Transport, Targeting, and Applications of Metallic Functional Nanoparticles for Degradation of DNAPL Chlorinated Organic solvents

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George Redden

Paul Meakin

Harry Rollins

Dan Ginosar

CMU

Gregory V. Lowry

Kris Matyjewski

Sara Majetich

David Sholl

Robert Tilton

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DOE Issues Addressed

- Primary: DNAPL contamination
  - Source zone remediation
- Secondary:
  - Colloid migration in porous media
  - Use of engineered colloids to affect subsurface fate and transport.
  - Innovative methods to manipulate subsurface processes

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Potential advantages of a particle-based approach to remediation:

- Concentration of active agents
- Ability to combine separate agents
  - Catalysts
  - Multiple particle types
- Engineered properties for:
  - Time release of reagents
  - Delayed release of reagents
  - Release of reagents in response to environment
- Transport processes different from solutes
  - Flow paths
  - Pore sizes
  - Surface interactions

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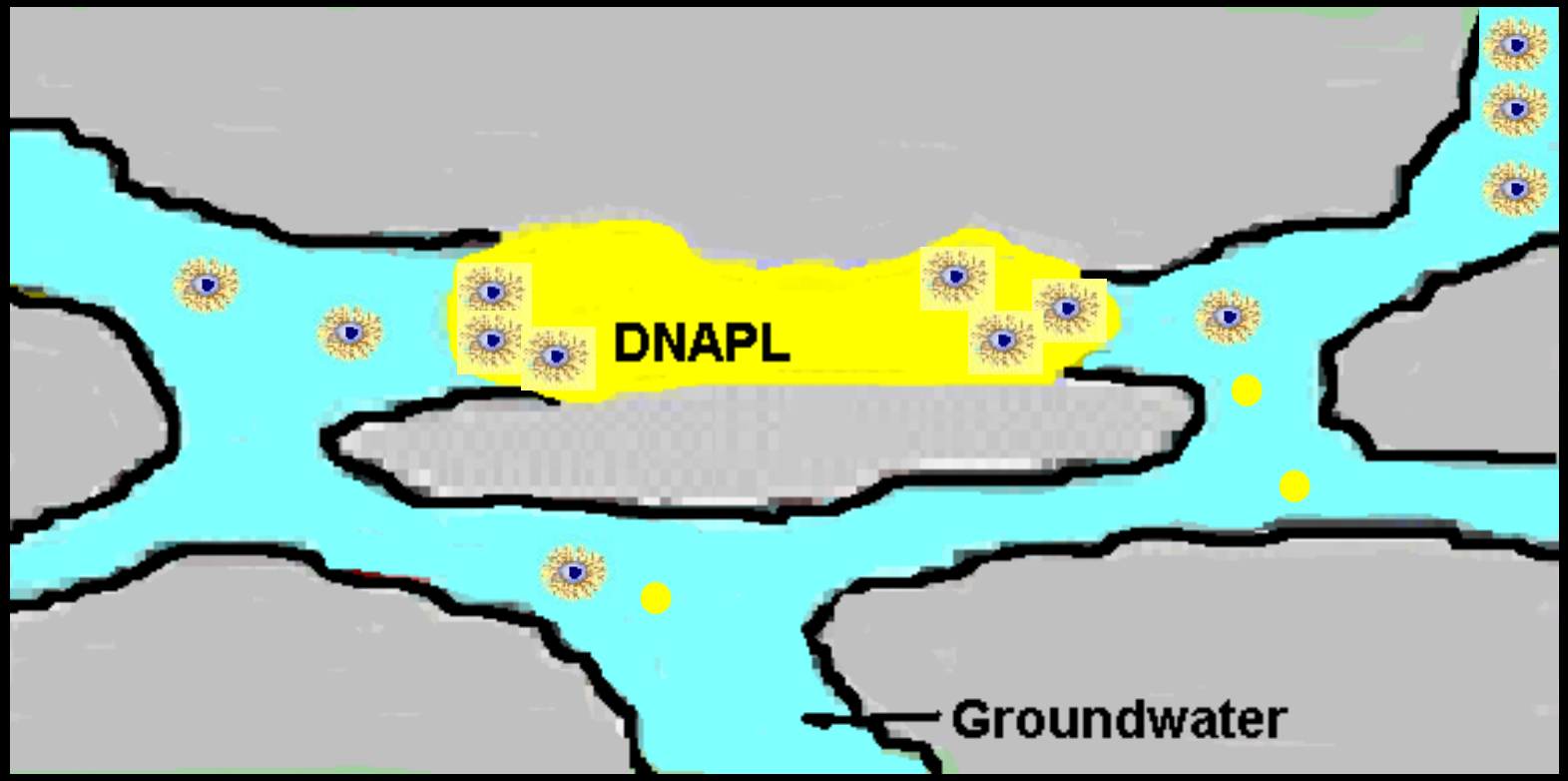
Conceptual Model



: surface-modified, reactive, catalytic nanoparticles

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Working Hypothesis

- Reactive colloid (nanoparticle) surfaces can be modified to:
  - Be transported through a porous matrix in a fluid phase (water or organic)
  - Preferentially partition at a NAPL-water interface
  - Degrade the NAPL to non-toxic products.

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Objectives

- Develop/optimize reactivity and transport of metal-based nanoparticles
- Demonstrate DNAPL-targeting
- Develop predictive numerical models for nanoparticle transport and DNAPL degradation in the subsurface

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Innovative Aspects

- Targeted *in situ* delivery of reactants to contaminant sources (DNAPL)
- Particle-scale to meso-scale understanding of mechanisms that control colloid transport
- Coupling Browning Dynamics and pore-scale models for colloid transport

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Project Elements

1. Particle synthesis
2. Particle surface modification
3. Particle Characterization
   - composition, morphology, surface properties
   - reactivity
4. Physical experiments to test:
   - particle mobility and partitioning
   - Ability to degrade non-aqueous phase contaminant
5. Model development
   - colloid mobility, partitioning, chemical transformations

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Particle synthesis to optimize reactivity and transport properties

- Particle Size
- Morphology/distribution of Pd/Fe
  - Pd surface deposits on Fe particles
  - Pd/Fe Alloy particles
  - Layered or dendritic structures
- Synthesis method
- Surface coatings

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Particle Synthesis Methods

- Sonochemical decomposition of $Fe(CO)_5$
- Polyol Method (reduction in boiling alcohols)
- Supercritical alcohol processing (a high temperature, pressurized polyol process)
- Borohydrate reduction of Fe^{2+}

Particle Characterization

- TEM - particle size and morphology
- Electron and X-ray diffraction - phase and crystallinity
- X-ray analysis (electron microprobe) - mapping Pd/Fe
- Transport properties
- Reactivity

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Sonochemical preparation of Pd-Fe(0)

- ½” Sonochemical horn with 450W power supply
- Low temperature bath
- Argon purge

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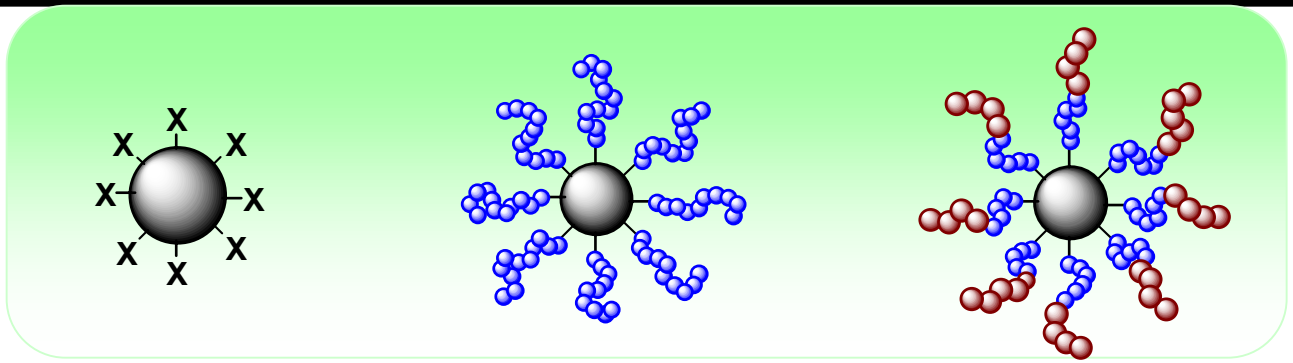
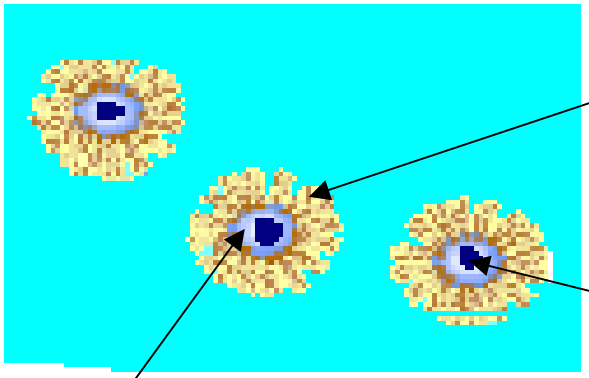
Surface Modification



Nanosized supported initiator

Hybrid-nanoparticles (hydrophobic block)

Hybrid-nanoparticles (hydrophobic-hydrophilic block-copolymers)



Hydrophilic block

Fe^0

Hydrophobic block

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Results: Fe(0) reactivity

- Nanoparticle reactivity a strong function of synthesis method (e.g. H_2O vs. EtOH as solvent)
- Polymer coating on Fe(0) surface does not inhibit reactivity
- Toda, Inc. commercially produces nano sized Fe(0)
  - ideal model particles (~100 nm)

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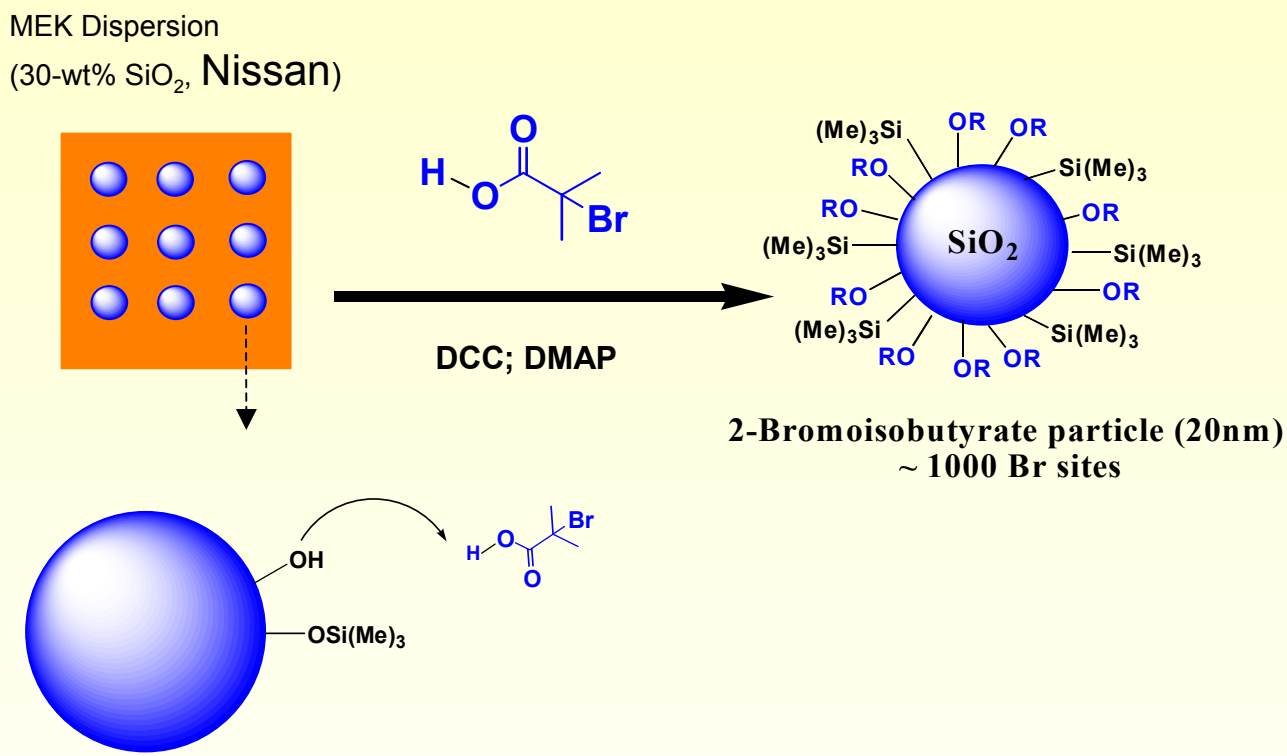
Results: Model SiO_2 Colloids



Reaction conditions: 30 min on ice-bath; than overnight at room temperature. Filtered, precipitated with MeOH-water (4:1), centrifuged, washed 10-15 times with MeOH-water (4:1). Dried in vacuum.

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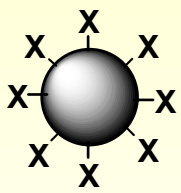
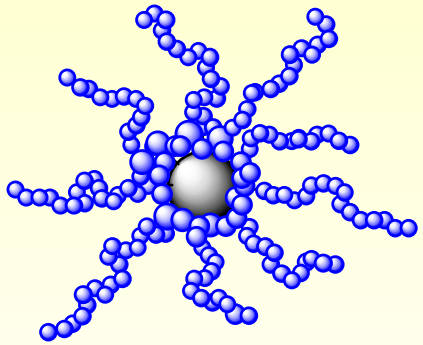
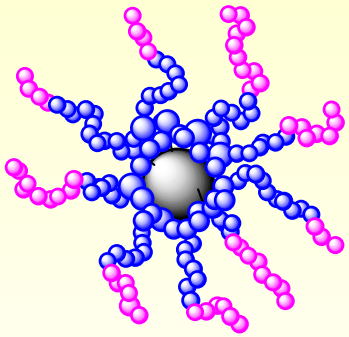
Results: PS/Sulfonated PS Hybrid Materials



Nanosized Si-supported initiator



Hybrid-nanoparticles (polystyrene as hydrophobic block)



Hybrid-nanoparticles (hydrophobic-hydrophilic block-copolymers) Sulfonated polystyrene as hydrophilic block

-soluble in DCE-hexane mixture

Sulfonation →

-insoluble in the reaction mixture

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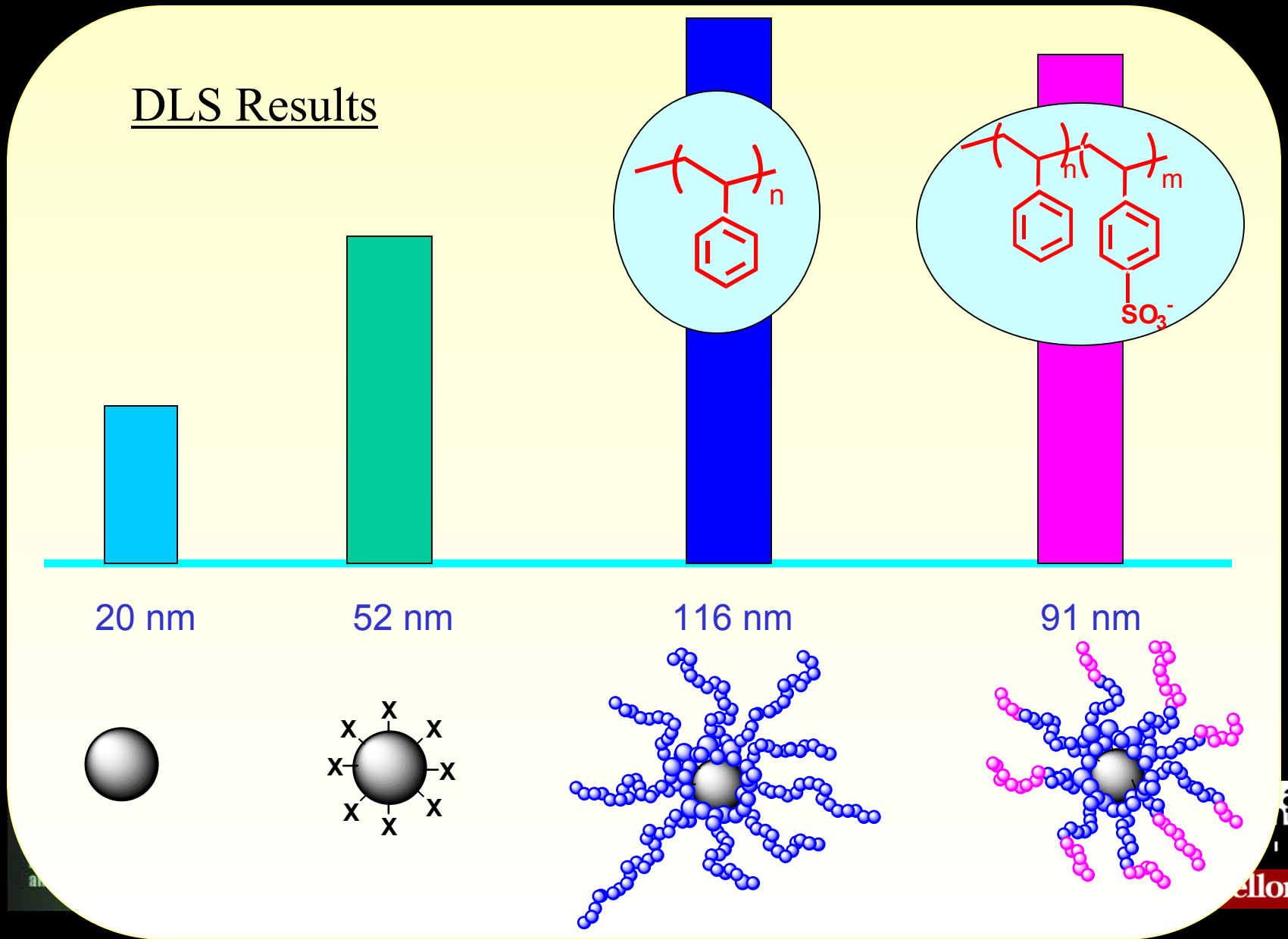
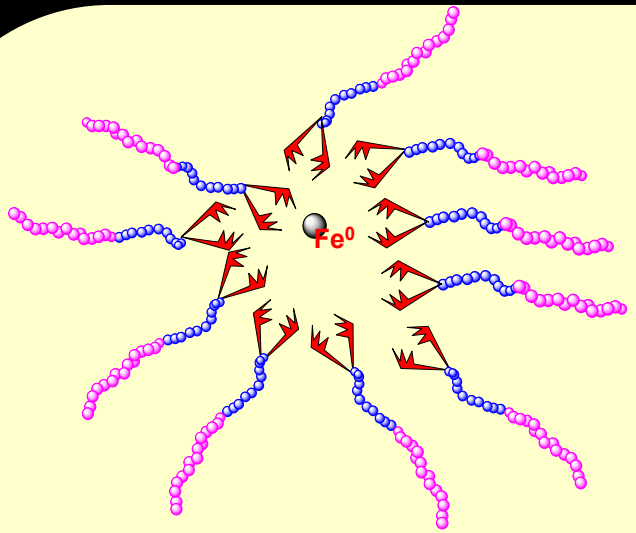
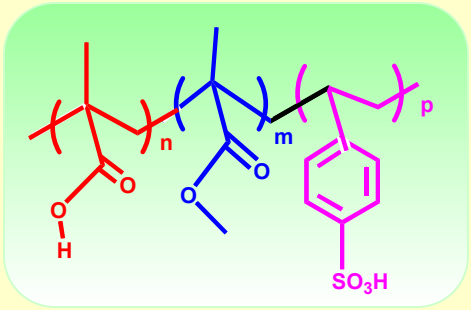
Results: PS/Sulfonated PS

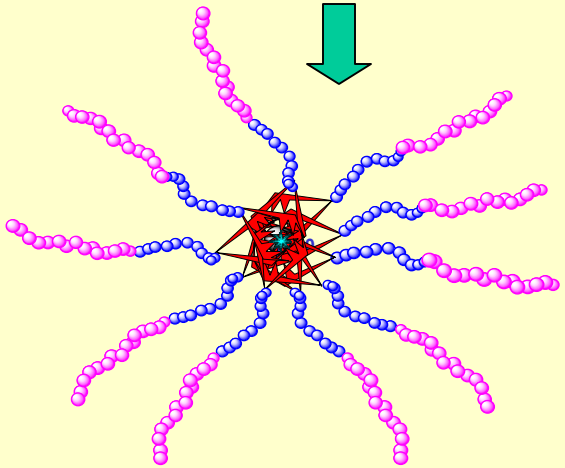


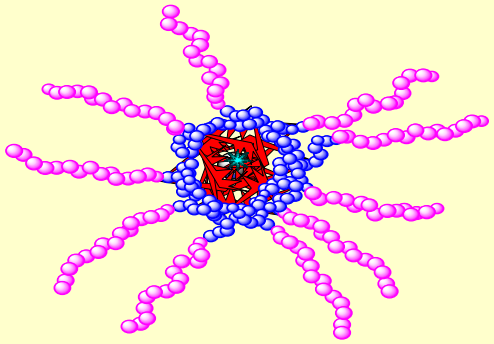
Results: Fe^0 Core-Shell Nanoparticles





Poly (tBMA)-b-poly(MMA)-b-poly(SST)





Triblock copolymers anchor Fe nanoparticles via poly(AA) groups

The hydrophobic blocks form a protective shell around the Fe nanoparticle

Near Future

- Begin construction of physical experiments
  - micro-models
  - Two-dimensional
  - Three-dimensional, “meso-scale” testing
- Initiate model development in coordination with physical experiments
  - Brownian Dynamics
  - Monte Carlo methods
- Particle Reactivity
  - Effect of size, age, history, morphology, and polymer

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Project Management

- Carnegie Mellon University
  - Polymer chemistry
  - Particle-contaminant reactions/characterization
  - Bench scale testing of particle transport
  - Modeling colloid behavior
- INEEL
  - Pore-scale modeling of colloid transport
  - particle synthesis
  - micro-model testing of particle transport
- INEEL/CMU
  - Meso-scale testing of particle transport and proof of concept

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