Mat E 272

Lecture 24b: A Brief Overview of Polymer Science

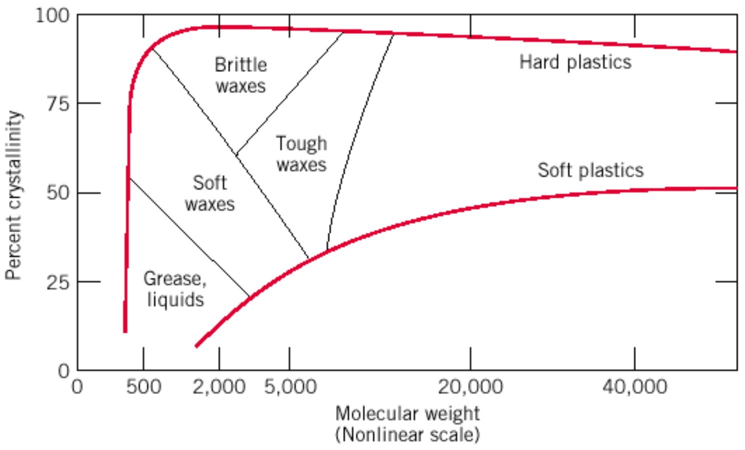
December 4, 2001

Introduction:

Don't make the mistake of associating the brevity of this lecture with a lack of importance of polymers in today's society. Polymers form a significant third distinct class of materials and enable such diverse products as tires, keyboard keys, styrofoam cups, plastic bags and bottles, fiber optic cables, water line pipes, and contact lenses. Clearly polymer science, with a history dating back to the early years of the nineteenth century, has a tremendous impact on our lives. The word "polymer" originates from the greek *polumeres*, which literally means `*having many parts'*. Polymers are essentially large molecules consisting of repeat units (called "mers") joined together. Polymers typically contain many thousands, or even millions, of mers, and the bonding between atoms in polymers is either covalent (strong) or van der Waals (weak).

Introduction to Polymers

Examples of polymers:



styrofoam cups
contact lenses
rubber tires
telephone housings
epoxies
sandwich bags
soda (or "pop") bottles
rubber bands
computer keyboard keys and cables

and on and on…

in fact, just look around your dorm or apartment room and you'll likely find plenty of examples of polymeric materials.

Introduction to Polymers

<u>Definition:</u> **A polymer is a molecule with a molecular weight on the order of several thousand, or more. Polymers are usually hydrocarbon-based (albeit with many exceptions) and contain many individual repeat units, or "mers."**

Suppose our repeat unit is an "X." Then, a linear polymer based on "X" would look like the following:

… --X--X--X--X--X--X--X--X--X--X--X--X--… where each "X" represents a "mer."

Sometimes, polymers contain functional side groups, called pendant groups:

```
                Y                       Y
                |                       |
… --X--X--X--X--X--X--X--X--X--X--X--X--X--X--…
                   |           |     |
                   Y           Y     Y
```

We call the primary linear chain the "backbone"

Introduction to Polymers

<u>Homopolymers vs. co-polymers:</u> If only one type of repeat unit is present, the polymer is called a *homopolymer*. If a second monomer is also present in the chain, the resulting material is called a *co-polymer*.

Model for a *homopolymer*:

--X--X--X--X--X--X--X--X--X--X--X--X-

Model for an *alternating co-polymer*:

--X--W--X--W--X--W--X--W--X--W--X--W-

Model for a *random co-polymer*:

--X--X--X--W--X--W--X--X--W--X--W--W-

Model for a *block co-polymer*:

--X--X--X--X--X--X--X--X--W--W--W--W--W--W--

<u>Graft co-polymer:</u> The resulting structure when chains of one type of monomer, say “W,” are grafted onto a backbone polymer chain of, say, “X.”

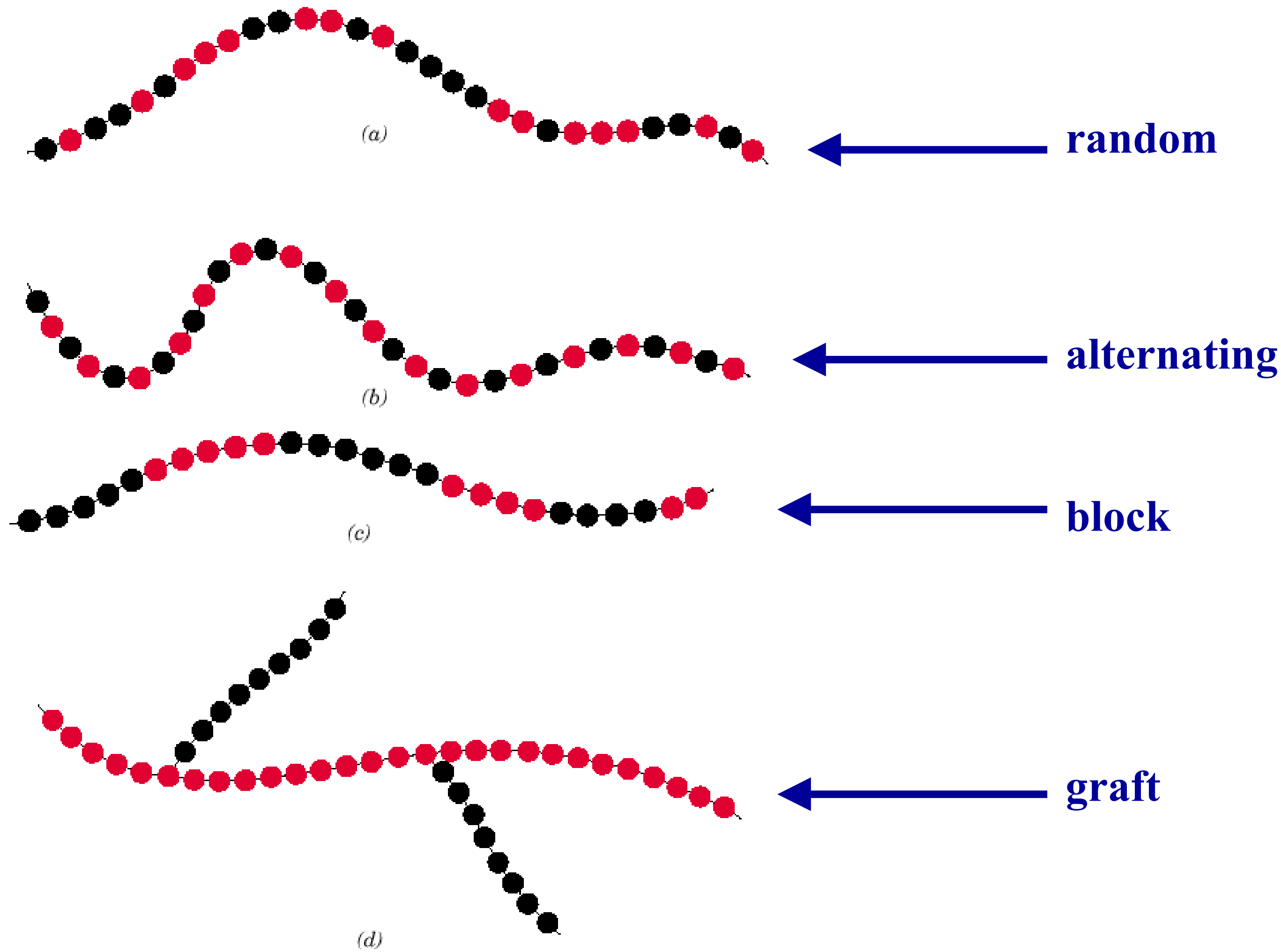
Model for a *graft co-polymer*:

```
                                         W
                                         |
              W                          W
              |                          |
              W                          W
              |                          |
              W                          W
              |                          |
--X--X--X--X--X--X--X--X--X--X--X--X--X--X--X--X--X--X--X--X--X--X--X--
                          |
                          W
                          |
                          W
                          |
                          W
```

Side branches like this tend to make a polymer harder and stronger.

Introduction to Polymers

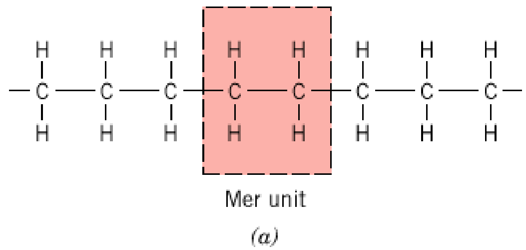
Another conceptual representation of various co-polymers:

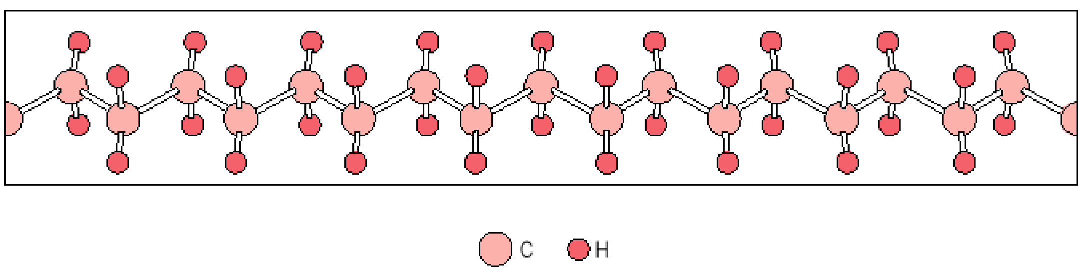


Introduction to Polymers

Examples of "real" monomers and their resulting polymers:

Polyethylene: **(the mer unit is C_2H_4)**





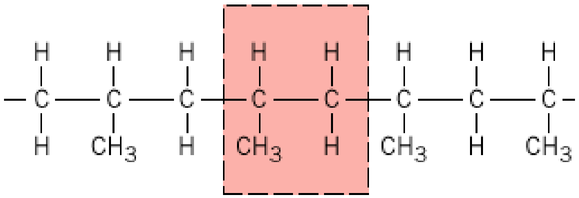
This is an example of a linear chain homopolymer, where the "X" in our model is replaced with the ethylene group.

Polyethylene is used for flexible bottles, toys, tumblers, battery parts, ice trays, and film wrapping materials. It is tough but possesses low strength. Trade names: Ethron, Fortiflex, Hi-fax, Rigidex, Zendel.

Introduction to Polymers

Examples:

Polypropylene: **(the mer unit is now C_3H_6)**




```
…--CH2--CH--CH2--CH--CH2--CH--CH2--CH--CH2--CH--
        |          |          |          |          |
       CH3        CH3        CH3        CH3        CH3
```

now, the repeat unit (or mer) is the propylene functional:

```
   H   H
   |   |
 --C--C--
   |   |
   H  CH3
```

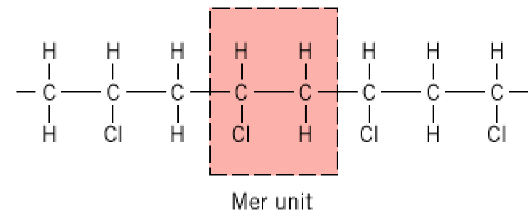
Polypropylene is used for such items as bottles, TV cabinets, luggage. It tends to be relatively strong and resistant to heat. It has the trade names Herculon, Meraklon, and Pro-fax.

Introduction to Polymers

Examples:

Polyvinyl chloride: (the mer unit is C_2H_3Cl)

```
   H  H   H  H  H   H  H  H   H   H
   |  |   |  |  |   |  |  |   |   |
--C--C--C--C--C--C--C--C--C--C--
   |  |   |  |  |   |  |  |   |   |
   H  Cl  H  Cl  H  Cl  H  Cl  H  Cl
```



Note that each carbon atom has 4 bonding electrons, which are depicted as dashed lines in the diagrams

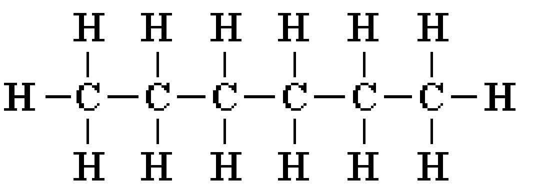
Polyvinyl chloride is a very popular, low cost rigid material (which can be made flexible by adding plasticizers). It is used as floor coverings, pipe, garden hose, electrical wire insulation, and (at one time) phonograph records. Tradenames: "PVC," Saran, Tygon, Darvic, Geon.

Introduction to Polymers

Molecular weight:

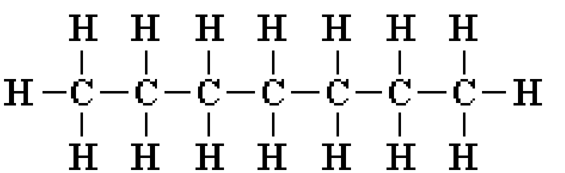
Determining the molecular weight of a polymer is easy; all you need to do is add the respective molecular weights of the components.

Consider hexane, C_6H_{14}



Hexane's molecular weight would be 6(12.01) + 14(1.01) = <u>86.2 g/mol</u>

Now look at heptane (obtained by adding another carbon), C_7H_{16}

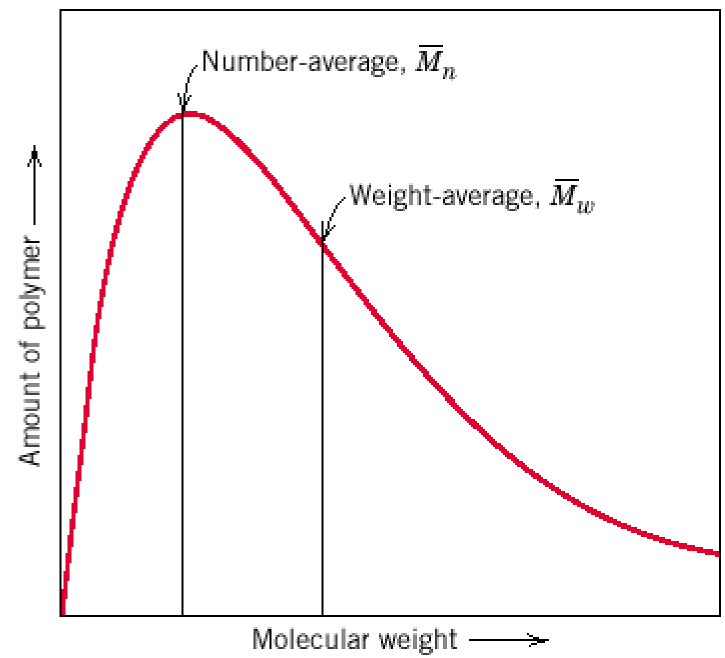


Heptane's molecular weight would be 7(12.01) + 16(1.01) = <u>100.2 g/mol</u>

Molecular weight:

Since many polymers contain thousands of repeat units, we generally speak of molecular weight in terms of an average value.

Polyethylene, for example, can contain chains with tens of thousands of carbon atoms. Some chains may contain a few more, some a few less. You won't find a group of polyethylene molecules all with exactly the same chain length; mostly, we see a skewed Gaussian-like distribution of molecular weight values:



Example problem

Problem:

A regular co-polymer of ethylene and vinyl chloride contains alternating mers of each type. What is the weight percent of ethylene in this co-polymer?

Solution:

Since there is one ethylene mer for each vinyl chloride molecule, one can write,

$$\text{wt. \% ethylene} = \frac{mol.wt.C_2H_4}{mol.wt.C_2H_4 + mol.wt.C_2H_3Cl} x100$$

substituting the known molecular weight values:

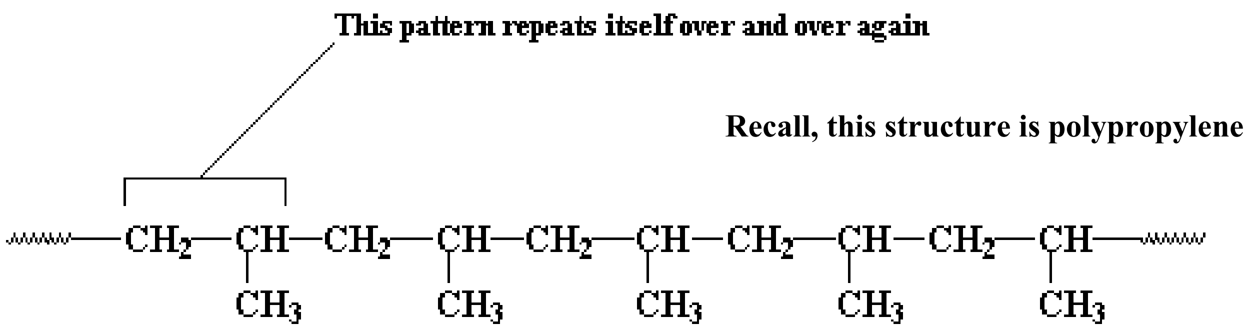
$$\text{wt. \% ethylene} = \frac{[2(12.01)+4(1.008)]}{[2(12.01)+4(1.008)]+[2(12.01)+3(1.008)+35.45]} x100$$

= 31.0 wt. %

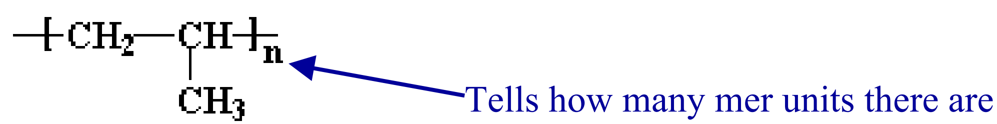
Introduction to Polymers

Degree of polymerization:

We need some way to indicate how many of these "mer" repeat units are present in a polymer. An obvious solution is to simply count them and indicate such in a compact chemical formula:



So we can write polypropylene more compactly then as follows:



Degree of polymerization:

We can easily determine the degree of polymerization if we know the total molecular weight, M, and the molecular weight per mer:

$$n_n = \frac{\overline{M}_n}{\overline{m}},$$

$$n_w = \frac{\overline{M}_w}{\overline{m}}$$

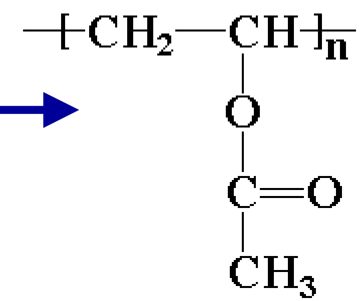
where the M and m represent the total and mer molecular weights, respectively. The subscripts n and w refer to number-averaged and weight-averaged, respectively.

by weight-averaged, we mean that a population of polymers is divided into a series of weight ranges. The weighted average molecular weight per range is just the mean molecular weight within each range, multiplied by the number fraction of chains within this weight range.

Example problem

Problem:

The formula for *vinyl acetate* is



It forms a polymer by addition polymerization (addition of mers to the base chain structure) with an average molecular mass of 4.5×10^4.
What is the degree of polymerization (take C = 12, H = 1, and O = 16)

Solution:

The molecular mass of the monomer is:

		total relative mass
H: 6 atoms x 1	=	6
C: 4 atoms x 12	=	48
O: 2 atoms x 16	=	32
		86 ← molecular mass of vinyl acetate

therefore, the degree of polymerization, n, = $(4.5 \times 10^4)/86 \approx 523$

PVA is used in adhesives, paper coatings, and water based paints

<u>Crosslinking:</u>

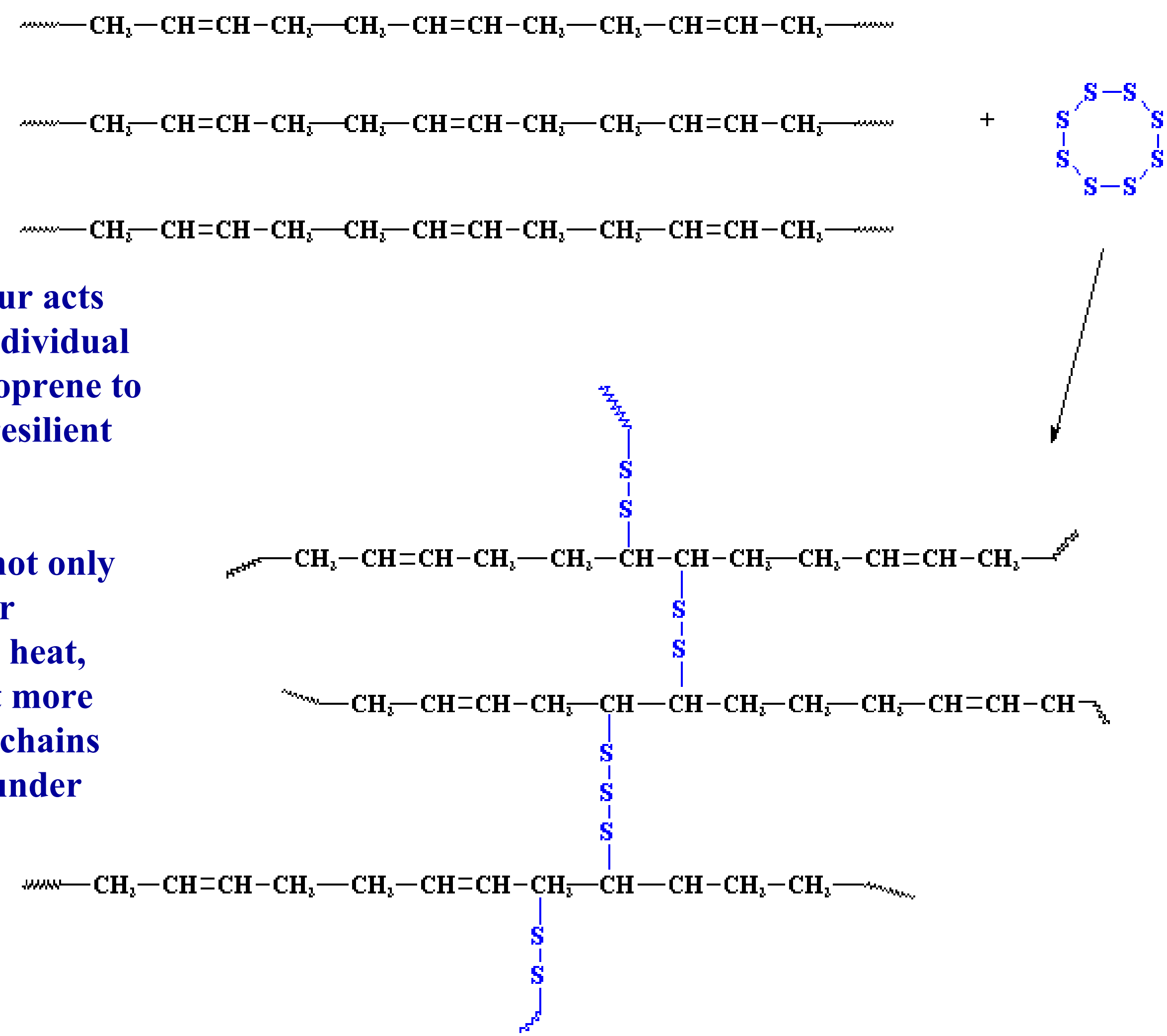
Individual chains can <u>covalently</u> bond together, resulting in a network structure. This occurs mainly in thermosetting polymers (to be discussed); the presence of strong covalent bonding means the resulting polymer remains strong at elevated temperatures.

On the next slide, we show an example of how sulfur acts to crosslink rubber latex (polyisoprene), a process known as *Vulcanization*. Vulcanized rubber was first invented by Charles Goodyear in 1839.

Without crosslinking, latex rubber becomes soft and sticky when warm

Introduction to Polymers

Crosslinking:



Addition of sulfur acts to link up the individual chains of polyisoprene to form a strong, resilient rubber.

The crosslinks not only make the rubber resilient against heat, but also make it more difficult for the chains to break apart under cold conditions.

The glass transition

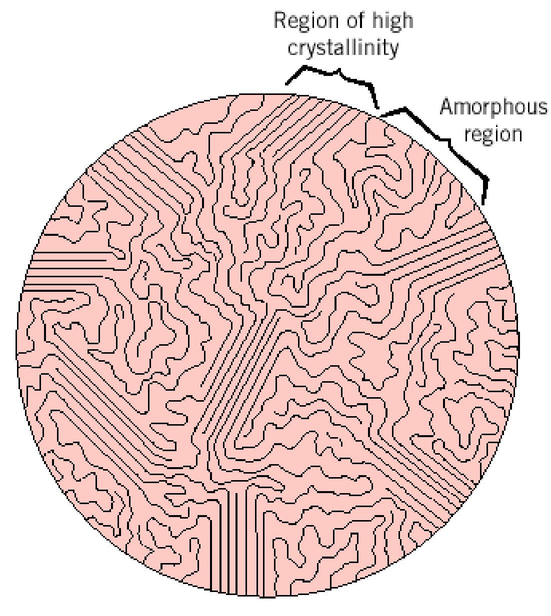
Similar to DBTT in BCC metals but completely different mechanism

Every polymer is characterized by a unique temperature, below which it becomes glass-brittle. This is referred to as the glass transition temperature, Tg.

Hard plastics (polystyrene and PMMA -- with Tg ~ 100^{o}C) are used *below* their Tg.

Rubber elastomers (polyisoprene and polyisobutylene) are normally used *above* their Tg

Note: the glass transition is a phenomenon that occurs in amorphous polymers, that is, polymers in which the chains possess no long-range crystalline order.



Most real polymers contain both amorphous and crystalline regions, as shown above.

The glass transition

Below the Tg, atoms do not possess sufficient kinetic energy to move in response to an applied stress. Consequently, the polymer shatters or breaks.

Above the Tg, there is sufficient kinetic energy so that the atoms can easily move and rearrange themselves in response to an applied stress. As a result, there is a change in shape but the polymer does not fracture.

Glass transition temperatures can sometimes be modified by adding chemical agents called *plasticizers*. Plasticizers (like carbon di-sulfide) are taken up by the chains and cause the average intermolecular spacing to increase. By increasing the average spacing between atoms, they can slide past each other more easily and this makes the polymer more pliable.

Fun fact: that infamous “new car smell” is just evaporation of plasticizers from various plastic components inside the cabin. Once the plasticizers have mostly evaporated away, the plastic becomes brittle and can crack on cold, winter days.

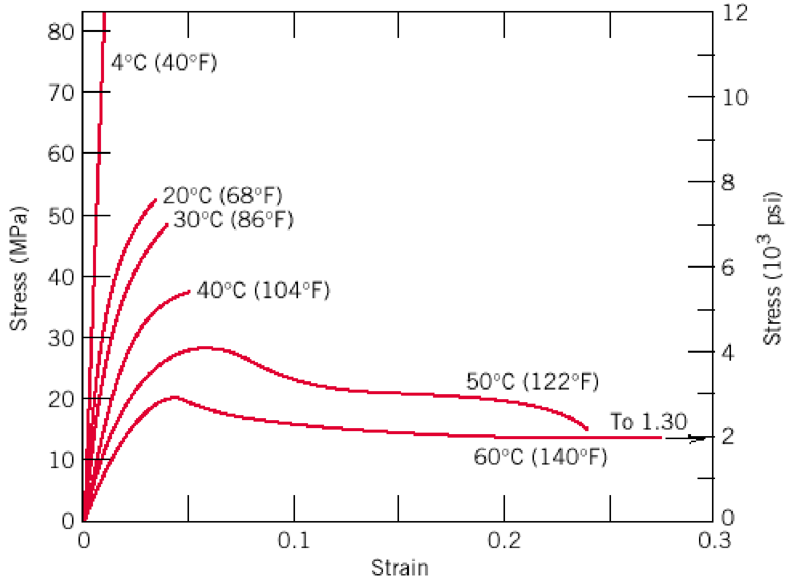
Introduction to Polymers

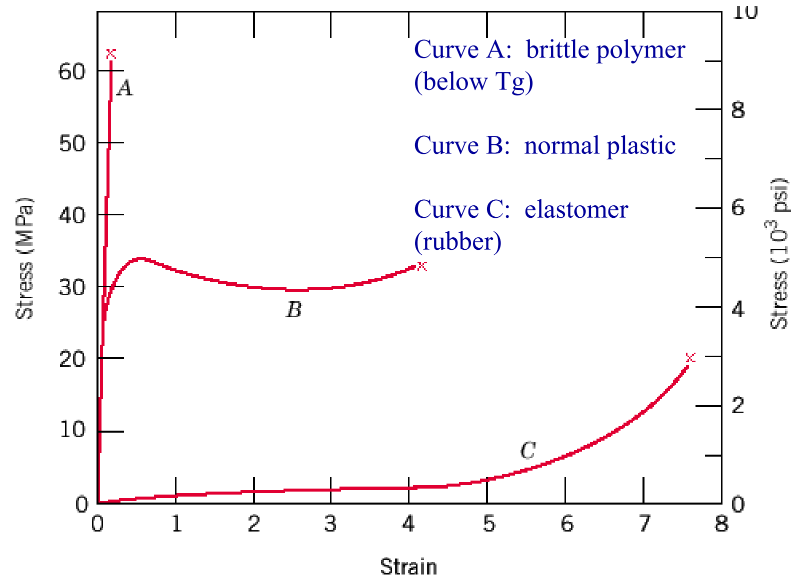
Thermoplastic vs. Thermosetting:

Some polymers become soft and deformable when heated. This type of polymer is characterized by weak van der Waals bonding between the molecules. As the molecules are heated up, their vibrational amplitude increases and can reach a point where the van der Waals bonds are broken. These thermoplastic polymers can be repeatedly softened and reshaped. Examples of thermoplastic polymers include polyethylene, PVC, polystyrene, polypropylene, acrylics, nylons, polycarbonates, polyesters, and fluoroplastics.

Others, like vulcanized rubber, remain strong with increased temperature (until finally melting). In fact, heat is used to form the links. Therefore, this type of polymer must be formed and shaped BEFORE heat is applied. Polymers which crosslink upon application of heat are called thermosetting polymers. Examples of thermosetting polymers include epoxies, silicones, polyesters, amino resins, polyurethane.

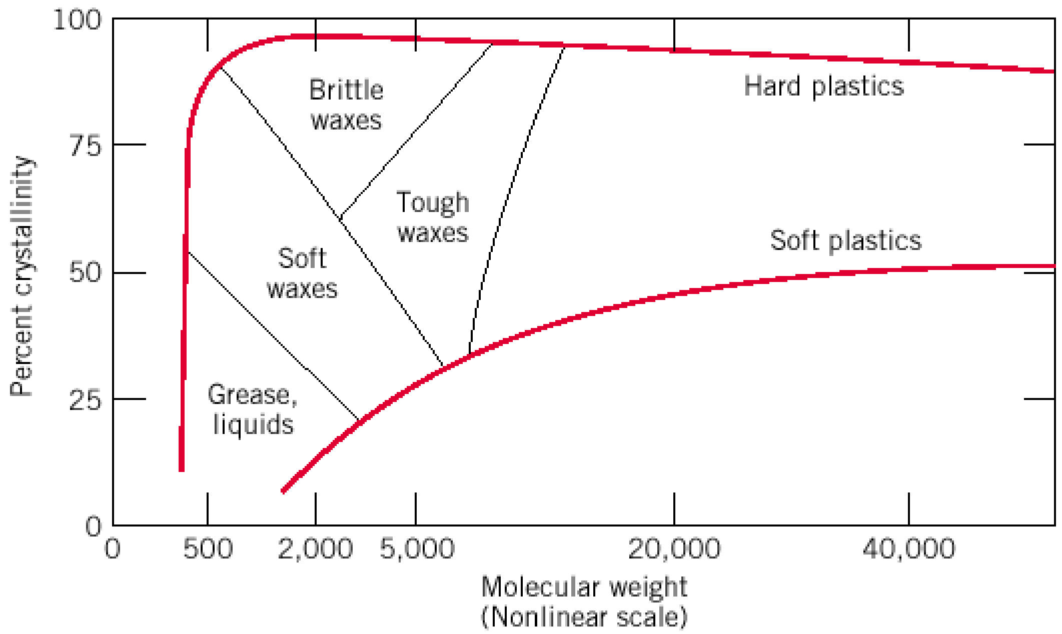
Mechanical properties of Polymers





Effect of temperature on stress-strain behavior of PMMA (left). Typical stress-strain behavior for three classes of polymers (right); curve A = brittle polymer, curve B = normal plastic polymer, curve C = elastomer (rubber)

Mechanical properties of Polymers



Influence of degree of crystallinity and molecular weight on the physical characteristics of a typical polymers.