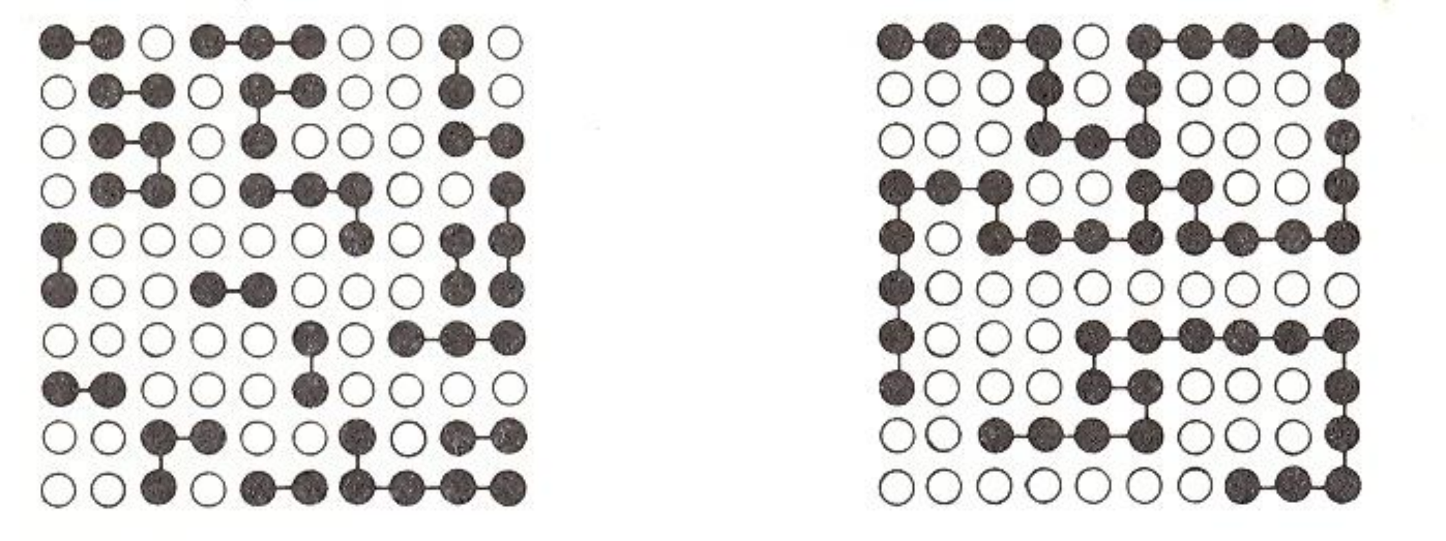
Lecture 27 *More Polymers*

Step

Chain



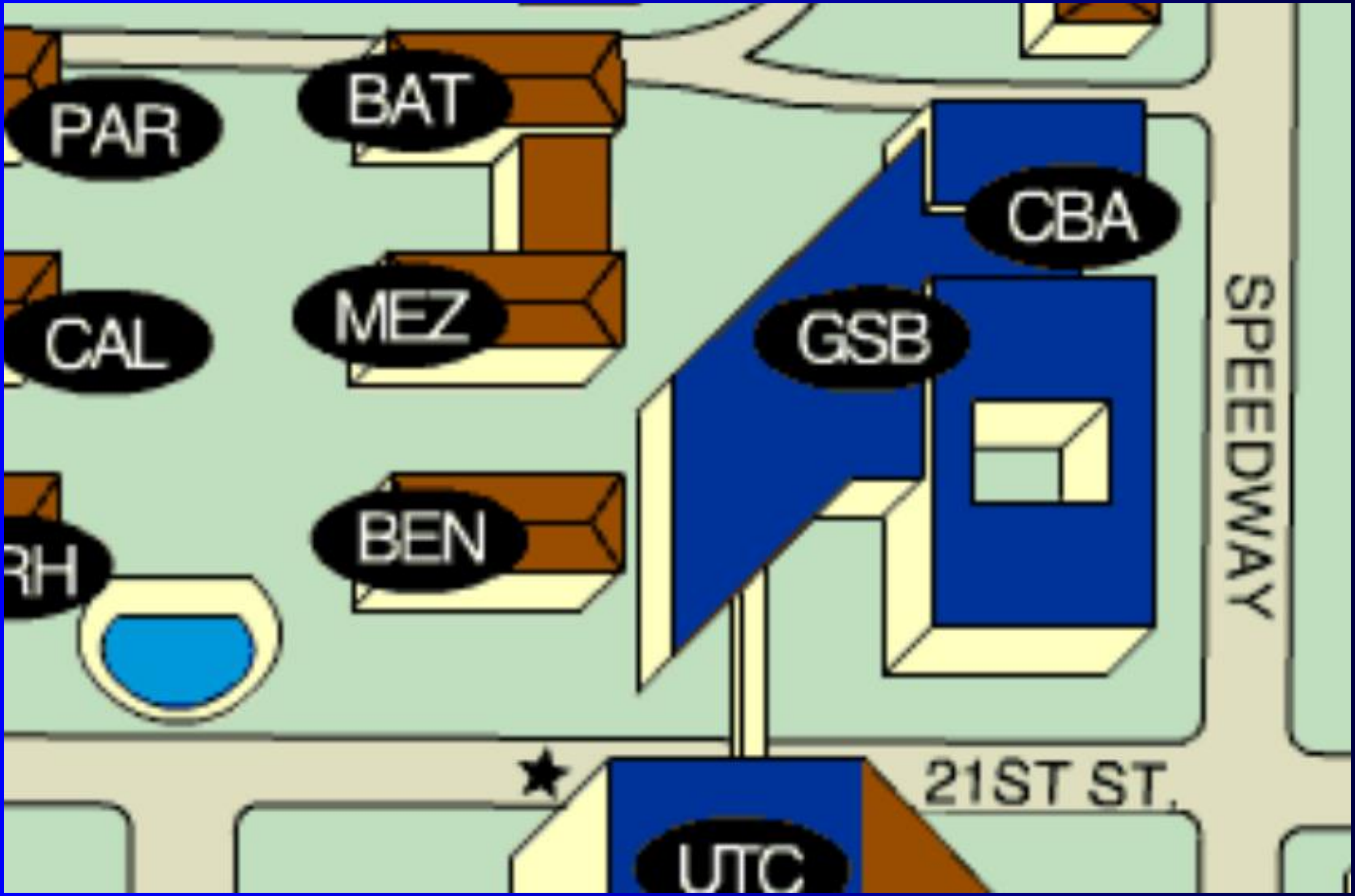
April 30, 2019

Final Exam

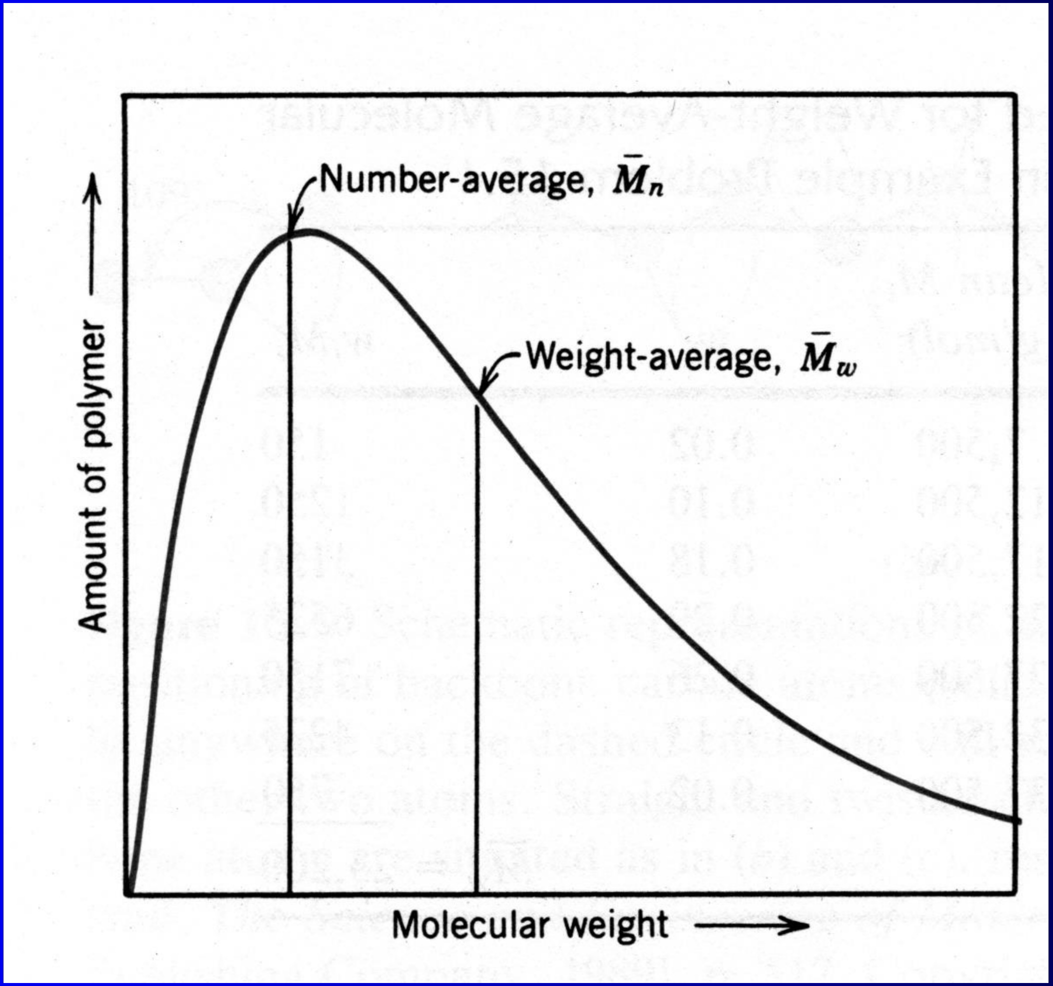
- Where: GSB 2.124!!
- When: Tuesday, May 21st , 9 AM – Noon
- Do: Study lecture notes, homework, reading
- Practice: Hydrolysis, signatures…and synthesis.
- Review: Spectroscopy and “unknowns”
- Please: Do a good job!

See web site for old exams

GSB 2.124



Distribution of Molecular Weights

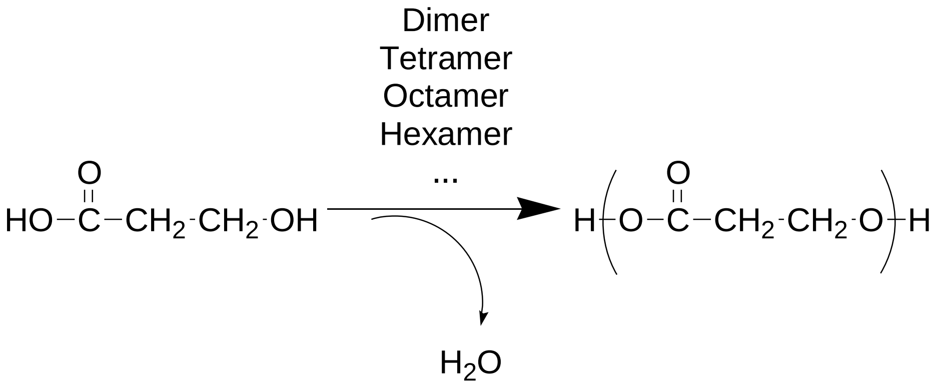


Polymers: Molecular Weight

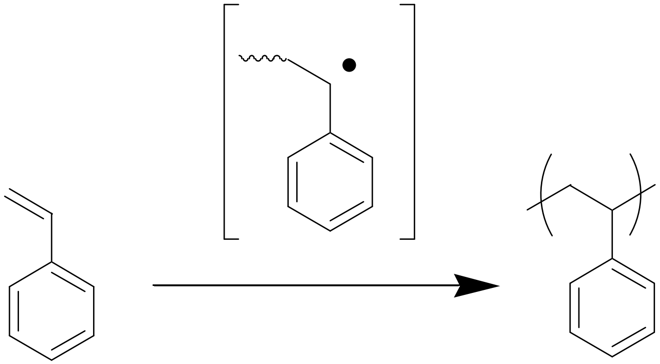
- Ratio of M_w to M_n is known as the polydispersity index (PDI) Đ
  - a measure of the breadth of the molecular weight distribution
  - Đ = 1 indicates $M_w = M_n$, i.e. all molecules have equal length (monodisperse)
  - Đ = 1 is possible for natural proteins whereas synthetic polymers have $1.1 < PI < 5$
  - At best Đ < 1.1 can be attained with special techniques

Basic Types of Polymerization Mechanisms

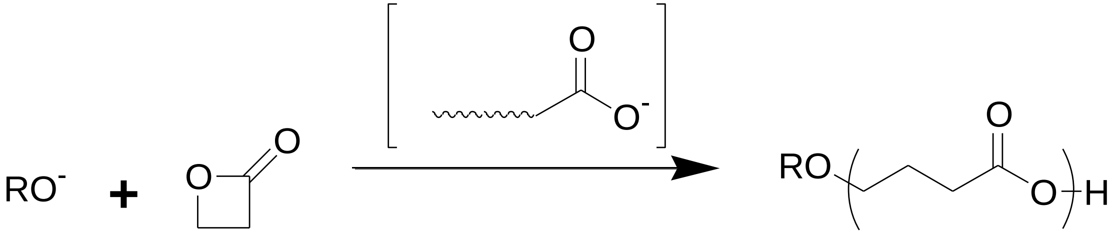
Step-growth



Chain-growth



Ring-opening



Chain growth system

The characteristic of a chain polymer is that *polymer growth takes place by monomer reacting only with the reactive centers.* Monomer does not react with monomer and the different-sized species such as dimer, trimer, and n-mer do not react with each other. If they do, they are no longer reactive. The polymerization ceases when the active center is destroyed by termination reaction(s).

Chain-Growth Polymers

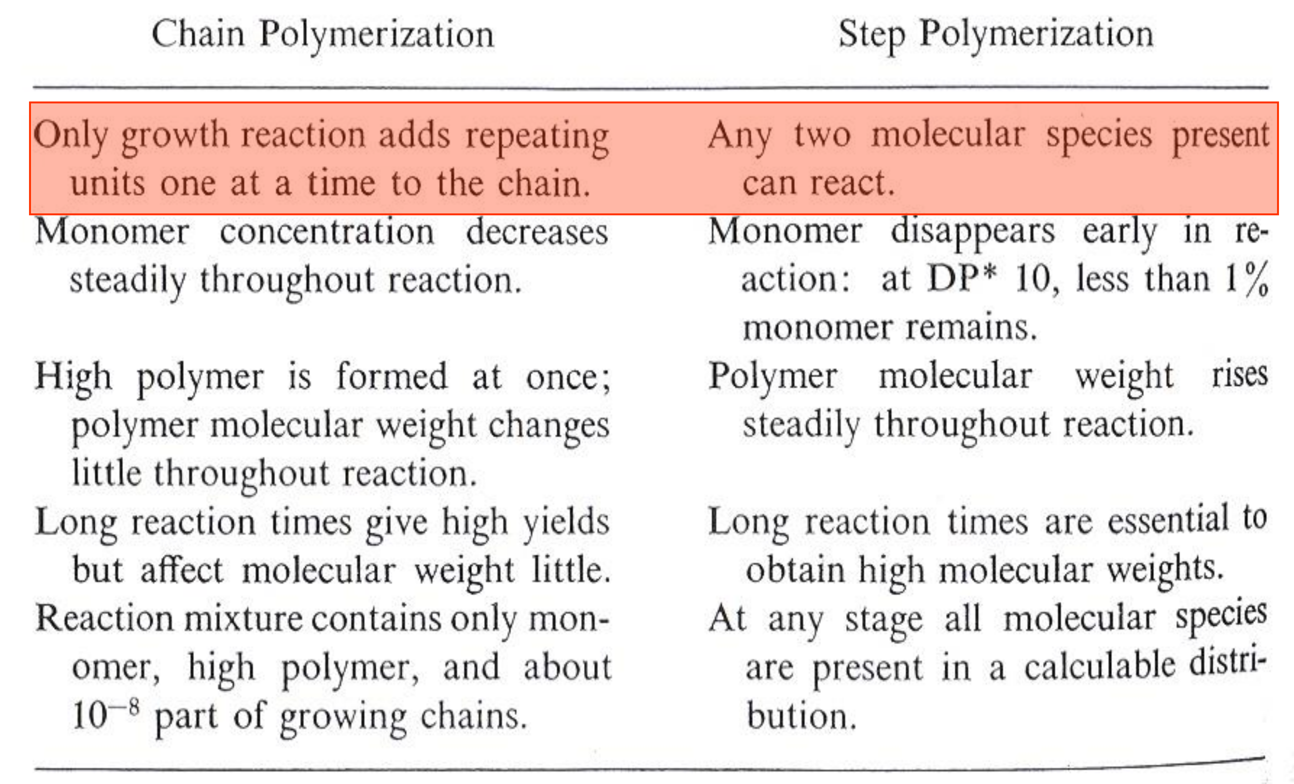
- **Chain-growth polymerization:** a polymerization that involves sequential addition reactions, either to unsaturated monomers or to monomers possessing other reactive functional groups

- Reactive intermediates in chain-growth polymerizations include radicals, carbanions, carbocations, and organometallic complexes

Step Growth system

A condensation takes place between two polyfunctional molecules to produce one larger polyfunctional molecule with the *possible* elimination of a small molecule such as water. The reaction continues until one of the reagents is used up.

Distinguishing features of chain- and step-polymerization mechanisms



Chain Polymerization	Step Polymerization
Only growth reaction adds repeating units one at a time to the chain.	Any two molecular species present can react.
Monomer concentration decreases steadily throughout reaction.	Monomer disappears early in reaction: at DP* 10, less than 1% monomer remains.
High polymer is formed at once; polymer molecular weight changes little throughout reaction.	Polymer molecular weight rises steadily throughout reaction.
Long reaction times give high yields but affect molecular weight little.	Long reaction times are essential to obtain high molecular weights.
Reaction mixture contains only monomer, high polymer, and about 10^{-8} part of growing chains.	At any stage all molecular species are present in a calculable distribution.

Comparison of Step and Chain

Step Growth

- Growth throughout the matrix between monomers, oligomers and polymers
- DP is low to moderate
- Monomer is consumed rapidly but Mw increases slowly
- No initiator needed and reaction same throughout process
- No termination step…chain ends still reactive
- Rate decreases steadily as funcional groups are consumed

Chain Growth

- Successive addition of monomer to a limited number of growing chain ends
- DP can be very high
- Initiation and propagation reactions are different
- Generally a chain termination step
- Polymerization rate increases initially remains relatively constant until monomer depleted

Chain Growth Polymerization

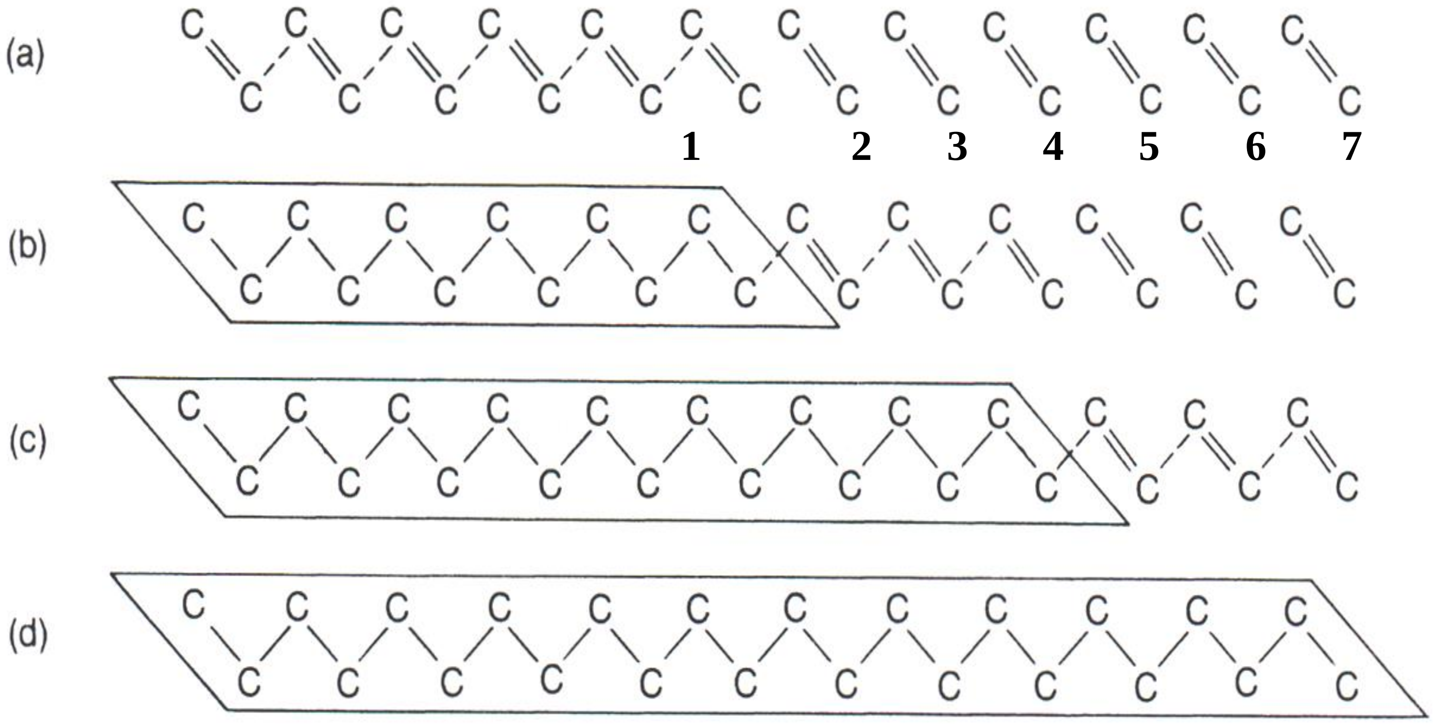


FIGURE 1.5. Chain-reaction polymerization: (a) unreacted monomer; (b) 50% reacted, $\overline{DP} = 1.7$; (c) 75% reacted, $\overline{DP} = 3$; (d) 100% reacted, $\overline{DP} = 12$. (Broken lines represent reacting species.)

$$DP = N_o/N = 12 / 7 = 1.7 \text{ (for 50\%, b)}$$

Step Growth Polymerization

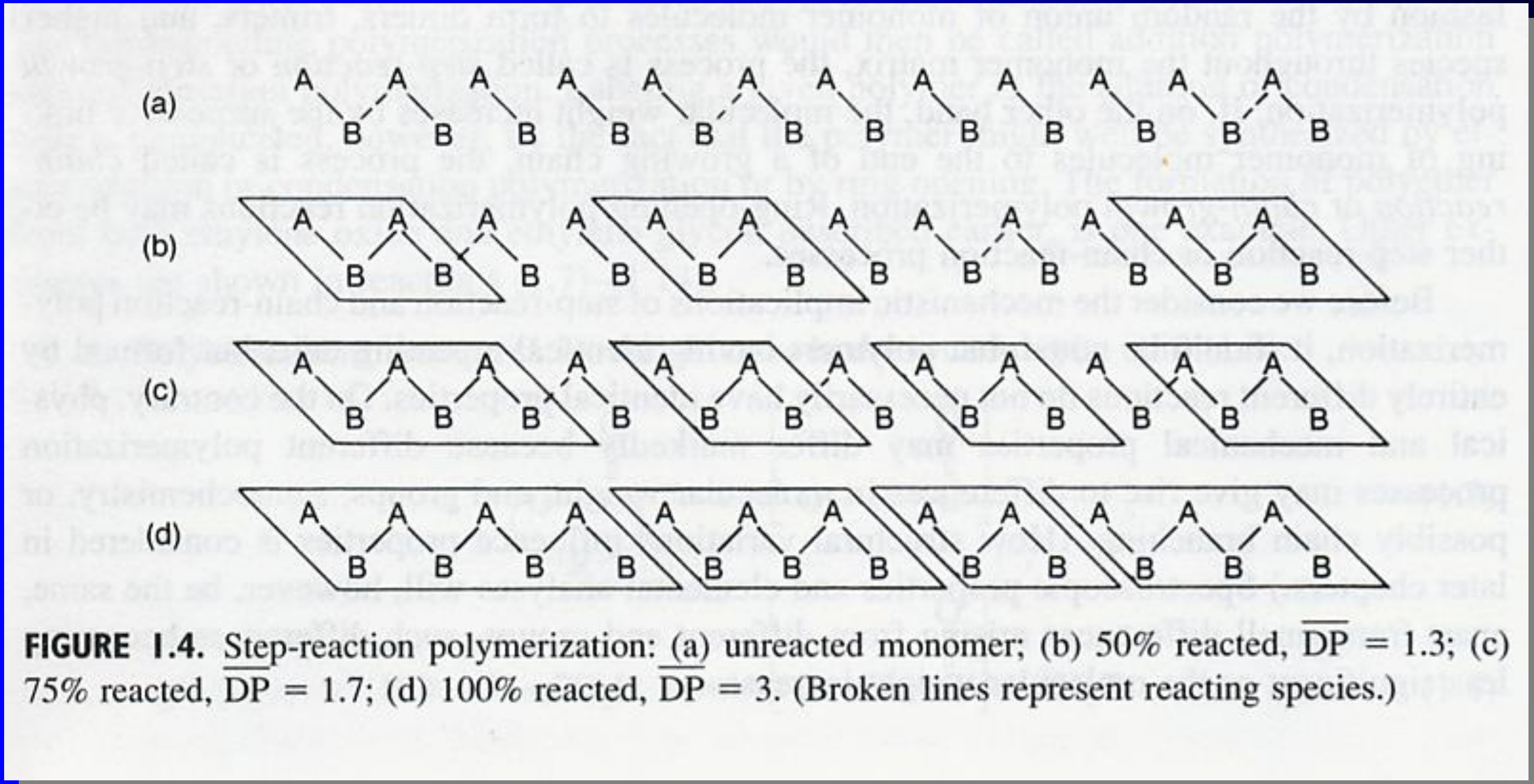
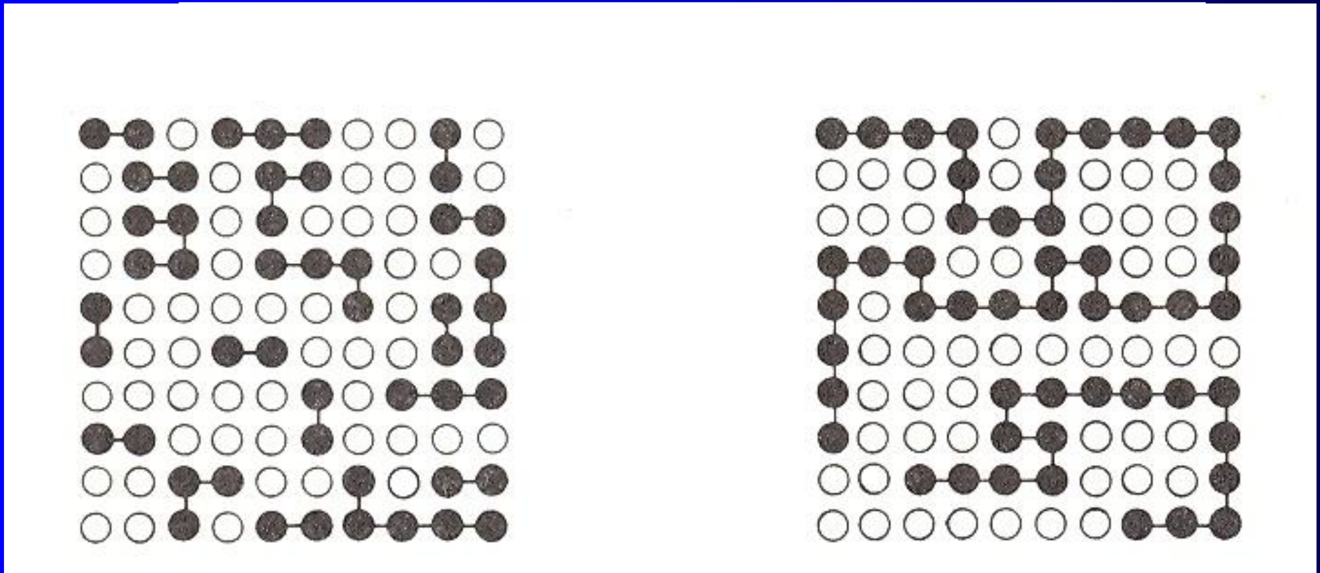


FIGURE 1.4. Step-reaction polymerization: (a) unreacted monomer; (b) 50% reacted, $\overline{DP} = 1.3$; (c) 75% reacted, $\overline{DP} = 1.7$; (d) 100% reacted, $\overline{DP} = 3$. (Broken lines represent reacting species.)

$$DP = N_o/N = 12 / 9 = 1.3 \text{ (for 50\%, b)}$$

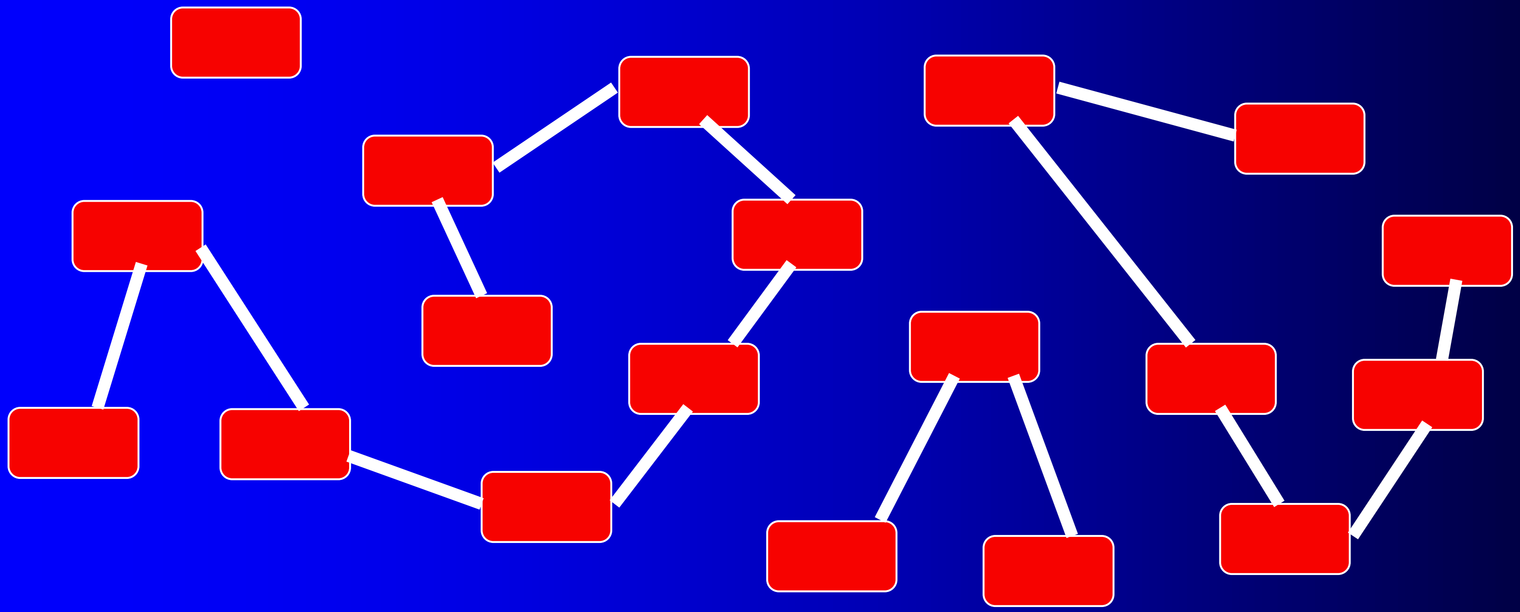
The chain growth vs. step growth



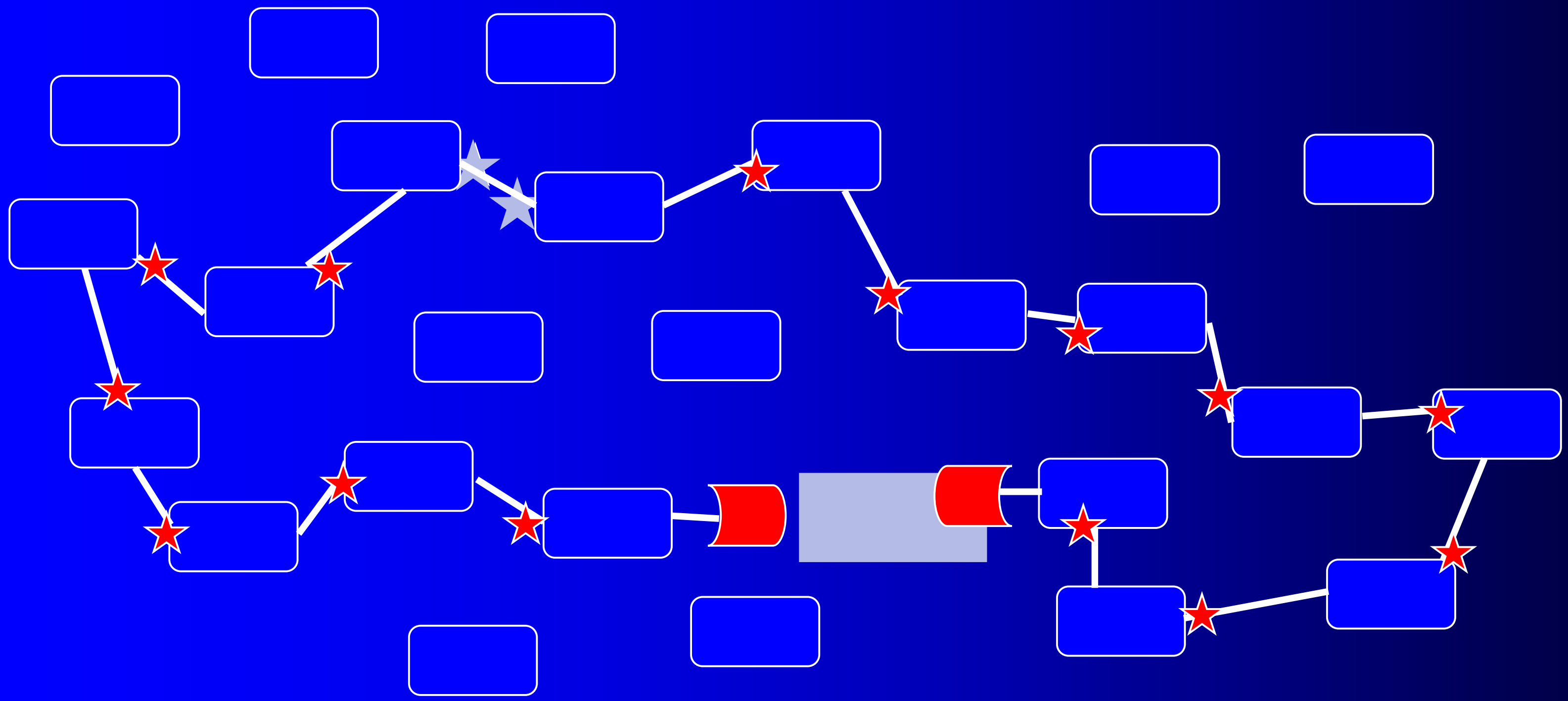
Step

Chain

- Step-growth polymerization



- Chain-growth polymerization



Let’s look at this Step Growth System more closely….

Consider a flask of monomer….If there are N_o molecules in the flask at time = 0 and N remaining at time t then the DP at time t is the average degree of polymerization… must just be N_0/N

The Carothers Equation

High Molecular weights are hard to get this way

If there are N_o molecules at time = 0 and N remaining at time t then the amount reacted is N_0-N and we can define p as a "conversion" or fraction reacted at time t then as

$P = (N_o - N) / N_o$ or

$N = N_o(1 - P)$

If DP is the average degree of polymerization… N_0/N ….substituting gives

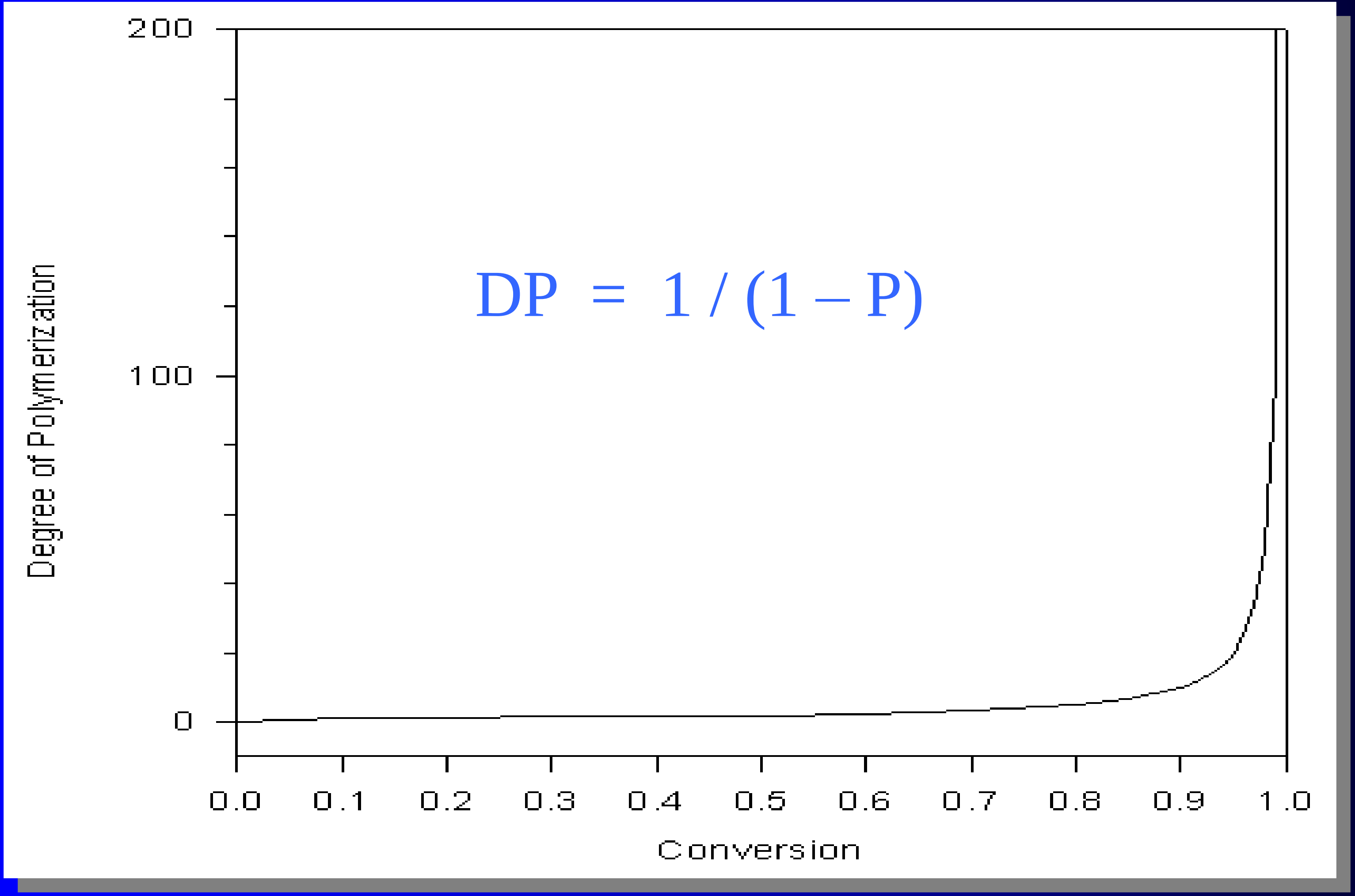
$N/No = (1 - P)$ or

$DP = 1 / (1 - P)$

and for $P = 0.98$ (98% conversion), DP = only 50!

The step growth system

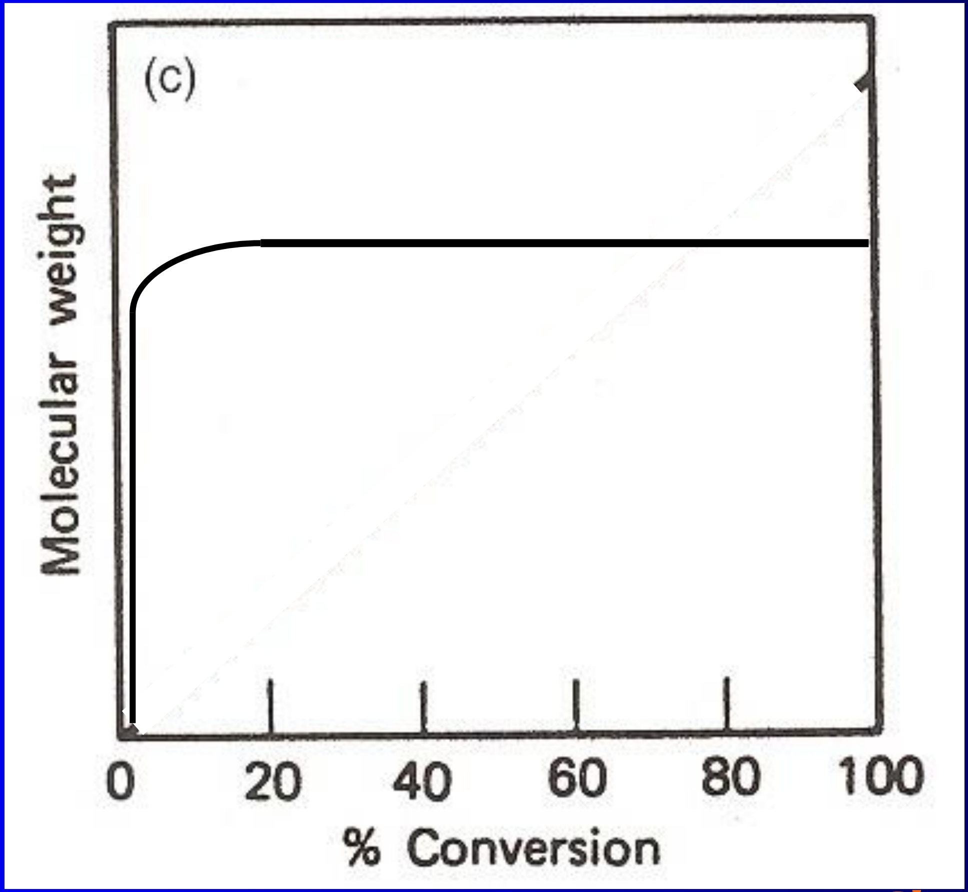
It all happens at the end!!!



$DP = 1/(1 - P)$

The chain growth system

The relationship between DP and conversion
With termination reactions…steady state



More Historical Figures

Wilhelm Schlenk

Michael Szwarc

Anionic polymerization

Some History

1914, Schlenk reacts Na with butadiene and styrene

1929, Ziegler proposes a mechanism

1952 Higginson, styrene, KNH_2, kinetic study

1956 Szwarc, sodium naphthalene, Styrene,

living polymerization conception

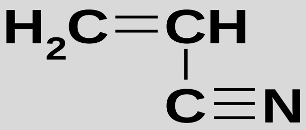
60's, commercial products were available

90‘s, study on the living polymerization of polar

monomers

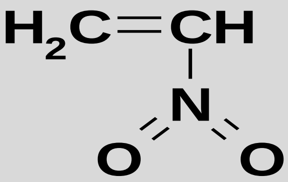
Alkenes with electron Withdrawing Groups undergo anionic polymerization

examples



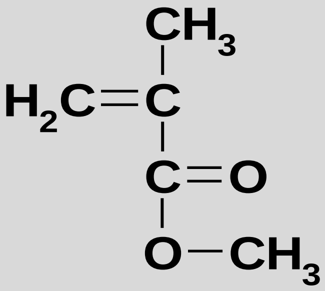
$H_2C{=}CH{-}C{\equiv}N$

Acrylonitrile



$H_2C{=}CH{-}NO_2$

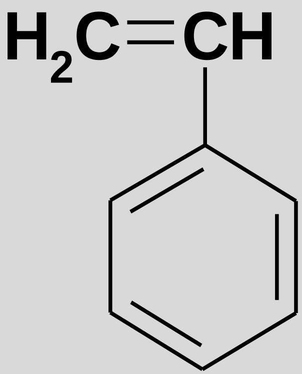
Nitroethene



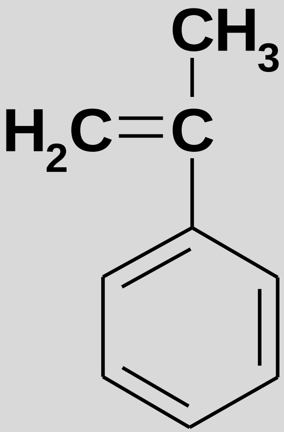
$H_2C{=}C(CH_3){-}C({=}O){-}O{-}CH_3$

Methyl methacrylate

Classical Monomers



styrene



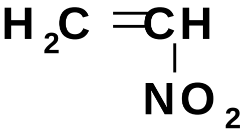
α-Me-styrene

Reactivity of monomers

Group A:

$H_2C{=}C(CN)_2$ >

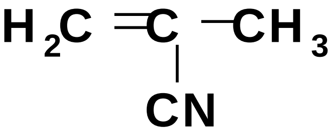
$H_2C{=}C(CN){-}COOC_2H_5$ >



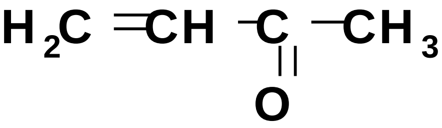
$H_2C{=}CH(NO_2)$

Group B:

$H_2C{=}CHCN$ >

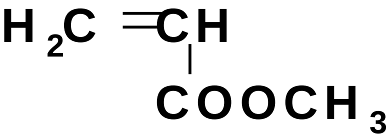


$H_2C{=}C(CN){-}CH_3$ >

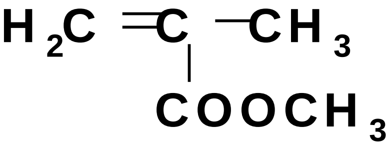


$H_2C{=}CH{-}C({=}O){-}CH_3$

Group C:



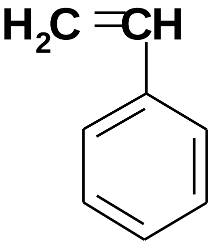
$H_2C{=}CH(COOCH_3)$ >

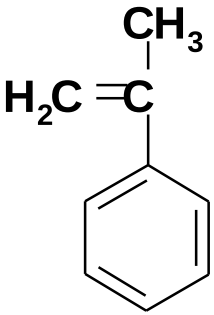


$H_2C{=}C(COOCH_3){-}CH_3$

Group D:

$H_2C{=}CH{-}CH{=}CH_2$



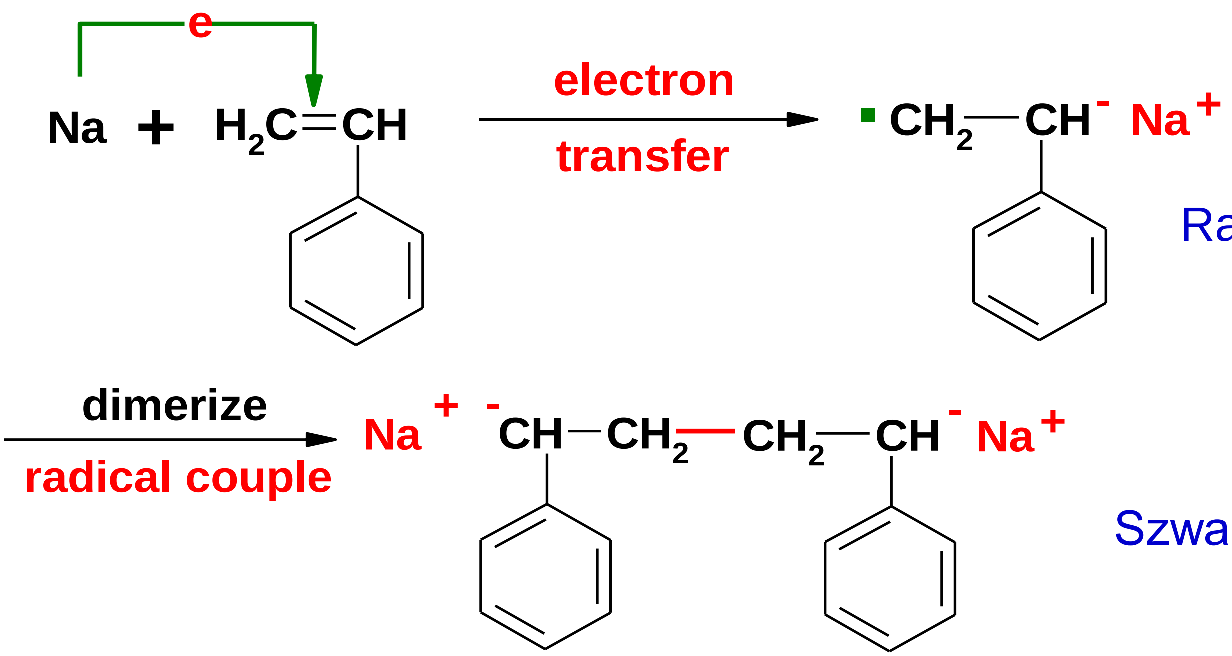


ob Berzelius

Anionic Initiators and initiation

(1) alkali metals ….one electron reductions

Lithium (Li) Sodium (Na) Potassium (K) as mirrors or fine dispersions.



Radical anion

Szwarc’s favorite

Break Seal Glassware

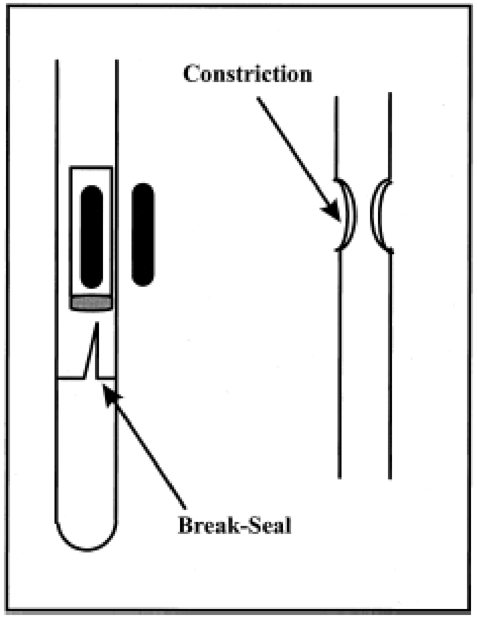


Figure 2. Breaker with break-seal and constri

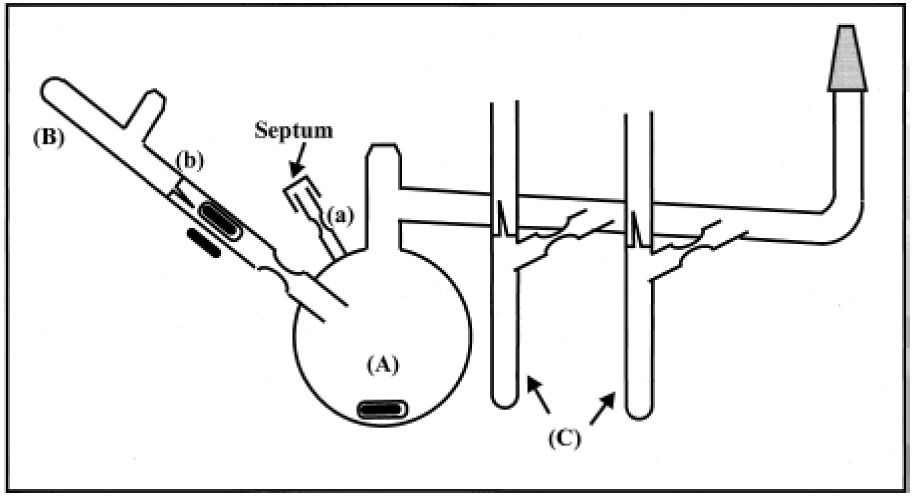
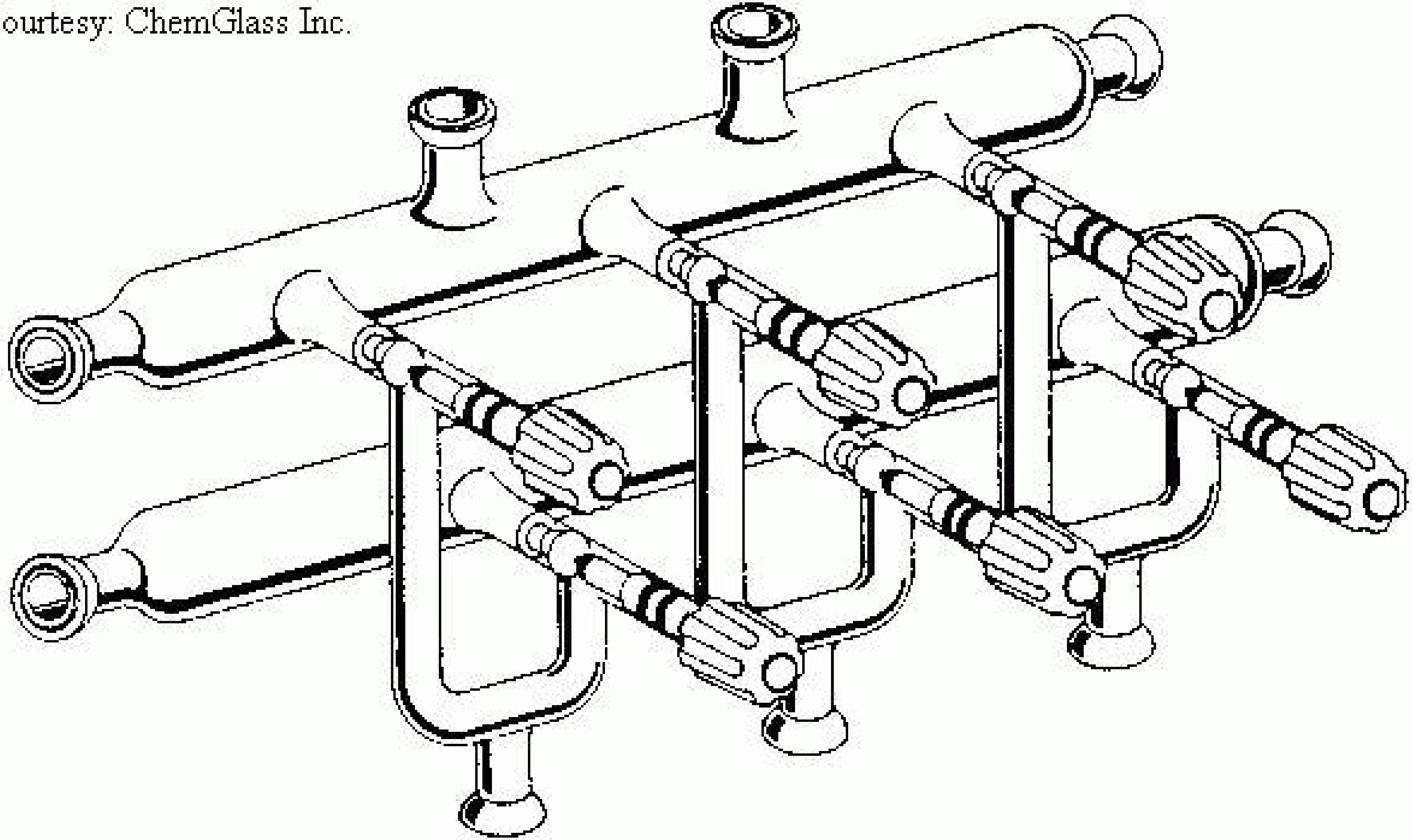


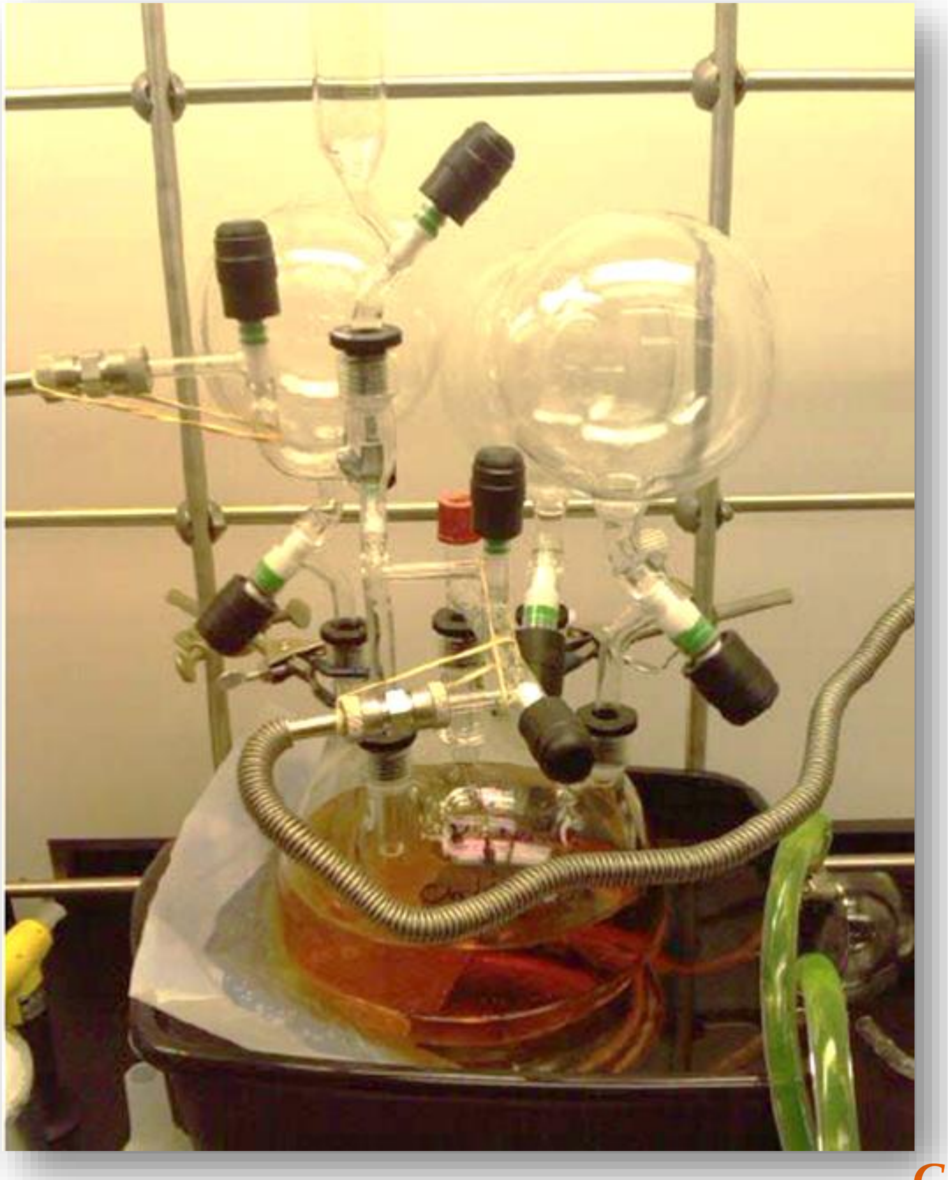
Figure 3. Apparatus for short-path distillation of high-boiling point substances.

Schlenk Tube Approach

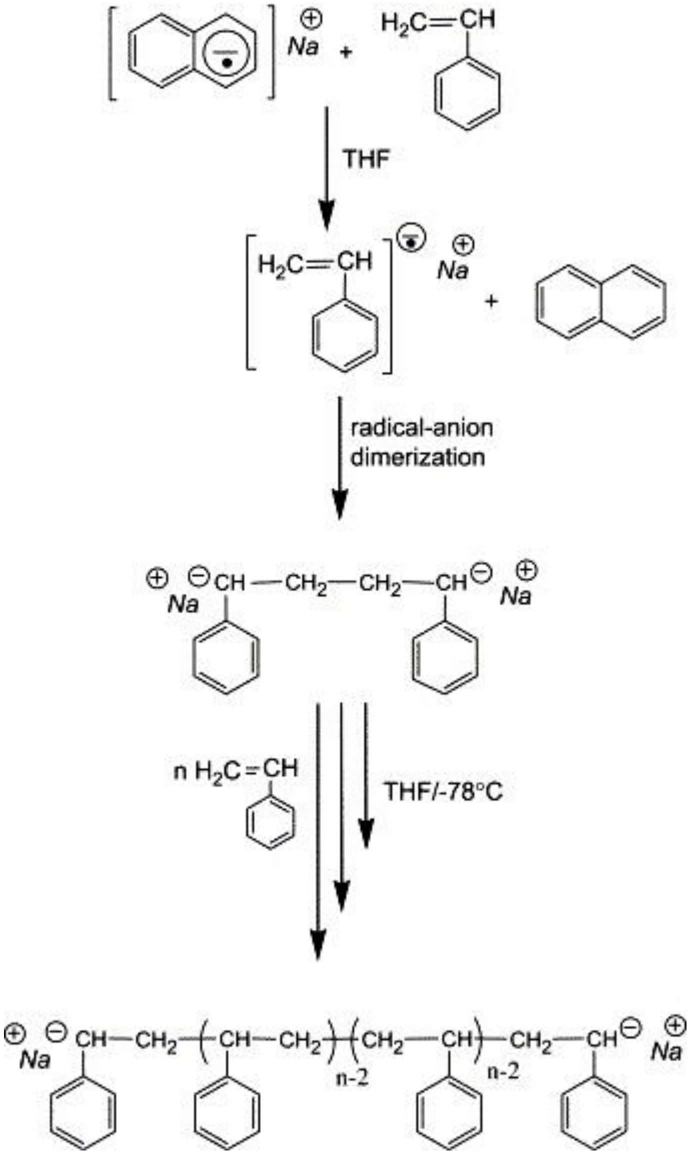


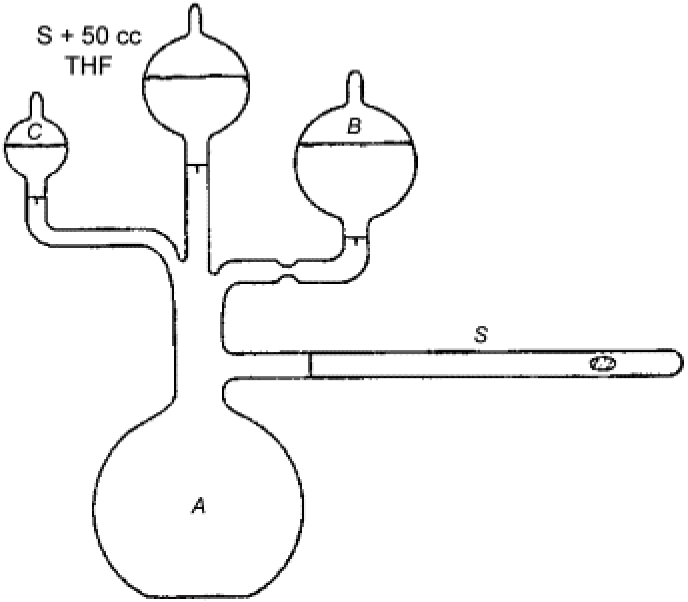
Courtesy: ChemGlass Inc.

Anionic Polymerization Apparatus



Szwarc's Experiment



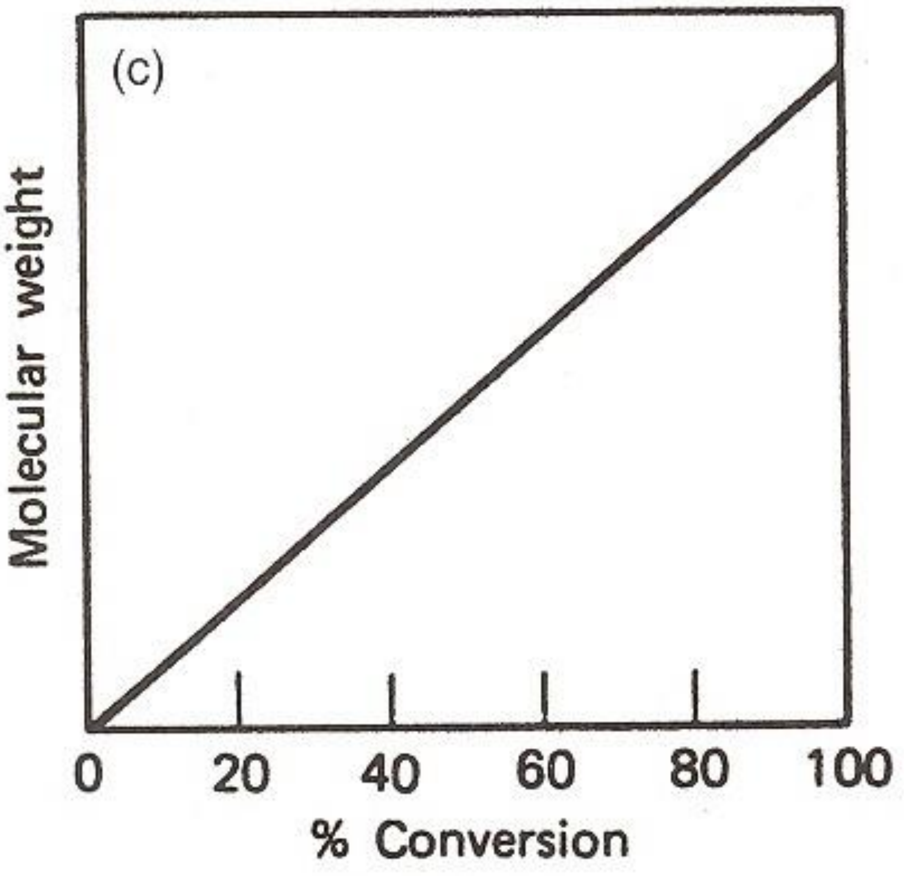


Living test

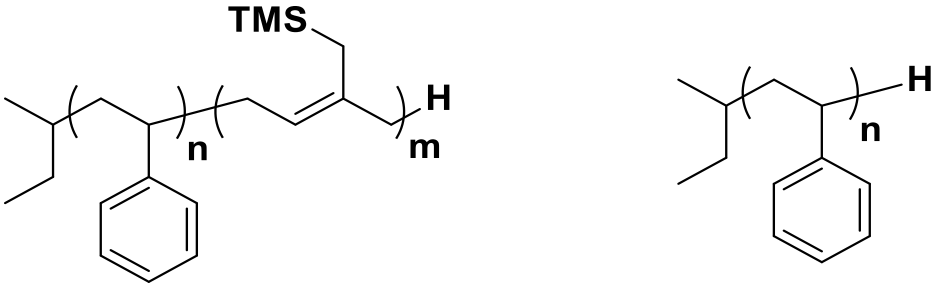
Reddish Orange

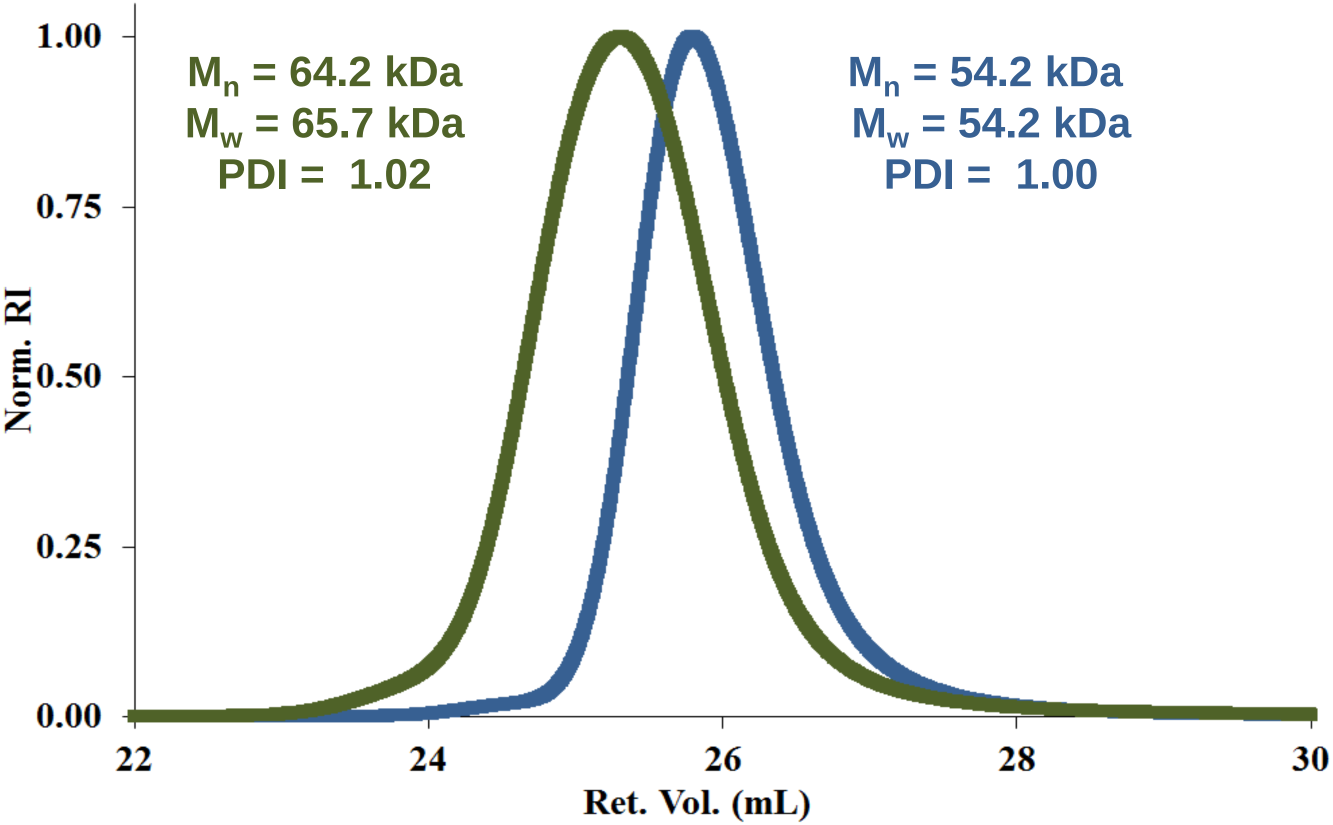
The Living Polymerization

$$DP_{t=\infty} = \frac{[M]}{[I]}$$



Anionic Polymerization of diblock copolymer



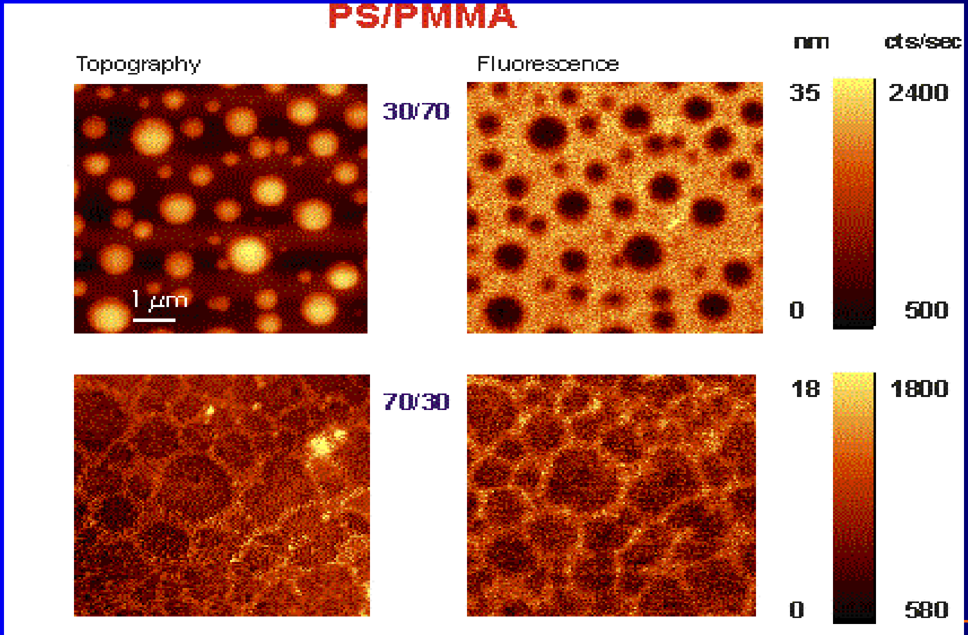


M_n = 64.2 kDa
M_w = 65.7 kDa
PDI = 1.02

M_n = 54.2 kDa
M_w = 54.2 kDa
PDI = 1.00

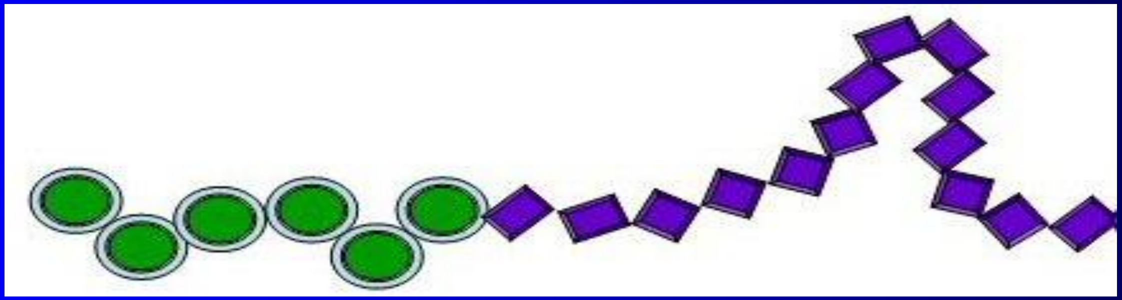
Polymer Blends

- Polymers do not generally form blends or “alloys”.
- About 99% of binary blends are heterogeneous except for small regions of the phase diagram
- Ethylene and propylene are mutually soluble, but polyethylene and polypropylene are not.

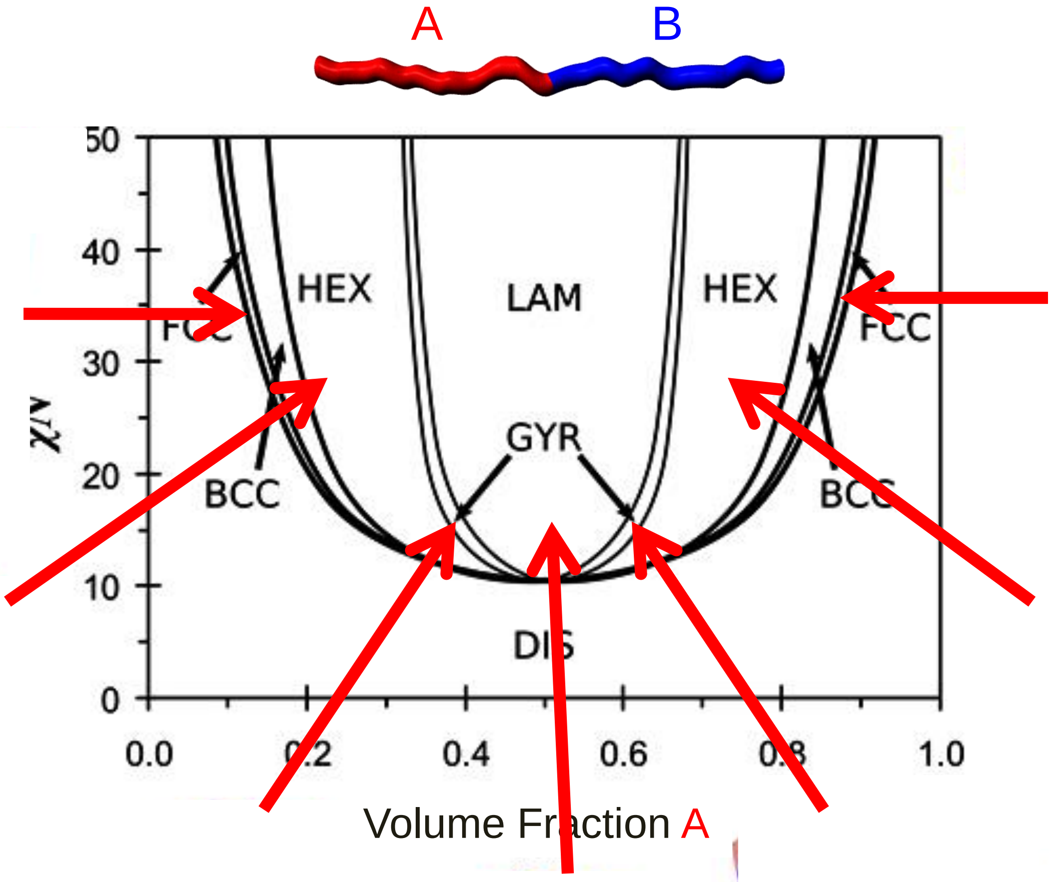


Block co-polymers

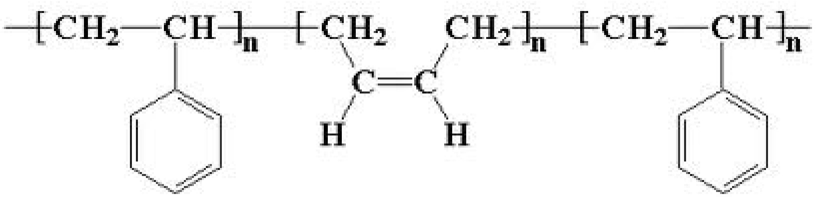
- Covalent linkage of two or more polymers that are intrinsically incompatible.
- Synthesis requires “special” techniques.



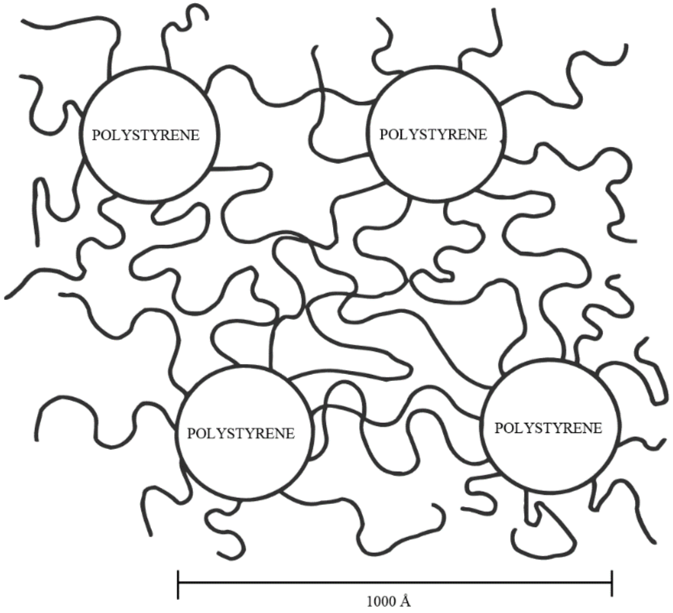
Miracle of Block Copolymers

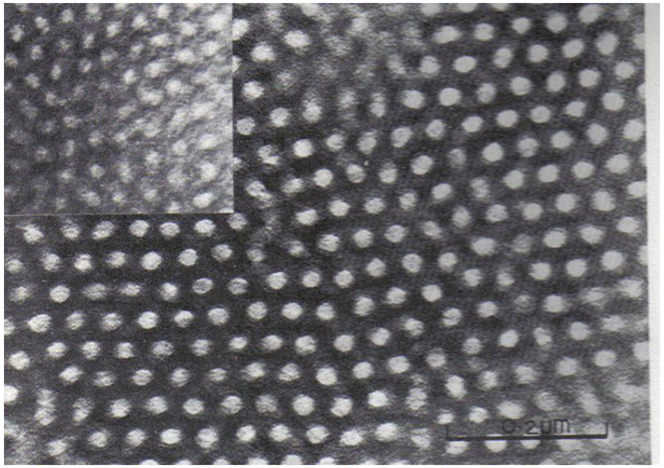


SBS Thermoplastic Elastomer

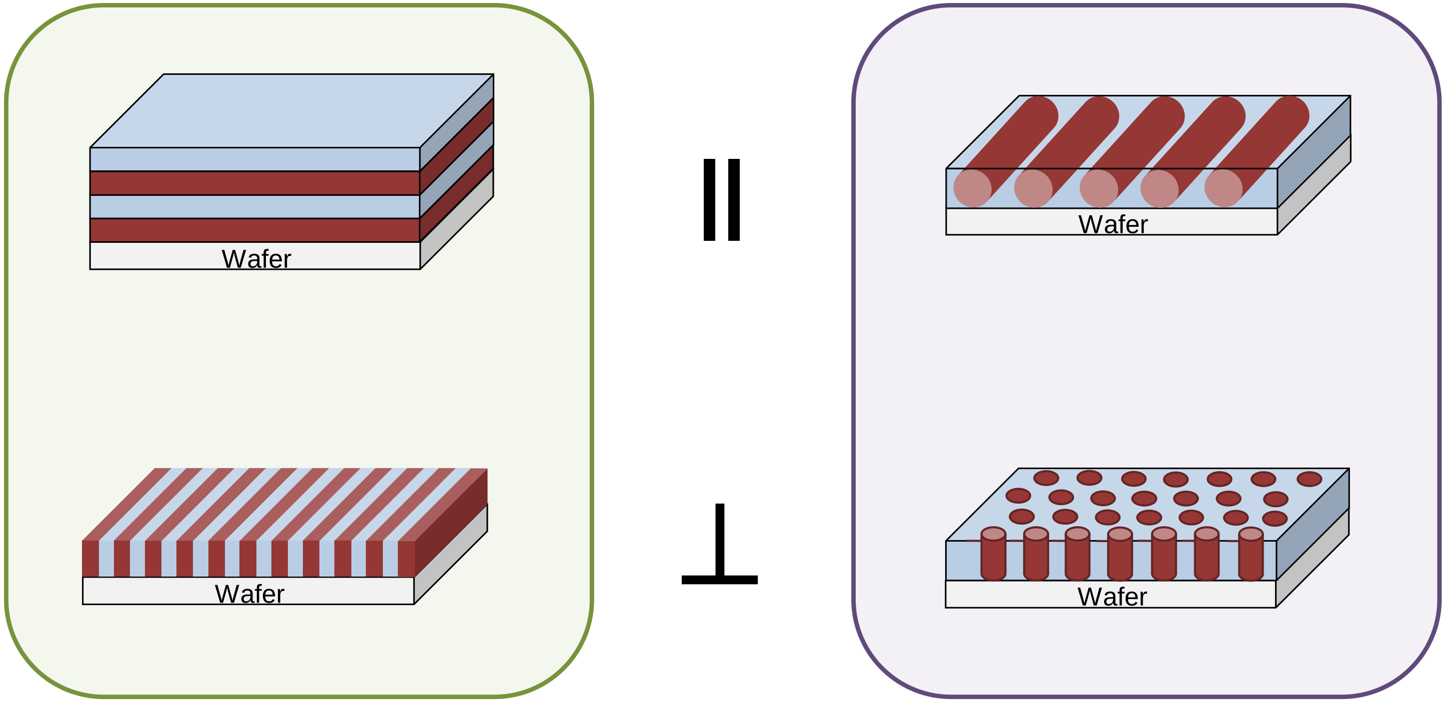


Krayton





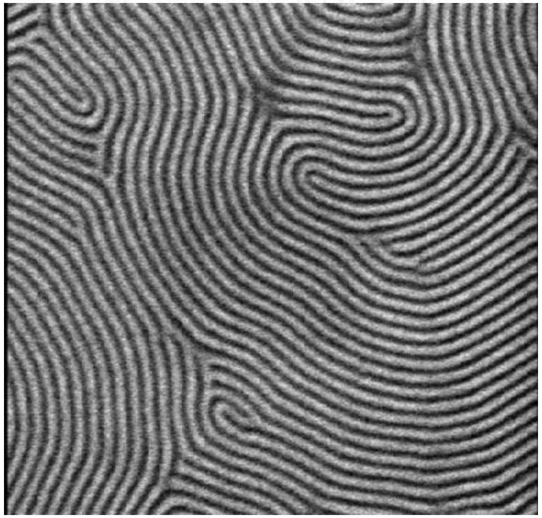
Orienting Block Copolymers



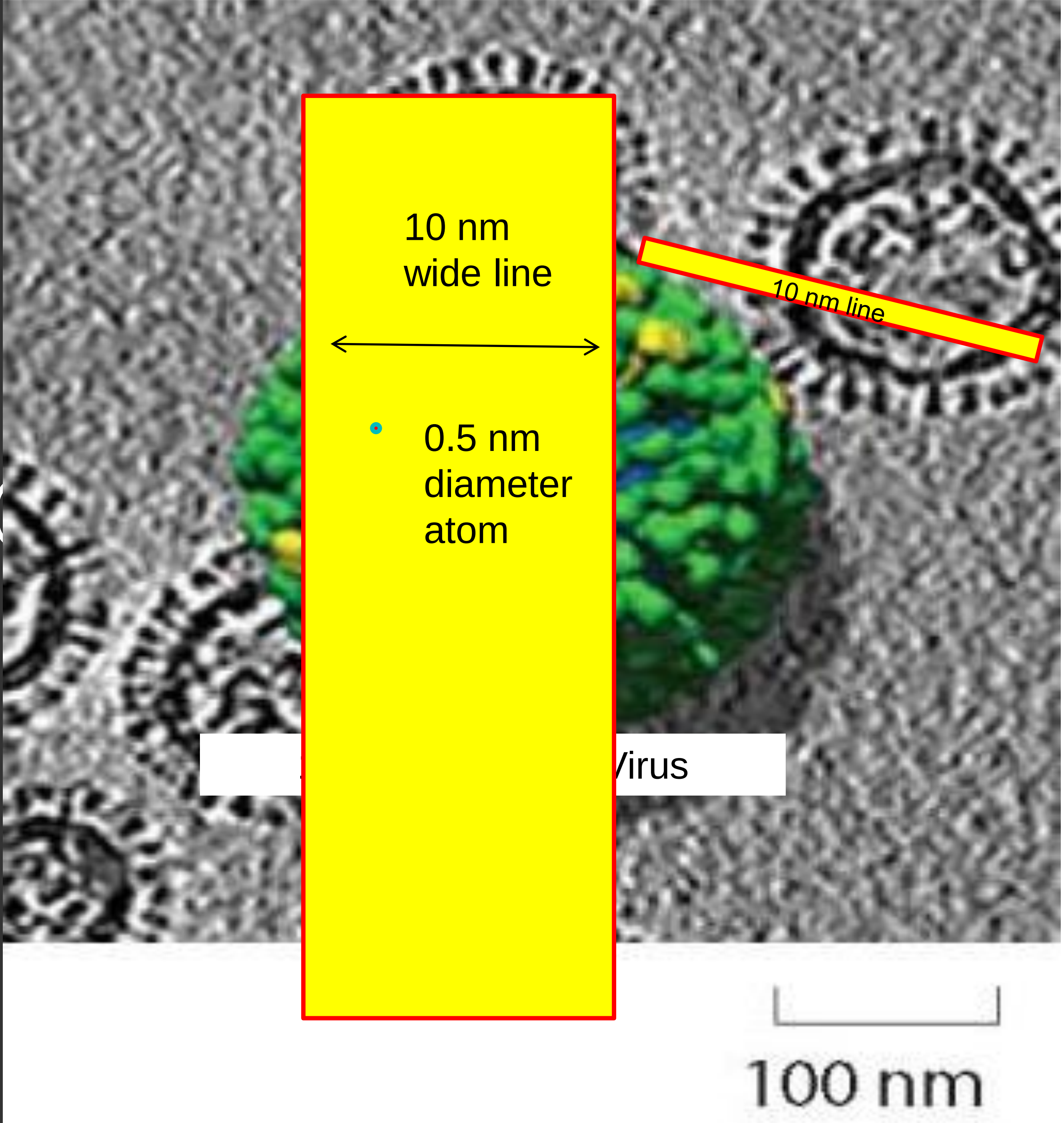
Lamellae

Cylinders

Directed self-assembly



How b



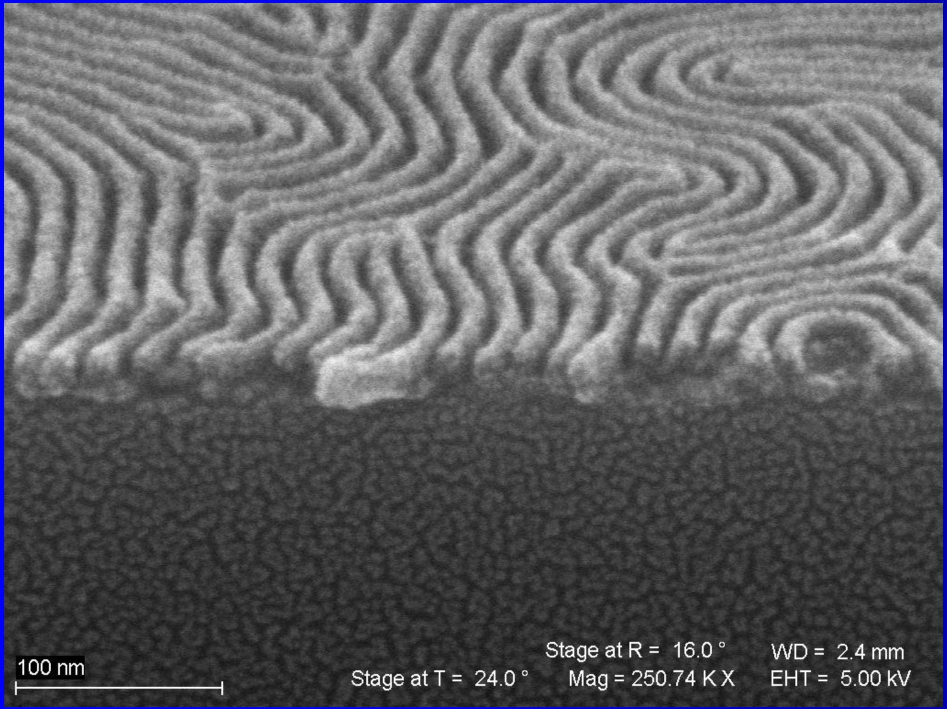
10 nm
wide line

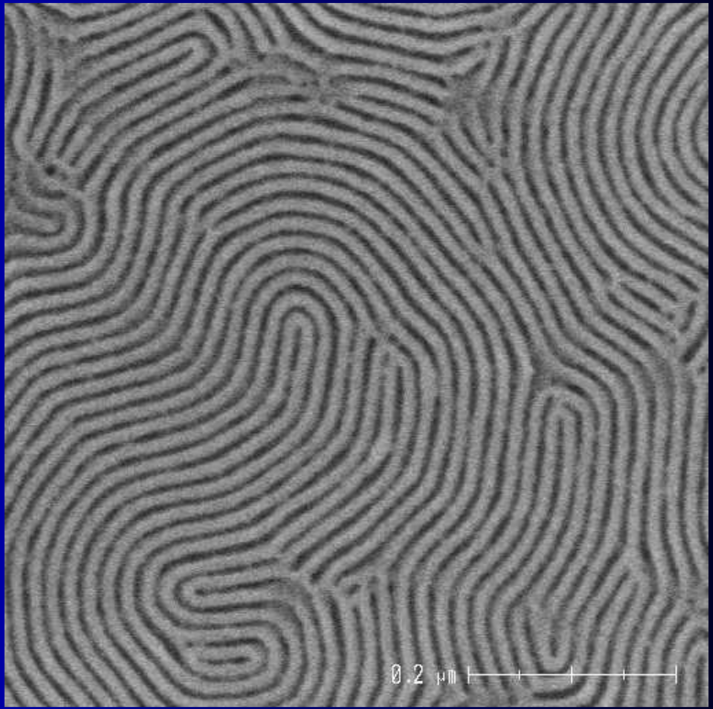
0.5 nm
diameter
atom

10 nm line

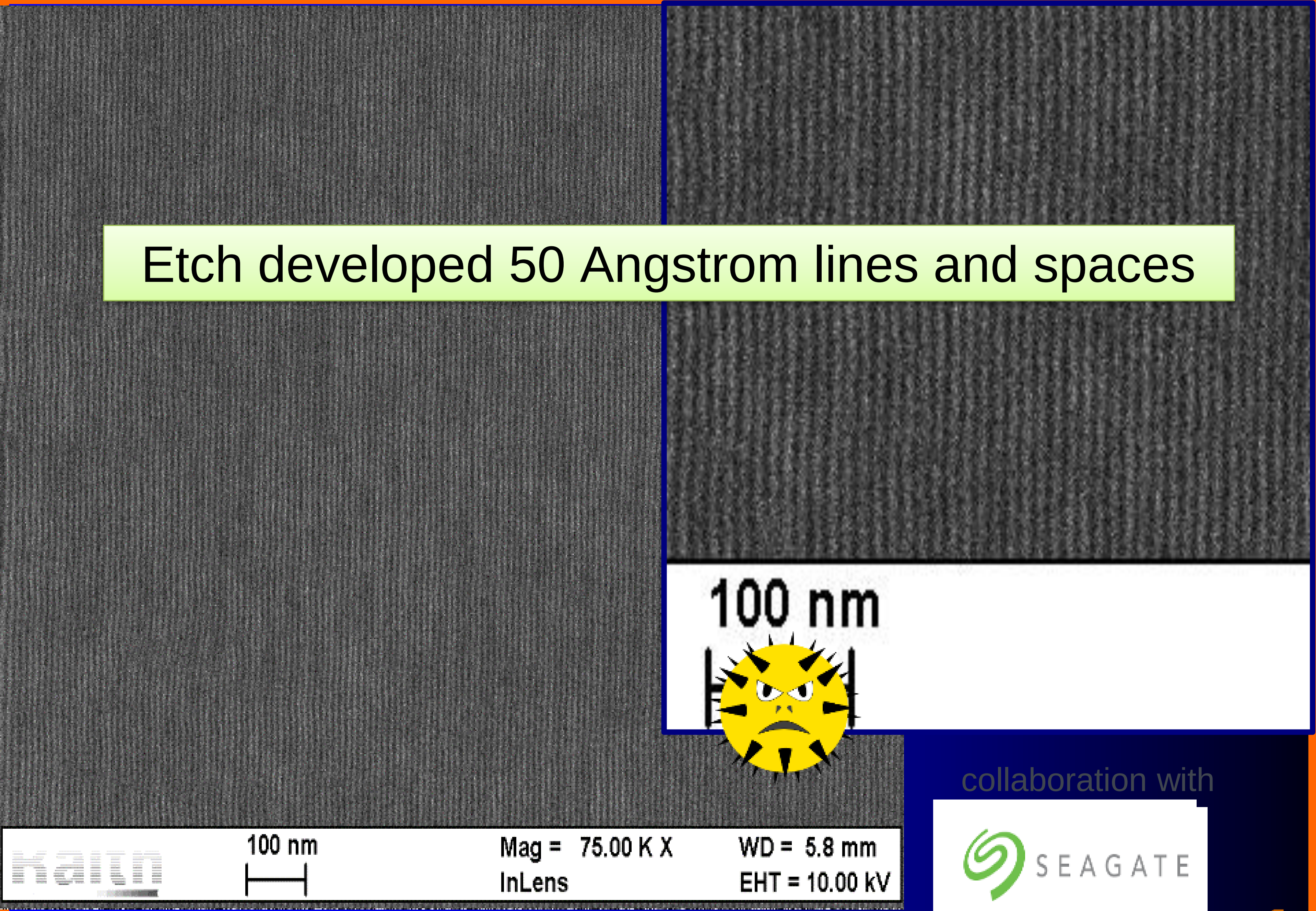
Virus

8nm lines in block copolymers





Etch developed 50 Angstrom lines and spaces



collaboration with

SEAGATE

Chemistry 328N