Stimuli Response and Solute Partitioning in Highly Branched Copolymers from Density Functional Theory

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Stimuli responsive polymers, including gels, brushes, and self-assembled structures, can swell or change shape in response to changes in temperature, pressure, and solvent or solute concentration. Understanding such behavior has the potential to enable design and control of unique chemical processes involving lubricants, viscosity modifiers, and surface coatings. To predict polymer swelling, conformational changes of polymer brushes, swelling of gels, and partitioning of components, a model must incorporate molecular architecture and intermolecular interactions across a range of length scales from solvent to polymers while remaining computationally tractable. Molecular density functional theory has shown great promise in modeling response of micelles, grafted copolymers, dendrimers, and bottlebrush polymers to associating solvents and solutes.

In this work, we present the response of associating dendrimers in explicit solvents using classical density functional theory. The existence of association enables uptake of solvent inside the dendrimer even for unfavorable Lennard Jones interaction between solvent and dendrimer. Depending on the distributions of associating sites, the dendrimer conformation can be either dense-core or dense-shell. The conformation of the associating dendrimer is greatly affected by temperature. Due to the interplay between association interaction and Lennard Jones attractions, we find lower critical solution temperature (LCST) behavior of dendrimer conformation and study how it changes as the dendrimer size or solvent size changes. The dendrimer in our study displays no LCST behavior at low generations and it has a maximum LCST at G4. Moreover, increasing the solvent chain length decreases the LCST. For solvents with self-association, the competition between solvent-solvent association and solvent-dendrimer association also tends to reduce the LCST. Qualitatively consistent with experiments, our results provide insight into the molecular mechanism of LCST behavior of associating dendrimers.