SIMULATIONS OF THE CONFIGURATIONAL ARRANGEMENTS OF PANI/BETA-CYCLODEXTRIN INCLUSION COMPLEXES UNDER DIFFERENT DIELECTRIC CONDITIONS

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Abstract

Inclusion complexation is a route to improve several physical properties and the morphology of a polymer substance without chemical reactions. In the case of π-conjugated polymers, electrical conductivity and dielectric behavior can be effectively controlled through morphological control. Beta-cyclodextrins (beta-CDs) act as excellent host materials for polymeric guest molecules due to the annular cavity size of their tapered-cone structures. However, the molecular configurations and arrangement of polymer/ beta-CD inclusion complexes is not completely understood due to experimental constraints caused by their size scale. Molecular dynamics studies are well suited to simulate the molecular arrangement in such systems under different conditions. We present the results of a set of MD simulations on polyaniline/beta-CD systems under different dielectric conditions using an implicit solvent method. Head-to-head, head-to-tail and random configurations of beta-CDs complexed with polyaniline were studied in the two dielectric media representing the solvent conditions of water and n-methyl pyrrolidone (NMP). The interaction energies between neighboring beta-CDs and between the polymer and beta-CDs indicate a stable head-to-tail configuration under high dielectric conditions. Electronic structure calculations of these inclusion complexes quantify how the dielectric behavior of the polymer is impacted by applied voltages. Correlations between these simulations and experimental results will be discussed.

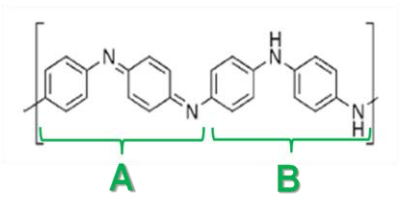


Figure 1: Schematic representation of the emeraldine structure of polyaniline (PANI) used in the simulations, which is 50% oxidized, as indicated by (A) above.

Computational Details

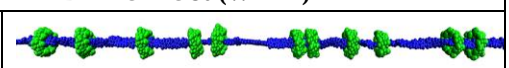
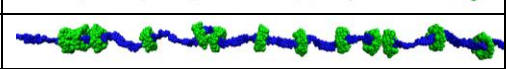
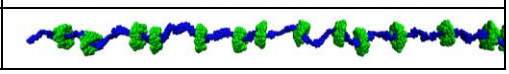
The polyaniline (PANI) polymer was built in the emeraldine form, which is an alternating block copolymer where one block is in its completely reduced form, and another block is completely oxidized, thereby making 50% of the chain in its oxidized state. (Emeraldine is considered to be the most useful form of PANI due to its electrical conductivity when doped and its stability at room temperature.) The polymer chain was built with 64 repeat units in total. The chemical structures for the polymer and the β-CD rings were generated using the Materials studio[1] package with the Discover module. The structure was minimized using the steepest decent algorithm employing energy tolerance cutoff of 10^{-5} kcal/mol.

MD simulations were performed with LAMMPS[2] software program. An NVT (constant number of molecules, temperature, and volume) ensemble at 300 K was done with no applied pressure, using the Nose-Hoover thermostat and the PCFF[3] force field. The simulations used a timestep of 1 fs, an equilibration time of 0.5 ns, and a simulation time of 3 ns for statistical analysis. Van der Waals and Coulombic cutoff radii were set to 8.5 Å and 10.0 Å respectively. The Debye screening effect of implicit solvent was implemented by using dielectric constants for water (80) and NMP (160). Initial configurations of the β-CDs and polymer chain were created by aligning the chain along the z-axis and then placing the rings as including hosts every roughly two repeats apart along the polymer chain. The simulations were performed by fixing the positions of the atoms of the polymer chain during the production run. There were three configurations explored of the β-CD rings: head-head, head-tail and random arrangements. Analysis was performed with VMD[4].

Results and Discussion

MD simulation trajectories. Error! Reference source not found.2 depicts the MD snapshots of various arrangements and configurations of the inclusion complex systems included in this study. In comparing the three different β-CD conformations, there is a significant difference in the interactions among neighboring β-CDs and the interactions with the PANI chain. The NMP allows the polymer to remain linear during the simulation. The β-CDs are able to thread onto the polymer chain more easily and move more readily. With water as the implicit solvent, the kinks in the polymer chain prohibit complete β-CD freedom to move along the chain. The β-CDs in the head-to-head orientation in both implicit solvents tend to clump together in somewhat pairwise interactions; in the head-to-tail orientations, pairwise interactions among β-CDs can be observed as well but to a much lesser extent. For the head-to-tail orientations, these pairs seemed to repel each other and spread across the length of the polymer. More bouncing as a function of time occurs with the β-CDs in the head-to-tail orientation, which could be due to the location of the β-CD on the alternating blocks of the PANI chain. Changing the structure of the polyaniline chain could possibly have an effect on this behavior. Both the water and the NMP solvent simulations have the same effects on the different conformations but the NMP results are generally more exaggerated.

Interaction energy calculations. *(Results not shown.)* The PANI/β-CDs interaction energies were found to have a maximum in the dielectric medium corresponding to NMP, although the PANI/β-CD interaction energies are indistinguishable among the three configurational arrangements of the rings. In most cases, the β-CDs have higher interaction energies among themselves in the NMP solvent simulations. It is evident that the β-CDs have higher interaction energy with the PANI chain (attractive force) in the head-to-tail orientation as compared to the head-to-head simulations. The β-CDs in the head-to-head orientation generally have continuous attractive forces throughout the entire simulation. The β-CDs undergo much more bouncing and spinning around the chain in the head-to-tail conformation. In addition, interaction energies among β-CDs suggest preferential arrangement being the head-head configuration among the three possible configurations.

DIELECTRIC 80 (WATER)	
Head-to-Tail	
Head-to-Head/ Tail-to-Tail	
Random	

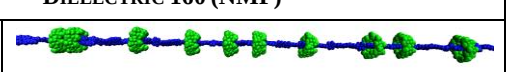
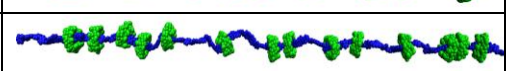
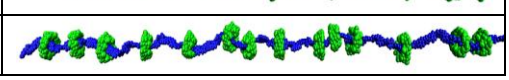
DIELECTRIC 160 (NMP)	
Head-to-Tail	
Head-to-Head/ Tail-to-Tail	
Random	

Figure 2: MD snapshots of the polyaniline/β-CD complexes in the different chosen dielectric conditions and configurations.

Conclusions

The dielectric medium applied during the simulations significantly affects the interaction energies and the trajectories of the inclusion complex simulations. The PANI/β-CD interactions are at a maximum under conditions of higher dielectric. The preferential arrangement of the β-CD rings is head-to-head under both the dielectric conditions. Electronic structure calculations from first principles are required to understand the dielectric behavior of the inclusion complexes.

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