



Towards Novel Multifunctional Polymer Nanocomposites

Elucidating the Role of Interfaces on Structure and Transport in Nanostructured Polymer Hybrid Materials

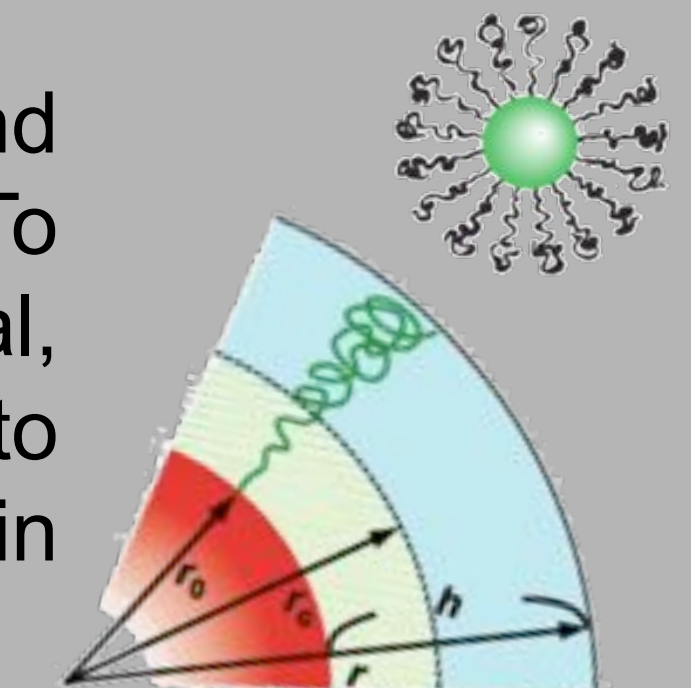
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Synopsis

Recent progress with engineered nanomaterials allows us to create very precise and well-defined polymer-grafted nanoparticles that can be used as additives to polymer matrices to enhance electrical, thermal, and mechanical properties of composite materials. However, a primary obstacle to the implementation of these novel composite materials exists in the control of dispersion/aggregation of the nano-filler additives. To overcome the existing challenges, it is necessary to understand the origin of miscibility in these blend systems. While neat nanoparticles tend to aggregate, leading to phase separation in the composite material, surface functionalized nanoparticles, 'particle brushes,' can be incorporated into polymer matrices with the optimization of polymer graft identity, degree of polymerization, and chain grafting density, which lead to thermodynamically favorable miscibility. An underlying theme in both projects described below is the development of understanding of the role of interfaces in the synthesis of new functional materials used in applications such as water filtration and sustainable energy.



I. Bioactive Microporous Polymer Nanocomposites for Self-Regulatory Membranes

Background

Block copolymers (BCPs) are segmented polymers containing two repeat units that microphase separate to form unique morphologies [1]. These structures can be used as templates for nano-fillers, such as particle brushes. In this study, PS-*b*-PMMA is used as a template for enzymes functionalized with PEG, a polymer compatible with only the PMMA block.

Challenge:

Although dispersion of inorganic nanoparticles and homopolymers in BCPs has been studied extensively, little is known about the dispersion of organic/biological nano-fillers, such as functionalized enzymes, in BCPs [3].

Motivation:

1. New Science: Elucidate to what extent the governing parameters of inorganic nanoparticle dispersion apply to organic/biological nano-filler dispersion
2. Application: Demonstrate a bioactive self-regulating membrane used for water purification, protective clothing, pharmaceutical purification, or nanoparticle filtration

Objectives

- Elucidate the **governing parameters that control structure formation/dispersion** in a BCP/organic filler system
- Determine to what extent **sequestration affects biological functionality** in the organic fillers
- Evaluate whether sequestration of enzymes can **trigger phase transformations** in the BCP matrix

Research Plan

There are three main thrusts in this research plan:

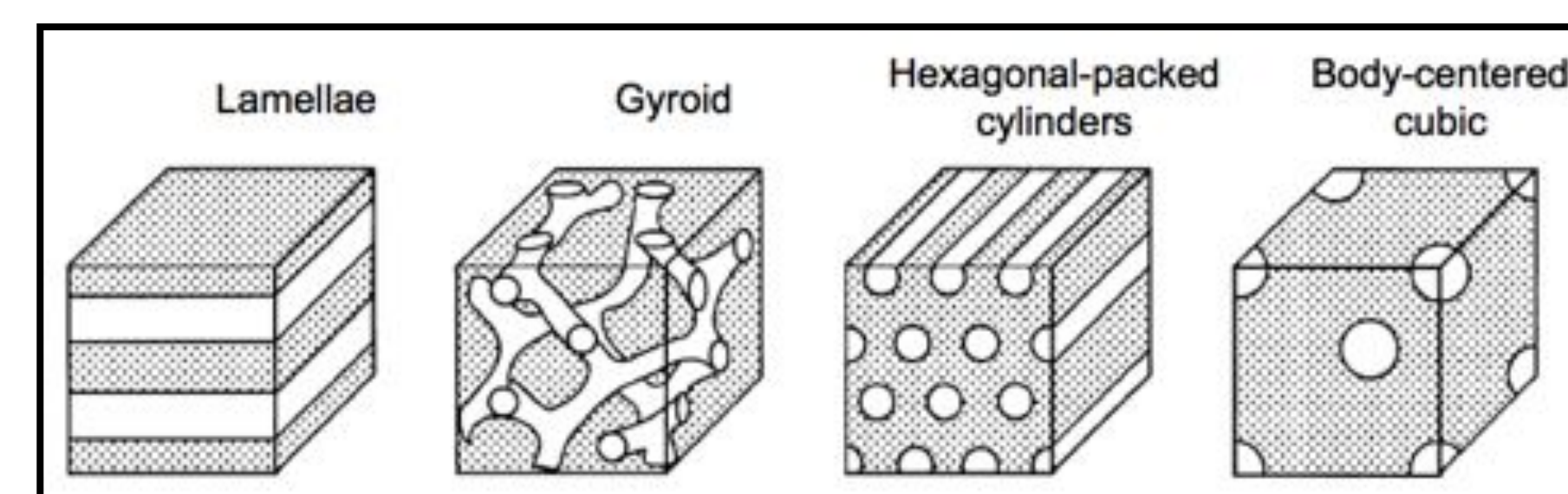
1. Synthesis and characterization of polymer-stabilized enzymes: Matrix-Assisted Laser Desorption/Ionization-Time of Flight (MALDI-TOF) and Dynamic Light Scattering (DLS)
2. Characterization of lamellar BCP (PS-*b*-PMMA model system): Transmission Electron Microscopy (TEM) and Small Angle X-ray Scattering (SAXS)
3. Synthesis and characterization of BCP/functionalized enzyme blend systems: TEM and SAXS

Results to Date

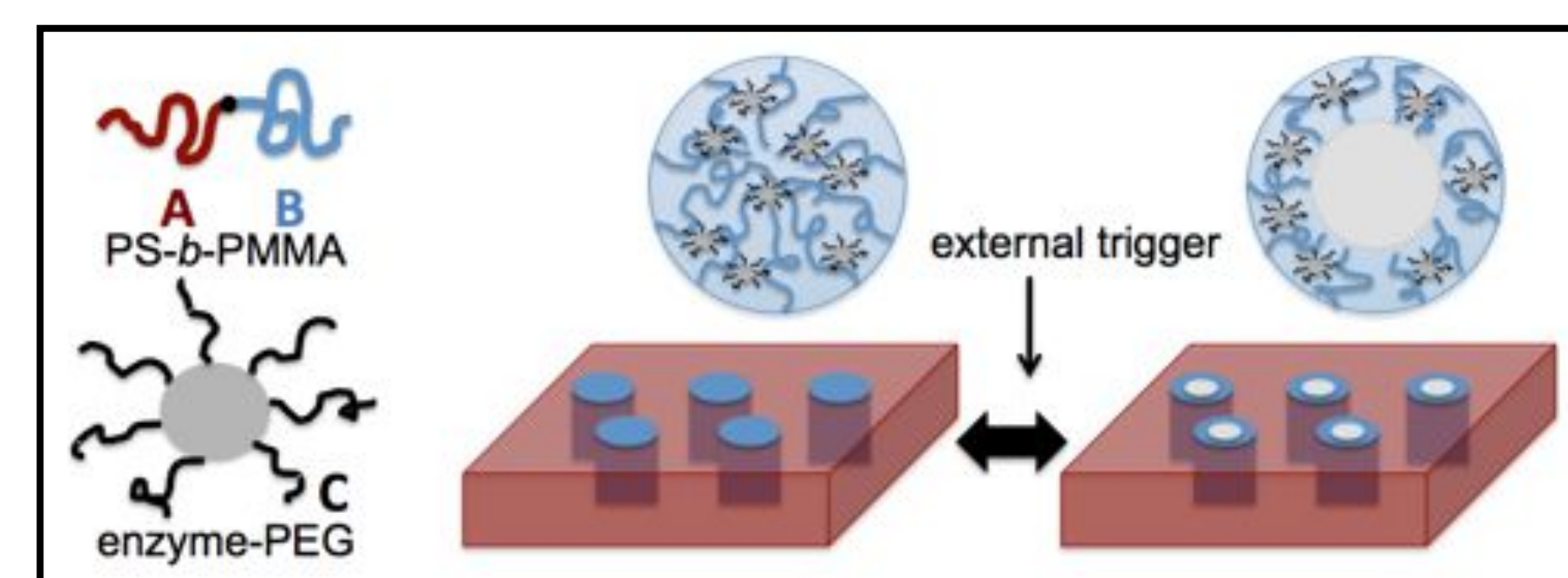
MALDI-TOF performed on PEGylated Trypsin shows a distribution in the degree of functionalization of the enzyme. Characterization using TEM and SAXS reveals a lamellar structure for the neat BCP. This lamellar structure was retained after the addition of 1 wt. % PEG-Trypsin [5].

Conclusions

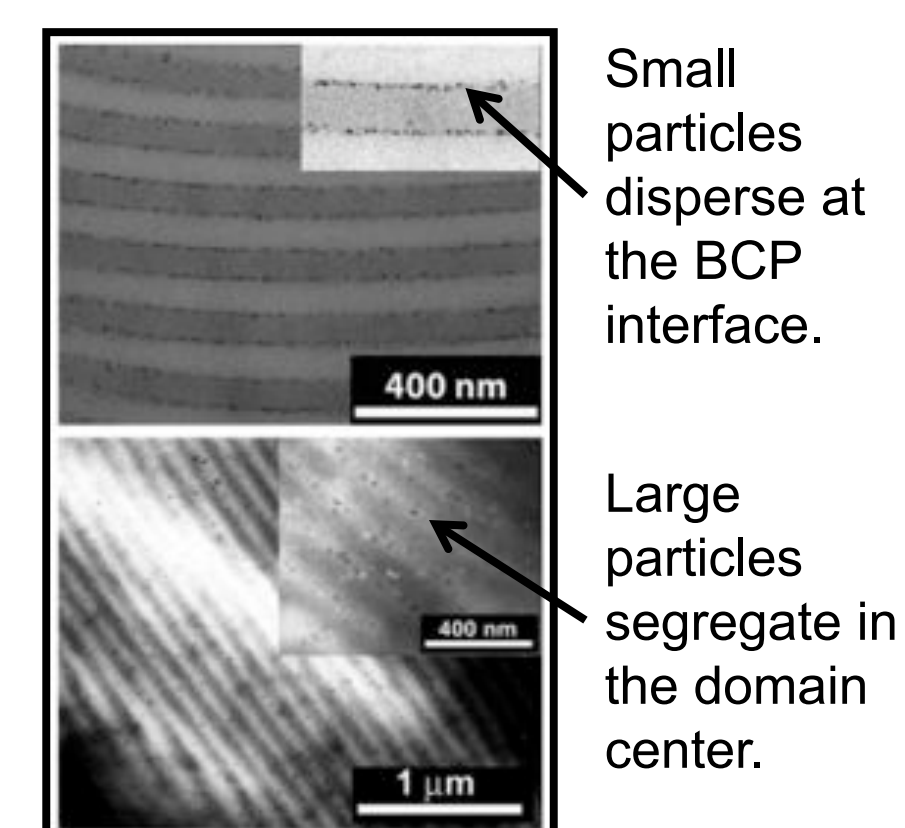
- ✓ Enzymes can be selectively functionalized with polymeric ligands to form bioactive particle brush analogs.
- ✓ Completion of the blend system studies will allow for the determination of functionalized enzyme dispersion.



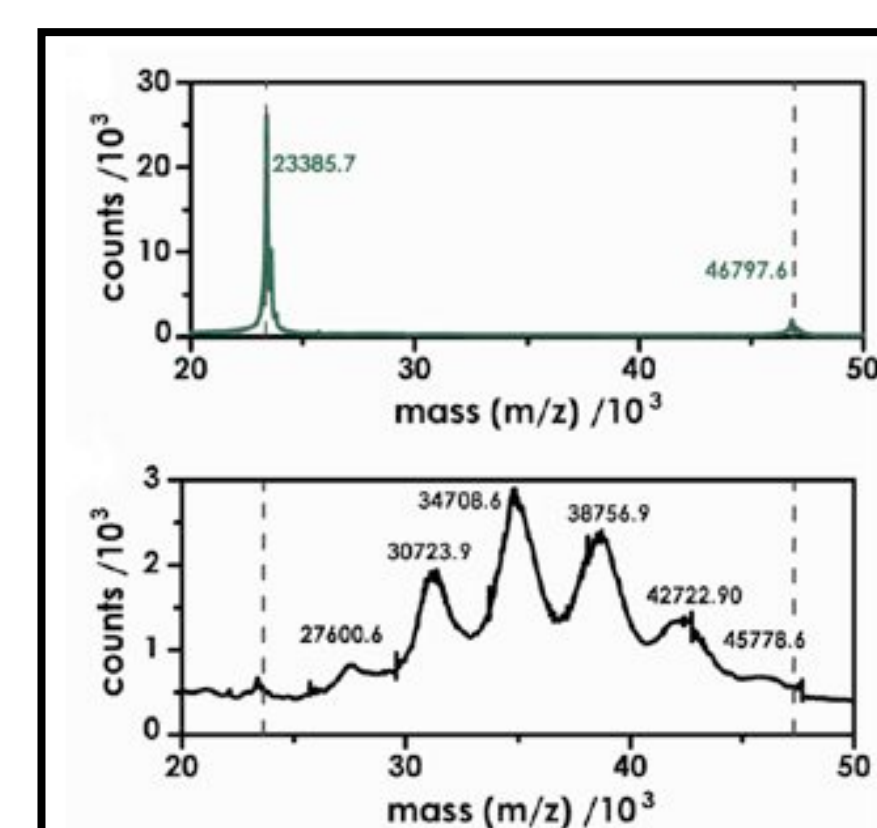
Morphologies that arise due to microphase separation in BCPs: Lamellar and Cylindrical are of interest to this study [2].



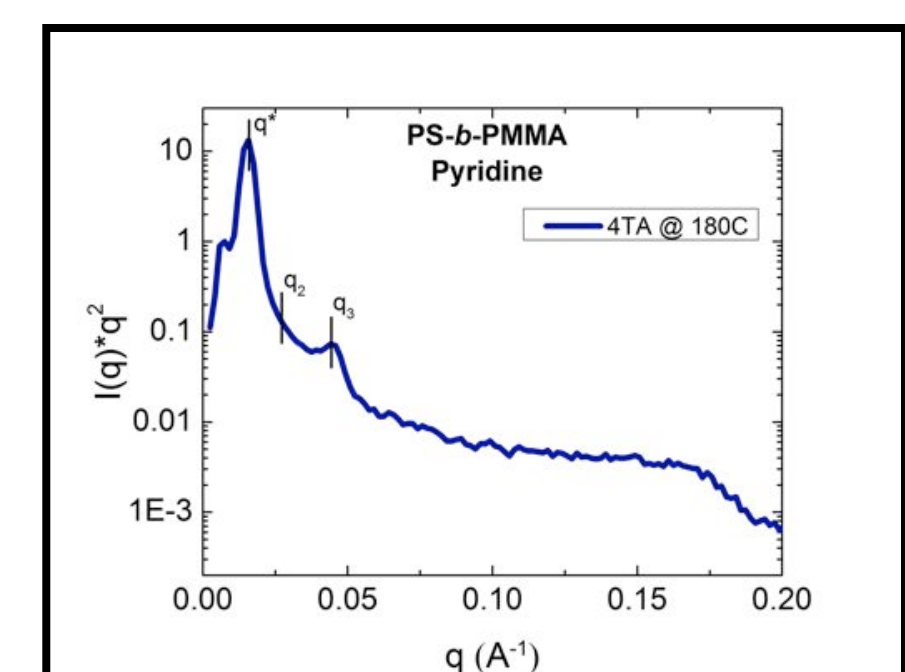
Dispersion of functionalized enzymes in a cylindrical BCP can lead to a tunable membrane with open and closed states.



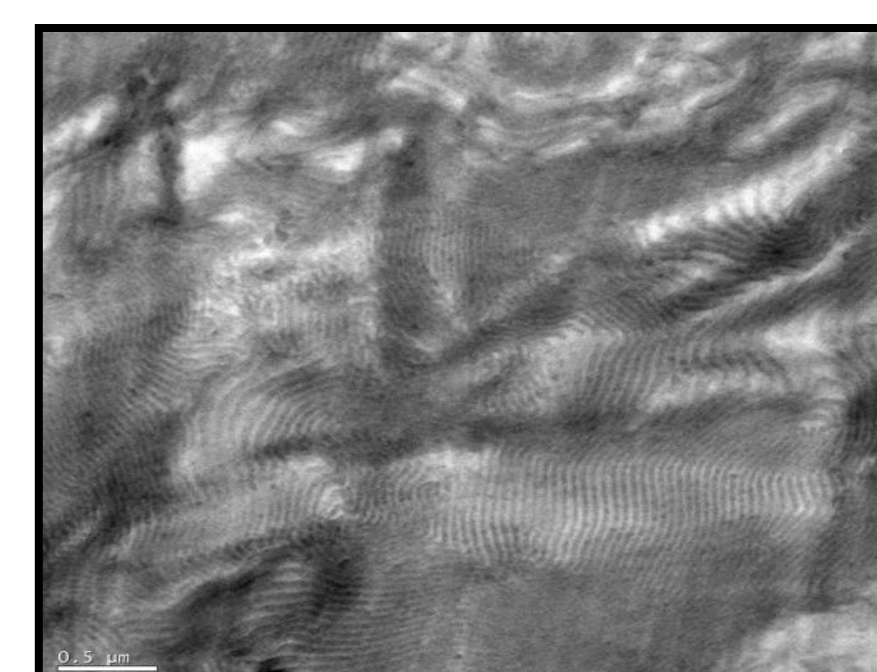
TEM: dispersion of inorganic nanoparticles in BCPs has been widely studied [3].



MALDI-TOF: number of ligands ranges from 1-5 for PEG-Trypsin [4].



SAXS: q/q^* ratios indicate a lamellar structure in the neat BCP (no fillers present).



TEM: PS-*b*-PMMA retains a lamellar structure after the addition of 1 wt.% PEG-Trypsin.

II. Multifunctional Polymer Nanocomposites

Background

The progression of sustainable environmental technologies requires materials with property combinations unattainable using current materials. However, embedding inorganics in polymeric media often comes with challenges. One example is inorganic additives in polymer glasses that usually act as light scattering centers, leaving the glass opaque.

This scattering caused by additives is proportional to the particle volume, and polarizability

$$C_{sca} \sim V_p^2 (\Delta\alpha^2)$$

Where polarizability is defined as the mismatch between dielectrics of the polymer and particle

$$\Delta\alpha \sim (\epsilon_p - \epsilon_m)$$

With controlled surface modification of additives and use of the Maxwell Garnett effective medium approximation, we aim to modulate the effective dielectric constant of the brush particle and significantly decrease light scattering in the inorganic/polymer blend [6].

Objective

The objective of this research is to attain high filling fractions of inorganic additives to polymer glasses for enhanced functionality while still maintaining optical transparency. Using effective medium concepts, we aim to design brush particles that will improve properties in polymeric media without losing transparency.

Research Plan

This research is divided into four main thrusts:

1. Synthesis of particle brushes of varying sizes and identities
2. Elucidation of the phase diagram / thermodynamics of the composite
3. Optical and thermal characterization of each particle brush dispersion in polymer glasses
4. Comparison of experimental data with theoretical effective medium models

Results to Date

In collaboration with the Matyjaszewski lab, controlled synthesis of the first particle brush systems using ATRP (Atom Transfer Radical Polymerization), 7.7SiO₂SAN24 (SiO₂ nanoparticle with radius 7.7 nm, random copolymer poly(styrene-*r*-acrylonitrile) with a degree of polymerization $N = 24$) was accomplished. According to Maxwell Garnett theory, this system will render the dielectric constant of the particle brush identical to PMMA [10].

Conclusions

- ✓ SiO₂ nanoparticles grafted with SAN are miscible with PMMA.
- ✓ The nanoparticles with the ratio of SAN:SiO₂ grafting predicted by the Maxwell Garnett theory show significant suppression of scattering when compared to all other systems.
- ✓ Future work includes studying the limitations and boundaries of the Maxwell Garnett effective medium approximation in high volume fraction inorganic polymer nanocomposites.

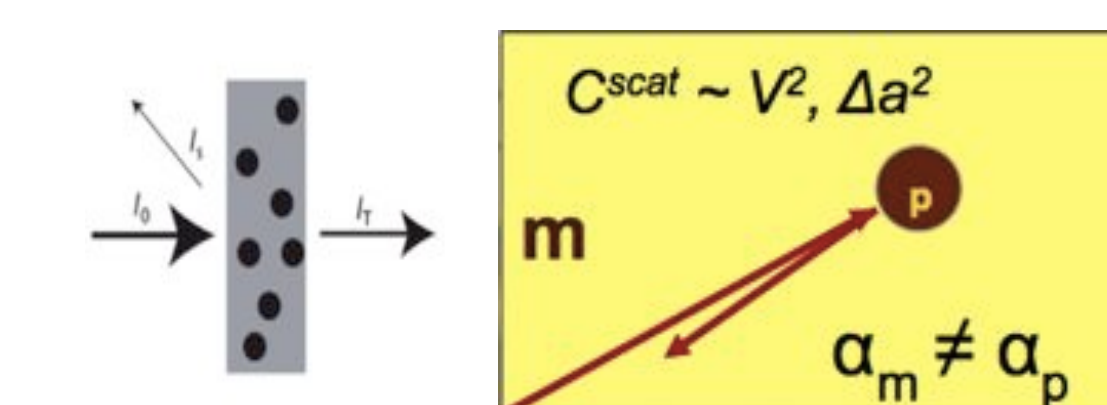
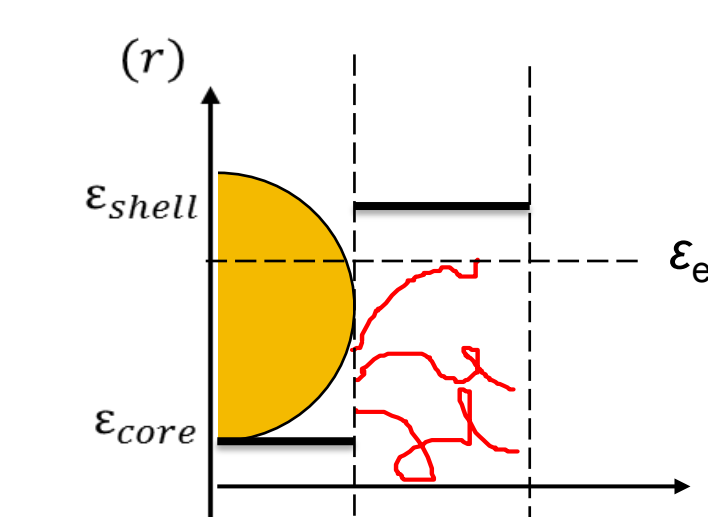
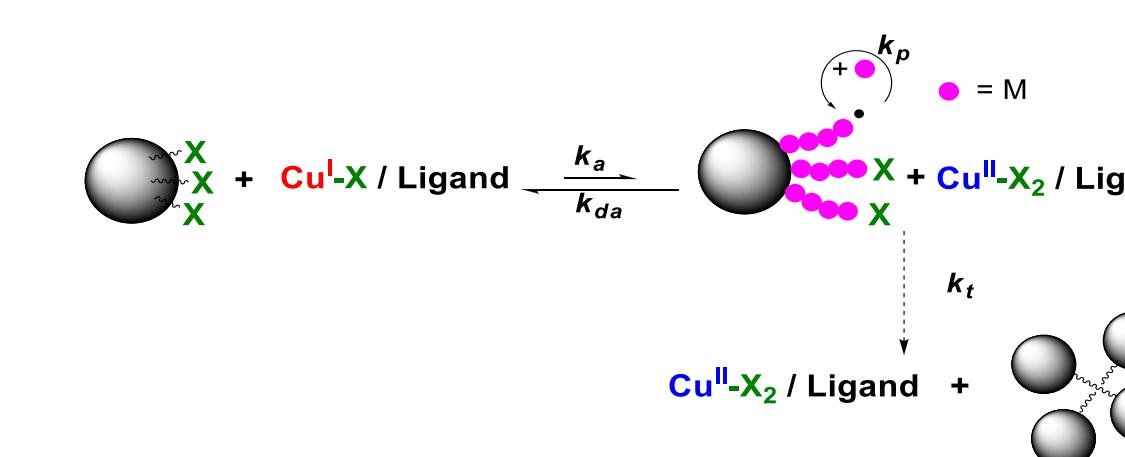


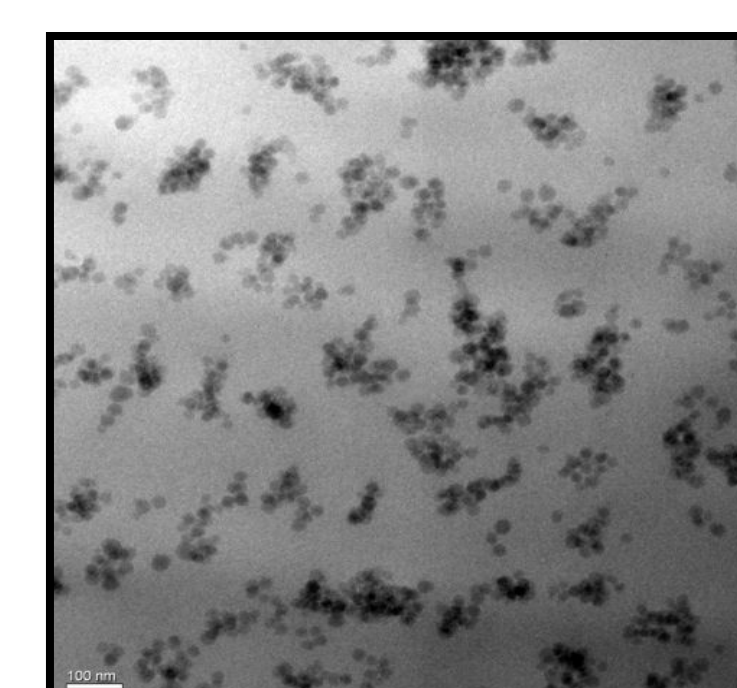
Illustration of light scattering in a particle filled polymer, highlighting the relevant parameters that affect scattering: particle volume and polarizability [6,7].



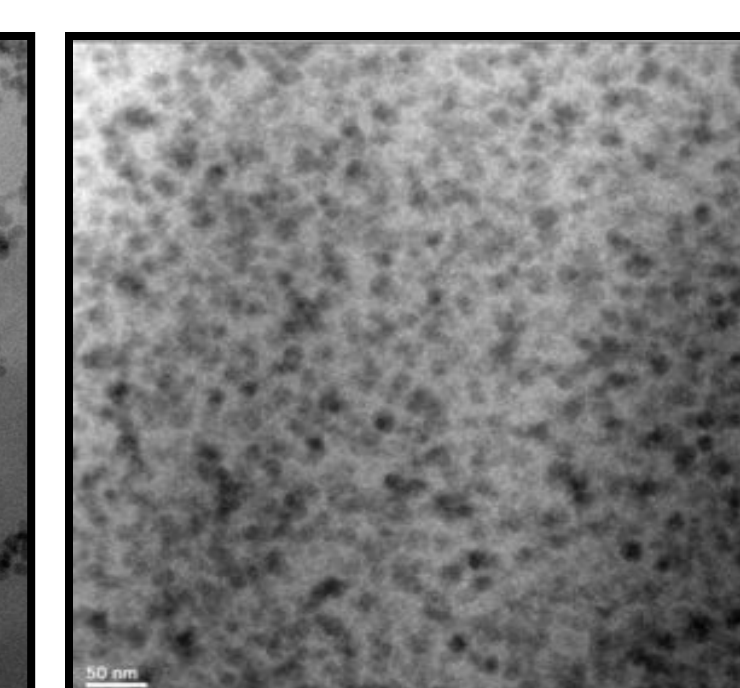
According to the Maxwell Garnett approximation, we aim to modulate the "effective" dielectric of a particle brush to null dielectric mismatch [7].



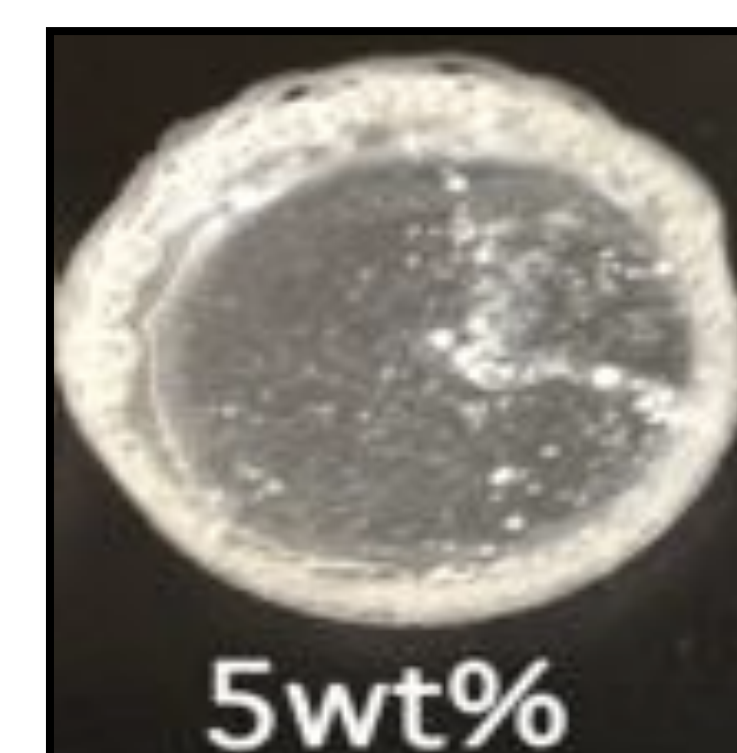
Schematic of ATRP (Atom Transfer Radical Polymerization). Particles are synthesized using MIBK as the initiator and CuBr/PMDETA for the ligand [8,9].



TEM of 5 wt% non-index matched brush particles in PMMA. Scale: 100nm



TEM of 5 wt% index matched brush particles in PMMA. Scale: 50nm



5 wt% non-index matched particle brush in PMMA.



30 wt% index matched particle brush in PMMA.

References

[1] F. S. Bates, G. H. Fredrickson, *Annual Review of Physical Chemistry* **1990**, 41, 525-57.
 [2] I. W. Hamley, *Introduction to Block Copolymers*, John Wiley & Sons, Ltd., **2004**.
 [3] M. R. Bockstaller, R. A. Mickiewicz, E. L. Thomas, *Advanced Materials* **2005**, 17, 1331-1349.
 [4] Hakem et al. *J. Am. Chem. Soc.*, **2010**, 132, 16593-16598.
 [5] Ferebee et al. *in preparation*.
 [6] Mie, G., *Ann. Phys.* **1908**, 25, 377-445.

[7] Ojha, S. (2012). *Fabrication of Transparent Nanocomposites with High Inorganic Concentration: An Enthalpic Approach*. Carnegie Mellon University.
 [8] Hui, C. (2011). *Uniform Distribution of Inorganic Particles in a Polymer Matrix Driven by Enthalpic Interactions*. Carnegie Mellon University.
 [9] J. Pietrasik, K. Matyjaszewski, et al. *Macro. Rap. Comm.*, **2011**, 32, 295-301.
 [10] Mahoney et al. *in preparation*.

Acknowledgements

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