10.569, Synthesis of Polymers
Prof. Paula Hammond
Lecture 1: Introduction

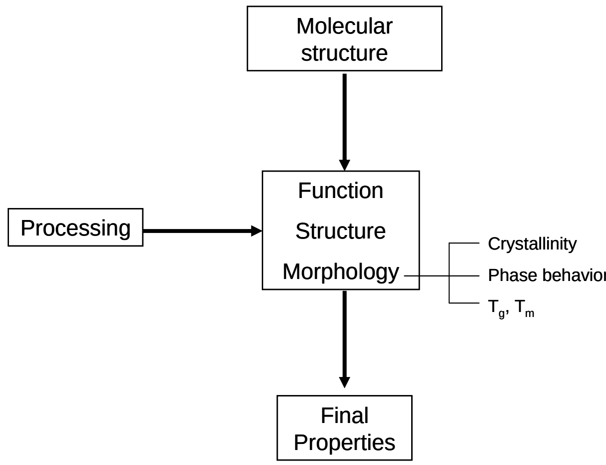
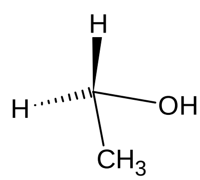


Figure 1: Processing and molecular structure of a polymer determines its function, structure, and morphology, which in turn determines its final properties

Diversity of Polymer Chains (two types):

A) Low molar mass (small) molecules

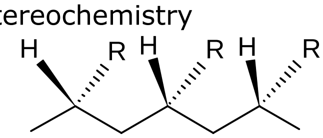
Example:



Synthesis determines molecular structure
One goal of synthesis is to avoid side reactions and achieve a pure product

B) Polymer

- Control molecular structure
- Control regularity of backbone
  - Ex: stereochemistry



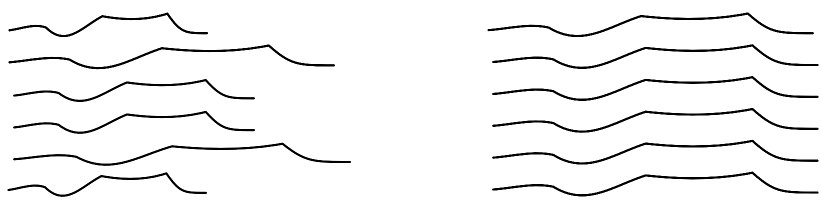
Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 course materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.

- Ex: sequencing in copolymers

  These three polymers are different even though they have the same number of monomers:

abababab	regular copolymer
abbaaaba	random copolymer
aaaabbbb	block copolymer

- Control molecular weight
  - Impacts polydiversity:

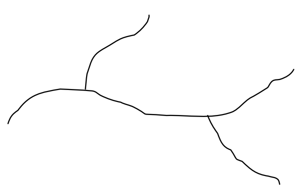


Polydisperse vs. Monodisperse

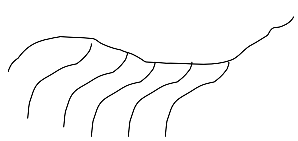
  - Overall molecular weight (MW) or mass
    - If a polymer has low MW, it acts like a fluid above T_g
    - If a polymer has high MW, it acts like a rubber above T_g
    - MW also determines mechanical properties, viscosity, rheology

- Control architecture

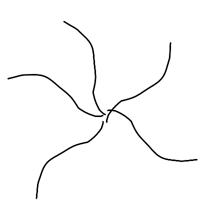
linear chain polymer



lightly branched polymer



"combed" polymer



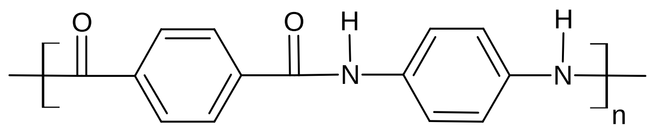
"star polymer"

Course Goals

Goal 1: Structural and architectural control

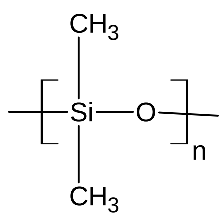
- To gain a sense of rational design and synthesis
- To develop an intuition about the impact of a structure on property
- The following two examples demonstrate how structure determines the polymer's physical and chemical properties:

    - Ex 1: polyamides (Kevlar® by DuPont)



- Kevlar®'s very low flexibility makes it a rigid structure
- The hydrogen bonding enhances rigidity and makes it solvent-resistent
- The long backbone gives it high mechanical strength
- In fact, Kevlar® has a liquid crystalline structure

    - Ex 2: polydimethylsiloxane (PDMS)



- The longer Si—O bond makes PDMS very flexible
- CH_3 makes the polymer hydrophobic
- $T_g \approx -100°C$

Goal 2: Apply knowledge to processes in industrial and commercial settings

- Determine which process is best for certain applications (Ex: there are ways to synthesize PDMS)
- There are variables in polymer approach, synthetic route, starting materials and/or catalysts, and solvent conditions

Goal 3: Awareness of new tools and approaches to materials design

- Less traditional approaches
- Functionalization of polymers
- Self-assembly approaches

Description of Molecular Weight in Polymers

Each MW can be represented as M_i

N_i = number of molecules of MW=M_i

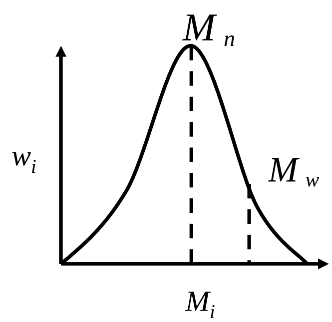
w_i = weight fraction of given system of chains with MW=M_i

$$w_i = \frac{N_i M_i}{\sum N_i M_i}$$

$$\overline{M_n} = \text{number average MW} = \frac{\text{total weight}}{\text{total \# molecules in sample}} = \frac{\sum N_i M_i}{\sum N_i}$$

$$\overline{M_w} = \text{weight average MW} = \frac{\sum (N_i M_i) M_i}{\sum (N_i M_i)} = \frac{\sum N_i (M_i)^2}{\sum N_i M_i}$$

The following graph shows the relationship between w_i *and* m_i:



Polydispersity can be measured by PDI (polydispersity index): $z = \frac{\overline{M_w}}{\overline{M_n}} \geq 1.0$.

z = 1.03 or 1.05 is considered close to monodisperse

Types of Polymerization

A) Chain growth

- In chain growth, a monomer is activated and polymerization propagates by activating neighboring monomers. The process is very rapid and high MW polymers are achieved quickly.
- The following describes the chain growth reaction in which * represents the activated monomer M. This can be a free radical, negative charge, or positive charge:

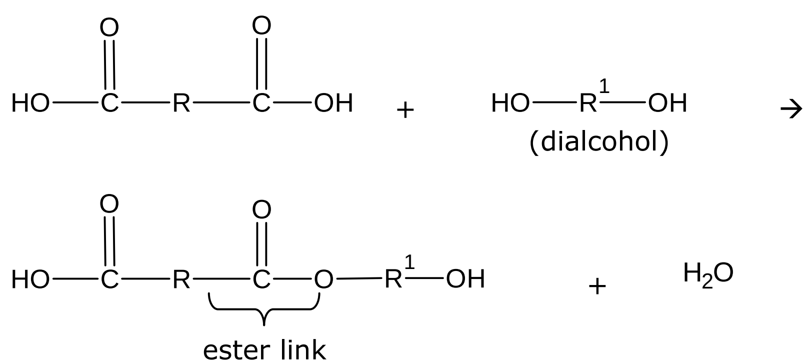
1.	R*	+	M	→	RM*
2.	RM*	+	M	→	RMM*
	…				
	RM_n*	+	M	→	RM_{n+1}*
3.	Event that terminates				

B) Step growth

- In chain growth, bifunctional monomers are added systematically to form covalent bonds. It generally involves 2 (or more) functional groups: "a" and "b." Molecular weight increases "slowly" as dimers become trimers, which in turn become tetramers.
- Examples of polymers formed by chain growth: nylons, polyesters, polypeptides (proteins)
- [Handout] These are typical a and b groups:

a + b → c + d   where c = covalent link
                  d = byproduct

1. a—a + b—b → a—c—b + d



2. a—c—b + a—a → a—c—c—a

3. a—c—c—a + b—c—c—c—a → $a(c)_6a$ + d