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:

```
H
/  \
H-OH
/   \\
CH3
```

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
- aaaaabbb 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-resistant
  - 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
  - CH₃ makes the polymer hydrophobic
  - Tg ≈ -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=$M_i$

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

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

$\overline{M}_w$ = 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:

\[
\begin{align*}
1. & \quad R^* + M \rightarrow RM^* \\
2. & \quad RM^* + M \rightarrow RMM^* \\
& \quad \vdots \\
3. & \quad RM_n^* + M \rightarrow RM_{n+1}^*
\end{align*}
\]

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:

\[
\begin{align*}
a + b & \rightarrow c + d \\
& \quad \text{where } c = \text{covalent link} \\
& \quad d = \text{byproduct}
\end{align*}
\]

1. \[a--a + b--b \rightarrow a--c--b + d\]

\[
\begin{array}{c}
\text{HO--C--R--C--OH} \\
\text{dialcohol}
\end{array} + \begin{array}{c}
\text{HO--R^1--OH} \\
\text{ester link}
\end{array} \rightarrow \begin{array}{c}
\text{HO--C--R--C--O--R^1--OH} \\
\text{H_2O}
\end{array}
\]

2. \[a--c--b + a--a \rightarrow a--c--c--a\]

3. \[a--c--c--a + b--c--c--c--a \rightarrow a(c)_a a + d\]