Response of Ionizable Block Copolymer Assemblies to Solvent Dielectrics: A Molecular Dynamics Study

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Abstract

Ionizable co-polymers assembly in solutions is driven by the formation of ionic clusters. The fast clustering of the ionizable blocks often leads to formation of far-from equilibrium structures that ultimately impact the structure of polymer membranes and affect their many applications. Using large scale atomistic molecular dynamics simulations, we probe the effects of electrostatics on formation of ionizable co-polymer micelles that dominate their solution structure, with the overarching goal of defining the factors that control the assembly of structured ionizable co-polymers. A symmetric pentablock ionizable copolymer, with a randomly sulfonated polystyrene center tethered to polyethylene-r-propylene block, terminated by poly (t-butyl styrene), in solvents of varying dielectric constants from 2-20, serves as the model system. We find that independent of the solvents, this polymer forms a core-shell micelle with the ionizable segment segregating to the center of the assembly. The specific block conformation, however, strongly depends on the sulfonation levels, and the dielectric constant and the polarity of the solvents.

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Introduction

Ionizable block co-polymers, which consist of ionic blocks covalently tethered to one or more non-ionic segments, are at the center of many current and potential applications such as clean energy,[1,2] separation devices[3,4] and bio-medical aplications.[5,6] Combining ionizable blocks that can facilitate transport of water and ions with van der Waals blocks that can provide mechanical stability opens up numerous possibilities for a wide range of new materials. These polymers are governed by two different energy scales, strong, long-range, electrostatic interactions and van der Waals forces. The strong electrostatic interactions drive clustering that enable the function of these polymers in their many applications. However, these assemblies often trap the polymers in far-from equilibrium structures that keep transforming as the polymer environment changes.

Because of their high glass transition temperature resulting from clustering, the transformation of these polymers to viable materials is often carried out from solution through solvent casting. Therefore, their micellar characteristics in solution propagates through processing, determining the membranes structure and functionality.[7,8] The current study focuses on the effect of solvents with varying dielectric constants on the assembly of ionizable co-polymers, at the onset of micelle formation, at high temperature, high pressure, which are typical of industrial processing of ionizable polymers, into solutions.[9,10]

Using atomistic molecular dynamics (MD) simulations, the current study probes the effects of electrostatic interactions exerted by solvents on the formation of structured ionic polymer assemblies. Specifically, we probe the response of a symmetric pentablock co-polymer with a sulfonated polystyrene (PSS) center tethered to polyethylene-r-propylene (PEP) and terminated by poly(t-butyl styrene) (t-BPS) to polar and non-polar solvents. This polymer was designed by Kraton™ with the premise that the PSS block controls the transport of ions and water, while the

PEP blocks provide flexibility, and the t-BPS blocks enhance mechanical stability. The polymers are dissolved at high temperature and are cast into films as the solvents evaporate. In non-polar solvents, this pentablock forms micelles with spherical and elliptical symmetries[11,12] with the PSS blocks residing at the core of the micelle surrounded by the PEP segments. The t-BPS blocks are distributed across the hydrophobic regions with a slight preference to the PSS interface. These micellar assemblies formed in the solution are directly transferred into membranes and control the functionality of the membrane. As the blocks are highly incompatible, they exhibit distinctive affinities to different solvents.

The technological potential of these polymers has driven experiment and computational studies of these polymers leading to a knowledge base that underlies the current study. Using x-ray scattering and STEM, Choi et al.[11] suggested that in cyclohexane/heptane mixtures, these pentablocks form spherical aggregates with an inner ionic core and outer non-ionic corona. Further insight was obtained from small angle neutron scattering by Etempawala et al.[12] that were able to distinguish the core and corona of these micelles. They showed that these copolymers form ellipsoidal core-shell assemblies, with the PSS block in the core and a swollen PEP and t-BPS corona. With increasing solution concentration, they found that the size of the micelle, the thickness of the corona, and the aggregation number increase, while the solvent fraction in the core decreases. Aryal et al.[13] using MD simulations of this pentablock in water and in a cyclohexane/heptane mixture found that the core of the aggregates consists of a network of PSS with the hydrophobic blocks partially intertwined in the core but predominantly residing in a highly swollen corona. In water, the PSS blocks reside largely at the water-polymer interface, while in a mixed solution of cyclohexane and heptane, a more tightly packed ionic network is formed. The ionic network serves as a long-lived skeleton of the assembled nanoparticle where the

hydrophobic blocks can migrate in and out of this structure depending on the nature of the solvent. The correlation of solution structure and the membrane morphology was demonstrated by Huang et al.[7] who showed that a random distribution of discrete sulfonated domains dominates membranes cast from a cyclohexane-heptane solution, but ordered pentablock morphology consisting of lamella and hexagonally packed ion groups are formed in films cast from a THF solution. Though the fact that solvents affect solution structure and consequently membrane morphology, molecular understanding of these effects, critical for deriving controlled processing conditions for this class of technologically important polymers, remains a challenge.

Here, we probe the response of micellar assemblies of this pentablock with sulfonation level f = 0.15, 0.30 and 0.55, across the ionomer/polyelectrolyte boundary, in three solvents: cyclohexane, THF and propanol using fully atomistic MD simulations. Cyclohexane is a non-polar solvent with a polarity index of 0.2 and a dielectric constant of 2.02. It is a poor solvent for the PSS and PS at room temprature. It is a good solvent for the PEP block. Propanol and THF are significantly more polar, with a polarity index of 4, but differ in their dielectric constants with 7.58 for THF and 20.33 for propanol. The polarity index captures the ratio of molecular volume to the dipole moment of the molecules. It is measured experimentally and is available as part of the specification provided by the manufacturers of different solvents. It often serves as a qualitative measure of solvent interactions.

Model and Methodology

Polymer characteristics including sulfonation level and molecular weights were chosen to match previous experimental[11,12] and computational studies.[13-15] The molecular weight of each of the chains is ~50,000 g/mol with a weight percent (wt%) of the center atactic PSS block of ~40%,

each of the randomly substituted PEP blocks is ~20%, and each of the t-BPS blocks is ~10% with Na^+. counterion. The polystyrene center block was randomly substituted with sulfonated groups with fractions f = 0.15, 0.30, and 0.55 of the available sites. The three solvents, cyclohexane, tetrahydrofuran (THF) and propanol, were chosen to cover the broad range of solvent polarity and dielectric constants that match the industrially used solvents to cast the films. The number of molecules per micelle for this study was chosen to be 5 pentablock chains. In very dilute solutions, very small micelles have been observed by neutron scattering. At higher concentrations the number of molecule per micelle formed in non-polar solvent varies from 25-70. [12] Alongside, it has been shown that the critical micelle concentration of ionic block copolymers can be extremely low,[16] and unimolecular micelles are formed. Subsequently, we have chosen a viable compromise that provides insight into the effect of solvent polarity on the local packing while probing the systems on the atomistic level within realistic computer resources. All simulations were run at 500K, a temperature that is above the glass transition temperature of the ionic domain of PSS in melts. This temperature is consistent with the temperature range in which these polymers are dissolved to form parent solutions for casting.

Molecular dynamics simulations of multi-chains of ionic pentablock were carried out using the Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).[17] The chains and solvent molecules are modelled using the Optimized Potentials for Liquid Simulations All Atoms (OPLS-AA) force fields developed by Jorgensen et al.[18,19] with updated parameters for the polyethylene-r-propylene block.[20] All Lennard-Jones interactions are truncated at cutoff radius r_c = 1.2 nm. Coulomb interactions are treated with long-range particle−particle particle-mesh algorithm (PPPM)[21] Ewald with a real space cutoff of 1.2 nm and a precision of 10^{-4}. The

pentablock molecules and three solvents were constructed using Polymer builder and Amorphous Cell modules of Materials Studio®.

Atomistic MD simulations are among the very few methods that that provide molecular insight into the factors that control formation of micelles. However, following the actual aggregation of polymer molecules to form micelles in dilute solutions is computationally challenging due to large system size and the slow diffusion of the chains. Here, an alternative route was taken [13] in which the five polymer chains were first collapsed into a spherical micelle in an implicit poor solvent and then merged with the explicit solvents. This was done by placing the chains with a large spherical cavity which was reduced in radius by 0.5 nm/ns until the micelle reached a density of 1.0 g/cm^3, using the 'fix indent' command in LAMMPS[22].

Two paths were tested as shown Figure 1a. One confines the ionizable blocks to form a dense core shown in Figure 1a (top) and the second compresses the five polymer chains to form a spherical

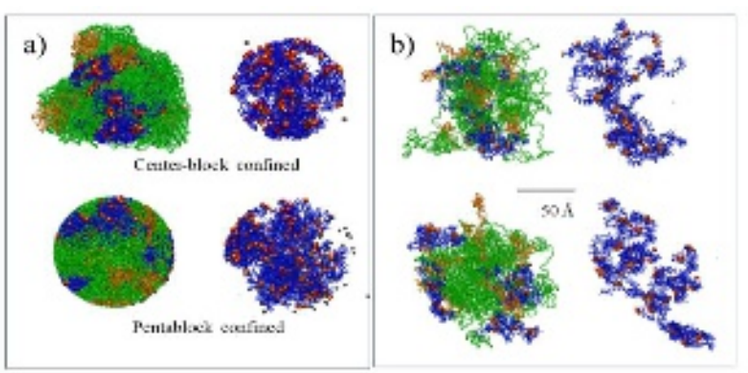

Figure 1. a) Visualization of condensed micelles with sulfonation fraction f = 0.15 and the corresponding center block, formed by compression of the ionic blocks (top) and the entire pentablock (bottom) in implicit poor solvent. b) The corresponding micelles to those presented in a) and the center blocks after 100 ns in propanol following the exposure to solvent. The solvent molecules are removed for clarity. The t-BPS block is shown in orange, the PEP in green, polystyrene in blue, oxygen atoms in red, sulfur atoms in yellow and sodium counterions in gray.

aggregate as shown in Figure 1a, (bottom). Constraining the ionizable segments only is based on experimental[11,12] and computational[13] studies that showed that the ionic blocks form the core of the micelle. Separately we equilibrated systems of 97,200 cyclohexane molecules, 83,500 THF molecules and 120,000 propanol molecules in a cubic simulation cell with periodic boundary conditions. After slowly increasing the diameter of a cavity in the center of each solvent system large enough to accommodate the collapsed micelle, the micelle and solvent were merged and equilibrated at constant pressure P = 100 atm and temperature T = 500 K for 50 ns. The temperature and pressure were maintained by coupling the system weakly to a thermostat and barostat with a damping time of 100 ps. The final dimensions of the simulation were ~ 30 nm for cyclohexane and propanol and 26.0 nm for THF. The systems were then run for at least another 150 ns at constant volume. After 100 ns, the condensed micelles relax and assume the same shape and molecular conformation, independent on the path taken towards assembly as show in Figure 1b for the entire micelles and their cores.

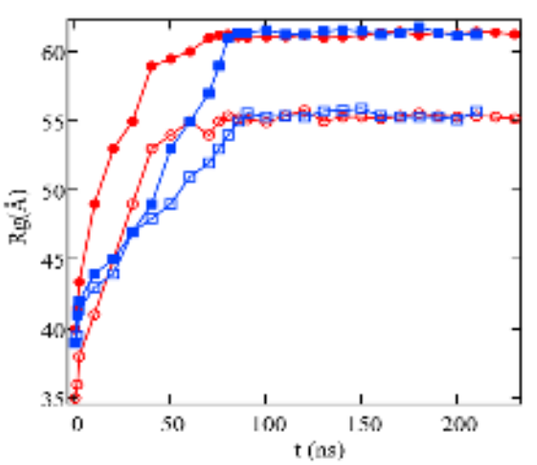

Figure 2. Radius of gyration R_g of the entire micelle (filled) and the ionic blocks (open) as a function of time for f = 0.15 in propanol. Red circles correspond to spherically compressing the center blocks and blue squares correspond to compressing the whole system to form the micelles.

The time for the two starting states to reorganize and form a stable micelle was determined by calculating the radius of gyration R_g as function of time for the whole micelle and for the ionic segments is shown in Figure 2. Here t = 0 is the time the condensed micelles and solvent were merged. These results show that the size of the micelle as well as that of ionic segments reach a steady state after approximately 100 ns. Similar times were observed for the micelles in cyclohexane and THF. In subsequent discussions, results are presented for the micelles formed by compressing the ionic blocks, though the two give very similar results.

Results

The condensed micelles were immersed in solvents and followed as a function of time as the solvent penetrates and the blocks rearrange. Visualization of the entire micelle and the ionizable block assemblies 100ns after immersion are presented Figure 3. At first glance, the micelles

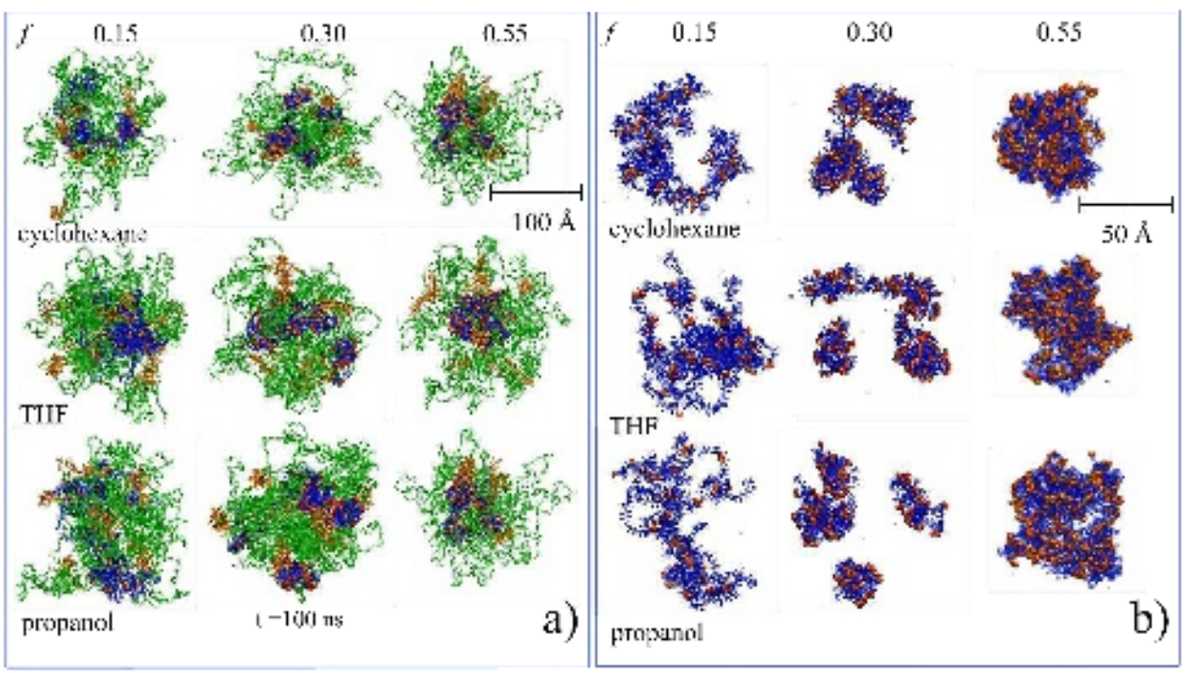

Figure 3. Visualization of a) the micelle and b) the PSS center blocks in cyclohexane, THF and propanol for f = 0.15, 0.30 and 0.55 at 500 K. The solvent molecules are removed for clarity. The t-BPS block is shown in orange, the PEP block in green, polystyrene in blue, oxygen atoms in red, and sulfur atoms in yellow.

(Figure 3-a) appear to be spherical in all three solvents. However, a closer look shows that the packing and conformation of the individual blocks and their distribution across the assemblies vary with the solvent and the overall shape depends on the degree of sulfonation. At *f=0.15,* the condensed micelle relaxed into an assembly with a relatively extended ionizable domain in the core, surrounded by the rest of the blocks. The micelles exhibit similar characteristics to that observed by neutron scattering,[12] for all solvents, where the PEP and t-BPS, reside in the corona. The detailed structure of the corona is driven by the solvent quality differences of the PEP and t-BPS blocks and to the PSS core. A sulfonation level of f = 0.15 is sufficient to drive the formation of a well-defined core. In THF and propanol, the t-BPS block mostly resides at the solvent interface.

At the highest sulfonation fraction *f=0.55*, the ionizable blocks collapse in a dense core for all three solvents. The core swells with increasing dielectric constant of the solvent. The distribution of the PEP and tBPS blocks in cyclohexane remains similar to that of the corona of the *f=0.15*

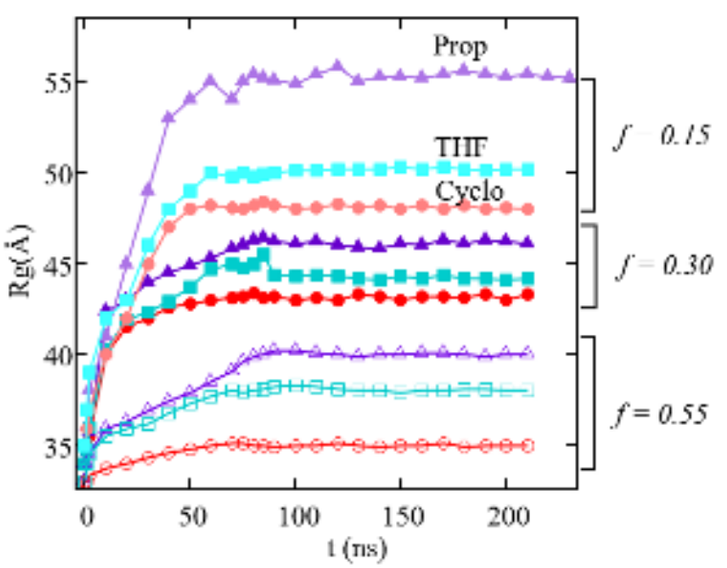

Figure 4. Radius of gyration Rg of the PSS domains as a function of time at indicated sulfonation levels and solvents. Prop corresponds to propanol, THF to tetra hydro furane and Cyclo to cyclohexane. The time the condensed micelle was merged with the solvent is defined as t=0.

micelle. However, they reside across the entire corona in THF and propanol. For the intermediate sulfonation fraction 0.3, a transitional state is observed, where the density of the ionic domains is increased though the core is not fully contiguous, nevertheless the micelle remains stable.

The dimensions of the entire micelle and that of the PSS domains in the different solvents are shown in Figure 4. For all systems, Rg of the condensed micelle first increase with time and then plateaus as the condensed micelle swells. Two distinctive features associated with differences in electrostatics of either the polymer or the solvent are observed. The time from immersion in the solvents to reaching the plateau increases with sulfonation level. Further the higher the dielectric constant of the solvent, the more swollen the core becomes for all sulfonation levels. The evolution of R_g at different f and ε of the solvent together with the dimensions of the PSS domains provide a first direct insight into the delicate electrostatic balance that controls the assembly of ionizable polymers.

The structural nanoscale changes were depicted by calculating the static structure factor $S(q)$. $S(q)$ is given by

$$S(q) = \sum_{i,j=1}^{N} b_i b_j \langle \exp\left[i\boldsymbol{q}.\left(\boldsymbol{r_i} - \boldsymbol{r_j}\right)\right]\rangle / \sum_{i=1}^{N} b_i^2, \qquad (1)$$

where b_i are the scattering lengths for neutrons and $\boldsymbol{r_i}$ the position of atom i. To compare with any experimental solution structure determination method, the scattering density needs to be chosen to reflect the interactions of the atoms of the system with the scattered waves. Here choosing the scattering lengths b_i for neutrons allows comparison with our previous experimental neutron results.[23,24] $S(q)$ patterns for entire micelle and for the ionizable blocks are shown in Figure 5. $S(q)$ is calculated averaging over 200 configurations with 500 random $\boldsymbol{q}$ vectors for each q value. All $S(q)$ patterns exhibit well defined signatures at low q indicative of formation of discrete micelles. At the intermediate q regime, $S(q)$ scales as $q^{-\alpha}$ where the value of α depends on the

shape of the aggregate. For the entire micelle, α increases from 3.6 to ~4.0 as the sulfonation level *f* increases, in all solvents. This indicates that as *f* increases the micelle becomes more spherical, consistent with the visual observations shown in Figure 3. The static structure factor *S(q)* of just the ionic blocks depends on both the sulfonation fraction and solvent dielectrics. For $f = 0.15$ in cyclohexane $\alpha = 3.8$, which suggests a close to spherical aggregate. With increasing solvent dielectric constant, α decreases whereas in propanol, $\alpha \sim 1$ for S(q) of the core, which captures the more elongated structure of the ionic blocks. However, for higher sulfonation, $\alpha \sim 4$ for all solvents as the ionic blocks form a more spherical core. All S(q) patterns exhibit a signature at intermediate q range which arises from the core. These lines are rather distinctive at high sulfonation levels where the core is well defined. It becomes significantly broader at lower sulfonation level, where the ionizable segments form a more open structure in the center of the micelle.

A full analysis of the structure was obtained by fitting *S(q)* for the entire micelle to core-shell form factor developed by Pedersen,[25,26] as was done for SANS data for larger micelles,

$$P_{micell}(q) = N_{agg}^2\beta_{core}^2 P_{core}(q) + N_{agg}\beta_{brush}^2 P_{brush}(q) +$$

$$2N_{agg}^2\beta_{core}\beta_{brush}S_{brush-core}(q) + N_{agg}(N_{agg}-1)\beta_{brush}^2 S_{brush-brush}(q). \qquad (2)$$

This complex form factor encapsulated four terms that allow description of the core, the shell, and their interrelation. Capturing the interrelation between the core and the corona is particularly critical for the low *f* systems where the ionizable PSS segment is not fully collapsed into a dense core. $P_{core}(q)$ and $P_{brush}(q)$ are the form factors for the core and the corona. $S_{brush-core}(q)$ and $S_{brush-brush}(q)$ are cross terms between core-corona and the corona-corona. $P_{core}(q)$ describe the interactions of chains in the homogeneous core in the center and decaying core segments density at core-corona interface. $P_{brush}(q)$ describes the Gaussian chains in corona and

it follows the Debye function. $S_{brush-core}(q)$ addresses the roughness of the interface between core and corona and $S_{brush-brush}(q)$ describes the interaction between chains in the corona. Here, β_{core} and β_{brush} are the total excess scattering length densities of the core and the corona. $P_{core}(q)$, $P_{brush}(q)$, $S_{brush-core}(q)$, and $S_{brush-brush}(q)$ are mathematically defined in set of functions which account for the aggregate dimensions. $N_{agg}$is the number of polymer chains in the micelles. In an ideal core-shell model, the surface of the core is smooth and well defined, and the shell is homogeneously distributed around the core. With the presence of three different blocks which have different flexibility and interactions, there is some intermixing of the core and corona that is captured in the complex form factor we used. During the fitting, the scattering length density

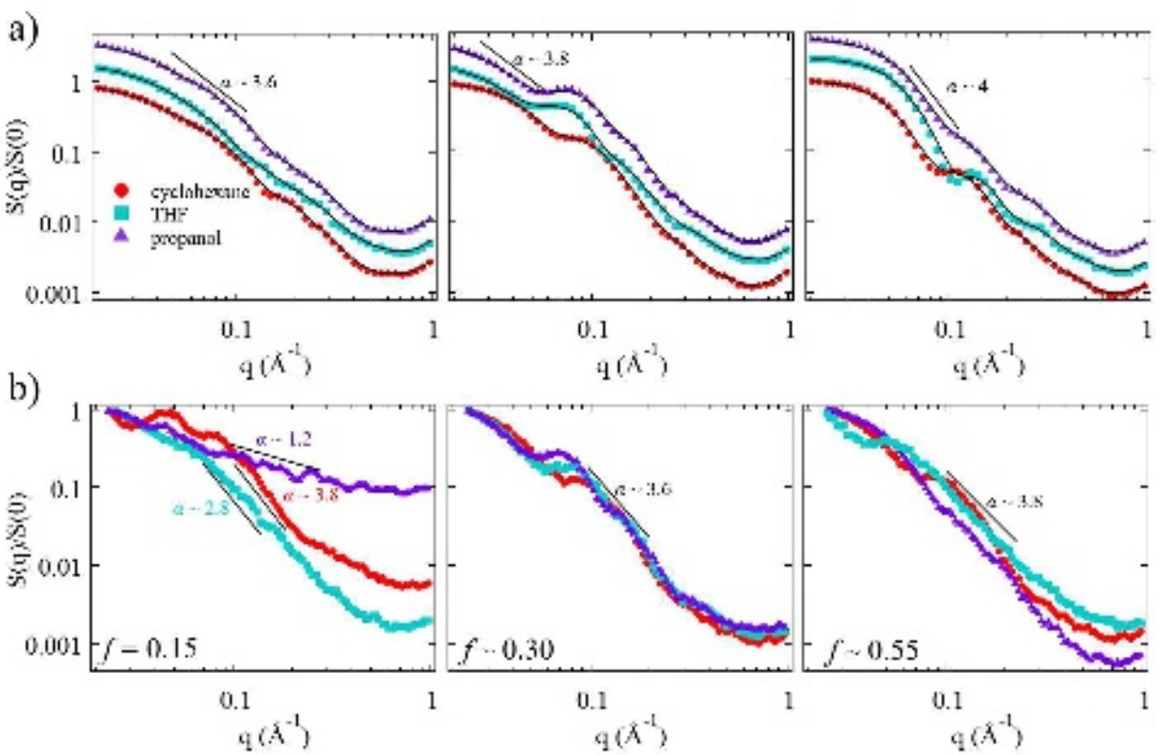

Figure 5. Static structure factor *S(q)* as a function of wave vector *q* for a) the micelle and b) for the ionic blocks in cyclohexane (red circles), THF (blue squares) and propanol (purple triangles) for different sulfonation fractions f = 0.15 (right), f = 0.30 (center), f = 0.55 (left). Solid lines correspond best fits to the core-shell model. *S(q)* for the micelle in a) for THF and propanol are shifted vertically for clarity.

(SLD) of solvent is set to that of the deuterated solvents (D-THF, D-Propanol and D-Cyclohexane), and N_{agg} = 5, the number of chains in a micelle. Also, an elliptical or spherical core fit was used depending on the value of α. Best fits were obtained by minimizing the χ^2, and it is assumed that fits are acceptable with χ^2 less than 2. For f = 0.15, the data for $S(q)$ is best fit with an elliptical core-shell model with high degree of intermixing (d_{im} = 0.1-0.2) of core and the corona

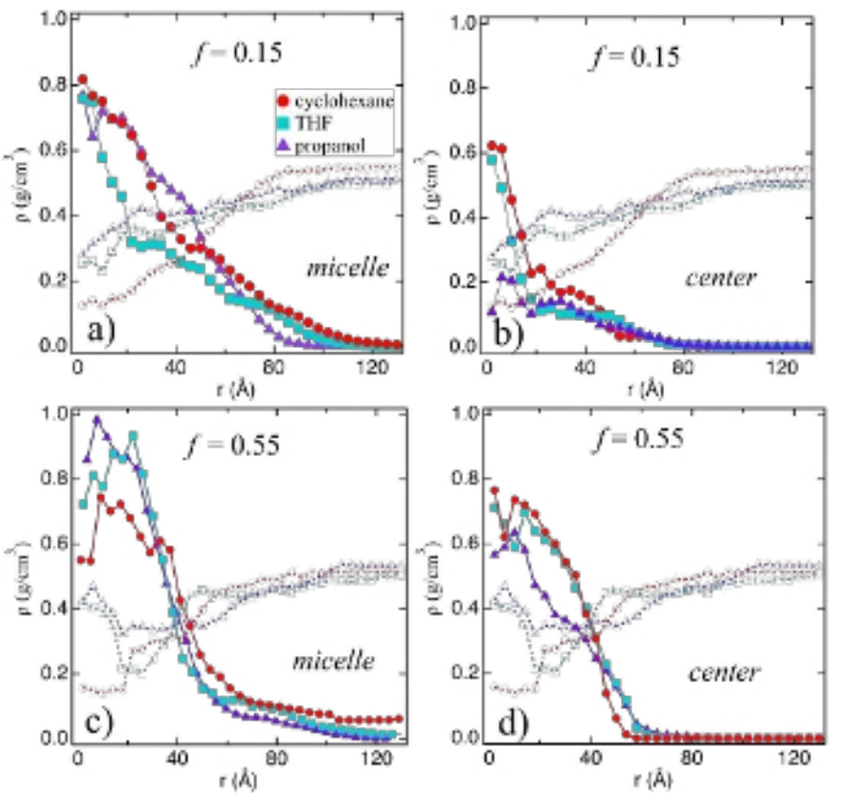

Figure 6. Radial density as function distance r from the center of mass of (a) micelle and (b) ionic blocks for f = 0.15 and (c) micelle and (d) ionic blocks for f = 0.55 (solid symbols) in cyclohexane, THF and propanol. Open symbols are the solvent density.

For f = 0.30, spherical-core shell model gave the best fit with significant intermixing (d_{im} = 0.4-0.5) of core and corona while f = 0.55, the best fit is for a spherical core-shell model with very little intermixing (d_{im} = 0.6-0.8) of ionic blocks in the core and the non-ionic blocks in corona. Further, the core radius decreases (R_{core} = 8-7 nm for f = 0.30, and 5-6 nm for f = 0.55) with

increasing sulfonation fraction. These fits are consistent with the visible observations that for the higher sulfonation levels, core is more homogeneous and spherical.

The distribution of the atoms within the micelles and the ionic blocks are captured as radial density profile as a function of distance from the center of mass of the micelle. Results for $f = 0.15$ and 0.55 are shown in Figure 6. These mass density profiles support the visual observations of the micelles shown in Figure 3 and reveal further details about the aggregates. In all three solvents, the overall density of the ionic blocks is more diffusive for $f = 0.15$ but much larger with a sharper interface for $f = 0.55$. The radius of the micelle is largest (~ 9 nm) for cyclohexane is ~90 Å and decreases as the polarity of the solvent increases. For $f = 0.55$, the overall size of the micelle is very similar for all three solvents. The solvent density shows that while all three solvents penetrate the core, there is about twice as much propanol and THF in the core than cyclohexane.

The ionic groups of the center block aggregate into clusters. For $f = 0.15$ average cluster size is ~ 4 in cyclohexane and decreases ~ 2 for the more polar solvents. Here two sulfonated groups are considered to be in the same cluster if the sulfur atoms are separated by 0.6 nm or less. This distance encompasses all sulfur pairs within the first peak in the pair correlation function. Increasing the cutoff does not change the qualificative results. For the highest sulfonation fraction $f = 0.55$, the average cluster size increases to ~20 for propanol and THF and 24 for cyclohexane. The effects of solvent polarity on cluster formation in ionic core is further explored by probing the association of the solvent molecules with the ionic groups.

The association of cyclohexane and propanol molecules for $f = 0.15$ and $f = 0.55$ is shown in Figure 7. The closest distance between sulfur in the ionic group and the oxygen in the solvent molecule is ~0.5-0.6 nm, accounting for the geometry of the solvent molecule. Therefore, solvent molecules are assumed to be associated with an ionic group if the distance between the S and any atom in the

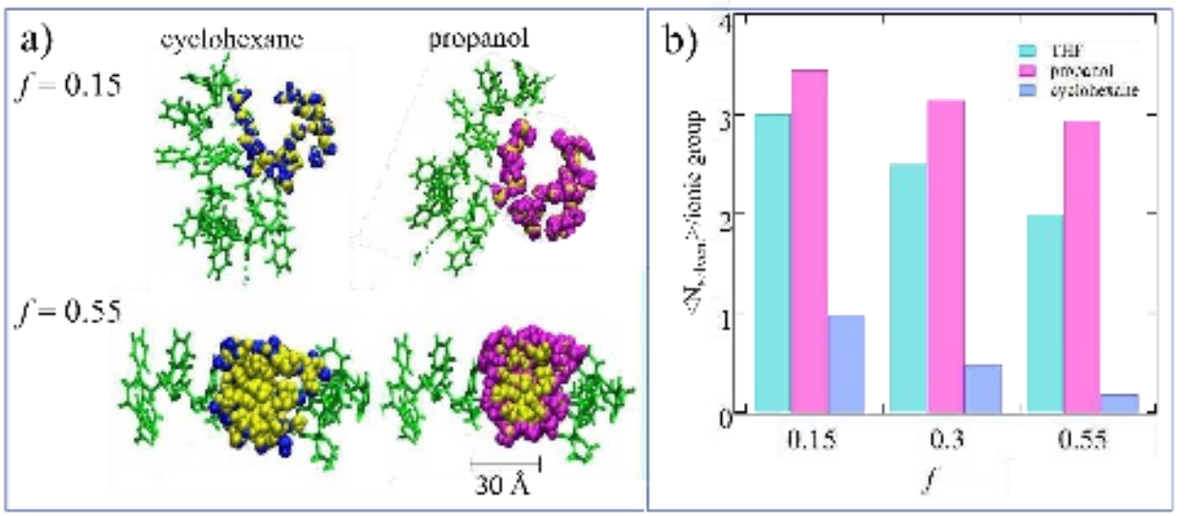

Figure 7. a) Cross section of the ionic block and associated solvents for cyclohexane (blue) and propanol (pink) with ionic groups for $f = 0.15$ (top) and $f = 0.55$ (bottom). Yellow corresponds to the sulfur atoms, green represents the backbone and the phenyl rings. b) Number of solvent molecules per ionic group associated with an ionic group for different sulfonation levels.

solvent molecules are within 0.7 nm. Figure 7a visualizes the cross section of the ionic blocks and associated solvent for $f = 0.15$ and 0.55. For low sulfonation fraction, all three solvent molecules associate with the ionic groups to some extent as seen in Figure 7b. However, more propanol and THF molecules are associated with the ionic groups for all sulfonation levels compared to cyclohexane, which is largely excluded from the core. The THF and propanol molecules which penetrate the core weaken the ionic interaction, resulting in a slightly swollen ionic core compared to cyclohexane (Figure 7b).

Conclusions

Here using molecular dynamics simulations, we isolated the delicate balance of electrostatic interactions at the onset of micelle formation, on the structure and assembly process of micelles of structured ionizable block copolymers. We first developed and validated a computational methodology to build complex assemblies with structures as close as possible to long lived agglomerates in the physical world, followed by probing the formation of micelles formed by an ionizable co-polymer.

We find that the micelles formed from this pentablock copolymer response differently depending on the dielectric constant of the solvent balance with the direct electrostatic interactions of the ionizable blocks, coupled directly with the explicit chemical interactions of the solvents with the different blocks. In cyclohexane, at low f values the ionizable blocks segregate into an ionic domain surrounded by a corona of the PEP and t-BPS blocks. With increasing *f*, a dense spherical core is formed while non-polar blocks form a swollen state. In this solvent, the interaction of the solvent with both hydrophobic blocks affect the corona structure whereas the t-BPS block resides at the interface of the PSS core where the solvent-micelle interface is dominated by the PEP. In contrast to cyclohexane, in THF and propanol and the ionizable blocks are more swollen and non-polar blocks slightly more collapsed. With increasing sulfonation, ionic blocks condense to form a more stable ionic core. The t-BPS however is distributed across the entire corona.

These results clearly show that in structured ionizable co-polymers a delicate balance between solvent dielectrics and direct electrostatic interactions between the ionizable groups controls the evolution of the micelles and their final dimensions. Further the results demonstrate that the overall distribution of the segments in the low dielectric environment corona is controlled by their direct interactions with the solvent.

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