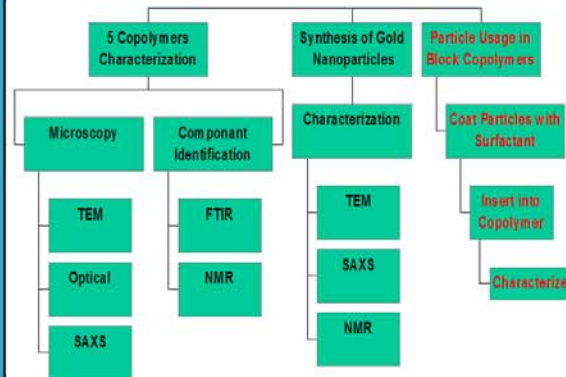


CHARACTERIZATION OF BLOCK COPOLYMERS AND GOLD NANOPARTICLES

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SCOPE OF PROJECT



WHAT IS A BLOCK COPOLYMER?

- A Copolymer is a polymer which contains at least two different materials.
- A Block Copolymer is a copolymer where polymers are chemically joined (via covalent bonds) to form repeating blocks of each polymer.
- Block Copolymers show...
 - Properties of each of the individual polymers.
 - New properties that are explained by the chemical bonds. (Not specific to any one of the polymers contained in the blocks)

MORPHOLOGY

- Block Copolymers 'self-assemble' into morphologies. The morphology can be controlled by varying
 - % composition
 - the temperature at which the copolymer was formed
 - the degree of polymerization
- The most common morphology is lamellar. Others include hexagonal-packed cylinder and body centered cubic.
- Morphologies can be determined using SAXS and TEM.

BLOCK COPOLYMERS

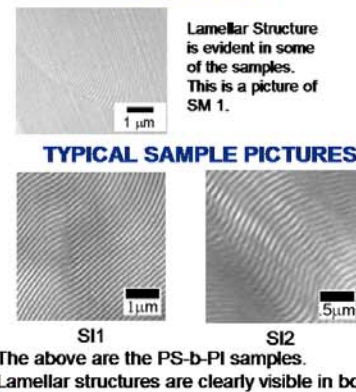
Five samples were characterized.

- **Polystyrene-b-Poly(methylmethacrylate) (PS-b-PMMA)**
 - ~ 85k-b-91k SM 1
 - ~ 50k-b-54k SM 2
 - ~ 38k-b-37k SM 3
- **Polystyrene-b-Polyisoprene (PS-b-PI)**
 - ~ 40k-b-33k SI 1
 - ~ 26k-b-20k SI 2

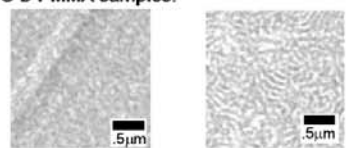
MICROSCOPY

- ♦ **Optical Microscopy**
 - ↪ This method is a quick way to see if the sample's morphology is or is not 3D symmetric. Lamellar structures are not 3D symmetric and therefore should be birefringent.
 - ♦ Samples SI 1 and SI 2 (PS-b-PI) and SM 1 (PS-b-PMMA) were confirmed to be birefringent using an optical microscope and a 1 lambda waveplate.
 - ↪ All samples theoretically should be birefringent.
- ♦ **PREPARATION FOR TRANSMISSION ELECTRON MICROSCOPY (TEM)**
- ♦ **Microtoming**
 - ↪ Determine whether sample is glassy or rubbery
 - ↪ PS-b-PMMA: glassy → cut at room temperature
 - ↪ PS-b-PI: rubbery → using liquid N₂, cut below glass transition temperature
 - ↪ Face the sample with a glass knife until all edges are smooth.
 - ↪ Use a diamond knife to cut slices to < 70 nm.
 - ↪ Collect the slices onto copper grids
- ♦ **Staining**
 - ↪ PS-b-PI samples were stained in OsO₄
 - ↪ PS-b-PMMA samples were stained using RuO₄

TEM RESULTS

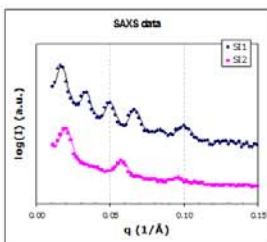
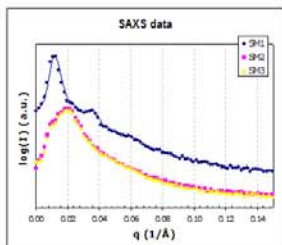


TYPICAL SAMPLE PICTURES

- No structure is clearly visible in either of the PS-b-PMMA samples.
- 
- SM1 SM2
- Are SM1 and SM2 actually PS-B-PMMA?**
- FTIR performed on both samples.
 - Peaks showed evidence of an aromatic ring (styrene) and were similar to results found on PMMA.
 - NMR – Hydrogen and Carbon
 - Results concluded that both PS and PMMA were in our questionable samples

SAXS DATA

Results inconclusive for 2 of the PS-b-PMMA samples.



Results confirmed lamellae in the PS-b-PI samples.

CHARACTERIZATION CONCLUSIONS FOR FIVE ORIGINAL SAMPLES

	TEM Results		SAXS Results		NMR	FTIR
	Birefringent	Lamella?	Lamellar?			
SM1	Yes	Yes	Yes	N/A	N/A	
SM2	No	No	No	confirmed to be PS & PMMA	confirmed to be PS & PMMA	
SM3	No	No	No	confirmed to be PS & PMMA	confirmed to be PS & PMMA	
SI1	Yes	Yes	Yes	N/A	N/A	
SI2	Yes	Yes	Yes	N/A	N/A	

SYNTHESIS OF GOLD NANOPARTICLES

Reaction performed as described in the

Journal of the American Chemical Society 2000, 122 12890-12891

"Improved Synthesis of Small (d_{core}=1.5nm) Phosphine Stabilized Gold Nanoparticles"

by Weare, Reed, Warner, and Hutchinson

This synthesis was chosen because the ligand that in the end surrounds the particles is PPh₃. This ligand makes the particles soluble in organic solvents and it is easy to put other molecules onto it.

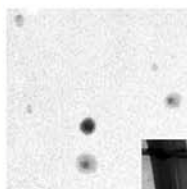
CHARACTERIZATION OF Au PARTICLES

NMR – Check Particles to make sure that all Phosphine has been rinsed off of them.

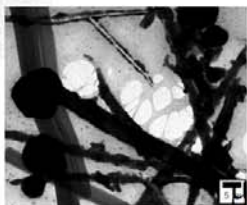
TEM – Place some particles onto a grid and using the TEM get an approximate size of the particles.

SAXS – If the particles are small enough (<40 nm), the SAXS camera can be used to determine the particle sizes.

Au PARTICLES

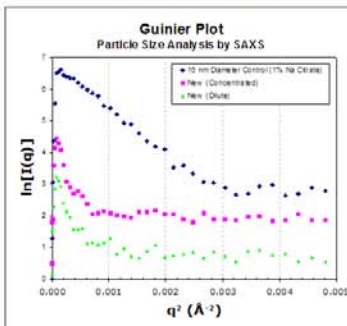


Au Particles on Carbon Coated Grid



Unknown objects on Formvar Grid

SAXS RESULTS FOR Au NANOPARTICLES



CONCLUSIONS

Of the 5 original Block Copolymer Samples, 2 were disordered and 3 formed lamellar structures as predicted.

The Gold Nanoparticles are larger than 16nm judging by the SAXS and TEM results. The particles either crashed out during the reaction or formed aggregates.

FUTURE WORK

After the Au particles have been synthesized to be approximately 1.5 nm and characterized completely, they will be coated with a variety of surfactants.

Each of the original five copolymers will be prepared again, this time with the addition of the Au nanoparticles.

Characterization of each of the 5 samples will be repeated.

ACKNOWLEDGEMENTS

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