

Chapter Outline: Characteristics, Applications, and Processing of Polymers

- Mechanical properties
 - Stress-Strain Behavior
 - Deformation of Semicrystalline Polymers
- Crystallization, Melting, Glass Transition
- Thermoplastic and Thermosetting Polymers
- Viscoelasticity
- Deformation and Elastomers
- Fracture of Polymers
- Polymerization
- Elastomers

Optional reading: 15.6, 15.17-15.19, 15.21-15.24

“The Graduate” 1967:

Mr. McGuire: *I want to say one word to you. Just one word.*

Benjamin: *Yes, sir.*

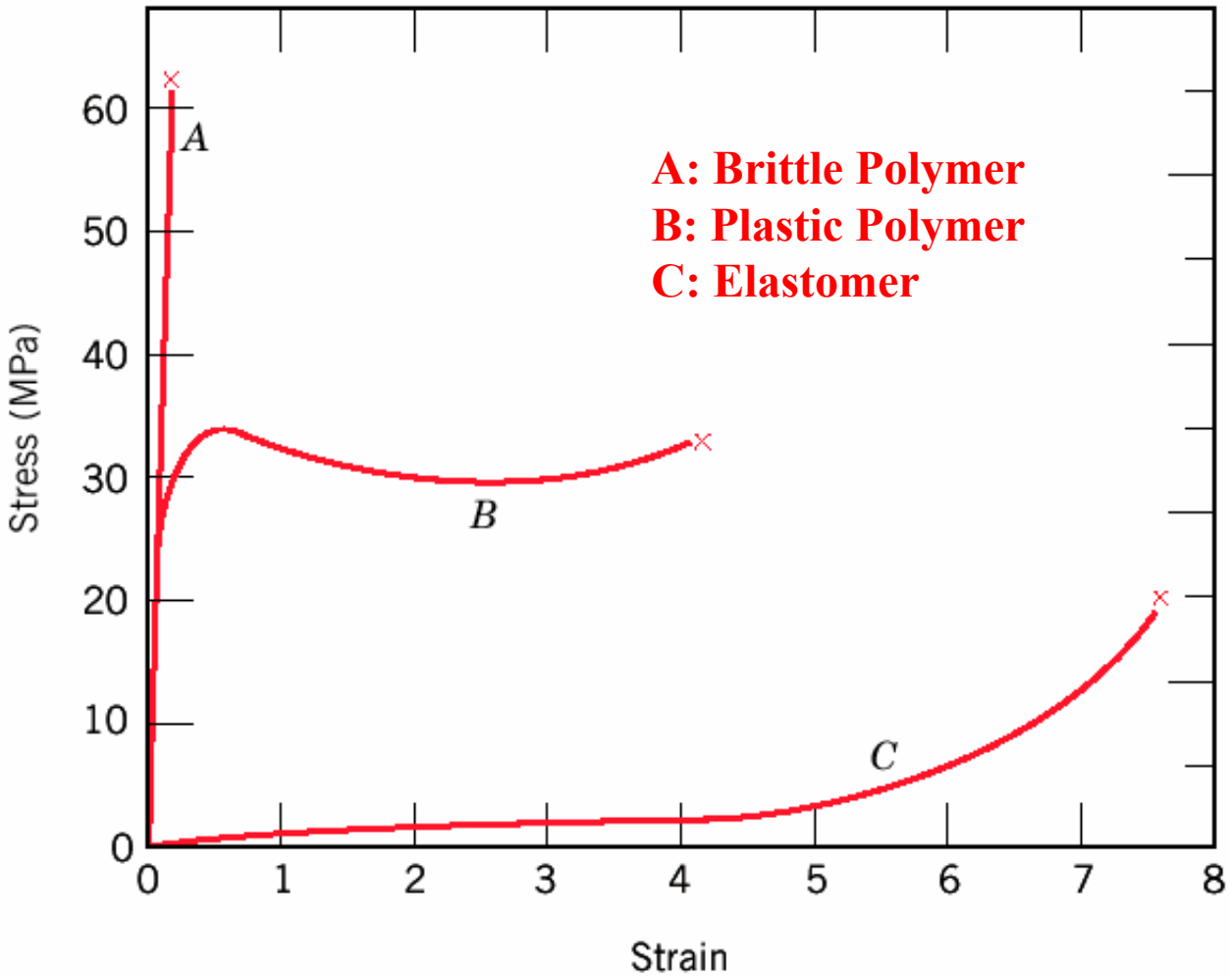
Mr. McGuire: *Are you listening?*

Benjamin: *Yes, I am.*

Mr. McGuire: *Plastics.*

Stress – Strain Behavior (I)

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

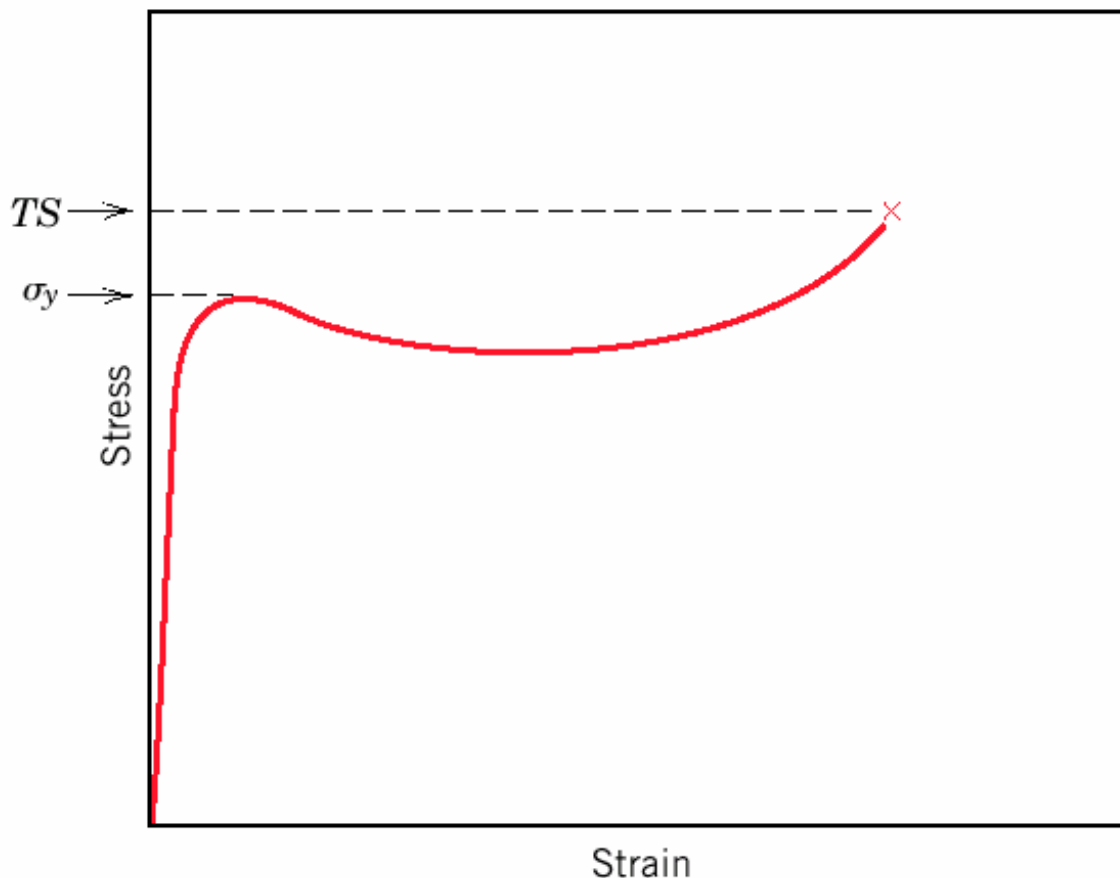


Polymers can be brittle (**A**), plastic (**B**), or highly elastic (**C**). Deformation shown by curve **C** is totally elastic (rubber-like elasticity, large recoverable strain at low stress levels). This class of polymers - **elastomers**

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)



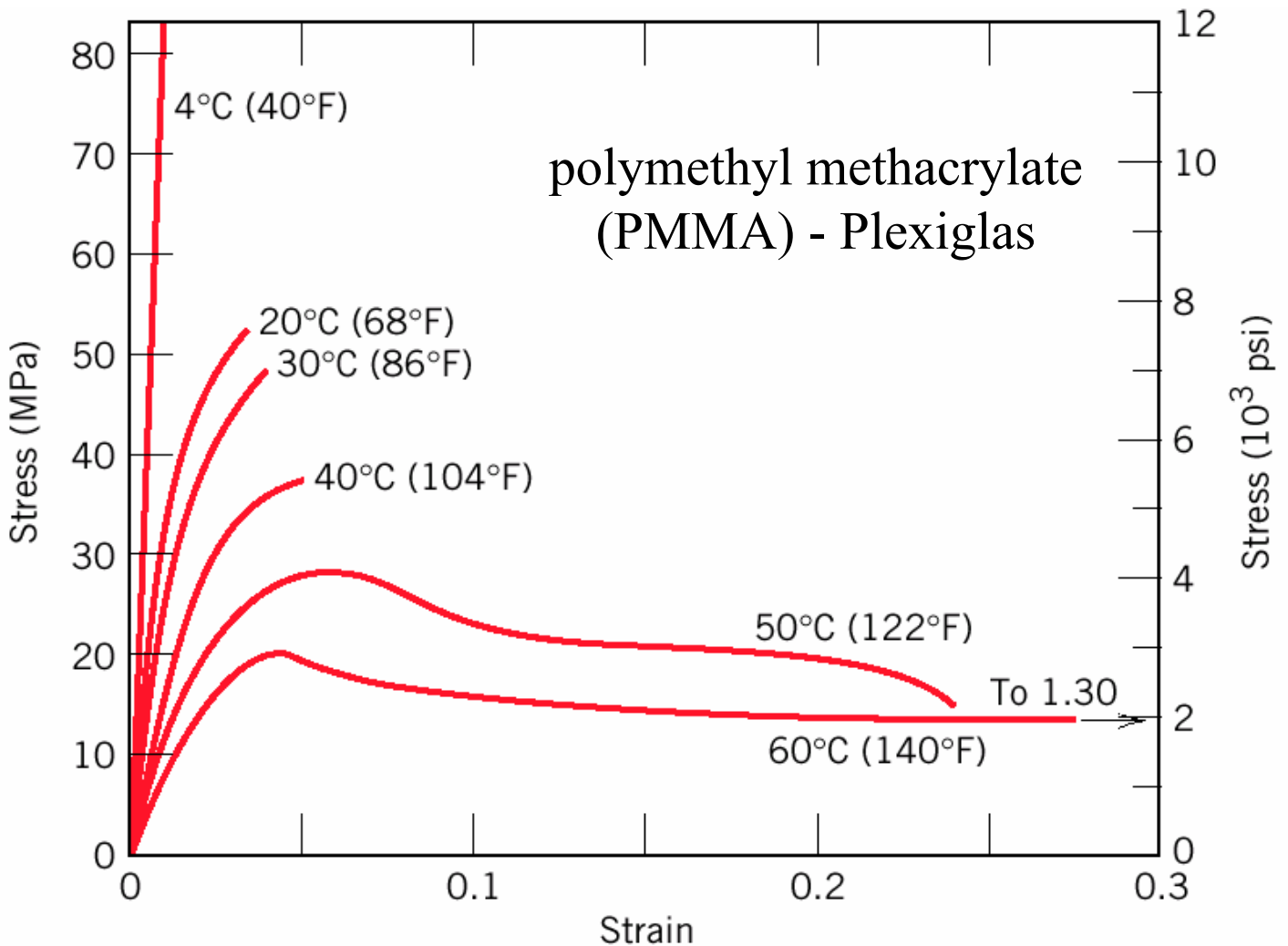
Stress – Strain Behavior (III)

- 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:

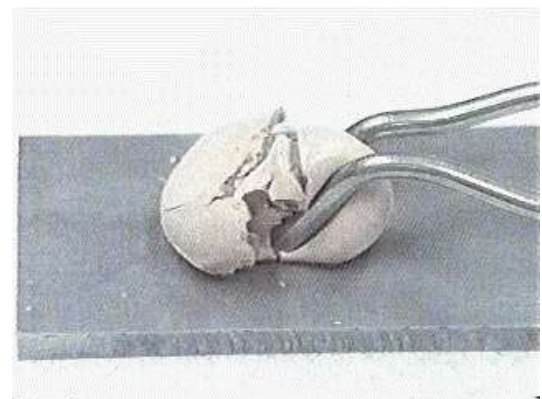
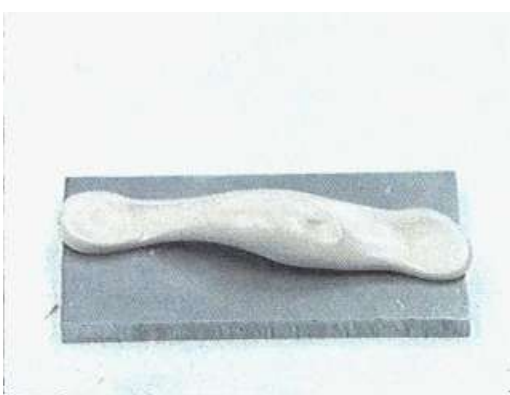
- ✓ Decrease in elastic modulus
- ✓ Reduction in tensile strength
- ✓ Increase in ductility



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

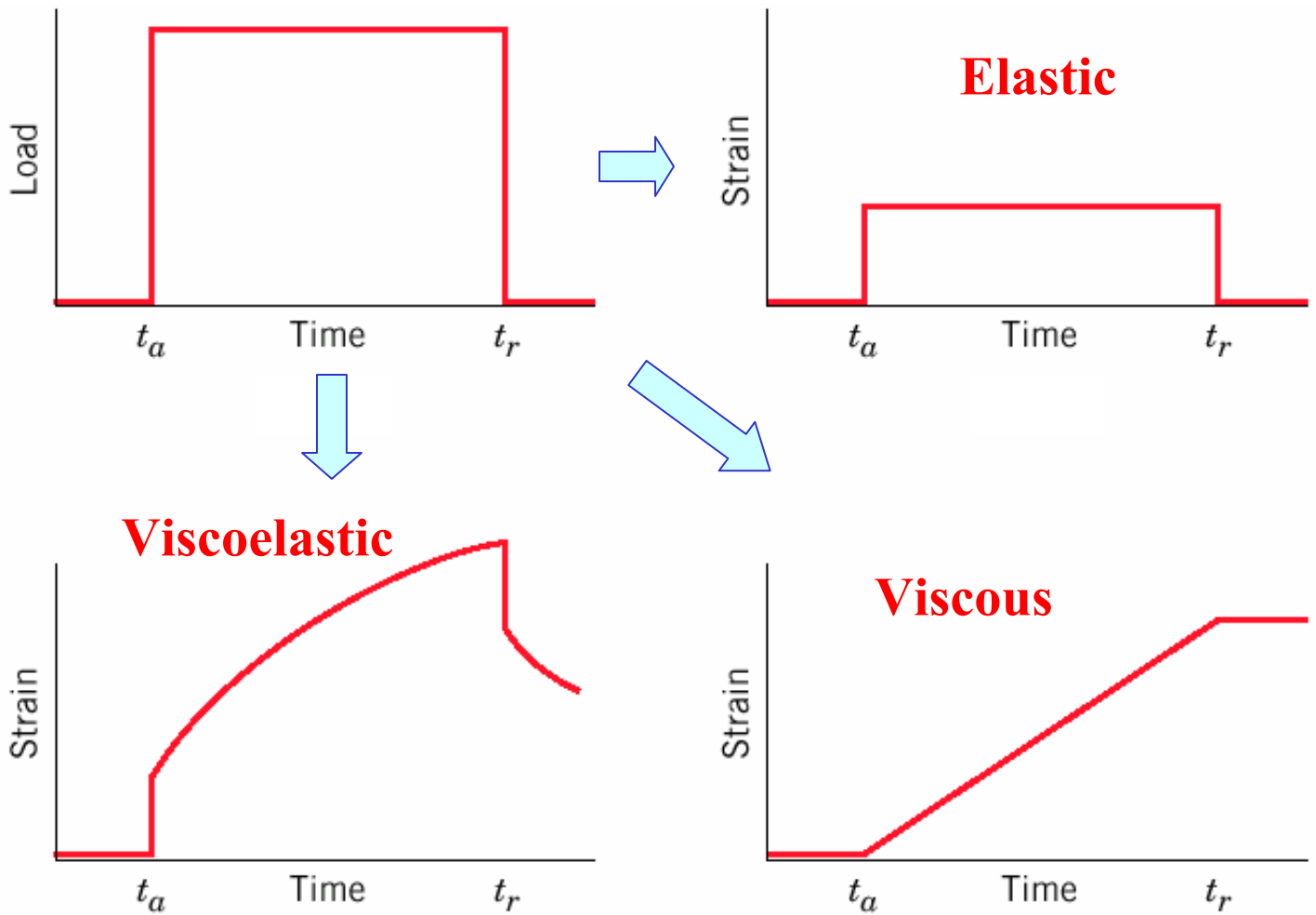
Viscoelasticity (I)

- 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 (II)



Load is applied at t_a and released at t_r

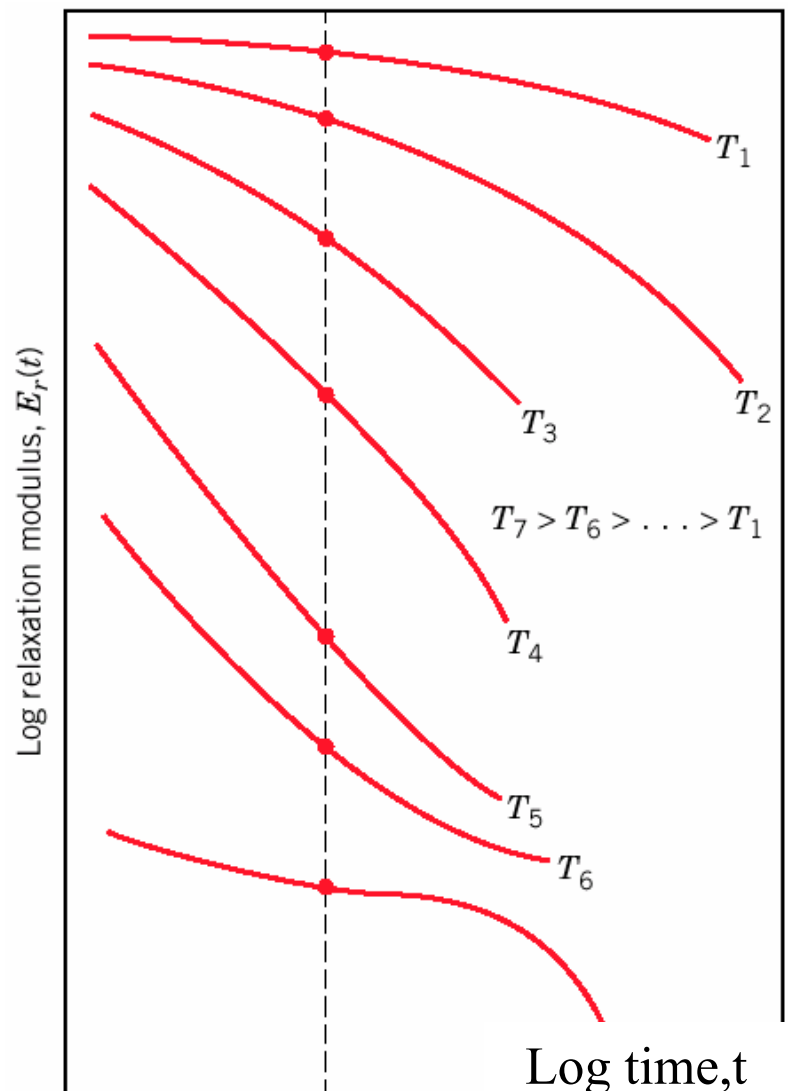
Viscoelasticity (III)

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

- Sample is strained rapidly to pre-determined strain
- Stress required to maintain this strain ϵ_0 over time is measured at constant T
- Stress decreases with time due to molecular relaxation processes
- Relaxation modulus can be defined as

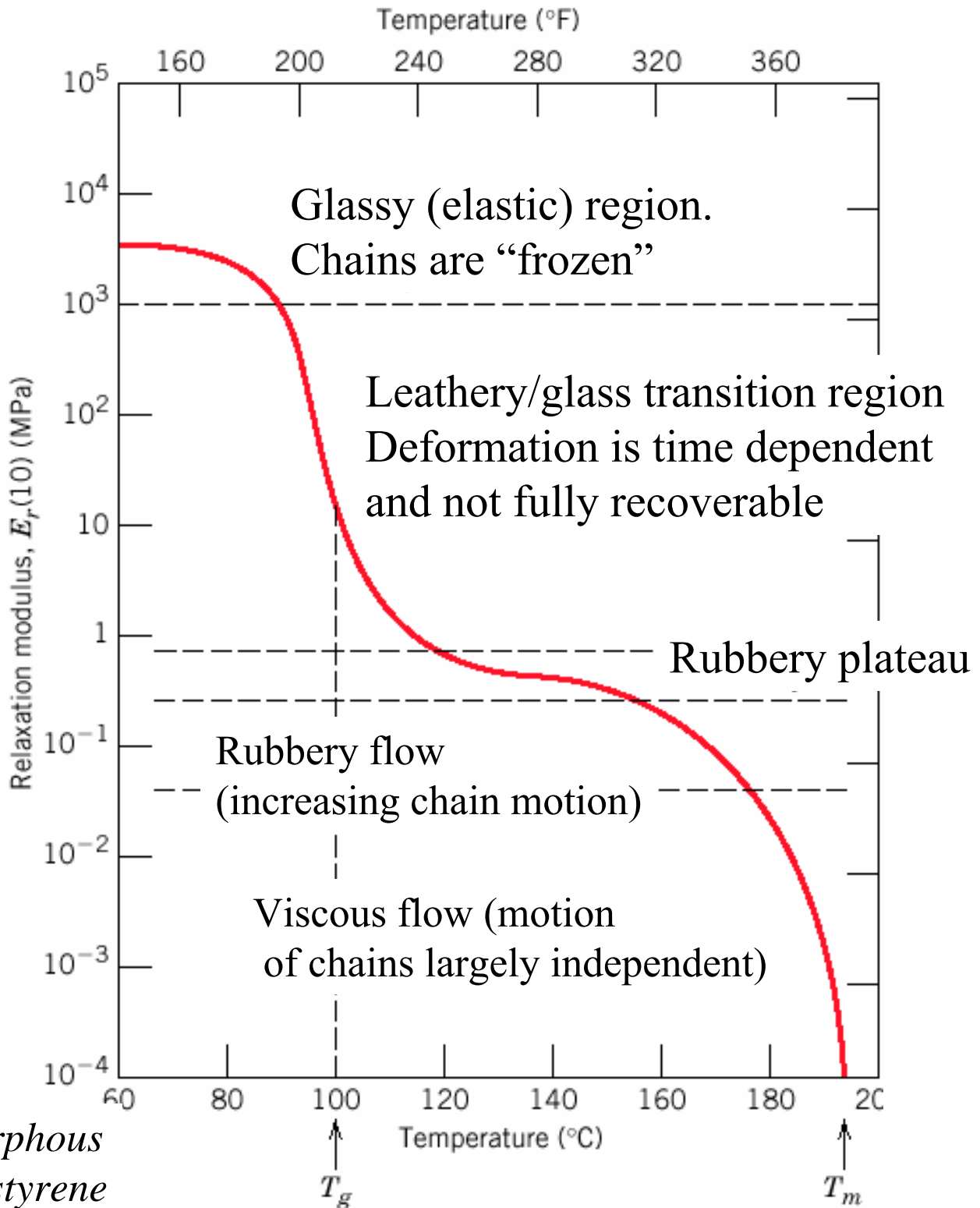
$$E_r(t) = \sigma(t)/\epsilon_0$$

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



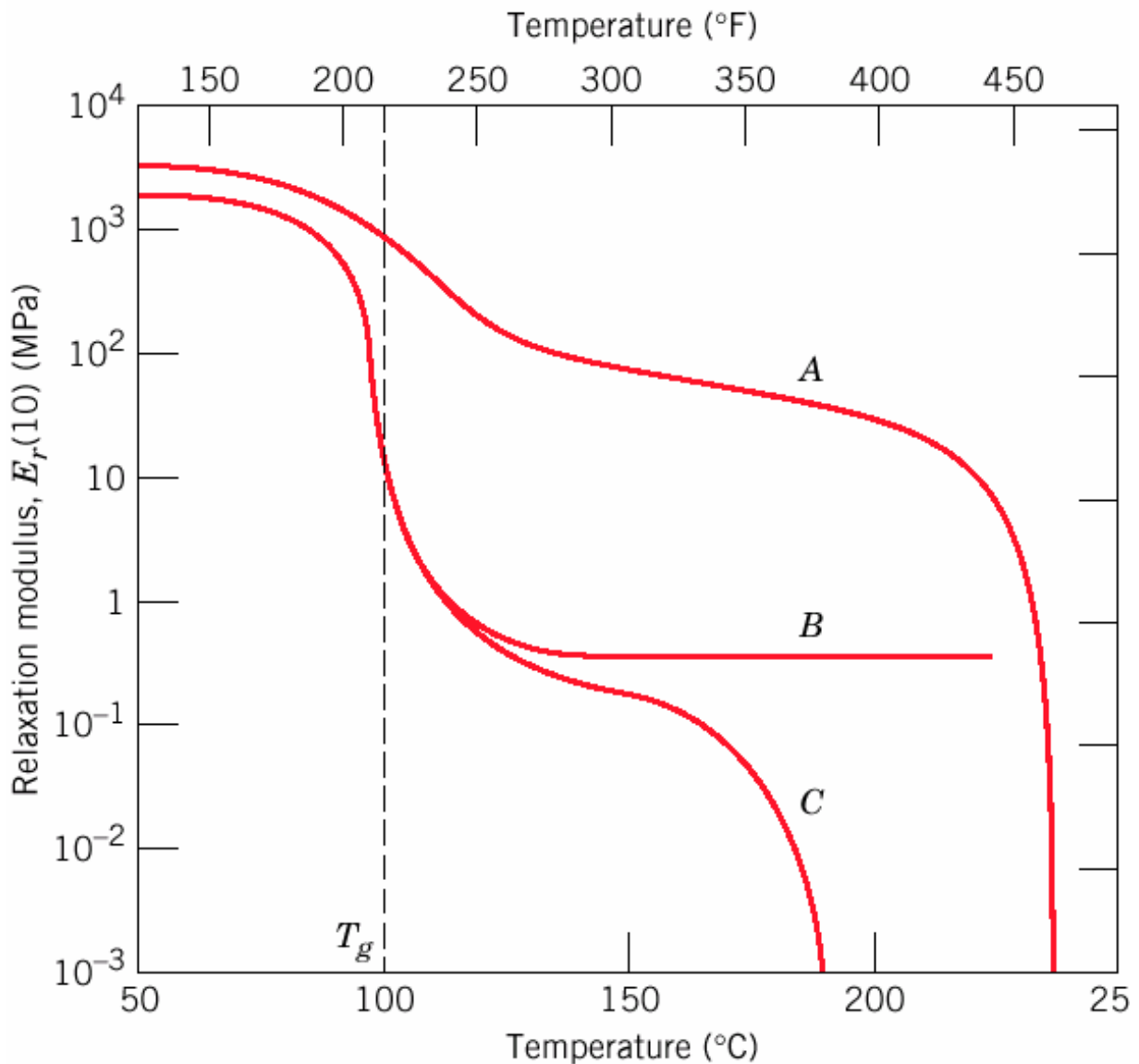
Viscoelasticity (IV)

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



Viscoelasticity (V)

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

Viscoelastic Creep

Many polymers susceptible to time-dependent deformation under constant load – viscoelastic creep

Creep may be significant even at room temperature and under moderately low stresses (below yield strength)

Results of creep tests are described by time dependent creep modulus:

$$E_c(t) = \sigma_0 / \epsilon(t)$$

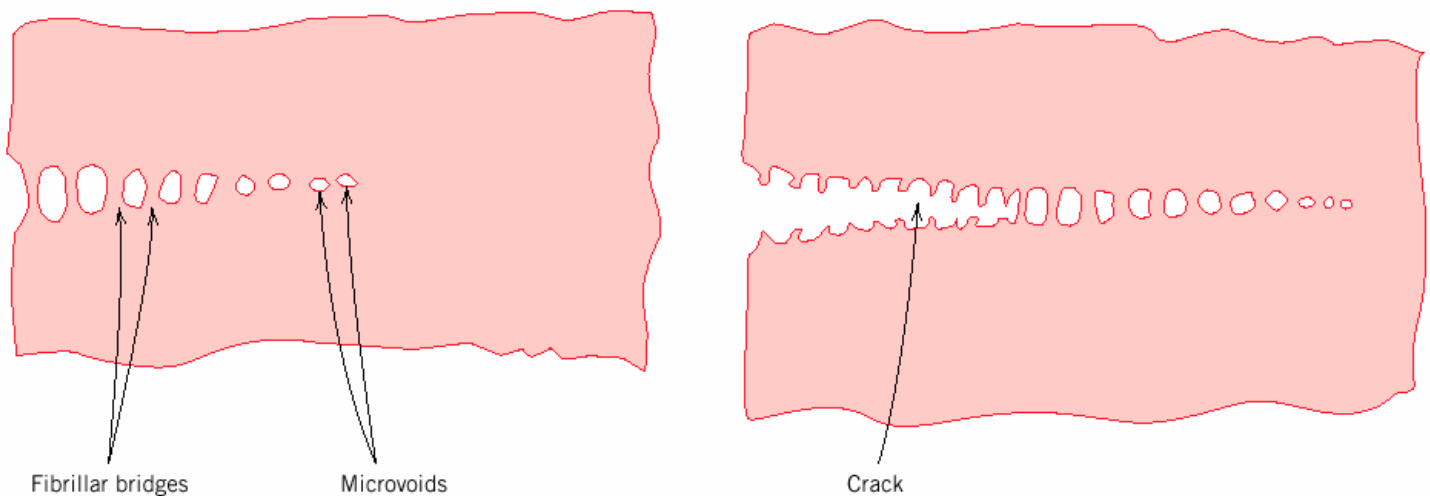
Amount of creep decreases as crystallinity increases

Fracture of Polymers

- Fracture strengths of polymers are low compared to metals and ceramics
- Brittle fracture occurs in thermosetting polymers. Fracture is initiated at stress concentrators (scratches, notches, etc). Covalent bonds are severed during fracture
- In thermoplastic polymers, both ductile and brittle fracture are possible. Brittle fracture is favored at lower temperatures, higher strain rates, and at stress concentrators
- Brittle to ductile transition often occurs with increasing temperature

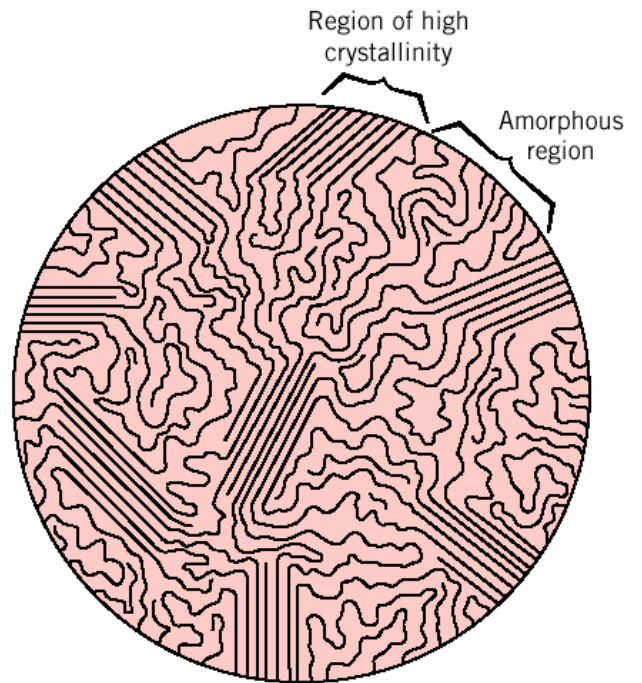
Fracture of Polymers: Crazeing

- Fracture of glassy thermoplastic polymers often proceeds through crazing. Crazing occurs when localized regions yield, forming an interconnected array of microvoids. Fibrillar bridges of oriented molecular chains form between voids.
- At high enough tensile loads, these bridges elongate and break, enabling crack propagation
- Crazeing absorbs fracture energy and increases fracture toughness



Deformation of Semicrystalline Polymers

Semi-crystalline polymers: crystalline regions separated by amorphous material (Chapter 14)



Elastic deformation:

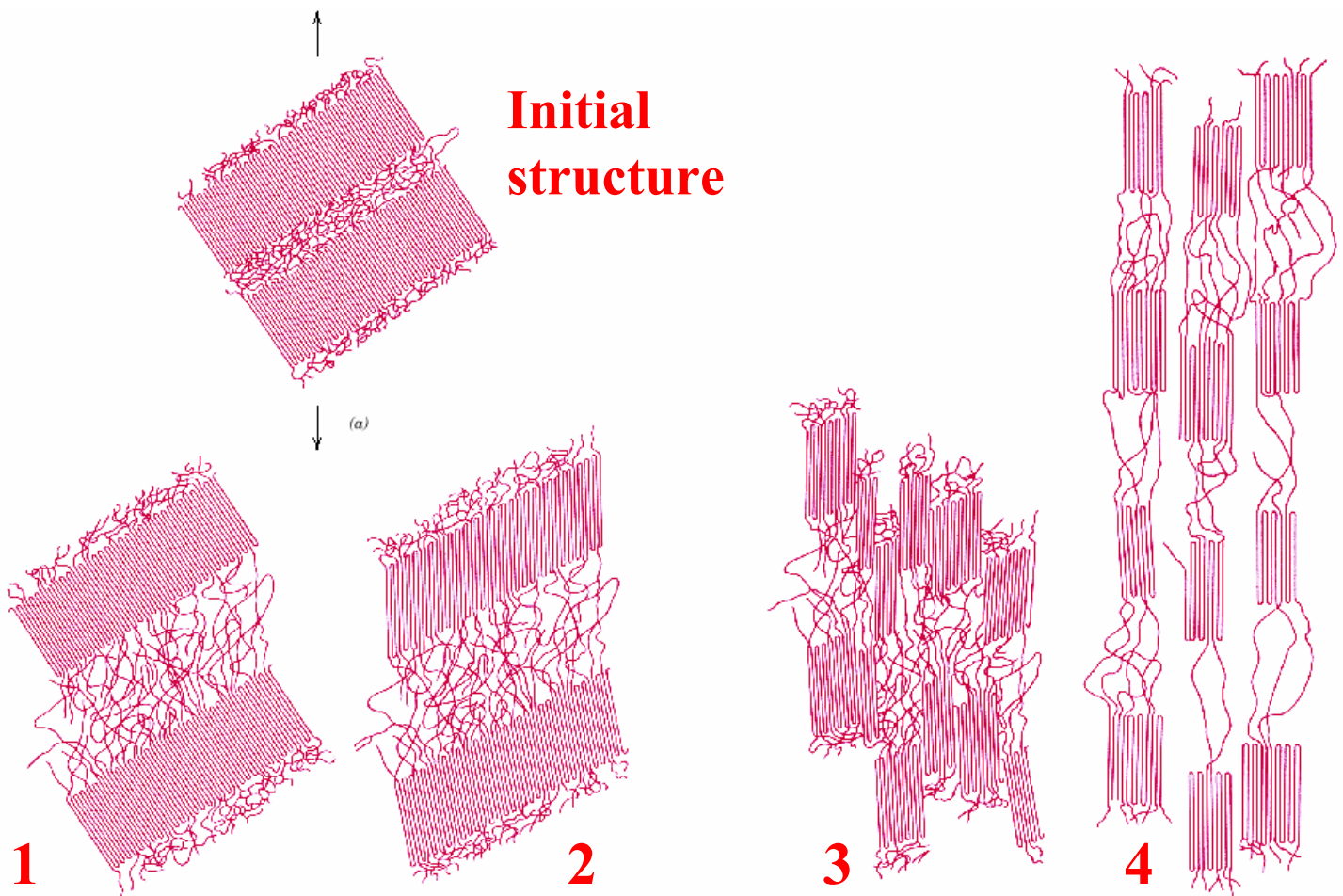
Basic mechanism of elastic deformation is elongation (straightening) of chain molecules in the direction of the applied stress. Elastic modulus is defined by elastic properties of amorphous and crystalline regions and by the microstructure.

Plastic Deformation of Semicrystalline Polymers

Plastic deformation is defined by the interaction between crystalline and amorphous regions and is **partially reversible**.

Stages of plastic deformation:

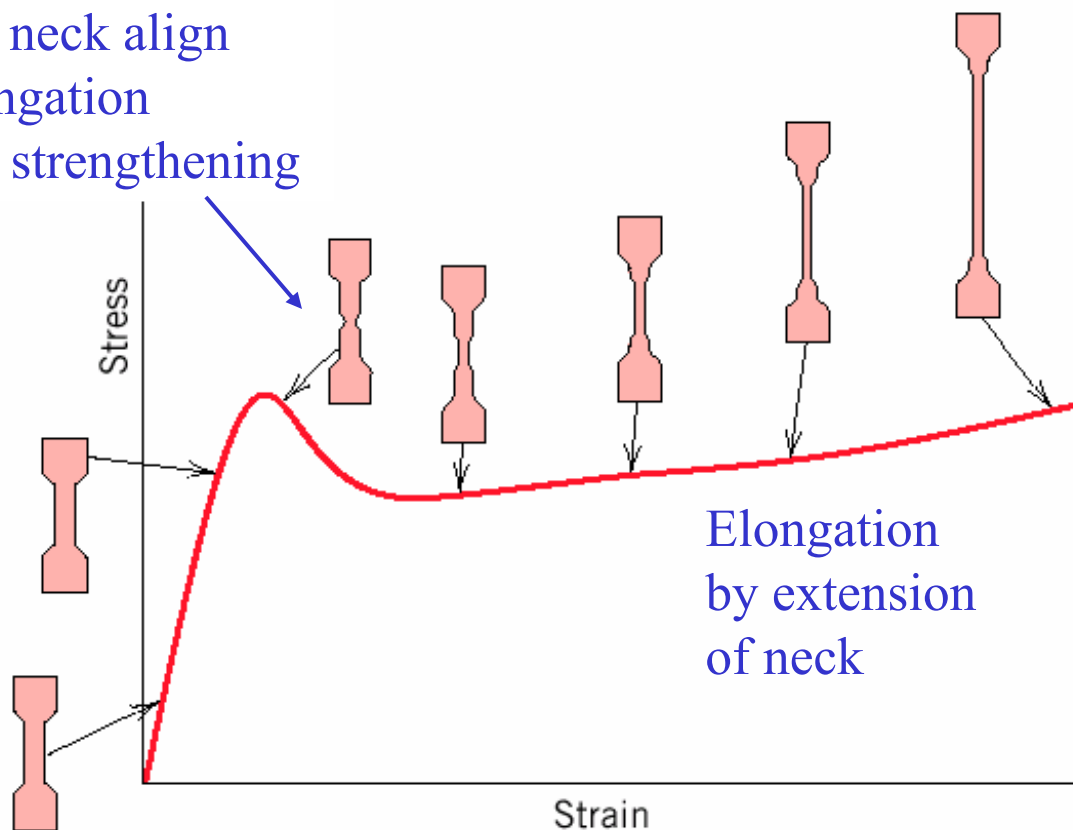
1. elongation of amorphous tie chains
2. tilting of lamellar crystallites towards the tensile axis
3. separation of crystalline block segments
4. stretching of crystallites and amorphous regions along tensile axis



Plastic Deformation of Semicrystalline Polymers

The macroscopic deformation involves necking. Neck gets stronger since the deformation aligns the chains and increases local strength in the neck region (up to 2-5 times) \Rightarrow neck is expanding along the specimen.

Chains in neck align
along elongation
direction: strengthening



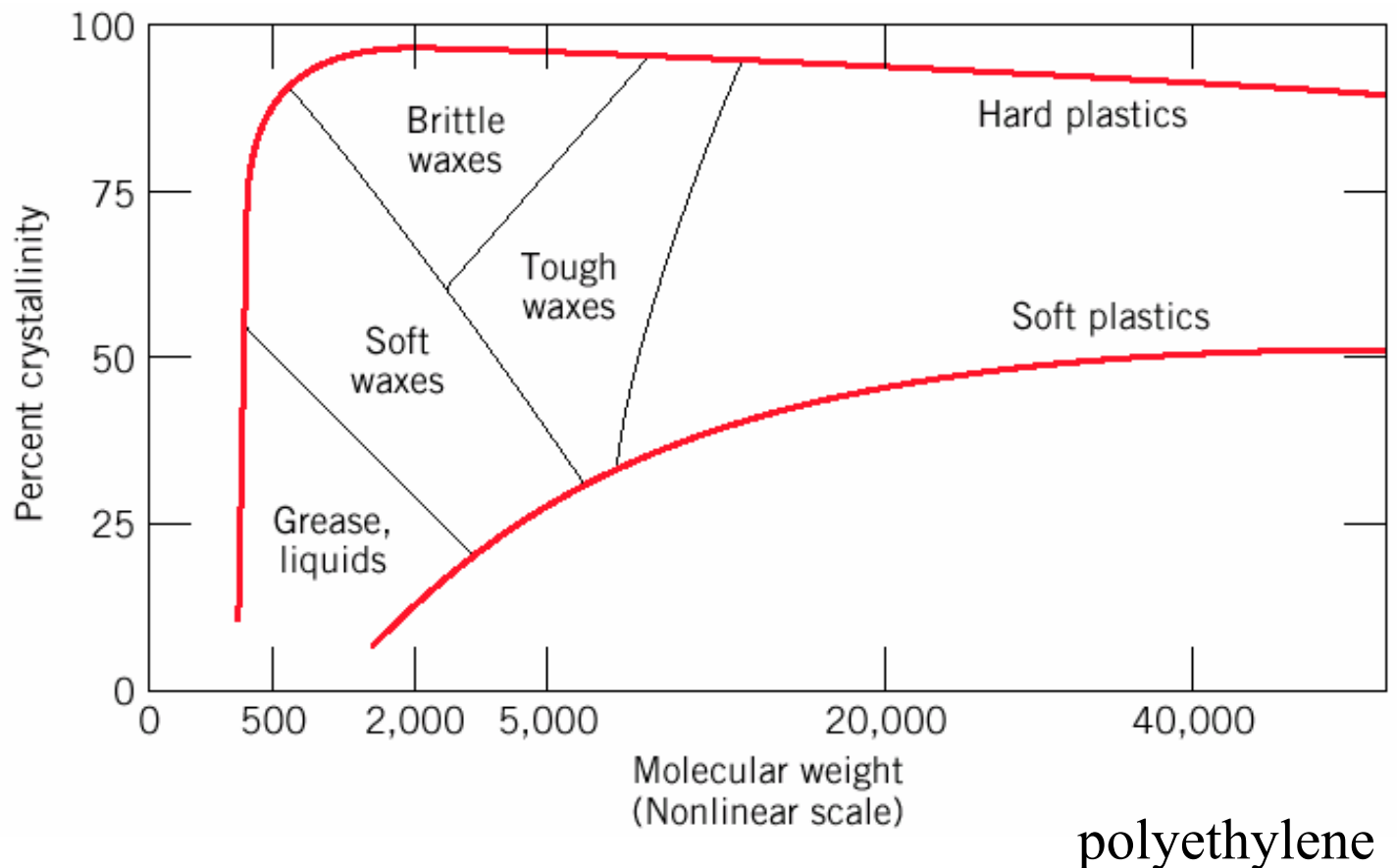
Different from ductile metals where the deformation is confined in the initial neck region.

Factors that Influence Mechanical properties (I)

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

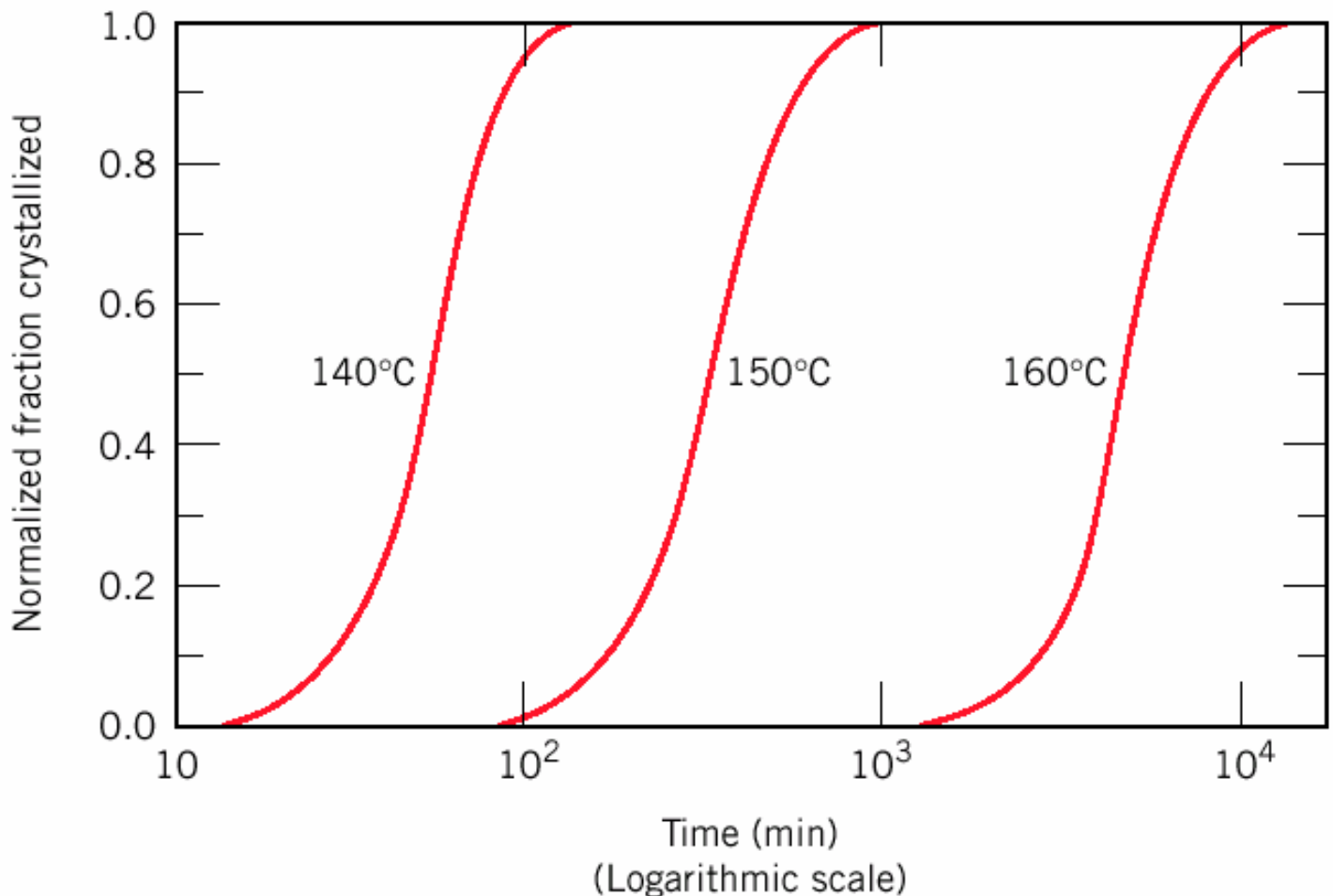
Factors that Influence Mechanical properties (II)

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



Crystallization, Melting, Glass Transition (I)

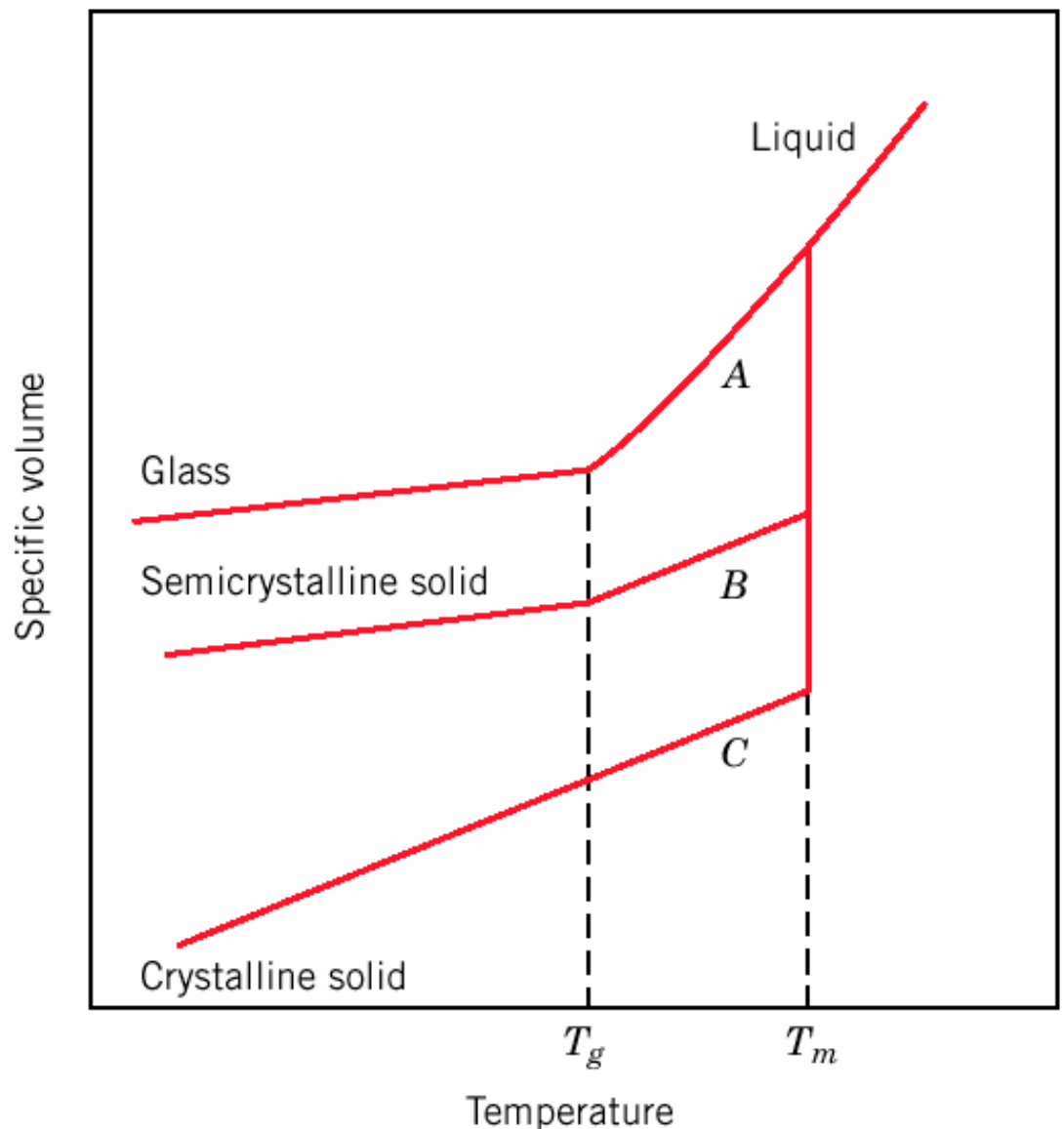
Crystallization: crystalline nuclei form and grow, chains align and order. Crystallization rates can be defined from the same type of S-curves we saw for metals - can be described by the same Avrami equation: $y = 1 - \exp(-k t^n)$



Glass transition: polymer become rigid solids (viscosity is increasing) upon cooling yet retain the disordered molecular structure characteristic for liquids

Crystallization, Melting, Glass Transition (II)

Melting behavior of semicrystalline polymers is intermediate between that of crystalline materials (sharp density change at a melting temperature) and that of a pure amorphous material (melting can be only defined from changes in viscosity).



The glass transition temperature is between 0.5 and 0.8 of the melting temperature.

Crystallization, Melting, Glass Transition (III)

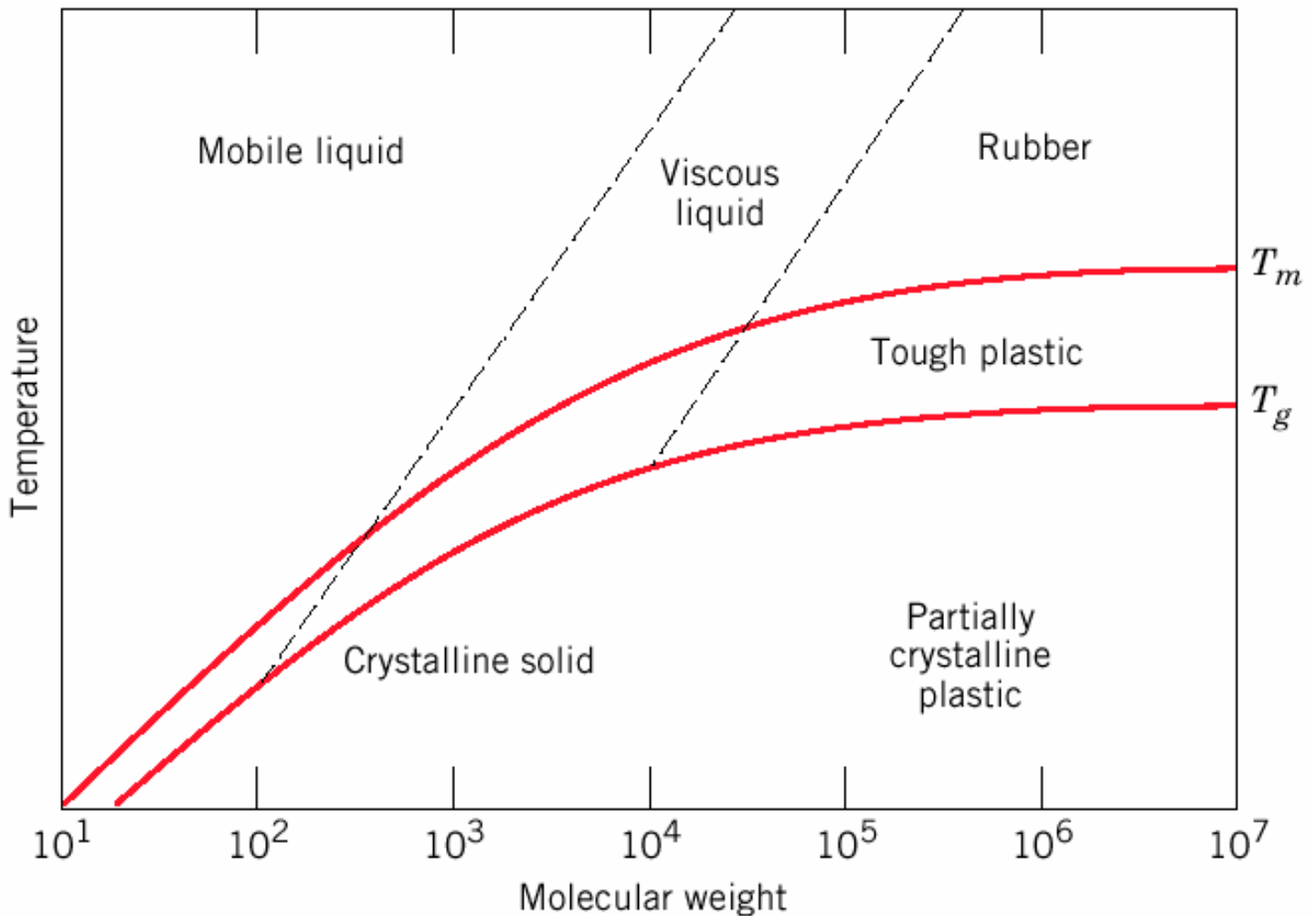
The melting temperature increases with the rate of heating, thickness of the chain-folded crystalline lamellae, and depends on history of material, especially crystallization temperature.

Melting involves breaking of the inter-chain bonds, therefore the glass and melting temperatures depend on:

- chain stiffness (e.g., single vs. double bonds) - rigid chains have higher melting temperatures
- size/weight of molecule - increasing molecular weight increases T_m (range of M produces range of T_m)
- size, shape of side groups, side branches, cross-linking, defects, etc.

Essentially the same molecular characteristics rise and lower both melting and glass transition temperatures.

Crystallization, Melting, Glass Transition (IV)



Dependence of melting and glass transition temperatures and polymer properties on molecular weight

Thermoplastic and Thermosetting Polymers

Thermoplastic polymers (thermoplastics): soften *reversibly* when heated (harden when cooled)

At elevated temperatures inter-chain bonding is weakened allowing deformation at low stresses. Most thermoplastics are linear polymers and some branched structures

Thermosetting polymers (thermosets): harden *permanently* when heated.

Covalent crosslinks (~ 10 - 50% of mers) formed during heating. Cross-linking hinder bending and rotations. Thermosets are harder, more dimensionally stable, and more brittle than thermoplastics. Examples: vulcanized rubber, epoxies, resins.

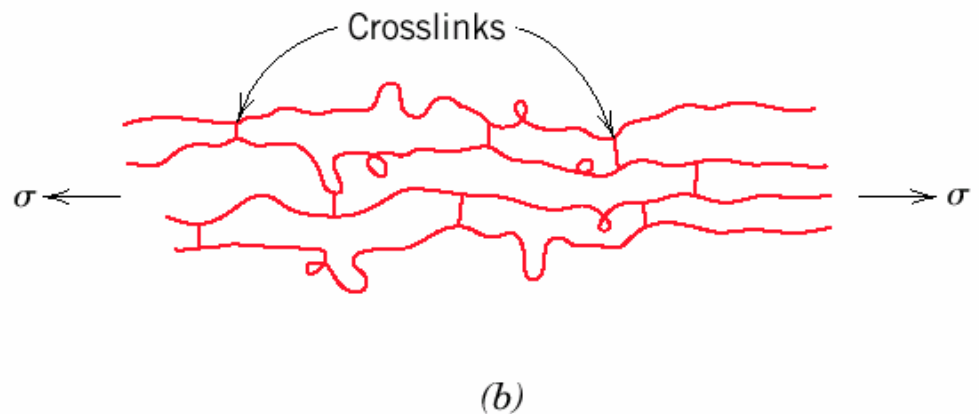
Classification by the end use in applications (plastics, elastomers, fibers, etc.)

Plastics – a broad class of polymeric materials that exhibit some structural rigidity under mechanical loading and are used in general-purpose applications.

Elastomers

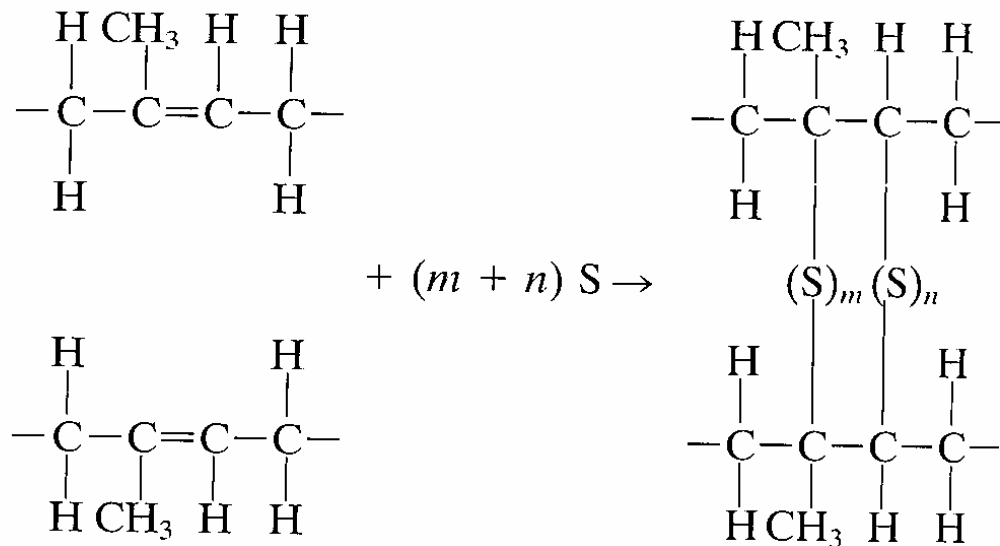
Elastomers can be deformed to **very large strains** and then spring back elastically to the original length, a behavior first observed in natural rubber. To be elastomeric, the polymer needs to meet several criteria:

- Resistance to crystallization (elastomers are amorphous)
- Relatively free chain rotations (unstressed elastomers have coiled/twisted structure – uncoil during deformation)
- Certain degree of cross-linking (achieved by vulcanization) that increases resistance to plastic deformation
- Temperature is above the glass transition temperature (below T_g elastomer becomes brittle)



Elastomers: Vulcanization (I)

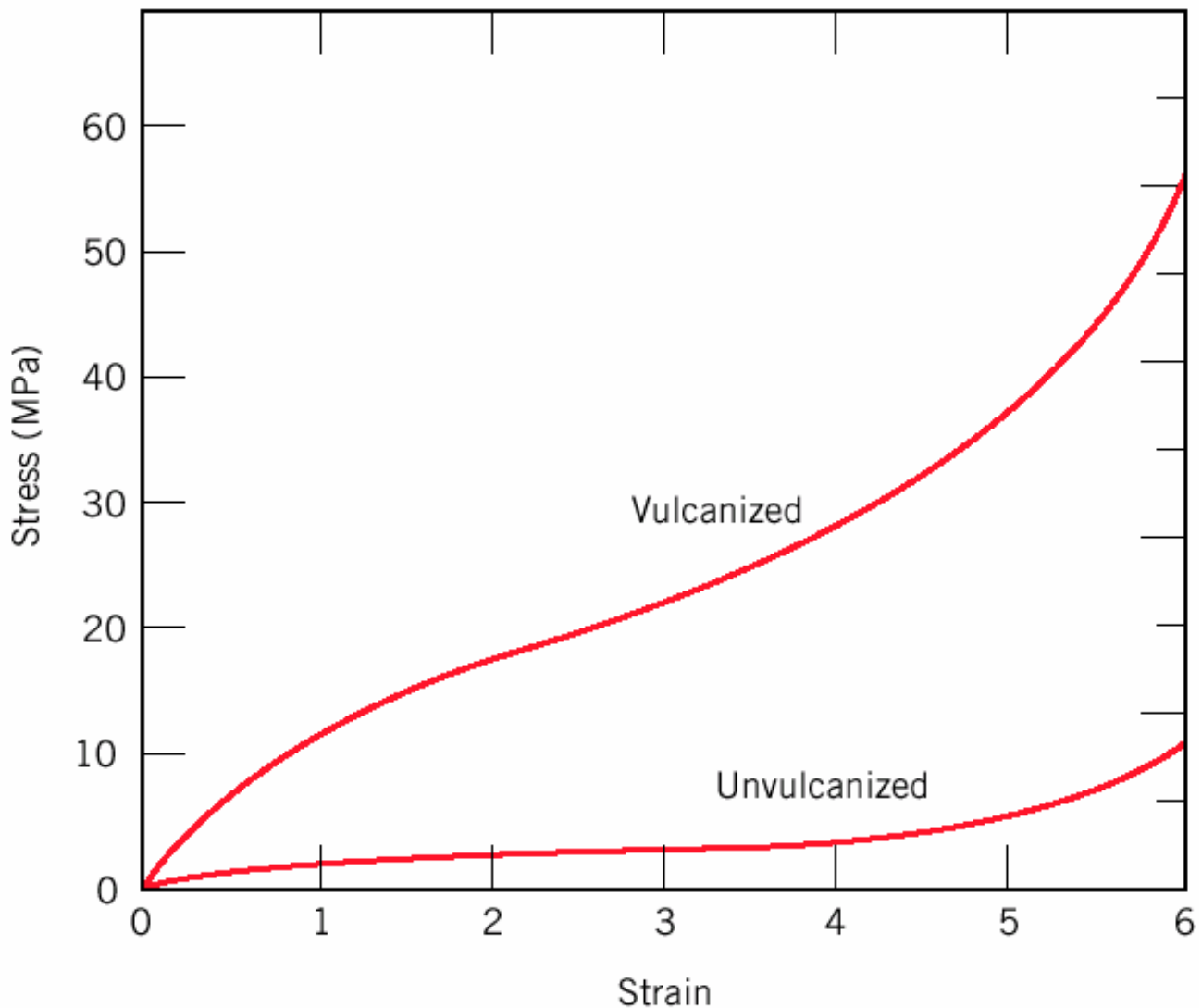
- Crosslinking is one of the requirements for elastomeric behavior.
- It can be achieved by **vulcanization** - an irreversible chemical reaction usually at high temperatures, and usually involving the addition of sulphur compounds.
- Sulfur atoms bond with double-bonded C in chain backbones and form the bridge cross-links.



Unvulcanized rubber suffers from softening at high ambient temperatures and hardening at low temperatures. Ways were sought to overcome this by treating the rubber with all sorts of chemicals, eventually (in 1839) Charles **Goodyear** found vulcanization by accidentally heating sulphur-coated rubber which he observed became firm and was stable under heating and cooling.

Elastomers: Vulcanization (II)

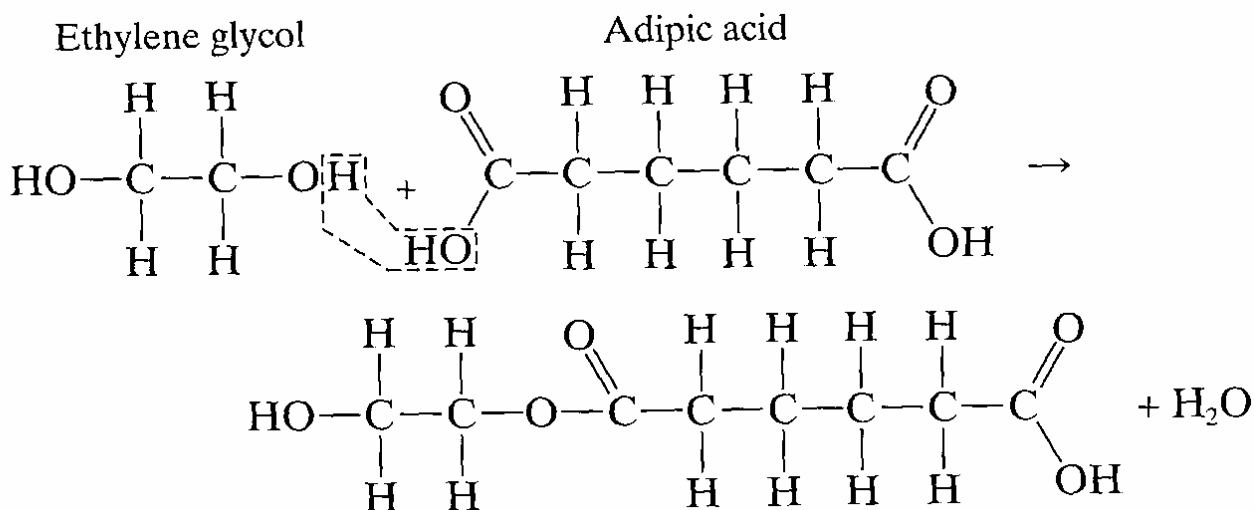
- Because they are cross-linked, elastomeric materials are **thermosetting polymers**
- Elastic modulus, tensile strength, oxidation resistance increased by vulcanization - magnitude of E proportional to number of cross-links. Too many cross-links reduces extensibility



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 Chapter 14). 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



Summary

Make sure you understand language and concepts:

- Addition polymerization
- Condensation polymerization
- Crazing
- Creep modulus
- Deformation of semicrystalline polymers
- Effect of molecular weight, crosslinks, drawing, degree of crystallinity on mechanical properties
- Elastomer
- Fracture of polymers
- Glass transition temperature
- Plastics
- Relaxation modulus
- Thermoplastic polymer
- Thermosetting polymer
- Viscoelasticity
- Vulcanization