Introduction:
Block copolymers have been used as a template to produce nanoparticles (using micro-emulsion techniques). In the case of a tensegrity-inspired material, block copolymers are ideal candidates. The copolymers can act as "nanoreactors" (through micelle formation) and as the tensile agent in the material. The nanoparticles that are synthesized inside the micelles would act as the compression agent.

Hydroxyapatite (HAp), Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, is the selected material for the nanoparticles, which can be synthesized from various calcium and phosphate precursors. The material of interest for the block copolymers are triblocks and diblocks of polycaprolactone (PCL) and polyethylene glycol (PEG). These materials were chosen for its potential usage in the biomedical field. Although synthesis of controlled HAp particle shape is possible with conventional surfactants, the processing takes a relatively long time due to multiple washings required after synthesis; usage of block copolymers can potentially simplify the process. The hypothesis of this experiment is that factors involving the block copolymers have an effect on the shape of the nanoparticles (spherical/rod-like/lamellar).

Procedure:
A stock solution of 0.375g triblock copolymers of PCL/PEG/PCL with molecular weights of 10k/8k/10k, respectively, (which will be denoted as PEG 8k) was dissolved in 15mL Tetrahydrofuran (THF) and 0.375g PEG 1.5k was dissolved in 15mL THF. 0.375g PEG 8k was also dissolved in 15mL N, N, Dimethylformamide (DMF). Further, a 0.025 g/mL PCL/PEG diblock copolymer (molecular weights of 10k/5k amu, respectively) THF solution was made. Additionally, various 0.5M Ca$^{2+}$ and 0.3M PO$_4$$^{3-}$ precursors dissolved in distilled water were prepared.

Sample solutions were prepared by adding the appropriate amount of copolymer solution and the corresponding solvent (THF or DMF). The Ca$^{2+}$ precursor was added and stirred with a magnetic stirrer on a stirring plate for ~10 minutes. Then, the PO$_4$$^{3-}$ precursor was added to the sample and stirred for 20 minutes. The amount of precursor varied, but the ratio of Ca$^{2+}$ to PO$_4$$^{3-}$ was kept at 1.6. On some of the experiment sets, the pH of the samples was raised by addition of ammonium hydroxide. Also, the order in which the precursor and NH$_4$OH were added varied between experiment sets.

After the synthesis of the samples were complete, the samples were allowed to age until the particles settled to the lower part of the vial. TEM and FTIR tests were conducted on selected samples to see the effects of a variable on the HAp particle shape.

Results and Discussion:
Figure 1 shows TEM images of samples 21, 23, 28, and 30 (all four were dissolved in THF and synthesized with the same amount and type of precursors). The [PEG 8k] was increased between samples 21 and 23, respectively and the pH was increased between samples 21, 28, and 30, respectively. By observing the TEM images, all four samples produced similar brush-like particles; thus, changes in [PEG 8k] and pH had negligible effect on particle shape.

Figure 2 shows the FTIR results for pure PEG 8k and Sample 30. Sample 30 shows characteristic PCL carbonyl stretches (1725cm$^{-1}$) and CH stretches (2945cm$^{-1}$). Also, P-O and O-P-O stretches is evident at 1092 cm$^{-1}$ to 1040 cm$^{-1}$ and 600cm$^{-1}$ to 570 cm$^{-1}$, respectively. Thus, formation of HAp with [PEG 8k] could be possible, but additional confirmation is needed.

Figure 1: TEM pictures showing similar brush-like particles for samples 21, 23, 28, and 30.

Figure 2: FTIR characterization of pure triblock PEG 8k (blue) and Sample 30 (red).

Conclusion:
TEM images and FTIR characterization were conducted on selected samples from the THF system. From the TEM images, variance in [PEG 8k] and pH had minimal effect on particle shape. However, from the FTIR characterization, synthesis of HAp particles is possible, but further affirmation is required.

Acknowledgments:
I would like to thank Dr. Shofner for allowing me to participate in her research group. Also, I want to thank Ji Hoon Lee for mentoring me throughout my learning experience in the SURF program and Jasmeet Kaur for her time in taking the TEM images.