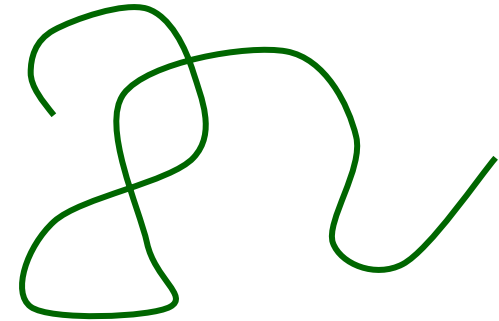


Polymers: an overview

Polymers are long molecules

They can be flexible (e.g., silicone polymers).



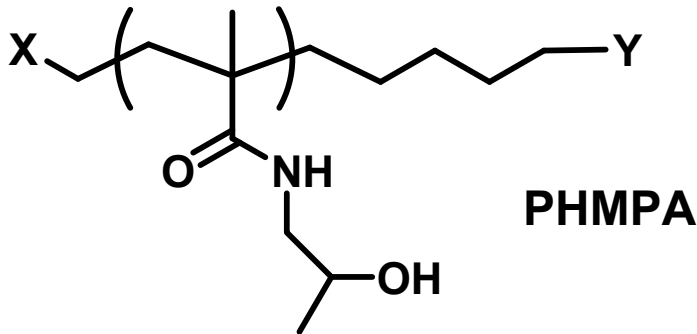
They can be stiff (DNA, polysaccharides), with periodic conformations such as helices, or random conformations.



All of their interesting properties derive from the fact that the monomer units act cooperatively because of backbone connectivity.

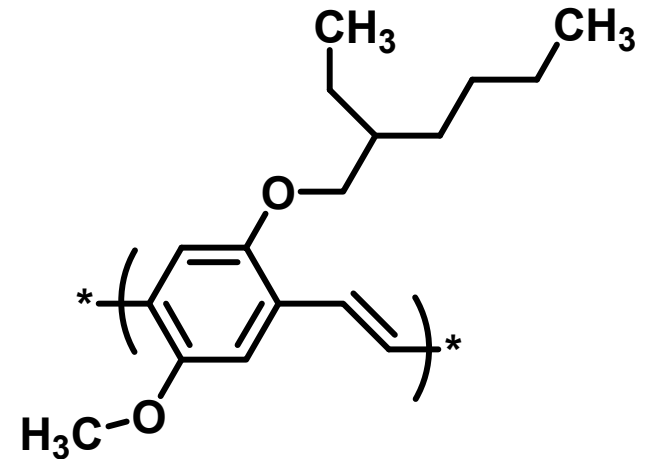
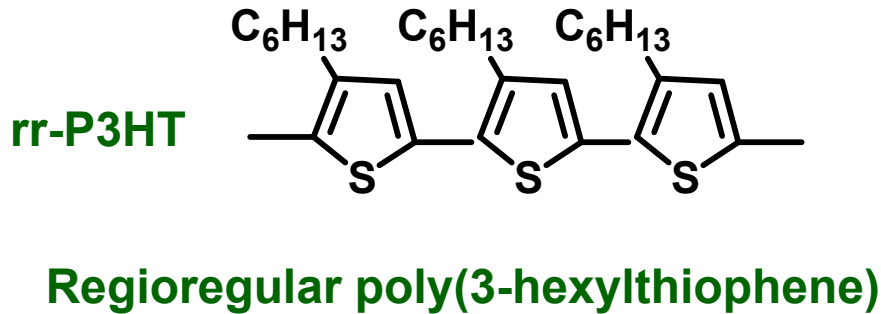
Some functional polymers

Poly(hydroxypropyl methacrylate)



a biocompatible polymer

Conjugated polymers



Classifying polymers by their properties

Plastics (hard)

They can be semi-crystalline or amorphous (glassy).

Thermoplastics will flow under shear when heated. They can be compression- or injection- molded.

Thermosets will not flow when heated. The monomers (or pre-polymers) are 'cured' in a mold ('RIM').

Elastomers (soft)

Rubbery cross-linked solids that will deform elastically under stress.

Thermoplastic elastomers are a special type of elastomer in which the cross-linking becomes reversible upon heating.

Solutions

Viscosity modifiers, polymeric surfactants, lubricants.

Polymer Chemistry, Part I

We will focus on how polymers are synthesized and the mechanisms of different polymerization methodologies.

Condensation (step-growth) polymerization

Anionic polymerization

Free radical polymerization

Controlled radical polymerization

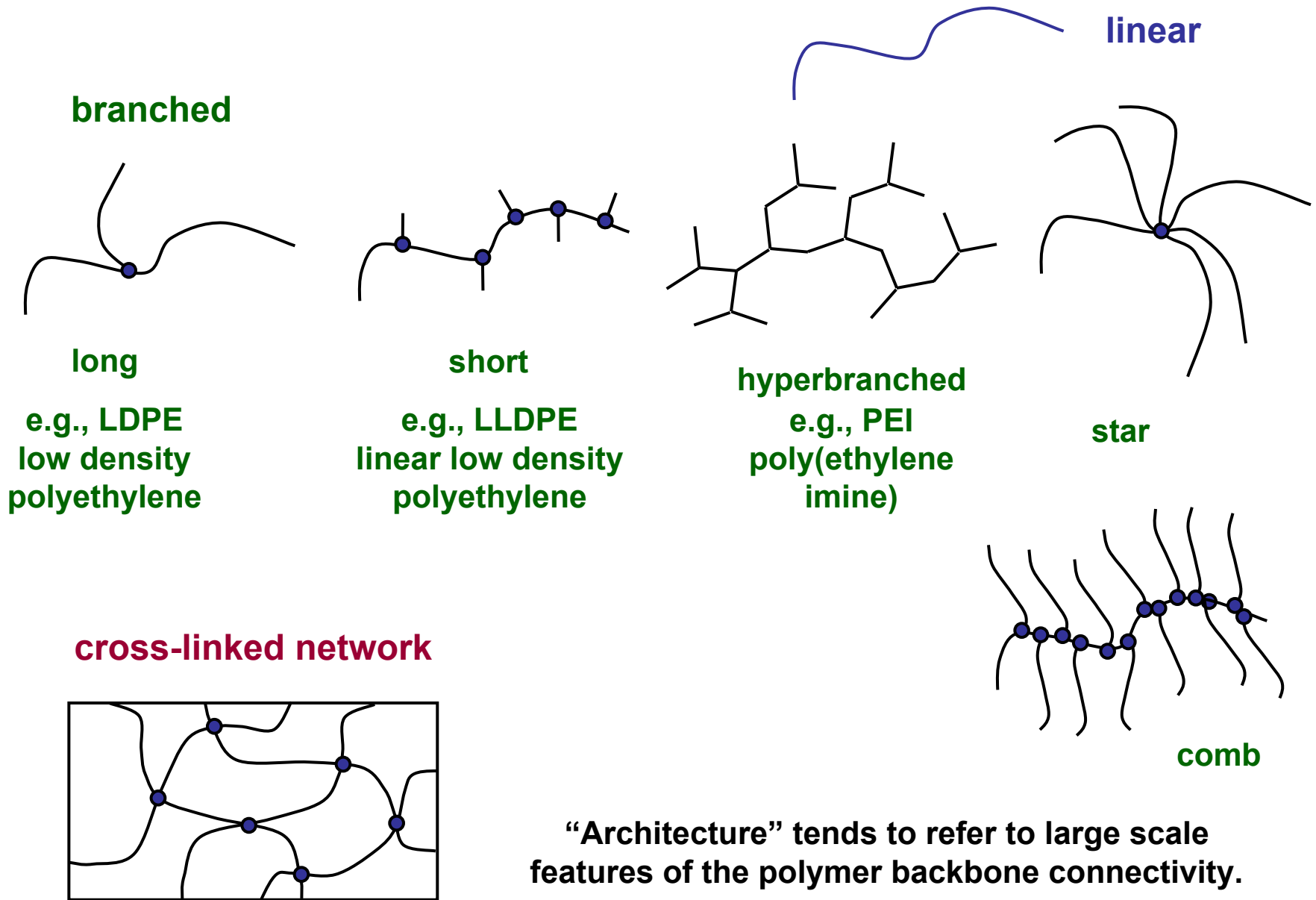
**Catalytic Ziegler-Natta and metathesis
polymerization of olefins**

Ring-opening metathesis polymerization

We will pay particular attention to how the polymerization mechanism affects the groups on the ends of the polymer molecules.

But first, some general principles.

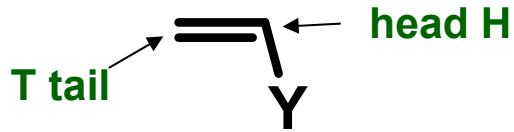
Polymer architecture and microstructure



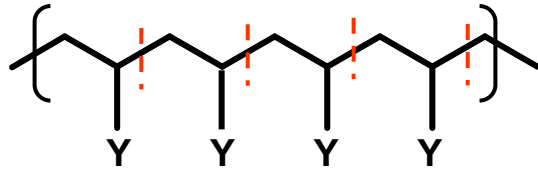
“Architecture” tends to refer to large scale features of the polymer backbone connectivity.

Polymer microstructure

monomer

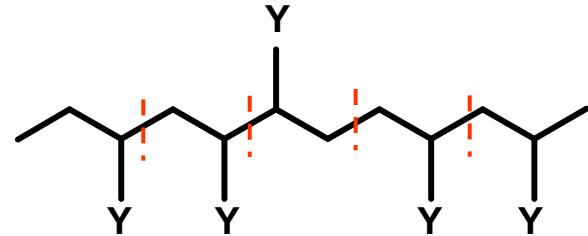


“Microstructure” tends to refer to details of the local chemical structure.



HT HT HT HT

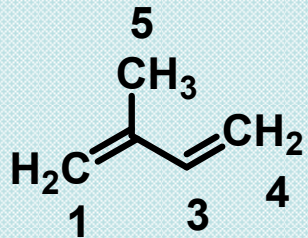
most polymers form as HT sequences



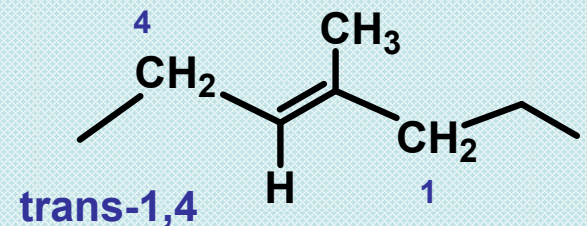
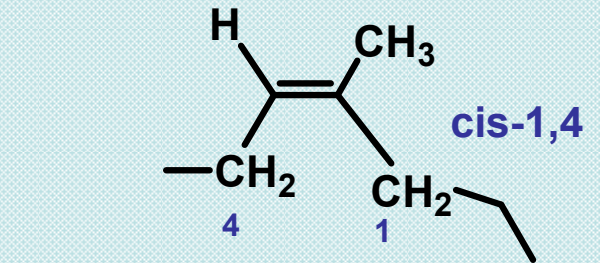
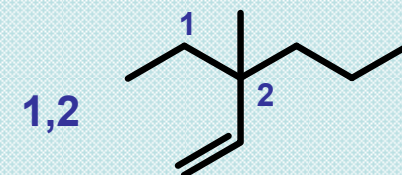
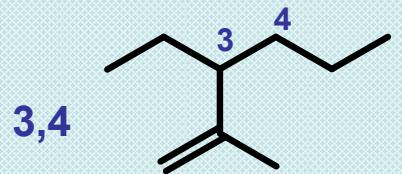
HT HH TT HT

here we have HH and TT defects

diene monomer

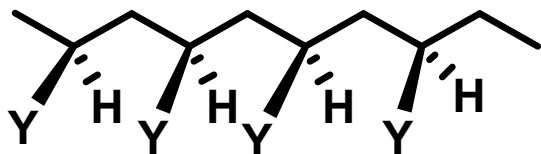


isoprene

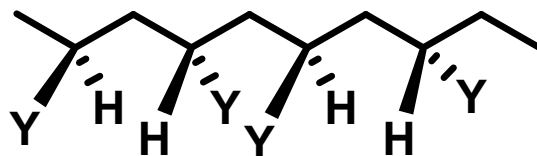


Polymer microstructure

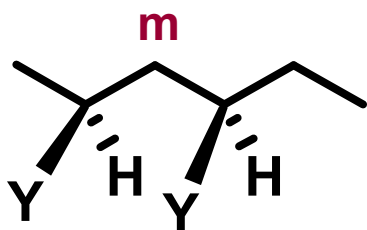
TACTICTY



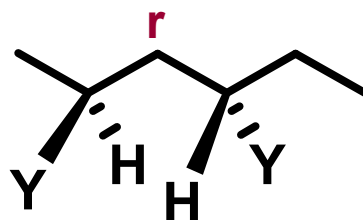
isotactic



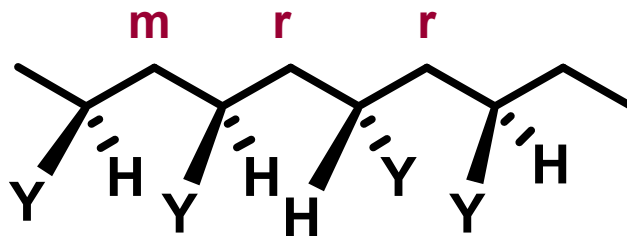
syndiotactic



meso dyad



racemic dyad



atactic

Polymer microstructure

COPOLYMERS

alternating

A-B-A-B-A-B-A-B-A-B

random (statistical)

A-B-B-A-B-A-A-B-A-A-A-A-B-B-A-B

block

A-A-A-A-A-A-A-B-B-B-B-B-B-B

diblock copolymer

A-A-A-A-A-A-A-B-B-B-B-B-B-B-A-A-A-A-A-A

triblock copolymer

graft

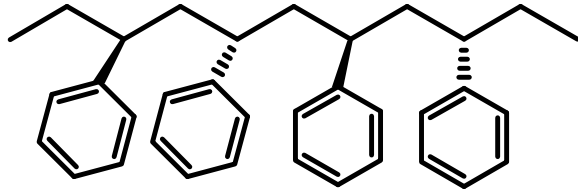
B-B-B-B-B-B-B-B-B-B-B-B-B-B-B-B-B-

A-A-A-A-A-

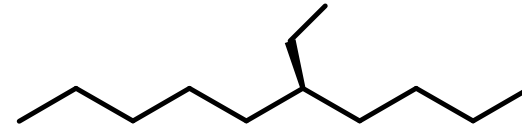
A-A-A-A-A-A-A-A-A-

A-A-A-A-A-

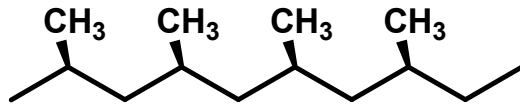
Some examples



syndiotactic polystyrene

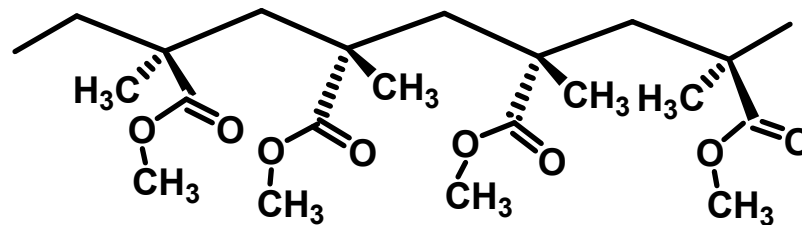


poly(ethylene-co-butene)
LLDPE (EB)

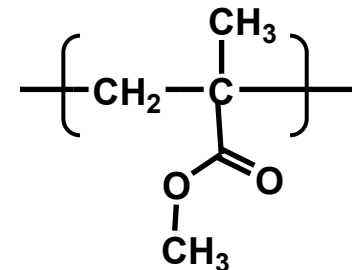


isotactic polypropylene

atactic poly(methyl methacrylate)

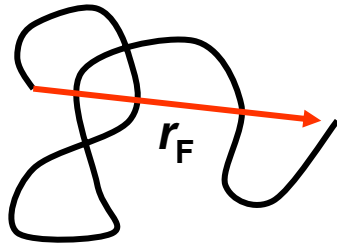
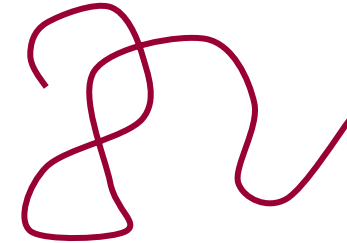


PMMA



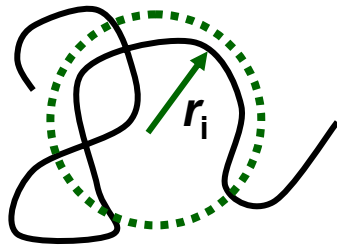
Polymers have a distribution of conformations.

The overall shape is described in terms of the mean dimensions of the molecules.



$$R_F^2 = \langle r_F^2 \rangle$$

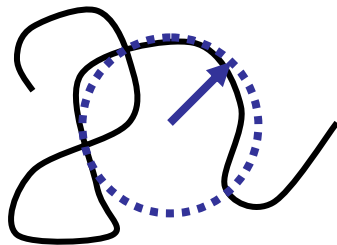
Mean-squared end-to-end length



$$R_G^2 = \frac{\sum_i m_i r_i^2}{\sum_i m_i}$$

Mean-squared radius of gyration

The distribution of mass around the center-of-mass.

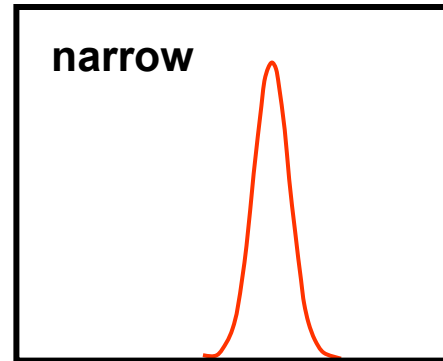
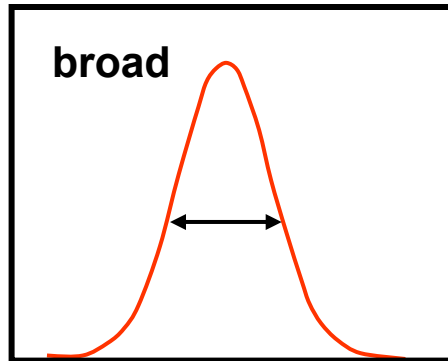


$$R_H$$

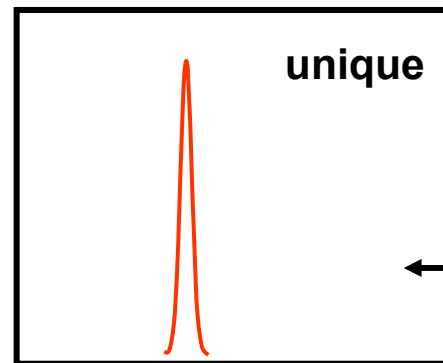
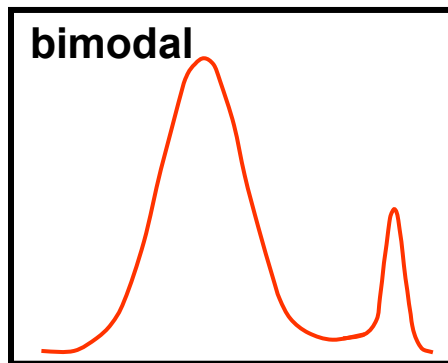
Hydrodynamic radius

The radius of the hard sphere with the same diffusion constant.

Synthetic polymers are characterized by a distribution of molar mass



σ
↔
breadth of the
distribution



Some
biomacromolecules:
proteins, DNA

←

We are interested in various averages over
this distribution: M_n , M_w , M_z
(as well as a measure of the width of the
distribution): (M_w/M_n)

Painter and Coleman notation pp 15 - 17

M_0	monomer molar mass
N_0	number of monomers
N	total number of molecules
N_x	number of molecules of length x
M_x	molar mass of molecules of length x
W_x	weight (mass) of molecules of length x
w_x	weight fraction of molecules of length x
x	length of a given polymer $M-(M)_{x-2}-M$
X_x	number fraction (mole fraction) of molecules of length x
\bar{x}_n	number average degree of polymerization
\bar{x}_w	weight average degree of polymerization

Important relationships

N total number $N = \sum N_x$

X_x number fraction $X_x = N_x / \sum N_x$

w_x weight fraction $w_x = W_x / \sum W_x$

\bar{x}_n number average chain length $\bar{x}_n = N_o / N$

M_n number average molar mass

$$M_n = \frac{\sum N_x M_x}{\sum N_x} \quad M_n = M_o \bar{x}_n \quad M_n = \sum X_x M_x$$

M_w weight average molar mass

$$M_w = \frac{\sum W_x M_x}{\sum W_x} \quad M_w = \frac{\sum N_x M_x^2}{\sum N_x M_x} \quad M_w = M_o \bar{x}_w$$

$$M_x = x M_o$$

$$W_x = N_x M_x = x N_x M_o$$

$$w_x = x N_x M_o / N_o M_o$$

Molar mass distribution

We are interested in various averages: M_n , M_w , M_z

N_x is the number of chains of length x , and M_x is its mass.

$$M_n = \frac{\sum_x N_x M_x}{\sum_x N_x}$$

M_n is the number-averaged molar mass. (1st moment)

$$M_w = \frac{\sum_x N_x M_x^2}{\sum_x N_x M_x}$$

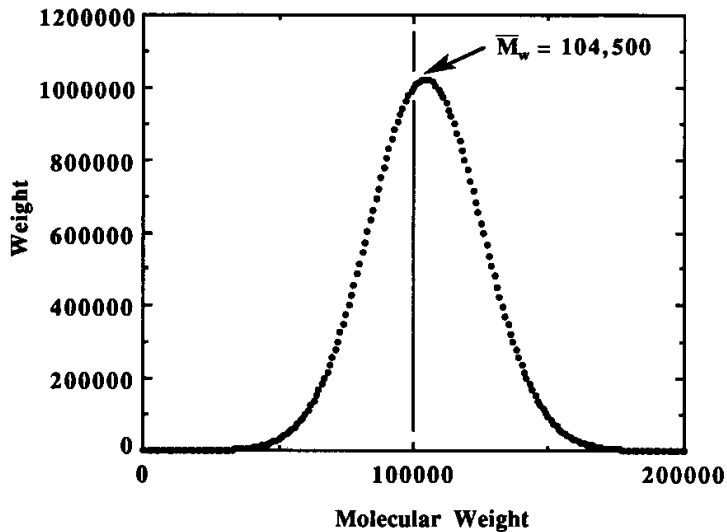
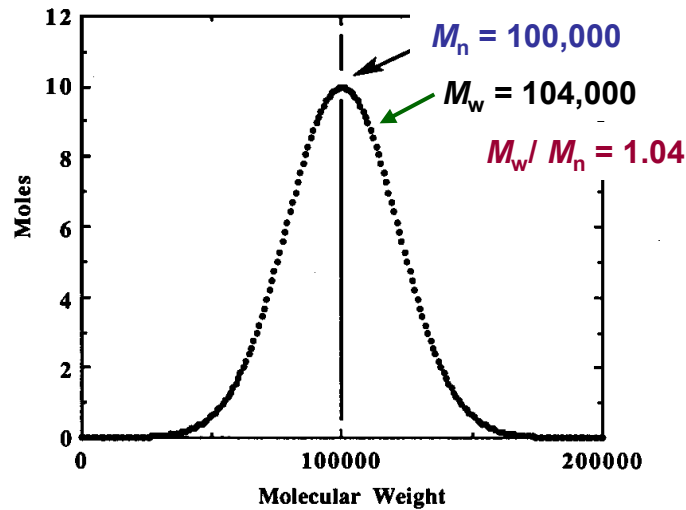
M_w is the weight-averaged molar mass. (2st moment)

$$M_w = \frac{\sum_x W_x M_x}{\sum_x W_x}, \quad \text{and} \quad W_x = N_x M_x$$

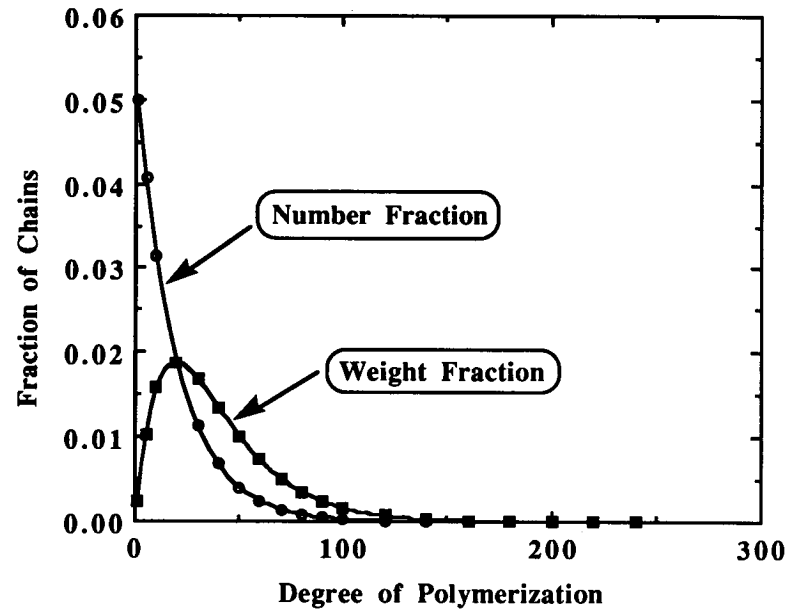
$$M_z = \frac{\sum_x N_x M_x^3}{\sum_x N_x M_x^2}$$

M_z is the 3rd moment of the mass distribution

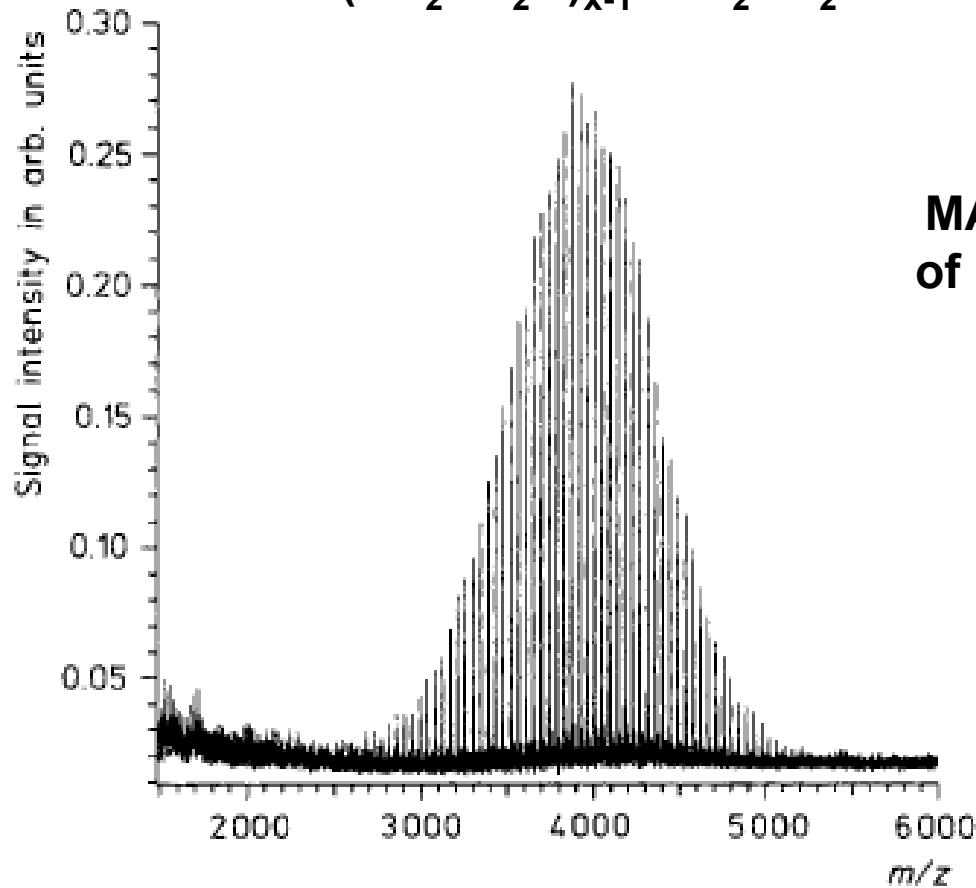
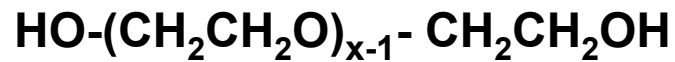
Polystyrene of narrow MWD ($M_w/M_n = 1.04$)



Number and weight distribution ($M_w/M_n = 2$) for a typical step-growth (condensation) polymerization



polyester, polyamide (nylon), ...



**MALDI mass spectrum
of poly(ethylene glycol)
 $M_n = 4000$**

$M_n = 4000$; $M_w/M_n = 1.01$

M_n and M_w

$$M_n = \frac{\sum_x N_x M_x}{\sum_x N_x} \quad M_w = \frac{\sum_x N_x M_x^2}{\sum_x N_x M_x}$$

note that $W_x = N_x M_x$, and that $M_x = x M_0$.

$$M_w = \frac{\sum_x w_x M_x}{\sum_x w_x} = \frac{\sum_x N_x M_x^2}{\sum_x N_x M_x}$$

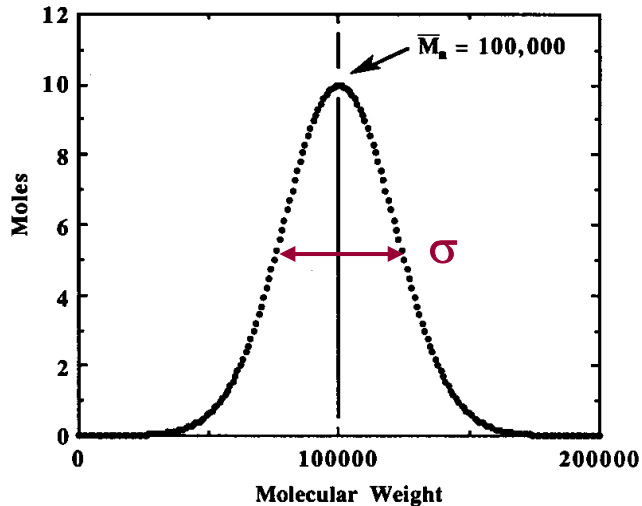
Calculate M_n and M_w for a polymer mixture that contains
10 chains of $M = 1000$ g/mol +
2 chains of $M = 100,000$

$$M_n = \frac{10 \times 1000 + 2 \times 100,000}{10 + 2} = \frac{210,000}{12} = 1.75 \times 10^4$$

$$M_w = \frac{10 \times (1000)^2 + 2 \times (100,000)^2}{10 \times 1000 + 2 \times 100,000} = \frac{2.0 \times 10^{10}}{2.1 \times 10^5} = 9.52 \times 10^4$$

$$M_w/M_n = (9.5/1.75) = 5.5 \text{ (very broad!)}$$

Standard deviation of the mass distribution



$$\sigma^2 = \frac{\sum_x N_x (M_x - \bar{M})^2}{\sum_x N_x}$$

definition

$$\sigma^2 = \frac{\sum_x N_x M_x^2}{\sum_x N_x} - 2\bar{M} \frac{\sum_x N_x M_x}{\sum_x N_x} + \bar{M}^2$$

multiply it out

$$\sigma^2 = (\bar{M}^2 - 2\bar{M}^2 + \bar{M}^2) = \bar{M}^2 - \bar{M}^2$$

key concept

$$M_w = \frac{\sum_x N_x M_x^2}{\sum_x N_x M_x} = \frac{\sum_x X_x M_x^2}{\sum_x X_x M_x} = \frac{\bar{M}^2}{M_n}$$

$$\bar{M}^2 = M_w M_n$$

$$\bar{M} = M_n = \sum_x X_x M_x$$

The important message is that $[(M_w/M_n) - 1]$ is a quantitative measure of the standard deviation of the molar mass distribution in a polymer sample.

$$\left(\frac{\sigma}{M_n}\right)^2 = \frac{M_w}{M_n} - 1$$

Polymer Synthesis: mechanisms and kinetics

Classifying polymers by how they are synthesized

Synthetic polymers (by functional group):

polyamides, polyesters, acrylates, methacrylates, polyolefins,.....

Synthetic polymers (by mechanism):

step-growth, addition, insertion,.....

condensation, free radical, anionic, cationic, metathesis, ring opening

Synthetic polymers (by catalyst):

Ziegler-Natta, metallocene, metathesis,...

Biopolymers (including synthetic polymers made by genetic engineering):

proteins and polypeptides, polysaccharides, polynucleic acids, ...

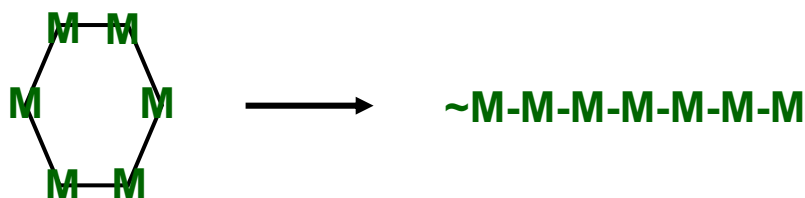
Polymer Synthesis: mechanisms and kinetics

Thermodynamics of polymerization: $\Delta G < 0$

$$\Delta G = \Delta H - T\Delta S$$

ENTROPY

Loss of translational entropy is the largest contributor to ΔS



For some ring-opening polymerizations, $\Delta S > 0$.

ENTHALPY

All successful polymerization reactions: $\Delta H < 0$ and $|\Delta H| > |T\Delta S|$

Rare: $\Delta H \geq 0$, $\Delta S > 0$: e.g., ring opening of cyclo- S_8 .

CEILING TEMPERATURE

The ceiling temperature (T_c) is the value of T where $\Delta H = T\Delta S$.

When $T > T_c$, depolymerization is favored.

Polymer Synthesis: mechanisms and kinetics

Step-growth polymerization

Slow step-by-step growth in chain length

We will examine the kinetics and then use statistical methods to examine the distribution of chain lengths generated.

Free radical polymerization

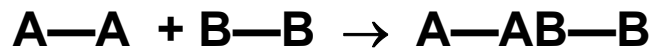
Rapid growth of individual chains throughout the reaction

We will examine the kinetics and mechanism, and then use the kinetics to help understand microstructure for copolymers.

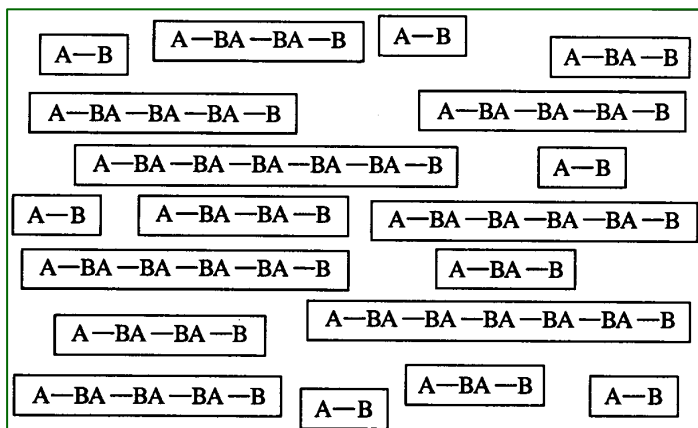
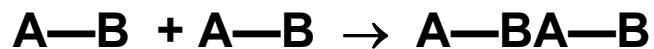
'Living' polymerization

We will have a brief look at anionic polymerization, and a longer look at some mechanisms of controlled radical polymerization to understand how one can prepare polymers of narrow mass distribution.

Step-growth polymerization



or

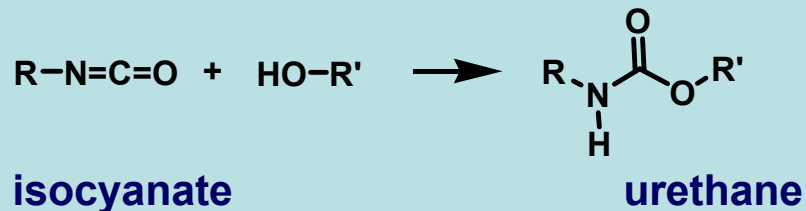
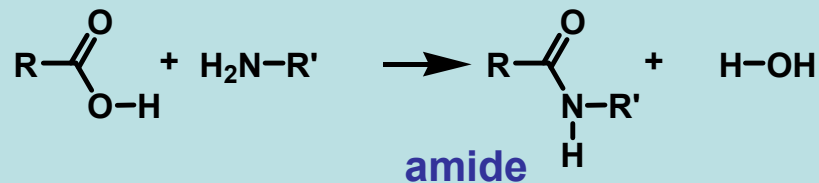
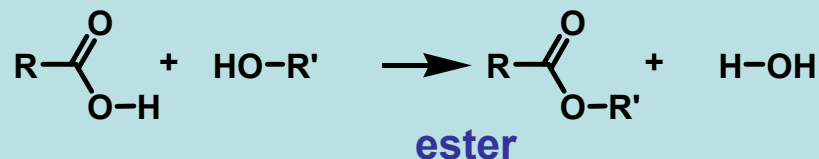


The chains grow from both ends, one step at a time

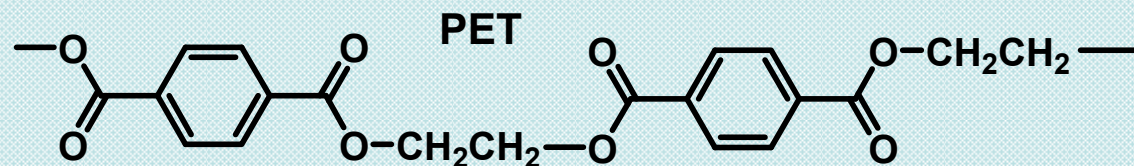
analogous small molecule reaction



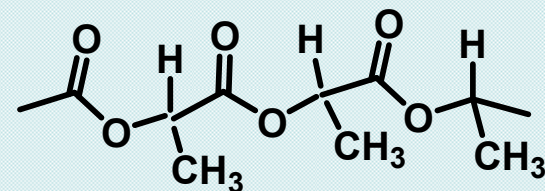
In a condensation reaction, a small molecule is often expelled with each coupling step.



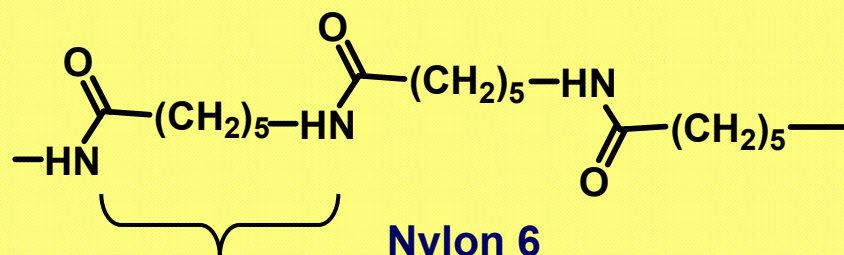
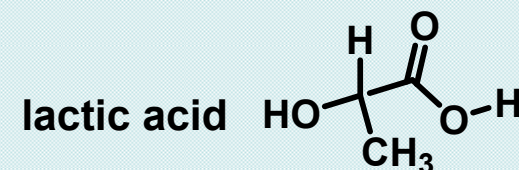
Some polyesters and polyamides



Poly(ethylene terephthalate)

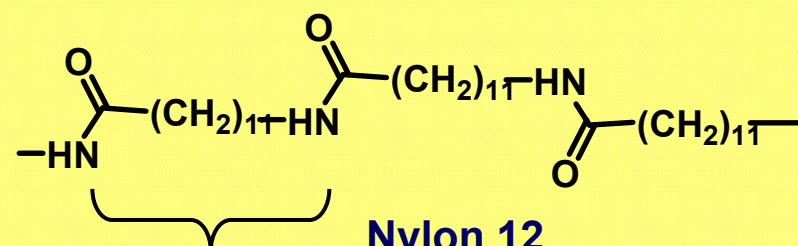


poly(lactic acid)



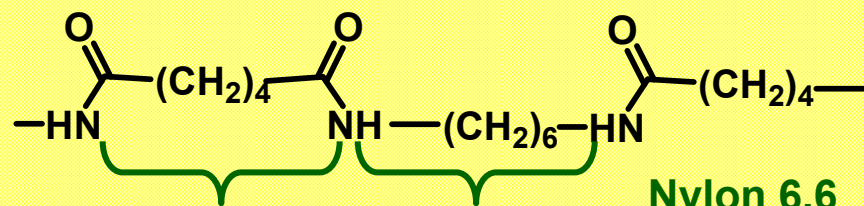
Nylon 6

6 carbons



Nylon 12

12 carbons



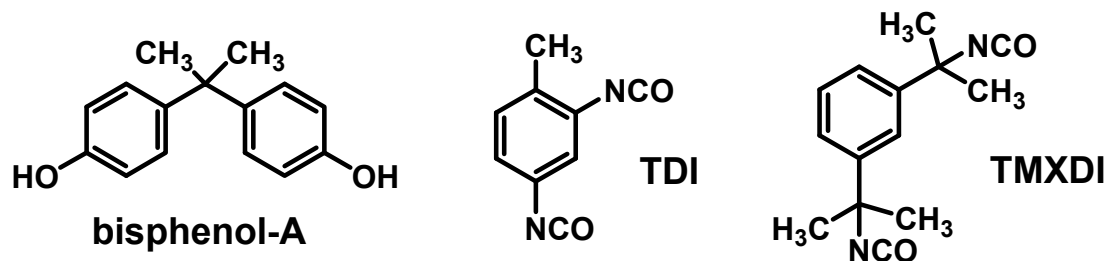
Nylon 6,6

6 carbons 6 carbons

Some exercises **Draw two repeat units**

Draw the structure of the poly(lactic acid) formed by polymerization of R-lactic acid; and of racemic lactic acid.

Polyurethanes formed from aliphatic diisocyanates are much more stable to hydrolysis than those formed from aromatic diisocyanates. Draw the structures of the polyurethanes formed by reaction of polycaprolactone diol with a) toluene-diisocyanate (TDI) and b) tetramethylxylene-diisocyanate (TMXDI).



Bisphenol-A polycarbonate is formed from the reaction of bisphenol-A and phosgene. Draw the structure of this polymer.

What you should know

- **Definitions of M_n , M_w . Relationships on slide 11.**
- **Tacticity: be able to draw a segment of a polymer backbone showing isotactic, syndiotactic, atactic microstructure.**
- **Be able to draw representative structures of a branched polymer, as well as random, alternating, graft and diblock copolymers.**
- **Given a diisocyanate and a diol, be able to draw the structure of the polyurethane they would form.**
- **Be able to draw the structures of PET, nylon 6, nylon 12, nylon 6,6, bisphenol-A polycarbonate**
- **Define ceiling temperature and understand what it means.**