Studying Structure and Thermodynamics in Macromolecular Materials Using Theory and Simulations

Arthi Jayaraman

Professor

Dept. of Chemical and Biomolecular Engineering

Dept. of Materials Science and Engineering

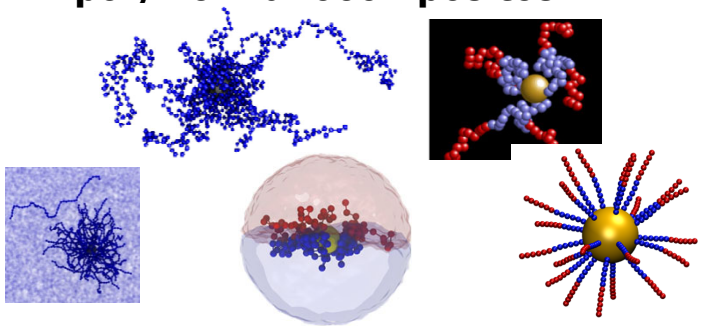
University of Delaware, Newark

Associate Editor, *Macromolecules*

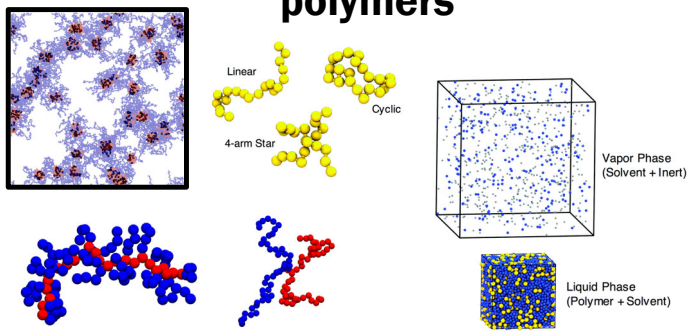
Research Thrusts and Interests in the Jayaraman Lab

Linking molecular features to macroscopic morphology and thermodynamics

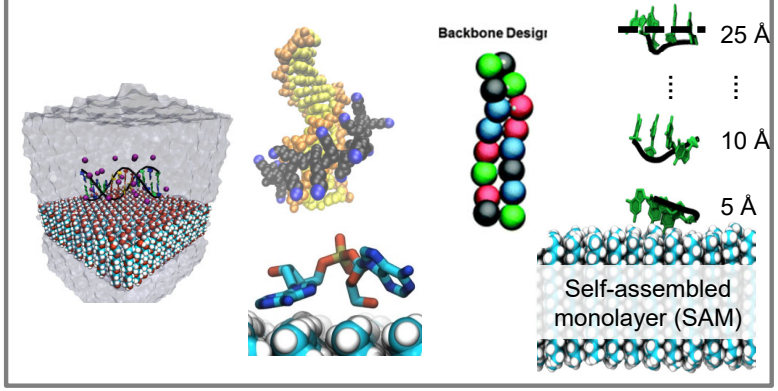
Functionalized nanoparticles in polymer nanocomposites



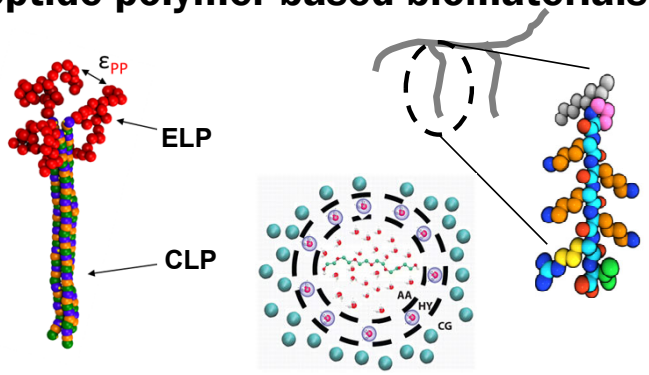
Solvent role in assembly of colloids & polymers



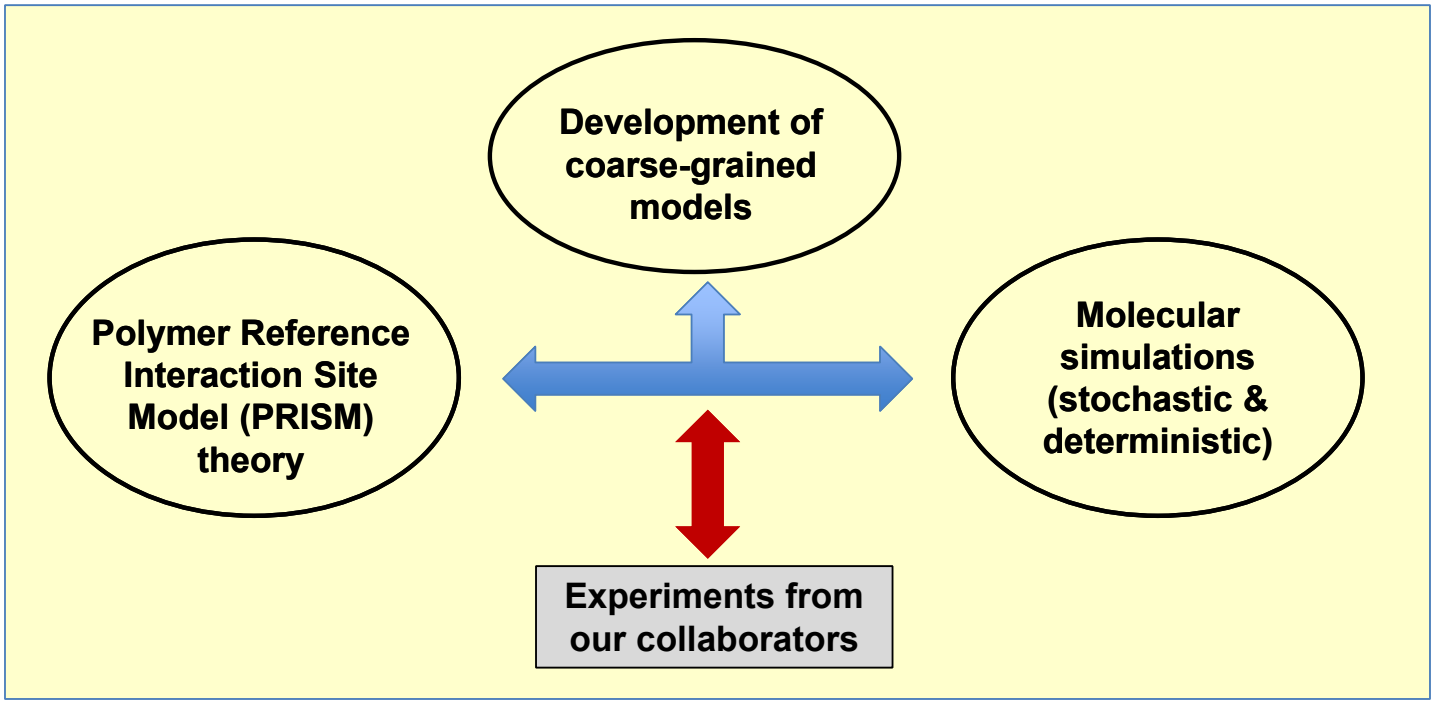
Nucleic acids based materials



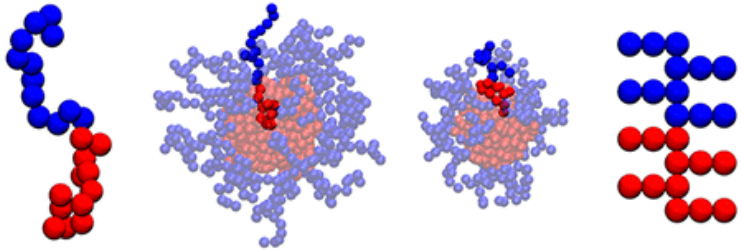
Peptide-polymer based biomaterials

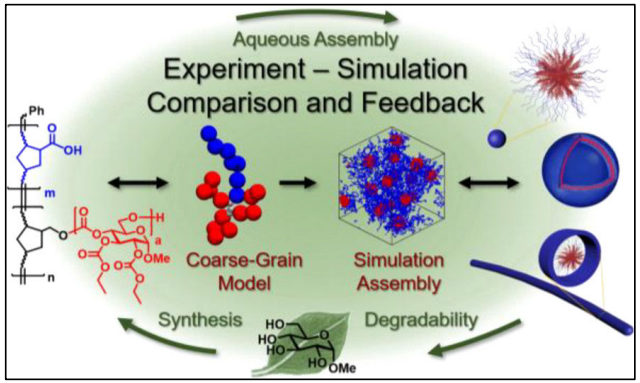


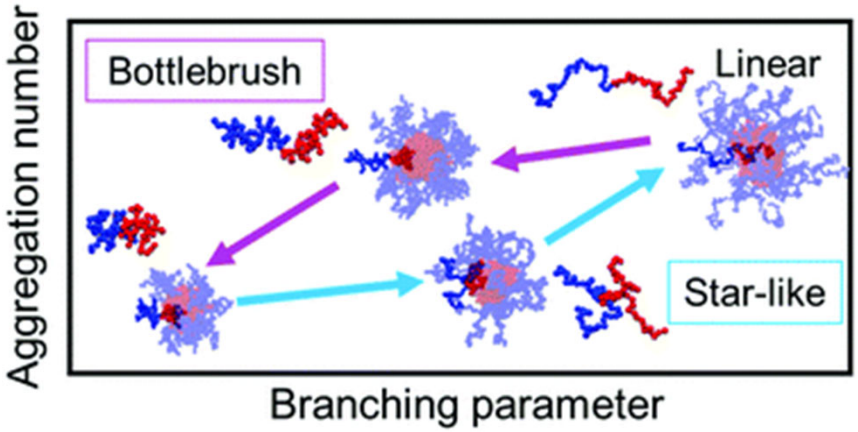
Past and current projects funded by


Development of coarse-grained models
Polymer Reference Interaction Site Model (PRISM) theory
Molecular simulations (stochastic & deterministic)
Experiments from our collaborators

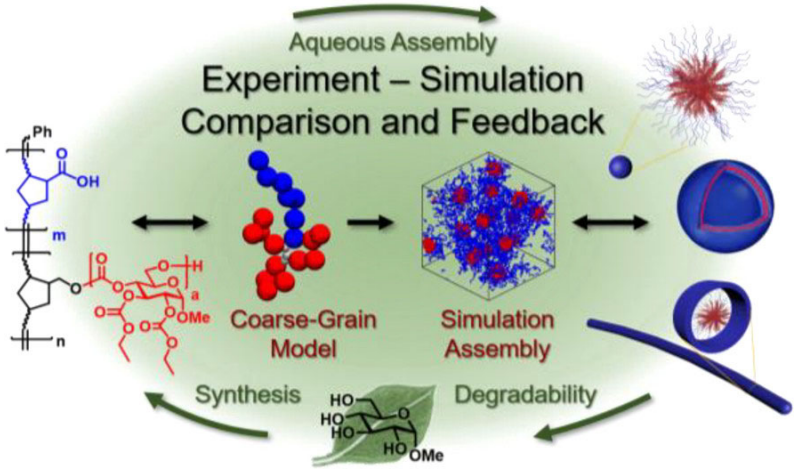
I. Assembly of amphiphilic non-linear polymers in solution: Theory-simulation (my group) & experiment (collaborators)



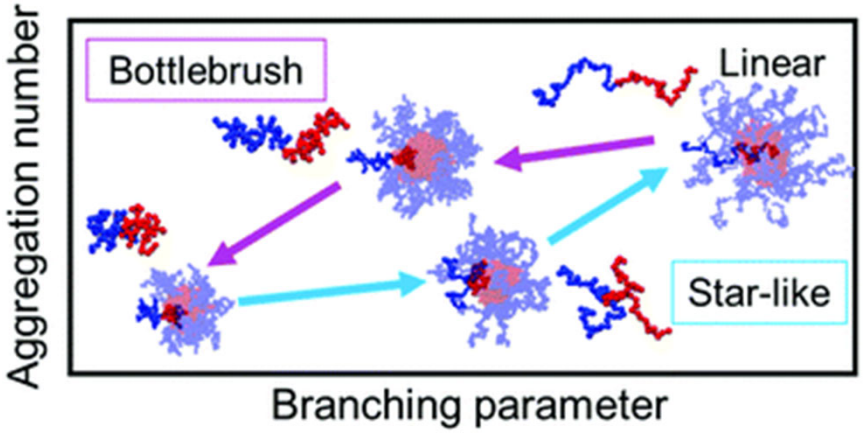




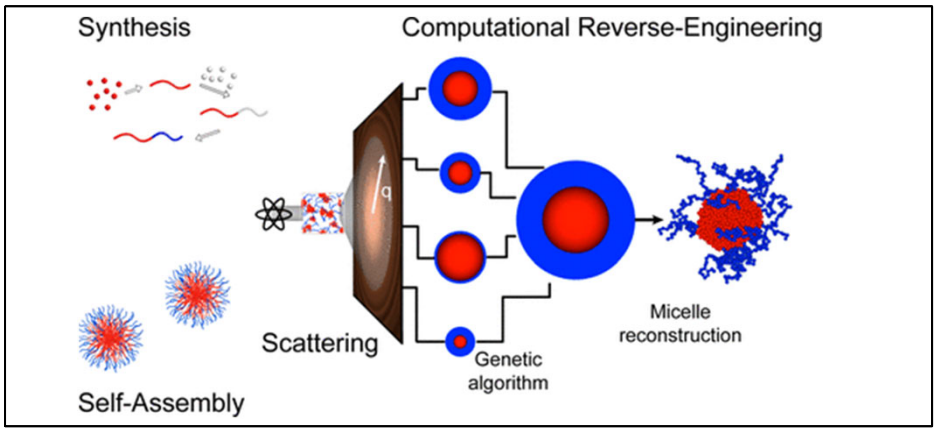
Validation of Coarse-grained Model



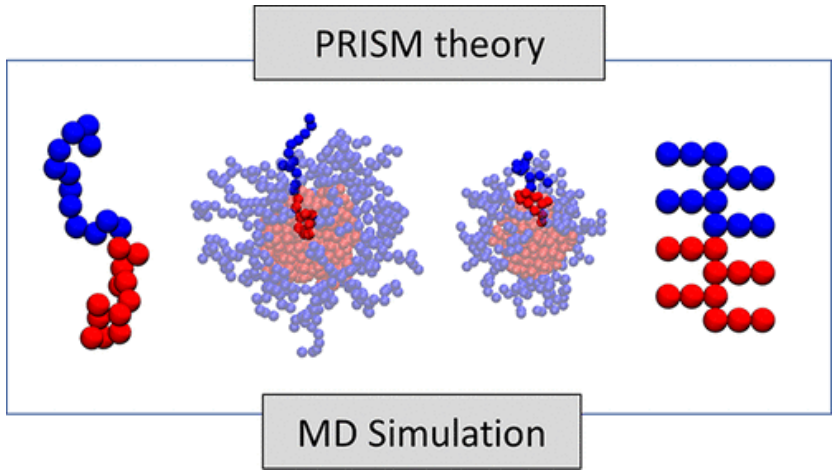
Simulation – Effects of Varying Architecture



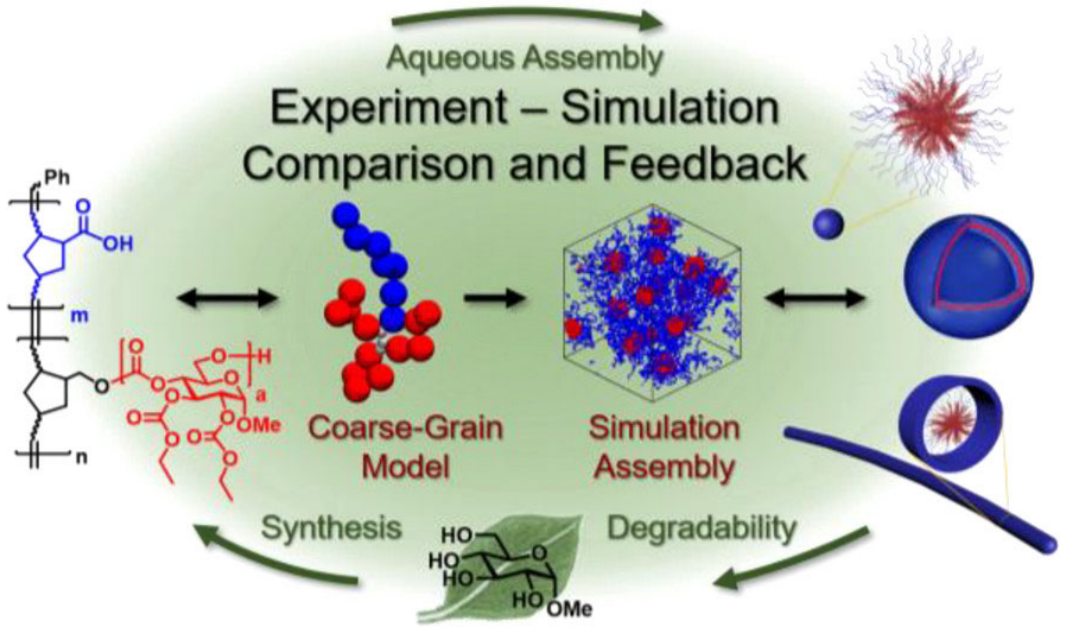
Computational Reverse Engineering from Scattering Data



Theory – Simulation Link



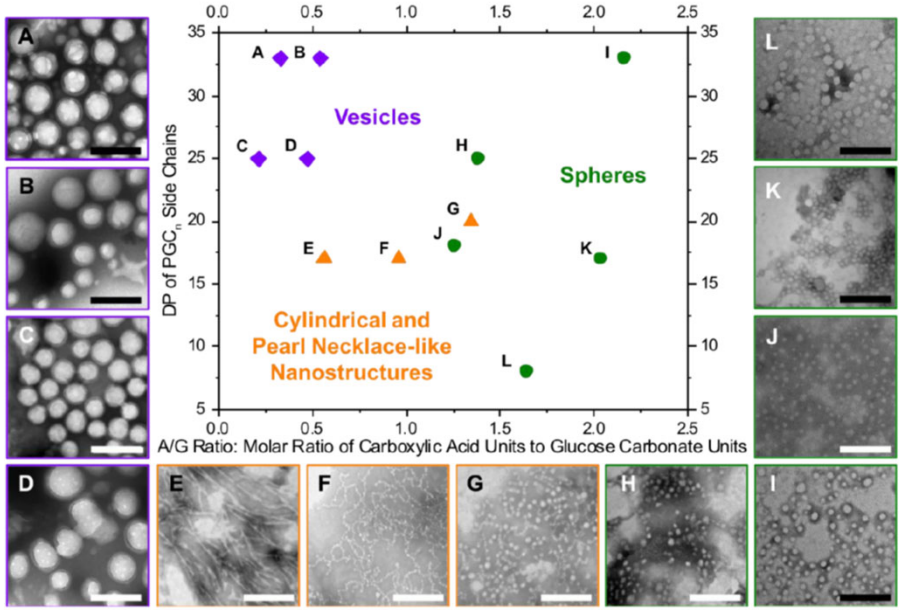
Coil-brush amphiphilic copolymers



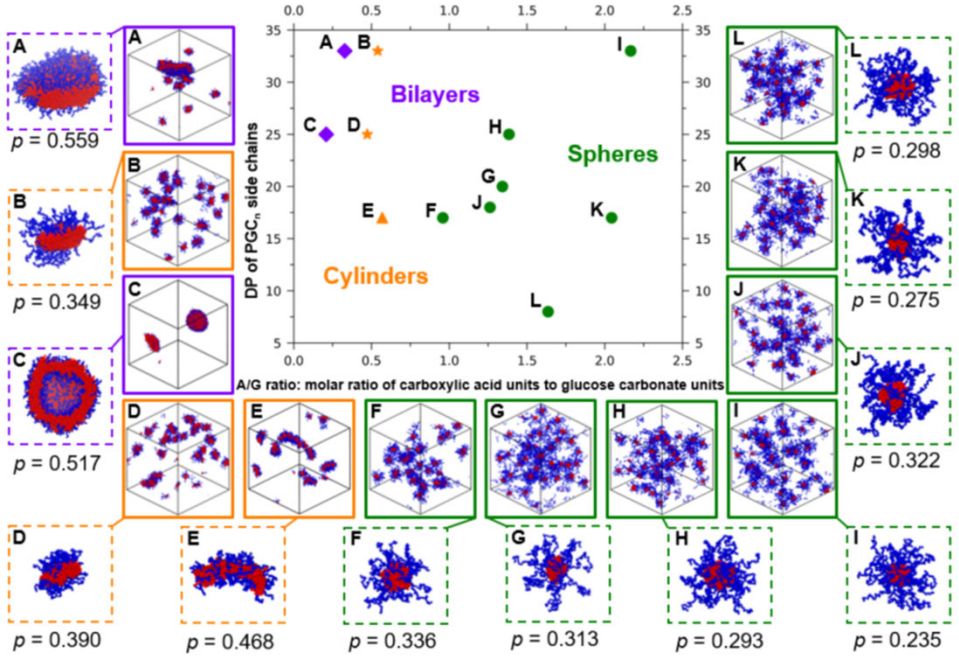
Synthesis by Ms. Mei Dong & Prof. Karen L. Wooley at Texas A&M
Characterization by Ms. Jee Young Lee & Prof. Darrin Pochan at Univ. of Delaware
Simulations by Mr. Michiel Wessels & Prof. Arthi Jayaraman at Univ. of Delaware

M. Dong, M. Wessels, J. Young Lee,…, D. Pochan, A. Jayaraman, K. Wooley ***ACS Nano*** (2019), 13, 5147-5162

Phase Diagram - Experiments vs. Simulations



Experiments



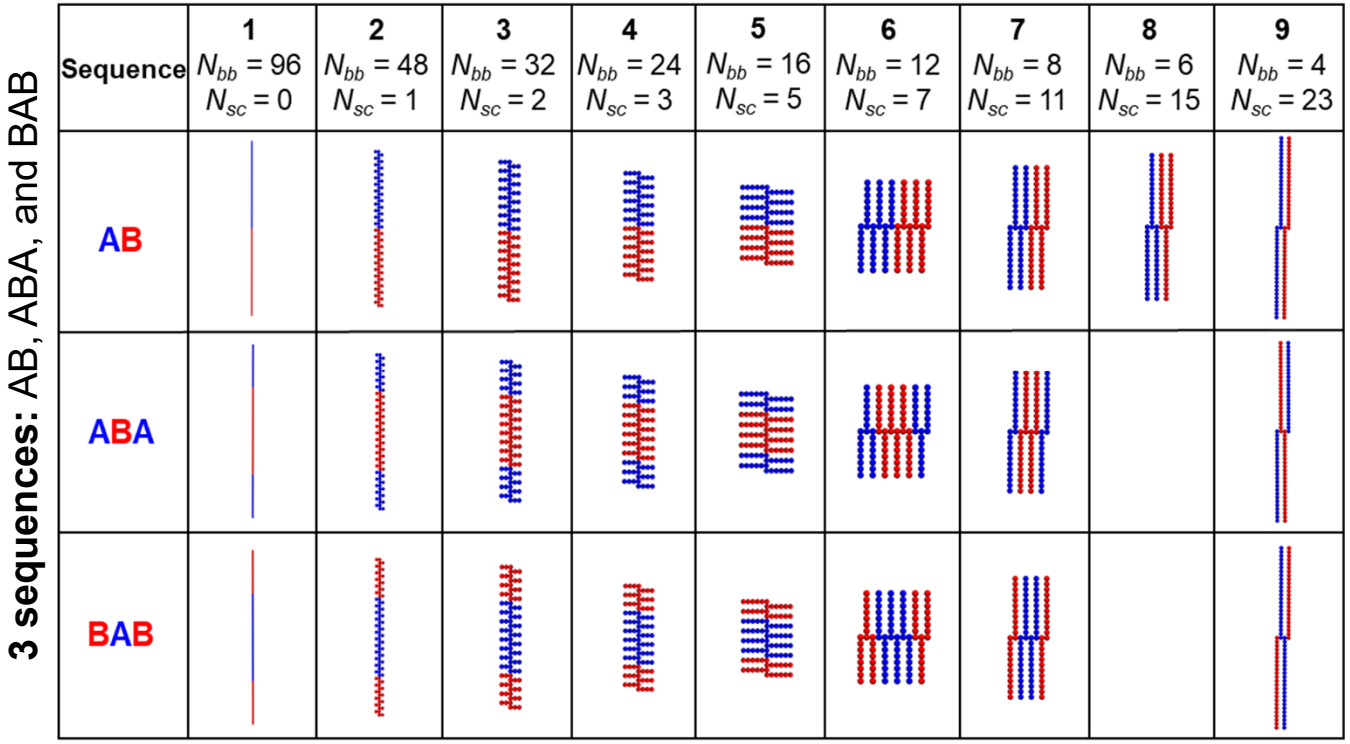
Simulations

The coarse-grained model and simulation approach is appropriate to capture the regions of micelle structures seen in phase diagram from experiments as a function of the design parameters relevant to branched amphiphiles

M. Dong, M. Wessels, J. Young Lee,…, D. Pochan, A. Jayaraman, K. Wooley ***ACS Nano*** (2019) 13, 5147-5162

Exploration of varying non-linear polymer architectures, sequence and composition using theory and simulations

9 polymer architectures



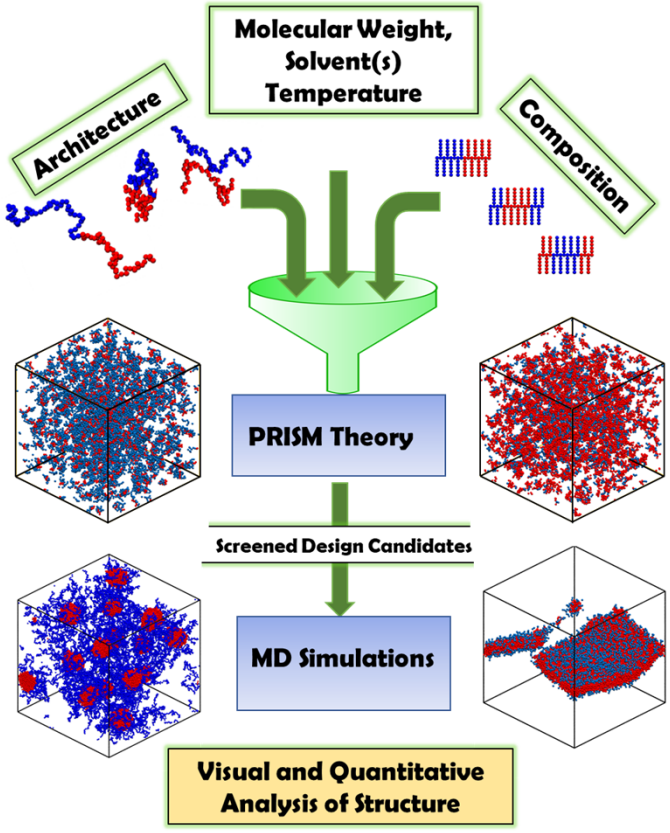
3 compositions: A:B 50:50, A:B 25:75, and A:B 75:25

M. Wessels, A. Jayaraman*, Self-assembly of amphiphilic polymers of varying architectures near attractive surfaces, ***Soft Matter*** (2020) 16, 623-633

M. Wessels, A. Jayaraman*, Molecular dynamics simulation study of linear, bottlebrush, and star-like amphiphilic block polymer assembly in solution, ***Soft Matter***, (2019) 15, 3987-3998

Combining PRISM theory and MD simulations

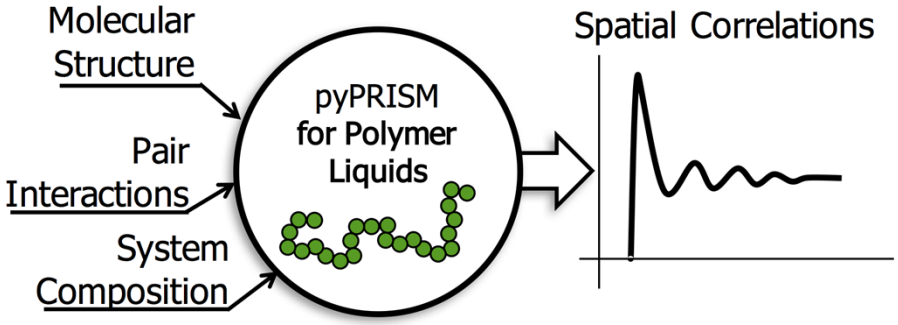
PRISM theory can be used to explore a wide design space of polymer architectures to predict phase transitions and guide use of MD simulations only for the exciting design parameters



LINEAR COPOLYMERS
I. Lyubimov, M. Wessels, A. Jayaraman,
***Macromolecules,* 2018, 51 (19), 7586**

BOTTLEBRUSH COPOLYMERS
I. Lyubimov, D. J. Beltran-Villegas, A. Jayaraman,
***Macromolecules,* 2017, 50, 7419**

pyPRISM: An Open Source Package for PRISM Theory



pyPRISM is an open source package for PRISM theory that predicts the structure and thermodynamics of polymer blends, solutions and nanocomposites

Dr. Tyler Martin
Dr. Ron Jones
Dr. Chad Snyder
Mr. Thomas Gartner
Prof. Arthi Jayaraman

GitHub
github.com/usnistgov/pyPRISM

Read the Docs
pyPRISM.readthedocs.io

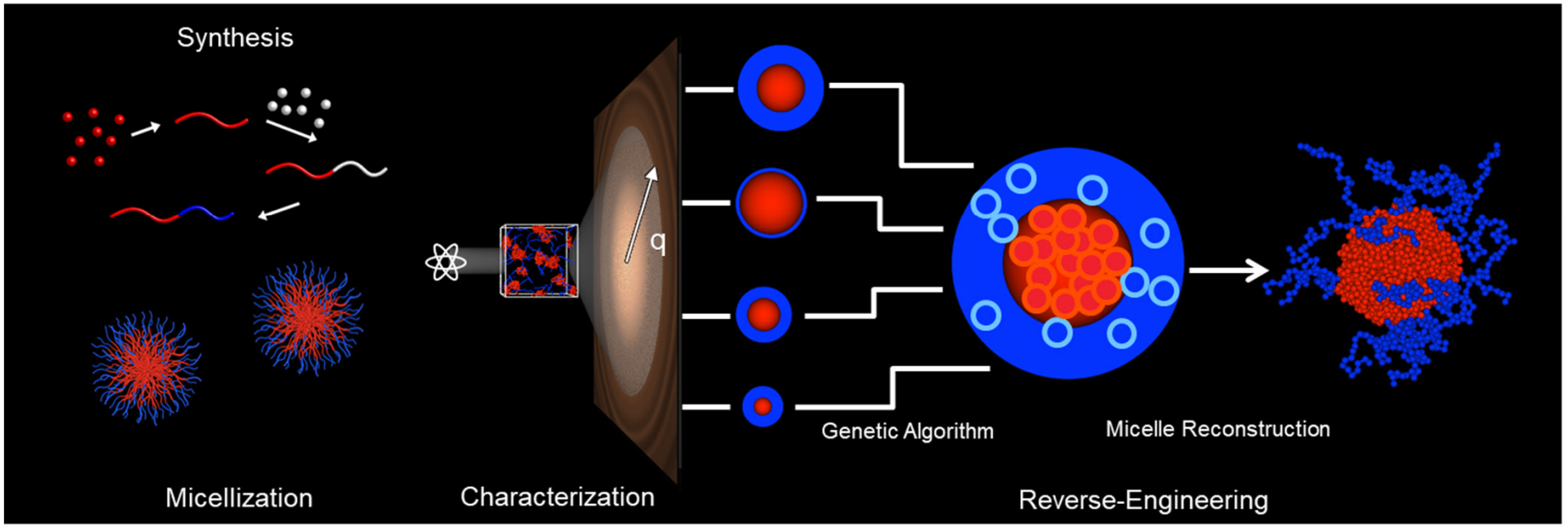
pyPRISM Tool Article

T. B. Martin, T. Gartner, R. Jones, C. Synder, A. Jayaraman, ***Macromolecules*** 51 (8), 2906 (2018)

PRISM Theory Article

K. S. Schweizer, J. Curro, *Phys. Rev. Lett.,* 58 (3) 246 (1987)

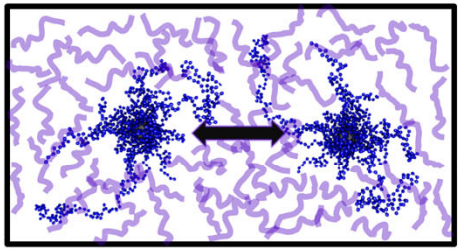
Using genetic algorithm and simulations to interpret scattering profiles of the micelles in amphiphilic polymer solutions

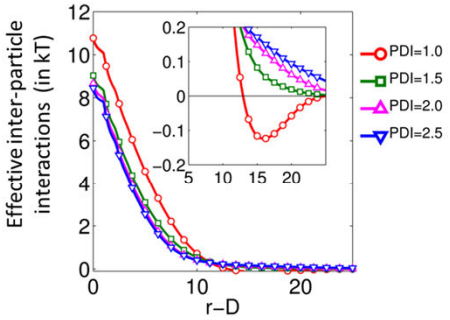


Computational Reverse-Engineering Analysis for Scattering Experiments on Amphiphilic Block Polymer Solutions
Daniel J. Beltran-Villegas, Michiel G. Wessels, Jee Young Lee, Yue Song, Karen L. Wooley, Darrin J. Pochan, and Arthi Jayaraman
JACS (2019) 141 (37), 14916-14930

PRISM theory and MD simulations for polymer nanocomposites

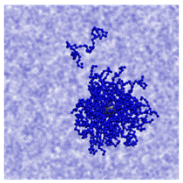
Polydisperse Graft Polymers Improve Particle Dispersion in Matrix Polymers

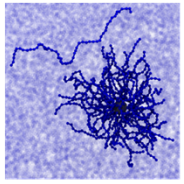


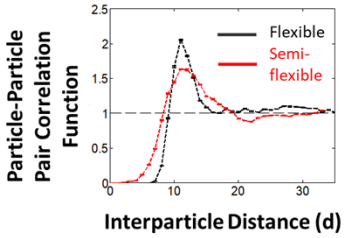


T. B. Martin, P. Dodd, A. Jayaraman, Phys Rev Lett (2013) 110, 018301

Improving Particle Dispersion using Semi-Flexible Graft and Matrix Polymers

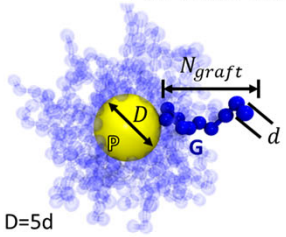






B. Lin, T. B. Martin, A. Jayaraman, ACS Macro Lett. (2014) 3, (7), 628

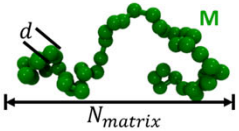
Graft-Matrix Polymer Wetting-Dewetting Transition Distinct from Particle Dispersion-Aggregation Transition

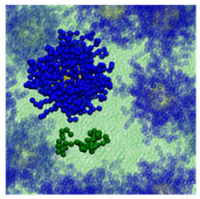


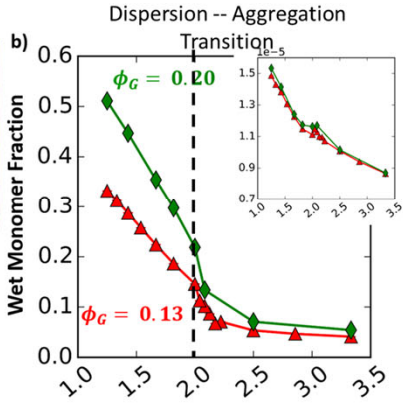
D=5d

N_{matrix} = 50; N_{graft}=10

Grafting Density= 0.76 $chains/d^2$





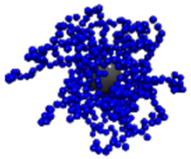


T. B. Martin, A. Jayaraman et al., JACS (2015) 137, (33), 10624

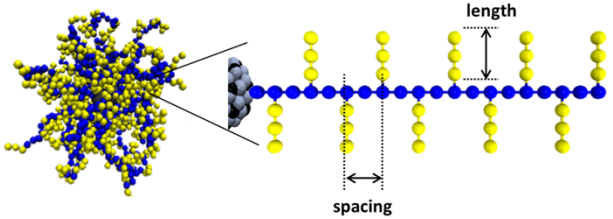
T. B. Martin. A. Jayaraman, Macromolecules (2016) 49, (24), 9684

Branched versus Linear Graft Polymers

Linear Polymer Grafted Particle



Comb Polymer Grafted Particle



K. Modica, T. B. Martin, A. Jayaraman, Macromolecules (2017) 50, (12), 4854

Simulations of macromolecular materials with directional interactions

Proteins

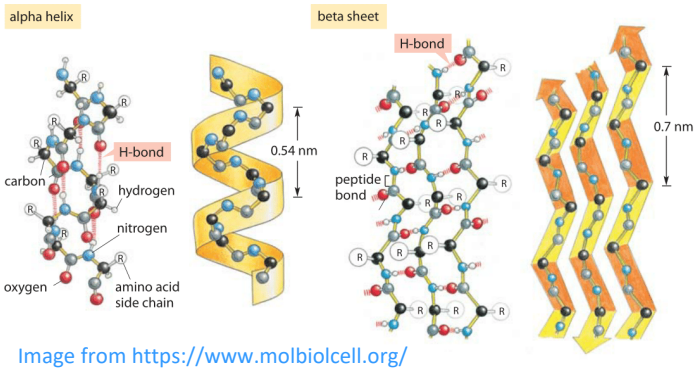


Image from https://www.molbiolcell.org/

DNA

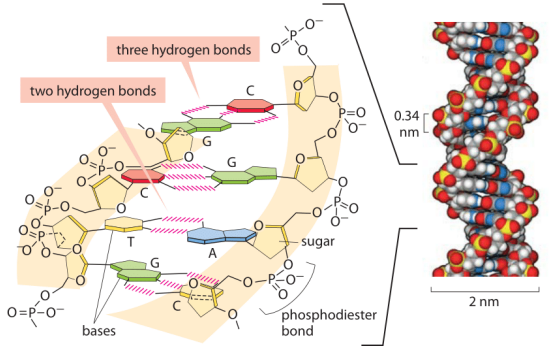
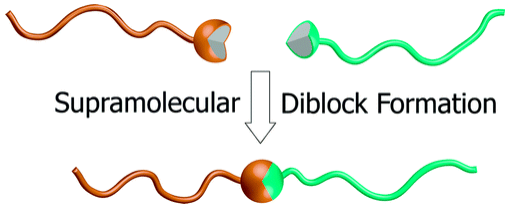


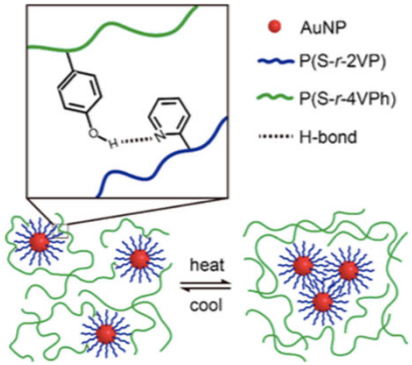
Image from http://book.bionumbers.org/

Polymers with Multiple Hydrogen-Bonded End Groups



Feldman, Kade, de Greef, Meijer, Kramer and Hawker
Macromolecules, 41, 4694-4700, (2008)

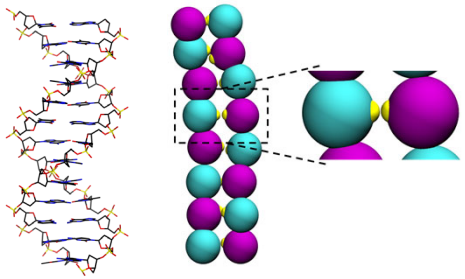
Polymers Nanocomposites with H-bonding Chemistries



Heo, K., Miesch, C., Emrick, T. & Hayward, R. C.. *Nano Letters* 13,5297–5302 (2013).

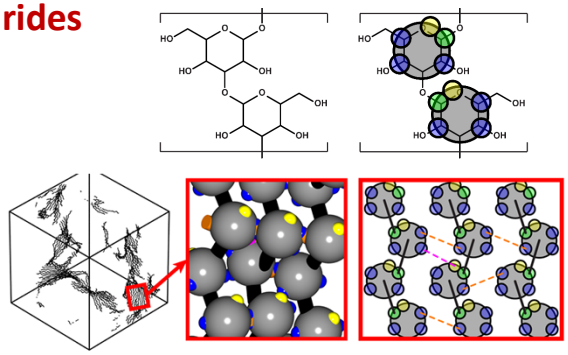
New coarse-grained models for macromolecules with directional interactions

Starting from our previous DNA models …



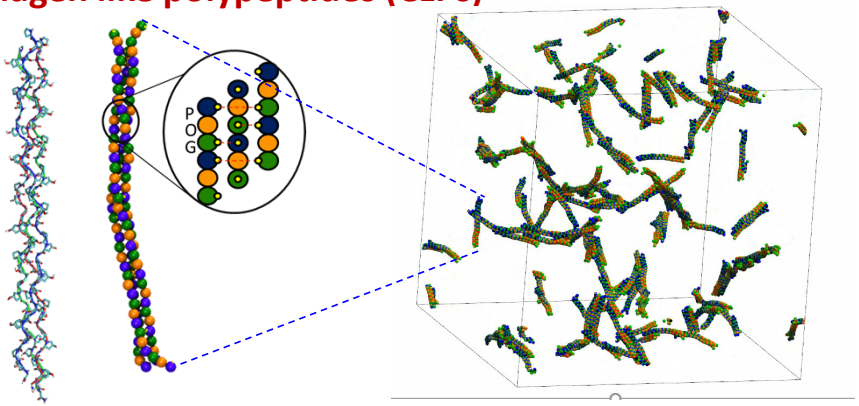
… we have now built **CG models for polymers with directional interactions** enabling studies of a broad range of polymeric materials

Polysaccharides



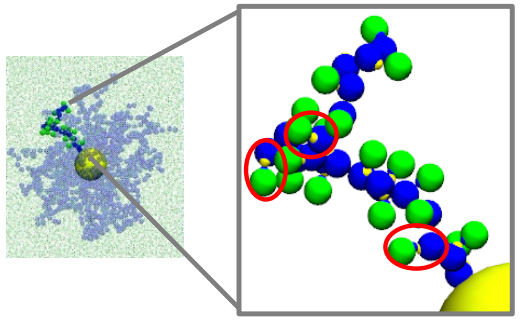
D. J. Beltran-Villegas, D. Intriago, K. Kim, N. Behaptu, J. D. Londono, A. Jayaraman*, Coarse-grained molecular dynamics simulations of α-1,3-glucan, ***Soft Matter*, (2019) 15, 4669-4681**

Collagen like polypeptides (CLPs)



J.E. Condon and A. Jayaraman, Development of Coarse-Grained Model of Collagen-like Peptide (CLP) for Studies of CLP Triple Helix Melting " ***J. Phys. Chem B* (2018) 122 1929–1939**

Polymer Nanocomposites (PNCs)



A. Kulshreshtha and A. Jayaraman, Impact of Hydrogen Bonding Interactions on Graft–Matrix Wetting and Structure in Polymer Nanocomposites, ***Macromolecules* (2019) 52 (7), 2725-2735**