Chapter 10 **Polymer Characteristics**

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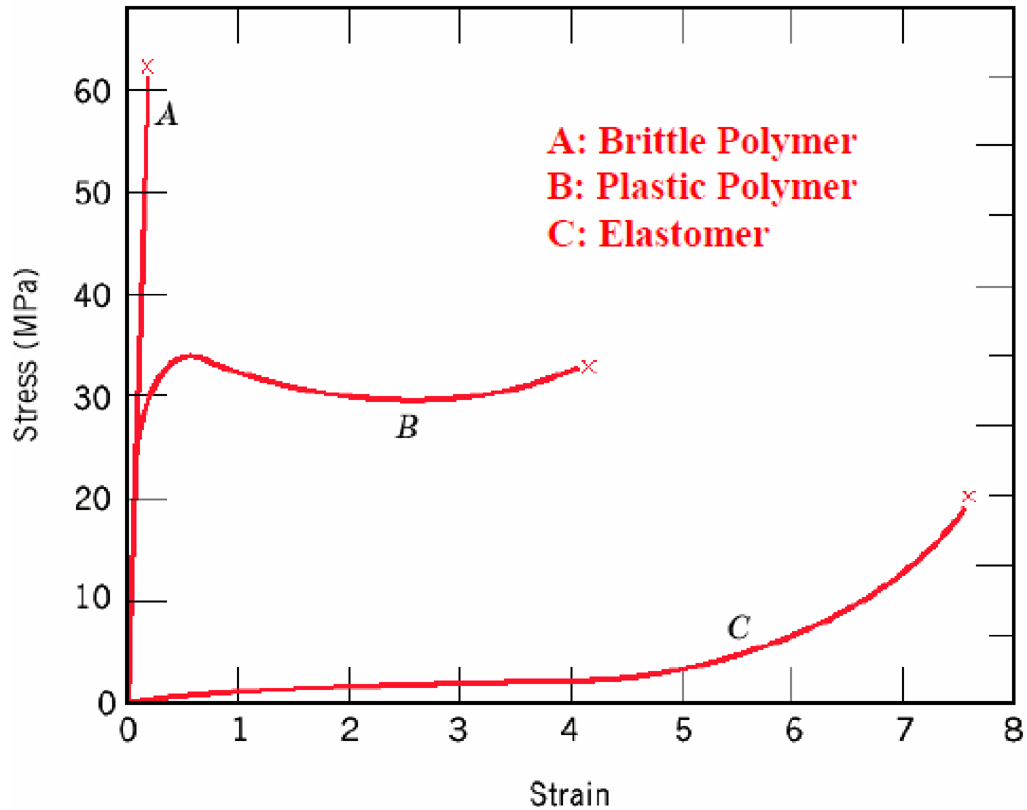
Stress – Strain Behavior (I)

- The description of stress-strain behavior is similar to that of metals



Polymers can be **brittle** (**A**)**, plastic (B), or highly elastic, or elastomer** (**C**)**. Deformation shown by curve C is totally elastic** (rubber-like elasticity, large recoverable strain at low stress levels).

Stress – Strain Behavior (II)

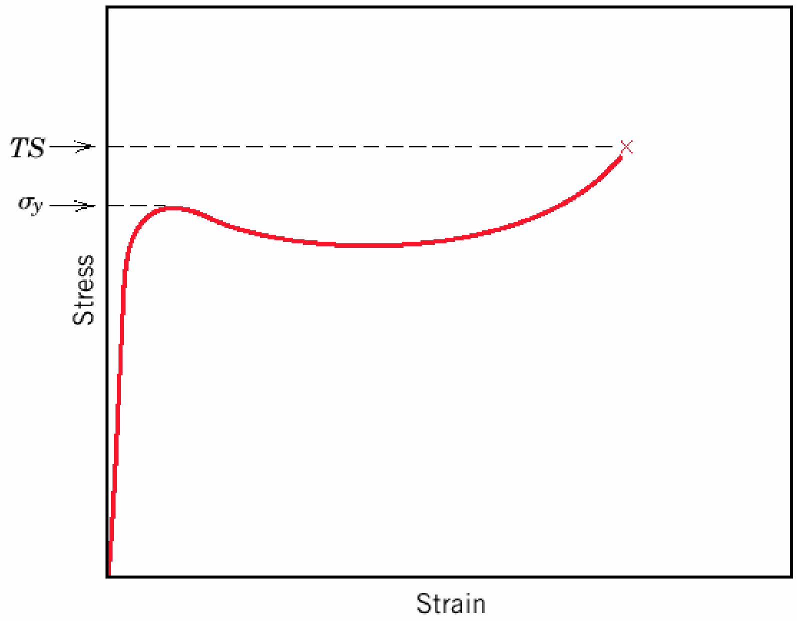
- Characteristics of stress-strain behavior:

✓ **Modulus of elasticity – defined as for metals**

✓ **Ductility (%EL) – defined as for metals**

❖ **Yield strength - For plastic polymers (B), yield** strength is defined by the maximum on curve just after the elastic region (different from metals)

❖ **Tensile strength is defined at the fracture point and can** be lower than the yield strength (different from metals).



Stress – Strain Behavior (III)

- Moduli of elasticity for polymers are ~ 10 MPa - 4 Gpa (compare to metals ~ 50 - 400 GPa)
- Tensile strengths are ~ 10 - 100 MPa (compare to metals, hundreds of MPa to several GPa)
- Elongation can be up to 1000 % in some cases (< 100% for metals)

❑Mechanical properties of polymers change dramatically with temperature, going from glass-like brittle behavior at low temperatures to a rubber-like behavior at high temperatures.

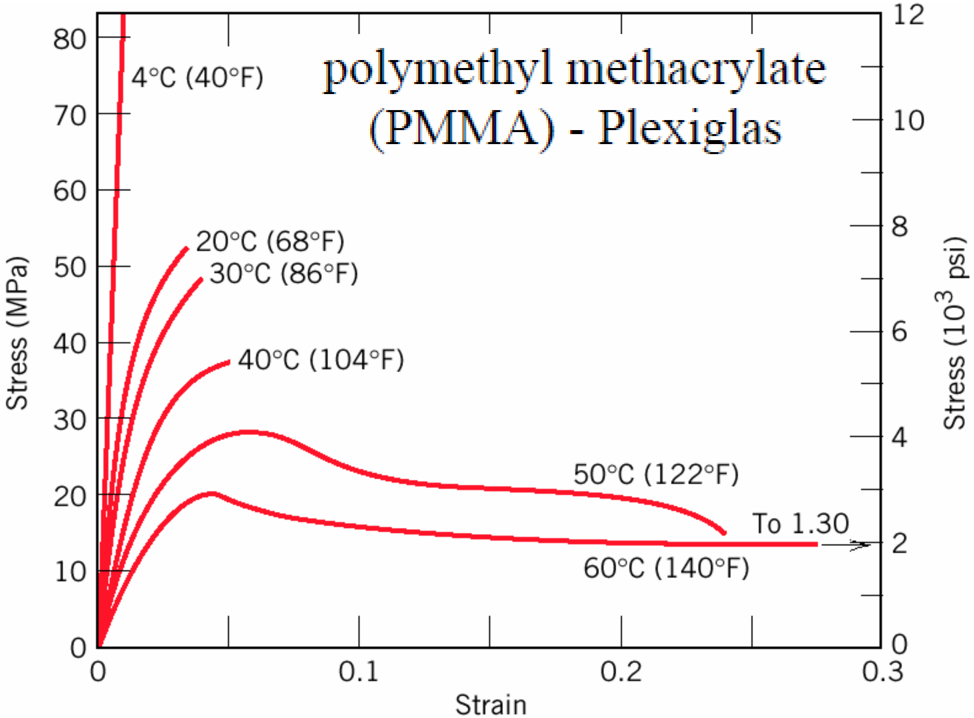
❑Polymers are also very sensitive to the rate of deformation (strain rate). Decreasing rate of deformation has the same effect as increasing T.

Stress – Strain Behavior (IV)

Temperature increase leads to:

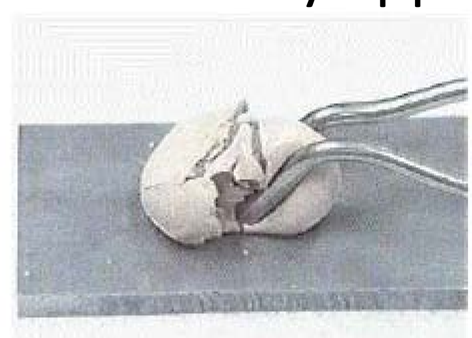
- Decrease in elastic modulus
- Reduction in tensile strength
- Increase in ductility

The glass transition temperature (Tg) of PMMA ranges from 85 to 165 °C – all of the above curves are for temperatures below Tg.



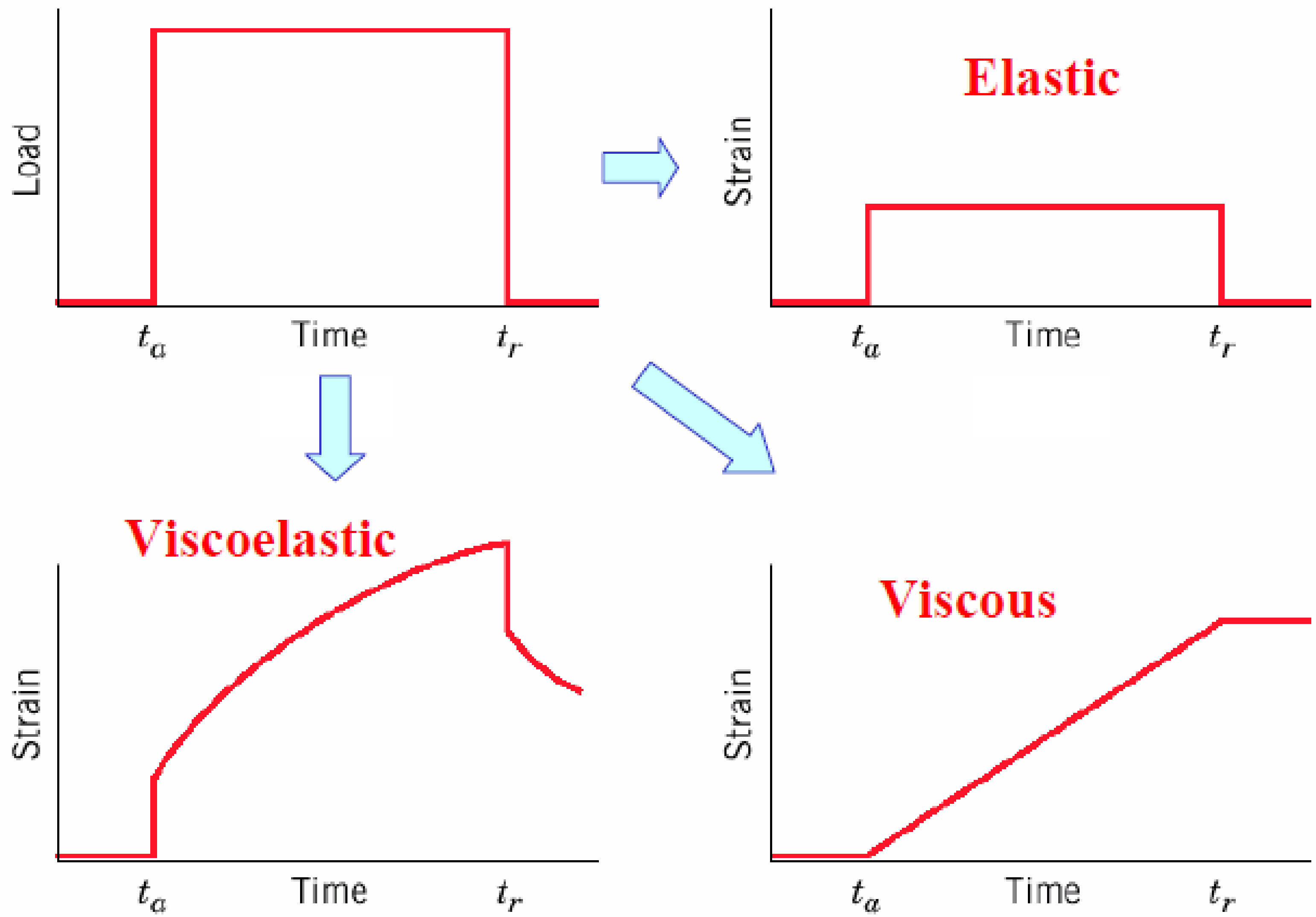
Viscoelasticity

- Amorphous polymer: glass at low temperatures, rubber at intermediate temperatures, viscous liquid at high T.
- Low temperatures: **elastic deformation at small strains** ($\sigma = E\varepsilon$). Deformation is instantaneous when load is applied. Deformation is reversible.
- High temperatures: **viscous behavior. Deformation is** time dependent and not reversible.
- Intermediate temperatures: **viscoelastic behavior.** Instantaneous elastic strain followed by viscous time dependent strain.
- Viscoelastic behavior is determined by rate of strain (elastic for rapidly applied stress, viscous for slowly applied stress)



Rate dependence of viscoelastic properties in a silicone polymer (Silly Putty). Picture by Geon Corp.

Viscoelasticity



Load is applied at t_a and released at t_r

Viscoelasticity

- Viscoelasticity can be characterized by the **viscoelastic relaxation modulus:**

✓ Sample is strained rapidly to pre-determined strain

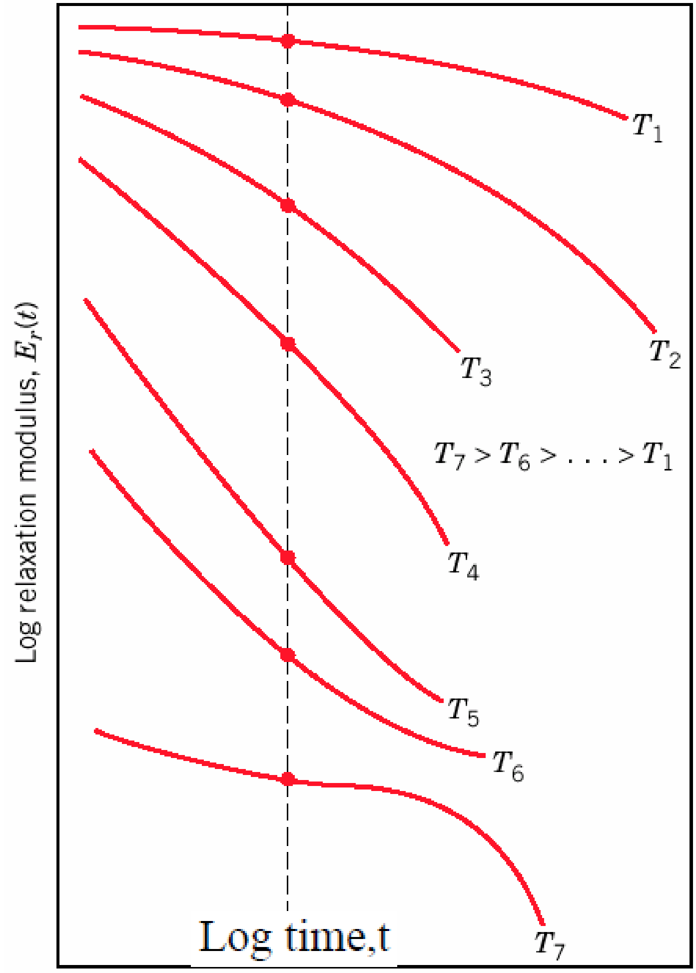
✓ Stress required to maintain this strain ε0 over time is measured at constant T.

✓ Stress decreases with time due to molecular relaxation processes.

✓ Relaxation modulus can be defined as

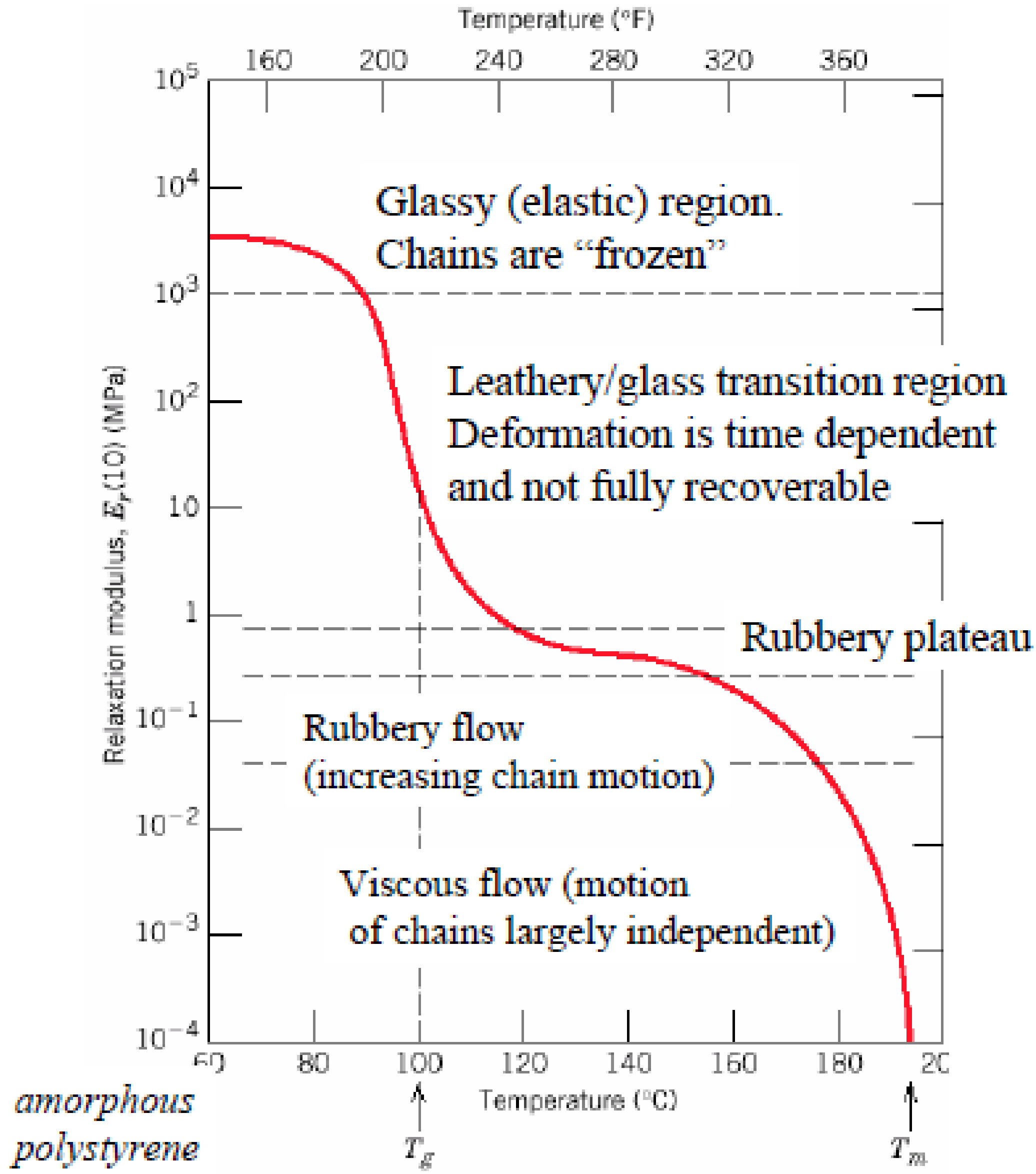
$$E_r(t) = \sigma(t)/\varepsilon_0$$

$E_r(t)$ is also a function of temperature



Viscoelasticity

To show the influence of temperature, the relaxation modulus can be plotted at a fixed time for different T:



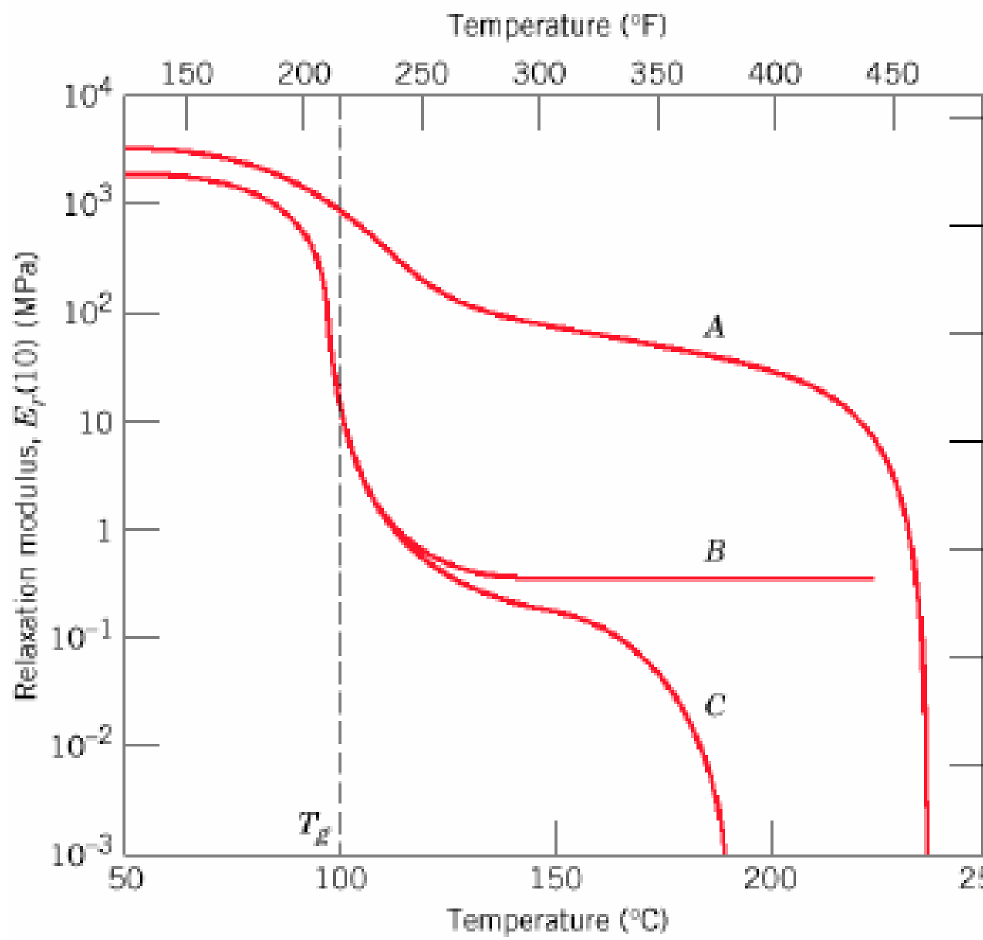
Viscoelasticity

Temperature dependence for different **polymer structures**

A : Largely crystalline isotactic polystyrene. Glass transition region limited – small amount of amorphous material

B: Lightly cross-linked atactic polystyrene – leathery region extends to decomposition temperature: no melting

C: Amorphous polystyrene



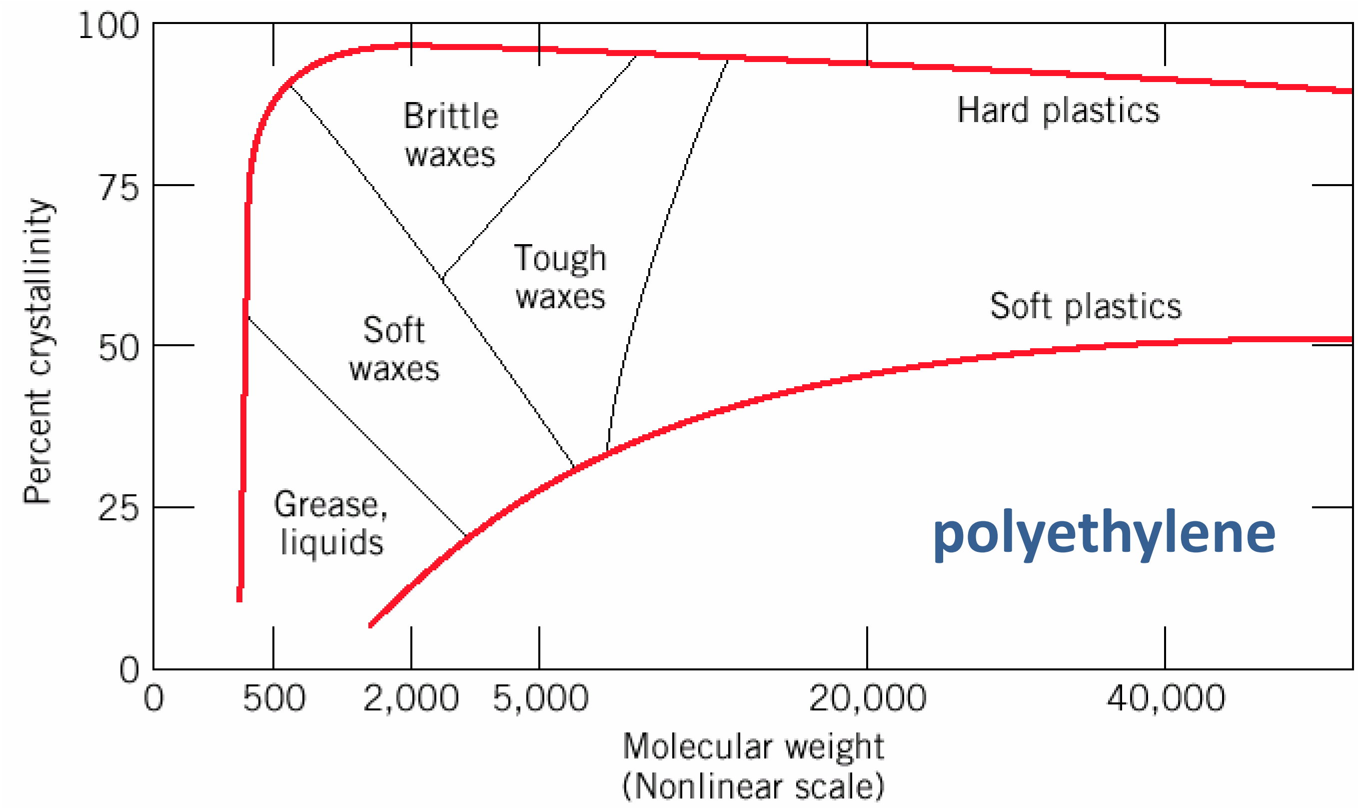
Factors that Influence Mechanical properties

- **Temperature and strain rate (already discussed)**
- **Chain entanglement, strong intermolecular bonding** (van der Waals, cross-links) increase strength
- **Drawing, analog of work hardening in metals,** corresponds to the neck extension. Is used in production of fibers and films. Molecular chains become highly oriented ⇒ properties of drawn material are anisotropic (perpendicular to the chain alignment direction strength is reduced)
- **Heat treatment - changes in crystallite size and order**
  - **undrawn material**: Increasing annealing temperature leads to
    - ✓ increase in elastic modulus
    - ✓ increase in yield/tensile strength
    - ✓ decrease in ductility

    Note that these changes are opposite from metals
  - **drawn material**: opposite changes (due to recrystallization and loss of chain orientation)

Factors that Influence Mechanical properties

- Tensile strength increases with **molecular weight –** effect of entanglement
- Higher **degree of crystallinity – stronger secondary** bonding - stronger and more brittle material



Polymerization

- Polymerization is the synthesis of high polymers from raw materials like oil or coal. It may occur by:

1. Addition (chain-reaction) polymerization, where monomer units are attached one at a time (discussed in previous Chapter). Has three distinct stages: initiation, propagation, and termination.
2. Condensation (step reaction) polymerization, by stepwise intermolecular chemical reactions that produce the mer units.
    - ✓ Usually there is small by-product that is then eliminated
    - ✓ Significantly slower than addition polymerization
    - ✓ Often form trifunctional molecules that can form cross-linked and network polymers

Ethylene glycol   Adipic acid