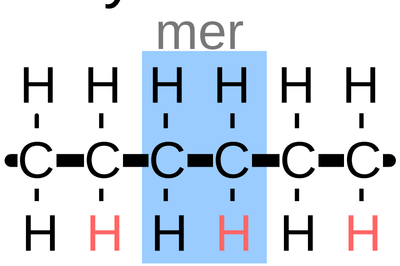
CHAPTERS 14/15: Polymer structures, applications, & processing

ISSUES TO ADDRESS...

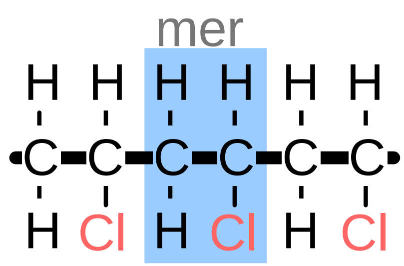
- What are the basic microstructural features?
- What dictates polymer mechanical properties?
- How do these features dictate room T tensile response?
- How does elevated temperature mechanical response compare to ceramics and metals?

Polymer microstructure

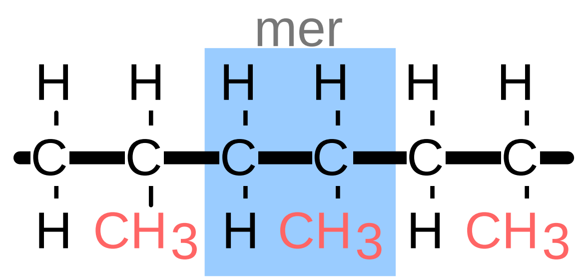
- Polymer = many mers



Polyethylene (PE)

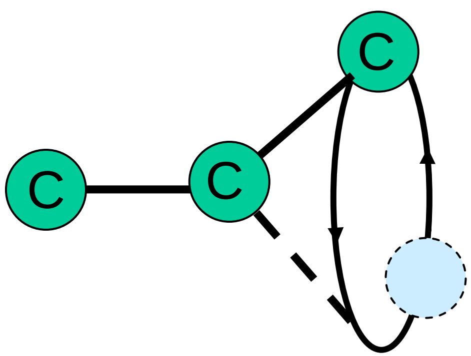


Polyvinyl chloride (PVC)



Polypropylene (PP)

Adapted from Fig. 14.2, *Callister 6e.*



Chain rotation

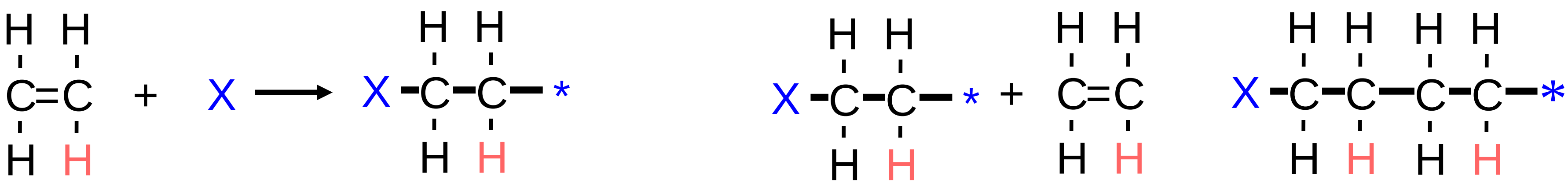
The C-C bond has rotational freedom; provided there are no steric hindrance from bulky side groups (polystyrene)

Weakness of polymers is due to weak van der Waals bond <u>between</u> chains

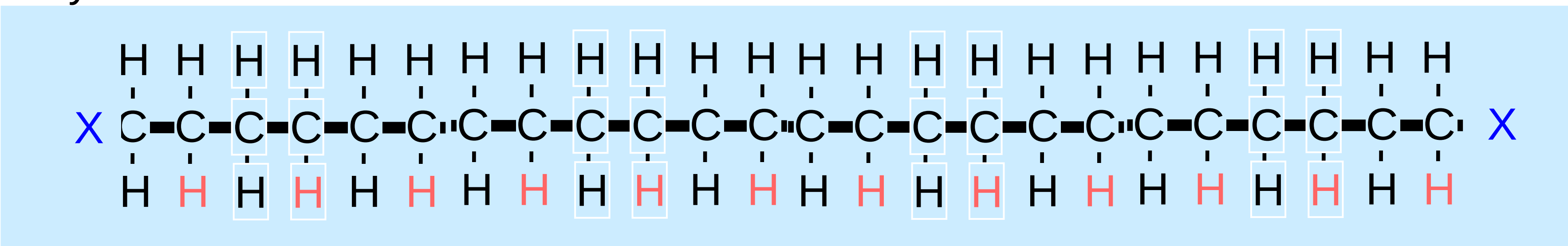
Adapted from Fig. 14.7, *Callister 6e.*

Polymerization of ethylene

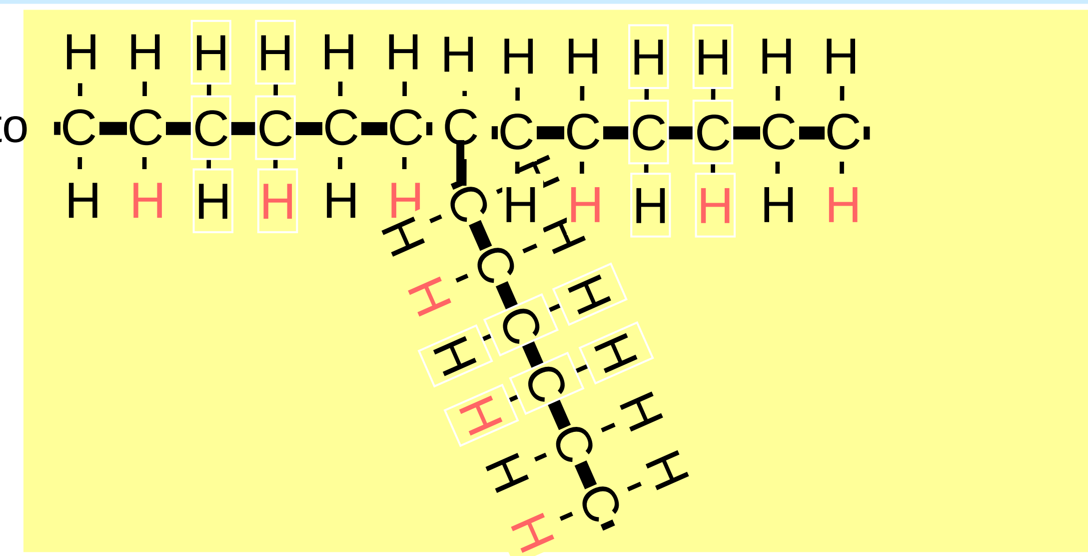
Addition polymerization



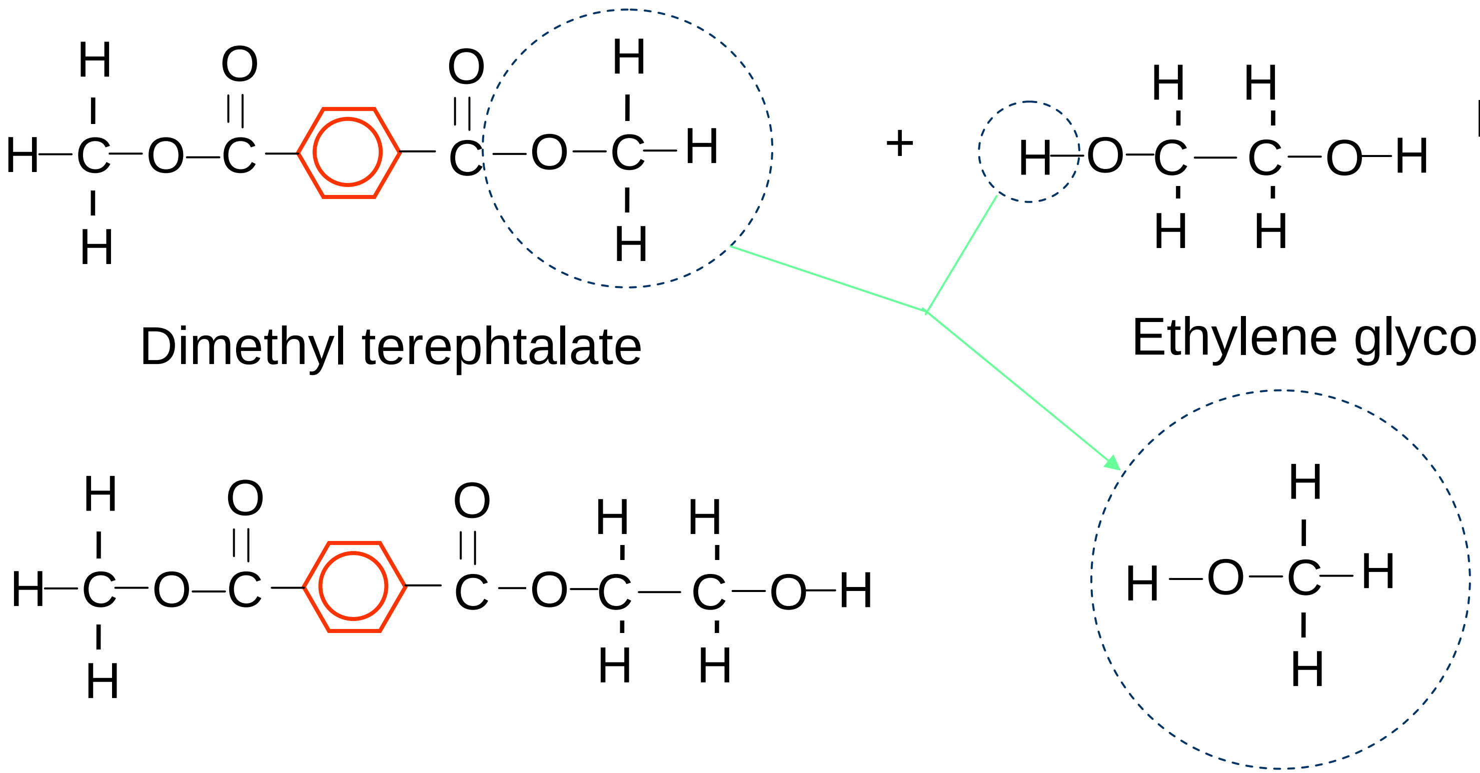
Polymerization and termination



However, mistakes do happen during polymerization, leading to branching



Condensation polymerization



Dimethyl terephtalate

Ethylene glycol

Repeating unit for polyethylene terephtalate (PET)

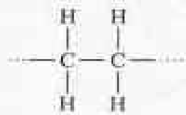
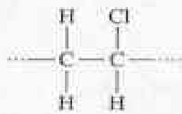
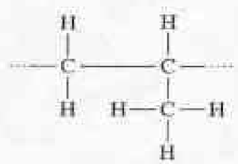
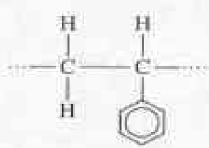
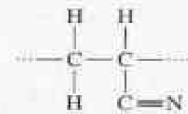
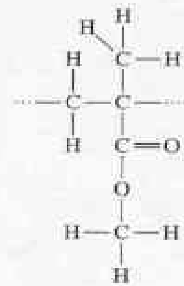
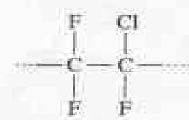
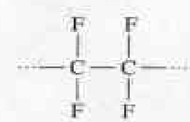
Methyl alcohol by-product

Polymer properties

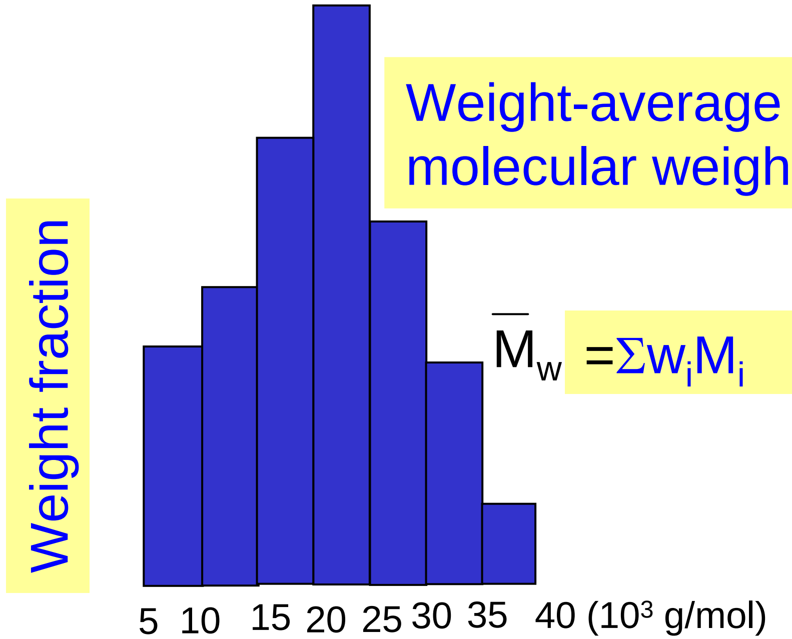
- Molecular characteristics
  - Chemistry (Mer composition)
  - Size (Molecular weight)
  - Shape (Chain twisting, entanglement)
  - Structure
    - Linear
    - Branched
      - (Linear, Branched) → Configuration
        - Stereoisomers
          - Isotactic
          - Syndiotactic
          - Atactic
        - Geometrical isomers
          - cis
          - trans
    - crosslinked
    - network

Polymer chemistry

TABLE 15-3 *Repeat units and applications for selected addition thermoplastics*

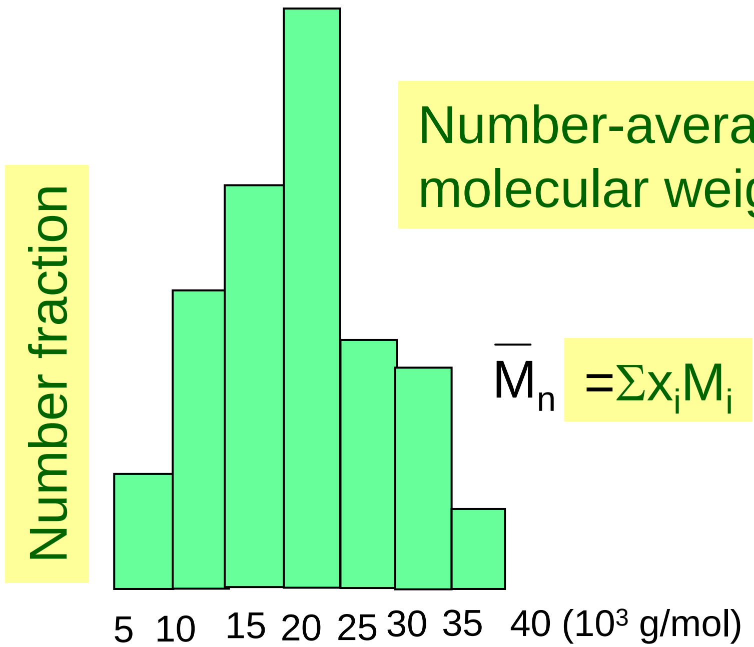
Polymer	Repeat Unit	Application
Polyethylene (PE)		Packing films, wire insulation, squeeze bottles, tubing, household items
Polyvinyl chloride (PVC)		Pipe, valves, fittings, floor tile, wire insulation, vinyl automobile roofs
Polypropylene (PP)		Tanks, carpet fibers, rope, packaging
Polystyrene (PS)		Packaging and insulation foams, lighting panels, appliance components, egg cartons
Polyacrylonitrile (PAN)		Textile fibers, precursor for carbon fibers, food container
Polymethyl methacrylate (PMMA) (acrylic-Plexiglas)		Windows, windshields, coatings, hard contact lenses, lighted signs
Polychlorotri-fluoroethylene		Valve components, gaskets, tubing, electrical insulation
Polytetrafluoro-ethylene (Teflon) (PTFE)		Seals, valves, nonstick coatings

Degree of polymerization



Weight-average molecular weight

$\overline{M}_w = \Sigma w_i M_i$

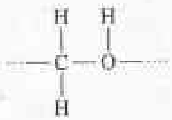
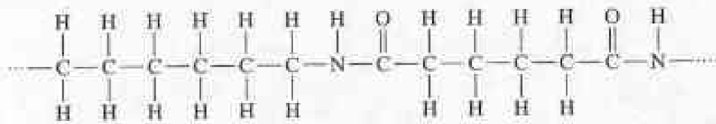
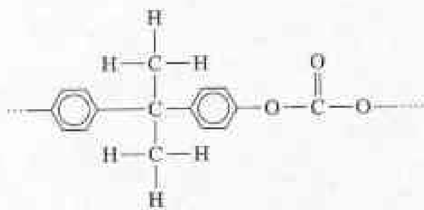
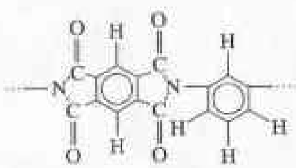
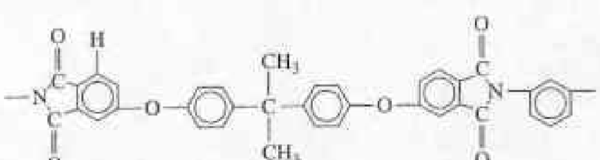


Number-average molecular weight

$\overline{M}_n = \Sigma x_i M_i$

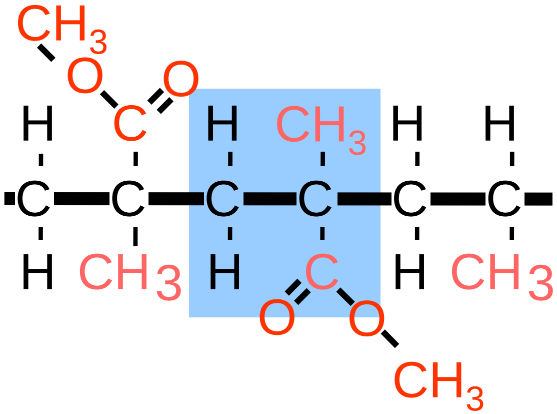
$$\text{Degree of polymerization} = \frac{\text{Average molecular weight of polymer}}{\text{Molecular weight of repeat unit}}$$

TABLE 15-4 ■ *Repeat units and applications for complex thermoplastics*

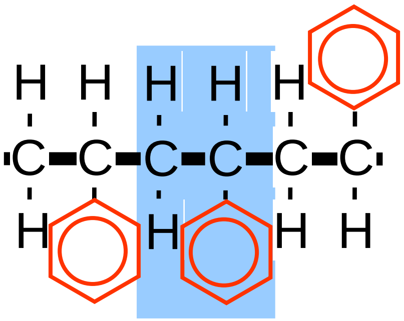
Polymer	Repeat Unit	Applications
Polyoxymethylene (acetal)(POM)		Plumbing fixtures, pens, bearings, gears, fan blades
Polyamide (nylon) (PA)		Bearings, gears, fibers, rope, automotive components, electrical components
Polyester (PET)		Fibers, photographic film, recording tape, boil-in-bag containers, beverage containers
Polycarbonate (PC)		Electrical and appliance housings, automotive components, football helmets, returnable bottles
Polyimide (PI)		Adhesives, circuit boards, fibers for space shuttle
Polyetheretherketone (PEEK)		High-temperature electrical insulation and coatings
Polyphenylene sulfide (PPS)		Coatings, fluid-handling components, electronic components, hair dryer components
Polyether sulfone (PES)		Electrical components, coffeemakers, hair dryers, microwave oven components
Polyamide-imide (PAI)		Electronic components, aerospace and automotive applications

Chain stiffeness

Bulky side groups offer steric hindrance to polymer chains and kinking



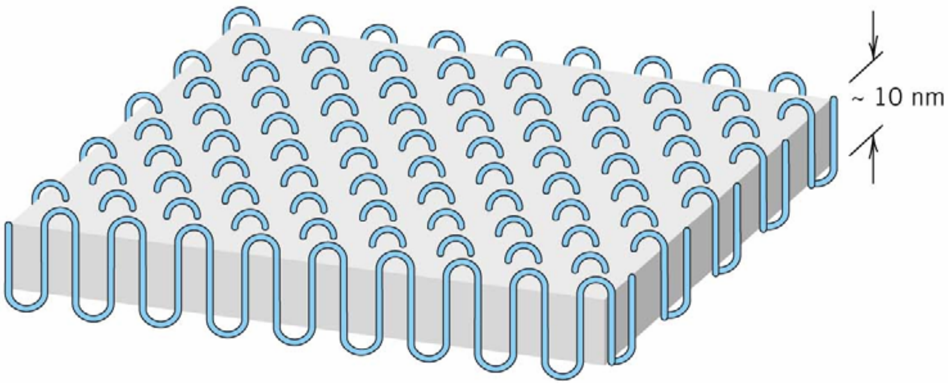
Polymethyl Methacrilate (PMMA)



Polystyrene (PP)

Chain crystallization

Chain-folded structure



Chain crystallinity influenced by:

- Chemistry (simple mers)
- Regularity in
  - Structure (linear)
  - stereoisomerism (isotactic, syndiotactic)
  - Co-polymerization (alternating and block)

Polyethylenes

Chain length (Molecular Weight) →

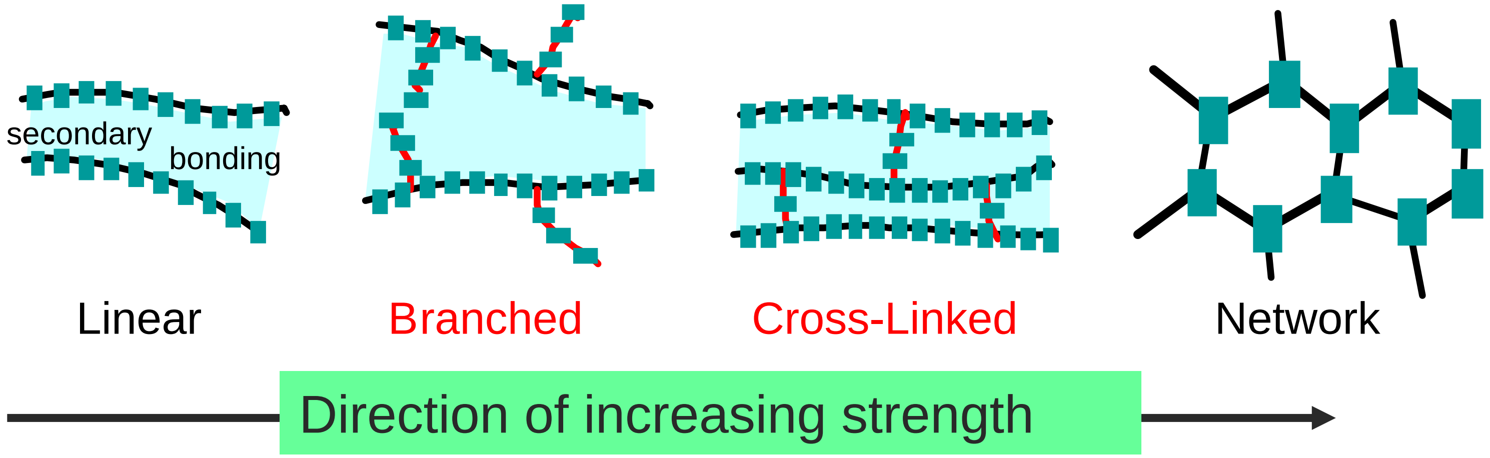
Propane gas | Baby oil | Parafin wax | Polyethylenes

	HDPE	LDPE
Density g/cm^3	0.96	0.92
Tensile strength (psi)	5,500	3,000
Young's modulus (psi)	180,000	40,000
Applications	Garbage cans dish pans, pipes	Plastic wrap Plastic bags
	Some crystallinity	Short length branched • low density • amorphous • weaker

UHMWPE has very long molecular chains (70,000 C atoms), crystalline, inert lines sockets of artificial joints

Structure

- Structure – 4 Covalent chain configurations and strength:



Chain configuration

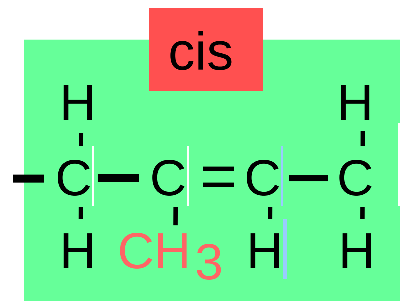
Stereoisomers

Isotactic | Syndiotactic | Atactic

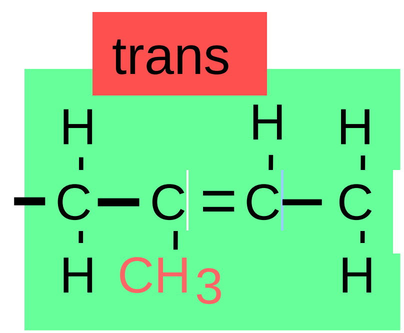
Geometrical isomers

cis | trans

- *isotactic* (side group is *ordered* on one side)
- *syndiotactic* (side group is *ordered* on opposite sides)
- *atactic* (side group is <u>*random*</u> along the chain)



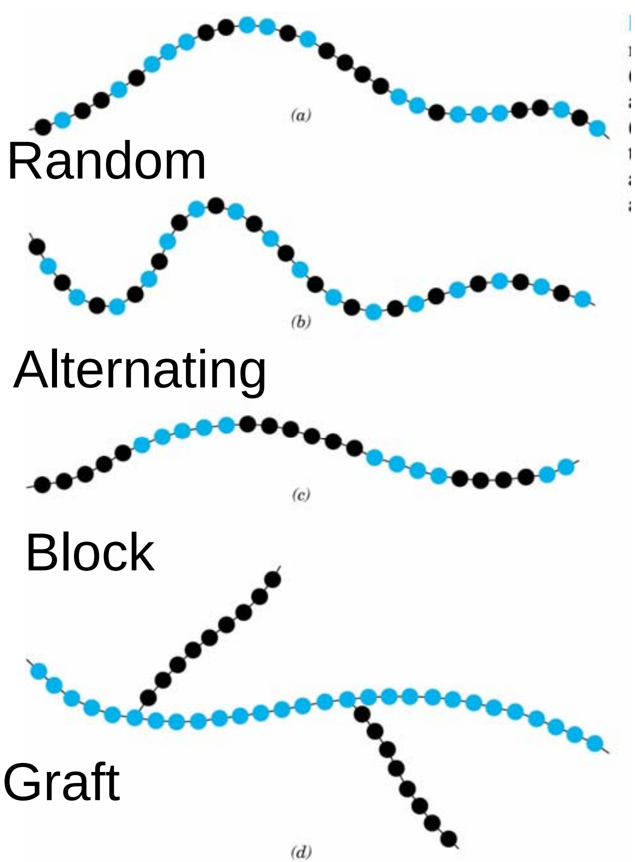
Natural Rubber



Gutta-percha

Other polymer characteristics

Co-polymers



HIP – High Impact Polystyrene

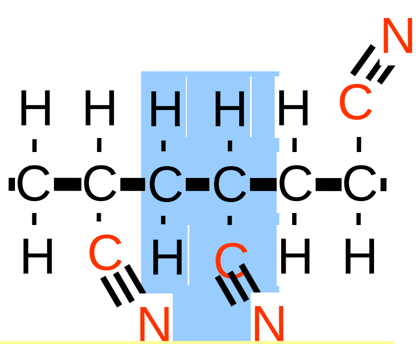
Styrene mer (PS)

Butadiene mer (PB)

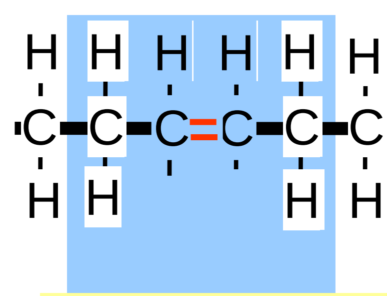
ABS – High Impact Polystyrene

Styrene + Acrylonitrile (PS + PA)

Butadiene + Acrylonitrile (PB + PA)



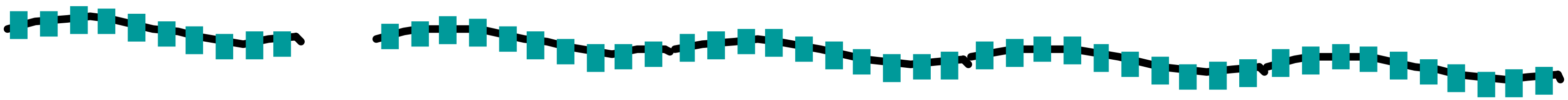
Polyacrylonitrile



Polybutadiene

Molecular weight & crystallinity

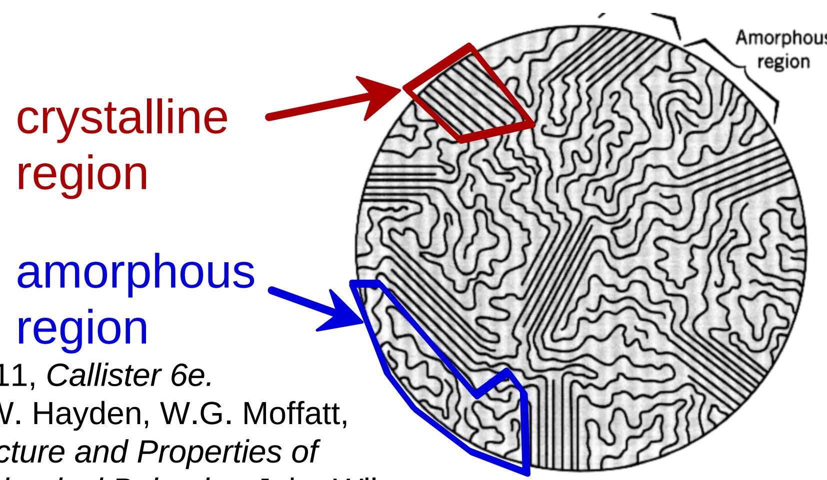
- Molecular weight, M_W: Mass of a mole of chains.



smaller M_W larger M_W

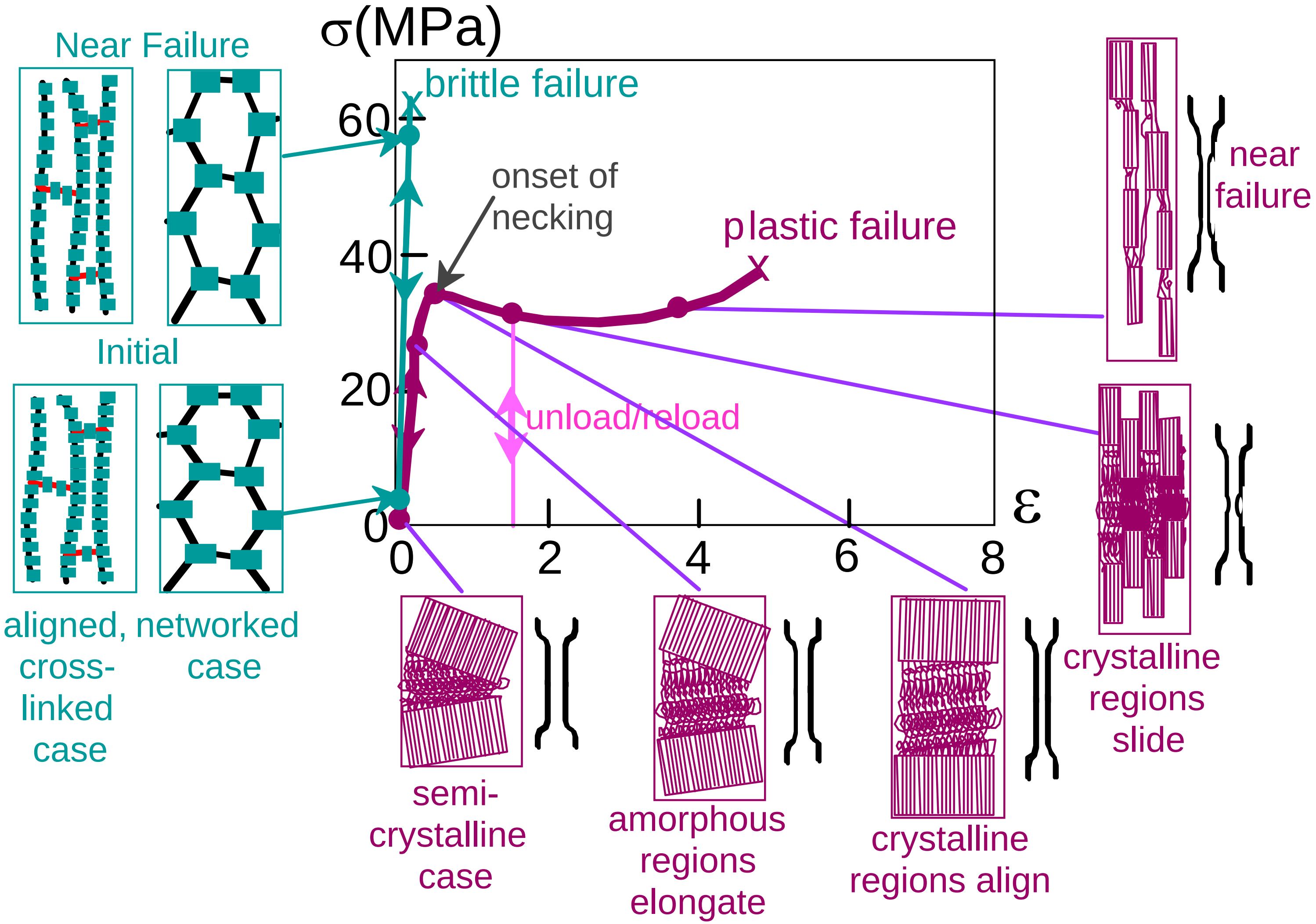
- Tensile strength (TS):
  --often increases with M_W.
  --Why? Longer chains are entangled (anchored) better.

- % Crystallinity: % of material that is crystalline.
  --TS and E often increase with % crystallinity.
  --Annealing causes crystalline regions to grow. % crystallinity increases.



Adapted from Fig. 14.11, *Callister 6e.* (Fig. 14.11 is from H.W. Hayden, W.G. Moffatt, and J. Wulff, *The Structure and Properties of Materials*, Vol. III, *Mechanical Behavior*, John Wiley and Sons, Inc., 1965.)

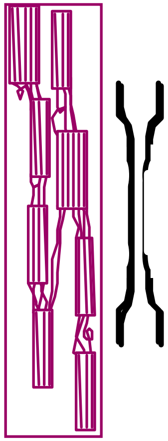
Tensile response: brittle & plastic



Stress-strain curves adapted from Fig. 15.1, *Callister 6e.* Inset figures along plastic response curve (purple) adapted from Fig. 15.12, *Callister 6e*. (Fig. 15.12 is from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)

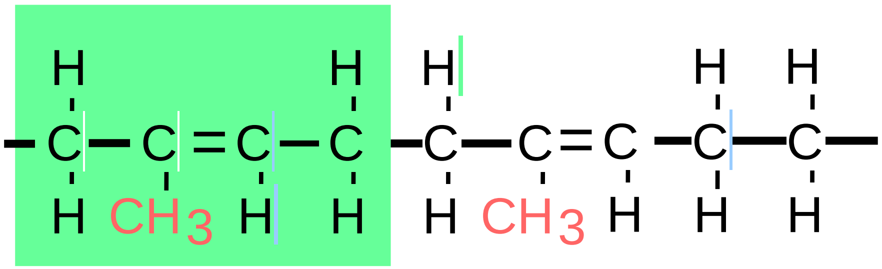
Predeformation by drawing

- Drawing...
  --stretches the polymer prior to use
  --aligns chains to the stretching direction
- Results of drawing:
  --increases the elastic modulus (E) in the stretching dir.
  --increases the tensile strength (TS) in the stretching dir.
  --decreases ductility (%EL)
- Annealing after drawing...
  --decreases alignment
  --reverses effects of drawing.
- Compare to cold working in metals!



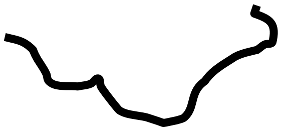
Adapted from Fig. 15.12, *Callister 6e*. (Fig. 15.12 is from J.M. Schultz, *Polymer Materials Science*, Prentice-Hall, Inc., 1974, pp. 500-501.)

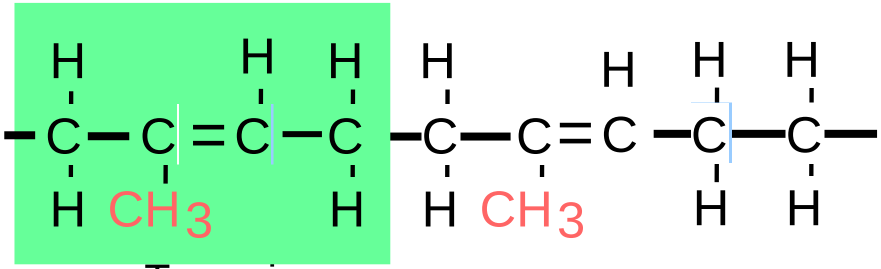
Rubber



Cis-isoprene

Crowding causes kinking and chain rotation

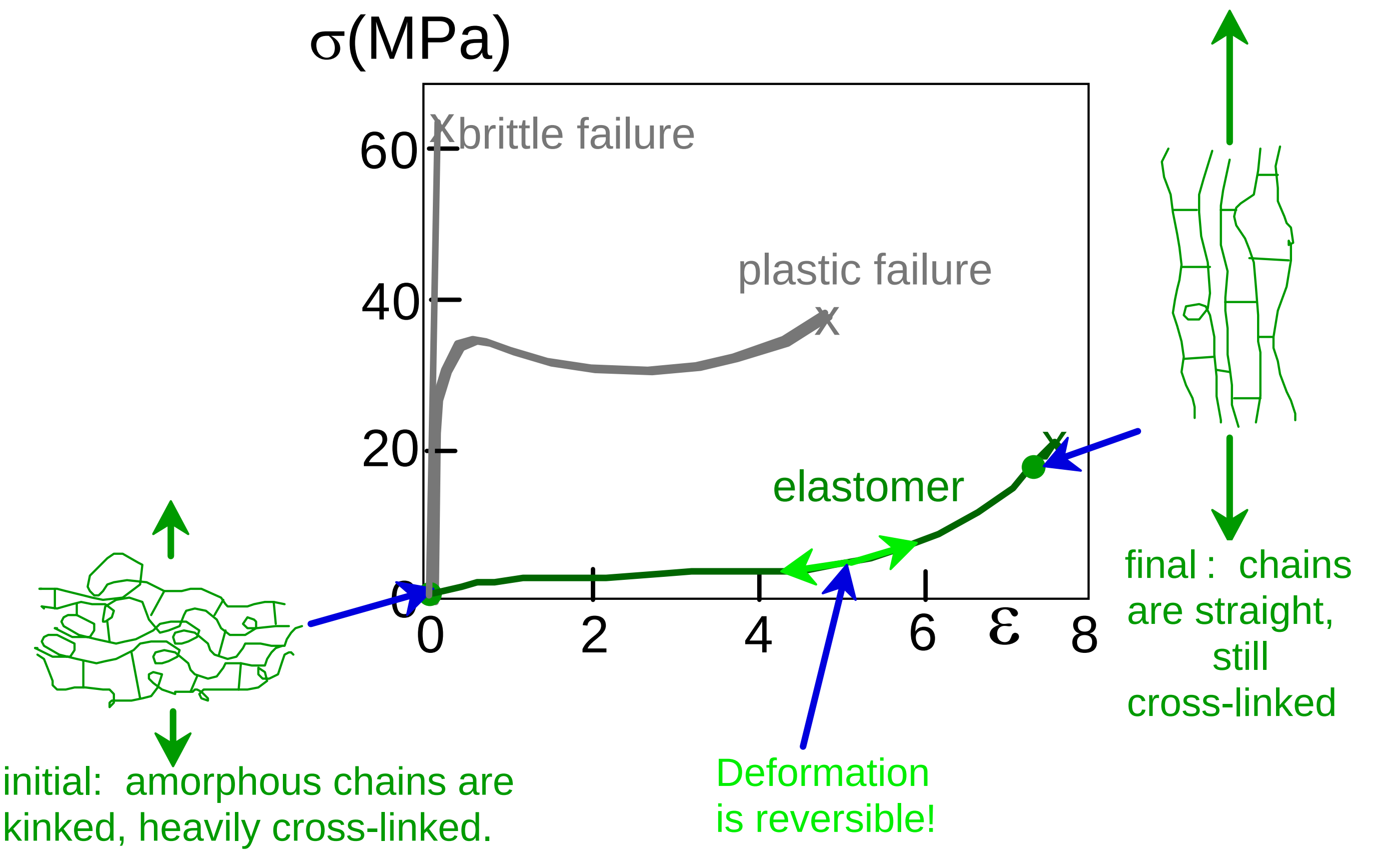




Trans-isoprene

Linear chain is stiffer

Tensile response: elastomer case

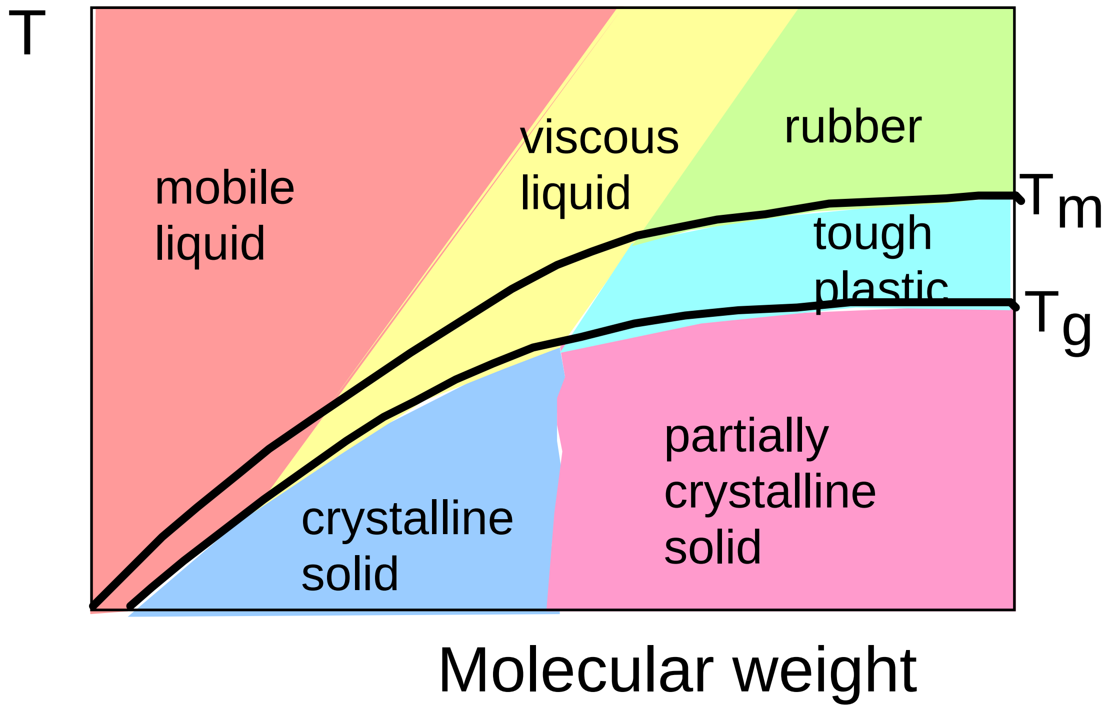


Stress-strain curves adapted from Fig. 15.1, *Callister 6e.* Inset figures along elastomer curve (green) adapted from Fig. 15.14, *Callister 6e*. (Fig. 15.14 is from Z.D. Jastrzebski, *The Nature and Properties of Engineering Materials*, 3rd ed., John Wiley and Sons, 1987.)

- Compare to responses of other polymers:
  - --brittle response (aligned, cross linked & networked case)
  - --plastic response (semi-crystalline case)

Thermoplastics vs thermosets

- **Thermoplastics**:
  --little cross linking
  --ductile
  --soften w/heating
  --polyethylene (#2)
  polypropylene (#5)
  polycarbonate
  polystyrene (#6)



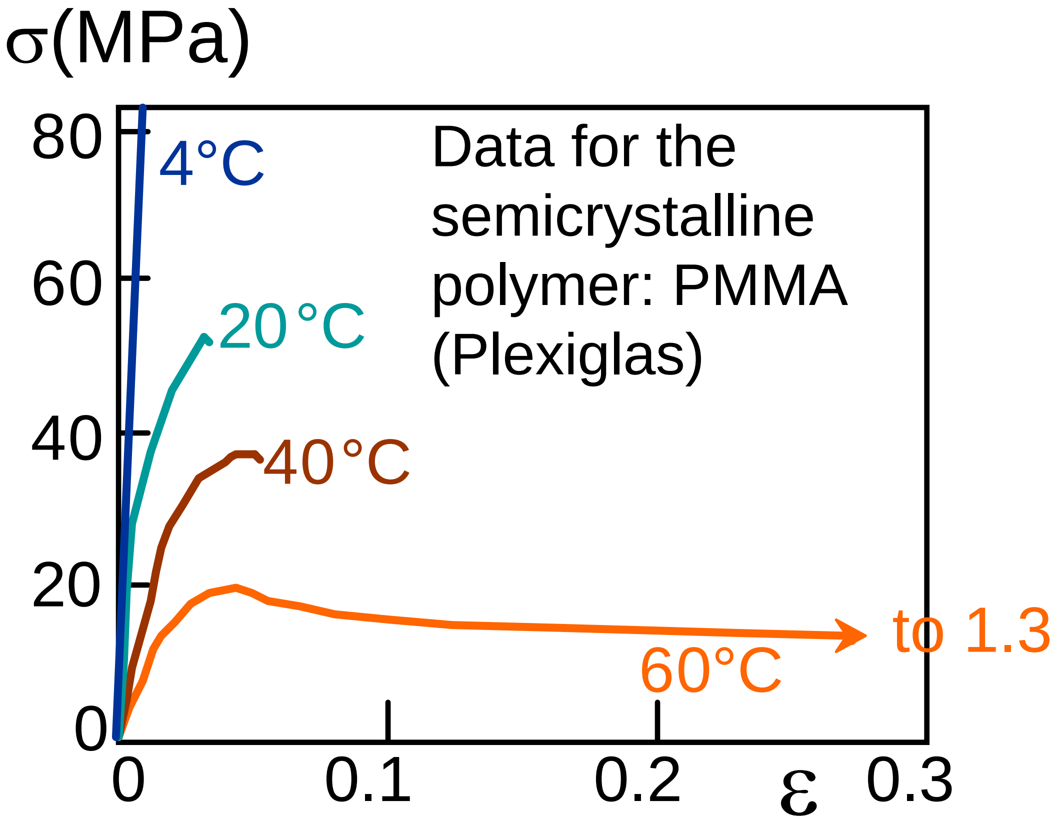
Adapted from Fig. 15.18, *Callister 6e*. (Fig. 15.18 is from F.W. Billmeyer, Jr., *Textbook of Polymer Science*, 3rd ed., John Wiley and Sons, Inc., 1984.)

- **Thermosets**:
  --large cross linking
  (10 to 50% of mers)
  --hard and brittle
  --do NOT soften w/heating
  --vulcanized rubber, epoxies,
  polyester resin, phenolic resin

T and strain rate: thermoplastics

- Decreasing T...
  - --increases E
  - --increases TS
  - --decreases %EL

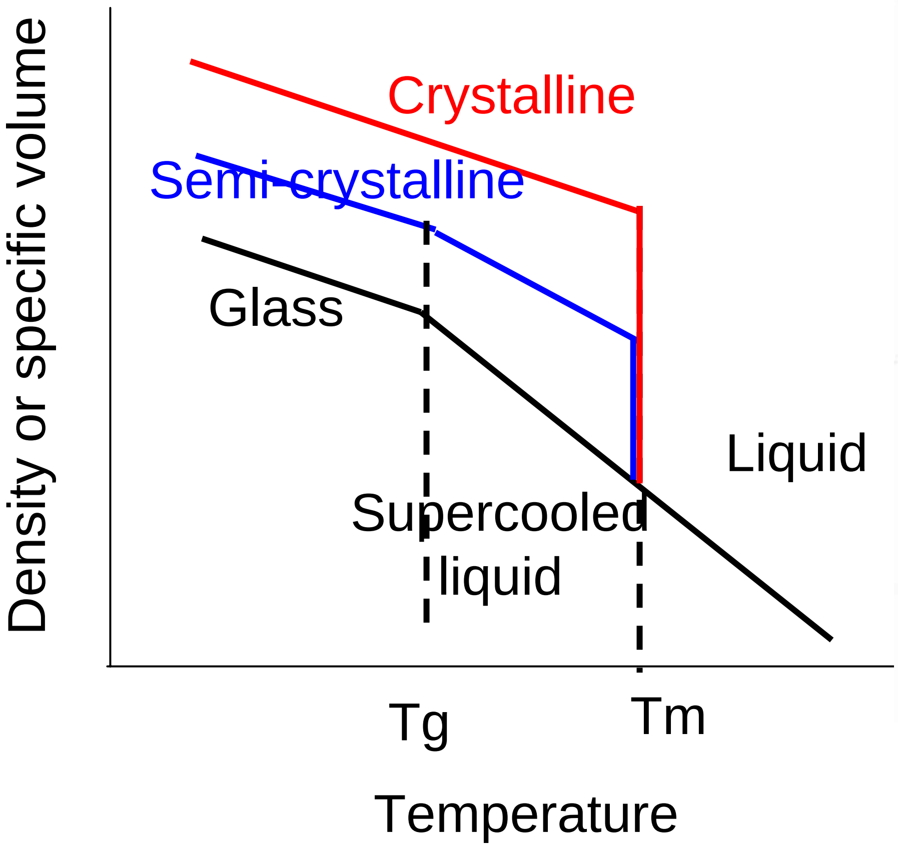
- Increasing strain rate...
  - --same effects as decreasing T.



Adapted from Fig. 15.3, *Callister 6e*. (Fig. 15.3 is from T.S. Carswell and J.K. Nason, 'Effect of Environmental Conditions on the Mechanical Properties of Organic Plastics", *Symposium on Plastics*, American Society for Testing and Materials, Philadelphia, PA, 1944.)

Melting vs Glass transition temperature

Temperature at which upon cooling a noncrystalline polymer transforms into from a supercooled liquid to a rigid glass



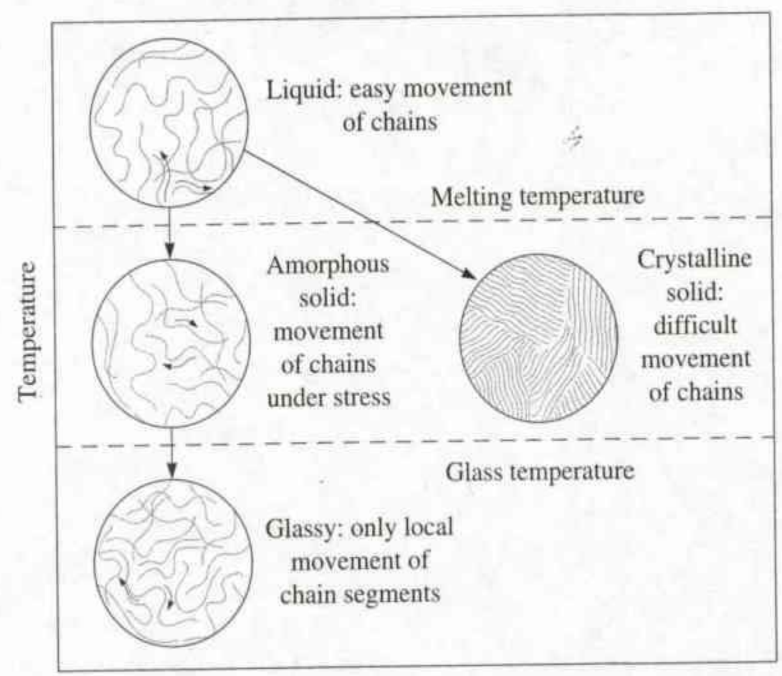
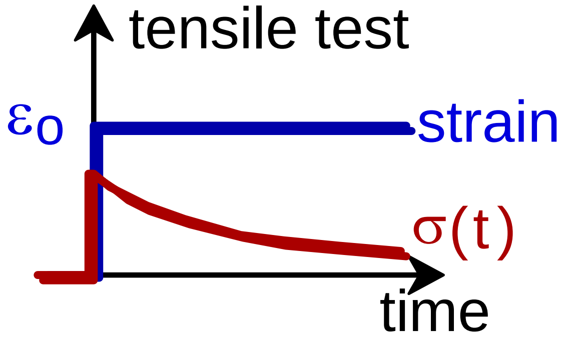


Figure 15-12 The effect of temperature on the structure and behavior of thermoplastics.

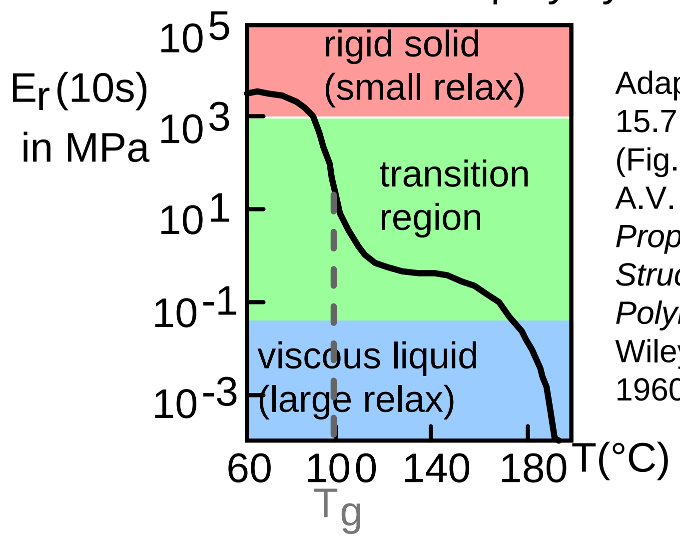
time dependent deformation

- Stress relaxation test:

  --strain to ε_o and hold.
  --observe decrease in stress with time.



- Data: Large drop in E_r for $T > T_g$. (amorphous polystyrene)



Adapted from Fig. 15.7, *Callister 6e*. (Fig. 15.7 is from A.V. Tobolsky, *Properties and Structures of Polymers*, John Wiley and Sons, Inc., 1960.)

- Relaxation modulus:

$$E_r(t) = \frac{\sigma(t)}{\varepsilon_o}$$

- Sample T_g(C) (Glass transition) values:

PE (low M_w)	-110
PE (high M_w)	- 90
PVC	+ 87
PS	+100
PC	+150

Selected values from Table 15.2, *Callister 6e*.

Summary

- General drawbacks to polymers:
  - -- E, σ_y, K_c, $T_{application}$ are generally small.
  - -- Deformation is often T and time dependent.
  - -- Result: polymers benefit from composite reinforcement.
- Thermoplastics (PE, PS, PP, PC):
  - -- Smaller E, σ_y, $T_{application}$
  - -- Larger K_c
  - -- Easier to form and recycle
- Elastomers (rubber):
  - -- Large reversible strains!
- Thermosets (epoxies, polyesters):
  - -- Larger E, σ_y, $T_{application}$
  - -- Smaller K_c

Table 15.3 *Callister 6e*:

Good overview
of applications
and trade names
of polymers.

ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems: