# Supporting Information

## Soft Nanoparticles: Nano Ionic Networks of Associated Ionic Polymers

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Thirty randomly sulfonated chains of the pentablock were placed in a large simulation cell and aggregated in an implicit poor solvent. This aggregate of 30 chains, where all blocks are collapsed and randomly distributed, is the starting point of the simulation. A spherical void was formed in the center of the simulation box for both solvents using the indenter command in LAMMPS. The pentablock assembly was introduced into the void. Any overlapping atoms that resulted from the extended pentablock molecules were removed by running for a few thousand steps with the *fix NVE/limit* routine in LAMMPS. The temperature of the system was increased to 500 K, above the glass transition of polystyrene, to allow for the molecules to rearrange. An example of the time evolution of the aggregate in cyclohexane/heptane is shown in Figure S1 for $f = 0.30$. As time progresses, the center blocks segregate and are surrounded by the swollen flexible blocks and end blocks. To quantify the dimension of the micelle and center blocks, we calculated the radius of gyration $R_g$ as a function of time. As seen in Figure S2, $R_g$ initially increased in size for first 25 ns and then leveled off, while $R_g$ of the center blocks decreased for first 40 ns and the remained constant. The time evolution of the radial density for micelle, center blocks, and cyclohexane/heptane molecules from the center of mass of the micelle are shown in Figure S3. Initially, the polymers are tightly packed resulting in a homogenous density, however

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as time processes, the density decrease as solvent penetrates into the micelle. The center blocks migrate towards the center of micelle as the density of the core increases with time. After ~50 ns, the radial density profiles for the micelle, center blocks, and solvent are time independent. These results are further supported by tracking the number of solvent molecules inside the micelle as a function of time where solvent uptake leveled off after ~50 ns as seen an insert in Figure S3b.

The LAMMPS classical MD code[1] was used to perform all the simulations. The Newton equations of motions were integrated using the velocity-Verlet algorithm. The reference system propagator algorithm (REPSA)[2] with multi-time scale 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 for micelle in mixture of cyclohexane/heptane and 2.0 fs for micelle in water was used to accelerate the simulation. Temperature of the system was maintained by using a Langevin thermostat with a 100 fs damping constant. The Nose-Hoover thermostat was used with the same damping constant to equilibrate the system at constant pressure and temperature after merging the polymer chain with the solvent.

The mixed solvent system was run for 100 ns and the water system for 105 ns at 500 K and then cooled to 300 K at constant pressure P = 1 atm. Each system was then run at constant volume for an additional 40 ns. The dimensions of the simulation cell at T = 300 K was L= ~40 nm for both solvents, sufficient to prevent interaction of the micelle with itself through the periodic boundaries.

The dynamic structure factor S(q,t) is given by

$$S(q,t) = \sum_{i,j=1}^{N} b_i b_j < \exp\left[iq.(r_i(t) - r_j(0))\right] >$$

Where q is the momentum transfer vector, t is time, b is the scattering length of atom $i,j$ where

the sum is over all atoms. The position of the atoms at time t is given by $r_i(t)$. $S(q,t)$ results are

fitted with double exponential $S(q,t) = A_1 e^{-\Gamma_1 t} + A_2 e^{-\Gamma_2 t}$, where $A_1$ and $A_2$ are constants, and

$\Gamma_1$ and $\Gamma_2$ are effective diffusion coefficients. $A_1$ and $A_2$ are treated as independent parameters.
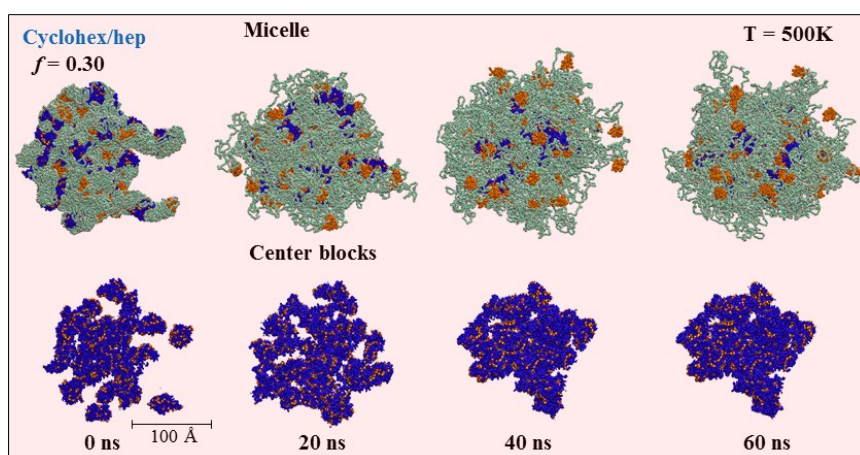


**Figure S1** Time evolution of micelle (upper panel) and center blocks of pentablock (lower panel) for $f = 0.30$ in cyclohexane/heptane at 500 K.
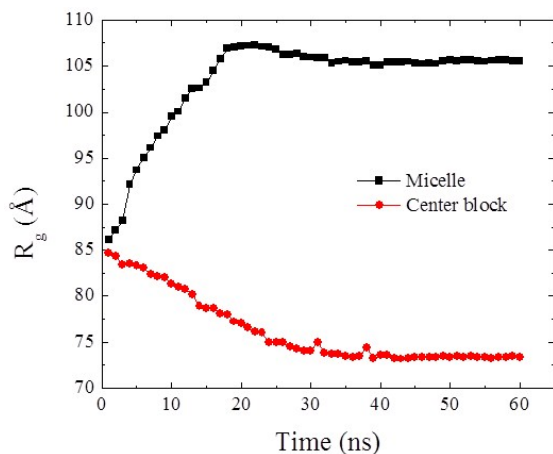


**Figure S2** Radius of gyration ($R_g$) as the function of time for micelle [■], and center blocks of pentablock_[●] for $f = 0.30$ in cyclohexane/heptane at 500 K.
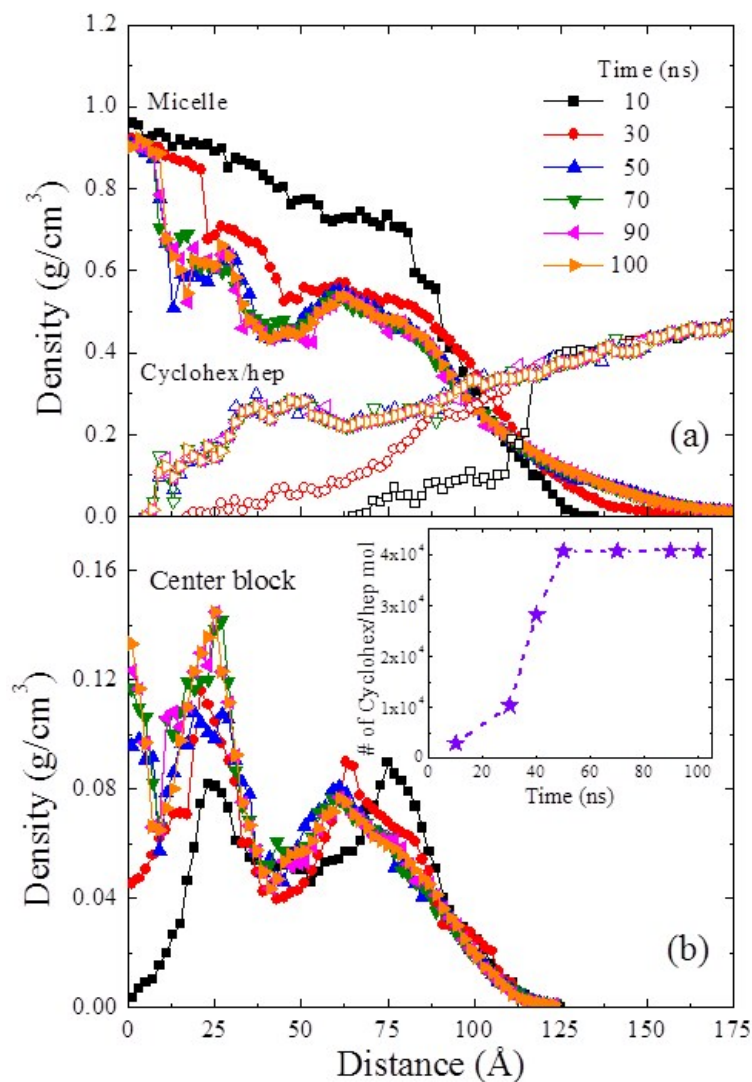
**Figure S3** Radial mass density for (a) both micelle and cyclohexane/heptane molecule and (b) center block for $f$ = 0.30 in cyclohexane/heptane at 500 K at 10 ns [■], 30 ns [●], 50 ns [▲], 70 ns [▼], 90 ns [◄], and 100 ns [►]. Solid symbol are for micelle and open for cyclohexane/heptane molecules. Insert shows number of cyclohexane/heptane molecules inside the micelle as a function of time.
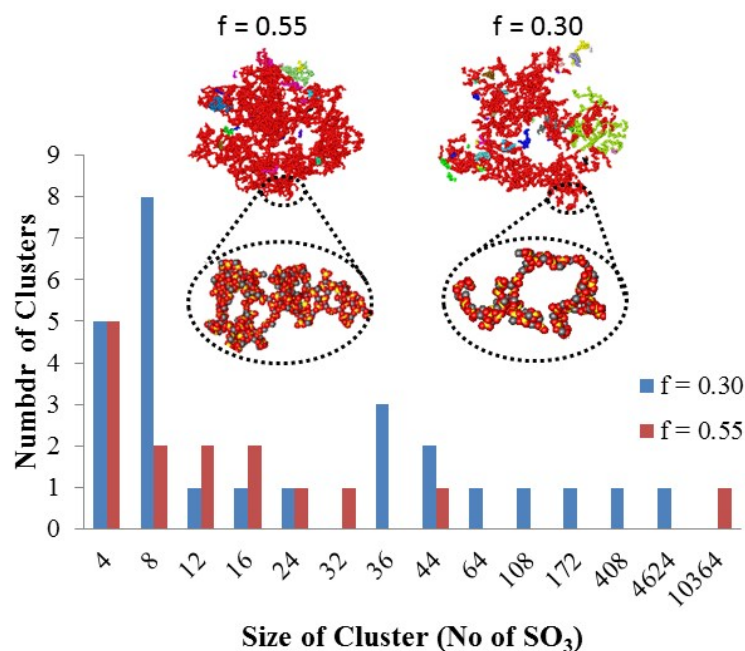
**Figure S4** Cluster distribution of $SO_3$ groups for f=0.30 (■) and f=0.55 (■) in mixture of cyclohexane/heptane at 300 K. Insert shows images only $SO_3^- Na^+$ clusters that are within 6 Å of each other from micelles for f=0.30 and 0.55. Different colors represent distinct clusters.
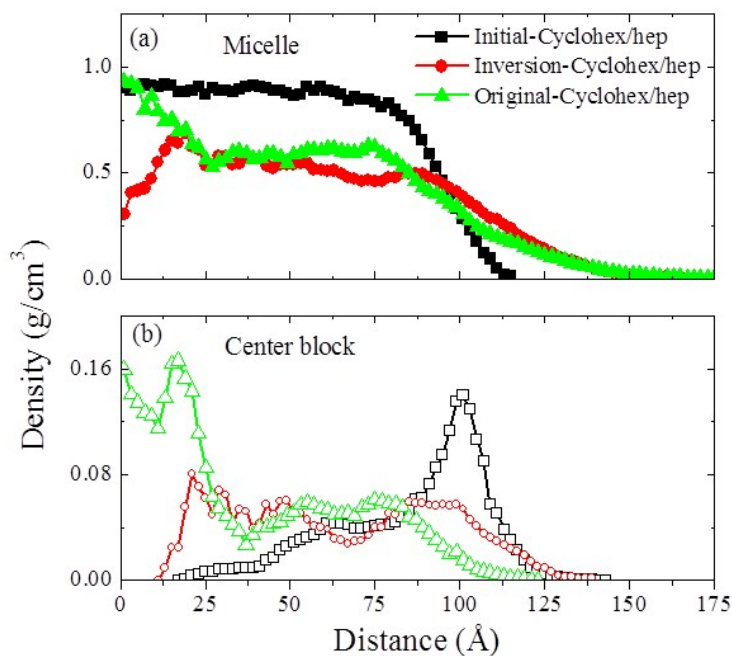


**Figure S5** Radial mass density for (a) micelle and (b) center blocks of pentablock in the mixture of cyclohexane/heptane (solvent inversion: water to cyclohex/hep) for $f = 0.55$ at 500K. Solid symbol for the micelle and open for center blocks. Original-Cyclohex/hep corresponds to the system shown in Figure 1b.

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TABLE 1: Root mean square of average radius of gyration $<Rg^2>^{1/2}$ and moments of inertia for micelle for both f in cyclohexane/ heptane and in water at 300 and 500 K.

| Solvents | T (K) | f | $<Rg^2>^{1/2}$ (Å) | $\lambda_2/\lambda_1$ | $\lambda_3/\lambda_1$ |
|---|---|---|---|---|---|
| Cyclohexane/ heptane | 300 | 0.30 | $101.2 \pm 0.5$ | 1.15 | 1.50 |
| | | 0.55 | $95.5 \pm 0.4$ | 1.10 | 1.40 |
| | 500 | 0.30 | $105.5 \pm 0.6$ | 1.20 | 1.55 |
| | | 0.55 | $98.4 \pm 0.5$ | 1.25 | 1.50 |
| Water | 300 | 0.30 | $74.5 \pm 0.2$ | 1.08 | 1.15 |
| | | 0.55 | $77.4 \pm 0.2$ | 1.10 | 1.20 |
| | 500 | 0.30 | $77.2 \pm 0.3$ | 1.10 | 1.20 |
| | | 0.55 | $79.9 \pm 0.3$ | 1.15 | 1.25 |

# References

[1] S. Plimpton, *Journal of Computational Physics.* 1995**, 117**, 1.

[2] M. Tuckerman, B. Berne, G. Martyna, *J.Chem.Phys.* 1992*, 97*, 1990.