The Intermaterial Dividing Surface (IMDS)

Can think of the microdomain structure as comprised of a set of surfaces that define the changeover in composition from Block A to Block B

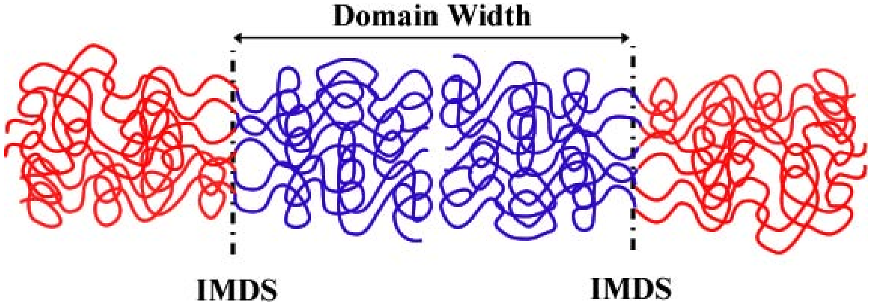
The IMDS in an AB diblock copolymer system:

Image removed due to copyright restrictions.

Please see Fig. 1 in Winey, K.I., Thomas, E.L. and Fetters, L.J. "Ordered Morphologies in Binary Blends of Diblock Copolymer and Homopolymer and Characterization of their Intermaterial Dividing Surfaces." *Journal of Chemical Physics* 95 (December 15, 1991): 9367-9375.

Characterize the IMDS

Mean curvature: Arithmetic average of the two *principal* curvatures:



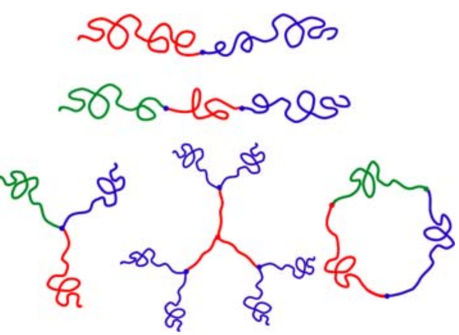


Image removed due to copyright restrictions.

Please see Fig. 2b in Thomas, E. L., et al. “Phase Morphology in Block Copolymer Systems.” *Philosophical Transactions: Physical Sciences and Engineering* 348 (July 15 1994): 149-166.

IMDS Shapes of Physical Interest

- Embedded surfaces (non self-intersecting)
- Closed surfaces
- Periodic surfaces (1, 2, or 3D periodic)

3-3 Bicontinuous Structures: L. E. Scriven, *Nature*, 263, 123-125, (1976)

Detailed Structure of the IMDS

- Energy functional to define surface

$$\varepsilon(S) = \iint_S F(C_1, C_2)\, dS'$$

Variational problem:

$$\delta\, \varepsilon(S) = 0$$

$$F(C_1, C_2) = \alpha\,(H - H_o)^2 + \beta K$$

α = surface tension
β = chain stretching, junction localization

Since morphology is at fixed composition.
This suggests cmc surfaces

Surfaces of Constant Mean Curvature

Specify Conditions: 1. Minimize area
2. Enclose a fixed volume

$$\int_{\alpha} \alpha'(s)\,ds \quad \rightarrow \quad \text{Min}$$

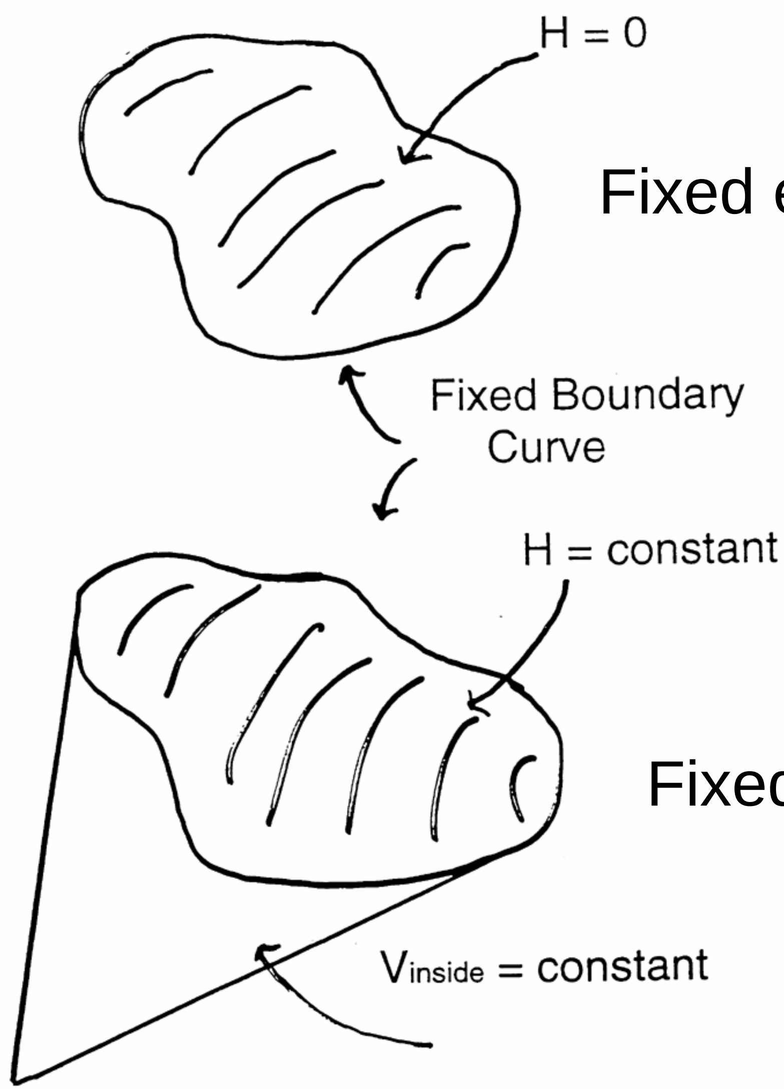
$$V_{\alpha} \equiv \text{constant}$$

Variational equation:

$$H \equiv \text{constant}$$

Surfaces of CMC cont'd

H = 0



Fixed enclosed boundary

H = constant

Fixed enclosed volume

Periodic Surfaces as Candidate Microdomain Structures

- **Constant Thickness Surfaces (CT)**

  Originally developed for surfactant-oil-water systems. Chain packing requirements of one component satisfied; Reference base surface is usually IPMS

- **Constant Mean Curvature Surfaces (CMC)**

  Minimization of interfacial area at fixed volume fraction

- **Surface defined by Level Sets (LS)**

  Connected microdomain structures of specified symmetry; the curvature and domain thickness vary; can be generated systematically using a crystallographic approach:

Wohlgemuth, M., Yufa, N., Hoffman, J., Thomas, E.L., "Triply Periodic Bicontinuous Cubic Microdomain Morphologies by Symmetries", *Macromolecules*, 34. 6083-6089, (2001).

Model IMDS Patterns for Microphase Separated Morphologies

- Minimize interfacial area – (H term in free energy)
  Constant Mean Curvature Surface

- Maximize chain conformational entropy – (S term)
  Constant Thickness Surface

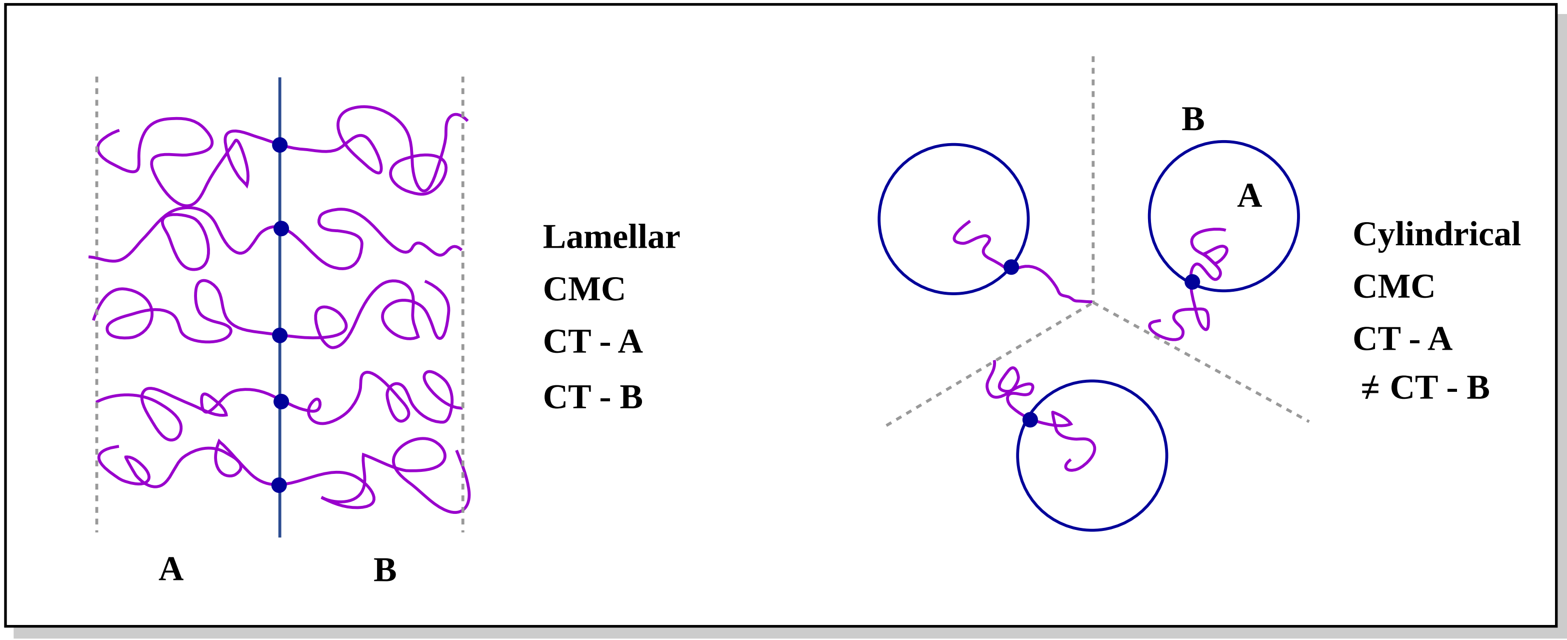


Figure by MIT OCW.

Optimum surface structure must respect both H and S terms

Constant Thickness (CT) Model

Parallel surfaces

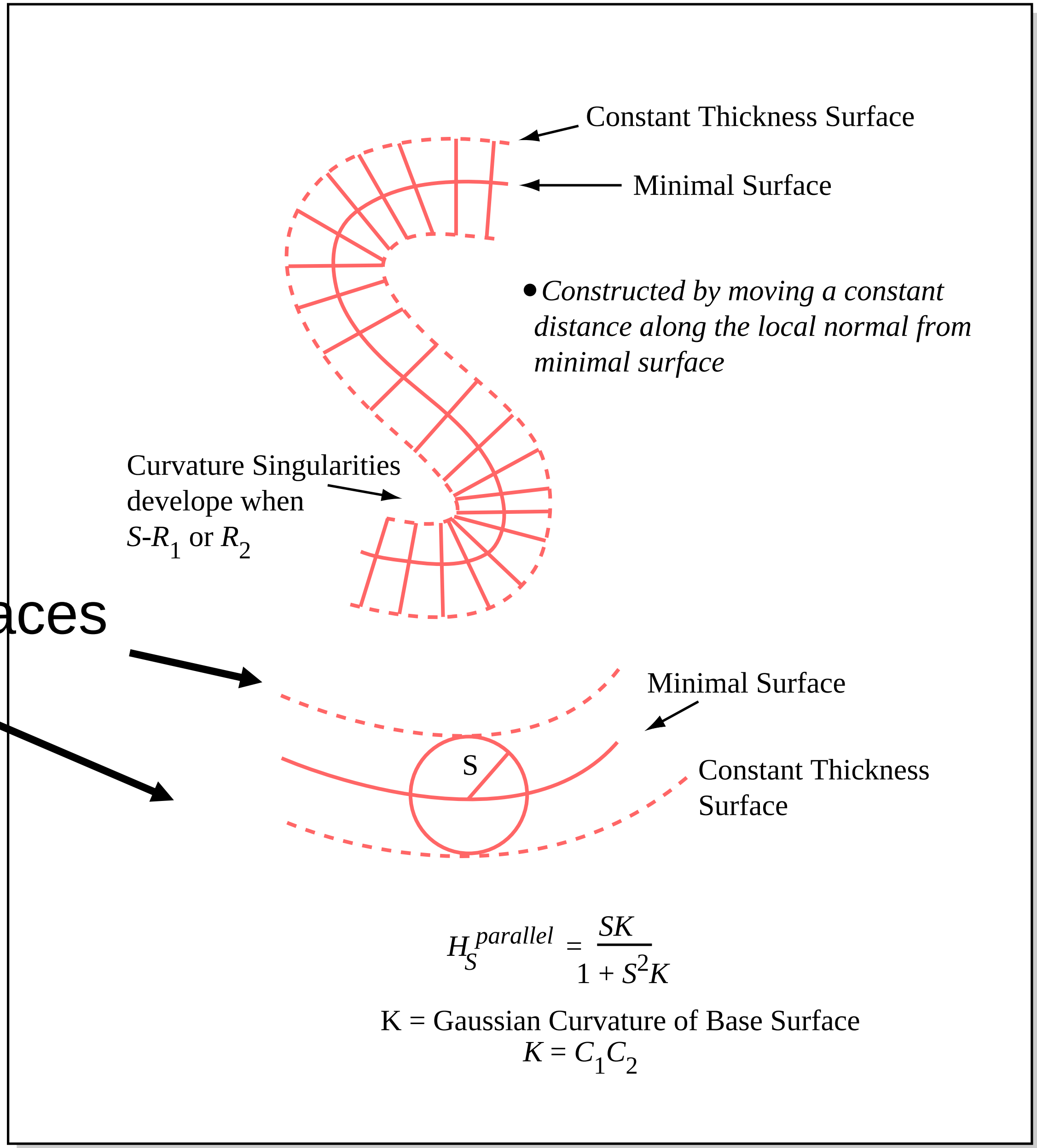
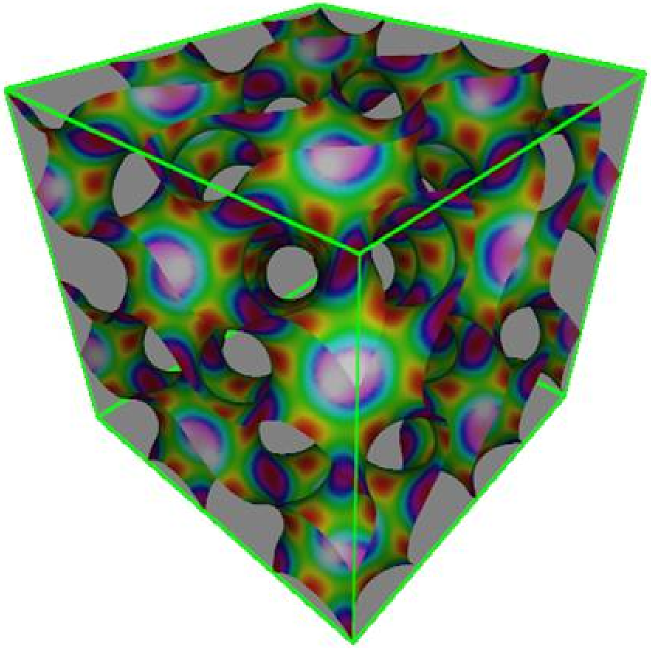


Figure by MIT OCW.

CT – Gyroid Model

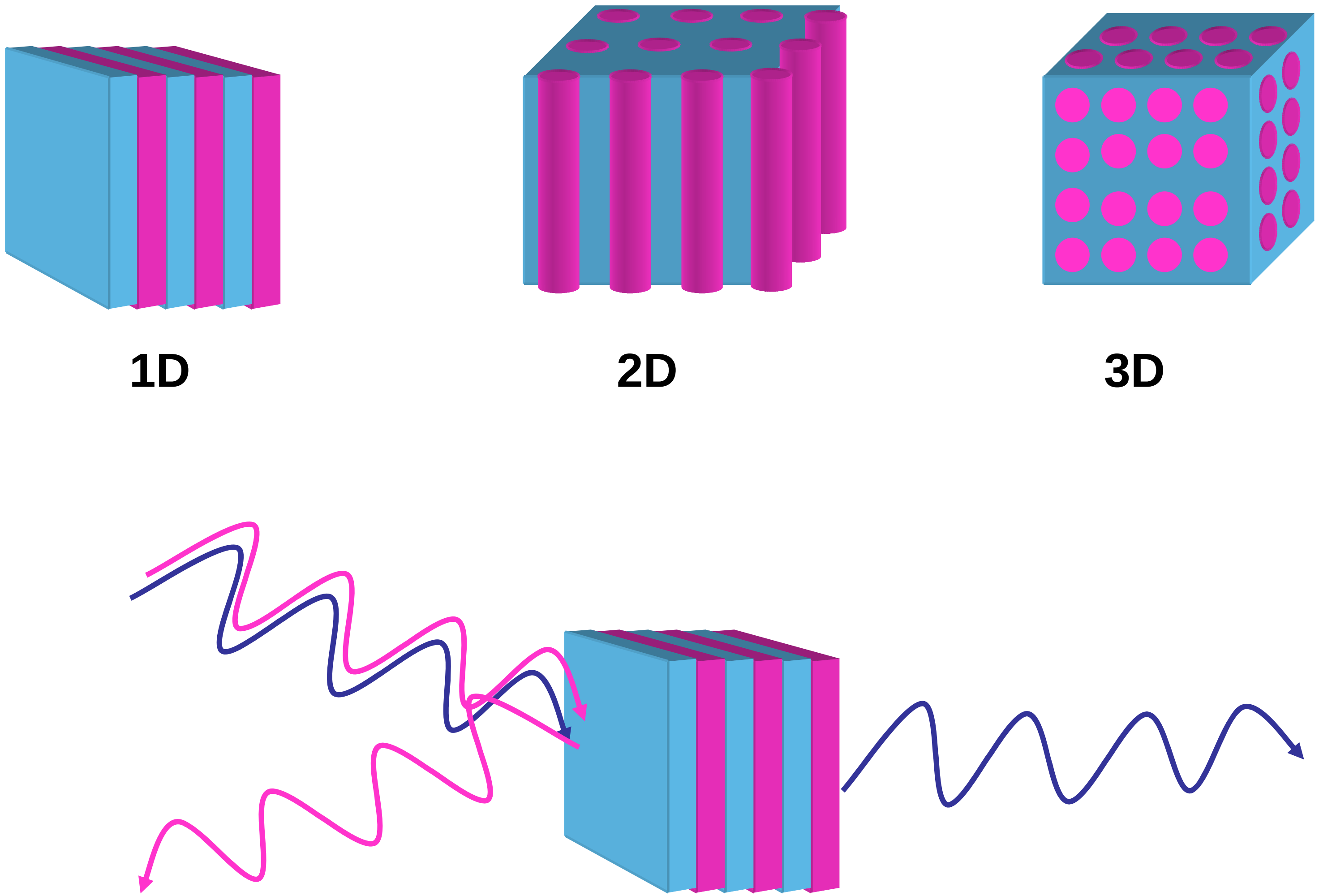


A/B BCP microdomain structure is the double gyroid

Schoen's G Minimal Surface used as Base Surface

	Space groups
Double Gyroid Network:	$Ia\bar{3}d$
Gyroid Minimal Surface:	$I4_132$
Single Gyroid Network:	$I4_132$

PHOTONIC CRYSTALS FROM SELF-ASSEMBLED BLOCK COPOLYMERS



4 Microdomain Morphologies for A/B Diblocks

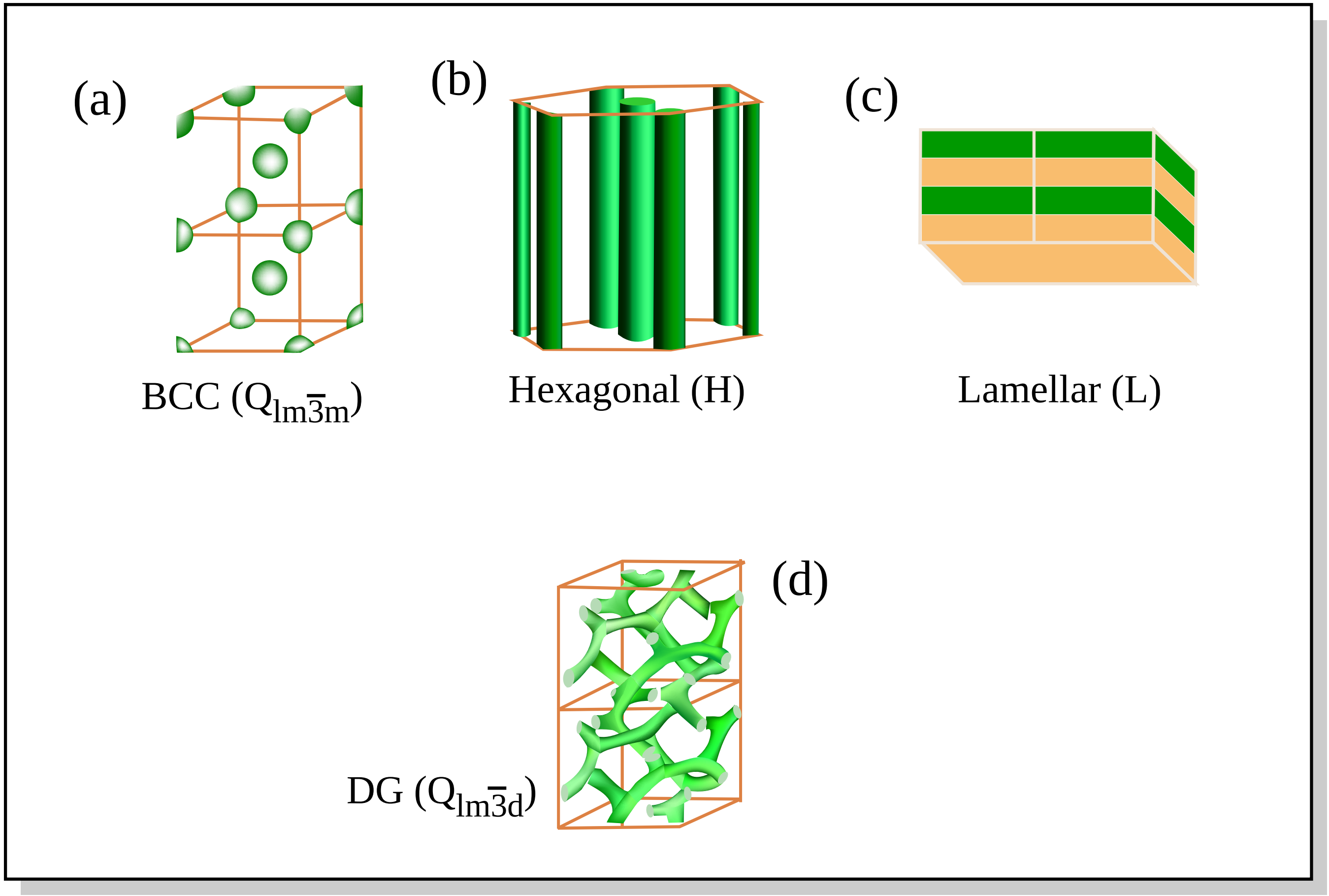


Figure by MIT OCW.

Photonic Block Copolymers

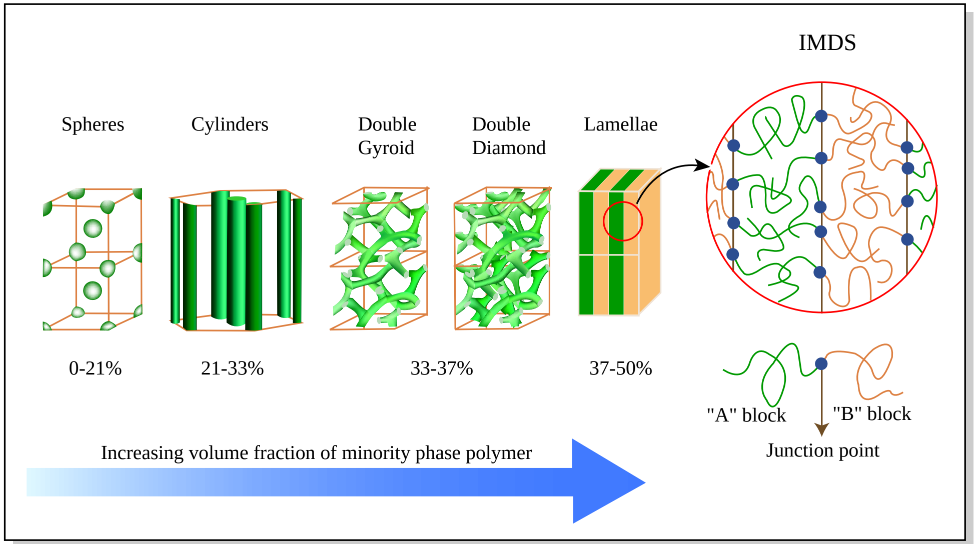


Figure by MIT OCW.

$0.34<f_{PS}<0.62$

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

Lamellae

$0.28<f_{PS}<0.34$

Please see Fig. 1 in Urbas, Augustine, et al. "Bicontinuous Cubic Block Copolymer Photonic Crystals." *Advanced Materials* 14 (December 17, 2002): 1850-1853.

Double gyroid

$0.17<f_{PS}<0.28$

Please see:Fig. 1a, 11 in Park, Cheolmin, et al. "Enabling Nanotechnology with Self-assembled Block Copolymer Patterns." *Polymer* 44 (2003): 6725-6760.

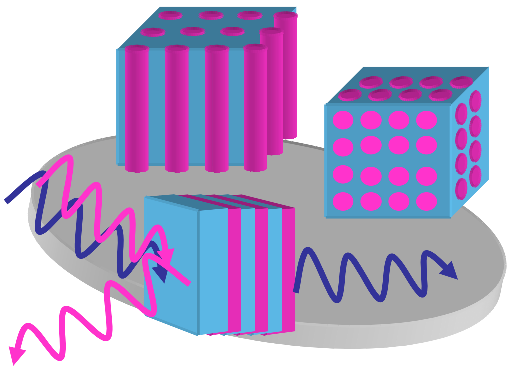
HCP cylinders

$f_{PS}<0.17$

Please see Fig. 8 in Lammertink, Rob G. H., et al. "Periodic Organic-Organometallic Microdomain Structures in Poly(styrene-block-ferrocenyldimethylsilane) Copolymers and Blends with Corresponding Homopolymers." *Journal of Polymer Science* B 37 (1999): 1009-1021.

BCC sphere

POLYMER-BASED PHOTONIC CRYSTALS



OMNIREFLECTIVITY - 1D PBG

Image removed due to copyright restrictions.

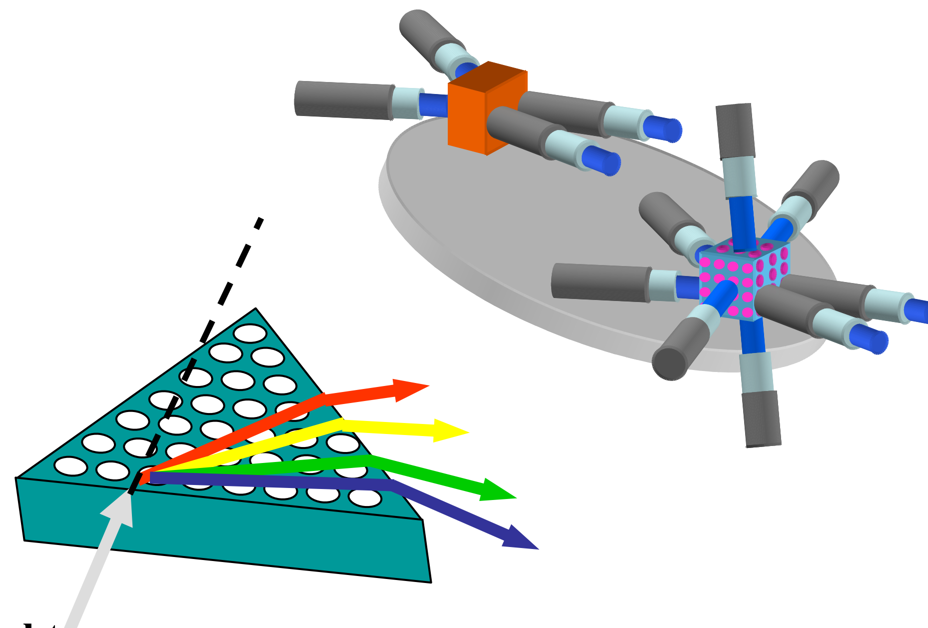
Please see Fig. 2b in Fink, Yoel, et al. “A Dielectric Omnidirectional Reflector.” *Science* 282 (November 27, 1998): 1679-1682.

3M GBO plastic reflectors

Image removed due to copyright restrictions.

Please see Fig. 4 in Weber, Michael F., et al. “Giant Birefringent Optics in Multilayer Polymer Mirrors.” *Science* 287 (March 31, 2000): 2451-2456.

PMMA - polyester



Photonics and Self Assembly

Self Assembly enables the fabrication of materials with periodic variations in properties (dielectric constant)

Patterning in 3-D is simple via self assembly

Design Considerations for Photonic Crystals

- **Geometrical structure with periodic index variations**
- **Components with large difference in the indices of refraction**
- **Optically transparent in the frequency range of interest**
- **Control over the length scale of the morphology**
- **Highly ordered structures with specific (controlled) defects**

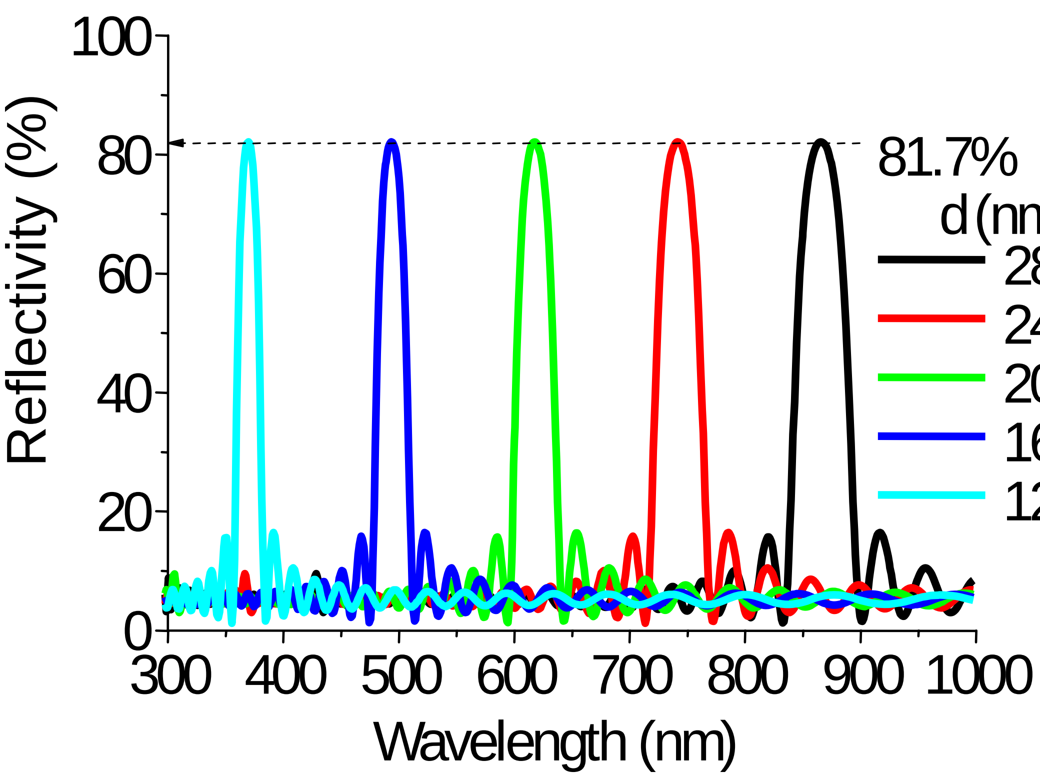
Band Gap Design Criteria

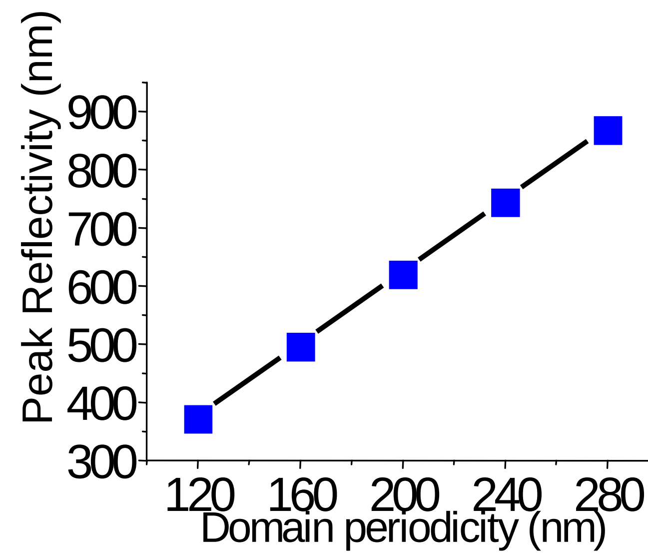
Peak position ~ Lamellar period

BG center wavelength ∝ Optical thickness (n x d)

BG width ∝ Index contrast n_2/n_1

n_H = 1.59, n_L =1.51, L = d_H+d_L, 2N = 50

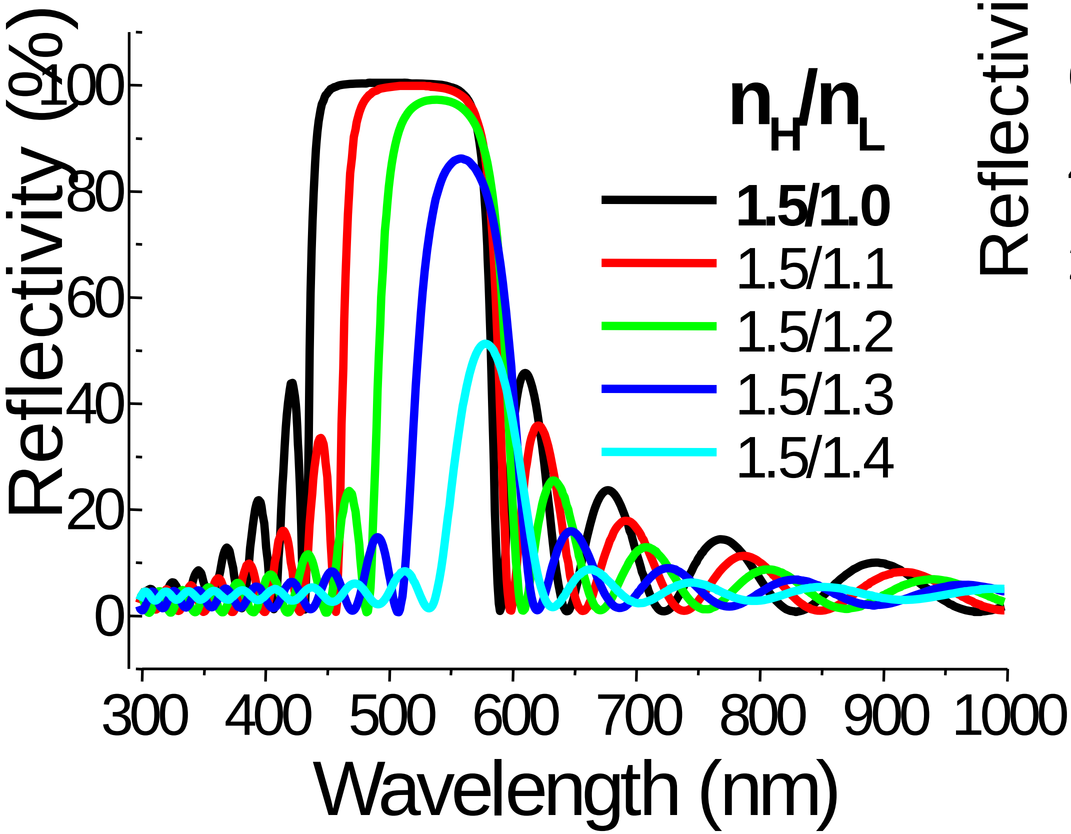


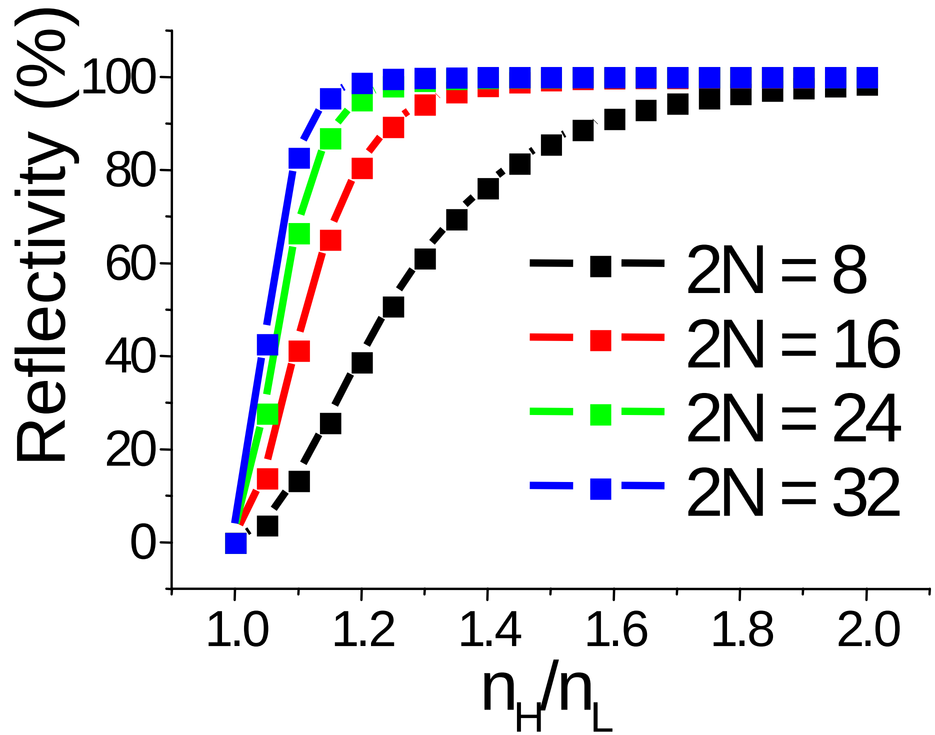


Design Criteria

Refractive index contrast and number of periods

$d_H = d_L = 100$ nm, 2N = 20



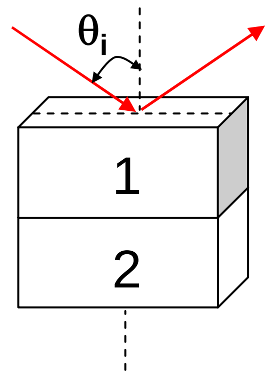


$$R = \left\{ \frac{1 - \left(\frac{n_L}{n_H} \right)^{2N}}{1 + \left(\frac{n_L}{n_H} \right)^{2N}} \right\}^2$$

Influence of Dielectric Contrast on Reflectivity

Image removed due to copyright restrictions.

Please see Fig. 1c in Yoon, Jongseung, et al. “Self-Assembly of Block Copolymers for Photonic-Bandgap Materials.” *MRS Bulletin* 30 (October 2005): 721-726



Urbas, A., Fink, Y., and Thomas, E.L., "One Dimensionally Periodic Dielectric Reflectors from Self-Assembled Block Copolymer-Homopolymer Blends", *Macromolecules*, 32, 4748-4750 (1999).

Material and Optical Parameters

PS: d_1 = 100 nm; n_1 = 1.59

PI: d_2 = 100 nm; n_2 = 1.52

40 periods (80 layers)

Fink, Y., Winn, J.N., Fan, S., Chen, C., Michel, J., Joannopoulos, J.D., Thomas, E.L., "A Dielectric Omnidirectional Reflector," *Science*, 282, 1679-1682 (1998)

Material and Optical Parameters

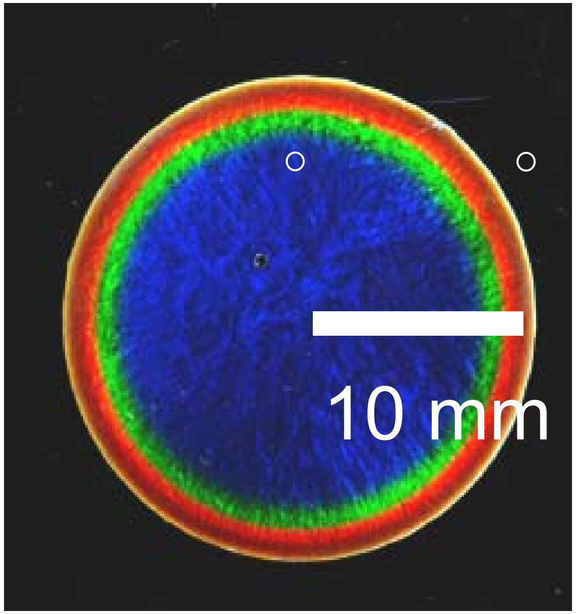
Te: d_1 = 0.8 μm ; n_1 = 4.6

PS: d_2 = 1.65 μm; n_2 = 1.59

4.5 periods (9 layers)

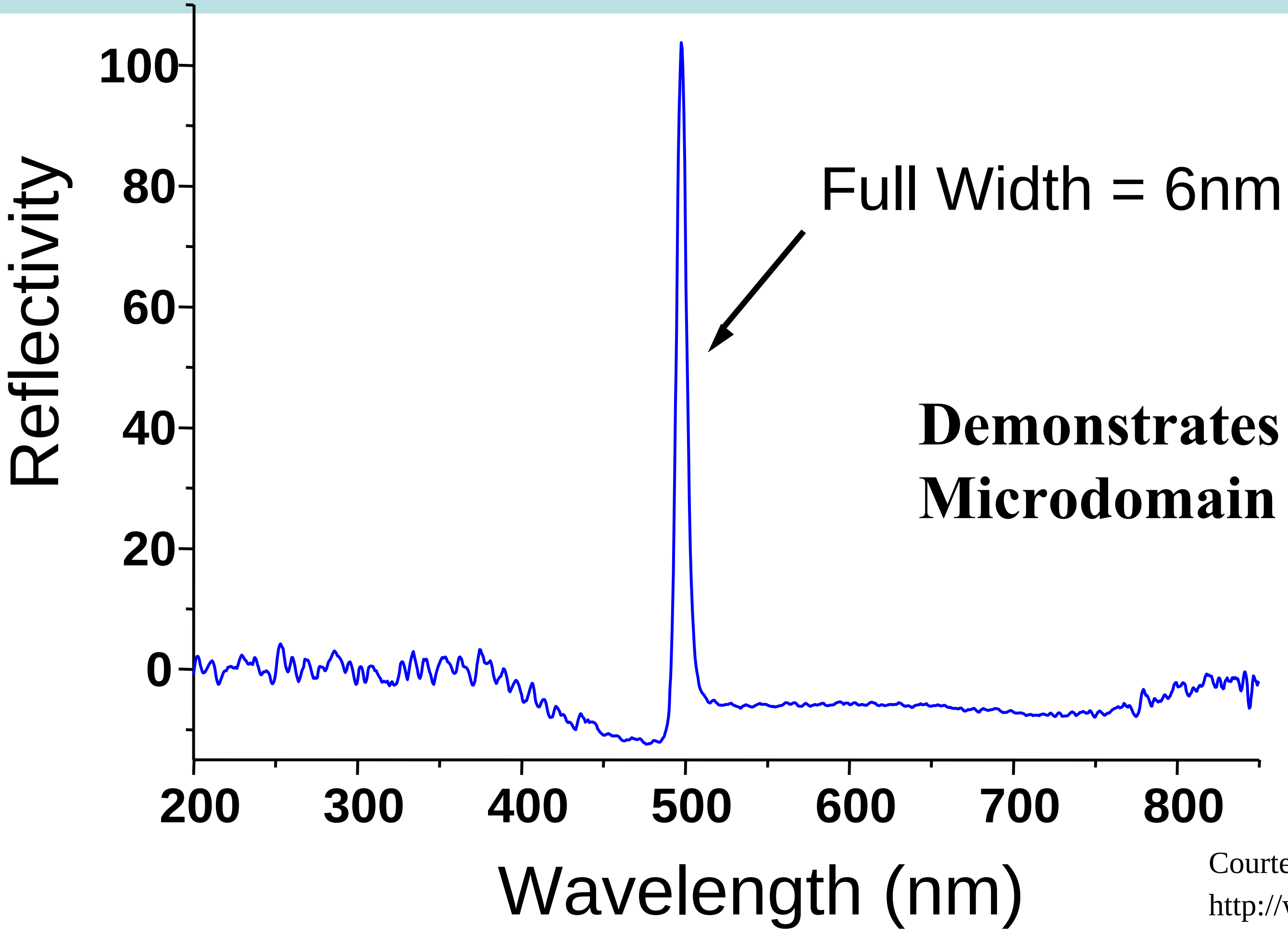
Reflectivity of BCP Lamellae

- Observed shift in color of reflectivity as gels dry



Green reflector:
PS/PI BCP

Highly Reflective Self Assembled Mirrors



Demonstrates Excellent Microdomain LRO

12% solution of PS/PI 480k/560k in Toluene

Self Assembled Metallodielectric Mirror

Concept: Sequester Nanoparticles in a Particle-phobic A/ Particle-philic B Diblock Copolymer and achieve High Dielectric Contrast

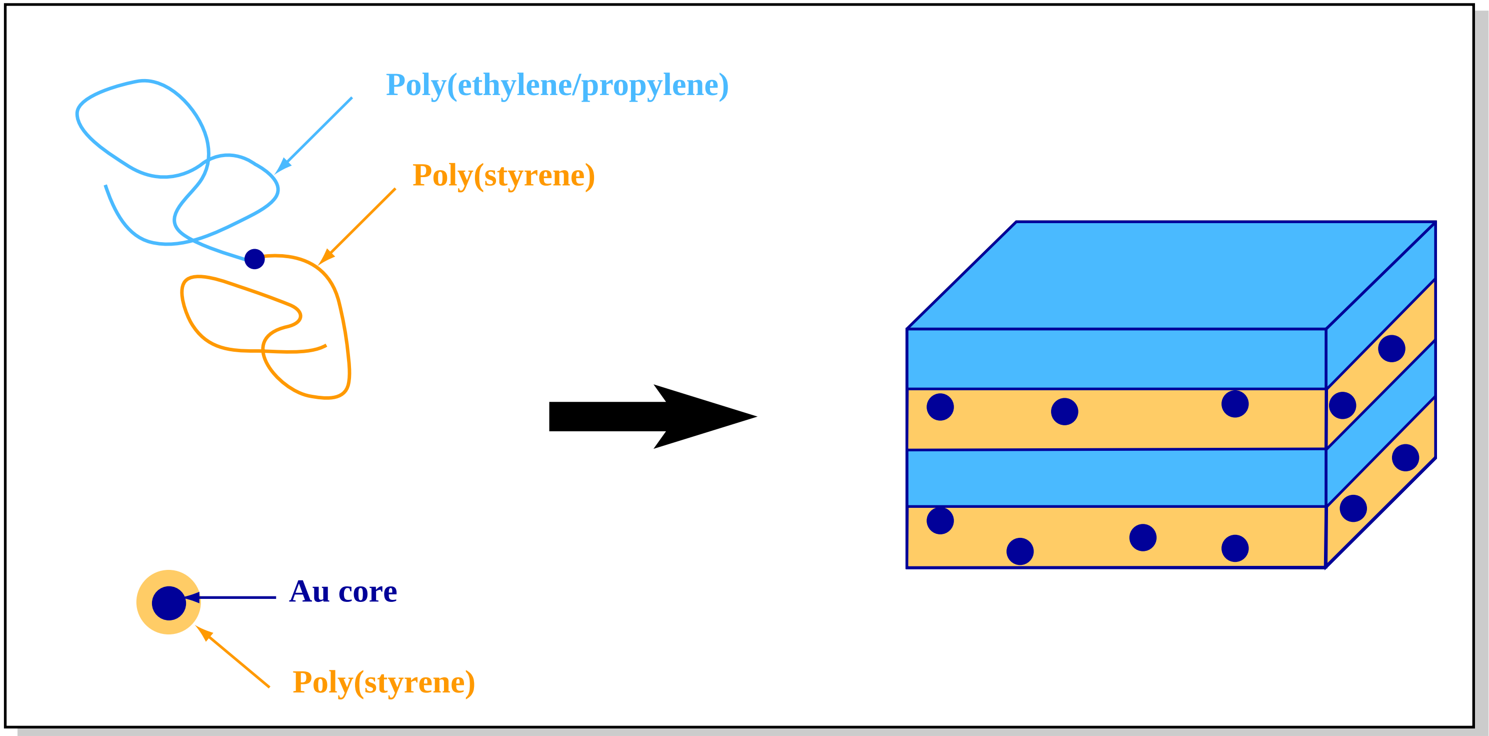


Figure by MIT OCW.

M. Bockstaller, R. Kolb and E. L. Thomas, *Adv. Mater.*, **13**, 23, (2001), 1783-1786.

Block Copolymer PBG - Template Approach To Increase Dielectric Contrast

Idea: Sequester high index quantum dots (nanoparticles) in a dot phobic A- dot philic B diblock copolymer

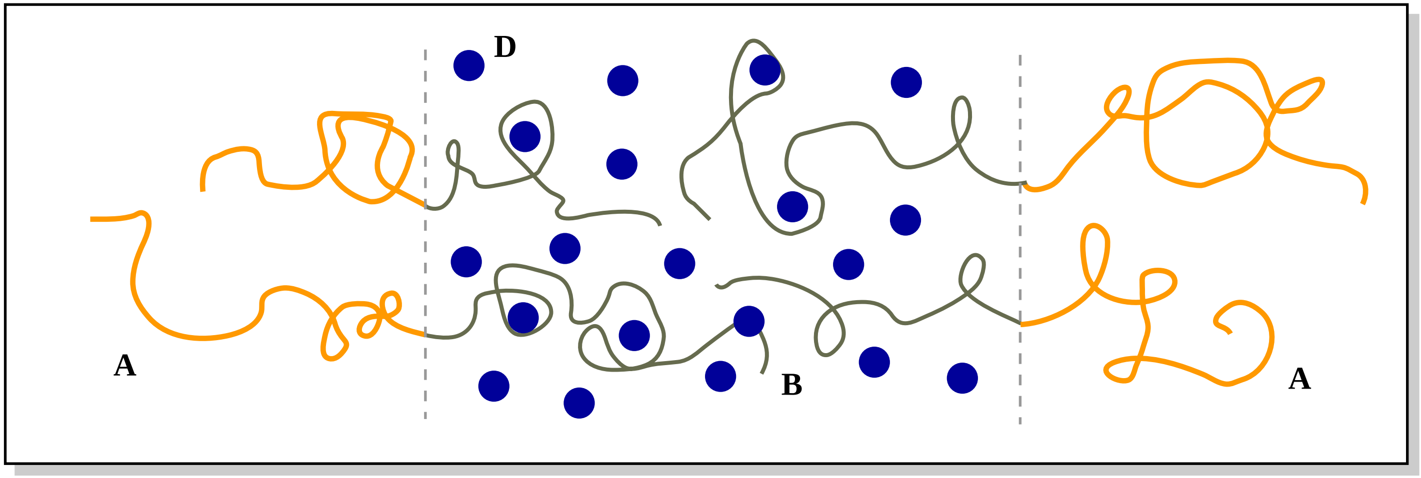


Figure by MIT OCW.

$<\varepsilon_A> = n_A^2$ $\quad$ $<\varepsilon_B> = \varepsilon_B \phi_B + \varepsilon_D \phi_D$

Effective $\varepsilon_D \phi_D$?

Ternary Nanocomposite (2 types of particles)

Demonstrate 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." *JACS* 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

M. Bockstaller et al. *J. Am. Chem. Soc.*, **125**, (2003), 1572-1573.

Self Assembled Omni-Directional Metallodielectric Mirror

Transfer Matrix Method

assumptions:
- quasistatic approximation
- effective medium theory

Image removed due to copyright restrictions.

Please see Fig. 3 in Bockstaller, Michael R., et al. "Metallodielectric Photonic Crystals Based on Diblock Copolymers." *Advanced Materials* 13 (December 3, 2001): 1783-1786.

✓ effective medium model
➔ red shift of reflectance

✓ Omnidirectional Reflector predicted for f=0.2

Block Copolymers Photonic Crystals

Towards

Self-Assembled Active Optical Elements

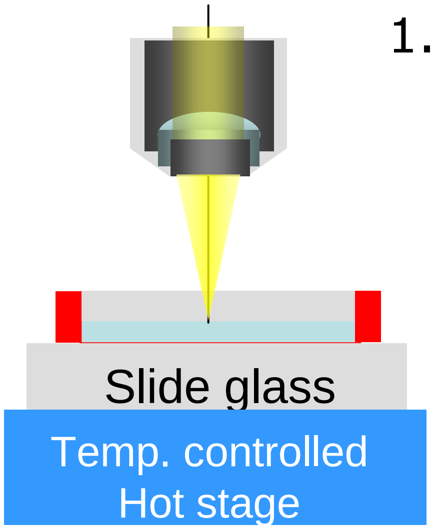
"Make it *do something*…"

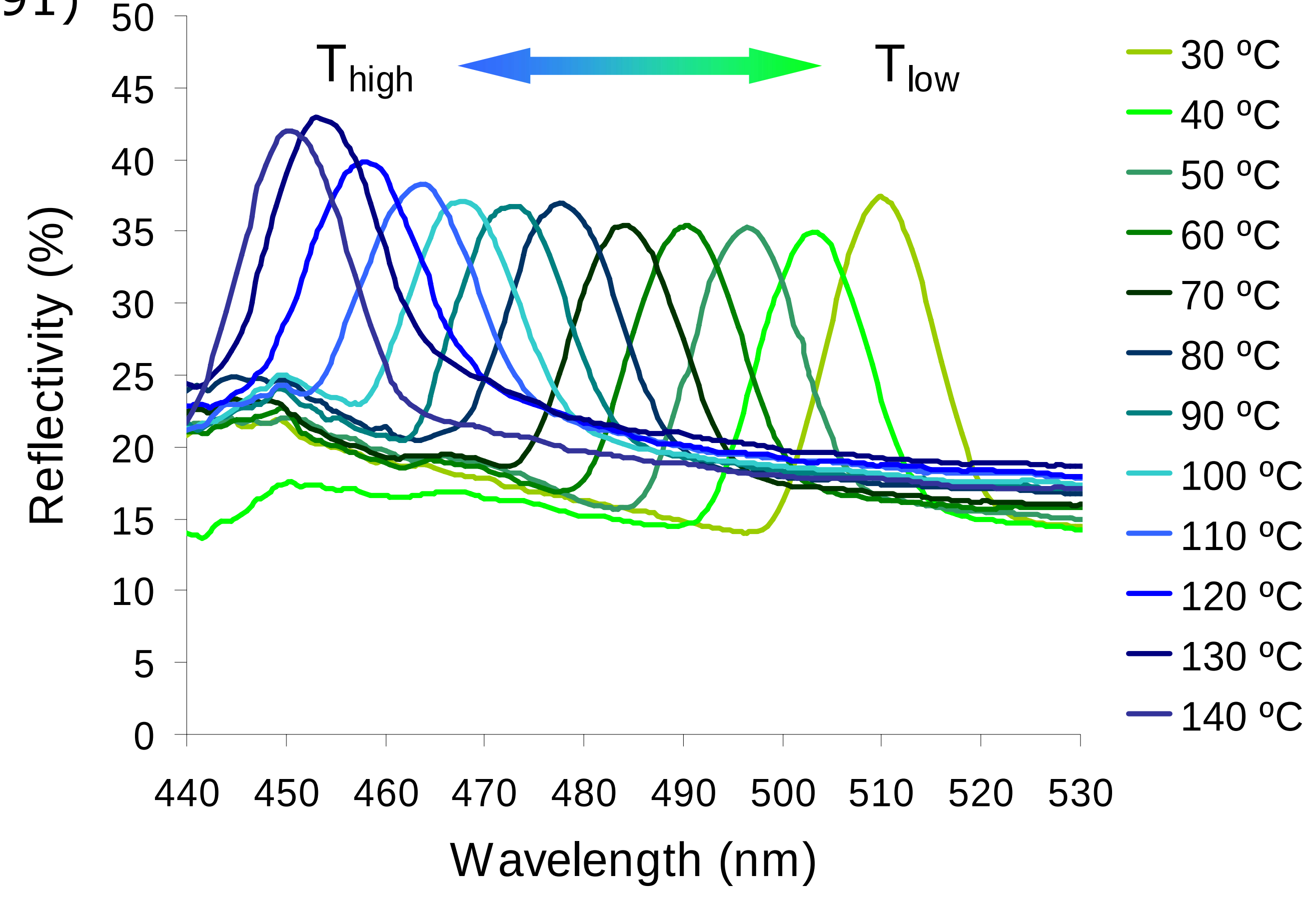
Variation of temperature (dn/dT, χ_{AB})
Concentration of solvent (swelling and χ_{AB})
Mechanical strain (layer spacing)
Polyelectrolyte gel (layer spacing and index)

Thermochromism

- Strong temperature dependence of peak reflectivity

PS/PI 480k/360k with cumene (n = 1.491)





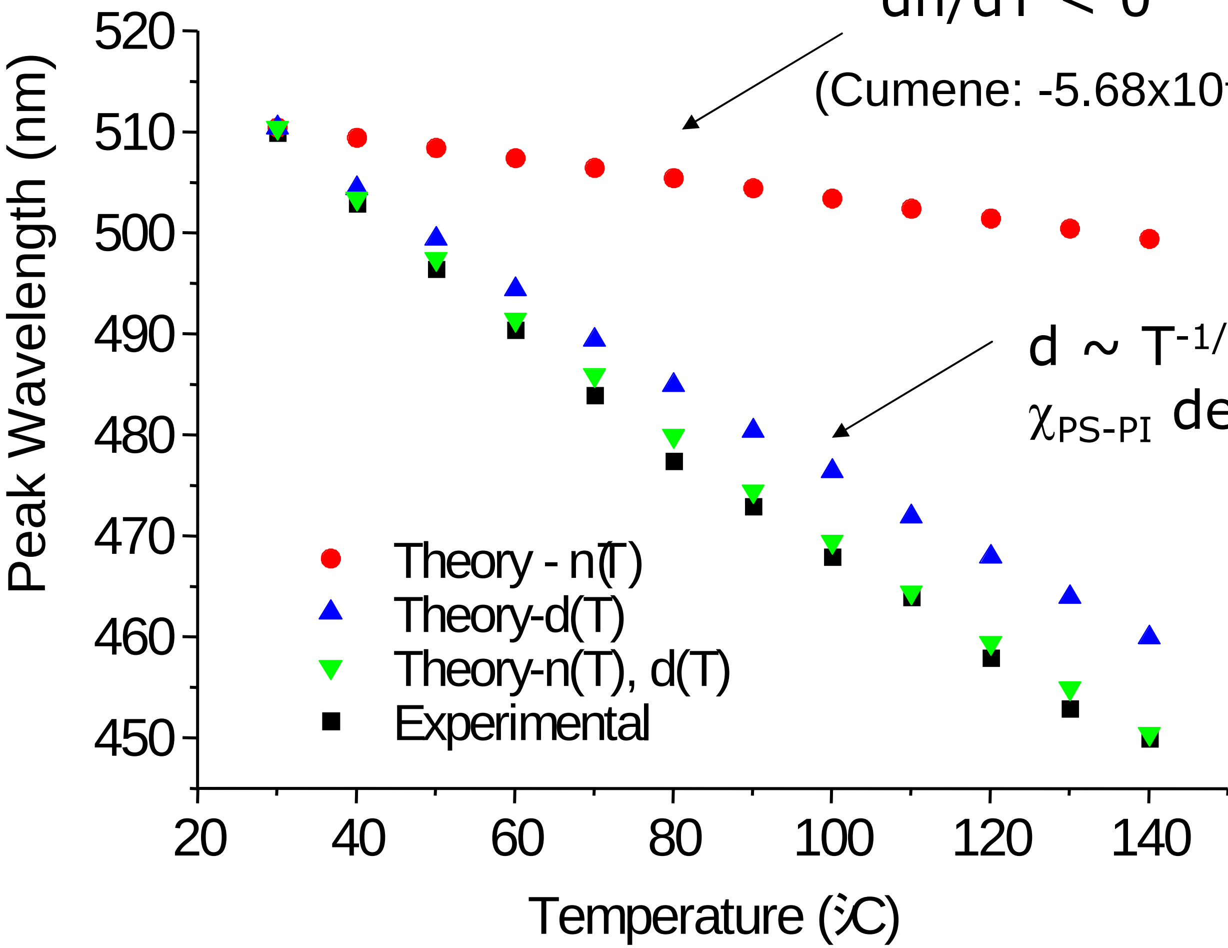
J.S. Yoon, unpublished

Thermochromism

Experiment vs. Theory

dn/dT < 0

(Cumene: -5.68×10^{-4}/K, PS/PI: -1.27×10^{-4}/K)



$d \sim T^{-1/3}$

$\chi_{PS\text{-}PI}$ decreases with Temp

Theory accounts for the measurements

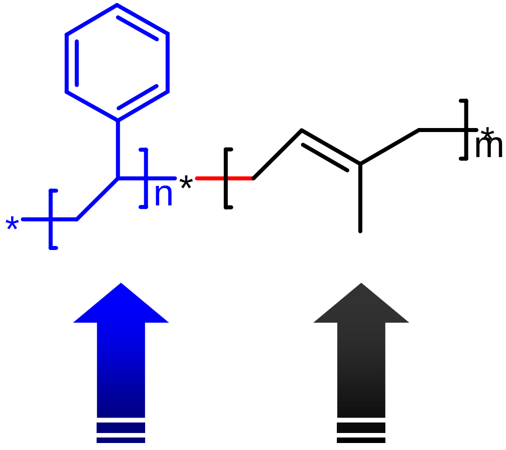
J.S. Yoon, unpublished

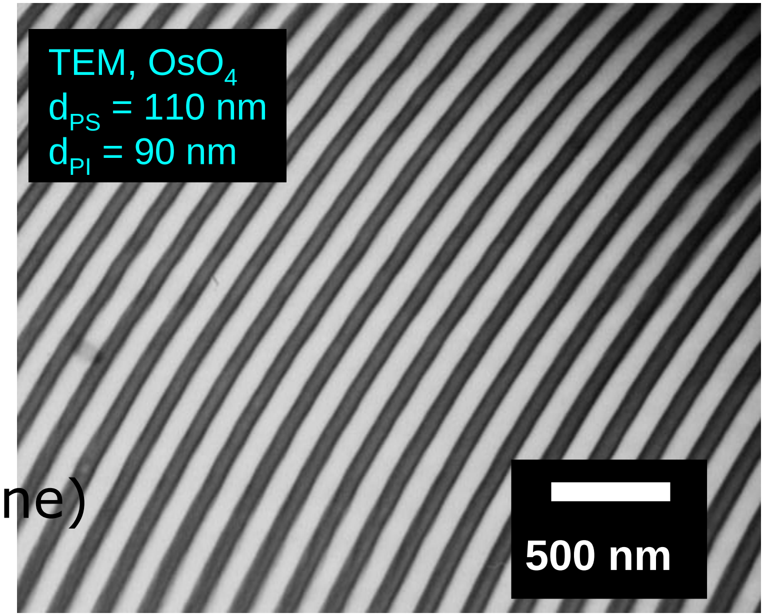
Self-Assembled Responsive Reflectors

- Mechanochromic BCP Photonic Gels

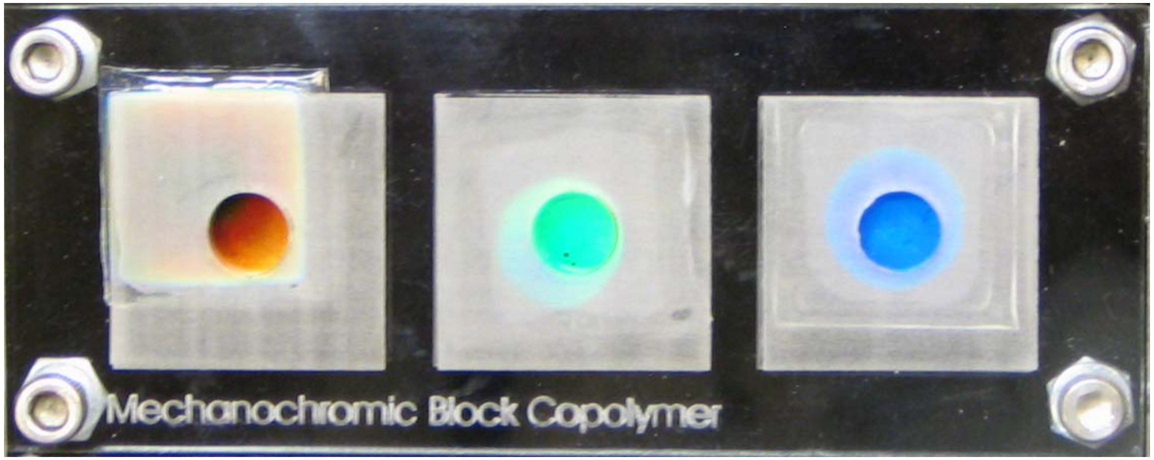
  (MW: 5×10^5 ~ 15×10^5 g/mol)

  - lamellar PS-b-PI BCP
  - neutral plasticizer (DOP or cumene)





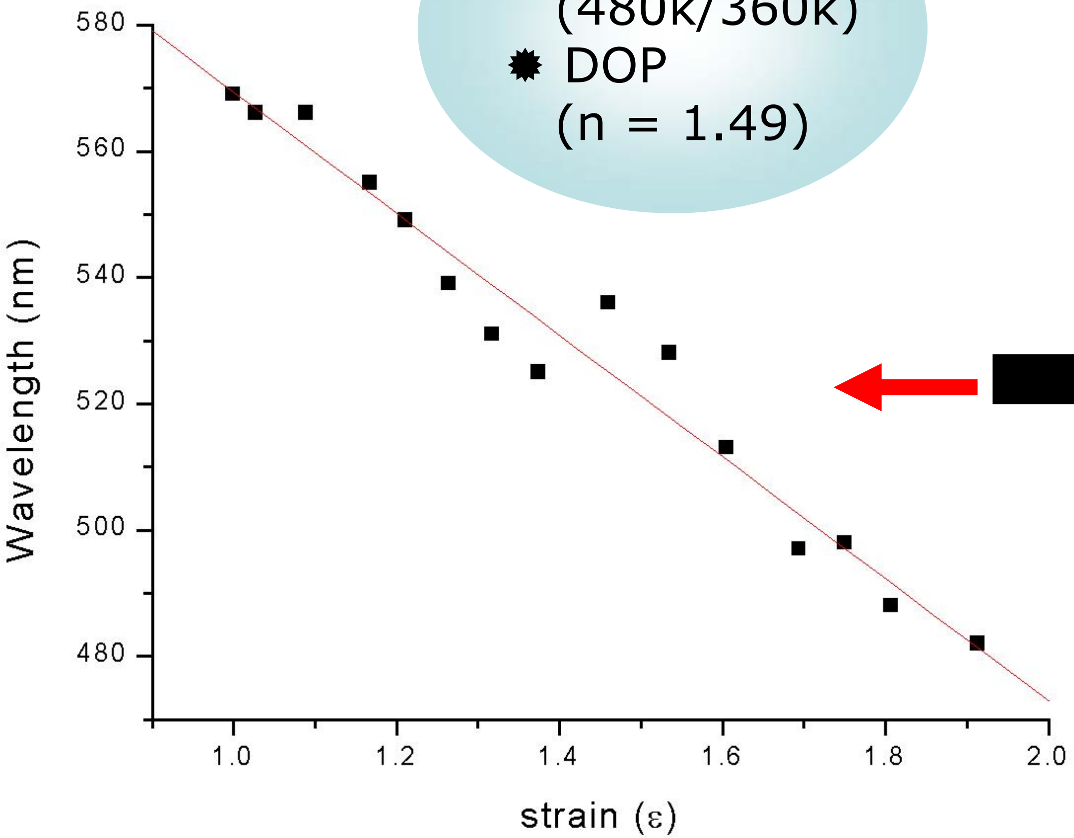
- PS-b-PI (480k/360k)



Mechanochromism

- Tensile/compressive strain

- PS-b-PI
  (480k/360k)
- DOP
  (n = 1.49)

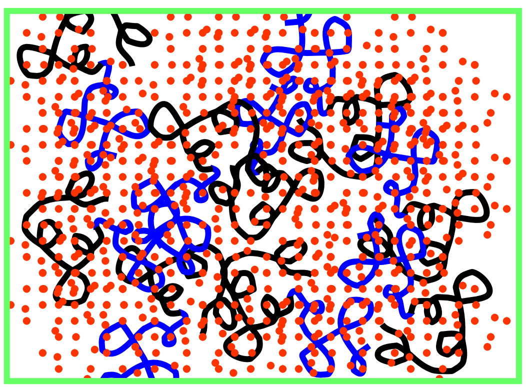


Solvatochromism

- Use a solvent to change layer spacings d_{LAM}

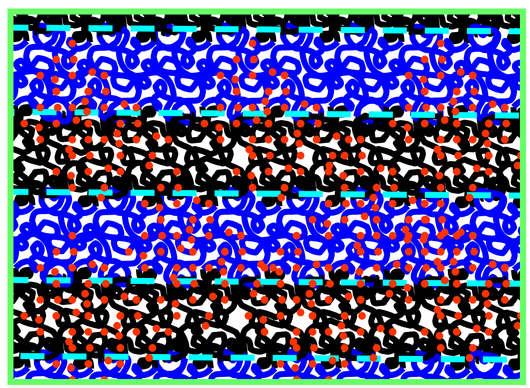
- Layers shrink as ϕ_p increases during solvent evaporation
- Layers expand as χ_{PS-PI} increases during solvent evaporation

Polymer solution



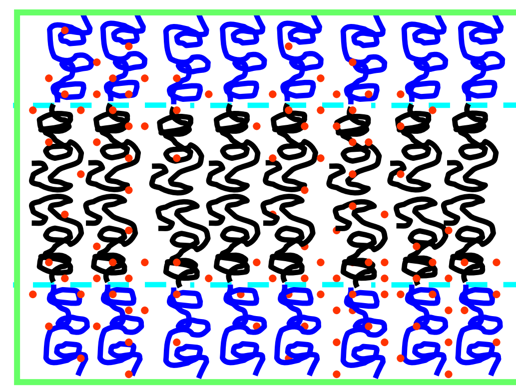
$\phi < \phi_{ODC}$

Swollen Gel



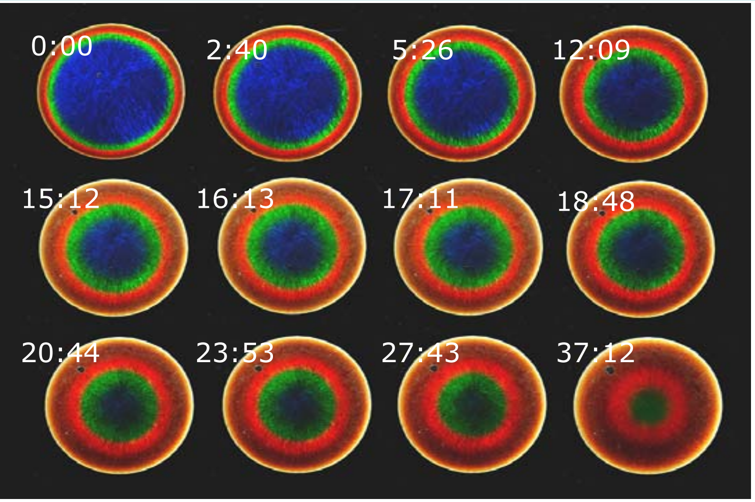
$\phi_1 > \phi_{ODC}$

Dry Polymer Film

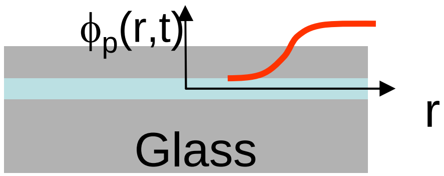


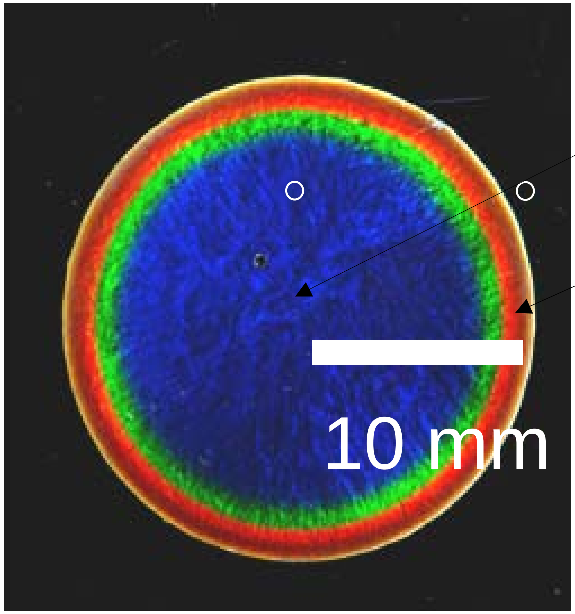
$\phi_2 > \phi_1$

Solvatochromism



Time series





Spectral properties