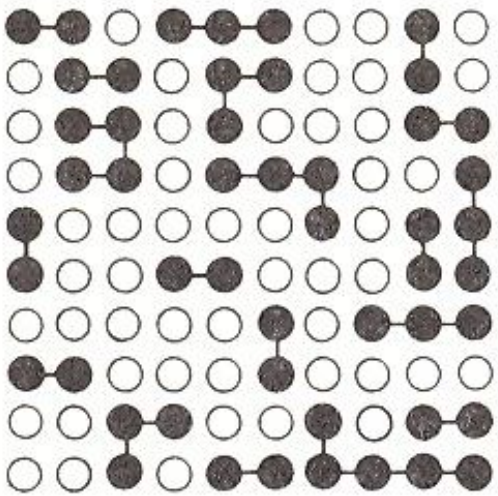
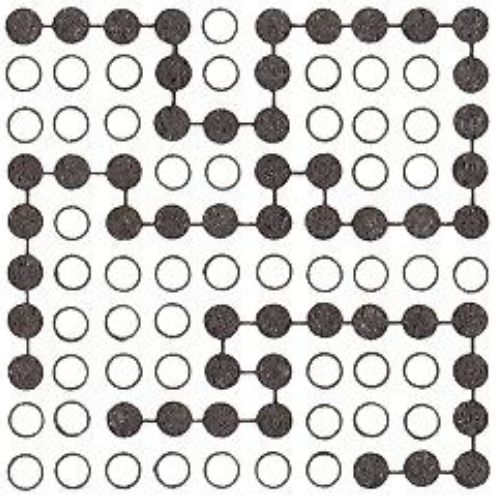
Lecture 27 *More Polymers*

Step



Chain



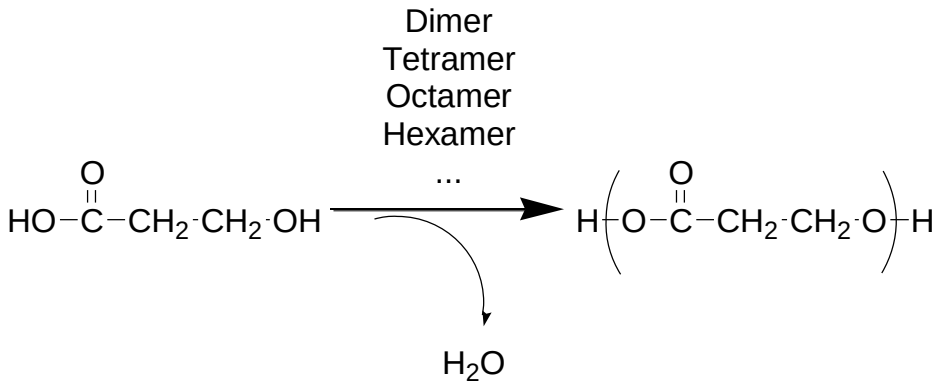
Midterm Exam III

- Where: WEL 1.316!!
- When: Wed., May 4th , 7:00 – 9:00 PM
- What: Covers lectures through 4/28
- Review Session: Mon & Tues. 5-6 PM
  - Monday PAI -3.02, Tue. PAI – 2.48
- Do: Study lecture notes, homework, reading assignments and practice hydrolysis and synthesis. Know signatures…
- Please: Do a good job!

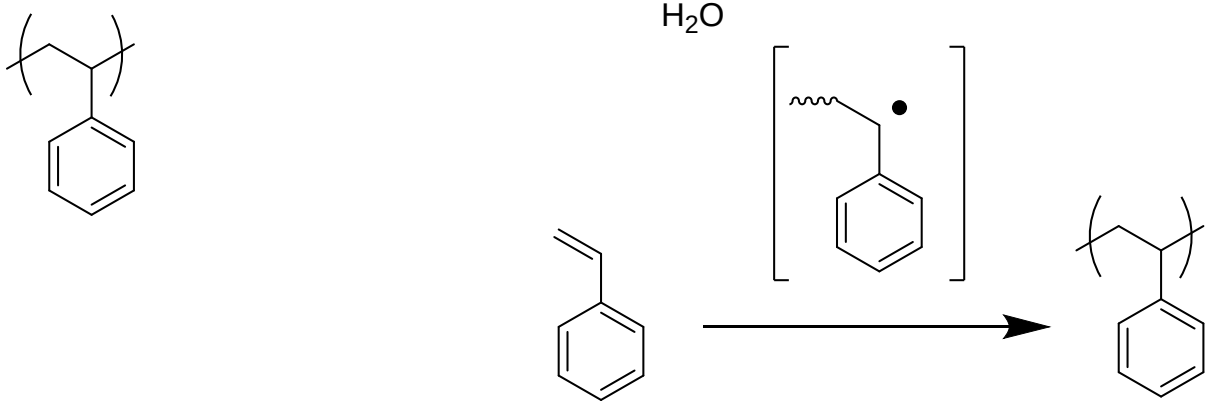
See web site for old exams

Flory's Classification by Polymerization Mechanisms

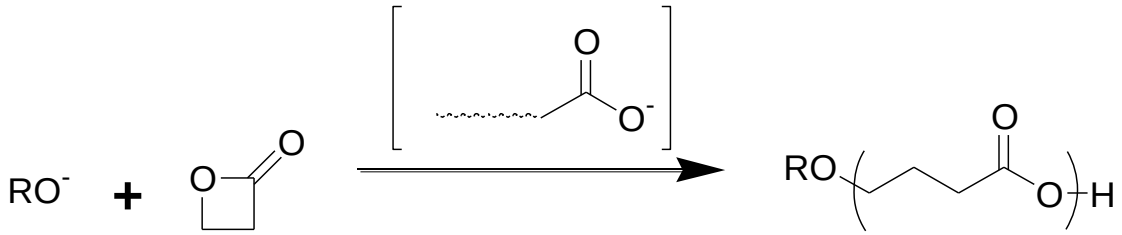
Step-growth



Chain-growth



Ring-opening



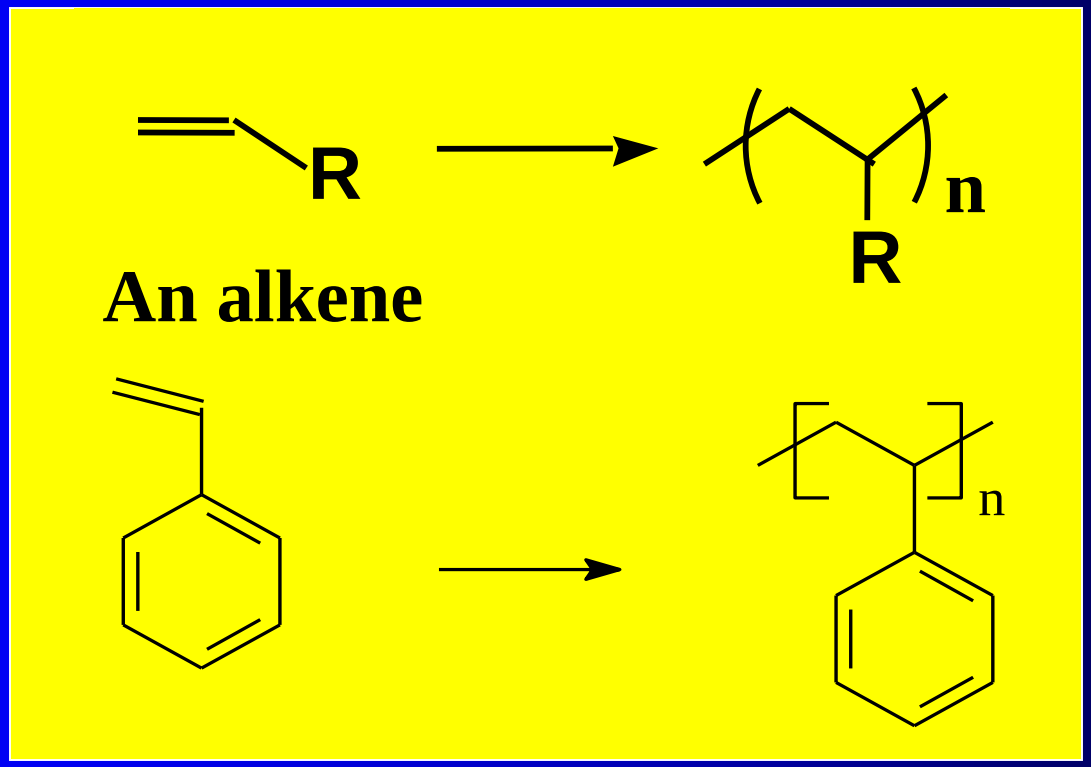
Chain-Growth Polymers

- **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

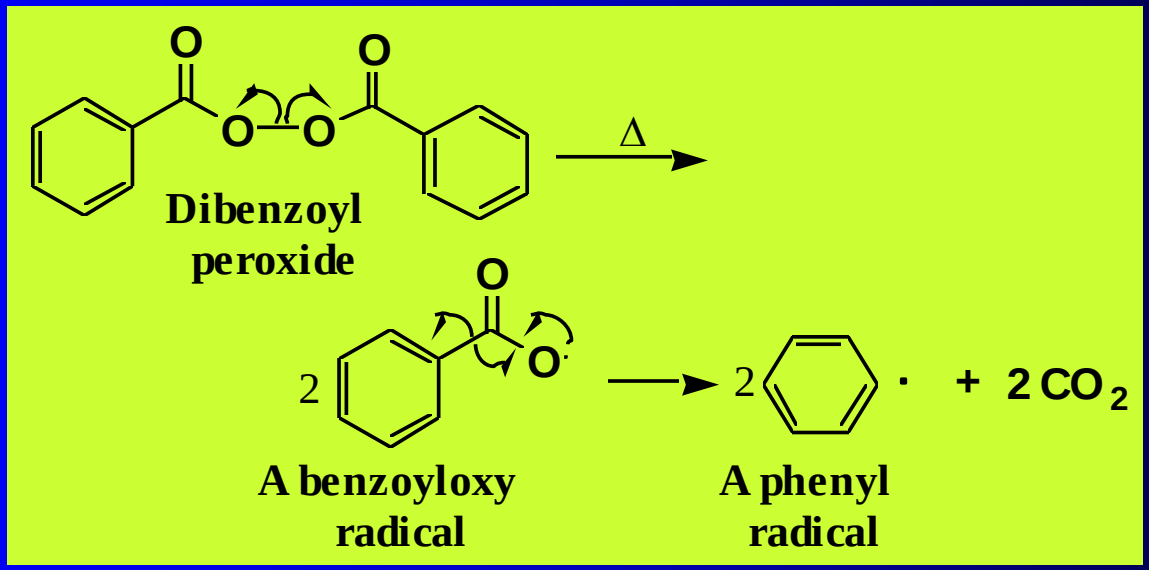
Chain-Growth Polymers

- We will concentrate on chain-growth polymerizations of ethylene and substituted ethylenes



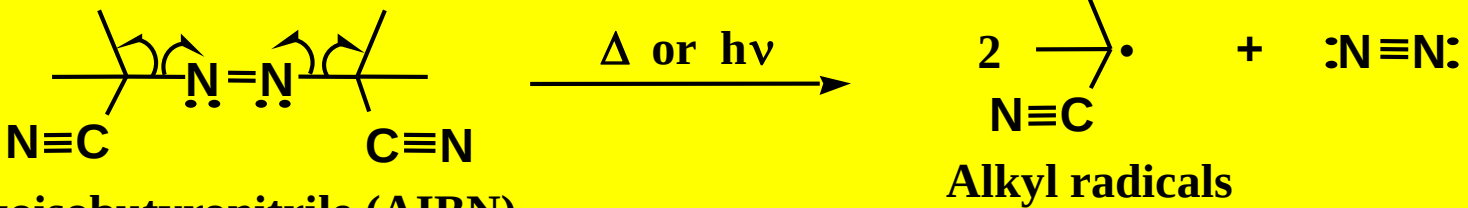
Radical Chain Growth Polymerization

- Among the initiators used for radical chain-growth polymerization are diacyl peroxides, which decompose as shown on mild heating



Radical Chain Growth Polymerization

- Another common class of initiators are azo compounds, which also decompose on mild heating or with absorption of UV light

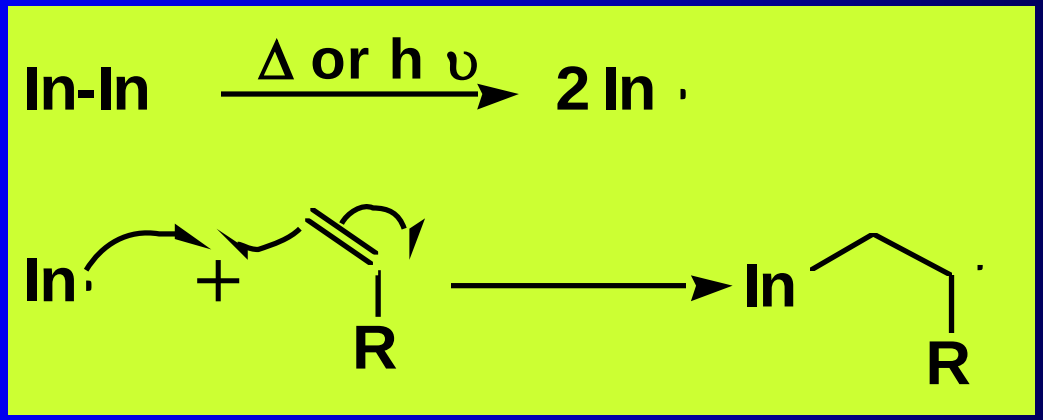


Azoisobutyronitrile (AIBN)

Alkyl radicals

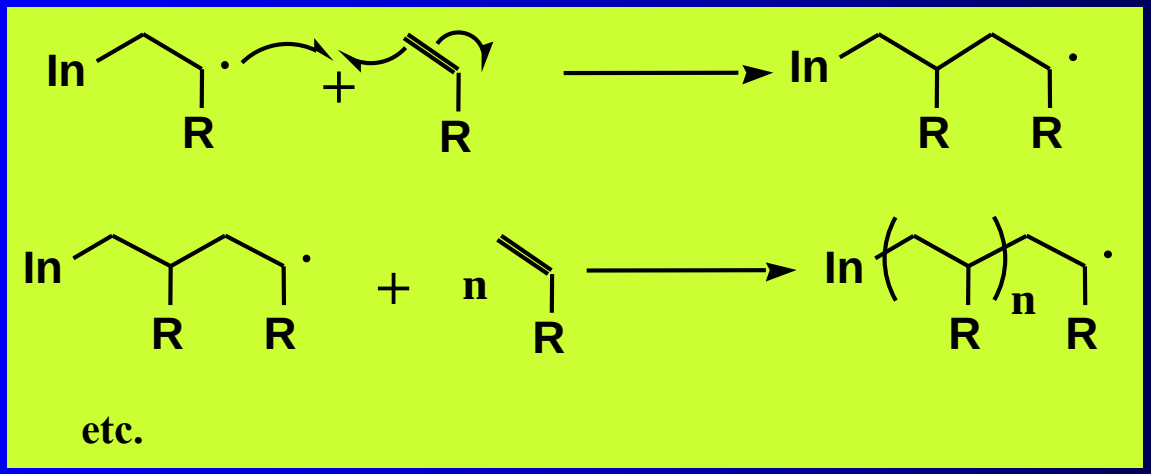
Radical Chain Growth Polymerization

- Chain initiation, chain propagation, and chain termination steps for radical polymerization of a substituted ethylene are shown for the monomer $RCH=CH_2$
  - chain initiation



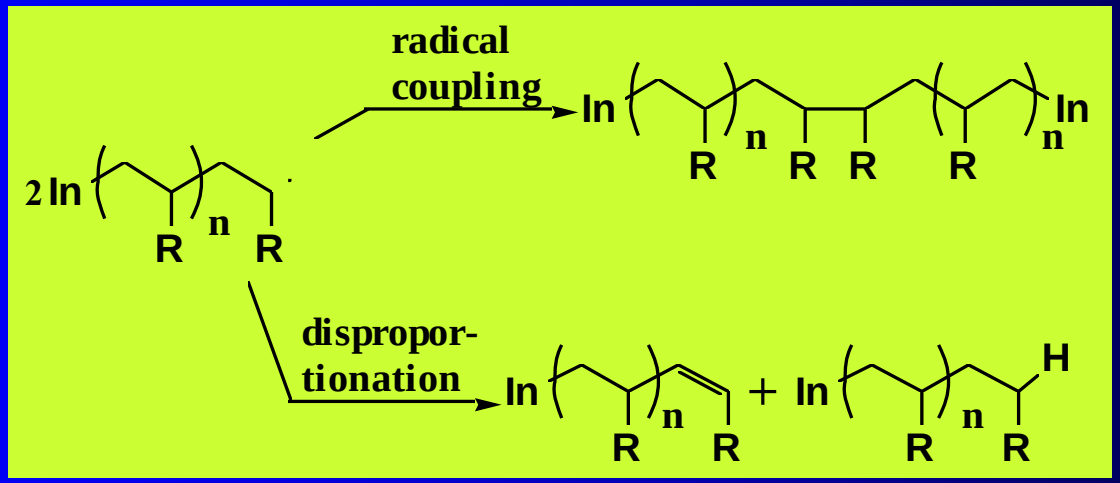
Radical Chain Growth Polymerization

– chain propagation



Radical Chain Growth Polymerization

– Chain termination

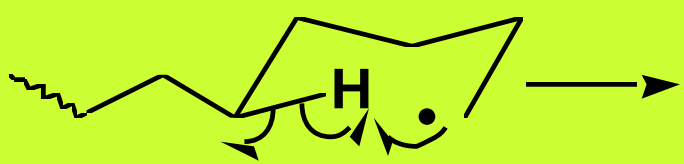


Radical Chain-Growth

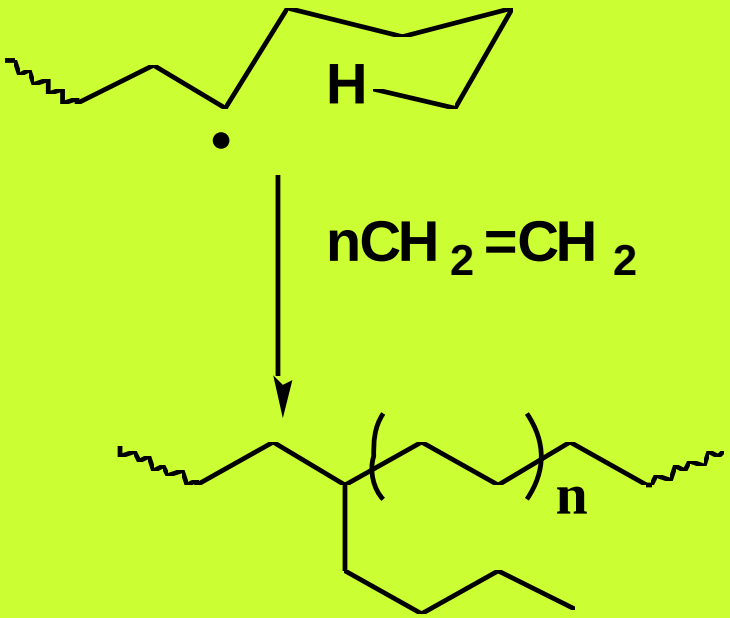
- Chain-transfer reaction: the reactivity of an end group is transferred from one chain to another, or from one position on a chain to another position on the same chain
  - polyethylene formed by radical polymerization exhibits a number of butyl branches on the polymer main chain
  - these butyl branches are generated by a “back-biting” chain transfer reaction in which a 1° radical end group abstracts a hydrogen from the fourth carbon back
  - polymerization then continues from the 2° radical

Radical Chain-Growth

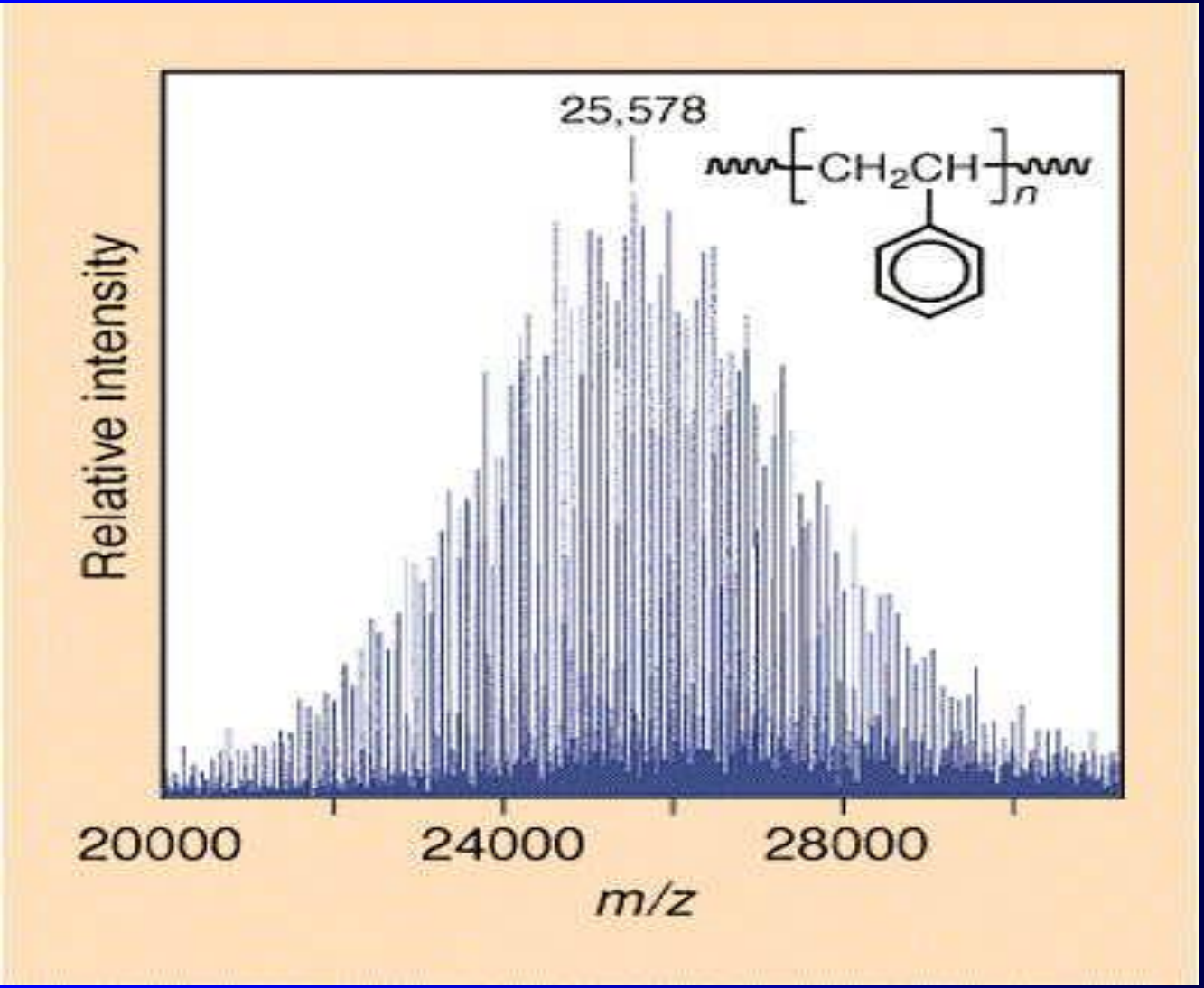
Back biting



A six-membered transition state leading to 1,5-hydrogen abstraction



MALDI Mass Spectrum of Polystyrene



Molecular Weight

- All polymers are mixtures of individual polymer molecules of variable MWs
  - Number average Mn: count the number of chains of a particular MW, multiply each number by the MW, sum these values, and divide by the total number of polymer chains

$$Mn = \frac{\sum MiNi}{\sum Ni}$$

  - weight average Mw: record the weight of each chain of a particular length, sum these weights, and divide by the total weight of the sample

$$Mw = \frac{\sum WiMi}{\sum Wi} = \frac{\sum NiMi^2}{\sum NiMi}$$

What the Weights Mean

M_n: This gives you the true average weight

Let's say you had the following polymer sample:

2 chains:	1,000,000 Dalton	2,000,000
5 chains:	700,000 Dalton	3,500,000
10 chains:	400,000 Dalton	4,000,000
4 chains:	100,000 Dalton	400,000
2 chains:	50,000 Dalton	100,000
		10,000,000

10,000,000/23 = 435,000 Dalton

1 Dalton = 1 g/mole

Weight Average Molecular Weight

M_w: Since most of the polymer mass is in the heavier fractions, this gives the average molecular weight of the most abundant polymer fraction by mass.

$$\frac{2{,}000{,}000}{10{,}000{,}000} = 0.20 \times 1{,}000{,}000 = 200{,}000$$

$$\frac{3{,}500{,}000}{10{,}000{,}000} = 0.35 \times 700{,}000 = 245{,}000$$

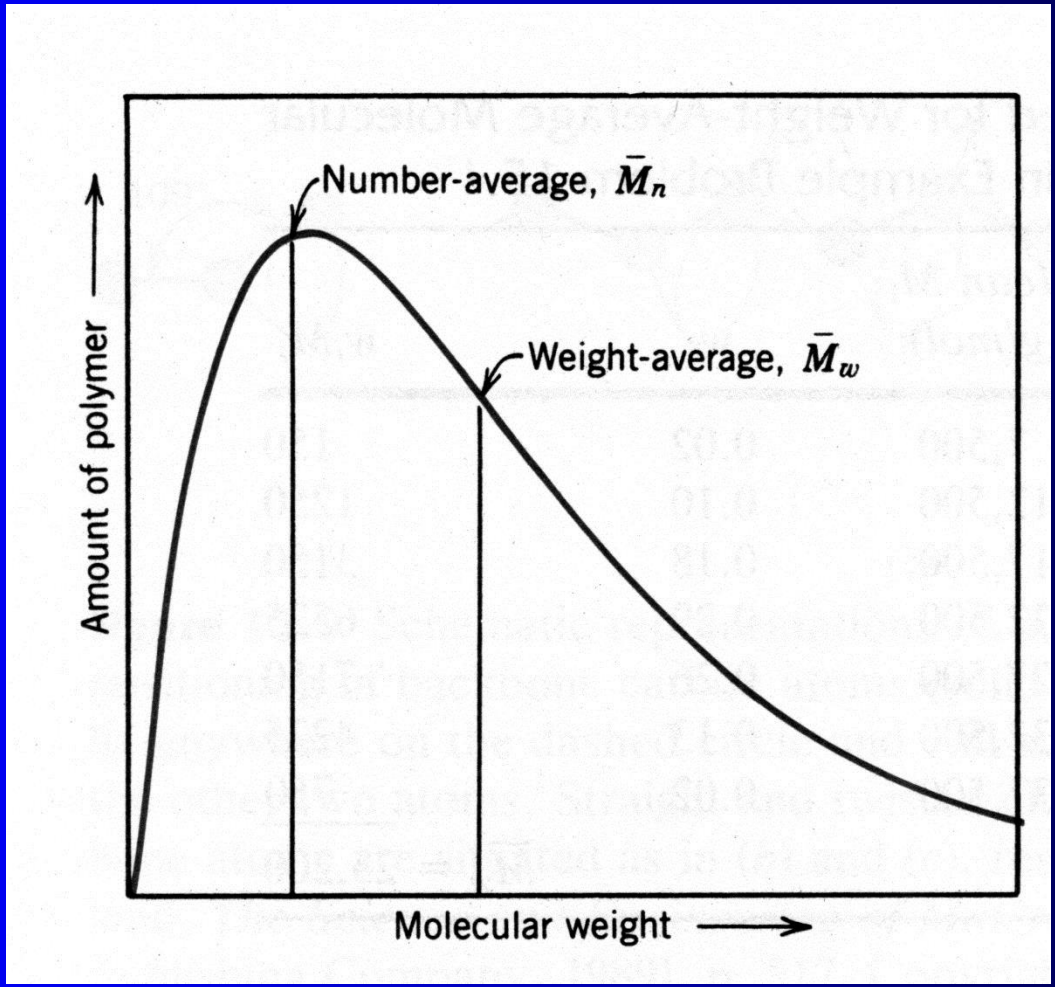
$$\frac{4{,}000{,}000}{10{,}000{,}000} = 0.40 \times 400{,}000 = 160{,}000$$

$$\frac{400{,}000}{10{,}000{,}000} = 0.04 \times 100{,}000 = 4{,}000$$

$$\frac{100{,}000}{10{,}000{,}000} = 0.01 \times 50{,}000 = 500$$

$$\text{Total} = 609{,}500$$

Distribution of Molecular Weights

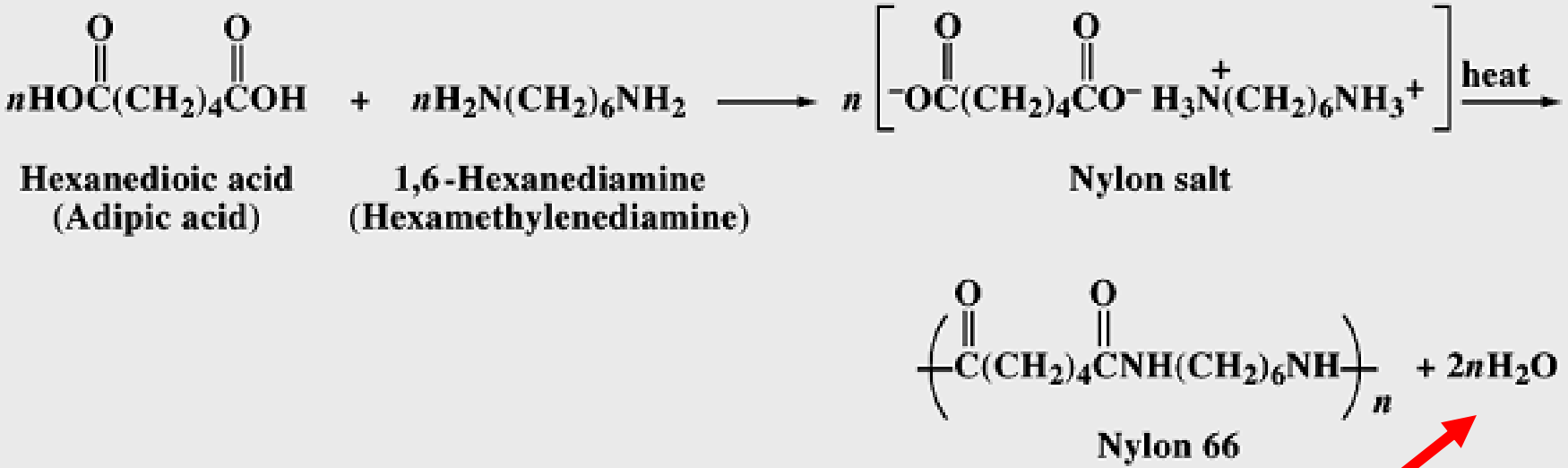


Polymers: Molecular Weight

- Ratio of M_w to M_n is known as the polydispersity index (PDI) Đ
  - a measure of the breadth of the molecular weight
  - 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 1.5 < PI < 5
  - At best Đ < 1.1 can be attained with special techniques

Step Growth: The Carothers Legacy

Synthesis of nylon 66

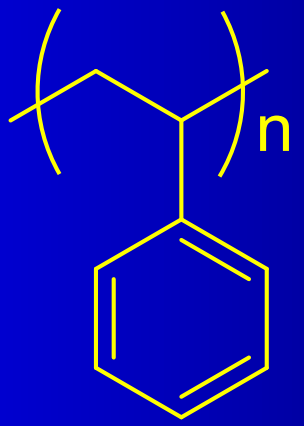


Stuff is lost in this reaction

Let's look at this 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 $\overline{DP}$ at time t is the average degree of polymerization… must just be N_0/N!

The "Degree of Polymerization" , $\overline{DP}$ is the number of monomer units in the average chain…it is the subscript n in this notation:



Chain Growth Polymerization

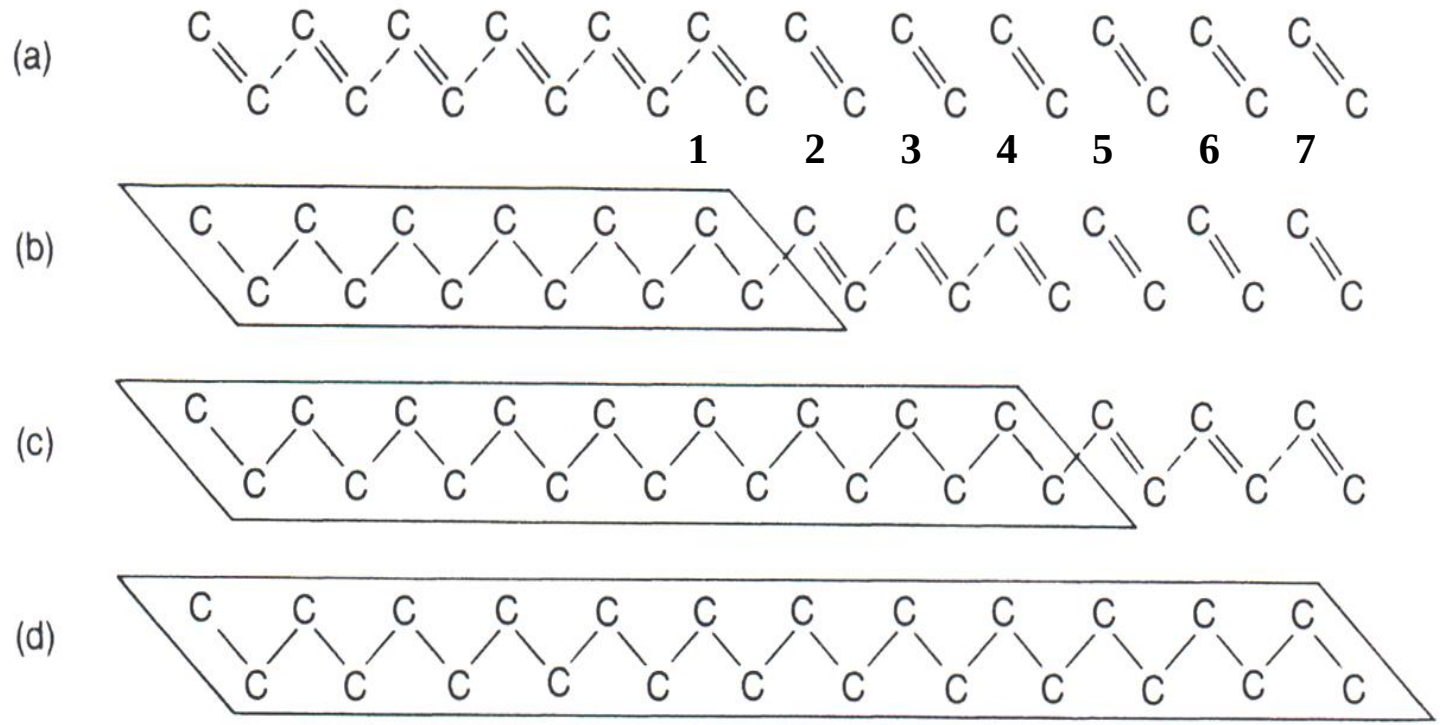


FIGURE 1.5. Chain-reaction polymerization: (a) unreacted monomer; (b) 50% reacted, $\overline{DP} = 1.7$; (c) 75% reacted, $\overline{DP} = 3$; (d) 100% reacted, $\overline{DP} = 12$. (Broken lines represent reacting species.)

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

Step Growth Polymerization

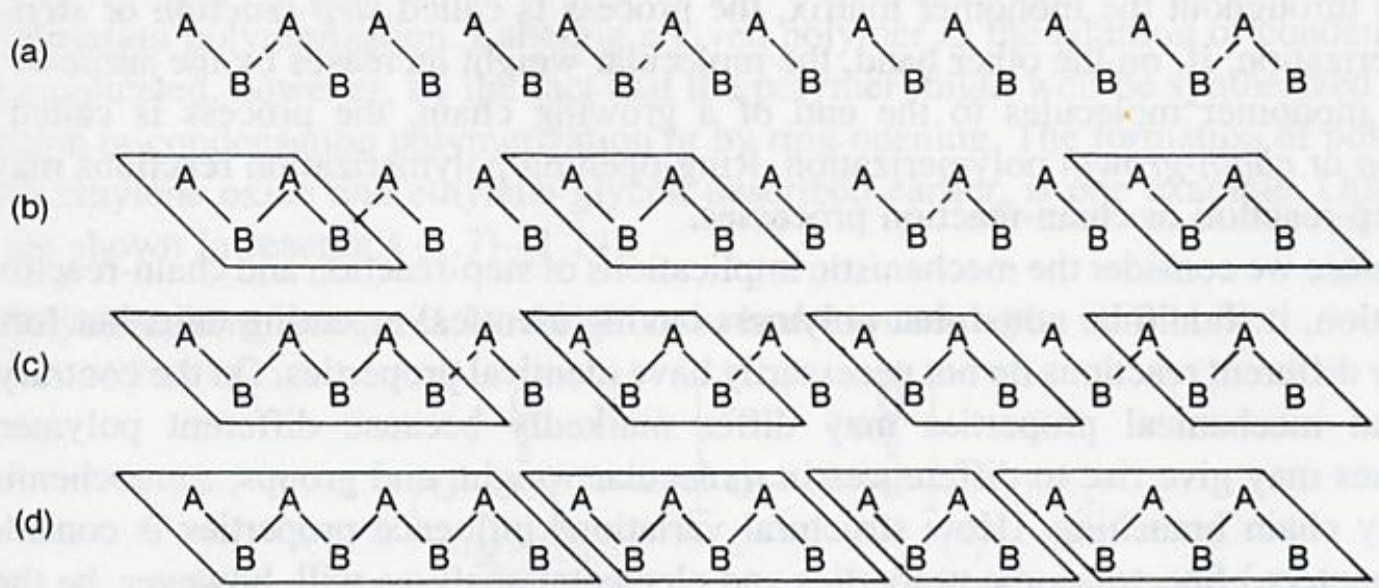
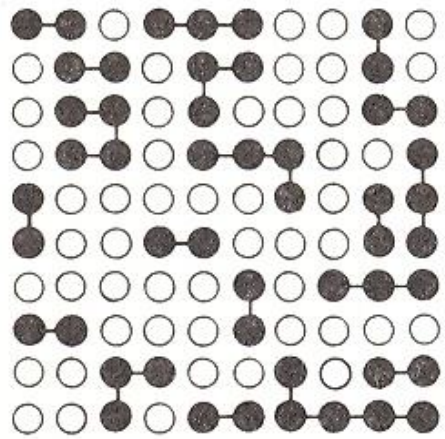


FIGURE 1.4. Step-reaction polymerization: (a) unreacted monomer; (b) 50% reacted, $\overline{DP} = 1.3$; (c) 75% reacted, $\overline{DP} = 1.7$; (d) 100% reacted, $\overline{DP} = 3$. (Broken lines represent reacting species.)

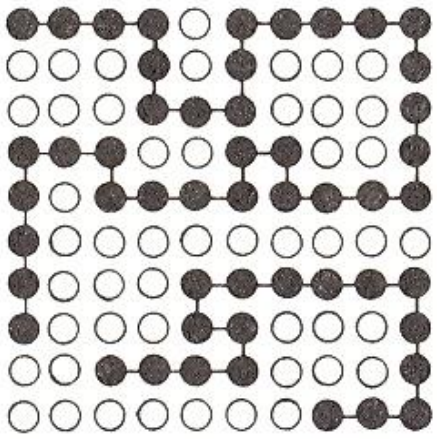
$DP = N_o/N = 12 / 9 = 1.3$ (for 50%, b)

The chain growth vs. step growth

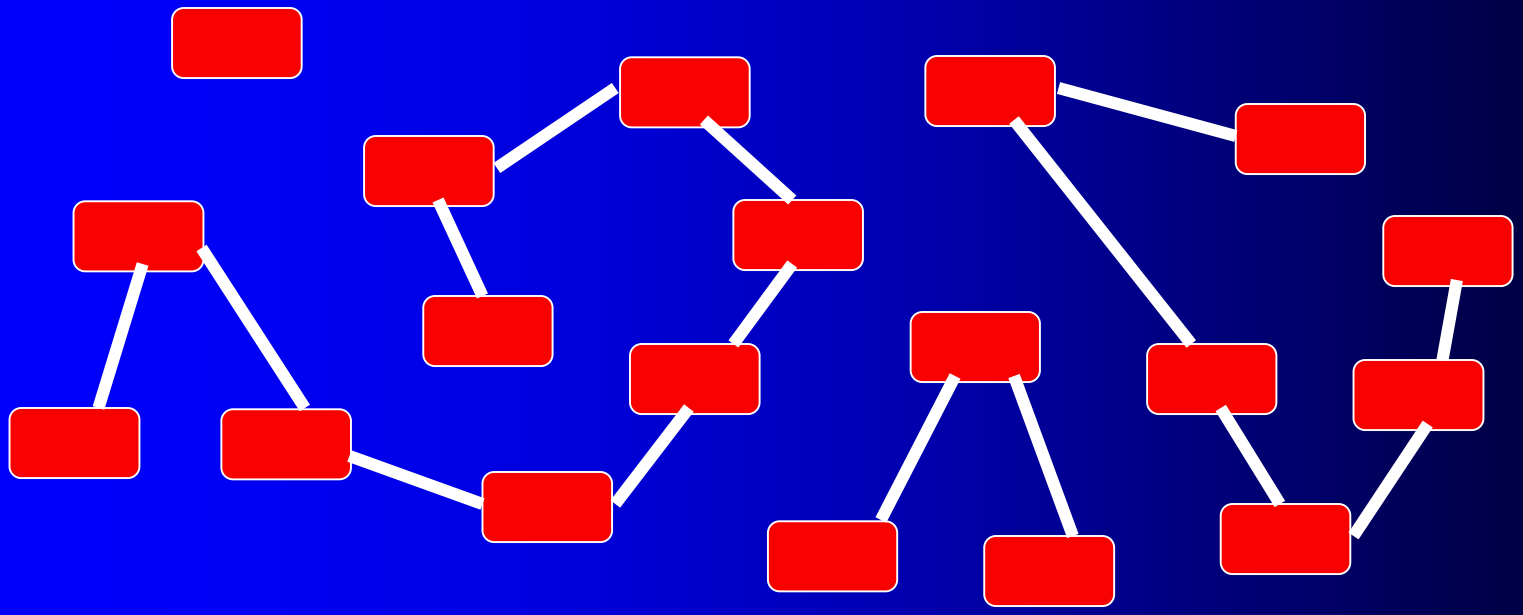
Step



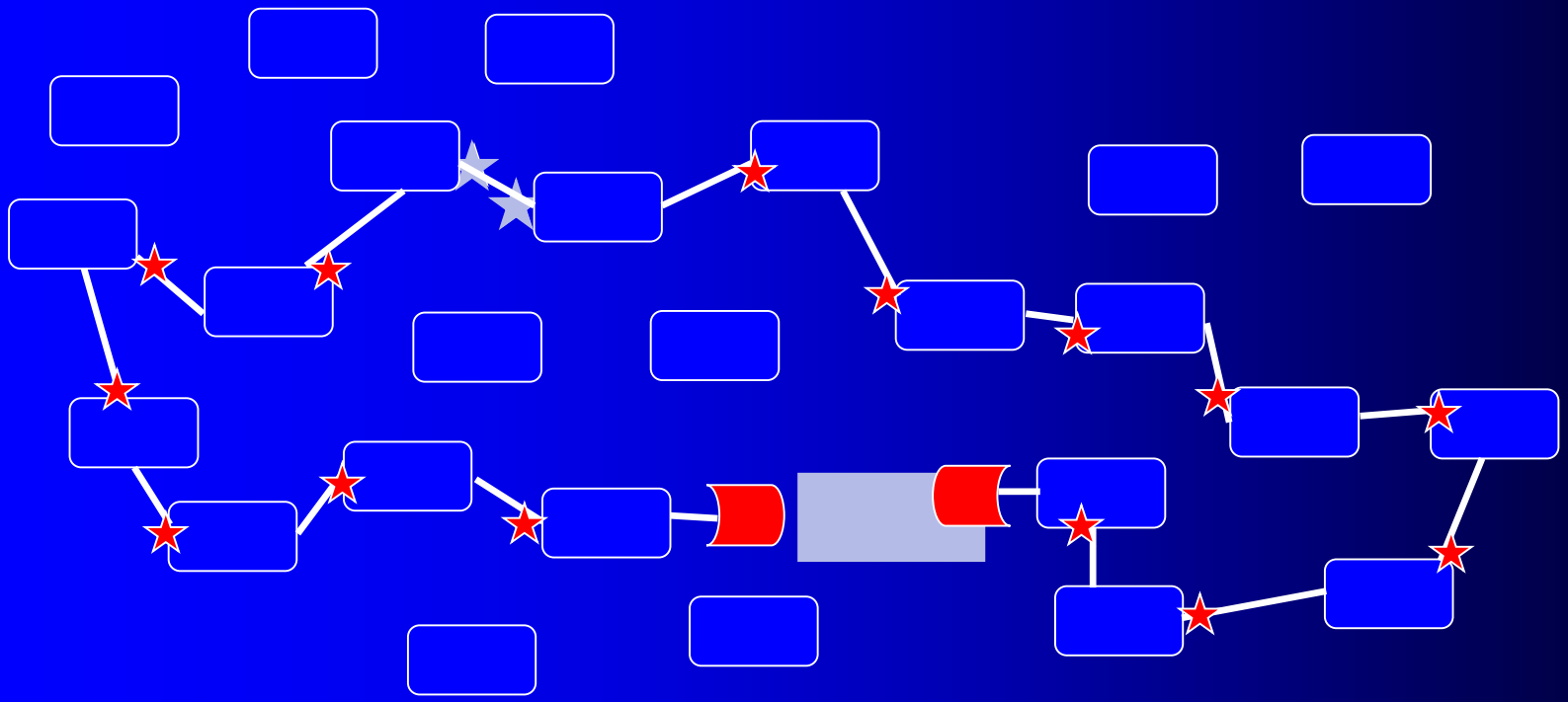
Chain



- Step-growth polymerization



- Chain-growth polymerization



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 the "conversion" or fraction reacted then as

$$P = (N_o - N) / N_o \quad \text{or}$$

$$N = N_o(1 - P)$$

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

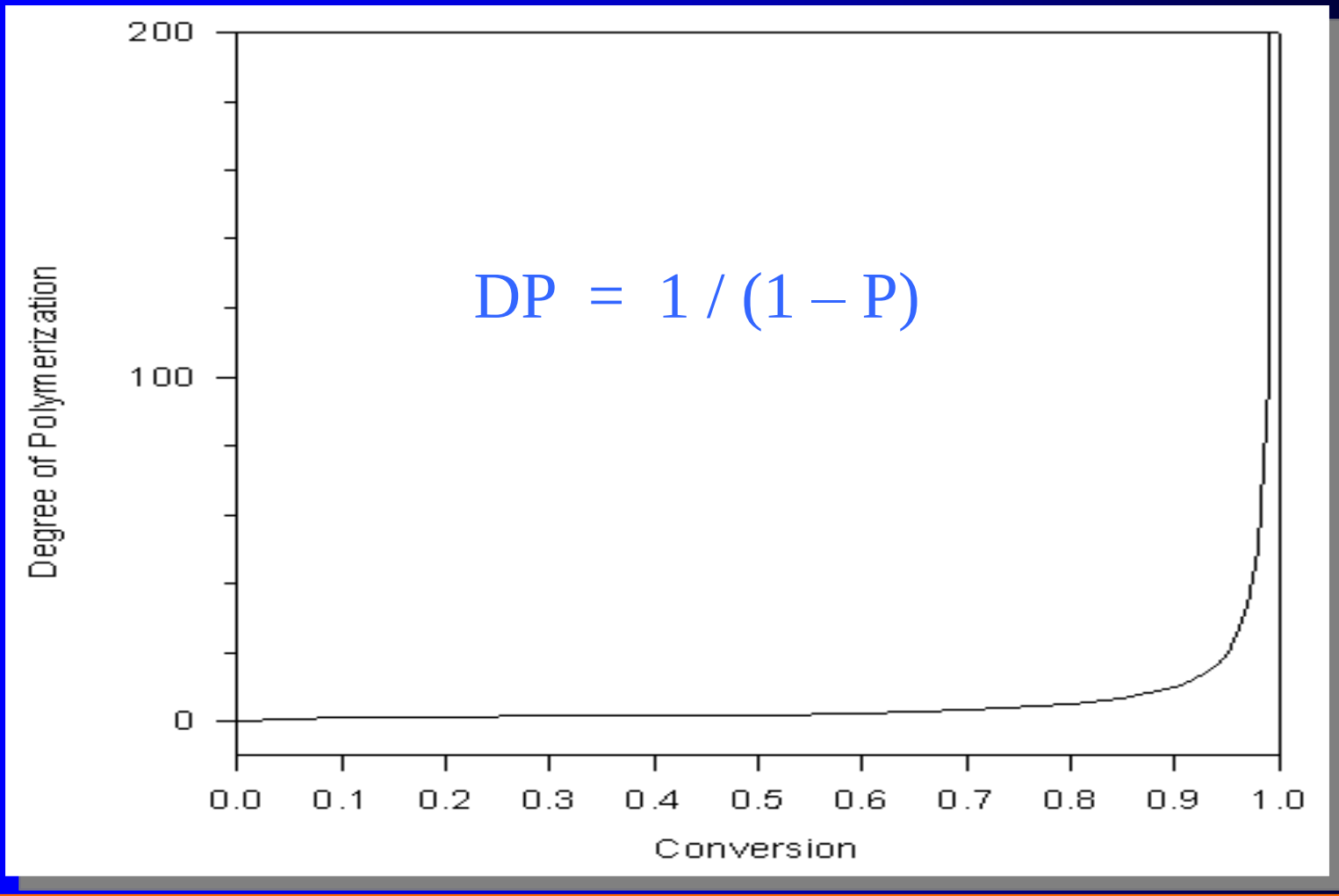
$$N/N = N_o/N(1 - P) \quad \text{or}$$

$$DP = 1 / (1 - P)$$

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

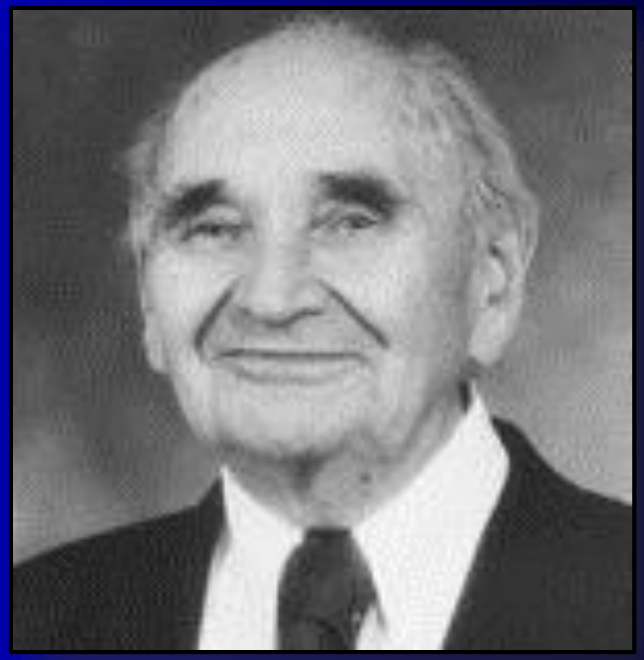
The step growth system

It all happens at the end!!!



More Historical Figures

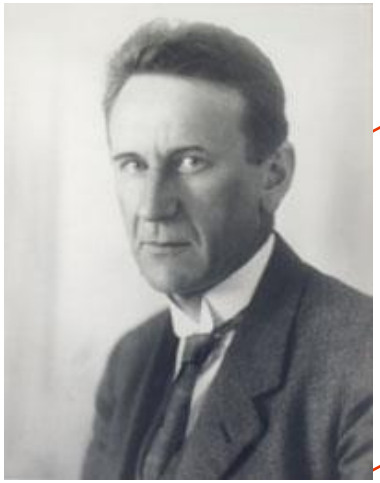
Wilhelm Schlenk

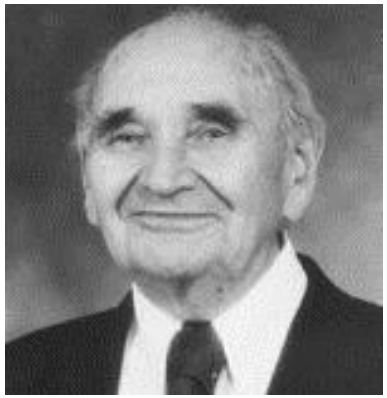


Michael Szwarc

Anionic polymerization

Some History





1914, Schlenk reacts Na with **butadiene and styrene**

1929, Ziegler proposes a mechanism

1952 Higginson, styrene, KNH_2, kinetic study

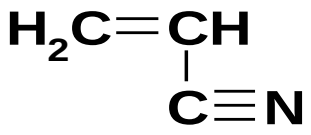
1956 Szwarc, sodium naphthalene, Styrene, living polymerization conception

60's, commercial products were available

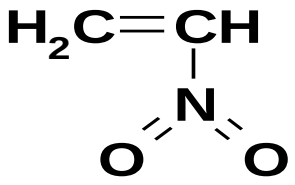
90‘s, study on the living polymerization of polar monomers

Alkenes with electron Withdrawing Groups undergo anionic polymerization

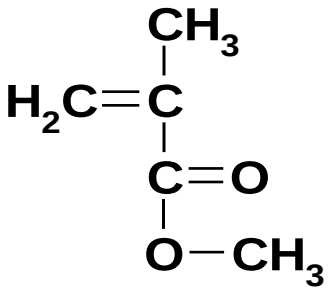
examples



Acrylonitrile

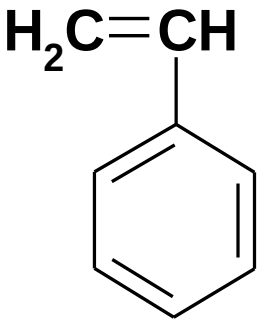


Nitroethene

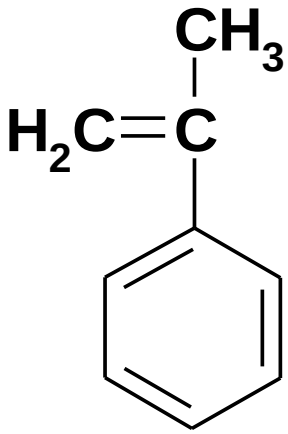


Methyl methacrylate

Classical Monomers



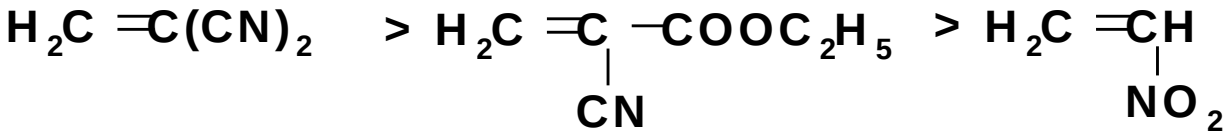
styrene



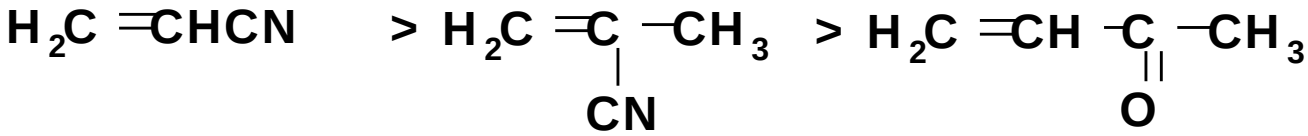
α-Me-styrene

Reactivity of monomers

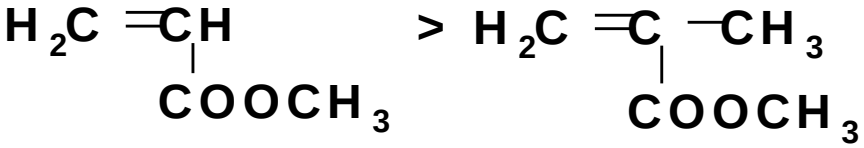
Group A:



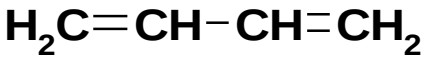
Group B:

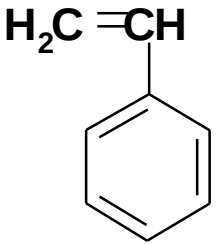


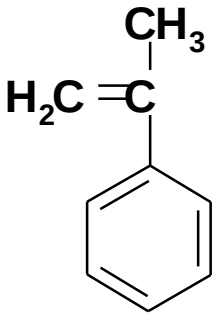
Group C:



Group D:





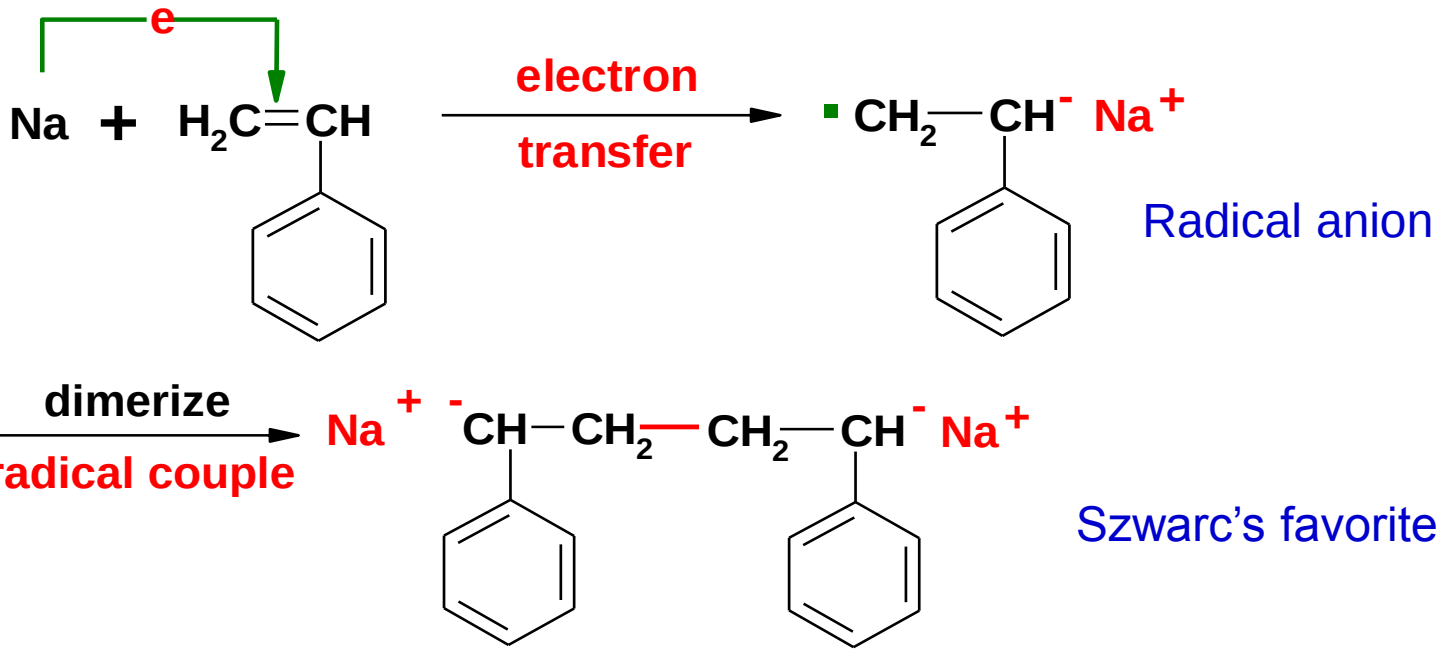


DR. BOHAN
EDGAR ARGO
"HAVE YOU TRIED SUPER GLUE?"

Initiators and initiation

(1) alkali metals ….one electron reductions

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



Break Seal Glassware

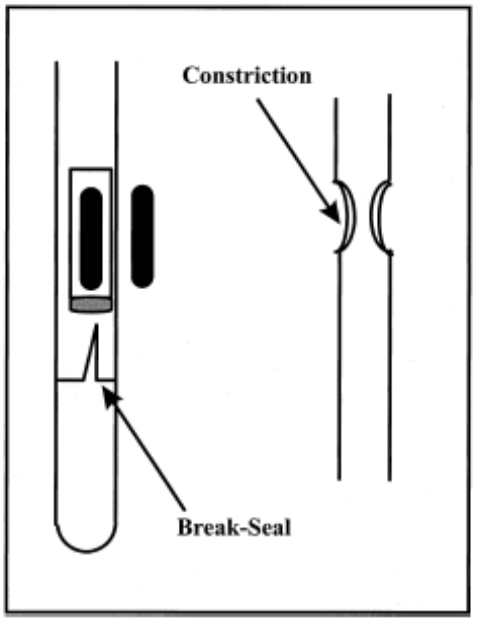


Figure 2. Breaker with break-seal and constriction.

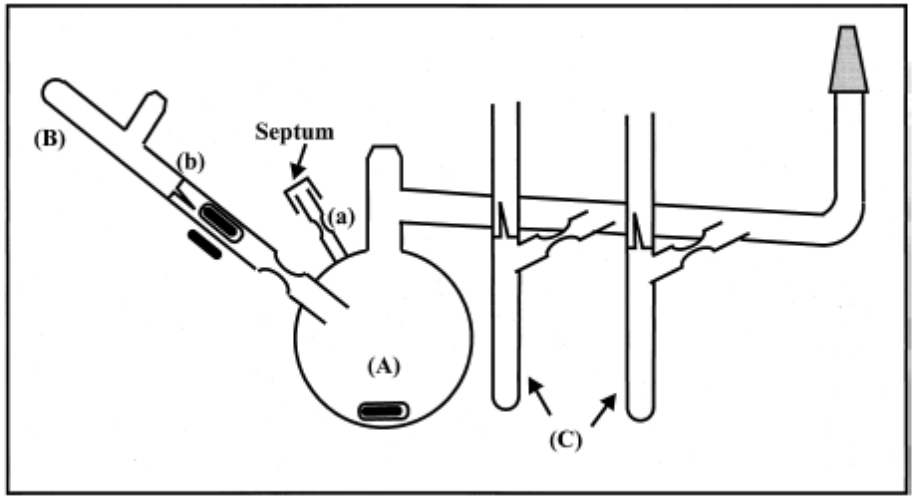
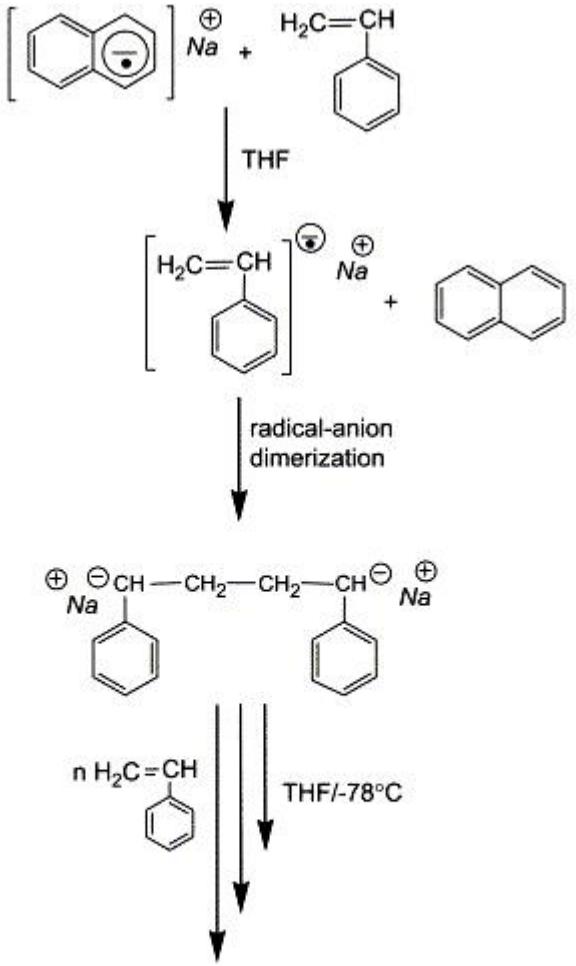
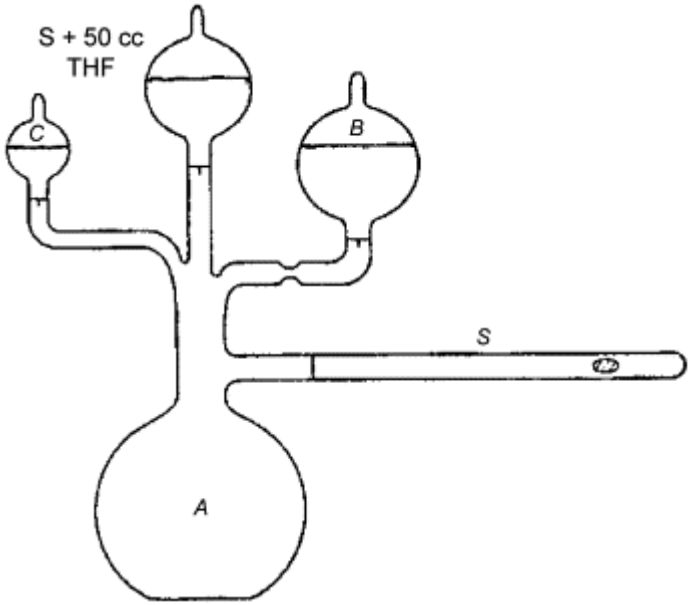


Figure 3. Apparatus for short-path distillation of high-boiling point substances.

Anionic Polymerization Apparatus

Szwarc's Experiment



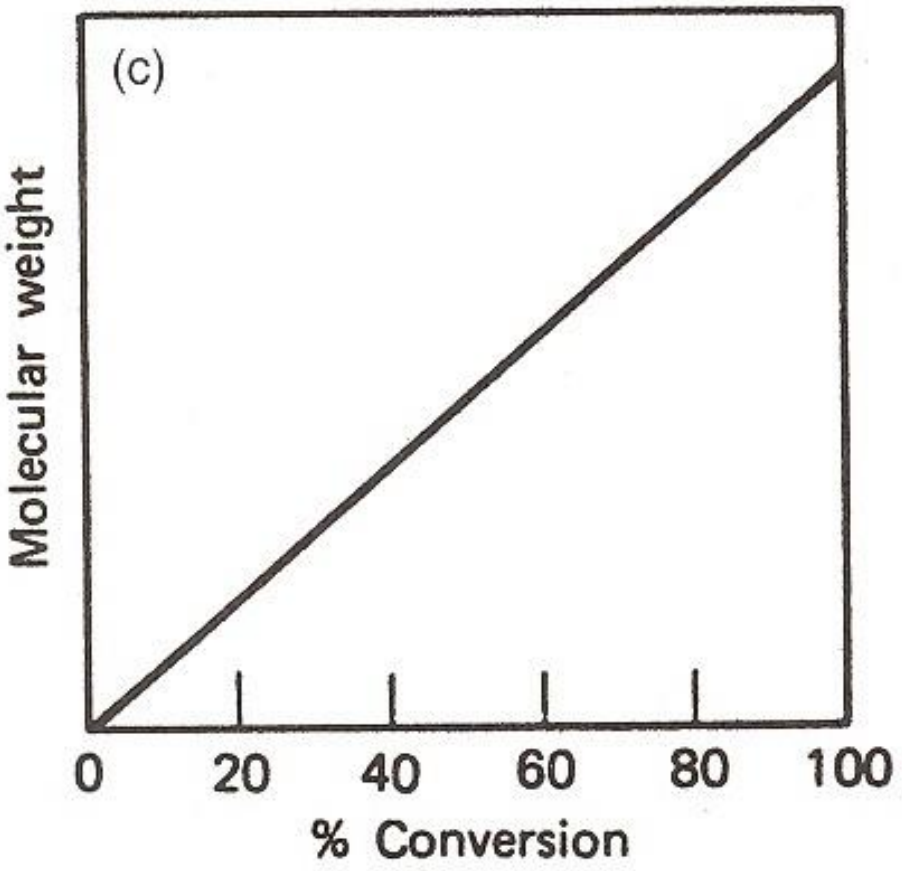


Living test

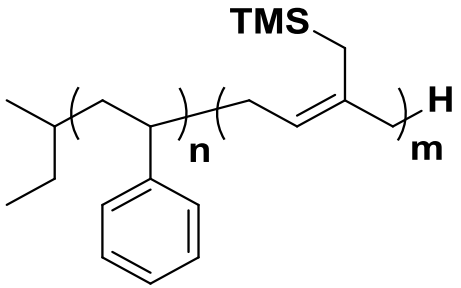
Reddish Orange

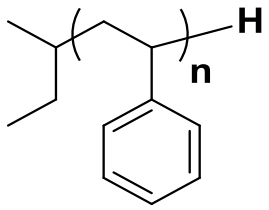
The Living Polymerization

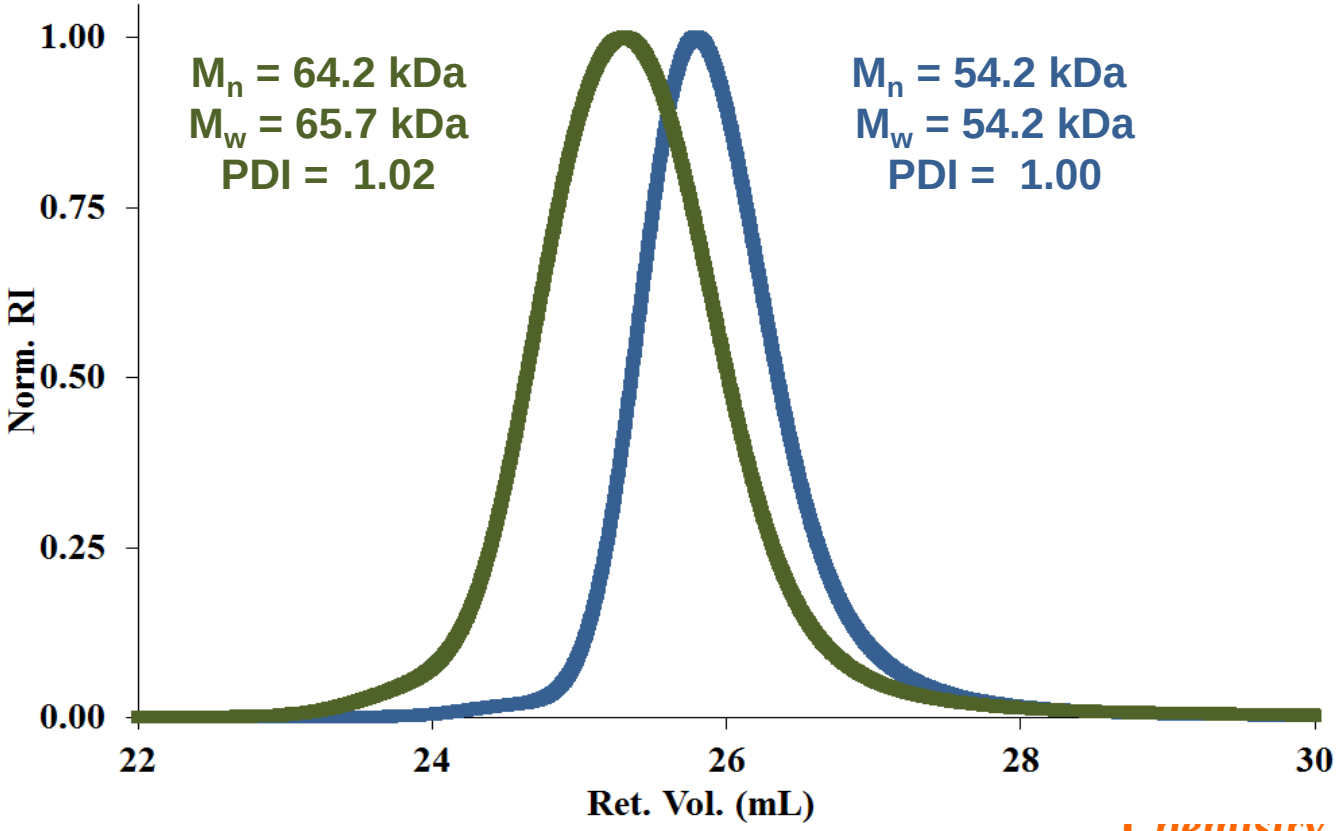
$$DP_{t=\infty} = \frac{[M]}{[I]}$$



Anionic Polymerization of diblock copolymer

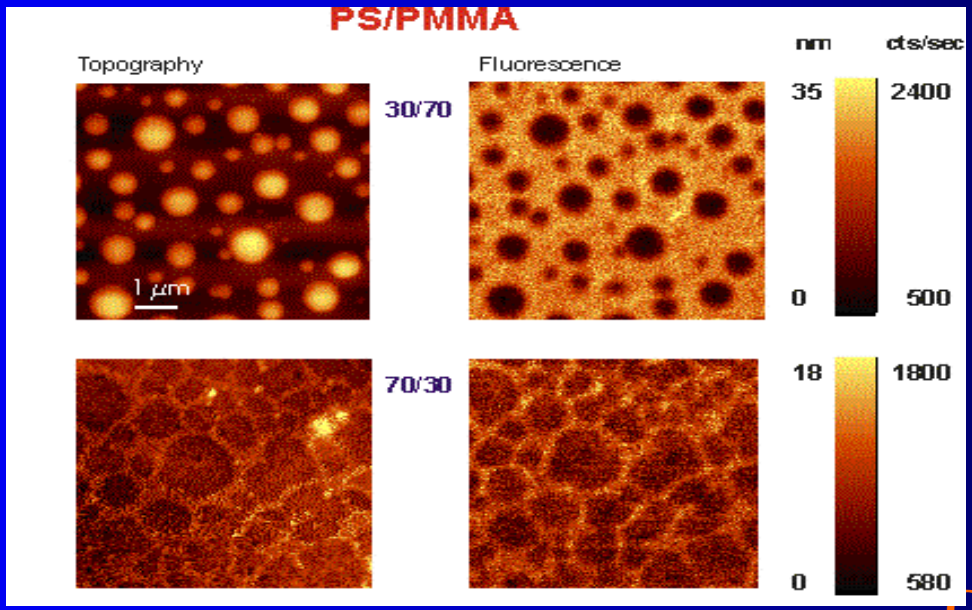






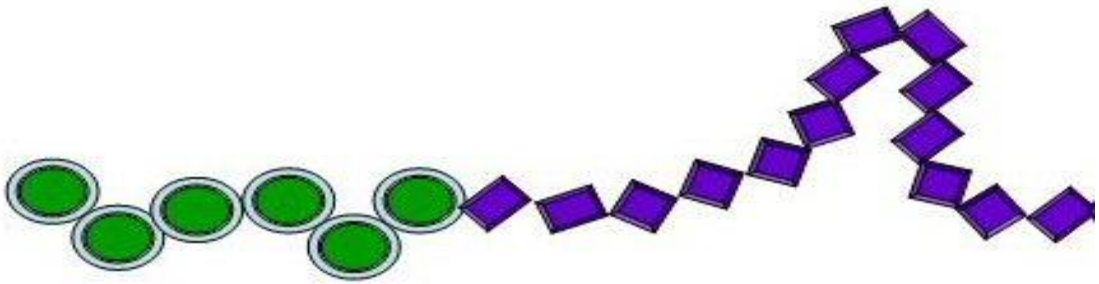
Polymer Blends

- 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.

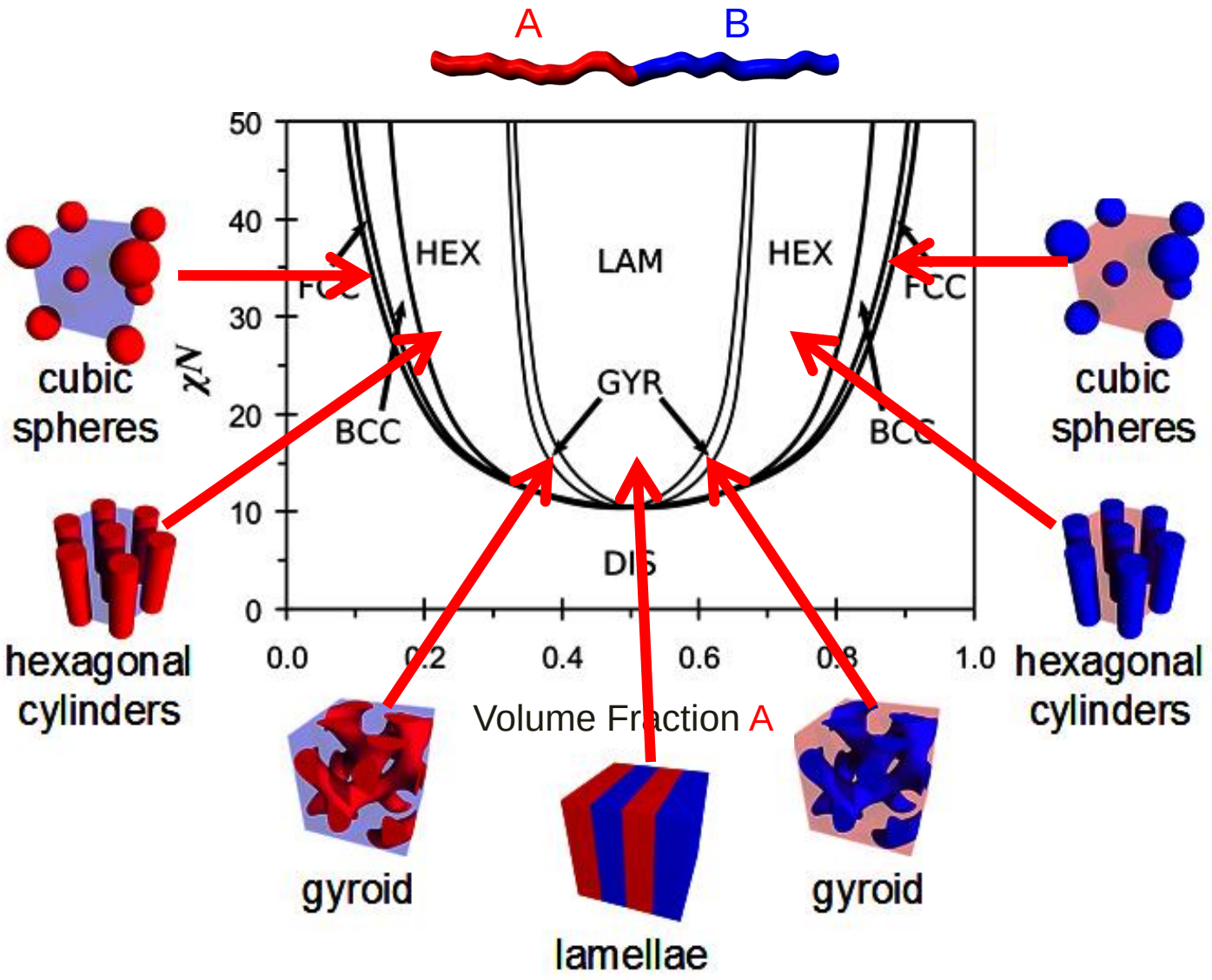


Block co-polymers

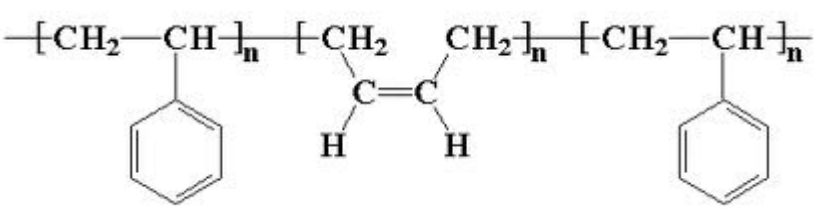
- Covalent linkage of two or more polymers that are intrinsically incompatible.
- Synthesis requires “special” techniques.

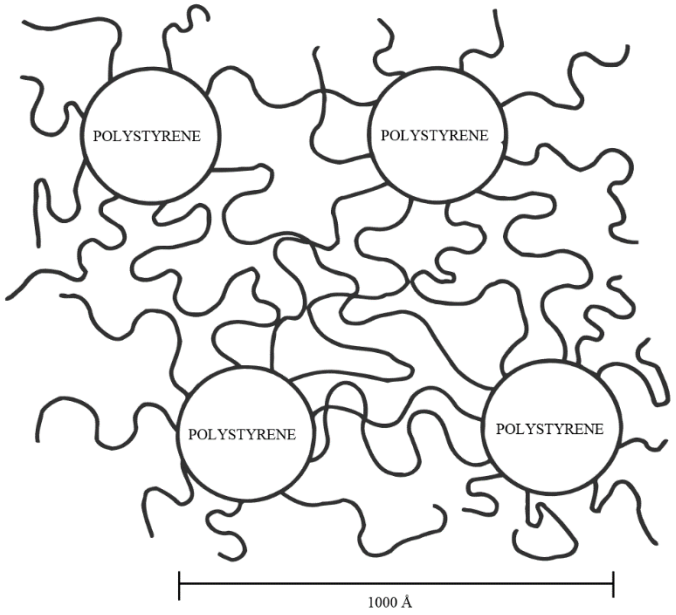


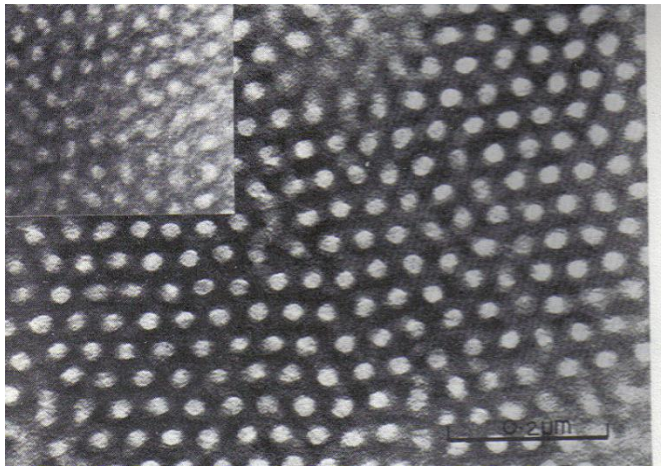
Miracle of Block Copolymers



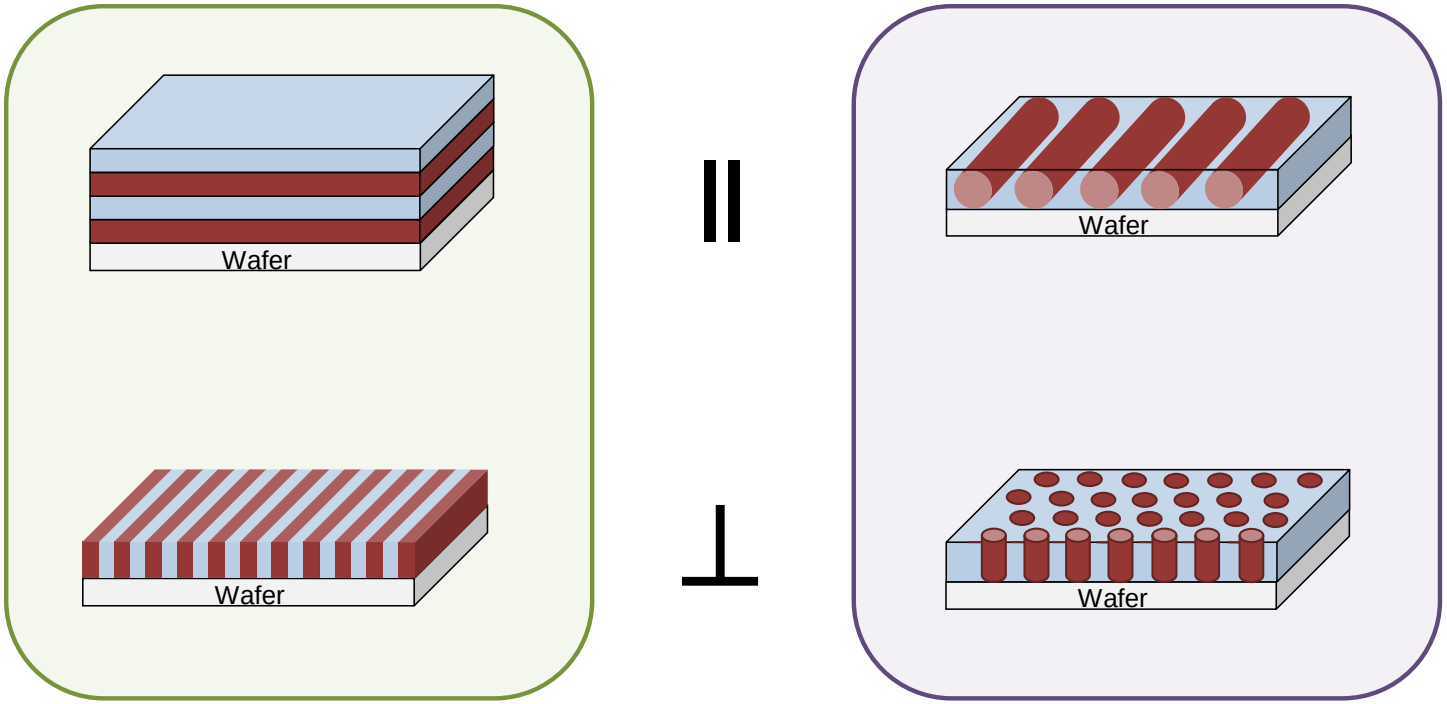
SBS Thermoplastic Elastomer







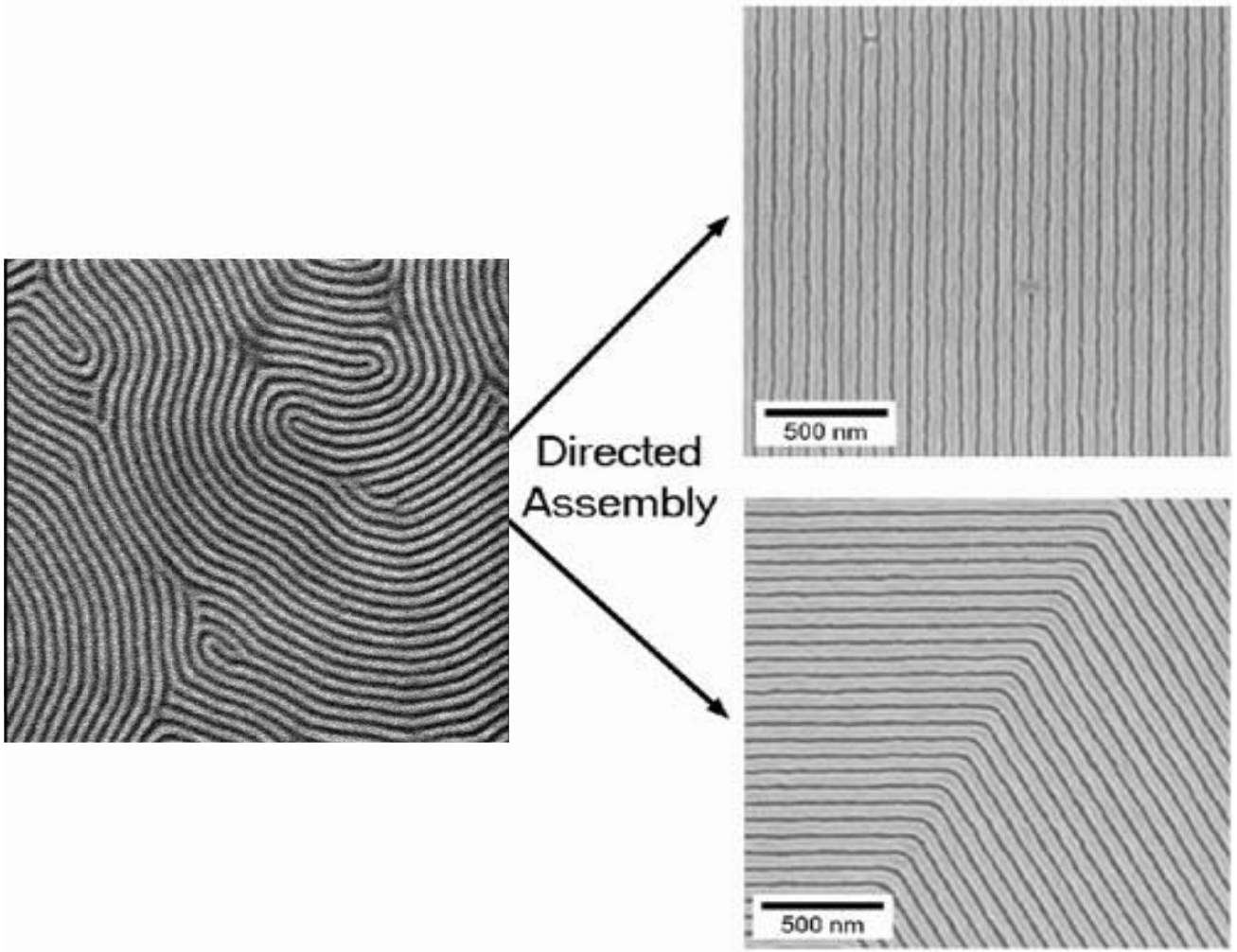
Orienting Block Copolymers



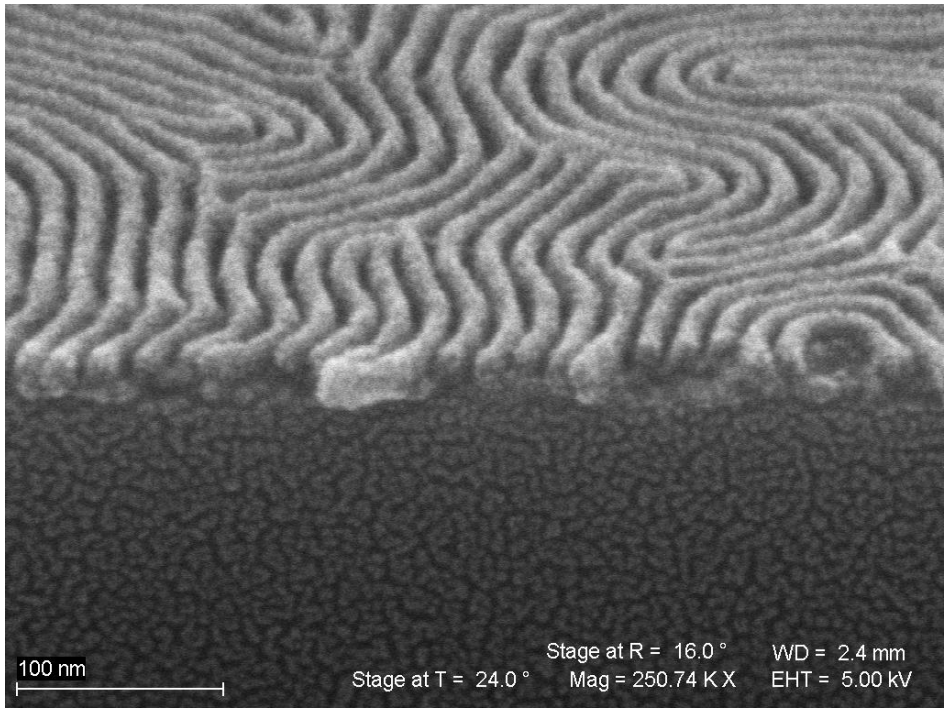
Lamellae

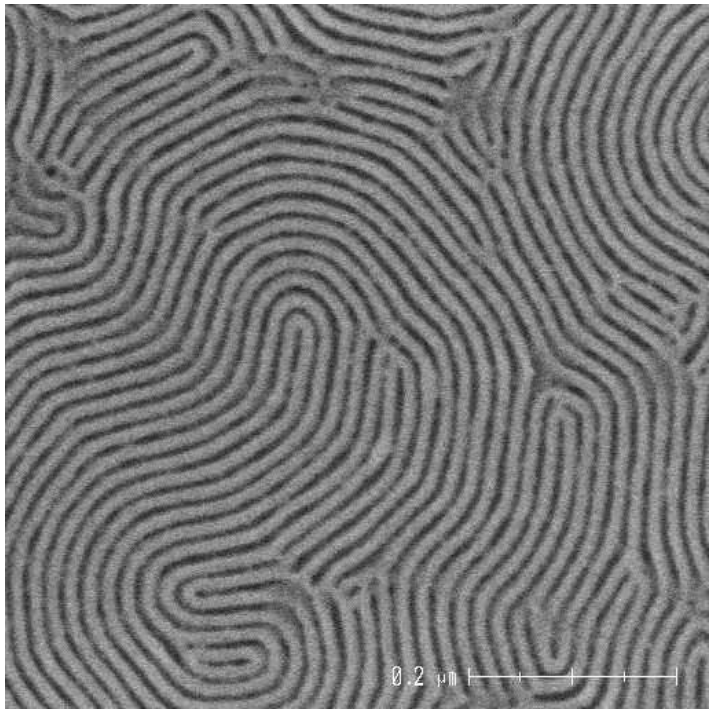
Cylinders

Directed self-assembly



8nm lines in block copolymers





Arthur K. Doolittle Award

The Arthur K. Doolittle Award, established by the Union Carbide Corporation, is given to the authors of an outstanding paper presented before the PMSE Division at each national meeting of the ACS. A prize in the amount of $1,000.00 is financed with the gift of royalties from A. K. Doolittle's book, *Technology of Solvents and Plasticizers*. All papers are evaluated on the basis of content, with emphasis on originality and development of new concepts, and on the quality of presentation. Recipients are selected by an anonymous panel of judges appointed by the Chairman of the Doolittle Award Committee.