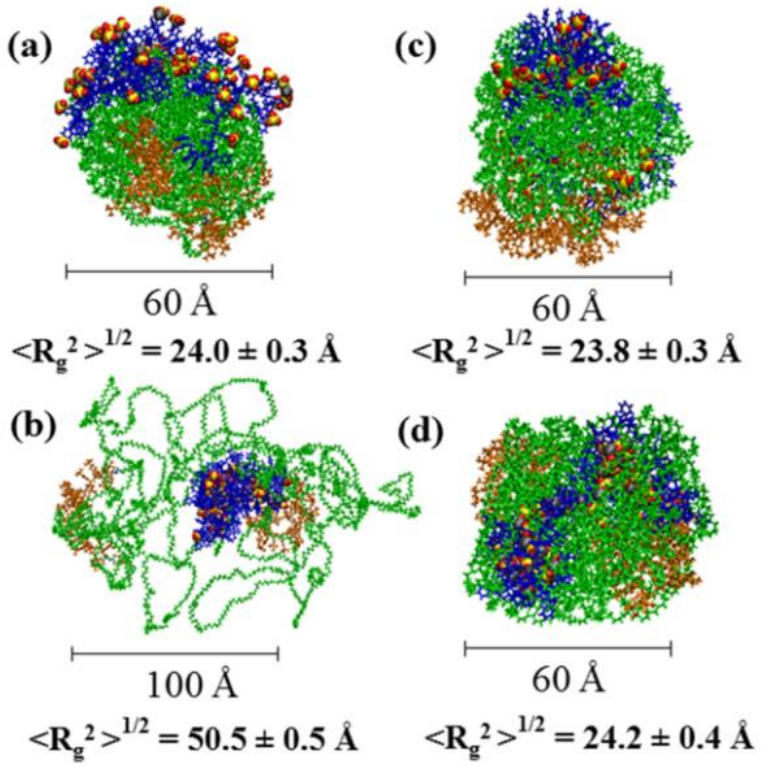

Figure 2. Snapshots of pentablock for f = 0.30 at T = 300K (a) in water, (b) in a 1:1 mixture of cyclohexane and heptane, (c) in poor solvent with ε = 77.73, and (d) in poor solvent with ε = 1.0.

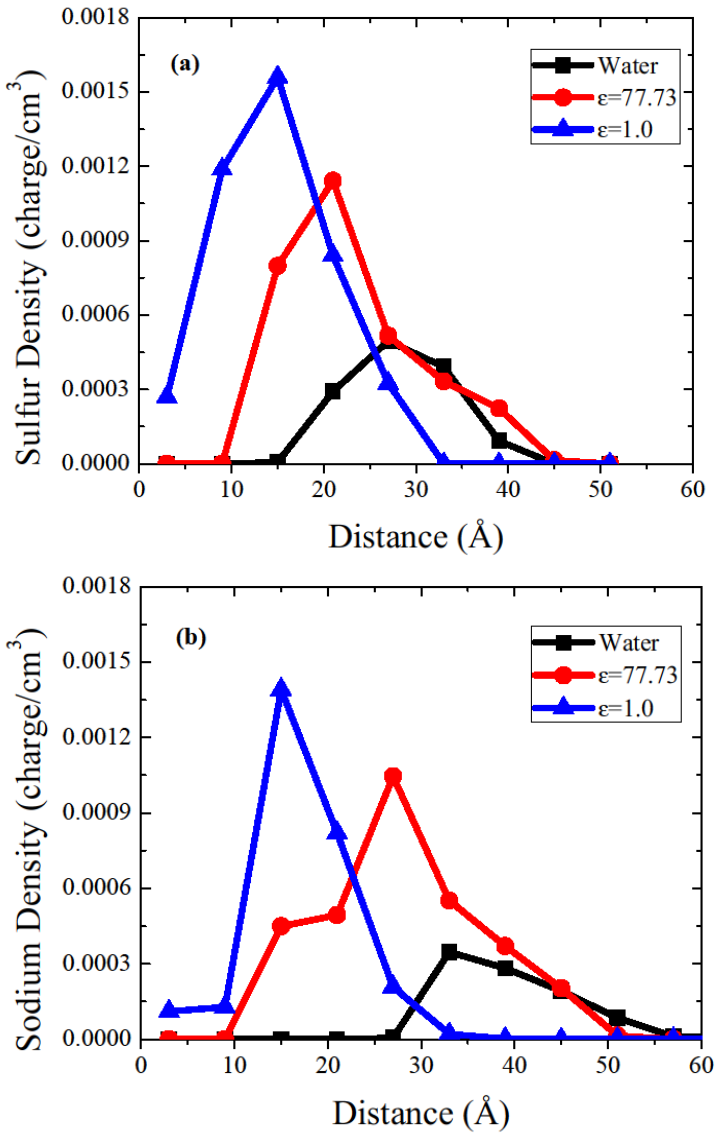

Figure 3. Density distribution function from the center of mass of pentablock for (a) sulfur atoms and (b) sodium atoms (b) at 300K in water (black) and in poor solvent with ε = 77.73 (red) and ε = 1.0 (blue) for the entire pentablock.

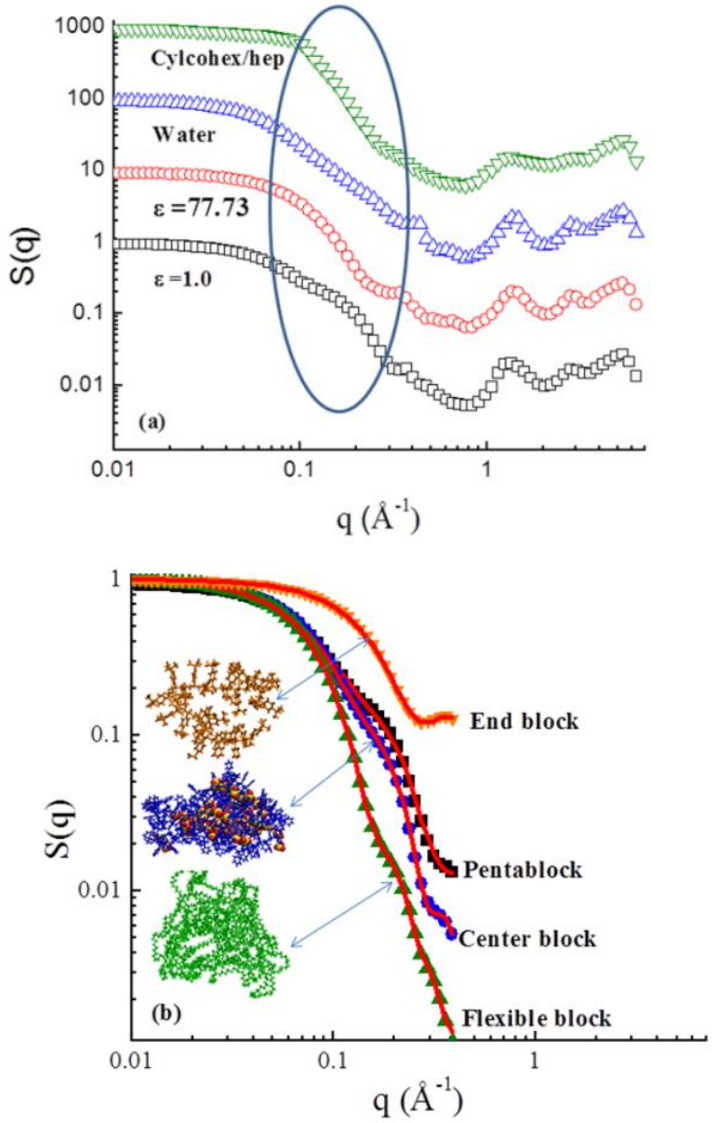

Figure 4. S(q) for f=0.30 at 300K as a function of q (a) pentablock in poor solvent with ε = 1.0 (squares) , in poor solvent ε = 77.73 (circles), in water (triangles) and in a 1:1 mixture of cyclohexane and heptane (down triangles). Data has been shifted vertically for clarity. (b) pentablock (squares), center block (circles), flexible block (triangles), and end block (down triangles) in poor solvent with ε = 1.0. Symbols represent the data and solid lines represent the best fit to the models described in text.

Table of Contents Entry:
Conformation of a structured pentablock ionic polymer in a mixture of cyclohexane and heptane and in water. In the mixed solvent, the flexible and end blocks are swollen while the

sulfonated polystyrene center block is collapsed. In water all the blocks of the pentablock are collapsed into a nearly spherical shape.

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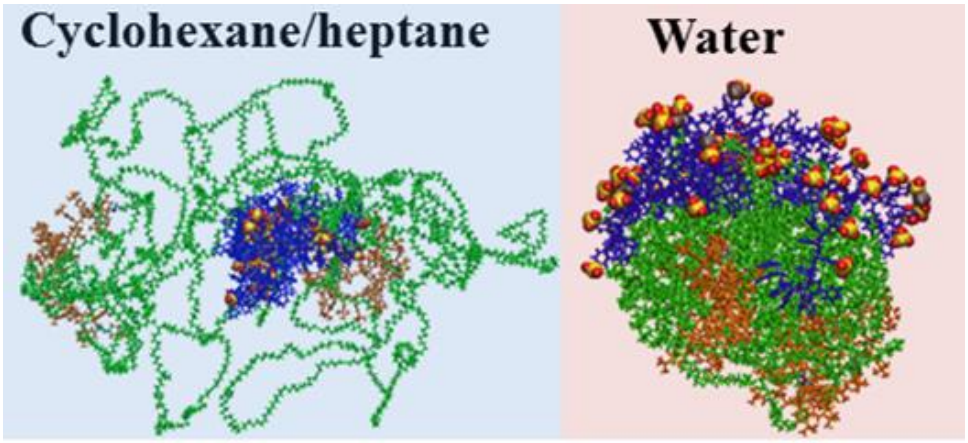
TABLE OF CONTENTS FIGURE



Supporting Information

Phase Behavior of a Single Structured Ionomer Chain in Solution

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1. Model and Methodology

Molecular dynamics simulations of an ionic pentablock were carried out using Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).[1] The single pentablock and solvent molecules are modeled using the Optimized Potentials for Liquid Simulations - All Atoms (OPLS-AA) framework of Jorgensen et.al.[2, 3] Non-bonded interactions are calculated between all atom pairs of different molecules and all pairs on the same molecule separated by three or more bonds, though the interaction is reduced by a factor of 1/2 for atoms separated by three bonds. All Lennard-Jones interactions are cut-off at r_c = 12 Å. For atom pairs, all electrostatic interactions closer than 12 Å are calculated in real space; those outside this range are calculated in reciprocal Fourier space by using the particle-particle particle-mesh algorithm (PPPM) [4] with precision of 10^{-4}.

The Newton equations of motions were integrated using a velocity-Verlet algorithm with a time step δt =1 fs for the implicit solvent and for the cyclohexane-heptane and water simulations. The reference system propagator algorithm (REPSA) [5] with multi-timescale integrator with a time step of 1.0 fs for the bond, angle, dihedral, van der Waals interactions and direct interactions part of the electrostatic interactions and a time step 4.0 fs for long range electrostatic interactions was used to accelerate the simulation. To maintain the system temperature a Langevin thermostat with a 100 fs damping constant was used for all of the runs in implicit solvents and for the constant volume runs of the explicit solvents. The pentablock molecules and 1:1 mixture of cyclohexane and heptane molecules were constructed separately using Polymer Builder and Amorphous Cell modules in Accelrys Materials Studio©. The pentablock co-polymers were merged with the solvent, and the systems were equilibrated initially at constant pressure and temperature using a Nose-Hoover thermostat with the same damping constant.

Simulations were carried out for two explicit solvents, water modeled by TIP4P/2005 model[6] and a 1:1 mixture of cyclohexane and heptane molecules described by OPLS and two implicit, poor solvents. For the two implicit solvent simulations, all the interactions

between atoms on the pentablock molecule were cutoff at radius r_c = 12 Å. To model water we set the dielectric constant ε=77.73 while ε=1.0 for a vacuum. The single pentablock molecules were initially fully stretched and collapsed at 300K. However this led to a metastable which was effectively frozen over the accessible simulation times. Therefore, each pentablock was heated in an implicit poor solvent to 500K, ran from 15 ns and then cooled back to 300K and run for an additional 20 ns. To simulate the pentablocks in explicit solvent we first equilibrated systems of 256000 water molecules and a 1:1 mixture of 21600 cyclohexane molecules and 21600 heptane molecules at 300K in a cubic simulation cell. Periodic boundary conditions were used for all explicit atom simulations. Overlapping atoms that resulted from merging the pentablock molecules and the explicit solvents were removed by running for a few thousand steps with the *fix NVE/limit* routine in LAMMPS. We ran the water system for 20 ns and mixed solvent system for 30 ns at 500K and then cooled each to 300K. Each system was then run for 30 ns at constant pressure with P = 0, followed by a run of 20 ns at constant volume. The dimensions of the simulation cell after equilibration at T=300K was L=19.6 nm for water and 21.8 nm for the mixed solvent, sufficient to prevent interaction of pentablock with its periodic image.

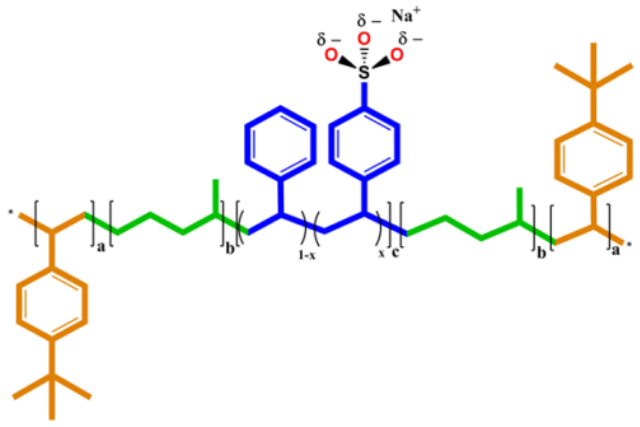

Figure S1. Chemical structure of the pentablock poly(t-butyl-styrene)-b-ethylene-r-propylene-b-styrene-r-styrenesulfonate-b-ethylene-r-propylene-b-poly(t-butyl-styrene) co-polymer with a, b and c are the number of the monomers and δ^- is a partial charge associated with the oxygen atoms. The sulfonation of the center block is random.

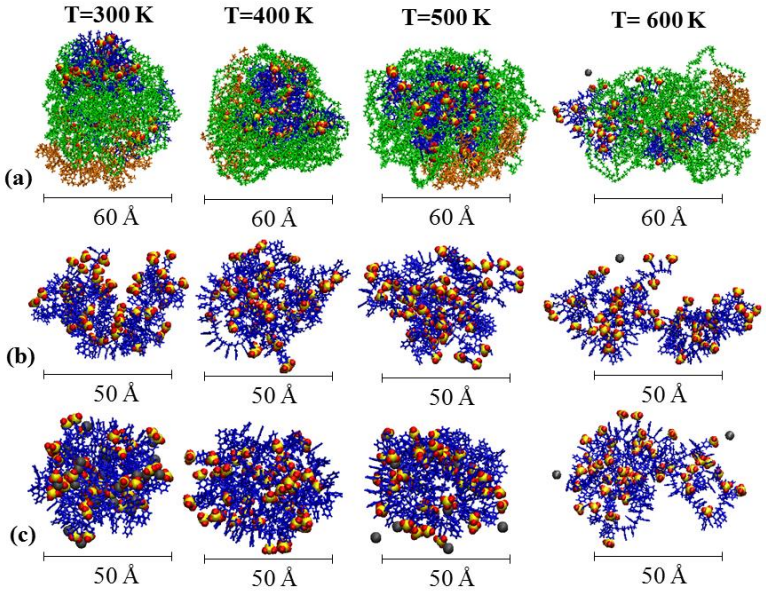

Figure S2. Snapshots of (a) pentablock, (b) center block of pentablock and (c) sulfonated PS for f = 0.30 in an implicit poor solvent with ε =77.73 at T=300, 400, 500 and 600K. Colors are the same as in Figure 1 in text.

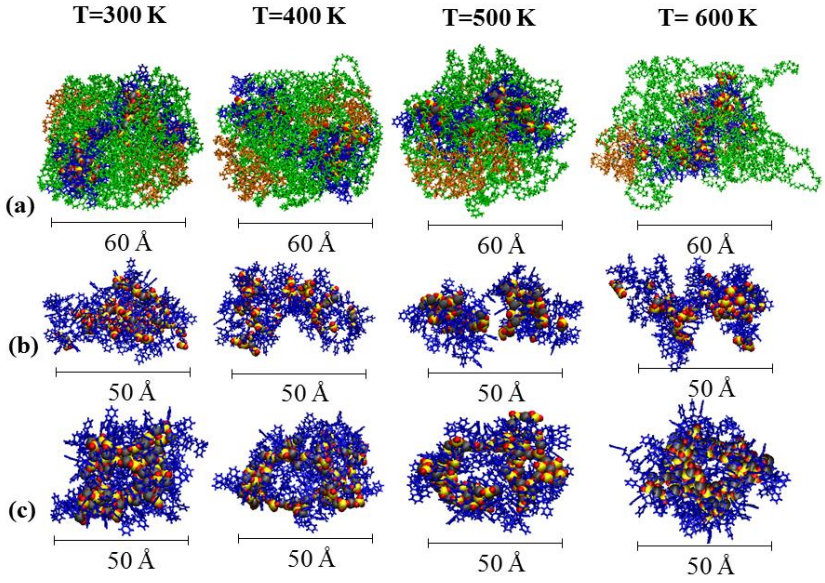

Figure S3. Snapshots of (a) pentablock, (b) center block of pentablock and (c) sulfonated PS for f = 0.30 in an implicit poor solvent with ε =1.0 at T=300, 400, 500 and 600K. Colors are the same as in Figure 1 in text.

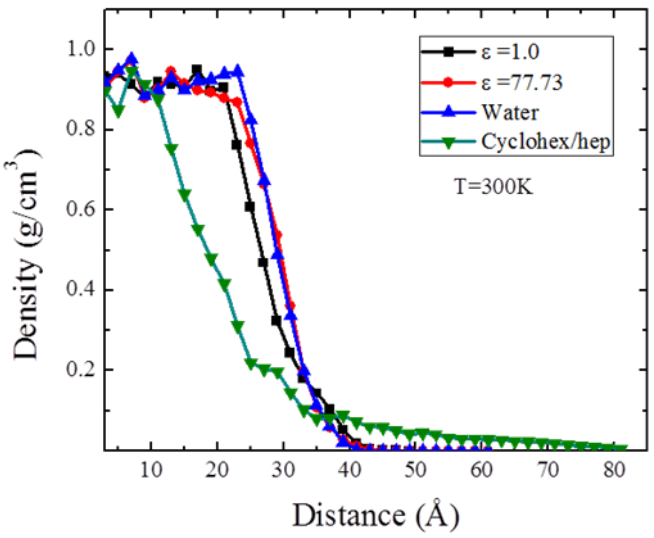

Figure S4. Density of pentablock as a function of distance from the center of mass for f=0.30 at 300K in water (blue-up triangles), poor solvent with ε =1.0 (black-squares) and ε =77.73 (red-circles) and cyclohexane/heptane (green-down triangles).

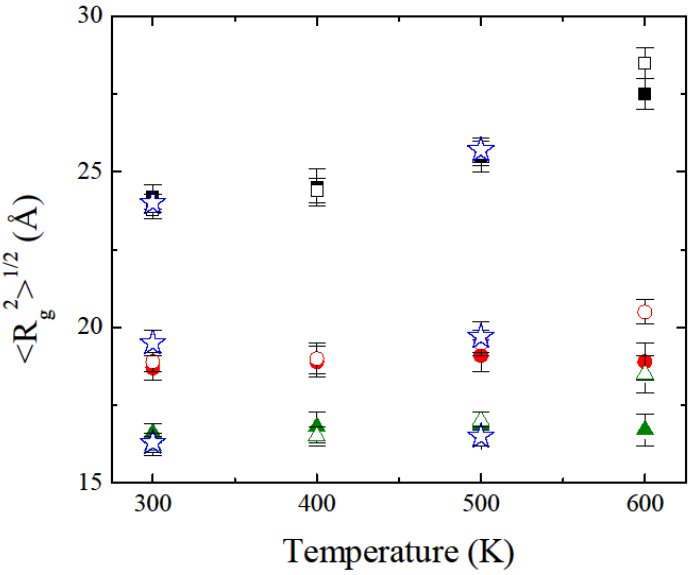

Figure S5. Square root of the mean square average radius of gyration of pentablock (squares), center sulfonated PS block of pentablock (circles), and sulfonated PS (triangles) as a function of temperature. Closed symbols represent results for ε=1.0 and opened symbols for ε = 77.73. Results for pentablock in water are shown as stars.

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