

## Supramolecular Star Polymers: Programming Macromolecules to Self-Assemble into Complex Architectures using Hydrogen Bonding

Eric M. Todd and Steven C. Zimmerman

The increasing interest in polymer architectures with defined structures and narrow polydispersities arises from their wide ranging applications in drug delivery, catalysis, and advanced materials. In this regard, tremendous advances have been made in preparing conventional and novel polymers by living/controlled polymerization methods. The programmed self-assembly of hydrogen-bonding modules provides an alternative, bottom-up, approach to the creation of complex polymeric structures, but has received considerably less attention.

With the engineering of complex supramolecular structures in mind, hydroxyl functionalized Bis(ureidodeazapterin), **Bis-DeAP**, has been designed and prepared on the gram scale. The orientation of the heterocycles and the entropic preference for discreet structures enables **Bis-DeAP** to assemble into robust cycle structures in nonpolar organic solvents. The hydroxyl group provides a synthetic handle to modify **Bis-DeAP** for any desired application and has been used to initiate the polymerization of cyclic esters and further functionalized to initiate the polymerization of styrene and methylmethacrylate through atom transfer radical polymerization (ATRP). The resultant polymers self-assemble into higher molecular weight structures with a lower molecular weight distribution. The largest discrete nanoscale polymeric assembly is proposed to be a hexameric star, stabilized by 30 hydrogen bonds, with a molecular weight of ca. 92.7 kDa. All polymeric assemblies generally exhibit PDI values of 1.3 to 1.5, which are lower than the PDI value of the corresponding polymeric arms.

