

# Definitions:

Greek

Polymer  $\Rightarrow$  Poly = many mer  $\Rightarrow$  meros = units  
many units IUPAC  $\Rightarrow$  A substance composed of macromolecules

Monomer  $\Rightarrow$  One unit

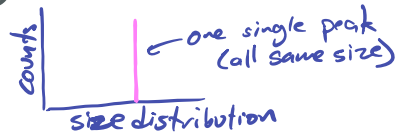
Oligomer  $\Rightarrow$  Oligos = "few" = Few units

Macromolecule  $\Rightarrow$  A molecule of high molecular mass composed of units of low molecular mass

Two types:

- Biopolymers: All macromolecules are composed of the same monomer sequence & molec. mass.

Nature:



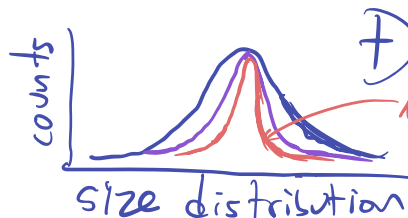
Dispersity  $\downarrow$   
 $\overline{D} = 1$

- Synthetic polymer: Contains a distribution of molecular weights & sequence

Laboratory:



Various sizes per batch.



$\overline{D} > 1.01$

Narrow distribution

How to draw a polymer

Linear

coiled

flexible  
Rigid

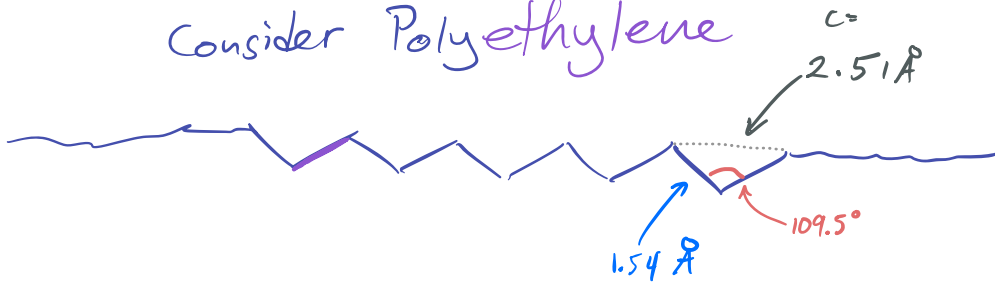
entangled

cross-linked

How Long is a polymer?

$$c^2 = a^2 + b^2 - 2ab \cdot \cos(109.5)$$

Consider Polyethylene



$$\text{CH}_2\text{CH}_2 = \underline{\underline{28 \text{ g/mol}}}$$

if  $\text{MW} = 10,000 \text{ g/mol} \Rightarrow 357 \text{ monomers}$

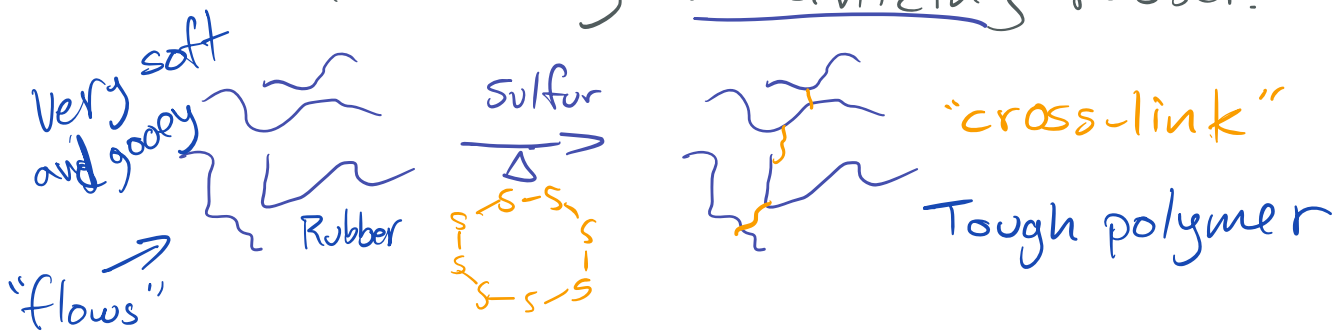
(or  $10 \text{ kg/mol}$ )

$\therefore$  the length = 90 nm

History: 1200-400 BC: Olmecs began to use Natural Rubber from the "Rubber Trees".

mesoamerica: "inhabitants of the rubber country"

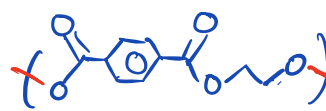
in 1839 = Charles Goodyear solved the "sticky gum" Problem by vulcanizing rubber.



1920: First time that polymers are considered to be large covalent molecules

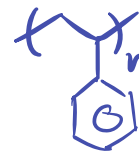
(Hermann Staudinger)

# Current Commodity Plastics



Smallest Repeat unit

number of repeat units



See Bruice, 27.3, pg 1184 for nomenclature.

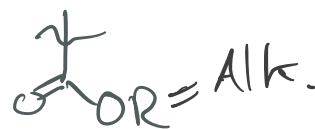
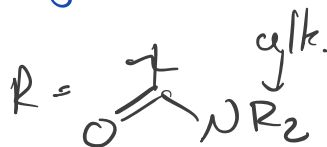
Two classes of Polymerizations:

A Chain Growth & Step Growth

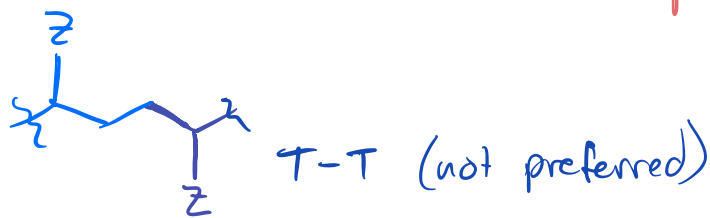
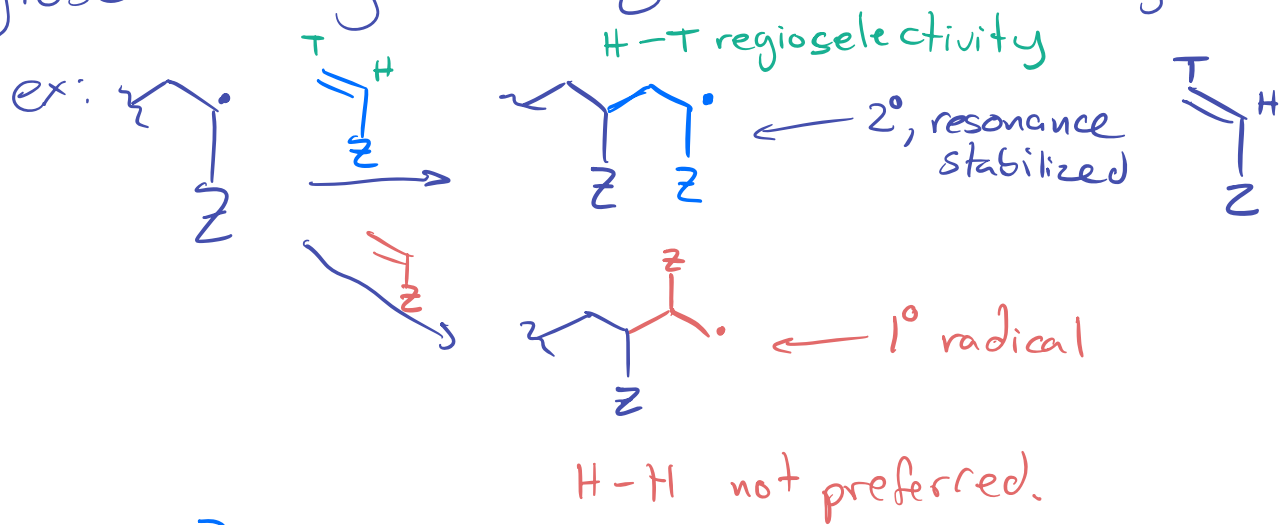
1) Controlled Radical Polymerization

Wow

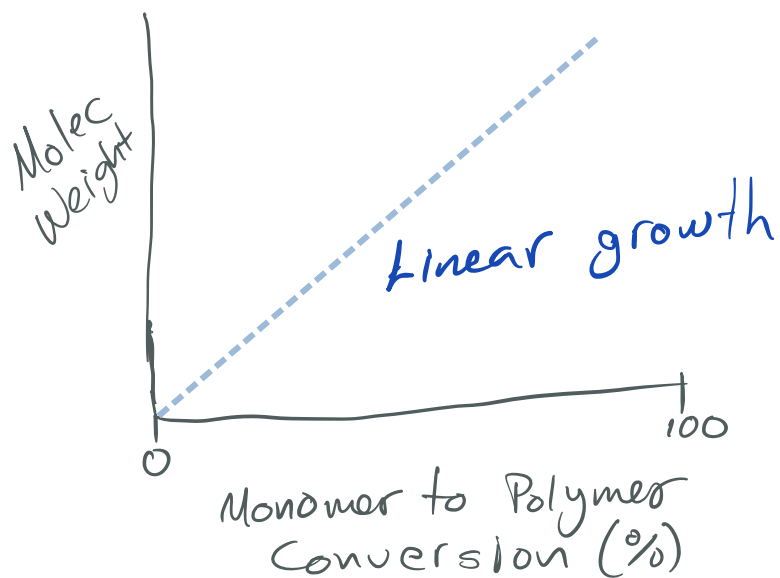
Types of monomers: Acrylamides & Acrylates



# Regioselectivity driven by radical stability.



## Kinetics of Polymerization:- controlled.



Because it's uncontrolled:



Average number molecular weight  $M_n$

(obtained by size exclusion chromatography)

COPOLYMERS allow us to tune the physical & mechanical properties: PS  $\Rightarrow$  stiff & Brittle

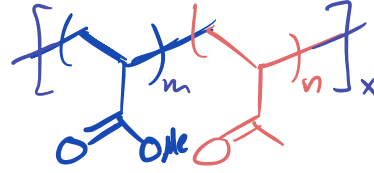
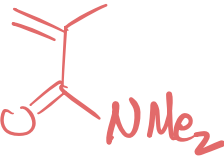
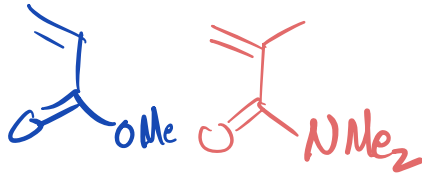
PnBA  $\Rightarrow$  Goopy

methyl acrylate.

thioxanthone

TX

Statistical (Random)



softer, more pliable

N,N-dimethyl acrylamide



ex  $\begin{matrix} 0+0 \\ m=9 \\ n=11 \\ x=20 \end{matrix}$

Poly(dimethylacrylamide-co-methyl acrylate)

or

P(DMAA-co-MA)

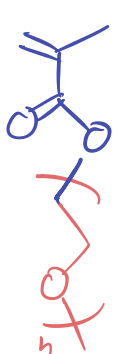
Side note

if perfectly alternating:

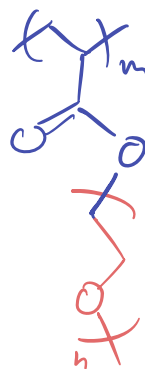
ABABABABABAB

Poly(A-alt-B) name.

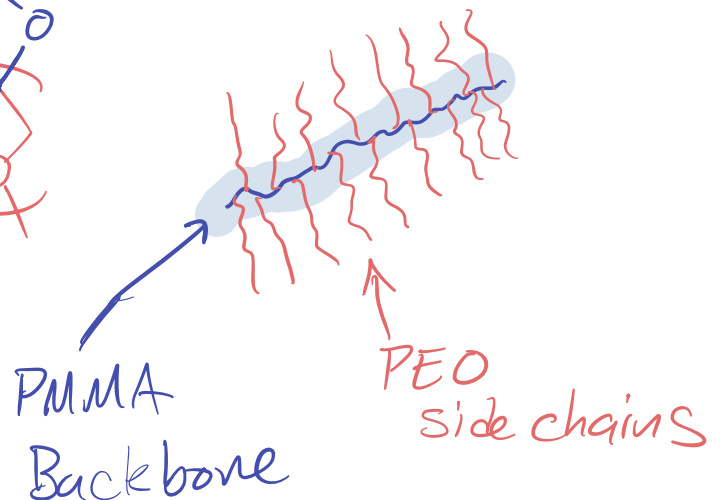
Controlled radical polymerizations  $\Rightarrow$  New architectures



"CRP"



"Graft copolymer"



# Ionic chain-growth polymerization

- cationic
- Anionic

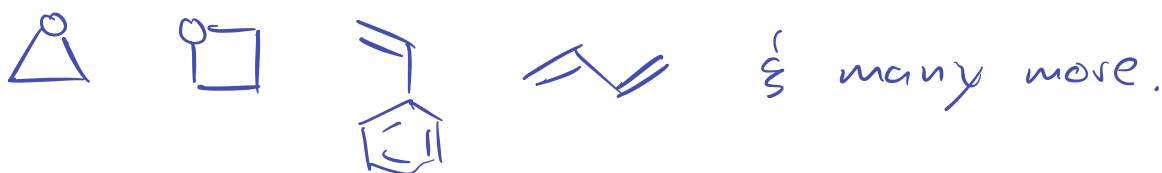
Cyclic ethers

Wow 2

Need: initiator ROH

R = H, Alkyl, Aryl, Vinyl

Monomers: Many options. Examples



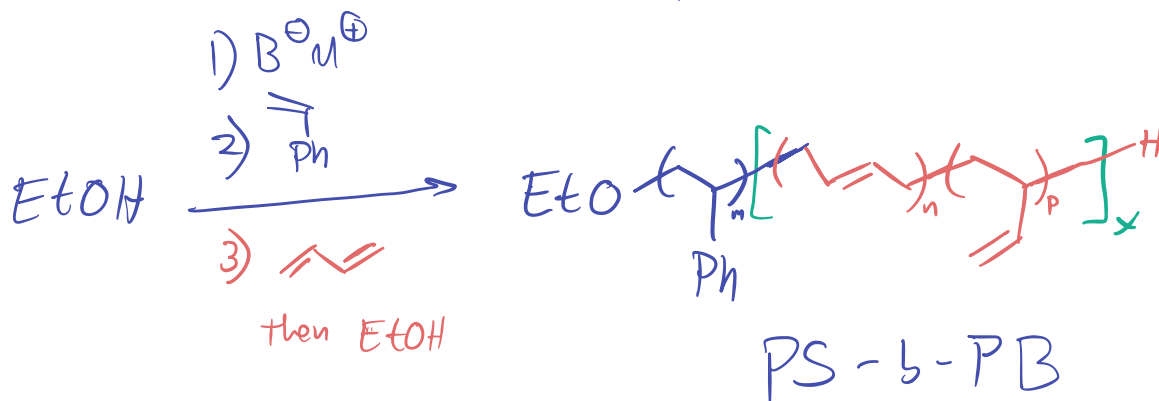
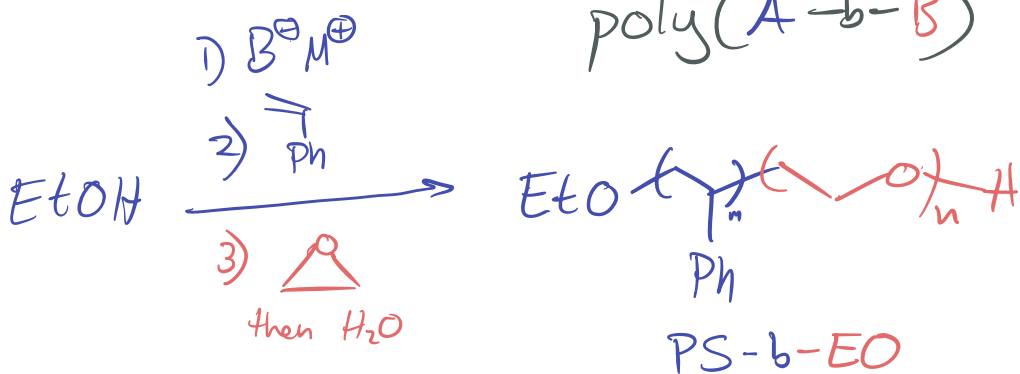
Block Copolymers!



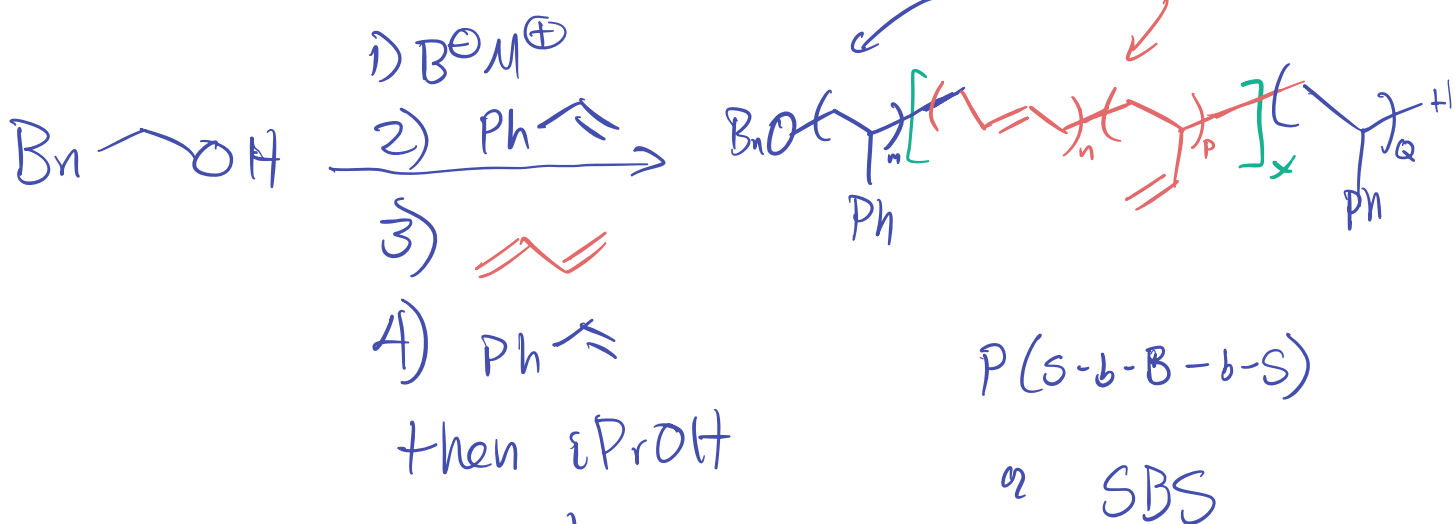
$\text{poly}(A-b-B)$

Diblock  
Copolymer

ex.



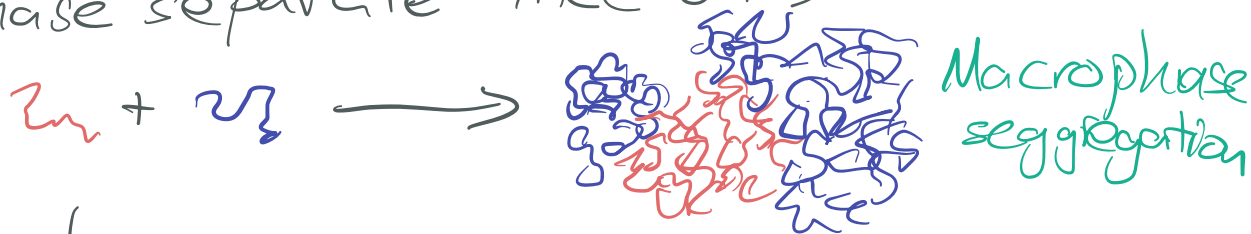
# Triblock Copolymers



Why do we need  
multiblock copolymers?  
- different polymers  
that are covalently bound.

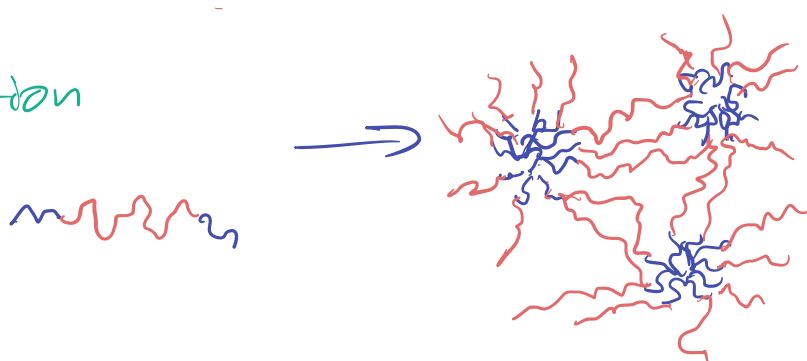
Used in a lot  
of materials,  $\phi$   
including shoe  
soles

If two different polymers are mixed,  
they phase separate like oil & water.



If covalent:

microphase  
segregation



PS = Links &  
holds the  
strands

PB = Bouncy,  
rubbery