Abstract Submitted
for the MAR16 Meeting of
The American Physical Society

Assembly, Conformation, and Thermodynamics of Star-Branched Poly(N-isopropylacrylamide) (PNIPAM) in Solution MICHAEL J. A. HORE, XIAOLONG LANG, WILLIAM R. LENART, Case Western Reserve University — The synthetic route and molecular architecture of poly(N-isopropylacrylamide) (PNIPAM) affects its assembly and thermoresponsive behavior. Here, the structure and assembly of star-branched PNIPAM is studied in water using a new model based on the random phase approximation (RPA), and small-angle neutron scattering (SANS) for $f = 3$, 4, and 6 arm star polymers, synthesized using either click chemistry, RAFT, or ATRP. Unlike linear PNIPAM, we find that for star-branched polymers, the radius of gyration scales with the degree of polymerization N as $R_g \sim N^{0.65}$ indicating physical excluded volume effects in the polymer chain conformation. R_g decreases monotonically as the system temperature approaches the lower critical solution temperature (LCST). Interesting, PNIPAM chains begin to associate well below the LCST, depending on whether the polymers were synthesized via ATRP or RAFT, and a strong structure factor peak can be observed as T increases. Finally, the Flory-Huggins interaction parameters between PNIPAM and water are extracted from the scattering data, and indicate that molecular architecture does not substantially influence the interaction between water and PNIPAM. These observations are compared to recent studies in the literature.

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Date submitted: 26 Oct 2015

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