

POLYMERS ;

AMORPHOUS \Rightarrow NO LONG RANGE ORDERING

- they are not crystalline!

$\left. \begin{array}{l} \text{glass} \\ \text{rubber} \end{array} \right\}$ same stuff but depends on Temperature

above $T_g \Rightarrow$ rubber (MOLECULAR REARRANGEMENT)
 under $T_g \Rightarrow$ glass no molecular rearrangement (FROZEN) temperature

Volume is function of Temperature

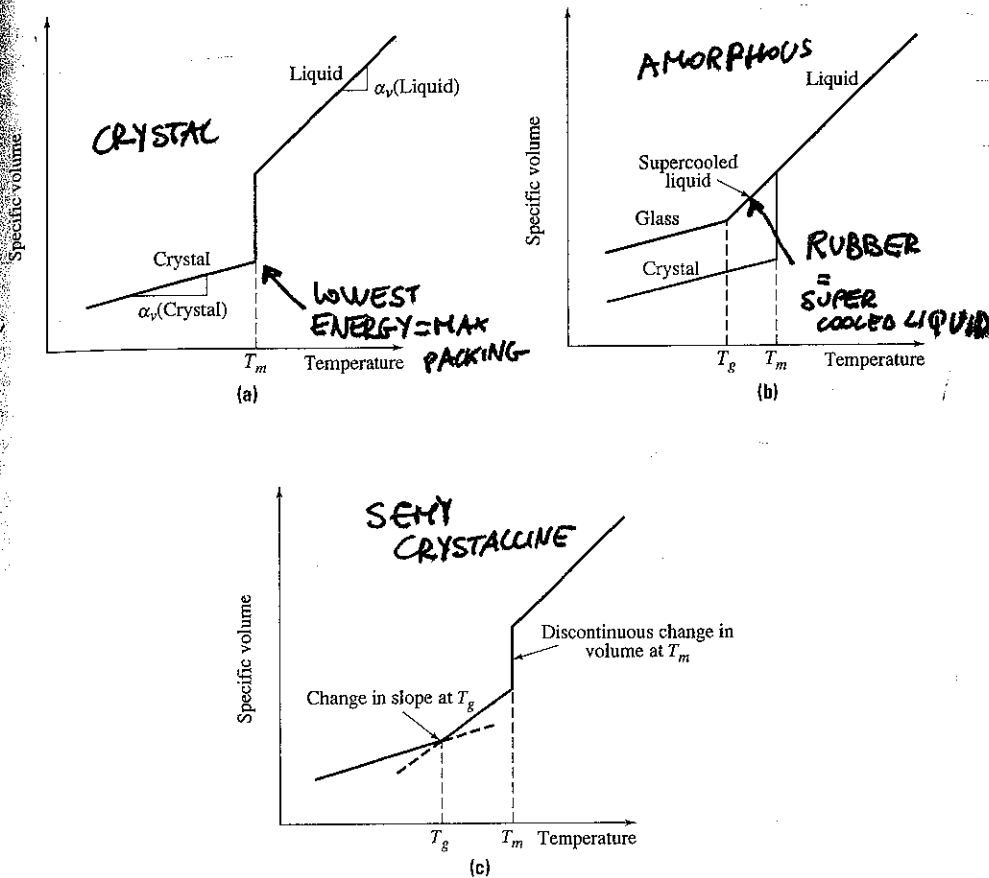
on times comparable with exper. time

$$\Rightarrow \alpha_v = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

thermal expansion

$$\alpha_L = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_P$$

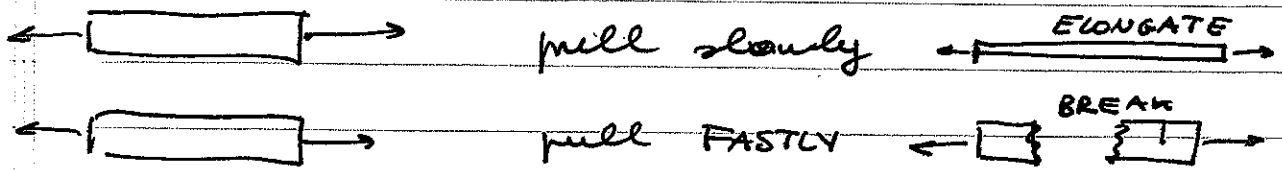
$$\alpha_v \sim 3\alpha_L$$



$\alpha_v^{\text{Liq}} > \alpha_v^{\text{sol}}$
 MOST OF MATERIALS

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 \Rightarrow depends on time frame of experiment
 REARRANGEMENT



$\Rightarrow T_g$ depends on Time frame of events!

EXAMPLE OF POLYMERS = POLY + (MER)
 \uparrow
 many times * mer.

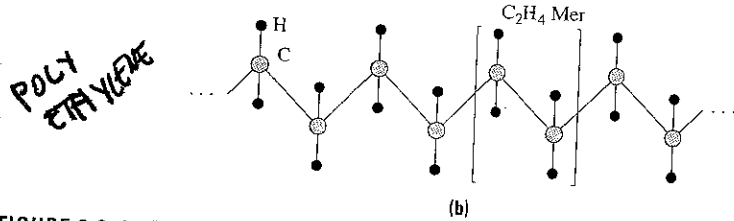
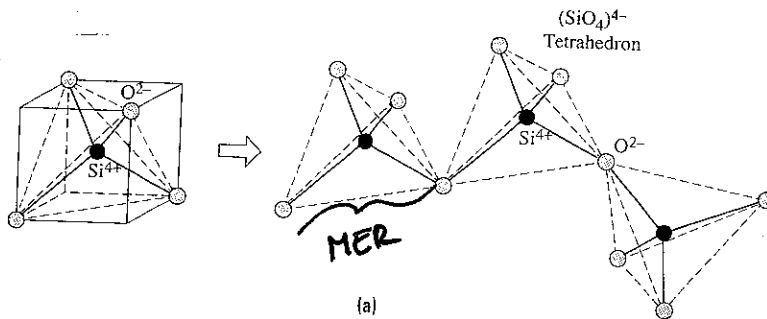
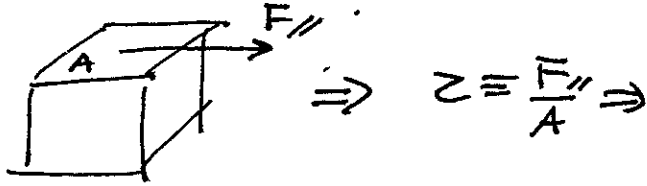


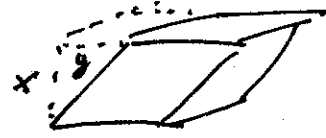
FIGURE 6.2-2 Repeat units in two different structures: (a) the $(\text{SiO}_4)^{4-}$ tetrahedron in SiO_2 , and (b) the C_2H_4 mer in polyethylene. In this figure we show the polymer molecule in a simplified linear (stretched-out) orientation. In fact, as discussed later in the chapter, polymer molecules 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.

VISCOSITY

SHEAR STRESS

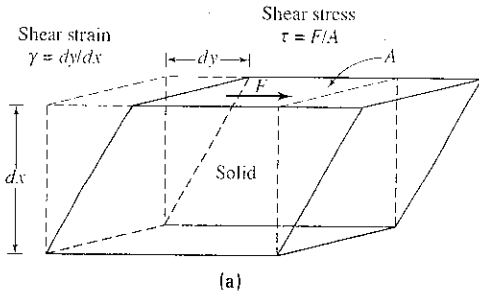


SHEAR STRAIN



$\frac{y}{x}$ is shear strain;

even better $\frac{dy}{dx} \equiv \gamma$ SHEAR STRAIN



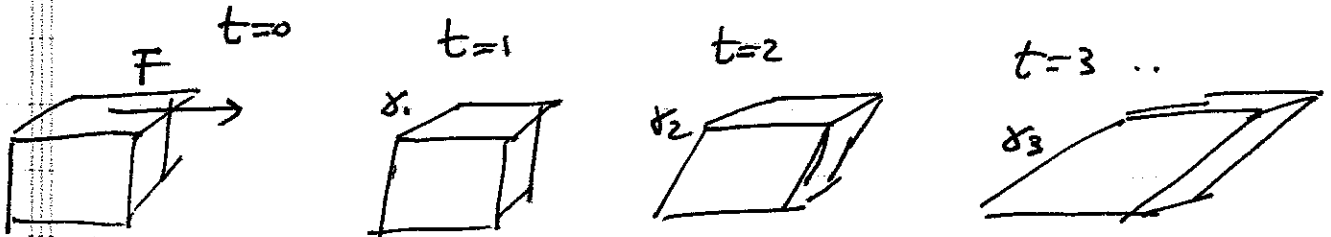
SOLID RESPONSE

$z \Rightarrow \gamma \propto z$ $z = G\gamma$
 \downarrow
 SHEAR MODULUS

A liquid responds to shear STRESS?

NO STRAIN but STRAIN RATE

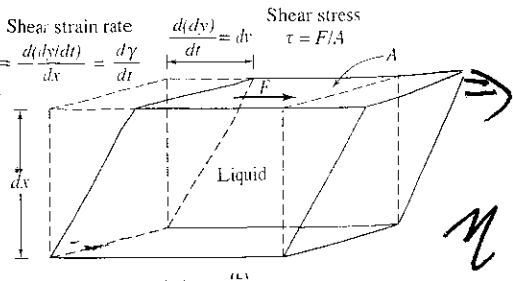
\Rightarrow constant deformation



$\gamma \uparrow$ $\gamma(t) \uparrow$ is function of time

P3

\Rightarrow $\frac{\partial \gamma}{\partial t} \propto z$ bigger z & faster $\frac{\partial \gamma}{\partial t}$
 $\Rightarrow \tau \propto \frac{\partial \gamma}{\partial t}$



$$\tau = \eta \frac{\partial \gamma}{\partial t}$$

NEWTON VISCOSITY LAW

η is measure of work done for deformation

η (?)

$$\left(\frac{F}{A}\right) = \eta \frac{1}{s} \frac{m}{m} \Rightarrow \left(\frac{g \cdot m}{s}\right) \text{ POISE}$$

$$\Rightarrow \frac{g \cdot m}{s} \frac{1}{m} = \frac{g}{s}$$

$\eta \downarrow$ water, solvent, } still liquid
 $\eta \uparrow$ ~~liquid metals,~~ }
 viscous materials

liquid metals (Hg)
 $H_2O \sim 0.01 P$
~~Metal liquid metal~~

CARAMEL $\sim 10^5 P$

WINDOWS glasses 10^{25}

FLUIDITY

$$\phi \equiv \frac{1}{\eta}$$

viscosity (& fluidity) are TEMPERATURE DRIVEN PROCESSES

$T \uparrow \Rightarrow \eta \downarrow, \phi \uparrow$

\Rightarrow
 when the system is viscous
 at good FIT @ $T > T_g$

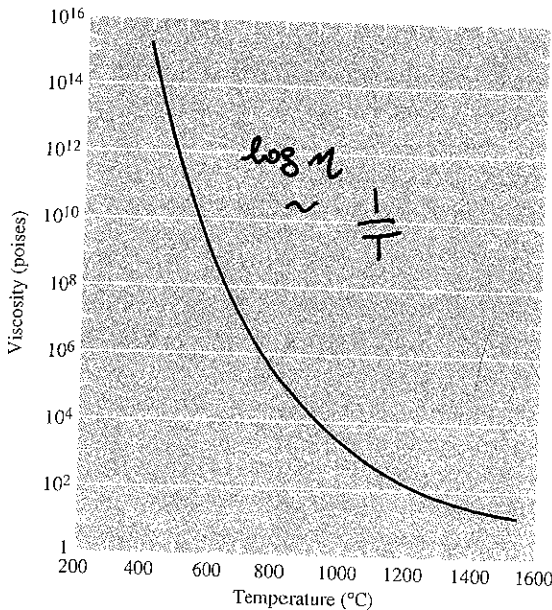
ARRHENIUS

$$\phi \equiv \frac{1}{\eta} = \phi_0 \exp\left(-\frac{Q}{RT}\right)$$

activation energy

$$\eta = \eta_0 \exp\left(\frac{Q}{RT}\right)$$

T in Kelvin,
 NOT Celsius

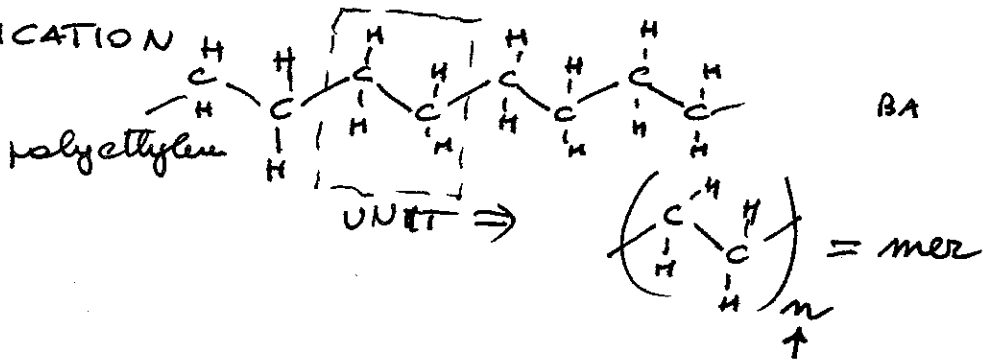


P4

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

STRUCTURES!

- CLASSIFICATION

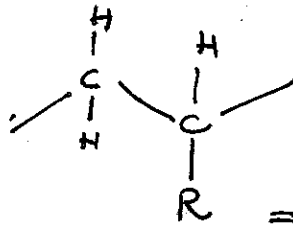


BA

if n small \Rightarrow polyethylene
 \downarrow
 HUNDREDS.
WAX OR PARAFFIN OR OIL

Degree of polymerization
 $n \sim 50K, 500K$
 MILLIONS

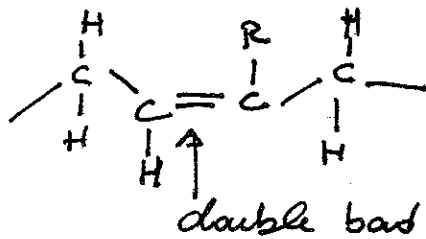
VINYL POLYMER



R = VINYL POLYMER

R = CH₃ \Rightarrow POLYPROPYLENE

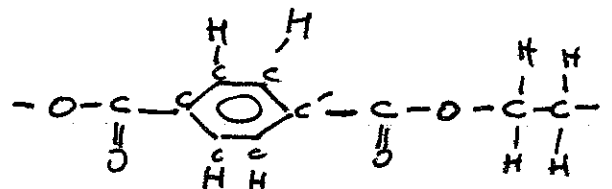
HYDROCARBONS RUBBERS (with double bond)



R = H POLYBUTADIENE

• POLYOLEFIN (with C & H only) = FAMILY
 if not only C in BACKBONE \Rightarrow

• POLYESTER ESTER $-O-C(=O)-$
 FAMILY
 PET
 POLYESTER



NYLON, DACRON, FORTREL,
 TERYLONE

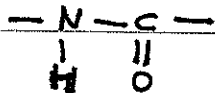
P5
 FILMS & FIBERS
 TRANSPARENT, PROJECTOR

AMIDE GROUP

● POLYAMIDES

OR NYLON

CARPET, SILK, WOOL,

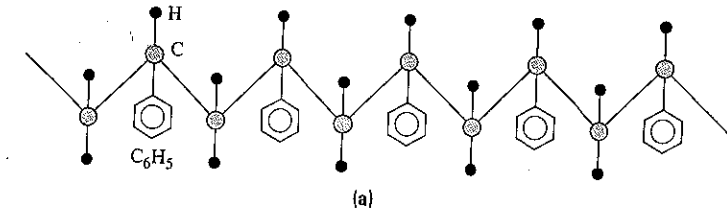
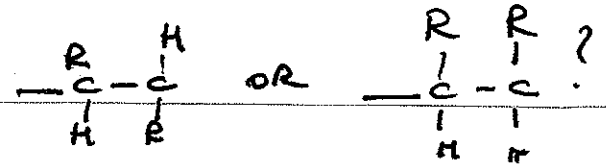


Polymer	Structure	Applications
Vinyls and related polymers		
Polyethylene	$CH_2=CH_2 \rightarrow [CH_2-CH_2]$	Clear film, flexible bottles
Polyvinylchloride	$CH_2=C \begin{array}{c} H \\ \\ Cl \end{array} \rightarrow [CH_2-C \begin{array}{c} H \\ \\ Cl \end{array}]$	Floors, pipes, hoses
Polystyrene	$CH_2=C \begin{array}{c} H \\ \\ \text{C}_6\text{H}_5 \end{array} \rightarrow [CH_2-C \begin{array}{c} H \\ \\ \text{C}_6\text{H}_5 \end{array}]$	Containers (clear or foam), toys
Polypropylene	$CH_2=C \begin{array}{c} H \\ \\ CH_3 \end{array} \rightarrow [CH_2-C \begin{array}{c} H \\ \\ CH_3 \end{array}]$	Sheet, pipe, film, containers
Polyacrylonitrile	$CH_2=C \begin{array}{c} H \\ \\ C \equiv N \end{array} \rightarrow [CH_2-C \begin{array}{c} H \\ \\ C \equiv N \end{array}]$	Fibers—synthetic wool
Polytetrafluoroethylene (Teflon)	$CF_2=CF_2 \rightarrow [CF_2-CF_2]$	Nonstick coatings, gaskets, seals
Polymethylmethacrylate (Plexiglas)	$CH_2=C \begin{array}{c} CH_3 \\ \\ C=O \\ \\ O-CH_3 \end{array} \rightarrow [CH_2-C \begin{array}{c} CH_3 \\ \\ C=O \\ \\ O-CH_3 \end{array}]$	Lenses, transparent enclosures, windows
Rubbers		
Polybutadiene	$\begin{array}{c} H & H & H & H \\ & & & \\ C=C & -C=C & -C=C & -C=C \\ & & & \\ H & H & H & H \end{array} \rightarrow [C \begin{array}{c} H \\ \\ C=C \\ \\ H \end{array} - C \begin{array}{c} H \\ \\ C=C \\ \\ H \end{array}]$	Tires and molded parts
Polyisoprene (natural rubber)	$\begin{array}{c} H & H & CH_3 & H \\ & & & \\ C=C & -C=C & -C=C & -C=C \\ & & & \\ H & H & H & H \end{array} \rightarrow [C \begin{array}{c} H \\ \\ C=C \\ \\ H \end{array} - C \begin{array}{c} H \\ \\ C=C \\ \\ H \end{array}]$	Tires and gaskets
Polychloroprene	$\begin{array}{c} H & H & Cl & H \\ & & & \\ C=C & -C=C & -C=C & -C=C \\ & & & \\ H & H & H & H \end{array} \rightarrow [C \begin{array}{c} H \\ \\ C=C \\ \\ H \end{array} - C \begin{array}{c} H \\ \\ C=C \\ \\ H \end{array}]$	Belts, bearings, and foams
Polydimethylsiloxane (silicone rubber)	$\begin{array}{c} CH_3 & & HCl \\ & & \\ Cl-Si-Cl & - & H-O-H \\ & & \\ CH_3 & & \end{array} \rightarrow [Si \begin{array}{c} CH_3 \\ \\ Si-O \\ \\ CH_3 \end{array}]$	Gaskets, insulation, and adhesives

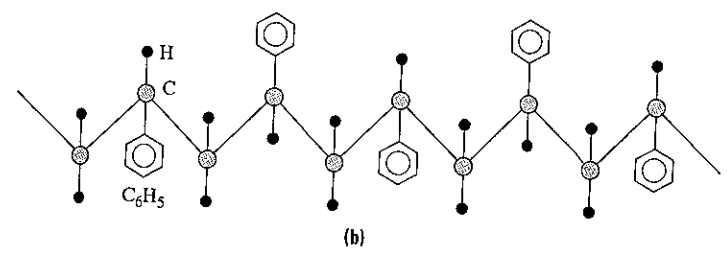
Polymer	Structure	Applications
Polyesters Polyethyleneterephthalate (Thermoset variation)	$\text{H}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H} + \text{H}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{H}$ $\xrightarrow{-\text{H}_2\text{O}}$ $\left[\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\text{CH}_2 \right]_n$ $\text{H}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H} + \text{H}-\text{O}-\text{CH}_2-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2-\text{O}-\text{H}$ $\xrightarrow{-\text{H}_2\text{O}}$ $\left[\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2 \right]_n$	Films (magnetic tape), fibers, and clothing Boat and auto body parts (fiberglass), helmets, and chairs
Polyamides Nylon 6,6 Kevlar, or poly p-phenyleneterephthalamide (PPTA)	$\text{H}-\text{N}-(\text{CH}_2)_6-\text{N}-\text{H} + \text{H}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$ $\xrightarrow{-\text{H}_2\text{O}}$ $\left[\text{N}-(\text{CH}_2)_6-\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O} \right]_n$ $\left[\text{N}-\text{C}_6\text{H}_4-\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O} \right]_n$	Carpets, parachutes, rope, gears, insulation, and bearings Fibers, bulletproof vests
Other common polymers Polyacetal Polycarbonate Phenolformaldehyde Polyurethane Epoxy	$\text{H}-\text{C}(\text{H})-\text{O} \rightarrow \left[\text{C}(\text{H})-\text{O} \right]_n$ $\text{H}-\text{O}-\text{C}_6\text{H}_4-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{O}-\text{H} + \text{H}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$ $\xrightarrow{-\text{HCl}}$ $\left[\text{O}-\text{C}_6\text{H}_4-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}} \right]_n$ $\text{H}-\text{C}_6\text{H}_4-\text{OH} + \text{H}-\text{C}_6\text{H}_4-\text{OH} + \text{H}-\text{CHO} \xrightarrow{-\text{H}_2\text{O}}$ $\left[\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{O} \right]_n$ $\text{H}-\text{O}-\text{R}-\text{O}-\text{H} + \text{H}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-\text{R}-\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{H}$ $\xrightarrow{-\text{H}_2\text{O}}$ $\left[\text{O}-\text{R}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-\text{R}-\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O} \right]_n$ $\text{H}-\text{O}-\text{R}-\text{O}-\text{H} + \text{H}-\text{C}(\text{H})_2-\text{CH}_2-\text{Cl}$ $\xrightarrow{-\text{HCl}}$ $\left[\text{O}-\text{R}-\text{O}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\text{CH}_2 \right]_n$	Gears and machine parts Lenses, helmets, lamp casings, machine parts Castings, (motor and telephone), electrical components, distributor caps Foam, sheet and tubing, in-line skate wheels Adhesives, used in composites

P7

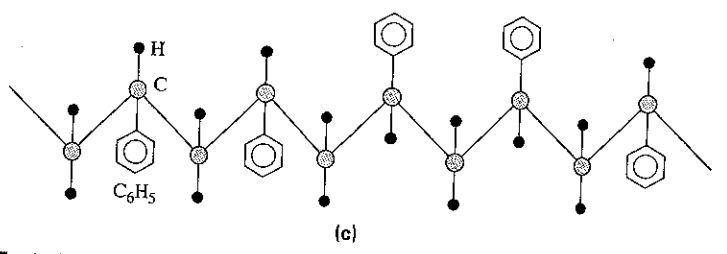
Relation with adjacent groups



ISOTACTIC



SYNDIOTACTIC



ATACTIC

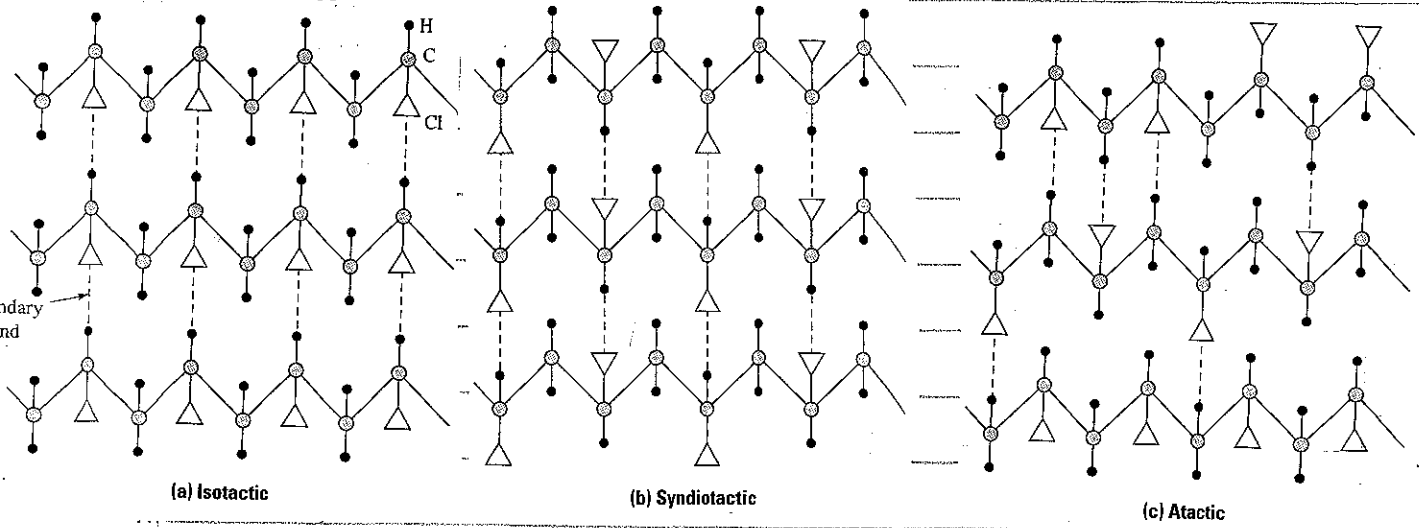
Random.

it's decided during

production

FIGURE 6.4-5 A planar illustration of the (a) isotactic, (b) syndiotactic, and (c) atactic configurations of polystyrene. Note: The C₆H₅ rings are actually much larger than indicated in these sketches.

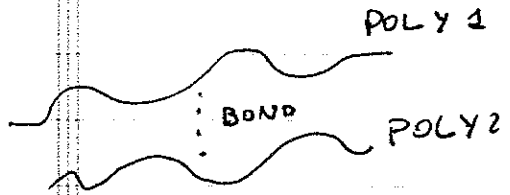
TACTICITY (STEREOCHEMISTRY) ~~is~~ depends on polymer function
 (can be modified randomly at HIGH TEMP)
 because they affect secondary bonds:



P11

⇒ CRYSTALS?
 Some do!

THERMO PLASTIC & THERMOSET



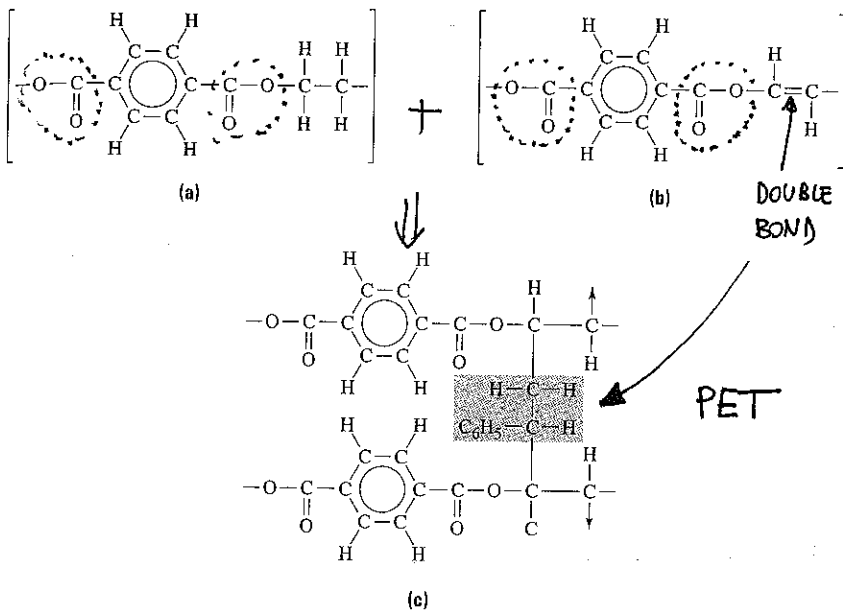
BOND: 1) secondary; (VDWALS, DIPOLE) \Rightarrow weak, can be destroyed by Temperature $\Rightarrow T \uparrow \Rightarrow$ polymer melts
THERMO PLASTIC (TP)

2) primary \leftarrow 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



PHENOL FORMALDEHYDE (BAKELITE)

PHENOL FORMALDEHYDE (BAKELITE) \Rightarrow POLYMER SURFACE

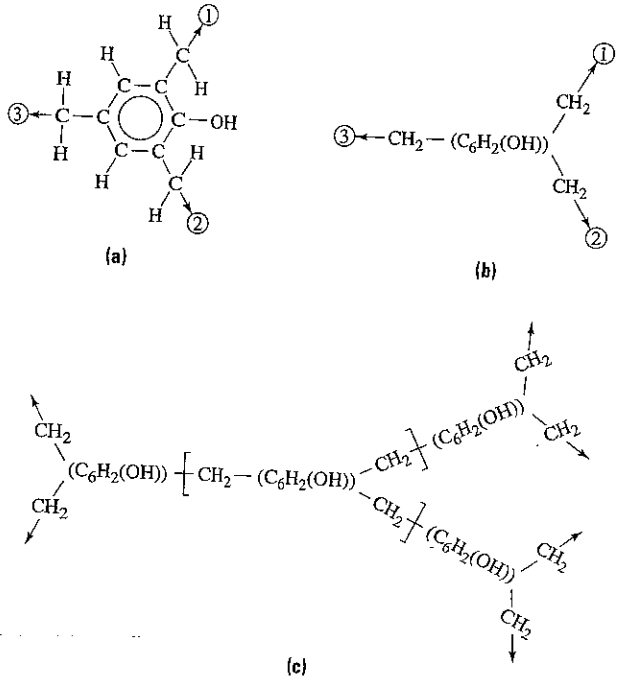


FIGURE 6.4-2
The structure of the TS polymer phenol formaldehyde (Bakelite®) showing: (a) the basic building block for the structure (the numbers 1-3 correspond to the three sites for primary bond formation with neighboring monomers), (b) a simplified representation of the basic building block, and (c)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

CELLULOSE

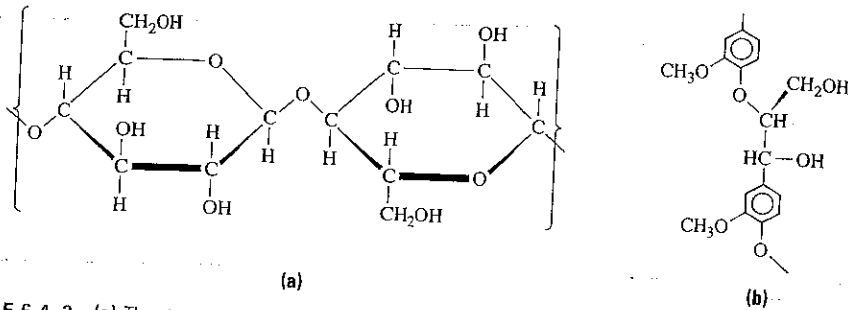
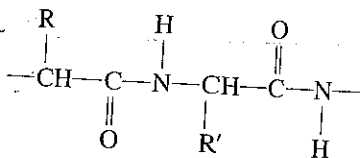


FIGURE 6.4-3 (a) The structure of cellulose, and (b) schematic of the structure of lignin.

PROTEINS



DIFFERENT

R & R' moieties

different amino acids!

MOLECULAR WEIGHT

1 mer = m
 & degree of polymerization n } $(MER)_n \Rightarrow M = mn$

if a bunch of different polymers \bar{M}
 \Rightarrow different molecular weights \Rightarrow

$N_i = \#$ of polymers with weight $M_i \Rightarrow$

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

different definitions:

$w_i =$ total weight of polymers with weight $M_i \Rightarrow w_i = N_i M_i$

$$\Rightarrow \bar{M}_w = \frac{\sum w_i M_i}{\sum w_i}$$

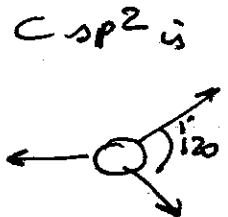
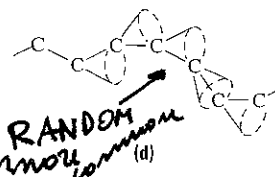
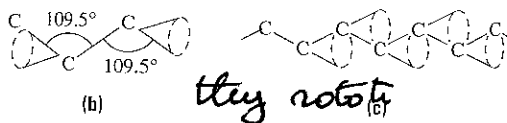
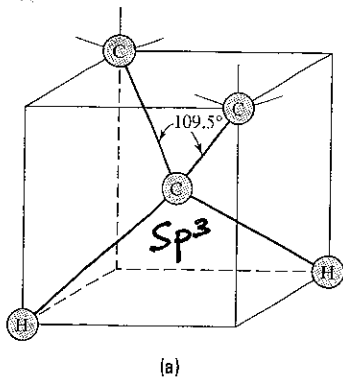
$$PD = \bar{M}_w / \bar{M}_n$$

Polydispersity ~ 2 to 20

$PD = 1.0 \Rightarrow$ all same polymers.

POLYMERS CONFIGURATION

very rarely they are linear —X—
 usually KINKED :



P10

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 Pol.

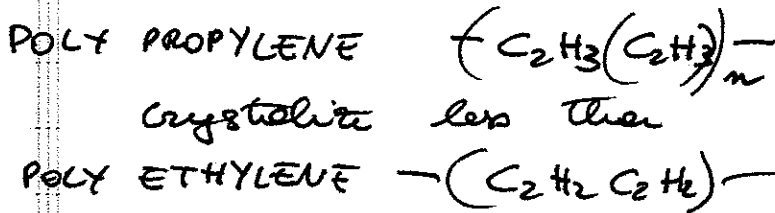
THERMOPLASTIC partially crystallize

→ go T↑ and cool slowly.

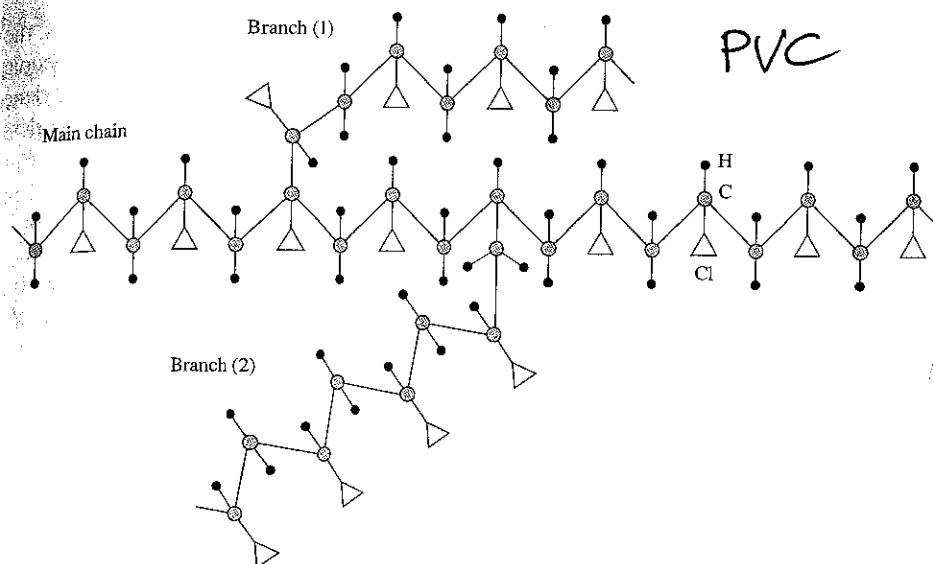
CRYSTALLIZATION DEPENDS ON

- 1) SIZE OF SIDE GROUPS (R)
 - 2) EXTENT OF BRANCHING
 - 3) TACTICITY
 - 4) COMPLEXITY OF MER
 - 5) TYPE OF SECONDARY BONDS (DIPOLE OR VDW)
- DEFECTS.

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



2) BRANCHING



More branches
less crystal!
small concentration
of branches



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 boxes

3) TACTICITY affects crystallization

Atactic (random) with big side groups cannot ~~only~~ only be packed.

It's easier to pack ~~isotactic~~ ISOTACTIC (-H H H H)
and SYNDIOTACTIC (-H H H H H H)

⇒ this influences properties.

EX: POLYPROPYLENE ^{ISOTACTIC} (~50% crystalline) = HARD & RIGID

POLYPROPYLENE ATACTIC (~0% crystalline) = USELESS
gummy substance

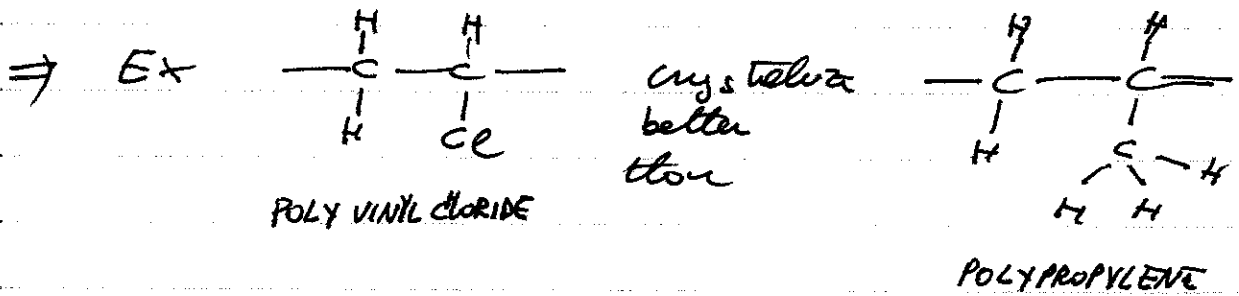
4) COMPLEXITY OF MER

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

↓
⇒ they crystallize slowly.
then short mer

5) TYPE OF SECONDARY BONDS

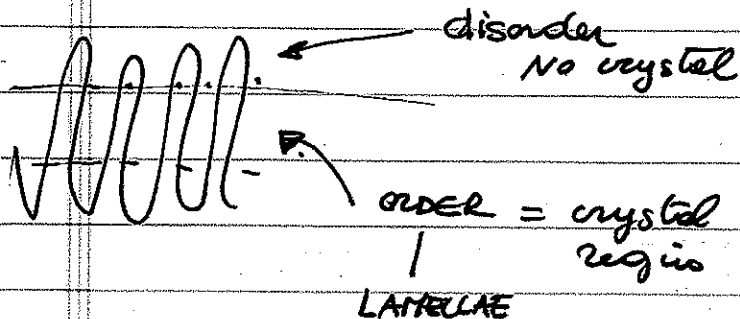
existence of small space polar side groups
helps formation of crystals



⇒ PVC stronger than PP

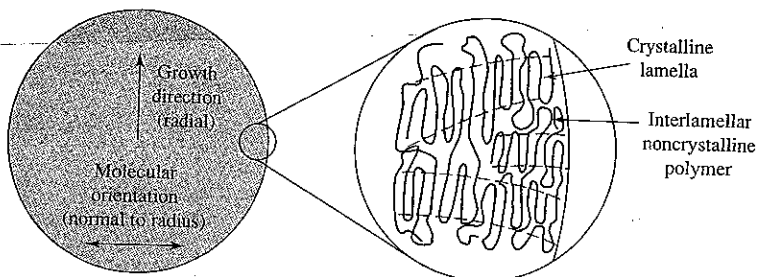
SEMICRYSTALLINE POLYMER

polymers = long spagetti need to roll up

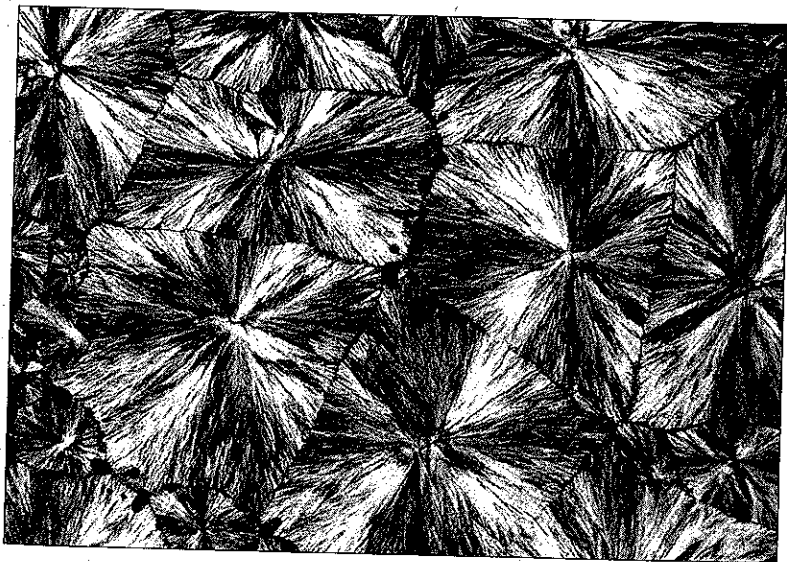


~~SPEER~~ SPHERULITE
= AGGLOMERATE OF
LAMELLAE

+ INTERLAMELLAR NONCRYSTALLINE
POLYMER



(a)



(b)

SEMI CRYSTAL



✓ DEGREE OF
CRYSTALLINITY

= % of the
polymer that
is crystalline

(METAL, CERAMICS $\sim 99\%$)

POLY ~ 90 to 95%

non crystal $\sim 0\%$

T_g vs. T_m

Simple rule: longer MERs, HEAVIER side groups
 \Rightarrow ~~higher~~ ^{increase} T_g (RUBBER simple and light)
 because you need higher T to get the "motion" going on.

in ADDITION Symmetric MER (C₂H₄ PE for instance)
 $T_g \sim \frac{T_m}{2}$

Asymmetric MER (-C₂H₃Cl PVC)
 $T_g \sim T_m \frac{2}{3}$

It's an entropy EFFECT (Symmetric MER HAS ONE MORE DEGENERATION $\rightarrow S = k \log R$ is \downarrow for symmetric !!)

TABLE 6.5-3 Observed melting and glass transition temperatures for selected polymers.

Polymer	T _m (°C)	T _g (°C)
High density polyethylene	137	-120
Polyvinylchloride	—	87
Polypropylene	170	-16
Polystyrene	240	110
Polyacrylonitrile	320	107
Polytetrafluoroethylene	327	—
Polychlorotrifluoroethylene	220	—
Polymethylmethacrylate	—	100
Acetal	181	-85
Nylon-6,6	265	50
Cellulose acetate	230	—
Polycarbonate	230	145
Poly(ethylene terephthalate)	255	90
Silicone	—	-123
Polybutadiene	120	-90
Polychloroprene	80	-50
Polysoprene	30	-73

GLASSES

STRUCTURE & PROPERTY

take a piece of a window \Rightarrow X-RAY, wait it becomes

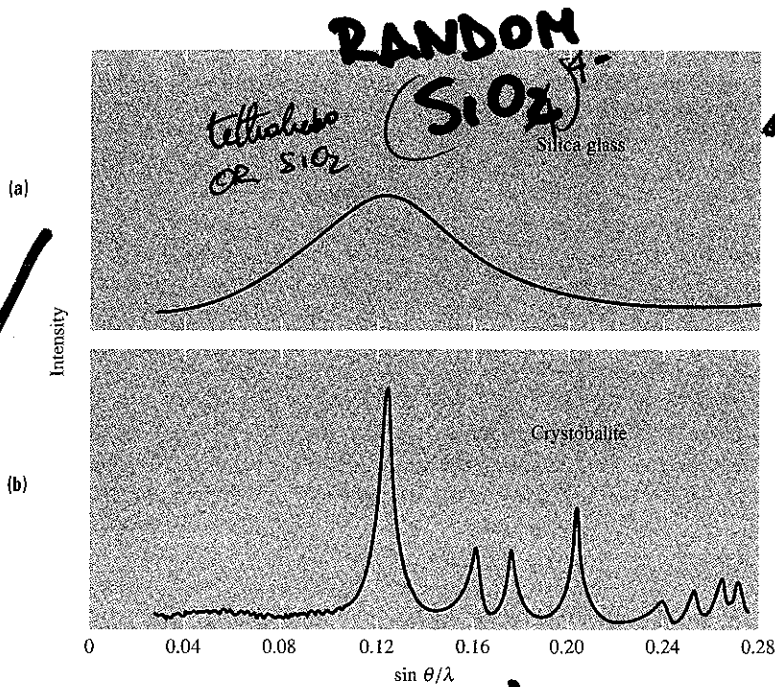


FIGURE 6.5-1

A comparison of the X-ray scans for (a) amorphous silica and (b) a crystalline polymorph of silica (cristobalite). (Source: Adapted from B. E. Warren and J. Biscoe, Journal of American Ceramic Society, 2149, 1938.)

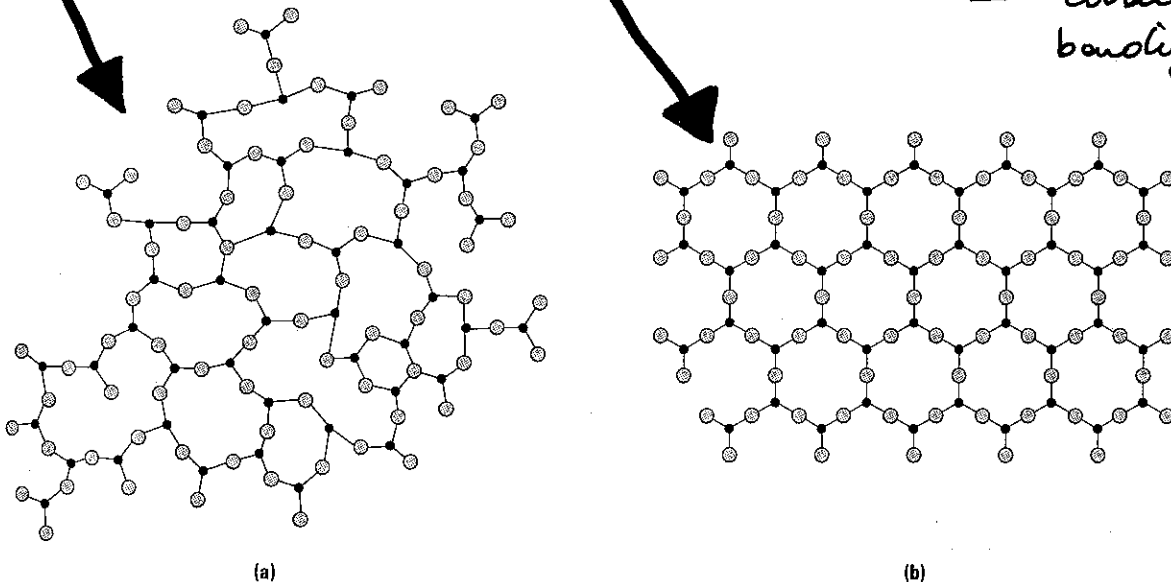


FIGURE 6.5-2 The 2-D representations of (a) silica glass and (b) a crystal of silica.

crystalline

Silica glass = covalent bonding

Glass: variety of materials (AMORPHOUS) \equiv RANDOM
 \neq metal, ionic & covalent

REQUIREMENT: MATERIAL MUST BE COOLED FROM LIQUID PHASE, RAPIDLY ENOUGH TO "FREEZE" THE LIQUID PHASE, AND KINETIC TO OF CRYSTALLINE PHASE MUST BE SLOW SO THE SYSTEM DOES NOT ~~BE~~ BECOME ORDERED FAST,

(MELT MUST BE VISCOUS)

TABLE 6.5-1 Glass-forming systems.

Elements:	S, Se, P
Oxides:	B ₂ O ₃ , SiO ₂ , GeO ₂ , P ₂ O ₅ , As ₂ O ₅ , Sb ₂ O ₃ , In ₂ O ₃ , SnO ₂ , PbO ₃ , and SeO ₂
Halides:	BeF ₂ , AlF ₃ , ZnCl ₂ , Ag(Cl, Br, I), Pb(Cl ₂ , Br ₂ , I ₂), and multicomponent mixtures
Sulfides:	As ₂ S ₃ , Sb ₂ S ₃ , CS ₂ , and various compounds of B, Ga, In, Te, Ge, Sn, N, P, and S
Selenides:	Various compounds of Tl, Sn, Pb, As, Sb, Bi, Si, and P
Tellurides:	Various compounds of Tl, Sn, Pb, As, Sb, Bi, and Ge
Nitrides:	KNO ₃ -Ca(NO ₃) ₂ and many other binary mixtures containing alkali and alkaline earth nitrates
Sulfates:	KHSO ₄ and other binary and ternary mixtures
Carbonates:	K ₂ CO ₃ -MgCO ₃ ← STATUES
Polymers:	Polystyrene, polymethylmethacrylate, polycarbonate, polyethylene terephthalate, and nylon
Metallic alloys:	Au ₂ Si, Pd ₂ Si, (Fe-Si-B) alloys

OXIDES

Source: Robert H. Doremus, *Glass Science*, 1st ed., Copyright © 1973 by John Wiley & Sons. Reprinted by permission of John Wiley & Sons, Inc.

IONIC GLASSES

If IONIC COMPOUND CAN LIVE IN A DISORDERED STATE,
 \Rightarrow 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

NEED NETWORKS: METAL + OXYGEN.

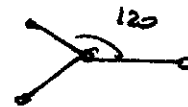
- 1) OXIDE GLASS NETWORKS ARE COMPOSED OF OXYGEN POLYHEDRA → METAL + OXYGEN
- 2) COORDINATION OF OXYGEN IS 2! $CN(O) = 2 \Rightarrow O^{2-}$
- 3) COORDINATION OF METAL IS 3 OR 4

$CN(M) = 4 \Rightarrow$ TETRAHEDRA $(SiO_4)^{4-}$
 or SILICA (SiO_2)

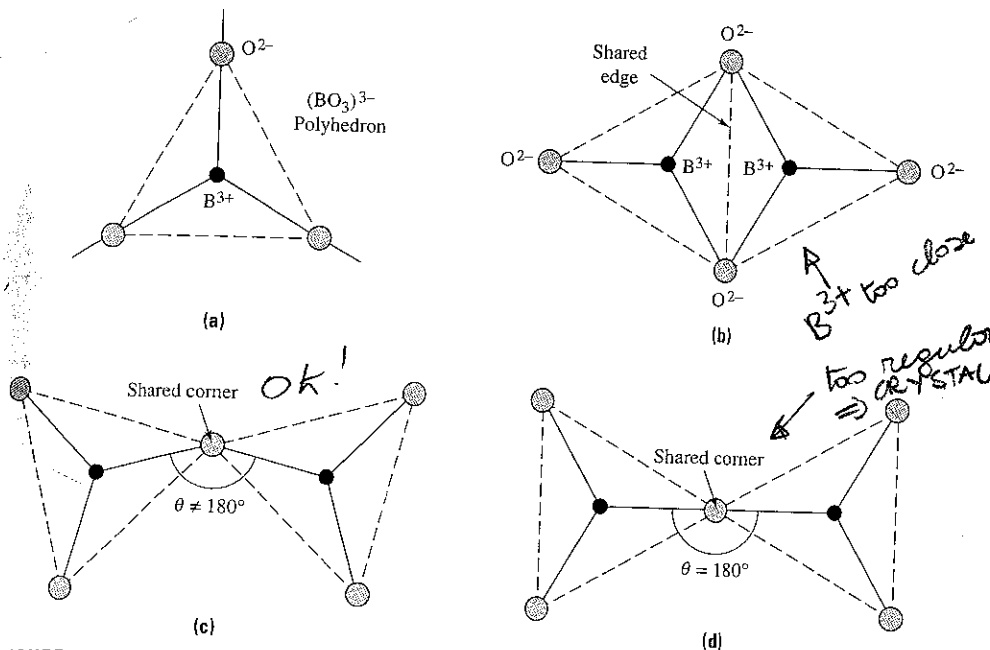


$CN(3) = 3 \Rightarrow$ TRIANGLES Li^+
 LIKE $(BO_3)^{3-}$ or B_2O_3 & Boron oxide

- 4) OXYGEN POLYHEDRA SHARE CORNERS, NOT EDGE OR FACE (TO MINIMIZE METAL+ REPULSION!!)



- 5) EACH POLYHEDRA SHARES at least 3 CORNERS



RANDOM NETWORK
 ⇒ FORMERS

FIGURE 6.5-3 The structure of amorphous B_2O_3 : (a) the basic building block, a triangular polyhedron $(BO_3)^{3-}$; (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 ~~still~~ oxide glasses!

what about covalent glasses:?

MUST BE POLYMERS, with & have $T_g > T_{room}$

& must be able to

COOL DOWN FAST &

Must have viscous melt,

GLASS = NO DEFECTS

ISOTROPY

TABLE 6.5-3 Observed melting and glass transition temperatures for selected polymers.

Polymer	T_m (°C)	T_g (°C)
High-density polyethylene	137	-120
Polyvinylchloride	—	87
Polypropylene	170	-16
Polystyrene	240	110
Polyacrylonitrile	320	107
Polytetrafluoroethylene	327	—
Polychlorotrifluoroethylene	220	—
Polymethylmethacrylate	—	100
Acetal	181	-85
Nylon 6,6	265	-50
Cellulose acetate	230	—
Polycarbonate	230	145
Poly(ethylene terephthalate)	255	90
Silicone	—	-123
Polybutadiene	120	-90
Polychloroprene	80	-50
Polyisoprene	30	-73

SEMICONDUCTORS: usually

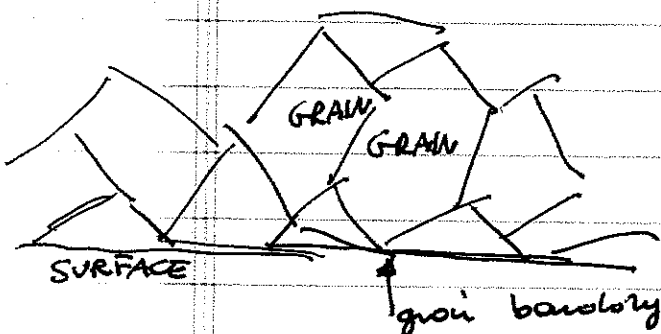
build from crystals (reduce defects to increase μ),

but when μ is not a problem, then we can use

amorphous semiconductors

EXAMPLES: solar cells, need

surface \Rightarrow very expensive Si crystalline, but amorphous Si works fine & no grain boundaries which are the places where corrosion starts!!



© surface \Rightarrow start corrosion

METALLIC GLASSES

metals are very fluid once melted

⇒ hard to remove heat fast

Removing 10^5K/s (huge) we can make max 20% glass of a metal material ⇒ 80% ^{crystalline} metal & 20% glassy ^{metal}!

⇒ ONLY SMALL PARTS & STRIPS & RIBBONS & WIRES

DOPE WITH
IF I ~~NEED~~ A NON METAL OR BAD METAL

Au-Si (80 & 20), Fe-Si-B (78, 9, 13) ⇒ then the 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 ⇒

1) strong against corrosion

2) isotropic properties (used for magnetic applications)

METALLIC FOAMS

increase temperature, melt, and decrease fast while bubbling with inert gas ⇒ METALLIC FOAMS, LIKE SPONGES

USED FOR BIOMATERIALS ⇒ STRONG & ADSORBENT & LIGHT
(BONES) ↑ good ↑ tissue ↑ good

RUBBERS & ELASTOMERS

it's when $T_g < T_{room}$, but NOT ONLY

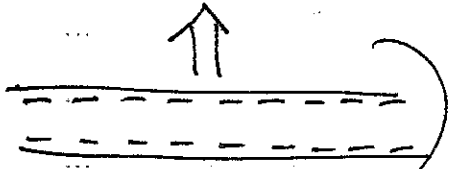
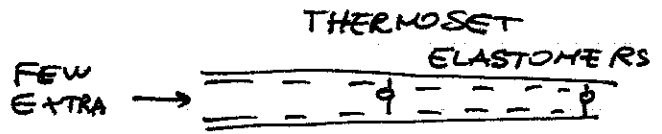
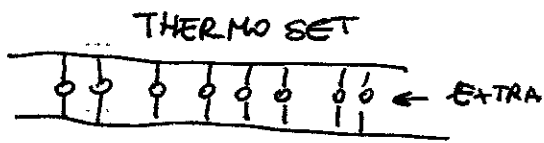
REMEMBER

THERMOPLASTIC \Rightarrow NO secondary bonds, \Rightarrow when $T > T_g$ VISCOSITY DEFORMABLE

THERMOSET \Rightarrow PLENTY OF ~~secondary~~ ^{double} bonds $\Rightarrow T > T_g$ get cross linked!! and material gets strong

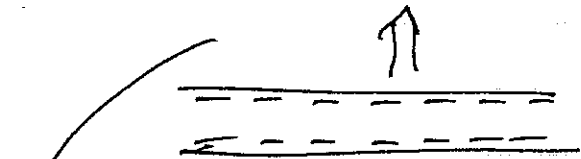
THERMOSET ELASTOMER

\Rightarrow low few available bonds to make few cross links



MUCH CROSS LINKING (1/10)

HEAVY BRITTLE STIFF



LITTLE CROSS LINKING (1/1000) (1/100000)

SOFT, RUBBER, RUBBER BAND STYLE!!

CONTROLLING CONCENTRATION OF "EXTRA"
WE CAN CONTROL FINAL PRODUCT

MEDIUM (1/100)
~ TIRES FOR CARS!

THERMOSET ELASTOMERS DO NOT REALLY MELT,
THEY GET STIFFER & THEN BURN!

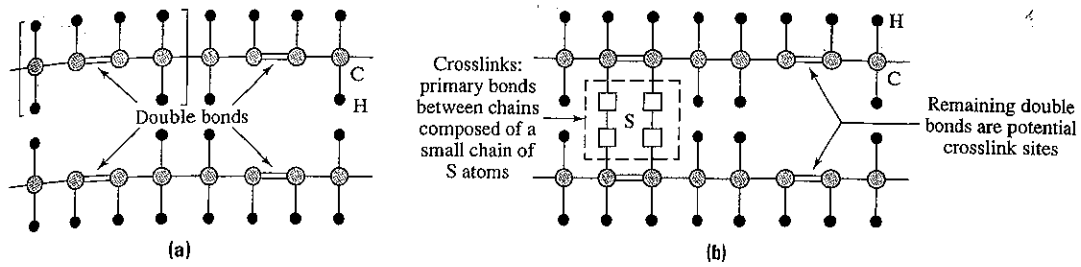
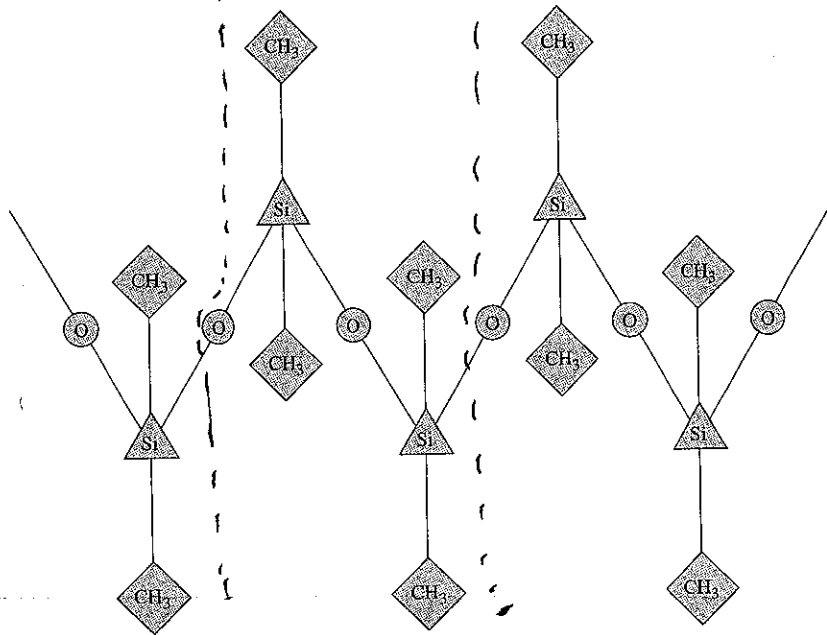


FIGURE 6.6-1 The structure of polybutadiene: (a) as a thermoplastic polymer, and (b) as a crosslinked rubber.



↑ SILICONE RUBBER (CAULKING COMPOUNDS)
 POLY DIMETHYL SILOXANE
 Si + Oxygen

THERMOPLASTIC ELASTOMERS

when thermoplastic is heated, becomes viscous: loses shape

⇒ How can we fix the shape and make it elastic?

⇒ NEED TO FIGHT VISCOSITY KEEPING ELASTICITY

BLOCK COPOLYMERS!!

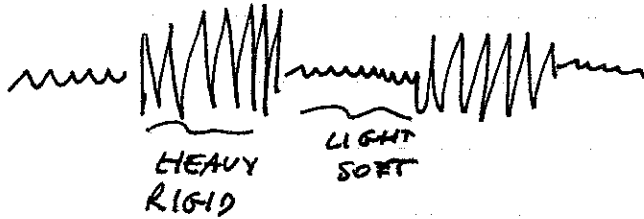


A N_A times

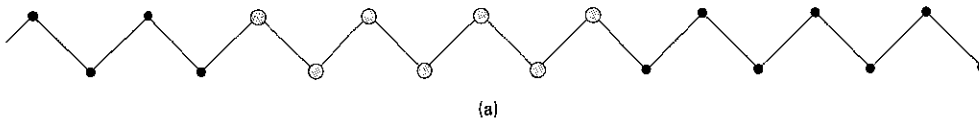
B N_B times

KEEP FLEXIBLE
& NOT CROSS LINKED!
⇒

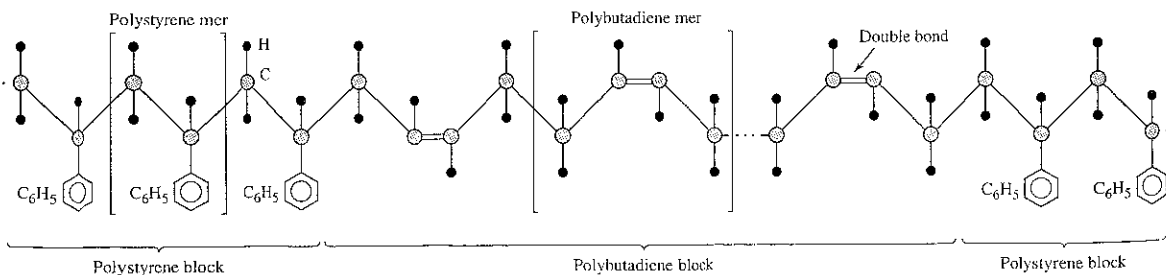
DOUBLE BONDS (UNSATURATED)
SO IT MAKES CROSS LINKS
& GETS HARD & RIGID



⇒ ELASTIC &
When high temperature melts because the light & soft mers (no secondary bonds) but at lower temperature is elastic



(a)

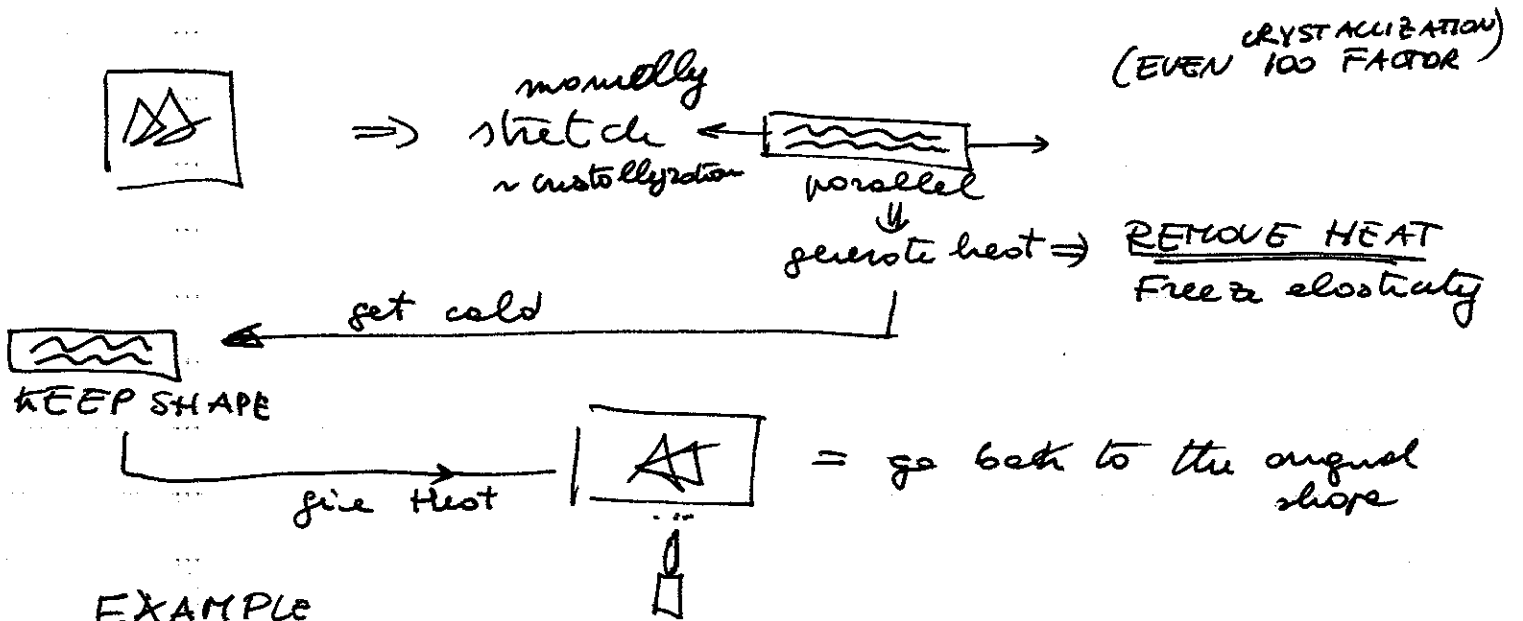


(b)

can decide property with size of blocks!

FIGURE 6.6-3 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



EXAMPLE

THERMO SHRINKING MATERIALS !!

usefull in electronics
PIPES that shrink with
heat gun !!

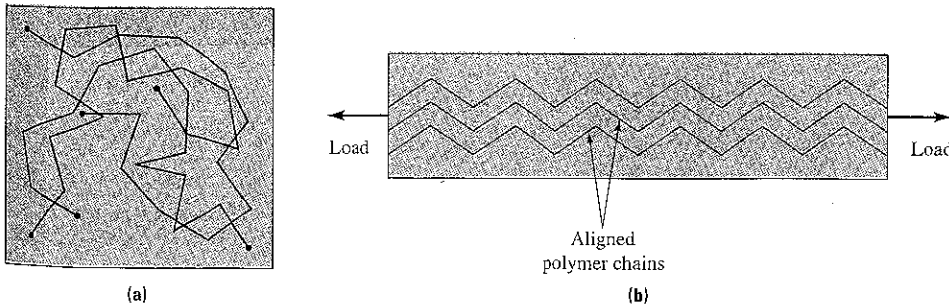
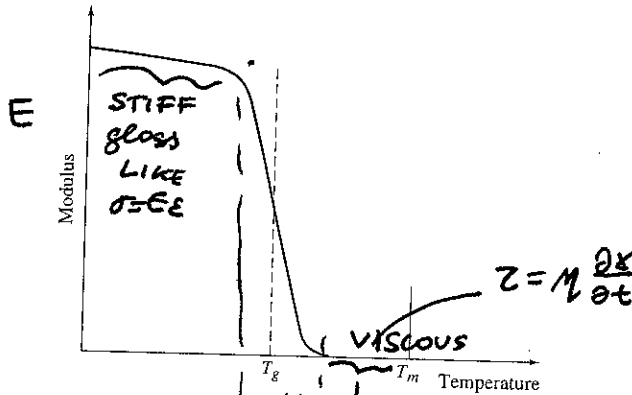


FIGURE 6.6-4 Changes in polymer structure as a result of an applied load: (a) unaligned chains in an unloaded polymer, and (b) chains aligned under an applied load.

YOUNG'S MODULUS & TEMP

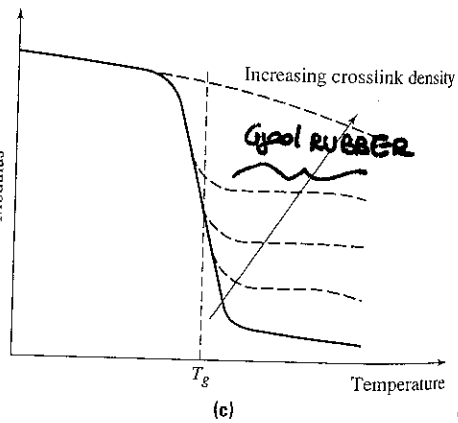
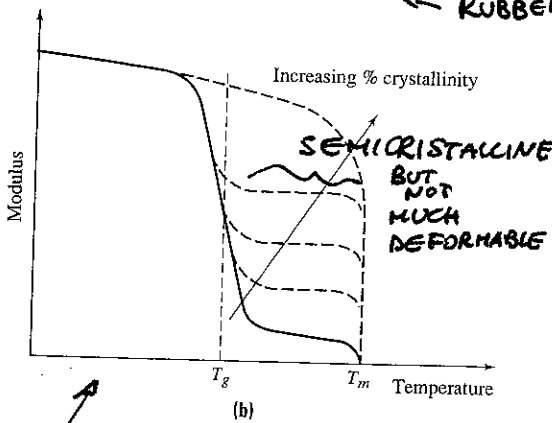
$$\sigma = E \epsilon$$

$$E(t)$$



TOO NARROW ← RUBBER

VISCOSITY
NEWTON LAW'S



GOOD RUBBER
MODERATE CROSS-LINK,
BUT NO VISCOSITY!!

FIGURE 6.6-5 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.

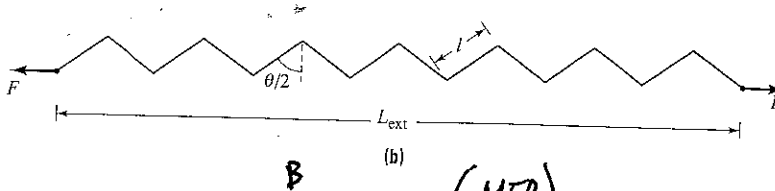
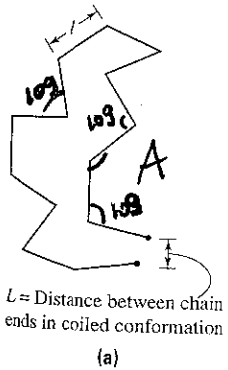
→ EPOXIES & PHENOLICS

with semicrystalline and cross-link density the glossy transition "disappears", softens!!

RUBBER ELASTICITY

ELASTOMERS. = stretch 10 times and come back to original shape !!

How? stretching original fiber directions



(MER) ~~1000~~ m
↑
number of L

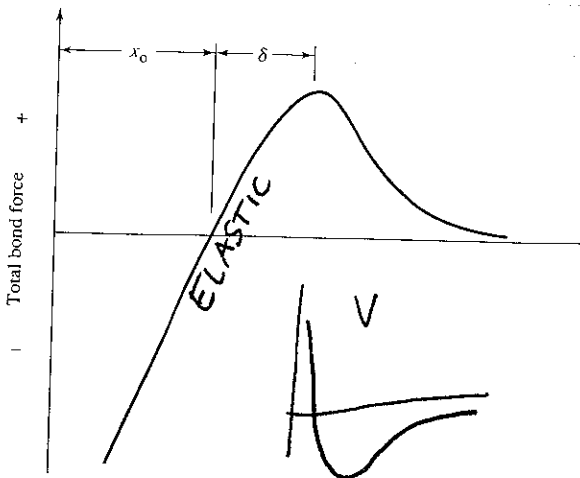
FIGURE 6.6-6 A comparison of (a) the random coil conformation of an unstretched rubber, and (b) the stretched, or planar zigzag, conformation in which the separation distance between the chain ends is maximum.

Stretch A to get B

Reorientation of bond directions!

S_A & S_B (which is bigger)
PRODUCE OR ADSORB HEAT?

No elongation of bonds \Rightarrow $\Delta U \approx 0$ No
Therefore ELASTIC ENERGY, ~~heat~~ does not go
in bond stretching but in ENTROPY CHANGE



← FROM BOND STRETCHING
ONLY FEW %

now all logs of $c \frac{c}{l} c$ are along the same direction!!!

$\Rightarrow L_{ext} = m l \cos\left(\frac{\theta}{2}\right)$ for extended

$L_{COILED} \approx l \sqrt{m} \frac{1 + \cos\theta}{1 - \cos\theta}$

$L_{COILED} \ll L_{EXT}$

$m \gg 1 \Rightarrow \sqrt{m} \gg 1$

Max stretch = $\frac{L_{EXT} - L_{COIL}}{L_{COIL}} = \frac{L_{EXT}}{L_{COIL}} - 1 \approx 1.15 \sqrt{m} = \text{HUGE}$

$m \approx 10^2 - 10^5$

Max stretch ~ 10 to 300 times

~~mx~~

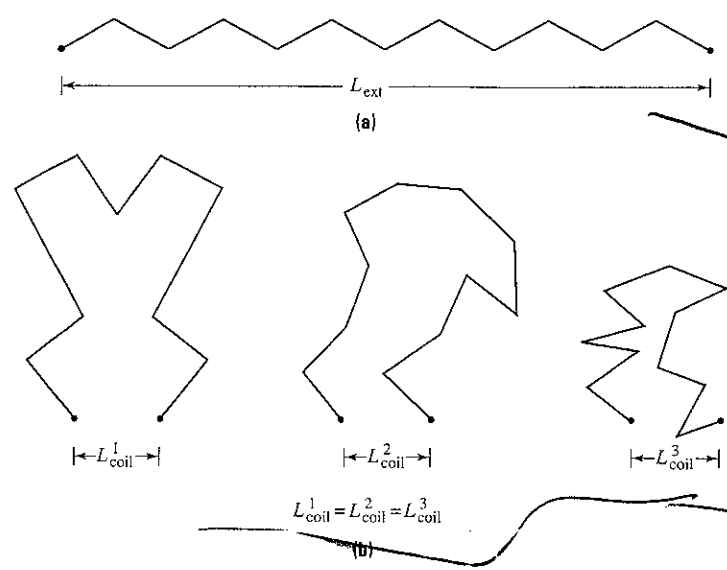
HUGE

all elastic energy goes in uncoiling.

ENTROPIC EFFECT

$S = k \log \Omega(E)$

of configurations with Energy E



1 confi
 $S \approx 0$

many conf

$S = \text{HIGH}$

on stretching $S \downarrow$

$\Rightarrow T \Delta S \rightarrow \Delta Q$ produced

FIGURE 6.6-8 A comparison of the number of equivalent conformations for (a) the planar zigzag conformation and (b) a partially coiled chain.

P27

ELASTOMERS SHRINK UPON HEATING