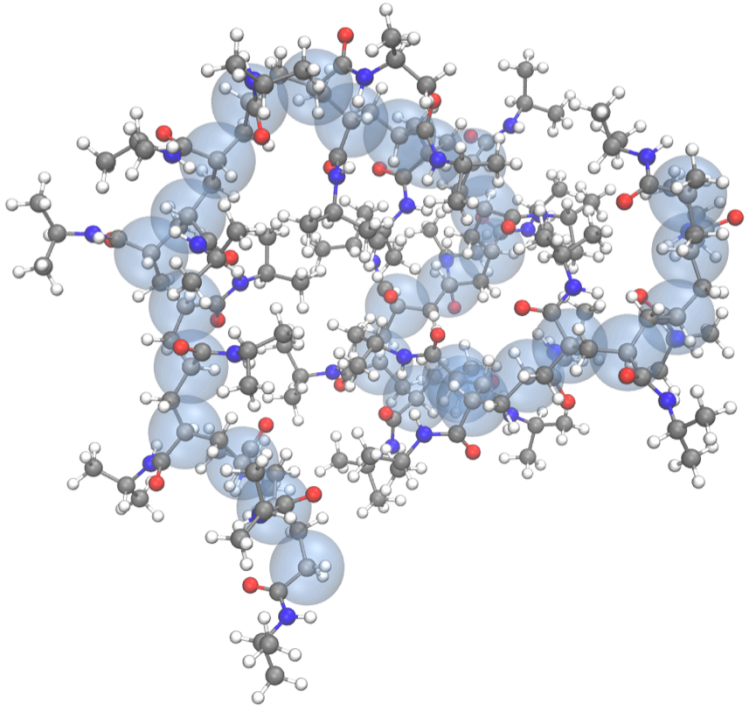
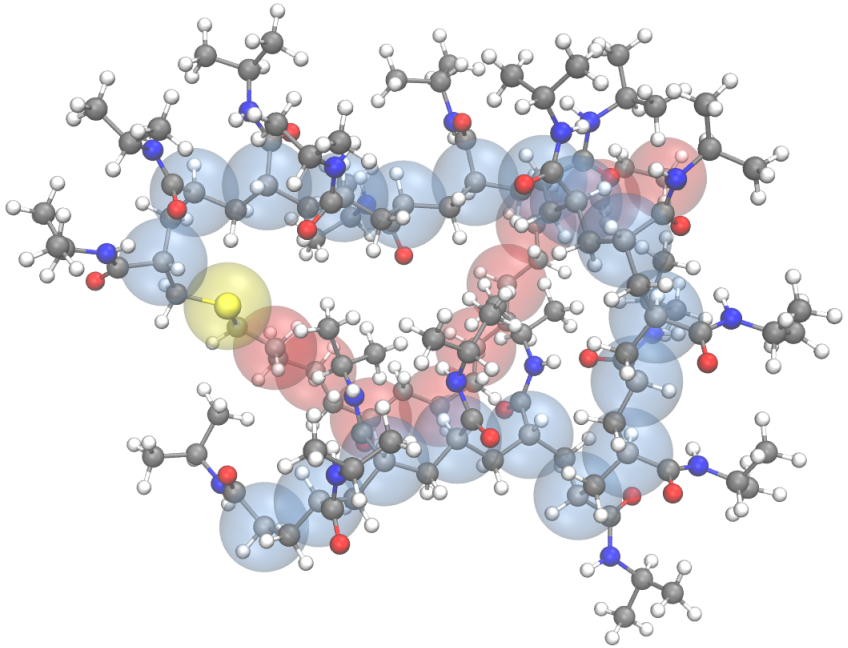
Atomistic Simulations of Thermoresponsive Poly(*N*-isopropylacrylamide) Polymers





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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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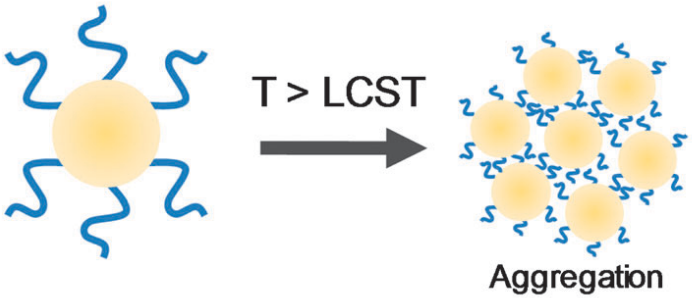
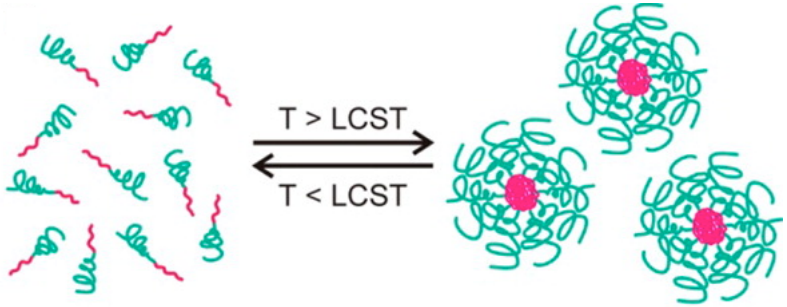
Temperature-responsive behavior useful for many applications

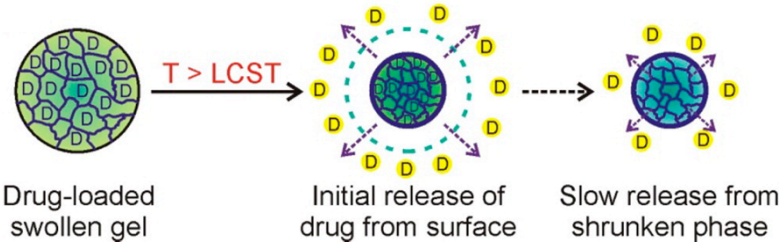
Responsive surface coatings
(e.g., sensors, catalysis)

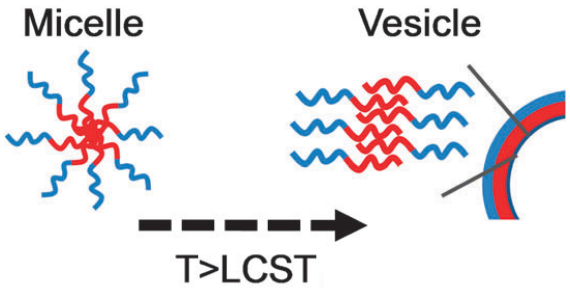


Responsive self-assemblies



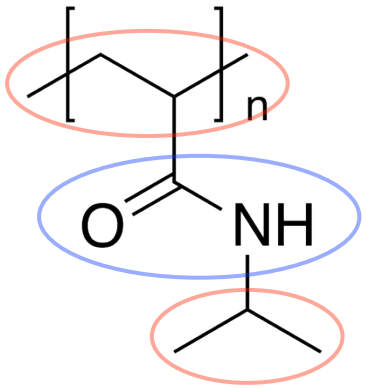
Responsive hydrogels
(e.g., drug delivery, tissue engineering)

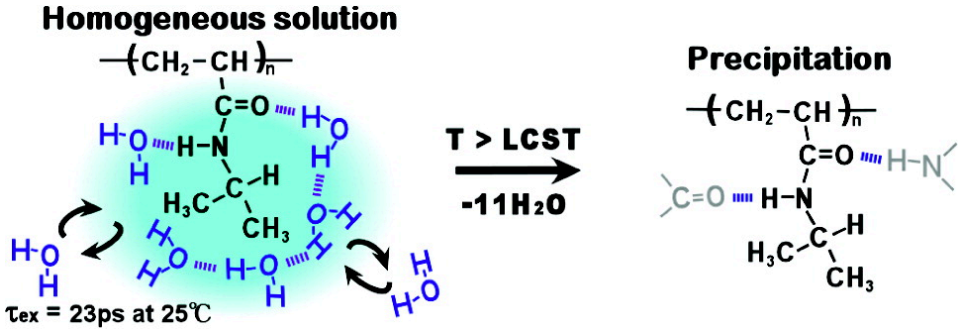


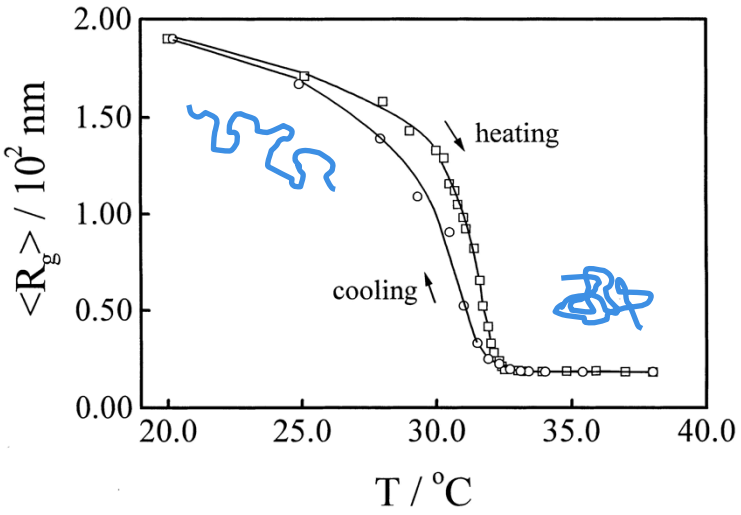


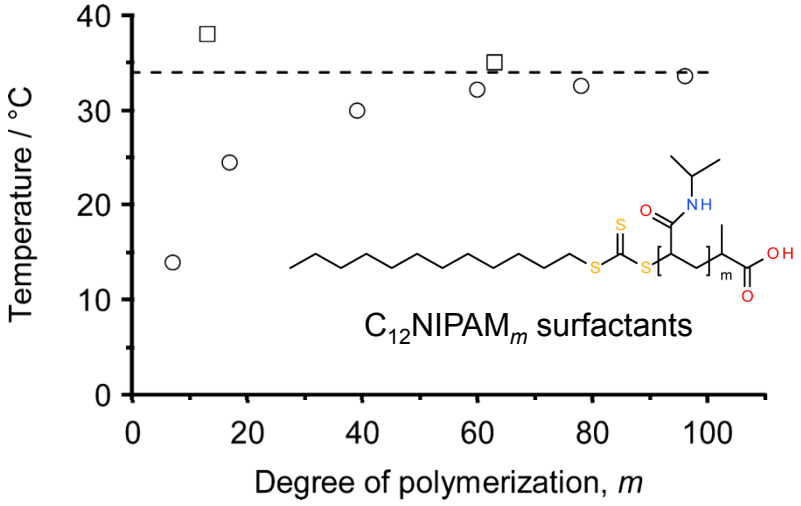
(1) Gibson, *Chem. Soc. Rev.*, 2013; (2) Lee, *Macromolecules*, 2013

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









(1) Wang, *Macromolecules*, 1998; (2) Ono, *JACS*, 2006; (3) FitzGerald, *Langmuir*, 2014

PNIPAM oligomers and surfactant studied in this work

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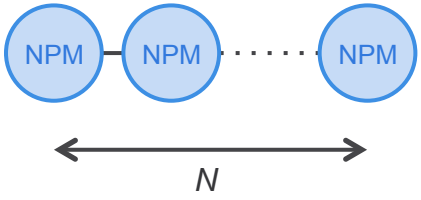
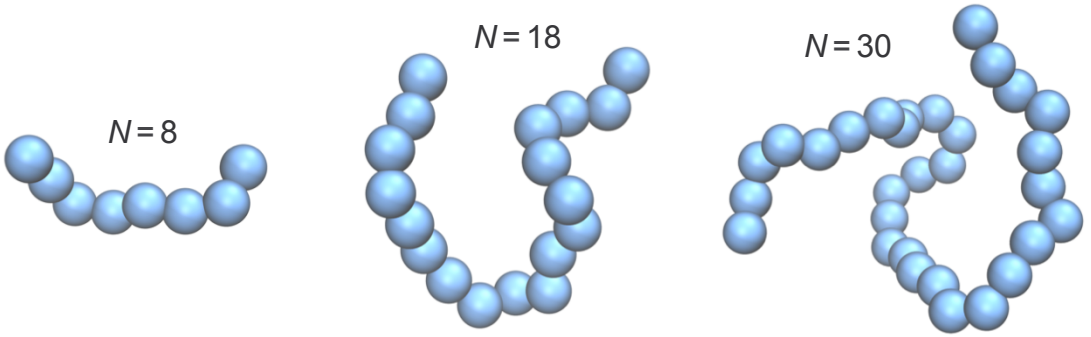
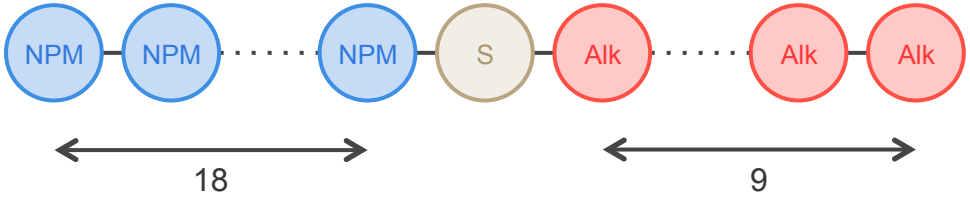
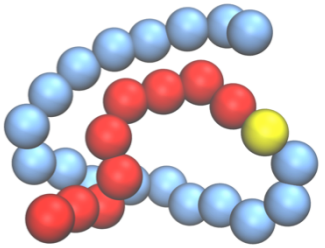
PNIPAM oligomers:



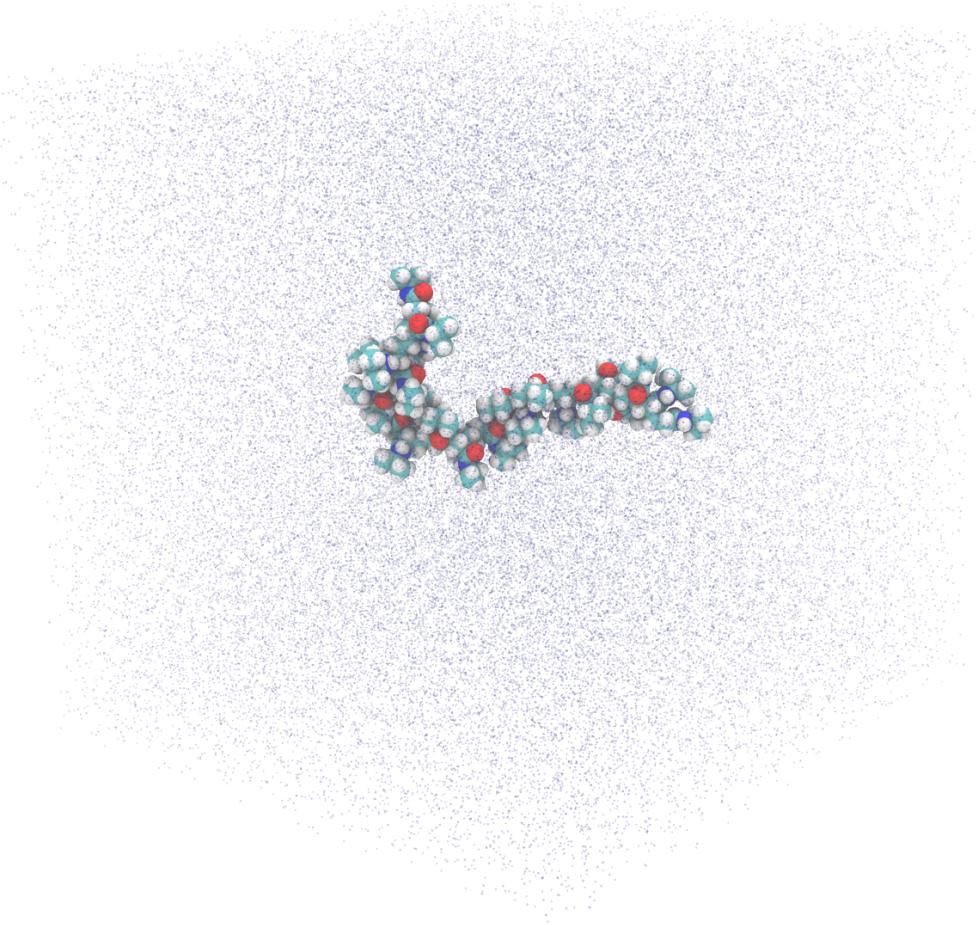


PNIPAM-C18 surfactant:





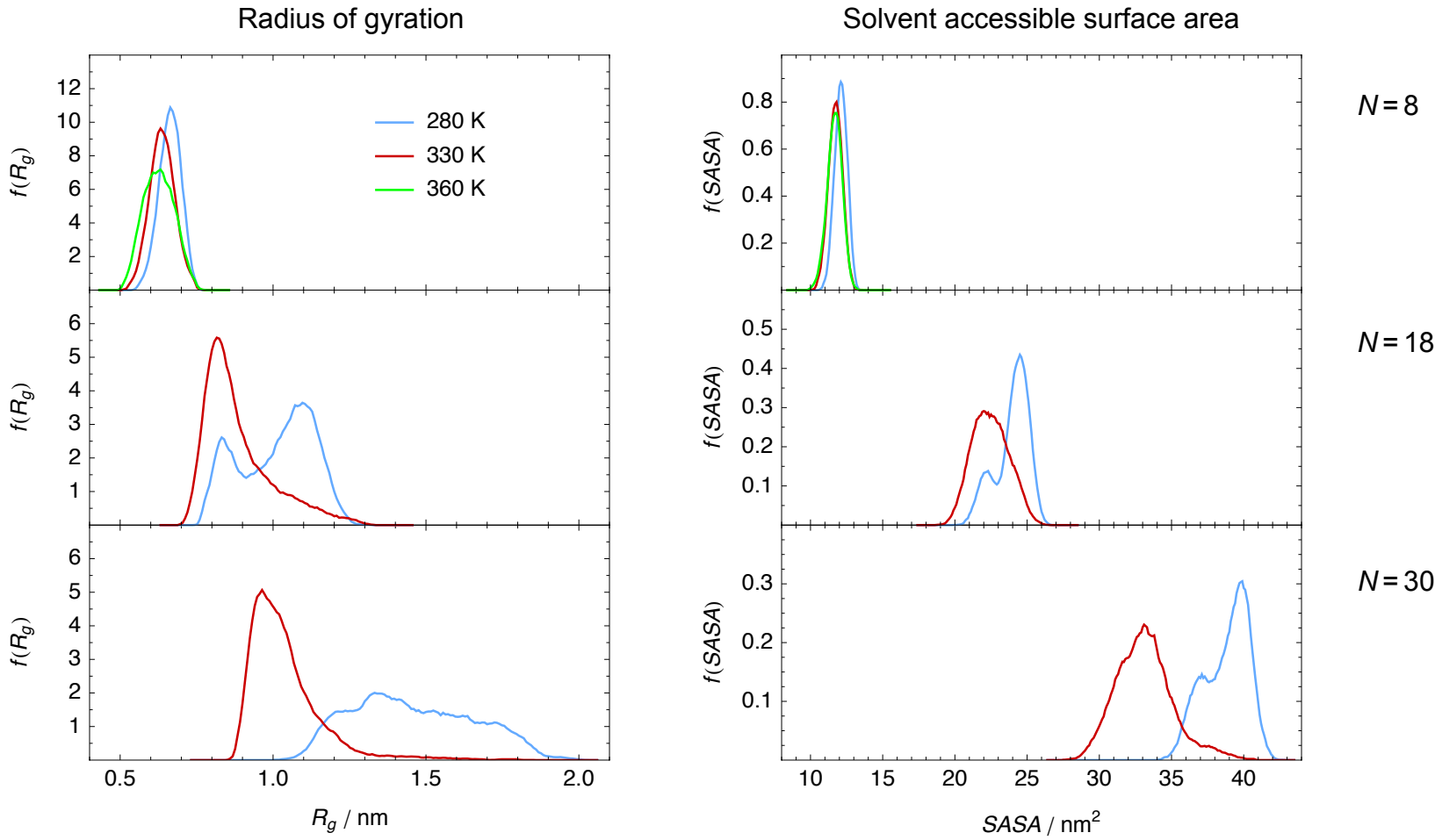
Details of the atomistic simulations



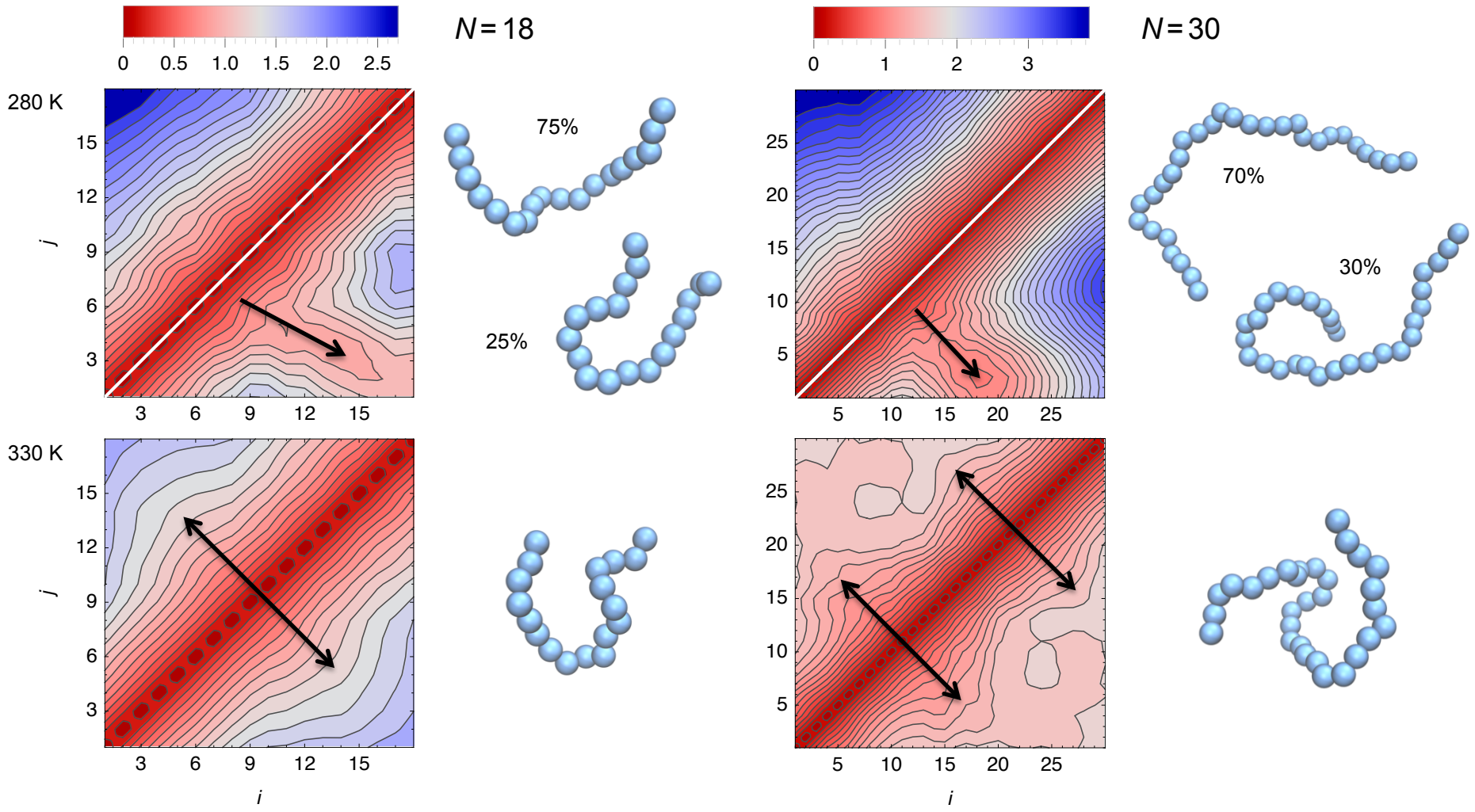
- OPLS with modified dihedrals[1]
- TIP4P/2005 water model
- Gromacs 4.6.5
- 100-400 ns production in NPT ensemble
- 2 fs time step
- Canonical thermostat
- Parrinello-Rahman barostat
- Short-range nonbond with 1.0 nm cutoff
- Long-range electrostatics with PME
- Cubic box, 4.0-9.0 nm

(1) Sui, *J. Chem. Theory Comput.*, 2012

Collapse observed only in longer PNIPAM oligomers

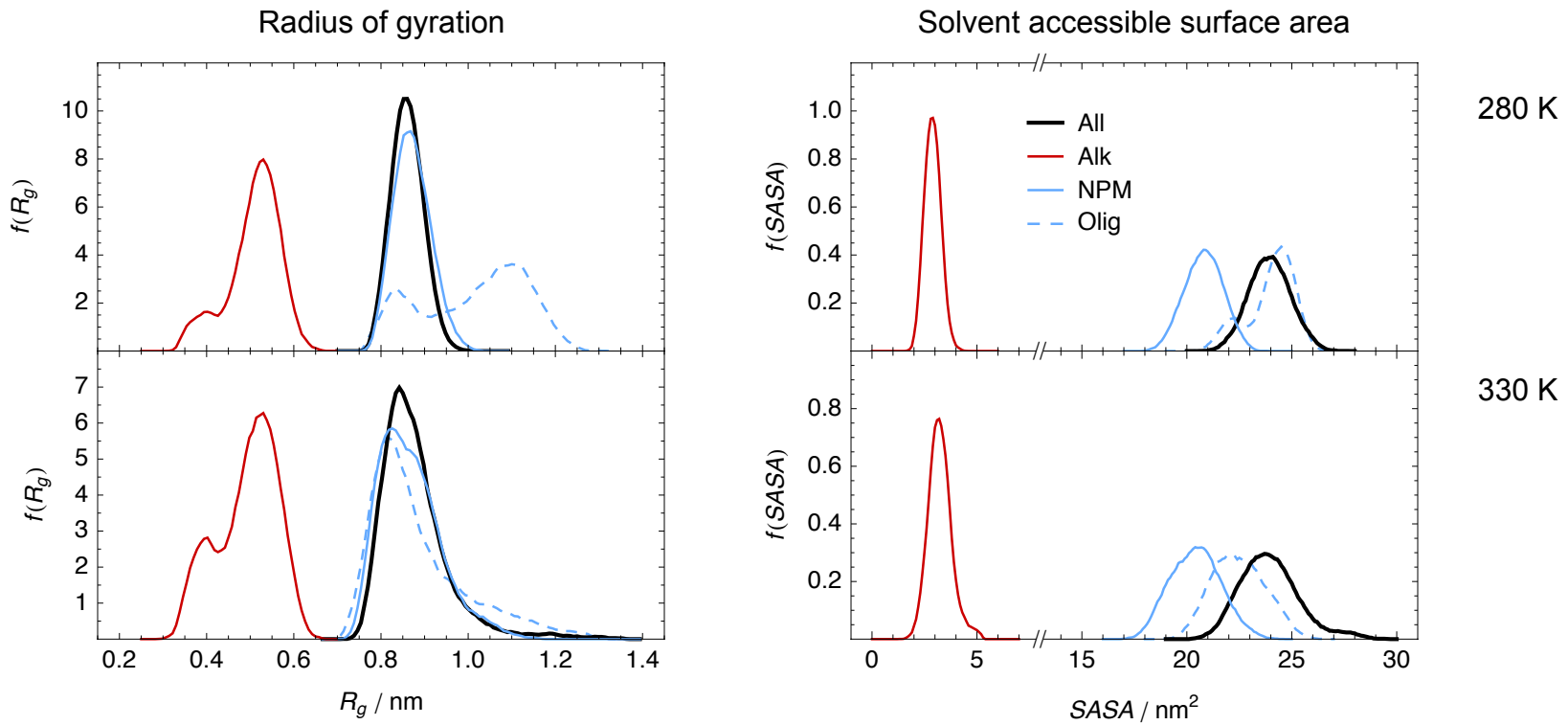


Distance maps identify average chain conformations



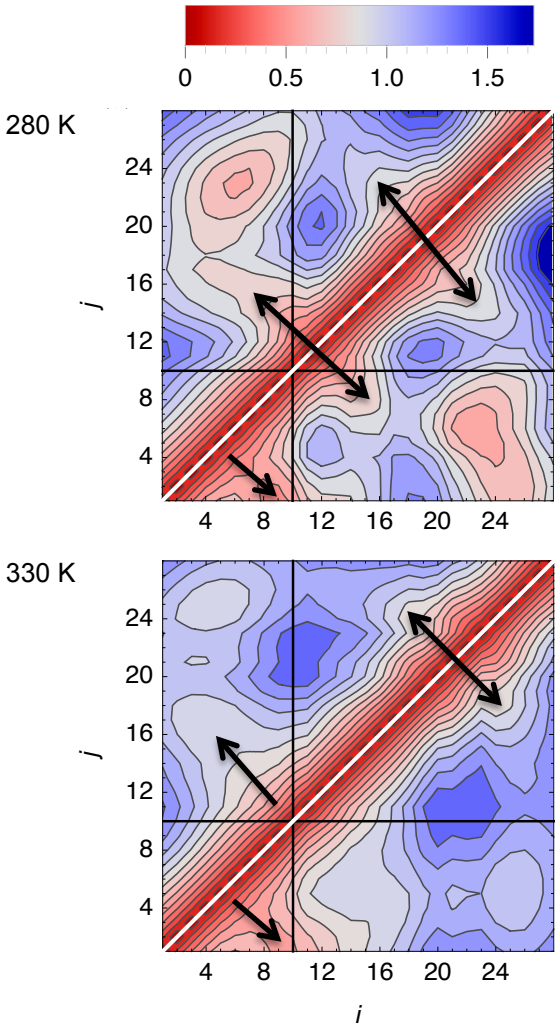
Segments of 9-10 monomers corresponds with persistence length of PNIPAM

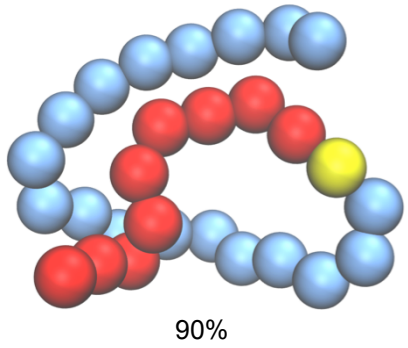
Surfactant single chain does not show responsive behavior

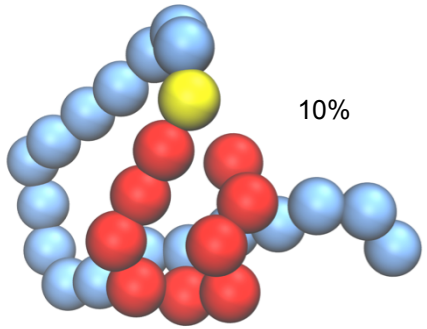


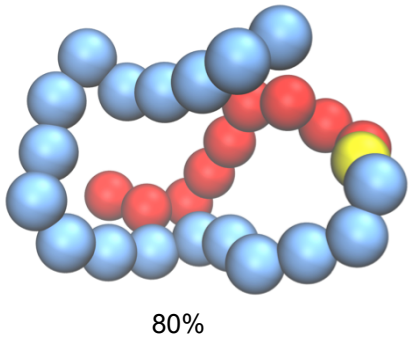
Transition temperature is effectively lowered by the addition of the hydrophobic alkyl tail

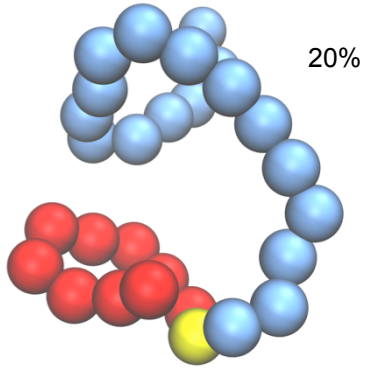
Surfactant structures are similar at both temperatures



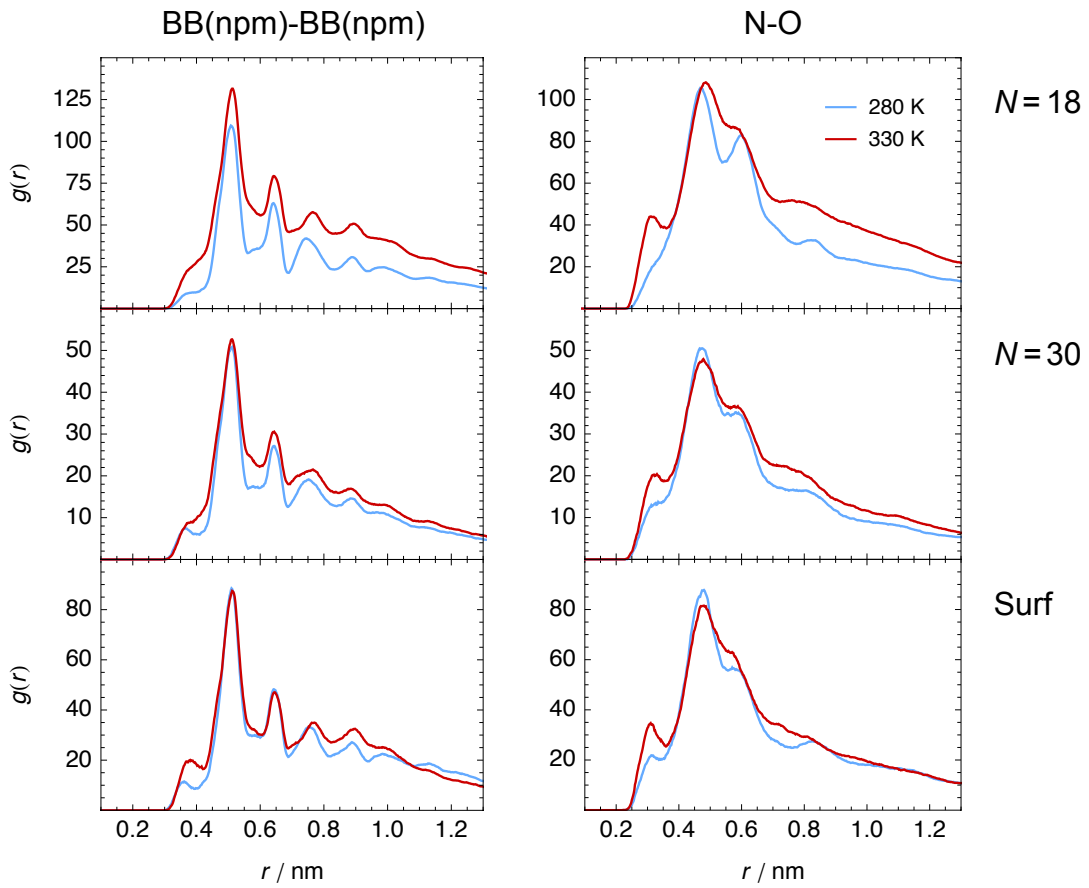


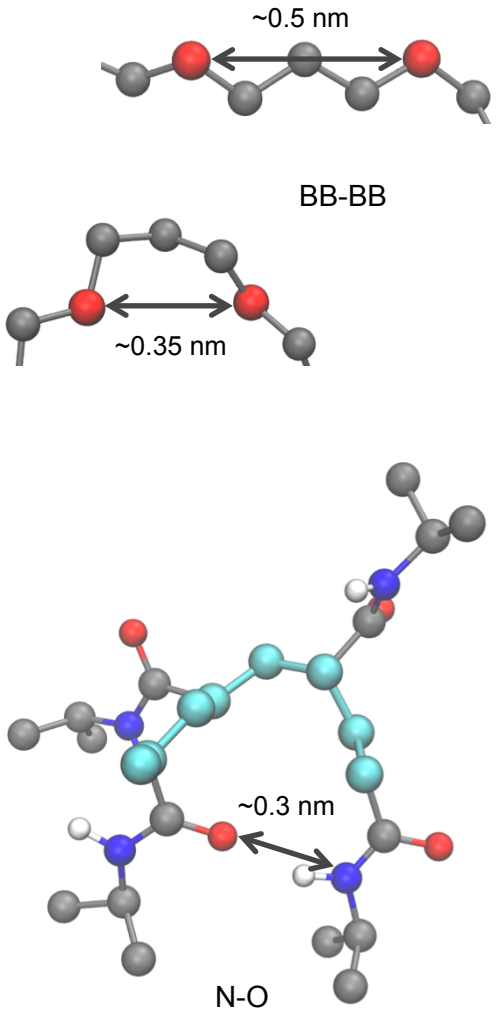






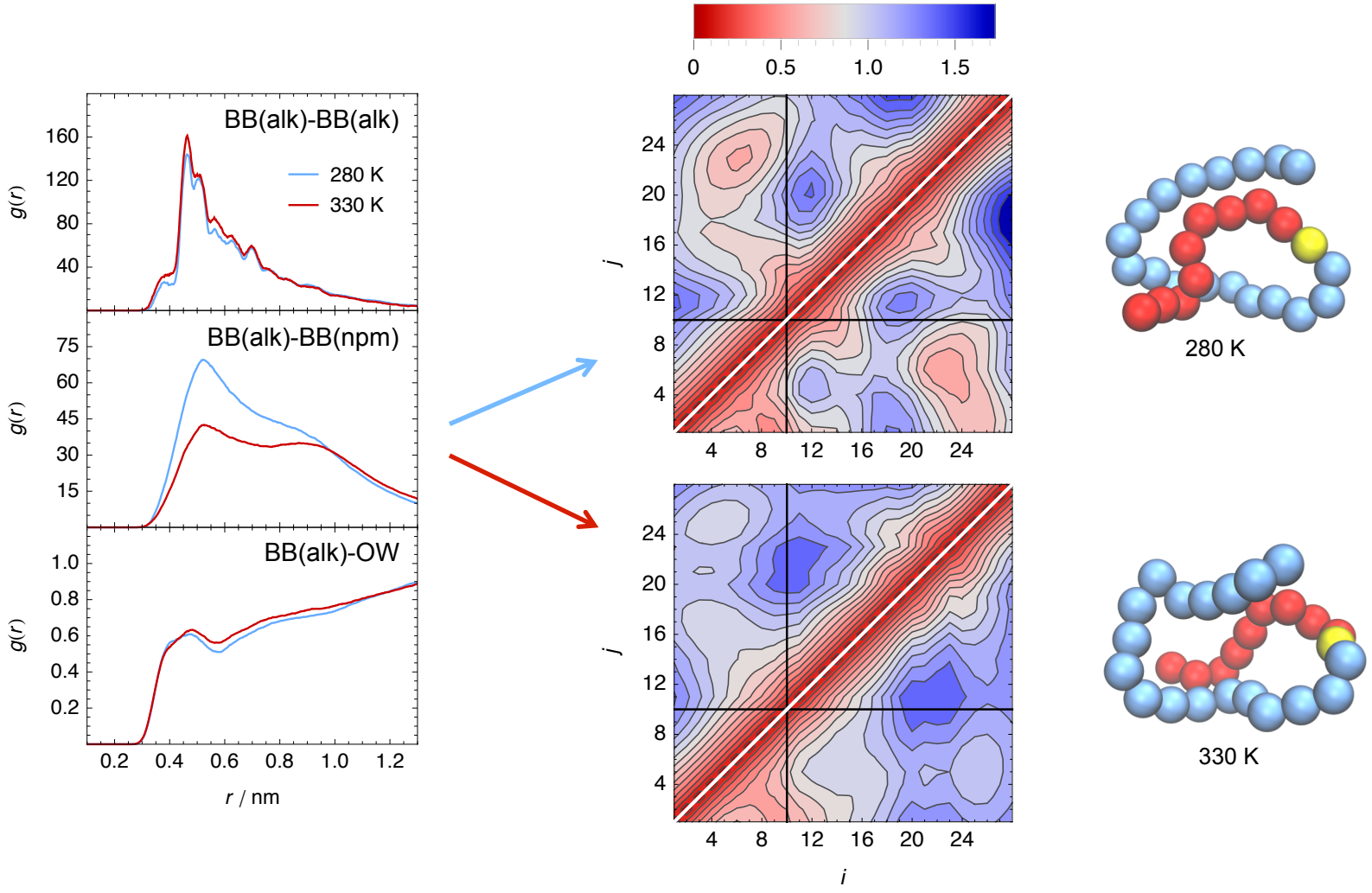
Polymer-polymer contacts increase above transition temperature



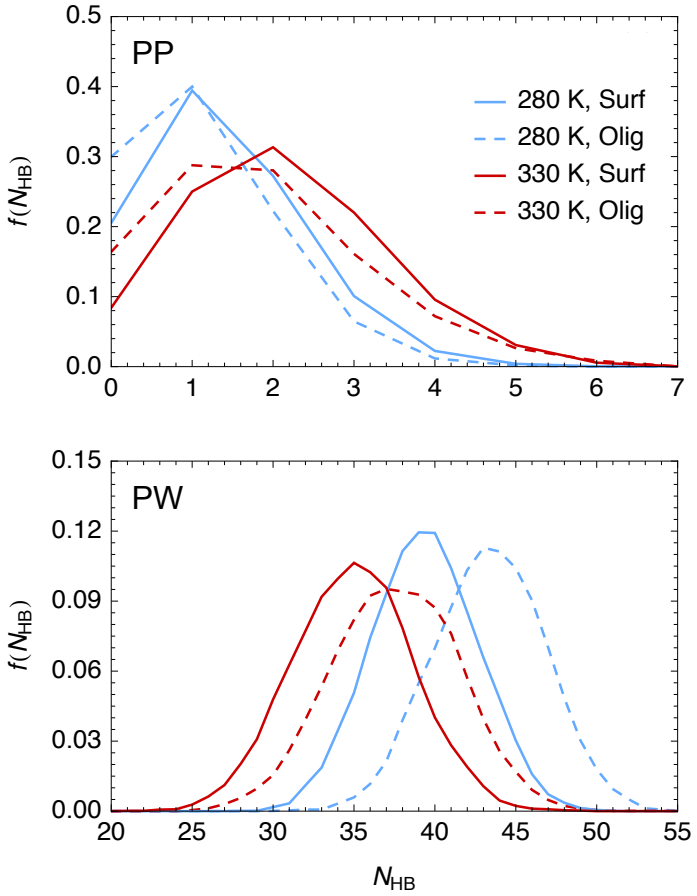


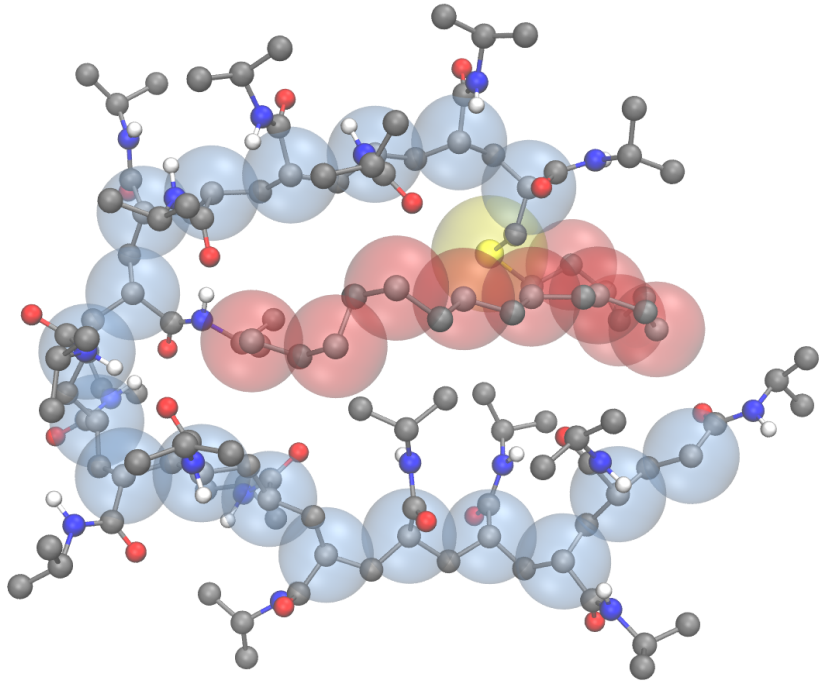
Change in RDF peaks corresponds to extent of structural change

Alkyl-PNIPAM contacts decrease above transition temperature



Alkyl tail interferes with hydrogen bond formation

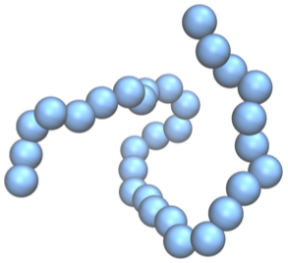


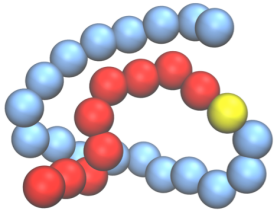


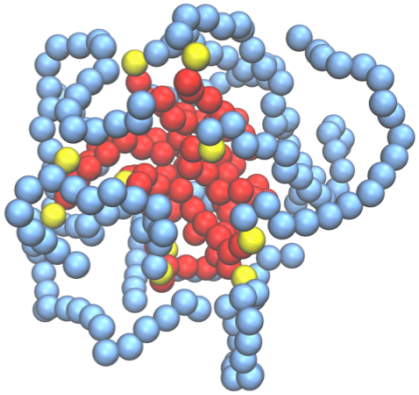
Chains remain partially hydrated even in collapsed state (~2 waters per NIPAM monomer)

Conclusions

- Structural transition observed in longer PNIPAM oligomers
  - Collapse to minimize hydrophobic surface in contact with water
  - Segments of 9-10 monomers consistent with persistence length
- PNIPAM-C18 collapsed at both temperatures
  - Addition of hydrophobic alkyl tail leads to drop in transition temperature
  - Having alkyl tail alone in water is highly unfavorable
- Polymer-polymer contacts increase above transition temperature
  - Except PNIPAM-alkyl contacts, which decrease
  - Similar trends for polymer-polymer hydrogen bonds
- Polymer-water hydrogen bonds decrease at higher temperatures
  - Alkyl tail interferes with hydrogen bond formation
  - Chains remain partially hydrated in collapsed state
- Temperature-responsive behavior achievable for PNIPAM surfactants
  - Increasing size of PNIPAM segment
  - Formation of aggregates (e.g., micelles)







Acknowledgements

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