Lecture Notes on Polymer Physics

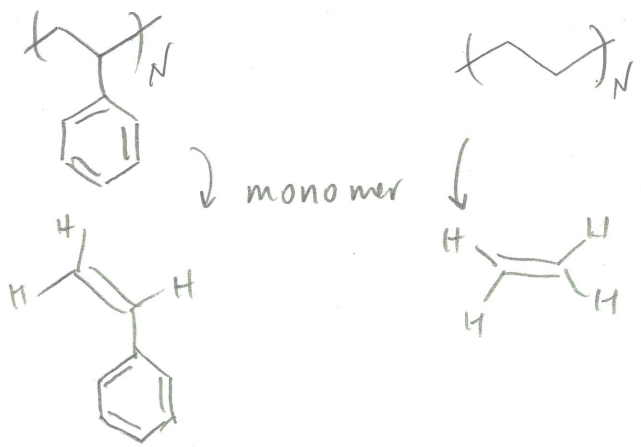
Prepared in Spring 2022

Lecture 1: Introduction

A. Polymers as macromolecules

* Polymers are very large molecules. They are made up of many repeating units. "chain molecules"
  - Poly : many (Greek)
  - meros: parts

Example: Polystyrene, Polyethylene



* Many examples: DNA, proteins, rubber, etc.
* Polymers were "discovered" about 100 years ago (1920). Controversial at first. Nobel prize to Staudinger in 1953.

* N is called the degree of polymerization.

$$N = \frac{M}{M_0}$$

M ← molecule molecular weight

M_0 ← monomer molecular weight

"# of monomers"

"oligomer" → $N < 100$ "oligo" = few (greek)

$N \approx 100$ usually the threshold for polymers

$N \approx 10^4$ is typical for synthetic polymers

$N \approx 10^6$ is not uncommon, esp. for biopolymers

↳ dsDNA of E. coli = 4.6×10^6 base pairs

* Polymers are part of a class of molecules called "macromolecules." Macromolecules are "big" molecules. Sometimes the terms are used interchangably. Sometimes people distinguish other objects (e.g. proteins, lipids) from polymers. I am in the former camp.

B. Polymer Variety

* Polymers can have chemical, architectural, and isomeric variety.

1. Chemical variety

* A polymer made with more than one kind of repeat unit is called a "heteropolymer." A polymer with only one kind of repeat unit is a "homopolymer"

* Heteropolymers with two monomer types are called "co-polymers". Three monomer types = "terpolymer"

2 = copolymer (or bipolymer)

3 = terpolymer

4 = quaterpolymer

and so on.

* The sequence of the chemical structure can be important.

random ...A-B-B-A-A-A-B-A...

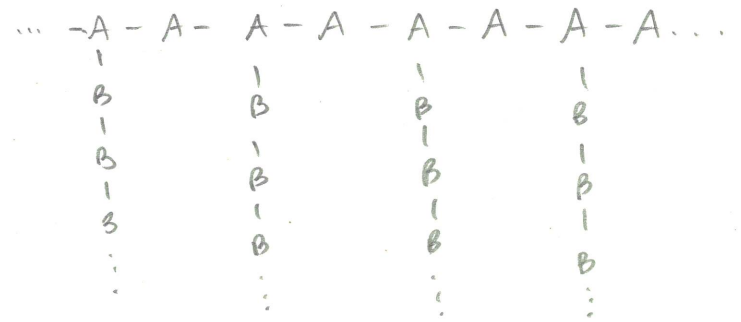
alternating ...A-B-A-B-A-B-A-B...

diblock ...A-A-A-A-B-B-B-B...

triblock ...-A-A-A-B-...-B-A-A-A...

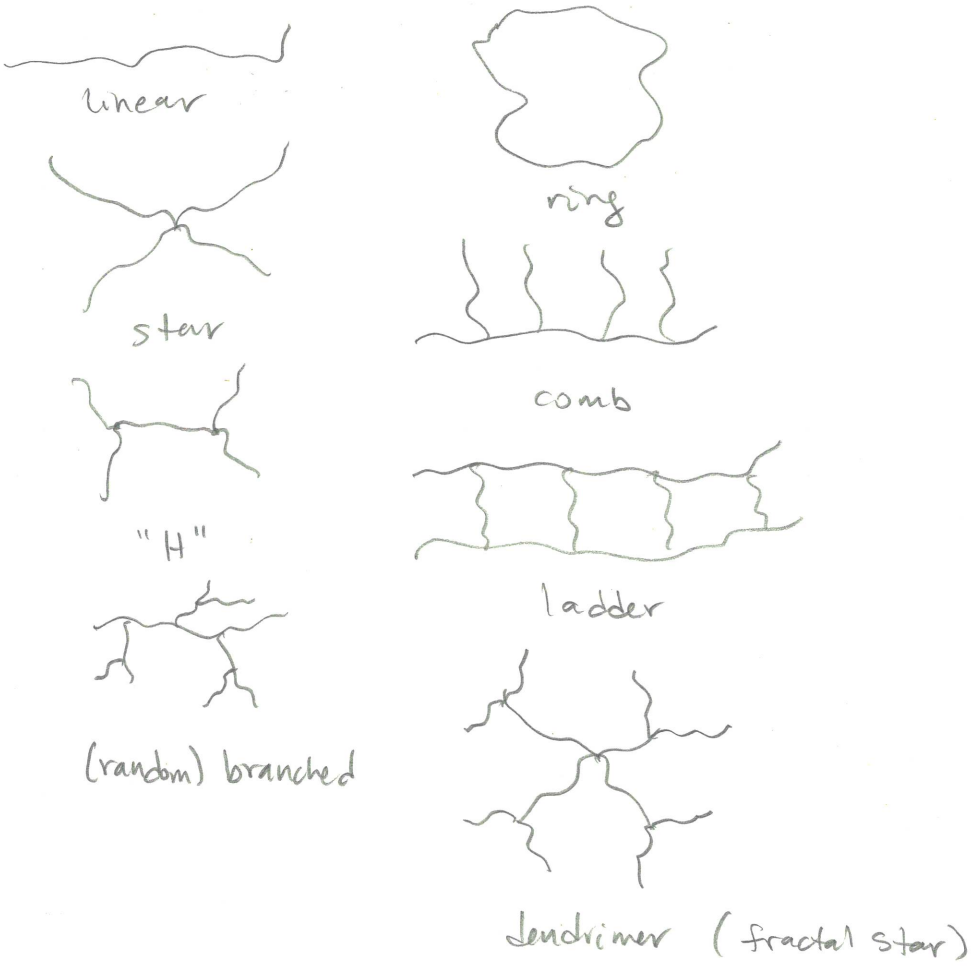
(multiblock also possible)

graft



2. Architectural variety

* Like we just saw with the graft copolymer, polymers can also have non-linear bonding patterns. Let's look at a few examples.



3. Isomeric variety

* Isomers are molecules with the same molecular formula, but a different spatial configuration.

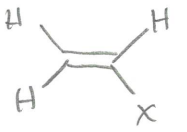
  There are three types of polymeric isomers:

  positional, structural / geometric, stereochemical

* Key concept: polymerization of a monomer "locks in" the spatial configuration of chemical bonds.

* Positional isomers.:

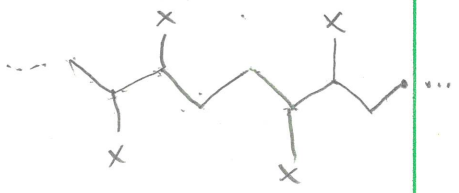
- monomer has an "orientation" with a head & tail:

eg. 

≈ 

- two positional isomers:

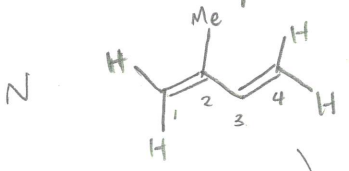
"head-to-tail" 

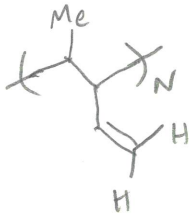
"head-to-head" 

* structural/geometric isomers:

- This isomerism is similar to positional, but monomer variety can be more complex.

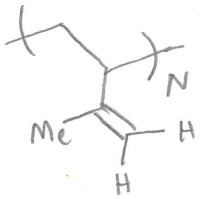
For example: 1,3-isoprene can polymerize





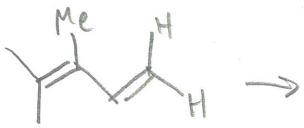
1,2-polymerization

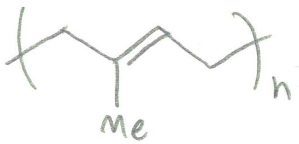
or



3,4-polymerization

- A second example with 1,3-isoprene



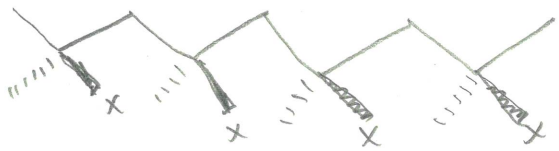


1,4-polymerization

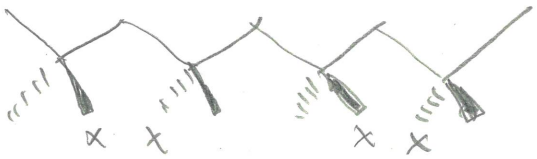
but now, the double bond can't rotate, so this forms:

cis-1,4-polyisoprene trans-1,4-polyisoprene

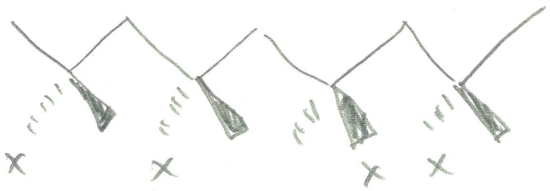
* Finally, chiral monomers give rise to stereoisomers: (tacticity)



isotactic (same side of a chain)



syndiotactic (alternate)



atactic (irregular)

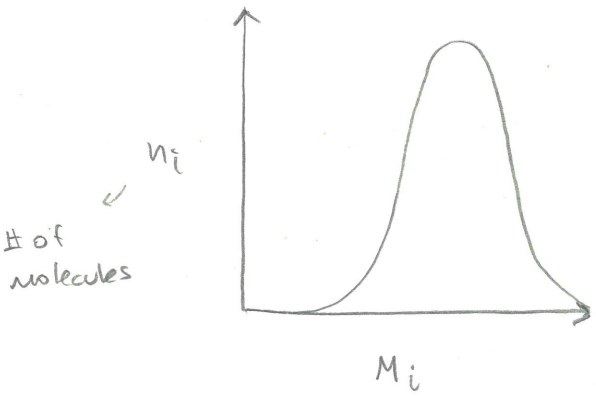
* Polymerization chemistry is not very precise. As such, all of these types of variety are common. As such, (non-biological) polymers are not a chemically homogeneous mixture. Instead, they are a closely-related set of different molecules with near infinite variety.

* The variety of a polymer is sometimes called its "microstructure" or "configuration". Latter not to be confused w/ "conformation".

C. Molecular weight Distributions

* Just as the chemical structure of polymers varies, the number of monomers in a mixture is also variable (exception: biopolymers, DNA).

* Consequently, we have a molecular weight distribution.



monodisperse: mixture w/ a single molecular weight

polydisperse: mixture w/ a distribution of mol. wt.

* we characterize distributions with moments (e.g. mean & variance).

$$M_n = \frac{\sum_{i=1}^{N} n_i M_i}{\sum_{i=1}^{N} n_i} = \frac{M_0 \sum_i i\, n_i}{\sum n_i} = M_0 \langle i \rangle$$

↑ number-averaged molecular weight.

↑ mean! (1st moment)

$$M_n = \sum_{i=1}^{N} x_i M_i \qquad x_i = \frac{n_i}{\sum n_i}$$

- M_n tells us about the mean or "typical" size of the polymer

$$M_w = \sum_i w_i M_i = \frac{\sum_i n_i M_i^2}{\sum n_i M_i} \qquad w_i = \frac{n_i M_i}{\sum_i n_i M_i}$$

↑ weight-averaged Molecular weight.

- M_w is related to the 2nd moment, but it isn't quite it. We use it because it is easy to measure.

- The 2nd moment, the variance is given by:

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

- Because of this, we often use the polydispersity index (PDI)

$$PDI = \frac{M_w}{M_n} \qquad PDI \geq 1$$

to describe the variance of MW distributions

$$\frac{\sigma^2}{M_n^2} = PDI - 1$$

PDI < 1.5 : "narrow"

PDI > 2 : "broad"

($\star$) Variance is the 2nd moment centered about the mean:

$$\sigma^2 = \frac{\sum_i n_i (i - \langle i \rangle)^2}{\sum n_i}$$

D. States of Polymer Materials

* Having discussed some of the chemical properties of polymers, let's categorize their phase behavior as well.

* Gases: Polymers do not appear in the gas phase. They have too high a vapor pressure. The will decompose before volatilizing.

* Liquids: Neat polymers at high temperature form a melt.

  In addition, polymers can be solvated in a solution with a good solvent.

  - As we will see later, polymers have a certain size, R, in solution.

This size is much larger than the bare space taken up by the monomers.

$V_{dry} \approx v_0 \cdot N$ $\quad v_0$: monomer volume.

$V_{sdn} \approx R^3$ (*) $\quad R >> (v_0 N)^{1/3}$

- let $\phi = \dfrac{v_0 n \cdot N}{V}$ ← total # of monomers / ← system volume

(*) "pervaded volume"

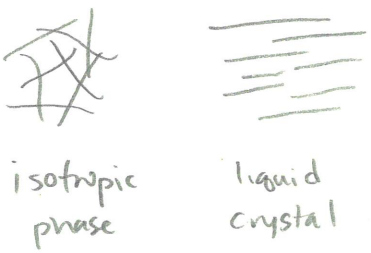
- There is a special ϕ in a polymer solution where the polymer "size" fills the solution. This is called ϕ^*, the overlap concentration.

ϕ^* happens when $V \approx nR^3$

$$\phi^* \approx \frac{v_0 N}{R^3}$$

$\phi^* \ll 1$! still lots of space left.

* Liquid-crystals ; Polymers that are stiff can form phases that have orientational order, even if they are not positionally ordered on a lattice. This phase is known as a liquid crystal.



mesogen: rod-like macromolecule

liquid crystal phases:
nematic, smectic, chiral
(oriented) (layers) (twisted)

* Solids: Melts that are cooled can form either a semi-crystalline phase or a glass.

glass: - ordered like a liquid
- characterized by Tg "glass transition temp"
- "frozen" atoms can't re-arrange, non-equilibrium

semi-crystalline: - local positional order on a lattice
- characterized by Tm, melting temp.
- "equilibrium" phase, except not all of melt can form in crystals. Some crystals w/ some glassy regions in between.

* networks: Polymers can be chemically cross-linked to form very large networks. A whole material might be one big molecule.

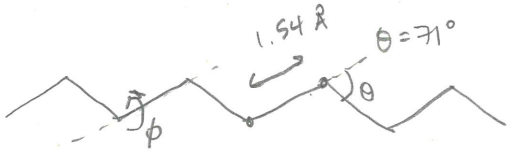
- A neat polymer network above Tg is a "rubber." It has local mobility, but crosslinks give it solidity & elasticity
- A solvated polymer network is called a "gel". It is usually quite soft, especially as more solvent is added.

E. Polymer Conformations

* A polymer conformation is the instantaneous shape of the molecule.

  - Polymers are quite flexible. They can adopt many conformations.

* Example: polyethylene



why "soft matter" is soft!

- Relevant energy: k_BT, $T \approx 300\,K$

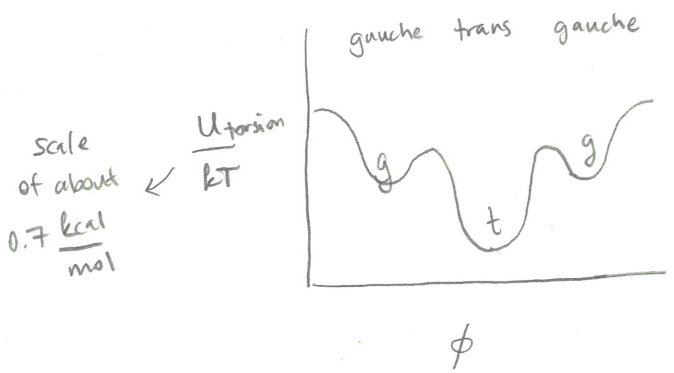
$1.38 \times 10^{-23} \frac{J}{K}$ $\quad k_BT \approx 4.14 \times 10^{-21} J$

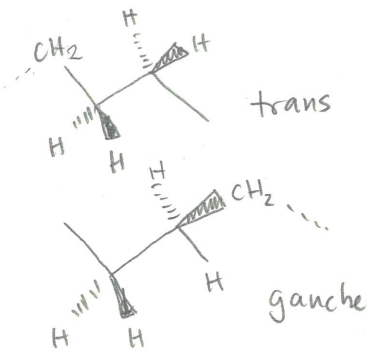
$\approx 1/40\ eV$

$\approx 0.6 \frac{kcal}{mol}$

$\approx 2.5 \frac{kJ}{mol}$

- Covalent bond energy $\approx 1\ eV$
  - ↳ bonds will not break
- Bond length fluctuation ($1\text{Å} \approx 1000 \frac{kJ}{mol}$)
- Bond angle fluctuation ($\frac{\pi}{10} \approx 80 \frac{kJ}{mol}$) (*)
- Torsional angle:





From Trapp-UA for PE.

(*) Ramos, Vega, & Martinez-Salazar. Macromolecules. 2015

Doi: 10.1021/acs.macromol.5b00823

- key takeaway: Torsional rotation is responsible for molecular flexibility.

* A polymer has significant conformational entropy. Many, many states.

* Polymer physics hypothesis: The conformational energy & entropy dominates the behavior of macromolecules.

  - chemical identity is secondary.
    (e^- interactions don't dominate like in small molecules).