



REU PROGRAM 2005  
NANOMATERIALS AND NANOTECHNOLOGY  
DARTMOUTH COLLEGE

# Self-Assembled Organometallic Copolymers as Templates for Ordered Arrays of Bimetallic Nanomagnets

Sean Haggerty – University of Vermont

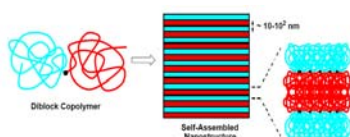
## Big Picture

- Why: Create a molecular switch for potential applications in magnetic storage devices (molecular size computer switch)
- Idea: Create bi-metal (alloy) nanowires
- How: Attach metal ligand (organometallic) structures to self-assembling nanostructures (block copolymers)
- Fabrication Method Comparison:
  - Engineering Method: Use lithography or electroplating; "top down" approach; more expensive and resource intensive
  - Chemistry Method: Use nature to form materials that self assemble on the nanometer scale to form a nanostructure; "bottom up" approach; simpler and cheaper; this poster outlines the bottom up method

Glueck, David S.; Grubbs, Robert P.; Soh, Yeong-An. Self Assembled Organometallic Block Copolymers as Templates for Ordered Arrays of Metal Nanomagnets. NSF-NIRT proposal 2004.

## Theory

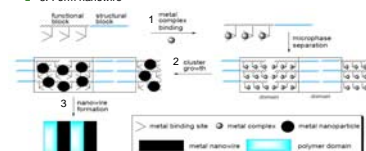
- Create a framework, out of polymers, then attach metals to one of the functional blocks
- How? Use a diblock copolymer: chains of two different polymers chemically linked at ends
- Polymers naturally phase separate to form distinct periodic layers



Glueck, David S.; Grubbs, Robert P.; Soh, Yeong-An. Self Assembled Organometallic Block Copolymers as Templates for Ordered Arrays of Metal Nanomagnets. NSF-NIRT proposal 2004.

## Theory

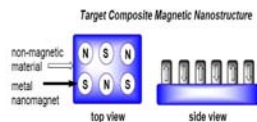
- Steps used to create diblock copolymer-template formation of metal nanowires
  1. Attach metal to polymer
  2. Heat to burn off carbon monoxide attached to metal
  3. Form nanowire



Glueck, David S.; Grubbs, Robert P.; Soh, Yeong-An. Self Assembled Organometallic Block Copolymers as Templates for Ordered Arrays of Metal Nanomagnets. NSF-NIRT proposal 2004.

## Aligned Metal Nanomagnets for Data Storage

- Single domain metal nanowires with two magnetization states in non-magnetic matrix (polymer)
- Possible one-bit per particle media recording using up or down spin characteristic of metal alloy, this is equivalent to a computer switch which uses binary code, a 1 or 0
- Detection of the up or down spin using magnetic force microscopy

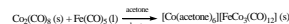


Glueck, David S.; Grubbs, Robert P.; Soh, Yeong-An. Self Assembled Organometallic Block Copolymers as Templates for Ordered Arrays of Metal Nanomagnets. NSF-NIRT proposal 2004.

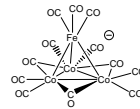
## My Project Goals

1. Make 3 organo-bimetallic compounds from literature references
2. Use alkyne-functionalized polymers to exploit known binding characteristics of cobalt carbonyl fragments to make precursors to bi-metallic nanoparticles
3. Characterize using IR (Inferred Spectroscopy), TEM (Transmission Electron Microscopy), AFM (Atomic Force Microscopy) and DSC (Differential Scanning Calorimetry)
4. Heat compound to drive off CO to reorganize and form bimetallic nanoparticle clusters
5. Characterize using IR, TEM, AFM and DSC

## Metal Complex 1: Co<sub>3</sub>Fe - Purple



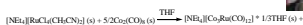
- Reactant for 2<sup>nd</sup> reaction not commercially available, synthesized using literature reference
- Metal complex formed stabilized by CO
- 1<sup>st</sup> attempt to synthesize failed because reaction carried out in air, the purple-sludge could not be collected, indicated the compound is air sensitive
- 2<sup>nd</sup> attempt successful when reaction performed under nitrogen gas
- Characterized product using infrared spectroscopy



1. Braunstein, P.; Rose, J.; Bars, O. J. Organomet. Chem. 1983, 252, C101-C105.  
2. Dehand, J.; Rose, J. Inorg. Chim. Acta 1979, 37, 249-253.

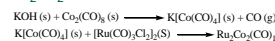
## Metal Complexes 2 and 3

### Co<sub>3</sub>Ru - Red



1. Roland, E.; Vahrenkamp, H. Angew. Chem.Int. Ed. 1981, 20, 679-680.  
2. Ellis, J. E.; Barger, P. T.; Winzenburg, M. L.; Warnock, G. F. Journal of Organometallic Chemistry 1990, 383, 521-530.

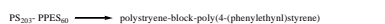
### Ru<sub>2</sub>Co<sub>2</sub> - Black



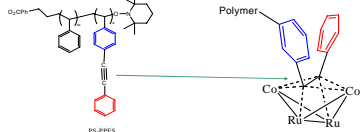
1. Coske, C. G.; Mays, M. J. J. Organomet. Chem. 1974, 74, 449-455.  
2. Aime, S.; Oestli, D.; Gobetto, R.; Johnson, B. F. G.; Milane, L. Inorganica Chimica Acta 1983, 68, 141-145.

## The Polymer and Bonding

- Alkyne-functionalized polymers chosen for known binding ability to cobalt carbonyl fragments
- Metal complex coordinates to triple bond between the two aromatic rings
- Polymer consists of polystyrene connected to the phenylethyne

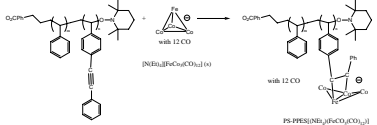
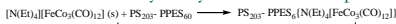


PS - 64%, PPES 36% Molecular Weight = 33641 g/mol  $M_w/M_n$  (SEC) = 1.27



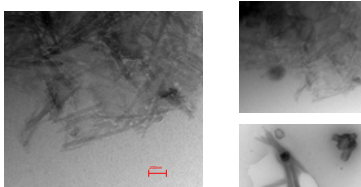
1. Braunstein, P.; Rose, J.; Bars, O. J. Organomet. Chem. 1983, 252, C101-C105.  
2. Roland, E.; Vahrenkamp, H. Organometallics 1983, 2, 183-184.

## New Chemistry: Polymer-Metal Complex



- Heated under reflux at 40°C for six hours
- Methylene chloride used as solvent
- Re-crystallized product from solution with petroleum ether, filtered to collect precipitate, washed solid with petroleum ether and collected purple fluffy powder
- Repeated procedure with [Co<sub>2</sub>Ru(CO)<sub>12</sub>] metal complex to form a pink fluffy solid

## Results



TEM images of PS-PPES[Ni(Et)<sub>2</sub>][FeCo<sub>2</sub>(CO)<sub>12</sub>]  
Width of wires is approximately 100nm

## Conclusion

- Results from IR indicate metal attached to polymer
- Results from TEM promising for positive formation of polymer-metal complex
- Further analysis of TEM needed to better ascertain if desired product formed
- Annealing of polymer-metal compound needed to break the CO bonds and create nanowires

## Acknowledgments

- Liliana Miinea for synthesizing the polymers and her guidance
- Charles Daghljan for TEM
- Funded by the NSF REU program and the DoD ASSURE program

