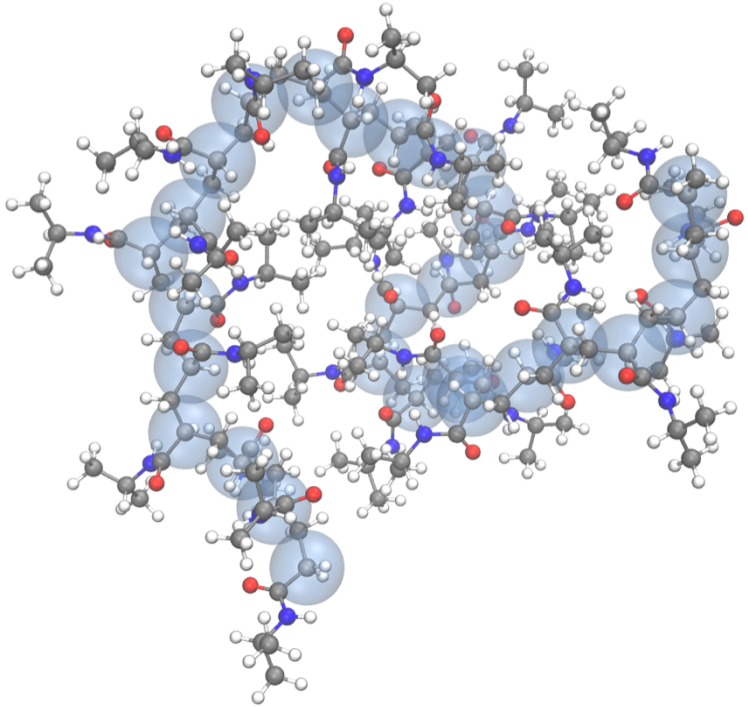
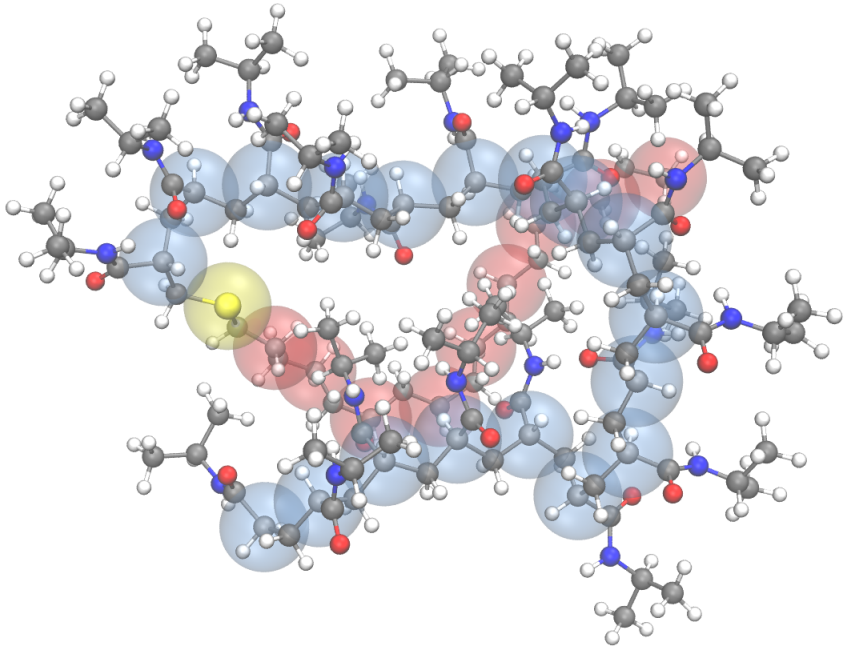
SAND2015-1244C

Atomistic Simulations of Poly(*N*-isopropylacrylamide) Surfactants in Water





Lauren J. Abbott and Mark J. Stevens

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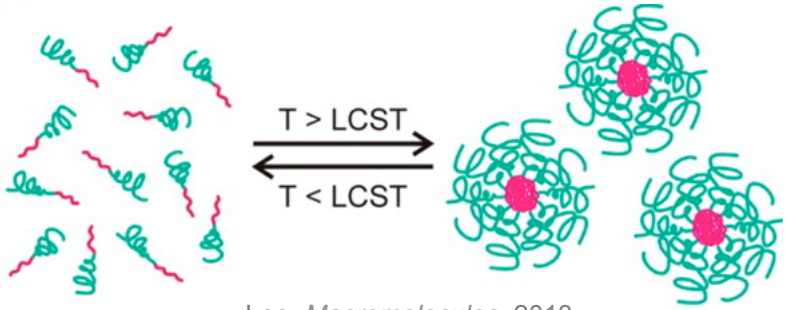
Temperature-responsive behavior useful for many applications

Responsive surface coatings
(e.g., sensors, catalysis)

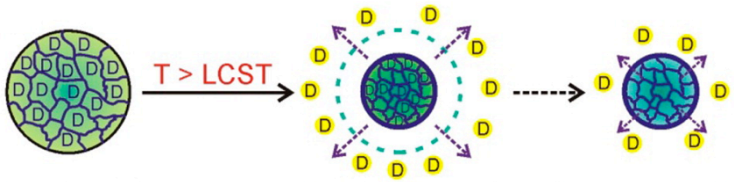
Gibson, *Chem. Soc. Rev.*, 2013

Responsive self-assemblies

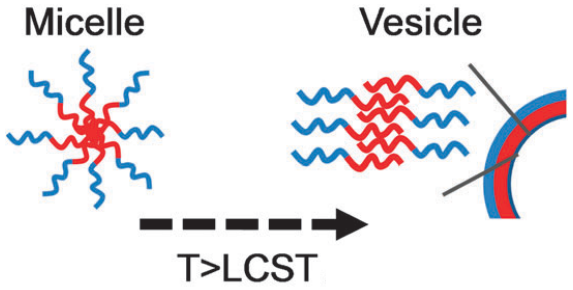


Lee, *Macromolecules*, 2013

Responsive hydrogels
(e.g., drug delivery, tissue engineering)

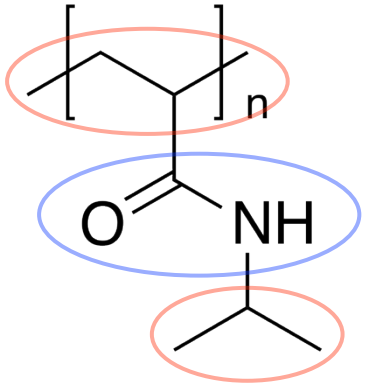


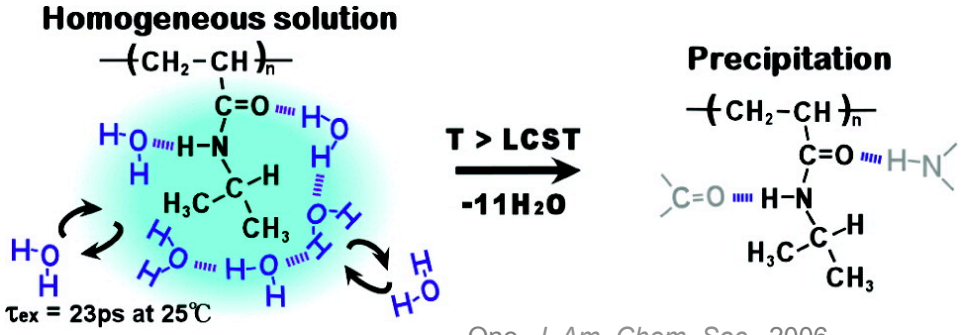
Lee, *Macromolecules*, 2013



Gibson, *Chem. Soc. Rev.*, 2013

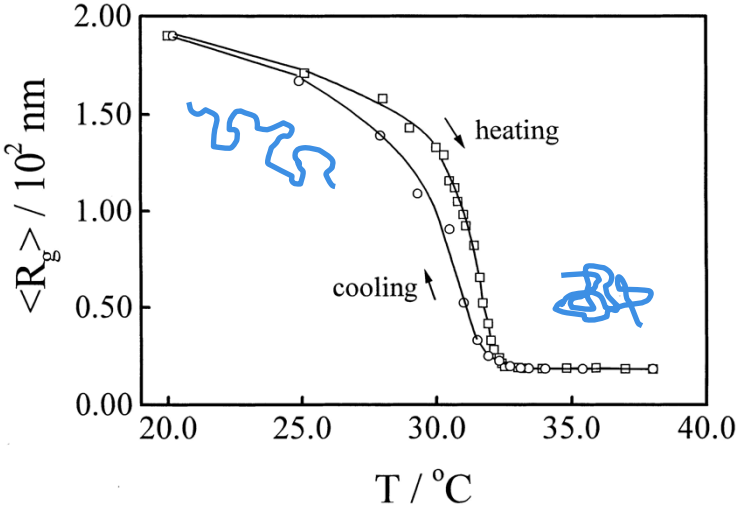
PNIPAM displays a sharp transition at its LCST ~32 °C



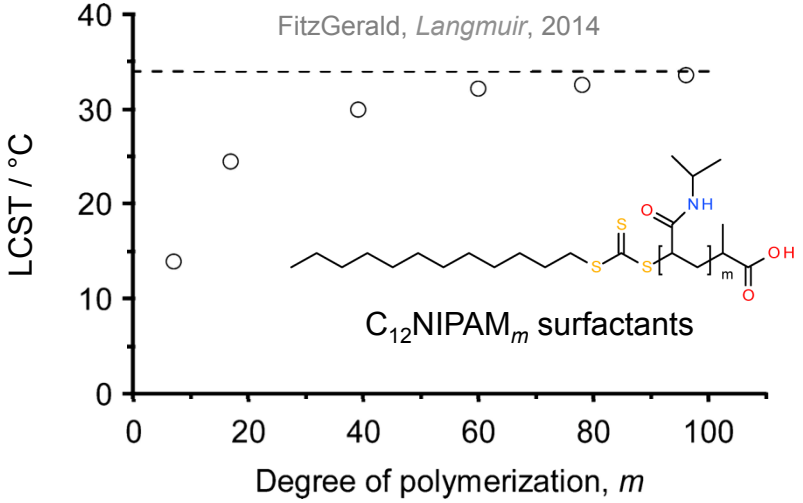


Ono, *J. Am. Chem. Soc.*, 2006

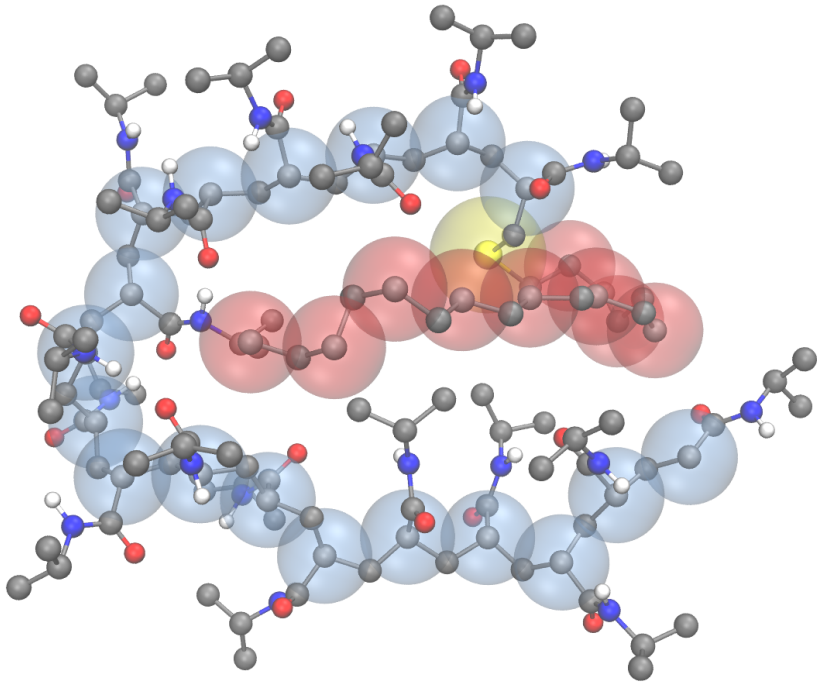
Wang, *Macromolecules*, 1998



FitzGerald, *Langmuir*, 2014



Details of the atomistic simulations

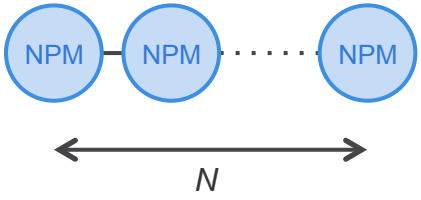


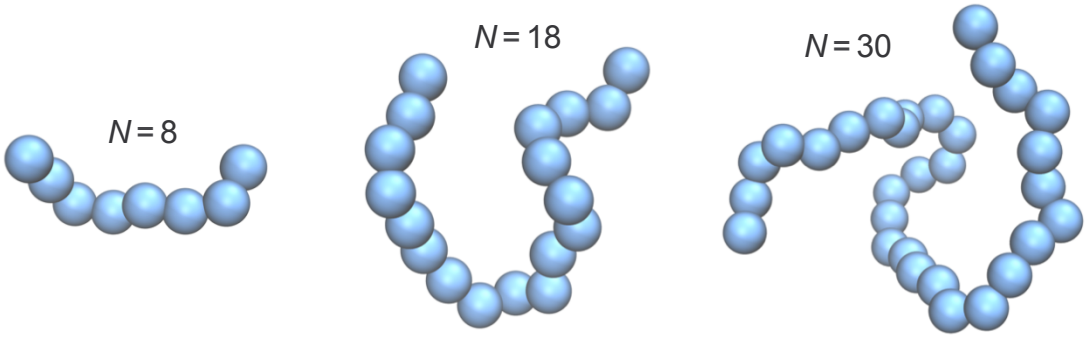
- OPLS with modified dihedrals (Siu, *JCTC*, 2012)
- TIP4P/2005 water model
- Gromacs 4.6.5
- 100-400 ns production in NPT ensemble
- 2 fs time step
- Canonical thermostat
- Parrinello-Rahman barostat
- Short-range nonbond with 1.0 nm cutoff
- Long-range electrostatics with PME
- Cubic box with PBC, 4.0-9.0 nm

PNIPAM oligomers and surfactant studied in this work

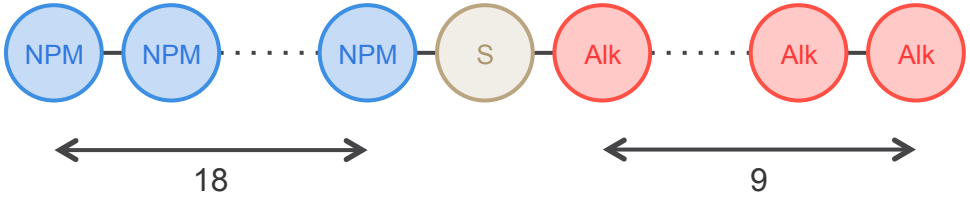
Sandia National Laboratories

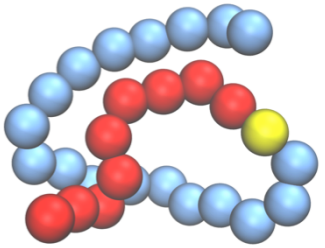
PNIPAM oligomers:



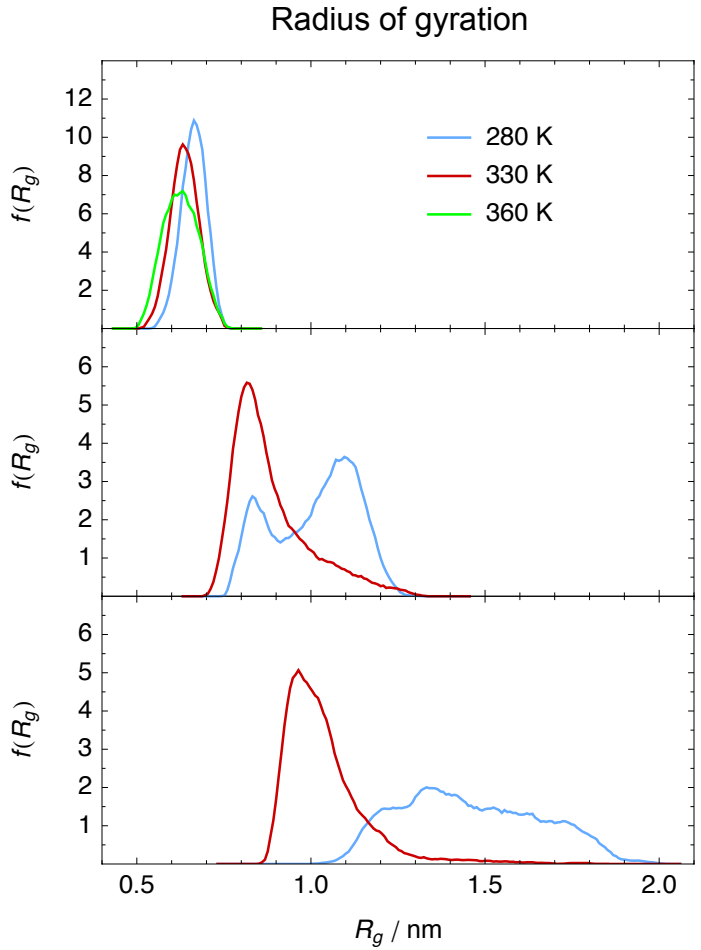


PNIPAM-C18 surfactant:





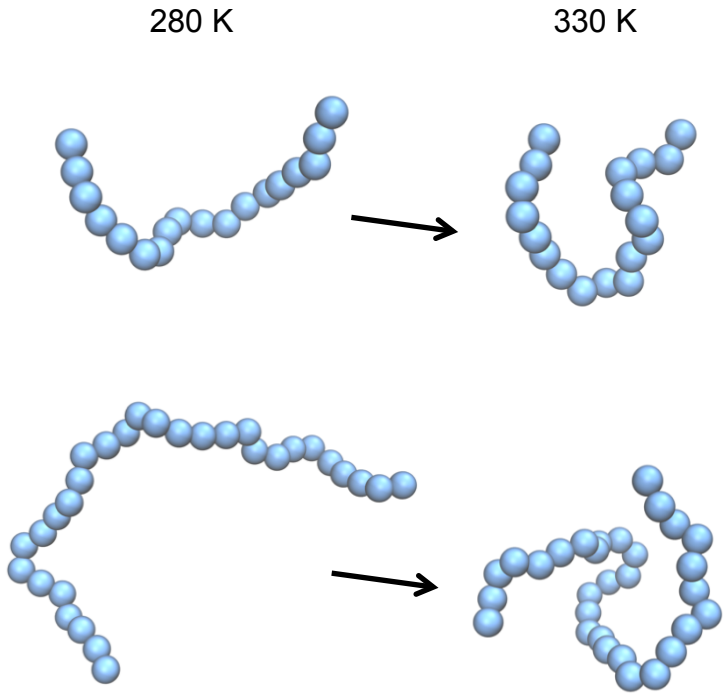
Collapse observed only in longer PNIPAM oligomers



$N = 8$

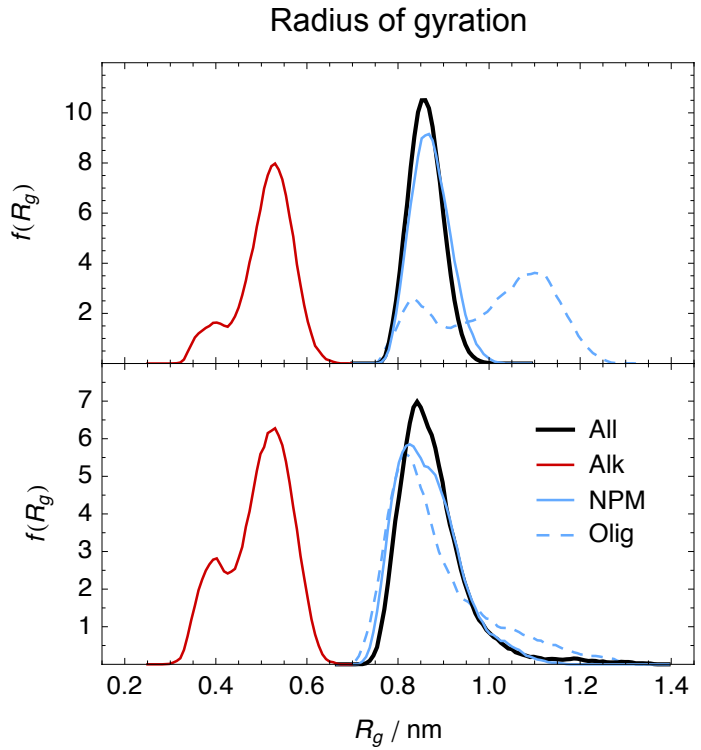
$N = 18$

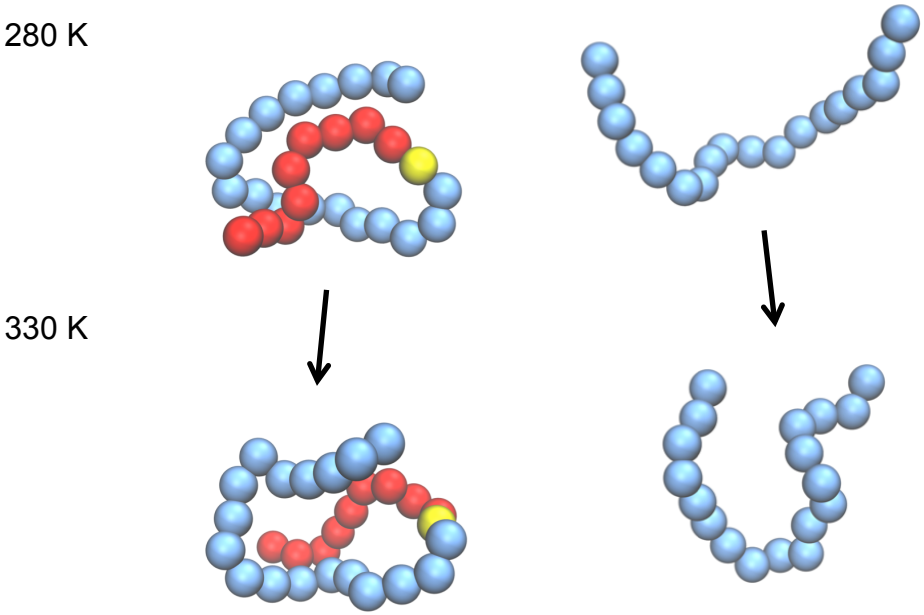
$N = 30$



Segments of 9-10 monomers corresponds with persistence length of PNIPAM

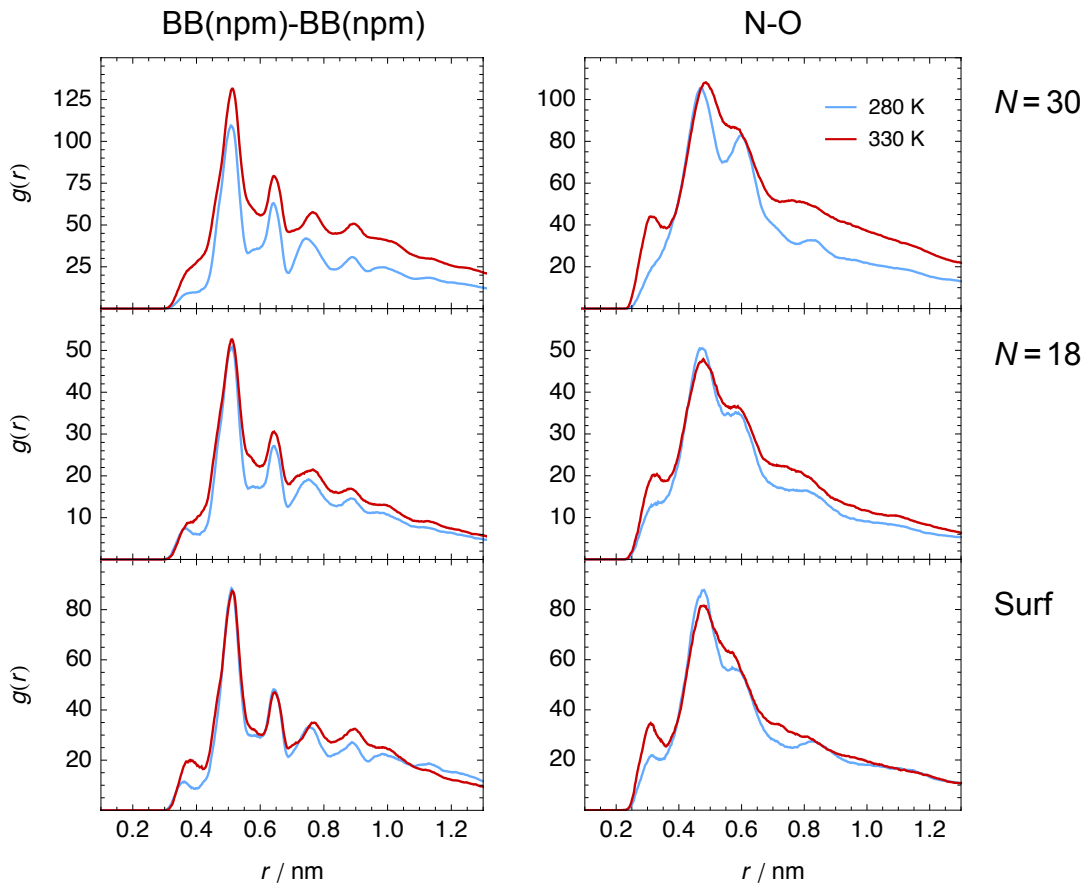
Surfactant single chain does not show responsive behavior

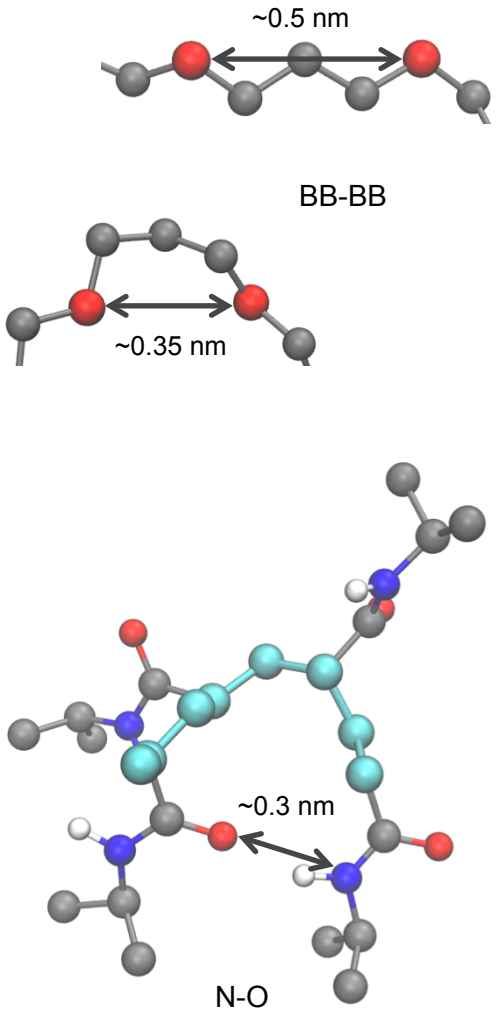




Transition temperature is effectively lowered by the addition of the hydrophobic alkyl tail

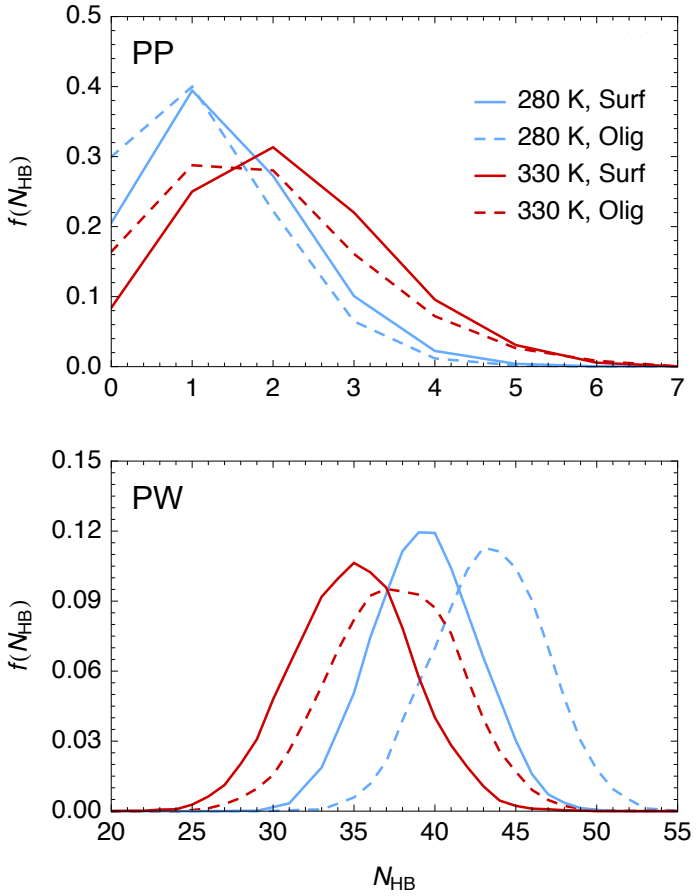
More polymer-polymer contacts above transition temperature

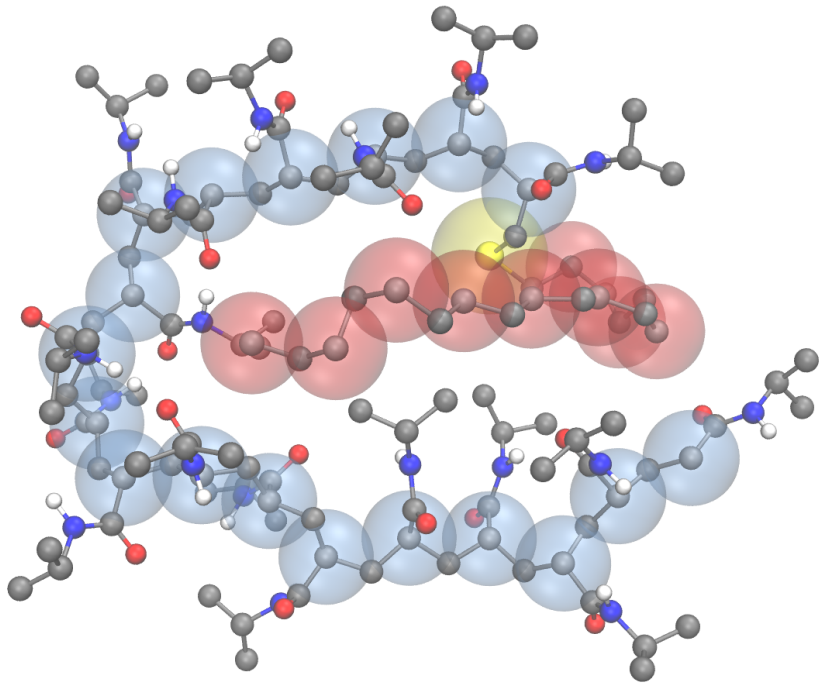




Change in RDF peaks corresponds to extent of structural change

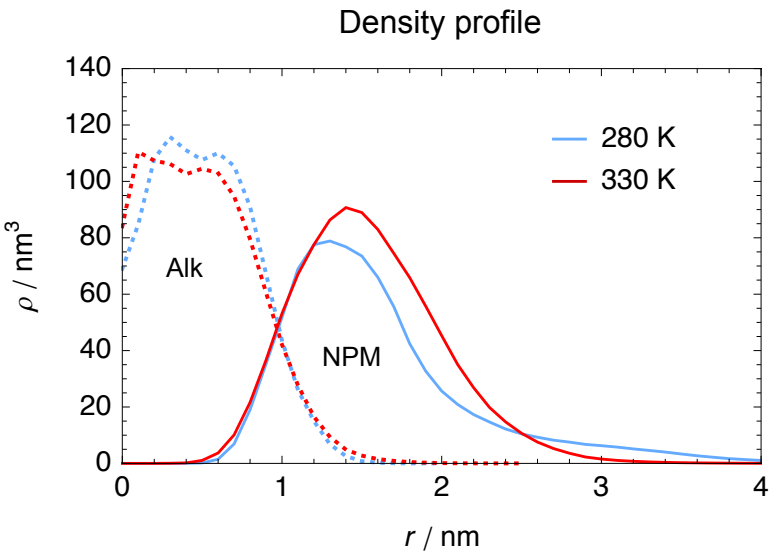
Alkyl tail interferes with hydrogen bond formation

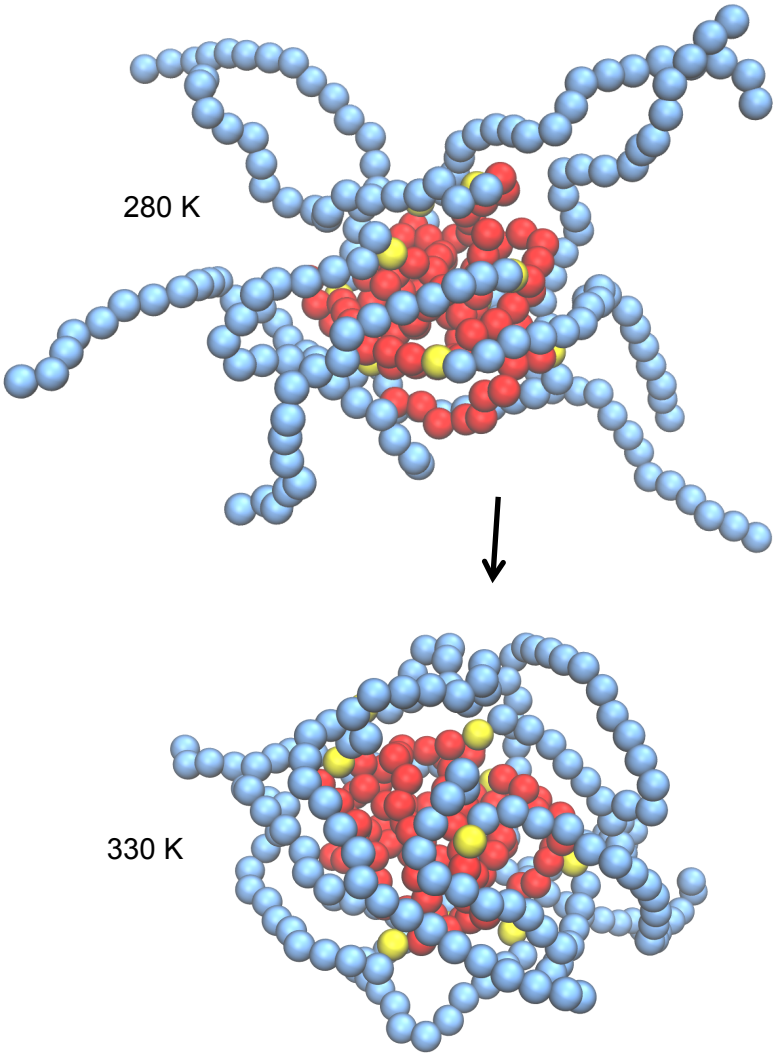




Chains remain partially hydrated even in collapsed state (~2 waters per NIPAM monomer)

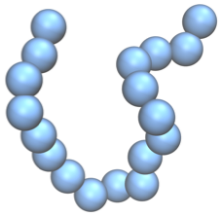
Micelles show some temperature-responsive behavior

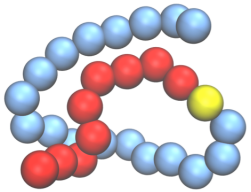


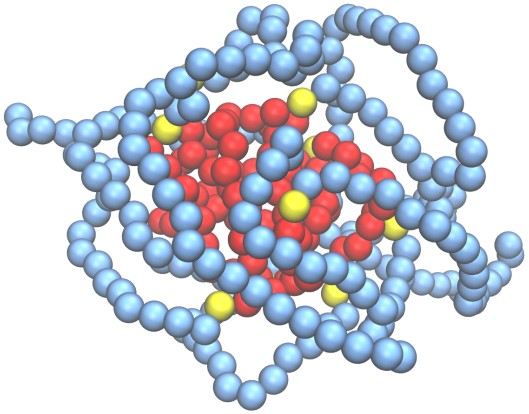


Conclusions

- Structural transition observed in longer PNIPAM oligomers to minimize hydrophobic surface in contact with water
- PNIPAM-C18 surfactant collapsed at both temperatures due to addition of hydrophobic alkyl tail
- Polymer-polymer contacts increase above transition temperature, polymer-water contacts decrease
- Temperature-responsive behavior observed for micelles







LJ Abbott, AK Tucker, MJ Stevens.
J Phys. Chem. B, DOI: 10.1021/jp511398q

Work was supported by the US Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division