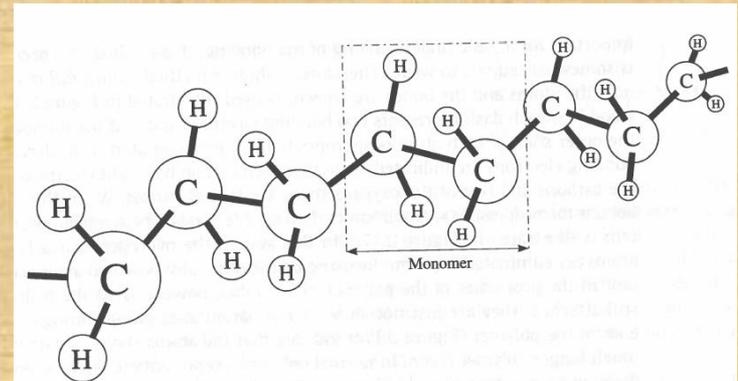


Structure and Properties of Engineering Polymers

Lecture: **Microstructures in Polymers**

Nikolai V. Priezjev



Textbook: *Plastics: Materials and Processing* (Third Edition), by A. Brent Young (Pearson, NJ, 2006).

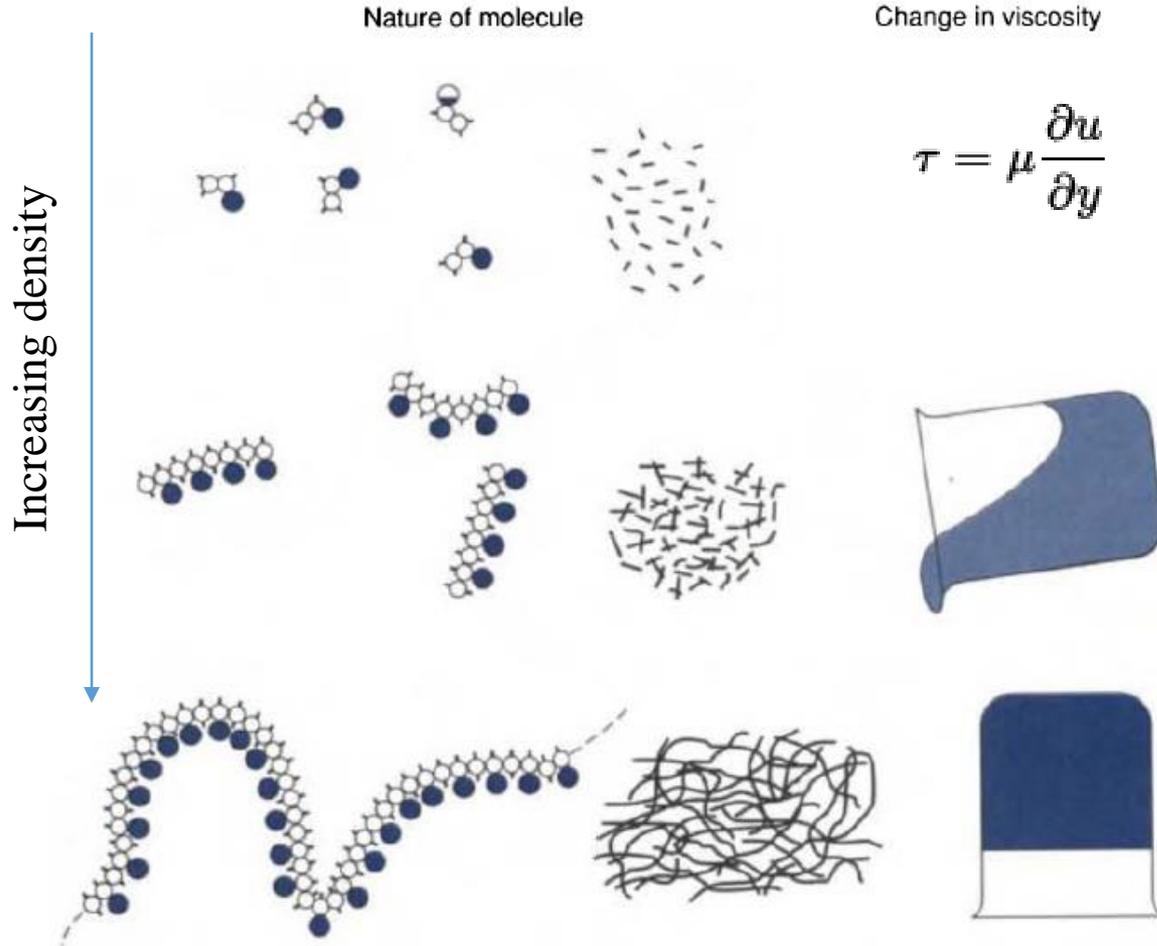
Microstructures in Polymers

- Gas, liquid, and solid phases, crystalline vs. amorphous structure, viscosity
- Thermal expansion and heat distortion temperature
- Glass transition temperature, melting temperature, crystallization
- Polymer degradation, aging phenomena
- Molecular weight distribution, polydispersity index, degree of polymerization
- Effects of molecular weight, dispersity, branching on mechanical properties
- Melt index, shape (steric) effects

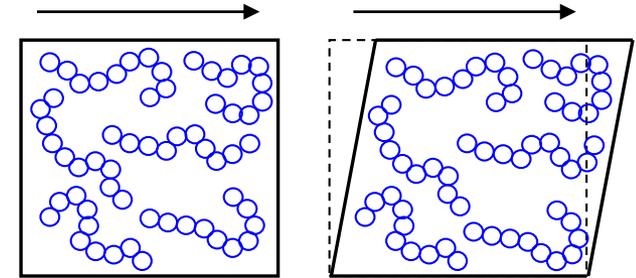
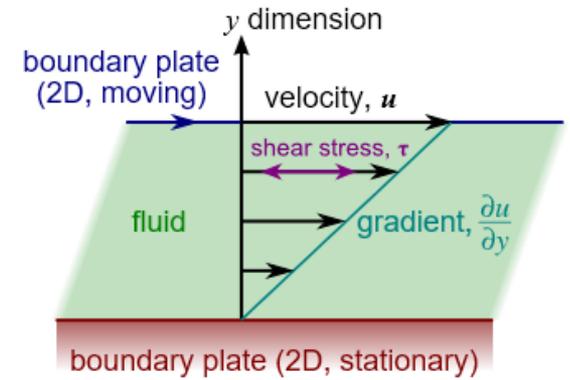
Reading: Chapter 3 of *Plastics: Materials and Processing* by A. Brent Strong

Gas, Liquid and Solid Phases

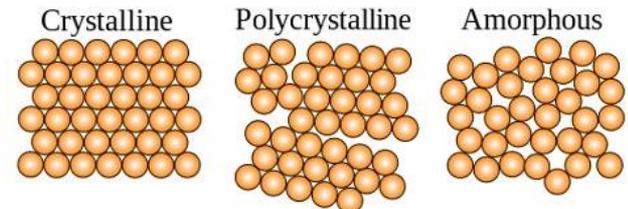
At room temperature



$$\tau = \mu \frac{\partial u}{\partial y}$$



Solid or liquid?



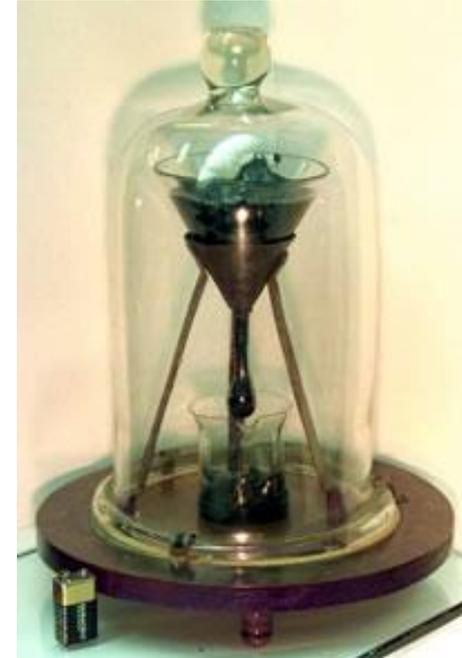
Stages in the polymerization of a vinyl polymer and the relative changes in viscosity they produce. From R. A. Higgins, *The Properties of Engineering Materials*, R. E. Krieger, Huntington, NY (1977).

Pitch Drop Experiment

Pitch (derivative of tar) at room T feels like solid and can be shattered by a hammer. But, the longest experiment shows that it flows!

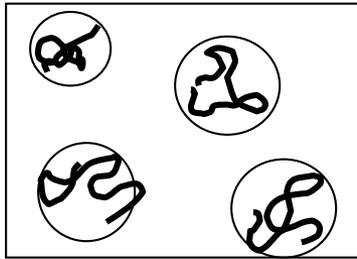
In 1927, Professor Parnell at UQ heated a sample of pitch and poured it into a glass funnel with a sealed stem. Three years were allowed for the pitch to settle, and in 1930 the sealed stem was cut. From that date on the pitch has slowly dripped out of the funnel, with **seven drops falling between 1930 and 1988**, at an average of one drop every eight years. However, the eight drop in 2000 and the ninth drop in 2014 both took about 13 years to fall. **It turns out to be about 100 billion times more viscous than water!**

Pitch, before and after being hit with a hammer.

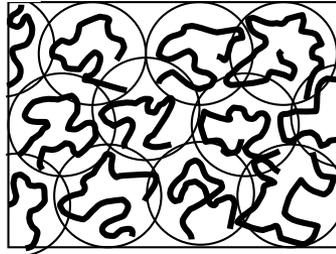


Liquid phases: polymer melt vs. polymer solution

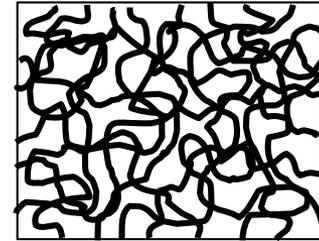
Dilute solution:



Semi-dilute solution:



Polymer melt:



Chains in solvent do not overlap:
-- Can consider that each polymer chain acts in isolation.

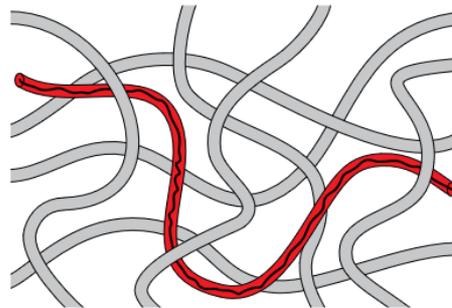
In semi-dilute solutions concentration of polymer chains is sufficient for chains to just overlap.

No solvent/only polymer chains

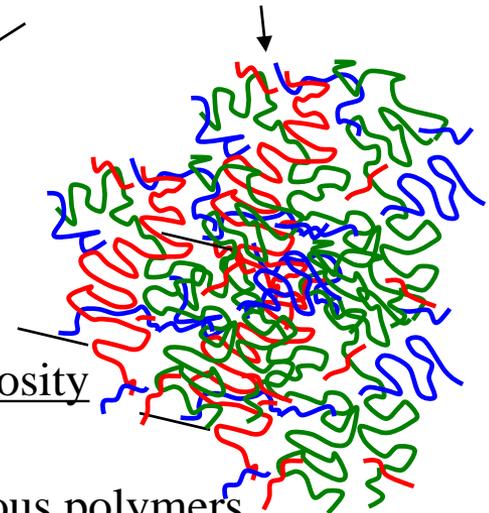
Entangled/unentangled

T up, viscosity down

High viscosity

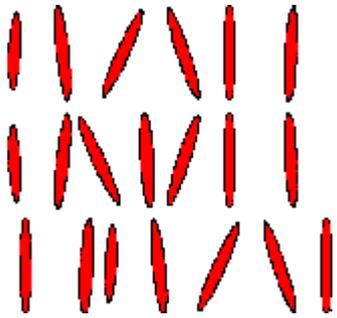


Low viscosity



Reptation—motion of long linear, entangled macromolecules amorphous polymers.

Liquid Crystal Phases

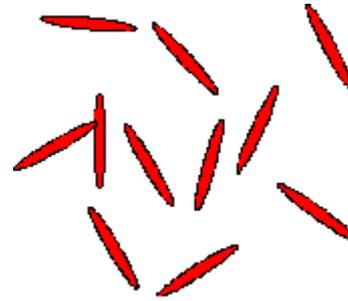


Smectic A

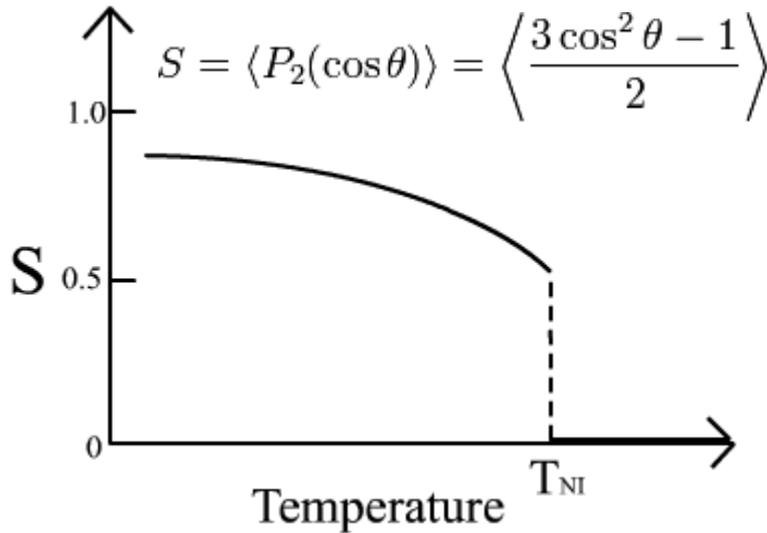
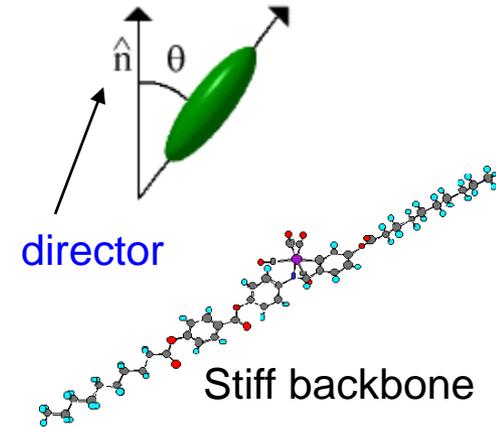


Nematic phase

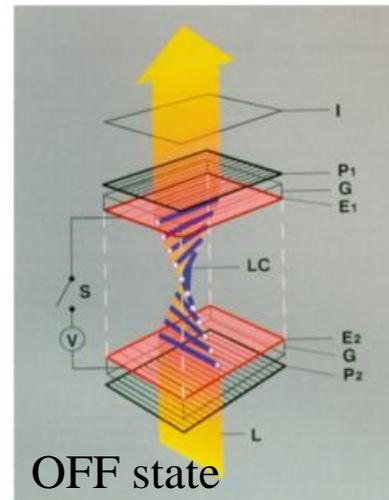
No positional but orientational order!



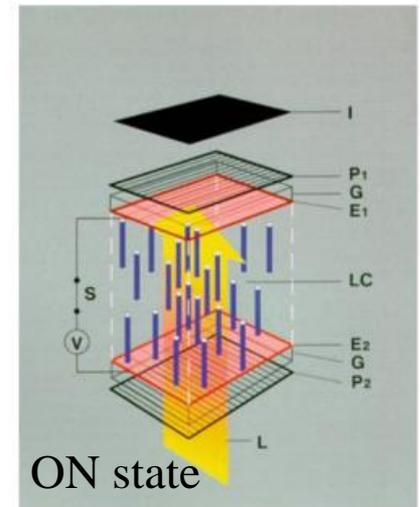
Isotropic phase



Liquid crystal displays:



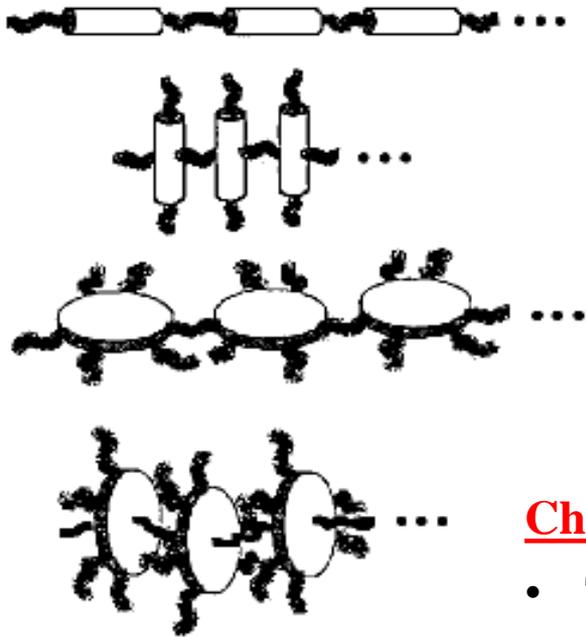
OFF state



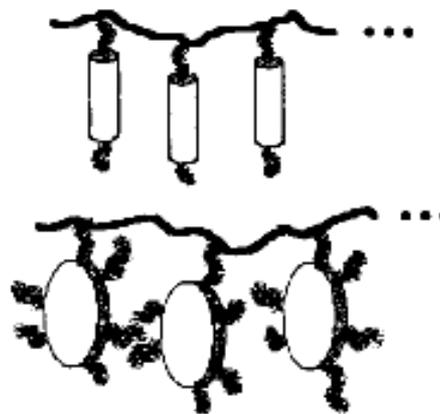
ON state

Liquid Crystal Polymers

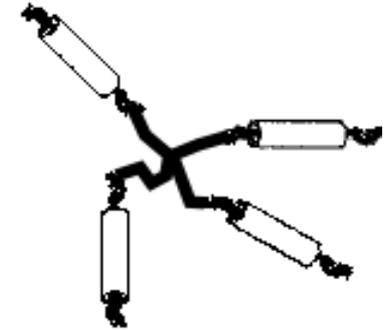
main chain



side chain



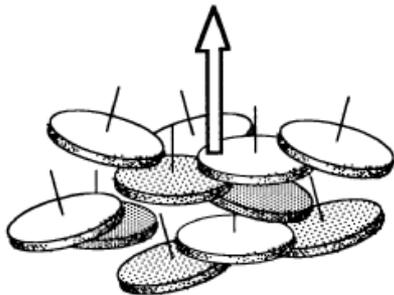
dendritic



Characteristics:

- These are a class of aromatic polymer.
- Extremely unreactive and inert.
- Highly resistant to fire.

Kevlar, the most widely used body armor is made up of intertwined liquid crystal polymers.



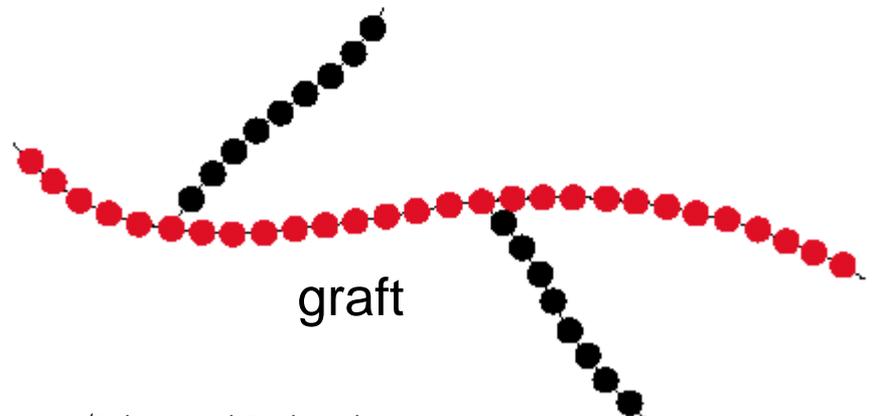
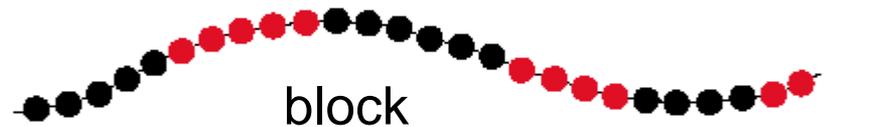
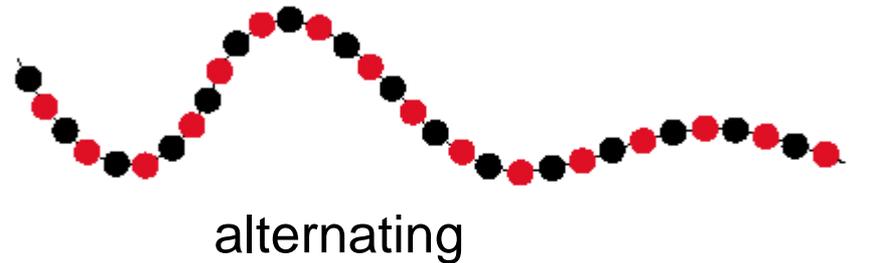
Discotic nematic liquid crystals



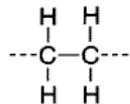
Copolymers

two or more monomer polymerized together

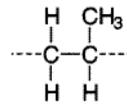
- **random** – A and B randomly vary in chain
- **alternating** – A and B alternate in polymer chain
- **block** – large blocks of A alternate with large blocks of B
- **graft** – chains of B grafted on to A backbone



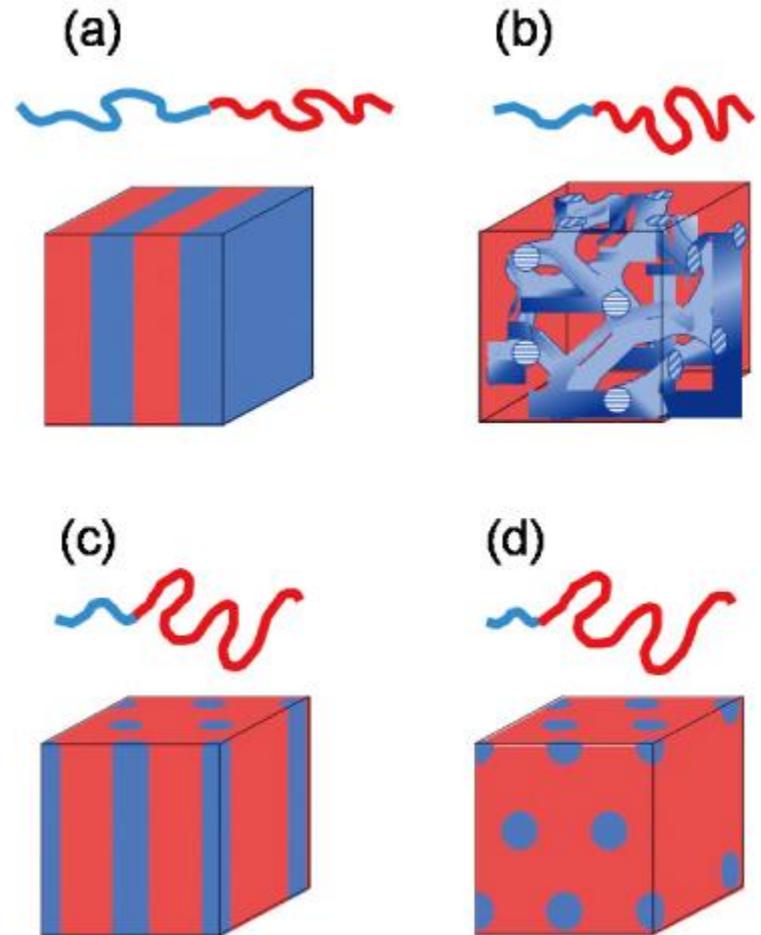
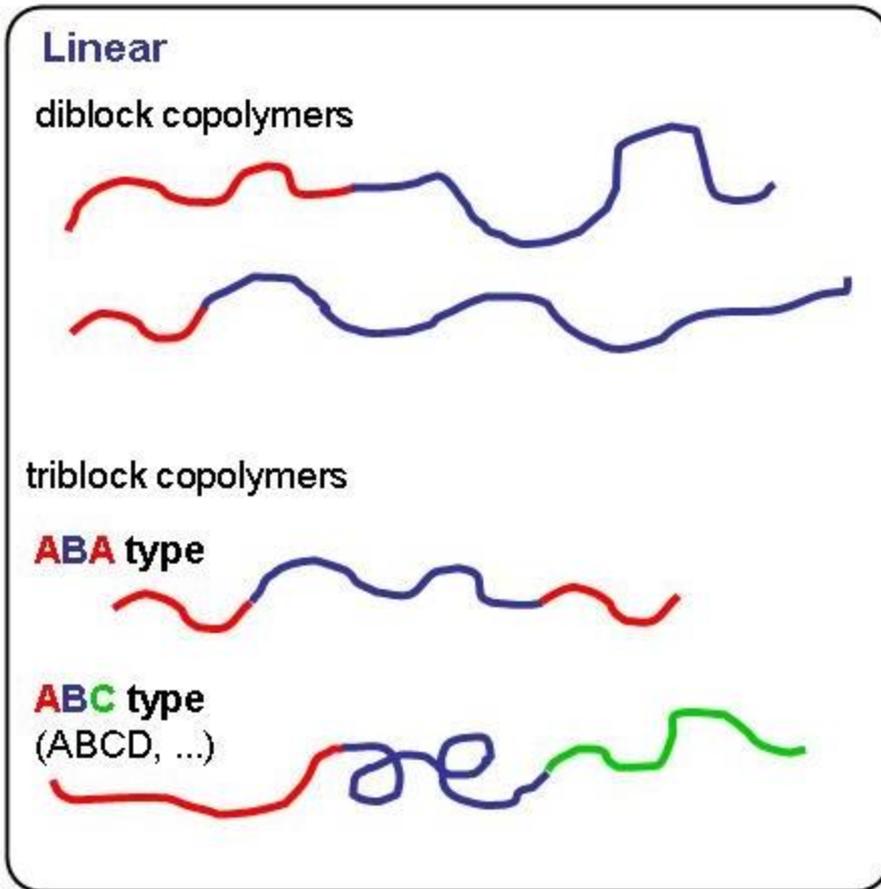
A –



B –

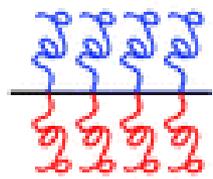
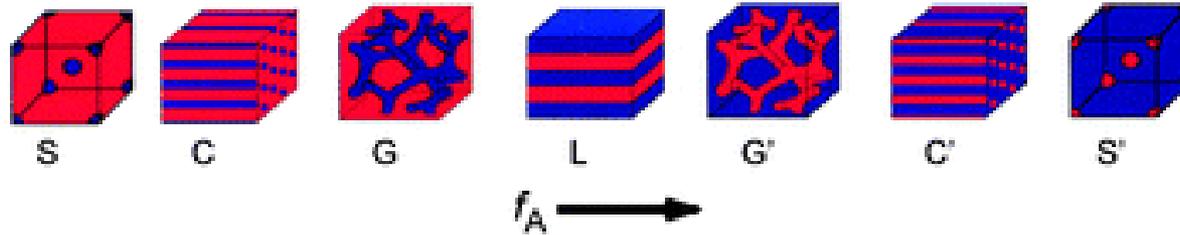


Block Copolymer Microstructures



a Lamella structure. **b** Double gyroid (bicontinuous) structure. **c** Cylindrical dispersion structure. **d** Spherical dispersion structure.

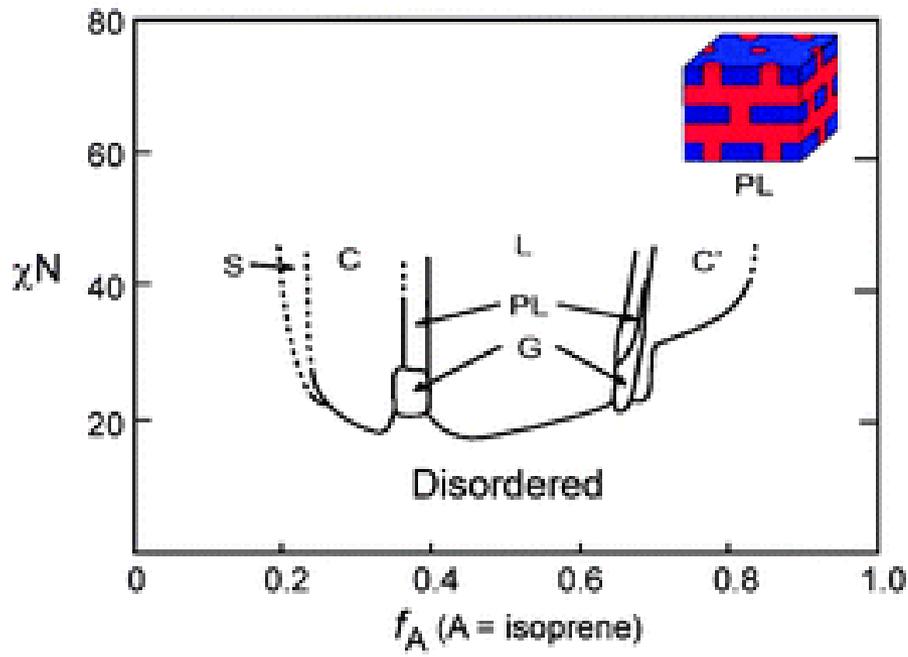
(Di) Block Copolymer Microstructures



lamellar



cylinder
gyroid
sphere

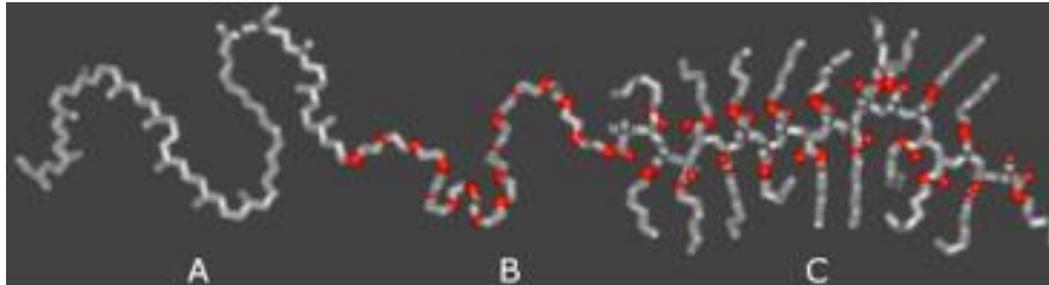


x , the relative volume fractions of the dissimilar segments

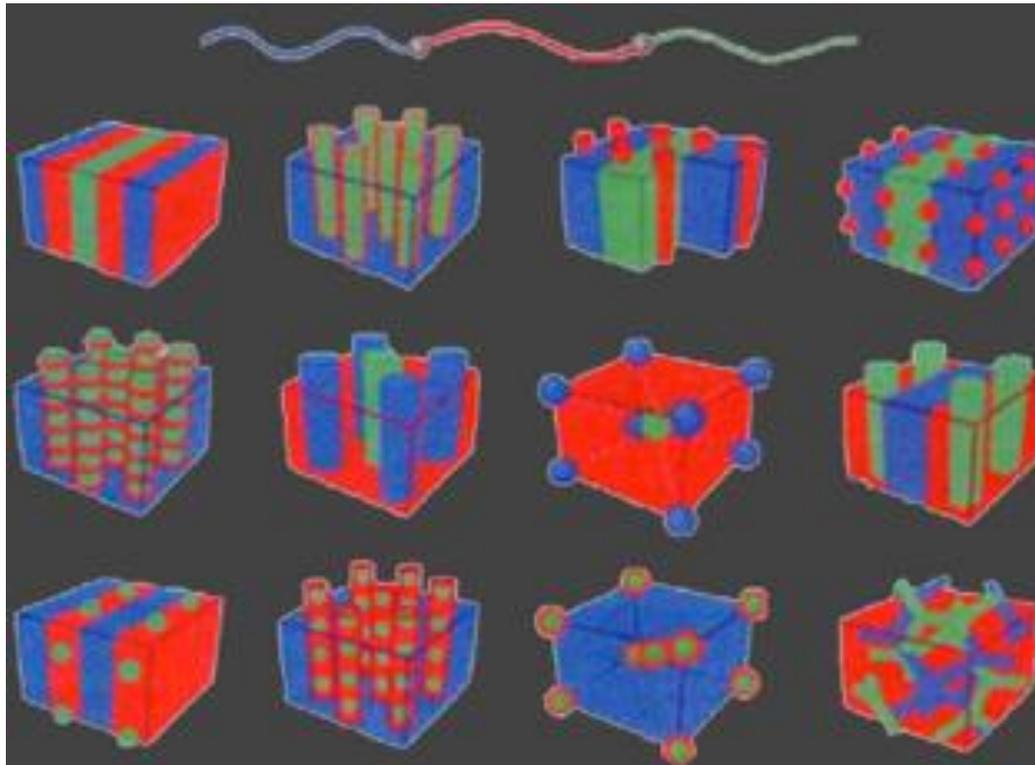
N , molecular weight

Block copolymer microstructures and the phase diagram for the polystyrene-polyisoprene diblock copolymer system. The metastable perforated lamellar microstructure is illustrated in the upper right corner of the phase diagram.

Triblock Terpolymers Microstructures



Tri-block terpolymers may be thought of simply as a diblock copolymer (AB) upon which a third block (C) is grown.



Polymer Crystallinity

Crystallization in linear polymers: achieving a very regular arrangement of the *mers*

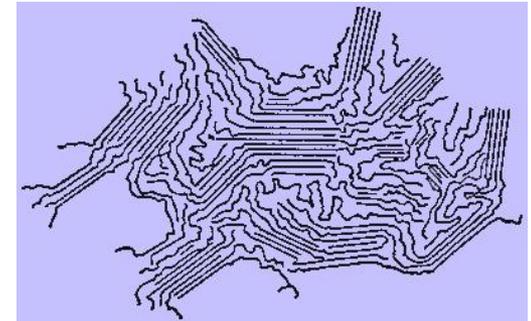
Induction of crystallinity

- cooling of molten polymer
- evaporation of polymer solution
- annealing — heating of polymer at a specific temperature
- drawing — stretching at a temperature above T_g

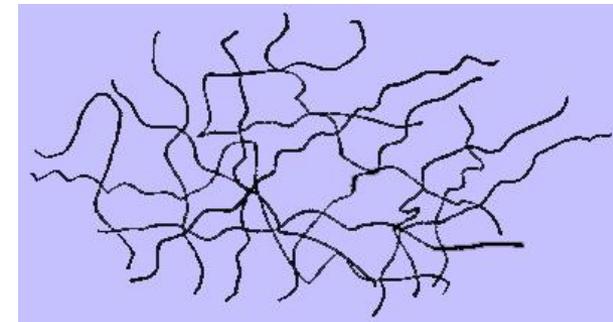
Effects of crystallinity:

- Increased Density
- Increases Stiffness (modulus)
- Reduces permeability
- Increases chemical resistance
- Reduces toughness

Semi-crystalline



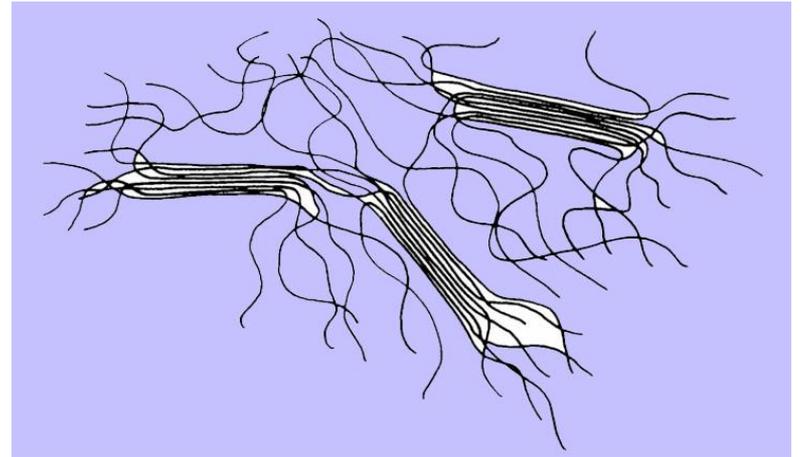
Amorphous



Polymer Crystallinity

Crystalline polymers (vs amorphous polymers)

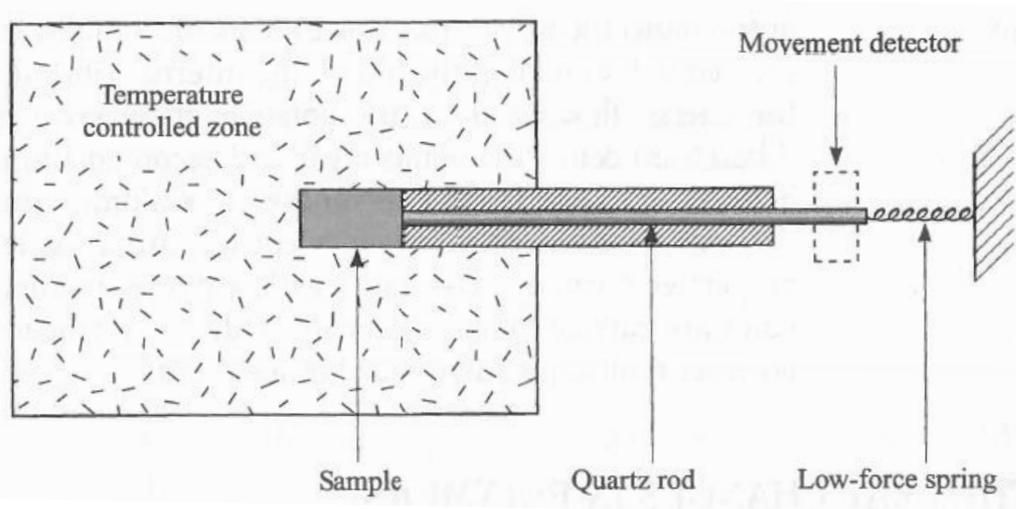
- ❑ **tougher, stiffer** (due to stronger interactions)
- ❑ **higher density, higher solvent resistance** (due to closely packing morphology)
- ❑ **more opaque** (due to light scattering by crystallites)



Crystalline morphologies

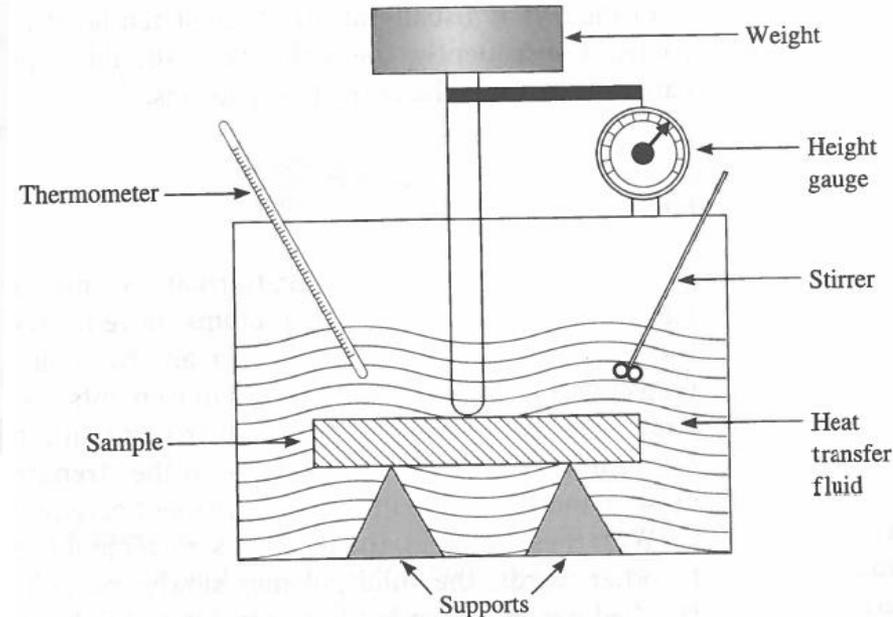
- Spherulite — aggregates of small fibrils in a radial pattern (crystallization under no stress)
- Drawn fibrillar — obtained by drawing the spherulitic fibrils
- Epitaxial — one crystallite grown on another; lamella growth on long fibrils; the so-called shish-kebab morphology (crystallization under stirring)

Thermal Expansion and Heat Distortion Temperature



Test apparatus (*dilatometer*) used for measuring the coefficient of thermal expansion ($CTE = \Delta l / l_0 / \Delta T$).

Changes in length compared to original length ($\Delta l / l_0$) called *linear expansion*.



Deflection Under Load test to determine *heat distortion temperature* (HDT). Test time: ~10,000 hours!

Table 3.1 Typical Thermal Conductivities, Heat Capacities, and Coefficients of Thermal Expansion for Plastics and Metals

| Material | Thermal Conductivity | Heat Capacity | Thermal Expansion (CTE) |
|----------|---|---|--|
| Plastic | 0.03 to 0.06 Btu/h-ft °F (0.05 to 1.0 W/m · K) | 0.4 to 0.9 Btu/lb °F (0.4 to 0.9 cal/g °C) | 9 to 12 in./in. °F × 10 ⁻⁵ (5 to 7 cm/cm °C × 10 ⁻⁵) |
| Metal | 30 to 60 Btu/h-ft °F (50 to 500 W/m · K) | 0.1 to 0.3 Btu/lb °F (0.1 to 0.3 cal/g °C) | 2 to 8 in./in. °F × 10 ⁻⁵ (1 to 4 cm/cm °C × 10 ⁻⁵) |

Aromatic content, crosslink density, crystallinity, secondary bonding can raise T at which distortion occurs.

The Glass Transition Temperature, T_g

- The glass transition, T_g , is temp. below which a polymer OR glass is brittle or glass-like; above that temperature the material is more plastic.
- The T_g to a first approximation is a measure of the strength of the secondary bonds between chains in a polymer; the stronger the secondary bonds; the higher the glass transition temperature.

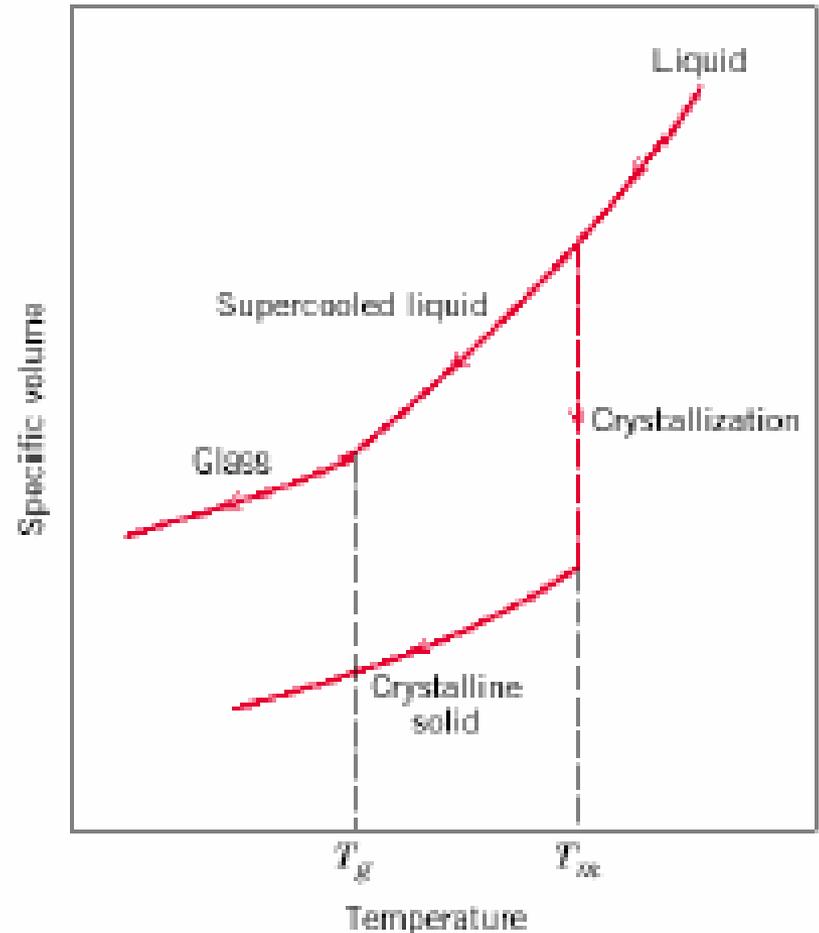
Polyethylene $T_g = 0^\circ\text{C}$;

Polystyrene = 97°C

PMMA (plexiglass) = 105°C .

Since room temp. is $< T_g$ for PMMA, it is brittle at room temp.

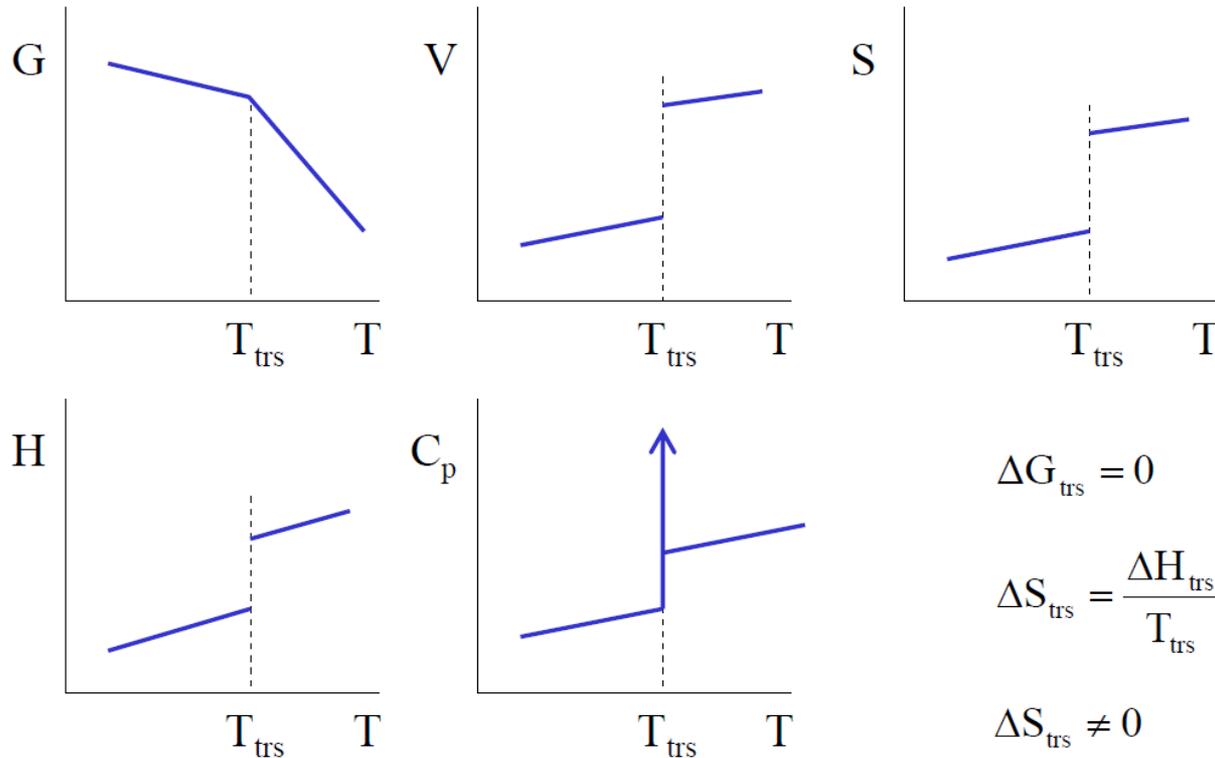
For rubber bands: $T_g = -73^\circ\text{C}$



First-order and second-order phase transitions (I)

The classification of phase transitions proposed by Ehrenfest is based on the behavior of G near the phase transformation.

First-order phase transition



$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{- discontinuous}$$

e.g. melting, boiling, sublimation, some polymorphous phase transitions.

$$G = H - TS$$

First-order phase transition: first derivatives of G are discontinuous.

$$\Delta G_{\text{trs}} = 0$$

$$\Delta S_{\text{trs}} = \frac{\Delta H_{\text{trs}}}{T_{\text{trs}}}$$

$$\Delta S_{\text{trs}} \neq 0$$

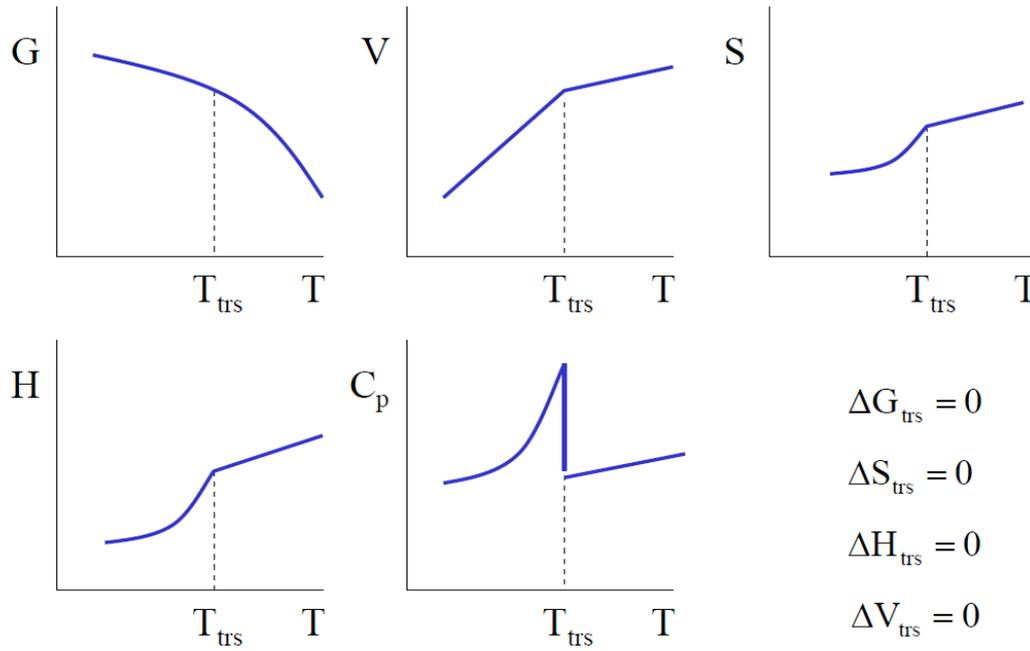
$$\Delta H_{\text{trs}} \neq 0$$

$$C_p = \left(\frac{dH}{dT}\right)_P$$

Second-order phase transition: first derivatives of G are continuous, but second derivatives of G are discontinuous.

First-order and second-order phase transitions (II)

Second-order phase transition



$$G = H - TS$$

First-order phase transition: first derivatives of G are discontinuous.

Second-order phase transition: first derivatives of G are continuous, but second derivatives of G are discontinuous.

$$\Delta G_{\text{trs}} = 0$$

$$\Delta S_{\text{trs}} = 0$$

$$\Delta H_{\text{trs}} = 0$$

$$\Delta V_{\text{trs}} = 0$$

$$C_p = \left(\frac{dH}{dT} \right)_p$$

$$\left(\frac{\partial G}{\partial T} \right)_p = -S \quad \left(\frac{\partial G}{\partial P} \right)_T = V$$

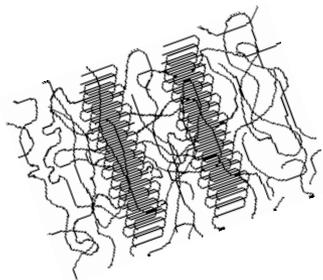
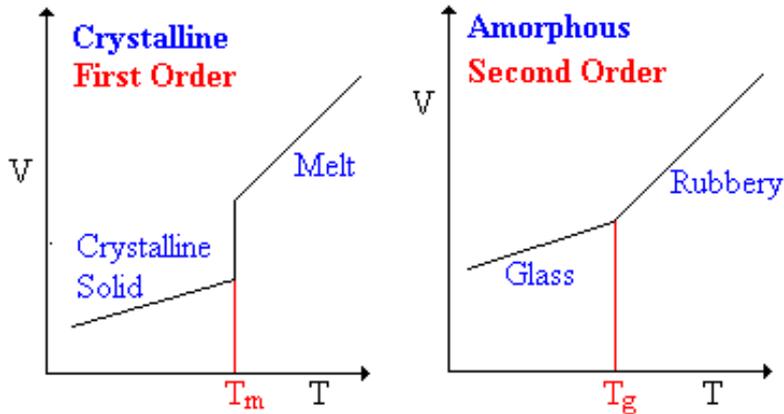
- continuous (S and V do not jump at transition)

$$\left(\frac{\partial^2 G}{\partial T \partial P} \right) = \left(\frac{\partial V}{\partial T} \right)_p \quad \left(\frac{\partial^2 G}{\partial P \partial T} \right) = - \left(\frac{\partial S}{\partial P} \right)_T \quad \text{- discontinuous}$$

e.g. conducting-superconducting transition in metals at low temperatures.

The Glass Transition Temperature, T_g

Glass transition temperature of a polymer is the temperature at which there is enough thermal energy for the polymer chains to move freely (wiggle around).

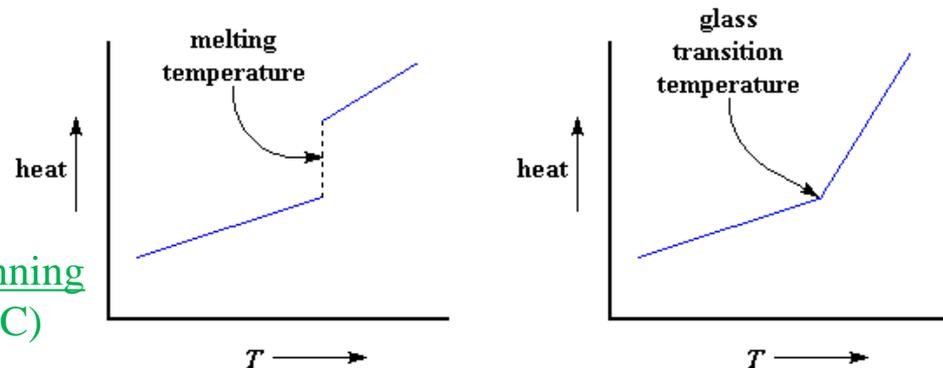


Thermomechanical analysis (TMA) = volume expansion

Differential scanning calorimetry (DSC) method

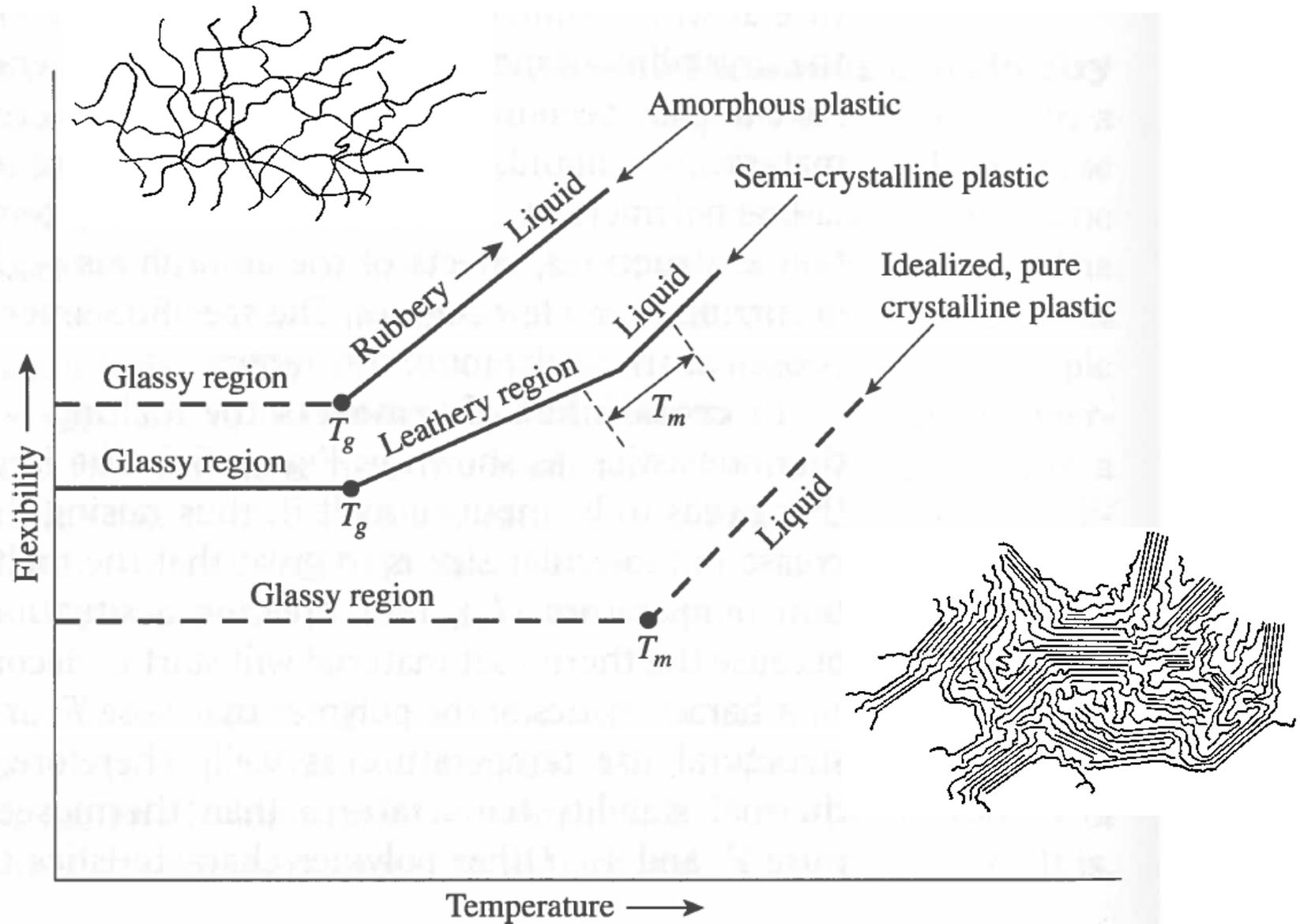
Dynamic Mechanical Analysis (DMA): response to oscillatory shear

| Amorphous Thermoplastic | Semi-crystalline Thermoplastic | Thermoset |
|-------------------------|--------------------------------|------------------------|
| Decomposition T_d | Decomposition T_d | Decomposition T_d |
| Liquid | Liquid | Softening |
| Gummy | T_m | Semirigid |
| Rubbery | Flexible | T_g |
| Leathery | T_g | HDT |
| Pliable | | Creep |
| T_g | | |
| HDT | HDT | |
| Creep | Creep | |
| Volume increases | Volume increases | |
| Stiff | Stiff | Stiff |
| Hard | Hard | Hard |
| Glass-like | Glass-like | Glass-like |



A heat vs. temperature plot for an crystalline polymer, on the left; and a amorphous polymer on the right.

Glass Transition and Melting Point for Thermoplastics



Glass Transition and Melting

- **Amorphous polymers change between a brittle or rigid glassy state – at lower T – and a rubbery state. This transition occurs at a polymer's **glass transition temperature** (T_g). Important in elastomers.**
- **Crystalline polymers change between a crystalline state – at lower T – and a viscous fluid state. This transition occurs at a polymer's **melting temperature** (T_m). Important in thermoplastics.**
- **Polymers with both amorphous *and* crystalline regions exhibit both transitions:**
 - **Amorphous regions region undergo glass transition *only*.**
 - **Crystalline regions undergo melting *only*.**

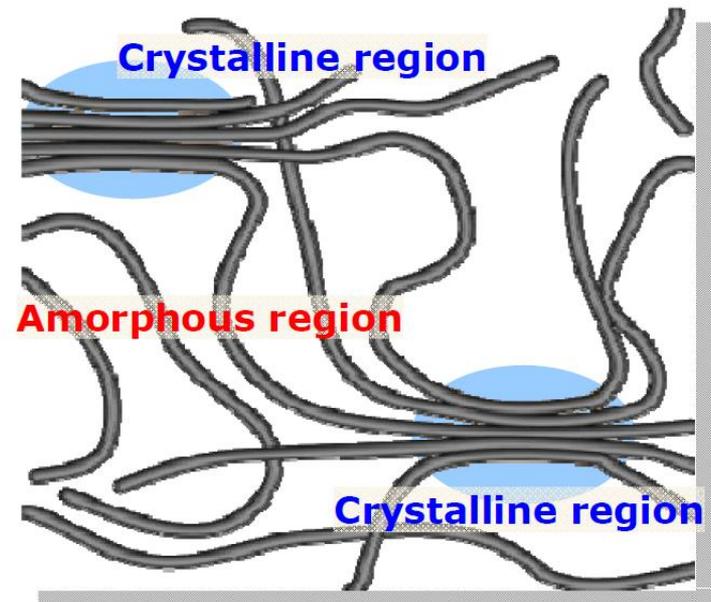
Thermal Properties of Selected Plastics

| Polymer | T_g | T_m | Processing Temp |
|---------------------------------------|-----------------------------------|----------------------------------|----------------------------------|
| Polyethylene—low density (LDPE) | −130° to −13°F (−90° to −25°C) | 208° to 240°F (98° to 115°C) | 300° to 450°F (149° to 232°C) |
| Polyethylene—high density (HDPE) | −160°F (−110°C) | 266° to 280°F (130° to 137°C) | 350° to 500°F (177° to 260°C) |
| Polypropylene (PP) | −103° to −94°F (−25° to −20°C) | 320° to 356°F (160° to 180°C) | 374° to 550°F (190° to 288°C) |
| Acrylonitrile butadiene styrene (ABS) | 212°F (100°C) | 230° to 257°F (110° to 125°C) | 350° to 500°F (177° to 260°C) |
| Nylon (6,6) | 120°F (49°C) | 470° to 500°F (243° to 260°C) | 500° to 620°F (260° to 327°C) |
| Polyethylene terephthalate (PET) | 150° to 175°F (66° to 80°C) | 413° to 509°F (212° to 265°C) | 440° to 660°F (227° to 349°C) |
| Polycarbonate (PC) | 300°F (149°C) | 284° to 300°F (140° to 149°C) | 520° to 572°F (271° to 300°C) |
| Polyphenylene oxide (PPO) | 375° to 428°F (190° to 220°C) | 500° to 900°F (260° to 482°C) | 400° to 670°F (204° to 354°C) |

Melting temperature, T_m : Influence of Structure

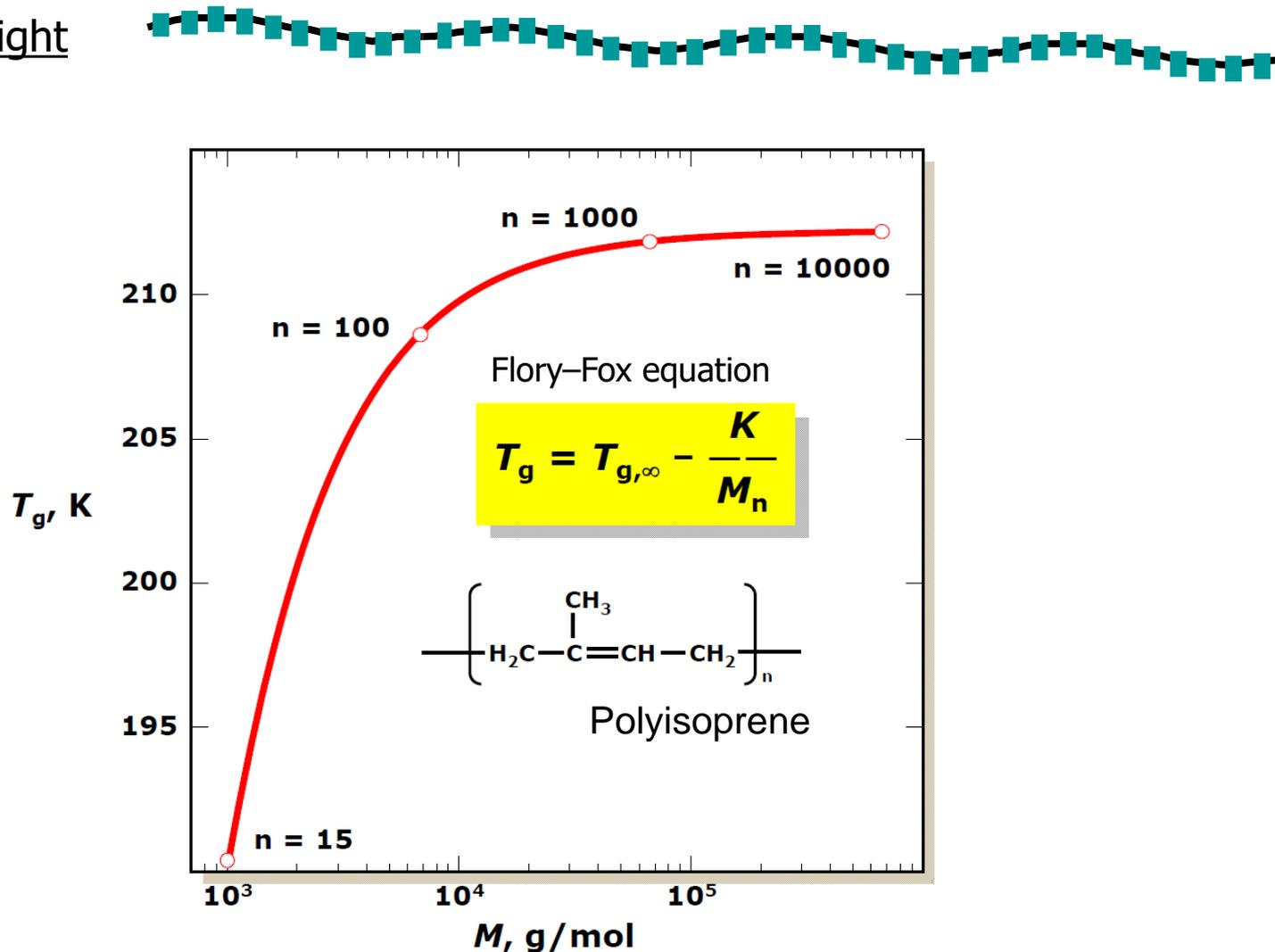
| | Polyethylene Crystallinity, % | | |
|----------------------------|----------------------------------|------|------|
| | 55 | 70 | 85 |
| T_m , °C | 109 | 125 | 133 |
| Density, g/cm ³ | 0.92 | 0.94 | 0.96 |
| Yield stress, MPa | 12 | 23 | 35 |

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



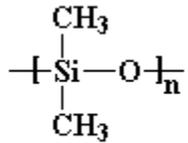
Factors that affect the glass transition temperature, T_g

Molecular Weight



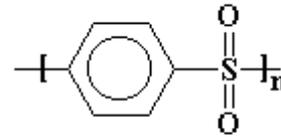
Factors that affect the glass transition temperature, T_g

Backbone Flexibility



polydimethylsiloxane

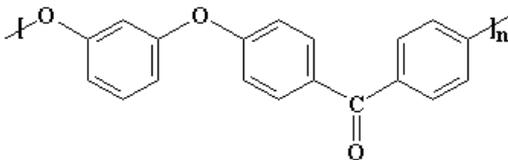
This backbone is so flexible that polydimethylsiloxane has T_g way down at -127°C !



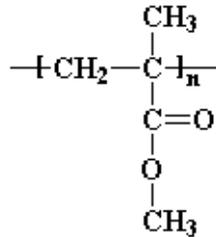
poly(phenylene sulfone)

The backbone is very stiff. It's so rigid that it doesn't have a T_g ! You can heat it to over 500°C and it will still stay in the glassy state. It will decompose from all the heat before it lets itself undergo a glass transition!

Pendant Groups

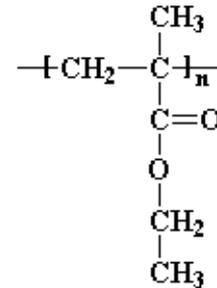


This poly(ether ketone) has a T_g of 119°C



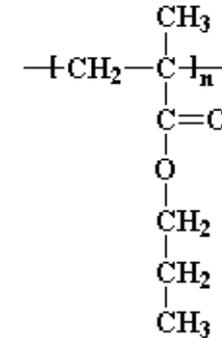
Poly(methyl methacrylate)

$T_g = 100\text{--}120^\circ\text{C}$



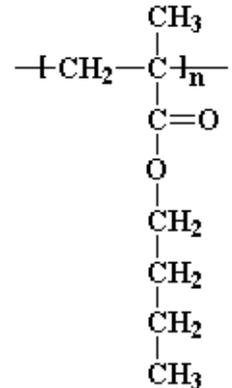
Poly(ethyl methacrylate)

$T_g = 65^\circ\text{C}$



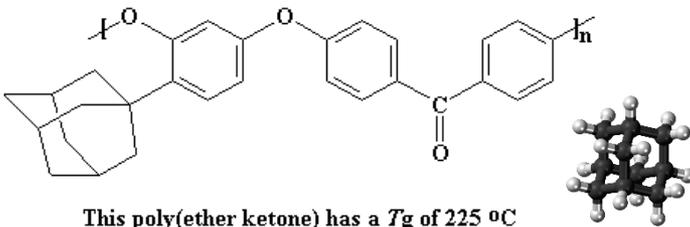
Poly(propyl methacrylate)

$T_g = 35^\circ\text{C}$



Poly(butyl methacrylate)

$T_g = 20^\circ\text{C}$



This poly(ether ketone) has a T_g of 225°C



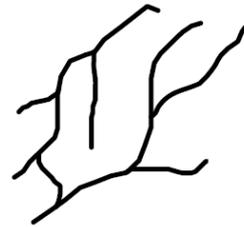
$\text{C}_{10}\text{H}_{16}$

Adamantine act like a hook that catches on nearby molecules and keeps the polymer from moving.

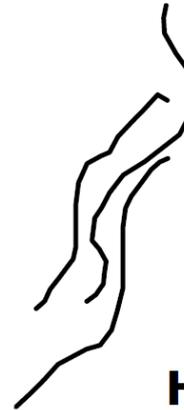
But big bulky pendant groups can lower the T_g , too. Pendant groups limit how closely the polymer chains can pack together. The further they are from each other, the more easily they can move around. This lowers the T_g , in the same way a plasticizer does.

Factors that affect the glass transition temperature, T_g

Linearity

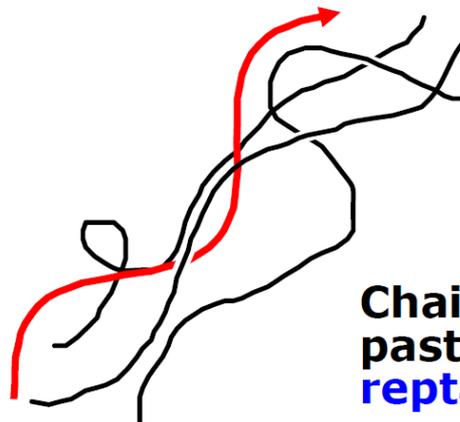


LDPE
branched
lower density



HDPE
linear
higher density

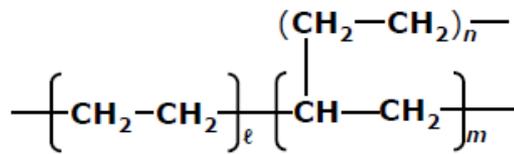
Entanglements



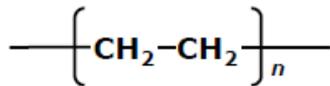
Chains must slide
past each other by
reptation

Factors that affect the glass transition temperature, T_g

| Polymer | T_g , °C | T_m , °C | Tensile Str., MPa |
|---------------------------|------------|------------|-------------------|
| Low-density Polyethylene | -125 | 105-120 | 12 |
| High-density Polyethylene | -78 | 130-135 | 26-33 |
| Nylon-6,6 | 50 | 255-265 | 45-75 |



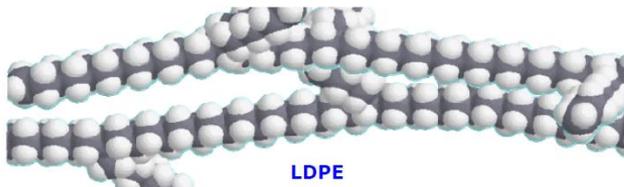
LDPE



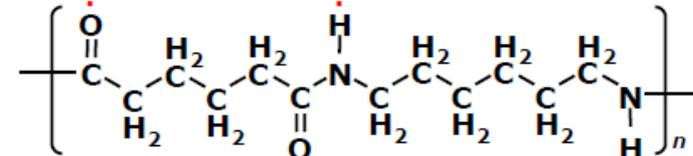
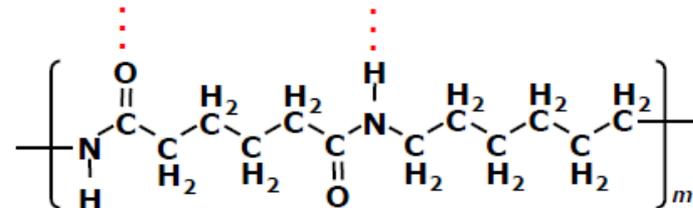
HDPE



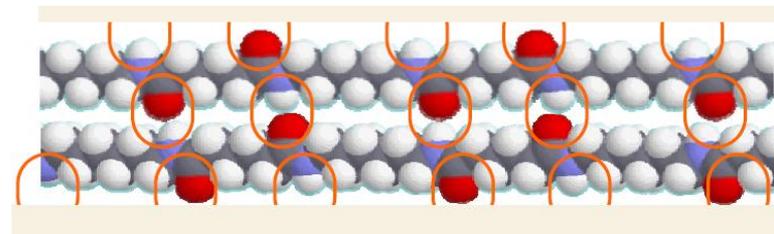
HDPE



LDPE



Nylon-6,6



Nylon-6,6

Phase Transitions and Structure

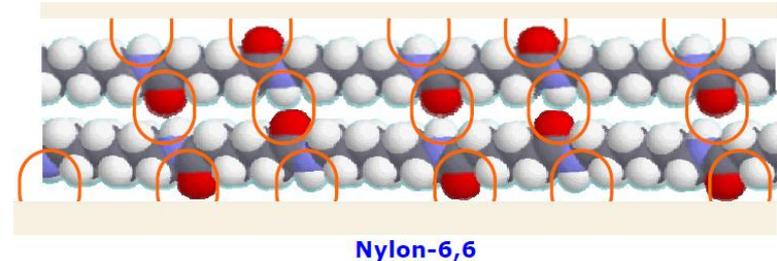
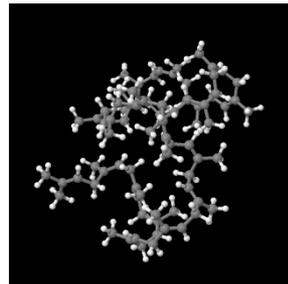
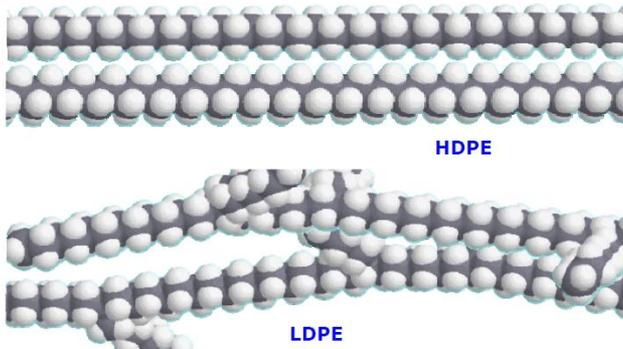
T_m and T_g increase with

- **Increasing intermolecular forces**
- **Increasing intra- and intermolecular barriers to chain rotation**
- **Bulky, stiff backbone and side groups**
- **Shorter flexible side groups**

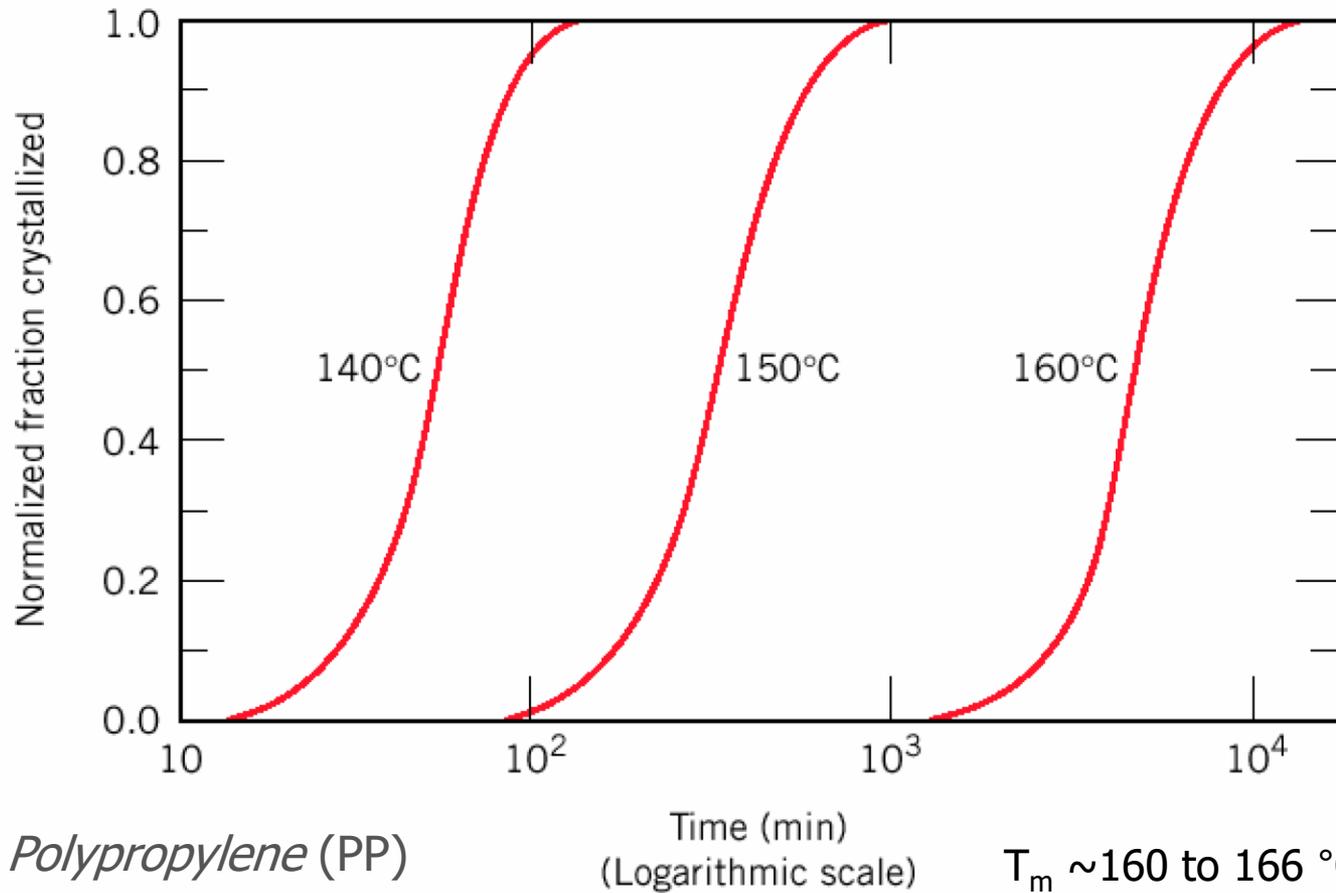
Quiz

Which of the following polymers would most likely have the *highest* T_g ?

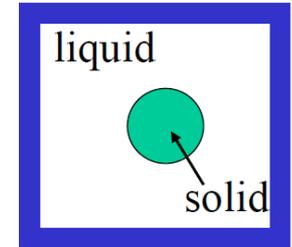
- a) A linear polyethylene with $M_w = 1,000,000$.
- b) A branched polyethylene with $M_w = 1,000,000$.
- c) A linear polyisoprene with $M_w = 1,000,000$.
- d) A linear nylon-6,6 with $M_w = 1,000,000$.



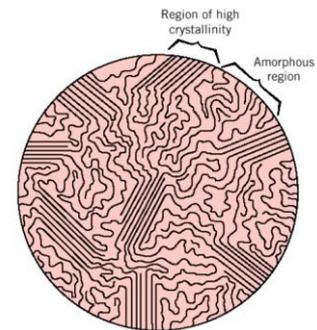
Crystallization, Melting, Glass Transition



$$\Delta G_v = \frac{\Delta H_m \Delta T}{T_m}$$

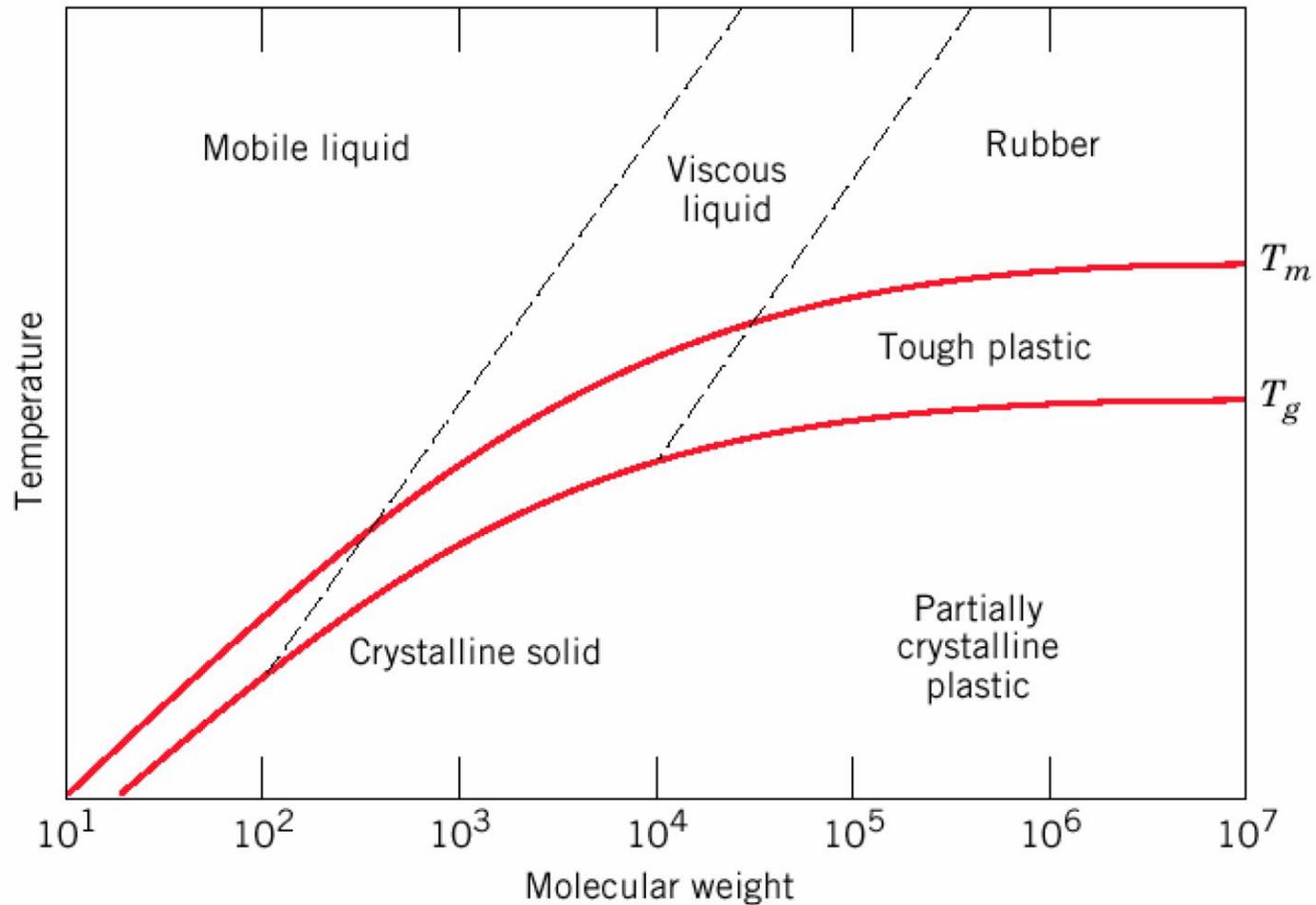


$$r^* = \left(\frac{2\gamma_{SL} T_m}{H_m} \right) \frac{1}{\Delta T}$$

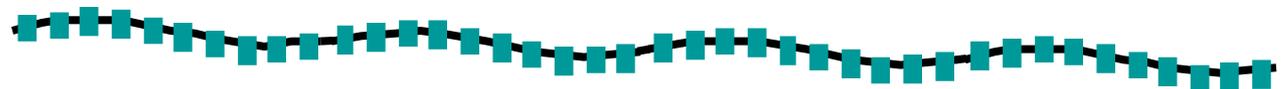


Crystallization: crystalline nuclei form and grow, chains align and order. Crystallization rates can be defined from the same type of S-curves we saw for metals - can be described by the Avrami equation: $y = 1 - \exp(-k t^n)$

Crystallization, Melting, Glass Transition



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



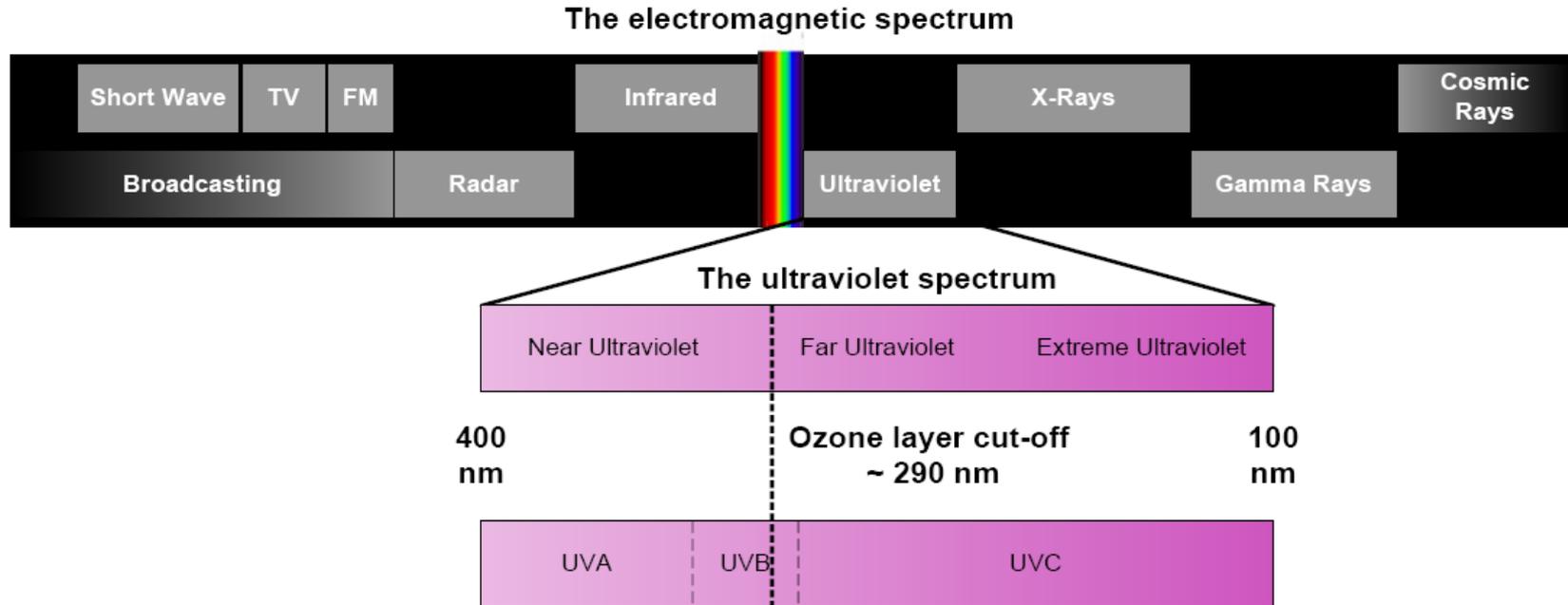
Polymer Degradation

- Polymer degradation is a change in the properties like tensile strength, color, shape, etc.
- Polymer-based product under the influence of one or more *environmental* factors such as heat, light or *chemicals* such as acids, alkalis and some salts. Main factors: solar radiation, temperature, moisture, oxygen. **These changes are usually undesirable, such as *cracking* and chemical disintegration of products.**

Solar radiation:

- **Physical changes** resulting from exposure to the environment are initiated by **chemical bond breaking reactions** caused by the **absorbed light**.
- The **ultraviolet portion** of solar energy, with the shortest wavelengths often having the **greatest effect**.
- Solar absorptivity is closely related to **color**, thus samples of different colors will reach different on-exposure temperatures.

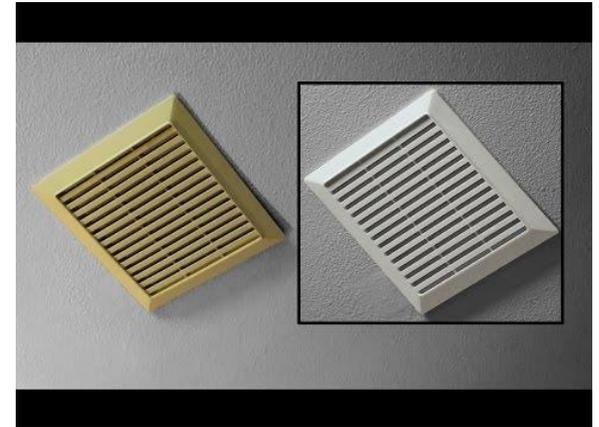
UV radiation



- The lower boundary in Earth's atmosphere solar UV spectrum is caused by ozone shielding. Ozone O₃ layer.
- UV radiation can be classified as near, far or extreme UV but it is also possible to classify UV radiation in terms of UVA, UVB and UVC

Polymer Degradation (cont.)

- **Short** wavelength UV radiation causes **yellowing**; **long** wavelength UV (penetrate deeper in the material) is primarily responsible for **degradation of physical properties**, such as tensile strength and impact strength.



Photoinduced degradation:

- Most polymers can be degraded by photolysis to give lower molecular weight molecules. Electromagnetic waves with the energy of visible light or higher, such as ultraviolet light-rays and gamma rays are usually involved in such reactions.
- Photo degradation of poly alpha – methyl styrene



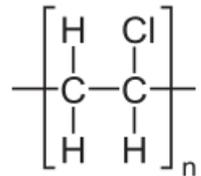
UV rays



Polymer Degradation (cont.)

Thermal degradation:

- Chain-growth polymers like poly(methyl methacrylate) PMMA can be degraded by hemolysis at high temperatures to give monomers, oils, gases and water.
- For example the PVC eliminates HCl, under 100–120 °C.
- $\text{CH}_2(\text{Cl})\text{CHCH}_2\text{CH}(\text{Cl}) \rightarrow \text{CH}=\text{CH}-\text{CH}=\text{CH} + 2\text{HCl}$ Hydrochloric acid



Biological degradation:

- Biodegradable plastics can be biologically degraded by microorganisms to give lower molecular weight molecules. To degrade properly biodegradable polymers need to be treated like compost and not just left in a landfill site where degradation is very difficult due to the lack of oxygen and moisture.
- The mechanism of biodegradation is by anaerobic processes, where oxygen is not present.



Polymer Degradation (cont.)

Moisture:

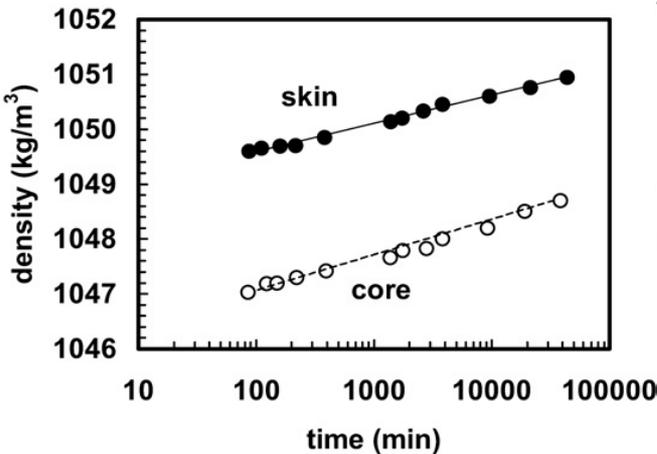
- Moisture, in combination with solar radiation, contributes significantly to the weathering of many polymeric materials
- **Mechanical stresses** imposed when **moisture is absorbed or desorbed** and to the chemical participation of moisture in the chemical evolution cause weathering
- **The span of time over which the precipitation occurs** and the **frequency of wetness** are important in the weathering of materials
- **Water absorption** in the surface layers produces a **volume expansion** which places **mechanical stress on the dry subsurface layers**.
- **Drying out of the surface layers** would lead to a **volume contraction**.
- The **hydrated inner layers resist this contraction**, leading to **surface stress cracking**.



Physical Ageing in Polymers

Polymer ageing may involve *physical ageing* without chemical reaction occurring; *chemical* changes such as crosslinking during curing of a thermoset; *thermal* conditioning at elevated temperature; *photochemical* ageing, as occurs in weathering.

Volumetric relaxation after rapid cooling



Density versus ageing time at room temperature of samples extracted, respectively, from the skin and the core of an injection moulded polystyrene bar. Ageing took place in a density column at 23 °C.

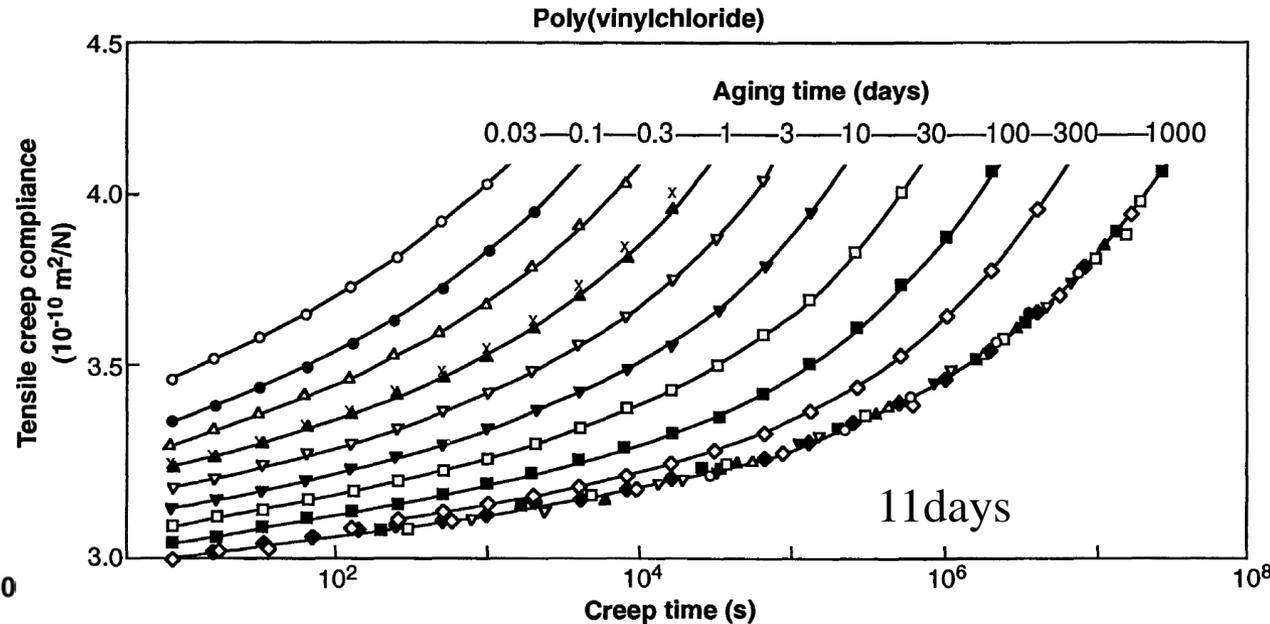


Fig. 3. Small-strain tensile creep curves of rigid PVC quenched from 90°C (i.e., about 10°C above T_g) to 40°C and further kept at 40 ± 0.1°C for a period of 4 years. The different curves were measured for various values of the time t_a elapsed after the quench. The master curve gives the result of a superposition by shifts which were almost horizontal; the shifting direction is indicated by the arrow. The crosses refer to another sample quenched in the same way, but measured for creep at a t_a of 1 day only.

L. C. E. STRUIK

Molecular Weight

- **Molecular weight, M :** Mass of a mole of chains.



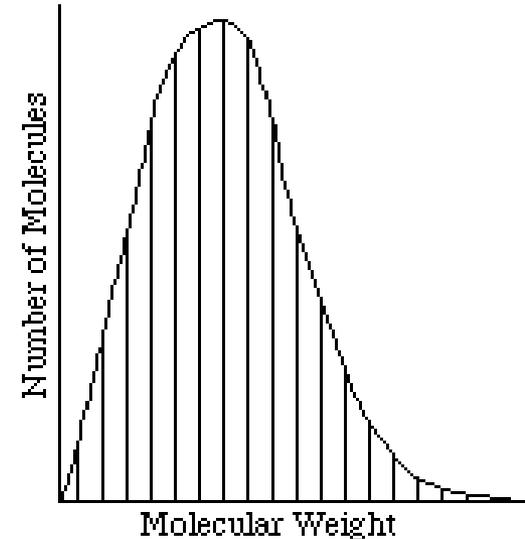
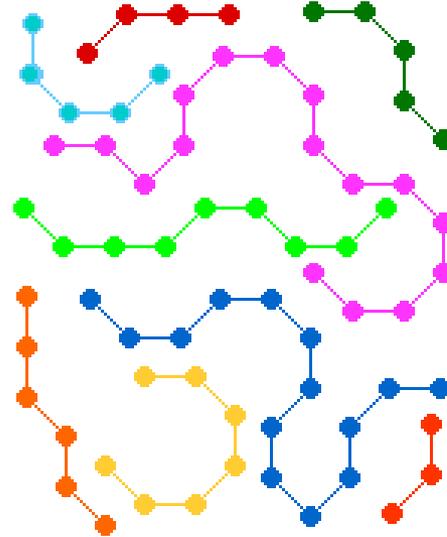
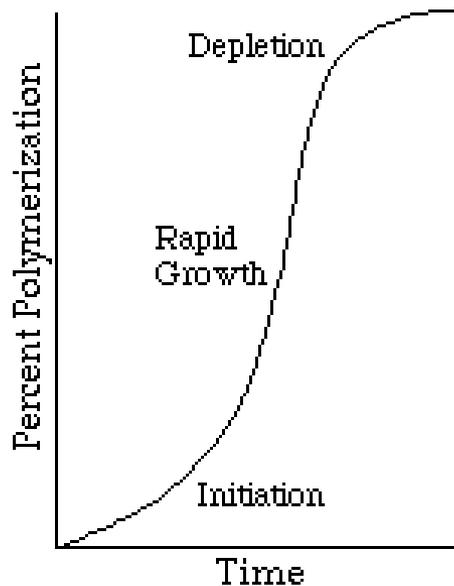
Low M



high M

Not all chains in a polymer are of the same length
— i.e., there is a distribution of molecular weights
polydispersity

Molecular Weight Distribution

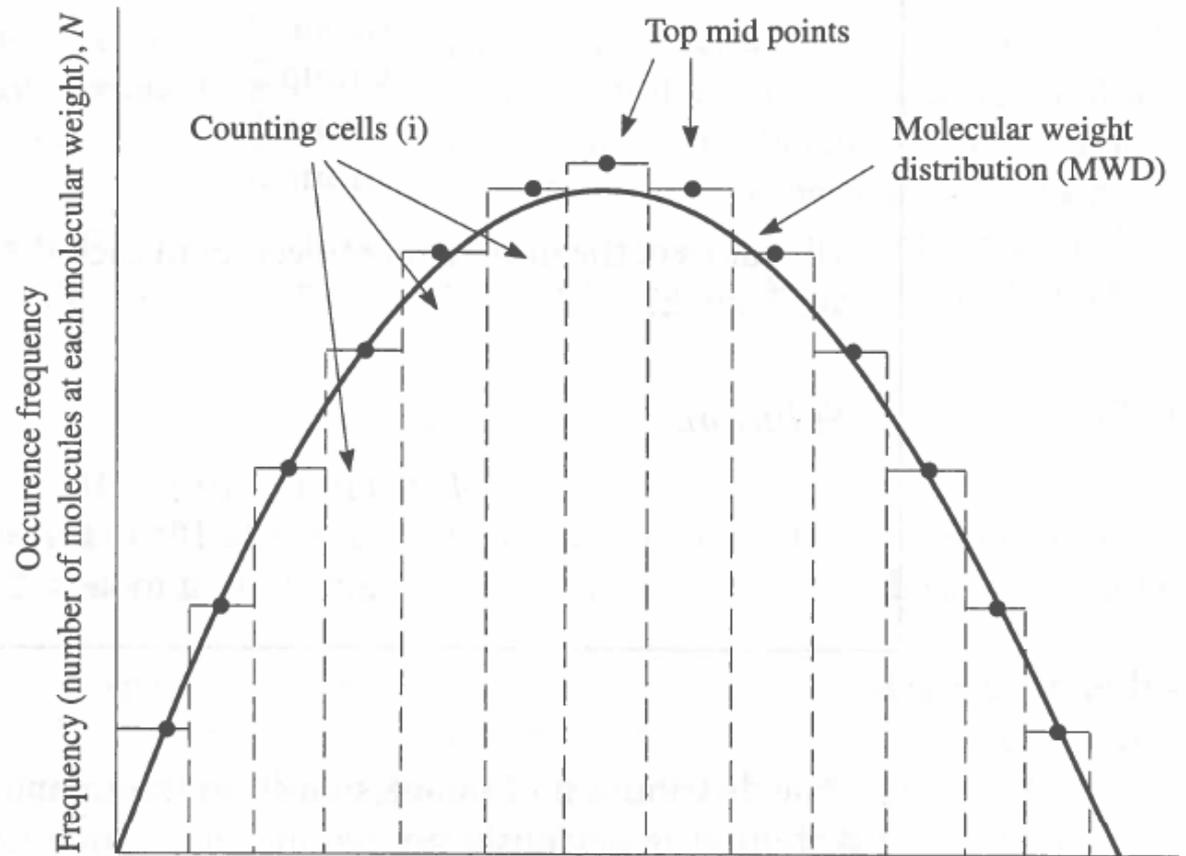
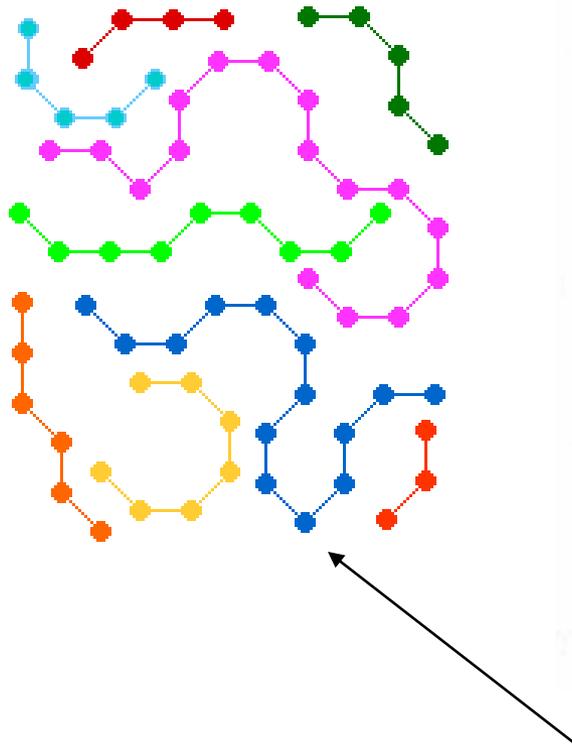


Arrhenius equation

$$rate = Ae^{-(E/RT)}$$

Most polymers are *polydisperse* — they contain more than one chain length
— i.e., there is a distribution of molecular weights

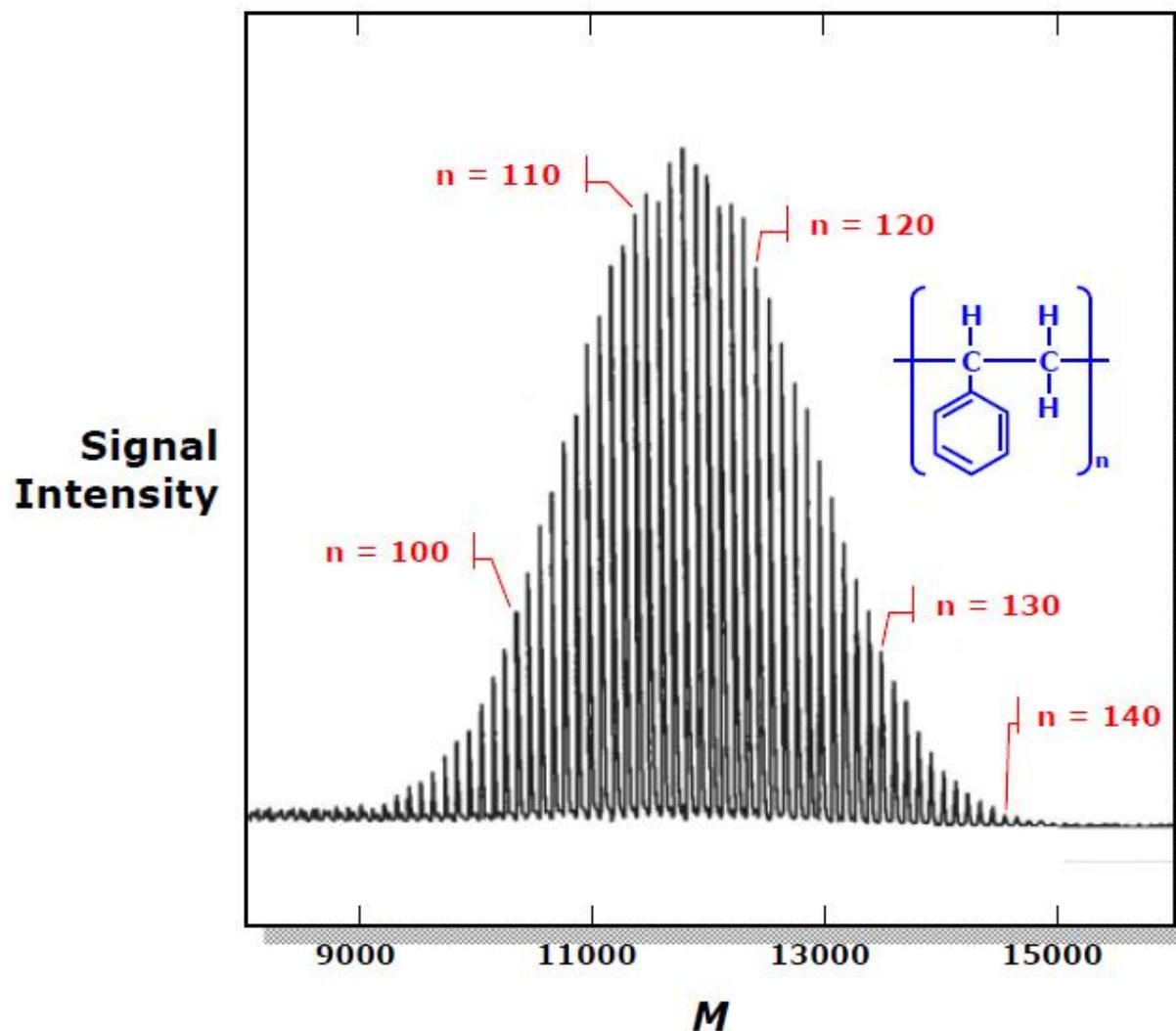
Molecular Weight Distribution



Molecular weight of ethylene $C_2H_4 = 2 \times 12 + 4 \times 1 = 28$ g/mole

Molecular weight of polyethylene $1000 \times C_2H_4 = 1000 \times 28$ g/mole = 28,000 g/mole

Mass Distribution in Low-MW Polystyrene

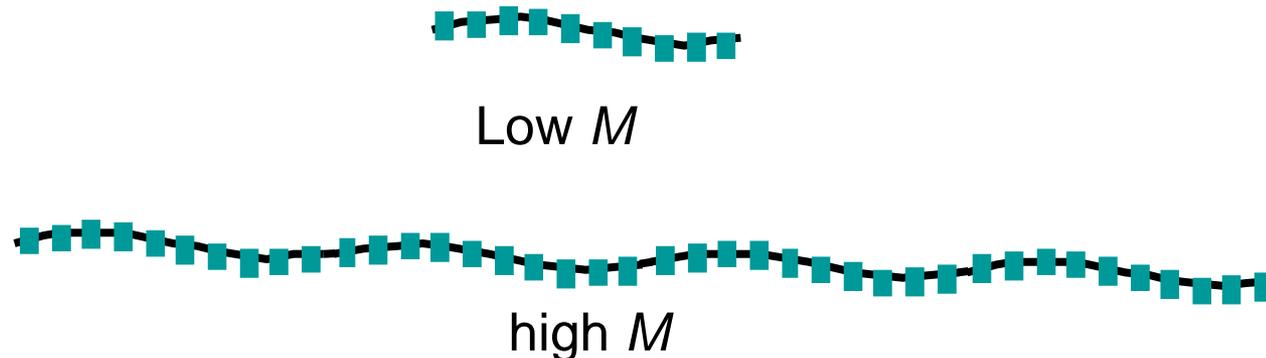


Adapted from "The Characterization of Polystyrene Oligomers by Field-desorption Mass Spectrometry", K. Rollins *et al.*, 1990 *Rapid Commun. Mass Spectrom.*, 4, 355-359

Molecular Weight Distribution

The average distribution of chain masses can be described in more than one way:

- M_n , the **number-average** molecular weight
- M_w , the **weight-average** molecular weight
- M_z , the **z-average** molecular weight
- $M_z \geq M_w > M_n$
- PDI, **polydispersity index**, is the ratio of the weight-average molecular weight to the number-average molecular weight



Molecular Weight Calculation

Example: average mass of a class

| Student | Weight mass (lb) |
|---------|---------------------|
| 1 | 104 |
| 2 | 116 |
| 3 | 140 |
| 4 | 143 |
| 5 | 180 |
| 6 | 182 |
| 7 | 191 |
| 8 | 220 |
| 9 | 225 |
| 10 | 380 |

What is the average weight of the students in this class:

- Based on the **number fraction** of students in each mass range?
- Based on the **weight fraction** of students in each mass range?

Molecular Weight Calculation (cont.)

Solution: The first step is to sort the students into weight ranges. Using 40 lb ranges gives the following table:

| weight range | number of students | mean weight |
|--------------|--------------------|-------------|
| mass (lb) | N_i | mass (lb) |
| 81-120 | 2 | 110 |
| 121-160 | 2 | 142 |
| 161-200 | 3 | 184 |
| 201-240 | 2 | 223 |
| 241-280 | 0 | - |
| 281-320 | 0 | - |
| 321-360 | 0 | - |
| 361-400 | 1 | 380 |

Calculate the number and weight fraction of students in each weight range as follows:

$$x_i = \frac{N_i}{\sum N_i} \quad w_i = \frac{N_i W_i}{\sum N_i W_i}$$

For example: for the 81-120 lb range

$$x_{81-120} = \frac{2}{10} = 0.2$$

$$w_{81-120} = \frac{2 \times 110}{1881} = 0.117$$

total number $\longrightarrow \sum N_i$
10

$\longleftarrow \sum N_i W_i$ total weight
1881

Molecular Weight Calculation (cont.)

| weight range | mean weight W_i | number fraction x_i | weight fraction w_i |
|--------------|----------------------|--------------------------|--------------------------|
| mass (lb) | mass (lb) | | |
| 81-120 | 110 | 0.2 | 0.117 |
| 121-160 | 142 | 0.2 | 0.150 |
| 161-200 | 184 | 0.3 | 0.294 |
| 201-240 | 223 | 0.2 | 0.237 |
| 241-280 | - | 0 | 0.000 |
| 281-320 | - | 0 | 0.000 |
| 321-360 | - | 0 | 0.000 |
| 361-400 | 380 | 0.1 | 0.202 |

$$\bar{M}_n = \sum x_i M_i = (0.2 \times 110 + 0.2 \times 142 + 0.3 \times 184 + 0.2 \times 223 + 0.1 \times 380) = 188 \text{ lb}$$

$$\bar{M}_w = \sum w_i M_i = (0.117 \times 110 + 0.150 \times 142 + 0.294 \times 184 + 0.237 \times 223 + 0.202 \times 380) = 218 \text{ lb}$$

$$\bar{M}_w = \sum w_i M_i = 218 \text{ lb}$$

Molecular Weight Distribution

M_n : Number-Average Mol. Wgt.

The number-average molecular weight (molar mass) of a polymer containing N_i molecules of mass M_i is the arithmetic mean of the molar mass distribution:

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

M_w : Weight-Average Mol. Wgt.

The weight-average molecular weight (molar mass) is the sum of the products of the molar mass of each fraction multiplied by its weight fraction (w_i).

In terms of w_i or numbers of molecules, M_w is

$$M_w = \sum w_i M_i$$

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

Molecular Weight Distribution

M_z : Z-Average Mol. Wgt.

The z-average molecular weight (molar mass) is:

$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$

M_z is especially sensitive to the presence of high-MW chains.

PDI: Polydispersity index

The molecular weight distribution, or polydispersity index, is the ratio of the weight-average molecular weight to the number-average molecular weight:

$$\text{PDI} = \frac{M_w}{M_n}$$

The polydispersity index of a monodisperse polymer is 1.00.

The polydispersity index increases as the polymer distribution broadens.

Molecular Weight Distribution

Example:

You have a polymer sample that contains the following molecules:

| M, Da* | N |
|----------------------------|-----------------------|
| 1,000,000 | 2 |
| 700,000 | 5 |
| 400,000 | 10 |
| 100,000 | 4 |
| 50,000 | 2 |
| Total: | 23 |

*Da = dalton, g/mol

What are M_n , M_w , and the polydispersity index?

Molecular Weight Distribution

Example:

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

$$M_n = \frac{10,000,000 \text{ Da}}{23}$$

$$M_n = 435,000 \text{ Da}$$

$$M_w = \sum w_i M_i$$

$$w_i = \frac{N_i M_i}{\sum N_i M_i}$$

$$M_w = 609,500 \text{ Da}$$

| <i>M</i> , Da | <i>N</i> | <i>N</i> · <i>M</i> , Da | <i>w</i> | <i>w</i> · <i>M</i> , Da |
|---------------|----------|--------------------------|----------|--------------------------|
| 1,000,000 | 2 | 2,000,000 | 0.20 | 200,000 |
| 700,000 | 5 | 3,500,000 | 0.35 | 245,000 |
| 400,000 | 10 | 4,000,000 | 0.40 | 160,000 |
| 100,000 | 4 | 400,000 | 0.04 | 4,000 |
| 50,000 | 2 | 100,000 | 0.01 | 500 |
| Totals: | 23 | 10,000,000 | 1.00 | 609,500 |

Molecular Weight Distribution

Example:

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

$$M_w = \frac{6.095 \times 10^{12} \text{ Da}^2}{1.000 \times 10^7 \text{ Da}}$$

$$M_w = 609,500 \text{ Da}$$

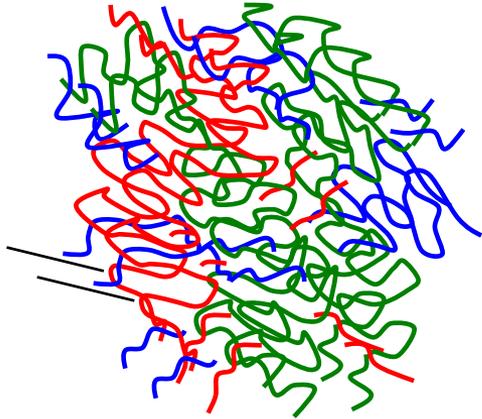
$$\text{PDI} = \frac{M_w}{M_n}$$

$$\text{PDI} = \frac{609,500 \text{ Da}}{435,000 \text{ Da}}$$

$$\text{PDI} = 1.40$$

| <i>M</i> , Da | <i>N</i> | <i>N</i> · <i>M</i> , Da | <i>N</i> · <i>M</i> ² , Da ² |
|---------------|----------|--------------------------|--|
| 1,000,000 | 2 | 2,000,000 | 2.000×10 ¹² |
| 700,000 | 5 | 3,500,000 | 2.450×10 ¹² |
| 400,000 | 10 | 4,000,000 | 1.600×10 ¹² |
| 100,000 | 4 | 400,000 | 0.040×10 ¹² |
| 50,000 | 2 | 100,000 | 0.005×10 ¹² |
| Totals: | 23 | 10,000,000 | 6.095×10 ¹² |

Molecular Weight and Dispersion - an example:



Here are:

10 chains of 100 molecular weight

20 chains of 500 molecular weight

40 chains of 1000 molecular weight

5 chains of 10000 molecular weight

Find \bar{M}_n , \bar{M}_w , polydispersity index:

$$\bar{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

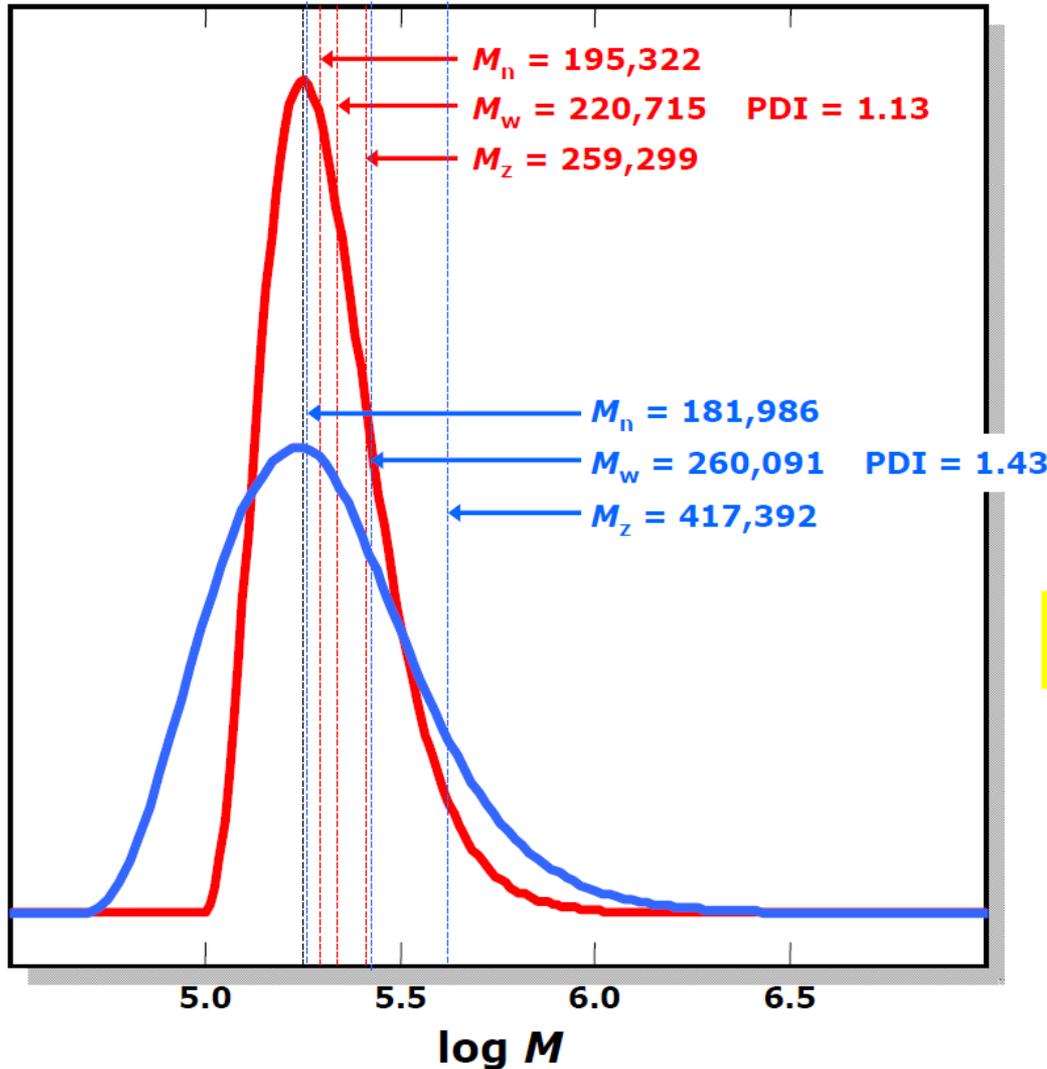
$$\bar{M}_n = \frac{(10 \cdot 100) + (20 \cdot 500) + (40 \cdot 1000) + (5 \cdot 10000)}{10 + 20 + 40 + 5} = 1347$$

$$\bar{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

$$\bar{M}_w = \frac{(10 \cdot 100^2) + (20 \cdot 500^2) + (40 \cdot 1000^2) + (5 \cdot 10000^2)}{(10 \cdot 100) + (20 \cdot 500) + (40 \cdot 1000) + (5 \cdot 10000)} = 5390$$

$$\text{Polydispersity} = \frac{\bar{M}_w}{\bar{M}_n} \approx 4$$

Molecular Weight Distribution



$$\text{PDI} = \frac{M_w}{M_n}$$

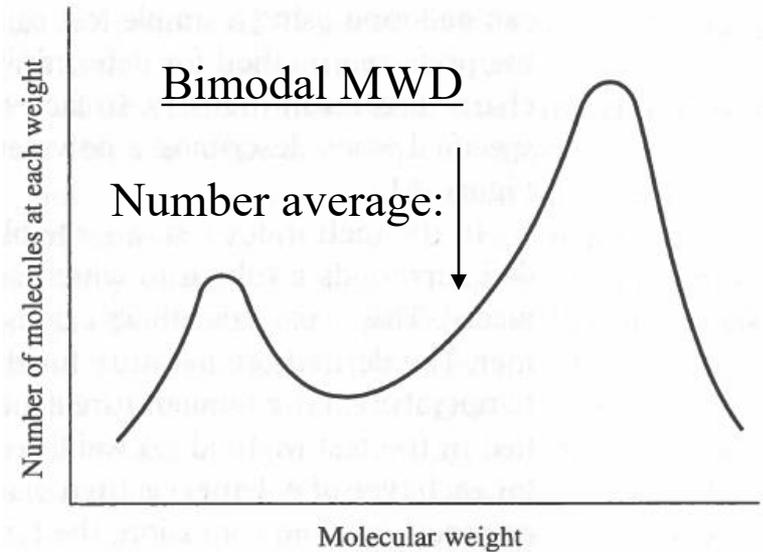
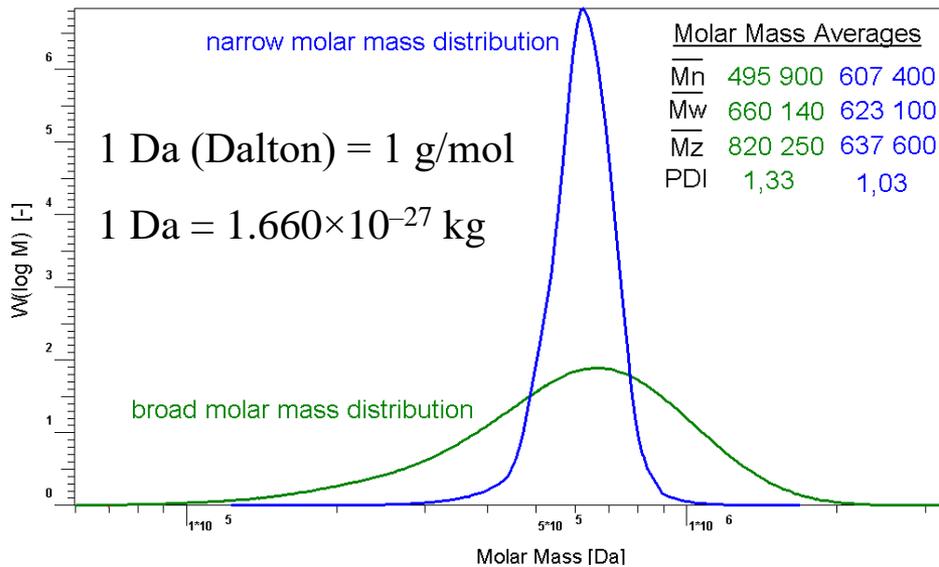
$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

$$M_w = \sum w_i M_i$$

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$

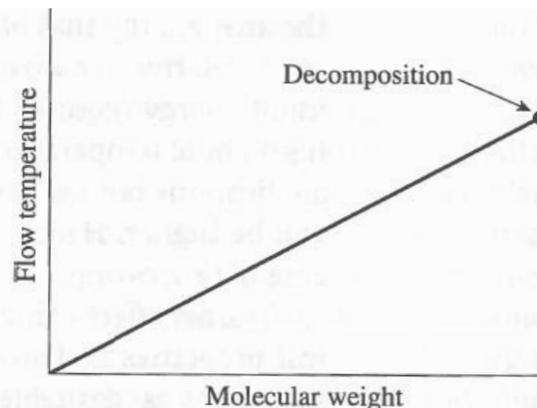
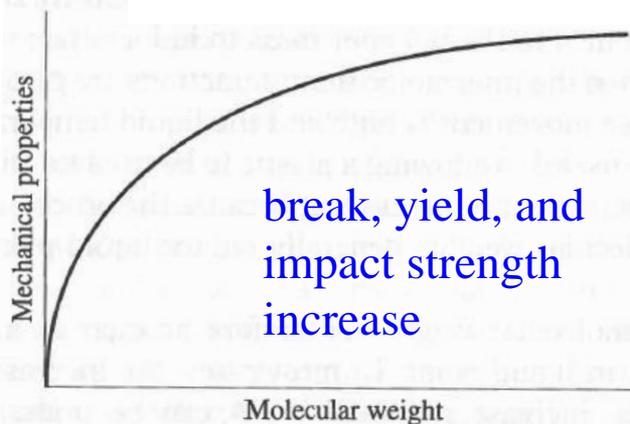
Molecular Weight Distribution



$$\bar{M}_n = \frac{\sum M_i \cdot n_i}{\sum n_i}$$

$$\bar{M}_w = \frac{\sum M_i \cdot w_i}{\sum w_i} = \frac{\sum M_i^2 \cdot n_i}{\sum M_i \cdot n_i}$$

$$PDI = \frac{\bar{M}_w}{\bar{M}_n}$$

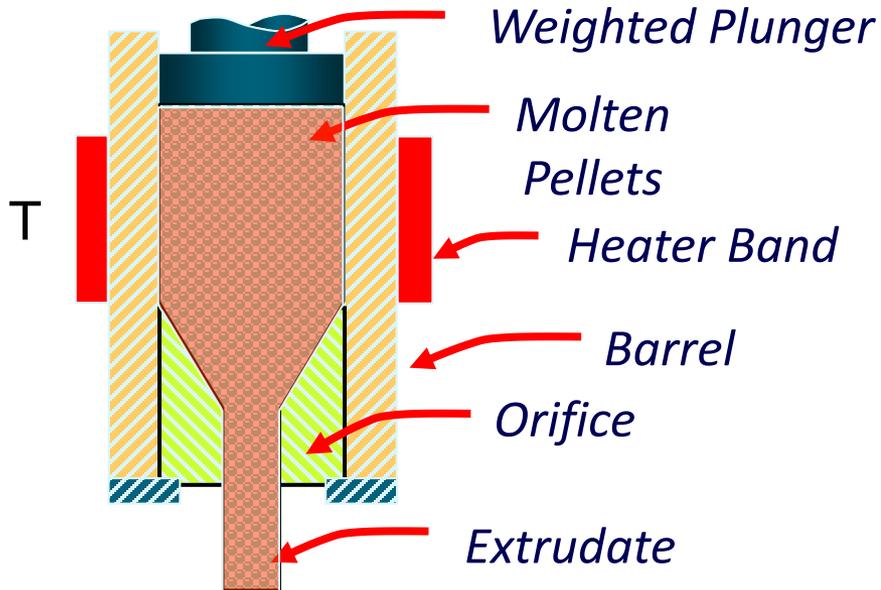


Polydispersity index (PDI) is a measure of the distribution of molecular mass in a given polymer sample. PDI=1, many chains with the same length (monodisperse). Otherwise, polydisperse PDI>1.

Figure 3.11 General mechanical and melting properties as a function of molecular weight.

Melt Index

Simple melt index test



Melt Flow Index

grams of flow per 10 minutes

For example: PE 190C/1.0kg

Not intrinsic or fundamental property of polymer melt, rather convenient and easy method for expressing flow properties useful for processing.

High melt index = low molecular weight; low melt index = high molecular weight.

Table 3.3 Comparison of Melt Index and Average Molecular Weight

| Weight Average Molecular Weight (g/mole) | Melt Index (g/10 min) |
|--|-----------------------|
| 100,000 | 10 |
| 150,000 | 0.3 |
| 250,000 | 0.05 |

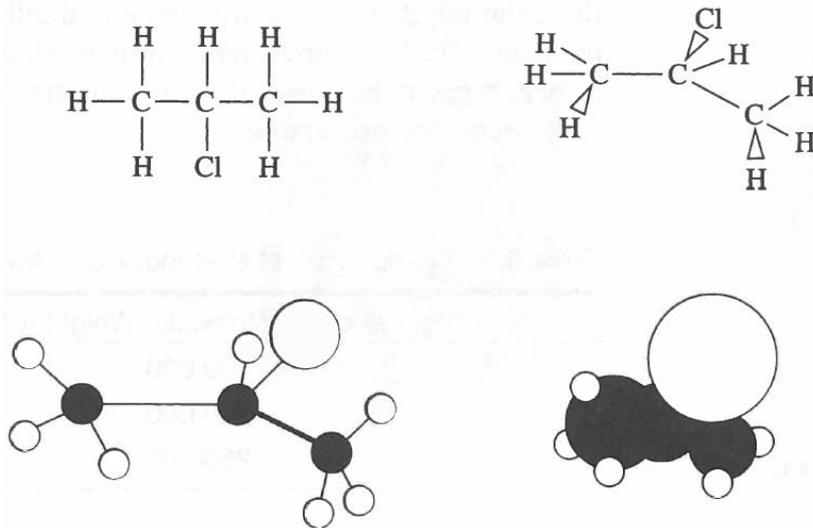


Effects of molecular weight, dispersity, branching

- The molecular weight, dispersity and branching has a significant effect on the mechanical and physical bulk properties of polymers. In general, a higher molecular weight improves the mechanical properties, that is, break, yield, and impact strength increase. However, a *higher molecular weight also increases the melt and glass transition temperature* as well as the solution and melt viscosity, which makes processing and forming of the polymeric material more difficult.
- The dispersity has the opposite effect; a wider molecular weight distribution lowers the tensile and impact strength but increases the yield strength, or in other words, a lower dispersity (narrower distribution) leads to better mechanical properties. The low-molecular weight portion of the distribution has a similar effect as a plasticizer, that is, it reduces the brittleness and lowers the melt viscosity which improves the processability, whereas the high-molecular weight portion causes processing difficulties because of its huge contribution to the melt viscosity.
- Branching is another important performance parameter. In general, **branching lowers the mechanical properties**. For example, it decreases the break and yield strength. The effect on toughness is less clear; if the length of the branches exceed the entanglement weight it improves the toughness, otherwise it lowers the impact strength. Branching also lowers the brittleness, the melt temperature, the melt and solution viscosity and increases the solubility. In conclusion, the processability improves with increasing degree of branching.

Shape (Steric) Effects

The effects of the shape or size of the atoms or groups of atoms are called **steric effects**.



Various methods for representing the 2-chloropropane (C₃H₇Cl) molecule:
 reduced crystallinity => tensile strength,
 T_g lower. But hindered movement.

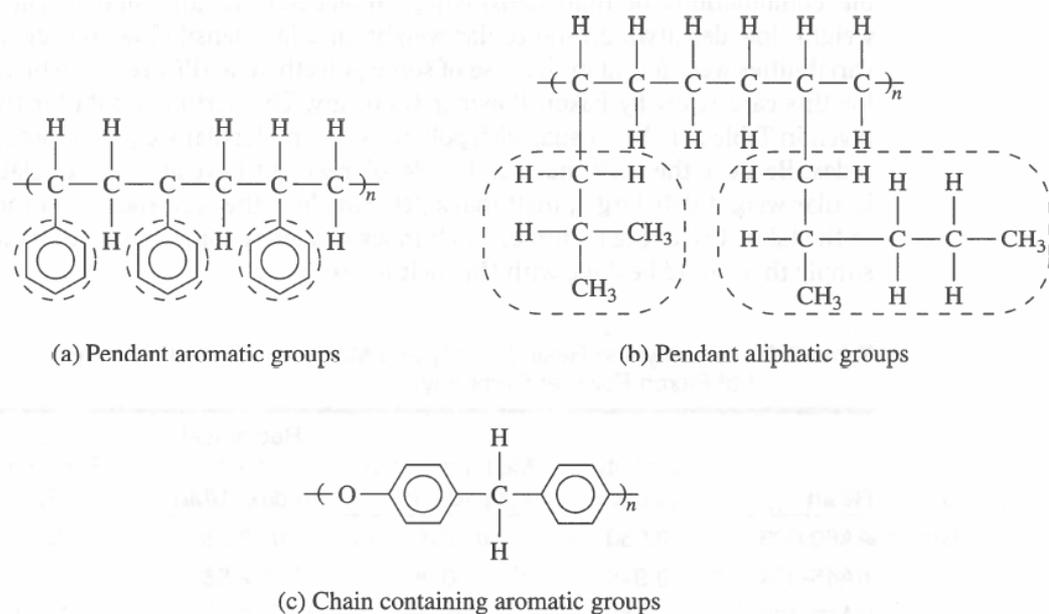


Figure 3.15 Aromatic and aliphatic pendant groups and backbone constituents.

Main physical properties of polymers

1 - Primary bonds: the covalent bonds that connect the atoms of the main chain

2 - Secondary bonds: non – covalent bonds that hold one polymer chain to another including hydrogen bond and van der Waals (dipole –dipole) attraction

3 - Crystalline polymer: solid polymers with high degree of structural order and rigidity

4 - Amorphous polymers: polymers with a low degree of structural order

5 - Semi – crystalline polymer: most polymers actually consist of both crystalline domains and amorphous domains with properties between that expected for a purely crystalline or purely amorphous polymer

6 - Glass: the solid form of an amorphous polymer characterized by rigidity and brittleness

7 – Crystalline melting temperature (T_m): temperature at which crystalline polymers melt

8 - Glass transition temperature (T_g): temperature at which an amorphous polymer converts to a liquid or amorphous domains of a semi crystalline polymer melt

9 – Thermoplastics (plastics): polymers that undergo thermally reversible conversion between the solid state and the liquid state

10 - Thermosets: polymers that continue reacted at elevated temperatures generating increasing number of crosslinks such polymers do not exhibit melting or glass transition

11 - Liquid–crystalline polymers: polymers with a fluid phase that retains some order

12 - Elastomers: rubbery, stretchy polymers the effect is caused by light crosslinking that pulls the chains back to their original state

Summary

- Gas, liquid, and solid phases, crystalline vs. amorphous structure, viscosity
- Thermal expansion and heat distortion temperature
- Glass transition temperature, melting temperature, crystallization
- Polymer degradation, aging phenomena
- Molecular weight distribution, polydispersity index, degree of polymerization
- Effects of molecular weight, dispersity, branching on mechanical properties
- Melt index, shape (steric) effects

Reading: Chapter 3 of *Plastics: Materials and Processing* by A. Brent Strong