Introduction: Comparison of Common Polymerization Methods

	Step-Growth	**Chain-Growth**	**Anionic**
Growth method	Cons. of small molecules	Free-radical transfer	Carbanion transfer
Ease	Fairly simple	Fairly simple	Difficult
Poly-Dispersity	Very high	High	Very low
Theoretical PDI limit	2	1.5 or 2	1.0

Other methods: Cationic, RAFT, ATRP

Anionic Disadvantages

- More difficult than many polymer techniques
  - Simple homopolymer requires 15-20 steps executed perfectly
- Generally not compatible with glycols, oxides, amines, etc.
  - Any labile proton source in the monomer terminates reaction
  - Mostly limited to pure carbon backbones (PS, PBd, PI, etc.)
- Difficult to initiate from a surfaces

Common Anionic Polymerization Schemes

	Solvent	Initiator
Polystyrene	Cyclohexane	sec/n-BuLi
Polybutadiene	Cyclohexane	sec/n-BuLi
Polyisoprene	Cyclohexane	sec/n-BuLi
PMMA	THF	LiαMeS*
PEO	THF	K-naphthalene
α-Methylstyrene	THF	sec-BuLi

*Poly(α-methylstyryl)lithium

Basic Components: Solvents

- Solvents need to be a-protic in all situations
- Most often saturated hydrocarbons either aromatic (i.e. benzene) or aliphatic (i.e. hexane)
- Boiling point and freezing point must be considered for low and high temperature reactions
- Solutions often need to be dilute because high concentration polymers are often insoluble
- Solvent selection also should minimize chain transfer reactions

Solvent Effects (cont.)

- Propagation
  - Different observed rate constant in each solvent
  - Controls tightness of polymer counter-ion pair
  - Strong effects on chain swelling

- Solubility
  - Concentrated polymers are often insoluble in most solvents
  - Polymer concentration must usually be low (5-10%) during whole procedure

Basic Components:
Solvent Effects on Initiation

- Initiation
  - Solvent choice can have an impact on overall reaction order for initiation
  - Difference between aliphatics and aromatics mainly
  - Reaction order higher in most cases in cyclohexane (aliphatic) than benzene (aromatic)
  - However reaction *rate* higher in aromatic solvent
    - Roovers and Bywater reported sec-BuLi initiated isoprene 2000 times faster in benzene than hexane
    - Difference between reaction order and reaction rate

Basic Components: Initiators

- Most common initiators are alkyllithium compounds
  - sec-BuLi, n-BuLi, etc.
  - Commercially available in solution
  - Alkyllithium compounds have a carbanion that is basic enough to initiate polymerization

- Other types used
  - Radical anions (used for dienes)
  - Alkali metals (used for dienes)
  - Cumyl Potassium

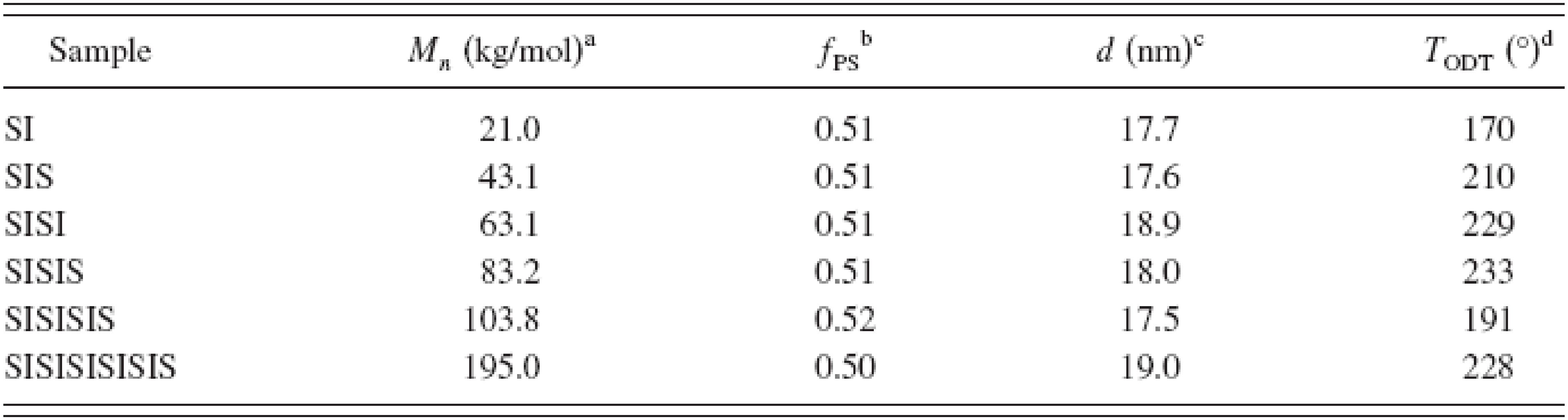
Basic Components: Initiators (cont.)

- Initiators can also contain functionalized end groups
  - Tertiary amines
  - Protected alcohols
  - Fluorescence Dyes

- Selection of initiator has significant effects on reaction rate
  - Styrene initiates faster with sec-BuLi than n-BuLi
  - Counter ion impacts structure (isomers of PI)
    - Li: 94% cis-1,4 6% 3,4
    - Na: 43% trans-1,4 51% 3,4 6% 1,2
    - K: 52% trans-1,4 40% 3,4 8% 1,2

Block Copolymers

- Highly controlled block copolymers were first enabled anionic polymerization
- Theoretically no limit to number of blocks or scale

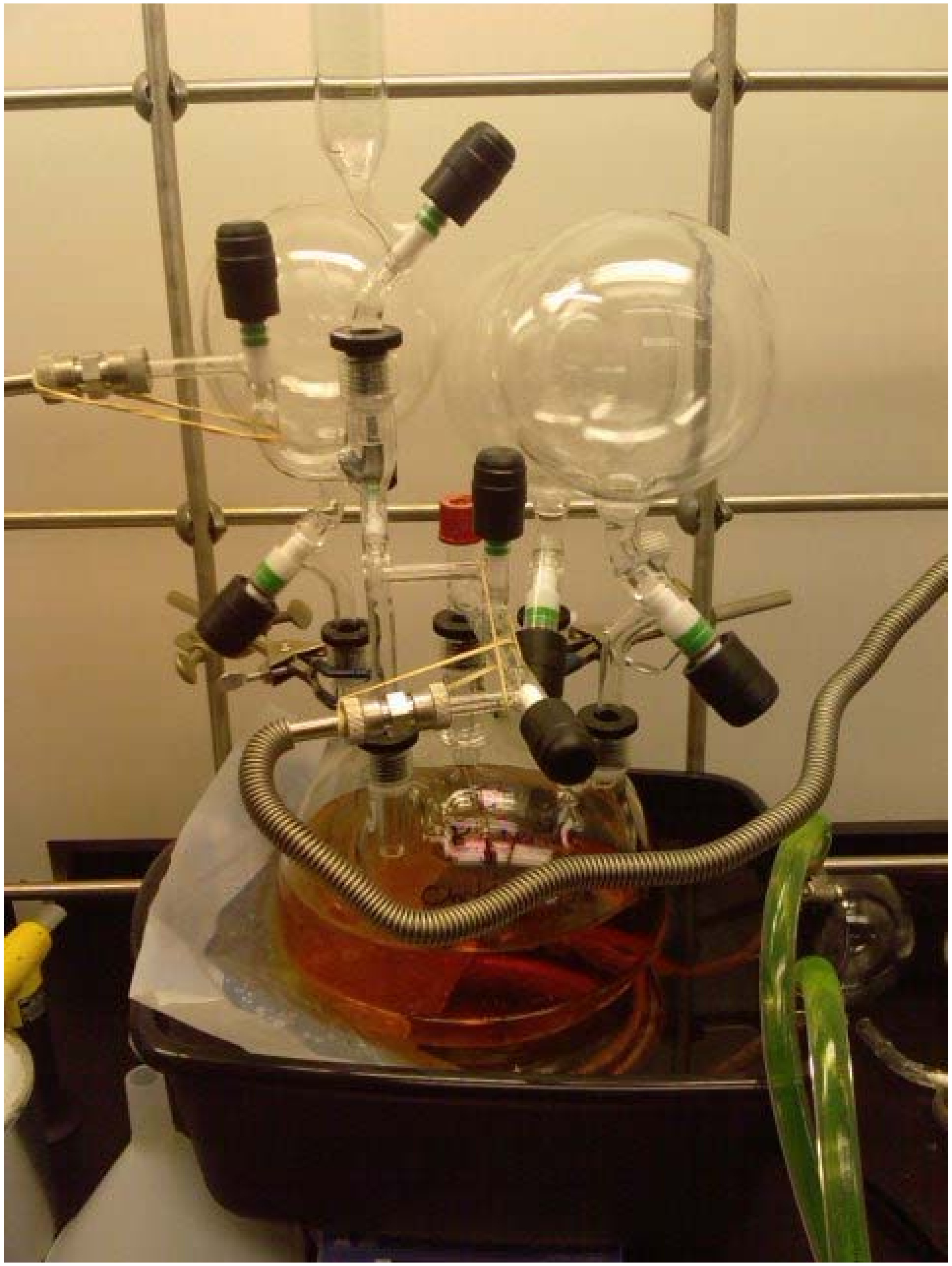


Sample	M_n (kg/mol)[a]	f_{PS}[b]	d (nm)[c]	T_{ODT} (°)[d]
SI	21.0	0.51	17.7	170
SIS	43.1	0.51	17.6	210
SISI	63.1	0.51	18.9	229
SISIS	83.2	0.51	18.0	233
SISISIS	103.8	0.52	17.5	191
SISISISISIS	195.0	0.50	19.0	228

Bates and Wu, J Rheology

- Three major methods:
  - – Sequential addition of monomers to one chain
  - – Multi- functional initiators (ABA, ABCBA, etc.)
  - – Coupling of living chains (ABA, ABCBA, etc.)

- 5L glass reactor for 500g SIS triblock



Block Copolymers

Sequential Monomer Addition

- Begin by polymerizing single monomer
- After first monomer is consumed add second monomer
- Best for AB di-blocks or asymmetric polymers

A	**B**	**Initiator**	**Solvent**
Styrene	EO	sec-BuLi	C_6H_6/DMSO
Styrene	MMA	sec-BuLi	THF
Isoprene	Styrene	Cumyl K	THF
Styrene	t-BuMA	n-BuLi	THF

Block Copolymers

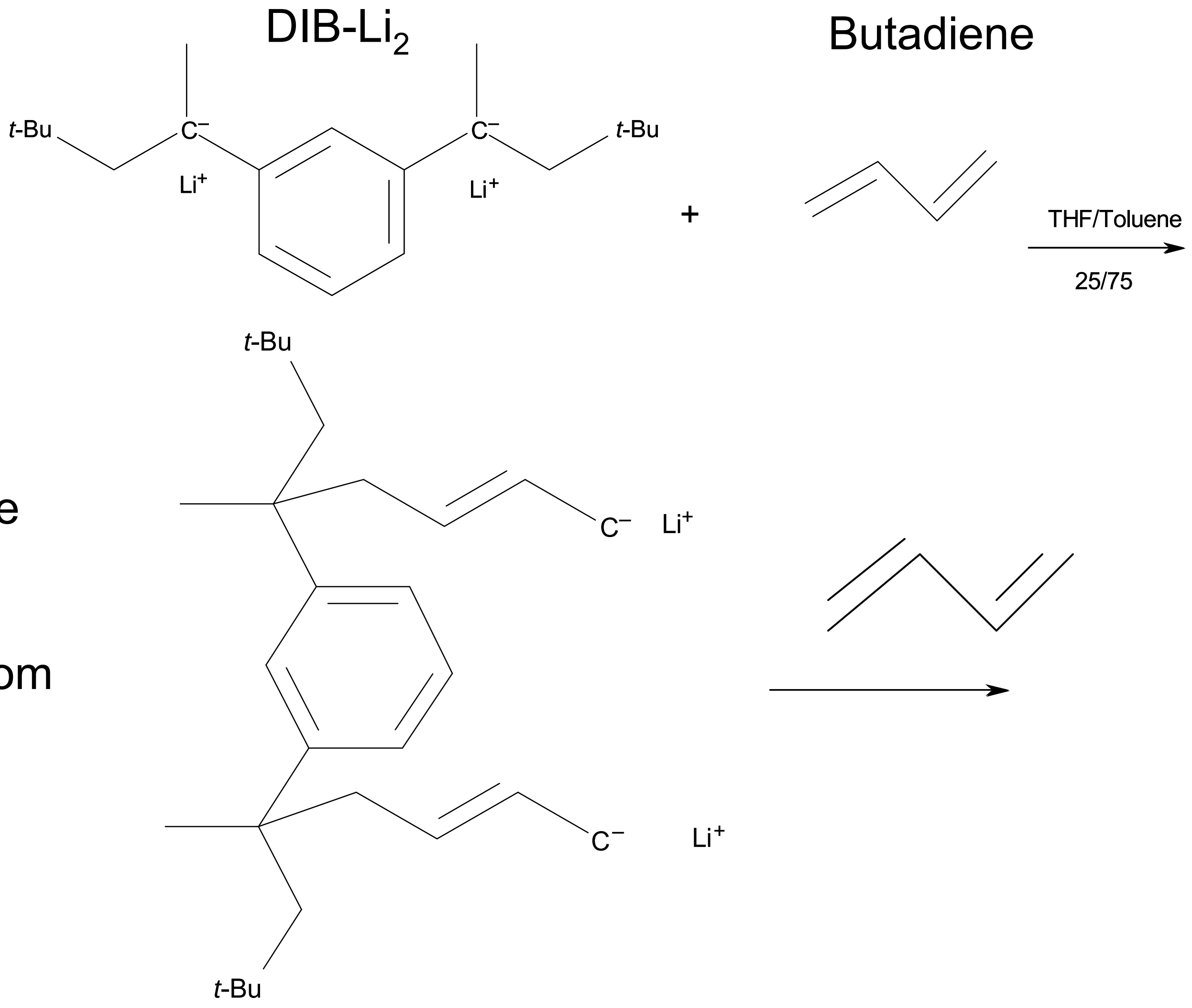
Multi-Functional Initiators

- Using a di-functional initiator the chain grows from two points at once with two active centers
- Second monomer will add to both ends
- Easiest method for symmetric block-copolymers (ABA, ABCBA, etc.)

A	**B**	**Initiator**	**Solvent**
Isoprene	EO	2 K-Naphthalene	THF
Butadiene	4-Vinylpyridene	DIB-Li_2	THF/Toluene
Butadiene	Styrene	DLI	C_6H_{14}/C_6H_6
t-BuA	MMA	DIB-Li_2	THF

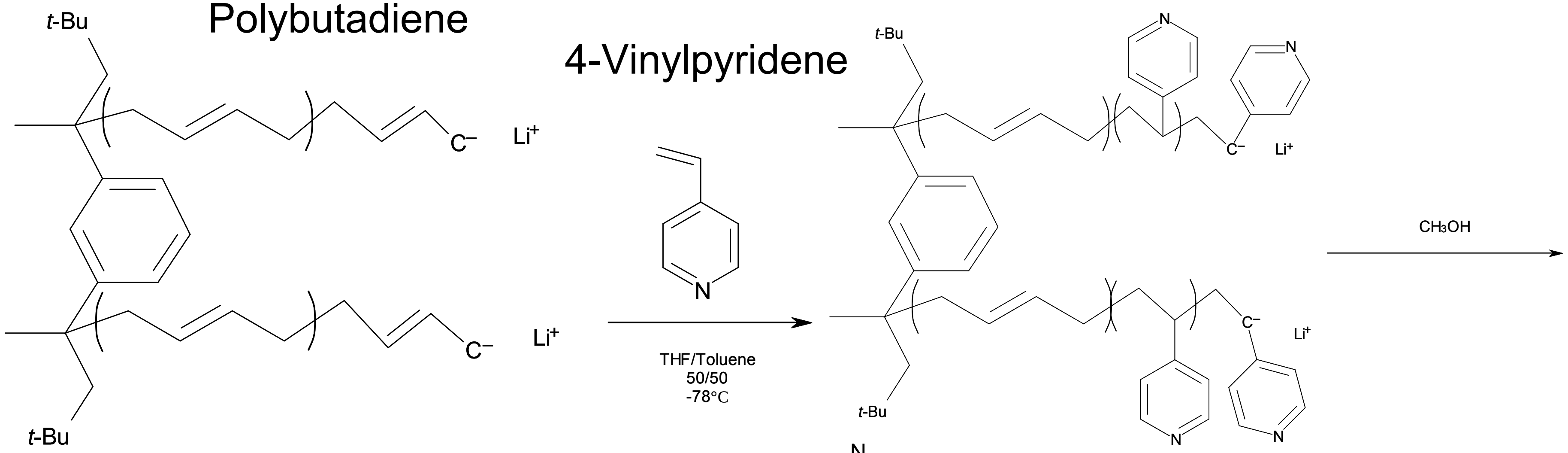
Table is all ABA co-polymers

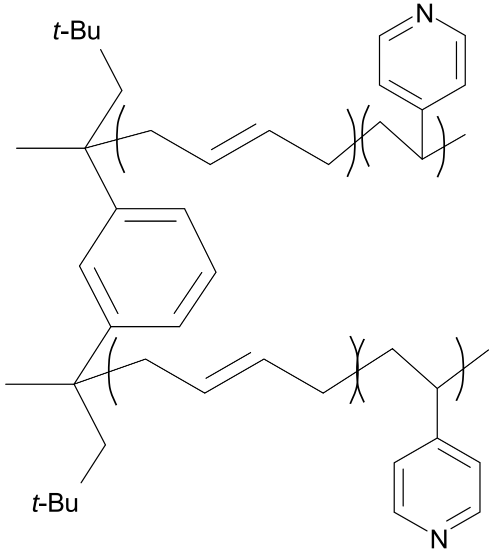
Block Copolymers Example Multi-Functional Initiator Scheme - Initiation



Note there are two active anions to polymerize from

Example Multi-Functional Initiator Scheme (cont.)

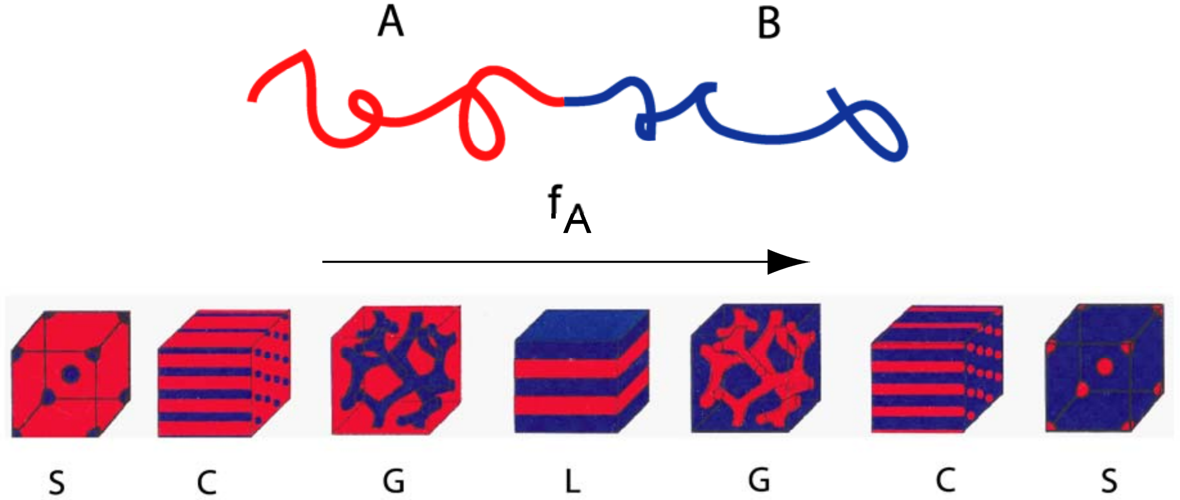


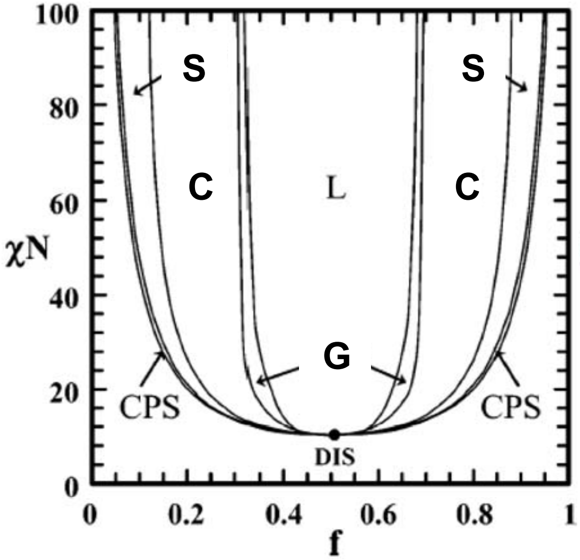


P4VP-PBd-P4VP

The second monomer adds to both ends of the growing chain creating an ABA pattern with the original monomer being the B block in the middle

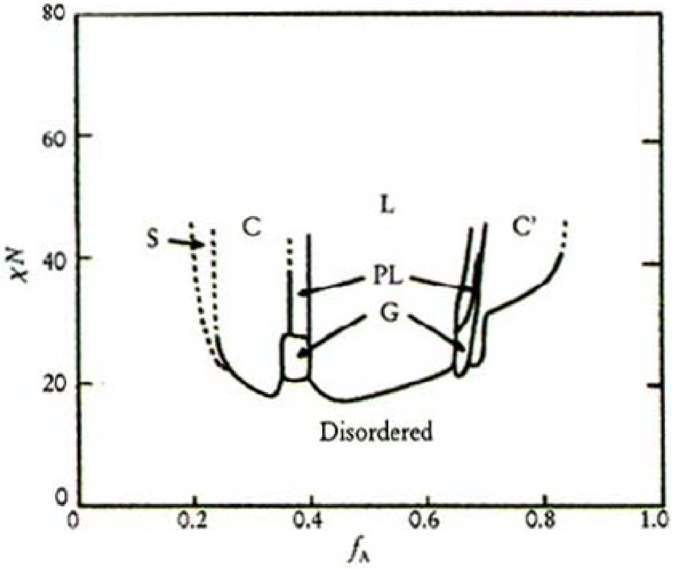
Phase Behavior of AB Diblock Copolymers





Theoretical phase diagram for AB diblock copolymer

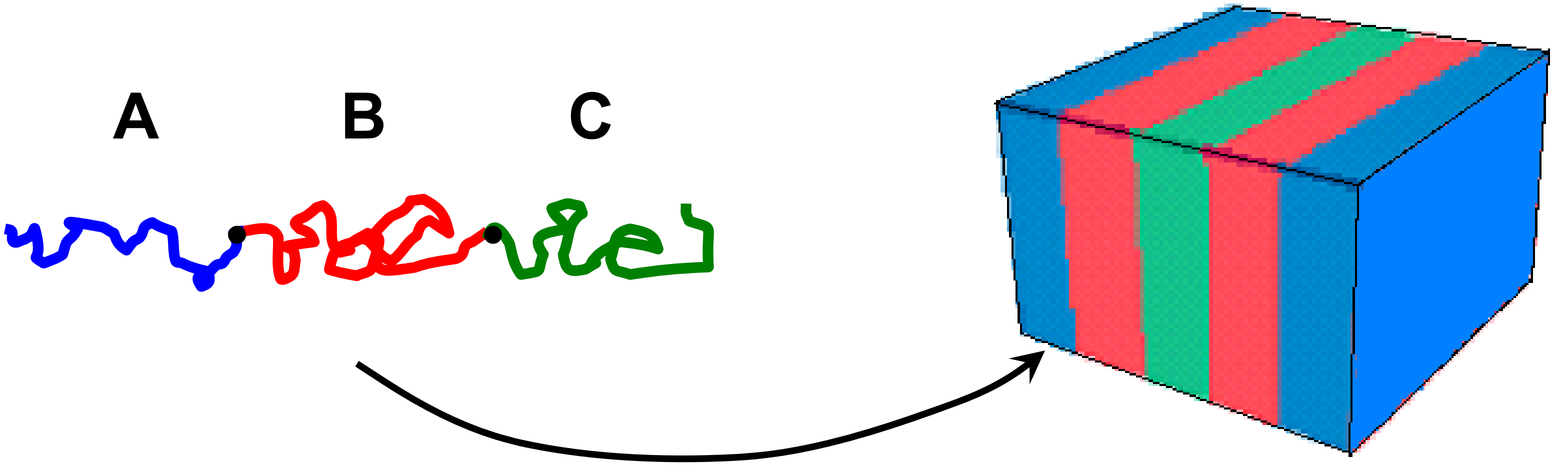
Cochran et al. *Macromolecules* **2006**



Experimental phase diagram of poly(styrene-*b*-isoprene)

Khandpur et al. *Macromolecules* **1995**

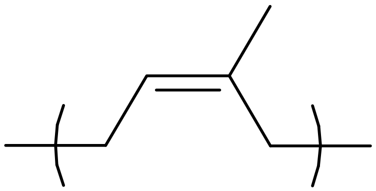
Phase Behavior for ABC Triblock Copolymers



- **Some of the key parameters governing the phase behavior:**
  - volume fractions: $f_A, f_B, f_C \ (f_C = 1 - f_A - f_B)$
  - segment-segment interaction parameters: $\chi_{AB}, \chi_{BC}, \chi_{AC}$
  - overall degree of polymerization: N
  - block sequence: ABC, BAC, ACB
  - statistical segment lengths: b_A, b_B, b_C

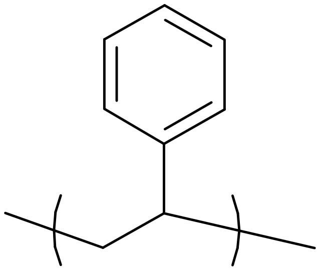
Universal organization of phase behavior for ABC triblocks not yet known

Poly(isoprene-*b*-styrene-*b*-ethylene oxide) (ISO)



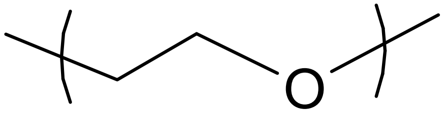
poly(isoprene)

I



poly(styrene)

S



poly(ethylene oxide)

O

- Extensively studied triblock terpolymer (monodisperse versions)
- Easily synthesized anionically
- Good contrast for x-ray scattering experiments

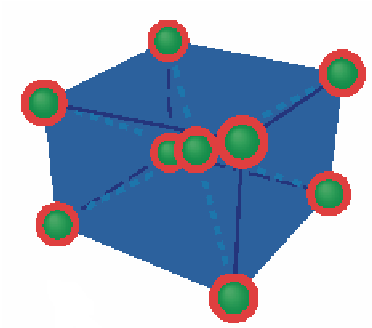
ISO represents a “nonfrustrated” ABC triblock copolymer:

$$\chi_{IO} > \chi_{IS} \approx \chi_{SO}$$

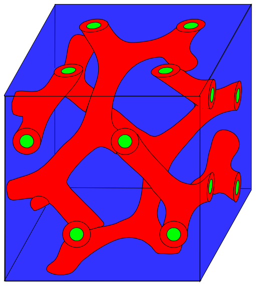
ISO Phase Behavior: Monodisperse

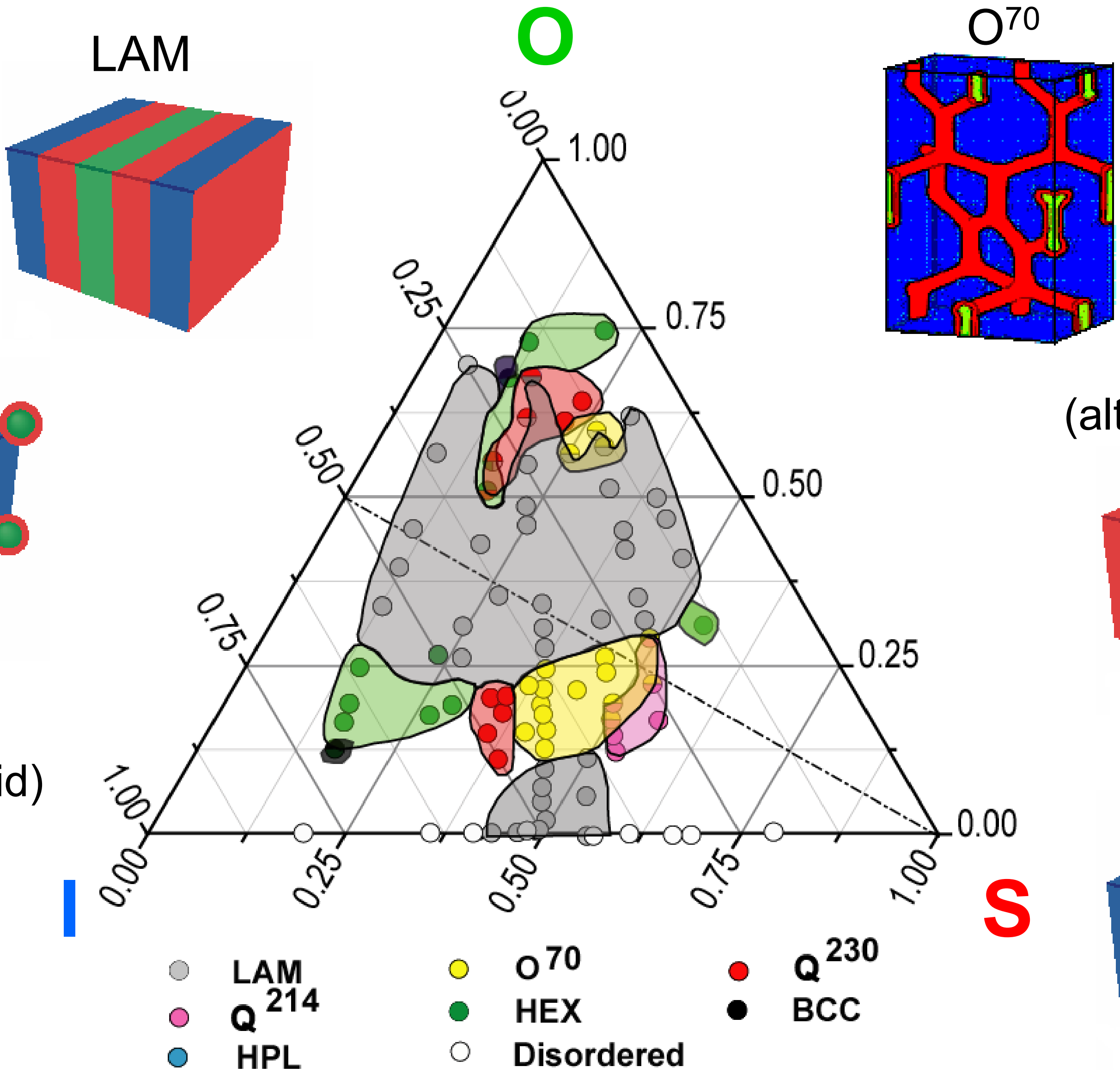
LAM

BCC



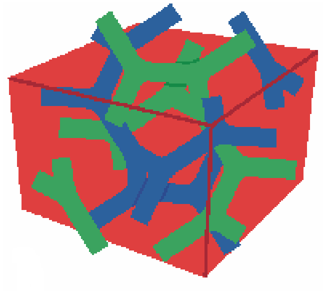
Q^{230}
(core-shell gyroid)



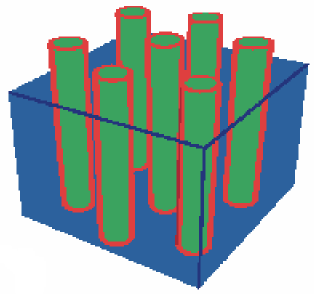


O^{70}

Q^{214}
(alternating gyroid)



HEX



Chatterjee, Jain and Bates, *Macromolecules* **2007**, *40*, 2882-2896.

Why are polydispersity effects important?

- **Living Anionic Polymerization, PDI < 1.1**
  - Commercial success (SIS, SBS triblocks)
  - Relatively expensive and highly sensitive to impurities
  - Limited number of monomers

- **Living Radical Polymerizations, PDI ~ 1.2-1.5 (lab)**
  - Relatively cheap and robust
  - Enhanced monomer compatibility
  - Low cost, large scale production of many block copolymers a reality

- **Potential beneficial effects…**
  - Expand toolbox for tuning block copolymer behavior

Impact of polydispersity effects?

"Much more important than fluctuation effects are those effects resulting from the polydispersity of the copolymer blocks. … it seems that even a small polydispersity of the sample may be crucial."

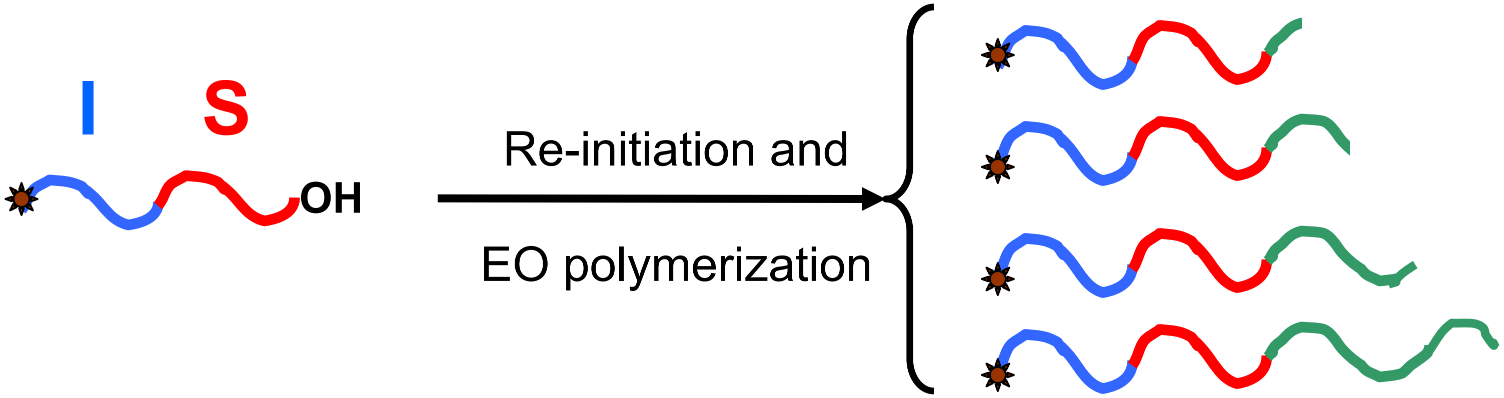
Leibler, L. *Macromolecules* **1980**, *13,* 1602-1617.

"Generally, self-assembly into highly ordered morphologies requires a fairly narrow molecular weight distribution (low polydispersity) for the BCP; a polydispersity less than 1.2 is typically required"

Malenfant, P.L. et al *Nature Materials* **2007**, *2,* 43-46.

Synthesis of ISO

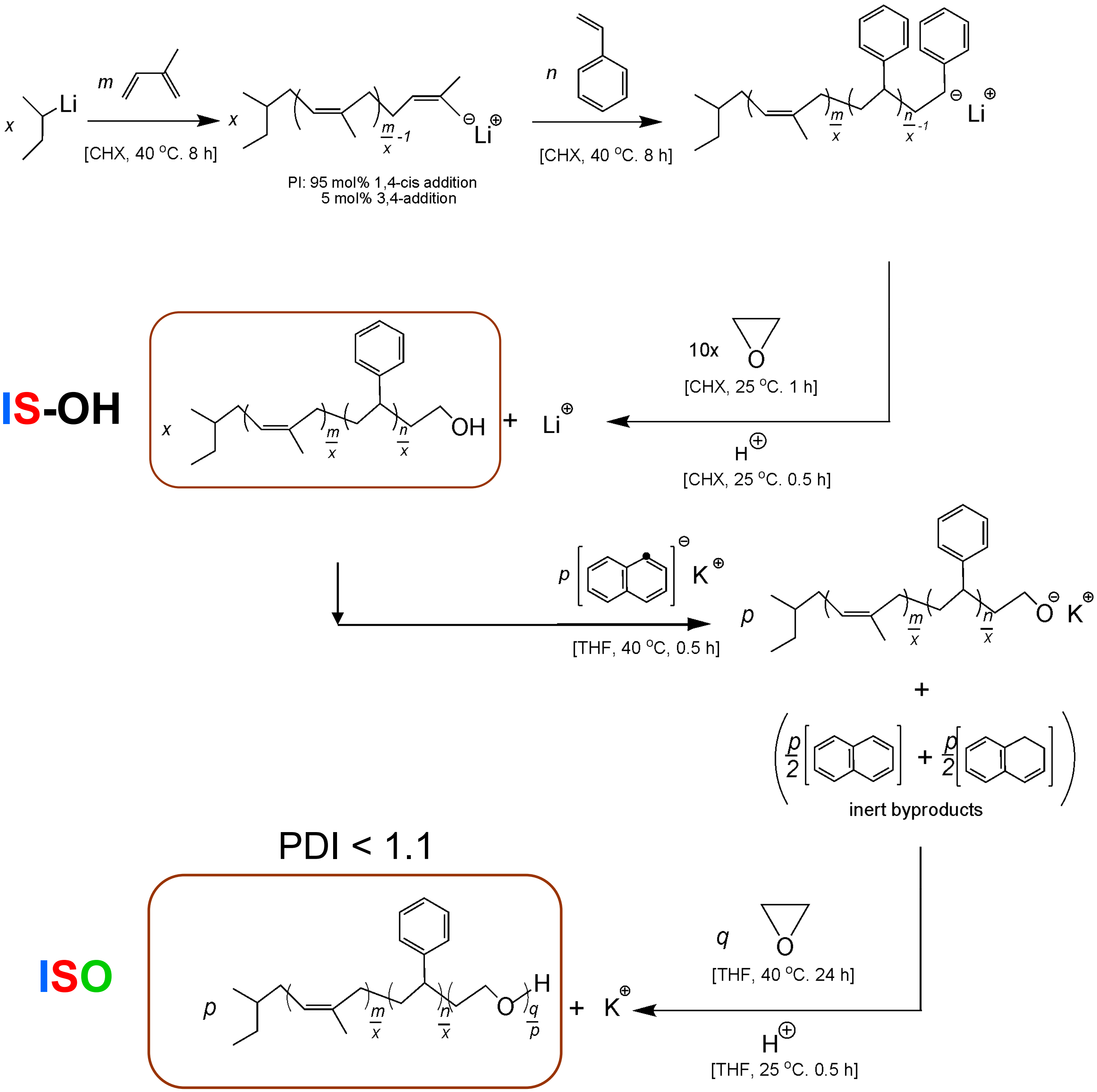
- **Sequential Living Anionic Polymerization**



PI-PS-PEO triblock copolymers

- **Initiation rate >> propagation rate, polydispersity < 1.1**

Sequential



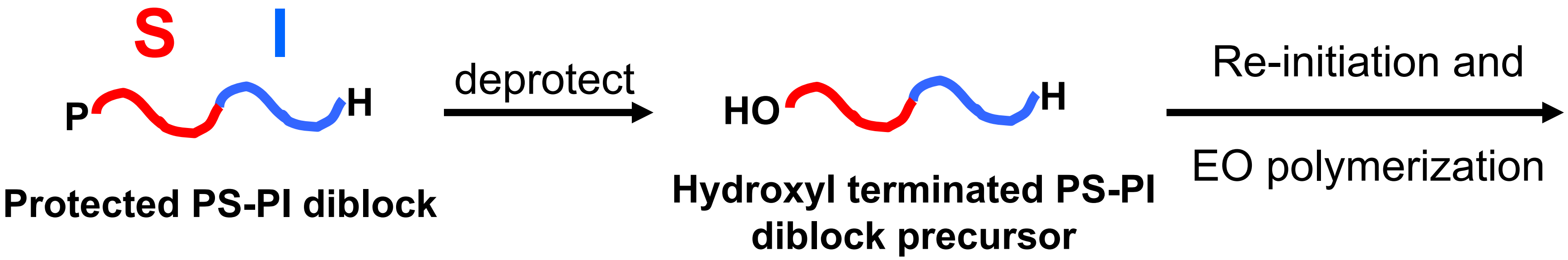
IS-OH

PDI < 1.1

ISO

Synthesis of ISO

- **Protected Living Anionic Polymerization**



Protected PS-PI diblock

deprotect

Hydroxyl terminated PS-PI diblock precursor

Re-initiation and

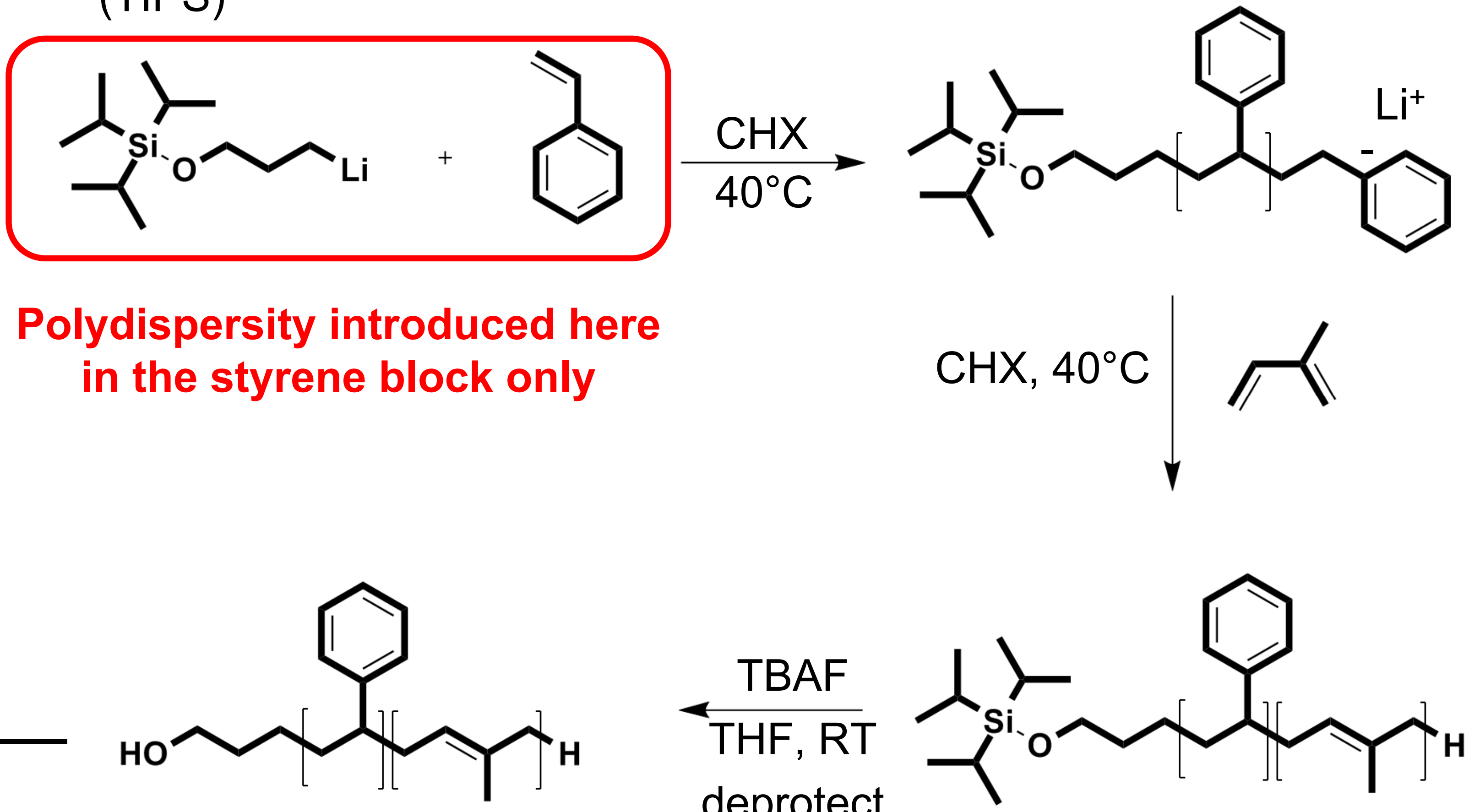
EO polymerization

- **Initiation rate ≥ propagation rate (due to initiator aggregates), PDI > 1.1**

  - **Polydispersity introduced into styrene block only**

Protected

Triisopropylsilyloxy-1-propyllithium
(TIPS)



Polydispersity introduced here in the styrene block only

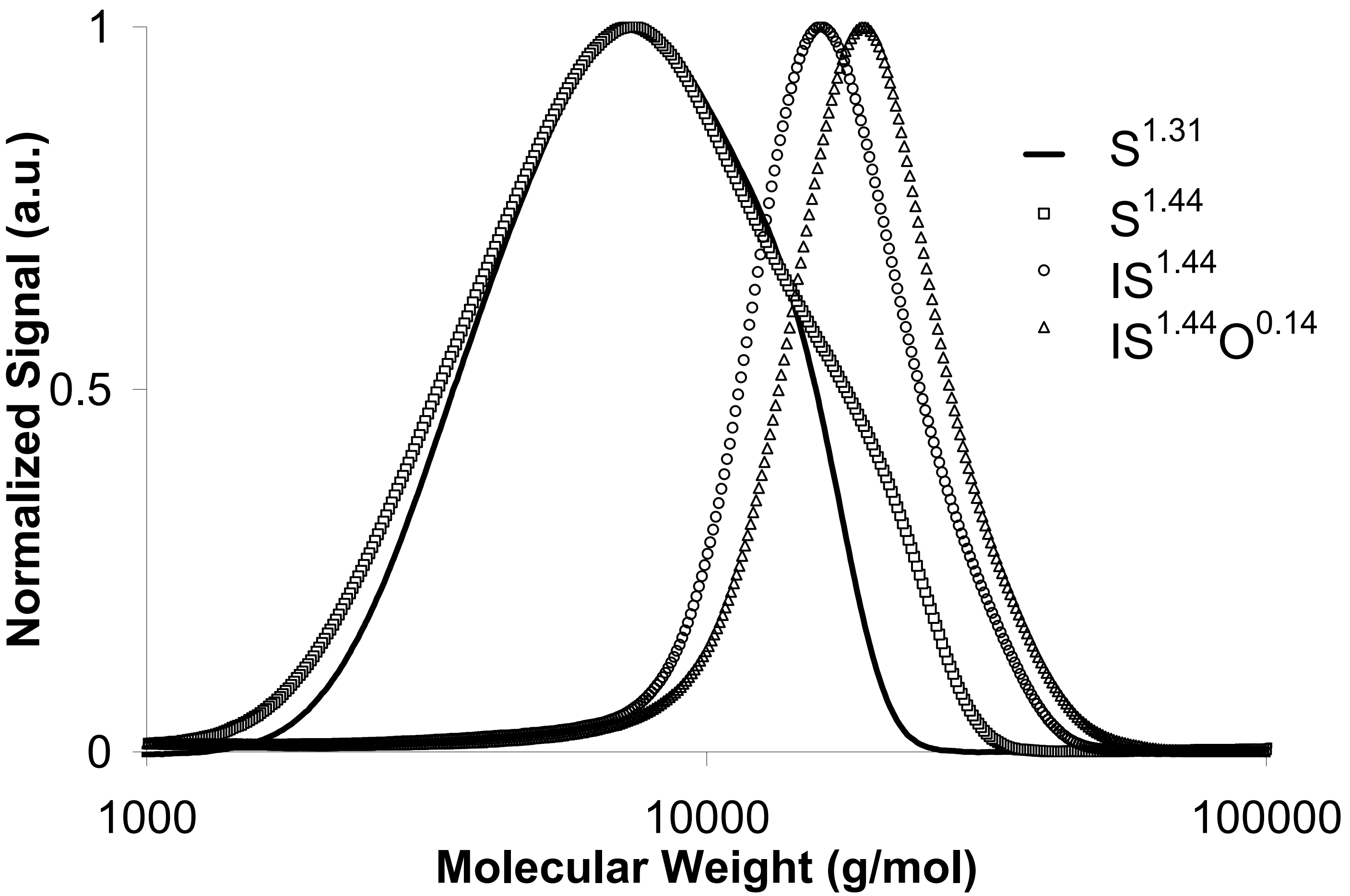
TIPS-SI

HO-SI

Re-initiation and
EO polymerization
as in sequential case

Meuler, Mahanthappa, Hillmyer and Bates, *Macromolecules* **2007**, 40, 760-762.

Molecular Weight Distribution

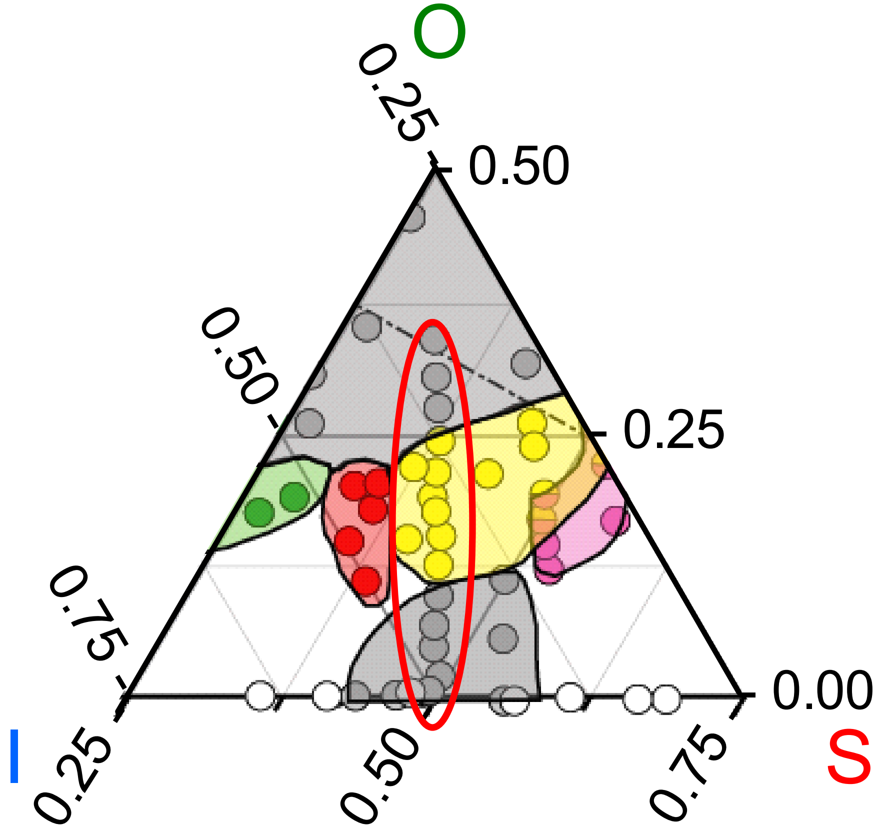


- room temperature, THF mobile phase, PS standards

Ellison, Meuler, Evans, Hillmyer and Bates, *Macromolecules* **2007**, *40*, 7072-7074.

ISO Containing "Monodisperse" S

- Focused on $f_I = f_S$ isopleth



M_n IS diblock = 13.6 kg/mol

PDI_S = 1.08

O^{70} window f_O = 0.13 – 0.24

Bailey, T. S., et al. *Macromolecules* **2002**, *35*, 7007-7017.
Epps III, T. H., et al. *Macromolecules* **2004**, *37*, 7085-7088.
Epps III, T. H., et al. *Macromolecules* **2004**, *37*, 8325-8341.

ISO Containing Polydisperse S

M_n IS = 11.5 kg/mol
PDI_S = 1.31

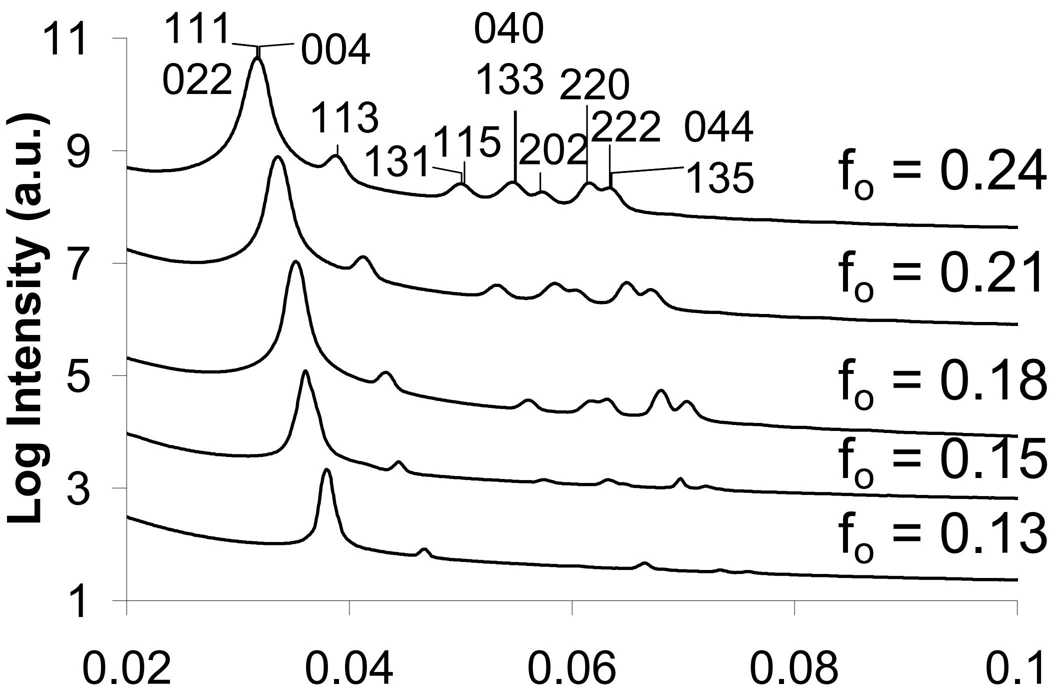
Polymer	f_O	Structure
$IS^{1.31}O^{0.04}$	0.04	LAM
$IS^{1.31}O^{0.09}$	0.09	LAM
$IS^{1.31}O^{0.11}$	0.11	LAM
$IS^{1.31}O^{0.14}$	0.14	LAM
$IS^{1.31}O^{0.17}$	0.17	LAM
$IS^{1.31}O^{0.18}$	0.18	LAM
$IS^{1.31}O^{0.24}$	0.24	LAM
$IS^{1.31}O^{0.30}$	0.30	LAM

M_n IS = 11.2 kg/mol
PDI_S = 1.44

Polymer	f_O	Structure
$IS^{1.44}O^{0.04}$	0.04	LAM
$IS^{1.44}O^{0.05}$	0.05	LAM
$IS^{1.44}O^{0.09}$	0.09	LAM
$IS^{1.44}O^{0.10}$	0.10	LAM
$IS^{1.44}O^{0.12}$	0.12	LAM
$IS^{1.44}O^{0.14}$	0.14	LAM
$IS^{1.44}O^{0.16}$	0.16	LAM
$IS^{1.44}O^{0.21}$	0.21	LAM

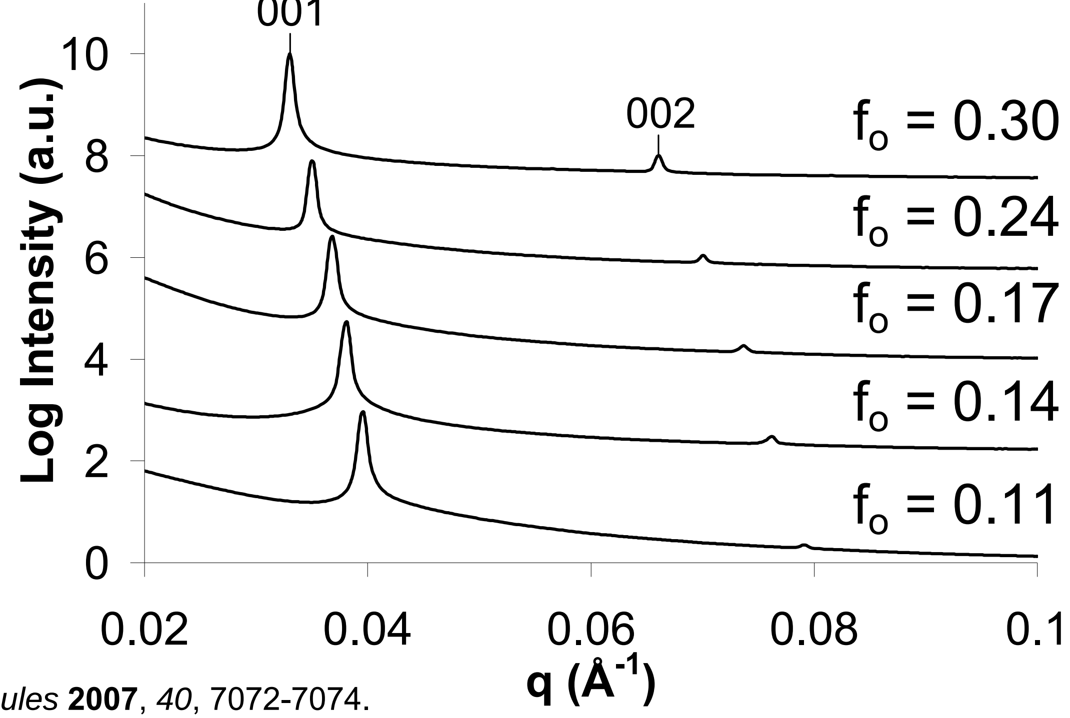
Ellison, Meuler, Evans, Hillmyer and Bates, *Macromolecules* **2007**, *40*, 7072-7074.

SAXS Comparison



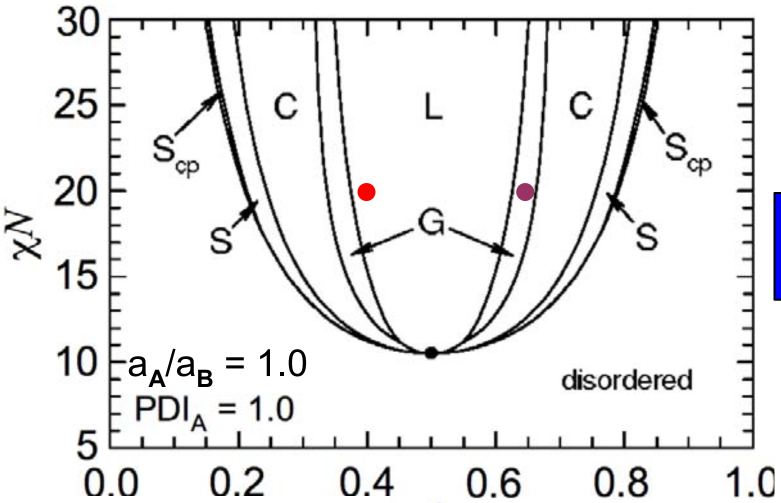
- “Monodisperse” ISO
- T = 160°C

- Polydisperse IS$^{1.31}$O
- T = 120°C

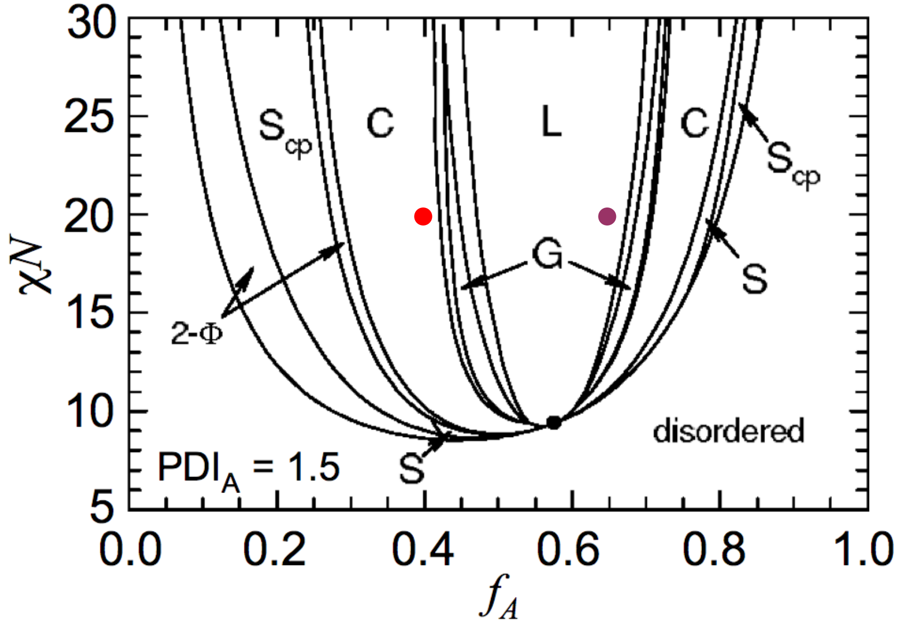


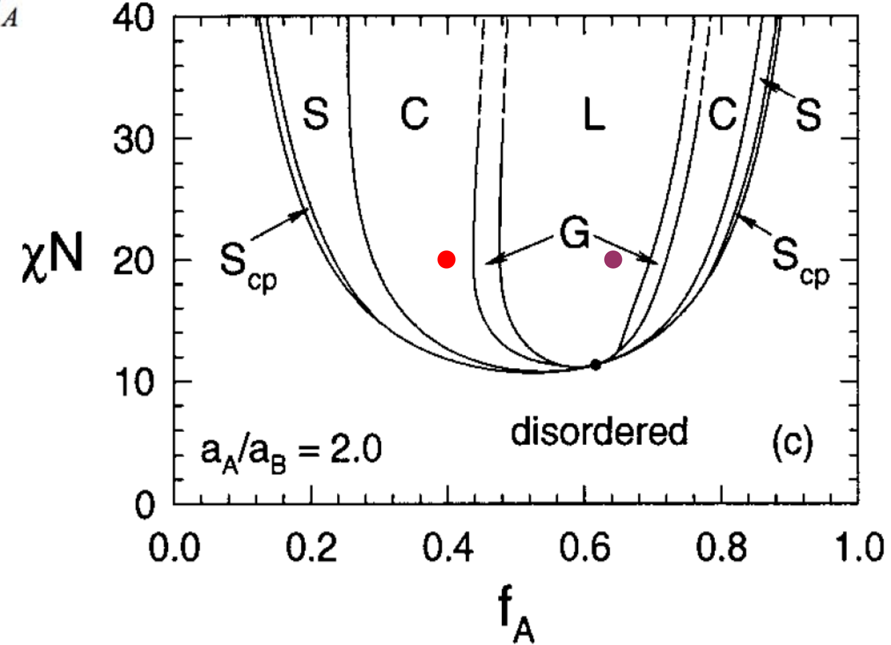
Ellison, Meuler, Evans, Hillmyer and Bates, *Macromolecules* **2007**, *40*, 7072-7074.

Polydispersity



Conformational Asymmetry





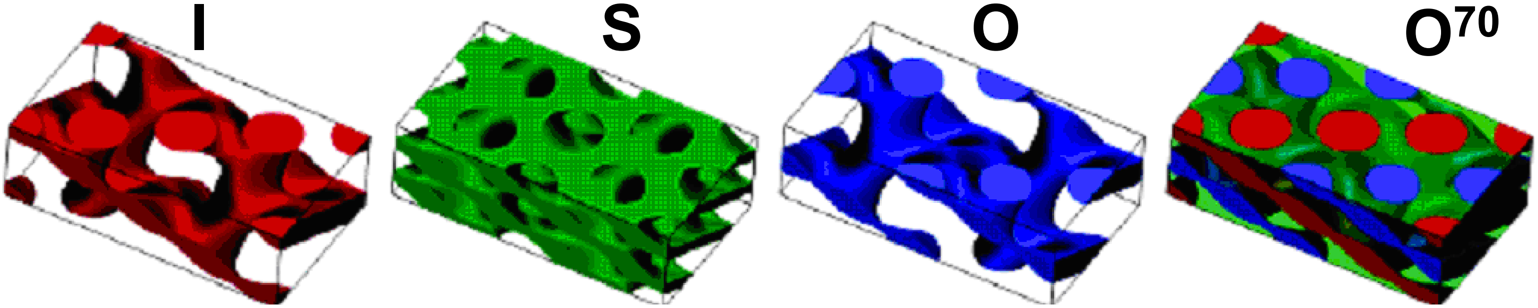
- longer blocks in A domain
  - less stretching required

Matsen, *Phys. Rev. Lett.* **2007**, *99*, 148304.

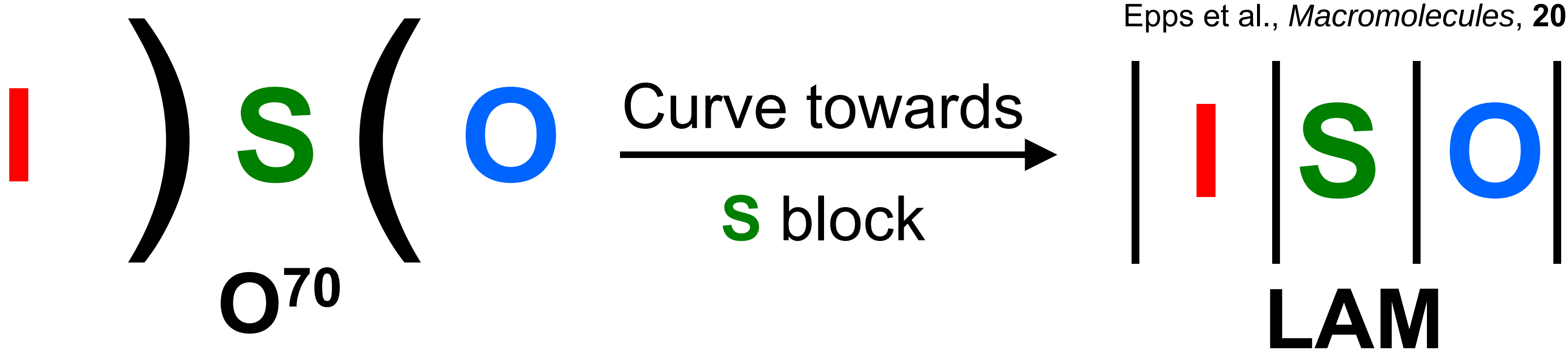
- Increased stat. seg. length
  - entropic penalty for stretching A is reduced

Matsen and Bates, *J. Polym. Sci. B* **1997**, *35*, 945.

Explanation: Curve Towards Polydispersity



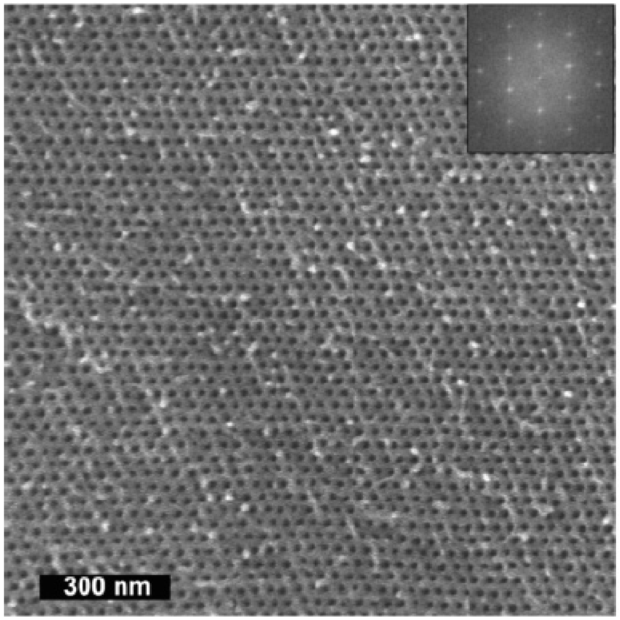
Epps et al., *Macromolecules*, **2004**.



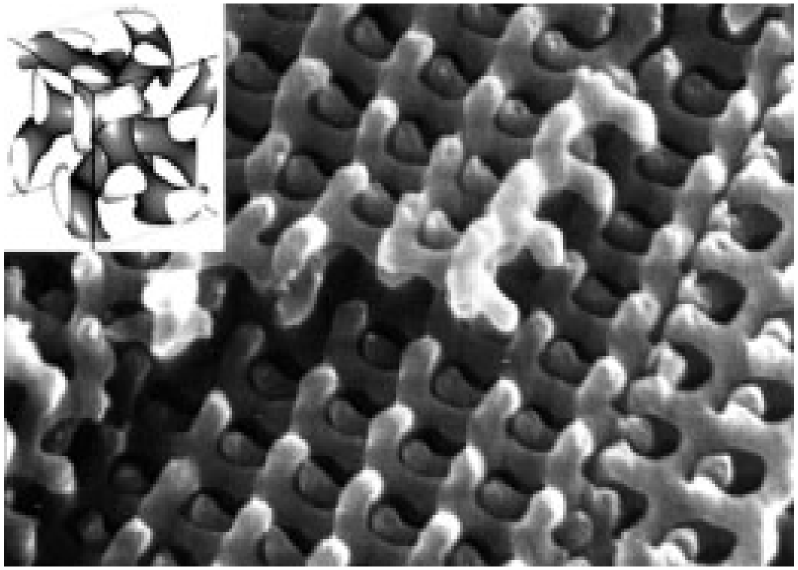
- Net mean curvature in O^{70} away from **S**
- Does not consider bridging
  - – short **S** chains must span domain
    - unable to relax near interface
  - – energetic balance changes

How will polydispersity be useful?

- Control order-disorder temperature (T_{ODT}) – processability
- Microstructures in “unconventional” regions of phase diagram
  - Nanoporous materials - etchable domains with controllable structure and size



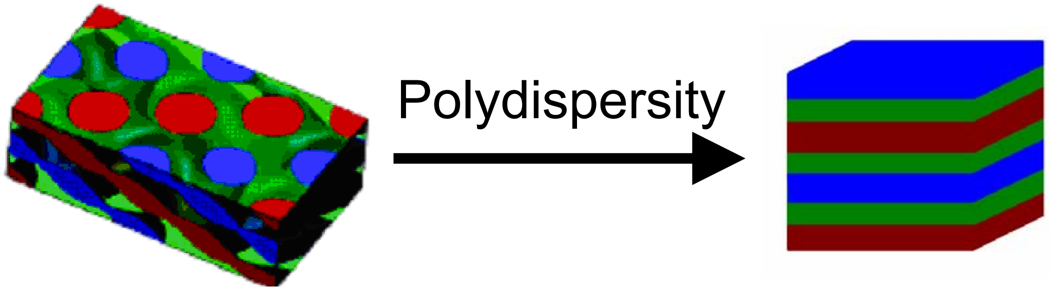
Rzayev, J.; Hillmyer, M. A. *J. Am. Chem. Soc.* **2005**.



Urbas, A. M., *et. al. Adv Mater* **2002**.

  - Control size and structure of functional domains / blocks (Ionic conductivity, moisture retention, mechanical props, etc.)

Conclusions

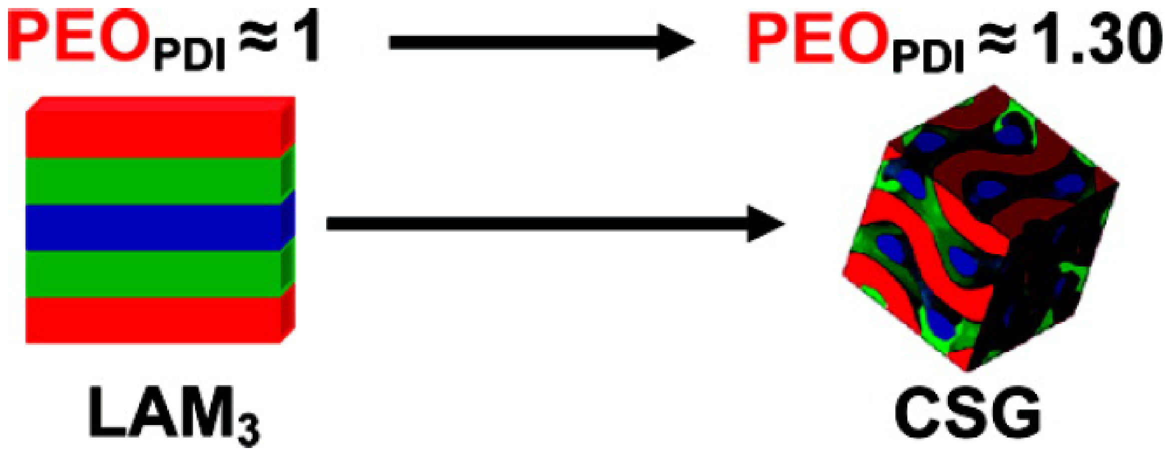


Bottom-up Approach

Design on molecular level (synthesis critical !!!!!)

Å’s up to 10’s nanometers

Thermodynamics exploited



Meuler, A.J., Ellison, C.J., Hillmyer, M.A., Bates, F.S., Macromolecules **2008** (17), 6272.

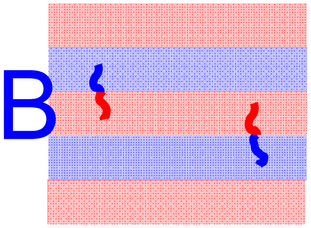
Anionic Polymer Common Commercial Uses

Polymer	Use
Polydiene	Synthetic Rubber
Polydiene-polystyrene	Wire coatings
PS-PI-PS (Kraton)	Shoe soles
Poly(methyl 2-cyanoacrylate)	Super glue[1]
PBd-PS (52/48)	Sponges

Thermoplastic Elastomers

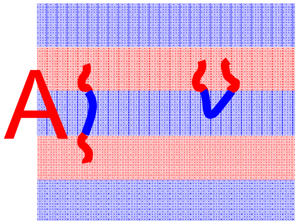
- SIS and SBS primarily
- Mechanically tough like rubbers, but moldable with heat

AB



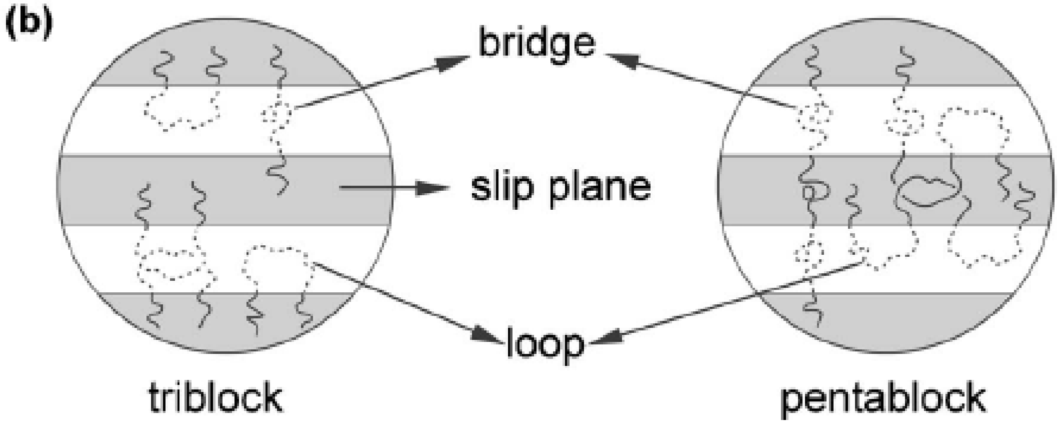
brittle
(poor mech.
props.)

ABA



tough to brittle
(tailored mech.
props.)

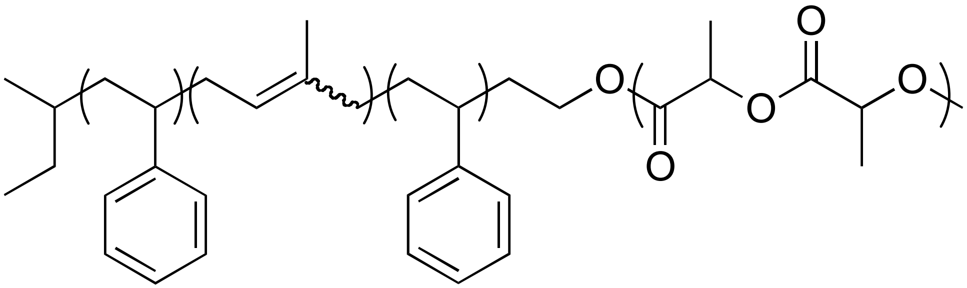
Glassy
Rubbery



- Actually, made with glassy cylinders and spheres

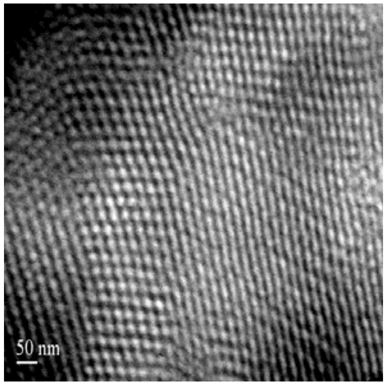
Mechanically Robust Nanoporous Materials

- Membranes (filtration, fuel cells, etc) (M.A. Hillmyer et al)

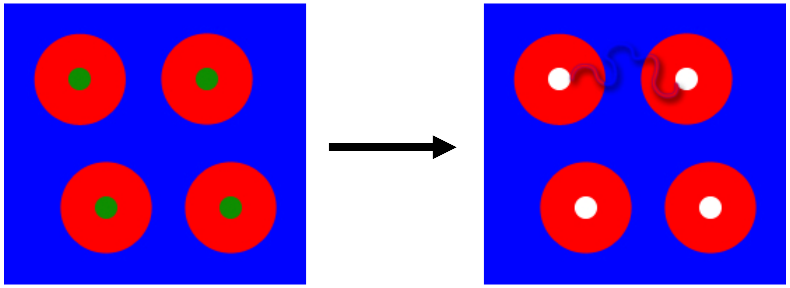


Poly(styrene)-poly(isoprene)-poly(styrene)-poly(lactide) (PS-PI-PS-PLA) tetrablock copolymer. The PLA phase is chemically etchable.

TEM image of PS-PI-PS-PLA



Schematic representation of nanoporosity generation from an ABAC tetrablock

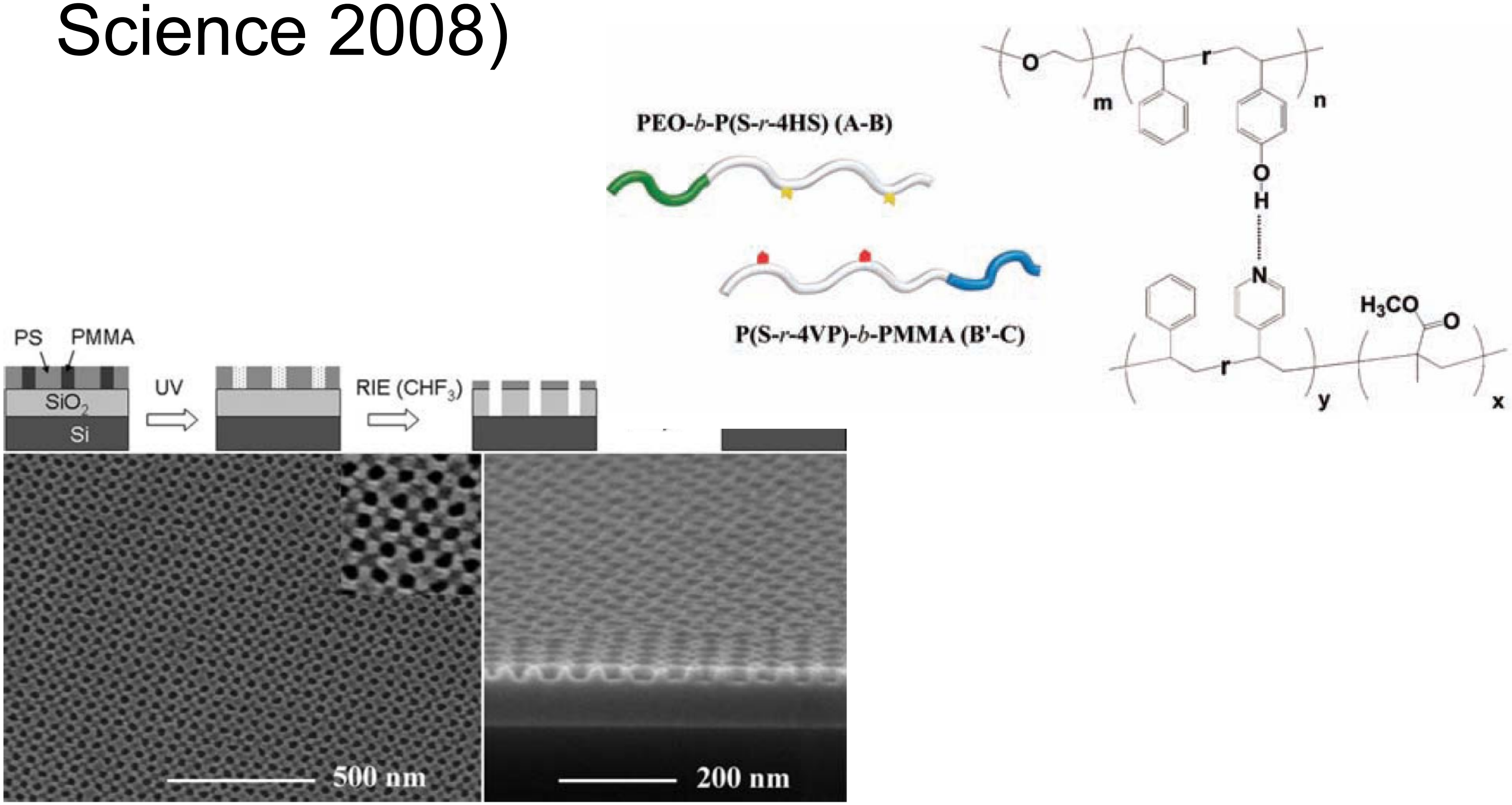


Ordered *tetra*block

Nanoporous *tri*block

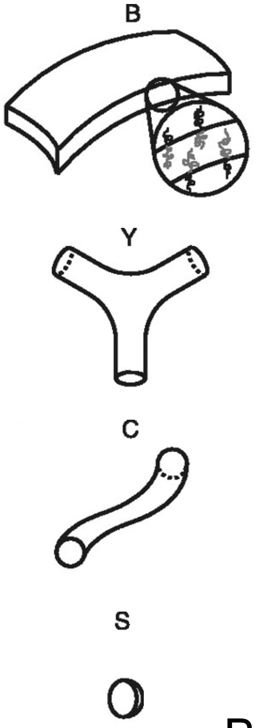
Lithography / Thin Films

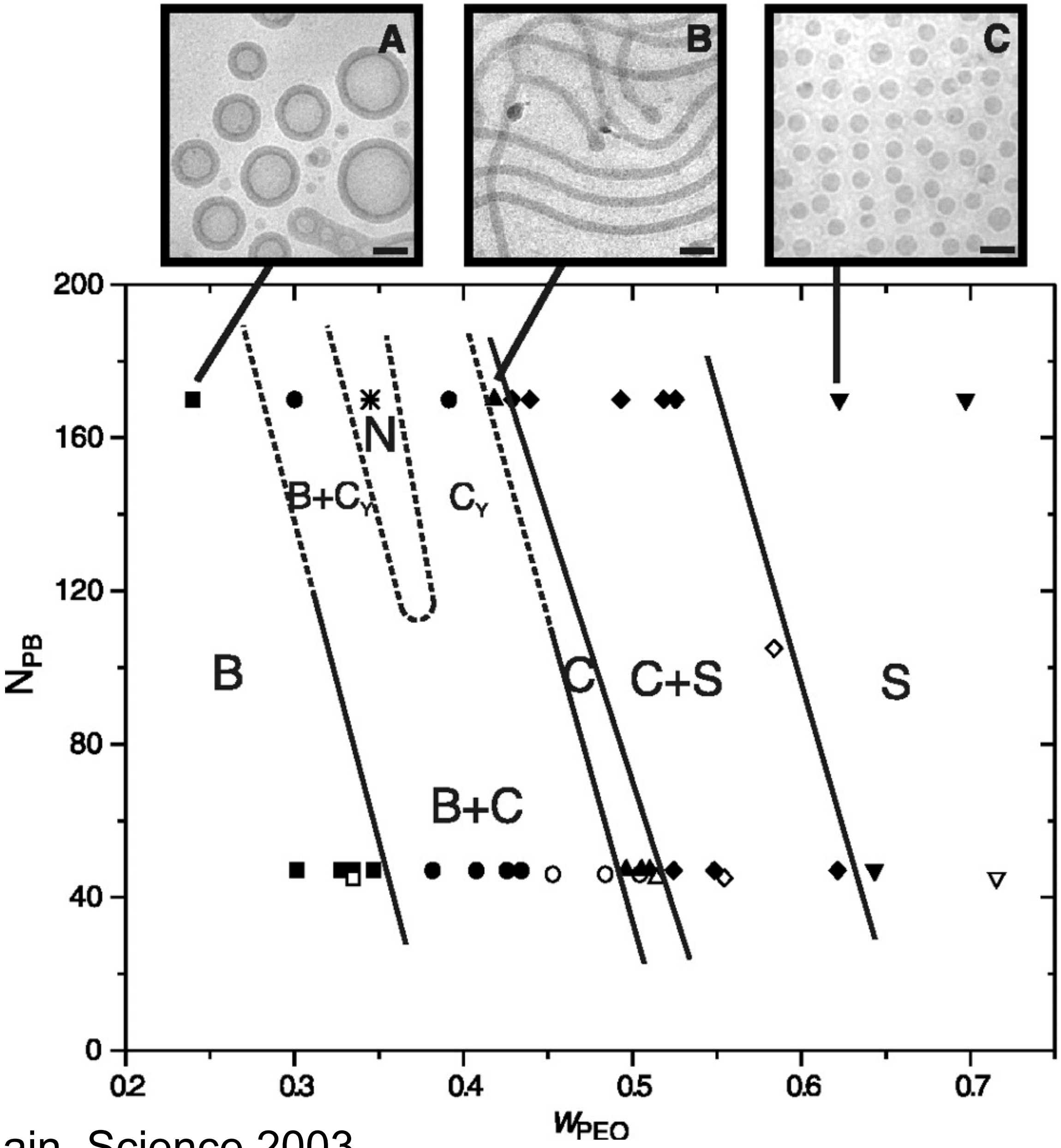
- Highly ordered square arrays for data storage (Hawker, Fredrickson and Kramer, Science 2008)



BCPs in Aqueous Solution

- Compartments for targeted drug delivery – solubilization of drugs inside





Bates and Jain, Science 2003