POLYMERS:

- They are not crystalline! < rubber < some stuff but depends on temperature.

Volume in function of temperature:

\[ \theta_v = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \]

Thermal expansion:

\[ \theta_l = \frac{1}{\ell} \left( \frac{\partial \ell}{\partial T} \right)_P \]

\[ \theta_v \sim 3 \theta_l \]

![Diagram](image)

**Figure 6.2-1** Specific volume as a function of temperature for a series of materials. (a) The liquid-to-crystalline solid transformation. A discontinuous change in volume occurs at the melting temperature \( T_m \). (b) The liquid-to-glass transformation (the liquid-to-crystal curve is shown for reference). The temperature range in which the slope of the liquid-glass curve changes is the glass transition temperature \( T_g \). (c) Specific volume versus temperature for a semicrystalline material. The discontinuous change in volume occurs at \( T_m \) and a change in slope occurs at \( T_g \).
**Molecular Motion** depends on time frame of experiment.

Pull slowly → **Elongate** → Pull fastly → **Break**

⇒ Tₜ depends on time frame of events!

**Example of Polymers** = Poly+(HER) + many times n mer.

---

**FIGURE 6.2-2** Repeat units in two different structures: (a) the (SiO₂)₄⁻ tetrahedron in SiO₂, and (b) the C₆H₄ mer in polyethylene. In this figure we show the polymer molecule in a simplified linear (stretched-out) orientation. In fact, as discussed later in the chapter, polymer molecules rarely look like this. When drawn in the linear fashion, however, the backbone carbon atoms are in the plane of the paper but the side groups (H, etc.) stick out of, or go into, the plane of the paper.
**VISCOMITY**

**SHEAR STRESS**

\[ \tau = \frac{F}{A} \]

**SHEAR STRAIN**

\[ \varepsilon = \frac{\Delta y}{x} \]

\[ \frac{dy}{dx} = \varepsilon \]

**SOLID RESPONSE**

\[ \varepsilon \geq \xi \]

\[ G = \frac{\tau}{\varepsilon} \]

**SHEAR MODULUS**

**A LIQUID RESPONSE TO SHEAR STRESS?**

**NO STRAIN but STRAIN RATE**

\[ \varepsilon \rightarrow \text{constant deformation} \]

\[ x \uparrow \quad \tau(t) \uparrow \quad \text{is function of time} \]

\[ \frac{\partial x}{\partial t} \uparrow \]

\[ \frac{\partial x}{\partial t} > \frac{x}{t} \quad \text{bigger } x \text{ & faster } \frac{\partial x}{\partial t} \]

\[ \tau = \frac{1}{2} \int \frac{\partial x}{\partial t} \]

\[ \eta \text{ is measure of work done for deformation} \]

**NEWTON VISCOSITY LAW**
\[ \eta (\cdot) \]

\[ \frac{F}{A} = \eta \frac{1}{s} \frac{m}{m} \Rightarrow \frac{g \cdot m}{s} \text{ Poise} \]

\[ \Rightarrow \frac{g \cdot m}{s} \cdot \frac{5 \cdot m}{m} = \frac{g \cdot m}{s} \]

\[ \eta \downarrow \text{ water, solvent} \]

\[ \eta \uparrow \text{ liquid metals (Hg)} \]

\[ \text{viscosities} \]

\[ \text{Caramel } \sim 10^5 \text{ Pa.s} \]

\[ \text{Windows glasses } 10^2 \text{ s} \]

\[ \text{Fluidity} \]

\[ \phi = \frac{1}{\eta} \]

\[ \text{Viscosity (and fluidity) are temperature driven processes.} \]

\[ T \uparrow \eta, \phi \]

\[ \Rightarrow \text{ Arrhenius} \]

\[ \phi = \frac{1}{\eta} = \phi_0 \exp \left( \frac{-Q}{kT} \right) \]

\[ \text{where the system is viscous enough to fit the Arrhenius equation} \]

\[ N = N_0 \exp \left( \frac{-Q}{kT} \right) \]

\[ \text{At Kelvin, not Celsius.} \]

**Figure 6.3-2** The effect of temperature on the viscosity of a soda-lime-silicate glass. (Source: W. G. Kingery, *Introduction to Ceramics*, 2nd ed. Copyright © 1976 by John Wiley & Sons. Reprinted by permission of John Wiley & Sons, Inc.)
STRUCTURES!

- CLASSIFICATION

polyethylene
\[ \text{UNIT} \Rightarrow \left( \frac{\text{C} \text{C}}{\text{H}} \right) = \text{MER} \]

If \( n \) small \( \Rightarrow \) polyethylene
WAX or PARAFFIN OR OIL

\( \downarrow \)

HUNDREDS.

If \( n \) small \( \Rightarrow \) polyethylene
WAX or PARAFFIN OR OIL

\( \downarrow \)

HUNDREDS.

VINYL POLYMER

\[ R = \text{VINYL POLYMER} \]

\[ R = \text{CH}_3 \Rightarrow \text{POLYPROPYLENE} \]

HYDROCARBONS  RUBBERS  CARE double bond

\[ R=H \Rightarrow \text{POLYBUTANENE} \]

- POLY OLEFIN (C \& H only) \( \Rightarrow \) FAMILY
- POLY ESTER  ESTER \( -O-C-\)  FAMILY
- PET  POLYESTER  \( \leftarrow \)

PET  POLYESTER  \( \leftarrow \)

NYCAR, OACRON, FORTREL, TERYLENE
# Polyamides (Polyamides)

- **NYLON**
  - Carpet, silk, wool

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Vinyls and related polymers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td>$\text{CH}_2=\text{CH}_2 \rightarrow \text{CH}_2-\text{CH}_2$</td>
<td>Clear film, flexible bottles</td>
</tr>
<tr>
<td>Polytetrafluoroethylene (Teflon)</td>
<td>$\text{CF}_2=\text{CF}_2 \rightarrow \text{CF}_2-\text{CF}_2$</td>
<td>Nonstick coatings, gaskets, seals</td>
</tr>
<tr>
<td>Polymethylmethacrylate (PMMA)</td>
<td>$\text{CH}_2=\text{C}=\text{O} \rightarrow \text{CH}_2-\text{C}=\text{O}$</td>
<td>Lenses, transparent enclosures, windows</td>
</tr>
<tr>
<td><strong>Rubbers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polybutadiene</td>
<td>$\text{CH} \equiv \text{CH} \rightarrow \text{CH}_2-\text{CH}=\text{CH}_2$</td>
<td>Tires and molded parts</td>
</tr>
<tr>
<td>Polyisoprene (natural rubber)</td>
<td>$\text{CH}_2=\text{C}=\text{C} \rightarrow \text{CH}_2=\text{C}=\text{C} \text{H}_3$</td>
<td>Tires and gaskets</td>
</tr>
<tr>
<td>Polychloroprene</td>
<td>$\text{CH} \equiv \text{CH} \rightarrow \text{CH}_2=\text{C}=\text{CH}_2$</td>
<td>Belts, bearings, and foams</td>
</tr>
<tr>
<td>Polydimethylsiloxane (silicone rubber)</td>
<td>$\text{H}_3\text{Si}=\text{O}-\text{Si}=\text{H}$</td>
<td>Gaskets, insulation, and adhesives</td>
</tr>
<tr>
<td>Polymer</td>
<td>Structure</td>
<td>Applications</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---------------------------------------------------------------------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>Polyesters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyallyl methacrylate</td>
<td></td>
<td>Films (magnetic tape), fiber, and clothing</td>
</tr>
<tr>
<td>(Thermoset variation)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyamides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nylon 6</td>
<td></td>
<td>Butt and auto body parts, fiberglass, helicis, and chairs</td>
</tr>
<tr>
<td>Polyarylate or poly 2-phenylethylamide (PPTA)</td>
<td></td>
<td>Fiber, bulletproof vests</td>
</tr>
<tr>
<td>Other common polymers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polymethyl acrylate</td>
<td></td>
<td>Gears and machine parts</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td></td>
<td>Lenses, helmets, lens-casting, machine parts</td>
</tr>
<tr>
<td>Polystyrene</td>
<td></td>
<td>Casing, moose and telephone, electrical components, distributor, tops</td>
</tr>
<tr>
<td>Polyurethane</td>
<td></td>
<td>Foam, paper and tubing, wire and cable insulation</td>
</tr>
<tr>
<td>Polypropylene</td>
<td></td>
<td>Adhesive, used in composites</td>
</tr>
<tr>
<td>Polyethylene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Relation with adjacent pairs

\[
\begin{array}{c}
\text{R} - \text{C} - \text{H} \\
\text{H} & \text{R} & \text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{R} - \text{C} - \text{R} \\
\text{H} & \text{R} & \text{H}
\end{array}
\]

ISOTACTIC

SYNDIOTACTIC

ATACTIC

it's decelerated during production

FIGURE 6.4-5 A planar illustration of the (a) isotactic, (b) syndiotactic, and (e) atactic configurations of polystyrene. Note: The C_6H_5 rings are actually much larger than indicated in these sketches.

TACTICITY (STEREOCHEMISTRY) is determined on polymer formation (can be modified randomly at HIGH TEMP) because they affect secondary bonds:

(a) Isotactic
(b) Syndiotactic
(c) Atactic

P11

→ CRYSTALS?
Some do!
THERMO PLASTIC & THERMOSET

BOND: 1) secondary; (VDWALCES, Dipoles) \( \Rightarrow \) weak, can be destroyed by temperature \( \Rightarrow \) \( T \uparrow \) \( \Rightarrow \) polymer melts

THERMO PLASTIC

2) primary & double bonds inside chain \( T \uparrow \) + extra atoms

\( \Rightarrow \) break double bonds inside chain \( \Rightarrow \) create EXTRA BOND CROSS LINK

THERMOSET \( (TS) \)

UNSATURATED: HAVE C=C
PHENOLFORMALDEHYDE (BAKELITE)

**PHENOLFORMALDEHYDE (BAKELITE) → POLYMER SURFACE**

**FIGURE 6.4-2**
The structure of the TS polymer phenolformaldehyde (Bakelite®) showing:
(a) the basic building block for the structure (the numbers 1–3 correspond to the three sites for primary bond formation with neighboring monomers), (b) a simplified representation of the basic building block, and (c) a 2-D representation of the 3-D primary bond network in this TS polymer.

CELLULOSE

**FIGURE 6.4-3** (a) The structure of cellulose, and (b) schematic of the structure of lignin.

PROTEINS

DIFFERENT

R & R' moieties

different amino acids!
**MOLECULAR WEIGHT**

\[(\text{MER})_n \Rightarrow M = mn\]

1. \(n\) = degree of polymerization
2. \(M\) = molecular weight

\(n\) = number of different polymers

\(\overline{M}\) = average molecular weight

\(N_i = \#\) of polymers with weight \(M_i \Rightarrow \overline{M} = \frac{\sum M_i N_i}{\sum N_i}\)

\(\overline{M_w} = \frac{\sum w_i M_i}{\sum w_i}\)

PD = 10 \Rightarrow all same polymers.

\[\text{PD} = \frac{\overline{M_w}}{\overline{M_n}} \approx 2 \text{ to } 20\]

**POLYMERS CONFIGURATION**

Very rarely they are linear \(-\times-\)

Usually **kinked**:

![3D structure of PE](image)

**Figure 6.4-4** The 3-D structure (conformation) of a polyethylene chain. (a) The C–C–C bond angle in PE. (b) The bond angle does not define the location of the neighboring C atoms but only restricts their location to a specific cone of rotation. (c) If all of the C atoms in the chain backbone lie in the same plane, the planar zigzag conformation results. (d) The more common (lower-energy) conformation of PE is the random coil structure.
CRYSTALLIZATION OF POLYMER

THERMOPLASTIC partially crystalline

→ go T↑ and cool slowly.

CRYSTALLIZATION DEPENDS ON

1) SIZE OF SIDE GROUPS (R)
2) EXTENT OF BRANCING
3) TACTICITY
4) COMPLEXITY OF MER
5) TYPE OF SECONDARY BONDS (DIPole or VOR)

1) SIZE — small polymers crystallize better
   simple polymers crystallize better

   POLY PROPYLENE \((\text{C}_2\text{H}_3\text{C}_2\text{H}_3)^n\)
   crystallize less than
   POLY ETHYLENE \((\text{C}_2\text{H}_2\text{C}_2\text{H}_2)^n\)

2) BRANCHING

   More branches
   → less crystalline

   Small concentration of branches
   → more open spaces,
   polymer
   less compact!!

FIGURE 6.4-7 A schematic illustration of chain branching in polyvinylchloride.

P12

HIGH density PE ⇒ structural
LOW density PE ⇒ storage
But
3) **TACTICITY** affects crystallization

Atactic (random) with big side groups cannot easily be packed. It's easier to pack isotactic (HLLH) and syndiotactic (HLLL).

⇒ This influences property.

Ex: Polypropylene isotactic (~50% crystalline) = hard & rigid
Polypropylene atactic (~0% crystalline) = useless gummy substance

4) **COMPLEXITY OF MER**

big repeated unit (mer) ⇒ need more extreme chain segment to create L.R.O.

⇒ they crystallize slowly.

Then short mer

5) **TYPE OF SECONDARY BONDS**

existence of small space polar side groups helps formation of crystals

⇒ Ex: \[ \text{PVC: } \frac{\text{H}}{\text{C}} \frac{\text{H}}{\text{C}} \] better than \[ \frac{\text{C}}{\text{C}} \text{Polypropylene} \]

⇒ PVC stronger than PP
SEMICRYSTALLINE POLYMER

Polymer = long spaghetti need to roll up

SPHERULITE = AGGREGATE OF LAMELLAR

ORDER = CRYSTAL REGION

+ INTERLAMELLAR NONCRYSTALLINE POLYMER

SEMICYSTAL

\[ \% \text{ DEGREE OF CRYSTALINITY} \]

\[ \% \text{ of the polymer that is crystalline} \]

METAL, CERAMICS \( X \approx 99\% \)

POLY \( \approx 90 \text{ to } 95\% \)

NON-CRYSTAL \( 0 \% \)
Tgloss V.S. Tmelting

Simple rule: longer MERS, HEAVIER side groups → higher Tg (rubber simple and brittle)

because you need higher T to get the "motion" going on.

In addition

Symmetric MER (C₂H₄ PE PE mixture)

\[ T_{g} \approx \frac{T_{m}}{2} \]

Asymmetric MER (C₂H₃ CE PVC)

\[ T_{g} \approx \frac{T_{m}}{3} \]

It's an entropy (symmetric MER has one more degeneration, \( S = k \log R \), 2 \( k \) for symmetric.)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( T_{m} ) (°C)</th>
<th>( T_{c} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-density polyethylene</td>
<td>197</td>
<td>-120</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>159</td>
<td>64</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>130</td>
<td>610</td>
</tr>
<tr>
<td>Polyamide</td>
<td>120</td>
<td>107</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>120</td>
<td>107</td>
</tr>
<tr>
<td>Polyethylene terephthalate</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Adipal</td>
<td>181</td>
<td>185</td>
</tr>
<tr>
<td>Nylon 6.6</td>
<td>205</td>
<td>205</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>230</td>
<td>230</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>230</td>
<td>230</td>
</tr>
<tr>
<td>Polystyrene terephthalate</td>
<td>255</td>
<td>90</td>
</tr>
<tr>
<td>Silicon</td>
<td>-</td>
<td>123</td>
</tr>
<tr>
<td>Polybutadiene</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>43</td>
<td>43</td>
</tr>
</tbody>
</table>
GLASSES
STRUCTURE & PROPERTY

Take a piece of a window + ray, wait it becomes crystalline.

Chapter 6  Noncrystalline and Semicrystalline Materials

**FIGURE 6.5-1**
A comparison of the X-ray scans for (a) amorphous silica and (b) a crystalline polymorph of silica (crystobalite). (Source: Adapted from B. E. Warren and J. Bosco, Journal of American Ceramic Society, 2149, 1538.)

**FIGURE 6.5-2** The 2-D representations of (a) silica glass and (b) a crystal of silica.
Gloss: variety of materials (amorphous) = random

 metall., ionic & covalent

Requirement: Material must be cooled from liquid phase, rapidly enough to "freeze" the liquid phase, and kinetic of crystallining phase must be slow so the system does not become ordered fast.

HINT MUST BE VISCOUS (HEAT MUST BE VISCOUS)

| Elements: | S, Se, P |
| Oxides: | B₂O₃, SiO₂, GeO₂, P₂O₅, As₂O₃, SnO₂, In₂O₃, SnO₂, PbO₂, and SeO₂ |
| Halides: | BeF₂, AlF₃, ZnCl₂, Ag(Cl, Br, I), Pb(Cl₂, Br₂, I₂), and multicomponent mixtures |
| Sulfides: | As₂S₃, Sb₂S₃, CS₂, and various compounds of B, Ga, In, Te, Ge, Sn, N, P, and S |
| Selenides: | Various compounds of Ti, Sn, Pb, As, Sb, Bi, Se, and P |
| Tellurides: | Various compounds of Ti, Sn, Pb, As, Sb, Bi, and Se |
| Nitrides: | KNO₃, Ca(NO₃), and many other binary mixtures containing alkali and alkaline earth nitrates |
| Sulfates: | KH₂PO₄ and other binary and ternary mixtures |
| Carbonates: | K₂CO₃, MgCO₃ |
| Polymeric: | Polysiloxane, polydimethylmethacrylate, polyvinyl, polyethylene terephthalate, and nylon |
| Metallic: | Au, Sn, Pb, Sn, (Fe-Cr-B) alloys |


IONIC GLASSES

An ionic compound can live in a disordered state, => can form glasses

Example: Oxide glasses (SiO₂) for which a set of rules was developed if oxygen + metal is present
ZACHARIASEN RULES FOR ionic Oxide GLASSES

1) Oxide Glass NETWORKS ARE COMPOSED OF OXYGEN POLYHEDRA \( \rightarrow \) METAL + OXYGEN

2) Coordination of Oxygen is 2! \( \text{CN}(O) = 2 \Rightarrow O^{--} \)

3) Coordination of Metal is 3 or 4
   \( \text{CN}(M) = 4 \Rightarrow \text{TETRAHEDRA} \quad (\text{SiO})_{4}^{2-} \)
   \( \text{of Silica} \quad (\text{SiO}_{2}) \)
   \( \text{CN}(3) = 3 \Rightarrow \text{TRIANGLES} \quad \text{like} \quad (\text{BO})_{3}^{-} \quad \text{of} \quad \text{B}_{2}O_{3} \quad \text{Boron O}^{+} \text{ion} \)

4) Oxygen Polyhedra Share Corners, Not Edge or Face (To Minimize Metal + Repulsion!)

5) Each Polyhedra Shares at Least 3 Corners

FIGURE 6.5–3 The structure of amorphous \( \text{B}_{2}O_{3} \) (a) the basic building block, a triangular polyhedron \( (\text{BO})_{3}^{3-} \);
   (b) two polyhedra shown sharing an edge; (c) two polyhedra sharing a corner, with the B—O—B angle slightly different from 180°; and (d) two polyhedra sharing a corner, with the B—O—B angle equal to 180°.
COVALENT GLASSES

lost time: ionic glasses & ZACHARIASEN'S Rule for stable ionic glasses!

What about covalent glasses?

MUST BE POLYMERS, weak & loose $T_g >$ Room

& must be able to

COOL DOWN FAST &

must lose viscosity melt,

GLASS = NO DEFECTS

----- ISOTROPY -----

SEMICONDUCTORS: usually

build from crystals (reduce defects to increase $\mu$),

but when $\mu$ is not a probe,

then we can use

amorphous semiconductors

EXAMPLES: solar cells, spread

surface $\Rightarrow$ very expensive Si

crystalline, but amorphous

Si works fine & no grain boundary which are the places where corrosion starts.

<p>|</p>
<table>
<thead>
<tr>
<th>Polymer</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-density polyethylene</td>
<td>127</td>
<td>150</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>129</td>
<td>67</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>179</td>
<td>710</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>280</td>
<td>100</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>330</td>
<td>100</td>
</tr>
<tr>
<td>Polystyrene adipate</td>
<td>340</td>
<td>320</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>320</td>
<td>320</td>
</tr>
<tr>
<td>Polychloroplastic</td>
<td>320</td>
<td>320</td>
</tr>
<tr>
<td>Azeesil</td>
<td>180</td>
<td>385</td>
</tr>
<tr>
<td>Nylon 6.6</td>
<td>265</td>
<td>90</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>220</td>
<td>140</td>
</tr>
<tr>
<td>Polychloroformaldehyde</td>
<td>285</td>
<td>30</td>
</tr>
<tr>
<td>Teflon</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Polychloroplastic</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>20</td>
<td>20</td>
</tr>
</tbody>
</table>
METALLIC GLASSES

Metals are very fluid once melted

\[ \Rightarrow \text{hard to remove best for} \]

Removing \(10^5 \text{K/s}\) we can make near 20% glass of a metal material \(\Rightarrow 80\% \text{ metal} \& 20\% \text{ glass}\).

\(\Rightarrow \text{only small parts} \& \text{strips} \& \text{ribbons} \& \text{wires}\)

Dope with

IF I NEED A NON METAL OR BAD METAL

Au-Si (80 \& 20), Fe Si B (78, 9, 13) \(\Rightarrow \text{low melt}\)

melt is more viscous and easy to form glasses.

GLASSY METALS are sensitive to heat!! HEAT destroys the glass \& becomes metal crystalline!!

Again, glass metals have no grain boundary \(\Rightarrow\)

1) Strong against corrosion

2) Isotropic properties (used for magnetic applications)

METALLIC FOAMS

Inenco temperature, melt, and decrease fast while bubbling with inert gas \(\Rightarrow\) METALLIC FOAMS, LIKE SPONGES

USED FOR BIOMATERIALS \(\Rightarrow\) STRONG \& ADSORBENT \& LIGHT

(BONES)

GOOD A TISSUE GOOD
RUBBERS & ELASTOMERS

It's when Tg < room, but not only

Remember

Thermoplastic ⇒ no secondary bonds, ⇒ when T > Tg viscosity decreases
Thermoset ⇒ plenty of covalent bonds ⇒ T > Tg get more linked!

And molecular gets strong

Thermoset elastomers

⇒ have few available bonds to make few cross links

Thermoset

Few extra

Thermoset elastomers

Little cross linking (1/100)

Soft, rubber, rubber band style

Much cross linking (1/10)

Heavy brittle stiff

Controlling concentration of "extra"

We can control final product

Medium (1/1000)

Tires for cars

Thermoset elastomers do not really melt,

They get stiffer & then burn!
Figure 6.6-1 The structure of polybutadiene: (a) as a thermoplastic polymer, and (b) as a crosslinked rubber.

Silicone Rubber (Crosslinked Compounds)

Poly Dimethyl Siloxane

\[ \text{Si} + \text{Oxygen} \]
Thermoplastic Elastomers

When thermoplastic is heated, becomes viscous; loses shape

How can we fit the shape and make it elastic?

Need to fight viscosity keeping elasticity

Block Copolymers!

\[
\begin{align*}
(MER_A) \cdots \cdots & (MER_A) - (MER_B) \cdots \cdots (MER_B) - (MER_A) \cdots \\
& \underbrace{A \ N_A \times} \quad \underbrace{B \ N_B \times} \\
\downarrow & \\
& \text{KEEP FLEXIBLE} \\
& \text{DOUBLE BONDS (UNSATURATED)} \quad \text{& NOT CROSS LINKED! SO IT MAKES CROSS LINKS}
\end{align*}
\]

\[ \Rightarrow \text{Elastic} \]

When high temperature melts, because the block softens (no secondary bonds) but at lower temperature is elastic

\[ \Rightarrow \text{Elastic} \]

Figure 6.1-3 Copolymers and thermoplastic rubbers: (a) a schematic illustration of a block copolymer, and (b) the structure of the triblock copolymer thermoplastic rubber polystyrene-polybutadiene-polystyrene.
CRYSTALLIZATION OF RUBBERS

CRystallization

Monodex

\[ \rightarrow \text{stetch} \quad \text{parallel} \quad \text{generate heat} \quad \text{REMOVAL HEAT} \quad \text{Free elasticity} \]

\[ \rightarrow \text{go back to the original shape} \]

EXAMPLE

THERMO SHRINKING MATERIALS!!

usefull in electronics

PIRES that shrinks with heat gun!!

**FIGURE 6.8-4** Changes in polymer structure as a result of an applied load: (a) unaligned chains in an unloaded polymer, and (b) chains aligned under an applied load.
YOUNG'S MODULUS & TEMP

\[ \sigma = E \varepsilon \]

\[ E(t) \]

**NEWTON LAW'S**

**VISCOITY**

\[ z = M \varepsilon t \]

Figure 6.5-5 The relationship between modulus and temperature. (a) An amorphous uncrosslinked polymer. (b) The influence of increasing percent crystallinity. (c) The influence of increasing crosslink density.

With semi-crystalline and cross-linked density the glossy transition "disappears", softens!!
RUBBER ELASTICITY

ELASTOMERS: stretch 10 times and come back to original shape!!

How? stretching original fiber directions

\[ F \]

\[ l_{\text{ex}} \]

\[ b \]

\[ \text{(HER)} \]

\[ m \]

\[ \text{distance between chain ends in coiled conformation} \]

(a)

FIGURE 6.6-6 A comparison of (a) the random coil conformation of an unstretched rubber, and (b) the stretched, or planar zigzag, conformation in which the separation distance between the chain ends is maximum.

Stretch A to get B

Rearrangement of bond directions!

No elongation of bonds

Therefore no Elastic Energy, does not go in bond stretching but in \underline{entropy change}.

\[ \varepsilon \text{ from bond stretching} \]

Only FEW %

\[ P26 \]
Now all logs of c_0^c are along the same direction!!

\[ L_{\text{ext}} = m \cos \left( \frac{\theta}{2} \right) \text{ for extended} \]

\[ L_{\text{coil}} \approx L_{\text{ext}} \sqrt{m \frac{1 + \cos \theta}{1 - \cos \theta}} \]

\[ L_{\text{coil}} \ll L_{\text{ext}} \quad m \gg 1 \Rightarrow \sqrt{m} \gg 1 \]

\[ \text{Max strain} = \frac{L_{\text{ext}} - L_{\text{coil}}}{L_{\text{coil}}} = \frac{L_{\text{ext}}}{L_{\text{coil}}} - 1 \approx 1.15 \sqrt{m} = \text{HUGE} \]

\[ m \approx 10^2 \text{ to } 10^5 \]

\[ \text{Max strain} \approx 10 \text{ to } 300 \text{ times} \]

All elastic energy goes in unwinding.

**ENTROPIC EFFECT**

\[ S = k \log 2^E \]

Folds configurations with energy

\[ S \approx 0 \]

Many configurations

\[ S = \text{HIGH} \]

on stretching S↓

⇒ TAS → AQ produced

P27

Elastomers shrink upon heating