POLYMER PROPERTIES

Polymer Properties

- Polymer Properties Depend on Temperature and Time

POLYMERS ARE VISCOELASTIC MATERIALS

BOTH ELASTIC AND VISCOUS BEHAVIOR

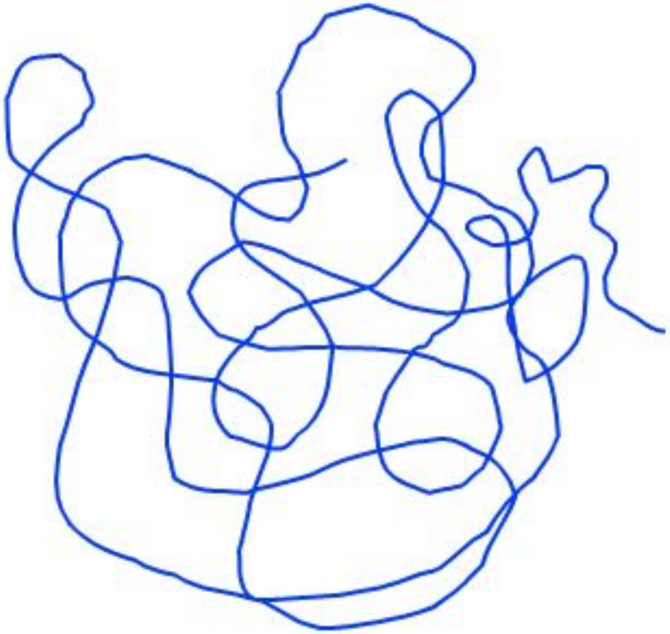
- Polymer Properties and related Temperature Dependence Depend on the Physical State of the Polymer
  - Amorphous States

Melt State	Hot cooked spaghettis no water
Glassy State	Frozen cooked spaghettis
Solution State	Hot cooked spaghettis in water

  - Partially Ordered Semicrystalline State: Mixture of Cooked and Raw spaghettis

AMORPHOUS STATE

Chain Conformation in the Amorphous State

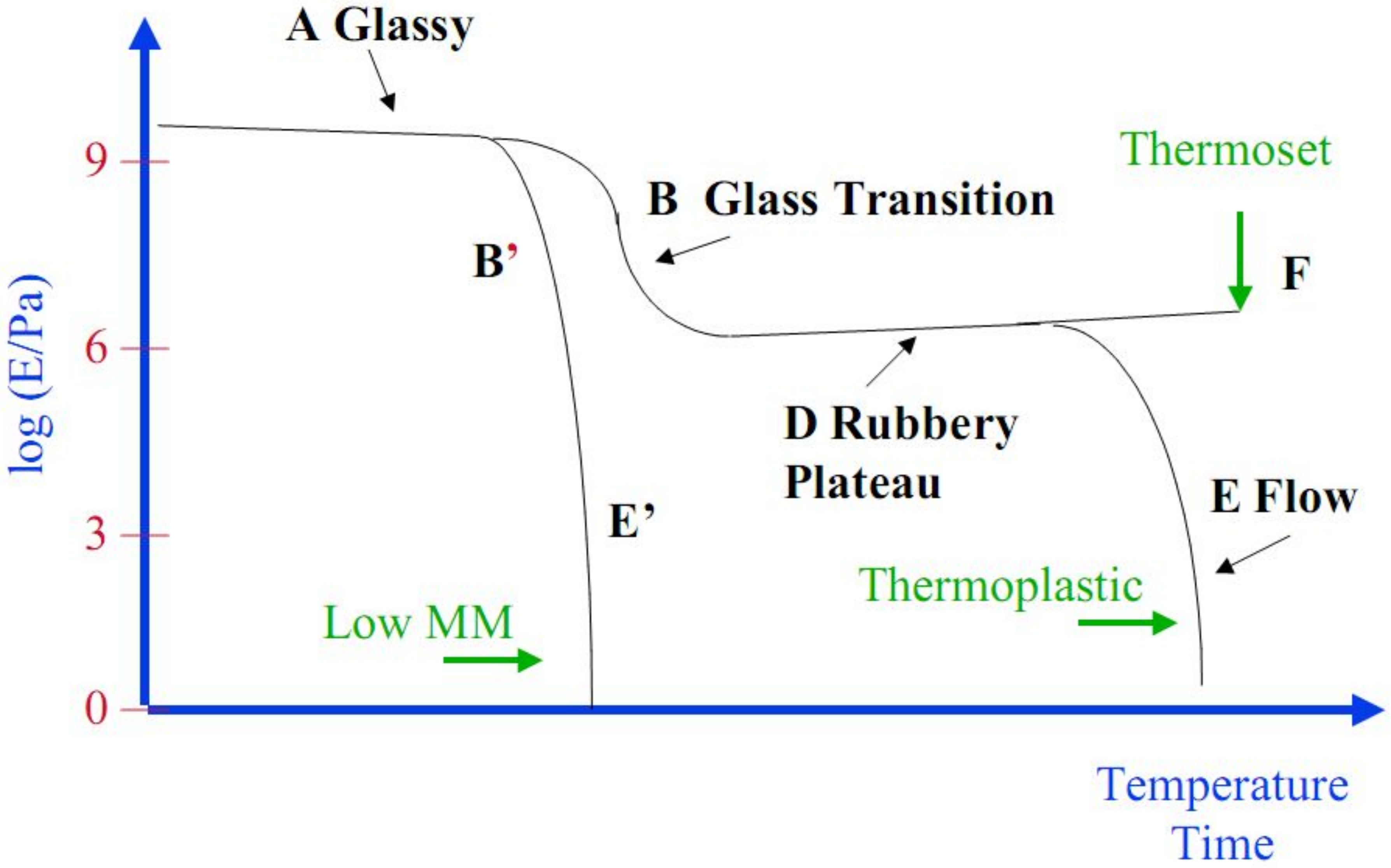


A polymer chain in
the amorphous state
is described as a
RANDOM COIL

The more flexible the chain, the more compact the coil (for a given number of repeat units).

Viscoelastic Behavior :

Strong Temperature and Time Dependence of Properties



When is a Polymer Amorphous ?

- **Glassy Polymer**
  Amorphous below T_g: PS, PMMA, Epoxy at Room Temperature

- **Rubbery Polymer**
  Amorphous above T_g: Crosslinked High Molar Mass Polyisoprene, Polychloroprene, Silicones, Polybutadiene at room temperature

- **Molten Semicrystalline Polymer**
  Crystallizable Polymer above T_m: PE ($T > 140°C$), it-PP ($T > 170°C$), PET ($T > 270°C$), PEEK ($T > 360°C$)

- **Between Crystals in Semicrystalline Polymers** ($T < T_m$)

Why is a Polymer Amorphous ?

- Amorphous state stable above Tm
- Some polymers do not crystallize Why ?
  - Crystallization kinetics too slow (next chapter)
  - Structure is not conducive to order
    - Tacticity defects
    - Regio defects
    - Branching (copolymerization)

Degree of Crystallinity of Statistical Ethylene Copolymers as a Function of Branch Content

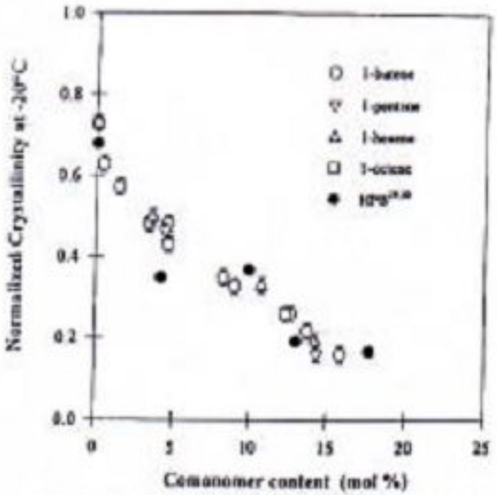


Figure 3. Normalized degree of crystallinity at −20 °C after cooling from the melt for ethylene/1-octene, ethylene/1-hexene, ethylene/1-pentene, and ethylene/1-butene copolymers. The normalized degree of crystallinity is obtained by dividing the actual degree of crystallinity by the weight fraction of ethylene sequences along the polymer backbone.

Macromolecules, 1999

Properties of Amorphous Polymers

- Below T_g
  Molecular motion is very localized (vibrations and few bond rotations)
  Hard, Brittle and High Modulus

- In the T_g Region
  Onset of large-scale molecular motions (vibration and significant bond rotations)
  Soft, tough and lower Modulus.
  Properties depend on time/speed/frequency of perturbation

- Rubbery Plateau Region

- Flow Region

CRYSTALLINE STATE

Chain Conformations in the Crystalline State

it-PP

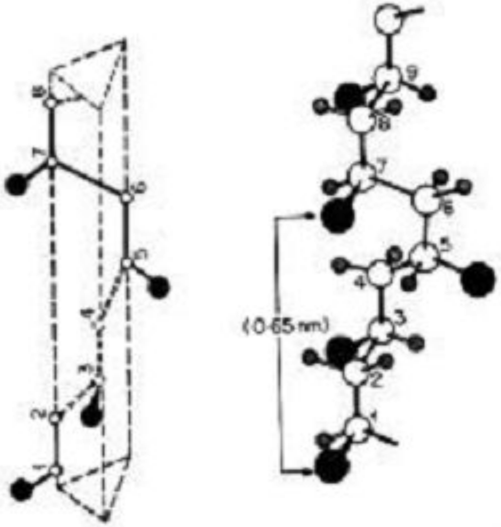


FIGURE 6.2. A 3_1-helix formed by a poly α-olefin, in this case polypropylene. This structure is also seen to fit a triangular template.

s-PP

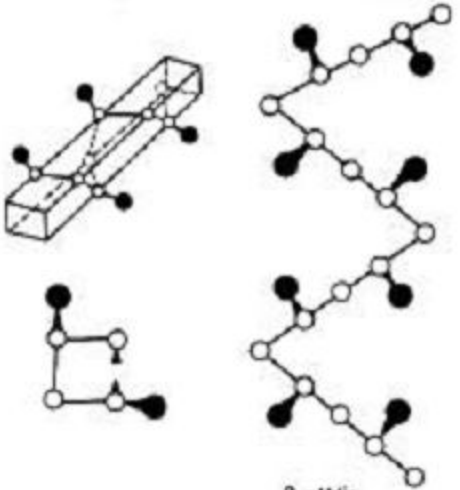


FIGURE 6.3. A poly α-olefin in the syndiotactic configuration showing the *ttgg* sequence along the chain, and the two fold helix which fits a square template.

Helical Conformations

-$(CH_2\text{-}CF_2)_n$-

Poly(tetrafluoroethylene) PTFE

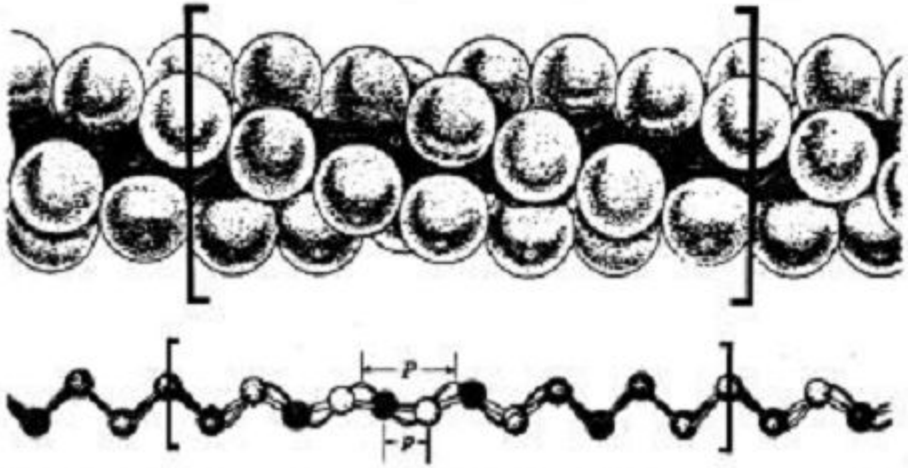
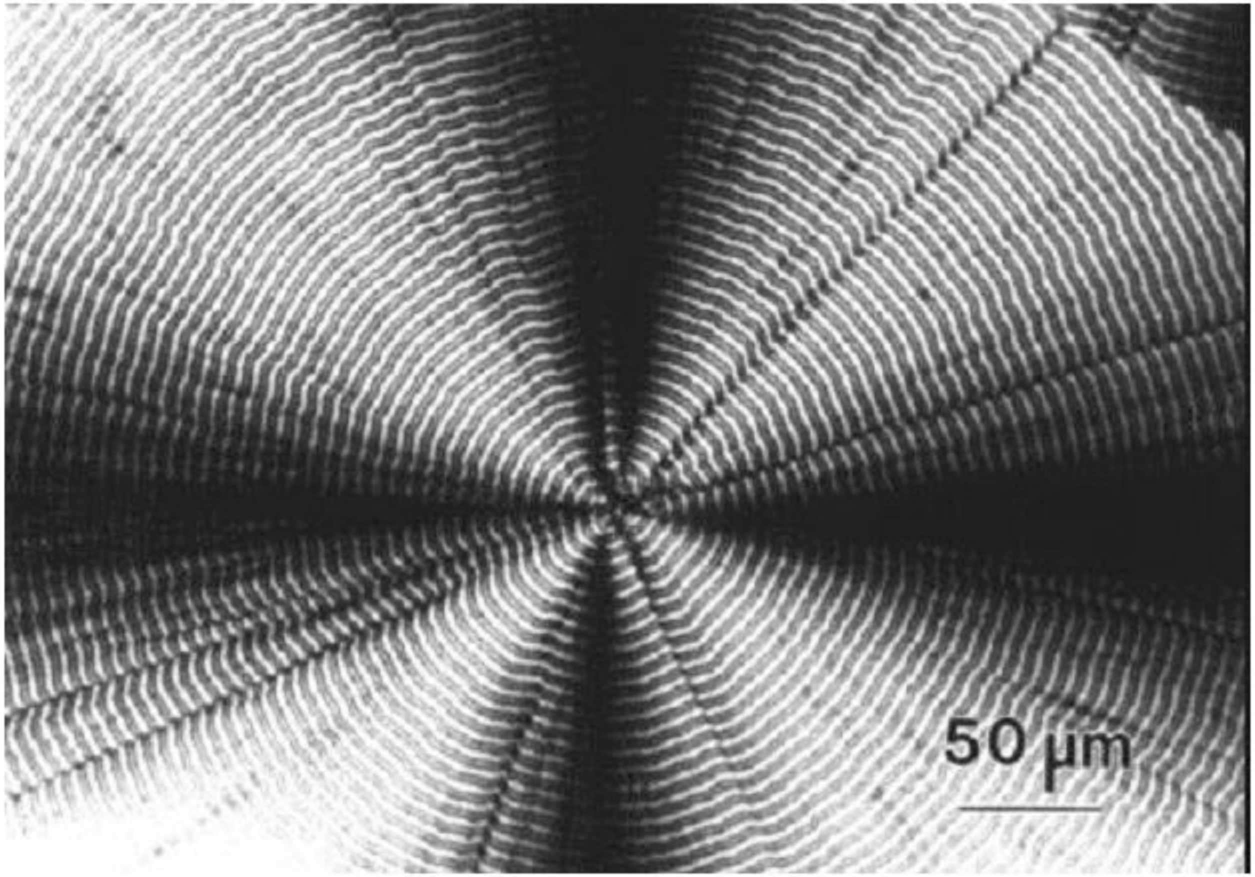


Figure 6-9 Molecular conformation of polytetrafluoroethylene: top—repeat unit of one molecule; bottom—carbon skeleton showing 13/6 helix. (Clark and Muus [27].)

Semicrystalline State: Spherulite



Poly(butylene sebacate) thin film observed
with polarized light in an optical microscope.

- Polymer Crystals:
  - Similar to small molecules/metallic crystals
    - Three dimensional positional order
    - First-order transition
  - Different from small molecules/metallic crystals
    - Degree of crystallinity ($T < T_m$) is less than 100%
    - Unit cell never contains the **whole** chain
    - Bonding differs greatly in different directions

- Crystallization Only Between T_g and T_m: Why ?
- Semicrystalline State: Properties depend on T !!
  - Hard and Rigid: $T < T_g < T_m$
    Modulus is independent of the degree of crystallinity
  - Flexible: $T_g < T < T_m$
    Modulus increases with the degree of crystallinity
- Degree of Crystallinity is controlled by:
  - Structure of polymer chain (defects, comonomers, etc..)
  - Thermal history: How so ?
- Kinetics of Crystallization

Polymer Crystal Melting Point

Techniques for its Detection

- Simple Visual Observation: Contrast solid and liquid phases
  - Flow behavior (solid vs liquid, viscosity, cross-linking, T_g)
  - Light scattering (haze, index of refraction fluctuations)

- Quantitative Evaluation:
  - X-ray Diffraction: [Bragg peaks vs Amorphous Halo]
  - Birefringence: [crystal phase: n $\parallel$ chain axis, n $\perp$ chain axis]
  - Calorimetry: C_p (T) [$C_p^{liq}(T)$, $C_p^{sol}(T)$, $H_{liq}-H_{sol} = \Delta H_f$ at T_m]
  - Dilatometry: V(T), [α_{liq}, α_{sol}, $V_{liq}-V_{sol} = \Delta V_f$ at T_m]
  - Infrared Spectroscopy: [Bond vibration, Conformers]
  - Raman Spectroscopy: [Bond vibration, Conformers]

Morphology of Semicrystalline Polymers:

Factors Controlling the Degree of Crystallinity

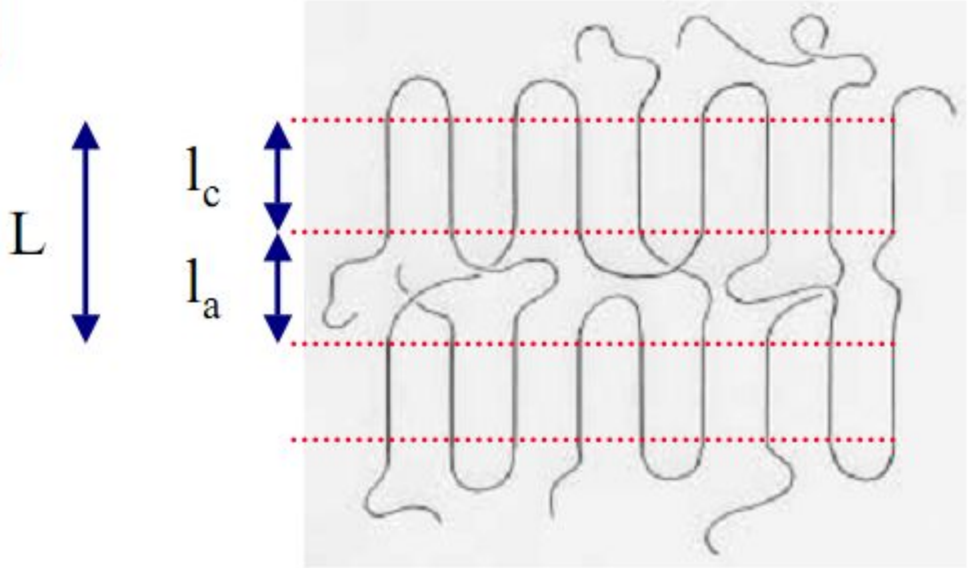
1) Crystallization Conditions (thermal history):

the higher the crystallization temperature, the higher the degree of crystallinity at the end of the primary crystallization stage (impingement).

2) Chain Structure:

Increasing the molar mass
Increasing tacticity defects
Increasing comonomer content
Increasing regio defects
Increasing chain stiffness

} Lead to a decrease in crystallinity



l_c : lamellar thickness
l_a: amorphous layer thickness
L : long spacing
local crystallinity = l_c / L

Crystal Structure

- Type of Information:
  - Unit Cell Type and Dimensions
  - Conformations of Polymer Chains and 3D Packing

- Techniques:
  - X-Ray Diffraction and Electron Diffraction
  - IR and Raman Spectroscopy, Atomic Force Microscopy

- Problems:
  - Case Study: Compare diffraction pattern from a large NaCl crystal and from a sample of polyethylene…..

Definition of Rubber Elasticity and Requirements

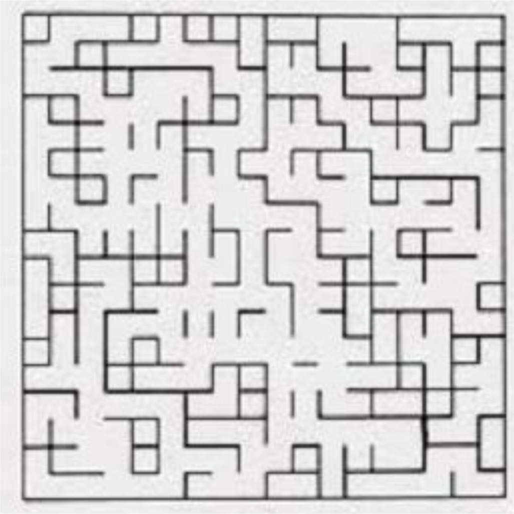
- Definition of Rubber Elasticity:
  Very large deformability with complete recoverability.

- Molecular Requirements:
  - **Material must consist of polymer chains.**
    Need to change conformation and extension under stress.
  - **Polymer chains must be highly flexible.**
    Need to access conformational changes (not w/ glassy, crystalline, stiff mat.)
  - **Polymer chains must be joined in a network structure.**
    Need to avoid irreversible chain slippage (permanent strain).
    One out of 100 monomers must connect two different chains.
    Connections (covalent bond, crystallite, glassy domain in block copolymer)

Cross-links, Networks and Classes of Elastomers

- Chemical Cross-linking Process:
  Sol-Gel or Percolation Transition

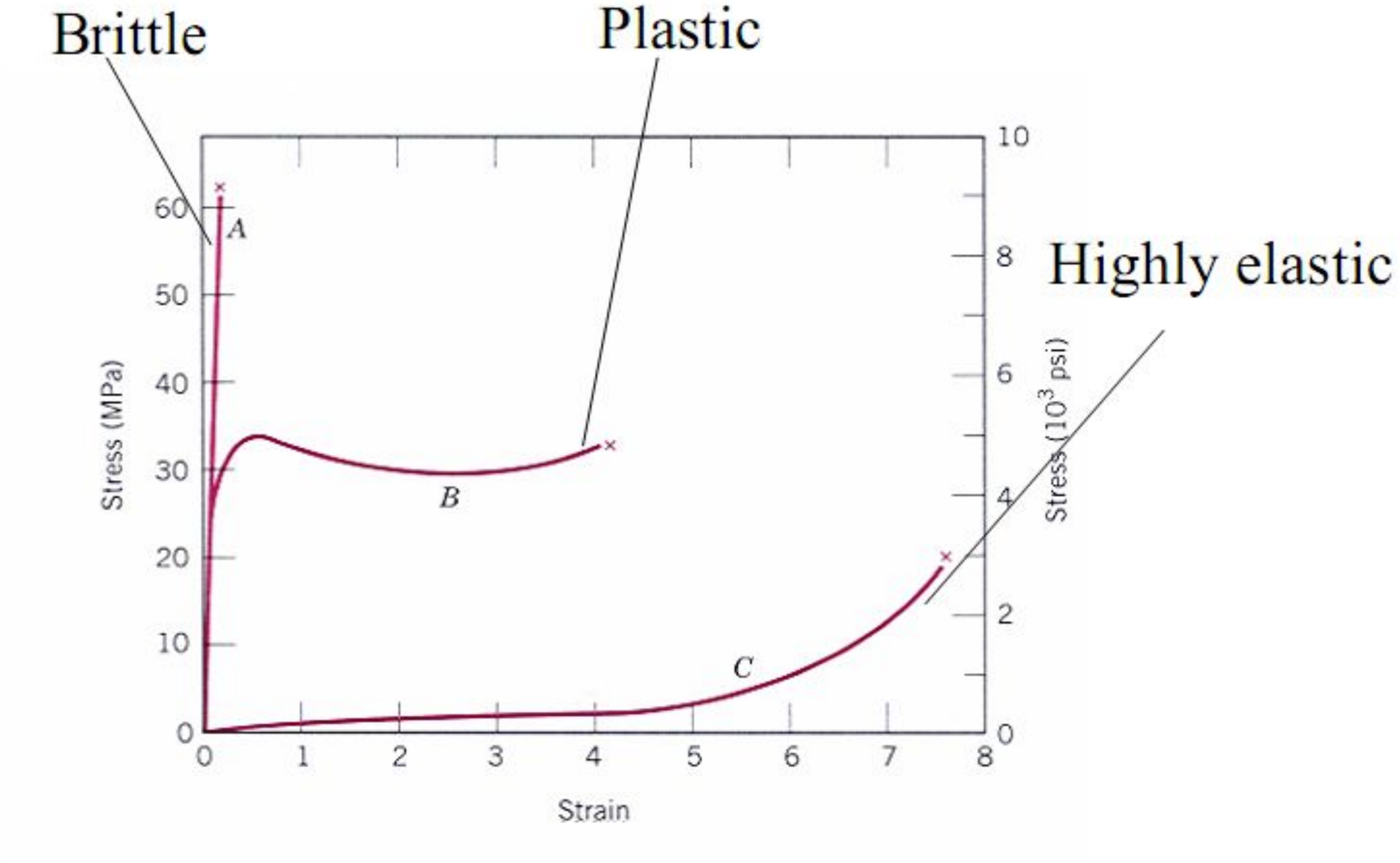
- Gel Characteristics:
  - Infinite Viscosity
  - Non-zero Modulus
  - One giant Molecule
  - Solid Polymer Network



- Step Polymerization (isocyanates, oxirane)
- Chain Polymerization (styrene with divinylbenzene)
- Post-polymerization Reactions (vulcanization with sulfur)

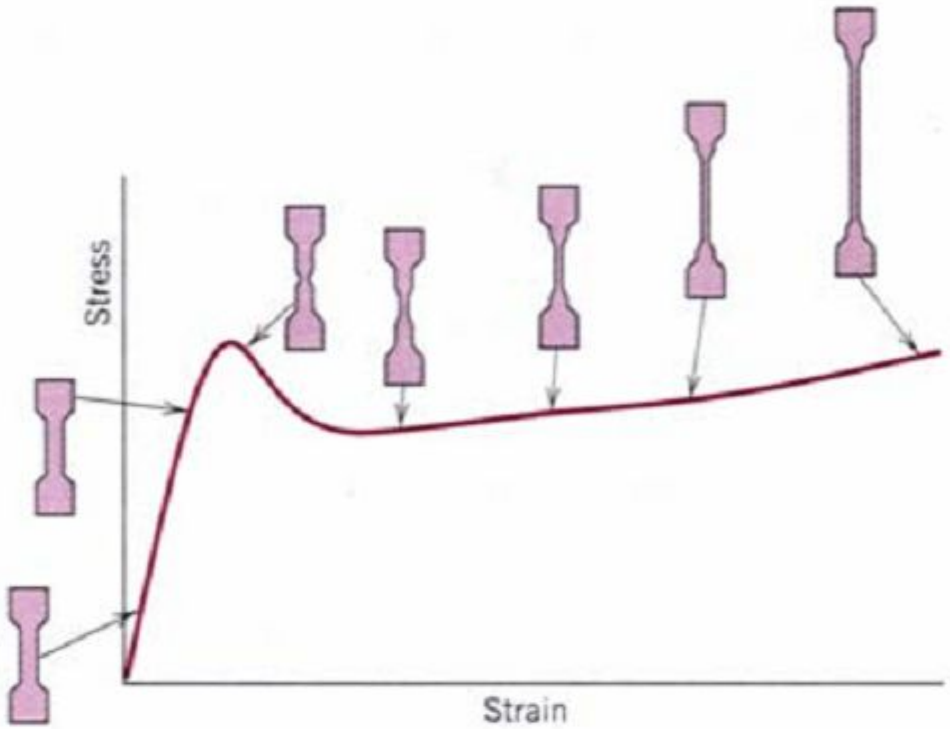
- Cross-linked and Gels in the Food/Health Care Industry:
  Globular protein example: the egg white ! (S_2 bridges)
  Jello®, contact lenses, liquid soaps, shampoos (proteins, polysaccharides)

Polymer stress-strain behavior

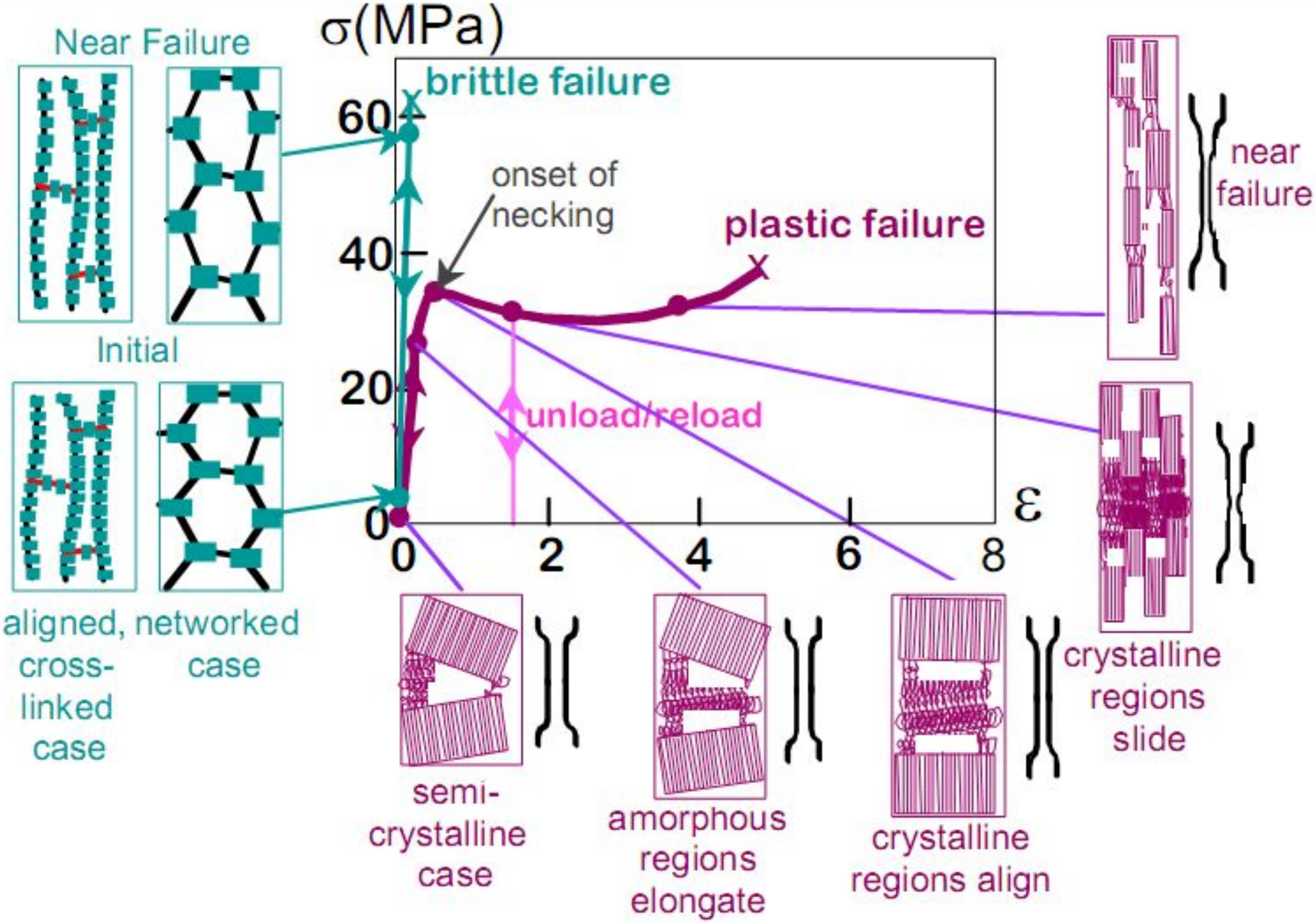


Deformation of semicrystalline polymers

- ☐ Mechanism of elastic deformation
- ☐ Mechanism of plastic deformation
- ☐ Stress-strain curve relation



Tensile response brittle & plastic



RESEARCH METHODS IN POLYMER CHEMISTRY

A variety of lab techniques are used to determine the properties of polymers:

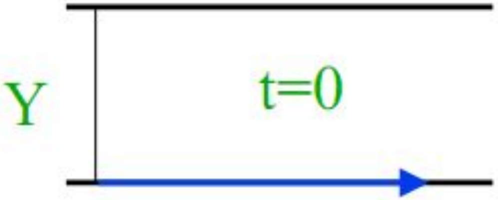
- Techniques such as wide angle X-ray scattering (WAXS), small angle X-ray scattering (SAXS) and small angle neutron scattering are used to determine the crystalline structure of polymers.
- Gel permeation chromatography is used to determine the number average molecular weight, weight average molecular weight, and polydispersity.
- Infrared or IR-spectroscopy is used to gather information about compound’s structure, to assess its purity, and sometimes to identify it.
- Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy and nuclear magnetic resonance (NMR) can be used to determine composition.

- Thermal properties such as the glass transition temperature and melting point can be determined by differential scanning calorimetry and dynamic mechanical analysis.
- Pyrolysis followed by analysis of the fragments is one more technique for determining the possible structure of the polymer.
- The scanning electron microscopy (SEM) is especially useful for routine examination of plastics, elastomers and biopolymers.
- There are many instruments that test the mechanical and viscoelastic properties of polymer materials. These instruments apply varied shear stress and shear rate to polymer samples to estimate their response to deformation and mechanical strength.
- Thermogravimetric analysis, or TGA, is commonly employed in research and testing to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of explosives, and solvent residues.

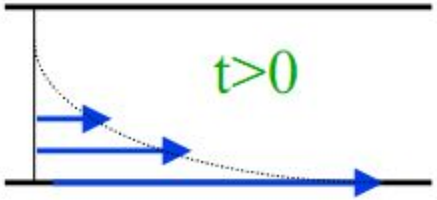
Viscosity of Fluids η

- Viscosity: physical property characterizing the resistance of fluids to flow.
- Newton's Law of Viscosity

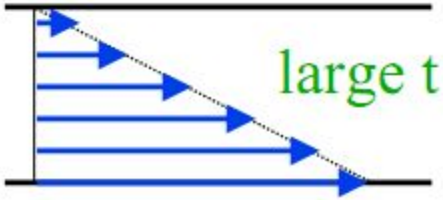
  Consider a fluid contained between two large plates of area A, separated by a small distance Y. We examine what happens when the lower plate initially at rest is set in motion at time t = 0 with a constant velocity V. As time proceeds the fluid gains momentum and after some time exhibits a steady-state velocity profile. When this state is reached, a constant force F is necessary to maintain the velocity of the lower plate at its initial value V.



Fluid is set in motion



Transient State



Fluid has reached Steady State

Newton's Law of Viscosity

Force

$$\frac{F}{A} = \eta \frac{V}{Y}$$

Velocity of lower plate
relative to upper plate

Area over which
the force is applied

Distance over which the
velocity is decreasing in
the direction
perpendicular to flow

Shear Stress
exerted in the
x-direction on a
fluid surface of
cst y by the
fluid of lesser y

$$\tau_{yx} = -\eta\left(\frac{\partial v_x}{\partial y}\right)$$

Local Velocity Gradient:
Velocity in x-direction
Gradient in y-direction

Polymers are Non-Newtonian Fluids

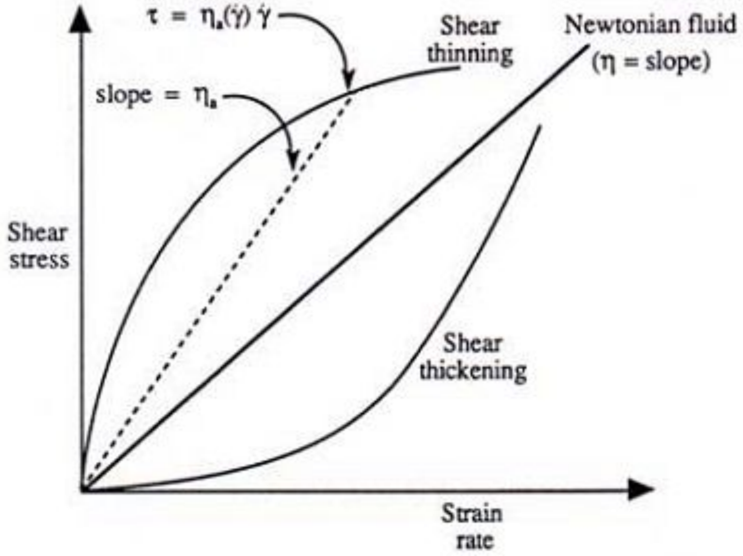


Figure 11.10 *Schematic plot of shear stress versus strain rate for Newtonian and non-Newtonian fluids.*

Polymer melts and solutions generally exhibit shear thinning:
Can you think of one very important application,
where this is very useful ?