

Matthew Herdiech

Advisor: David S. Glueck

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

**Abstract**

Metal nanoparticles are an area of interest that has many potential applications, including bimetallic nanomagnets and nanowires. However, fabrication of nanomaterials from “top-down” methods can be expensive and resource-intensive. By using the self-assembling and phase separating properties of copolymers, hopefully an efficient “bottom-up” approach to the fabrication of these materials can be developed.

**Introduction**

Metals provide many interesting and useful properties to materials. They have important roles in superconductors, electrochromic materials, catalysts, and magnetic materials used in data storage.<sup>1</sup> Combining metal particles with polymeric materials is currently a field of great interest, as combining metals with polymers has already, and will continue to lead to the development of hybrid materials having desirable properties.<sup>2</sup> A few of these hybrid materials that have already been developed include an osmium-polymer system that has led to the development of glucose sensors<sup>3</sup>, as well as a ruthenium-polymer system that has allowed for the development of self-oscillating gels, perhaps important in pulsatile drug delivery devices.<sup>4</sup> Other hybrid materials are used for their interesting electrical and optical properties.<sup>5</sup>

Another important aspect of metals, especially on the nanoscale, is their magnetic properties. The properties of metals on the macroscale differ from those on the nanoscale, as the size of the particles approaches fundamental magnetic lengths.<sup>6</sup> On the nanoscale, as changes in magnetization, coercivity, and hysteresis can occur, metals exhibit single-domain behavior.<sup>7</sup> For certain metals, if their size is not controlled, desirable magnetic properties can reverse themselves<sup>8</sup>, allowing their role in a specific application to become detrimental to the application itself. However, by creating anisotropic (having varying properties in different directions) metal nanowires, or nanomagnets, magnetization would occur perpendicularly to the surface of these one-dimensional nanowires, allowing for media recording, possibly even one bit per particle.<sup>9</sup>

Fabrication of metal nanowires is an area of research that can have multiple approaches and methods. Top-down approaches, where the starting material is large and is manipulated into a smaller scale, can often be expensive and resource intensive.<sup>10</sup> Current research has focused on using bottom-up approaches, where the smallest pieces are brought together using various assembling techniques. One such technique is self-assembly, where the placement of the metal nanoparticles is mediated by the natural self-assembly and phase separation of copolymers, specifically diblock copolymers (Figure 1).<sup>11,12</sup>

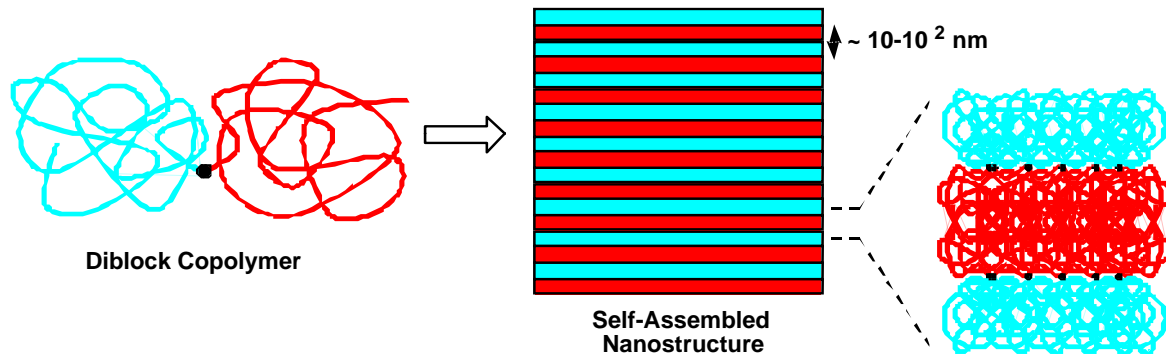


Figure 1: An illustration of the phase separation exhibited by a diblock copolymer.<sup>10</sup>

The result is essentially a metal nanomagnet in a nonmagnetic matrix (i.e. the polymer)

(Figure 2).

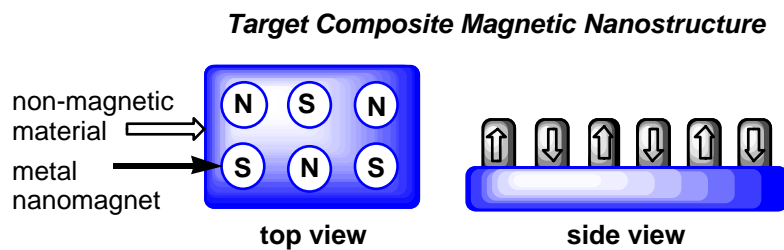


Figure 2: Single-domain metal nanowires with two magnetization states (up or down, North or South) in a nonmagnetic matrix: a target for one-bit/one-particle recording.<sup>10,13</sup>

An interesting example of pertinent research showed cobalt's ability to bind to the alkyne functional block of a diblock copolymer. PS-PPES was the polymer used, as PES monomers contain an alkyne. Results showed that cobalt clusters bound to the polymer, specifically to the PPES block (Figure 3,4).<sup>10</sup>

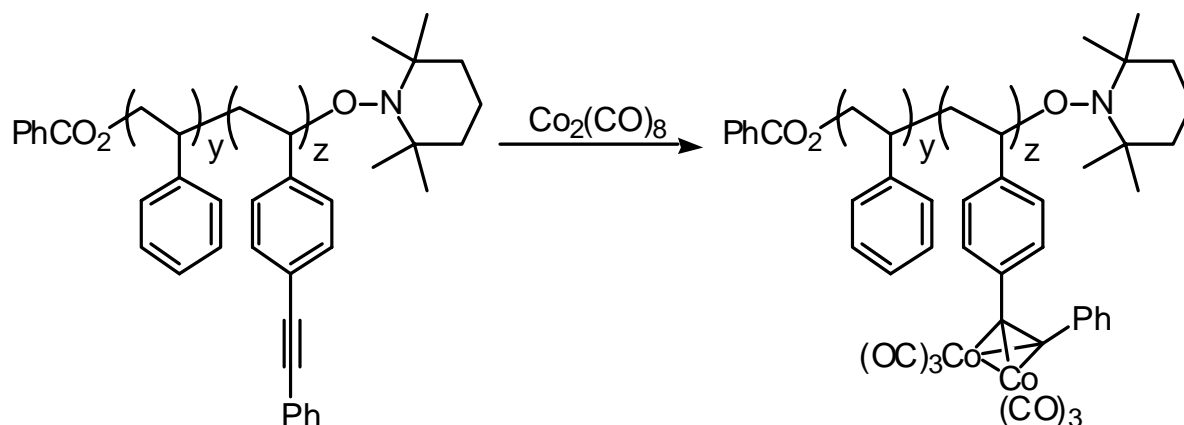


Figure 3: Illustrates the reaction between PS-PPES and a cobalt cluster to yield a metal-polymer hybrid.<sup>10</sup>

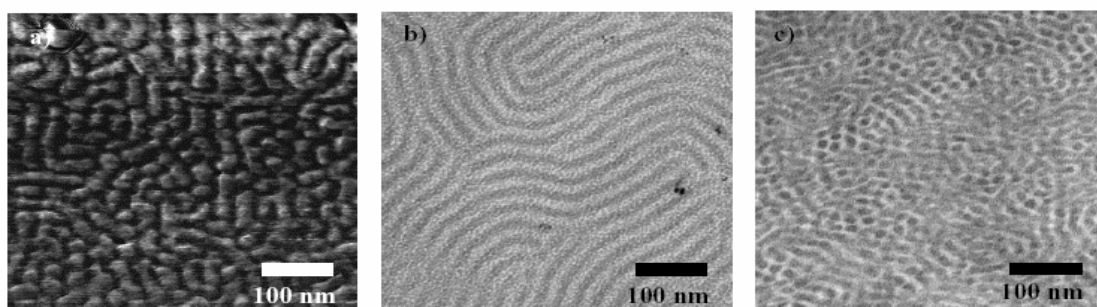


Figure 4: AFM and TEM images of the cobalt-polymer material.<sup>14</sup>

However, even with a bottom-up approach, problems do arise. Many of the applications of these metal-polymer hybrid materials will require that they be produced on a larger scale than the nanoscale.<sup>2</sup> The controlling of the placement of the metal nanoparticles themselves is still an area of concern. Even more complex, the issue of placement of the metal nanoparticles when there are various metallic elements being introduced into the polymer matrix is one of great difficulty.

## Experimental Section

**[FeCo<sub>3</sub>(CO)<sub>12</sub>][Et<sub>4</sub>N]**: Synthesis of the bimetallic cluster [FeCo<sub>3</sub>(CO)<sub>12</sub>][Et<sub>4</sub>N] (Figure 5) was attempted twice.

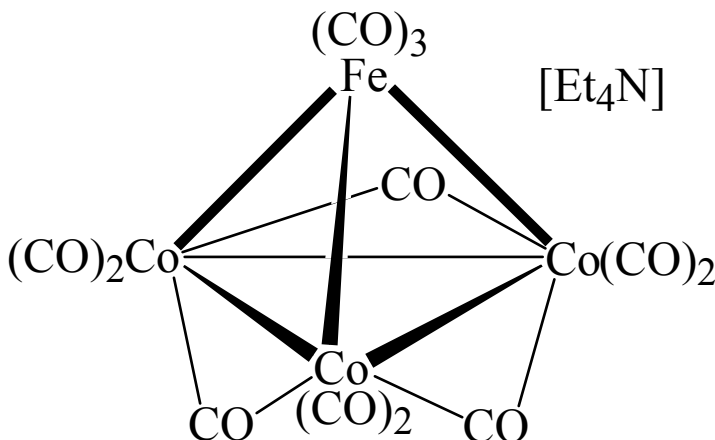


Figure 5: [FeCo<sub>3</sub>(CO)<sub>12</sub>][Et<sub>4</sub>N].

The first attempt was based on the procedure from (14) as well as (15). 3.00 g Co<sub>2</sub>(CO)<sub>8</sub> were reacted with 0.73 ml Fe(CO)<sub>5</sub>. The reaction was carried out assuming air sensitivity, so the Co<sub>2</sub>(CO)<sub>8</sub> was added to a flask inside of a glove box, and the Fe(CO)<sub>5</sub> was added using a cannula. The reaction was carried out on the Schlenk line to avoid exposure to air. The reactants were refluxed for approximately 9 hours in 95 ml of degassed acetone at 60°C. Throughout the reflux process, the reaction mixture remained dark in color. The reflux apparatus was set up to have nitrogen gas blowing in from the side of the reaction flask, as well as the top of it in an attempt to reduce the loss of solvent through the joints of the apparatus. Upon finishing refluxing, the solvent was pumped down, and the product was dissolved in a small amount of degassed acetone. An attempt to filter the product using a Schlenk filter was made, but it was difficult to use the Schlenk filter, as it kept getting clogged, so eventually it was just filtered using cannula filtration. It appeared as though impurities were filtered out with the Schlenk filter,

some product may have been lost due to clogging. 1.25 g  $\text{Et}_4\text{NCl}$  (although the procedure in the literature used  $\text{Et}_4\text{NI}$ , it should not have made a difference) was dissolved in 75.0 ml degassed, distilled water, and added to the product via a cannula. A precipitate did form, although the color was difficult to determine (some shade of dark). The precipitate was filtered using cannula filtration. At first, the filtrate was of a dark color (not the light pink that is described in the literature), so more  $\text{Et}_4\text{NCl}$  dissolved in water was added, but the filtrate never became pink. The precipitate was washed with water to rid it of excess  $\text{Et}_4\text{NCl}$ , and was then put under vacuum to remove the solvent, a process that lasted for 6 hours. An attempt was made to recrystallize it overnight in equal amounts of dichloromethane and hexane, but the product remained dissolved in solution (after one night in the refrigerator), and was filtered using a frit. The theoretical yield was 3.49 g, while the actual yield was 1.27 g (36% yield). IR (KBr): 2064, 2015, 1999, 1964, 1934, and  $1811\text{ cm}^{-1}$  (other small peaks were present, possibly the result of impurities; the peaks shown were the ones that most closely matched those described in literature).

After limited success with trying to bind the first metal cluster to a model alkyne, another attempt was made to make  $[\text{FeCo}_3(\text{CO})_{12}][\text{Et}_4\text{N}]$ . This time, the experiment was carried out closer to the procedure outlined in (15), deviating from it only when necessary. Instead of refluxing for 9 hours, this reaction was allowed to go the entire 14 hours described by the literature. At the end of the 14-hour period, the reaction mixture was a reddish brown solution, a promising sign, as that is what the paper described. After pumping down the remaining solvent, instead of bothering with the Schlenk filter, the flask was brought into the glove box, where it was dissolved in degassed acetone and

filtered with a frit inside of the box. Outside of the box, 1.25 g Et<sub>4</sub>NI dissolved in 75.0 ml degassed, distilled water was added to the product via a cannula. A precipitate that did appear to be reddish brown in color formed, but once again, the filtrate (it was filtered using cannula filtration) did not turn pink, even after additional Et<sub>4</sub>NI was added. The product was washed with water and dried under vacuum. The product was then recrystallized using warm dichloromethane and hexane. This time, a black powder formed after recrystallization, with a clear, supernatant layer on top, which was decanted using a pipette. The actual yield was less than in the previous attempt to produce the complex (around .8 g). IR (KBr): 2065.3, 2009.7, 1996.5, 1955.6, 1928.5, 1826.4, and 1810.4 cm<sup>-1</sup> (once again, other small peaks were present, possibly the result of impurities; the peaks shown were the ones that most closely matched those described in literature).

**[FeCo<sub>3</sub>(CO)<sub>10</sub>(Ph<sub>2</sub>C<sub>2</sub>)]**[Et<sub>4</sub>N]: To determine whether the metal cluster [FeCo<sub>3</sub>(CO)<sub>12</sub>][Et<sub>4</sub>N] was able to bind to an alkyne (and also, to see if what had been produced was in fact [FeCo<sub>3</sub>(CO)<sub>12</sub>][Et<sub>4</sub>N]), an experiment was performed by following a literature procedure (16) to produce [FeCo<sub>3</sub>(CO)<sub>10</sub>(Ph<sub>2</sub>C<sub>2</sub>)] [Et<sub>4</sub>N] (Figure 6).

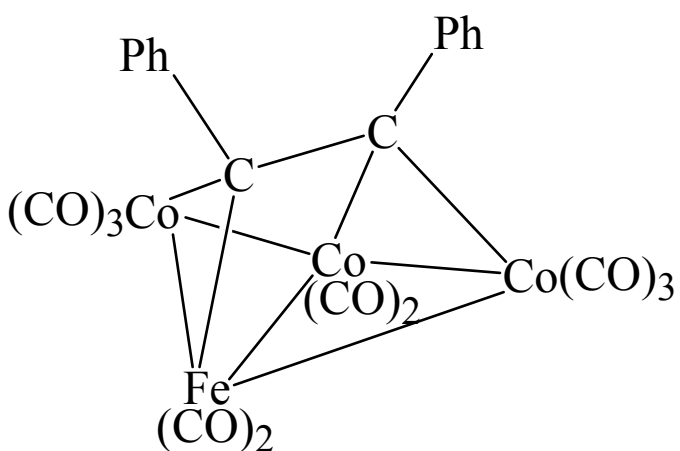


Figure 6: [FeCo<sub>3</sub>(CO)<sub>10</sub>(Ph<sub>2</sub>C<sub>2</sub>)] [Et<sub>4</sub>N].

The experiment was performed three times. The first time was performed using the sample of  $[\text{FeCo}_3(\text{CO})_{12}][\text{Et}_4\text{N}]$  that Sean Haggerty, last year's REU participant, had made. Because each time the experiment was performed the procedure was essentially the same, the way in which the experiment was performed will only be described once. The reaction was a 6 hour reflux using 0.50 g  $[\text{FeCo}_3(\text{CO})_{12}][\text{Et}_4\text{N}]$ , 0.65 g  $\text{Ph}_2\text{C}_2$ , and 50 ml acetone. The reaction was not air sensitive. When the reactants were first put into a flask, the reaction mixture was black/very dark red in color. Each time the experiment was performed, the reflux went for at least 5 hours, although 5 hours seems to be long enough (this is the time given in the literature procedure). The reflux temperature is  $60^\circ\text{C}$ . The reflux apparatus was set up so that nitrogen was coming through the side of the flask, as well as the top of it in an attempt to minimize the loss of solvent through the joints of the apparatus. The excess solvent was then pumped down, and the black powder left in the flask was recrystallized using acetone and ether. The product was then washed with ether once again, to ensure that any excess, unreacted alkyne had been washed away, as to not skew NMR results. The theoretical yield for these experiments was .59 g. The actual yield was generally around .4 g.

First attempt:  $^1\text{H}$  NMR (acetonitrile):  $\delta$  1.0 (t of t); 2.9 (q); 6.8 (very small peaks, indicating reacted alkyne); 7.2 (unreacted alkyne). IR (KBr): 2022.1, 2012.4, 2008.0, 2000.5, 1994.1, 1989.9, 1986.9, and  $1982.9\text{ cm}^{-1}$  (this IR did not show less than  $1970.0\text{ cm}^{-1}$ ).

Second attempt:  $^1\text{H}$  NMR (acetonitrile):  $\delta$  1.0 (t of t); 2.9 (q); 6.8 (very small peaks, indicating reacted alkyne); 7.2 (unreacted alkyne). IR (KBr): 2043, 2016, 2002, 1992, 1976, 1964, 1959, 1932, and  $1811\text{ cm}^{-1}$ .

Third attempt:  $^1\text{H}$  NMR (acetonitrile):  $\delta$  1.0 (t of t); 2.9 (q); 6.8 (very small peaks, indicating reacted alkyne); 7.2 (unreacted alkyne).

**[FeCo<sub>3</sub>(CO)<sub>12</sub>][Et<sub>4</sub>N]PS-PPES:** An attempt was made to bind [FeCo<sub>3</sub>(CO)<sub>12</sub>][Et<sub>4</sub>N] to two different types of the diblock copolymer PS-PPES (Figure 7): PS<sub>242</sub>-PPES<sub>98</sub> and PS<sub>179</sub>-PPES<sub>29</sub>. The polymers were synthesized by Liliana Miinea. In one experiment, .3 g PS<sub>242</sub>-PPES<sub>98</sub>, .067 g [FeCo<sub>3</sub>(CO)<sub>12</sub>][Et<sub>4</sub>N], and 80 ml of methylene chloride were put into a flask, and refluxed at 48°C for 5 hours. The stoichiometric amounts were determined by assuming five binding sites (alkynes) per metal complex. In the other experiment, .4 g PS<sub>179</sub>-PPES<sub>29</sub>, .093 g [FeCo<sub>3</sub>(CO)<sub>12</sub>][Et<sub>4</sub>N], and 80 ml of methylene chloride were put into a flask, and the same procedure was followed. Both reaction mixtures were black/very dark red in color.

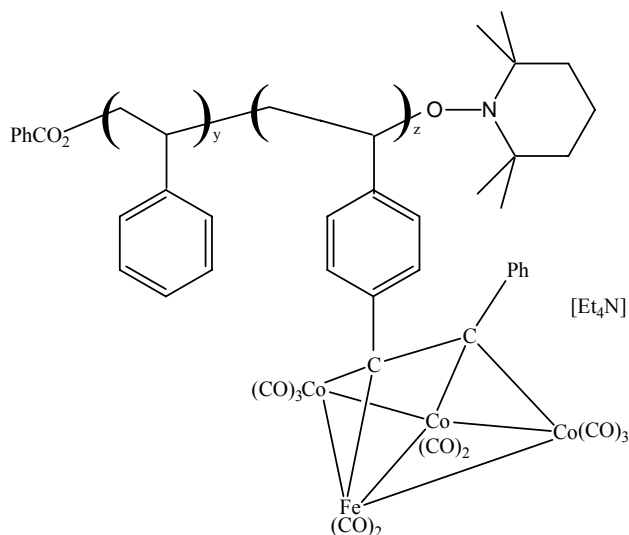


Figure 7: [FeCo<sub>3</sub>(CO)<sub>12</sub>][Et<sub>4</sub>N]PS-PPES.

For the reflux apparatuses, nitrogen was allowed to enter the flask from the top and side of the flasks to minimize the loss of solvent. After 5 hours, the solvent was pumped down, and brownish crystals remained. An attempt was made to dissolve excess, unreacted [FeCo<sub>3</sub>(CO)<sub>12</sub>][Et<sub>4</sub>N] by adding acetone (which PS-PPES does not readily

dissolve in) to the product, but all of the product seemed to dissolve, indicating that once PS-PPES reacts with  $[\text{FeCo}_3(\text{CO})_{12}][\text{Et}_4\text{N}]$ , it does dissolve in acetone.

$[\text{FeCo}_3(\text{CO})_{12}][\text{Et}_4\text{N}]\text{PS}_{242}\text{-PPES}_{98}$ : IR (KBr): 2024.0, 2011.2, 1995.9, 1988.6, 1980.5, 1970.0, 1818.7, and 1813.0  $\text{cm}^{-1}$ .

$[\text{FeCo}_3(\text{CO})_{12}][\text{Et}_4\text{N}]\text{PS}_{179}\text{-PPES}_{29}$ : IR (KBr): 2061.6, 2009.1, 1998.6, 1966.3, 1927.3, 1823.1, and 1809.6  $\text{cm}^{-1}$ .

**Experimenting with  $[\text{FeCo}_3(\text{CO})_{12}][\text{Et}_4\text{N}]$ :** During the first attempt to make  $[\text{FeCo}_3(\text{CO})_{10}(\text{Ph}_2\text{C}_2)][\text{Et}_4\text{N}]$ , it was noticed that although NMR data revealed a low yield of product, the reaction mixture changed color. The sample of  $[\text{FeCo}_3(\text{CO})_{12}][\text{Et}_4\text{N}]$  used in this experiment was that made by Sean Haggerty. At first, the metal cluster had a purplish color, but after the reflux reaction, the product was black, so clearly some reaction had to have happened. The first thought was that carbon monoxide (CO) had been burned off the metal cluster, resulting in metal nanoparticles. A control experiment was run in which a sample of the purple  $[\text{FeCo}_3(\text{CO})_{12}][\text{Et}_4\text{N}]$  was refluxed in acetone for 4 hours. At the end of this period, the cluster had changed color, as it was now black. TGA, mass spectrometry, and elemental analysis data were retrieved, but it was never determined what this black powder was.

## Results and Discussion

The goals of this research were to be able to selectively position metals into a three-dimensional polymeric matrix by exploiting the natural phase separation exhibited by diblock copolymers, and also to bind two distinct metals to the polymer, making this project unique to those performed in the past, which generally tried to put just one metal into a polymer. An iron-cobalt metal cluster was chosen for experimentation because of

cobalt's ability to bind to an alkyne, and also because literature procedures on how to synthesize the cluster were available.

Although the bimetallic cluster  $[\text{FeCo}_3(\text{CO})_{12}][\text{Et}_4\text{N}]$  was produced in some yield, this reaction is difficult to perform due to its sensitivity to air, and the fact that the product needs to be filtered multiple times under nitrogen. The best procedure to follow seems to be the one from (15). The procedure found in (14) is not as thorough, and is at times confusing. Despite the reaction being carried out as described by literature procedures, the sample of  $[\text{FeCo}_3(\text{CO})_{12}][\text{Et}_4\text{N}]$  that was synthesized was likely impure. The best indication of this came from its color, which was black. According to literature, it should have been reddish brown (although when the product was dissolved in acetone, the solution did appear to have a slightly reddish brown tint). Another indication of impurities in the sample was the IR spectroscopy data, which showed peaks similar to those described in the literature, but in addition to those peaks, there were other stray peaks throughout the spectrum. Most peaks occurred around 2000 and 1800  $\text{cm}^{-1}$ . There is a remote possibility that the starting materials,  $\text{Fe}(\text{CO})_5$  and  $\text{Co}_2(\text{CO})_8$  were not pure, or had changed composition, but this is unlikely as their colors indicated that neither of these had happened, and both materials had been stored properly.

In binding the metal cluster to an alkyne,  $^1\text{H}$  NMR showed that the reaction was successful, but that the product was in low yield. This was most likely due to the impurities in the starting metal complex, which may have impeded the cluster's ability to bind to an alkyne. The reaction between the metal complex and the alkyne was a simple reflux reaction that was not air sensitive, so it is unlikely that this is where the experiment went wrong. Literature describes the product of this reaction to be black crystals, while

this experiment produced black powder. IR spectroscopy data also showed that impurities were likely present, as additional peaks besides those mentioned in literature were shown, with most peaks occurring around 2000 and 1800  $\text{cm}^{-1}$ .

Despite the likely presence of impurities in the metal cluster, it was still used to bind to the diblock copolymer PS-PPES. This polymer was used because PPES is an alkyne functional block. The stoichiometric ratio used was 5 to 1 binding sites to metal clusters, as getting all metal clusters to bind was a concern, as separating unreacted metal clusters from the polymer would present a problem. After the reflux reaction between the polymer and metal clusters, acetone was added to the product to dissolve excess metal clusters, but the entire product dissolved, which was interesting since PS-PPES does not readily dissolve in acetone. This indicated that some reaction did occur.  $^1\text{H}$  NMR and IR characterization will hopefully determine what the product is.

## **Conclusion**

The most difficult step in accomplishing the project goals was synthesizing the bimetallic cluster. Producing this complex in high yield and with limited impurities is a challenge, but if accomplished, would likely allow for the successful binding of iron and cobalt to PS-PPES, or any other diblock copolymer with an alkyne functional block. The product of the reaction between the  $[\text{FeCo}_3(\text{CO})_{12}][\text{Et}_4\text{N}]$  and PS-PPES will continue to be analyzed using  $^1\text{H}$  NMR and IR spectroscopy. Future experimentation could include the use of more varying block lengths of PS-PPES, or another diblock copolymer that has an alkyne functional block. Once the products have been characterized, the polymers can be heated to burn off carbon monoxide, producing metal nanoparticles, whose placement

will be controlled through the phase separation exhibited by diblock copolymers (Figure 8).<sup>10</sup>

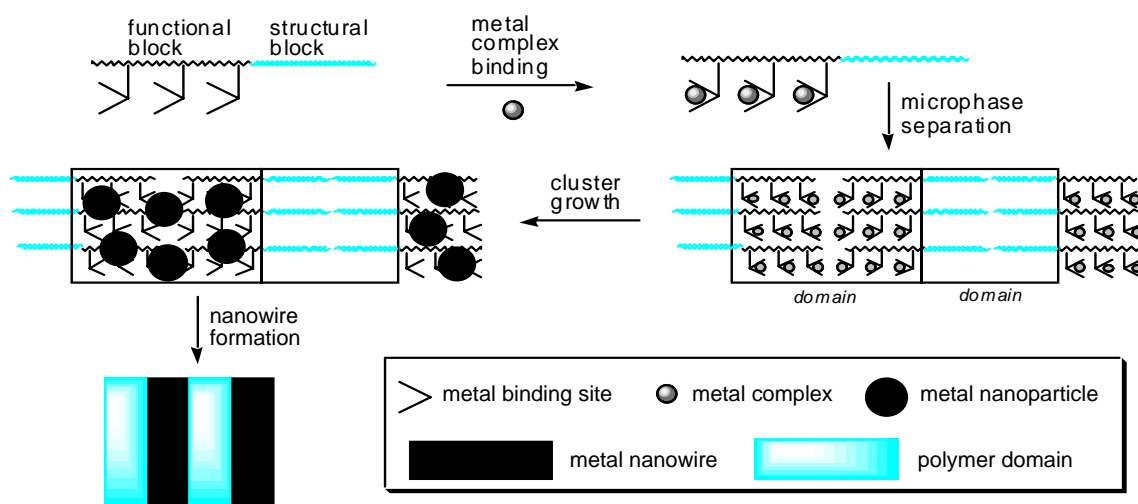


Figure 8: The result of combining a diblock copolymer where one of the blocks is alkyne functional with a metal cluster.<sup>10</sup>

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