

**Synthesis of Amphiphilic Diblock Copolymers as Precursors to Cobalt Nanoparticles**  
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**Introduction**

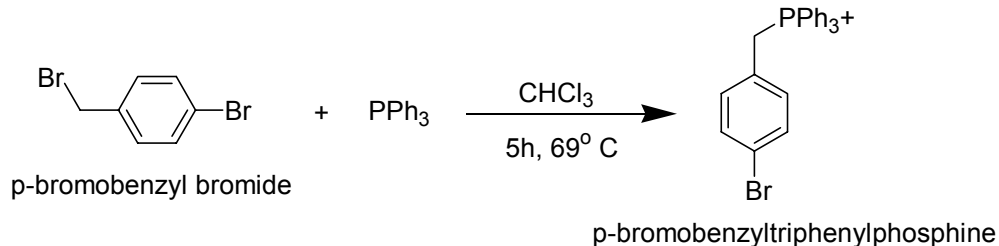
Diblock copolymers have been under study because of their range of applications, including those in nanotechnology. Using such polymers as precursors to nanoparticles is beneficial since self-assembly of the polymers causes the structures of the nanoparticles to be simple and orderly. Additionally, the size of the particles can be controlled<sup>2</sup>.

Amphiphilic diblock copolymers have the property where one block is hydrophobic and the other is hydrophilic. These polymers self assemble into different intriguing structures in solution depending on the ratio of each block and the polarity of solvent. For instance, spherical micelles form when the numbers of hydrophobic and hydrophilic blocks are equal and vesicles form when the number of hydrophobic blocks is much greater than the number of hydrophilic blocks<sup>1</sup>.

Alkynes are very reactive towards cobalt-containing compounds. Cobalt can thus be incorporated into amphiphilic diblock copolymers that contain an alkyne group. The phase separation of these polymers causes the orderly arrangement of the nanoparticles into micelles in aqueous solutions. Cross-linking of the micelles prevents the destruction of the micelles in non-aqueous solvents. These nanoparticles have potential for a wide array of applications because of their magnetic and electronic properties<sup>1</sup>.

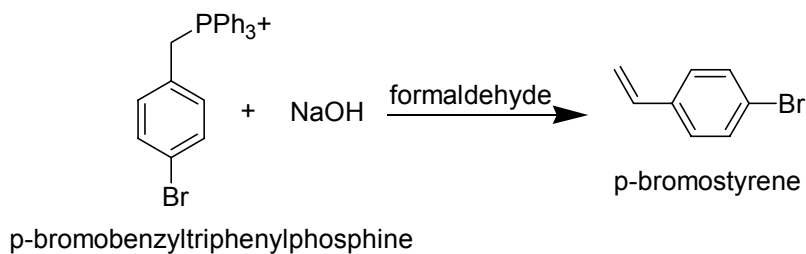
This study is focused on the preparation of an amphiphilic polymer with an alkyne functional group by atomic transfer radical living polymerization. Further the alkyne functional groups are complexed with cobalt carbonyl and crosslinked by exposure to UV light.

## Results and Discussion



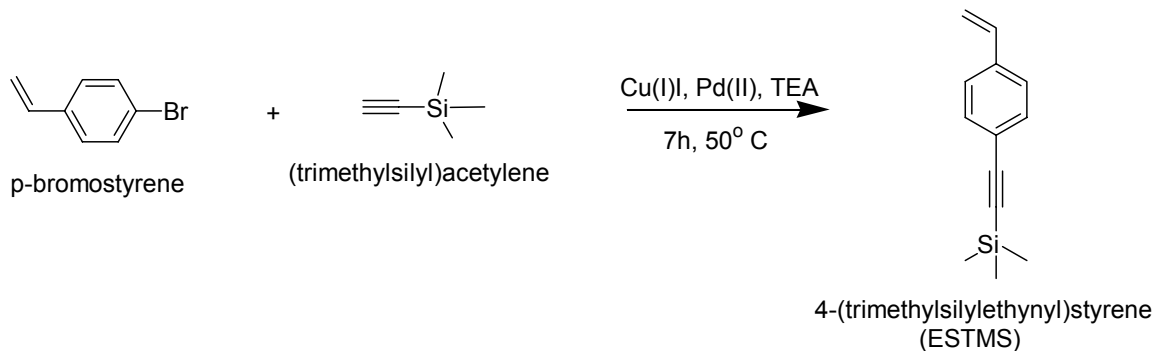
*P*-bromobenzyltriphenylphosphine salt was prepared by the reaction of *p*-bromobenzyl bromide with triphenylphosphine with a yield greater than 98%

### Preparation of *p*-bromostyrene



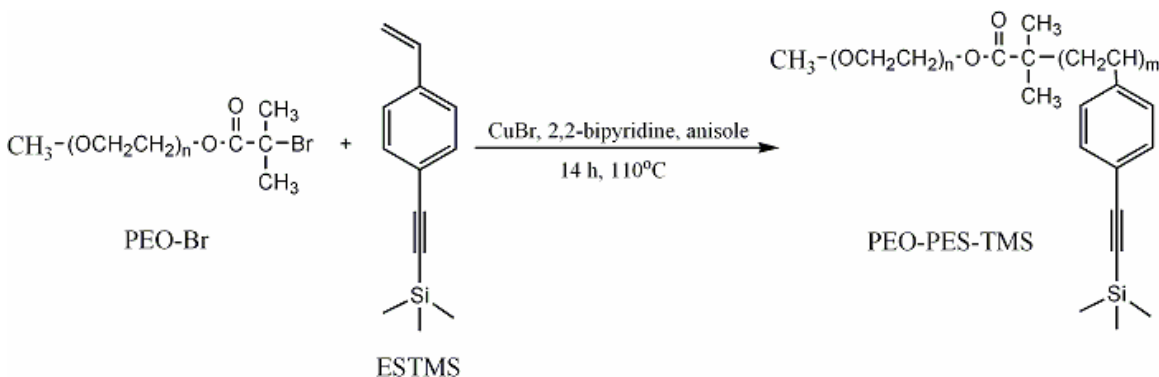
*P*-bromostyrene was prepared by the Wittig reaction between *p*-bromobenzyltriphenylphosphine and sodium hydroxide with a yield of 87%.

### Preparation of 4-(Trimethylsilylethynyl)styrene (ESTMS)



A Sonogoshira Coupling reaction was performed between *p*-bromostyrene and (trimethylsilyl)acetylene to synthesize 4-(trimethylsilylethynyl)styrene (ESTMS) with a yield of 48%. The product was confirmed by <sup>1</sup>H NMR where CDCl<sub>3</sub> was the solvent.

**Polymerization: Preparation of PEO-PES-TMS**



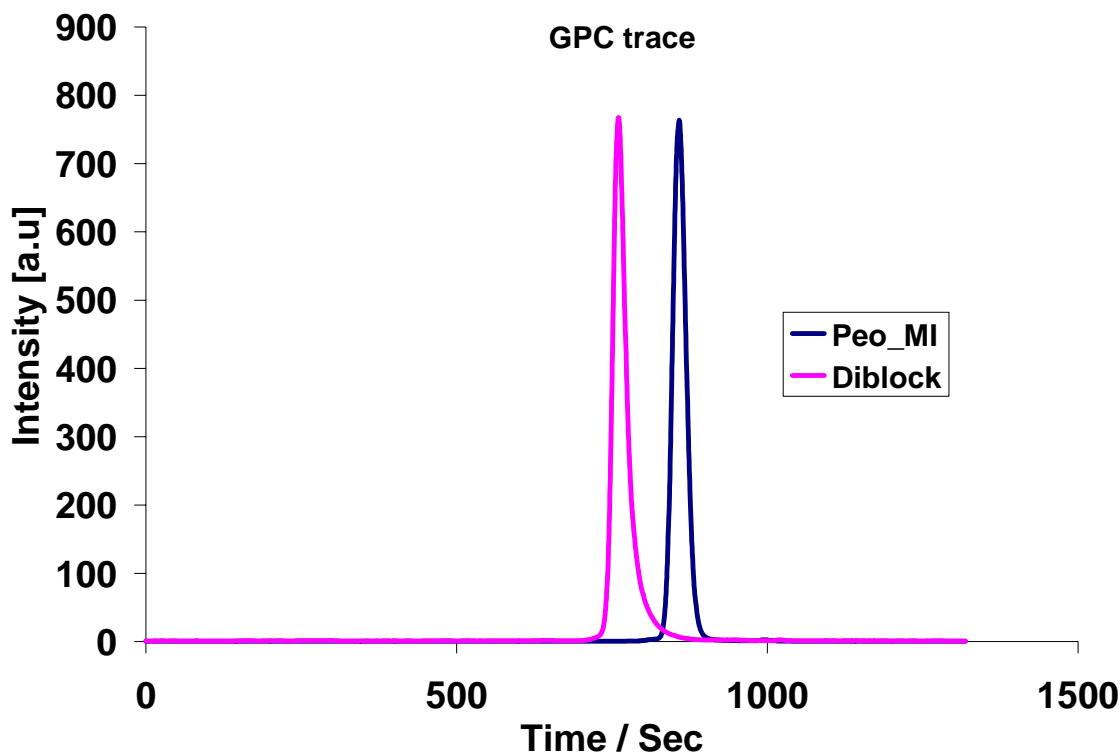
The synthesis of PEO-PES-TMS was carried out by atomic transfer radical polymerization where PEO-Br was the macroinitiator, CuBr was the catalyst, and 2,2-bipyridine was the ligand in a 1:50:0.001:0.003 ratio. Polymers of three different molecular weights were synthesized as shown in Table I.

**Table I.** Molecular weight data for PEO-PES-TMS from GPC and <sup>1</sup>H NMR analysis.

Polymer	Rxn Time (hr)	M <sub>n</sub> from GPC	M <sub>w</sub> from GPC	PDI	M <sub>n</sub> from NMR	Percent Conversion
1	6	11364	12372	1.0887	10455	69%
2	14	15551	17429	1.12076	15315	>98%
3	12	14976	15813	1.05589	12056	80%

The molecular weight number averages for the polymers obtained from both GPC and NMR matched fairly well. Additionally, the polydispersity indices of all the polymers were close to one, indicating that the molecular weight distributions were

narrow. The GPC trace, as shown in Figure 1, also shows the chain growth over the macroinitiator.



**Figure 1.** GPC traces for ER Polymer 1 and macroinitiator.

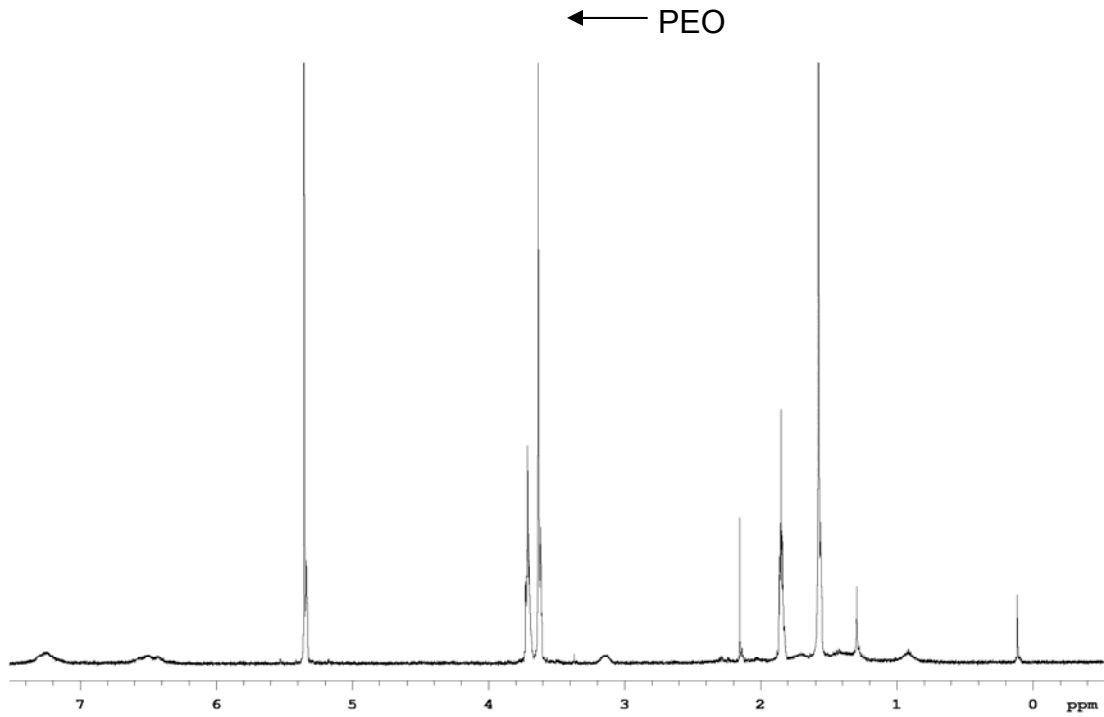
### Deprotection and Micellization: Preparation of PEO-PES

The deprotection of PEO-PES-TMS was carried out by reacting the polymer with KOH. The deprotection of the polymer was confirmed by  $^1\text{H}$  NMR (Table II), where the silyl peaks at  $\delta = 0.27$  ppm disappears and a new peak at  $\delta = 3.12$  ppm corresponding to the acetylene peak is observed.

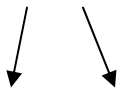
**Table II.** Distinctive NMR peaks for PEO-PES-TMS and PEO-PES

Polymer	SiMe <sub>3</sub> ( $\delta$ ppm)	C $\equiv$ CH ( $\delta$ ppm)
PEO-PES-TMS	0.27	--
PEO-PES	--	3.12

This confirms the deprotection of the acetylene peaks. The micellization of the polymer was performed by dialysis over a period of 3 days and continuous exchange of water. Micellization was also confirmed by  $^1\text{H}$  NMR, as seen in Figures 2a and 2b.



PES



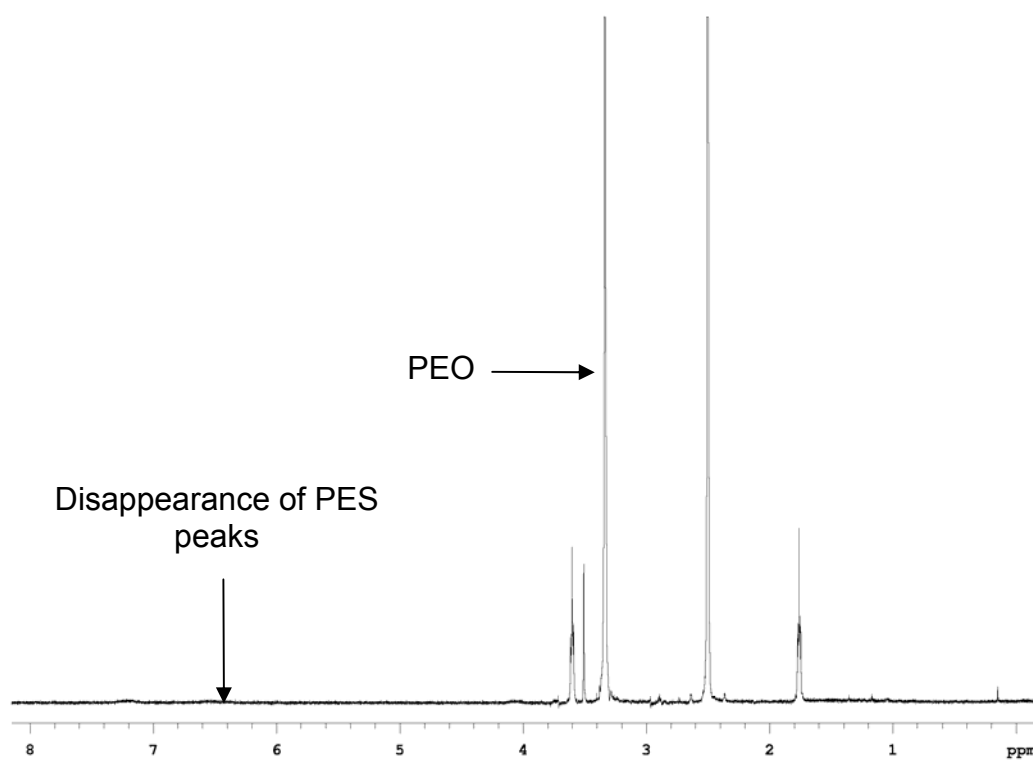
Styrene



Acetylene



**Figure 2a.**  $^1\text{H}$  NMR spectrum for PEO-PES micelles in  $\text{CD}_2\text{Cl}_2$ .

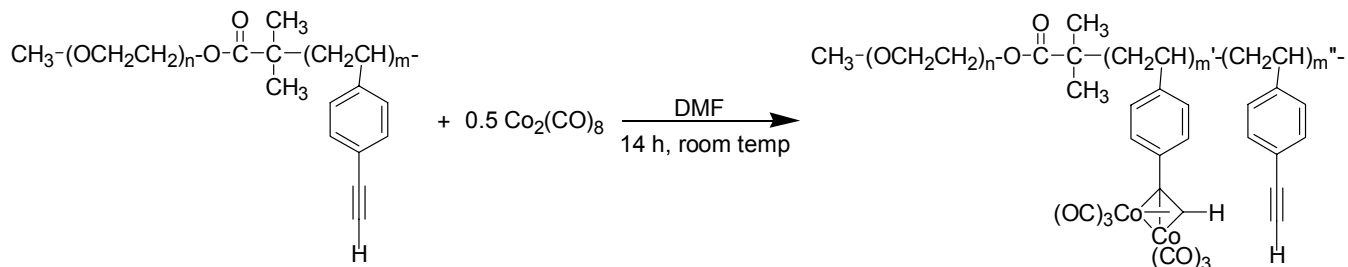


**Figure 2b.**  $^1\text{H}$  NMR spectrum for PEO-PES micelles in DMSO.

The  $^1\text{H}$  NMR spectrum of the polymer before micellation in  $\text{CDCl}_3$  showed peaks for both the PEO and PES blocks whereas the spectrum for the micellized polymer in deuterated DMSO, a strong polar solvent, did not show the peaks for the styrene block and acetylene peaks. This showed that the hydrophobic styrene block of the polymer was

probably at the center of the micelle and the hydrophilic PEO block of the polymer are at the outside of the micelle.

### Cobalt Addition to PEO-PES and Crosslinking



PEO-PES

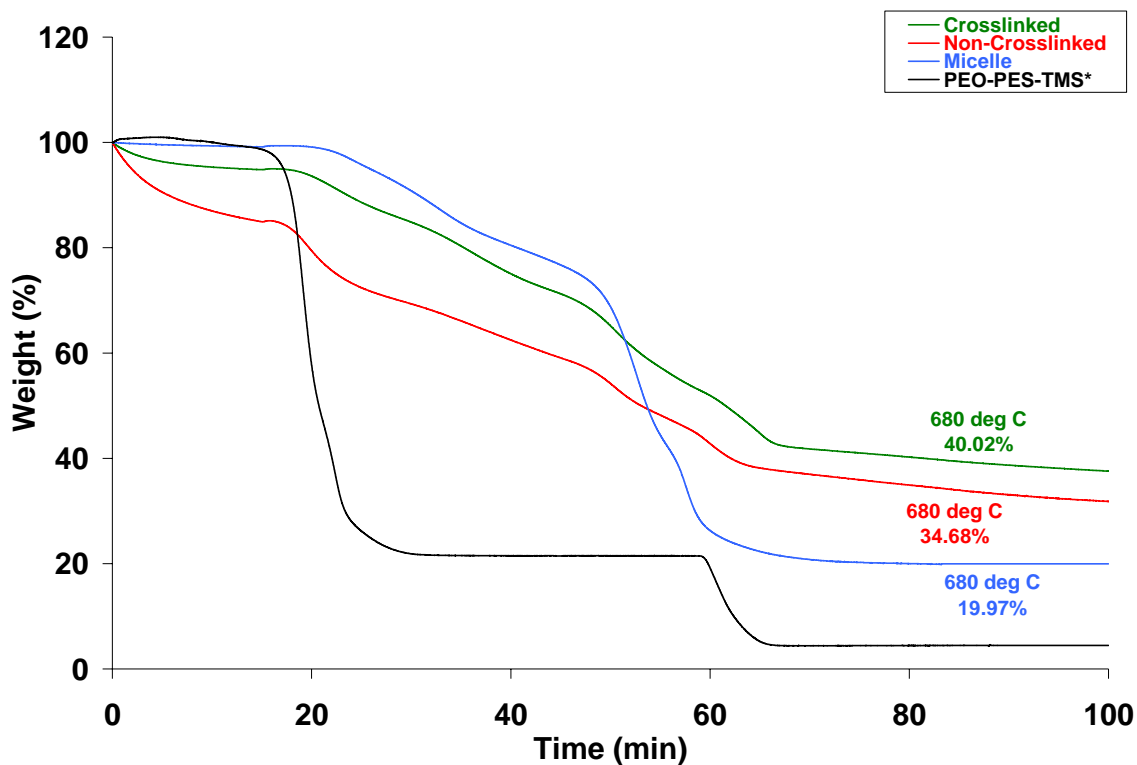
The ratio of PEO-PES to  $\text{Co}_2(\text{CO})_8$  in the synthesis of the cobalt containing polymer was 2:1 so that alkyne groups are available for further crosslinking. Cobalt addition and crosslinkage was confirmed by IR, as seen in Figure 3.



**Figure 3.** IR spectra (ZnSe) for PEO-PES-TMS, micellized, cobalt non-crosslinked, and cobalt crosslinked polymers.

The addition of cobalt was confirmed by the disappearance of the C≡C peak at 2105  $\text{cm}^{-1}$  appearance of the C=O peak at 2020  $\text{cm}^{-1}$ . Crosslinkage resulted in a decrease of peaks at 3402  $\text{cm}^{-1}$ (C-H) and 2360  $\text{cm}^{-1}$  (C-C).

The percent cobalt incorporated into the polymer was determined using TGA analysis, as seen in Figure 4.



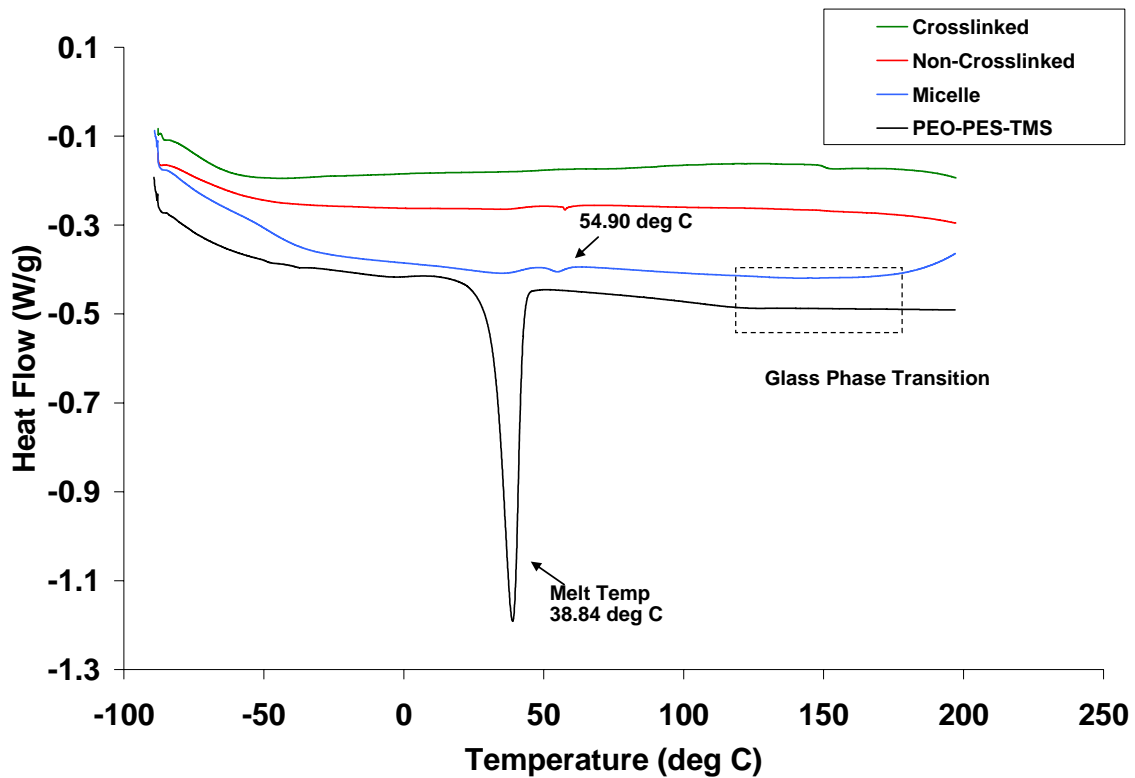
**Figure 4.** TGA analysis for silated, micellized, cobalt containing non-crosslinked, and cobalt containing crosslinked polymers.

The weight percent of the desilylatedmicellized polymer at 680°C was compared to the weight percent of the non-crosslinked cobalt-containing polymer at 680°C, the observed weight percent of the cobalt-containing polymer was 14.71% in comparison to

the calculated weight of 16%. The fact that the crosslinked cobalt-containing polymer had a higher weight percent at 680°C may indicate the greater stability of the crosslinked polymer.

### DSC Data

The melting points of the polymers was determined using DSC analysis, as can be seen in Figure 5.

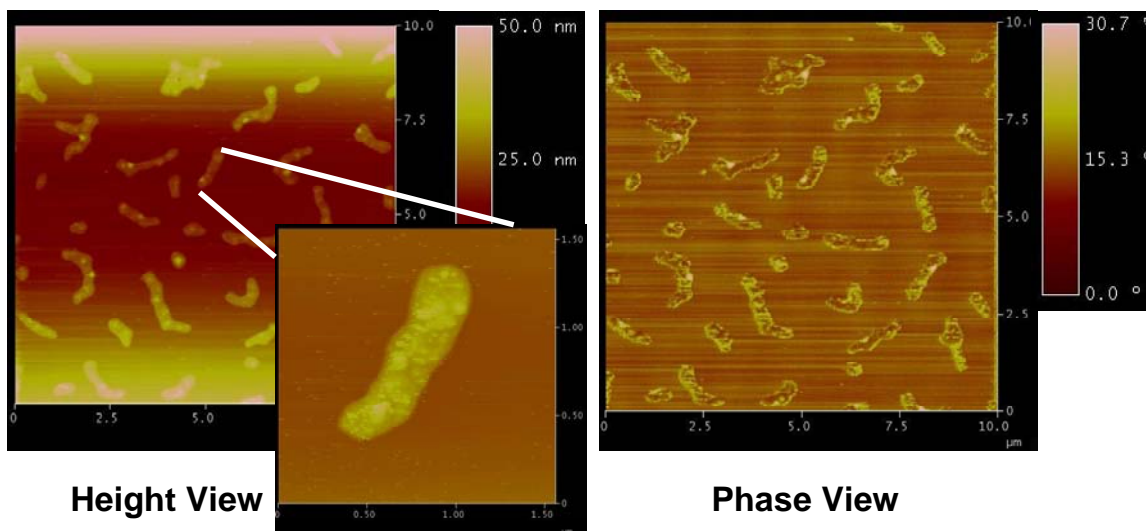


**Figure 5.** DSC data for silated, micellized, non-crosslinked cobalt containing, and crosslinked cobalt containing polymers.

PEO-PES-TMS had a well defined phase transition and strong melting point was found to be 38.84°C. The micellized polymer had a less defined phase transition and the

melting point was found to be 54.90°C. Interestingly, no phase transitions were observed for the cobalt containing polymers.

The morphology of the cobalt containing polymers were further investigated by atomic force microscopy (AFM) (Fig 6). Interesting worm-like structures were observed.



**Figure 6.** Possible encapsulation of the cobalt particles within the crosslinked polymers.

The average size of the polymers was determined using AFM and was found to be 1.2-1.4μm.

### **Experimental**

#### **Preparation of *p*-bromobenzyltriphenylphosphine<sup>3</sup>**

50.0 g *p*-bromobenzyl bromide, 53.6 g triphenylphosphine were dissolved in 100 mL chloroform and heated at 69°C for 5 hours, giving 114.6 g (> 98%) of a white crystal.

#### **Preparation of *p*-bromostyrene<sup>3</sup>**

114 g *p*-bromobenzyltriphenylphosphine bromide was dissolved in formaldehyde. A saturated solution of sodium hydroxide (10 g sodium hydroxide) was slowly added to the solution drop-wise. The solution was left stirring overnight and was then extracted with three portions of 300 mL of ether and washed with a 1000 mL brine solution. This

solution was then dried with magnesium sulfate, filtered, and the filtrate was evaporated. Salts were removed by passing the solution through a column of alumina in which 750 mL hexanes were used as the mobile phase. The hexanes were removed by evaporation, leaving 31.80 g (87%) of *p*-bromostyrene, a yellow liquid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.42 ppm, *j* = 5 Hz (d, aromatic proton); 7.34 ppm, *j* = 7 Hz (d, aromatic proton); 6.70 ppm, *j* = 11.0 Hz (d of d, vinylic proton); 5.63 ppm, *j* = 15 Hz (d of d, vinylic proton); 0.25 ppm (s, -SiMe<sub>3</sub>).

#### **Preparation of 4-(Trimethylsilylethynyl)styrene (ESTMS)<sup>4</sup>**

In a 1000 mL two-neck reaction flask, 15.0 g *p*-bromostyrene, 9.6 g (trimethylsilyl)acetylene, 167.4 mg copper(I) iodide, and 1.1 g dichlorobis-(triphenylphosphine) palladium(II) were combined with about 450 mL of TEA. The reaction flask was then purged with nitrogen for about 30 minutes. The reaction mixture was refluxed at 50°C for 7 hours, filtered, and the filtrate was evaporated for about 45 minutes. Eight grams of this solution were then passed through a column of silica where the mobile phase was a 1:1 pentanes/hexanes solution. The collected product was put under vacuum for about 40 minutes, isolating 5.2 g (28%) ESTMS, a clear yellow liquid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 7.42 ppm, *j* = 5 Hz (d, aromatic proton); 7.34 ppm, *j* = 7 Hz (d, aromatic proton); 6.70 ppm, *j* = 11.0 Hz (d of d, vinylic proton); 5.63 ppm, *j* = 15 Hz (d of d, vinylic proton); 0.25 ppm (s, -SiMe<sub>3</sub>).

#### **Preparation of PEO-PES-TMS<sup>4</sup>**

500 mg PEO-Br ( $M_n=5000$ ), 976.0 mg ESTMS, 14.0 mg CuBr, 45.6 mg 2,2-bipyridine, and 2.6 g anisole were combined in a 100 mL air-free flask under nitrogen. Three freeze/thaw cycles were performed on the reaction mixture, which was then heated at 110°C for 14 hours. The product was purified by passing the reaction mixture through a column of 10 g alumina with THF to remove salts. After the solvent was evaporated, the product was heated at 110°C for 2 hours, giving 830 mg (68%) PEO-PES-TMS, a yellow solid.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 7.24 ppm (m, aromatic proton); 6.39 ppm (m, ? proton); 3.67 ppm (s,  $\text{CH}_2\text{CH}_2\text{O}$ -); 3.39 ppm (s, methyl proton); 1.26 ppm (m, PES backbone), 0.27 ppm (s, - $\text{SiMe}_3$ ).

IR (ZnSe plate): 1098 (C-O-C), 2155 ( $\text{C}\equiv\text{C}$ ), 833 (Si-C).

#### **Preparation of PEO-PES (Deprotection and Micellization) <sup>4</sup>**

0.2 g PEO-PES-TMS and 10.0 mg KOH were combined in a 50 mL THF/50 mL methanol solution. The reaction mixture was left stirring overnight at room temperature. The polymer was then transferred to a semipermeable membrane (MWCO, 3500) and a dialysis was performed in water for 3 days to remove salts, with the water being changed about every 6 hours. The polymer was then dried at 50°C, giving 50.0 g (29%) of a pale yellow solid.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ): 7.24 ppm (m, aromatic proton); 6.39 ppm (m, ? proton); 3.67 ppm (s,  $\text{CH}_2\text{CH}_2\text{O}$ -); 3.39 ppm (s, methyl proton); 1.26 ppm (m, PES backbone), 0.27 ppm (s, - $\text{SiMe}_3$ ).

IR (ZnSe plate): 1096 (C-O-C), 2105 (C≡C), 2865 (C-H), 3238 (C≡C).

### **Cobalt Addition to PEO-PES<sup>5</sup>**

200 mg PEO-PES, 2.0 g DMF, and 10 mg Co<sub>2</sub>(CO)<sub>8</sub> were combined under nitrogen in a 100 mL air-free flask. The reaction mixture was left stirring for about 14 hours. The product was then dried on a vacuum line, giving a reddish-brown solid.

### **Crosslinking<sup>4</sup>**

The polymer-cobalt complex in DMF was put under UV light, stirring, for 6 hours. After the solvent was removed by vacuum, a brown solid was obtained.

### **References**

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