Hybrid Magnetic Amphiphilic Block Copolymer System for Pollutant Remediation in Aqueous Environments

Adriana Pavía-Sanders, Jeniree A. Flores, Jonathan E. Sanders, Karen L. Wooley

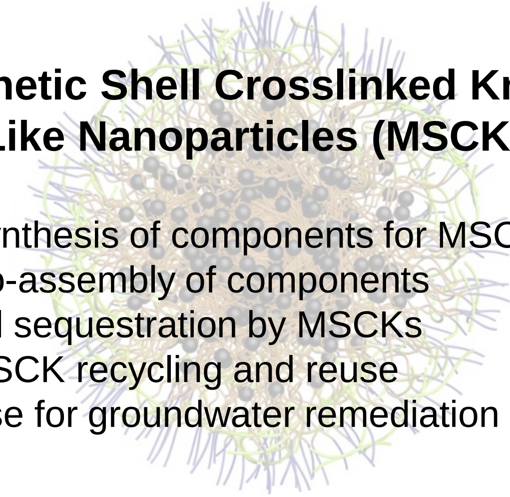
Polymer Chemistry

CHEM 466

Outline

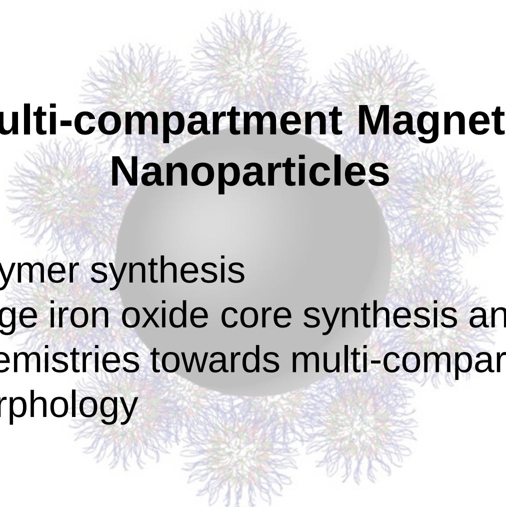
Background

Oil spills
Current remediation methods
Advancements in oil spill remediation



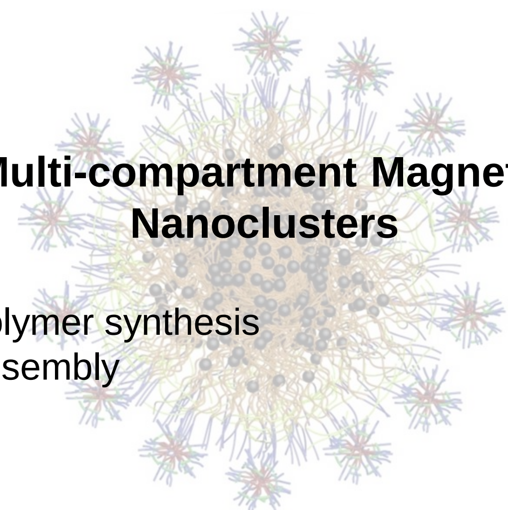
Magnetic Shell Crosslinked Knedel-Like Nanoparticles (MSCKs)

Synthesis of components for MSCKs
Co-assembly of components
Oil sequestration by MSCKs
MSCK recycling and reuse
Use for groundwater remediation



Multi-compartment Magnetic Nanoparticles

Polymer synthesis
Large iron oxide core synthesis and issues
Chemistries towards multi-compartment morphology

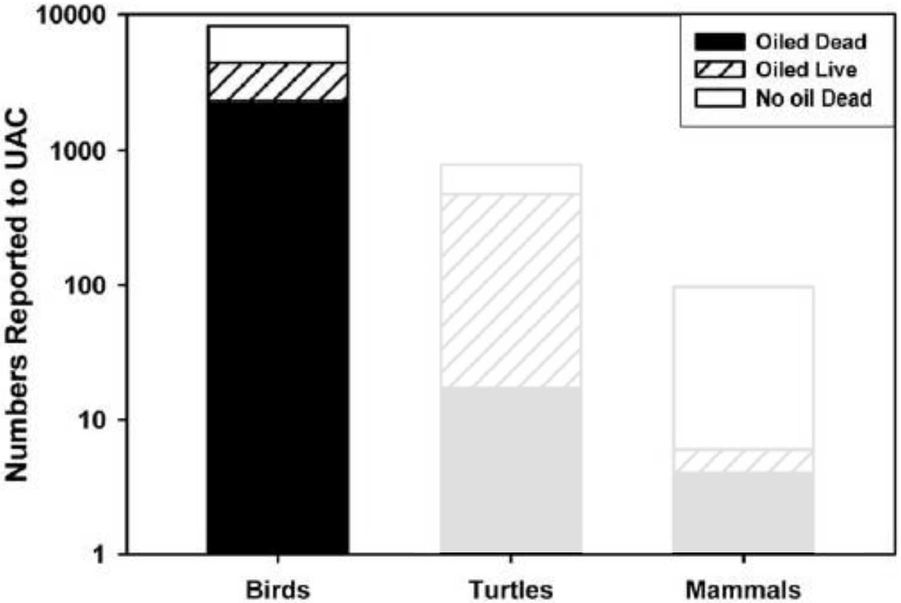


Multi-compartment Magnetic Nanoclusters

Polymer synthesis
Assembly

Oil Spills and Their Effects

- 20,000 oil spills reported in the United States annually
  - Severity varies
- Deepwater Horizon
  - 2,085 visibly oiled alive
  - 2,303 visibly oiled dead
  - Remaining: visibly no oil dead



Barron, M. G., *Toxicologic Pathology*. **2012,** *40* (2), 315-20.

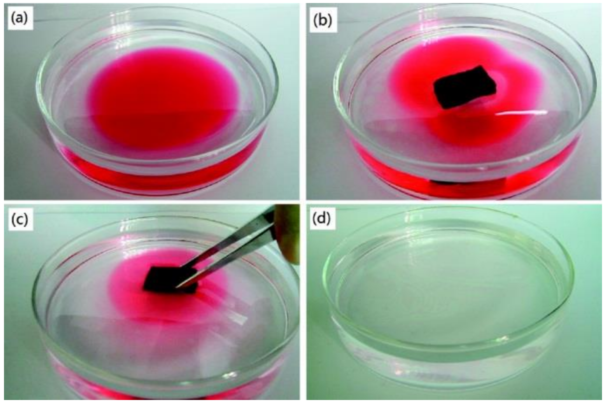
Oil Spill Response: Current Methods of Remediation

- Containment
  - Limits exposure
  - Facilitates recovery
- Bulk recovery
  - Current mechanical techniques
- Low concentrations
  - Sheen 0.04 to 50 µm on the water
- Current methods for sheen recovery

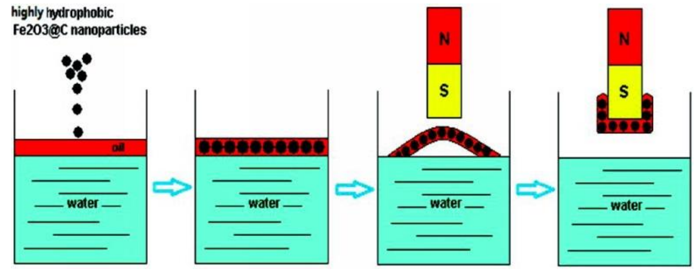
Images provided by Jonathan E. Sanders, MEC[X,] L.P.

Identification of Oil on Water: Aerial observation and identification guide. A. M. S. Authority. (**2009**).

Developments in Spill Remediation



1:13 max loading



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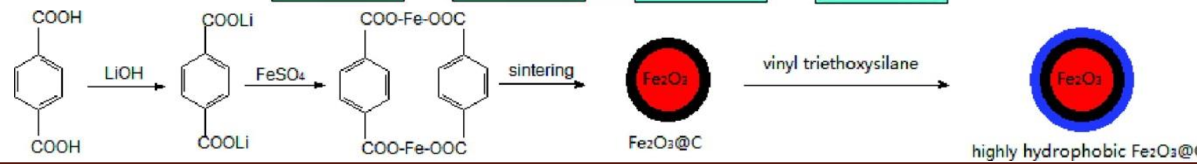
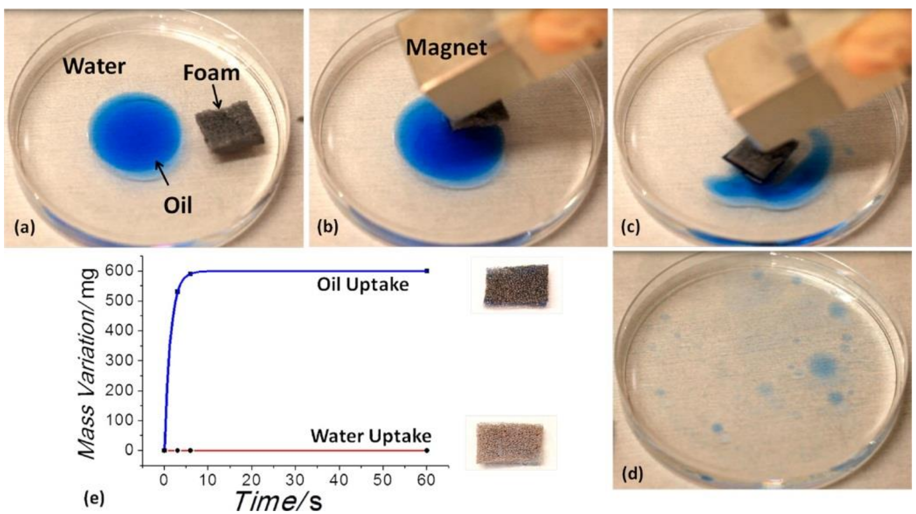
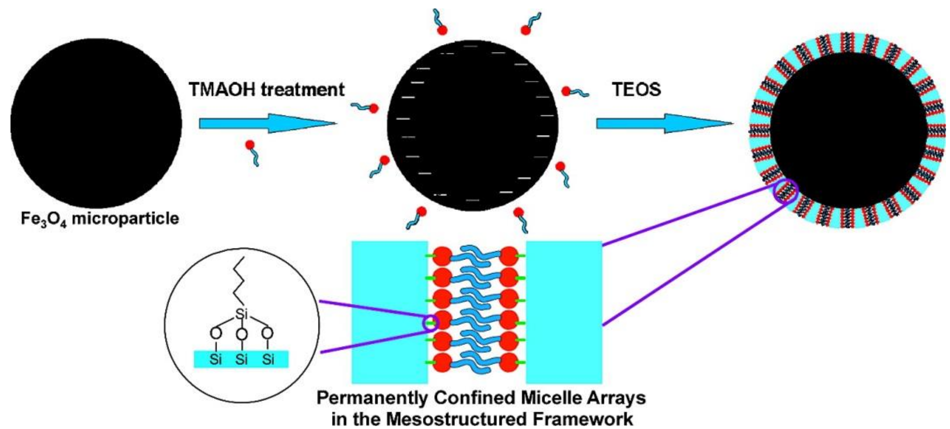


Tested against contaminants of limited complexities



1:13 max loading

1:3.9E^{-3} max loading

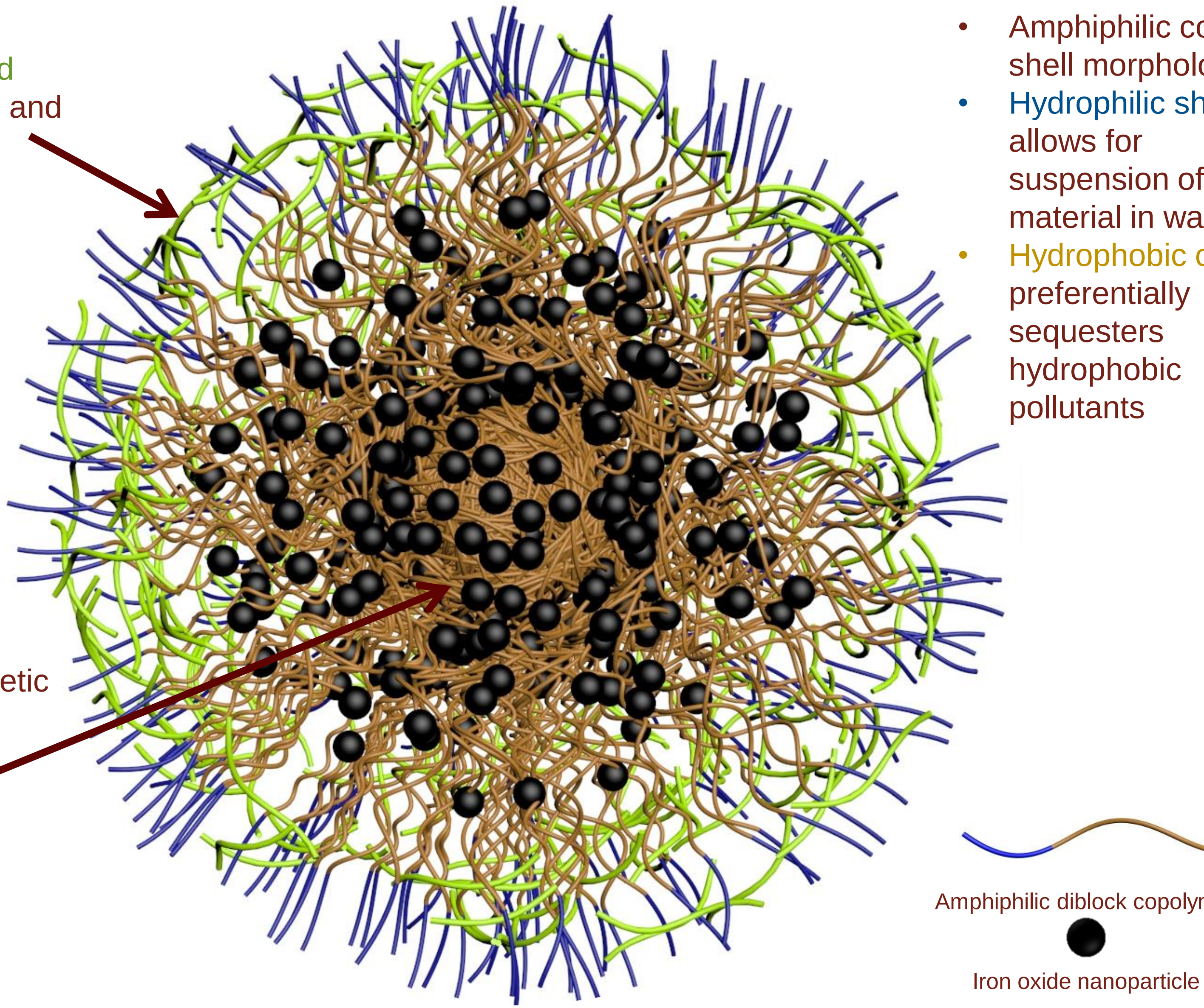


Calcagnile, P.; Fragouli, D.; Bayer, I. S.; Anyfantis, G. C.; Martiradonna, L.; Cozzoli, P. D.; Cingolani, R.; Athanassiou, A. *ACS Nano*. **2012**, *6* (6), 5413-5419.

Wang, P.; Shi, Q.; Shi, Y.; Clark, K. K.; Stucky, G. D.; Keller, A. A. *J. Am. Chem. Soc,* **2009**, *131* (1), 182-188.

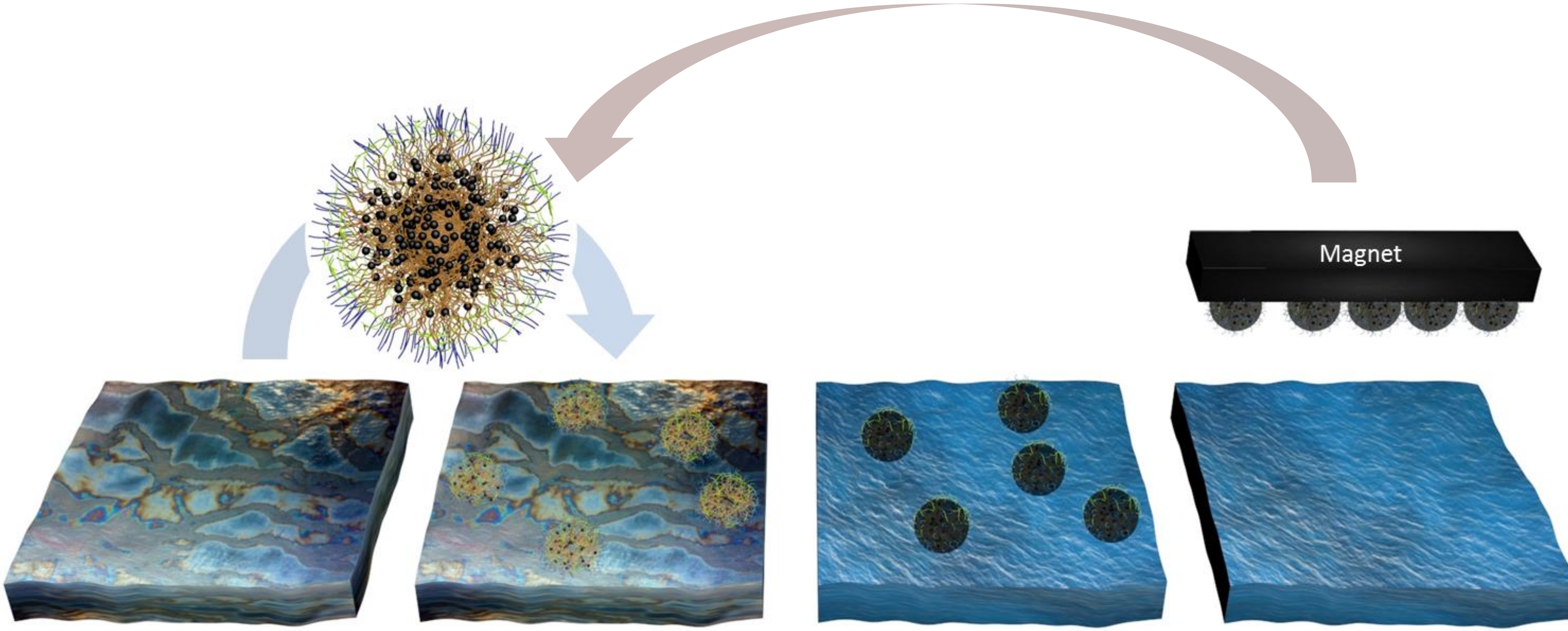
Magnetic Shell Crosslinked Knedel-like (MSCK) Nanoparticles

- Shell cross-linked protects micelles and stabilizes vessel
- Entrapped magnetic iron oxide nanoparticles
- High density NP loading



- Amphiphilic core-shell morphology:
- Hydrophilic shell allows for suspension of material in water
- Hydrophobic core preferentially sequesters hydrophobic pollutants

Mode of Deployment of MSCKs



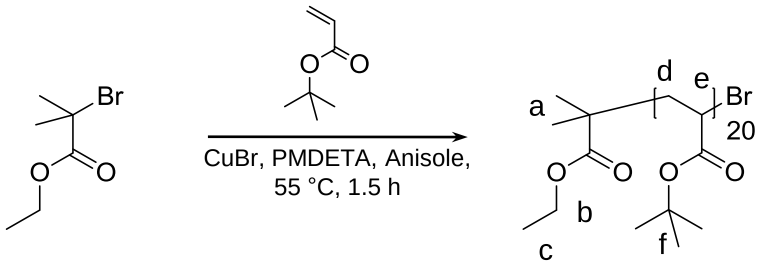
Addition of MSCKs to polluted water

Sequestration of pollutants by MSCKs

Removal of loaded MSCKs *via* magnetic force

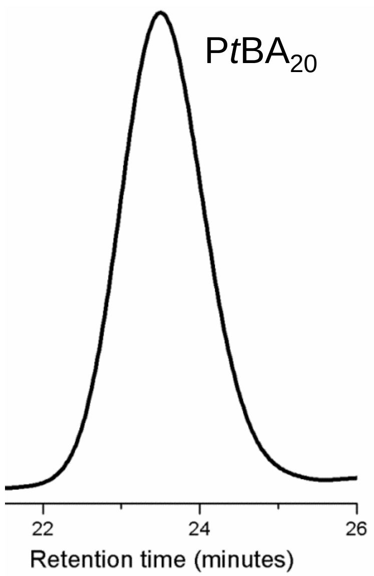
Synthesis of (PAA_{20}-*b*-PS_{280}) Amphiphilic Diblock Copolymer

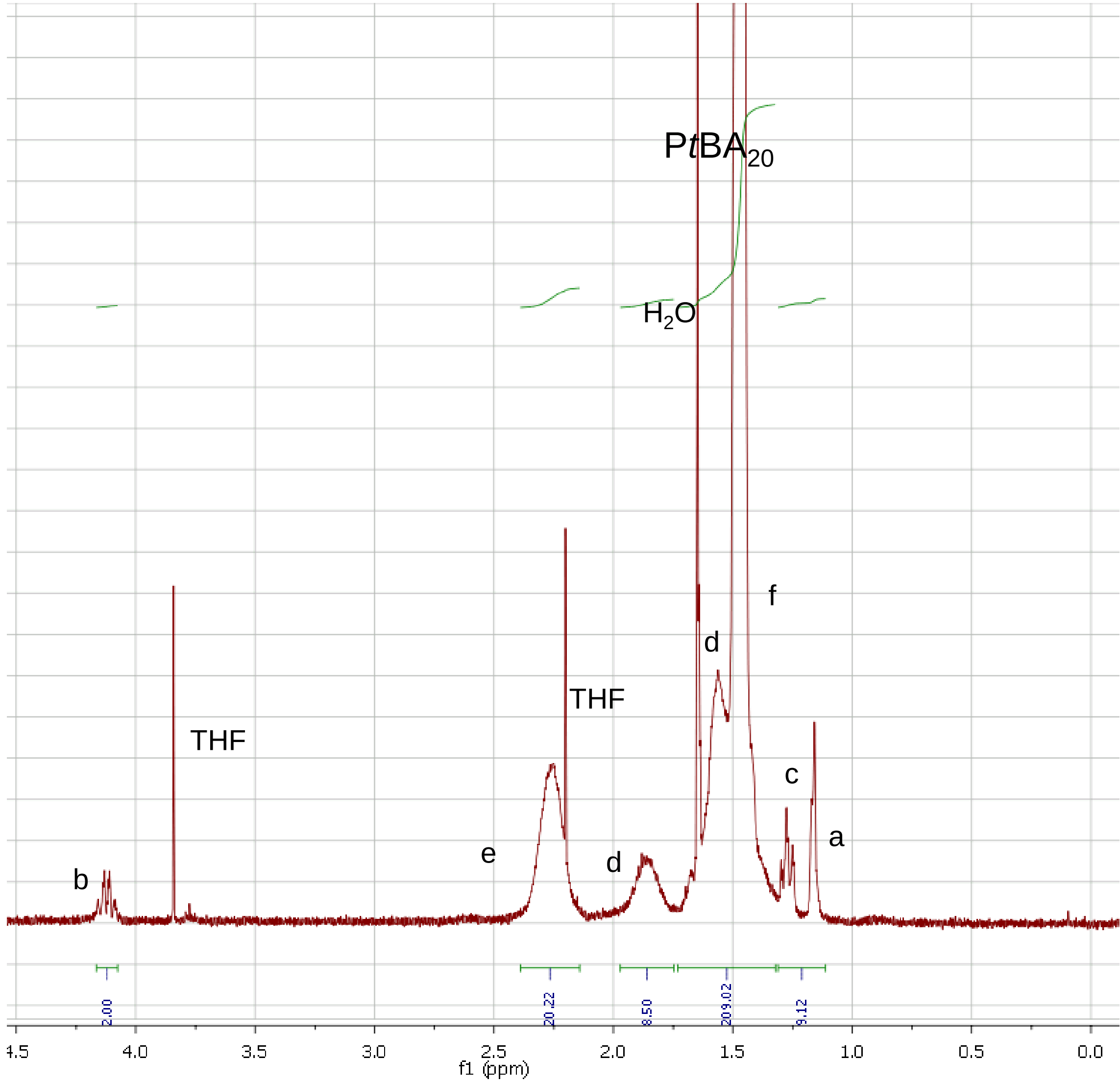
Atom Transfer Radical Polymerization (ATRP)



95%
conversion
40% yield

M_n (theo)= 3,600 Da
M_n (NMR)= 3,100 Da
M_n (GPC)= 3,200 Da
PDI= 1.11





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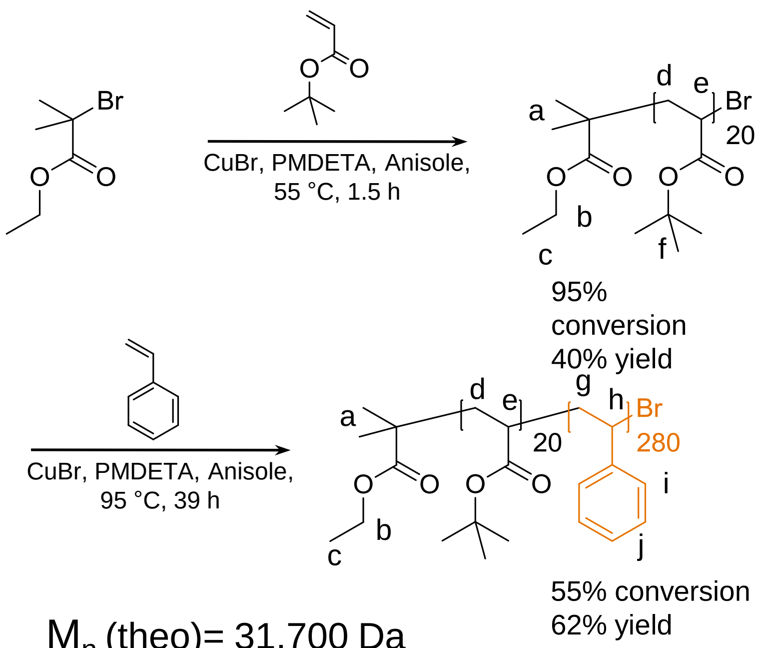
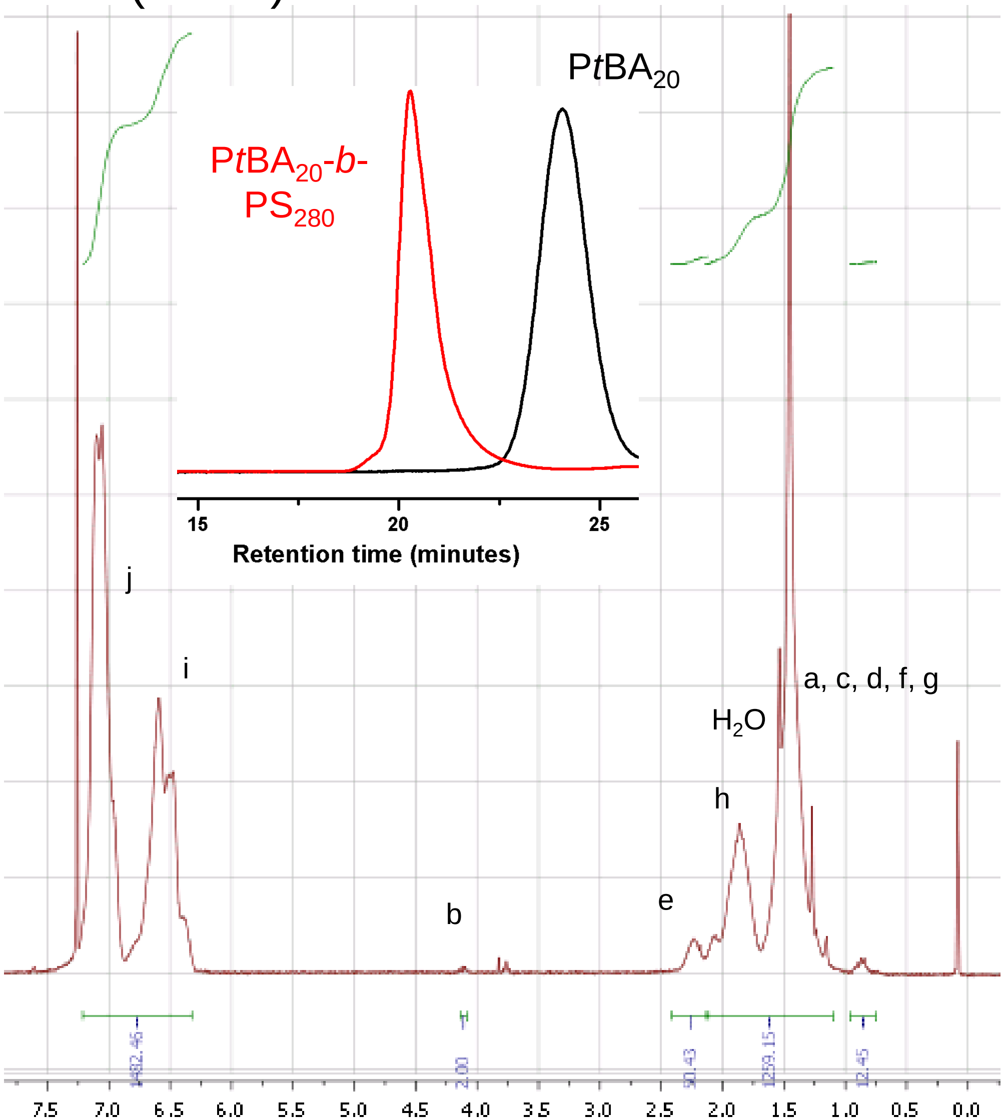


M_n (theo)= 31,700 Da
M_n (NMR)= 26,400 Da
M_n (GPC)= 32,200 Da
PDI= 1.12



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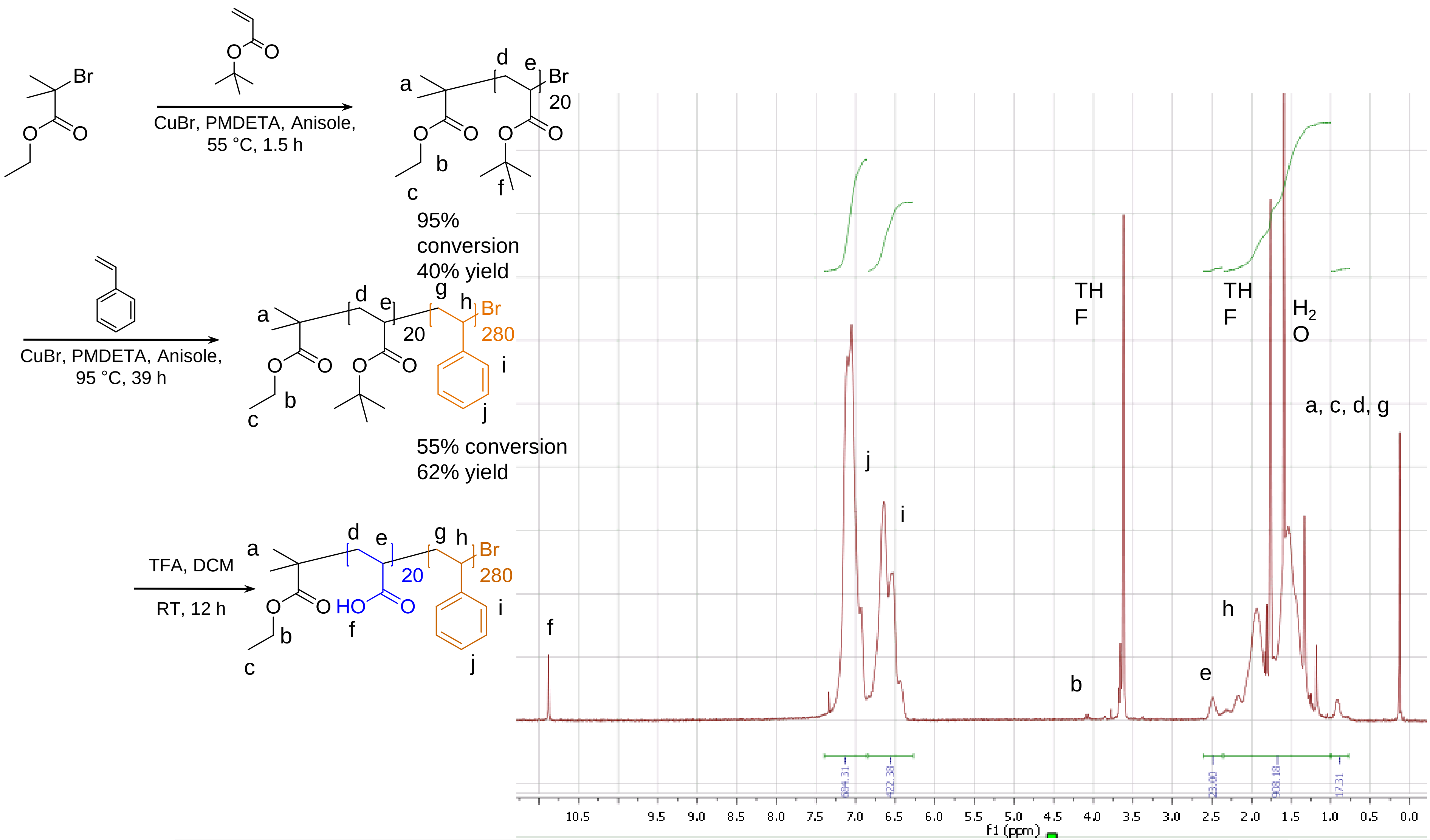
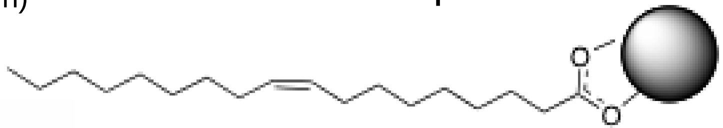
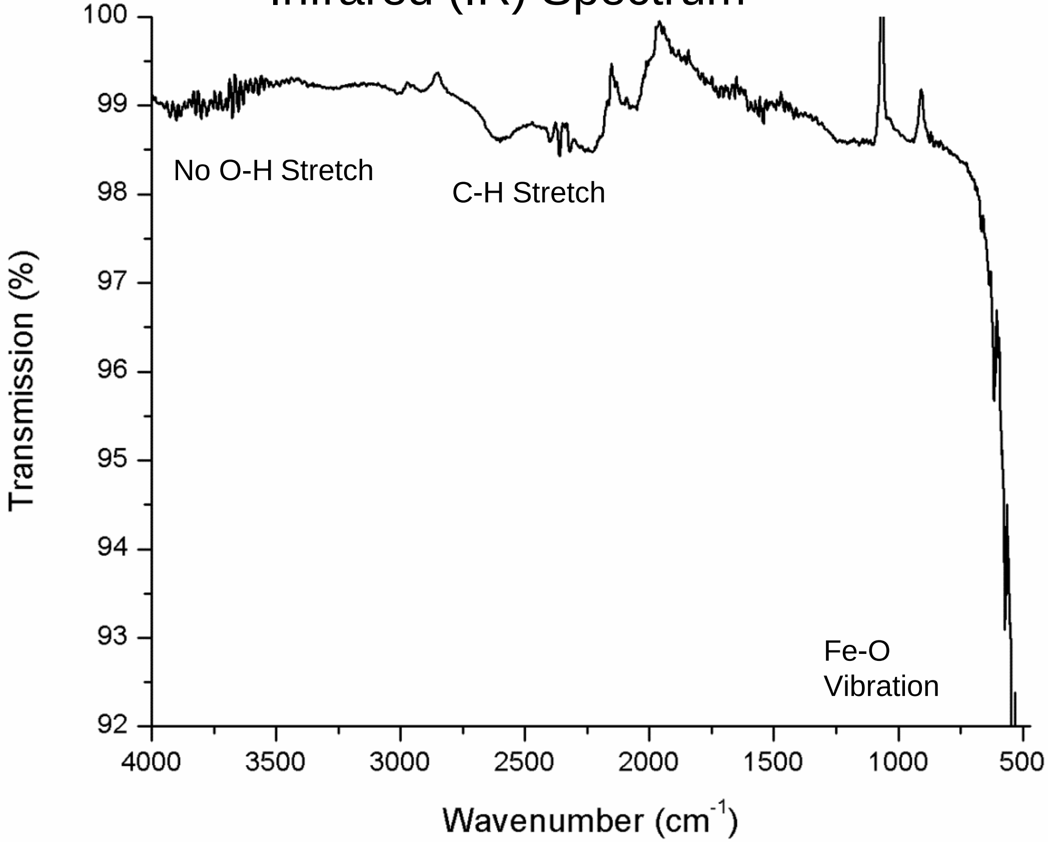


Thermolysis of Iron Oxide Nanoparticles

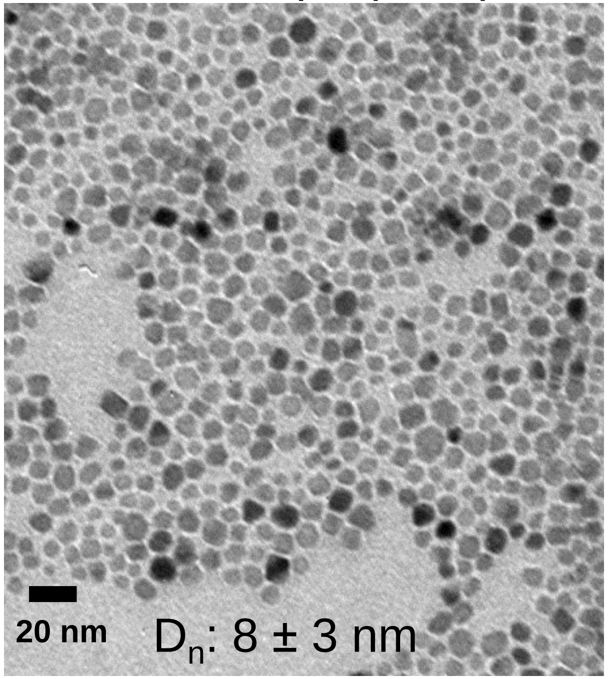
$Fe(acac)_3$ + Oleic acid —(Oleyl amine, 1,2-hexadecanediol, Benzyl ether; 140 °C→200 °C →250 °C (3 h))→ Iron oxide nanoparticles



Infrared (IR) Spectrum

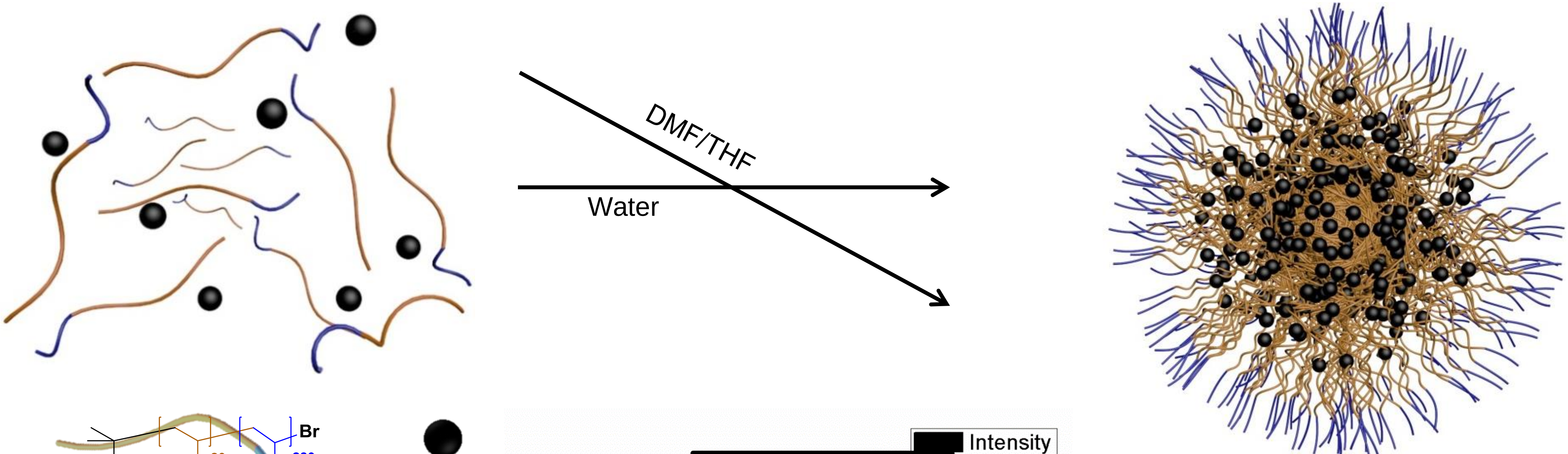


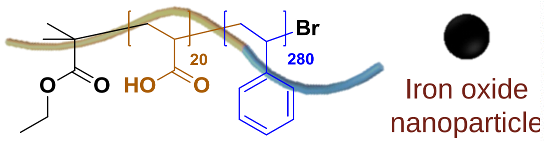
Transmission Electron Microscope (TEM)

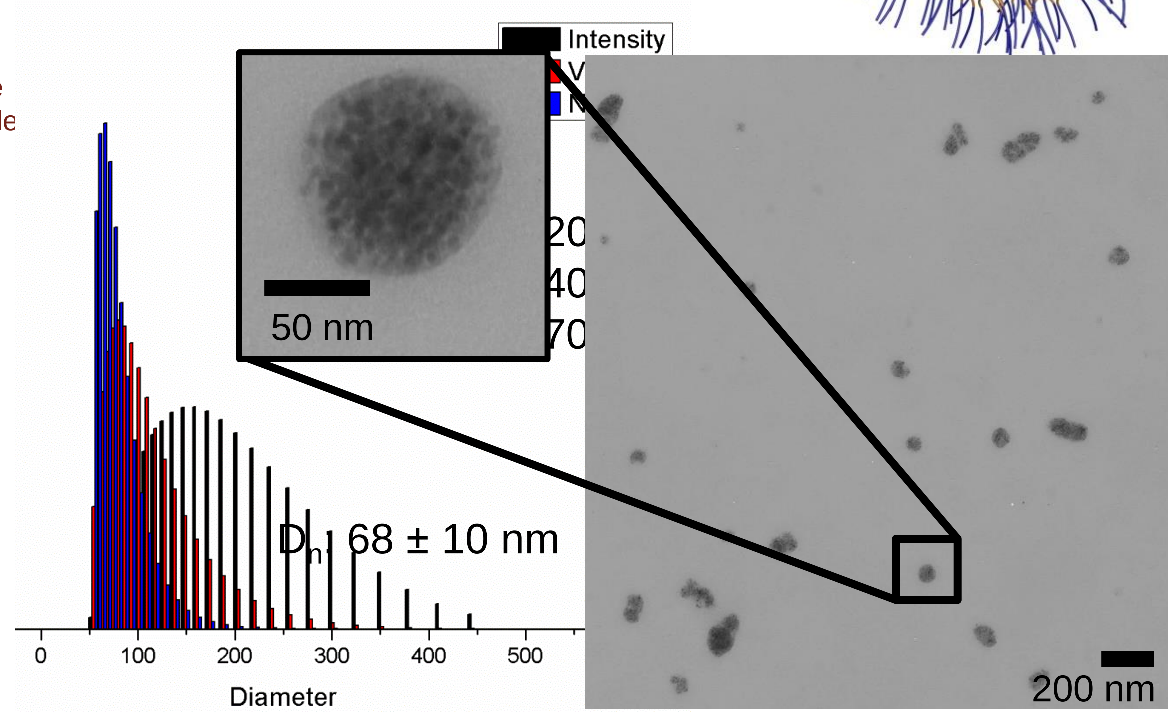


Superconducting Quantum Interference Device (SQUID) confirmed the magnetic character and determined the particle size to be 9.2 nm

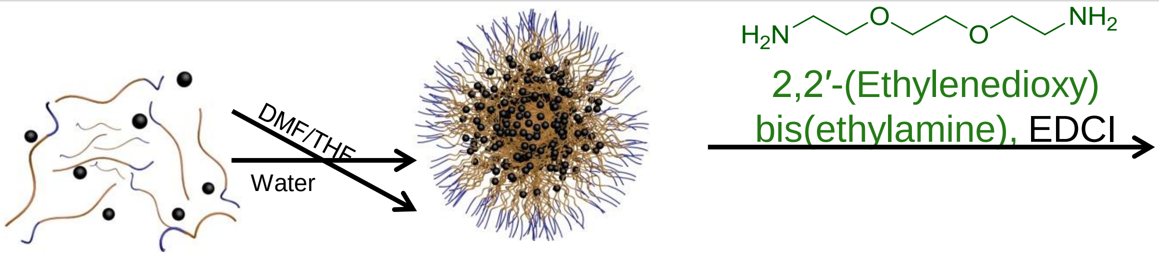
Co-Assembly and Characterization of Magneto Micelles

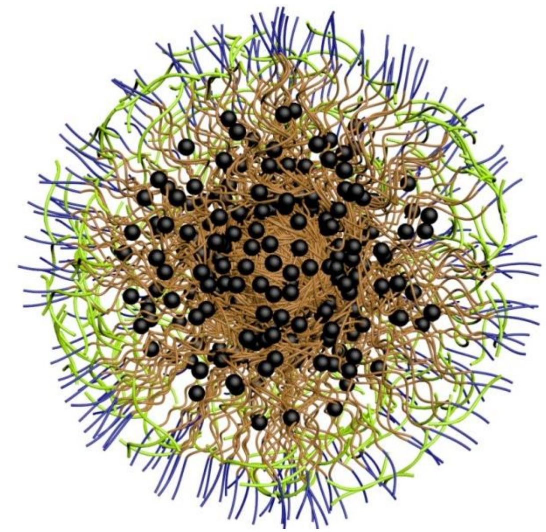






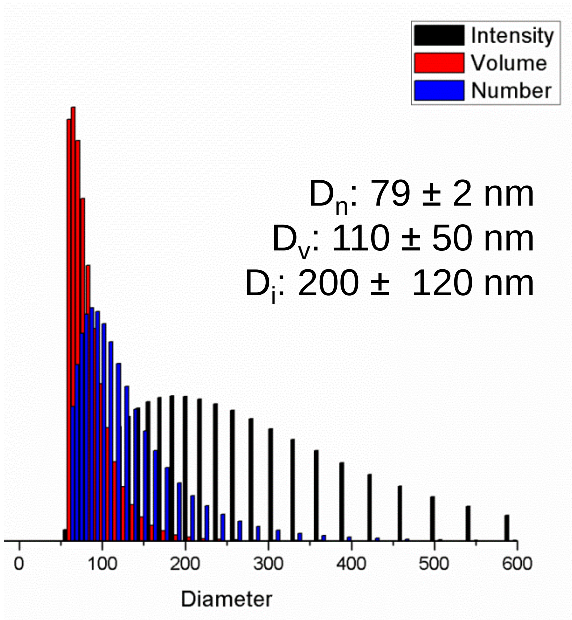
Crosslinking of Magneto Micelles

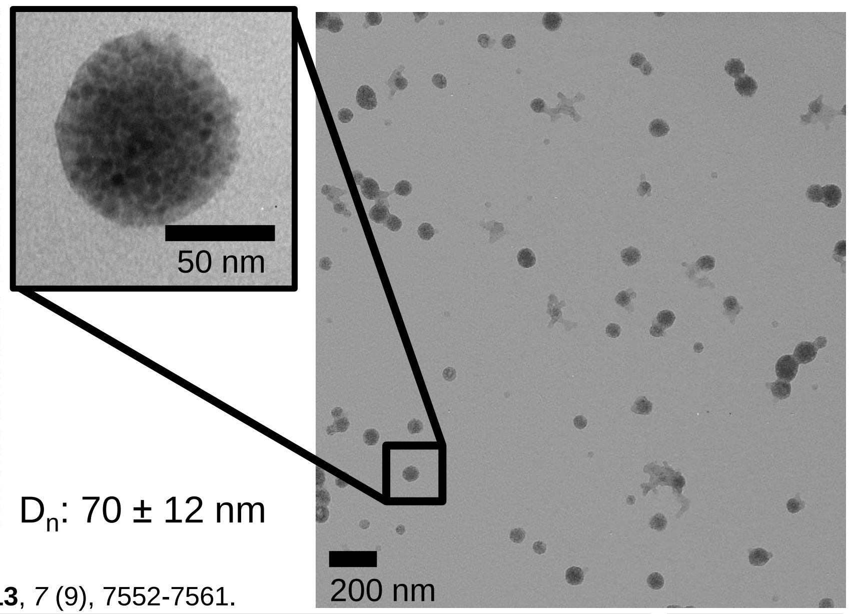




3D Tomography

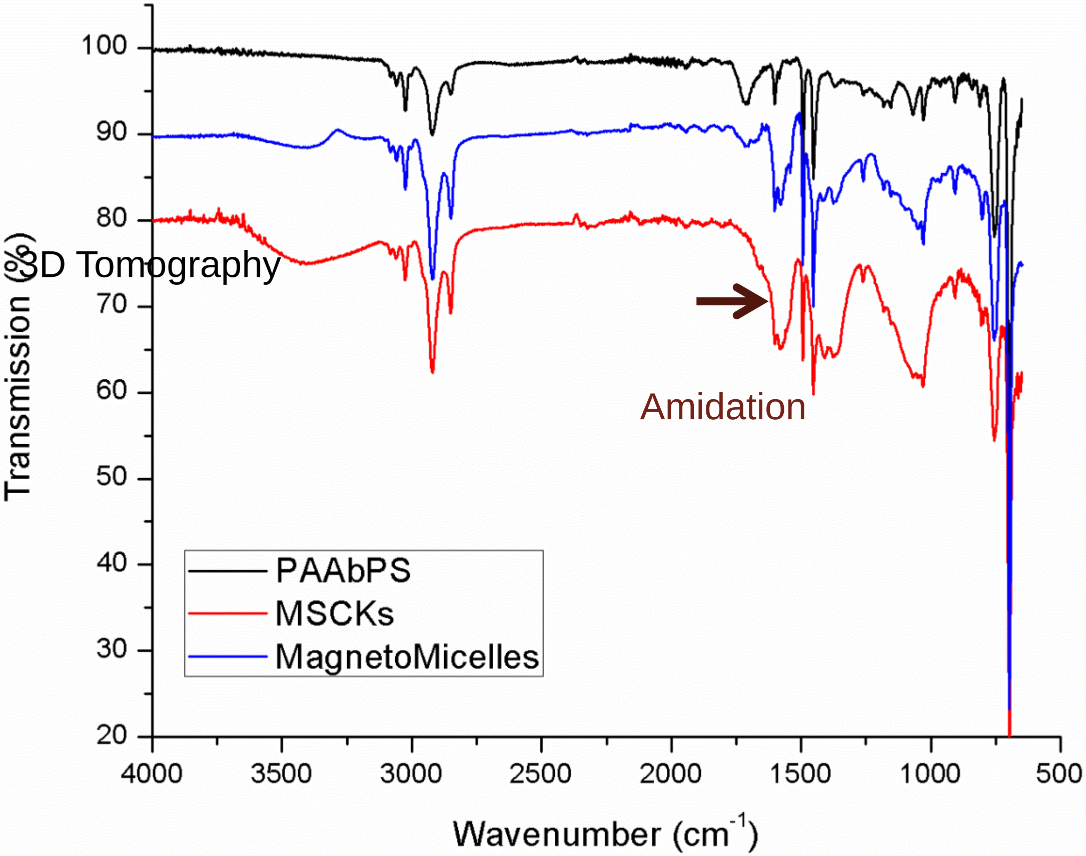
Well defined core-shell morphology observed in 3D scan



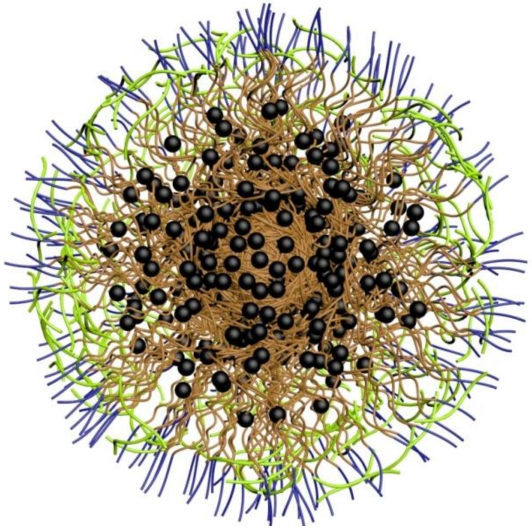


Pavia-Sanders, A.; Zhang, S.; Flores, J. A.; Sanders, J. E.; Wooley, K. L. *ACS Nano* **2013**, *7* (9), 7552-7561.

Crosslinking of Magneto Micelles



3D Tomography



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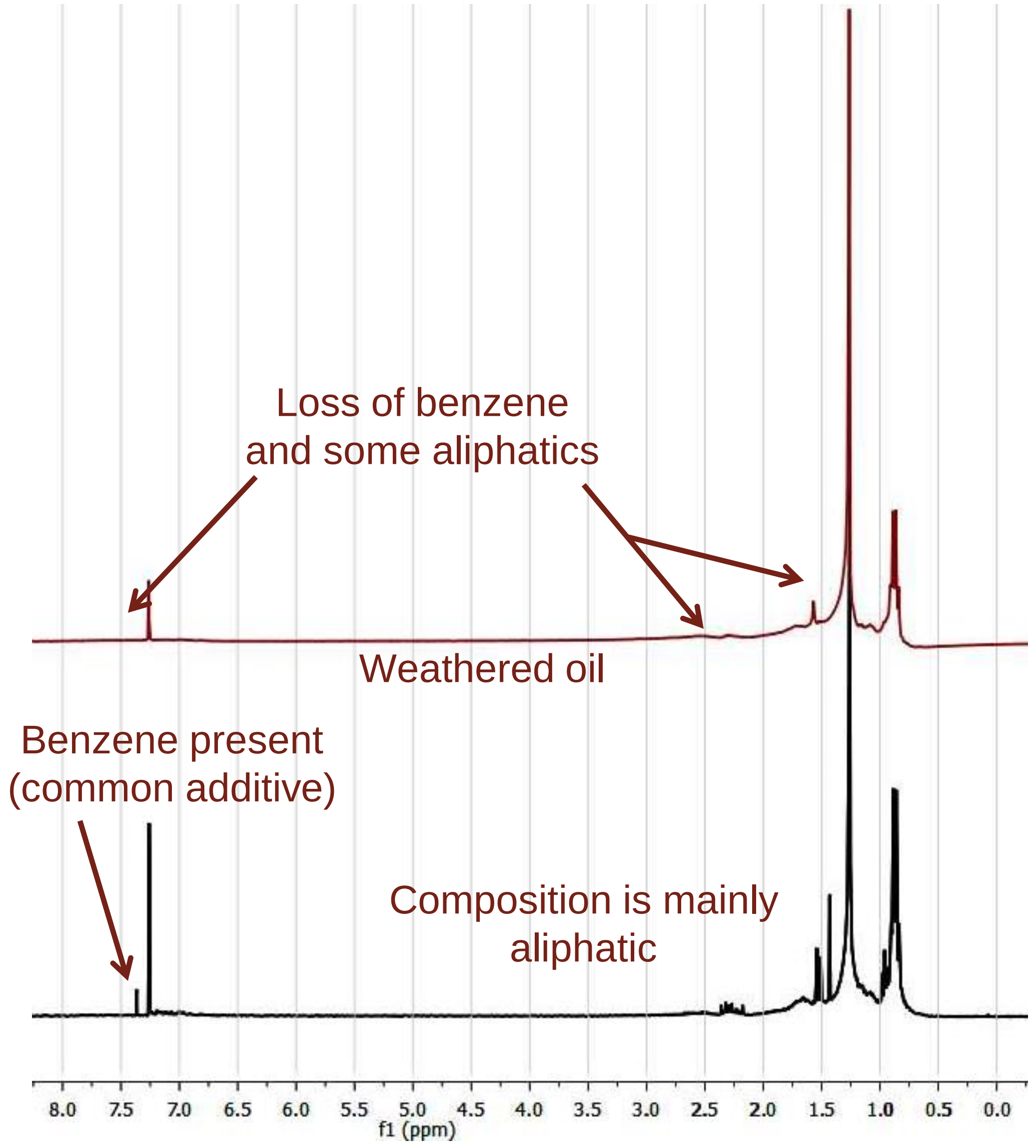
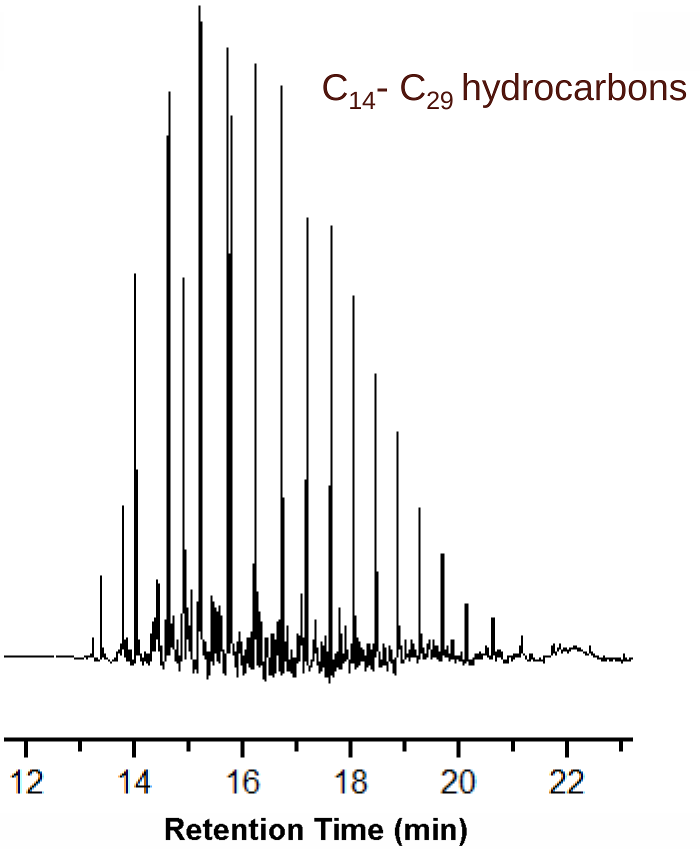
Crude Oil Characterization



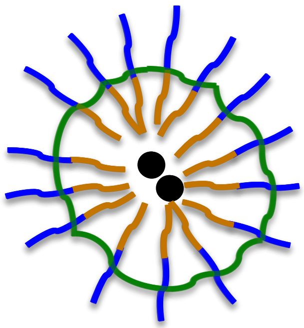
- Texas-Oklahoma pipeline
- Weathering of pollutant

Gas chromatography- mass spectrometry (GC-MS)



Crude oil provided by Enbridge Energy Partners, L.P.
U.S. Environmental Protection Agency

Oil Recovery Procedure

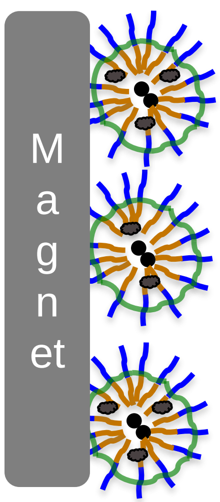


MSCKs

15-30 minutes

Crude oil

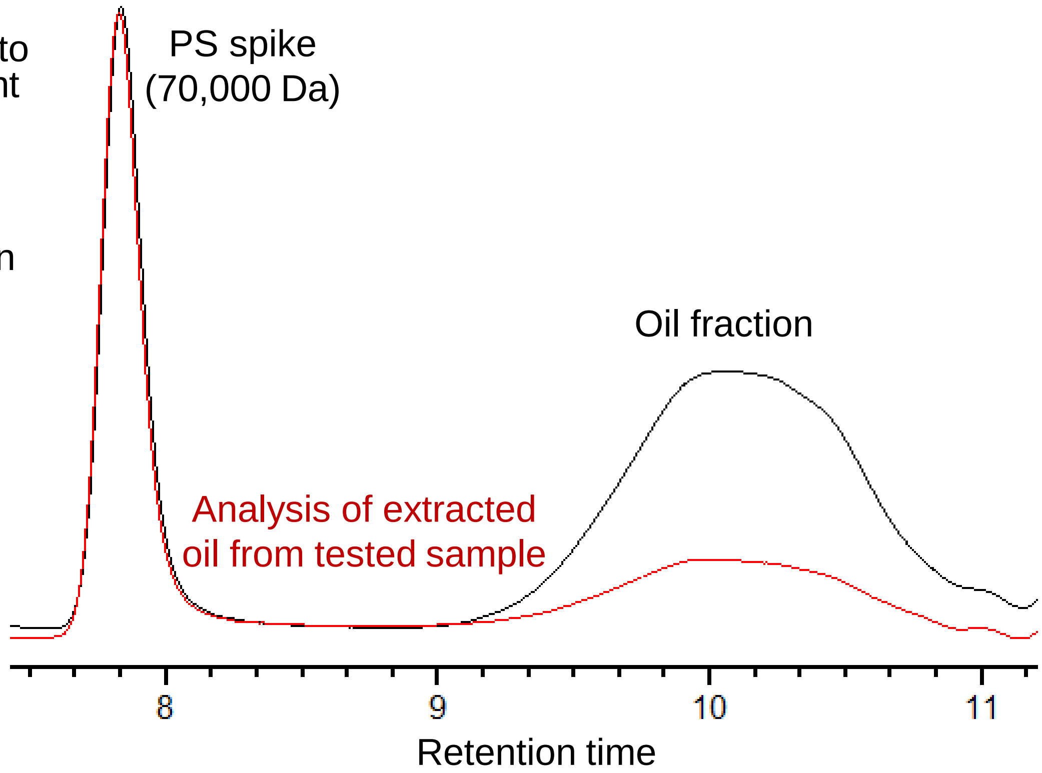
Extraction *via* magnet



- Water and remaining oil in tests were decanted into vial to allow for extraction without the presence of MSCKs
- Extraction of oil with chloroform
- GPC used for quantitative analysis

Oil Quantification

- Quantitative use of GPC
  - Refractive index (RI) is proportional to concentration and sample-dependent
- Control group and internal standard used
  - Determine relation between integration and sample concentration
- Quantify oil sequestered by MSCKs



$$k \cdot \frac{\int_{soil}}{\int_{spike}} = \frac{M_{oil}}{M_{spike}}$$

k: empirical coefficient

$$M_{oil} = \frac{M_{spike} \cdot \int_{soil} \cdot k}{\int_{spike}}$$

Representative Analysis

1:2.8 MSCK:Oil (Initial)

Sample	Oil (mV*Sec)	PS (mV*Sec)	Oil used (mg)
T1	116.1	155.2	13.6
T2	85.0	181.2	13.1
T3	136.5	184.5	14.8
C1	423.3	159.1	13.8
C2	414.5	190.5	13.7
C3	511.7	178.0	14.7

$$k = \frac{M_{oil} \cdot \int_{spike}}{M_{spike} \cdot \int_{soil}}$$

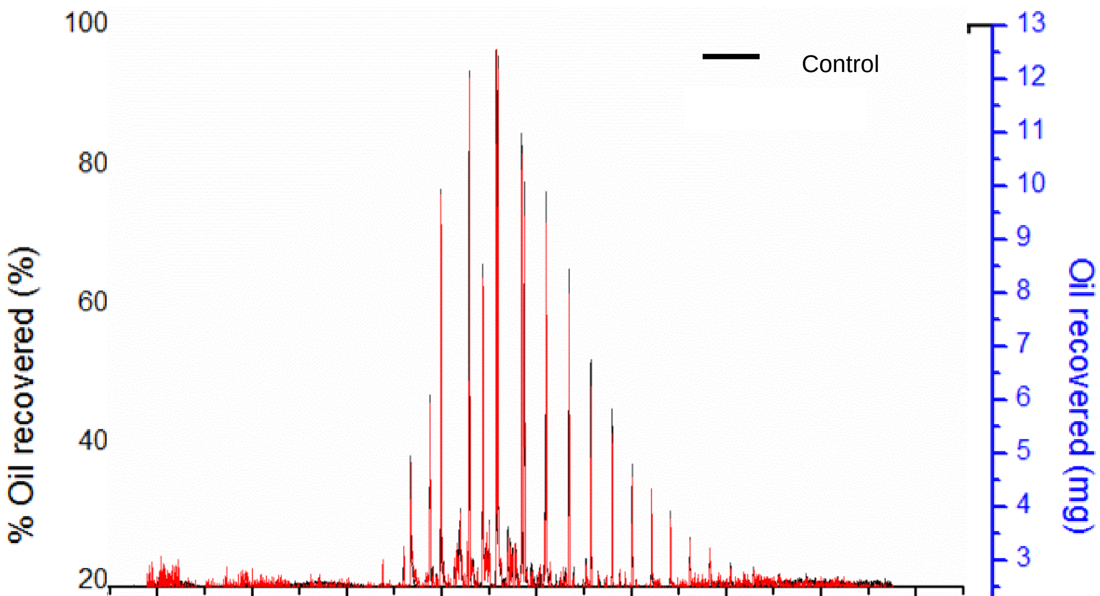
$$M_{oil} = \frac{M_{spike} \cdot \int_{soil} \cdot k}{\int_{spike}}$$

~10.2 mg of oil recovered
~5.0 mg of MSCKs used
1:2.1 ratio

~74% oil recovery

Sequestration Data and Oil Evaluation

Loading capacity plateauing ~10 mg oil/ 1 mg MSCK



Initial MSCK: Oil	Uptake ratio	% oil sequestered
1:2.8	1:2.1	74.0%
1:5.1	1:4.4	85.9%
1:11.5	1:9.6	81.2%
1:16.8	1:10.2	60.6%

MSCKs were washed in order to remove loaded oil
Reuse of system was tested at 1:15 and showed no loss of loading capabilities!

Initial MSCK: Oil	Uptake ratio	% oil sequestered
1:16.8	1:10.2	60.6%
1:15.7	1:10.9	67.0%

GC/MS analysis of extracted oil

No preferential uptake of oil fractions

Pavia-Sanders, A.; Zhang, S.; Flores, J. A.; Sanders, J. E.; Wooley, K. L. *ACS Nano* **2013**, *7* (9), 7552-7561.

MSCKs for Groundwater Remediation

- Aqueous environment *vs.* groundwater environment
  - Preferential flow paths
  - Adsorption
  - Absorption
  - Non-aqueous phase

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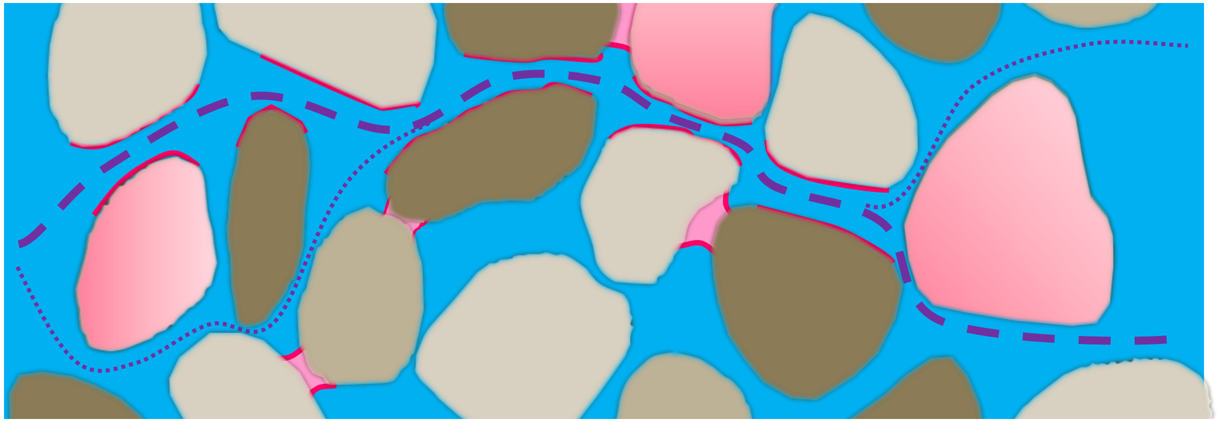
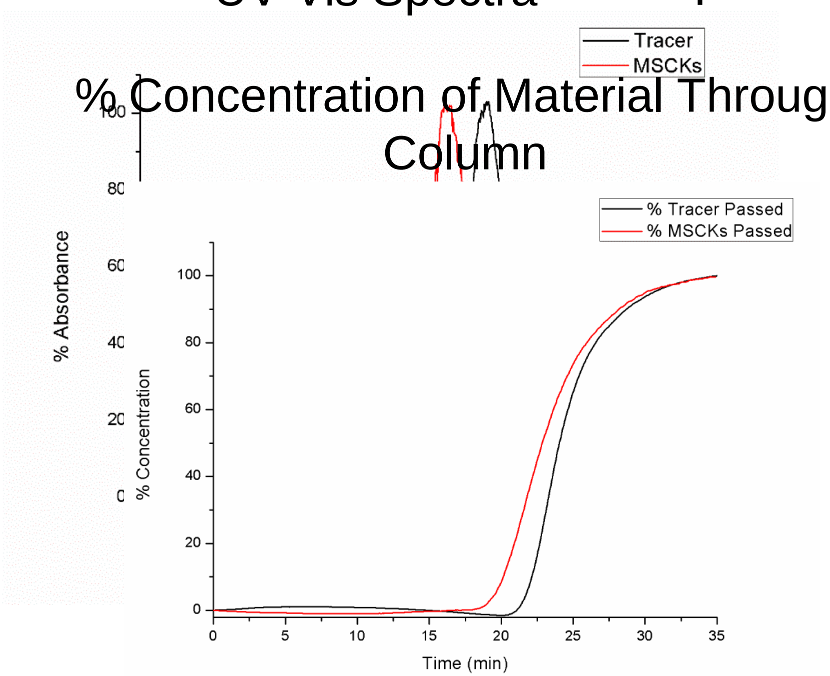


Experimental Setup & Breakthrough Curves

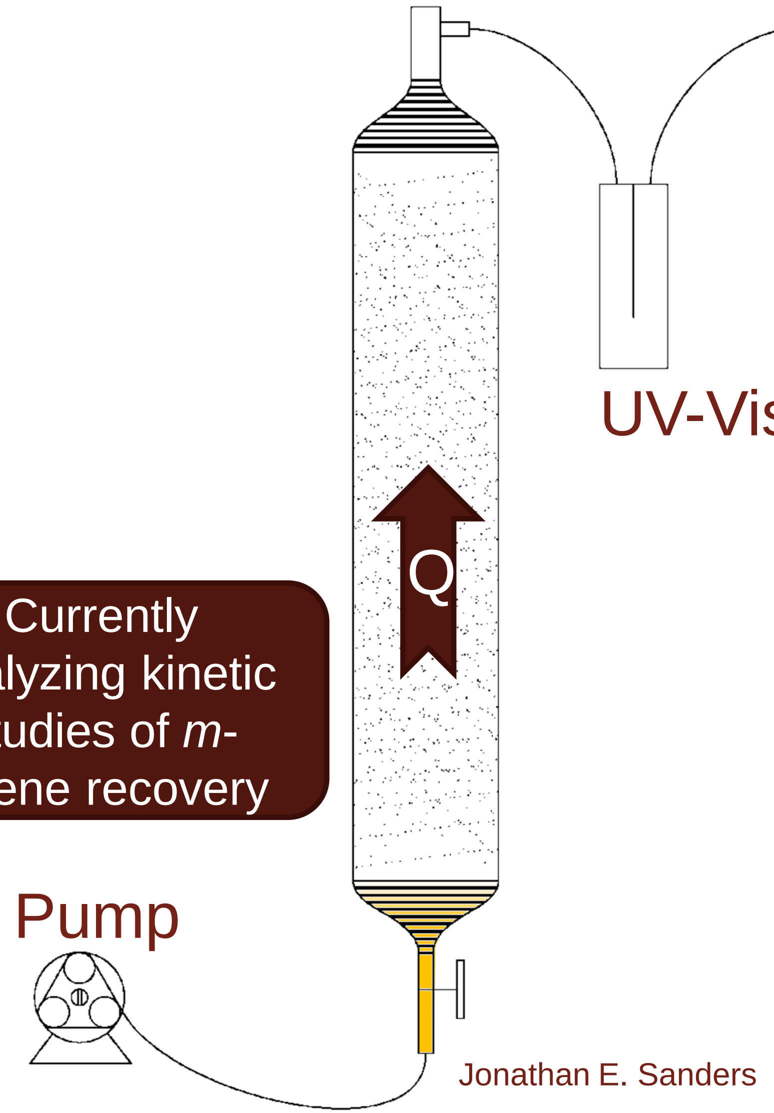
- Conservative tracer through saturated sand column (black)
- MSCKs through saturated sand column (red)
  - No adherence onto sand particles
- Quantitative yield of MSCKs calculated after column experiment

UV-Vis Spectra

% Concentration of Material Through Column



Currently analyzing kinetic studies of *m*-xylene recovery



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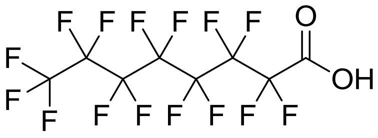
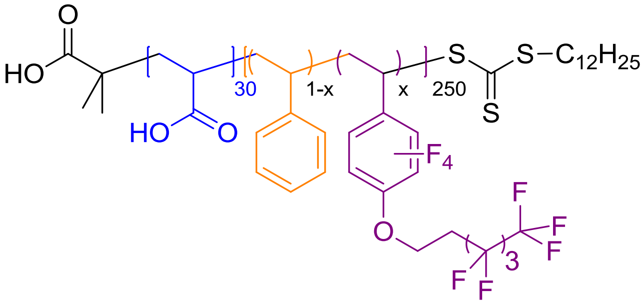
MSCKs for Groundwater Clean-up of Perfluorooctanoic acid



perfluorooctanoic acid

Broaden scope of MSCK system for environmental applications

- Persistent organic compounds (POC)
  - Perfluorooctanoic acid
- Common uses
  - Aqueous film-forming foams (AFFF)
  - Food packaging
  - Leveling agents for lubricants, paints, etc.
- Classified as persistent organic pollutants (POPs)
  - Found in virtually all people living in the industrialized world ($t_{1/2}$>4 yrs)
  - Growing evidence of toxicity
  - Resistant to biodegradation
  - Mobile in soils



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Advancements in oil spill remediation

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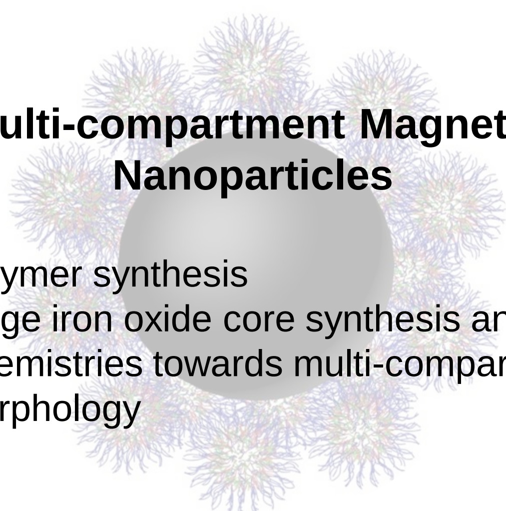
Oil sequestration by MSCKs
MSCK recycling and reuse
Use for groundwater remediation



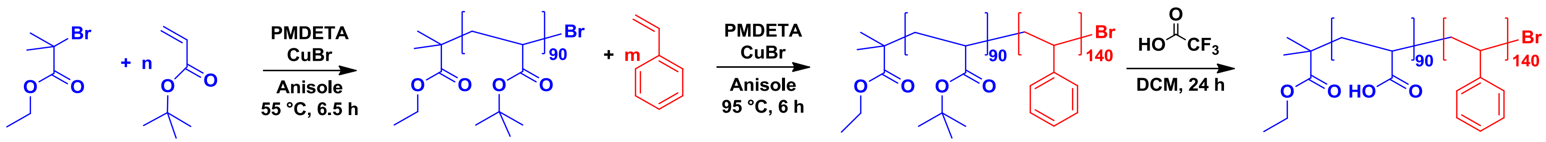
Multi-compartment Magnetic Nanoparticles

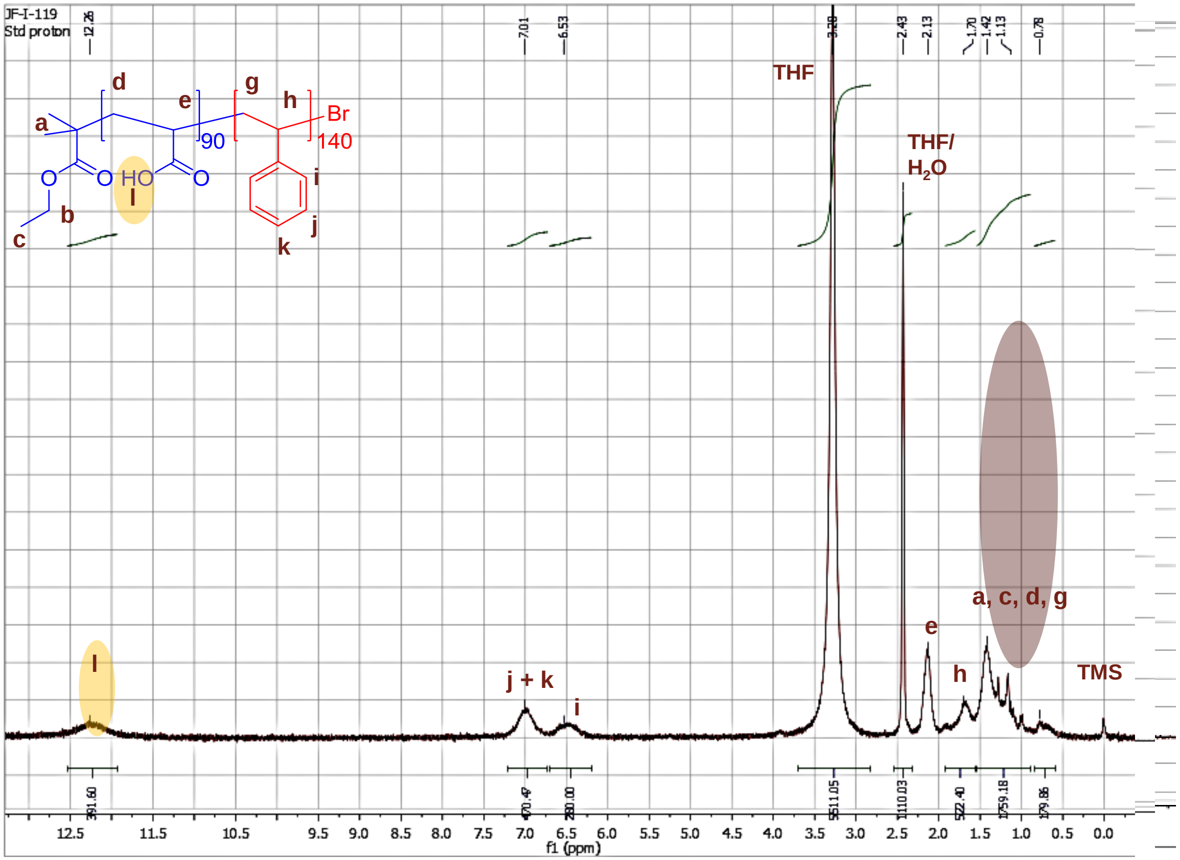
Polymer synthesis
Large iron oxide core synthesis and issues
Chemistries towards multi-compartment morphology

Multi-compartment Magnetic Nanoclusters

Polymer synthesis
Assembly

Synthesis of Block Copolymer for the Preparation of SCKs





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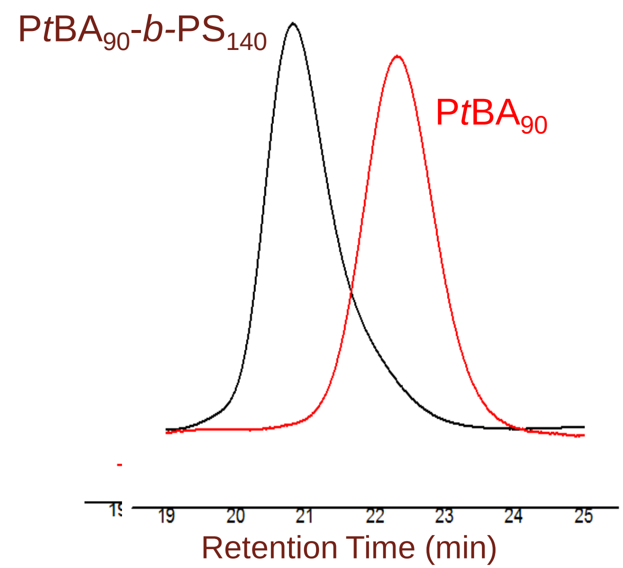


M_n (^{1}H NMR) = 13,400 Da

M_n (GPC) = 14,000 Da

PDI = 1.10

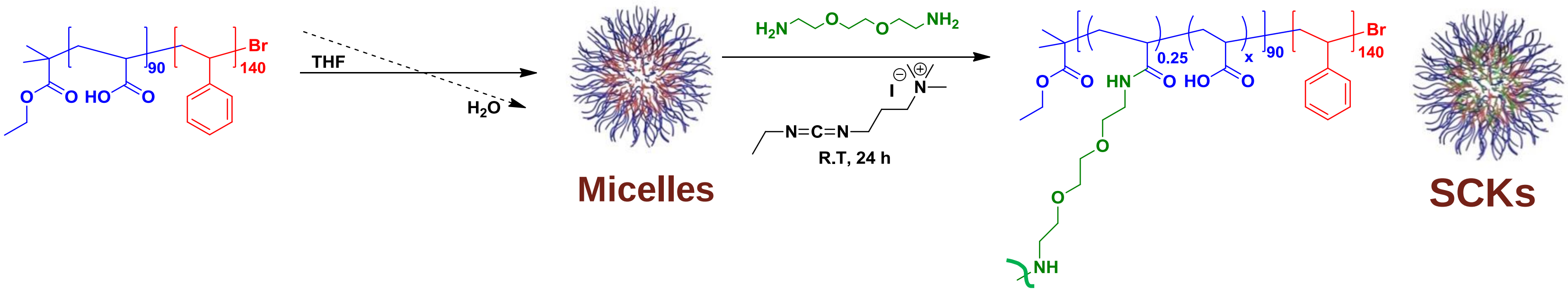
M_n (^{1}H NMR) = 28,000 Da

M_n (GPC) = 34,000 Da

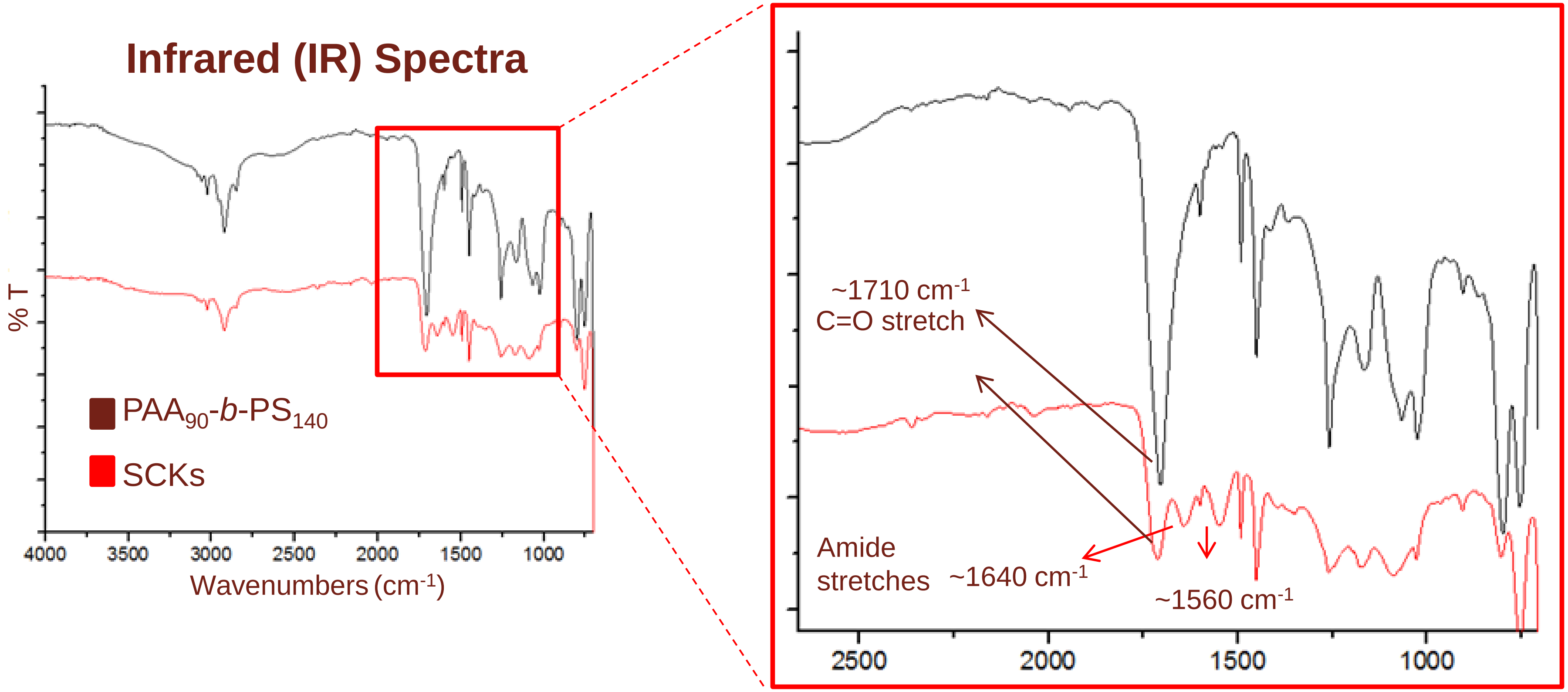
PDI = 1.12

ATRP: Atom Transfer Radical Polymerization

Self-assembly and Crosslinking of PAA_{90}-*b*-PS_{140} for the Synthesis of SCKs



Infrared (IR) Spectra



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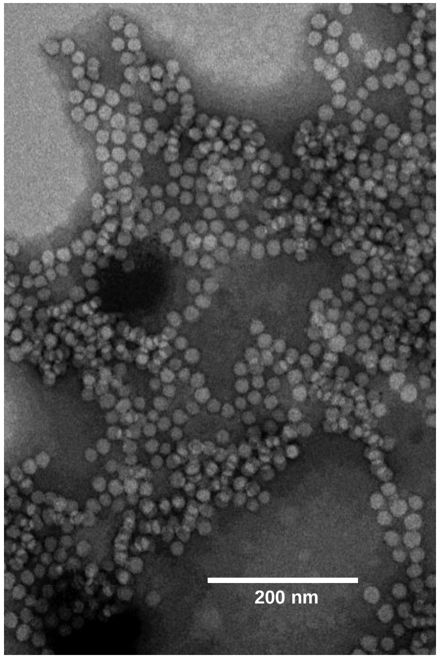
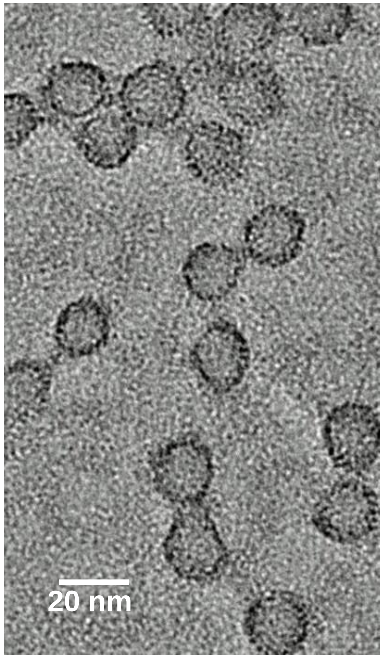
Characterization of SCKs

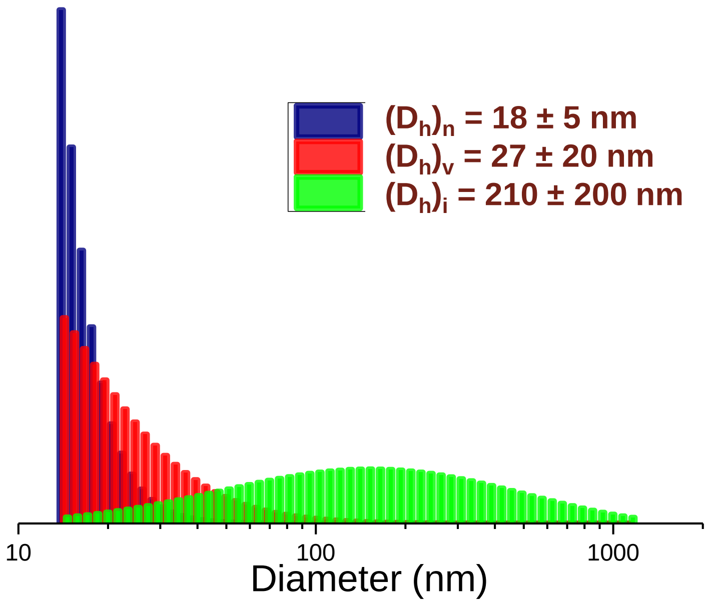
Transmission Electron Microscopy (TEM)





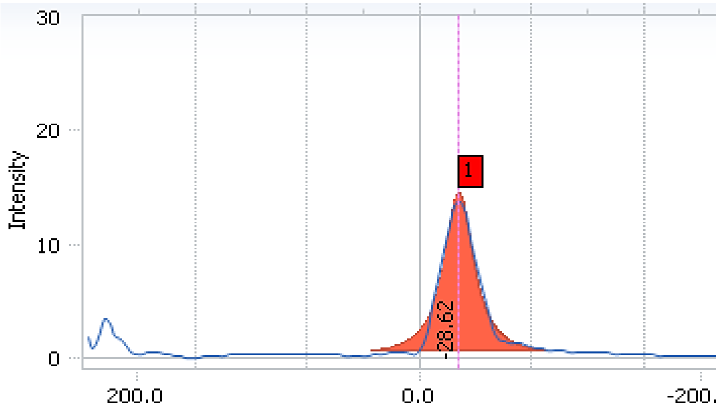
Average Diameter = 18 ± 2 nm

Dynamic Light Scattering (DLS)



Zeta Potential (mV)

ζ = -29 mV



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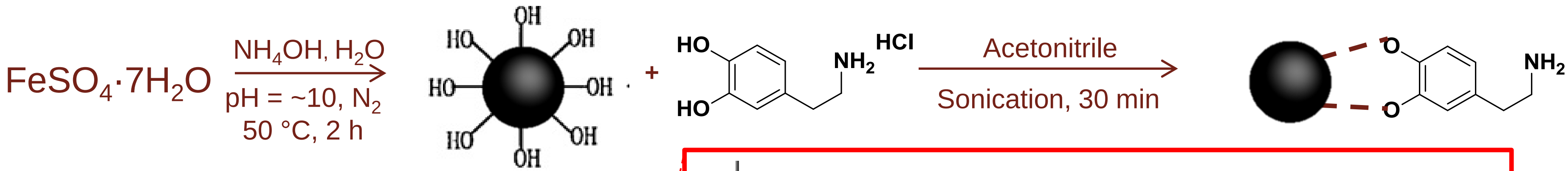
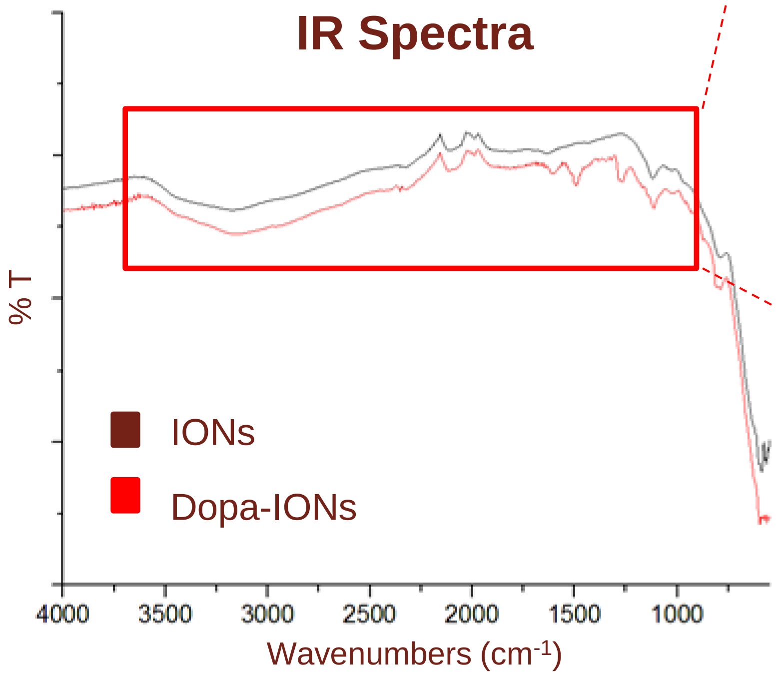
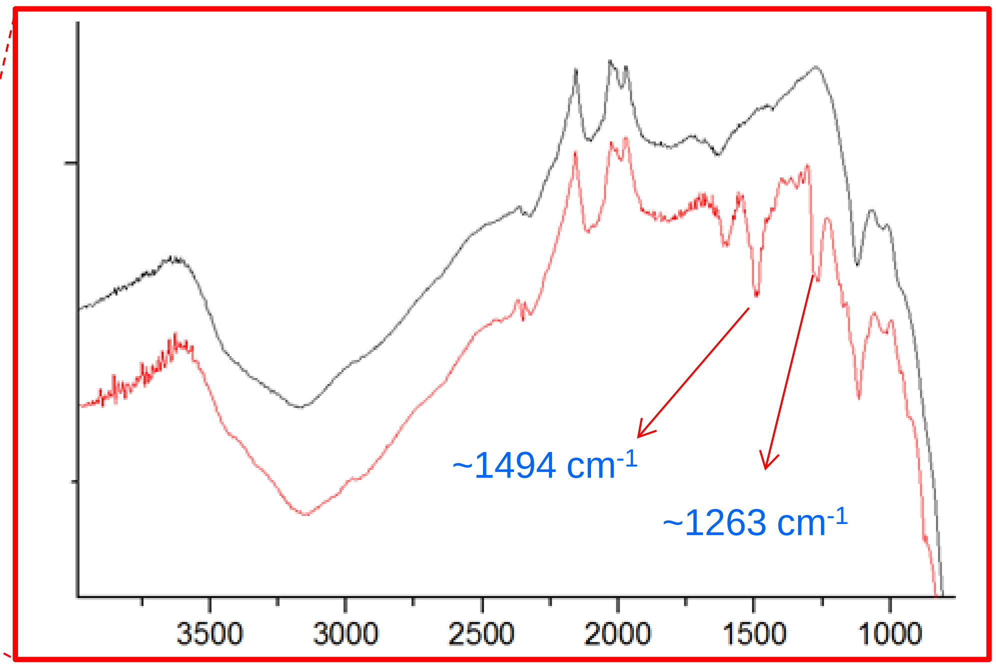
Synthesis and Characterization of Dopamine-coated Iron Oxide Nanoparticles (Dopa-IONs)







- ~ 1494 cm^{-1} overlap of C=C ring stretch band and CH_2 scissoring band

- ~ 1263 cm^{-1} C-O stretching of the catechol group

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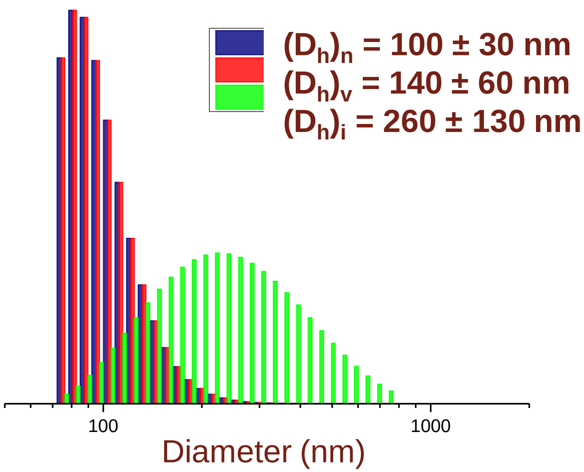
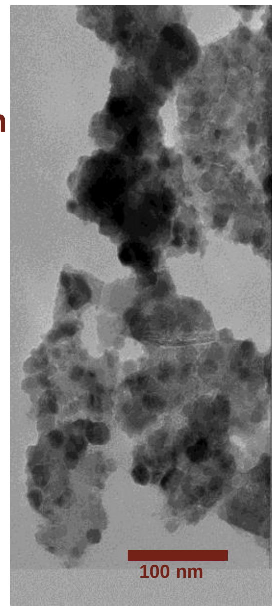
Characterization of Dopa-IONs and Comparison to Si-IONs

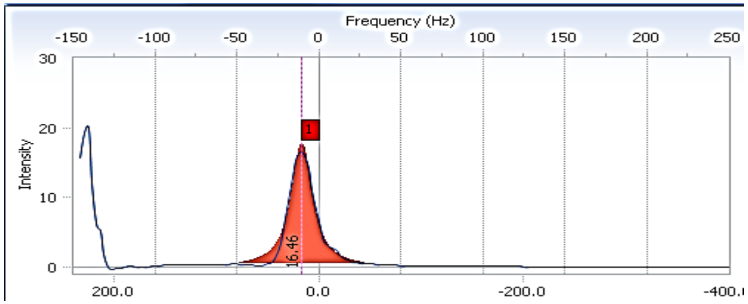
Characterization of Dopa-IONs



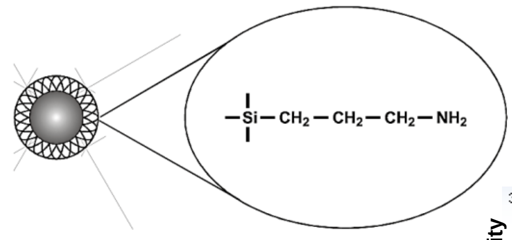


- TEM analysis showed agglomeration of particles in the dry state

ζ = 16 mV

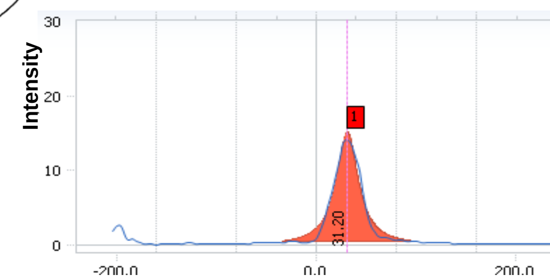


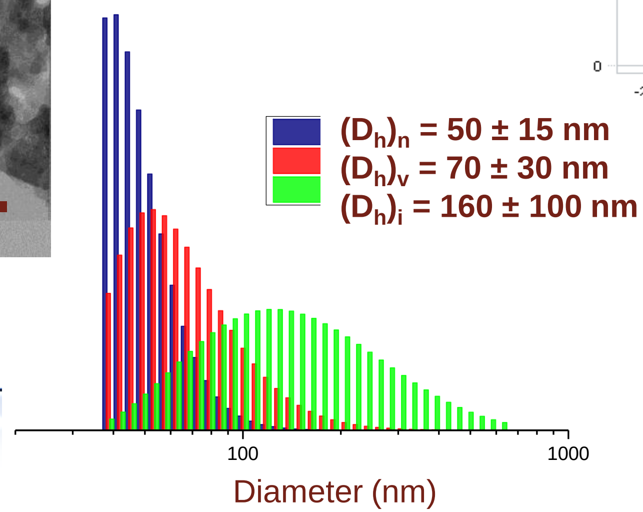
Characterization of Si-IONs

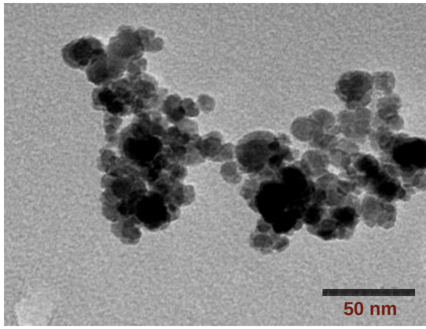


- Purchased from Chemicell GmbH

ζ = 31 mV

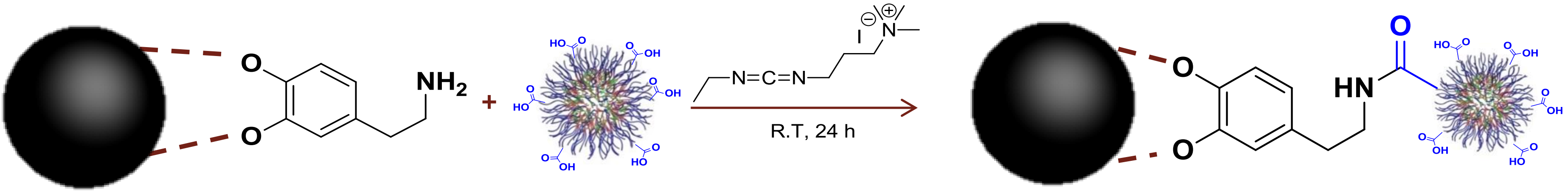




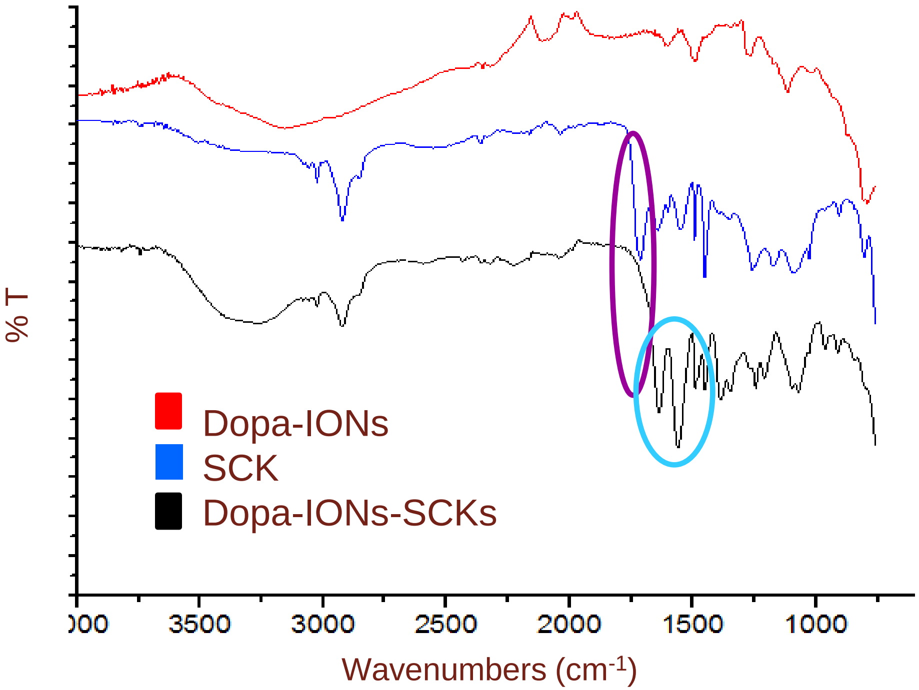


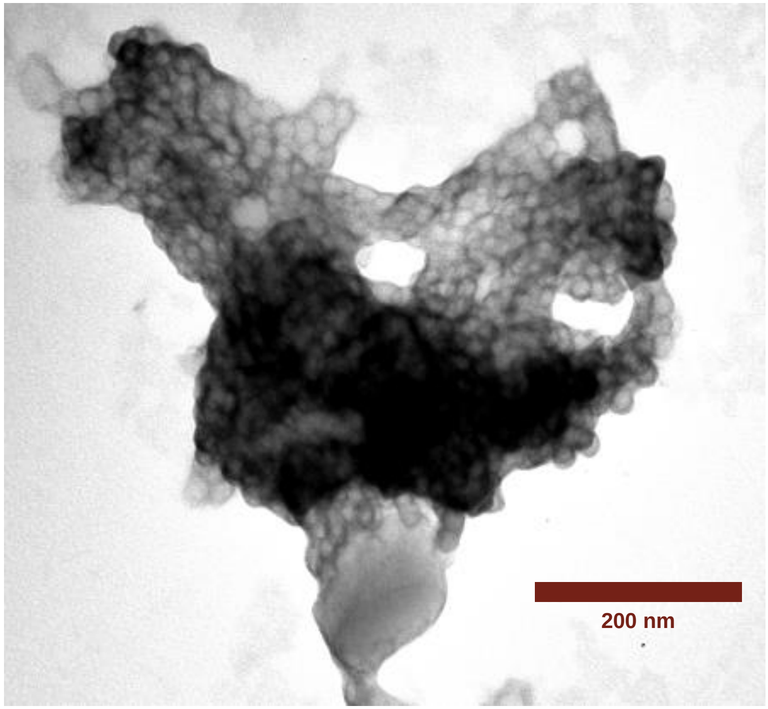
- TEM analysis showed a morphology similar to Dopa-IONs

Covalent Binding of Dopa-IONs to SCKs *via* Amidation Chemistry



IR Spectra





- Disappearance of the C=O stretch at *ca*. 1710 cm^{-1} and the increased intensity of amide signals at *ca.* 1560 cm^{-1} and 1640 cm^{-1}
- TEM analysis revealed formation of a hybrid network

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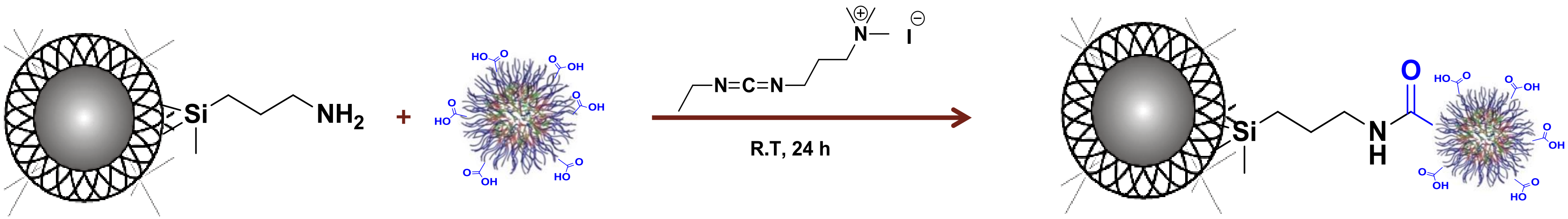
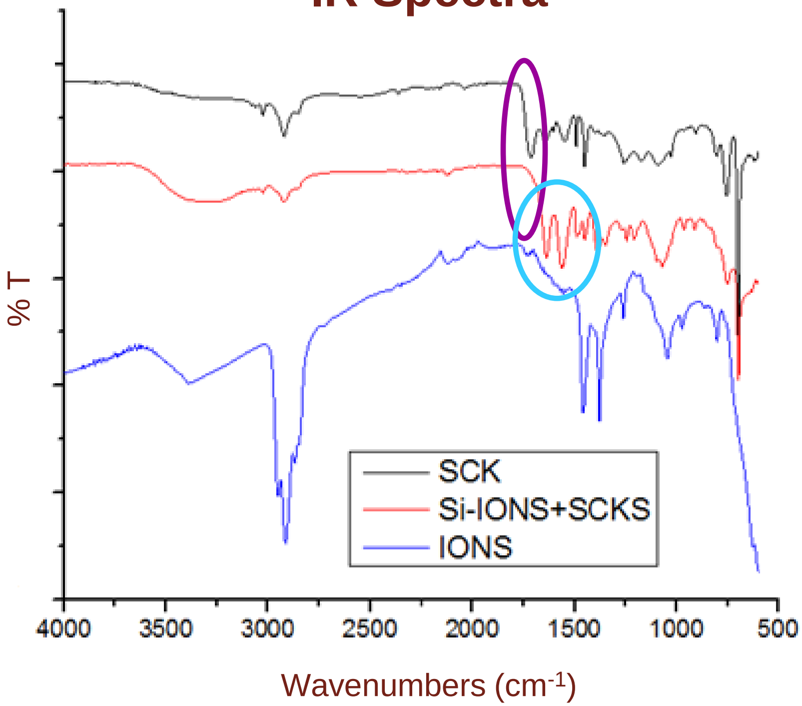
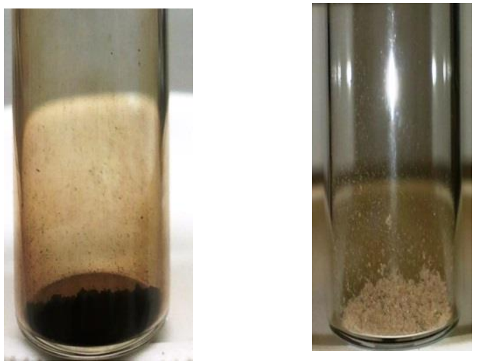
Covalent Binding of Si-IONs to SCKs *via* Amidation Chemistry







Si-IONs **Si-IONs-SCKs**

- IR spectra suggest formation of amide linkage

- Physical appearance indicates a combination of polymer and magnetic nanoparticles

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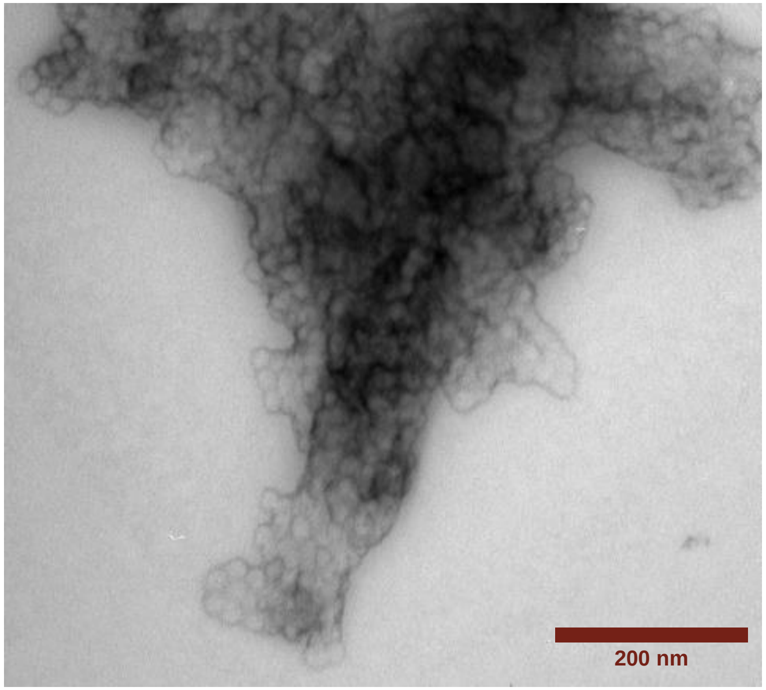
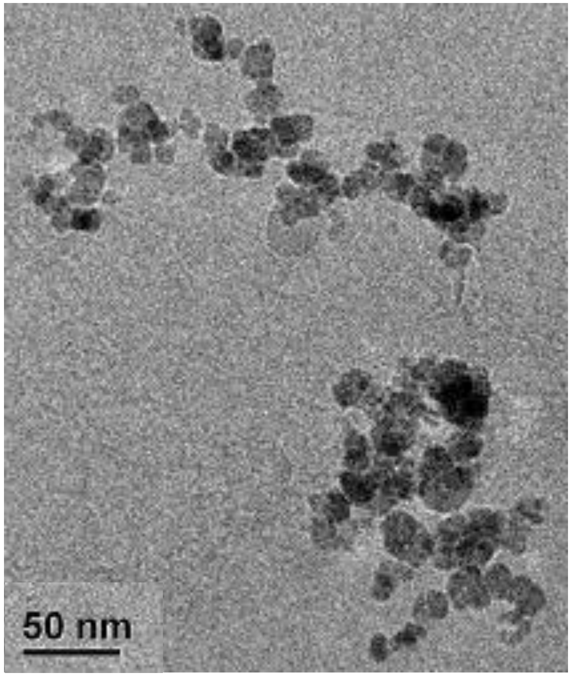
Characterization of Hybrid Nanoclusters and Future Directions

TEM Characterization of Si-IONs-SCKs



- Formation of a hybrid network
- Difficult to differentiate Si-IONs from areas of high concentration of stain
- Agglomeration of Si-IONs could be taking place even in solution

Cryogenic TEM Characterization of Si-IONs



- Agglomeration of particles is a problem even in solution

- Further morphological characterization: AFM and SEM
- Application towards the capture of crude oil

Outline

Background

- Oil spills
- Current remediation methods
- Advancements in oil spill remediation

Magnetic Shell Crosslinked Knedel-Like Nanoparticles (MSCKs)

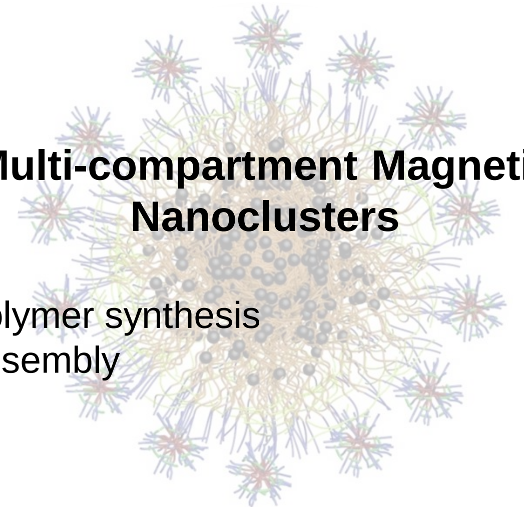
- Synthesis of components for MSCKs
- Co-assembly of components
- Oil sequestration by MSCKs
- MSCK recycling and reuse
- Use for groundwater remediation

Multi-compartment Magnetic Nanoparticles

- Polymer synthesis
- Large iron oxide core synthesis and issues
- Chemistries towards multi-compartment morphology

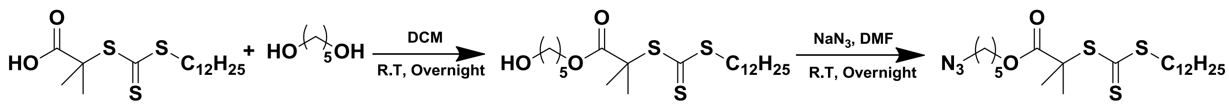
Multi-compartment Magnetic Nanoclusters

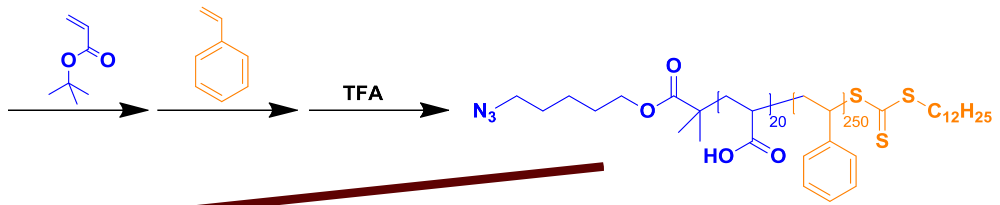
- Polymer synthesis
- Assembly

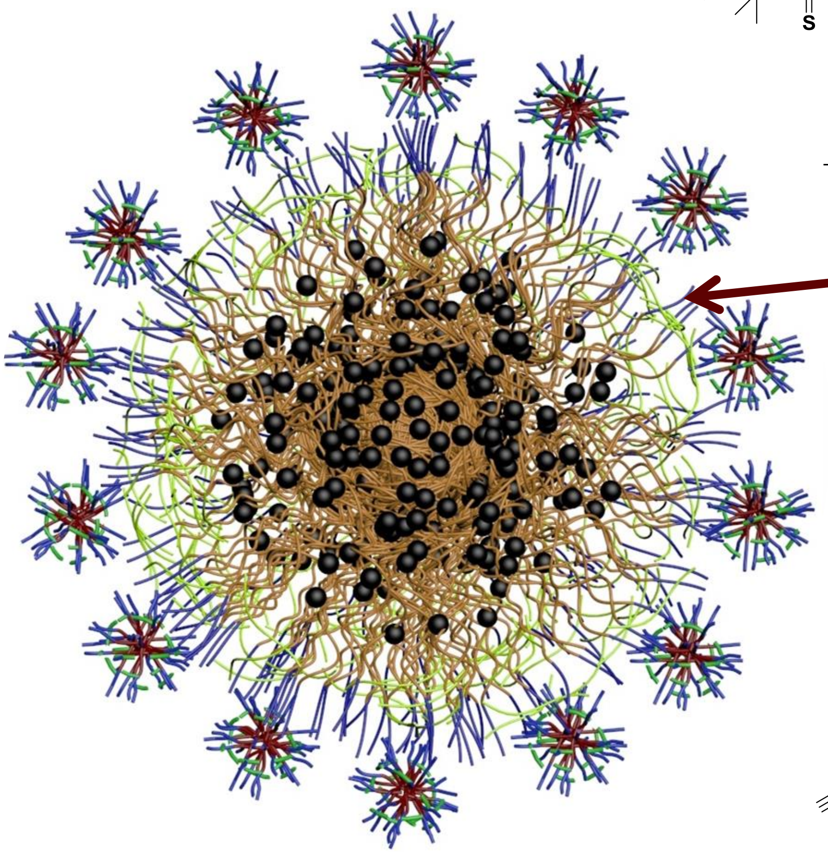


New Multi-compartment MSCK Nanoclusters

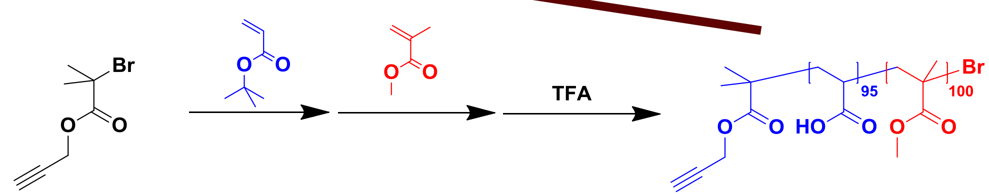
- Design for magnetic system incorporates MSCKs into the core of the structure
- Satellite shell crosslinked knedel-like nanoparticles (SCK)



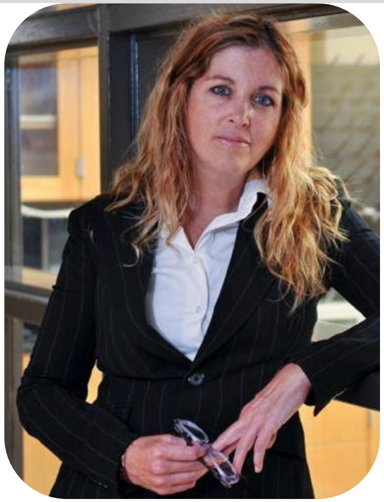




- Investigating conditions for the "click" chemistry of both components
- Determine other methods of characterization through anisotropy



Acknowledgements



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- Audience