Directing the Orientation of Nanoplate Particles Using Block Copolymer Domains to Control the Properties of Thin-Film Polymer Nanocomposites

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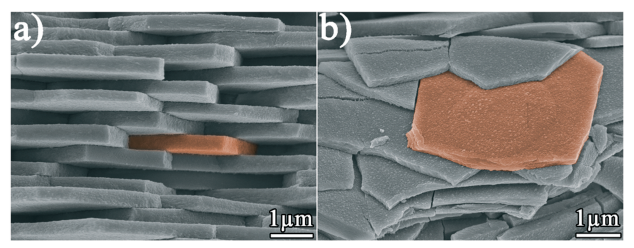
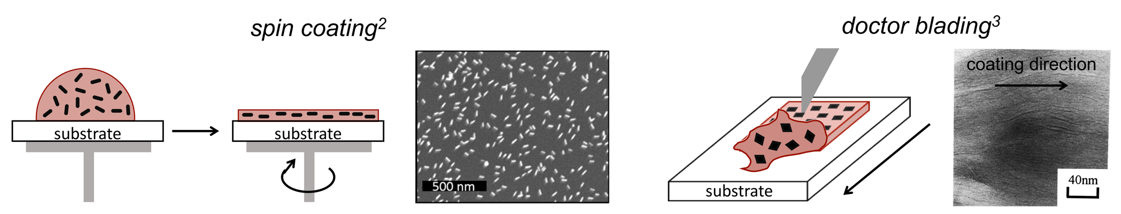
Introduction



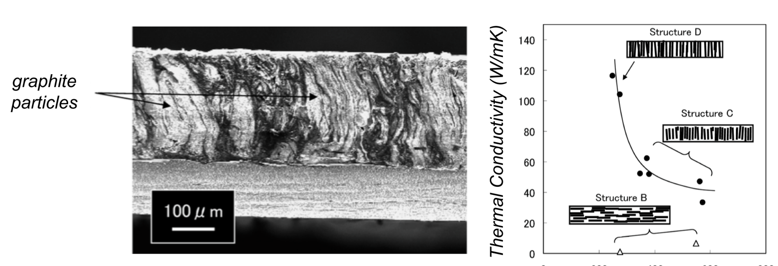
Fracture nacre (a) cross-section and (b) top surface[1]

Nature is successful at precisely controlling placement and orientation of anisotropic reinforcements for enhanced properties; model for synthesis composite system

- In polymer nanocomposites (PNCs), anisotropic nanoparticles (NPs) align along the direction of material flow
- Properties also orient parallel to the surface and the substrate



What if anisotropic NPs could align perpendicular to the substrate? *A new class of thin-film PNCs with a potential for unique set of properties could be revealed*



Morphology of Structure D

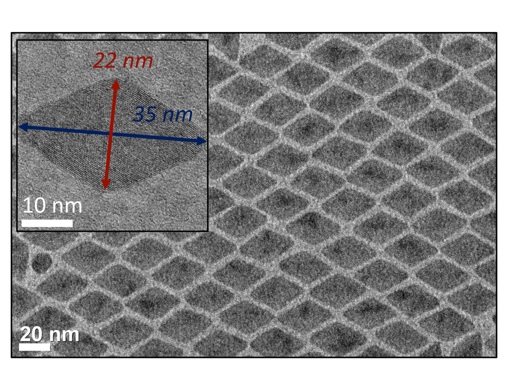
- Hitachi Chemical Company developed heat-dissipating sheets by vertically orienting graphite particles[4]
- Enhanced thermal conductivity (10x)
- Top-down approach: slicing and reassembly required

Research Goals

I. Synthesize model [gadolinium trifluoride (GdF_3)] nanoplate system
II. Create lamellar thin films with microdomains oriented vertically to the substrate
III. Chemically modify nanoplate surfaces for polymer compatibility and demonstrate particle dispersion in homopolymer matrices
IV. Incorporate chemically modified nanoplates first in parallel microdomains

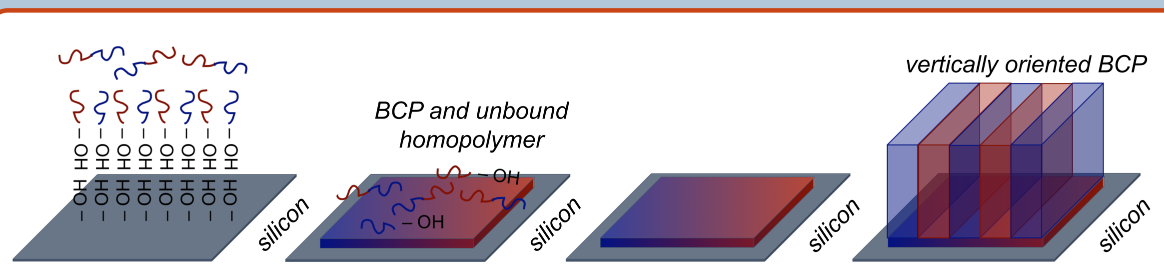
Employ block copolymer (BCP) templates to create ***self-assembled*** thin film PNCs with vertically oriented anisotropic NPs to improve out-of-plane transport

Goal I: Synthesis of GdF_3 Nanoplate System



- Synthesized via rapid thermal decomposition[5]
- Rigid, monodisperse, and tunable in size and shape
- Model nanoplate system
- Thickness of ~3 nm
- Oleic acid (OA) on particle surfaces

Goal II: Vertical PS-*b*-PMMA Lamellae



Step 1: spin-coat blend of PS-OH (6 kg/mol), PMMA-OH (6.5 kg/mol), and PS-*b*-PMMA (5k-*b*-5k g/mol)

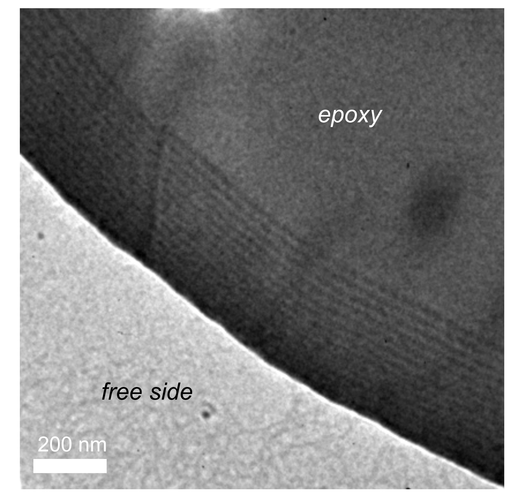
Step 2: thermally anneal

Step 3: sonicate in solvent to remove low molecular weight BCP and unbound homopolymer

Step 4: spin-coat lamellar-forming PS-*b*-PMMA (54k-*b*-52k g/mol) and thermally anneal[6]

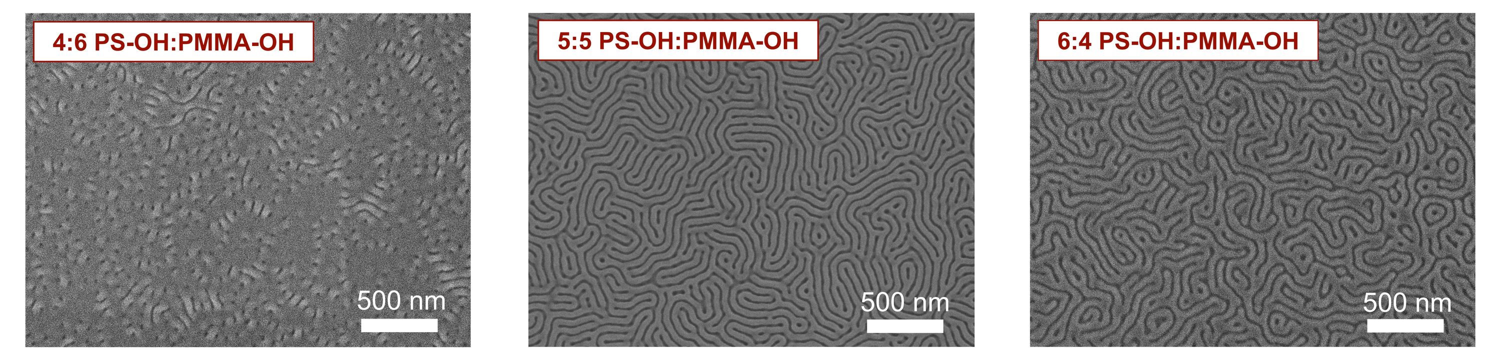
Goal II: Vertically Oriented PS-*b*-PMMA (54k-*b*-52k g/mol) Lamellae via a Neutralization Layer

Without neutralization layer, PMMA preferentially wets silicon leading to lamellae oriented parallel to the substrate.



TEM image of ultramicrotomed cross section of parallel PS-b-PMMA (38k-b-36.8k g/mol) lamellar film

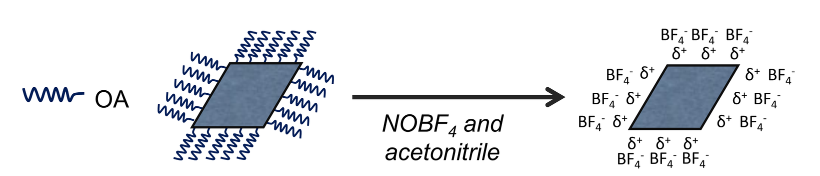
- Implemented a slightly asymmetric BCP compared to symmetric system used by Ji *et al.* (52k-*b*-52k g/mol)
- Achieved vertical ordering for film thicknesses ranging from ~50 nm to ~160 nm
- Varied ratio of the homopolymer brushes in neutrality layer underneath PS-*b*-PMMA films (~54 nm)



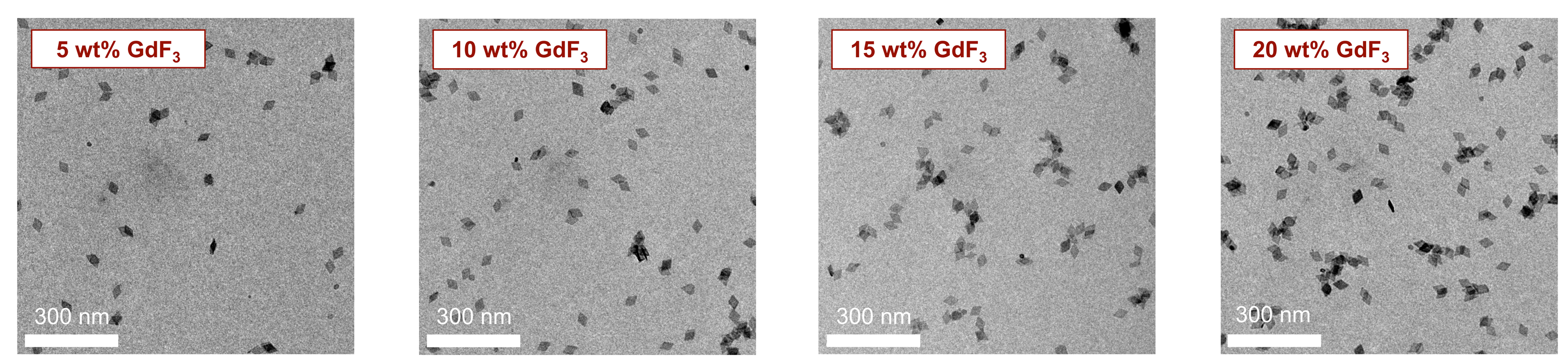
4:6 PS-OH:PMMA-OH	5:5 PS-OH:PMMA-OH	6:4 PS-OH:PMMA-OH
This study: >10 defects	**This study**: *no defects, most continuous*	**This study**: *no defects*
Ji et al.: *no defects*	**Ji et al.**: *no defects*	**Ji et al.**: *<10 defects*

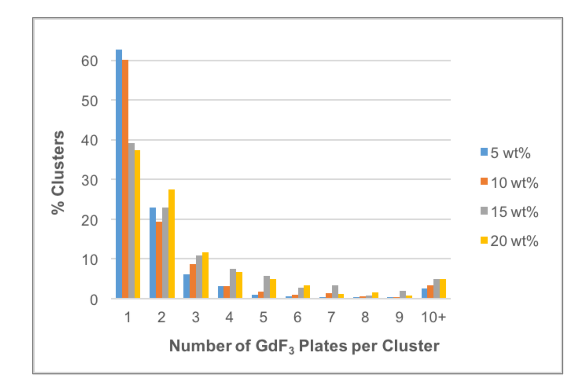
Shift in neutrality window to adjust for higher styrene content in asymmetric BCP

Goal III, Method 1: BF_4^- Stabilized GdF_3 Nanoplates Dispersed in PMMA



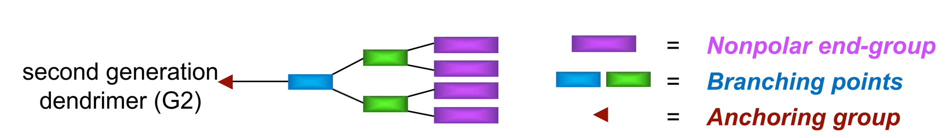
- Cleaved OA from as-synthesized GdF_3 platelets using nitrosonium tetrafluoroborate ($NOBF_4$) salt[7]
- Dispersed charge-stabilized GdF_3 in M_n = 212 kg/mol poly(methyl methacrylate) (PMMA)
- Spin-coated GdF_3/PMMA composites (~36 nm) as a function of particle wt%



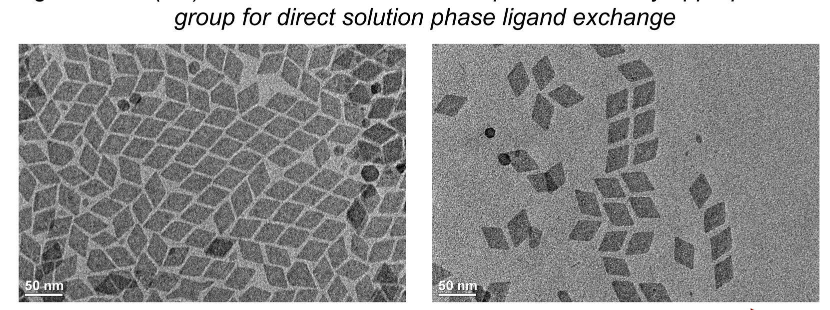


Charge stabilized GdF_3 results in particle aggregation in polymer matrix; As particle weight fraction increases, number of particles per cluster increases

Goal III, Method 2: PEG-PO_3H_2 Functionalized GdF_3 Nanoplates Dispersed in PMMA



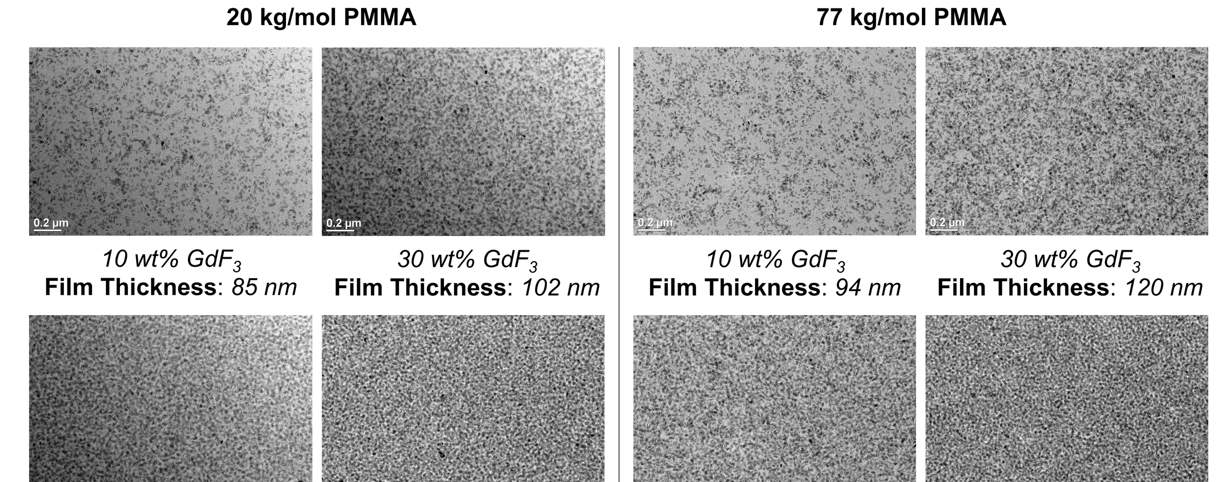
Second generation (G2) dendrimer[8] can serve as a probe to identify appropriate anchoring group for direct solution phase ligand exchange



Interparticle spacing increases (2.8 nm to 6.9 nm) with phosphonic acid (PO_3H_2) functionalized G2 from solution

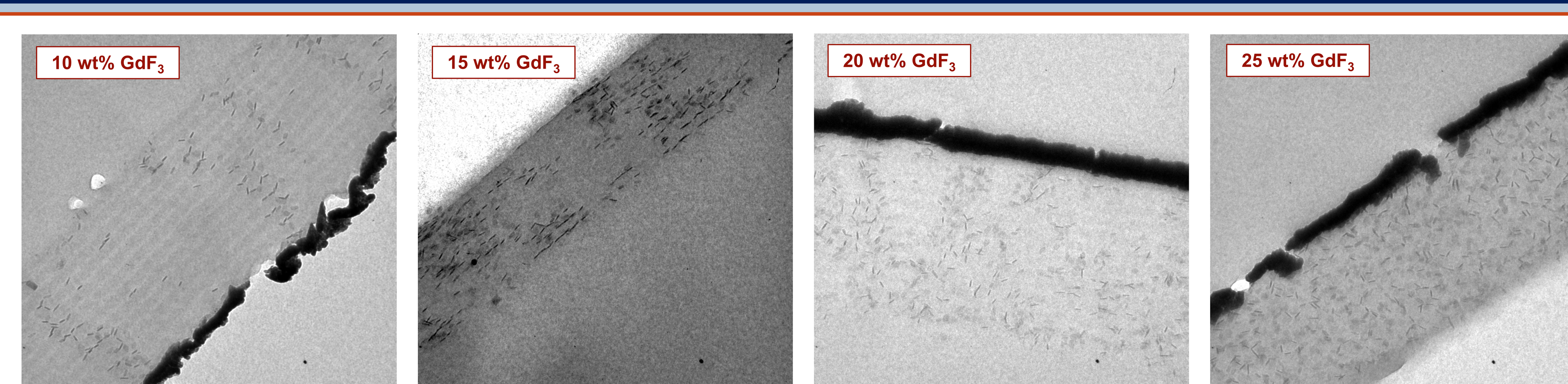
Phosphonic acid (PO_3H_2) is a suitable group for direct solution phase exchange on GdF_3

Good dispersion of M_n = 5 kg/mol PO_3H_2-poly(ethylene glycol) (PEG) modified GdF_3 achieved in PMMA independent of molecular weight



20 kg/mol PMMA		77 kg/mol PMMA	
10 wt% GdF_3 **Film Thickness**: *85 nm*	*30 wt% GdF_3* **Film Thickness**: *102 nm*	*10 wt% GdF_3* **Film Thickness**: *94 nm*	*30 wt% GdF_3* **Film Thickness**: *120 nm*
40 wt% GdF_3 **Film Thickness**: *120 nm*	*60 wt% GdF_3* **Film Thickness**: *156 nm*	*40 wt% GdF_3* **Film Thickness**: *130 nm*	*60 wt% GdF_3* **Film Thickness**: *177 nm*

Goal IV: Alignment of GdF_3 in PMMA Domain of Parallel PS-*b*-PMMA (38k-*b*-36.8k g/mol) Lamellae

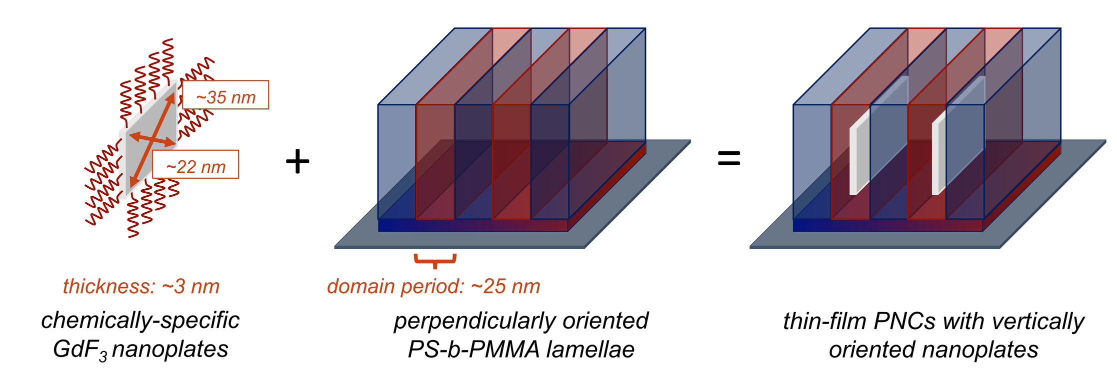


- 5 kg/mol PEG-PO_3H_2 functionalized GdF_3 preferentially segregate to PMMA domain
- Nanoplate alignment occurs up to 15 wt%
- GdF_3 orientation and BCP formation becomes disordered after 20 wt%

Conclusions

- Surface-modifiable, monodisperse GdF_3 nanoplates were synthesized and compatible with lamellae dimensions
- Without substrate modification, parallel PS-*b*-PMMA lamellae can be achieved
- Perpendicular PS-*b*-PMMA lamellae can be achieved with substrate modification for thin-film thicknesses ranging from ~50 nm to ~160 nm
- BF_4^- stabilized particles disperse in PMMA (212 kg/mol) up to 10 wt% GdF_3
- PEG-PO_3H_2 functionalized GdF_3 plates disperse in PMMA matrices of varying molecular weights independent of particle loading
- GdF_3 plates demonstrate directed alignment up to 15 wt% in the PMMA domain of parallel PS-*b*-PMMA lamellae

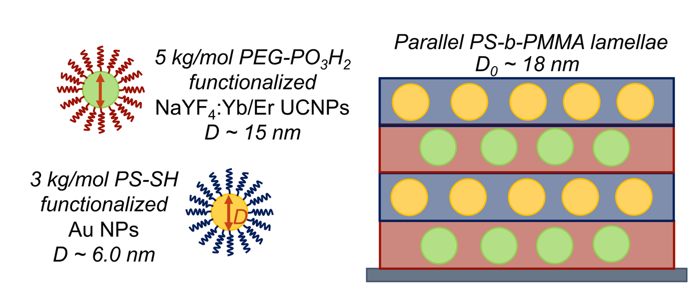
Future Work



- Explore the optimum parameter space for BCP molecular weight, nanoplate size and surface chemistry, and film thickness
- Guide studies with simulations performed in the Riggleman group

Can we establish a platform to align any planar particle in systems of technological relevance?

- Can we use BCPs as a platform to control placement and separation of any particle system?
- ***Goal***: develop flexible PNC coating with plasmon enhanced upconversion luminescence



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