



Mechanical Engineering Department
Dr. Khaled Mezghani

ME-578

*Mechanical Properties of
Engineering Polymers*

Objectives

- ***To broaden the knowledge of students about polymers, their applications, and their mechanical properties.***
- ***To study the yield behavior and breaking phenomena of polymers.***
- ***To study the viscoelastic behavior of polymers.***
- ***To study the behavior of polymer composites.***

Course Outline

- **Structure of polymers (Chapter 1 & notes).**
- **The deformation of an elastic solid (Chapter 2).**
- **Rubber-like elasticity (Chapter 3).**
- **Principles of linear viscoelasticity (Chapter 4).**
- **The measurement of viscoelastic behavior (Chapter 5).**
- **Time-temperature equivalence (Chapter 6).**
- **Yield and instability in polymers (Chapter 11).**
- **Breaking phenomena (Chapter 12).**
- **Polymer Composites: Macro- and Micro-scale (Ch. 8).**
- **Anisotropic mechanical behavior (Chapter 7).**

Textbook

I.M. Ward and J. Sweeney:

“An Introduction to the Mechanical Properties of Solid Polymers.”

John Wiley: NJ, USA, 2004.

Grading Policy

1) Homework	15%
2) Short Exams	25%
3) Term Project	25%
4) Midterm Exam	15%
5) Final Exam	20%

The term projects are intended to be real life problems related to the Theme:

Effect of Polymer Precursor on Carbon Fiber Mechanical Properties

CHAPTER 1

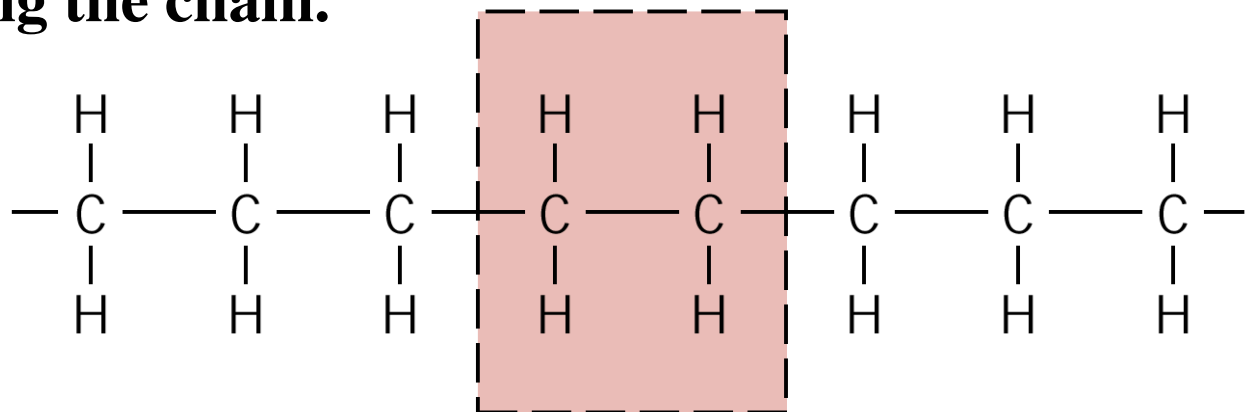
Structure of Polymers

Types of Polymers

1. **Thermoplastics:** They can be melted by heating, solidified by cooling and may be remelted repeatedly (PS, PE, PVC etc.)
2. **Thermosets:** They remain reactive in their fluid state and harden usually by application of heat and pressure due to crosslinking. They cannot be softened again to make them flow (phenol formaldehyde, epoxies, most polyurethanes)
3. **Elastomers:** They are cross-linked network structures with large deformability and essentially complete recoverability due to high degree of chain flexibility (natural rubber, rubbers). They solidify via thermally activated chemical crosslinking reactions, leading to lightly crosslinked network polymers (a process known as *vulcanization* in rubber technology)

Polymer Molecules

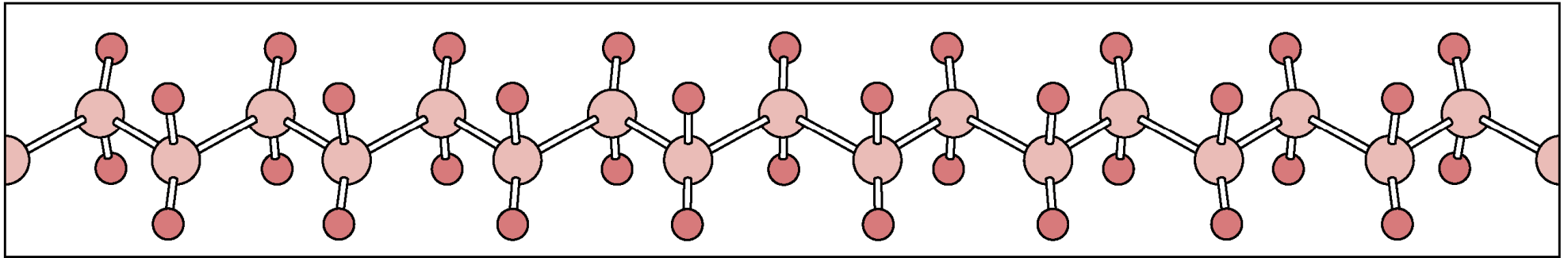
- ❖ They are very large molecules and often referred to as macromolecules.
- ❖ Within each molecule, the atoms are bound together by covalent interatomic bonds.
- ❖ For most polymers, these molecules are in the form of long and flexible chains.
- ❖ These long molecules are composed of structural entities called mer (unit), which are successively repeated along the chain.



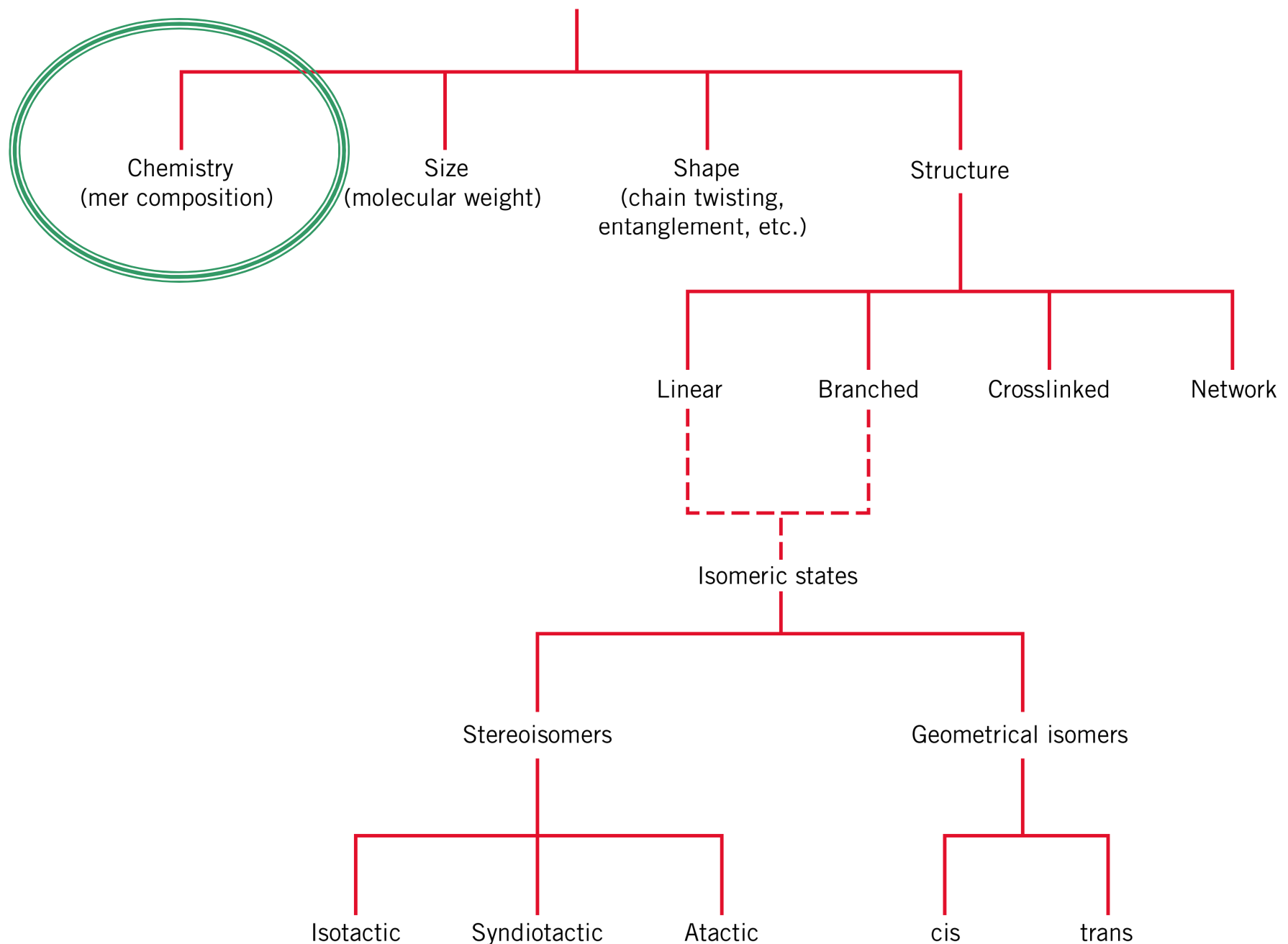
- ❖ Polymer means many mers.

Mer unit

Perspective of Polyethylene Molecule



Molecular Characteristics

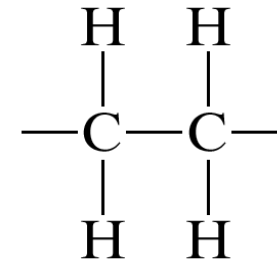


Mer Structures for Common Polymeric Materials

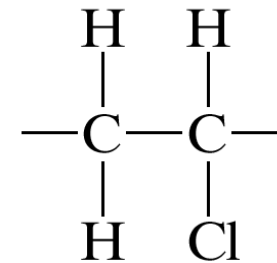
Polymer

Repeating (Mer) Structure

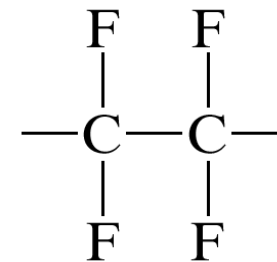
Polyethylene (PE)



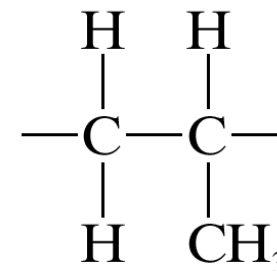
Polyvinyl chloride (PVC)



Polytetrafluoroethylene (PTFE)



Polypropylene (PP)

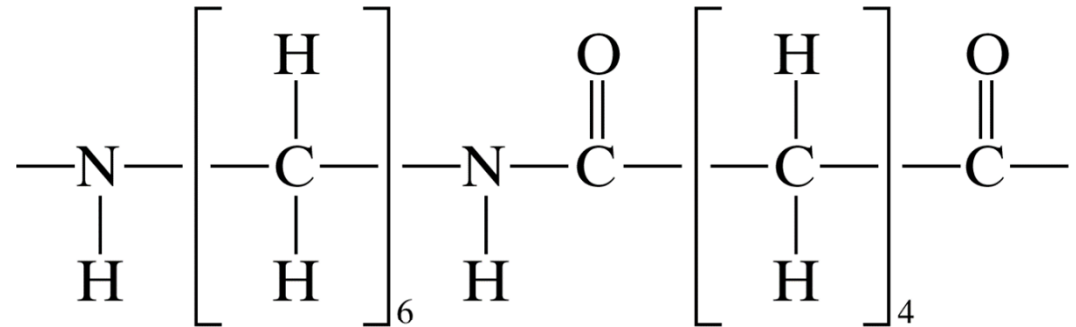


Mer Structures for Common Polymeric Materials

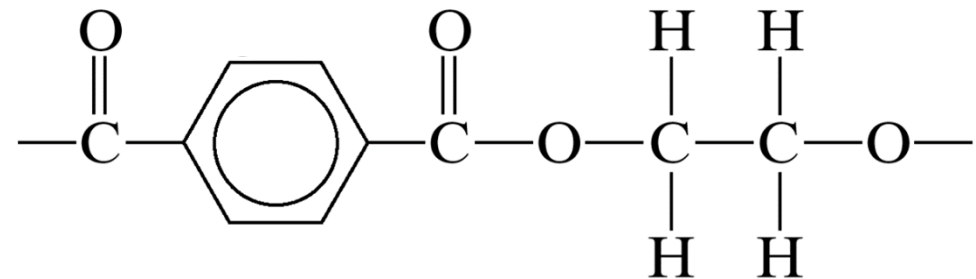
Polymer

Repeating (Mer) Structure

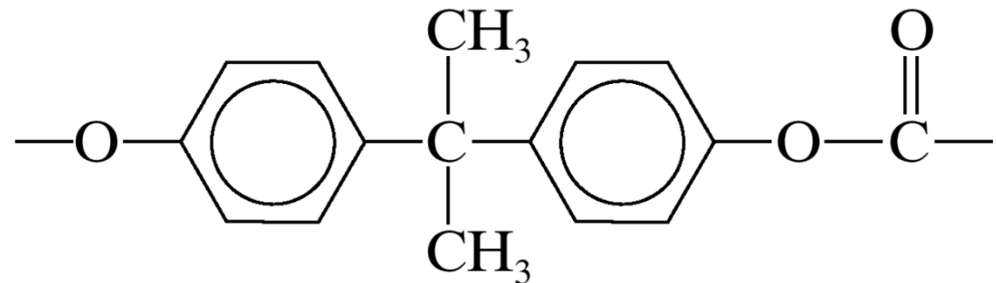
Polyhexamethylene
adipamide (nylon 6,6)



Polyethylene
terephthalate
(PET, a polyester)



Polycarbonate

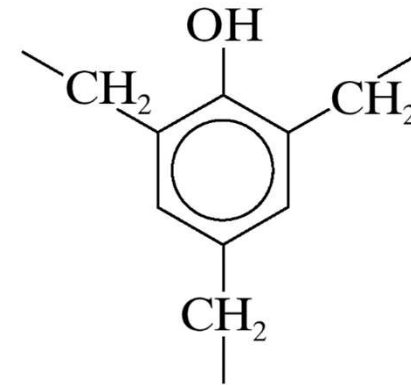


Mer Structures for Common Polymeric Materials

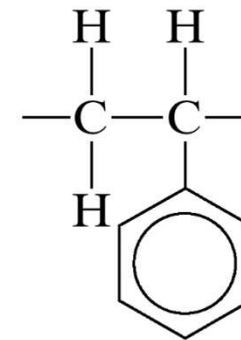
Polymer

Repeating (Mer) Structure

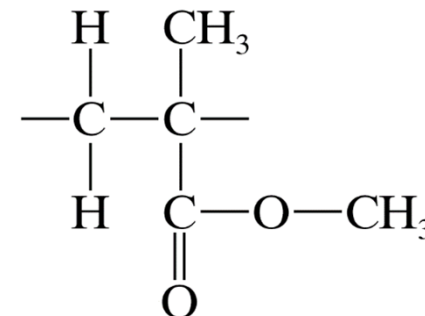
Phenol-formaldehyde (Bakelite)



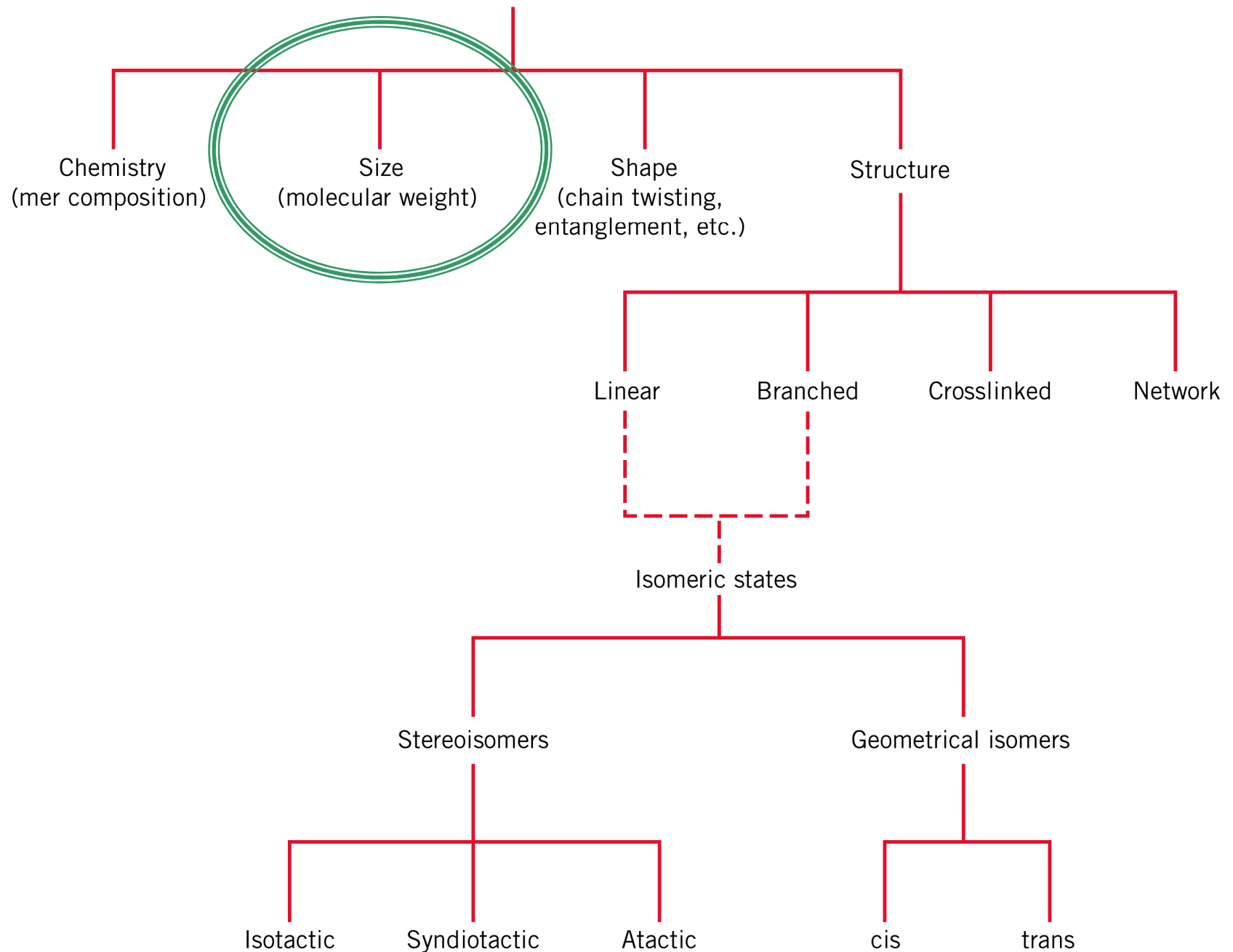
Polystyrene (PS)



Polymethyl methacrylate (PMMA)



Molecular Characteristics



Molecular Weight

- ❖ **During the polymerization process in which these large macromolecules are synthesized from smaller molecules, not all polymer chains will grow to the same length.**
- ❖ **This results in a distribution of chain lengths or molecular weights.**
- ❖ **There are several ways of defining average molecular weight:**
 1. Number-average molecular weight, \overline{M}_n
 2. weight-average molecular weight, \overline{M}_w

Number Average Molecular Weight

$$\bar{M}_n = \sum x_i M_i = \sum \frac{N_i}{N} M_i = \frac{\sum N_i M_i}{\sum N_i}$$

$$\bar{M}_n = \frac{W}{N} = \frac{\sum W_i}{\sum n_i} = \frac{W}{\sum (W_i / M_i)}$$

- Where:
- M_i represents the molecular weight of size i ,
 - x_i is the fraction of the total number of chains within the corresponding size i ,
 - N_i number of chains within the corresponding size i .
 - N total number of molecules,
 - W total weight of the material,
 - W_i weight of molecules of size i ,

Weight Average Molecular Weight

$$\overline{M}_w = \sum w_i M_i = \sum \frac{N_i M_i}{M_{total}} M_i = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

where M_i represents the mean (middle) molecular weight of size range i ,

w_i denotes the weight fraction of molecules within the same size interval.

and N_i number of chains within the corresponding size range.

Molecular Weight Distribution

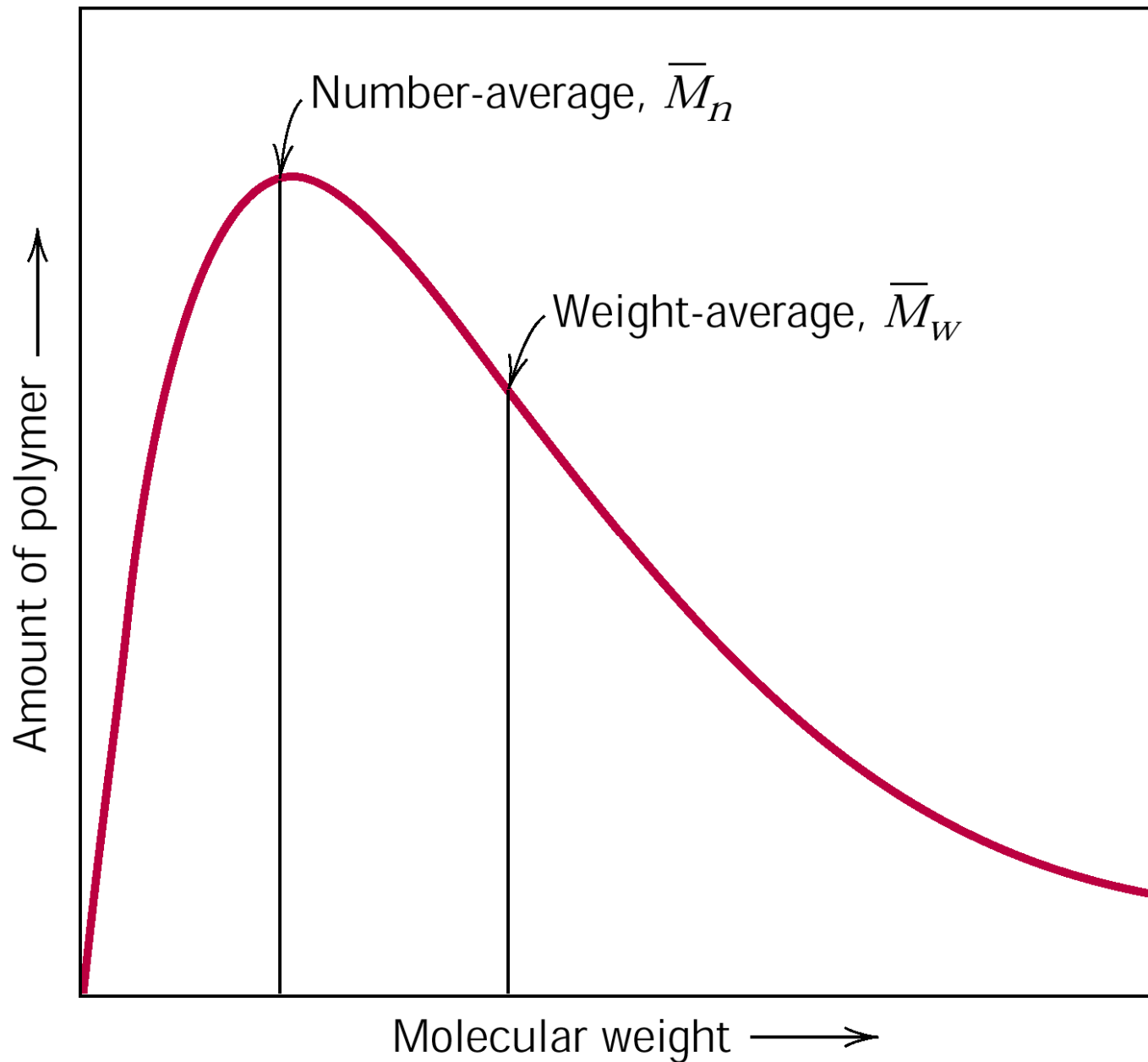
❖ *Also known as polydispersity index (PDI)*

$$MWD = \frac{\overline{M}_w}{\overline{M}_n}$$

where M_w represents the weight average molecular weight,

and M_n denotes the number average molecular weight.

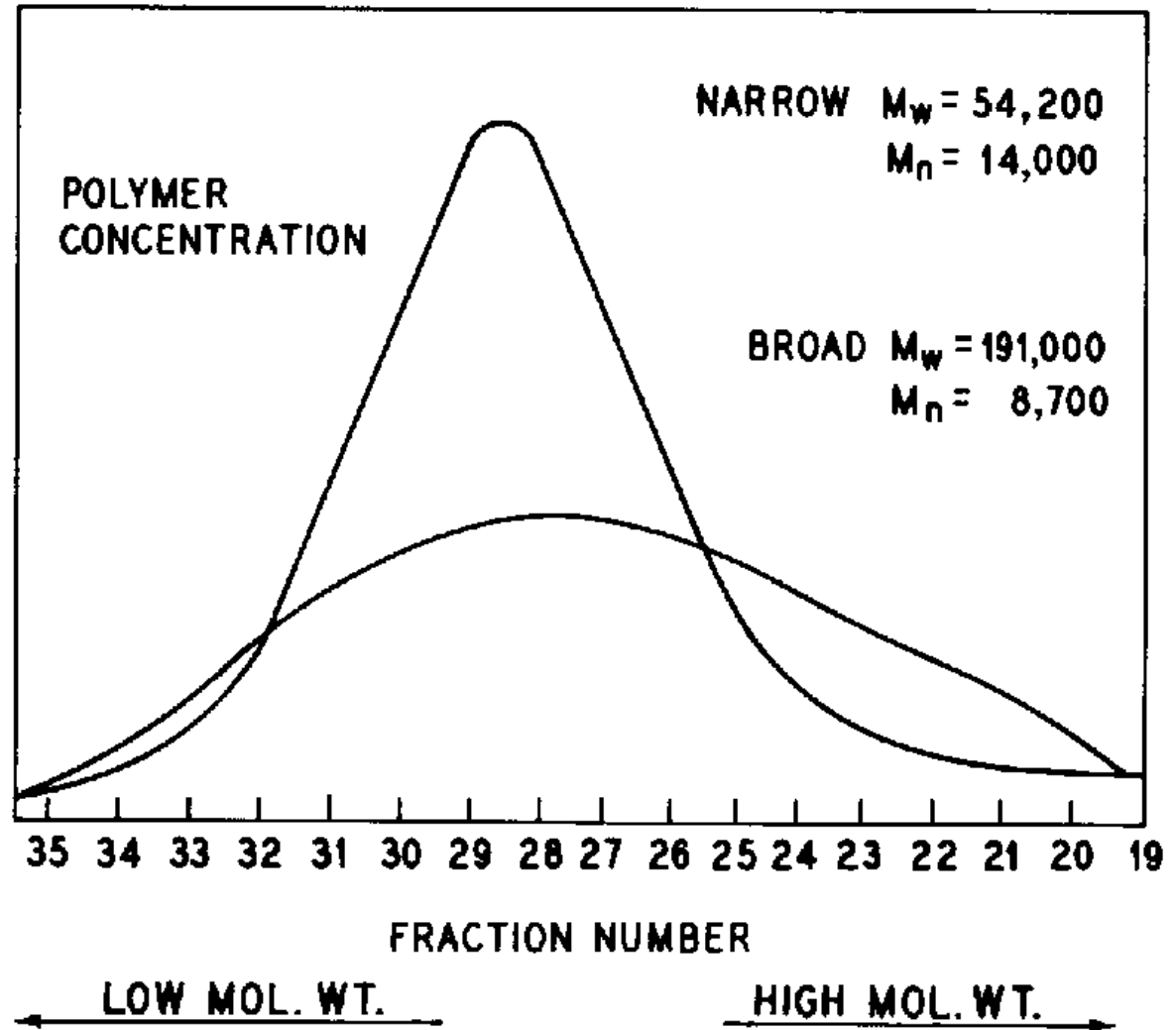
Molecular Weight Distribution



Polydispersity

By virtue of its definition, M_w cannot be less than M_n . It is influenced by the high molecular weight fraction of the material to a greater degree than M_n .

Low polydispersities (PDI \approx 2) generate higher melt viscosity, higher tensile strength and better toughness in polyethylene.



Degree of Polymerization

- **Number average degree of polymerization:**

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

- **Weight average degree of polymerization:**

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

Methods of Molecular Weight Determination

•Number Average Molecular Weight

- End-group analysis
 - determine the number of end-groups in a sample of known mass
- Colligative Properties
 - most commonly osmotic pressure, but includes boiling point elevation and freezing point depression

•Weight Average Molecular Weight

- Light scattering
 - translate the distribution of scattered light intensity created by a dissolved polymer sample into an absolute measure of weight-average MW

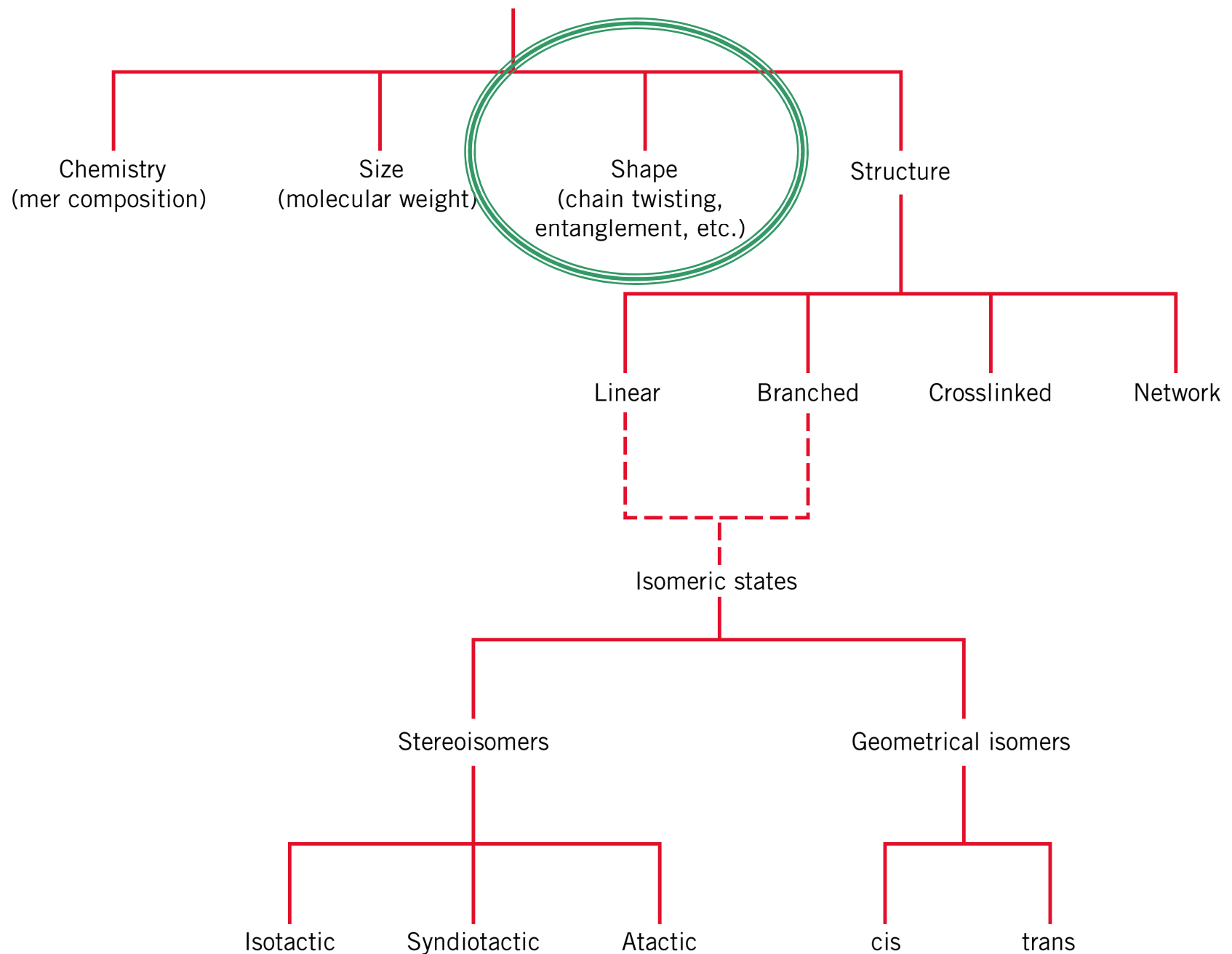
•Viscosity Average Molecular Weight

- Viscometry
 - the viscosity of an infinitely dilute polymer solution relative to the solvent relates to molecular dimension and weight.

•Molecular Weight Distribution

- Gel permeation chromatography (GPC)
 - fractionation on the basis of chain aggregate dimension in solution (See slide 1 for an example of GPC output).

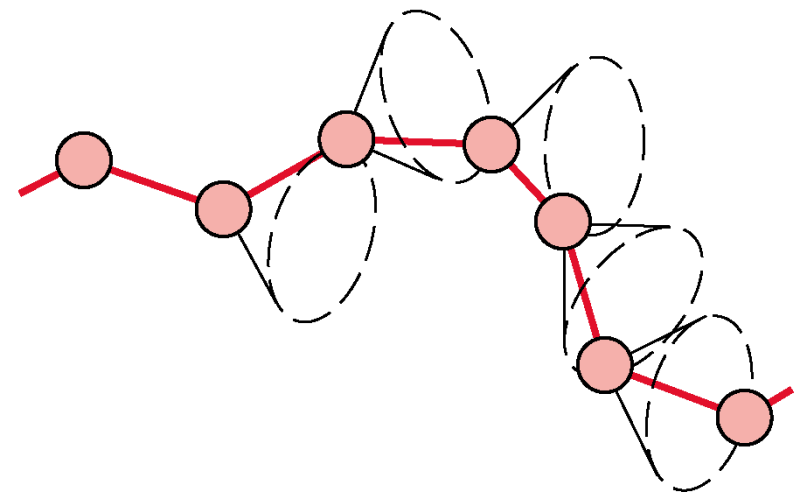
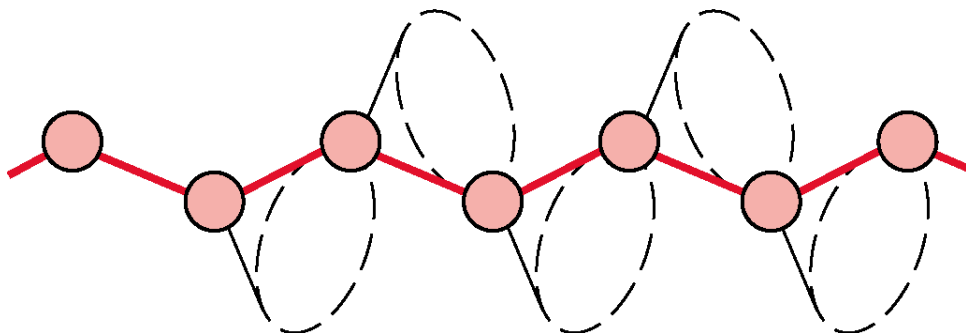
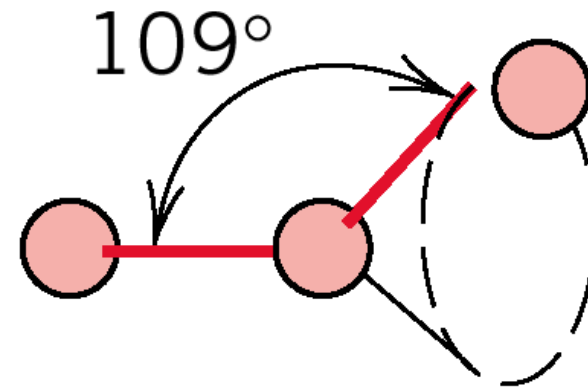
Molecular Characteristics



Molecular Shape

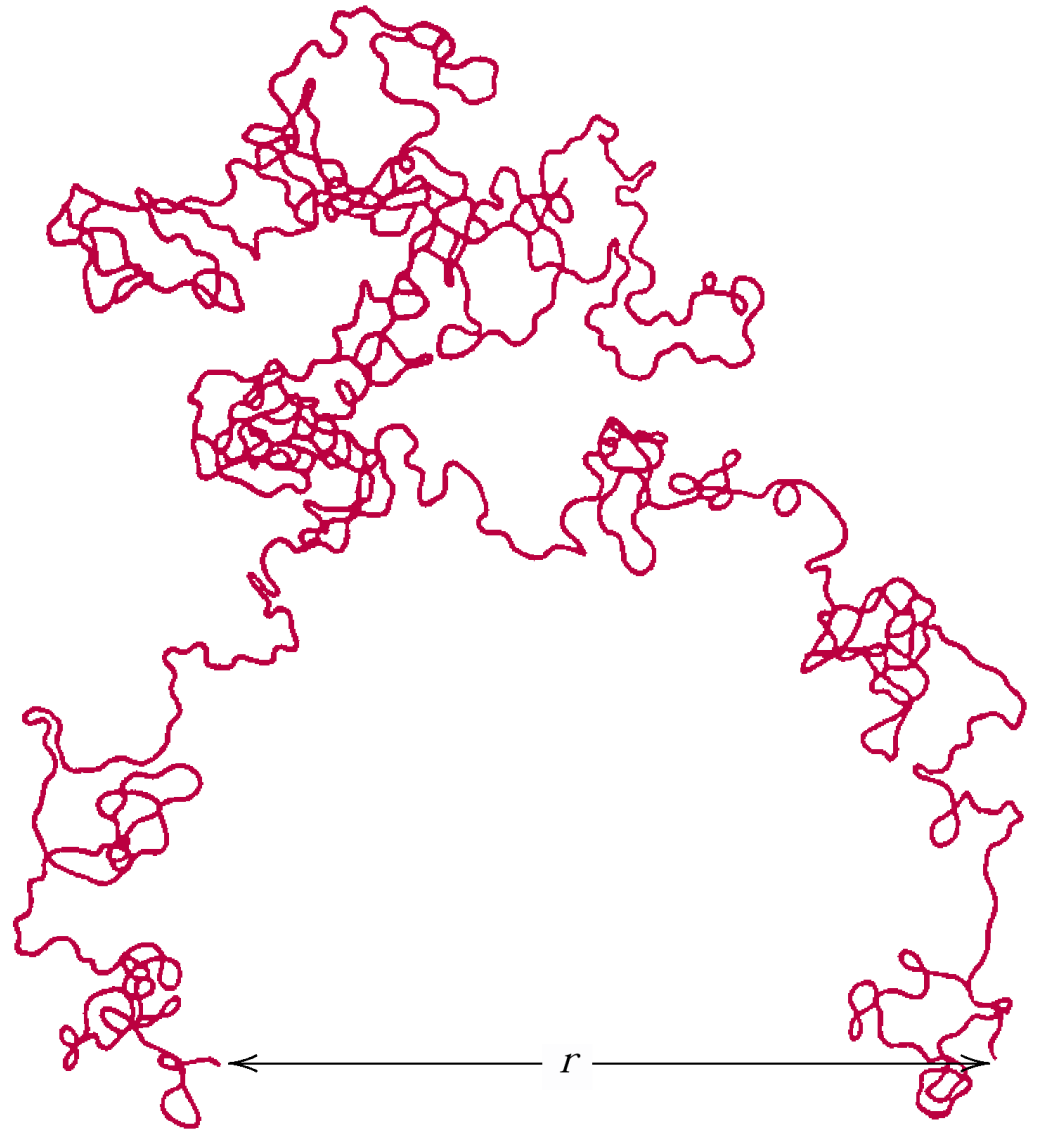
❖ Single chain bonds are capable of rotation and bending in three dimensions.

❖ Depending on the rotation the molecular shape can take



Single Chain Molecule

- ❖ **Polymers consist of large numbers of molecular chains, each of which may bend, coil, and kink.**
- ❖ **This leads to extensive intertwinning and entanglement of neighboring chain molecules.**
- ❖ **These random coils and molecular entanglements are responsible for a number of important characteristics of polymers, to include the large elastic extensions displayed by the rubber materials.**



Molecular Size

❖ Using the random walk approach with restricting rotational angle of 109.5° , the average **end-to-end distance** (r) and the **radius of gyration** (r_g) for a series of polymer molecules depends on the bond length (d) between chain atoms and the total number of bonds in the molecule N .

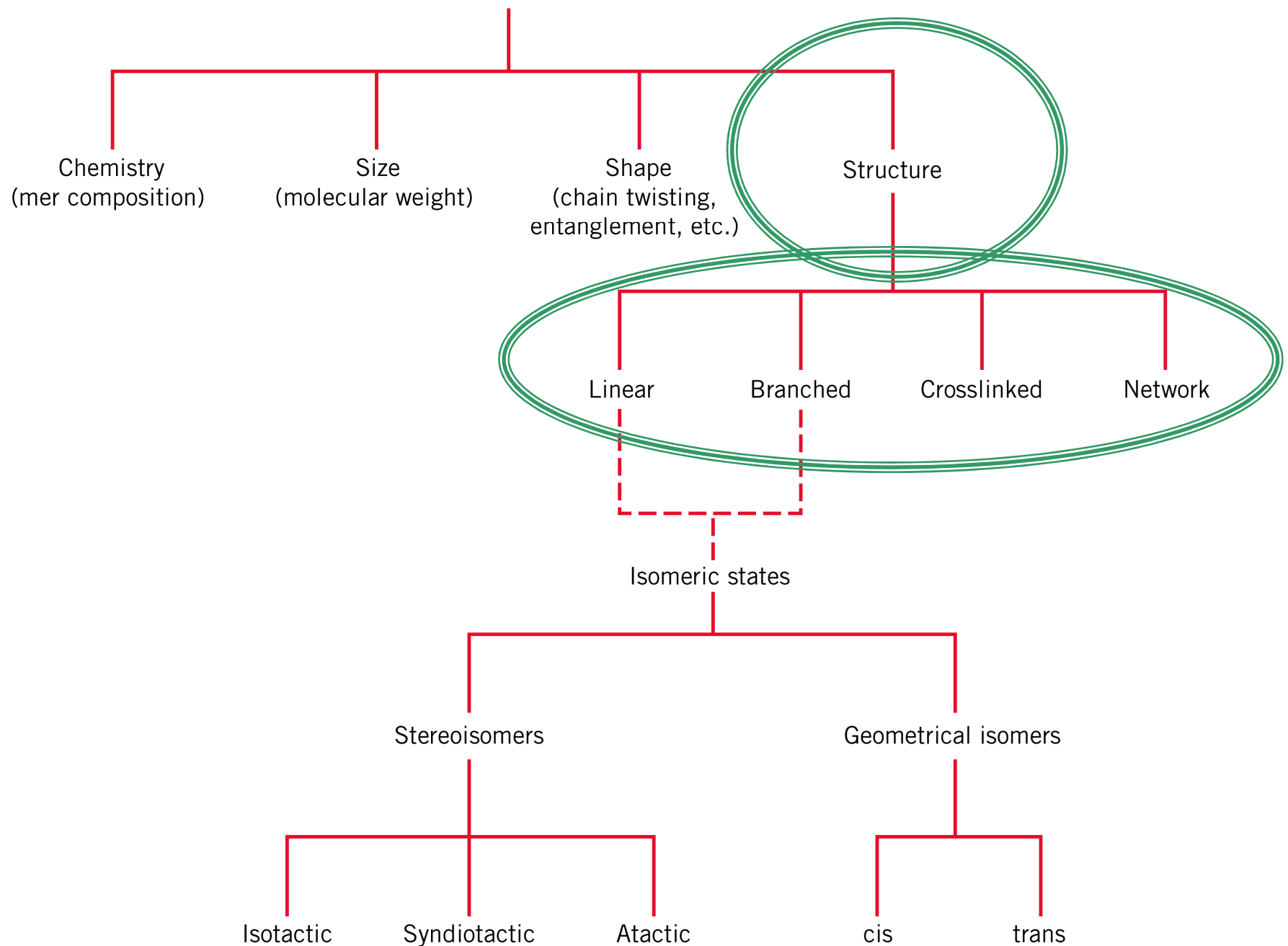
$$r = d \sqrt{2N}$$

$$r_g = \frac{r}{\sqrt{6}} = d \sqrt{\frac{N}{3}}$$

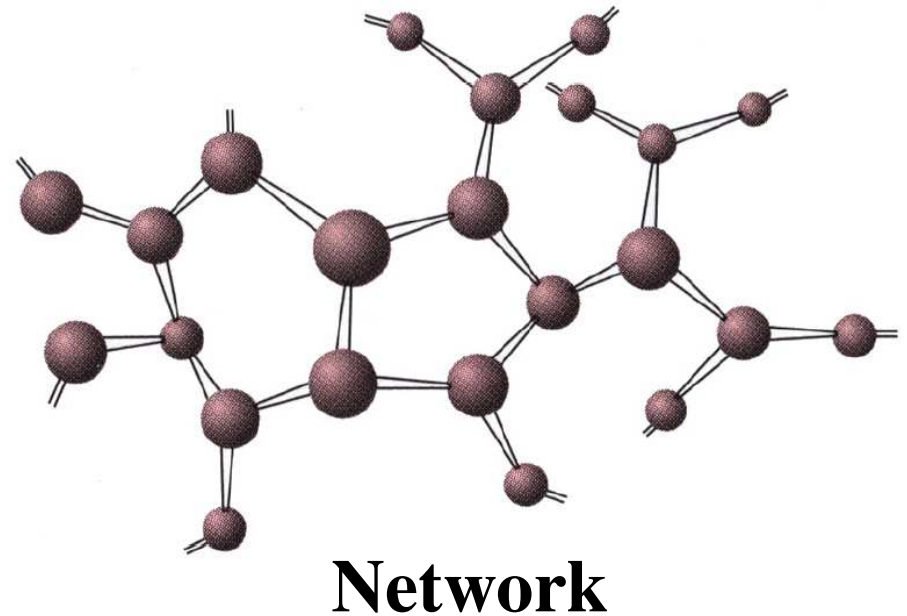
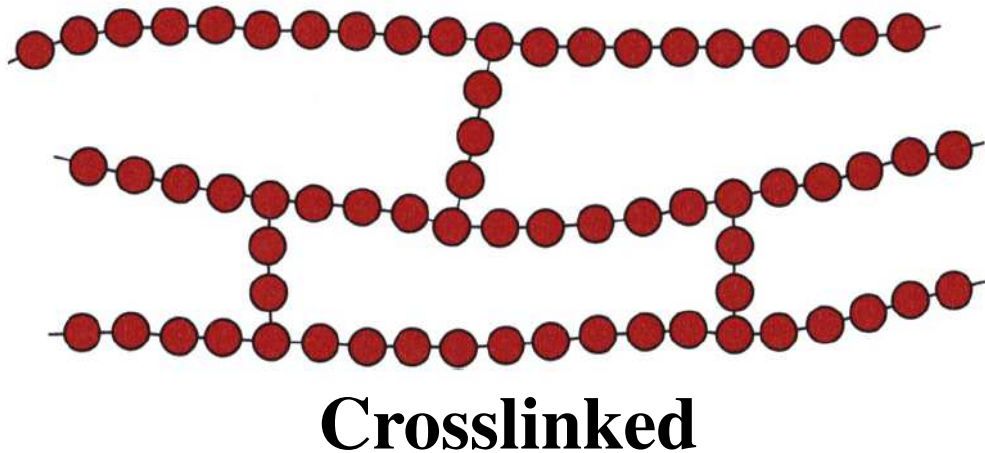
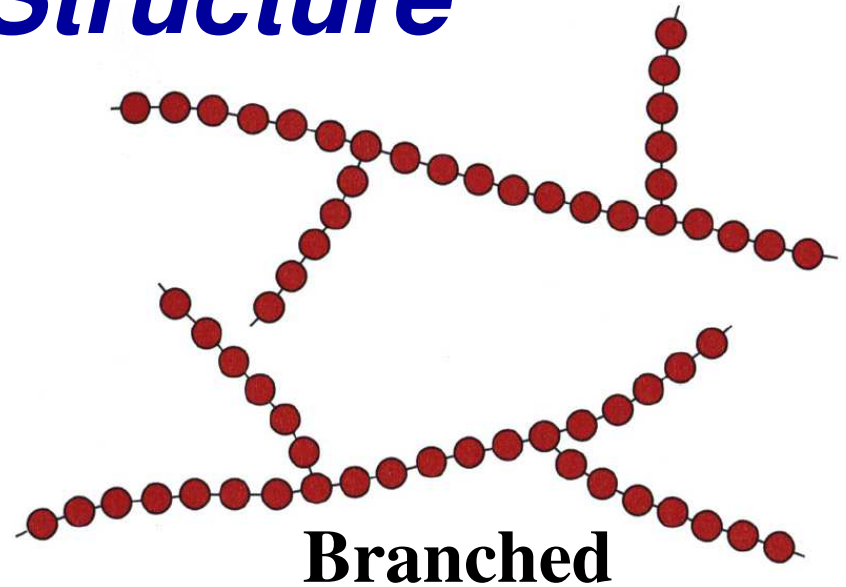
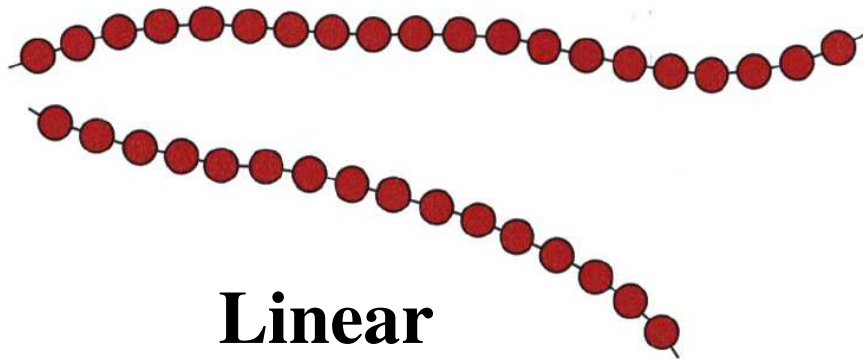
❖ For a linear polymer molecule, the **extended chain length** L depends on the bond length between chain atoms d , the total number of bonds in the molecule N , and the angle θ between adjacent backbone chain atoms.

$$L = Nd \sin \left(\frac{\theta}{2} \right)$$

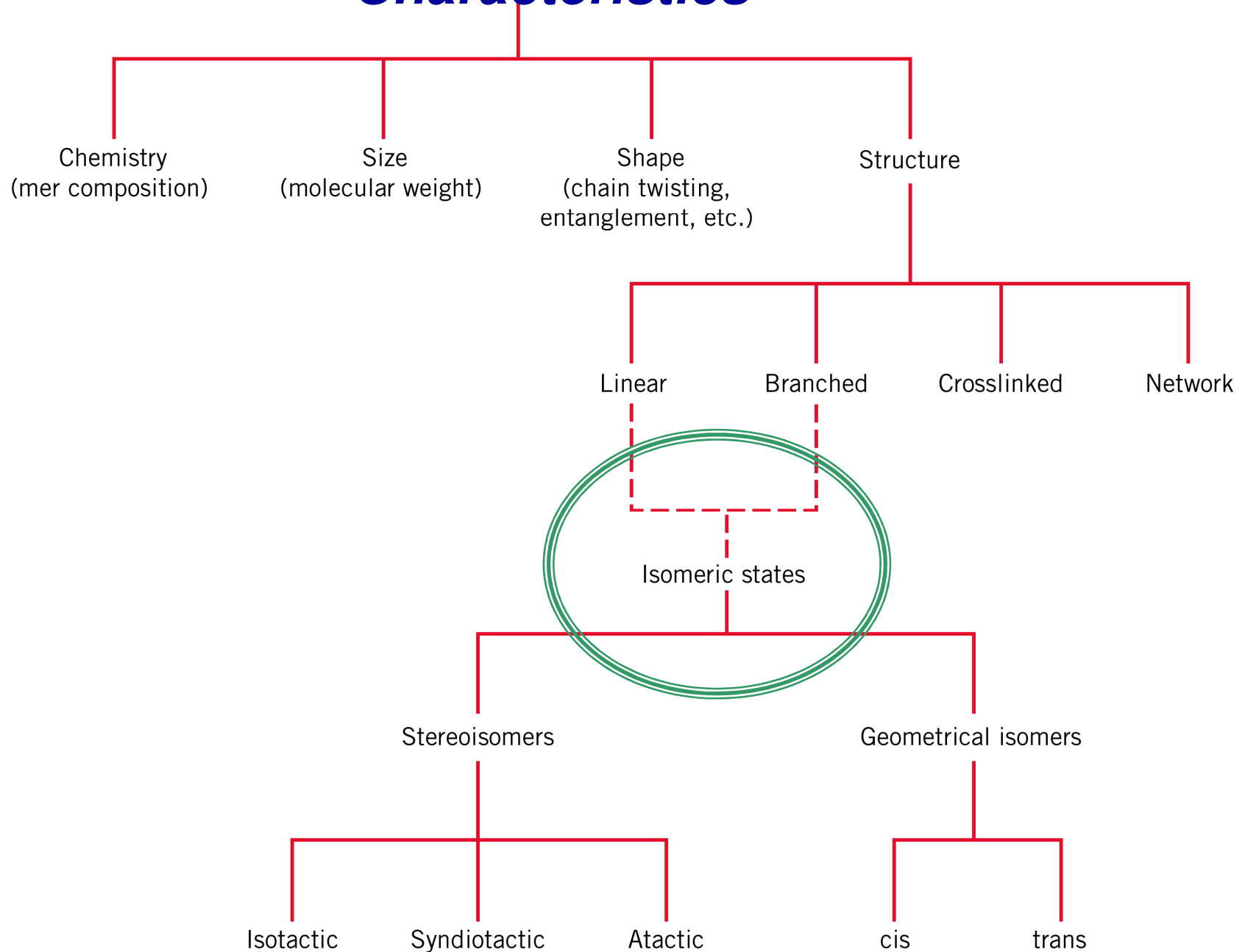
Molecular Characteristics



Molecular Structure

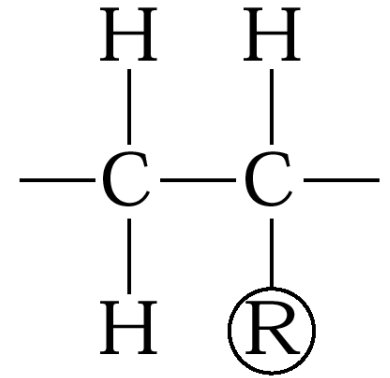


Molecular Characteristics



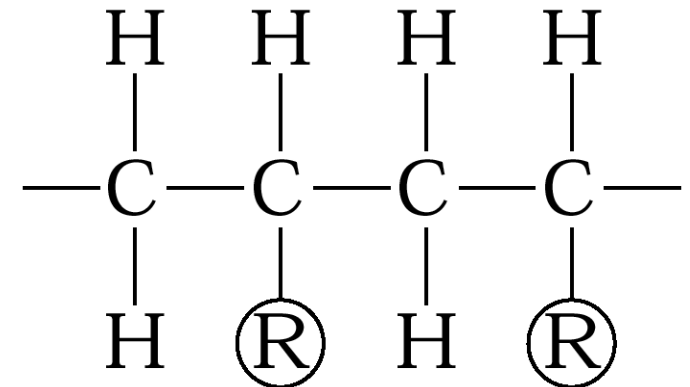
Molecular Configurations

- ❖ the regularity and symmetry of the side group arrangement can significantly influence the properties. Consider the mer unit in which R represents an atom or side group other than hydrogen (e.g., Cl, CH₃).

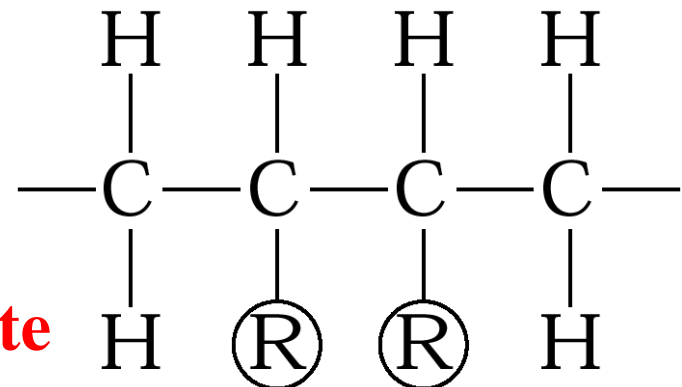


- ❖ Two configurations are possible:

1. Head-to-tail configuration.



2. Head-to-head configuration.

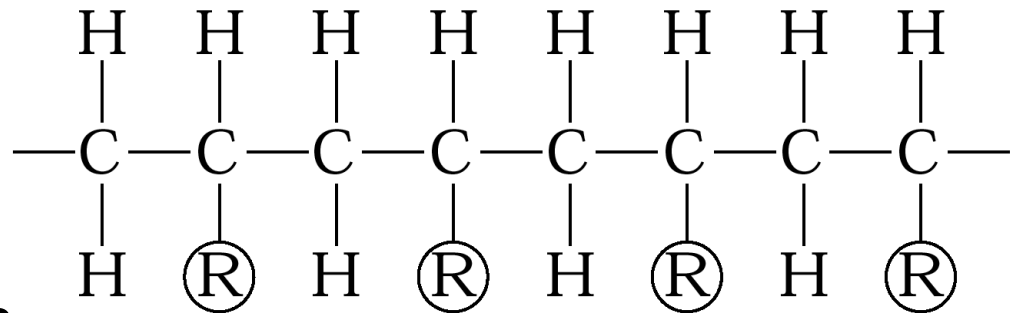


Head-to-tail configuration is predominate

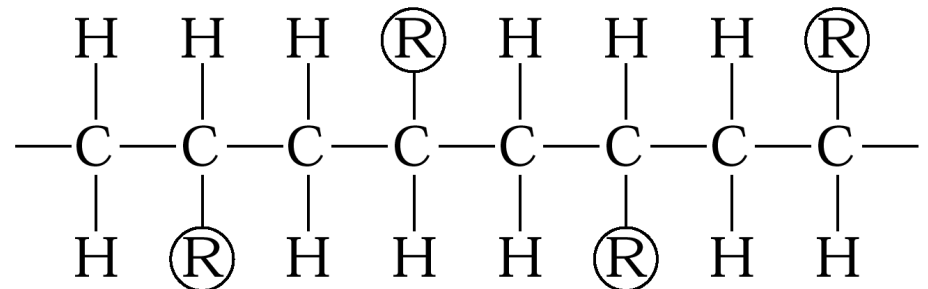
Stereoisomerism

❖ Stereoisomerism denotes the situation in which atoms are linked together in the same order (head-to-tail) but differ in their spatial arrangement.

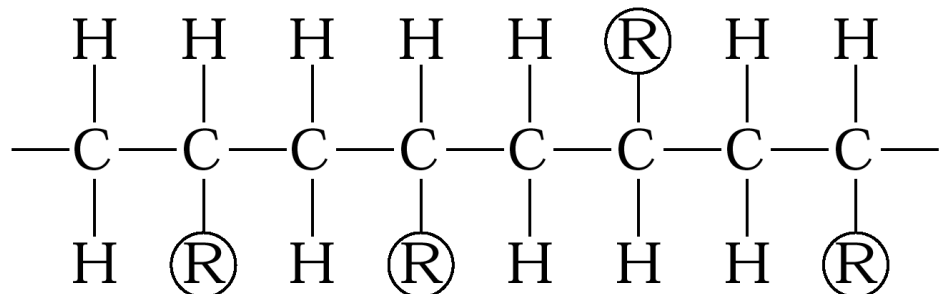
❖ Three configurations are possible:
1. Isotactic configuration.



2. Syndiotactic configuration.



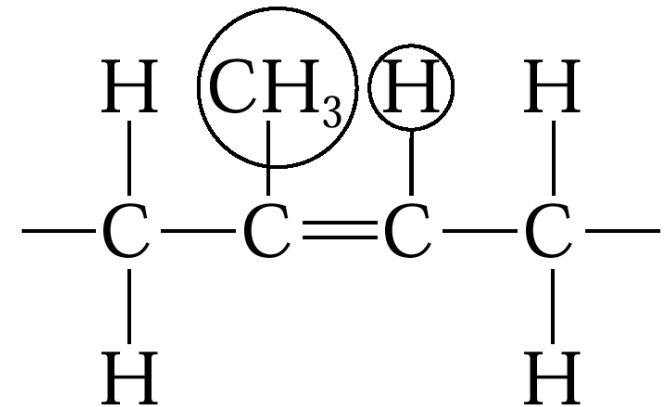
3. Atactic configuration



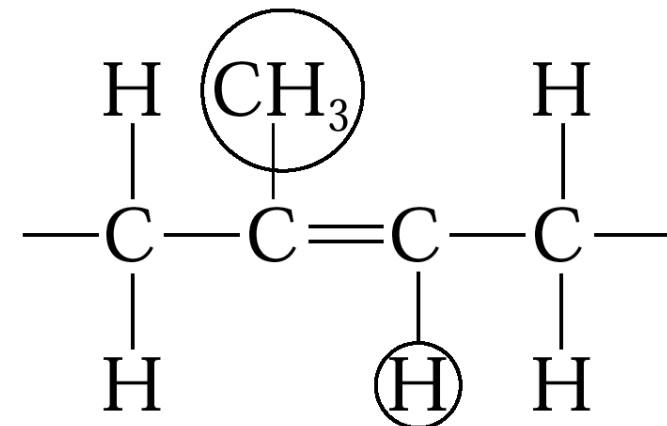
Geometrical Isomerism

- ❖ Geometrical isomers, are possible within mer units having a double bond between chain carbon atoms.
- ❖ Two configurations are possible:

1. Cis configuration (cis-polyisoprene, natural rubber).



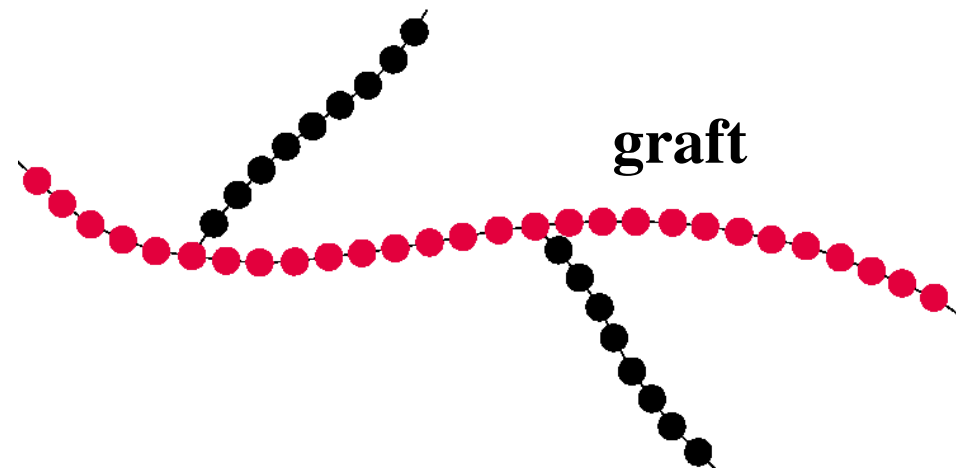
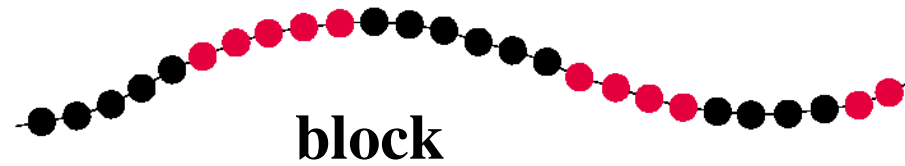
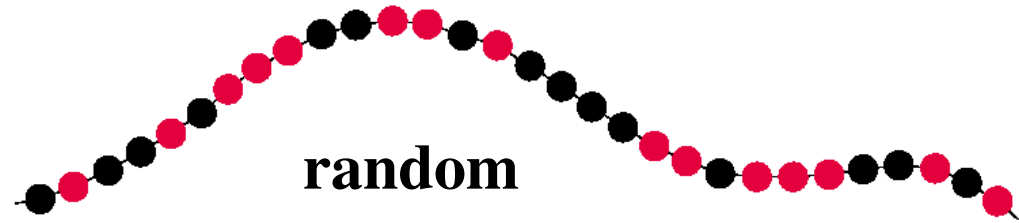
2. Trans configuration.



Summary

- ❖ **polymer molecules may be characterized in terms of their size, shape, and structure.**
- ❖ **Molecular size is specified in terms of molecular weight (or degree of polymerization).**
- ❖ **Molecular shape relates to the degree of chain twisting, coiling, and bending.**
- ❖ **Molecular structure depends on the manner in which structural units are joined together. Linear, branched, crosslinked, and network structures are all possible, in addition to several isomeric configurations (isotactic, syndiotactic, atactic, cis, and trans).**

Copolymers

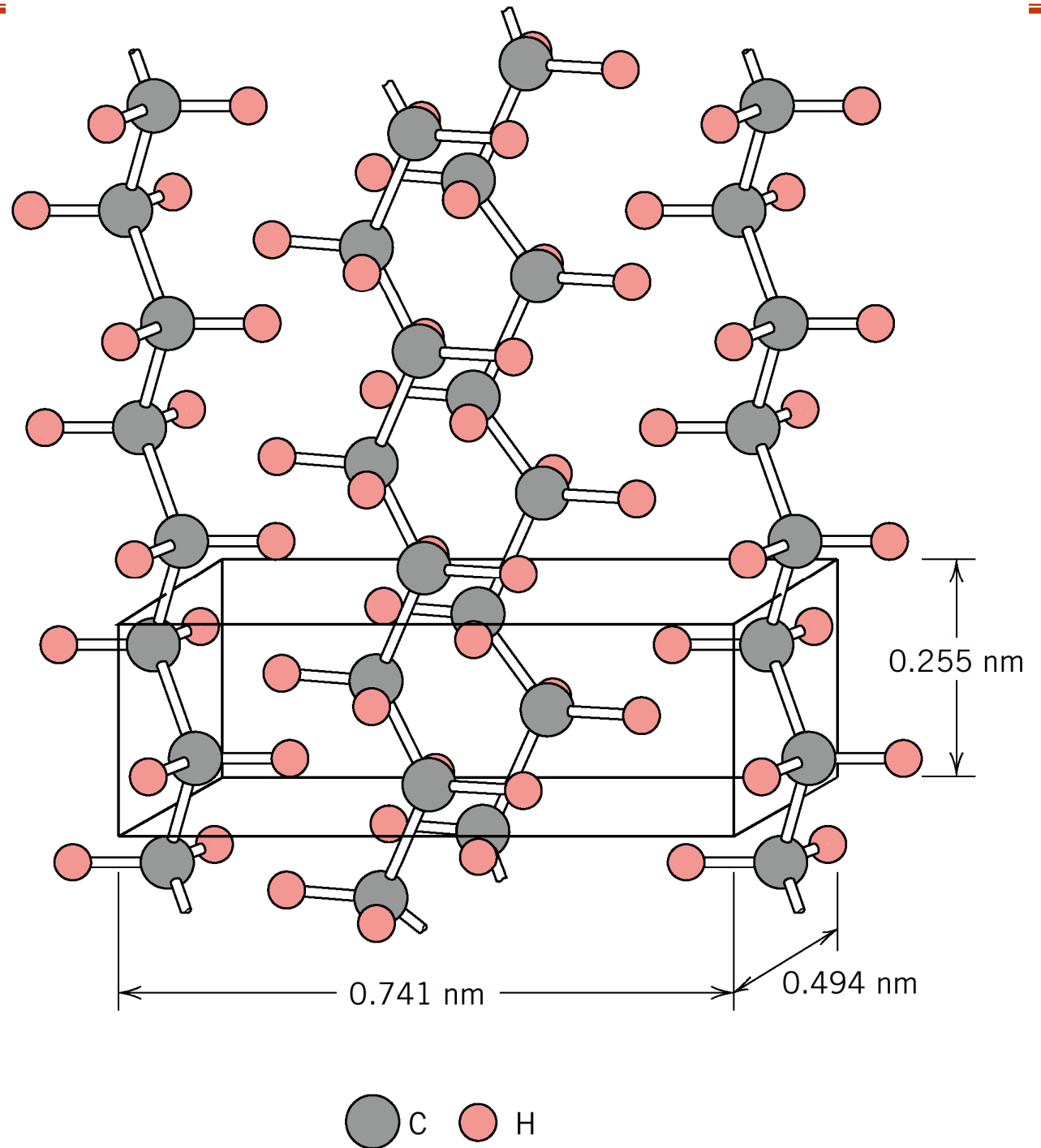


Polymer Crystallinity

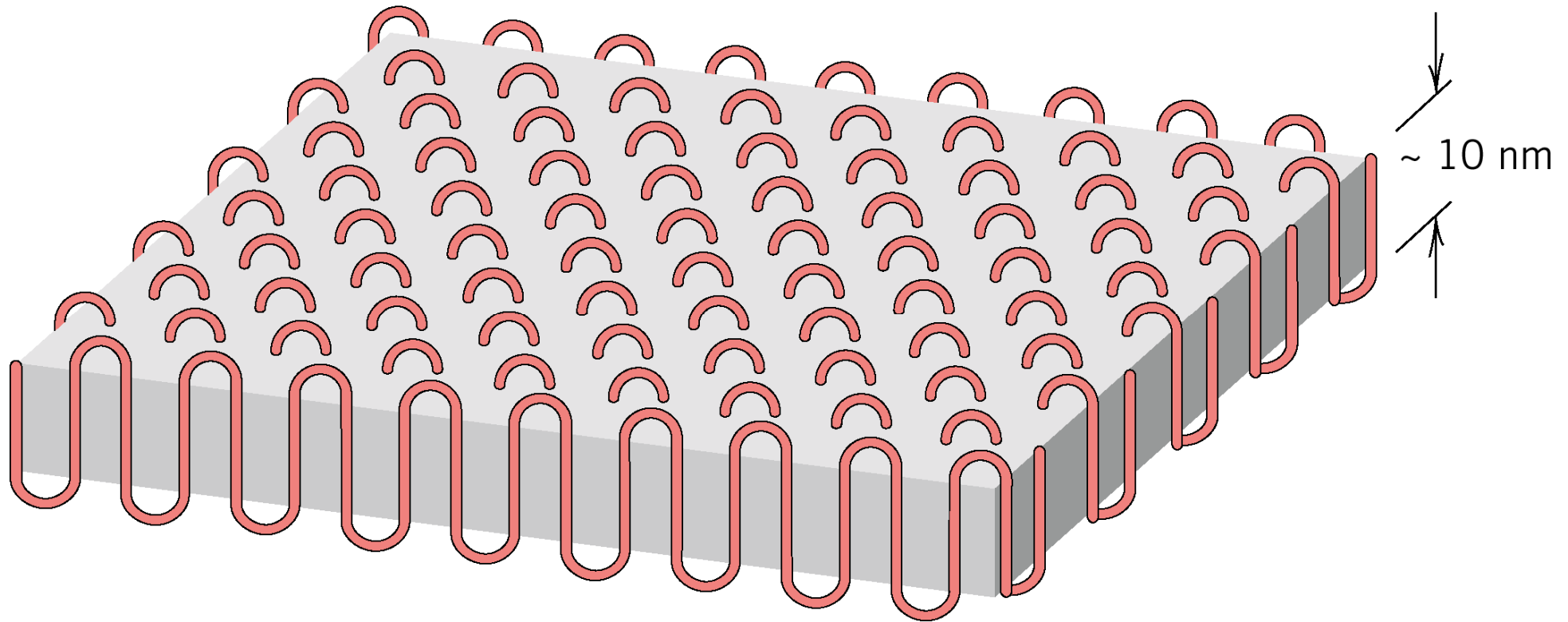
- ❖ **Molecular substances having small molecules (e.g., water, methane, metals...) are normally either totally crystalline (as solids) or totally amorphous (as liquids).**
- ❖ **As a consequence of their size and often complexity, polymer molecules are often only partially crystalline (or semicrystalline), having crystalline regions dispersed within the remaining amorphous material.**
- ❖ **Any chain disorder or misalignment will result in an amorphous region, a condition that is fairly common, since twisting, kinking, and coiling of the chains prevent the strict ordering of every segment of every chain.**
- ❖ **Other structural effects are also influential in determining the extent of crystallinity.**

Unit Cell of Polyethylene

Orthorhombic



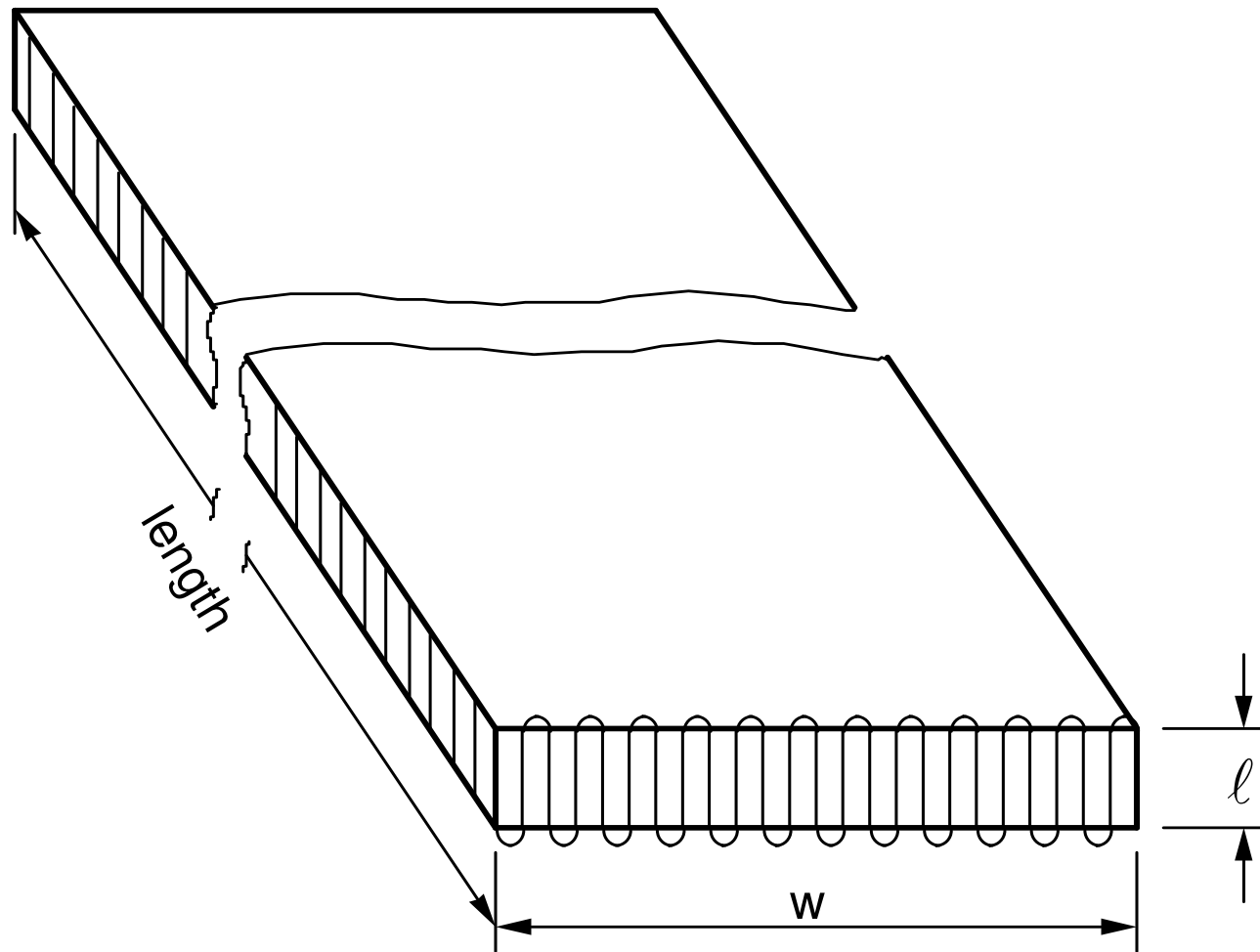
Polymer Crystals



Lamellar structure (10 to 20 nm thick and 10 μm long).

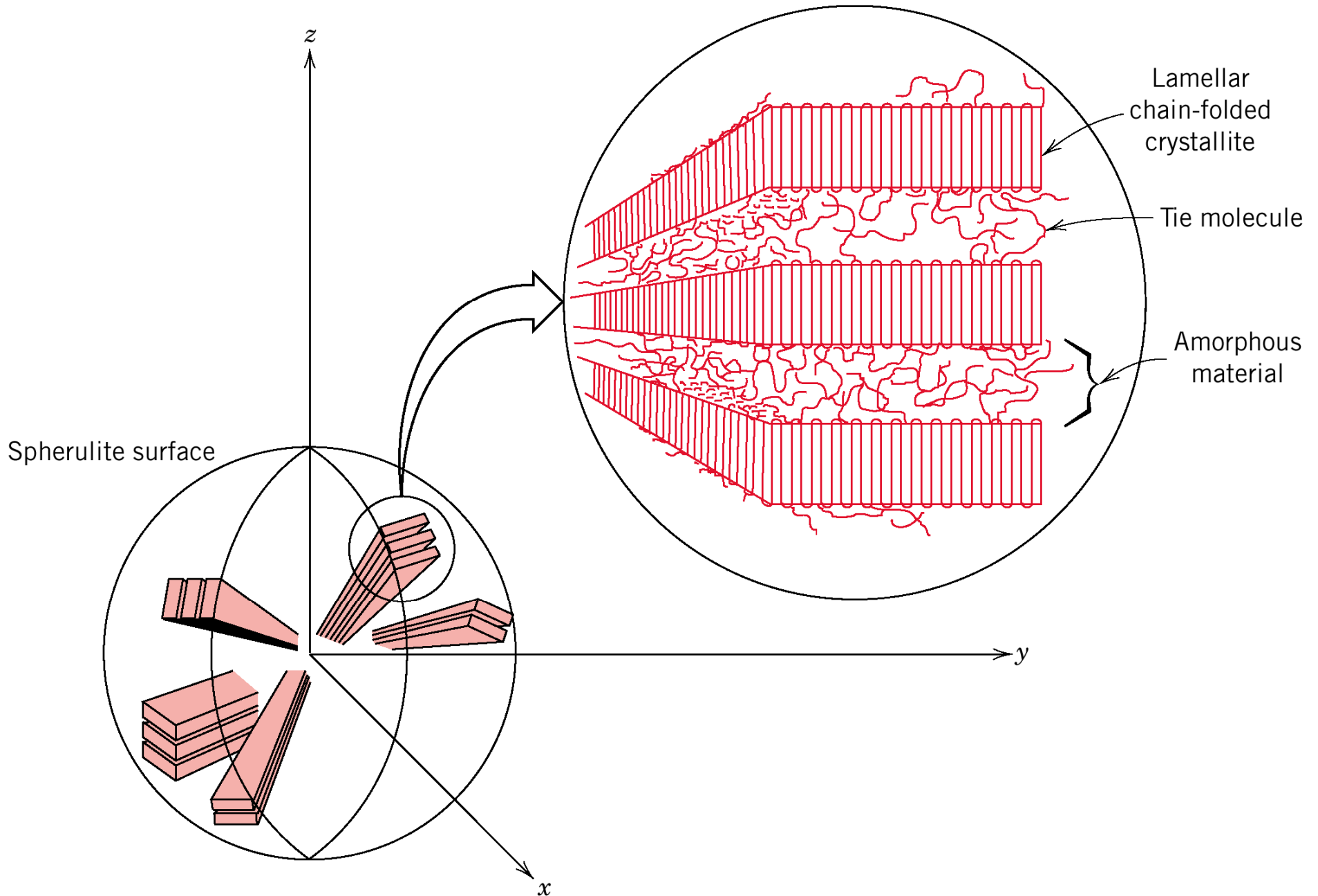
Molecular chains within each platelet fold back and forth on themselves, with folds occurring at the faces

Schematic of Lamellar Structure



ideally $l \ll w \ll \text{length}$

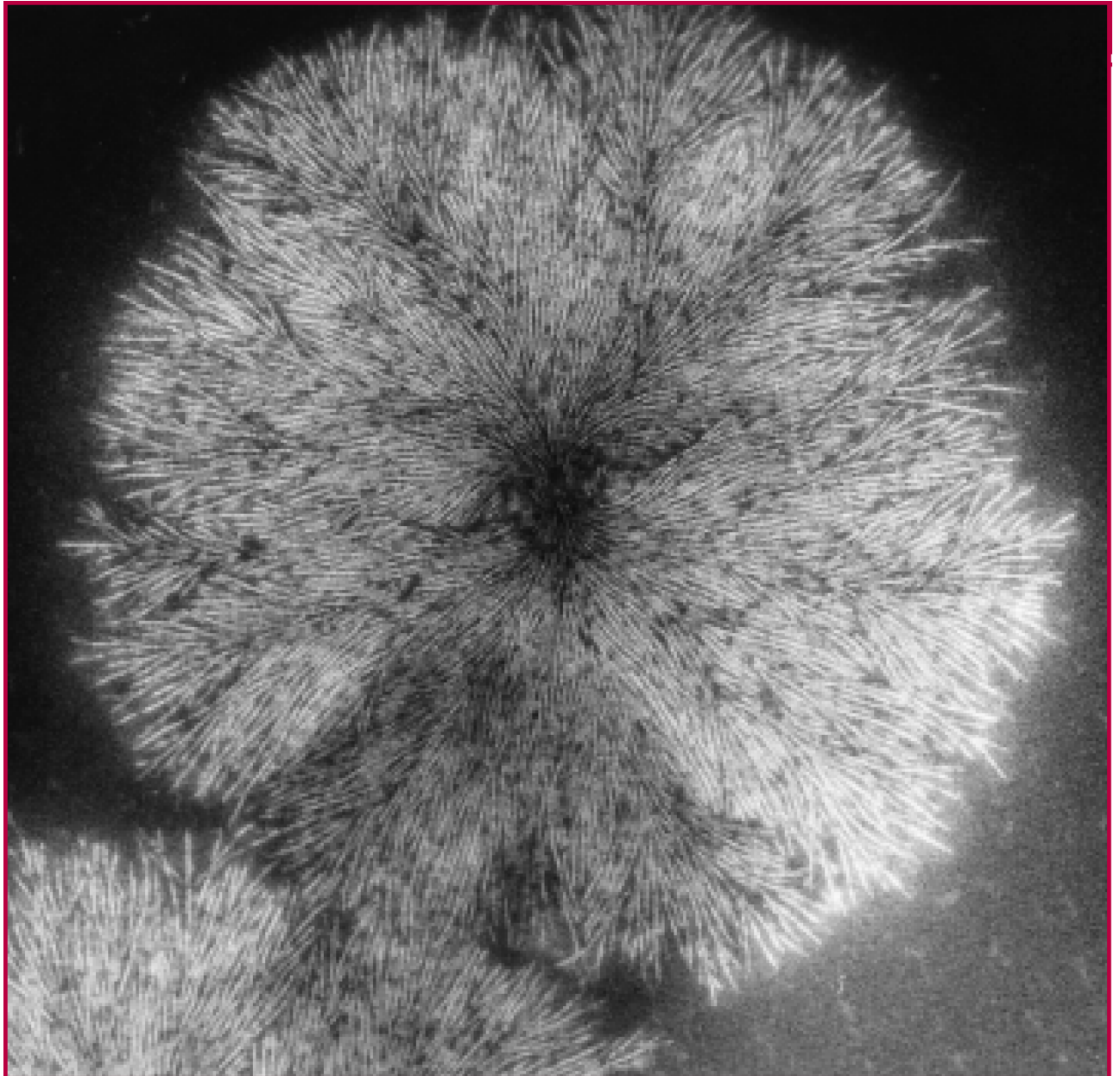
Schematic Representation of a Spherulite



Spherulites

The spherulite consists of an aggregate of ribbonlike chain-folded crystallites (lamellae) approximately 10 nm thick that radiate from the center outward.

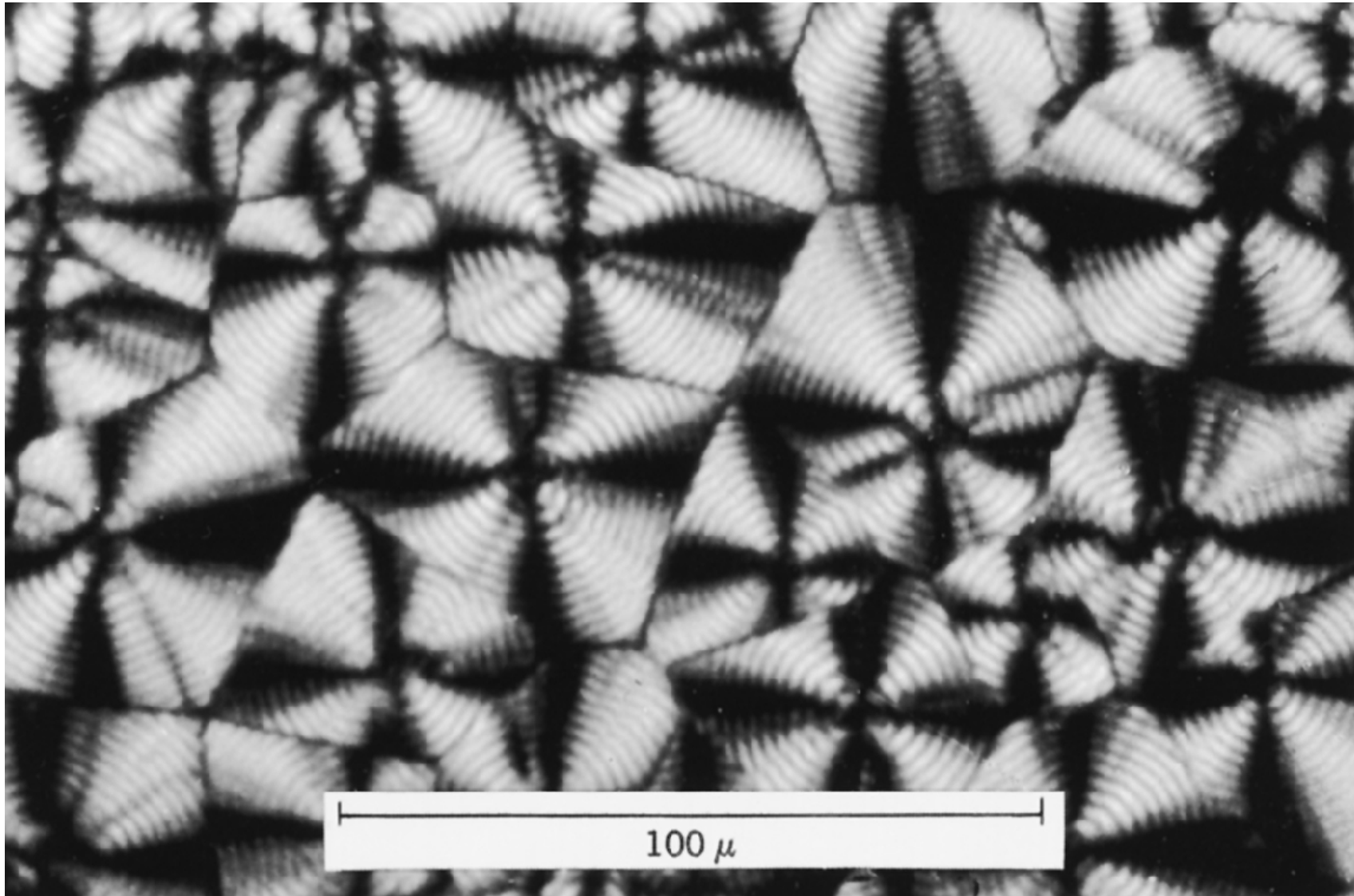
Many bulk polymers that are crystallized from a melt form spherulites.



Optical Microscope

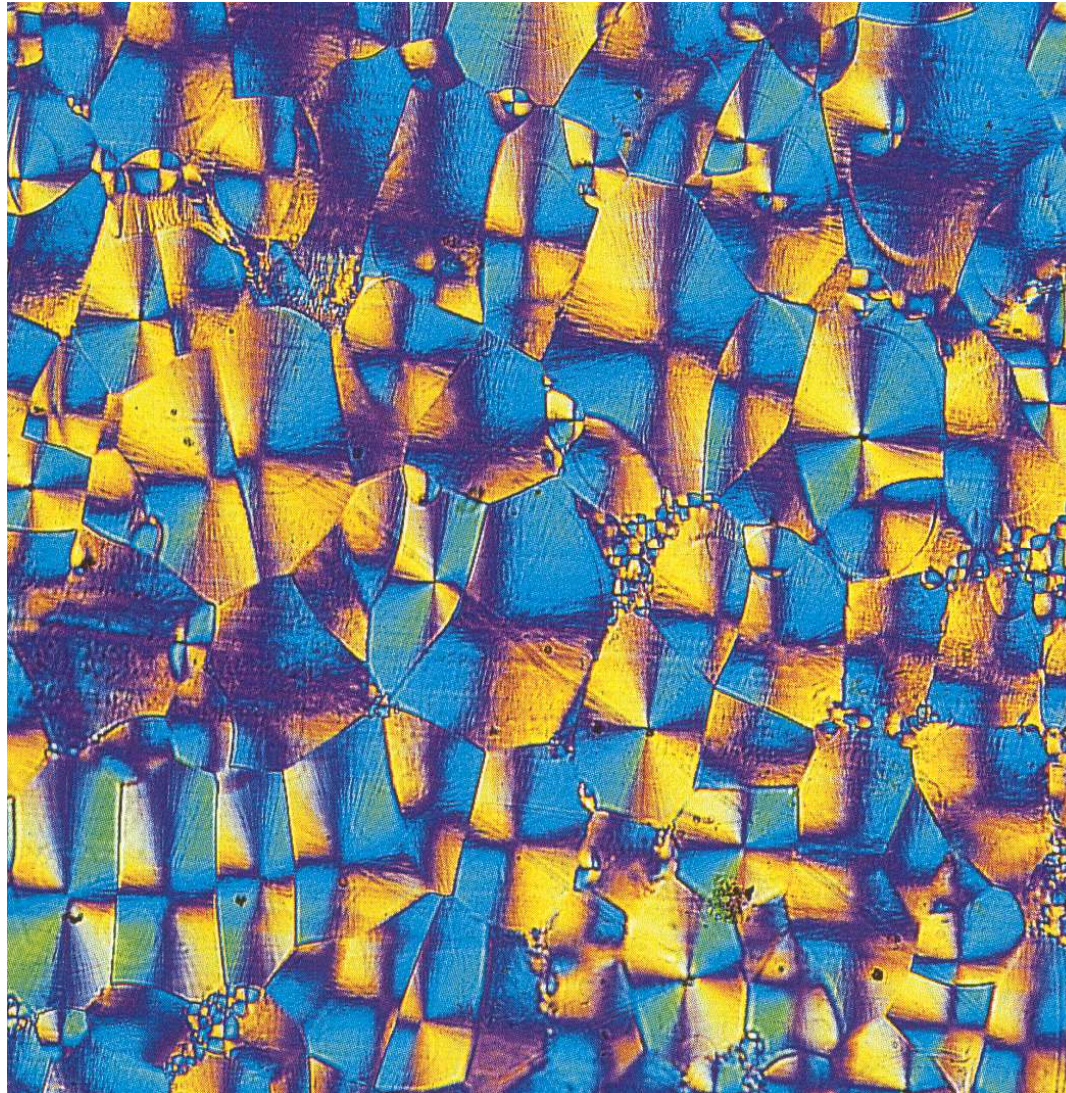


Microscopic Observation of PE Spherulite



Cross-polarized light photomicrograph showing the spherulite structure of polyethylene. Within each spherulite appears a Maltese cross. 525x

Microscopic Observation of Nylon Spherulites



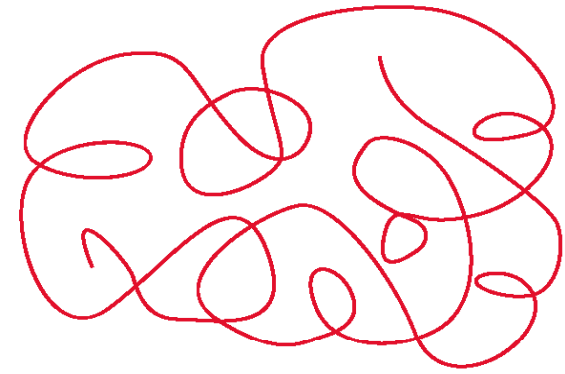
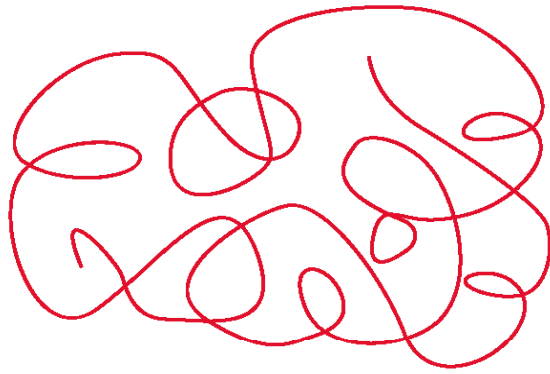
Cross-polarized light photomicrograph with 1/4-wave plate showing the spherulite structure of nylon.

Solid Structures

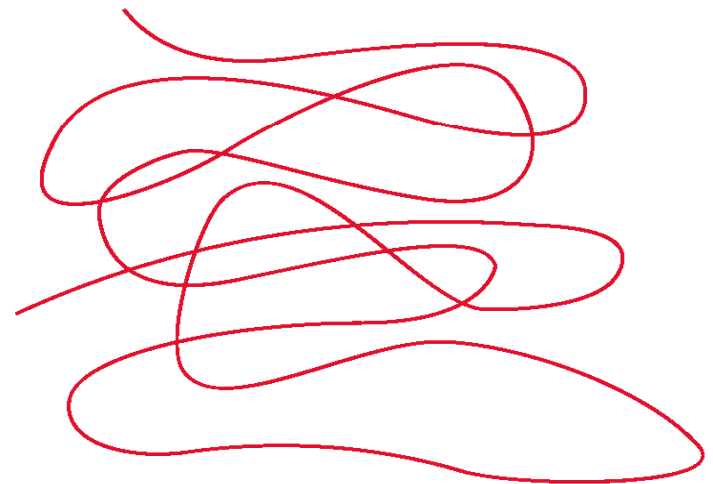
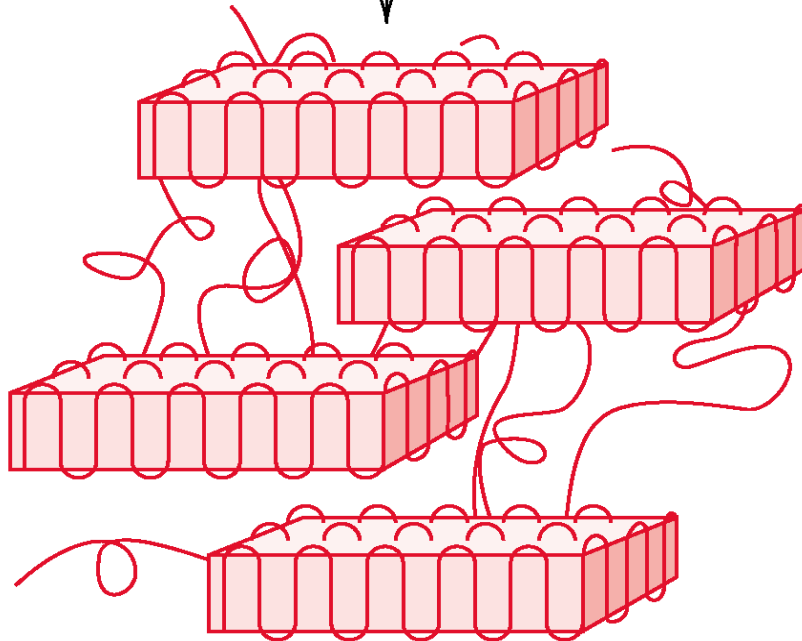
Semicrystalline

Amorphous

Melt



Solid



Degree of Crystallinity

$$\% \text{ crystallinity} = \frac{\rho_c(\rho_s - \rho_a)}{\rho_s(\rho_c - \rho_a)} \times 100$$

- ❖ **The degree of crystallinity of a polymer depends on the rate of cooling during solidification as well as on the chain configuration.**
- ❖ **Crystallization is not favored in polymers that are composed of chemically complex mer structures (e.g., polyisoprene).**
- ❖ **On the other hand, crystallization is not easily prevented in chemically simple polymers such as polyethylene, polypropylene and polytetrafluoroethylene, even for very rapid cooling rates.**

Degree of Crystallinity

❖ **Weight fraction:**
$$\%C_w = \frac{\rho_c (\rho_s - \rho_a)}{\rho_s (\rho_c - \rho_a)} \times 100$$

❖ **Volume fraction:**
$$\%C_v = \frac{(\rho_s - \rho_a)}{(\rho_c - \rho_a)} \times 100$$

❖ **DSC:**
$$\%C_{DSC} = \frac{\Delta H_{fs}}{\Delta H_{fc}} \times 100$$

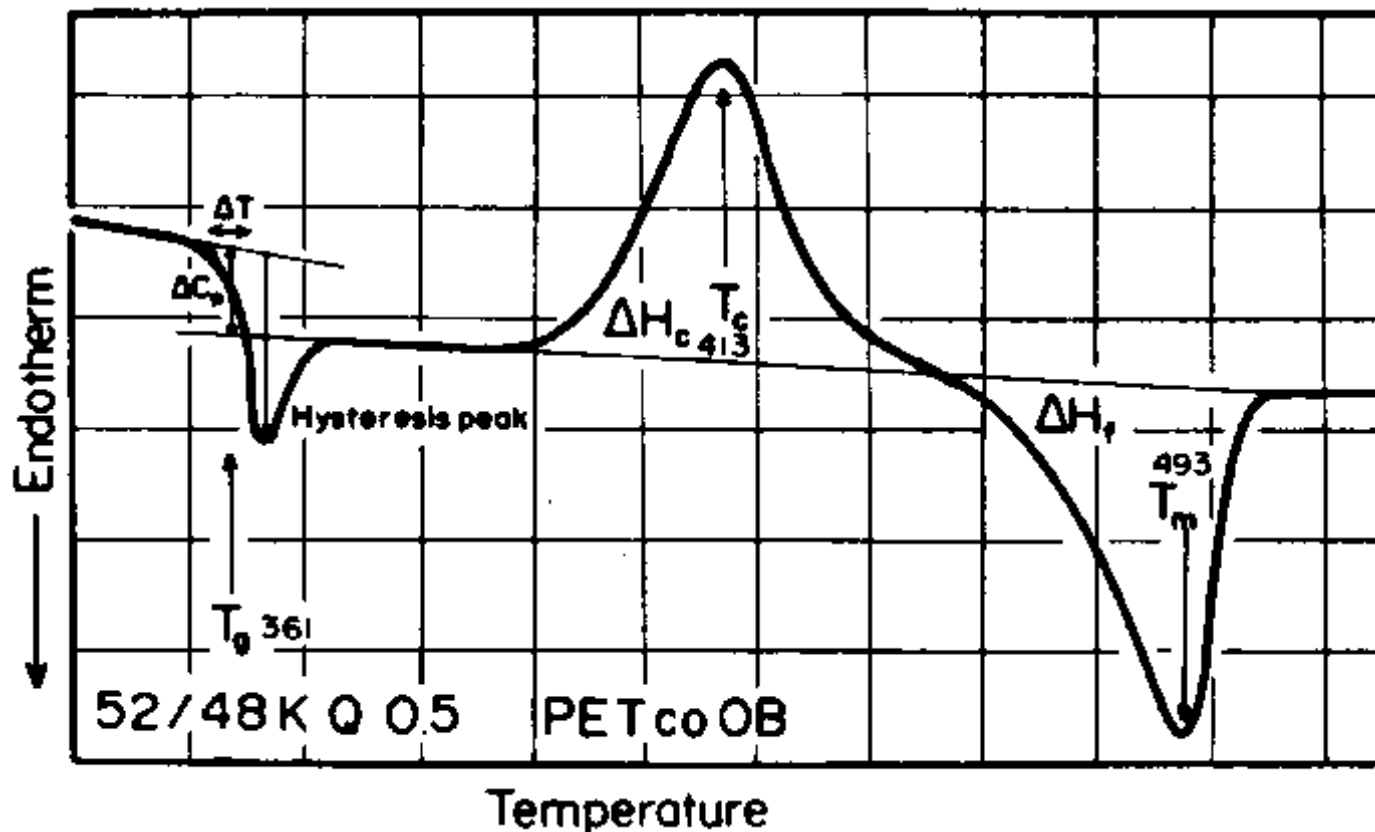
❖ **XRD:**
$$\%C_{XRD} = \frac{A_c}{A_{Total}} \times 100$$

Extent of Crystallinity: Calorimetry (DSC)

- Given independent knowledge of the heat of crystallization for a given polymer, one can readily determine the degree of crystallinity (ϕ) in a sample by DSC:

$$\phi = \frac{\Delta H_{f,\text{sample}}}{\Delta H_f}$$

- where $\Delta H_{f,\text{sample}}$ (J/g) is recorded from the melting endotherm and ΔH_f (J/g) is the heat of crystallization for a perfect crystal of the material.



Degree of Crystallinity

- ❖ Any side branches interfere with crystallization, such that branched polymers never are highly crystalline; in fact, excessive branching may prevent any crystallization whatsoever.
- ❖ Most network and crosslinked polymers are almost totally amorphous; a few crosslinked polymers are partially crystalline.
- ❖ With regard to stereoisomers, atactic polymers are difficult to crystallize; however, isotactic and syndiotactic polymers crystallize much more easily because the regularity of the geometry of the side groups facilitates the process of fitting together adjacent chains.
- ❖ Also, the bulkier or larger the side-bonded groups of atoms, the less tendency there is for crystallization.

Degree of Crystallinity

- ❖ For copolymers, as a general rule, the more irregular and random the mer arrangements, the greater is the tendency for the development of noncrystallinity.
- ❖ For alternating and block copolymers there is some likelihood of crystallization. On the other hand, random and graft copolymers are normally amorphous.
- ❖ To some extent, the physical properties of polymeric materials are influenced by the degree of crystallinity. Crystalline polymers are usually stronger and more resistant to dissolution and softening by heat.

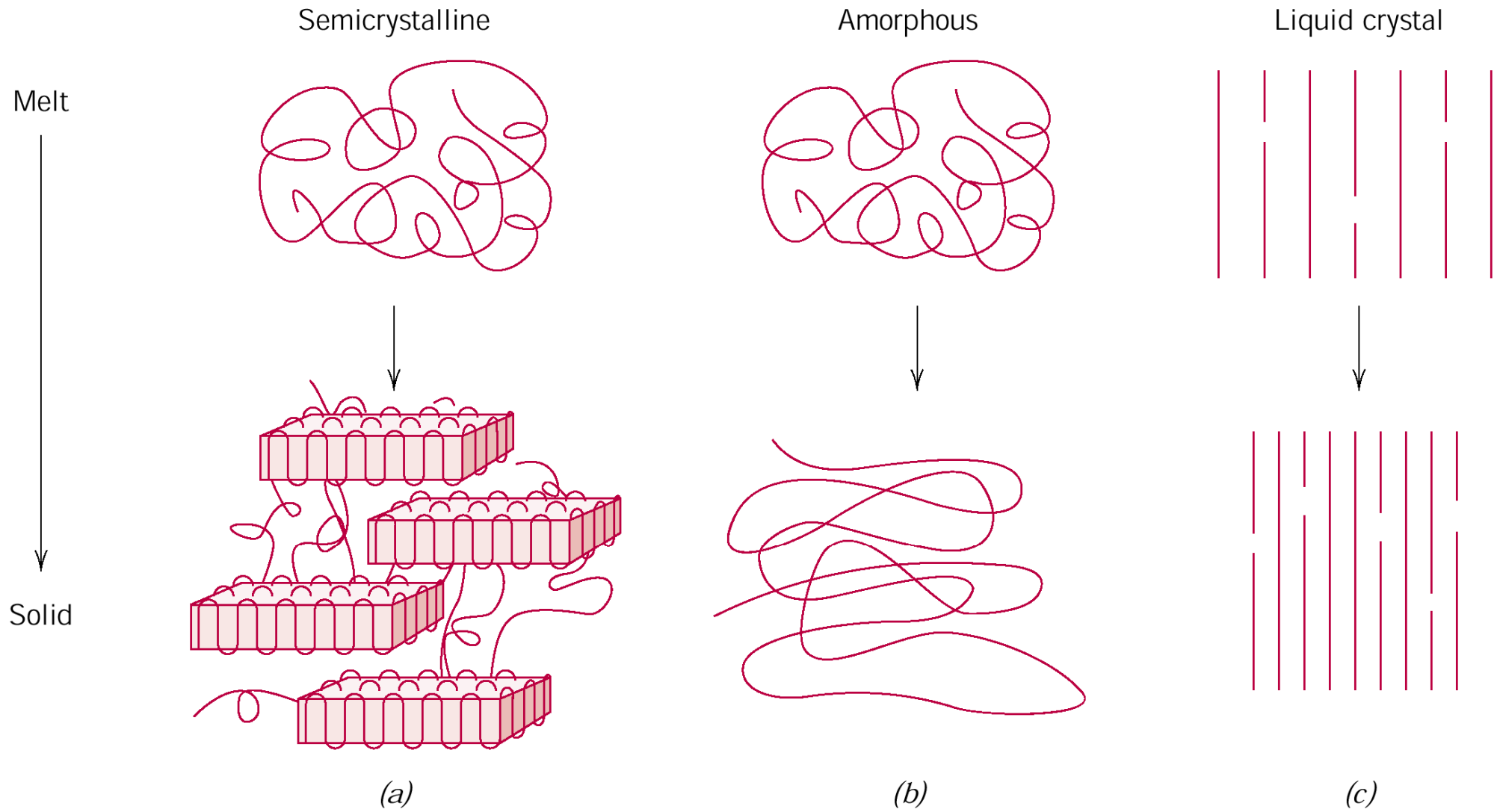
Summary

- ❖ Several molecular characteristics that have an influence on the properties of polymers were discussed.
- ❖ Molecular entanglements occur when the chains assume twisted, coiled, and kinked shapes or contours.
- ❖ With regard to molecular structure, linear, branched, crosslinked, and network structures are possible, in addition to isotactic, syndiotactic, and atactic stereoisomers, and the cis and trans geometrical isomers.
- ❖ The copolymers include random, alternating, block, and graft types.
- ❖ With regard to behavior at elevated temperatures, polymers are classified as either thermoplastic or thermosetting. The former have linear and branched structures; they soften when heated and harden when cooled. In contrast, thermosets, once having hardened, will not soften upon heating; their structures are crosslinked and network.

Summary (continued)

- ❖ **In addition to being entirely amorphous, polymers may also exhibit varying degrees of crystallinity; for the latter case, crystalline regions are interdispersed within amorphous areas.**
- ❖ **Crystallinity is facilitated for polymers that are chemically simple and that have regular and symmetrical chain structures.**
- ❖ **Many semicrystalline polymers form spherulites; each spherulite consists of a collection of ribbonlike chain-folded lamellar crystallites that radiate outward from its center.**

Schematic Representation of a Amorphous and Semicrystalline



Transitions in Polymers

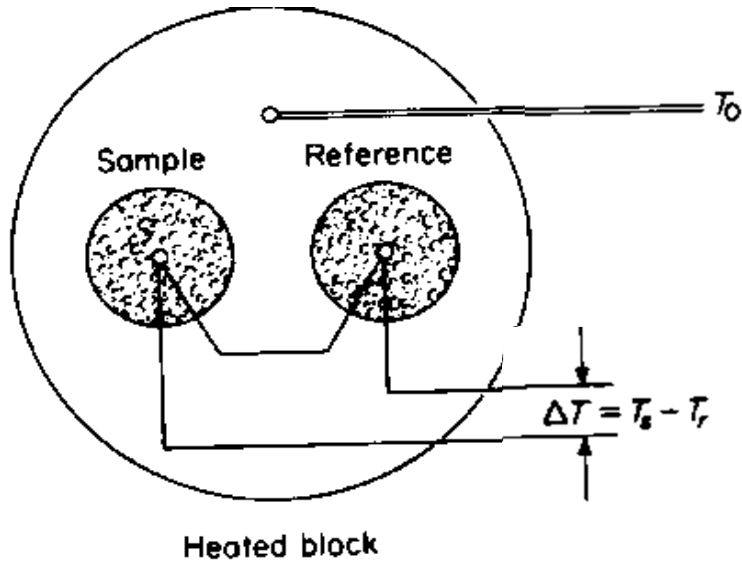
There are two major transition temperatures in polymers

- 1. Melting Temperature**
- 2. Glass Transition Temperature**

Melting

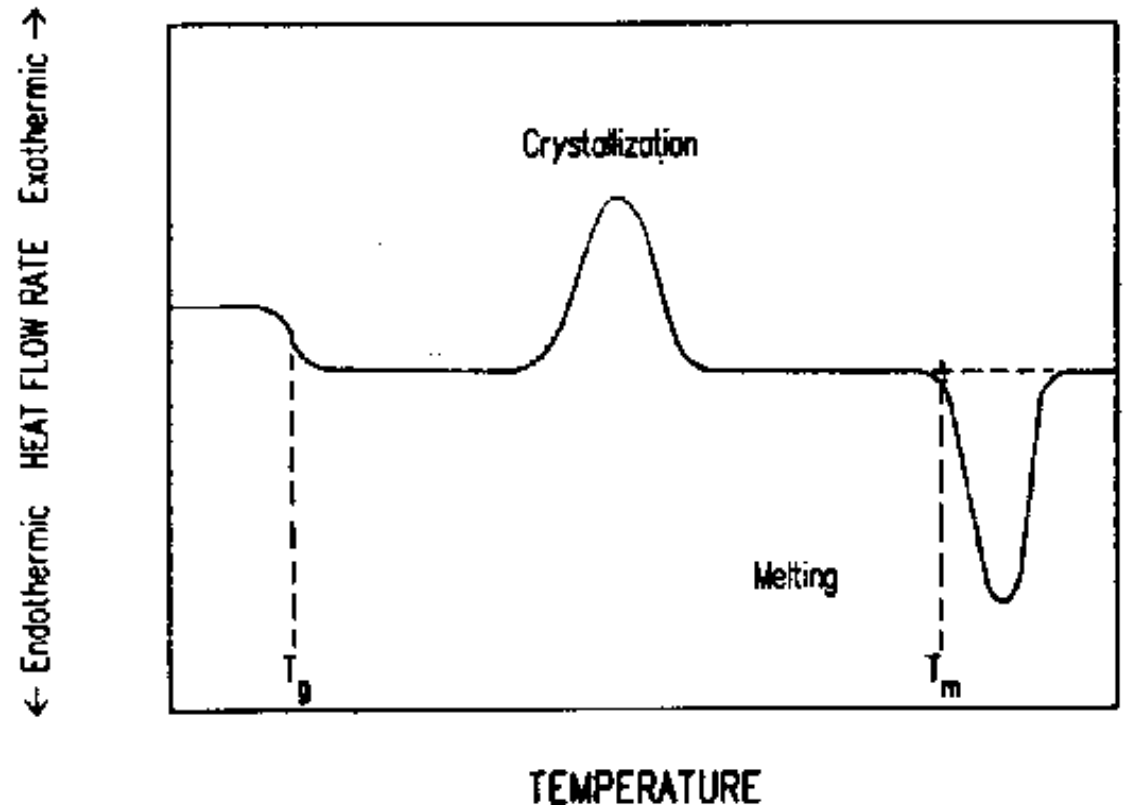
- ❖ **There are several features distinctive to the melting of polymers that are not normally observed with metals and ceramics; these are consequences of the polymer molecular structures and lamellar crystalline morphology.**
- ❖ **First of all, melting of polymers takes place over a range of temperatures.**
- ❖ **In addition, the melting behavior depends on the history of the specimen, in particular the temperature at which it crystallized.**
- ❖ **The thickness of chain-folded lamellae will depend on crystallization temperature; the thicker the lamellae, the higher the melting temperature.**
- ❖ **And finally, the apparent melting behavior is a function of the rate of heating; increasing this rate results in an elevation of the melting temperature.**

Identifying the Crystalline Melting Temperature



A Differential Scanning Calorimeter (DSC) controls the energy input to a sample and reference so they remain at the same T throughout a programmed temperature rise.

- A DSC trace is a plot of
- energy ($\Delta H = H_{\text{sample}} - H_{\text{ref}}$)
- as a function of T .



The Glass Transition Temperature

- ❖ **The glass transition occurs in amorphous (or glassy) and semicrystalline polymers, and is due to a reduction in motion of large segments of molecular chains with decreasing temperature.**
- ❖ **Upon cooling, the glass transition corresponds to the gradual transformation from a liquid to a rubbery material, and finally, to a rigid solid.**
- ❖ **The temperature at which the polymer experiences the transition from rubbery to rigid states is termed the glass transition temperature, T_g .**

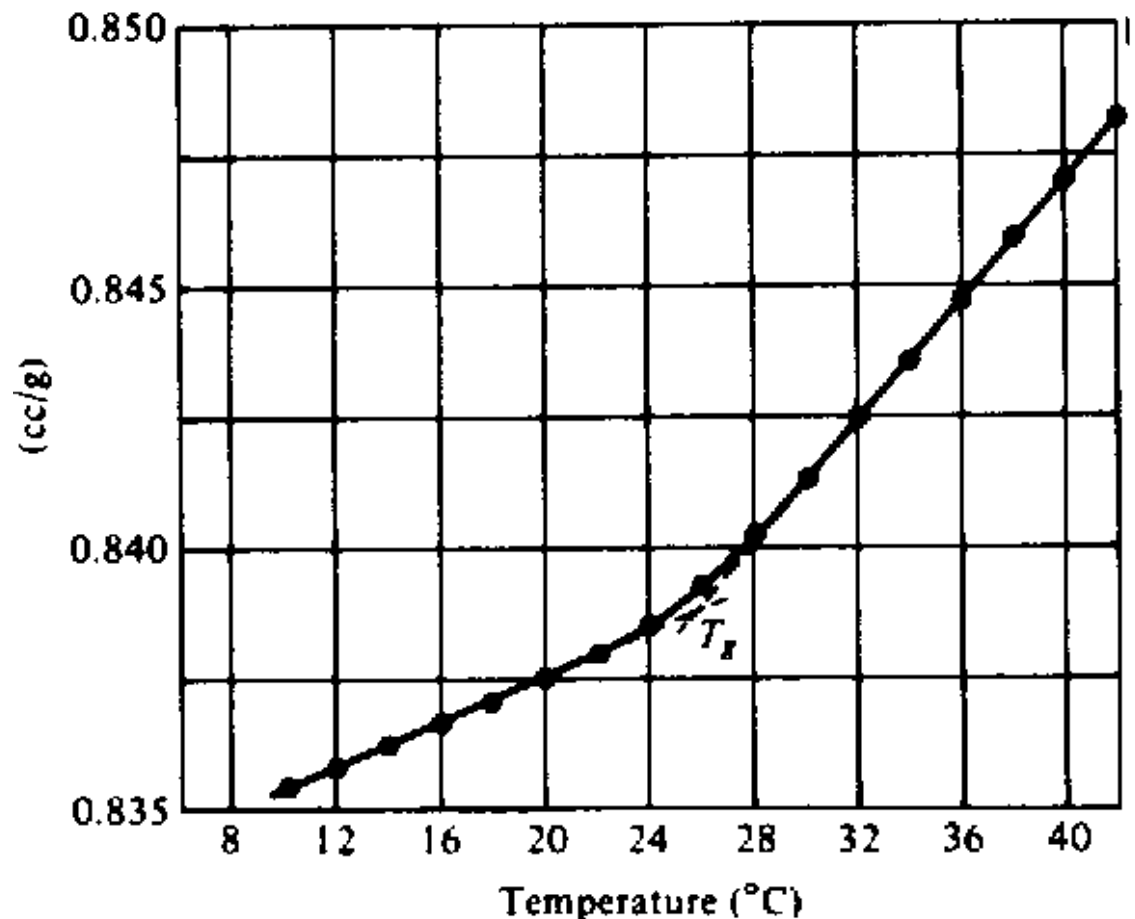
Identifying the Glass Transition Temperature

Transition from a glass amorphous state to a rubbery amorphous state can be detected by a number of methods.

- **Dynamic mechanical testing**
- **Specific volume determinations**
- **Differential Scanning Calorimetry**

Shown here is the specific volume vs. T plot for poly(vinyl acetate).

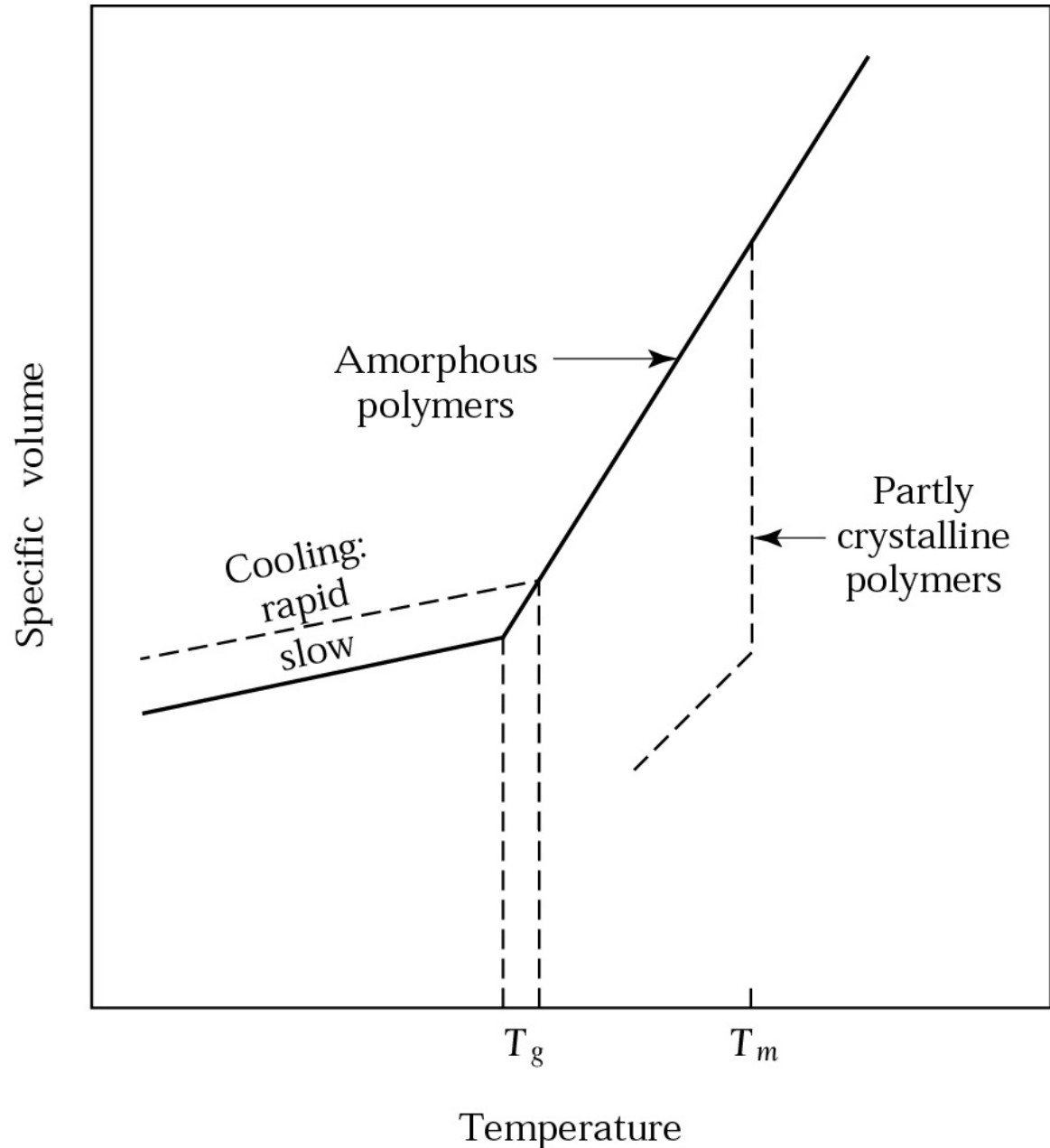
Note that the thermal expansion coefficient changes at T_g , and a discontinuity is observed at the glass transition point.



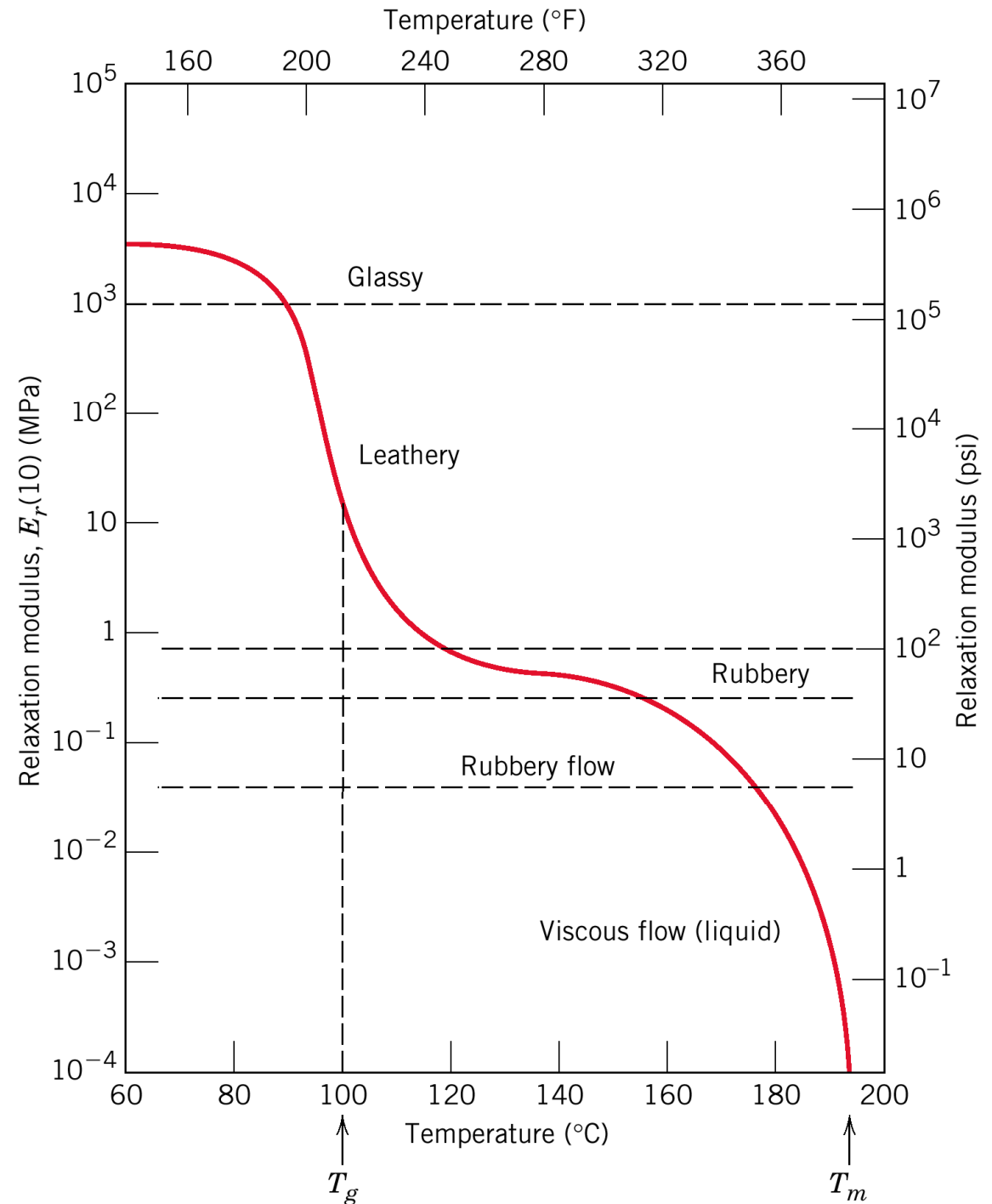
Specific Volume as a Function of Temperature

Specific volume of polymers as a function of temperature.

Amorphous polymers, such as acrylic and polycarbonate, have a glass-transition temperature, T_g , but do not have a specific melting point, T_m . Partly crystalline polymers, such as polyethylene and nylons, contract sharply while passing through their melting temperatures during cooling.



Relaxation Modulus Versus Temperature for Amorphous Polystyrene



Glass-Transition and Melting Temperatures of Some Polymers

TABLE 7.2

Material	T_g (°C)	T_m (°C)
Nylon 6,6	57	265
Polycarbonate	150	265
Polyester	73	265
Polyethylene		
High density	-90	137
Low density	-110	115
Polymethylmethacrylate	105	—
Polypropylene	-14	176
Polystyrene	100	239
Polytetrafluoroethylene	-90	327
Polyvinyl chloride	87	212
Rubber	-73	—

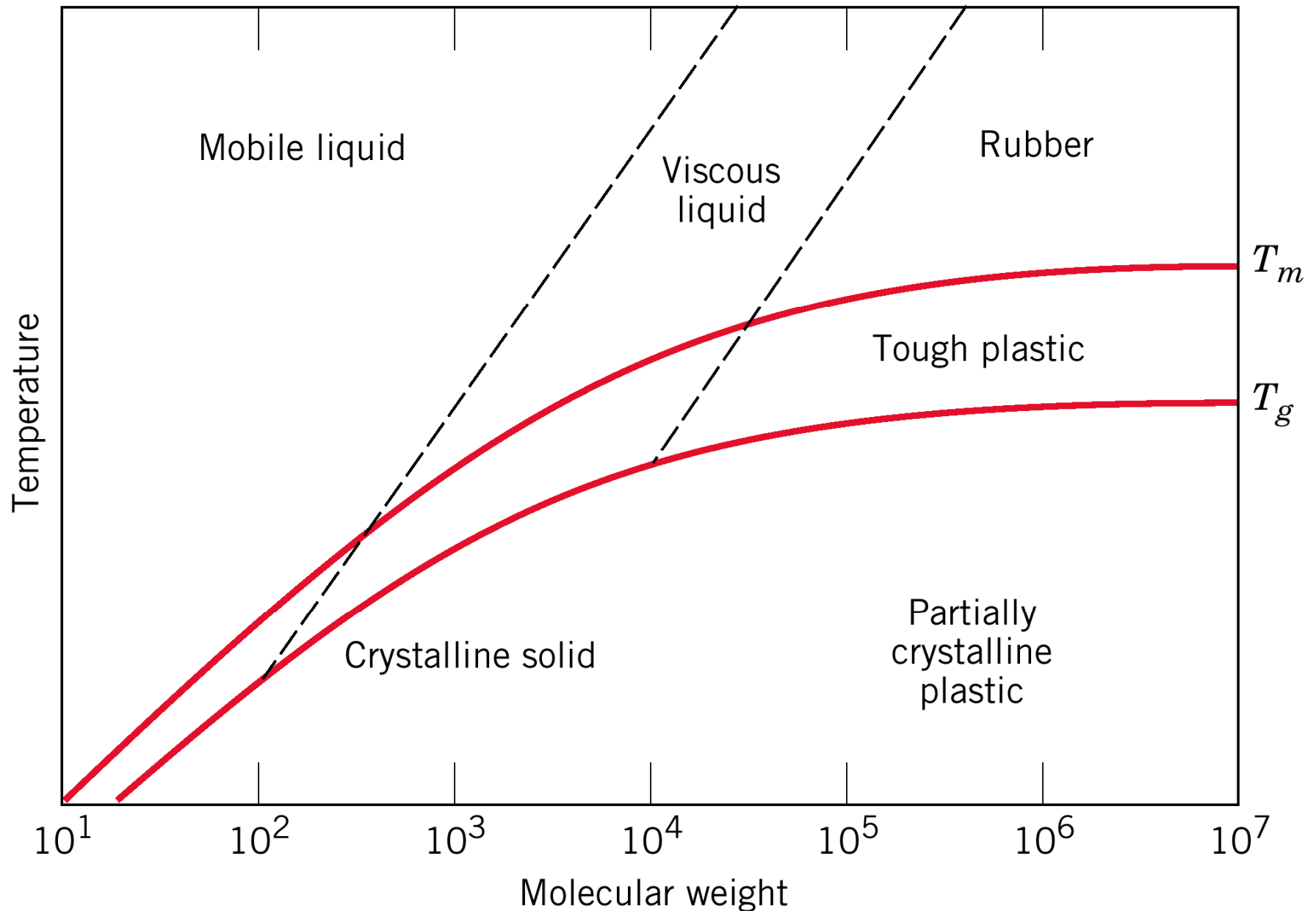
Factors That Influence Melting & Glass Transition Temperatures

- ❖ **Molecular chemistry and structure.**
- ❖ **Chain stiffness, which is controlled by the ease of rotation about the chemical bonds along the chain, has a pronounced effect.**
- ❖ **The presence of double-chain bonds and aromatic groups lowers chain flexibility and causes an increase in T_g and T_m.**
- ❖ **Furthermore, the size and type of side groups influence chain rotational freedom and flexibility; bulky or large side groups tend to restrict molecular rotation and raise T_g and T_m. For example polypropylene has a higher melting temperature than polyethylene (175°C versus 115°C).**

Factors That Influence Melting & Glass Transition Temperatures

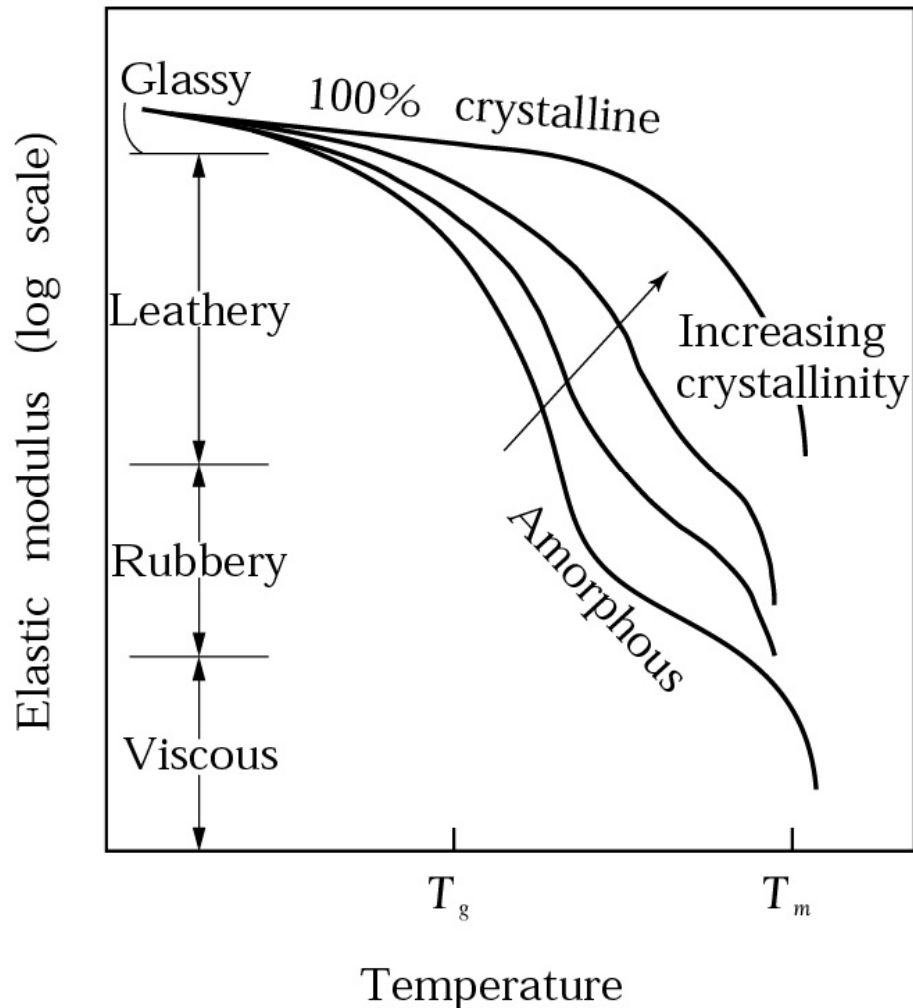
- ❖ For a specific polymer, melting and glass temperatures will also depend on molecular weight.
- ❖ Degree of branching will also affect the melting temperature of a polymer. The introduction of side branches introduces defects into the crystalline material and lowers the melting temperature. HDPE, being a predominately linear polymer, has a higher melting temperature (137°C) than low-density polyethylene (115°C) which has some branching.

Effect of Molecular Weight on Physical Properties

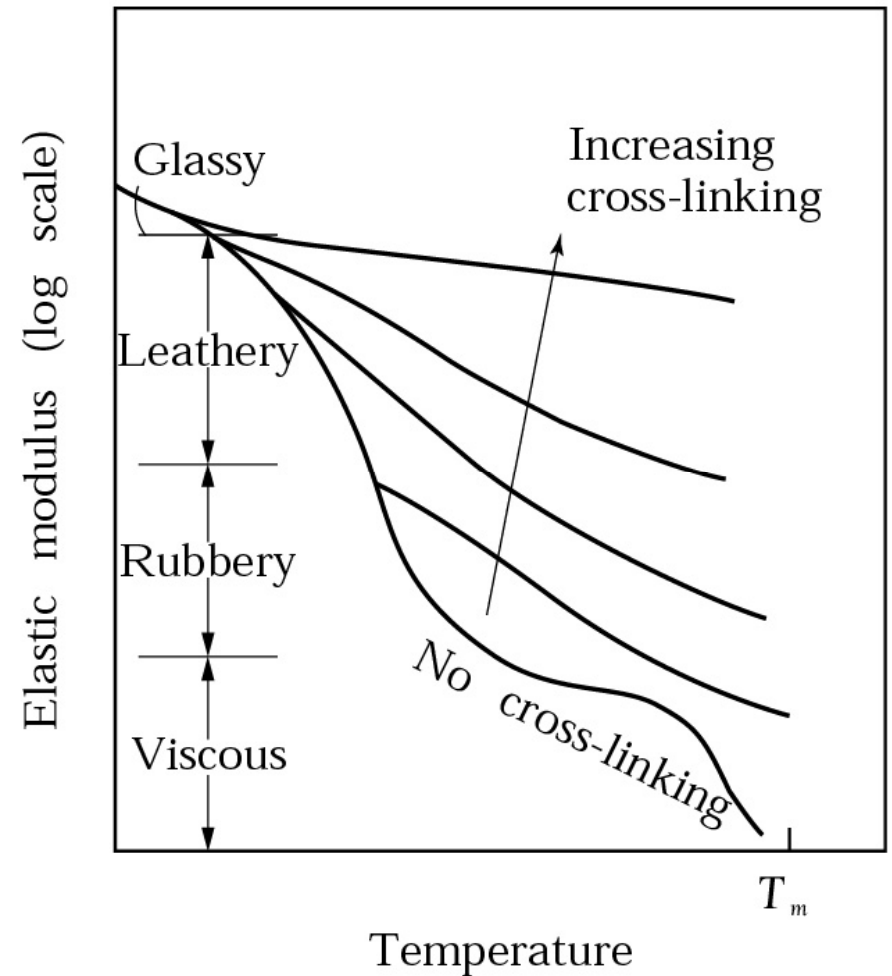


Polymer Behavior

(a)



(b)

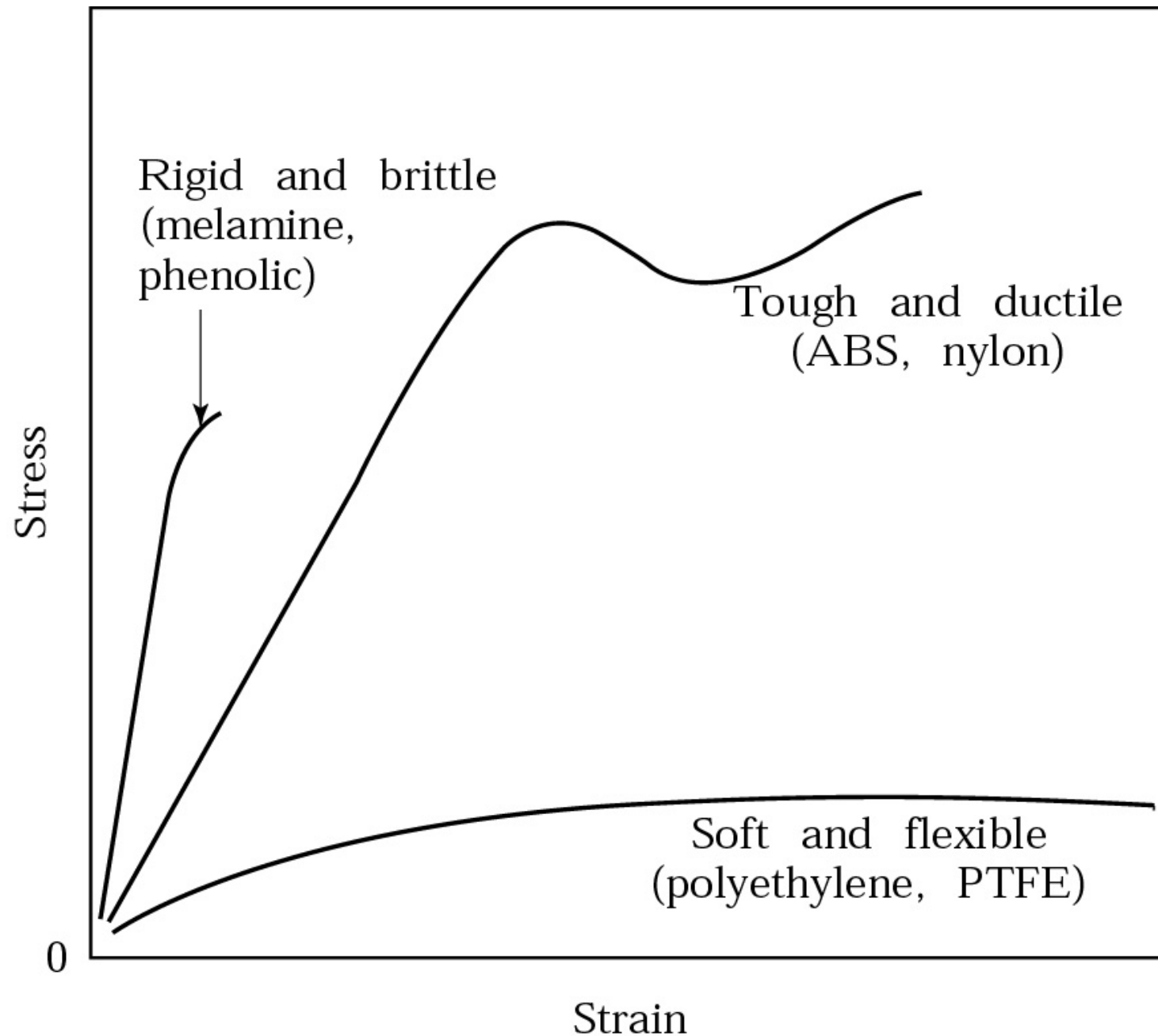


Behavior of polymers as a function of temperature and (a) degree of crystallinity and (b) cross-linking. The combined elastic and viscous behavior of polymers is known as viscoelasticity.

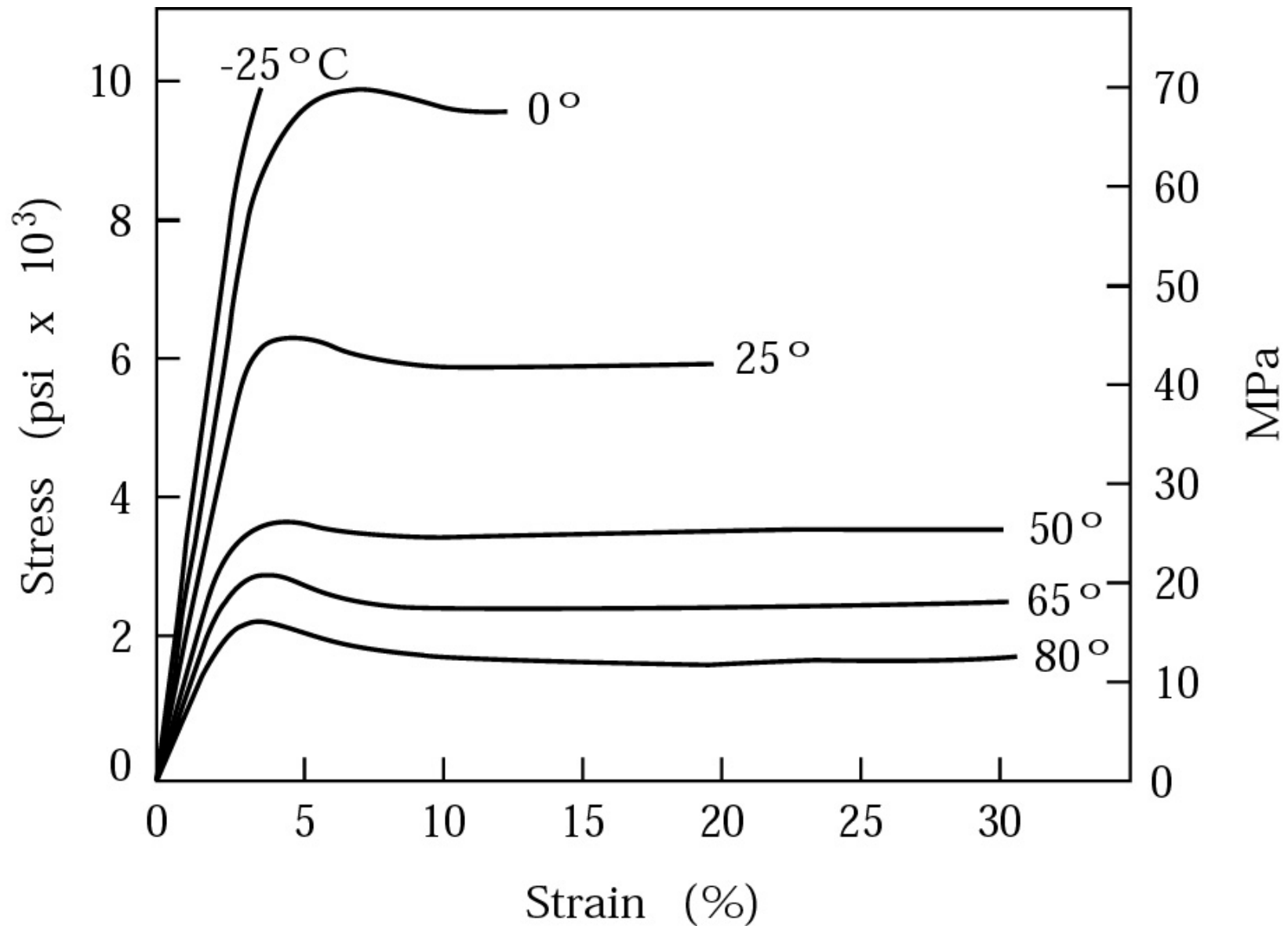
Important Characteristics of Polymers

- ❖ Melting Temperature (for crystalline and semicrystalline).**
- ❖ Glass Transition Temperature (for amorphous and semicrystalline).**
- ❖ Degree of Crystallinity (for semicrystalline).**
- ❖ Degree of Crosslinking (for rubber materials).**
- ❖ Molecular Orientation (from process).**
- ❖ Molecular Stability (due to: temperature, UV light, humidity).**

Behavior of Plastics



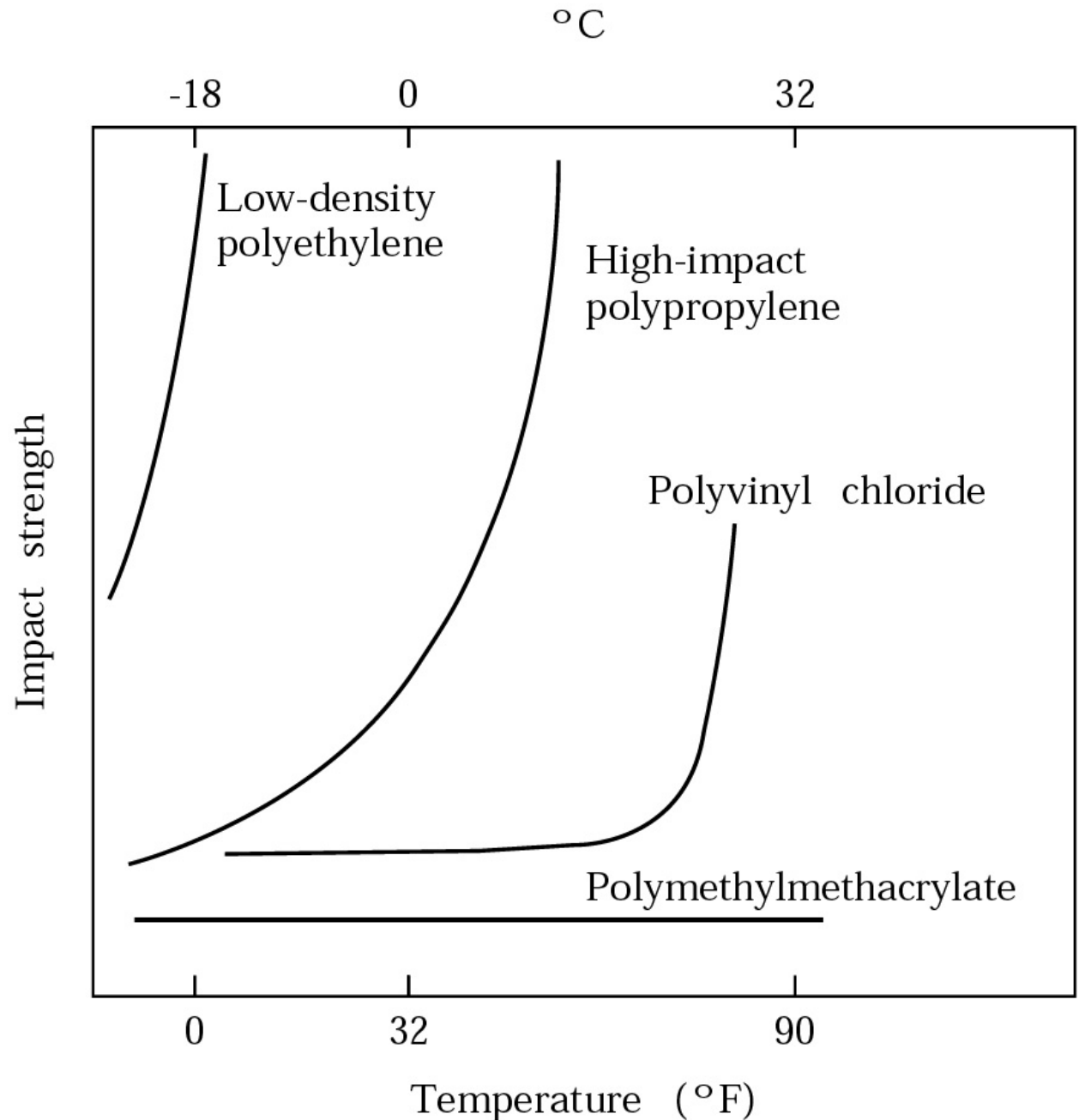
Temperature Effects



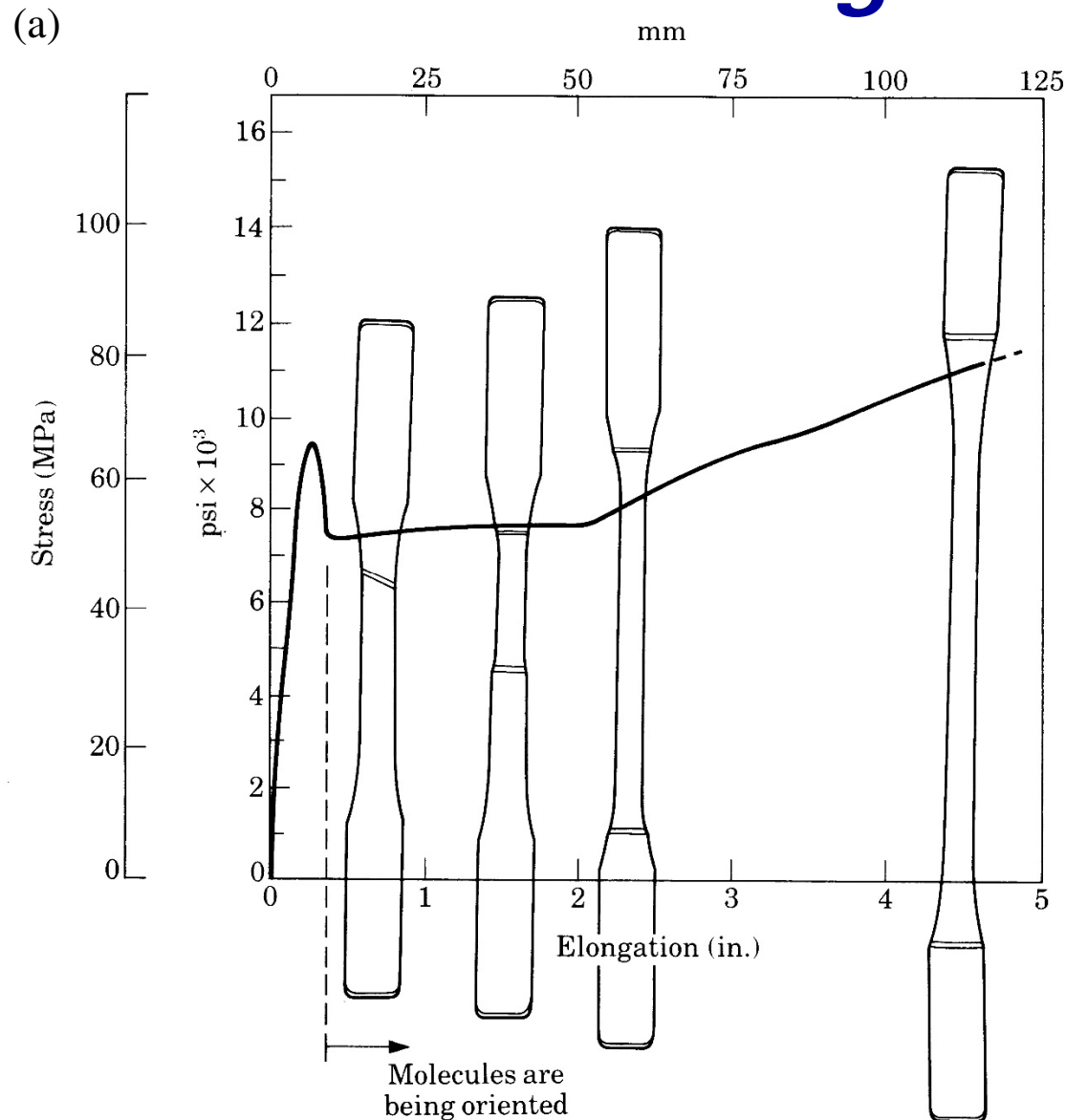
Effect of temperature on the stress-strain curve for cellulose acetate, a thermoplastic.

Temperature Effects

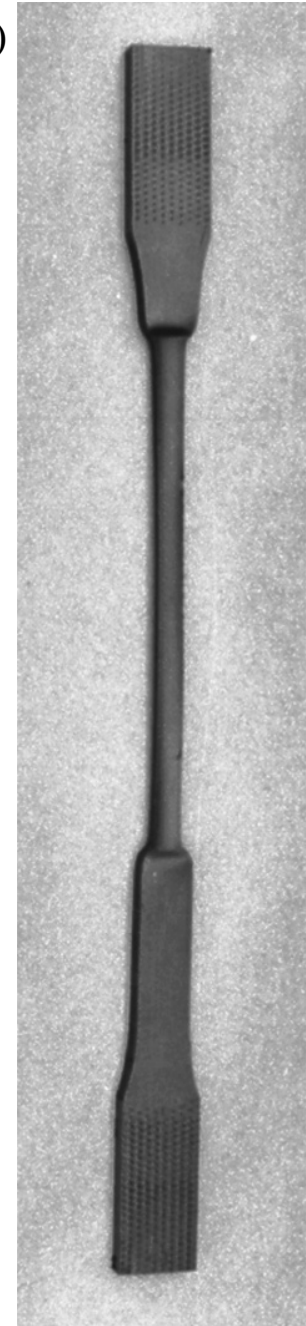
Effect of temperature on the impact strength of various plastics. Small changes in temperature can have a significant effect on impact strength.



Elongation



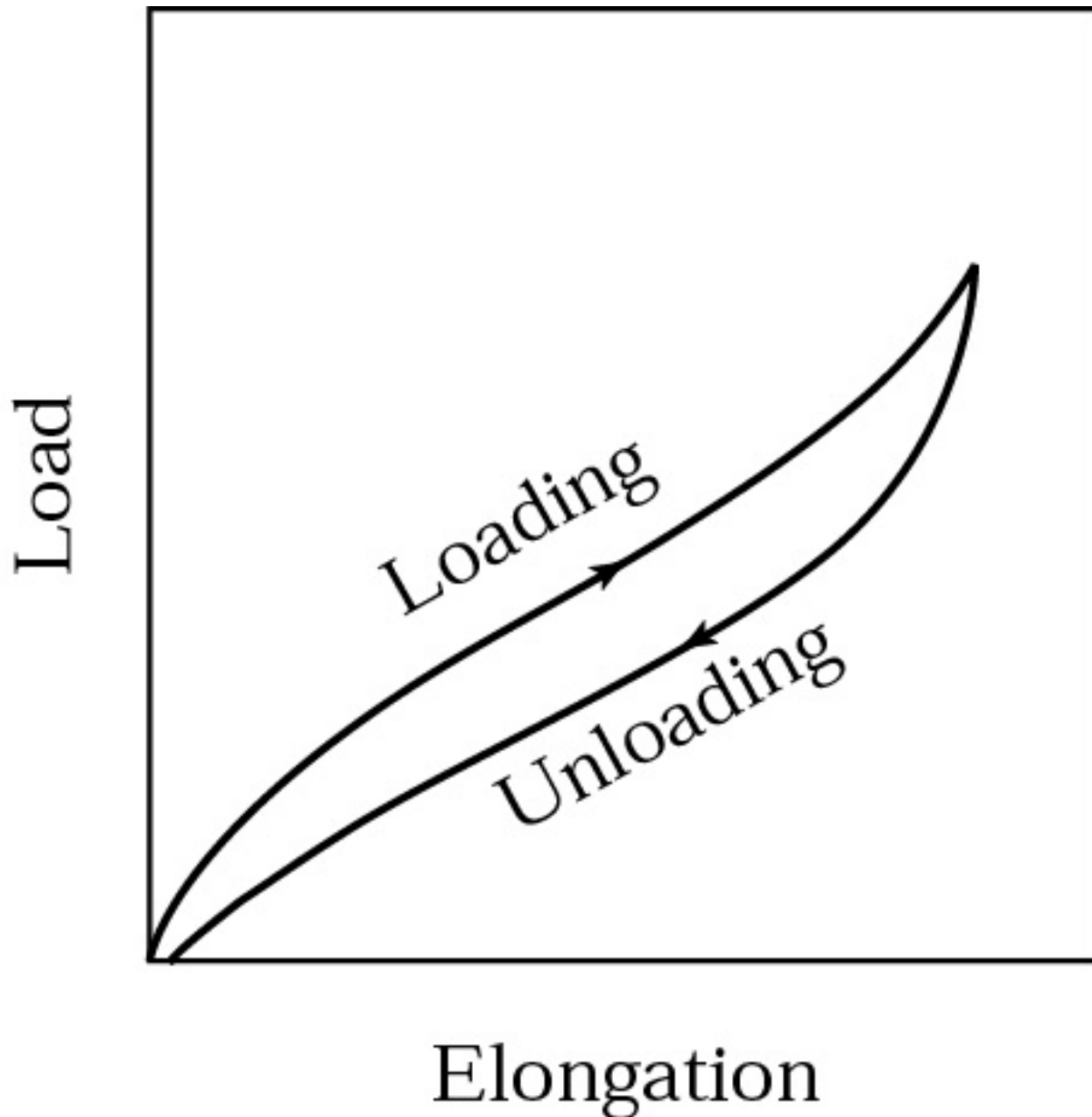
(b)



(a) Load-elongation curve for polycarbonate, a thermoplastic.

(b) High-density polyethylene tensile-test specimen, showing uniform elongation.

Load-Elongation Curve for Rubber



Typical load-elongation curve for rubbers. The clockwise loop, indicating the loading and the unloading paths, displays the hysteresis loss. Hysteresis gives rubbers the capacity to dissipate energy, damp vibration, and absorb shock loading, as is necessary in automobile tires and in vibration dampers placed under machinery.