Gowariker

The Genesis of Polymers.

— Life is based on protein polymers, wood, starch, cellulose, etc

— 15th Century

- Christopher Columbus
- natives of south america played a bouncing game with a solid mass collected from the exudate of a tree, which they called 'weeping wood'.

— Joseph Priestly.
showed that the solid mass could rub off pencil marks from paper — hence rubber.

— Christian Schonbein used cotton cloth to wipe (nitric acid + sulphuric acid) mixture. When ~~te~~ washed & left to dry near the fire place, it caught fire — discovery of 'gun cotton' or nitro derivative of polymer cellulose.

— mid - 19th century
Elephant tusks were used to make billiard balls. They became scarce.
James W Hyatt of New York developed 'celluloid' balls using heat & moulds.

- 19th century. Leo Baekeland found that certain materials were sticking to glass beakers. He found that phenol & formaldehyde could be used to produce a resin called Bakelite (after his name.).

1912 Jacques Brandenburger produced Cellophane.

Properties.

- High strength
- Light weight
- good flexibility
- special electrical properties
- resistance to chemicals,
- amenability for quick & mass production
- ~~fabrica~~ ,, ,, fabrication into complex shapes in a wide variety of colours.

Polymers can be converted into strong solid articles, flexible rubber-like masses, soft and resilient foams, smooth & fine fibres, clean and clear glass like sheets, swollen jelly like food materials, ~~et~~ and so on.

They can be used to bond objects seal joints, fill cavities, bear loads ~~and so on~~, make clothes, power spacecrafts, replace human organs, and so on.

What are polymers

- Complex & giant molecules different from low molecular weight compounds eg. common salt (58.5)

Polymer → can be several hundred thousands.

- These big molecules ~~of~~ or macromolecules are made up of much smaller molecules.
- The small molecules can be of one or more chemical compounds.

Rings of same size (representing molecules of same chemical)

Rings of different sizes (representing molecules of different chemicals

chains made of interlinked rings (representing polymer molecules)

The interlinking of many (poly) units ~~&~~ or parts (mer) = Polymer (Greek)

A gaseous compound called butadiene with a molecular weight of 54 combines nearly 4000 times to form Polybutadiene — synthetic rubber.

butadiene + butadiene + ... → Polybutadiene (Synthetic rubber)
4000 times

Contrast

~~One can thus see how.~~ 54 × 4000 = 200,000 mol. wt

Low M.W

$$\text{Benzene (solid)} \xrightarrow{5.5^\circ C} \text{benzene (liquid)} \xrightarrow{80^\circ C} \text{benzene (gas)}$$

~~Bs~~ ∴ behaviour on heating is well defin

Polymer

Polyethylene – does not melt sharply at one particular temp. into a clean liquid.

$$\text{solid polyethylene} \xrightarrow{\Delta} \text{Molten polyethylene} \xrightarrow{\Delta} \text{Various decomposition products, but not PE}$$

It becomes increasingly softer & turns into a very viscous and tacky (like paint, glu molten mass. Further heating converts it into various gases.

Another striking difference between the behavi of a polymer & that of a low molecular wt. compound concerns their solubility pattern

Add NaCl to ~~water~~ a fixed quantity of water. The salt which has low Mol. wt. dissolves in water upto a saturation point ∴ More additions settle at the bottom. The viscosity

~~The vis of salt so~~

of saturated salt solution is not very much different from that of water. But if we take polymer instead, say polyvinyl alcohol & add it to ~~water~~ a fixed quantity of water, the polymer does not go into solution immediately. The globules of PVA first absorb water, swell and get distorted in shape & after a long time go into solution. Also we can add a very large quantity of the polymer to the same quantity of water without the saturation point ever being reached. As more & more quantity of the polymer is added to the water, the time taken for the dissolution of the polymer obviously increases & the mix ultimately assumes a soft, dough like consistency. PVA never retains its original powdery nature in water ~~&~~ as the excess NaCl does in a saturated salt solution.

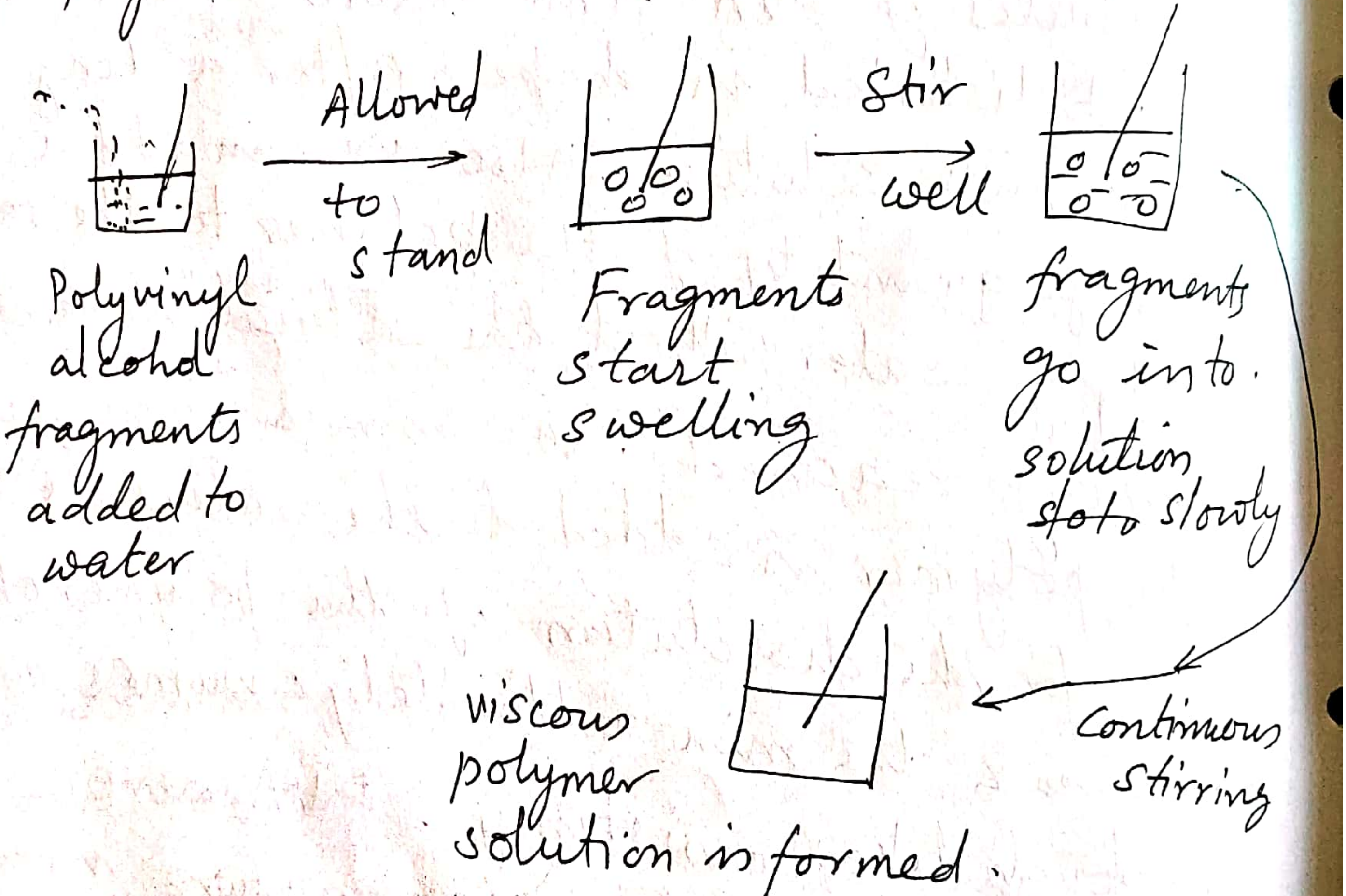
Conclusion :-

ⓐ the long time taken ~~to~~ by ~~polymer~~ polyvinyl alcohol for dissolution.

ⓑ the absence of a saturation point

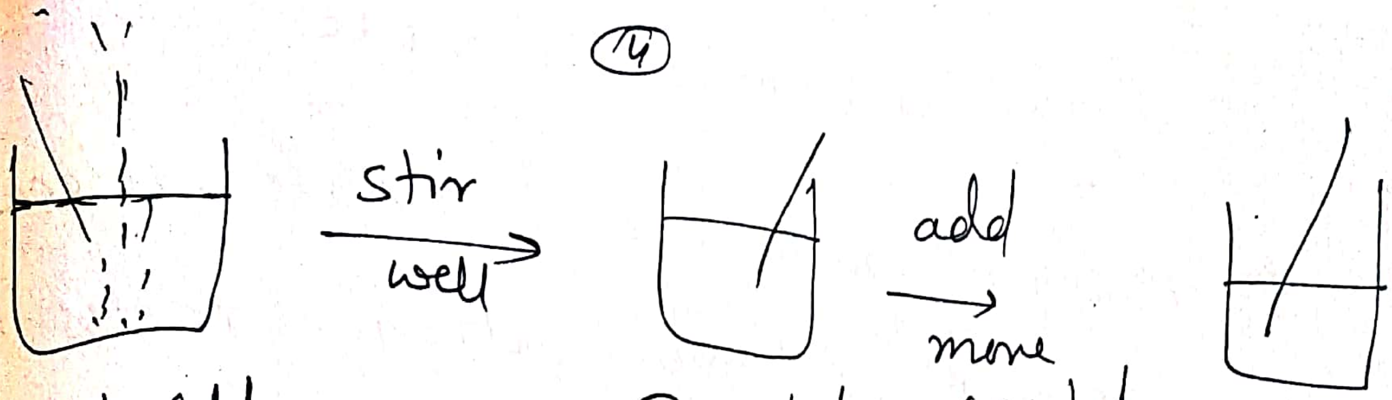
ⓒ the increase in the viscosity are all characteristics of a typical polymer being dissolved in a solvent ~~and these char~~

These characteristics are attributed ~~to~~ mainly to the large molecular size of the polymer.



Solution viscosity much higher than water viscosity

Polymer dissolution.



sod. Chl. crystals added to water.

Crystals go into solution
Solution viscosity not much different from water viscosity

saturated solution is formed.
Excess of crystals remains undissolved

NaCl dissolution

Difference in behaviour of a low mol. wt. compound (NaCl) and a polymer (polyvinyl ~~chlo~~ alcohol.)

How are polymers made

A polymer is made up of small molecules or monomers. Polymerization – process by which monomers are linked to form a large polymer molecule.

Two reactive sites (bifunctionality) of the monomer are pre requisites, for the molecular build up process to continue.

Polymerization is possible with molecules of the same or of different monomeric compounds. The monomer species in ~~this case~~ addition Polymerization retains its structural identity. Addition ~~meas~~ involves adding monomers to form a polymer.

$$\text{Ethylene} \xrightarrow{\text{Addition}} \text{Polyethylene.}$$

$$\text{Mol. wt} = M_1 \qquad = nM_1$$

Condensation Polymerization.

Molecules undergo some reaction in forming the polymer ~~app~~ apart from adding up. Two molecules ē same or different monomers condense to form a polymer.

Condensation takes place between two reactive functional groups, like the carbonyls group (of an acid) and hydroxyl group (of an alcohol). water molecules are eliminated

$5\,CH_2 = CH_2$ Ethylene monomer

Addition $\downarrow$ Polymerization

$- CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2$

① ② ③ ④ ⑤

or $\left[CH_2 - CH_2 \right]_5$ (Polyethylene molecule containing ⑤ repeat units of $-CH_2-CH_2-$)

DP=5

$4\ HO - R - COOH$ (Hydroxy acid monomer)

$\downarrow$ Condensation polymerization

$HO \vdots R-COO\cancel{H} \vdots R - COO \vdots R-COO \vdots R-COO \vdots H$

$\boxed{H\ OH}$ → H_2O $\quad H\ OH$ H_2O $\quad H\ OH$ H_2O

① ② ③ ④

(Polyester molecule containing 4 repeat units of $-R-COO-$)

$HO\left[R-COO \right]_4 H$ (DP=4) $+\ 3H_2O$ (3 molecules of water eliminated

---

Illustrations of Degree of Polymerization of ~~an~~ a polymer molecule.

Van Vlack

Ex 2-2.1

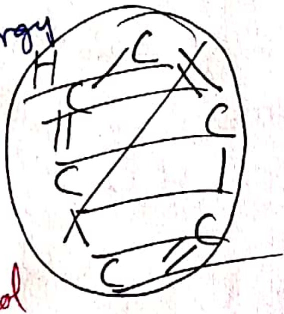
How much energy is required (+) or released (-) ~~if~~ if 2.6 kg of acetylene C_2H_2 reacts with hydrogen to produce ethylene, C_2H_4.

Procedure = For each molecule of C_2H_4 produced, one H-H bond and one triple carbon bond $C \equiv C$ are ~~b~~ eliminated. Conversely, a double carbon bond $C=C$ & two C-H bonds are formed. The energies involved are +435, +890, -680 & 2(-435) KJ/mol, respectively. A mole includes 0.6×10^{24} bonds

Energy is released when bond is formed (-ve)

Calculation reqd — broken (+ve)

Supply energy to break bond.



$$\frac{+435+890}{0.6\times10^{24}} + \frac{(-680)+2(-435)}{0.6\times10^{24}} \quad ①$$

890
-1115
-225 kJ/mol

$$\doteq -375\times10^{-21}\ J/C_2H_2$$

②

225 kJ/mol
× 100 mol
= 22.5×10^{6} J/

$$(2600\ gm)(0.6\times10^{24}\ amu/gm)/(26\ amu/C_2H_2)$$

Now one mole of C_2H_2 molecules weighs 26 gms.

$1\ gm = \frac{1\ \text{mole}\ C_2H_2}{26}$ $\quad 2600\ gm = \frac{2600 \times 1\ \text{mole}\ C_2H_2}{26} = 60\times10^{24}\ C_2H_2$ molecules

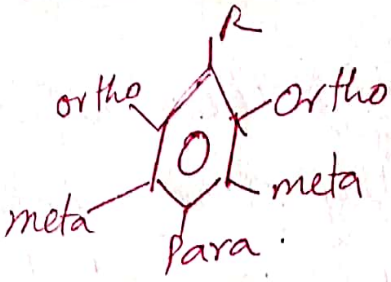
$$= -375\times10^{-21}\ J/C_2H_2 \cdot \times 60\times10^{24}\ C_2H_2$$

$$= -22.5\times10^{6}\ J$$

↑ energy is released. Thus once initiated the rxn could proceed spontaneously.

Van Vlack
2-2
p. 24

Molecules



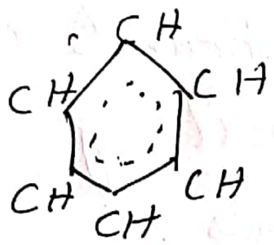
Common examples – H_2O, CO_2, CCl_4, O_2, N_2, HNO_3...

~~Use~~ Other Important molecules

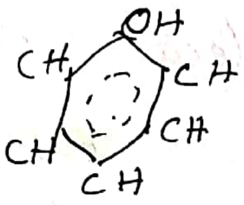
CH_3-OH
Methanol

CH_3CH_2OH
Ethanol

NH_3
ammonia

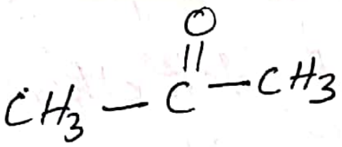


Benzene



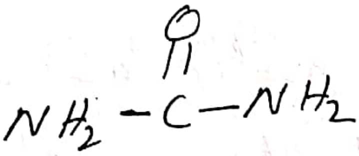
phenol

$CH_2=O$
Formaldehyde



$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

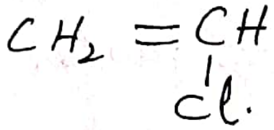
Acetone



$NH_2-\overset{\overset{O}{\|}}{C}-NH_2$

urea

$CH_2=CH_2$
Ethylene



$CH_2=\underset{\underset{Cl}{|}}{CH}$

Vinyl chloride

Fig Small molecules → Each C atom ~~to~~ is surrounded by four bonds, N – 3
O – 2, H – 1, Cl – 1

Within each of these molecules, the atoms are held together by strong intra molecular forces that produce covalent bonds. Unlike these strong forces, the inter molecular bonds ~~a~~ between molecules are weak. Consequently each molecule is free to act more or less independently. The following facts support these observations :-

① each of these molecular compounds has a low melting and a low boiling temperatu compared with other materials.

② the molecular solids are soft because the molecules can slide past each other with small stress applications.

③ the molecules remain intact in liquids and gases.

~~to~~ These molecules are comparatively small
Other molecules are large. 100s or 1000s of molecules

---

eg. $C_{35}H_{72}$ $CH_3 CH_2 CH_2 \dots CH_2 CH_2 CH_3$

pentatriacontane (35-ane)

$\rightarrow$ CH_4 (methane)

fig. Examples of molecules. → molecules are discrete groups of atoms. Primary bonds hold together the atoms within the molecule. Weaker, secondary forces attract molecules to each other.

Other materials like phenol-formaldehyde plastics have continuing 3-D structures of strong bonds. The difference between the structures of molecular materials & those with strong (primary) bonds continuing in all ~~th~~ 3-Dimensions produces major differences in properties.

Covalent bonds :-

Covalent bonds are stereospecific i.e. each bond is between a specific pair of atoms. The pair of atoms share a pair of electrons of opposite magnetic spins.

Each atom of a material is coordinated with its neighbours. ~~Th~~ The thermal vibrations in one atom influence the adjacent atoms; the displacements of one atom by mechanical forces, or by an electric field, leads to adjustments of the neighbouring atoms.

Covalent bonds are very strong.

Covalent bonds/atom or maximum CN

H	1	S	2
F	1	N	3
Cl	1	C	4
O	2	Si	4

Bond lengths and energies

(+ve)

The amount of energy required to break (or make) 1 mole (Avogadro's no.) of bonds.

e.g. 3,70,600 J — 1 mole C–C bonds

or $\frac{370}{N}$ kJ/~~mol~~ bond

$N = 0.602 \times 10^{24}$

(–ve)

Similiarly, energy released in forming C–C bond. (sign change)

	Bond energy	Bond length nm
C-C	370 kJ/mol	0.154
C=C	680	0.13
C≡C	890	0.12
C - H in CH_4	435	0.11
C-H in CH_3CL	435 - 5%	
C-H in $CHCl_3$	435 - 15%	

All values are -ve for forming bonds (energy is released) and are +ve for breaking bonds (energy is required.)

$2p^2$ ⇅ $2p$ ⇅ ↑

$2s^2$ ⇅ $2s$ ↑

$1s^2$ ⇅ $\boxed{1s + 3p.}$

= sp3.

Bond angles

sp3 hybrid orbital.

CH_4, CCl_4, diamond have sp3.

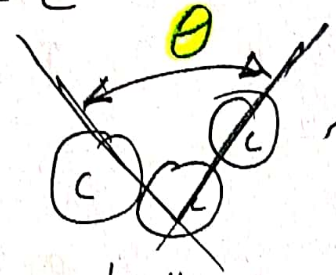
Bond angle = 109.5°

Greater distortions occur in hybrid orbitals when some electrons occur as lone pairs rather than in covalent bonds. NH_3 H_2O.

107.3°

104.5°

C-C-C bond angle in butane



value differs ~~de~~ slightly depending on whether ~~H_2 or~~ hydrogen or some other side radical is present, but we may assume for our purposes that the C-C-C angle is close to 120°.

Delocalized electrons.

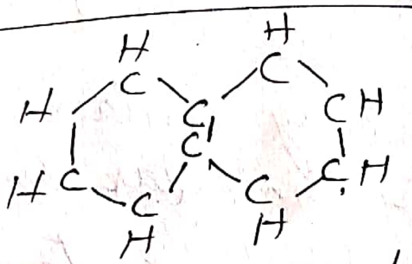
Most valence electrons enter into covalent bonds. These electrons are shared by specific atoms. ~~It~~ Bond is called sigma.

Benzene - 6 e⁻ are not included in the σ bonds. They ~~are~~ develop standing waves across the whole molecule. These electrons are called π. They respond to an electric field by moving their center of oscillation towards the side of the molecule that is nearer ~~to~~ the +ive electrode.

Example 2-2.2 The structure of napthalene is a double benzenes ring with two carbons of each ring in common. ⓐ How many de localized electrons are there? ⓑ How many wave patterns ~~are~~ (electron states) are available to the delocalized electrons?

Procedure Sketch the molecule. Determine the formula. Account for the valence electrons.

Napthalene ~~(example~~



A carbon is located at each hexagon corner. This leaves 10 delocalized electrons.

ⓐ Formula = $C_{10}H_8$ → valence electron balance

Total valence electrons

$C = 10C \times 4/C = 40$

$H = 8H \times 1/H = 8$

48

C-H bond(σ) = $8 \times 2 = 16$

C-C bond (σ) = $11 \times 2 = 22$

38

Remainder (π) delocalized = 10

ⓑ electron states = number of carbon atoms (like 1s, 2s, 2p, etc) = 10

$\boxed{\text{note} \mid \text{PTO}}$

Each state can contain two electrons of opposite spin. Therefore a total of 20 delocalized electrons could be acccomodated (were it not for a resulting imbalance of charges in the molecule).

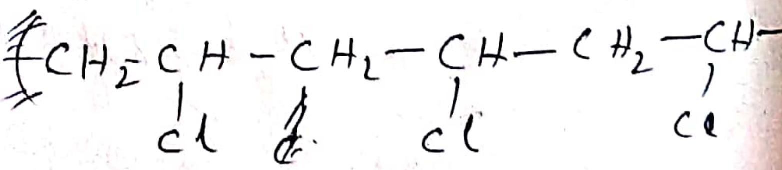
Macromolecules (Polymers)

Molecules may contain many atoms with strong intra molecular bonds. Materials such as PE typically contain thousands.

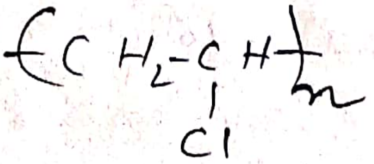
Cellulose is a natural macromolecule present in cotton, wood and most fibrous plants.

PE, PVC & PS are produced industrially.

C_2H_3Cl = mer
CH_2CHCl

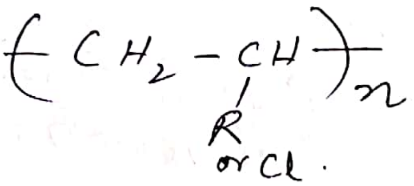


$$\text{-}\!\!\![CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-$$



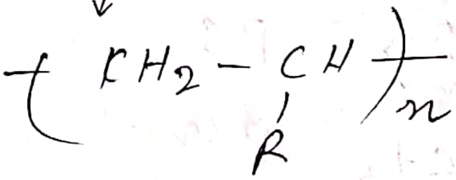
$$-\!\!\!\left[CH_2-\underset{Cl}{CH}\right]_n$$ Polymer or PVC

Linear molecules



$-(CH_2-\underset{R \text{ or } Cl}{CH})_n-$ is linear. There is no theoretical limit to its length. Strong covalent bonds exist along its length. Bonds of equivalent strength do not join molecules.

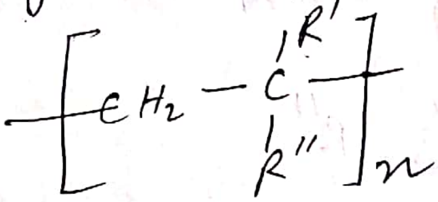
Polyvinyls & polyesters, etc are linear
↓



$-(CH_2-\underset{R}{CH})_n-$

n is the degree of polymerization or no of mers/molecule.

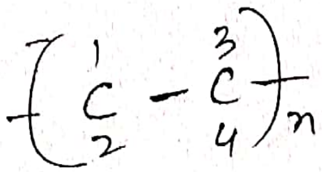
- vinylidene polymers :-



$\left[CH_2-\overset{R'}{\underset{R''}{C}}\right]_n$

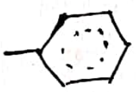
The mers of Polyesters, polyurethanes, etc are more complex & are commonly the product of two precursors. Like the vinyls they have a ~~a~~ chain of covalently bonded atoms that form a backbone structure.

Monomers must be bifunctional, i.e. they must be able to react with two adjacent molecules.



$$\left[\overset{1}{\underset{2}{C}} - \overset{3}{\underset{4}{C}}\right]_n$$

Selected vinyl polymers

Polymer	1	2	3	4	International abbreviation
Polyvinyls (general)	H	H	H	$-R$	
Polyethylene	H	H	H	$-H$	PE
Polyvinyl chloride	H	H	H	$-Cl$	PVC
Polyvinyl alcohol	H	H	H	$-OH$	PVA
Polystyrene	H	H	H		PS
Polypropylene	H	H	H	$-CH_3$	PP
Polyvinyl acetate	H	H	H	$-O\overset{\overset{O}{\|}}{C}CH_3$	PVAc
Polyacrylonitrile	H	H	H	$-CN$	PAN
Polyvinylidenes (general)	H	H	R'	R''	
Polyvinylidene chloride	H	H	$-Cl$	$-Cl$	PVDC
Poly methyl methacrylate	H	H	$-CH_3$	$-\overset{\overset{O}{\|}}{C}O\,CH_3$	PMMA
Polyisobutylene	H	H	$-CH_3$	$-CH_3$	PIB
Polytetrafluoro ethylene	F	F	F	F	PTFE

Secondary bonds.

Covalent bonds are very strong. Also called primary bonds.

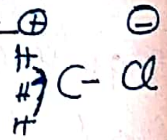
Weak intermolecular bonds are secondary bonds.

The forces of attraction that produce secondary bonds exist because of the local electric fields within and around uncharged atoms. The simplest (and weakest) of these secondary bonds arises from electron oscillations within the atom or molecule.

The center of the negative charges is displaced momentarily ($<10^{-15}s$), but repeatedly from the center of the positive charges that accompanies the protons in the nuclei. These oscillations produce small electric dipoles where the positive side of one atom or molecule is attracted to the negative side of an adjacent atom or molecule. The resulting dipoles provide the only forces of attraction in many of our ambient * vapors and gases. Only at very low temperatures where the thermal energy is nearly absent, are these attractive forces able to condense & solidify these ~~meta~~ materials.

eg. T_m of CH_4 is −185°C.

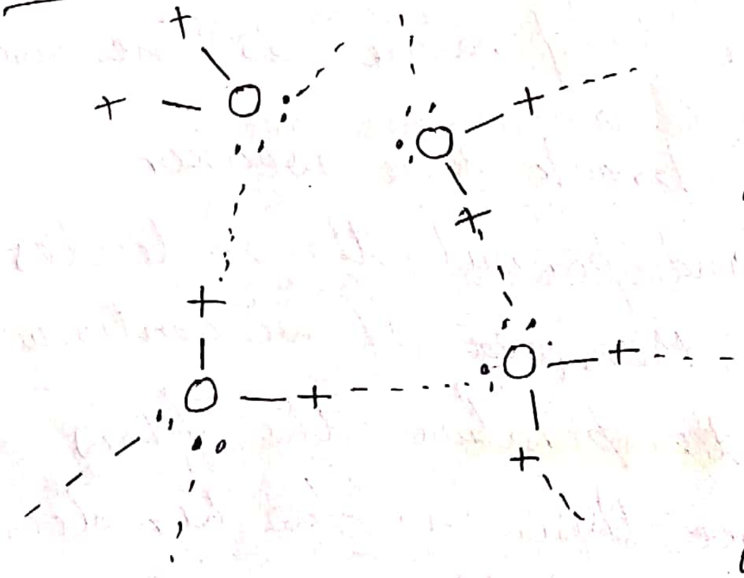
~~Polar molecules~~ Another type of secondary bonds exists with asymmetric molecules. Chloro methane CH_3Cl. The ~~e~~ 17 electrons of chlorine locate the negative center of charge away from the center of molecular mass. The hydrogen nuclei (protons) at the ends of the other three bonds cause the positive center of charge to locate in the opposite side of the center of mass. The result is an electric dipole, and the molecule is intrinsically polar.



Dipole moment $$\boxed{p = \underset{\text{charge}}{Q}\,\underset{\text{displacement}}{d}}$$

p of polar molecules is larger than those for comparable values in atoms & in nonpolar molecules. Thus materials possessing polar molecules remain solid at relatively high temperatures. These secondary forces have to be overcome to produce melting & vaporization.

Third type of secondary bond is the hydrogen ~~bon~~ bridge. It is the strongest secondary bond. Covalently bonded hydrogen atoms e.g. C—H & O—H expose bare protons on the ends of the bonds. These protons can easily be attracted to negative charges of other molecules, because the protons are not shielded by electrons. Similiarly lone pairs of e^- electrons in NH_3 & H_2O are unshielded.



Hydrogen bonding (in water). The hydrogen at the end of the orbital is an exposed proton (+). It is attracted to the ~~lon~~ electron lone-pairs of the adjacent water molecules.

The hydrogen bridge gives water the highest boiling point & melting point of any material with a low molecular wt (18 amu)

Similiarly its heat of vaporization $(\Delta H_v)_{100°C}$ is very high (2250 J/g)

The freezing expansion of water can also be related to the stereospecific nature of this type of bonding in solid ice.

Linear molecules are thermoplastic. They soften on heating and reharden on cooling (melting is the loss of crystallinity)

Relatively weak intermolecular forces along the molecular chain hold the molecules together. As the temperature is increased shear stresses can break these weaker secondary bonds and permit the molecules to move by each other. ~~ex~~ If we continue to increase the temperature the flow accelerates, since there is further decrease in the effectiveness of the secondary bonding ~~(as the temp. ↑)~~ with an addition of thermal energy. Conversely, cooling decreases the flow rate until these materials harden.

Ex. 2-3.1
P. 36

Teflon with a mer of C_2F_4 polymerizes to polytetrafluoro ethylene $(C_2F_4)_n$. What is the degree of polymerization of the mass of the molecule is 33,000 amu (Ⓐ or 33,000 gm/mol)? Ⓑ How many molecules are there per gram?

Procedure Ⓐ We want repeat units per molecule, therefore we need the mer weight. We consider C_2F_4 to be the repeat unit since CF_2 cannot be stable (The carbon must have four bonds). Ⓑ There are 33000 g per Avogadro's number of molecules

solution

Ⓐ Mer mass = $4(19) + 2 \times 12 = 100$ amu

$$\frac{33000}{100} \frac{\text{amu/molecule}}{\text{amu/mer}} = 330 \text{ mers/molecule}$$

Ⓑ $$\frac{(0.6 \times 10^{24} \text{ molecules})}{33,000 \text{ gm}} = 1.8 \times 10^{19}/\text{gm}$$

Comment = Teflon is a trade name PTFE — Poly tetra fluoro ethylene is generic.

Example 2.3.2

How much energy is given off when 70 g ~~is~~ of ethylene, C_2H_4, react to give polyethylene?

Procedure :- With each added C_2H_4 molecule one C=C bond is eliminated, and two C–C bonds are formed. ~~From~~ These changes involve +680 kJ per mole and 2 (−370 kJ/mol) of energy, respectively (+, for energy to break the bond; −, for energy released as a bond is formed)

A mole includes 0.602×10^{24} molecules

$$\begin{array}{r} -740 \\ 680 \\ \hline -6\cancel{0}_{15} \end{array} \times \frac{\cancel{70}}{\cancel{28}\,4} = -150\ \text{kJ}$$

Calculation

$$\frac{+680{,}000\ \text{J}}{0.602 \times 10^{24}\ \text{molecules}} - \frac{2(370{,}000\ \text{J})}{0.602 \times 10^{24}\ \text{molecules}} = -9.96 \times 10^{-20}\ \text{J}/C_2H_4$$

$$70\ \text{g}\,(0.602 \times 10^{24}\ \text{amu/g}) / (28\ \text{amu}/C_2H_4)$$

$$= 1.5 \times 10^{24}\ C_2H_4$$

$$(-9.96 \times 10^{-20}\ \text{J}/C_2H_4)(1.5 \times 10^{24}\ C_2H_4)$$

$$= -150{,}000\ \text{J}.$$

This reaction is the basic reaction for making large vinyl-type molecules that are used in plastics.

~~materials harden~~,

(2-4) 3-D Bonding

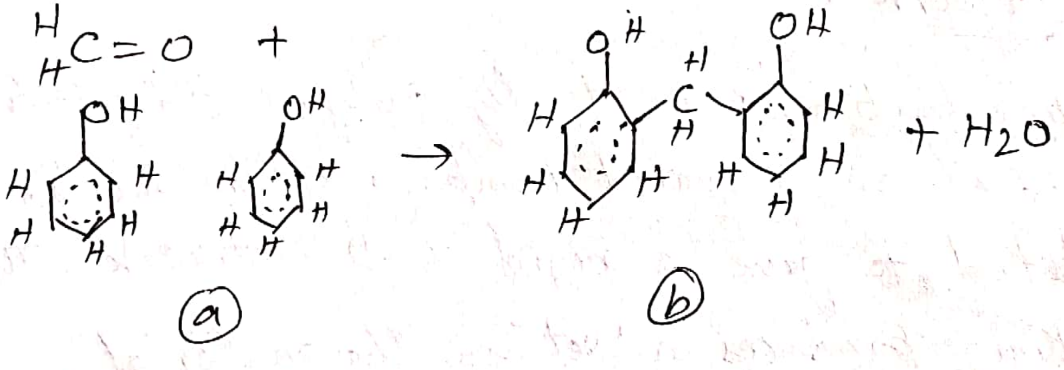
Precursor – Person or thing that comes before another of the same king, a forerunner.

Mechanical properties related to strength are ~~ele~~ improved if the primary bonds develop in all three dimensions.

Network structures :-

· Polymerization can lead to a network structure if some of the units are polyfunctional i.e. if the precursor molecules can react with ~~•~~ three or more ~~adjas~~ adjacent molecules.

eg. phenol formaldehyde – PF – trade name Bakelite



PF reaction → The phenols (C_6H_5OH) contribute hydrogen and the formaldehyde ($\cdot CH_2O$) contributes oxygen to produce water as a by product. The two rings are joined by a $-CH_2-$ bridge.

~~At room temp~~ ~~a~~ At room temp. Formaldehyde is a gas; phenol is a low-melting solid. The polymerization ~~that~~

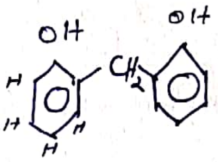
is a result of a reaction between the two. Formaldehyde supplies the CH_2 'bridge' between the ~~th~~ benzene rings of the two phenols. In the process, a hydrogen is stripped from each of the two phenols, and an oxygen is removed from the formaldehyde

$2H + O \rightarrow H_2O(g)$ Water volatilizes & escapes. This reaction can occur at several points around the phenol molecule. (Stereo hindrance limits the points to three)

This Polyfunctionality results in a molecular network.

In production a partially polymerized mixture is molded at an elevated temp., where the rxn is completed to give a rigid 3-D network. The heating produces a 'set' in the material.

In contrast to the earlier thermoplastic ~~material~~ products, PF is a thermosetting product. Reheating will not soften the 3D network significantly.



C_6H_5OH

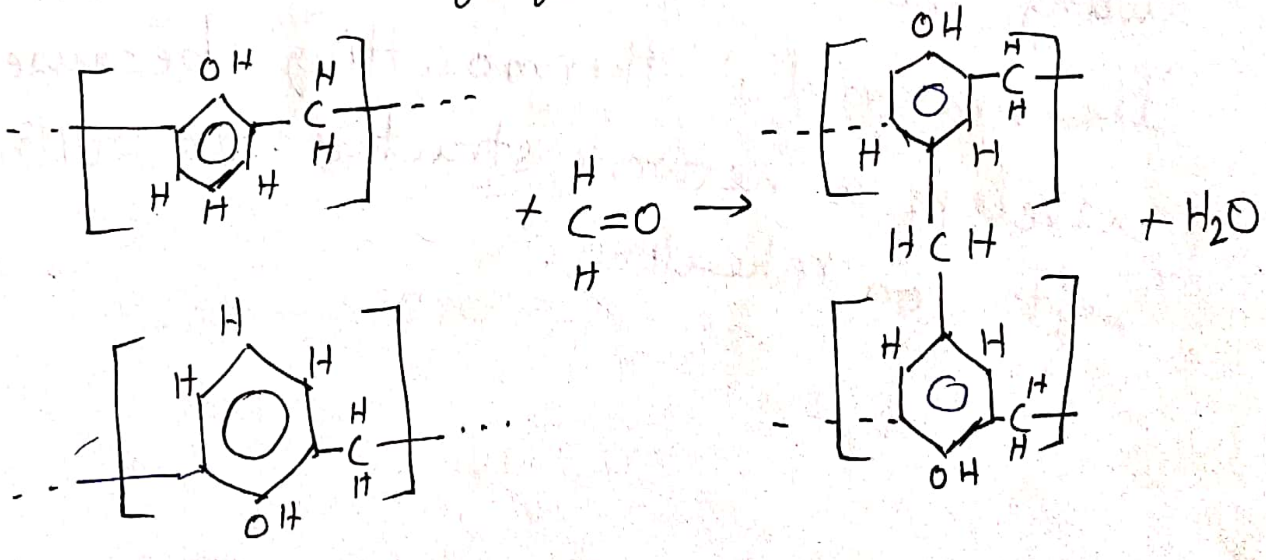
Example 2-4.1

A plastics molding company buys ~~of~~ a phenol formaldehyde raw material that is only two-thirds polymerized; that is, there is an average of only two $-CH_2-$ bridges joining each phenol, rather than the maximum three.

ⓐ How many gm of additional formaldehyde are required per kg of the above raw material to complete the network formation (that is, to make the phenols fully trifunctional)?

ⓑ How many gm of water will be formed in this thermosetting step?

Procedure :- The raw material corresponds to a linear polymer with the following structure & bridging reaction.



Calculation = using (g/mol)

Raw material

formaldehyde (x)

$$\underbrace{2[6(12)+3+16+1)+(12+2)]}_{212} + \underbrace{(12+16+2)}_{30} - $$

14
72
$\underline{20}$
$\underline{106 \times 2}$
212

$$\rightarrow \underset{\text{product}}{224} + \underset{\text{water }(y)}{18}$$

ⓐ $x/1\text{ kg} = \frac{30}{212}$; $x = 0.142\text{ kg}$

ⓑ $y/1\text{ kg} = 18/212$; $y = 85\text{g}$

Comments = The heated raw material is thermoplastic during molding, since it is essentially linear & lacks a network structure. While hot & still under pressure, the described 'curing' reaction gives a 'set' to the product. The material is thermosetting, because it develops a network structure. It will not soften on reheating.

Q - P31   A common polymer has C_2H_3Cl as a mer. It has an average mass of 35,000 amu/molecule.

ⓐ What is its mer mass?

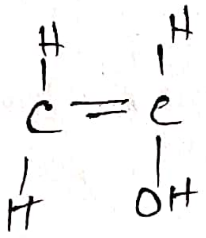
ⓑ What is its degree of polymerization

$C_2H_3Cl = 2 \times 12 + 3 \times 1 + 35.5 \times 1$

$= 62.5$ amu

$n = \frac{M}{m} = \frac{35,000}{62.5} = 560$ mer/molecule.

2 - P32   What is the net energy change as 18 g of vinyl alcohol polymerize to PVA?



kJ/mol

~~one~~ C=C bond break 680

C-C-

two~~one~~ C-C ~~two C-H~~ form 370.

$3+12+12+16+1 = 44g$
$= 1$ mole.

$\frac{18}{44} = 0.41$ mol.

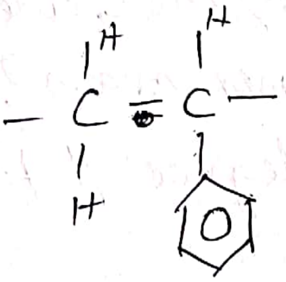
$+680 - 2 \times 370 =$

$$\begin{array}{r} 740 \\ 680 \\ \hline -60 \text{ kJ/mol} \end{array} \times 0.41$$

$\boxed{-24.5 \text{ kJ}}$

(P33) There are 9.2×10^{18} molecules per g of polystyrene
(a) what is the average molecular size?
(b) what is the D.P.?

Polystyrene



$$\begin{array}{r} 24+3 \\ +72+5 \\ \hline 96+8 \\ \hline \boxed{104} \end{array}$$ amu or g/mol.

mer

6.023×10^{23} molecules of mer in 104 g

9.2×10^{18} " " polymer in 1 g

$1 \text{ — } \frac{1}{9.2 \times 10^{18}}$

6.023×10^{23} molecules — $\frac{6.023 \times 10^{23}}{9.2 \times 10^{18}}$ g.

= 65467.4 g/mol.

⇒ avg molecular size = 65467 amu/molecule

$DP = \frac{65467}{104} = 629.5$ or 630 mer/molecule.

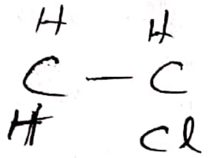
(P34) How many C=C bonds are eliminated per mer during polymerization of PVC
(b) How many additional C–C bonds are formed?

1, 2.

$C=C \cdot \Rightarrow \cdot C-C-$

−1 double bond per mer   +2 single bonds /mer

(P35) How much energy is released per mer ~~in~~ ?



$$24+3+35.5 = 62.5 \text{ amu/molecule}$$
$$62.5 \text{ g/mol}$$

$C=C = +680$
$2\times C-C = 2\times 370 = -740$ } −60 kJ/mol.

-60 kJ —— 6.023×10^{23} molecules (mer) —— 62.5g

~~1 molecule = $\frac{62.5}{6.023\times10^{23}}$ g~~

~~60 kJ~~

$$\frac{-60\text{ kJ}}{6.023\times10^{23}} = 9.9\times10^{-20} \text{ or } 0.99\times10^{-19}\ \text{J/molecule or mer}$$

or 1×10^{-19}

or $\boxed{10^{-19}\text{ J/mer}}$

Van Vlack
p 119

Order & Disorder in polymers

Materials like ice, C_6H_6 ($T_m = 6°C$), I_2 & dextrose sugar ($C_6H_{12}O_6$) retain their molecular structures when they crystallize. Their crystals may contain the imperfections like vacancies, interstitials, dislocations, etc, However the basic structure of the molecules is constant.

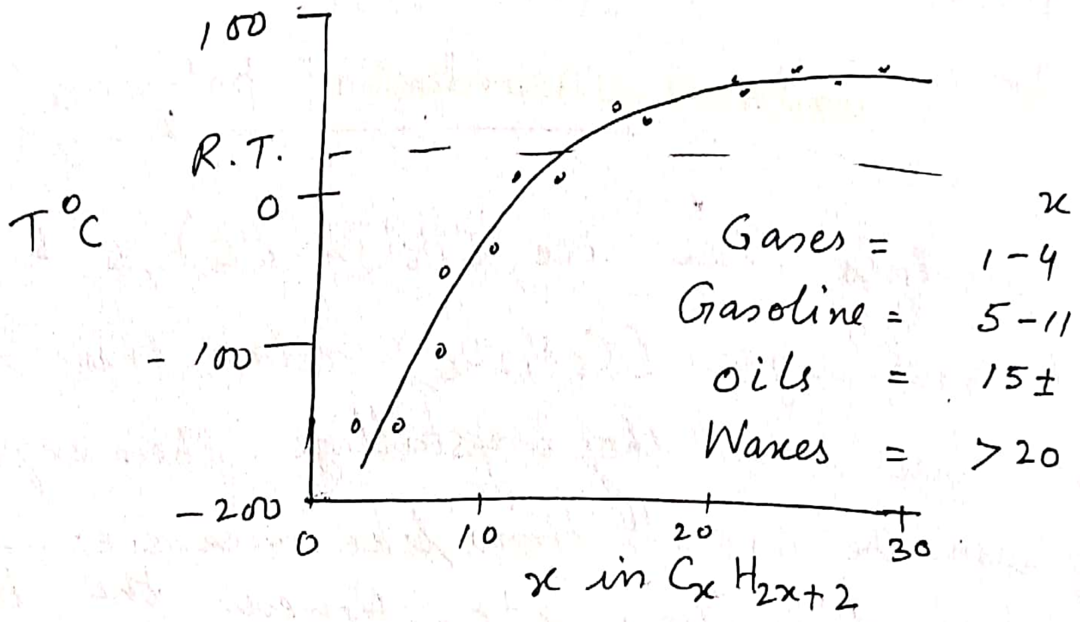
Macromolecules, are subject to variations in their molecular structure. e.g. Polyethylene may have 100 carbon atoms along its molecular chain, or it may have 1000. ~~In~~ Commonly it is kinked and coiled, like a cotton boll. Under stress the molecule may be pulled out nearly straight (except for the bond angles). These added variables lead to additional types of disorders in polymers. Properties are affected accordingly.

① Molecular wt
② Conformational disorder
③ Configurational variants
④ branching
⑤ Cross-linking.

Molecular weights:

Properties vary from different size molecules

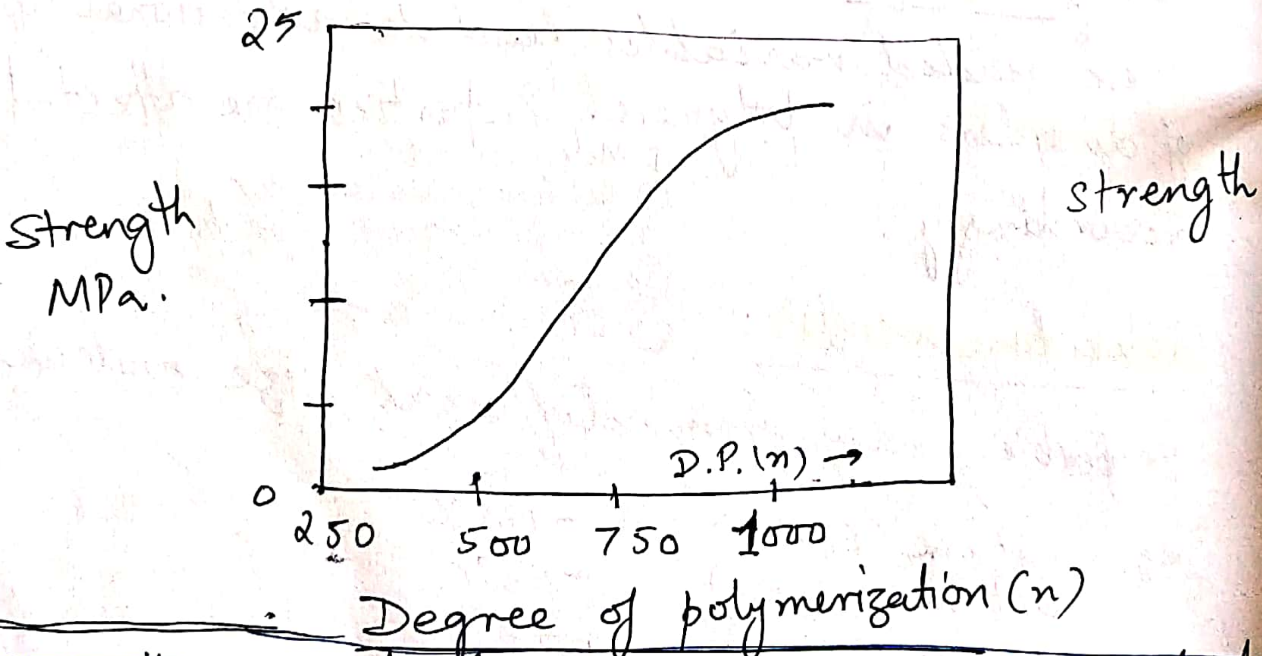
		T_m
eg.	butane (C_4H_{10})	−138 °C
	octane (C_8H_{18})	−56°C
	35 ane ($C_{35}H_{72}$	+75°C



Melting temperature vs molecular size in the C_xH_{2x+2} hydrocarbon series

~~The~~

Similiarly mechanical chemical & service stability of polymers are also dependenton molecular size.



Strength vs molecular size (PE) :- Larger molecules with more mers/molecule have increased mechanical and thermal properties, and thus are able to withstand more severe service requirements.

Molecular size can be reported in terms of the degree of polymerization, n. We do not determine the degree of polymerization by counting the mers. We determine the molecular wt. M.

Knowing the mer weight, m

$$n = \frac{M}{m} = \frac{\text{molecular weight}}{\text{mer weight}}$$

$$\frac{\text{amu/molecule}}{\text{amu/mer}} = \frac{\text{mers}}{\text{molecule}}.$$

PVC

$M = 35000$ amu (g/mol)

$m = C_2H_3Cl = 2(12)+3(1)+35.5$

$= 62.5$ amu.

The degree of polymerization is

$$\frac{35000}{62.5} = 560 \text{ mer/molecule}.$$

Mass-average molecular wt.

Molecular weights are obtained from lab tests. These tests use techniques that

① involve osmosis or

② use light scattering.

Molecular weights ~~as~~ also are measured indirectly against ~~at~~ caliberated standards by viscosity & gel permeation chromatographic procedures.

Reported values are average values since any polymer product contains many molecules, few of which ~~*~~ have grown identically.

Averages can be obtained on a

number basis or
weight basis.

eg. Syrup 18 g sugar ($C_6H_{12}O_6$, $M = 180$ amu) and 18 g water (H_2O with $M = 18$ amu)

50 : 50 wt ratio = Basis

mass-average molecular wt $\overline{M}_m$ is

$\therefore \overline{M}_m = 0.5(180) + 0.5(18) = 99$ amu or g/mol

Generalizing our calculation we have:

$$\overline{M}_m = \Sigma W_i M_i$$

W_i represents the weight fraction & M_i the molecular weight of each component i.

Number average Mol wt

18 g water ~~water~~ will involve 10 times as many molecules as will ~~18g~~ 18 g of sugar (because the molecular weights are 18 & 180 amu each). ~~A m~~

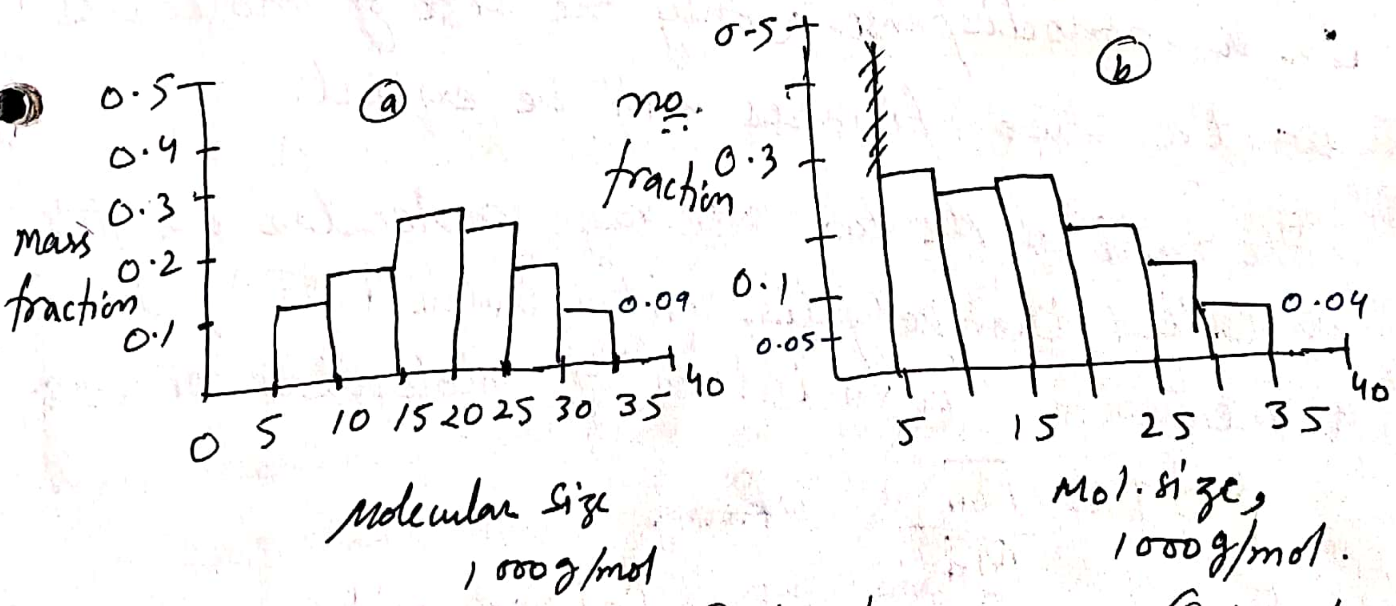
~~M~~ $\overline{M_n}$ = number average molecular wt

X_i = number fraction

$$\overline{M_n} = \Sigma X_i M_i$$

again M_i is the mol. wt of each component. Since we have 10 times as many water molecules as sugar molecules, the average molecular wt on a number ~~wt~~ fraction basis :-

$$\frac{10}{11}(18 \text{ amu}) + \frac{1}{11}(180 \text{ amu}) = 32.7 \text{ amu or g/mol.}$$



Polymer size distributions ⓐ based on mass ⓑ based on numbers.

ⓐ 12% of total mass is accounted for by molecules between 5000 amu & 10000 amu (mid value 7500 amu)

ⓑ 26% of the total number ~~is~~ of molecules fall in the 5000-10000 amu range.

These values of 26% for ⓑ vs 12% for ⓐ differ because it takes many of the small molecules to account for 12% of the mass. In contrast, 4% of the molecules account for 9% of the mass that is found in the interval from 30,000 to 35,000.

The no average molecular wt is less than the mass average molecular wt. in general in a polydisperse sample.

In a monodisperse (only one size of molecules) the two figures will be equal.

The ratio of the two average molecular weights is called the polydispersity index (PDI); it is a measure of the variation of molecular sizes:

$$PDI = \frac{\bar{M}_m}{\bar{M}_n}$$ ~~Rang~~

Range Lab. monodisperse = 1
commercial product = 4 or 5.

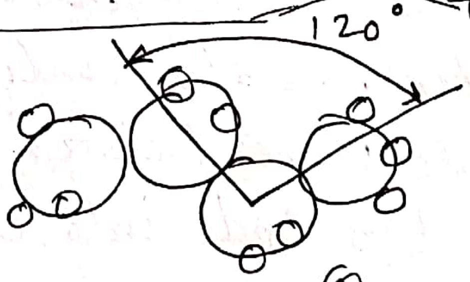
high PDI indicates a large quantity of small molecules that adversely affect thermal stability in service.

Conformation = any of the spatial arrangements of a molecule that can be obtained by rotation of the atoms about a single bond. *

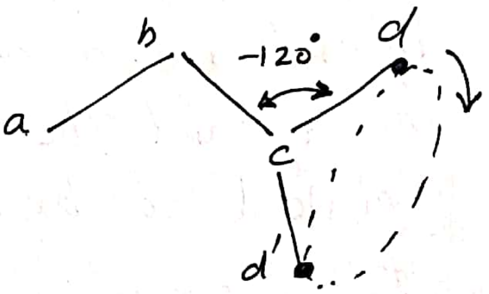
Conformational disorder

The average length of a polyethylene molecule ~~is~~ with $n = 500$ [i.e. $-(C_2H_4)-_{500}$] is 154 nm.

because each of the 1000 C–C bonds is 0.154 nm long. But the bond angle is ~120°



Bond rotation
(butane)



Although there is a 120° bond angle, the end to end distance can vary from a-d to a-d'. Large molecules ~~x~~ will have much more variation.

∴ Saw tooth length would be (154 nm) Sin 60° or 135 nm

Again this is an over simplification since the single bonds of ~~a~~ the carbon chain are free to rotate. This freedom is available at higher temperatures in amorphous (non crystalline) polymers and in polymers dissolved in a liquid solvent.

\# C–C bonds = 3 in butane

a – d = 0.4 nm   a – d' = 0.3 nm

The length varies randomly within these limits

~~The length v/s as the~~ as the thermal agitation rotates the bond angles. The ~~maxium~~ maximum limit for the end to end length of the polyethylene ~~in~~ with $n = 500$ is the 135 nm value. ~~we~~

The maximum end to end length would be a fraction of a nanometer (in the unlikely event that the molecule were twisted or kinked to bring the two ends into contact). The average or root mean square length L in non crystalline polymers lies between these two extremes and can be calulated on a statistical basis as.

$$L = l\sqrt{x}.$$ (Random walk statistics)

l = individual bond length.

x = number of bonds in the chain.

Kinked configuration (non crystalline molecules)

Since each C–C bond can rotate, a long molecule is normally kinked and has a relatively short mean length L.

$l = l\sqrt{2} = 1{\cdot}4\,l$ IV

Thus the doubling of the degree of polymerization of a polyvinyl increases the mean end to end length by 40%. The twisting and coiling arising from bond rotation is called conformational entropy, or disorder

This rotation is limited to single C–C bonds; however it is important to properties.

e.g. Above the Tg many polymers may be stretched from their kinked conformation to give high strains without changing the inter-atomic distances. Rubbers possess this characteristic, so they develop high strains at relatively low stresses. Furthermore, the molecules ~~of~~ recoil to their kinked ~~condition~~ conformation when the stress is removed. Rubber is visibly elastic because it has a very low elastic modulus.

Configuration - arrangement/layout
An arrangement of parts or elements in a particular form, figure or combination.

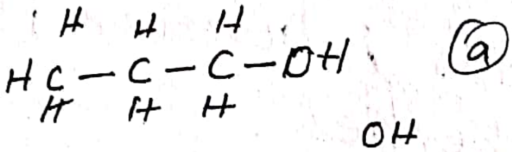
Configurational variants

Conf~~igura~~ormational disorder arises from bond rotation. Molecules also may possess more than one configuration. The change from one to another configuration involves bond breaking and new bond formation.

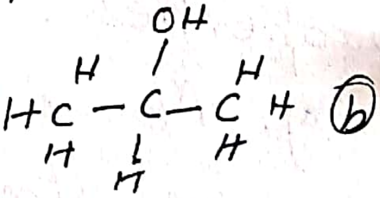
Isomers, for example, are two configurations of the same molecular composition. (same formula but different arrangement of atoms in the molecule)

n propyl alcohol.

iso propyl alcohol



$\mathrm{H\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH}$ ⓐ



$\mathrm{H\overset{H}{\underset{H}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}H}$ ⓑ

Fig: Isomers of propanol
ⓐ Normal propyl alcohol ⓑ Isopropyl alcohol.

The molecules have the same composition but different structures. Consequently, the properties are different. ~~Compare with polymorphism of crystalline~~

	Tm	Tv	ρ
n propyl alcohol	−127°C	97°C	0.8 g/cc
iso " "	−90°C	82°C	0.78 g/cc

Stereoisomers present more complex configurational variants..

Polypropylene is a polyvinyl with ~~$R=CH_3$~~ $R = -CH_3$

tacticity = stereochemical arrangement of the units in the main chain.

Tacticity = Stereochemical arrangement of the units in the main chain of a polymer   Greek Taktikos = relating to arrangement or order

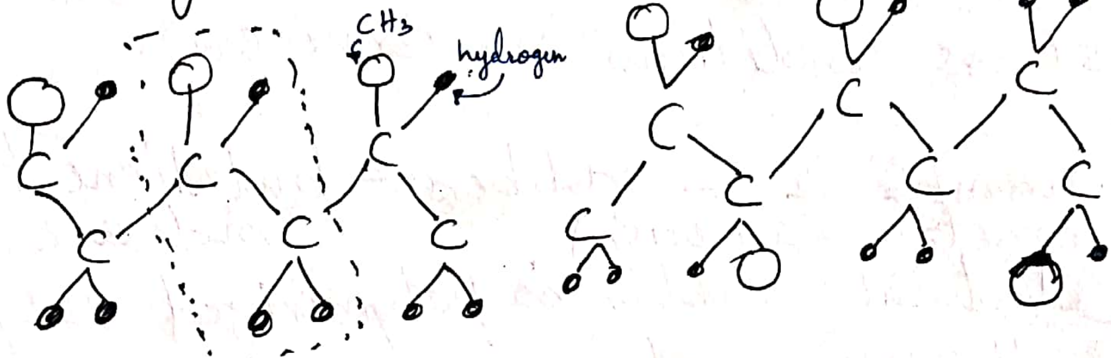
VI

Stereoisomers (P,P)

ⓐ Isotactic (same)   ⓑ Atactic (without pattern)

$C_2H_3CH_3$ mer has same spatial (stereo) arrangement

No spatial pattern.



ⓐ → mers show a high degree of regularity along the molecular chain. $C_2H_3CH_3$ units are added to form the linear polymer. There is an identical orientation of each propylene unit,

ⓑ The isomer has the same chain of propylene mers, but the geometric (or stereo) arrangement of the $-(C_2H_3CH_3)-$ units differ.

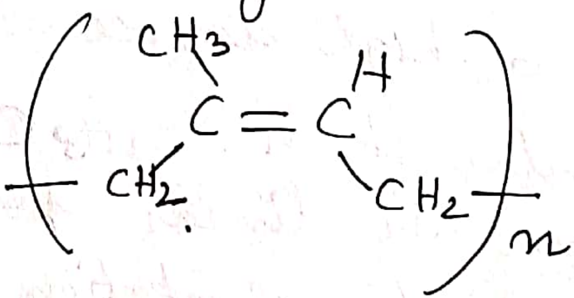
These molecules are stereo isomers.

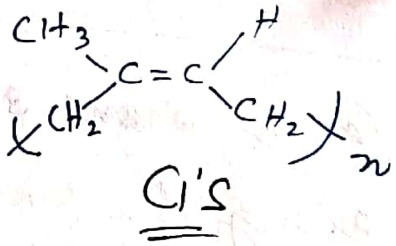
ⓐ iso tactic → same pattern.
ⓑ a tactic → no pattern.

The properties of these two isomers are different. eg. The isotactic molecules can mesh together better and require less volume. ~~Is~~. Isotactic molecules can crystallize ~~as~~. to a greater degree. The consequence is a slightly greater density and a measurably better resistance to adverse thermal & stress conditions in service.

Example 2 — rubbers – butadiene type molecule.
(Geometric Isomerism)

Natural rubber is polymerized isoprene with a mer of.

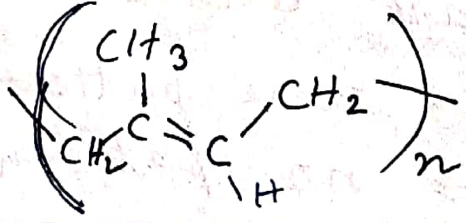




Cis

The two double bonded carbon atoms have a CH_3 group and a hydrogen on the same side of the chain. This cis isomer, with ~~the~~ occupancy on the same side of the chain arcs the mer.

Another modification has the CH_3 & H on opposite sides of the chain to give a trans isomer.



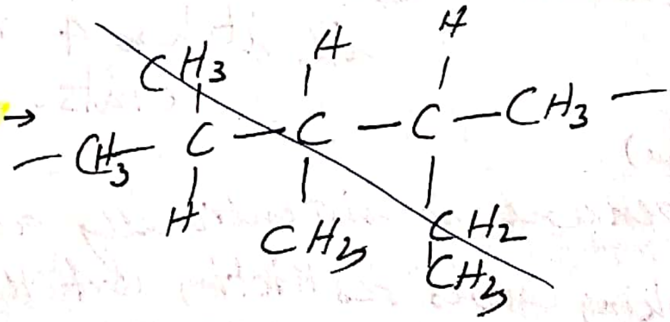
Syndiotactic = repeating units have alternating stereochemical configurations.

Although identical in compositions, these two isomers of $-(C_5H_8)-$ have different structures and therefore different properties.

Natural rubber with its cis type structure has a highly kinked chain, ~~as~~ due to the arc in the mer. Hence it exhibits very large elastic strain.

Polymer of the trans type is called gutta percha and has a bond angle pattern that is most typical of linear polymers. The unsaturated posetions balance each other across the double bond. It is plastic.

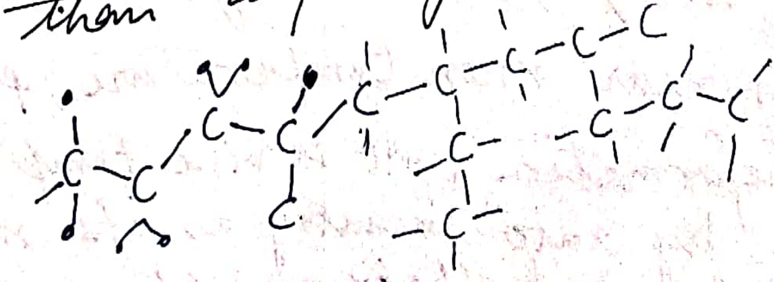
Branching →



Poly ethylene

Significance lies in 3D entanglements that can interfere with plastic deformation.

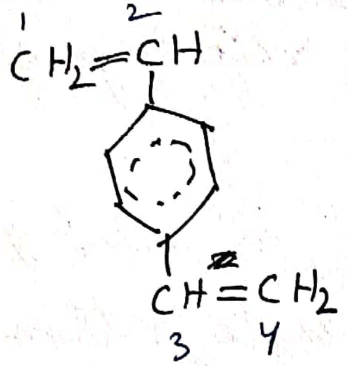
Pile of tree branches are more difficult to more than a pile of sticks.

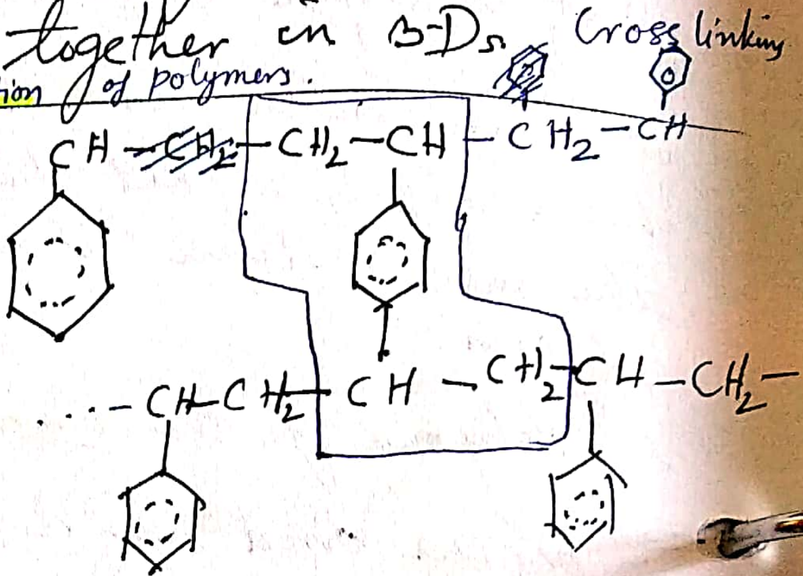


Cross-linking

Some linear molecules, by virtue of their structure can be tied together in 3-Ds. of polymers.

causes restrictions wrt plastic deformation of polymers.





Cross linking of polystyrene

Divinyl benzene ⓐ becomes part of two adj. chains. ⓑ becauz it is tetrafunctional i.e. it has 4 reaction points. 1,2,3,4

(Additive)
Divinyl benzene is intentionally added. Cross linking causes restriction wrt the plastic deformation of polymers.

Vulcanization of rubber — cross-linking by sulfur.

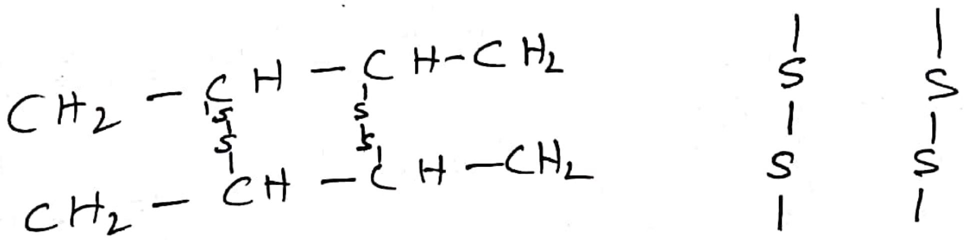
— Rubber is a soft, even sticky, material that, when it is near room temperature, flows by viscous deformation. At service temp it was unusable by auto industry as its molecules could slide past their neighbours, particularly at the pressures encountered.

Cross linking by sulfur at about 10% of the possible sites gives the rubber mechanical stability ~~in it~~ as a tyre, while enabling it to retain its flexibility.

Hard rubber has a larger percentage of Sulfur & ~~at~~ more cross links. pocket comb.

$CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2$

$CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2$



Vulcanization (butadiene type-rubbers)

Adjacent chains ⓐ are cross-linked by pairs of S atoms ⓑ other cross linking~~s~~ configurations like 2 single S atoms rather than two pairs may occur between 2C

4-3.1

A solution contains 15g of water, 4 g of ethanol (C_2H_5OH), and 1g of sugar ($C_6H_{12}O_6$).

ⓐ What is the mass fraction of each molecular component?

ⓑ What is the number fraction of each molecular component?

Solution

ⓐ Basis = 20gm

w_i

Water = $\frac{15}{20}$ = 0.75

Ethanol = $\frac{4}{20}$ = 0.2

Sugar = $\frac{1}{20}$ = 0.05

ⓑ Basis = 20 amu or 15 amu water
4 amu ethanol
1 amu sugar

Water = 2+16 = 18 amu

~~X_i =~~ $\frac{15}{18}$ = 0.833 molecules.

~~or 0.833x~~

Ethanol = $\cancel{\frac{4}{18}}$ = C_2H_5OH = $2_{\times 12} + 5 + 1_{\times 16} + 1$ = 24+6+16
= 46 amu

~~2+~~ = $\frac{4}{46}$ = 0.087 molecules.

Sugar = $C_6H_{12}O_6$ = 72 + 12 + 96 = 180
1/180 = 0.006 molecules.

$$\begin{array}{r} 0.833 \\ 0.087 \\ 0.006 \\ \hline 0.926 \end{array}$$ molecules.

~~100% basis~~. Number fraction

$\underline{\underline{X_i:}}$

$$\frac{0.833}{0.926} = 0.9$$

$$\frac{0.087}{0.926} = 0.094$$

$$\frac{0.006}{0.926} = 0.006$$

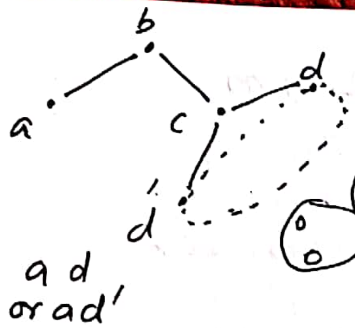
Example 4-3.3

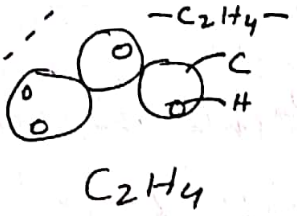
A polyethylene $-\!(C_2H_4)\!-$ molecule with the molecular mass of 22,400 amu is dissolved in a liquid solvent.

ⓐ what is the longest possible end-to-end distance of the polyethylene (without altering the 120° C–C bond angle)?

ⓑ what is the shortest?

ⓒ what is the most probable?





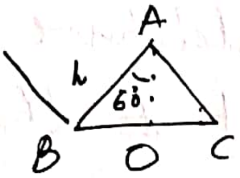
⑨

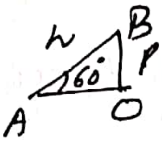
Bond length.

$l = 0.154$ nm.

C–C–C angle = 120°.

Molecular mass = 22400 amu.





sawtooth length

$\sin 60° = \frac{P}{h}$.

or $P = h \sin 60°$.

$C_2H_4 = 12 \times 2 + 4 \times 1 = 24 + 4 = 28$ amu

Degree of polymerization $= \frac{22{,}400 \text{ amu/molecule}}{28 \text{ amu/mer}}$.

$= 800$ mer/molecule.

$\Rightarrow 800 \times 2$ C–C bonds/mer $= 1600$ bonds/molecule.
mer/molecule.

ⓐ Total ~~to~~ end to end distance

$= 1600 \text{ bond} \times \underset{\text{Bond length}}{AB} \times \sin\left(\frac{120}{2}\right)$

$= 1600 \times 0.154 \text{ nm} \times \frac{\sqrt{3}}{2}$

$= 210$ nm.

ⓑ shortest distance = If ends are in contact it can be < 1 nm

ⓒ Root mean square length $\bar{L} = l\sqrt{x}$

l = individual bond length

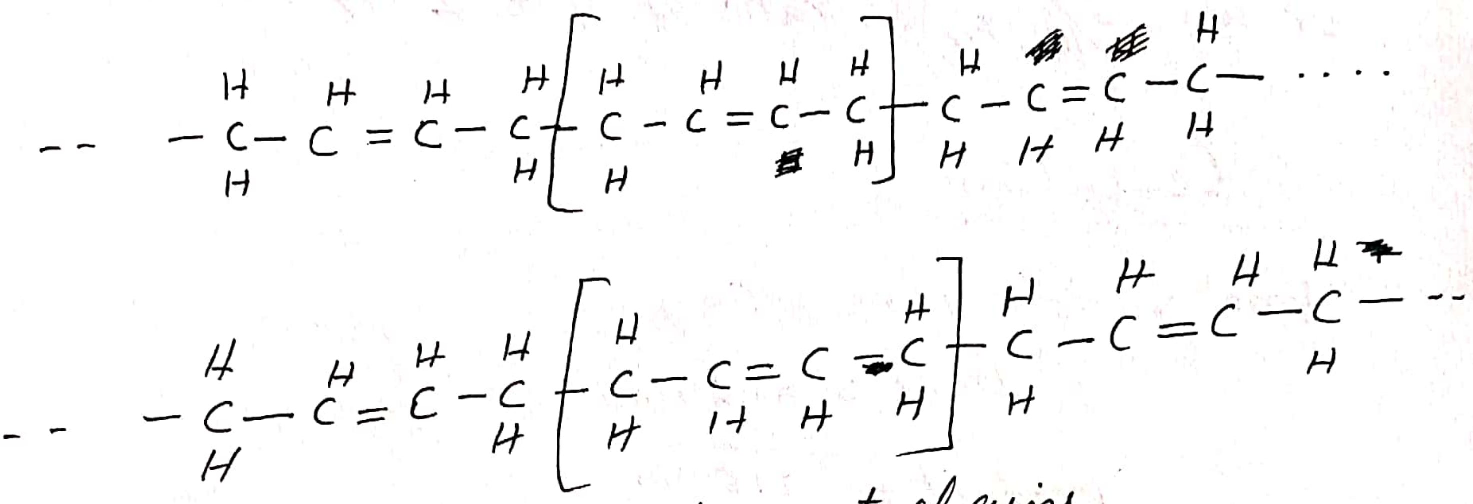
x = number of bonds in the chain

$L = 0.154 \text{ nm} \sqrt{1600} = \underline{\underline{6.2 \text{ nm}}}$

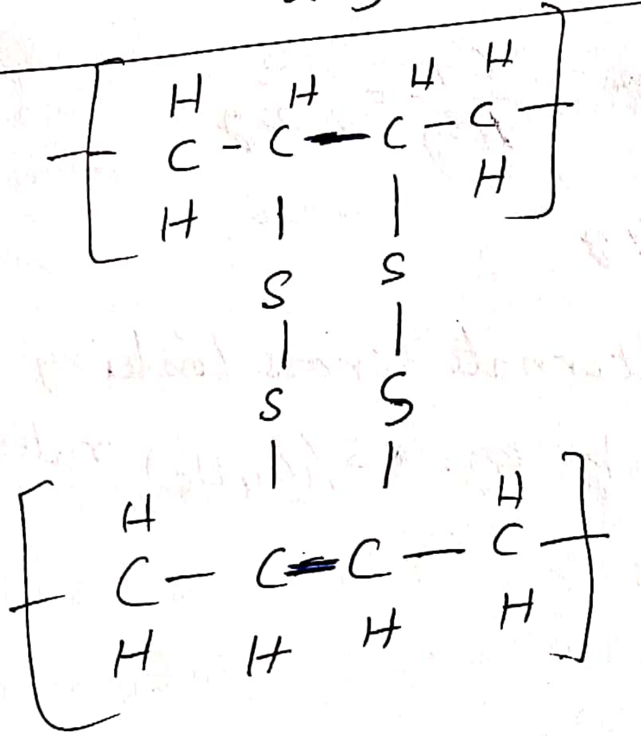
Comment = Since the molecule is under continuous thermal agitation, the probability of attaining a length of 200 nm is remote. A force would have to be used to stretch ~~on~~ it out to that length. Furthermore, the required force would become greater at higher temperatures, because the kinking becomes more persistent with increased thermal agitation.

Example 4-3.4

How many grams of sulfur are needed per 100 g of final rubber product to cross-link completely a polybutadiene $+ C_4H_6 +$ rubber with sulfur according to pattern in Figure.



adjacent chains



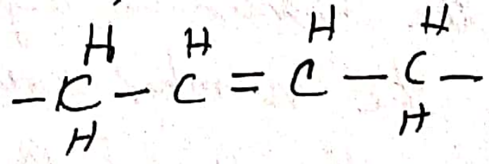
cross linked by pairs of S atoms

(single S atom instead of pairs may occur between chains too).

Vulcanization (Butadiene-type rubbers)

Procedure

In this rubber, the mer is



C_4H_6, or $-\overset{H}{\underset{H}{C}}-\overset{H}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}-$

Complete cross linking requires two sulfur molecules, S_2 for a pair of C_4H_6 mers or an $S/(C_4H_6)$ ratio of 4 to 2 or 2 to 1.

Calculation

1mol C_4H_6 = 48+6 = 54 g

2 atoms S = 64 gm

product = 118 gm

fraction sulfur = $\frac{64}{118g} = \frac{x}{100g}$

$x = 54g$

Comment = alternate cross linking structures can develop eg. $S/(C_4H_6)$ ratio of 1 to 1

Example 4-3.2

It has been determined that a PVC has the molecular wt distribution (shown in ~~fig.~~ table) for mass fraction & no fraction respectively.

ⓐ What is the mass-average molecular weight?

ⓑ What is the number average molecular weight?

ⓒ What is the D of P n based on M_n?

ⓓ what is the polydispersity index?

Procedure

Consider the six size classes as six molecular types with molecular weights of 7500 g/mol, 12500 g/mol & so on. Then determine the averages ~~as we did for~~ ~~the~~.

Molecular size interval amu	$(M)_i$ Mid value amu	M_m mass fraction	W_iM_i amu	x_i no. fraction	x_iM_i amu
5-10000	7,500	0.12	900	0.26	1,950
10-15000	12,500	0.18	2250	0.23	2875
15~~0~~-20000	17,500	0.26	4,550	0.24	4,200
20-25000	22,500	0.21	4,725	0.15	3,375
25-30000	27,500	0.14	3,850	0.08	2,200
30-35,000	~~0.09~~ 32,500	0.09	2,925	0.04	1,300
			$\Sigma = 19,200$ amu/molecule ⓐ M_m		$\Sigma = 15,900$ amu/molecule ⓑ M_n

ⓒ Amu/mer of PVC

$C_2H_3Cl = 24 + 3 + 35.5 = 62.5$ amu/mer

$DP = \frac{15,9000}{62.5} = 254$ mer/molecule based on $\overline{M}_n$

ⓓ $PDI = \overline{M}_m / \overline{M}_n = 19,200/15,900 = 1.2$

Comments:- Whenever there is a distribution of sizes, the number average molecular size is always less than the mass avg value, because of the large no. of smaller molecules per gm in the smaller size intervals. The two averages diverge more as the range of the size distribution increases.

P114

Non-crystalline materials

Long range order is absent in ~~so~~ liquids, glass, plastics & a few rapidly cooled ~~&~~ metals.

This lack of repetitive structure may be viewed as a volume, or 3-D, disorder.

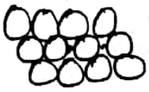
These materials are called amorphous (without form).

Liquids:- They are fluids (i.e. they flow under their own mass). Many liquids can become very viscous and even solid without crystallizing.

Take a single component metal and observe the disorder in it as it approaches melting & transforms to ~~met~~ a liquid. e.g. lead.

Greater thermal energy at higher temperatures introduces not only greater thermal vibrations ~~energy at higher temperatures~~ but also some vacancies.

Just short of the melting point, crystalline lead may contain upto 0.1 % vacancies in its lattice. When the vacancies approach 1% in a close-packed structure, "turmoil reigns". The regular 12 fold coordination is destroyed and the long range order of crystal structure disappears.



Crystalline metal
CN = 12
6 in the plane plus 3 above and 3 below.

Liquid metal
Long range order is lost
CN < 12 ∴
average interatomic distance increases slightly.

Energy is required to disrupt the crystalline structure at the time of melting. We call this energy the heat of fusion (ΔH_f). This is extra energy beyond the specific heat, or heat capacity, dE/dT, that is required for the increase in temperature. The energy for fusion or melting, differs from material to material, but in general reflects ~~fo~~ the strength of the atomic bonds. So ΔH_f can be correlated with T_m.

		T_m (°C)	ΔH_f (J/mole)
eg.	W	3410	32,000
	Fe	1538	15,300
	Cu	1084	13,500
	Al	660	10,500
	Pb	327.4	5,400

Solidification by crystallization releases $-\Delta H_f$ as the atoms ~~realli~~ reorder themselves into a crystalline array with specific interatomic distances.

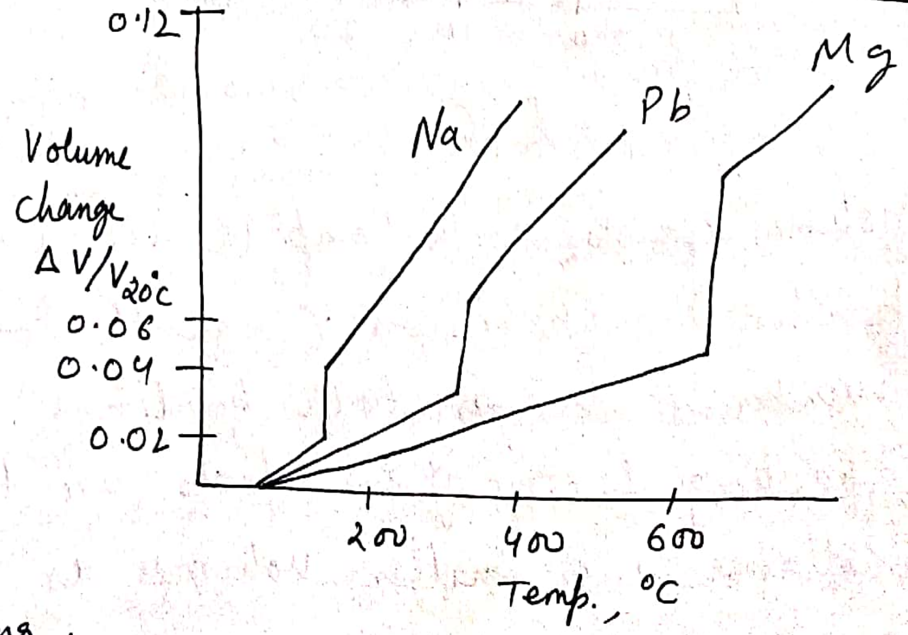
The disorder ~~a~~ that accompanies melting increases the volume of most metals ~~(fig 4.2.2)~~ and ionic solids because those crystals have high packing factors.

With the melting the CN in an fcc/hcp metal drops from 12 to 11 or 10. ~~Ther~~ The neighbors are not in a repetitive pattern. Consequently, the volume per atom and the average interatomic spacing is increased by a few %.

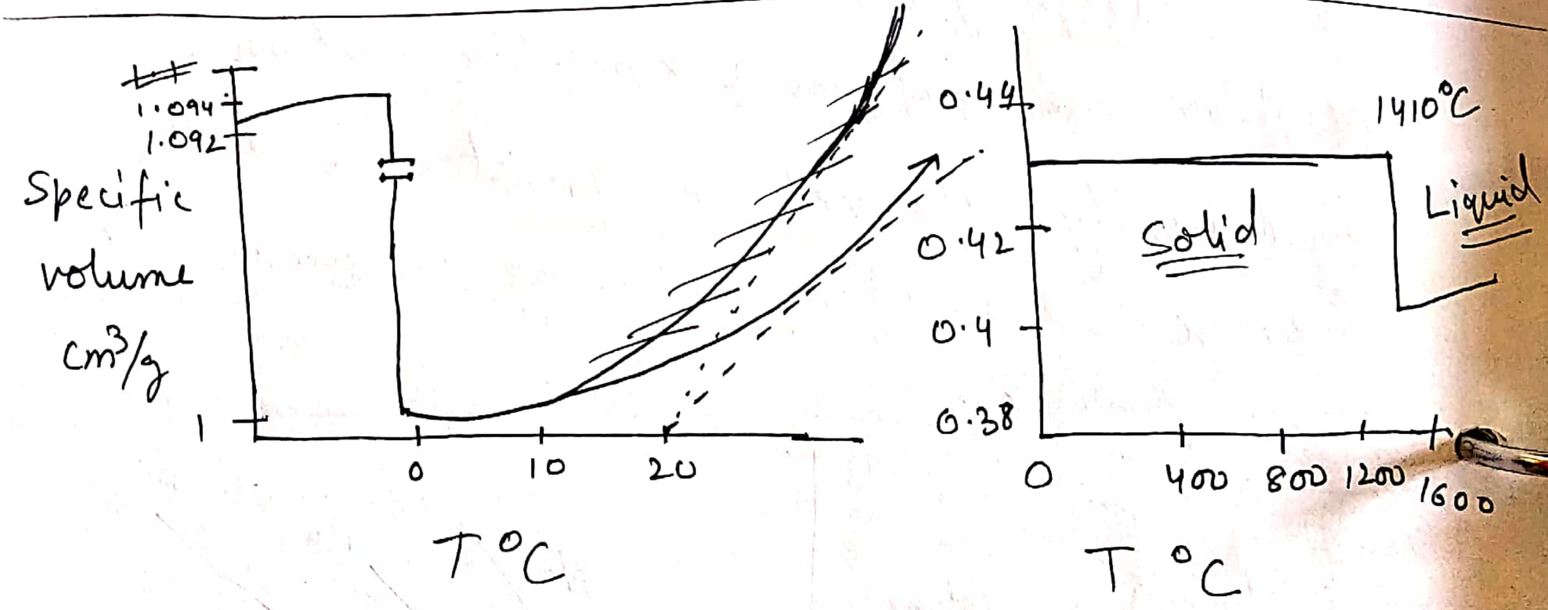
Volume changes with temp.

(Na – bcc
Pb – ~~f~~cc
Mg hcp)

metals with these structures expand on melting.



The disorder in melting ~~deg~~ decreases the volume of those materials that have network structures with stereo specific bonds, and therefore low packing factors. eg ① Silicon has a diamond cubic structure. ② ice has a predominance of hydrogen bridges. — These openly packed crystals collapse into denser liquids when their atoms are thermally excited into the molten state.

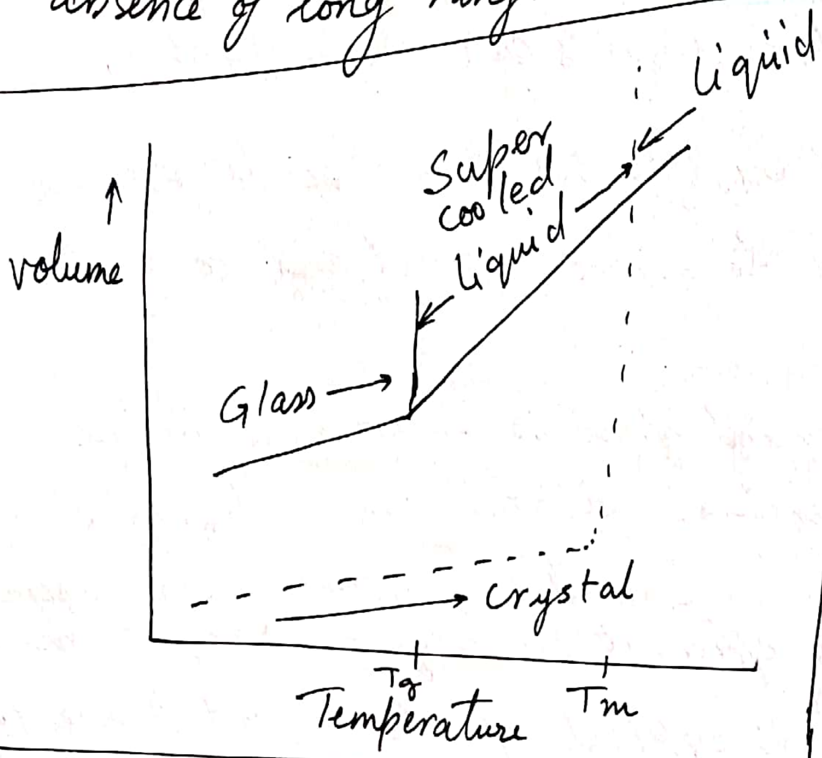


Volume changes with temp. ⓐ ice (hydrogen bridge bonding) ⓑ Silicon (covalently bonded). The coordination number is low for both bondings. Therefore, the packing factors of the solids are low. The structures collapse into smaller volumes as they melt.

Glasses

- They are non crystalline.
- ∴ sometimes considered to be very viscous liquids.
- However only a few liquids can make glasses.
- At high temperatures, glasses form true liquids. The atoms are free to move around and to respond to shear stresses.
- when a commercial glass is supercooled below its melting temperature without crystallizing, thermal contraction is caused by atomic rearrangements that produce more efficient packing of the atoms. This contraction is typical of all liquid phases (fig) However with more extensive cooling, there is an abrupt change in the thermal expansion coefficient, $\frac{dV}{dT}$ of glasses. Below a certain temperature, called the glass transition temperature, or more simply the glass temperature Tg, there are no further rearrangements of the atoms and the only volume change is a result of reduced thermal vibrations. This lower coefficient ~~can~~ is be comparable to the thermal expansion coefficient in crystals, where thermal vibrations are the only factor causing volume changes, and no rearrangement occurs. The term glass applies to those materials that have the expansion characteristics of (fig).

Glasses may be either inorganic or organic & are characterized by a short-range order (and an absence of long range order).

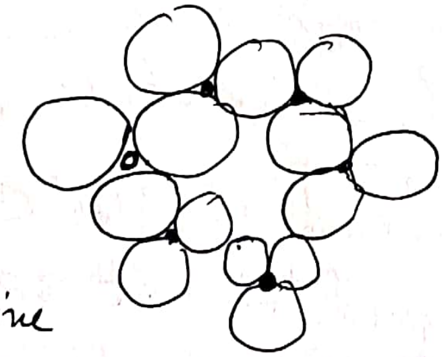


Volume changes in Supercooled liquids & glasses.

When a liquid is cooled, it contracts rapidly & continuously because with decreased thermal agitation the atoms develop more efficient packing arrangements, In the absence of crystallization, the contraction continues below Tm to the glass transition temperature Tg, where the material becomes a rigid glass. Below Tg, no further rearrangements occur, and the only further contraction is caused by reduced thermal vibrations of the atoms in their established locations.

The next fig. presents one of the simplest glasses B_2O_3 in which each small boron atom fits among three larger oxygen atoms. B has a valency of $3+$ & O ~~has~~ $2-$, ~~b~~ electrical balance is maintained if each oxygen atom is located between two boron atoms. ~~Thus~~ Accordingly a continuous structure of strongly bonded atoms is developed. Below Tg, where the atoms are ~~not~~ not readily rearranged, the fluid characteristics are lost and a noncrystalline solid exists. Such a solid has a significant resistance to shear stresses and therefore cannot be considered a true liquid.

~~The temperature-volume characteristics.~~



Structure of B_2O_3 glass = Although there is no long range crystalline order, there is a short range coordinational order. Each boron atom is among three oxygen atoms. Each oxygen atom is coordinated with two boron atoms.

~~The~~ Below the Tg, polymers are hard and brittle and have low dielectric constants. Above the Tg, a plastic becomes flexible & even rubbery, with countercurrent changes in its dielectric

Constant (K) ($K = \frac{D_m}{D_0}$ $\frac{\text{charge density with spacer material}}{\text{" " without " "}}$)

Tg of selected linear polymers

	Tg, °C (amorphous)	Tm, °C (If crystallized)
HDPE	-120	140
Polybutadiene	-70 ±	—* ($* =$ may not crystallize or very difficult to)
PolyPropylene	-15	175
Nylon 6/6	50	265
PVC	85	210*
PS	90	240*

Example 4-2.1

lead	ΔV/V
Liq 328°C	7%
Sol: 326°C	3%

From ~~Fig.~~ Table, Calculate the packing factor of

ⓐ of Solid lead at 326°C. ($\Delta V/V = 3\%$.

ⓑ of Liquid lead at 328°C. ($\Delta V/V = 7\%$)
(Assume the hard ball radius of 0.1750 nm is retained). PF of lead = 0.74.

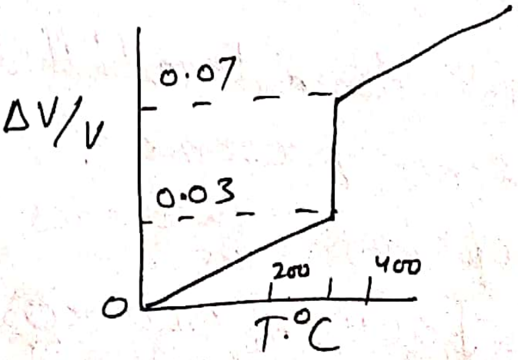
Procedure :- Lead is fcc with a calculated PF of 0.74;
Thus an increase in volume of 3% at 326°C and of 7% at 328°C decreases the PF accordingly.

Calculation

ⓐ $PF_{326°C} = \frac{0.74}{1.03} = 0.718$

ⓑ $PF_{328°C} = \frac{0.74}{1.07} = 0.692$

Comment= We could suggest that the radius increases by 1.0 % from 0.175 nm at 20°C to 0.1767 nm at 326°C to give the 3 v/o expansion. If so, the packing factor at 326°C would remain at 0.74 %, and the packing factor of the liquid would become 0.712. We cannot argue against that ~~that~~ suggestion, since one definition of radius is one-half of the closest interatomic distance. In either event, there is an abrupt discontinuity in packing efficiency at the melting temp.



Factors affecting Tg
(youtube - Polymer world. - Glass transition temp.)

① Mol. wt. — Tg is directly proportional to molecular weight of polymer

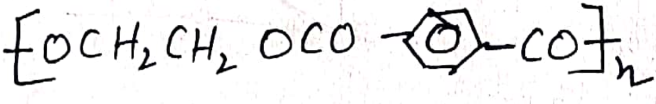
~~②~~ ∴ Short chains have more free volume. (low Mol wt) {more free ends of chains}
Tg for shorter chains will be lower than Tg for long chains

② Cross-links - Tg is directly proportional to the degree of cross links — restricted chain mobility ~~in~~

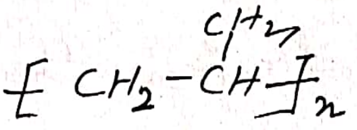
③ Plasticizer - Tg is inversely proportional to plasticization.
- Weaken intermolecular force between the polymer chains → reduce Tg [Plasticizers low mol. wt. compound improve processability)

④ Flexibility - Tg is inversely proportional to flexibility. eg. Poly(ethylene adipate) has Tg of -70°C $[OCH_2CH_2OCOCH_2CH_2CH_2CH_2-CO]_n$

Poly(ethylene terephthalate) has a Tg of 69°C ~~da~~ since presence of phenyl group in the chain back bone increases rigidity & Tg

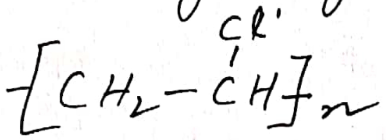


⑤ Intermolecular force - Tg is directly proportional to intermolecular force.

Atactic Polypropylene 
$\left[CH_2-\overset{CH_3}{CH} \right]_n$

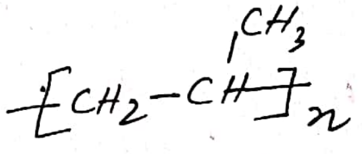
$T_g = -20°C$

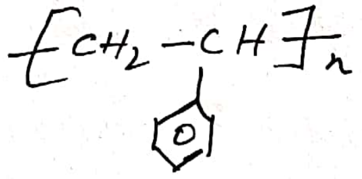
Atactic Poly(vinyl chloride) $T_g = 81°C$


$\left[CH_2-\overset{Cl}{CH} \right]_n$

(polar molecule
dipole-dipole interactions)

⑥ Chain branching - Polymers with more branching have more chain ends, so have more free volume, which reduces T_g - but the branches also hinder rotation, like large side groups, which increase T_g.

Atactic Polypropylene 
$\left[CH_2-\overset{CH_3}{CH} \right]_n$ $T_g = -20°C$

Atactic Polystyrene  $T_g = 100°C$

T_g is a property of the amorphous portion of a semicrystalline solid.

Higher the free volume — lower the T_g (easy chain mobility)

Higher the crystallinity - higher the T_g (restrict mobility of chains)

Measured using DSC, TMA (Thermal mechanical analysis (Differential scanning Calorimetry) & DMA (Dynamic mechanical Analyzer
Data

Data from these methods might vary to the tune of 25°C.

Q 4-P 24

Why is it easier to form a glass in a polymer than it is to do so in a metal?

Ⓐ Metals crystallize rapidly (in ms or μs), because each atom moves individually.

~~The or~~ Polymers → The ordering of molecules into a crystalline array involves the simultaneous rearrangements of large polyatomic groups.

Given a proper time period polymers can form glass.

4-P30 Is the elastic modulus of cross linked butadiene rubber greater than, approximately equal to or less than that of non vulcanized rubber?.

Ⓐ Greater

4-P31 Two gm of dextrose $C_6H_{12}O_6$. are dissolved in 14 g of water. What is the number-fraction of each type of molecule?

Ⓐ $C_6H_{12}O_6$

$12 \times 6 + 12 \times 1 + 16 \times 6 = 72 + 12 + 96 = 180$ amu

$H_2O = 18$ amu.

$2 + 14 = 16$ gm basis.

$\frac{2}{16} \times 180 + \frac{14}{16} \times 18$

✓ $\cancel{360} + \cancel{252}$

$22.5 + 15.75$

38.25 $\cancel{612}$ = mass avg M

✓

$\cancel{10+4}$ 140

$\cancel{10+8}$ $1\cancel{8}2$

$\cancel{100+120+32}$

$\cancel{252}$

~~2gm contains~~

180 gm ~~con suo~~ dextrose contains 1 mole

1

2 $\frac{1}{180} \times 2$ mole

18 gm H_2O —— 1 mole

14 gm —— $\frac{14}{18}$ mole

$\frac{2}{180} + \frac{14}{18} = \frac{2 + 140}{180} = \frac{142}{180}$ mole

$\frac{2}{180} / \frac{142}{180} = \frac{2}{142} = \frac{1}{71}$ molecule dextrose

$14/18 / \frac{142}{180} = \frac{140}{142} = \frac{70}{71}$ molecule water

$\frac{1}{71} \times (180) + \frac{70}{71}(18) = \frac{180 + 70 \times 18}{71} = \frac{180+1260}{71}$

$\frac{1440}{71} = \overset{20.28}{\cancel{1262.5}}$ amu. or g/mol $\underset{..}{no}$ avg molecular wt.

---

number fraction $= \frac{1}{71}$ dextrose & $\frac{70}{71}$ water

water = 0.986 ✓ dextrose 0.014 ✓

$0.986 \times 18 + 0.014 \times 180$ ✓

$= 17.75 + 2.52 = 20.27$ $\underset{..}{no}$ Avg M

4-P32 The following data were obtained from an analysis of a ~~p~~ polymeric sample.

	~~Wi~~ Mi	~~Wi~~	WiMi
Interval mid pt.	35 000 amu	1.25 g	43750
	25 000	2.65	66250
	15 000	2	30 000
	5000	1.9	9500
	ΣWi	7.8	$\frac{149500}{7.8}$

Compute the mass-average molecular size.

19166.67 or 19200 g/mol.

94-P33

ⓐ What is the mass avg molecular size of the molecule in Ex. 4-3.1(b) what is the no avg molecular size ?

Soln has 15 g water, 4 g C_2H_5OH/ethanol, and 1 g sugar $C_6H_{12}O_6$

a ~~H_2O~~ Basis 20g

		Wi
H_2O	15/20	0.75
C_2H_5OH	4/20	0.2
$C_6H_{12}O_6$	1/20	0.05

Basis 20 amu

			X_i
H_2O	15/18	0.833	0.9
C_2H_5OH	4/46	0.087	0.094
$C_6H_{12}O_6$	1/180	0.006	0.006
		0.926	

water = 18 amu C_2H_5OH = 46 amu $C_6H_{12}O_6$ = 180 amu

mass avg $0.75 \times 18 + 45 \times 0.2 + 180 \times 0.05 = 31.7$ amu ✓

~~$0.833 \times 18 + 0.087 \times 46 + 0.006 \times 180 = 15.01$~~

~~20.01 amu~~

number avg $0.9 \times 18 + 0.094 \times 46 + 0.006 \times 180 = (21.6)$ ~~Book~~

= amu ✓

Q4 - P34

PVC C_2H_3Cl is dissolved in an organic solvent.

ⓐ What is the mean square length of a molecule with a molecular mass of 28,500 g/mol

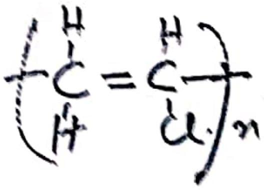
ⓑ What would be the molecular mass of a molecule with one-half ~~of~~ the mean square length of that in part ⓐ.

$$\overline{L} = l\sqrt{x}$$

$$C_2H_3Cl = 12\times2 + 3\times1 + 35.5 = 62.5 \text{ amu}$$

$$\frac{28500}{62.5} = \overset{456}{\cancel{114}} = n.$$

$\frac{P}{H} = \sin 6$



$$-\left(\overset{H}{\underset{H}{C}}=\overset{H}{\underset{Cl}{C}}\right)_n-$$

C-C bond = 0.154 nm ∠ = 120°.

$$0.154\sin60° = 0.135\,nm$$

$$\overset{0.135}{\cancel{0.154}}\sqrt{\underset{456\times2}{\cancel{114}}} = \cancel{0.154\times21.35}\ \underset{0.135\times30.2}{} = 3.29 = \underline{4.08}\,nm$$

$$0.135\sqrt{456} = 2.88.$$

C-C, ∠ = 109.5° $0.154\sin54.75 = 0.125$

$$0.125\sqrt{456} = 2.68\,nm.$$

$$\overline{L} = l\sqrt{x} = 0.154\sqrt{456\times2} = 4.65\,nm$$

ⓑ $\bar{L} = l\sqrt{x_1}$

$\frac{\bar{L}}{2} = l\sqrt{x_2}$

$\frac{1}{2}\frac{\bar{L}}{l} = \sqrt{x_2}$

$\left(\frac{\bar{L}}{l}\right)\frac{1}{2} = \sqrt{x_2} = \cancel{\frac{\sqrt{x_1}}{2}}$

$\left(\frac{\bar{L}}{l}\right)\left(\frac{1}{4}\right) = x_2$

$\frac{\bar{L}}{2} = l\sqrt{x}$

$\left(\frac{\bar{L}}{2l}\right)^2 = x$

$\frac{1}{4}\left(\frac{\bar{L}}{l}\right) = x$

$x = \frac{1}{4}$ th

$\Rightarrow \quad n = \frac{1}{4}$ th

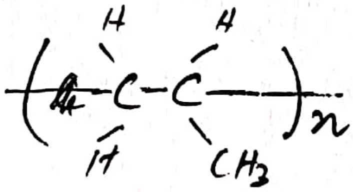
$n = \frac{28500}{4} = 7125$ g/mol ✓

↑ amu/ molecule

$n = \frac{62.5 \times 456}{4}$

P 4-35 Determine the degree of polymerization & the mean square length of the average molecule in problem P 431, if the polymer is polypropylene (number average).

Polypropylene =



C H
3×12 6×1
42 amu

(Mi) Mass	÷42 → no.	Xi	MiXi
35000 amu	833.33	0.43	15050
25000	595.24	0.31	7750
15000	357.14	0.19	2850
5000	119.05	0.06	300
	1904.73 ~~amu~~ molecules.		25,680 amu no. avg. mol. wt.

$$\frac{25680}{42} = 611.43 = n \text{ or degree of poly-}$$

bonds

$\sqrt{x} = \sqrt{611.43 \times 2} = 24.7\sqrt{2} = 34.93$

$\bar{L} = l\sqrt{x} = 0.\cancel{126}^{0.133} \times 2\cancel{4.7}^{34.93} = 3.1\text{ nm}$ ~~4.4~~ nm 4.66 nm

$l = 0.154 \sin\left(\frac{109.5^\circ}{2}\right) = 0.126.$

$\left(\frac{120}{2}\right) = 0.133$

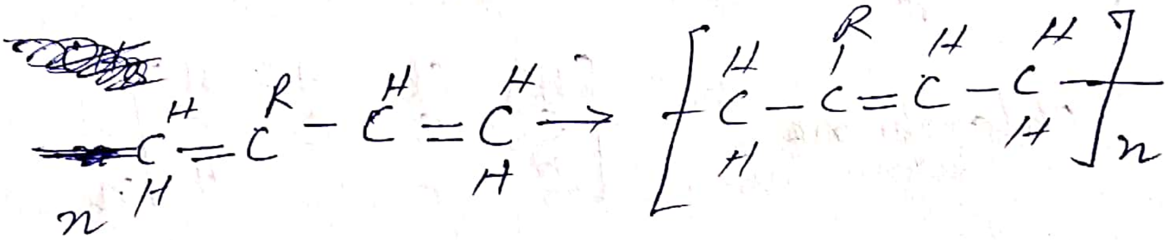
$\boxed{\text{Ans} = 3.7\text{ nm}}$

$\bar{L} = 0.154\sqrt{611.43 \times 2} = 5.4$

Q4-P36

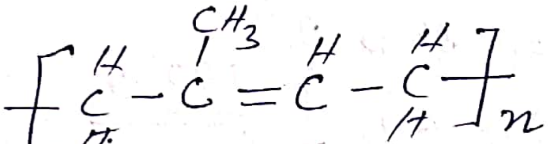
ⓐ What % sulfur would be present if it were used as a cross-link at every possible point in polyisoprene?

ⓑ What percent would be present if it were used in polychloroprene?



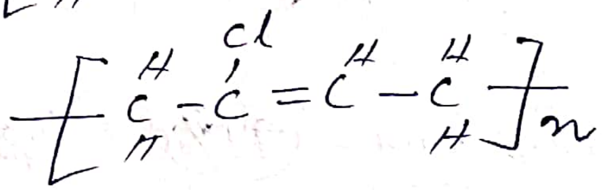
$$n\,\overset{H}{C}=\underset{H}{C}-\overset{R}{C}-\overset{H}{C}=\underset{H}{\overset{H}{C}} \rightarrow \left[-\underset{H}{\overset{H}{C}}-\overset{R}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}-\right]_n$$

cis-Polyisoprene



$$\left[-\underset{H}{\overset{H}{C}}-\overset{CH_3}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}-\right]_n$$

polychloroprene



$$\left[-\underset{H}{\overset{H}{C}}-\overset{Cl}{C}=\overset{H}{C}-\underset{H}{\overset{H}{C}}-\right]_n$$

Poly isoprene $C_4H_5CH_3 \rightarrow C_5H_8 = 12 \times 5 + 8 \times 1$

$= 68$

2 atoms S → 64 gm

Total (product) = 64 + 68 = 132

Fraction sulfur $= \frac{64}{132} =$ 48.5%

$C_4H_5Cl = 12 \times 4 + 5 \times 1 + 35.5 = 48 + 5 + 35.5$

$= 88.5$

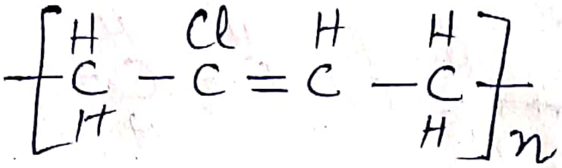
2 atoms S = 64 } = 152.5

$$\begin{array}{r} 48 \\ 35.5 \\ 5 \\ \hline 88.5 \end{array}$$

fraction sulfur $= \frac{64}{152.5} =$ 42%.

Q 4-P37 A rubber contains 91 w/o polymerized chloroprene and 9 w/o sulfur. What fraction of the possible cross-links is joined by vulcanization? (Assume that all the sulfur is used for cross-links of the type shown in fig. 4-3.10)

Chloroprene



$$\left[-\overset{H}{\underset{H}{C}}-\overset{Cl}{C}=\overset{H}{C}-\overset{H}{\underset{H}{C}}- \right]_n$$

① $C_4H_5Cl = 88.5$ } 152.5
Sulfur $S_2 = 64$ }

X ($152.5\text{ amu} = $ ~~91%~~   Chloroprene $= \frac{88.5}{152.5} = 58\%$

$\frac{64}{152.5} = $ ~~100~~ 41.97 w/o or 42%.)

$\frac{9}{41.97} = $ ~~2.38~~ 0.2144 or 21.44%

9% ~~910%~~
6/9

97.25 gm $= \frac{88.5}{91} \times 100.$

88.5 gm — 91%
1%
100%.

9% — 64 gm

42% — 100%. cross link
1% — $\frac{100}{42} \times 9 = \frac{900}{42} = 21.4$

② 9% Sulfur

$\frac{9}{100} = \frac{x}{88.5+x}$

$9 \times 88.5 = 100x - 9x$

$9 \times 88.5 = 91x$

8.75 gm

③ 88.5 gm —— 64 gm —— $\frac{100\%}{64} \times 8.75 = 13.6\%$.
88.5 —— 8.75 gm —— $= 0.14$.
88.5

Callister
p. 476 Ch. 13.

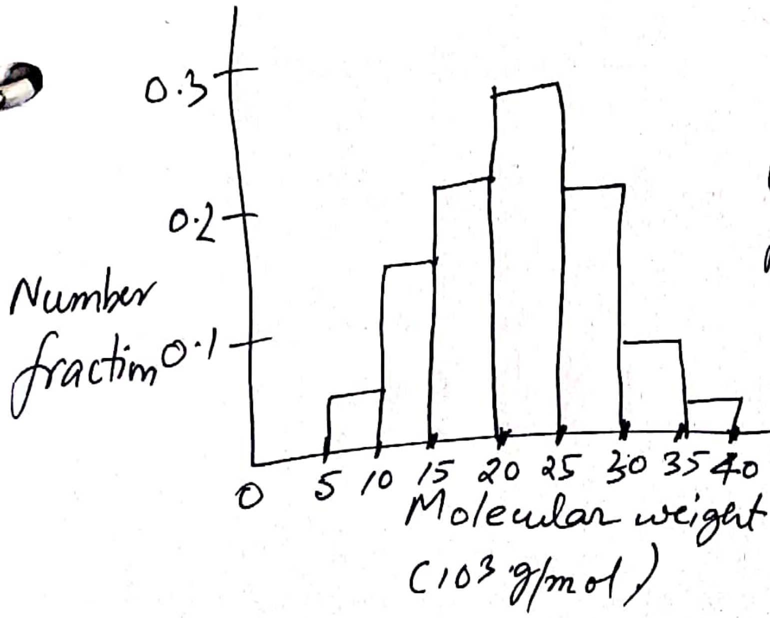
Assume that the molecular weights and degree of polymerization.

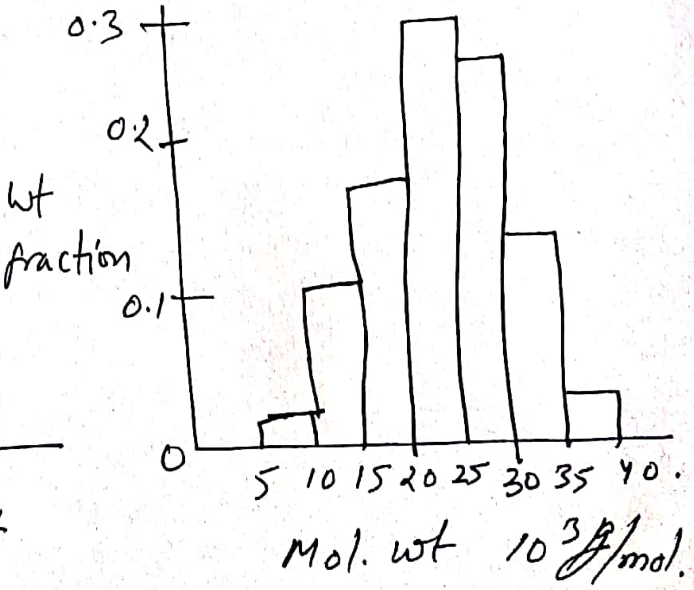
Assume that the molecular weight distributions shown in Fig. 13.3 are ~~four~~ for ~~p~~ PVC.

Compute ⓐ the number average molecular weight
ⓑ the degree of polymerization and
ⓒ the weight average molecular weight.

Solution.

ⓐ The data necessary for this computation, as taken from figure 13.3 a are presented in Table 13.4a. According to equation 13.5 a.



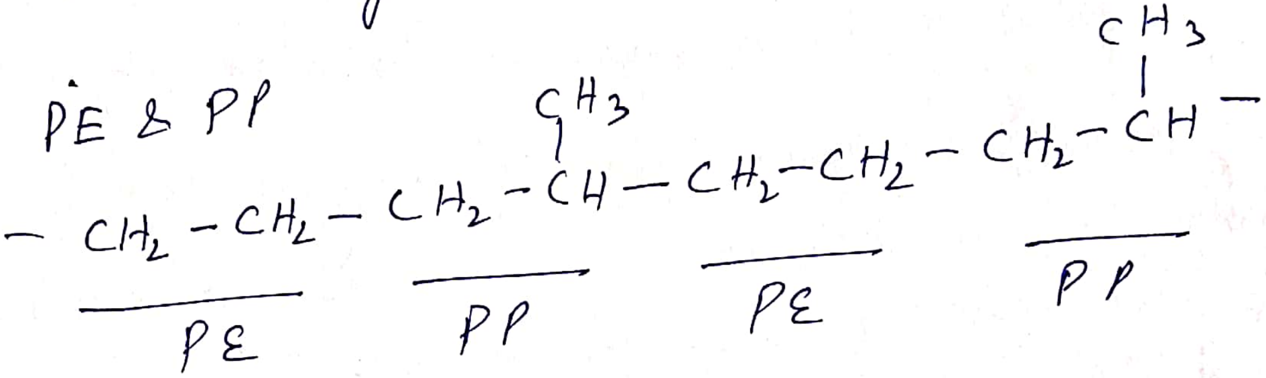


Rajesh
Prasad
IIT Delhi

Co Polymers

- analogous to solid solutions in metals
- ~~cont~~ A polymer consisting of more than one kind of monomers

PE & PP

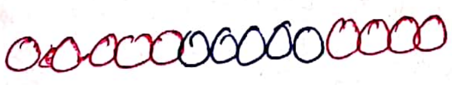


$$-\underbrace{CH_2-CH_2}_{PE}-\underbrace{CH_2-\overset{CH_3}{\overset{|}{CH}}}_{PP}-\underbrace{CH_2-CH_2}_{PE}-\underbrace{CH_2-\overset{CH_3}{\overset{|}{CH}}}_{PP}-$$

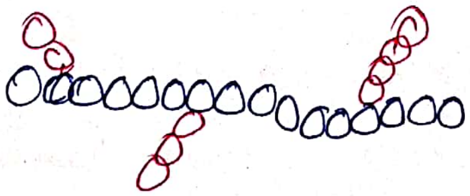
Types of copolymers

Random (disorde
soli
s

Alternating. (ordered
solid
soln)



Block



Branch.

9-6 Solid solutions in Polymers (copolymers)

Many commercial plastics consist of a single phase with two (or more) components & are therefore solid solutions. These are called copolymers. Although the most common copolymers are amorphous nonmetallic solids, we can consider them to be polymeric alloys.

Polymers may exist as homogeneous solid solutions in two forms. The first is a miscible (homogeneous) solution of two distinct molecular species. The molecules are distinct but form a single phase.

common copolymer = Polystyrene (PS) & polyphenylene oxide (PPO)

The 2nd type of copolymer contains more than one type of mer within a single polymeric molecule. eg. vinyl monomers: They are bifunctional with 2 principal C atoms. Each polymerizes with the rxn,

$$n\,C_2H_3R \rightarrow (C_2H_3R)_n$$

Two component polymers (schematic - conformation is never straight)

…… — S — S — S — S — …
…… — S — S — S — S-S — S — ……
…… PO — PO — PO — PO — PO — PO — …
…… PO — PO — PO — PO — PO — PO — ……
…… PO — PO — PO — PO — PO — PO — …

ⓐ Mutual solubity ~~be~~ of 2 polymers within a ~~a~~ single phase Styrene & polyphenylene oxide mers

— S — A — A — S — A — S — S — A — A — S —
— S — A — S — S — S — S — A — A — S — A — A —
— S — A — S — S — A — A — A — S — A — S — S — A — A

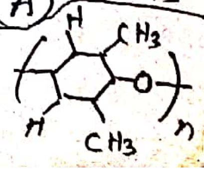
ⓑ Random copolymer with styrene mers (S) & acrylonitrile mers (A)

Polystyrene & Poly acrylonitrile have vinyl mers

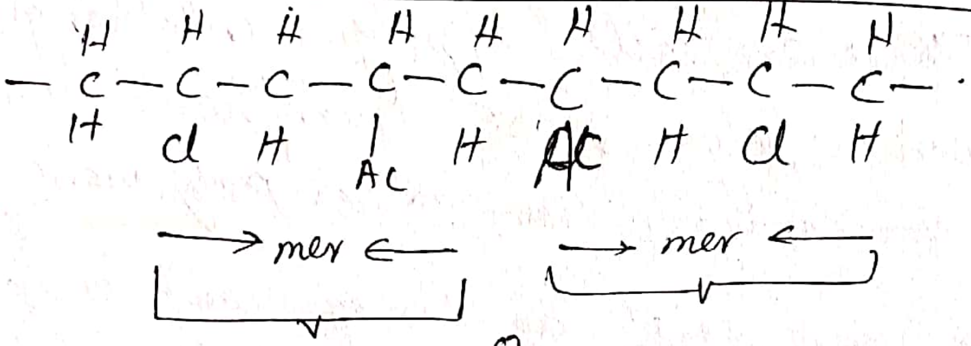
$CH_2CHC_6H_5$

PAN CH_2CHCN

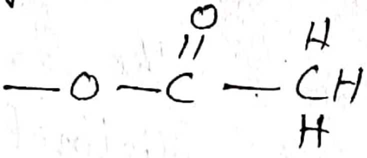
PPO =



A polymer molecule can have more than one type of mer. Fig above ⓑ & fig — Both are random copolymers.



Ac ·



$-O-\overset{\overset{O}{\|}}{C}-CH_3$

$OCOCH_3$

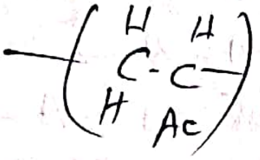
Copolymerization of vinyl chloride & vinyl acetate

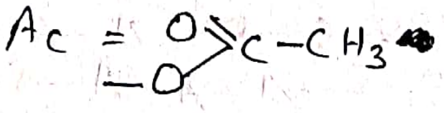
When randomly arranged, a copolymer is comparable to a solid solution in metallic and ceramic systems

Block copolymer → Section 7.5 ⇒ clustering of like mers along the molecular chain.

Example 4-6.1 A copolymer contains 10 m/o (mer %) vinyl acetate and 90 m/o vinyl chloride (m/o = mer percent) ⓐ what is the w/o vinyl acetate? ⓑ what is the w/o chlorine?

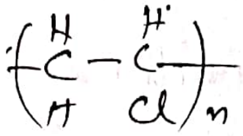
Solution :- vinyl acetate mer





mer
C = 4
H = 6
O = 2

vinyl chloride mer =



$$\left(-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{Cl}{C}}-\right)_n$$

mer
$\boxed{\begin{array}{c}2C\\3H\\1Cl\end{array}}$

Basics :

100 mers = 10 mers VA_c ~~#~~ (= 40 C + 20 O + 60 H)

= 90 mers VC (= 180 C + 270 H + 90 Cl)

10 mers V_{AC} = 40×12 + 20×16 + 60×1
= 480 + 320 + 60 = 860 amu

90 mer VC = 180×12 + 270×1 + 90×35.5
= 2160 + 270 + ~~900~~ 3195
= 5625 amu

ⓐ w/o vinyl acetate = 860/(5625 + 860)
= 13.3 w/o

ⓑ w/o chlorine = $\frac{3195}{(5625+860)}$ = 49.3 w/o.

Additional info :- A copolymer can be viewed as a solid solution of the contributing mers. ~~Just as with~~ The overall structural pattern exists with one, two, or several types of components.

~~Table 4-6~~ Example 4-6.2 = A copolymer contains ~~97 w/o~~ 92 w/o vinyl chloride & 8 w/o vinyl acetate. What is the mer fraction of VA_c?

Procedure = Since a copolymer is the molecular equivalent to a crystalline solid soln we will use similiar procedures

Choose a mass basis, and determine the numbers of each component.

$VC = -(C_2H_3Cl)- = 24+3+35.5 = 62.5$ amu/mer

$VAc = -(C_2H_3O.COCH_3)- = 24+3+59 = 86$ amu/mer

Basis: 100,000 amu = 92,000 amu VC
+ 8,000 amu VAc

VC 92,000/62.5 = 1472 mer = 0.941

VAc 8,000/86 = 93 mer = 0.059

Total = 1565 mers

Comment = This copolymer has ~16 PVC mers per acetate (PVAc) mer. Example of uses are indicated in Table

Vinyl chloride - acetate copolymers. Correlation between composition, molecular weight & applications

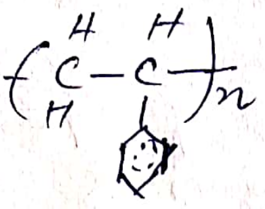
Item	w/o of vinyl chloride	No of chloride mers per acetate mer	Range of average mol. wts	Typical applications
Straight polyvinyl acetate	0	0	4800 - 15000	Limited chiefly to adhesives

Chloride acetate copolymers	85-87	8 - 9	8,500 - 9,500	Lacquer for lining food cans, sufficiently soluble in ketone solvents for ~~f~~ surface coating purposes.
	85-87	8 - 9	9,500 - 10,500	Plastics of good strength and solvent resistance molded by injection.
	88-90	10-13	16,000 - 23,000	Synthetic fibers made by dry spinning; excellent solvent & salt resistance
	95	26	20,000 - 22,000	Substitute rubber for electrical wire coating; must be plasticized; extrusion molded
straight PVC	100	—	—	Pipes, & similiar rigid products.

th

4-P-30 :: Is the elastic modulus of cross linked butadiene rubber greater than, approximately equal to, or less than that of nonvulcanized butadiene rubber?

4-P61 A copolymer has a 5 to 2 mer ratio of styrene and butadiene. What is the weight ratio of these two components?

Styrene = 

$C_2H_3C_6H_5$ or C_8H_8

$12\times8 + 8\times1 = 96+8 = 104$

Butadiene $\left(CH_2-CH=CH-CH_2\right)_n$

$C_4H_6 = 12\times4 + 6\times1 = 48+6.$
$= 54$

5 styrene + 2 BD = $5\times104 + 2\times54$
$520 + 108 = \underline{\underline{628}}$

~~520~~ $\frac{520}{628} = 82.8$ w%. $\frac{108}{628} = 17.2$ wt%

$\frac{82.8}{17.2} = \frac{4.8}{1}$ or $\boxed{4.8 \text{ to } 1}$ weight ratio of S & BD

4-P62 PVC & PVDC are copolymerized in a 2 to 1 weight ratio. They form a molecular chain similiar to that of fig 4-6.1(b). What fraction is of each type?

PVC $= \left(CH_2-CHCl\right)_n$ $C_2H_3Cl = \left.\begin{matrix}12\times2\\3\times1\\35.5\times1\end{matrix}\right\}\begin{matrix}24\\3\\35.5\end{matrix}$

$= 62.5$ amu

PVDC $\left(CH_2 - CCl_2 \right)_n$ = 2×12 = 24

35.5×2 71

2×1 2

$$\frac{}{97}$$

2 PVC + 1 PVDC = $2 \times 62.5 + 97$ = 222

They form a random copolymer with PVC & PVDC mers.

$f_{PVC} = 0.76$

$f_{PVDC} = 0.24$

w/o of PVC = $\frac{125}{222} = 0.563$

w/o of PVDC = $\frac{97}{222} = 0.437$

Basis = 1000 ~~mer~~ amu ⇒ ~~563~~

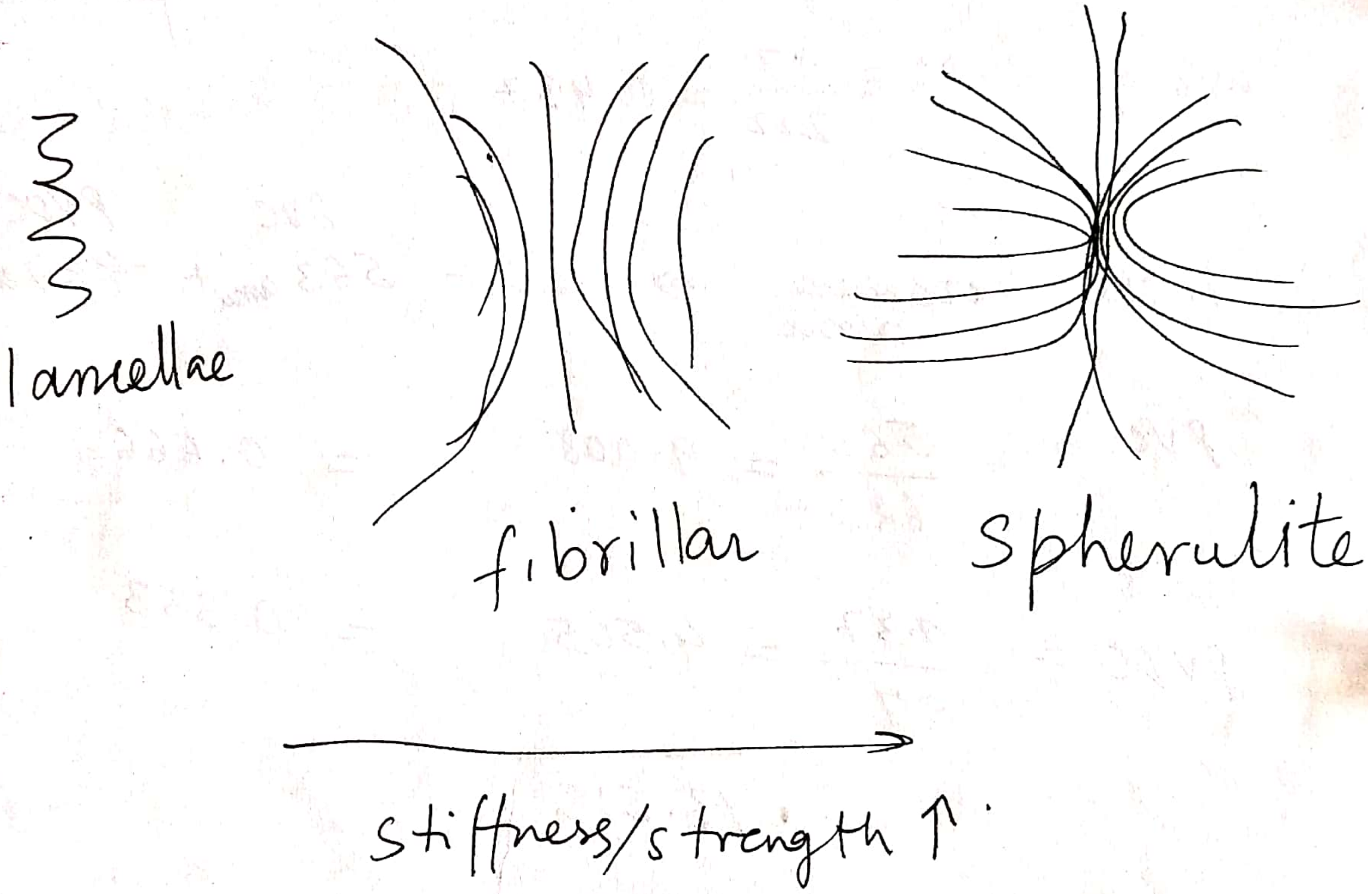
PVC	PVDC
563 amu +	437 amu

PVC = $\frac{563}{62.5} = 9.008$ = 0.666

PVDC = $\frac{437}{97} = 4.505$ = 0.333

13.513

$\frac{62.5}{222} =$


lamellae
fibrillar
spherulite
stiffness/strength ↑