Clustering effects in ionic polymers: Molecular dynamics simulations

Anupriya Agrawal, Dvora Perahia, and Gary S. Grest

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Clustering Effects in Ionic Polymers: Molecular Dynamics Simulations

Anupriya Agrawal,[1*] Dvora Perahia,[1] Gary S. Grest[2]

[1]Department of Chemistry, Clemson University, Clemson, SC 29634, USA
[2]Sandia National Laboratories, Albuquerque, NM 87185, USA

Abstract

Ionic clusters control the structure, dynamics and transport in soft matter. Incorporating a small fraction of ionizable groups in polymers reduces substantially the mobility of the macromolecules in melts. These ionic groups often associate into random clusters in melts, where the distribution and morphology of the clusters impact the transport in these materials. Here, using molecular dynamic simulations we demonstrate a clear correlation between cluster size and morphology with the polymer mobility in melts of sulfonated polystyrene. We show that in low dielectric media ladder-like clusters that are lower in energy compared with spherical assemblies are formed. Reducing the electrostatic interactions by enhancing the dielectric constant leads to morphological transformation from ladder-like clusters to globular assemblies. Decrease in electrostatic interaction enhances significantly the mobility of the polymer.

I. Introduction

Cluster formation in ionomers, macromolecules that consist of ionizable groups, is driven by a balance of electrostatic interactions and inherent segregation between hydrophilic and hydrophobic groups [1]. In contrast to polyelectrolytes [2,3] where the properties of the polymers are dominated by electrostatic interactions, the characteristics of ionomers are a result of a balance of both the conformation of the backbone and electrostatic forces. The ionic groups impart conductivity and electrolytic transport characteristics as well as mechanical behavior and adhesion strength [1]. Segregation of the hydrophobic matrix and ionic clusters dominates the structure of melts of flexible and semiflexible ionomers such as sulfonated polystyrene (SPS), polystyrene methacrylate and Nafion® [4-7]. The size, shape, number and distribution of the ionic assemblies, all affect the overall structure and dynamics of the polymers as well as their transport characteristics. Surprisingly, even addition of small number of ionizable groups impacts both the dynamics of the melts and the ability to transport ions and solvents. This impact is strongly manifested in recent rheology studies of Weiss and co-workers who have shown that lightly sulfonated short polystyrene melts, below the entanglement length are highly viscous and diffusion is significantly hindered in comparison with the non-sulfonated polymer with identical chain length [8-12]. The role of ionic clusters in the mobility of these polymers is one critical factor in controlling both transport characteristics and mechanical stability. Experimental studies revealed clusters with a predominantly spherical symmetry in melts, whose presence reduces significantly the mobility of the macromolecules. The direct correlation of clustering with mobility of ionic polymers however remains one critical open question. Here we probe the *clustering process and its impact on mobility* in sulfonated polystyrene, using molecular dynamics (MD) simulations. The rich manifold of available experimental data for polystyrene allows validation of our initial choice of force fields to describe polystyrene. Here the atomistic insight obtained from MD studies correlates the clustering effects on the polymer dynamics. In contrast to prior studies, we find that the morphology of the aggregates evolves with electrostatic interactions and impacts the polymer mobility.

The role of the ionic clusters in transport has driven numerous studies, pioneered by Eisenberg and co-workers [1,13,14]. They initially observed that the ionic groups segregate into multiplets, small, tightly packed ionic assemblies that in turn form clusters, using X-ray scattering [13]. They rationalized the stability of the clusters in terms of balance between electrostatic and elastic pulling forces of the polymer chains [13]. This initial model was further generalized by Forsman [15], Dreyfus [16], Datye and Taylor [17] and later by Mauritz [18]. Eisenberg, Hird and Moore [14] have successfully extended the original model of clustering to different types of ionomer environments. This model predicts that the mobility of atoms immediately surrounding the clusters is significantly reduced however they were not able to predict the morphology of the clusters. These clusters were further probed by several groups. Cooper and co-workers identified spherical ionic aggregates of size ~3 nm using electron microscopy and x-ray scattering in polystyrene sulfonate (SPS) [6,19]. Using scanning transmission electron microscopy and x-ray scattering, Winey and co-workers have observed ~2 nm spherical ionic aggregates that were independent of percent of sulfonation and the degree of ionization [7,20,21]. The clusters comprise multiplets, small, tightly packed ionic groups whose association is driven by columbic forces. The multiplets associate to form clusters or aggregates. The clusters' size and shape are generally affected by residual electrostatic energy between multiplets, the steric repulsion between monomers, and the energies needed to deform the polymer coils from their free, natural configuration due to confinement.

The significance of these ionic aggregates has driven further studies zooming in on the conformation of single molecules. Single chains of SPS with varying sulfonation, tacticity and ionization levels in different solvents were probed computationally [22-26]. Xie and Weiss have shown that the increase in sulfonation of SPS molecules resulted in the increase of the radius of gyration of chains [22]. Chialvo and Simonson have observed the like-charge attraction in the solvation of short chain SPS in aqueous solutions [23]. Carrillo and Dobrynin showed that with increasing fraction of sulfonation, a SPS chain adopts an elongated conformation [25]. These studies provide significant insight of single-molecules behavior in various solvents. Here, using MD simulations we probe the formation of ionic clusters in SPS melts and their impact on the polymer mobility. We demonstrate a quantitative correlation between cluster size and polymer dynamics. At low dielectric media, we find predominantly non-spherical, ionic clusters, predicted by Dreyfus [16] that transform into spherical ones with reduction of electrostatic interaction strength.

II. Methodology

Simulations were performed using the parallel molecular dynamics code Large Atomic Molecular Massive Parallel Simulator (LAMMPS) [27]. Atactic polystyrene chains of length $N = 40$ (20 chains) and 80 (40 chains) were made using Accelrys Materials Studio [28] with 0, 5 and 10% random sulfonation levels. $N = 80$ system was further replicated by a factor of 8 for a total system size of 320 chains. The percent sulfonation is defined as number of monomers, which are sulfonated with respect to the total number of monomers per chain. Polystyrene is modeled using the All Atom Optimized Potential for Liquid Simulations (OPLS-AA) force field by Jorgensen et al. [29,30]. Additional parameters for sulfonated group are obtained from Ref. 26, 31 and 32. The attractive r^{-6} dispersion term in the Lennard-Jones interaction as well as the electrostatic interactions were calculated using particle-particle particle-mesh algorithm [33]. As a result the Lennard-Jones interaction becomes a fully long range potential. Interactions closer than 1.2 nm are calculated in real space; those outside this range are calculated in reciprocal Fourier space with precision of 10^{-4}. The repulsive r^{-12} Lennard-Jones interaction was truncated at 1.2 nm. To understand the effect of the strength of the electrostatic interactions on the structure and dynamics of SPS melts, the dielectric constant ε of the $N = 80$, 10% sulfonation system was varied from $\varepsilon = 1$ to $\varepsilon = 30$.

The polymer chains were placed randomly in the simulation cell. After overlaps were removed using the 'nve/limit' fix in LAMMPS, each system was run for 1-2 ns using NPT ensemble with temperature 600K and 1 atm pressure where temperature and pressure were controlled using the Nosé-Hoover thermostat and barostat, respectively to set the density. Production runs for each sulfonation level and dielectric constant were run for at least 300 ns at constant volume. As discussed in more detail below, the average size of SO_3^- clusters increases over the 100 ns and then stabilizes. Newton equations of motions were integrated using a velocity-Verlet. The reference system propagator algorithm (REPSA) [34] 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. For all constant volume runs, each monomer was coupled weakly to a Langevin thermostat with a damping constant of 100 fs to maintain a constant temperature.

III. Results

The mobility of the polymer was followed by determining the mean square displacement (MSD) of the center of mass of the chains for three melts of 0, 5 and 10% sulfonation at $T = 600$K as shown in Figure 1. With increasing sulfonation level, the mobility of the chains is considerably reduced as was previously observed experimentally by rheology studies [4,11]. We further probed the internal dynamics of the polymers by comparing the MSD of non-sulfonated and sulfonated phenyl rings within SPS chains. As seen in Fig. 1 the sulfonated phenyl ring motion is significantly slower than that of the non-sulfonated rings whereas the overall motion of chains is similar to that of the sulfonated phenyl groups.

A snapshot of various clusters for a melt of chains of length $N = 40$ for 10% SPS at $T = 600$K is shown in the left panel of Fig. 2. Surprisingly, the sulfonated groups form ladder-like clusters, as shown in the zoomed-in image on the right panel. This cluster consists of eight $SO_3^-Na^+$ groups originating from three different chains. Assuming a dipole from

SO_3^- to Na^+, the geometry of this particular cluster can be described by ↑↓↑↓↑↓↑↓ where the arrows represent a dipole with the arrowhead representing Na^+. This ladder-like cluster was first postulated by Dreyfus [16]. Building on basic ionic pairs which constitute electrical dipoles, he showed that electrostatic interactions drive these dipole pairs to organize into multiplets of quadrupoles which further grow to form clusters. The size of a multiplet is limited by steric hindrance since each ionic pair is attached to the polymer backbone. The residual electrical energy between multiplets, the steric repulsion between monomers, and entropy loss due to disruption of polymer conformation all contribute to the overall shape of the cluster. In low dielectric media, the linear arrangement of these dipoles as found here minimizes the cluster energy.

To explore the thermal stability of the ladder morphology we probed the melt at 700K which is feasible in our model since the bonds are unbreakable. We find that the clusters remain stable even at this higher temperature as shown in Fig. 3. The mobility of the ionomers increases with increasing temperature as shown in the MSD data presented in Fig. S1b. While the clusters become more dynamic with increasing temperature, they do not dissociate under the conditions of our measurement. The tendency of the ionic groups to form clusters, also leads to increase in density with sulfonation level. The densities measured at 600K and pressure $P = 1$ atm are 0.84, 0.89 and 0.95 g/cc for sulfonation 0, 5 and 10% respectively. Concurrently, the average end-to-end distance of chains decreases with increasing sulfonation levels where $\langle R_g^2\rangle^{1/2}$ ~17.2 Å, 14.8 Å and 13.6 Å for 0, 5 and 10% sulfonation respectively.

As clustering affects the mobility, the impacts of the electrostatic interactions were further probed via increasing the dielectric constant ε of the melt. The dielectric constant impacts the residual electrostatic screening, which along with the hard core repulsive between monomers and polymer entropy determine the shape and stability of the ionic assemblies [16]. Here ε was varied between 1 and 30 as a means to tune this energetic term. Though increasing ε slightly decreases the density at constant pressure, all simulations for $\varepsilon = 1$-30 were carried out at the equilibrium density for $\varepsilon = 1$ for a direct comparison. Cluster evolution was followed as a function of time for different ε values. One typical cluster is shown Fig. 4 as time progresses for $\varepsilon = 1$ melt. Initially there are three smaller clusters as shown in Fig 4a. With time, the clusters form one string-like large aggregate. Once merged, the cluster rearranges and by 42 ns there are two ↑↓↑↓ multiplets joined by a string cluster. By 123 ns, all $SO_3^-Na^+$ ions form a single large multiplet. This cluster remains stable for an additional 300 ns apart from slight motion of the atoms.

The electrostatic interactions were then decreased by increasing the dielectric constant to $\varepsilon = 2$ for the same starting state as for $\varepsilon = 1$ described above. In this case, the clusters are significantly more dynamic; they break up and merge forming more globular assemblies as shown for one cluster after ~83 ns Fig 4b. The cluster are much more globular/spherical for $\varepsilon = 2$ than for $\varepsilon = 1$ with an average cluster size of 6 to 7 SO_3^- groups. On further increasing ε, the average cluster size decreases to 4.0 for $\varepsilon = 5$ and 1.7 SO_3^- for $\varepsilon = 10$. Distribution of SO_3^- for $\varepsilon = 1$, 2, 5 and 30 melt is shown in Fig. 5. Overall as the strength of the electrostatic interaction decreases, cluster size decreases.

Finally, starting at time 230 ns for the $\varepsilon = 1$ system, we followed the changes in the cluster shown in Fig. 3a with time after increasing ε from 1 to 2. Results are shown in Fig. 4c. After ~ 40-50 ns, the ladder morphology begins to distort but does not breakup until ~ 150ns. This cluster continues to deform as the simulation progresses. When switching back ε from 2 to 1 the globular clusters stretch out again to form ladder-like aggregates after approximately 100ns. This morphological change as a function of ε is attributed to screening of the residual electrostatic energy between ion pairs or multiples.

To further understand the morphological changes as a function of electrostatic strength, we compared energy of ladder-like and spherical aggregates of equal size and found that the potential energy is 32 kcal/mole lower in a ladder-like structure than in a spherical aggregate per SO_3^- group for $\varepsilon = 1$. This result was determined by calculating the potential energy of each aggregate for the melt with $\varepsilon = 1$ and comparing it with the melt run with $\varepsilon = 5$ but setting $\varepsilon = 1$. This shows that for $\varepsilon = 1$, ladder-like type clusters are most stable. However for large screening ($\varepsilon = 5$) the ladder-like and spherical aggregates of the same size have comparable potential energies. In this case the spherical aggregates would be likely favored due to a combination of entropy and interfacial energy, in agreement with our simulation results. This result is consistent with the overall energy of the ladder-like melt which is lower by 31 kcal/mol per SO_3^- group in comparison to that of a melt that consist of predominantly globular aggregates. This difference is due to a large gain in electrostatic energy at the expense of a small loss in the interfacial energy [35]. This result further demonstrates that the cluster morphology is dominated by the residual electrostatic interactions between multiples and is consistent with previous observations by coarse grained models [36that the cluster shape changes from disk-like to spherical as the strength of the attraction interaction between associating groups decreases.

Using the dielectric constant as a means to control the overall degree of association of the sulfonated groups, we probed the effects of cluster formation on the overall mobility of the polymers. The correlation between cluster formation and the mobility of the polymers as the dielectric constant is varied is summarized in Fig. 6 for a melt of chain length $N = 80$ with 10% sulfonation. With increasing ε the cluster size decreases, and their number increases as seen in Figure 7. The mobility of the polymers as reflected in the diffusion constant increases as the size of the clusters decreased. In this range the average end-to-end distance of chains remain constant (41.3 Å, 41.2 Å, 44.8 Å and 45.4 Å for $\varepsilon = 1$, 2, 5 and 30 respectively). The difference in the local mobility of the sulfonated versus non-sulfonated benzene rings also decreases as ε increases as shown in Figure 8. Even though the mobility of the polymers increases with increasing ε, for SPS, it remains slower in comparison with that of zero sulfonation polystyrene. The diffusion constant calculated for zero sulfonation polystyrene ($N = 80$) is 1.7×10^{-8} cm^2/s, which is considerably faster than all of the sulfonated systems and is in good agreement with experiment [38]. Part of this increase could be attributed to the reduction in density at $P = 1$ atm (0.84 g/cc for zero sulfonation compared to 0.95 g/cc for 10%).

IV. Conclusions

In summary, we have shown that the constrained dynamics in sulfonated polystyrene is directly correlated with cluster formation and is affected by the local movements of the group to which the ionizable group is tethered. The mobility of the SPS molecules decreases significantly with increasing sulfonation fraction in agreement with recent experiments [4]. However increasing the dielectric constant of the media decreases the dimensions of the clusters and consequently enhances dynamics. Surprisingly, the study revealed ladder-like cluster morphologies dominate at low dielectric media as predicted by Dreyfus [16] regardless of the percent sulfonation and chain length. These ladder-like clusters exhibit a lower potential energy compared to a globular morphology. We further show that small change in the electrostatic strength, leads to more spherical/globular clusters. In addition to unique new cluster morphologies, this study have demonstrated the delicate balance that controls cluster formation in ionic polymers and its correlation with the dynamics of the polymers in melts.

Acknowledgements

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*Present Address: Department of Mechanical Engineering and Materials Science, Washington University, St. Louis, MO 63130, USA

References:

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1. A. Eisenberg and J.-S. Kim, *Introduction to Ionomers* (John Wiley and Sons, Inc, 1998
2. D. T. Hallinan Jr. and N. P. Balsara, Annu. Rev. Mater. Res. **43**, 503 (2013)
3. C. E. Sing, J. W. Zwanikken and M. Olvera de la Cruz, Nat. Mater. **13**, 694 (2014)
4. Q. Chen, G. J. Tudryn and R. H. Colby, J. Rheol. **57**, 1441 (2013)
5. D. G. Peiffer, R. A. Weiss and R. D. Lundberg, J. Polym. Sci. Polym. Phys. Ed. **20**, 1503 (1982)
6. C. Li, R. A. Register and S. L. Cooper, Polymer (Guildf). **30**, 1227 (1989)
7. N. C. Zhou, C. D. Chan and K. I. Winey, Macromolecules **41**, 6134 (2008)
8. X. Qiao and R. A. Weiss, Macromolecules **46**, 2417 (2013)
9. R. A. Weiss and H. Zhao, J. Rheol. **53**, 191 (2009)
10. M. Rigdahl and A. Eisenberg, J. Polym. Sci. Polym. Phys. Ed. **19**, 1641 (1981)
11. R. A. Weiss, J. J. Fitzgerald, and D. Kim, Macromolecules **24**, 1071 (1991)
12. R. A. Weiss and W.-C. Yu, Macromolecules **40**, 3640 (2007)
13. A. Eisenberg, Macromolecules **3**, 147 (1970)

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14. A. Eisenberg, B. Hird and R. B. Moore, Macromolecules **23**, 4098 (1990)
15. W. C. Forsman, Macromolecules **1**, 343 (1968)
16. B. Dreyfus, Macromolecules **18**, 284 (1985)
17. V. K. Datye and P. L. Taylor, Macromolecules **18**, 1479 (1985)
18. K. A. Mauritz, in *Ionomers Synth. Struct. Prop. Appl.,* edited by M. R. Tant, K. A. Mauritz, and G. L. Wilkes (1997), pp. 95–157
19. D. J. Yarusso and S. L. Cooper, Macromolecules, **16**, 1871 (1983)
20. B. P. Kirkmeyer, R. A. Weiss and K. I. Winey, J. Polym. Sci. Part B Polym. Phys. **39**, 477 (2001)
21. A. M. Castagna, W. Wang, K. I. Winey and J. Runt, Macromolecules **44**, 2791 (2011)
22. R. Xie and R. A. Weiss, Comput. Theor. Polym. Sci. **7**, 65 (1997)
23. A. A. Chialvo and J. M. Simonson, J. Phys. Chem. B **109**, 23031 (2005)
24. A. Vishnyakov and V. J. Neimark, J. Chem. Phys. **128**, 164902 (2008)
25. J.-M. Y. Carrillo and A. V. Dobrynin, J. Phys. Chem. B **114**, 9391 (2010)
26. X. He, O. Guvench, A. D. J. Mackerell and M. L. Klein, J. Phys. Chem. B **114**, 9787 (2010)
27. S. Plimpton, J. Comput. Phys. **117,** 1–19 (1995)
28. "Materials Studio," Accelrys. © 2001-2007 Accelrys Software Inc.
29. W. L. Jorgensen, J. D. Madura, and C. J. Swenson, J. Am. Chem. Soc. **106**, 6638 (1984)
30. W. L. Jorgensen, D. S. Maxwell, and J. Tirado-Rives, J. Am. Chem. Soc. **118**, 11225 (1996)
31. W. R. Cannon, B. M. Pettitt, and A. A. McCammon, J. Phys. Chem. **98**, 6225 (1994)
32. J. Chandrasekhar, D. C. Spellmeyer, and W. L. Jorgensen, J. Am. Chem. Soc. **106**, 903 (1984)
33. R. E. Isele-Holder, W. Mitchell, and A. E. Ismail, J. Chem. Phys. **137**, 174107 (2012)
34. M. Tuckerman, B. J. Berne and G. J. Martyna, J. Chem. Phys. **97**, 1990 (1992)
35. J. L. Brédas, R. R. Chance, and R. Silbey, Macromolecules, **21**, 1633 (1988).
36. A. N. Semenov, I. A. Nyrkova, and A. R. Khokhlov, Macromolecules **28**, 7491 (1995)
37. P. G. Khalatur, A. R. Khokhlov, I. A. Nyrkova, and A. N. Semenov, Macromol. Theory Sim, 5, 711 (1996); 5, 749 (1996).
38. G. Fleischer, Polymer Bulletin, 11, 75 (1984)

Figures:

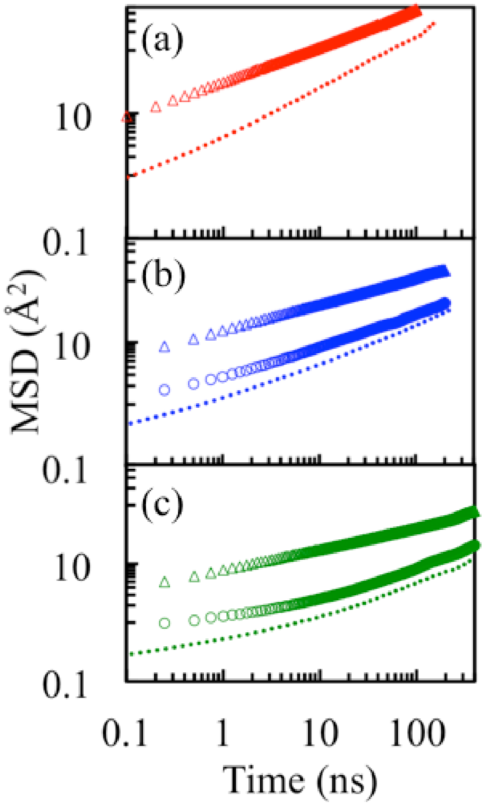


FIG. 1 (Color online) Mean square displacement versus time at 600K of a sulfonated polystyrene melt with f = 0, 0.05 and 0.10 of chain length N = 40. MSD of phenyl rings (Δ), sulfonated phenyl rings (o) and chain center of mass (dashed line)

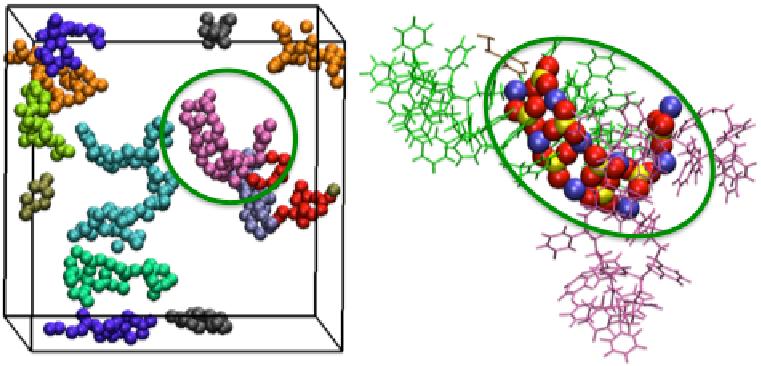


FIG. 2 (Color online) Left panel shows the snapshot of different ionic clusters for N = 40 with 10% sulfonation at 600K after 160ns, where 0 represent the start of the constant volume simulation. Different colors represent distinct clusters. Zoomed in green cluster at right show individual atoms S (yellow), O (red) and Na (blue).

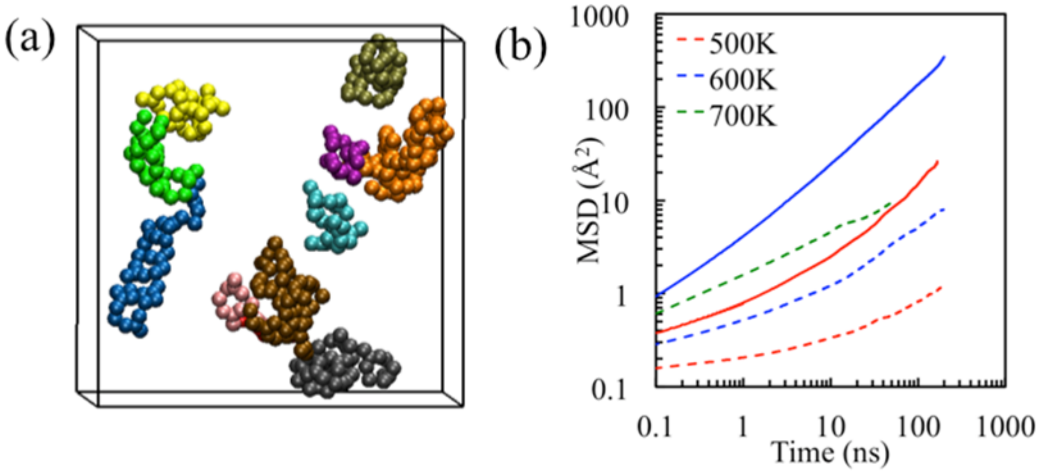
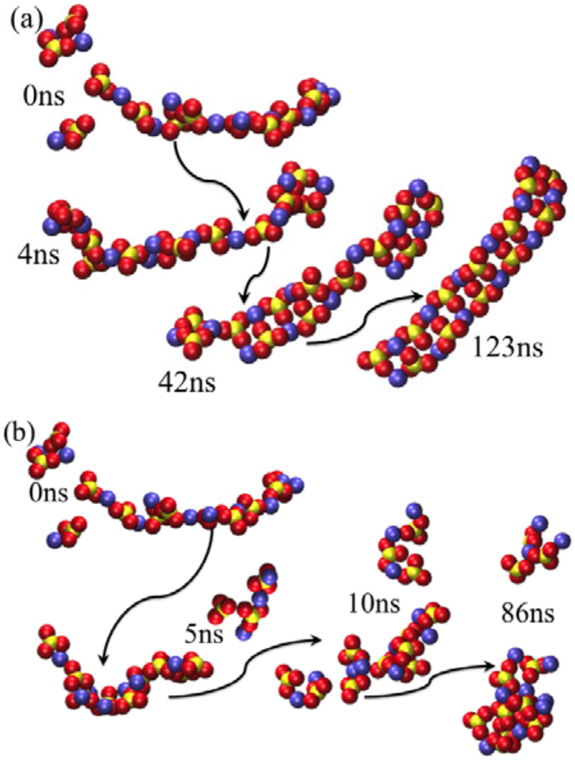


FIG. 3 (Color Online) (a) Clusters depicted in a melt of sulfonated polystyrene, $N = 40$ with 10% sulfonation at 700K. (b) Mean square displacement for same system (dashed lines). Solid lines are for zero sulfonation.



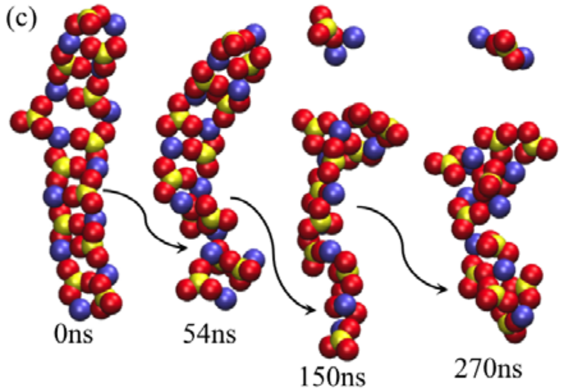


FIG. 4 (Color online) Time evolution of association and rearrangement of multiplets for a) $\varepsilon = 1$, b) $\varepsilon = 2$ and c) ε decreased from to 2 from 1 after 230 ns of simulation in a).

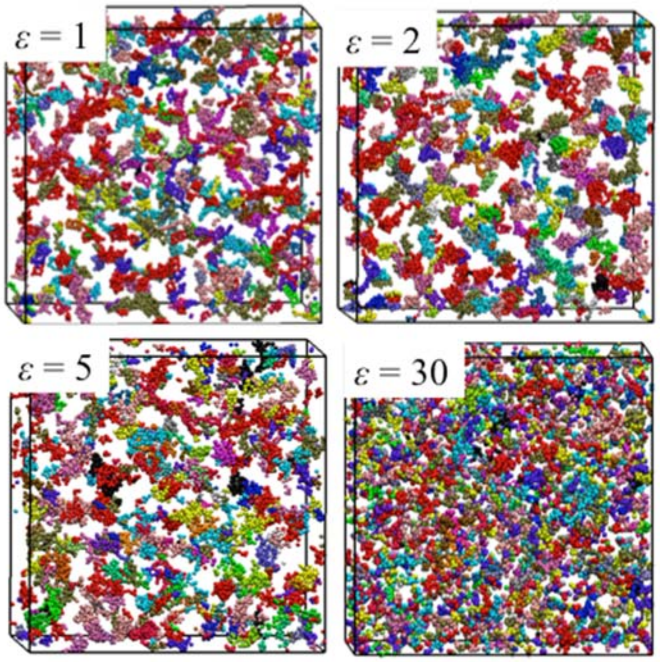


FIG. 5 (Color online) Ionic clusters for 10% sulfonated polystyrene ($N = 80$) for different values of ε at $T = 600$K.

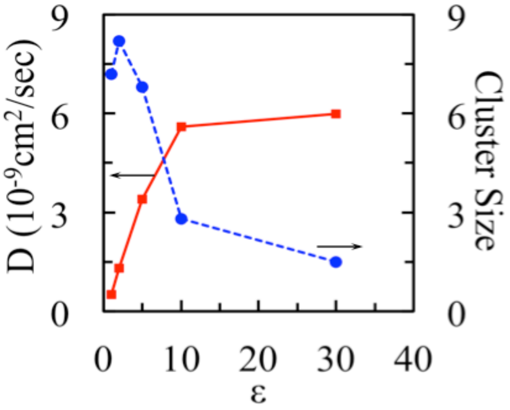


FIG. 6 (Color Online) Diffusion constant D (red squares) and average cluster size (blue circles) for the same sample for N = 80 polystyrene at T = 600K for 10% as a function of ionic strength.

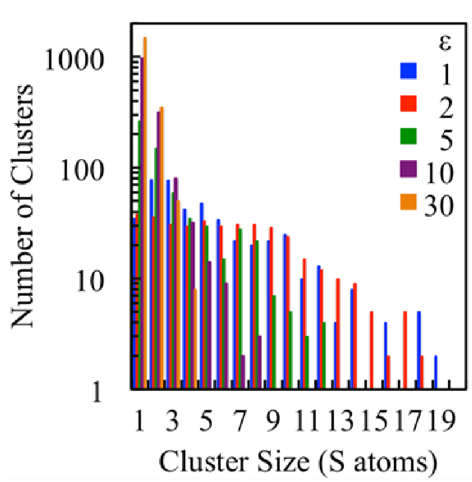


FIG. 7 (Color online) Cluster distribution for N = 80 polystyrene at T = 600K for 10% sulfonation with varying ionic strength.

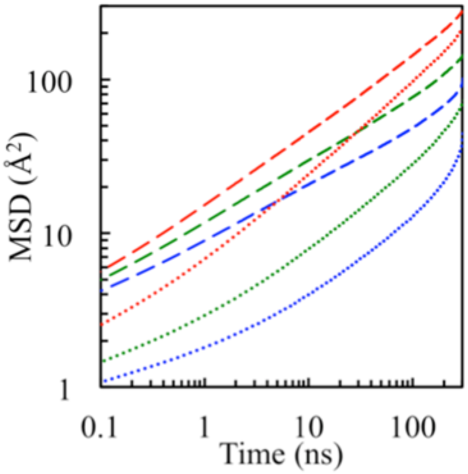


FIG. 8 (Color online) Mean square displacement of sulfonated (dotted) and non-sulfonated (dashed) benzene rings for chain length $N = 80$ with 10% sulfonation at 600K for $\varepsilon = 1$ (blue), $\varepsilon = 2$ (green) and $\varepsilon = 5$ (red).