3D Photonic Crystal structures

☞ Challenge: large index contrast & periodicity for the visible range 2-3:1 & ~ 200 nm

Nature's Photonic Crystals

1-D:

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

2-D:

Images removed due to copyright restrictions.

Please see

http://www.physorg.com/newman/gfx/news/2005/sem_mop.jpg

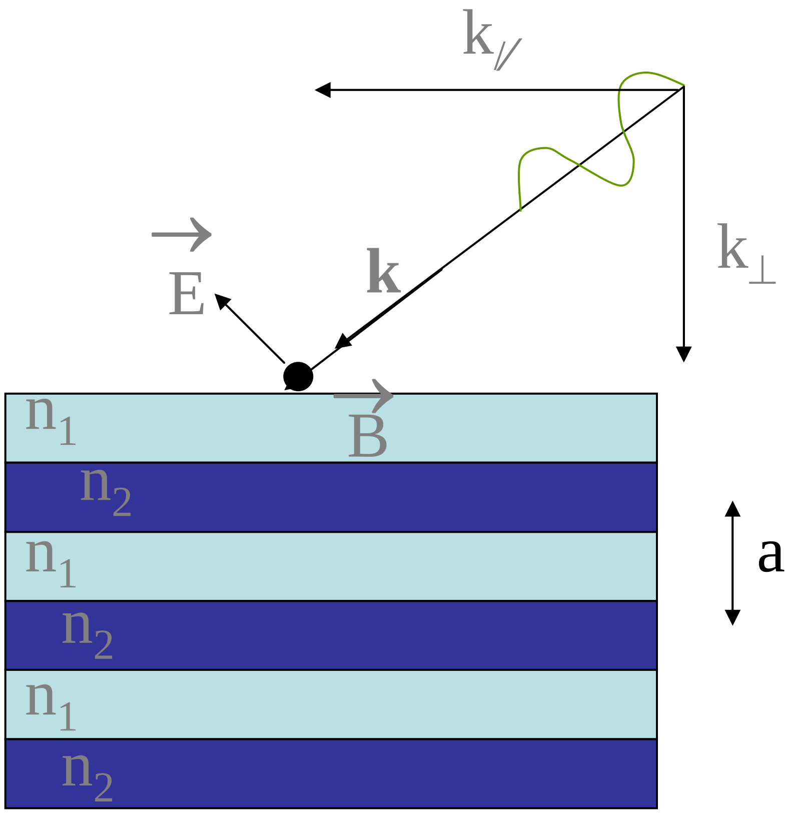
http://www.physics.usyd.edu.au/theory/seamouse/TheAnimal/spine.x64.jpg

http://www.physics.usyd.edu.au/theory/seamouse/TheAnimal/figure2.jpg

http://www.icmm.csic.es/cefe/Imagenes/manhattan.gif

3-D:

Photonic Materials

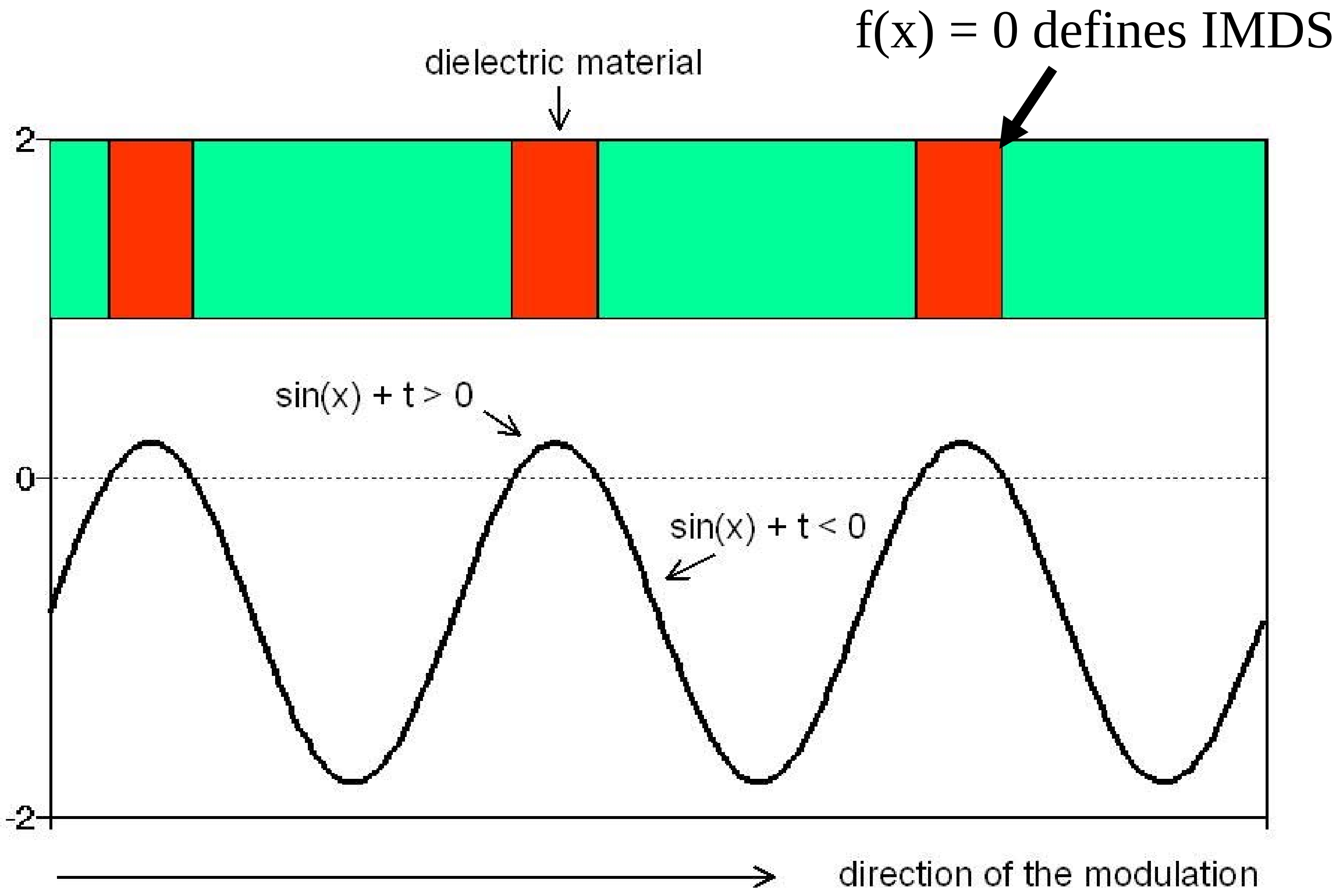


Periodic variations in dielectric properties cause particular propagating modes to be forbidden

E. Yablonovitch
PRL 1987

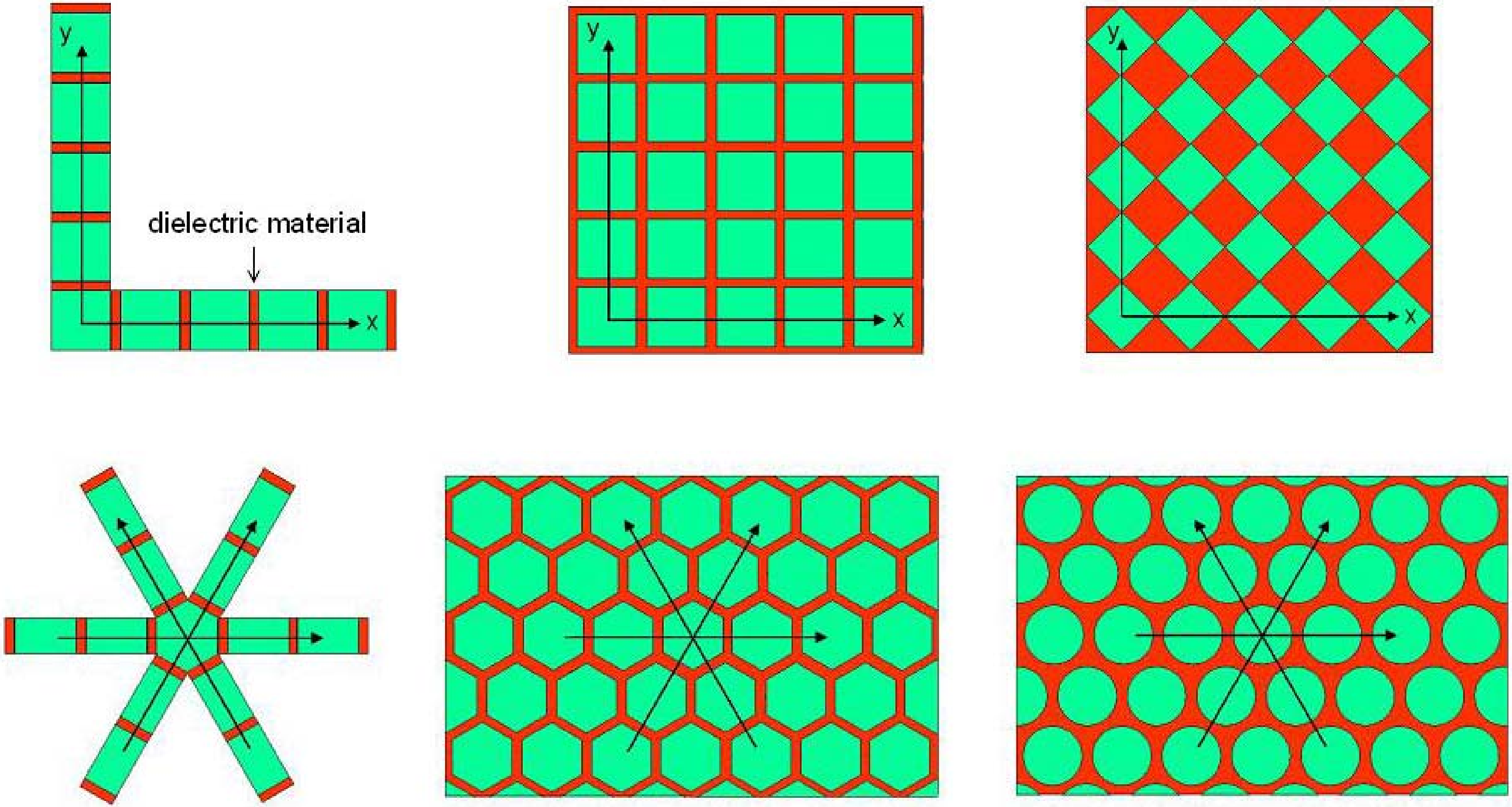
Periodicity can be 1-D, 2-D and 3-D giving rise to photonic properties of the same dimensionality.

Understanding Band Gaps: Periodic Dielectric Modulations



Modulations in Principal Directions

Superposition of Modulations in 2D



Periodic Bicontinuous Structures

Marine Biologists
"Cidaris Cidaris: Rectilinear"

Self Ass'y Community:
"Plumber's Nightmare"

Mathematicians:
"Schwarz's P Surface"

Image removed due to copyright restrictions.

Please see any image of the Schwarz P surface, such as
http://www.msri.org/about/sgp/jim/geom/minimal/library/P/imag/s_end.jpg

Sea Urchin: Cidaris Cidaris

Image removed due to copyright restrictions.

Please see any page on sea urchin anatomy.

- *Cidaris cidaris:* found off Shetland Isles
- Inhabit deep water (30m) and usually in predominantly sandy areas where they can sometimes be found in large numbers.

Cidaris Cidaris Stereom

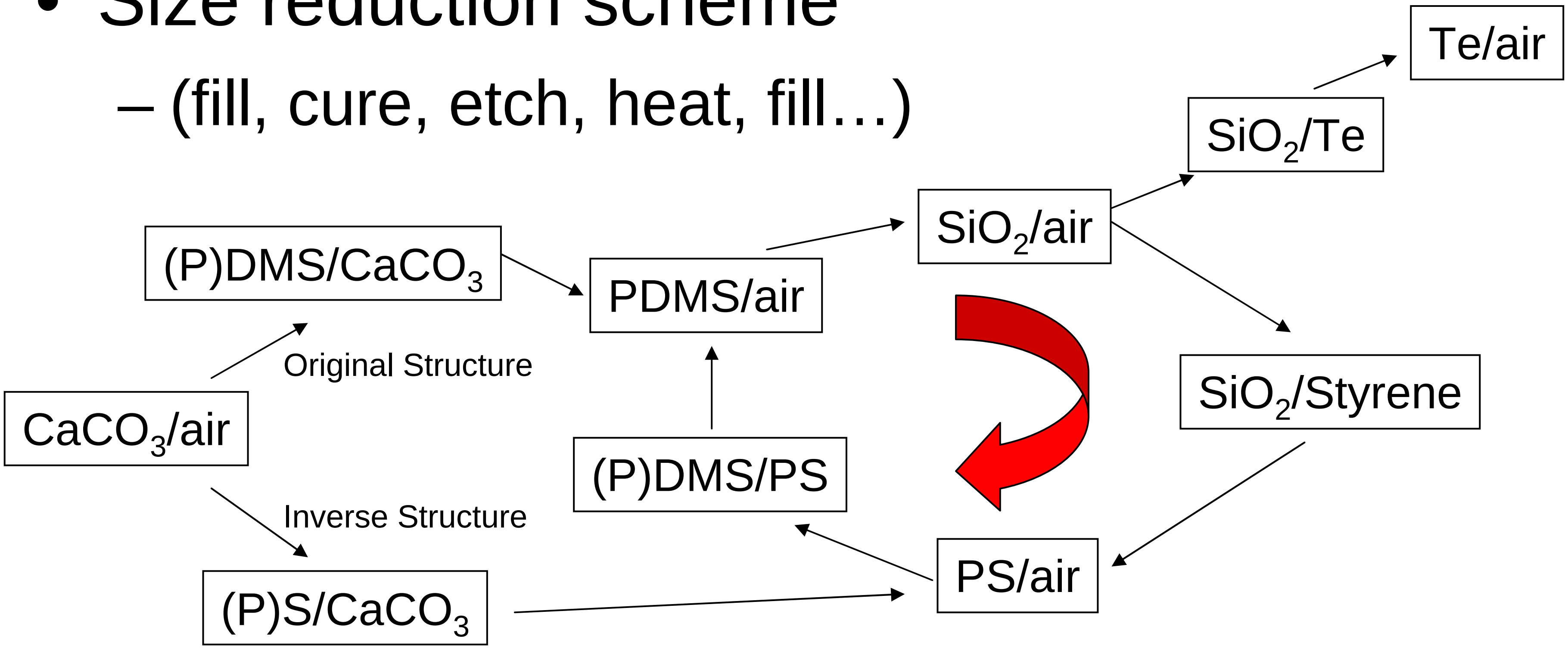
Image removed due to copyright restrictions.

Please see
http://www.ucmp.berkeley.edu/echinodermata/stereom.gif

- Composed of high magnesium calcite, a calcite ($CaCO_3$) that incorporates up to 15% $MgCO_3$.
- **The skeleton can be seen to be comprised of a three-dimensional meshwork, known in the mathematician's language as the P-surface.**

Photonic Crystal Engineering of Cidaris Cidaris

- For the native structure, the bandgap will appear approximately at λ=50 μm.
- Size reduction scheme
  - (fill, cure, etch, heat, fill…)



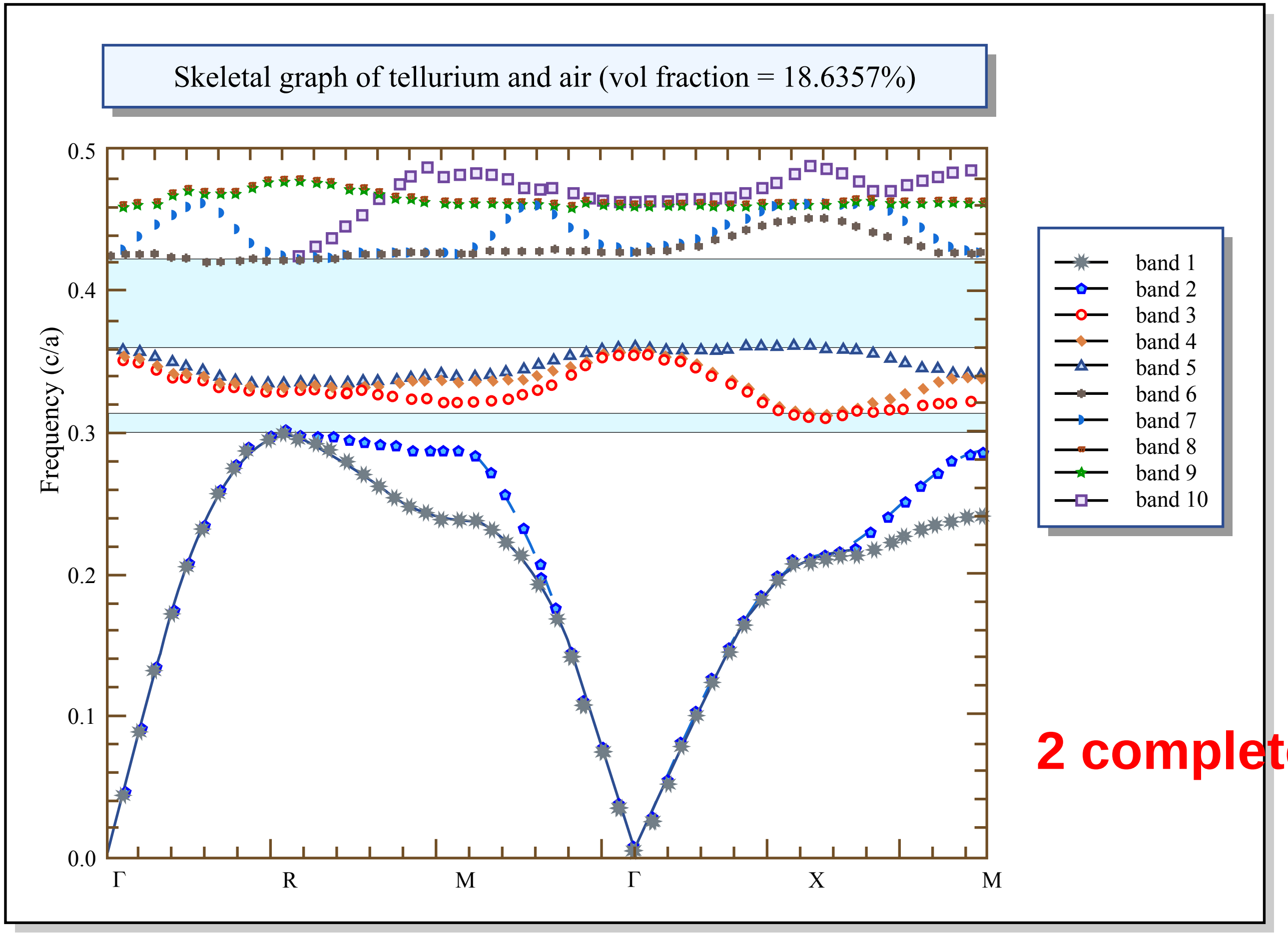
P-surface Family: 50% vol, $n_2/n_1 = 4.6$

Image removed due to copyright restrictions.

Please see Fig. 1c in Ma, Yung-Hoon, et al. “Three-Dimensional Network Photonic Crystals via Cyclic Size Reduction/Infiltration of Sea Urchin Exoskeleton.” *Advanced Materials* 16 (July 5, 2004): 1091-1094

No complete gap!

P-surface Family: 19 vol%, $n_2/n_1 = 4.6$



2 complete gaps!

Figure by MIT OCW.

Gap Map for $n_2/n_1 = 4.6$

Gap maps are useful for finding optimum structures and fill fractions

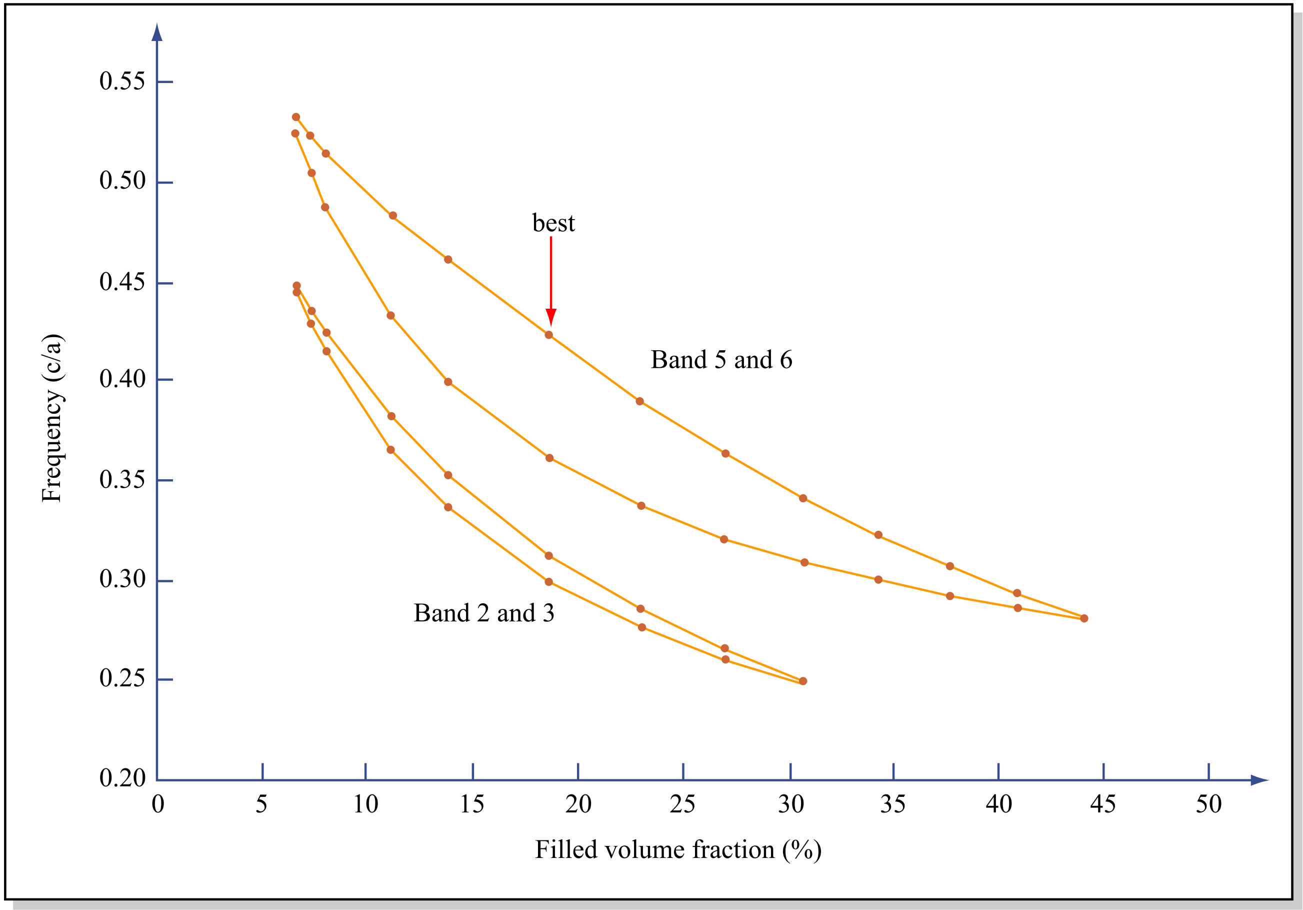


Figure by MIT OCW.

Modulations in Principal Directions

$$f(x,y,z) = \sin[2\pi x] + \sin[2\pi y] + \sin[2\pi z]$$

Superposition of sinusoidal modulations in 3D

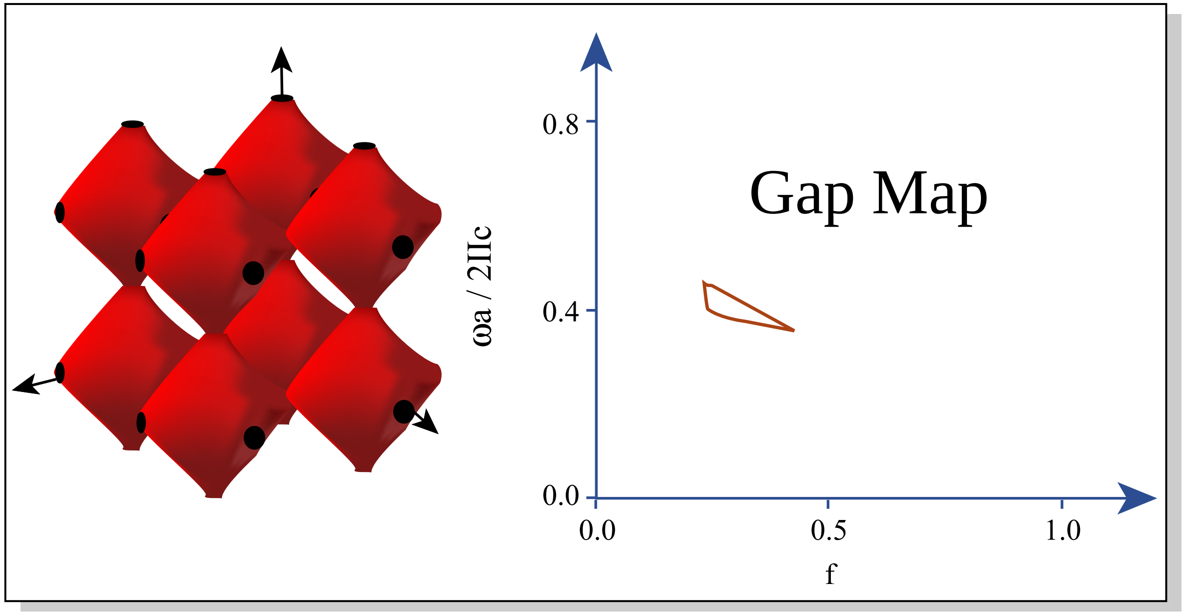


Figure by MIT OCW.

Complete Gap

f.o.m. ~ 13%

@ 0.26 dielectric network

$n_2/n_1 = 3.6$

BCP Photonic Crystals

1D: Lamellae

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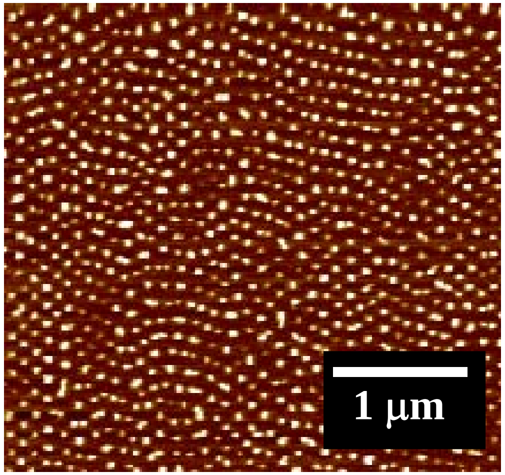
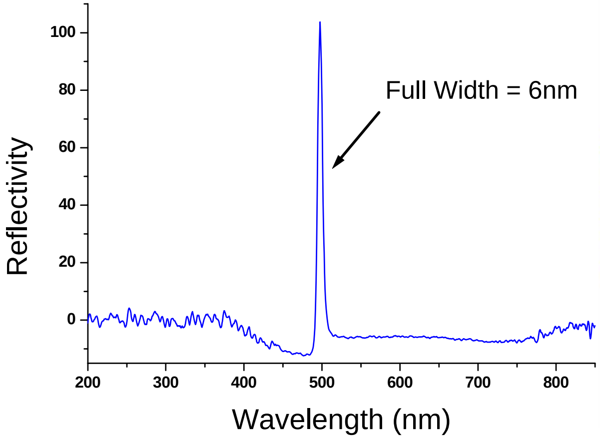
Please see Fig. 2a in Urbas, Augustine, et al. "Tunable Block Copolymer/Homopolymer Photonic Crystals." *Advanced Materials* 12 (2000): 812-814

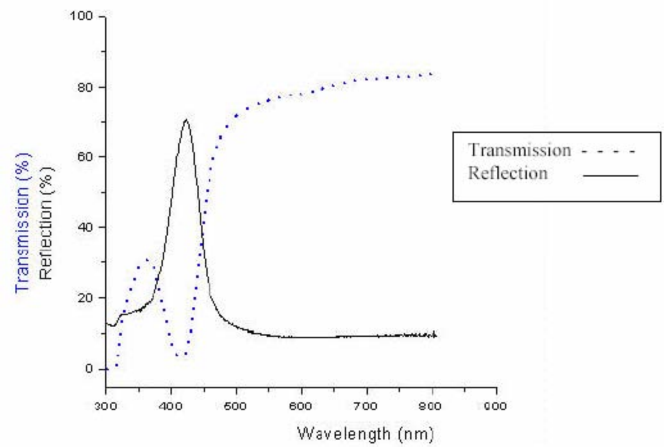
2D: Cylinders



3D: Double Gyroid

Please see Fig. 2 and 3 in Urbas, Augustine, et al. "Bicontinuous Cubic Block Copolymer Photonic Crystals." *Advanced Materials* 14 (December 17, 2002): 1850-1853



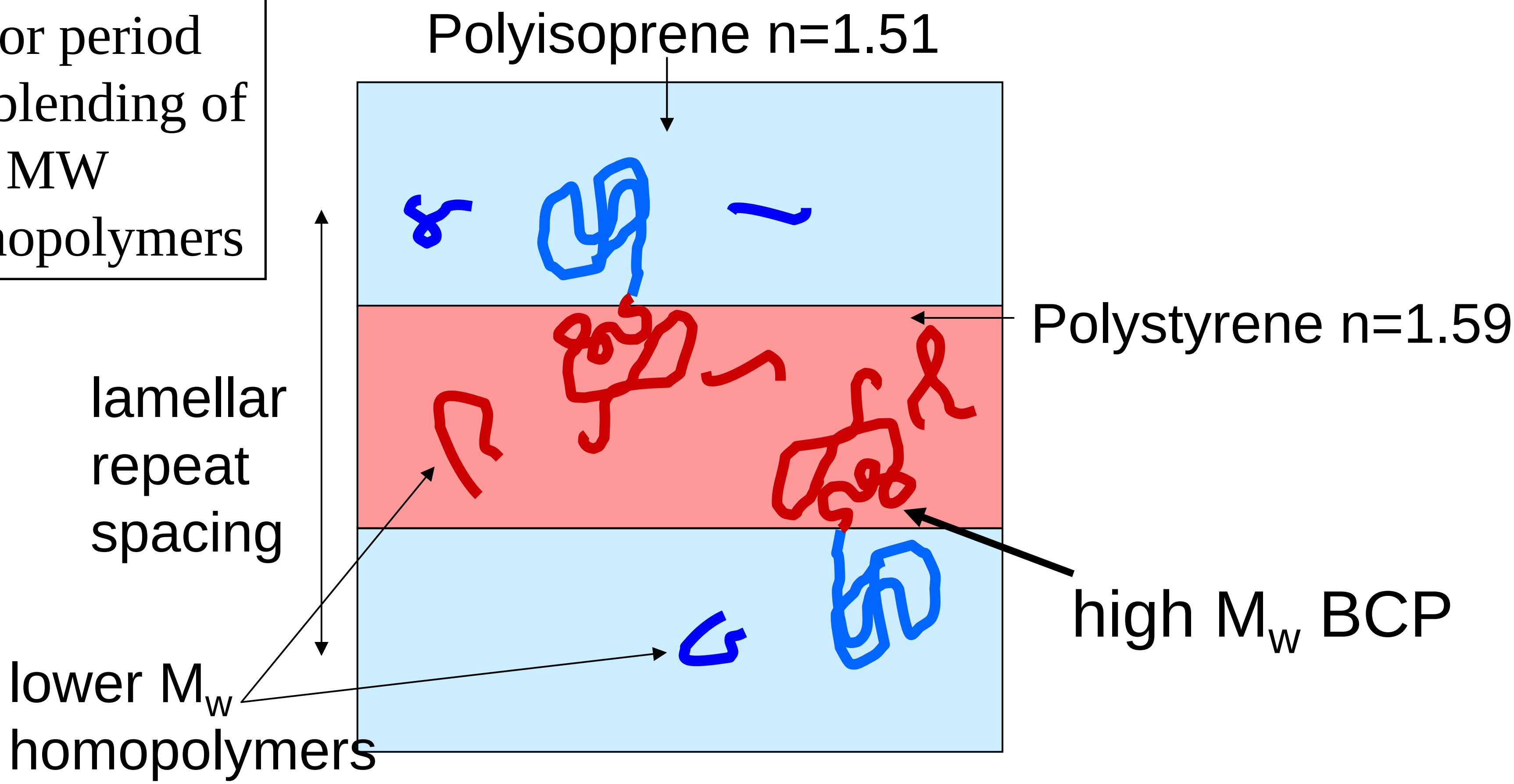


Courtesy Elsevier, Inc., http://www.sciencedirect.com. Used with permission.

1D Dielectric Stack: Multilayer Films from Lamellar Block Copolymers

Symmetric A/B BCP systems form regular lamellae

Tailor period via blending of low MW homopolymers

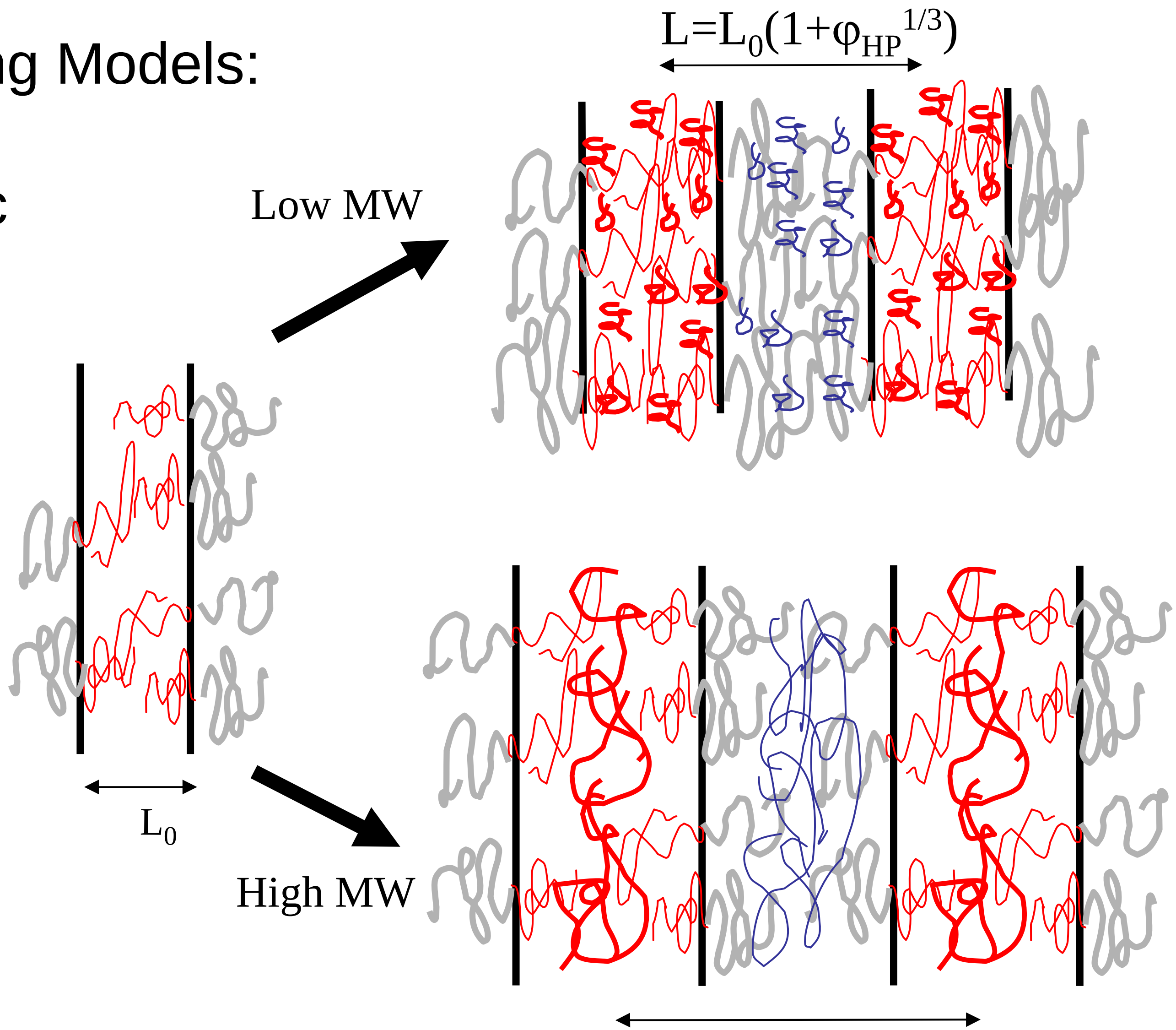


Ternary Blending: A/B, hPA, hPB

Two Swelling Models:

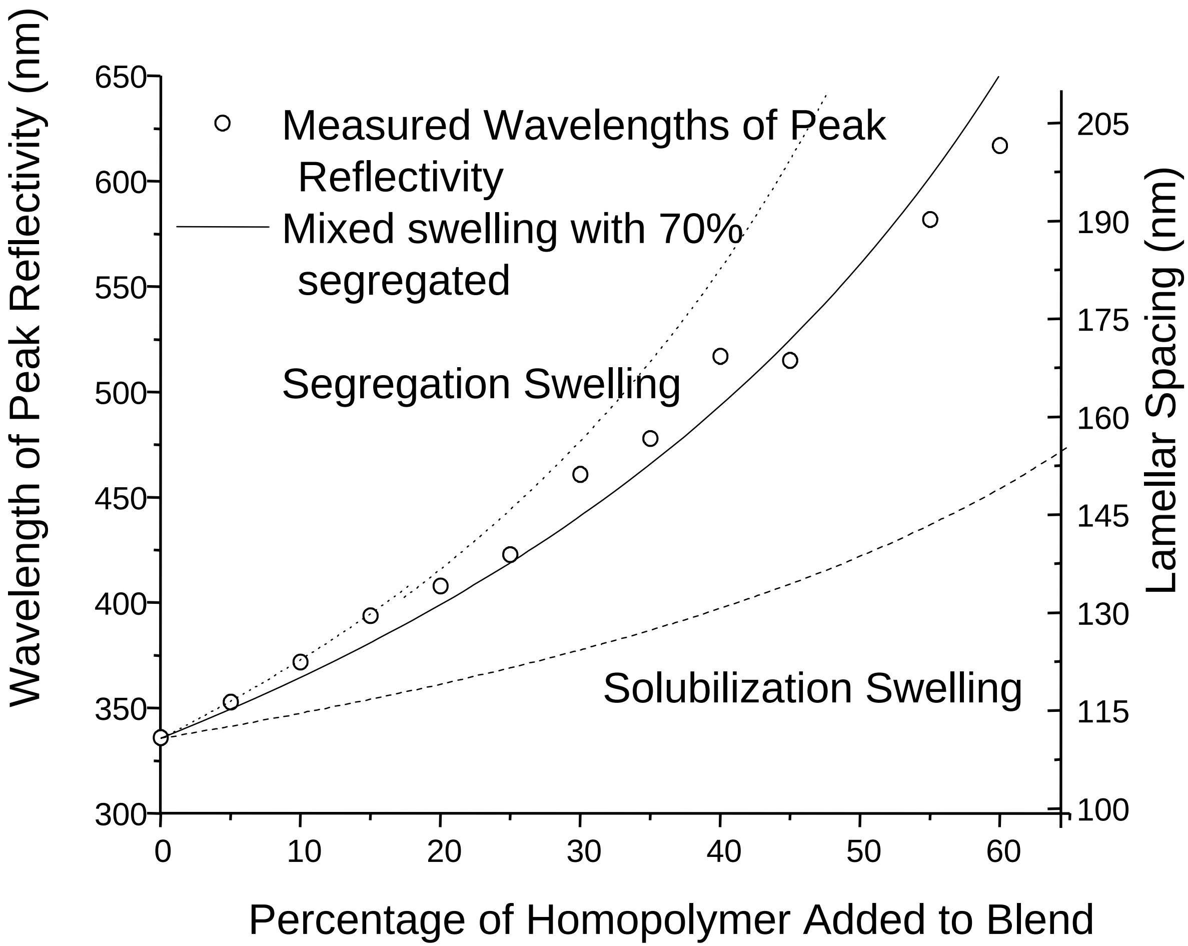
- Volumetric

- Linear



A. Semenov, Macromolecules 26, 2273 (1993)

Normal Incidence Band Gap Position vs Homopolymer Fraction



The reflectivity can be tuned to a selected wavelength

The morphology is maintained over this range of homopolymer fractions and the spacing changes by a factor of two

With a 3 component system, peak can span over visible spectrum

Reflectivity from Block Copolymer/Homopolymer Blends

Selected Blends of 194k/197k S/I BCP with 13k hPS and hPI

Samples are free cast in air from toluene.

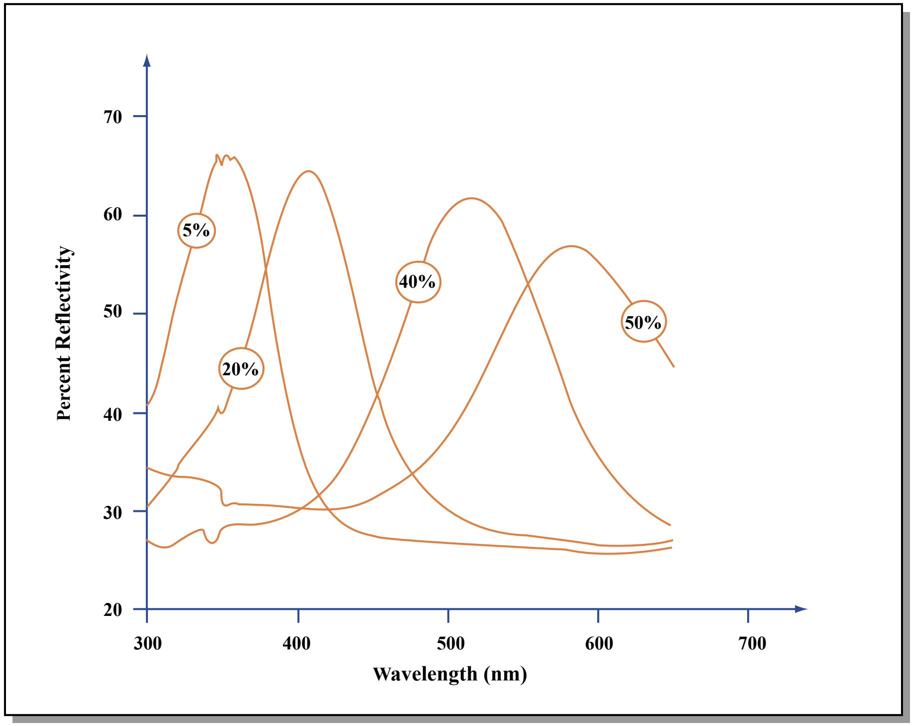


Figure by MIT OCW.

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Please see Fig. 1a and 2a in Urbas, Augustine, et al. “Tunable Block Copolymer/Homopolymer Photonic Crystals.” *Advanced Materials* 12 (2000): 812-814

Typical reflectivity is 60% and samples have a $\Delta\lambda/\lambda$ of 0.15-0.25

Block Copolymer Gels As Sensors

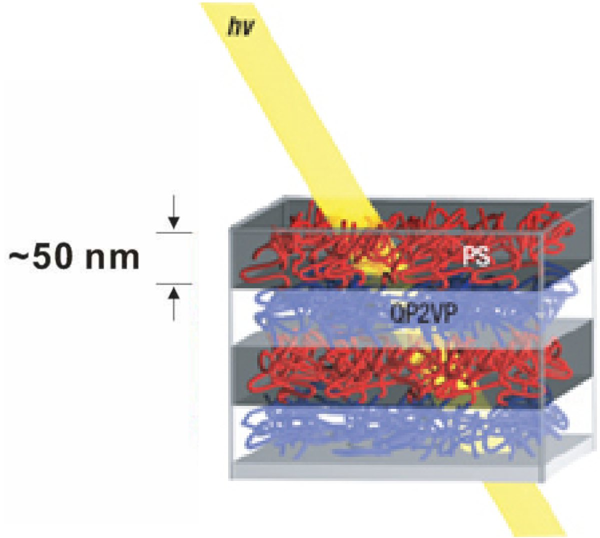
Paint-on pressure sensors

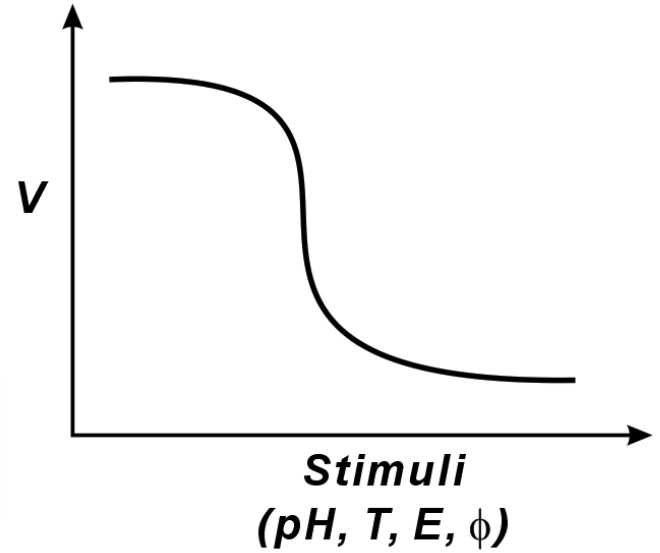
- Photonic polymer solutions from a BCP and a non-volatile solvent
- Highly viscoelastic with sufficient solvent
- The layer period is sensitive to mechanical deformation

Chemically Tunable Photonic Bandgap Gels

Lamellar PS(190K)-*b*-P2VP(190K)

P2VP block is crosslinked and quarternized





Concept: **Collapse Transition Gel Layers**

- Selectively modulate the optical thickness of the P2VP layer by swelling, consequently changing the photonic bandgap and the reflected color

- Gel layer volume can be up to 100 times of the initial polymer layer volume

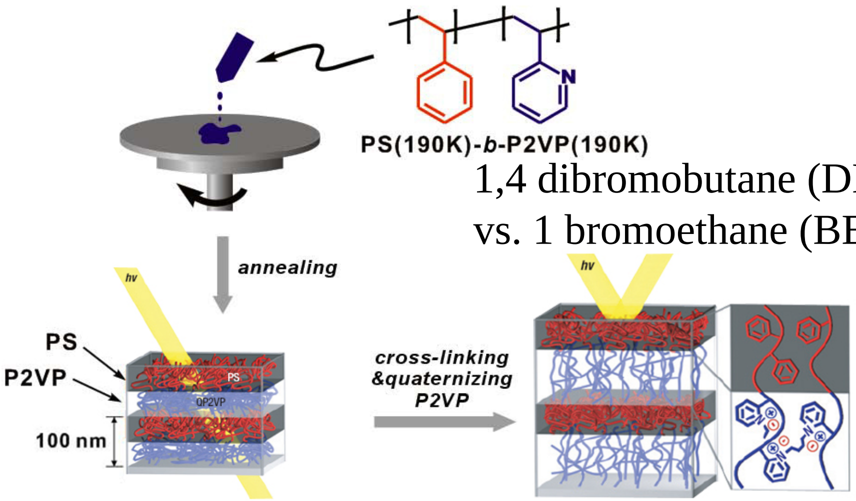
→ very large differences in refractive index and domain size;

→ reflected wavelength can be varied with the degree of swelling

Chemically Tunable Polyelectrolyte BCP Gels

Lamellar PS(190K)-*b*-P2VP(190K)

P2VP block is crosslinked and quaternized



1,4 dibromobutane (DBB)
vs. 1 bromoethane (BE)

2.5M NH_4Cl

Y. Kang et al., unpublished

Concept: **Rod - Coil Collapse Transition of Gel Layers**

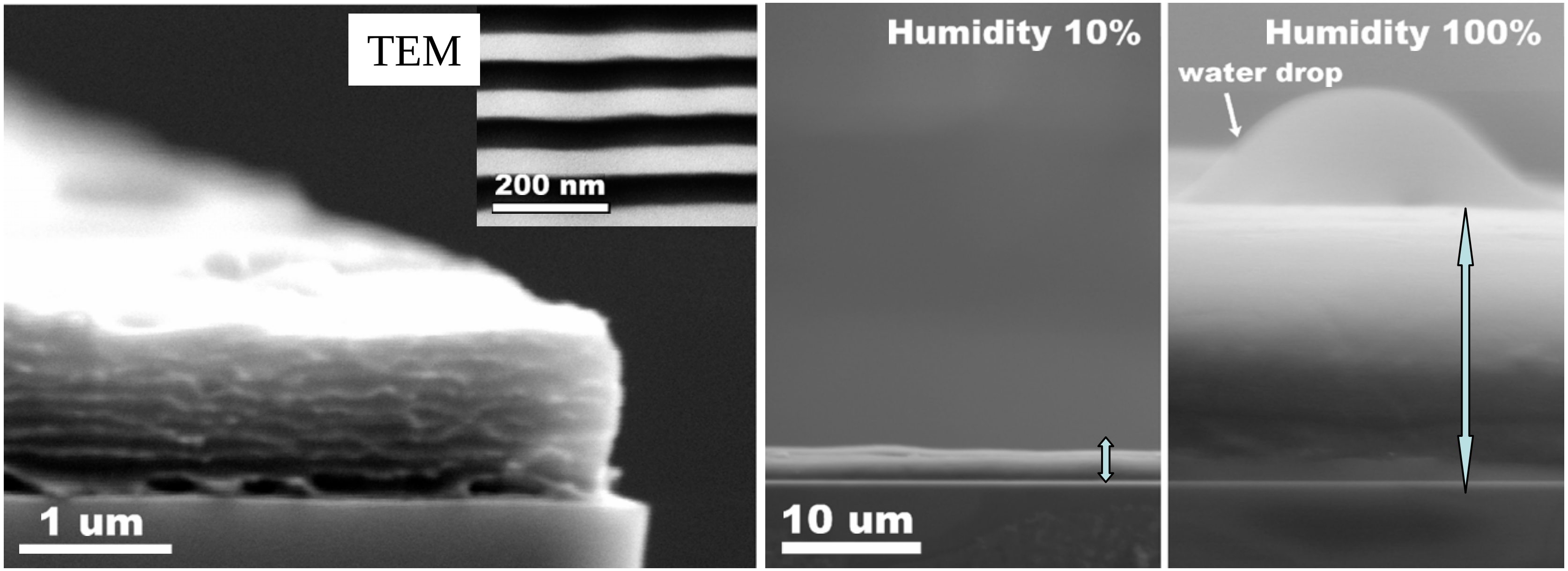
Selectively modulate the optical thickness of the QP2VP layer by swelling/deswelling, consequently changing the photonic bandgap and the reflected color

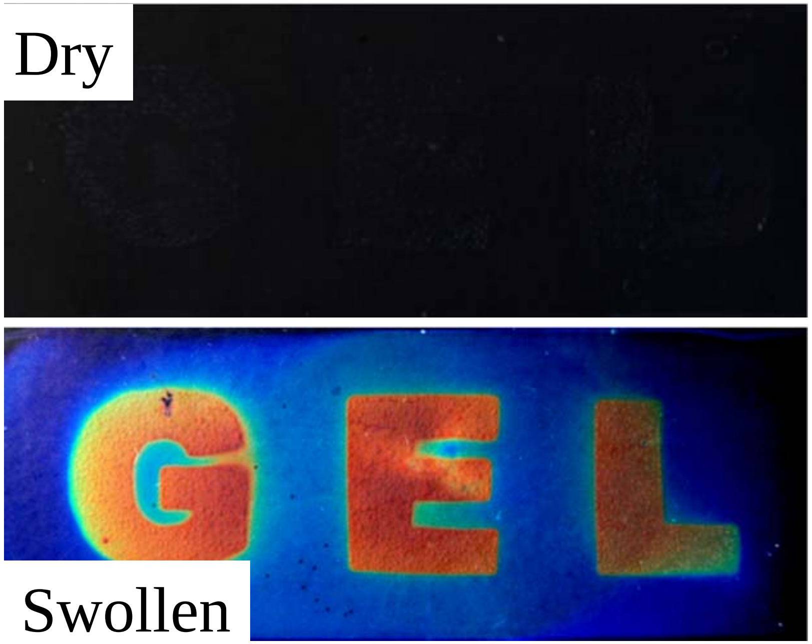
Gel layer volume can be up to *100 times* of the initial polymer layer volume

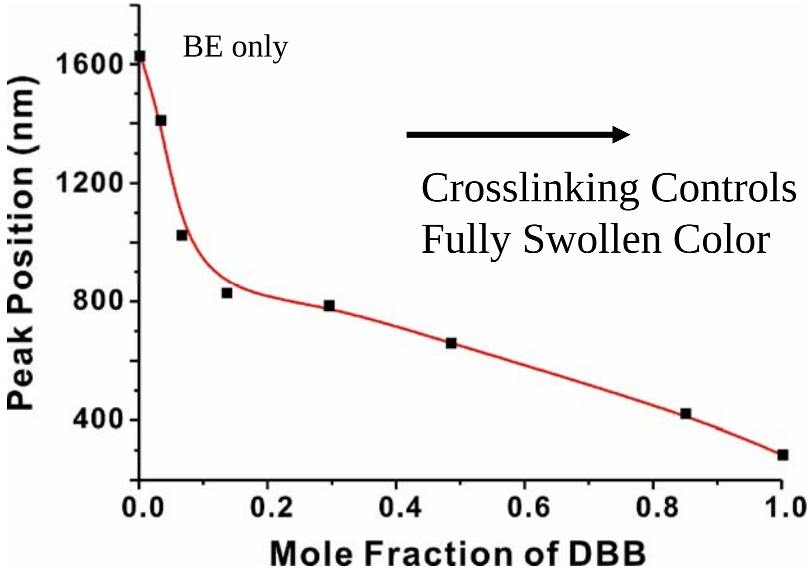
→ *Very large differences in refractive index and domain size;*

→ Reflected wavelength can be varied with the degree of swelling

Water Swelling of Polyelectrolyte BCP Gels

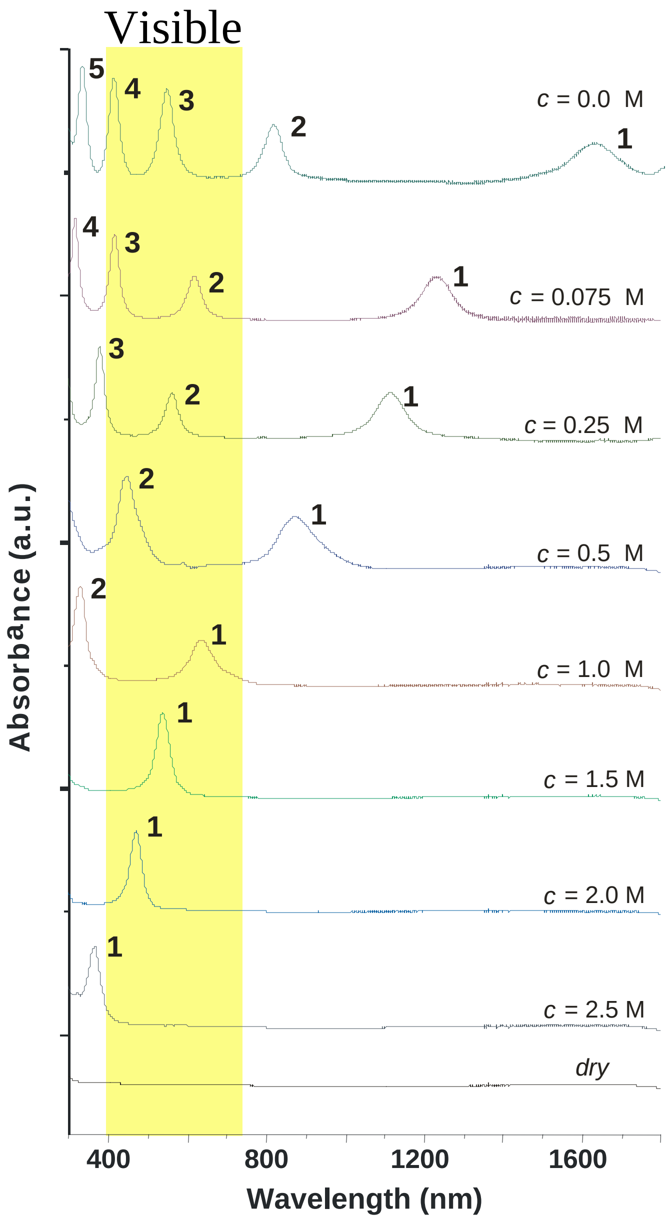


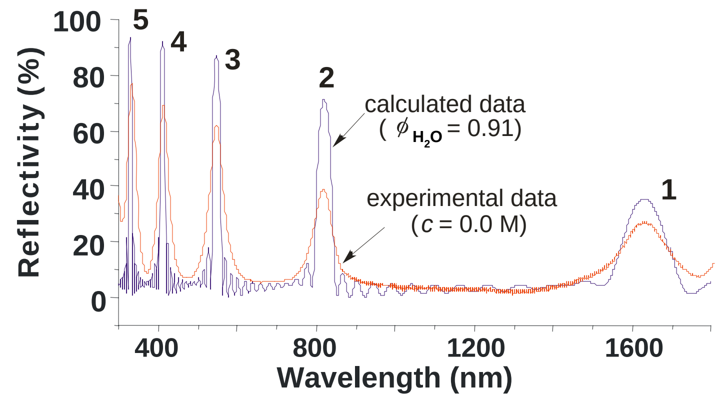


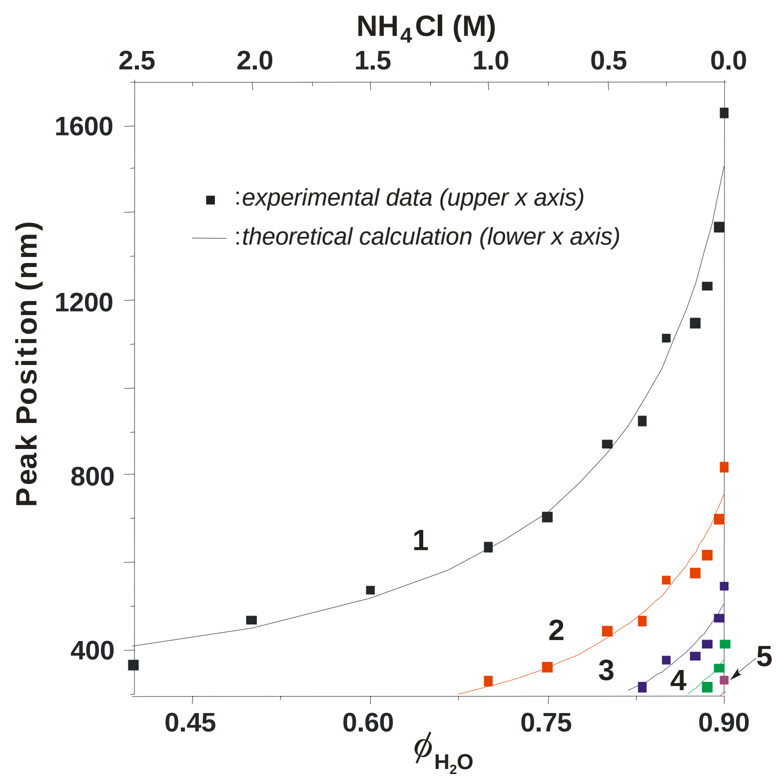


Crosslinking Controls Fully Swollen Color

Highly Responsive UV to IR Tunability and Multiorder Band Gaps







Photonic Block Polymers & Electro-optical Polymers

Using Block Copolymers As Host For Conjugated Sensory Polymers- Self-Assembled Lasing Cavities

Ability to microphase-separate
In 2D and 3D structures

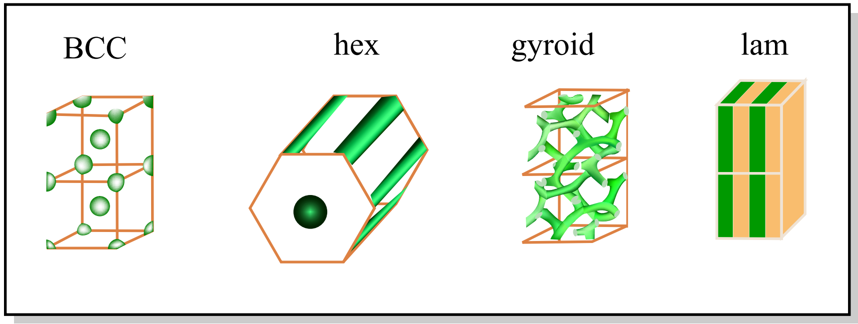
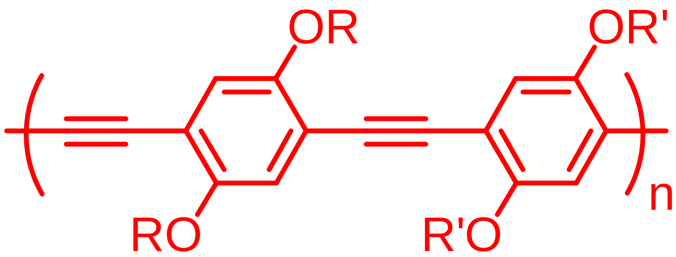
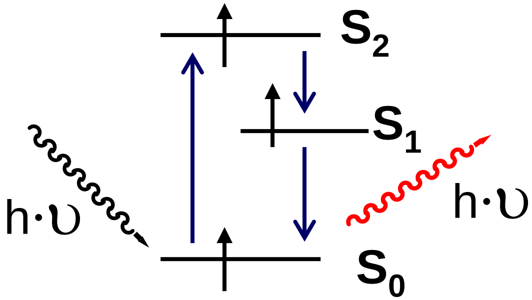


Figure by MIT OCW.

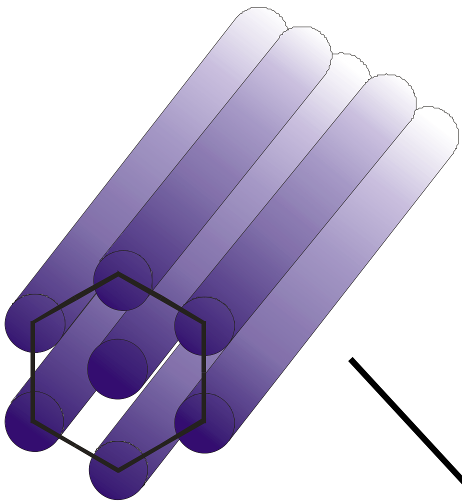
Increasing Weight Fraction
Block A

Stimulated emission in
conjugated polymers

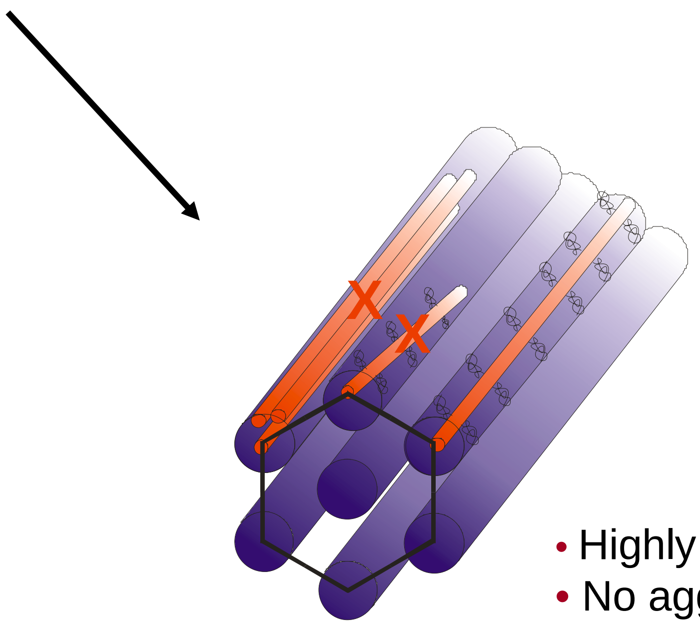


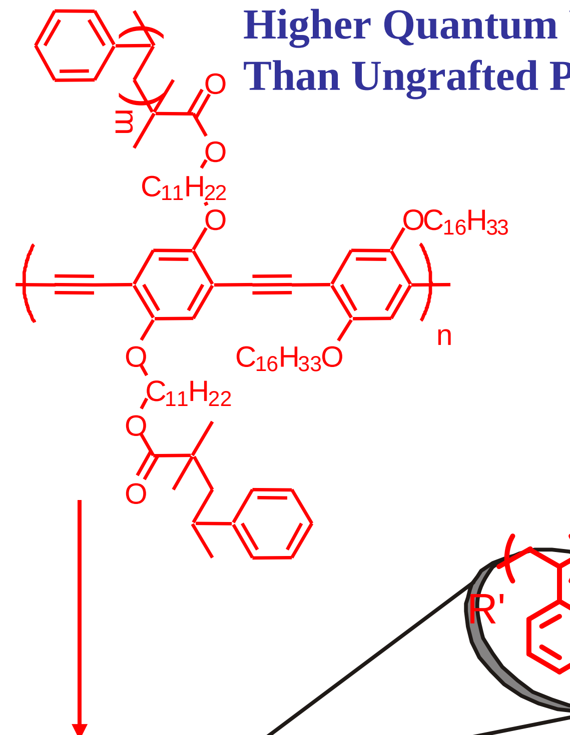


Grafted Poly(phenylene ethynylenes): Enhanced Emission and Alignment with Host Matrix

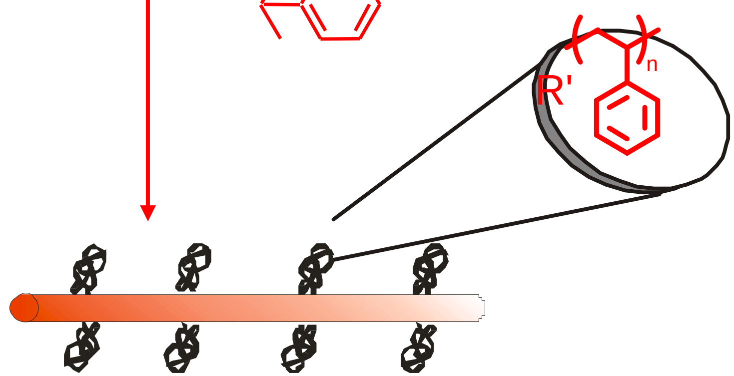


Using ABA block copolymer as template for PS grafted PPE





Higher Quantum Yield Than Ungrafted Polymer



- Highly anisotropic structure
- No aggregation