Lecture 15: Hierarchically Ordered BCP-Nanoparticle Composites

Polymer Based Nanocomposites

Matrix: Polymers and Block Copolymers

Filler: Nanoparticles

0, 1, 2D Fillers

Ligands for Dispersion

Co-assembly of BCP + Ex situ synthesized NP

BCP Template for Control of Location and Orientation of NP

Morphological Interplay and Emergent Properties

Nanocomposites

- **Nanocomposites:** Heterogeneous materials with at least one characteristic length scale in the nm range

- **Polymer Nanocomposites are comprised of a polymeric material and a nanoscale material.**
  - Typically made at 1-5 vol% of nanoparticles
  - New properties arising from: particle size and shape, particle locations and (possible) connectivity/proximity of particles

- **Many factors affect polymer nanocomposite structure:**
  - Synthesis method (melt compounding, solvent blending, in-situ polymerization, emulsion polymerization etc).
  - Type of nanoparticles and their surface treatments (ligand shells)
  - Polymer matrix (Crystallinity, Molecular Weight, Polymer Chemistry, Blocks…)
  - Nanocomposite morphology: ***Control of location and orientation of NP***

- **Understanding and optimizing composite properties is very challenging and important.**

NanoComposite Opportunities

Properties become **size and shape dependent** below some critical length scale.

Dynamically tunable materials and properties.

Hybrid material combinations ***unattainable*** in nature.

Sophisticated tailoring of Composite Properties

New materials, new properties, new phenomena
Hierarchical structures; gradients, proximity effects…

Spatial and Orientational Ordered NP --relatively unexplored regime - **lots of potential!**

Crystalline NanoParticles

- Optical properties determined by *quantum confinement effects*, (and scattering, absorption, dielectric constant)

The color of Gold

Image from Wikimedia Commons, http://commons.wikimedia.org

Metal: (plasmonics)

→ surface scattering affects electronic properties for particle size < mean free path of an electron (plasmon: coherent electron oscillation); energylevel discretization for size < 1.0 nm (metals become insulators!)

Variable size CdSe dots

Semiconductor:

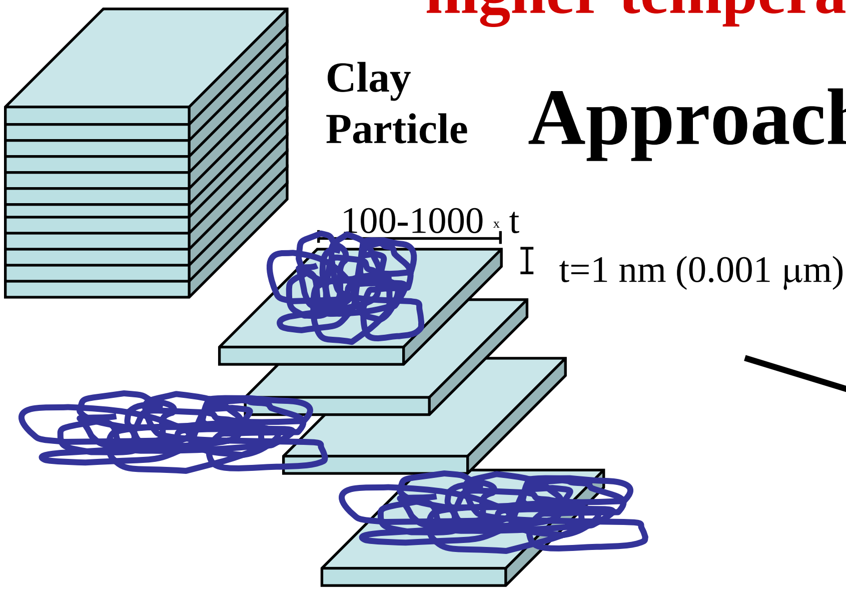
→ band gap widens for size < exciton radius (plus high photoluminescence efficiency)

Smallest QDs **Bawendi et al., MIT**

NanoWorld Surprises:

Mechanical Example: Polymer Nanocomposites

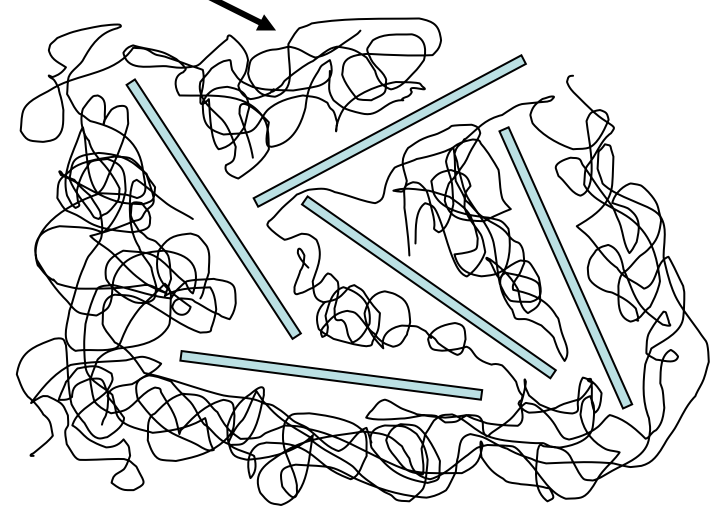
Objective: **Produce easily processable, mechanically robust, higher temperature polymers via inexpensive fillers**



Approach: Exfoliation of Clay

Surface Functionalized
mica-type layered silicate (clay)

Polymer (thermoplastic or thermoset)



Exfoliated Nanocomposite

Polymer Nanocomposites

Outstanding Property Enhancements

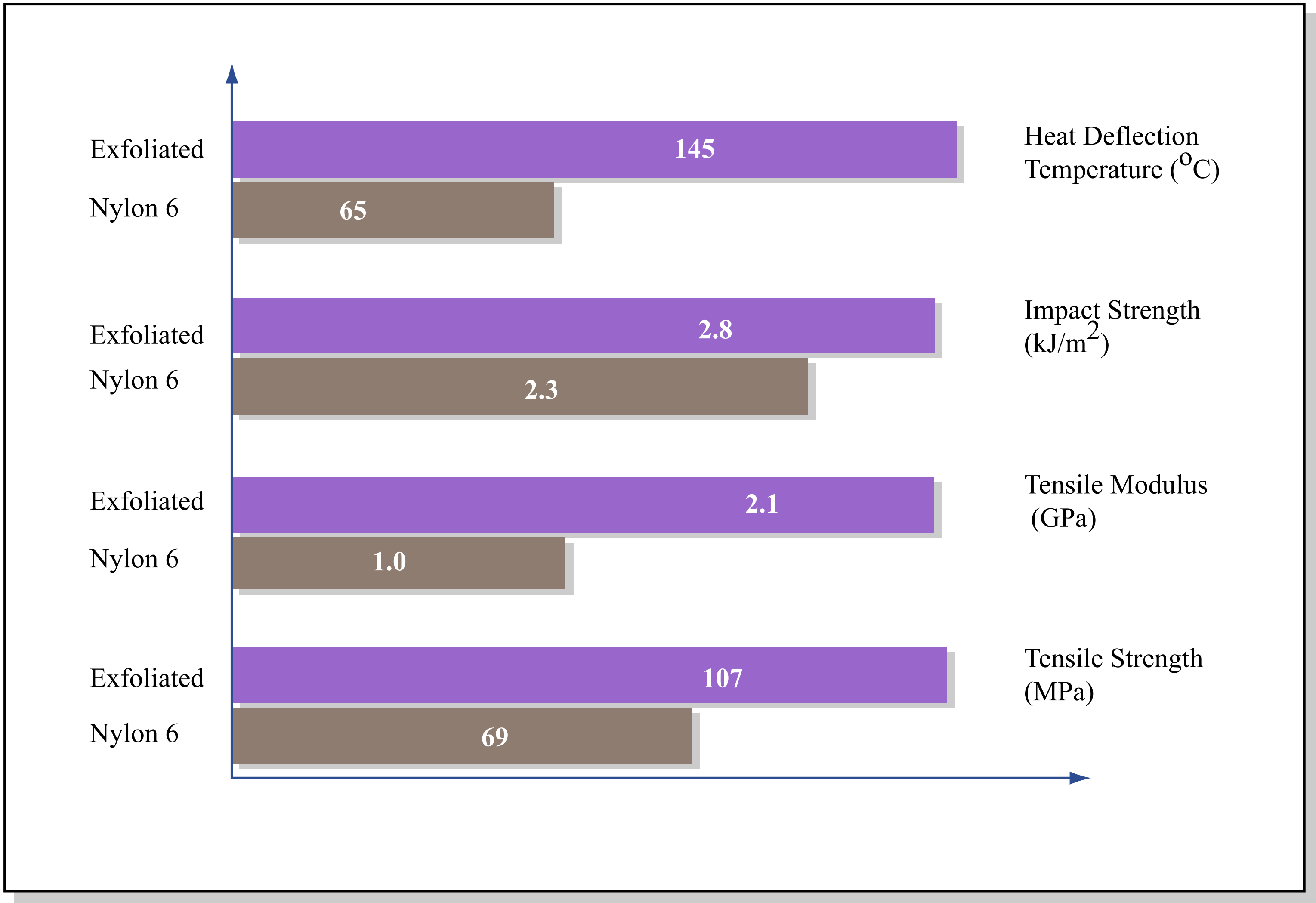


Figure by MIT OCW.

Characteristics of NP Composites

- Low vol % particle-particle correlation threshold
  - –Ultra low percolation threshold (~ 0.1 vol%)
- Particle number density up to ~ 10^{20} / cm^3
- S/V per particle of ~ 10^7 cm^2/cm^3
- Particle size, interparticle spacing and R_g of the polymer host are all comparable

Conventional Composites vs. NanoComposites

Image removed due to copyright restrictions.

Please see Fig. 1 in Bockstaller, Michael M., et al. “Block Copolymer Nanocomposites: Perspectives for Tailored Materials.” *Advanced Materials* 17 (2005): 1331-1349.

Economics of Additives

- MMT nanoclays
- Carbon fibers
- POSS®
- MWNT (multiwalled)
- SWNT (single walled)
- n-Silica
- n-Aluminum Oxide
- n-Titanium Dioxide

- $3.5/lb
- $95/lb
- $1,000/lb-R&D
- $3,178/lb ($7/g)-R&D
- $227,000/lb ($500/g)
- $8.5/lb
- $11.8/lb
- $11.8/lb

J Koo/R. Vaia

The Future - CNT the ultimate polymer ?

$E = 1$ TPa
(exp and calc)

$\sigma_f \sim 50 +$ GPa
(calc)

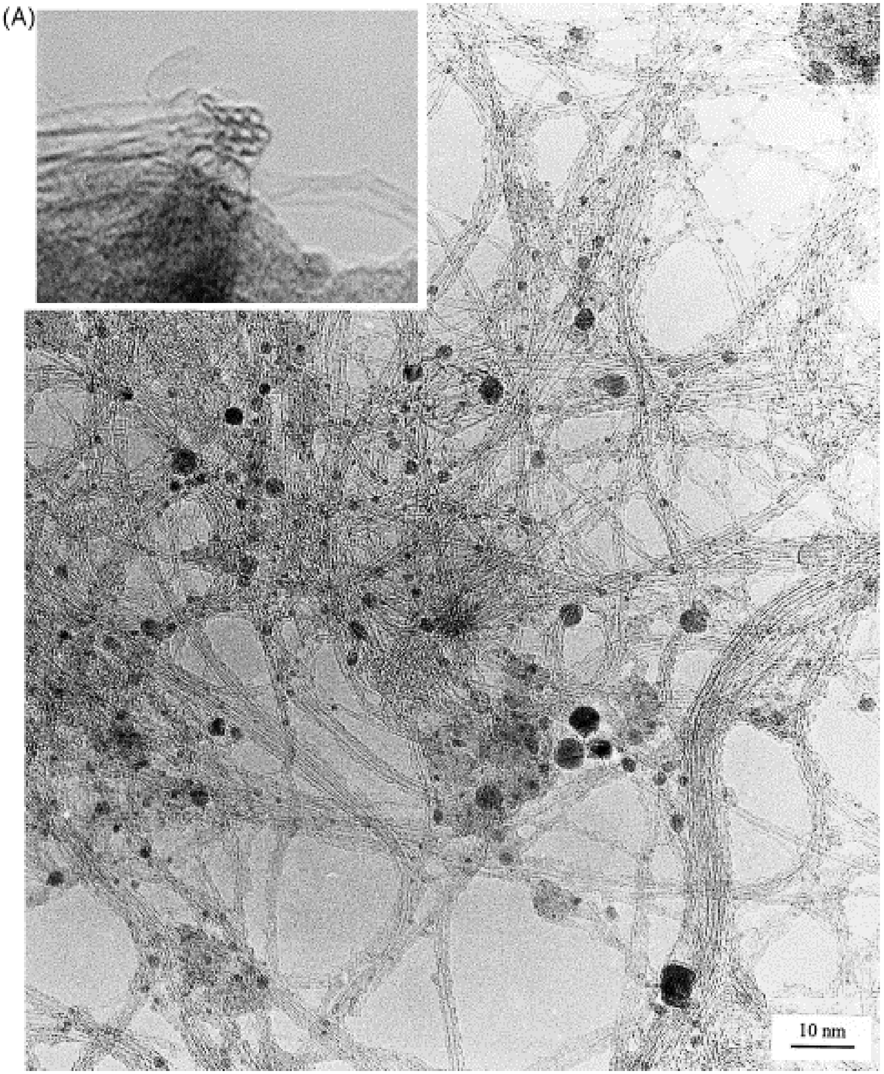
Values for individual tubes

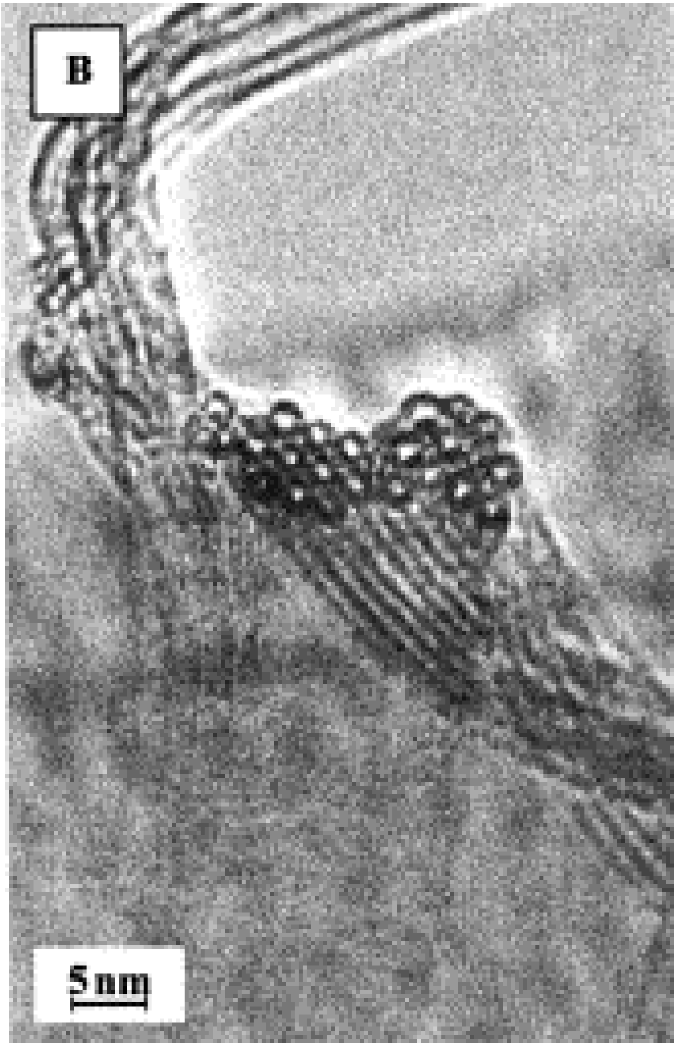
CNT Satellite Tether

Image removed due to copyright restrictions.

Please see the cover of *Scientist Today*, July/August 1997.

Single wall CNT fibres

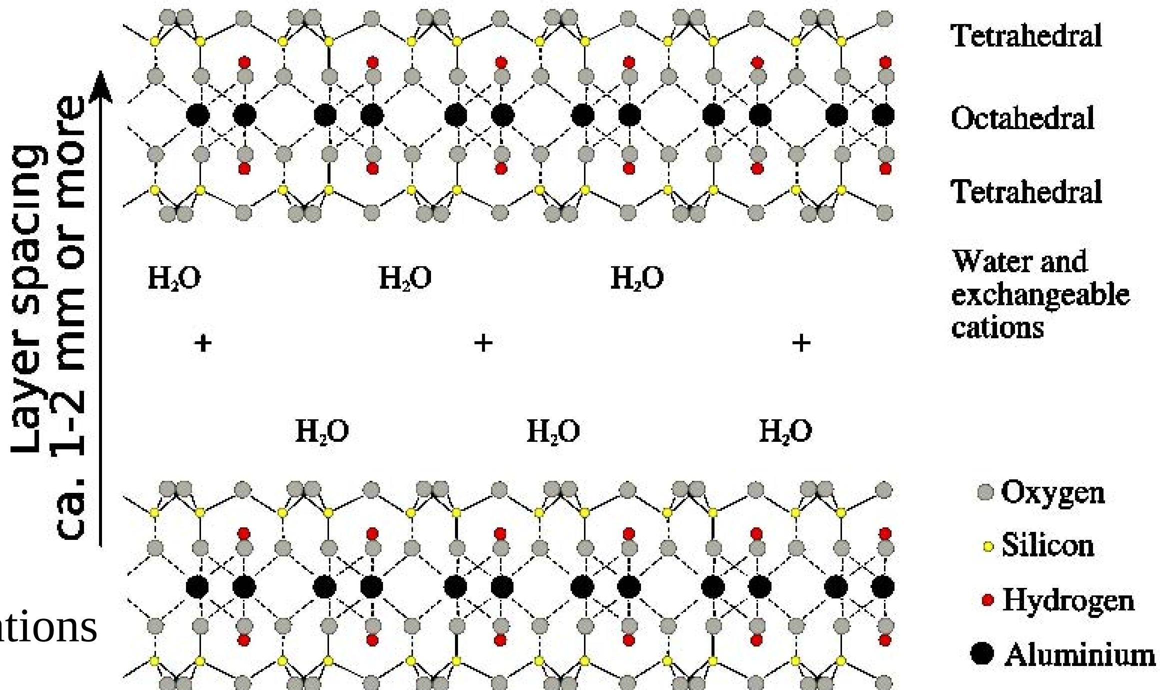




TEM images - note catalyst particles in left image.

2D Sheet-like NPs: Sodium Montmorillonite

- Clay
- 2D Sheet-like structure
- (2:1) phyllosilicate
- 300:1 Aspect ratio
- Isomorphoric substituted cations
- Counter ions in galleries hold individual sheets together to form 10-20 sheet stacks called “tactoids”



Courtesy Andreas Trepte and Itub. Image from Wikimedia Commons, http://commons.wikimedia.org.

Lateral dimensions > 300 nm,

Individual layer thickness ~ 1nm

NP-Block Polymer Materials Platform

BCP Host Properties:

mechanical, optical, gas transport…
conductive, electroactive, photoactive

but still ***limited*** (low index of refraction, nonmagnetic, relatively soft, permeable…)

Accessing New Properties via NP Additives

- 0, 1 and 2D particles (e.g. Q Dots, SWCNTs, Clays)
- spatial and orientational ordering of particles
- emergent properties from proximity effects

Nanoparticle Composites: MULTIFUNCTIONAL MATERIALS

Key Attributes of NP-BCP Composites

- Size, shape, symmetry of both the NP and the BCP host
- Thermodynamic interactions (ligands and polymer)
- At least one NP dimension < one BCP domain length
- Processing conditions - applied fields
- Emergent properties

2 Approaches to NP-BCP Composites

(1) ***In situ synthesis*** of NP within BCP matrix

Diffusion/reaction/nucleation but restricted NP synthesis pathways since chemistry must occur inside a polymeric matrix

(2) ***Ex situ synthesis*** of NP followed by blending into BCP matrix:

Synthesis is done under preferrred conditions (e.g. in solution w/o oxygen, well stirred, homogeneous reactions…)

Followed by Co-assembly of NP + BCP ~ (equilibrium thermodynamics)

Nanoparticle Block Copolymer Composites

Novel Microstructured Materials
With Tunable Properties

Ex situ Synthesis
&
Co-assembly

Nanoparticle

Strong,
Stiff,
High dielectric constant,
Luminescent,
Magnetic,
Impermeable
Conductive (thermal/electrical)
-*basically NPs provide property enhancements not available with polymers*.

Block Polymer

Self assembly in
1D, 2D, 3D
Processing
MultifunctionalPropertie
Glassy, rubbery

Unique properties of the Nanocomposite arise from :

Small distances between components
Confinement & Compartmentalization
Ultra-large interfacial area per volume

Stabilization of non-equilibrium phases
Multifunctionality-tailoring of properties
Size-dependent physics & chemistry

0-D Nanoparticles

TEM

GOLD

SiO_2

Image removed due to copyright restrictions.

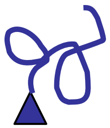
Please see Supporting Material for Bockstaller, Michael R., et al. "Size-Selective Organization of Enthalpic Compatibilized Nanocrystals in Ternary Block Copolymer/Particle Mixtures." *Journal of the ACS* 125 (2003): 5276-5277.

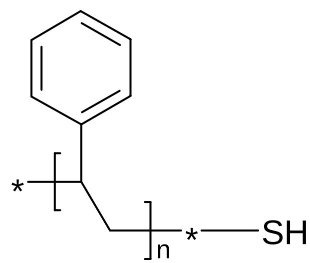
$\langle d \rangle$ = 3-5 nm

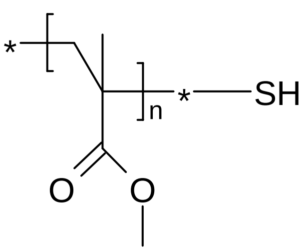
$\langle d \rangle$ = 45 nm

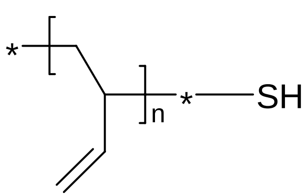
Ex situ Synthesis of NP Ligands

Grafting-To



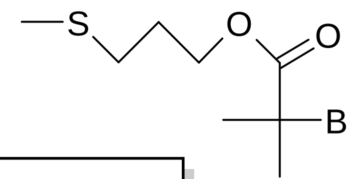


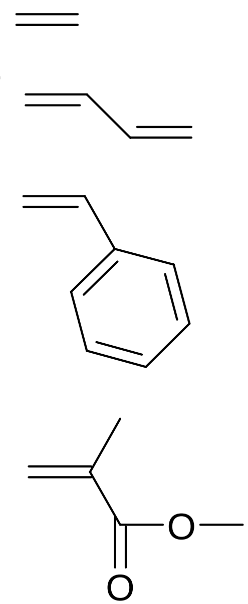




Grafting-From

monomer





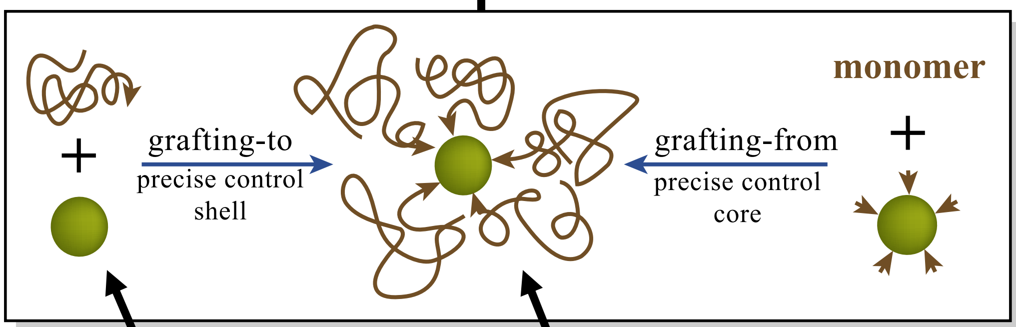


Figure by MIT OCW.

Gold NP

Corona - polymer ligands

Use thiol terminated chain to attach to gold NP surface

Self Organization via Co-assembly of *XD*-*YD* NP-BCP Materials

Parameters

- Nanoparticle: size and shape: a, b, c and *IPDS* *X = 0, 1, 2D dimensional*
- BCP domain size and shape: A, B, C and *IMDS* *Y = 1, 2, 3D periodic*
- Corona: ligand chemistry, grafting density, MW of ligand
- BCP: composition, architecture, MW
- Interaction parameters: χ_{ij}

Example:

1D NP in 2D BCP

Hex packed cylinders

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Please see Fig. 2 in Bockstaller, Michael M., et al. "Block Copolymer Nanocomposites: Perspectives for Tailored Materials." *Advanced Materials* 17 (2005): 1331-1349.

nanorod

Morphological Interplay: Co-assembly of NP-BCP Materials

- Order-Order Phase Transitions:
  - Volume fraction driven (NPs increase the effective vol fraction of the microdomains that they reside in)
  - Shape accomodation driven
    - e.g. NP Sheet + BCP cylinder domain -> BCP Lamellae
    - e.g. Curved NP rods + BCP cylinders -> BCP Lamellae
- NP Templating of BCP:
  - Heterogeneous nucleation of BCP domains on NP
  - Kinetics of transformation is enhanced
  - Orientational ordering of BCP by flow orienting NP
- Field Assisted Assembly: Top down <-> Bottom Up
  - Topographic confinement: commensuration to template
  - Flow, magnetic and electric fields

NP-BCP Symmetry Compatibility Map

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Please see Fig. 4 in Bockstaller, Michael M., et al. “Block Copolymer Nanocomposites: Perspectives for Tailored Materials.” *Advanced Materials* 17 (2005): 1331-1349.

Compatible NP-BCP Nanocomposites

0D - 3D

1D - 2D

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Please see Fig. 6 in Bockstaller, Michael M., et al. "Block Copolymer Nanocomposites: Perspectives for Tailored Materials." *Advanced Materials* 17 (2005): 1331-1349.

~2D - 3D

2D - 1D

Chain Topology Issues

Block Polymers

Diblock

Limited Interdigitation

Triblock

Bridges and Loops

junctions

NP/Block Polymer Composites

Next to NP: Loops only

Particle-Matrix Energetics

Incorporation of NPs into the microdomains, locally deforms the chains.

Chain deformation and IMDS area increase

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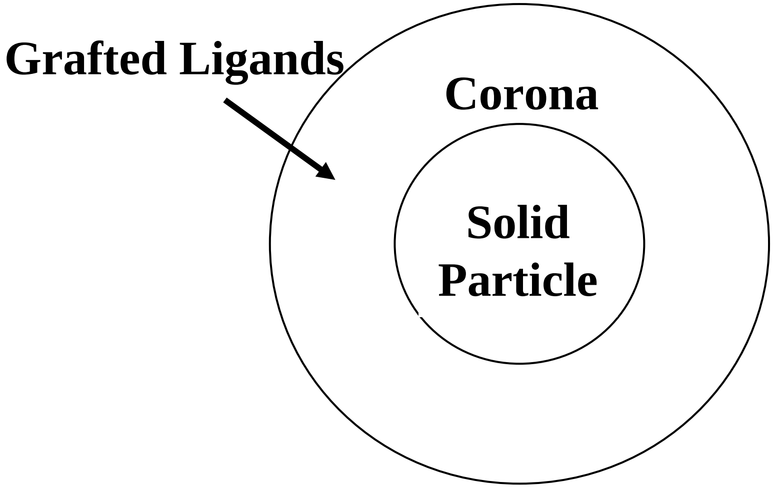
Please see Fig. 3 in Bockstaller, Michael M., et al. “Block Copolymer Nanocomposites: Perspectives for Tailored Materials.” *Advanced Materials* 17 (2005): 1331-1349.

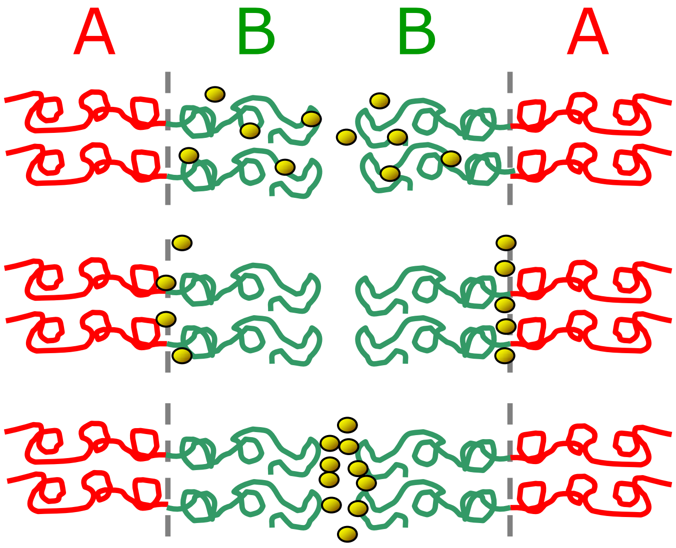
Location, Location, Location

- ❑ Target a specific domain

- ❑ Locate *within* the domain

  - Homogeneous
  - Interfacial
  - Central





0D-1D NP-BCP Nanocomposites

Location:Interfacial

Small Au particles

Gold NP

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Please see Fig. 9 in Bockstaller, Michael M., et al. "Block Copolymer Nanocomposites: Perspectives for Tailored Materials." *Advanced Materials* 17 (2005): 1331-1349.

Silica NP

Location:Center

Medium size SiO_2 particles

Ternary Nanocomposite

Locations:Interfacial & Center

(see next slide for details)

Ternary NP/BCP Nanocomposite
(2 types of particles)

Control of Particle Location

PS-PEP+SiO_2-R_2($\phi \sim 0.04$)+Au-S-$C_{18}H_{37}$ ($\phi \sim 0.04$)

Cross sectional TEM

Image removed due to copyright restrictions.

Please see Fig. 2 in Bockstaller, Michael R., et al. "Size-Selective Organization of Enthalpic Compatibilized Nanocrystals in Ternary Block Copolymer/Particle Mixtures." *Journal of the ACS* 125 (2003): 5276-5277.

Au	$\langle d \rangle$ = 3 nm	Located near the IMDS
SiO_2	$\langle d \rangle$ = 22 nm	Located near the domain center

Electrical Anisotropy in Nanocomposites

Ion transport is 100 times greater parallel to clay layers than when ions have to navigate around the high aspect ratio platelets

Images removed due to copyright restrictions.

GISAXS showing anisotropic orientation of clay platelets

Hybrid organic/inorganic systems

Please see Scheme 7 in Simon, Peter F. W., et al. "Block Copolymer-Ceramic Hybrid Materials from Organically Modified Ceramic Precursors." *Chemical Materials* 13 (2001): 3464-3468.

Mechanical properties can be tuned over several orders of magnitude !!!

The BCP is used as a "structure directing agent" for the inorganic precursor materials. A condensation reaction takes place leading to the formation of the inorganic material

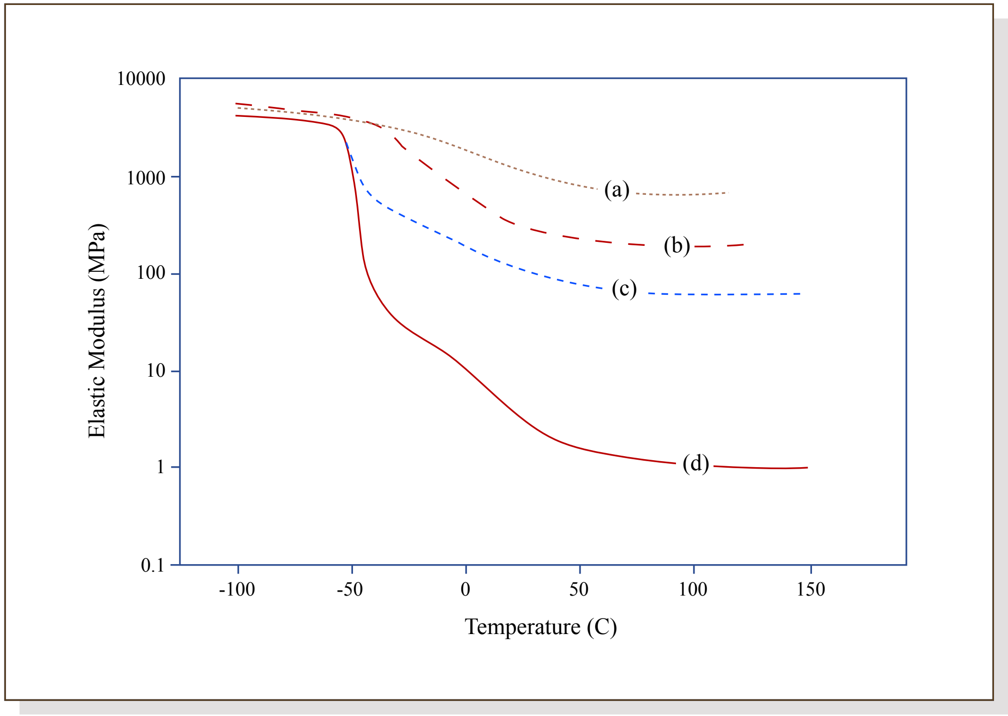

Figure by MIT OCW.