ENGINEERING CHEMISTRY

UNIT -5

MATERIALS

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11.11.2019
Monday

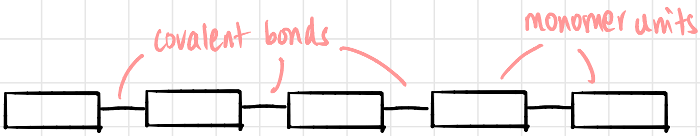
MATERIALS

polymers • nanomaterials

- Can be soft, harder than steel (bulletproof vests - kevlar)
- Can be used for making F1 racecars (kevlar, carbon nanotubes)
- Can be conducting in nature (electronically, not ionically; can be used as electrode)

- We have the ability to tailor-make a polymer.

POLYMER



- Giant molecules formed by repeated joining of several simple molecules which are linked through strong covalent bonds.
- Eg: Teflon, PVC

MONOMER

- Simple molecules with two or more binding sites which are the building blocks of polymers.
- Not all molecules can qualify as monomers (there must be binding sites)

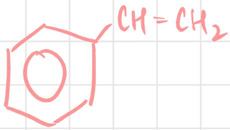
CH_3-CH_3 — not a monomer
ethane

$CH_2=CH_2$ — can qualify as monomer
ethene

$CH_3-\overset{O}{\overset{\|}{C}}-OH$ — can only form dimer (only one bonding site)
acetone

$HOOC-(CH_2)_4-COOH$ — can be used
adipic acid

$NH_2 - C(H_2)_5 - COOH$ — can be used
amino acid



— can be used

styrene

$CH_2 - OH$
$|$
$CH_2 - OH$ — can be used (bifunctional)
glycol

$CH_2 - OH$
$|$
$CH - OH$ — can be used (trifunctional)
$|$
$CH_2 - OH$
glycerol

POLYMERISATION

$$(CH_2 = CH_2)_n \xrightarrow[\text{polymerisation}]{\text{initiator}} \left(CH_2 - CH_2 \right)_n$$ — DP

Degree of polymerisation (DP)

The total number of repeat units in a polymer.
Gives us information on:
(i) length of the polymer chain
(ii) molecular weight of the polymer (DP × weight of monomer)

TYPES OF POLYMERISATION

(1) ADDITION POLYMERISATION

- self-addition of unsaturated monomers takes place without elimination of by-products.
- also called chain polymerisation

$$n \left(CH_2 = \underset{\underset{Y}{|}}{CH} \right) \xrightarrow{\text{initiator}} \left(CH_2 - \underset{\underset{Y}{|}}{CH} \right)_n$$

Y: H — Polyethylene
Y: $-CH_3$ — Polypropyline
Y: $-Cl$ — Poly vinylchloride
Y: $-C_6H_5$ — polystyrene
Y: $-CN$ — Polyacrylonitrile

MAIN FEATURES

1. Only for unsaturated compounds
2. Double bond provides two binding sites
3. No elimination of byproducts.
4. Self-addition takes place rapidly.
5. Polymerisation is brought about by either free-radical or ionic mechanism.
   (i) Free radical: benzoyl peroxide initiator
   (ii) Cationic mechanism: Lewis acid to generate cation (Carbonium)
   ↪ use Lewis acids.
   (iii) Anionic mechanism: organo metallic compound — RMgX
   ↪ use BuLi
   (iv) Coordination mechanism: Zeigler Natta Catalyst
   ↪ $Al(C_2H_5)_3 + TiCl_4$ (coordinate bond)
   - when molecules get adsorbed on catalyst, stereoregular polymer formed
6. Linear or branched polymers are formed.
7. Molecular weight of polymer is an integral multiple of that of the monomer.

HOMOPOLYMERISATION

- one type of monomer
- Teflon, PVC, polyethylene etc.

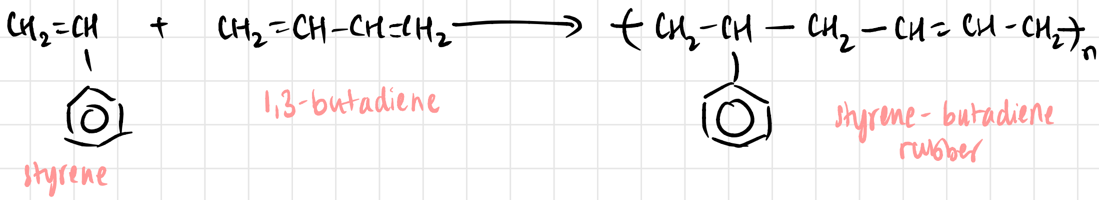
COPOLYMERISATION

- two different types of monomers

(1) $\underset{\text{vinyl chloride}}{CH_2=CH(Cl)} + \underset{\text{vinyl acetate}}{CH_2=CH(OCOCH_3)} \longrightarrow -\!\!\left[CH_2-CH(Cl)-CH_2-CH(OCOCH_3)\right]\!\!-_n$

polyethylene with hydrogens replaced

(2) SBR - Styrene-butadiene rubber



- speciality of SBR - polymer is that it is still unsaturated

TYPES OF COPOLYMERS

(i) Alternate

$-\!\!\left[M_1-M_2-M_1-M_2-M_1-M_n\right]\!\!-$

(ii) Random

$-\!\!\left[M_1-M_1-M_2-M_1-M_2-M_2\right]\!\!-$

(iii) Block

$-\!\!\left[\underbrace{M_1-M_1-M_1}-\underbrace{M_2-M_2-M_2}-\underbrace{M_1-M_1-M_1}-\underbrace{M_2-M_2-M_2}\right]\!\!-$

(iv) Grafting

12.11.2019
Tuesday

(2) CONDENSATION POLYMERISATION

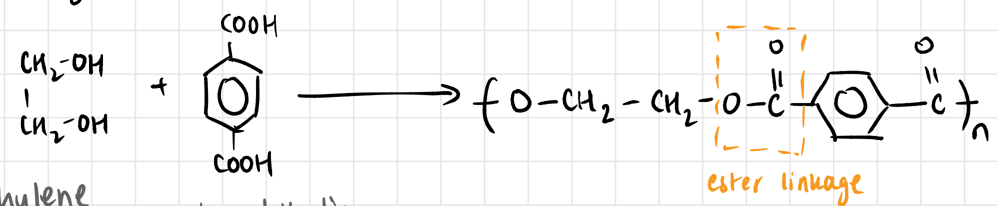
- Also called chain polymers
- Intermolecular condensation with continuous elimination of byproducts.
- Normally catalysed by acid or alkali
- At least two functional groups.

(i) Nylon 66

$$HOOC-(CH_2)_4-COOH + H-\overset{H}{N}-(CH_2)_6-NH_2 \xrightarrow{-H_2O} \left(\overset{O}{\overset{\|}{C}}-(CH_2)_4-\boxed{\overset{O}{\overset{\|}{C}}-NH}-(CH_2)_6-NH \right)_n$$

adipic acid — hexamethylene diamine — amide linkage

(ii) Terylene



ethylene glycol

terephthalic acid

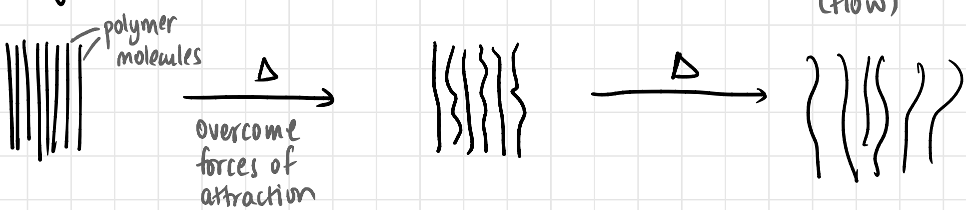
MAIN FEATURES

1. Two or more reactive functional groups should be present
2. Polymerisation is through intermolecular condensation.
3. Continuous elimination of byproducts.
4. Chain buildup is slow.
5. Catalysed by acid or alkali
6. Linear, branched or cross-linked polymers are produced.
7. Elemental composition of the polymer is generally different from that of its monomer.

STRUCTURE-PROPERTY RELATIONSHIP

GLASS-TRASITION TEMPERATURE (T_g)

glassy state $\xrightarrow{T_g}$ rubbery state $\xrightarrow{T_m}$ liquid state (flow)

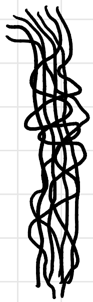


- Temperature at which polymer changes from glassy state to rubbery state
- Rubber balls cooled to -ve temp is brittle like glass

- Many properties of polymers

1. Crystallinity

- crystallites



periodic arrangement

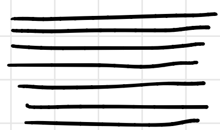
- depends on how close the polymer chains can come
- certain areas, periodic arrangement with strands close to each other.
- depends on structure and stereoregularity.

(i) Structure

(a) Bulky pendant groups

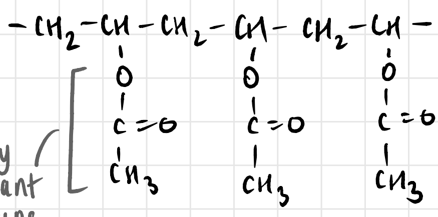
PE:

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

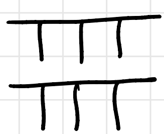


crystalline

PVac:

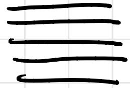


bulky pendant groups



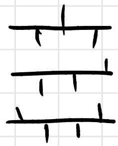
amorphous

PE $\xrightarrow{\text{ZN catalyst}}$ HDPE
high density
• bottles



uses Ziegler-Natta catalyst: stereoregular

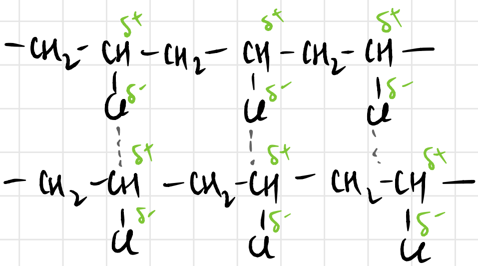
PE $\xrightarrow{\text{free radical}}$ LDPE
low density
• cling wrap



free radical mechanism; random arrangement.

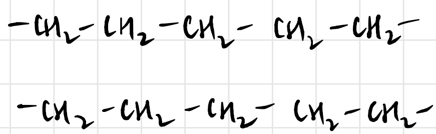
(b) Presence of polar group

PVC



dipole-dipole interaction

PE



van der Waals forces

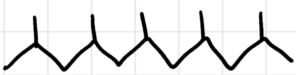
(ii) Stereoregularity

- arrangement of substituents in space
- atactic, isotactic, syndiotactic

(a) Atactic

random substituent arrangement

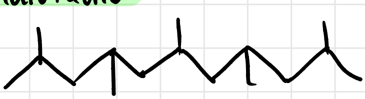
(b) Isotactic



or

same side

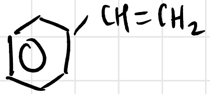
(c) Syndiotactic



- isotactic polystyrene for car bumper
- atactic polystyrene for gum sealants

Q1: Write the three stereoisomers for polystyrene. Which has the highest melting point? (DP = 5)
What is molecular weight? (styrene = 104)

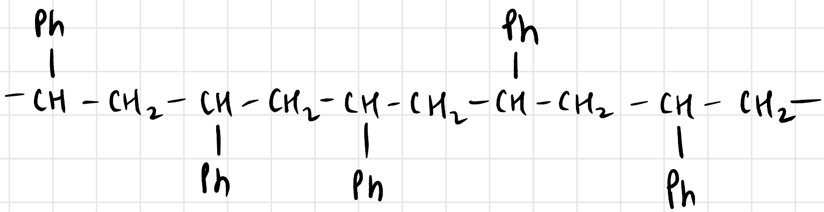
A1: Styrene:



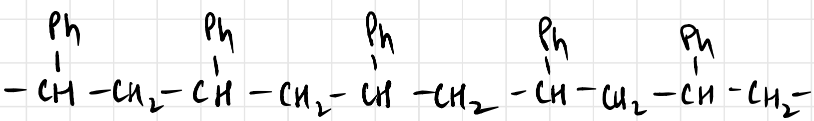
104g

Polystyrene: DP = 5 ⇒ molecular wt = 104 × 5 = 520 g mol^{-1})

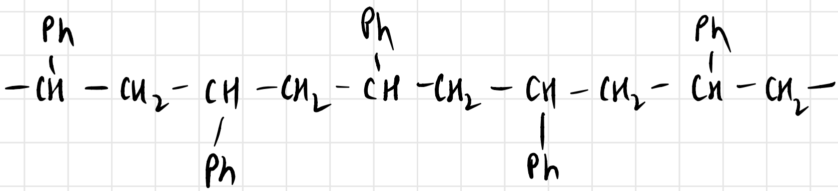
(i) Atactic



(ii) Isotactic – highest MP (orderly arrangement)



(iii) Syndiotactic



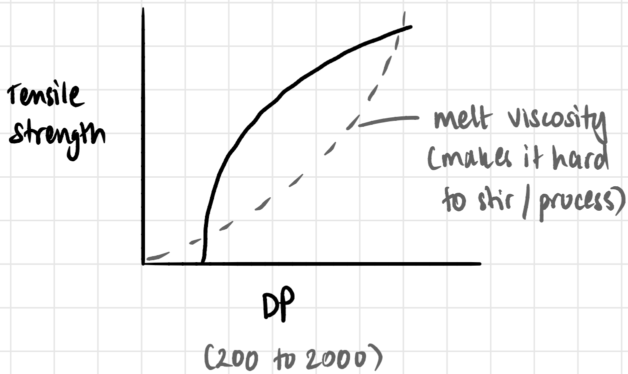
2. Tensile strength

- The amount of stress a polymer can take before suffering permanent deformation.

impact strength: when it is hit
glass: almost nil

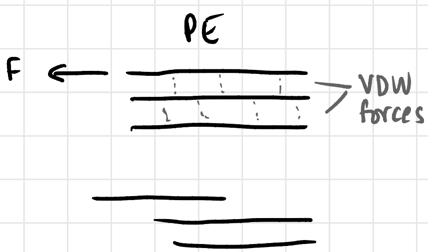
(i) Molecular weight

low wt. — soft to gummy
high wt. — tough

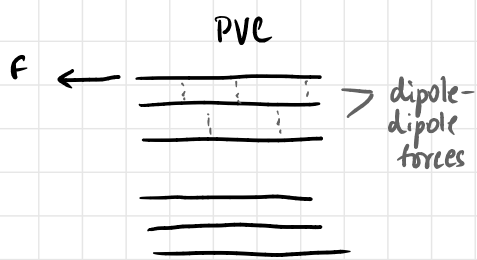


need to compromise between tensile strength & melt viscosity

(ii) Presence of polar groups



chains slip against each other



chains harder to move

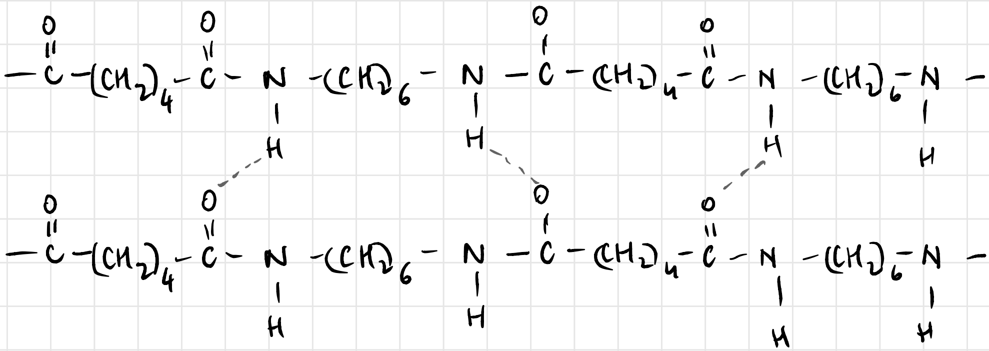
- cannot tear Nylon (H-bonding); very high tensile strength
- can only cut

13.11.2019

Wednesday

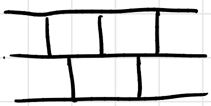
Nylon 66

H-bonds



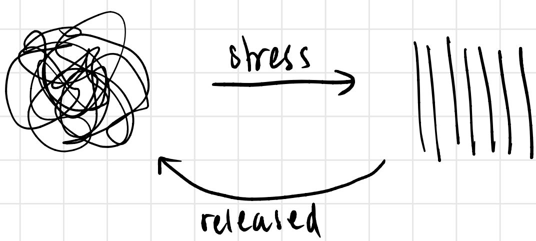
(iii) Cross linked

covalent bonds



3. Elasticity

- Property of a material to deform under stress and regain original shape when stress is released.
- Elastomers



- How to make polymer elastic (elastomer)

i) Introduce cross-linking

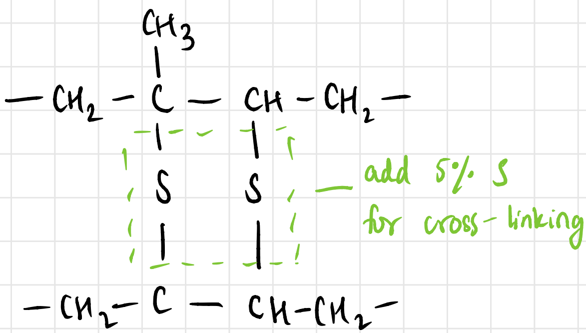
- natural rubber - isoprene

only VDW forces; chains slip

$$n\ CH_2{=}\underset{\substack{|\\CH_3}}{C}-CH{=}CH_2 \longrightarrow \left(CH_2-\underset{\substack{|\\CH_3}}{C}=CH-CH_2\right)_n$$

isoprene → natural rubber

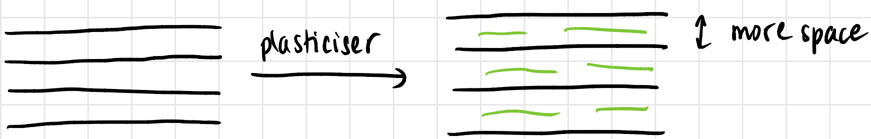
- natural rubber too weak; needs to have stronger forces
- vulcanise rubber at sites of unsaturation.
- formation of covalent bonds



- Should not add too much; needs to be flexible as well
- Add a small amount of S (5%) to the natural polymer.

ii) Introduce plasticiser into a hard molecule.

- PVC - dipole-dipole
- To gain elasticity, added (NOT BOUND)



- compounds added to hard polymers that are introduced to make it more flexible
- Eg: Ph_3PO_4
- New car seat smell: seat made of PVC (volatile; not escaping)
- Old car seats get brittle; cracks formed.

4. Chemical resistance

- The resistance to swell, dissolve or get degraded in the presence of a solvent or chemical — called chemical resistance.

(i) Like dissolves like (polar-polar, nonpolar- nonpolar)

polar polymers ⟶ polar solvents

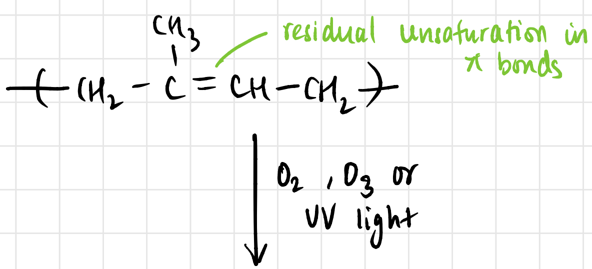
(H-bonds) polyvinyl alcohol, starch ⟶ water

- PVA added slowly to water in lab

nonpolar polymers ⟶ non polar solvents

PE, PStyrene ⟶ benzene, cyclohexane, gasoline

(ii) Residual unsaturation leads to oxidative degradation

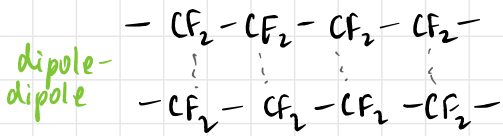


oxidative degradation

(iv) Presence of polar groups

- Solvent (H_2O) enters between polymer chains (raisins) and swells up

- Teflon: very high resistance



does not allow any solvents to enter

- Made by Dupont – nonstick
- Wonderplastic

(iv) Cross-linking

- Polymer does not allow solvent to enter chain
- Bakelite

5. Plastic deformation.

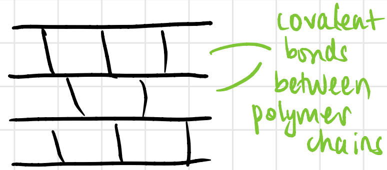
- On application of heat and pressure, polymers become soft, flexible and undergo deformation, melt and flow
- On cooling, they return to the original state.
- This property is called plasticity.

(i) Thermoplastic

- can be remoulded
- VDW, D-D, H-Bonds

(ii) Thermosetting plastic

- cannot be remoulded
- cross-linked



Thermoplastic	Thermosetting plastic
1. Soften on heating, harden on cooling	1. Fusible on initial heating, become permanently hard on cooling.
2. Undergo reversible changes on application of heat	2. Irreversible changes
3. Can be reshaped by heat cycle	3. Cannot be reshaped.
4. Soft and flexible	4. Hard and rigid.
5. Linear or branched structure	5. Cross-linked 3D structure
6. No change in chem. composition during moulding	6. Undergoes chemical changes and cross-linking during moulding
7. Swell or dissolve in organic solvents.	7. Neither swell nor dissolve
8. Moulded articles have to be cooled to room temperature before taking out from moulds to avoid deformation.	8. Can be removed while still hot without deformation.
9. PE, PVC.	9. Bakelite, P-F resin, urea-F resin

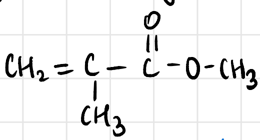
14.11.2019
Thursday

COMMERCIAL POLYMERS

1. PMMA - Polymethyl Methacrylate

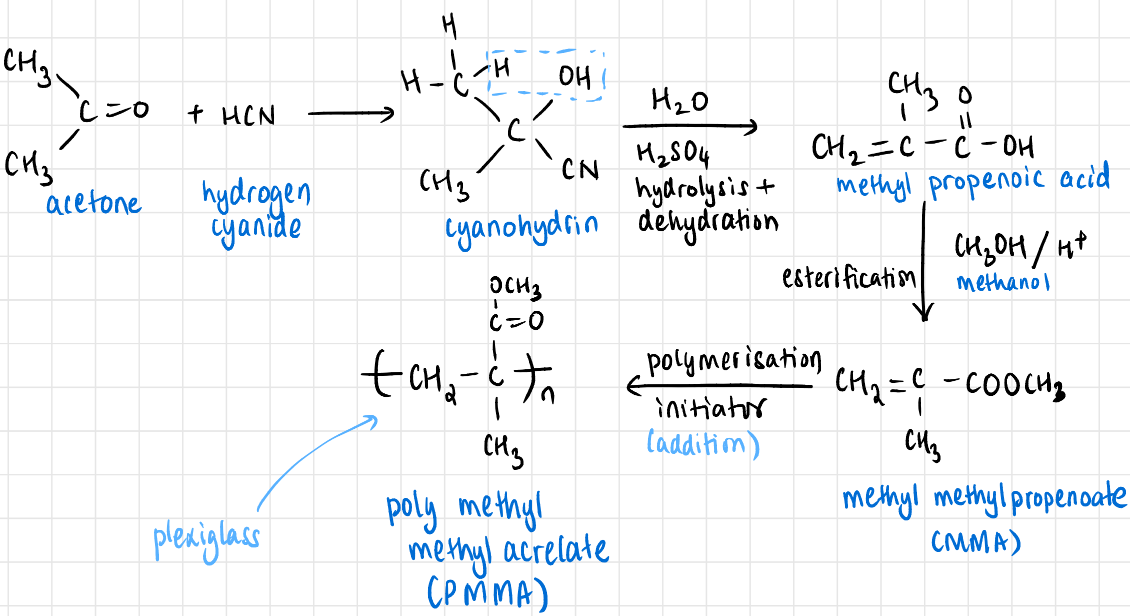
- plexiglass - tradename
- monomer: methyl methacrylate
- acrylic acid: propenoic acid
  $CH_2 = CH - COOH$
- acrelate: ester
  $CH_2 = CH - COCH_3$

- Methyl methacrylate



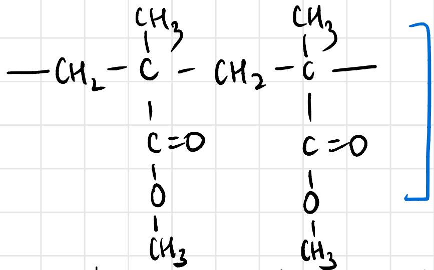
methyl methacrylate

(a) Synthesis



(b) Properties

(i) Thermoplastic (no cross-linking)



bulky pendant groups

(ii) Amorphous due to bulky pendant groups
(iii) Excellent optical clarity but poor scratch resistance

(c) Applications

(i) Used for making aircraft windows (instead of glass; lightweight)
(ii) Artificial eyes
(iii) Dentures - light and flexible
(iv) Making light fixtures (very good refractive index)
(v) Skylights in buildings (to let in sunlight)
(vi) Paints and adhesives
(vii) Attractive sign boards (shiny)

2. Elastomers

- materials which undergo deformation under stress but regain original shape when stress is released.
- long, entangled chains that become stiff when stretched.

- Natural rubber (polyisoprene)

$$\left[CH_2 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH - CH_2 \right]_n$$

isoprene: 2-methyl-1,3-butadiene

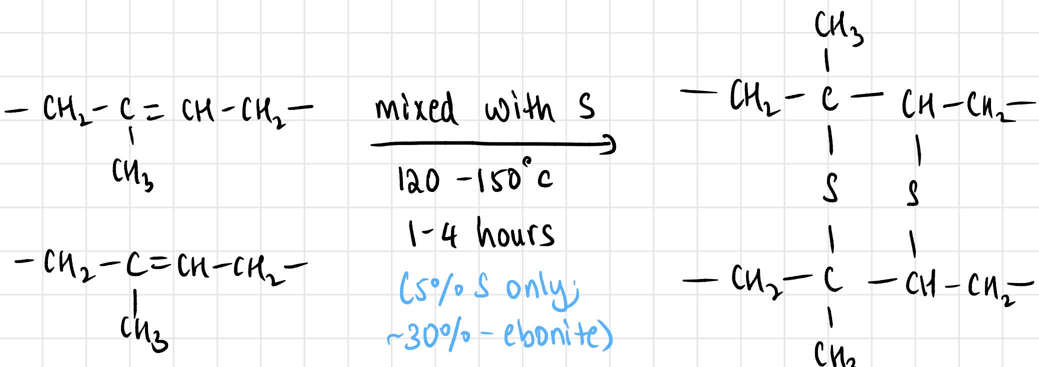
- not used as widely
- low tensile strength (VDW forces; slipping)

- residual unsaturation, oxidative degradation

Deficiencies of Natural Rubber

- hard & brittle at low temperatures
- soft & sticky at high temperatures
- soluble in many organic solvents
- undergoes oxidative degradation (residual unsaturation)
- low tensile strength (chains slip against each other).

Vulcanisation



polyisoprene

vulcanised rubber

- Vulcanisation was discovered by Charles Goodyear (tyres) by accident.
- Neoprene - don't use S; use ZnO, MgO (oxygen bonds, not sulphur) for polymers with Cl
- Introduce cross-links into polymer chain to increase tensile strength.

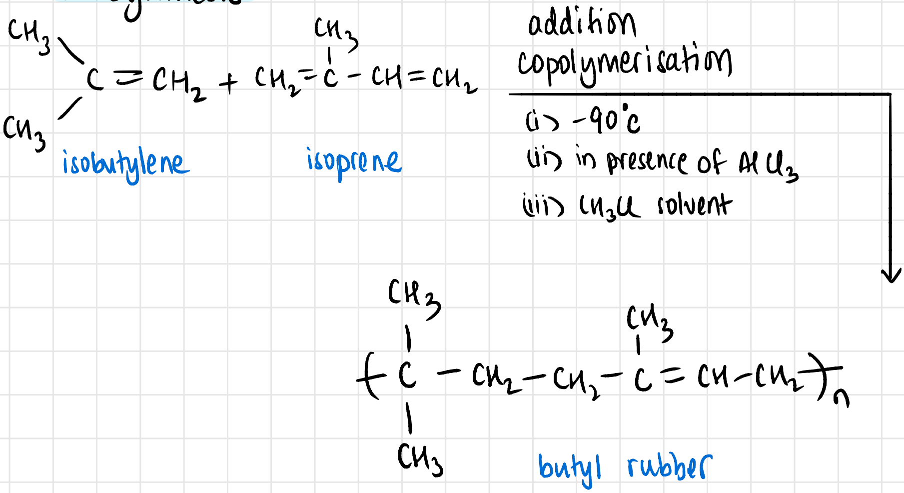
Advantages of synthetic rubber

- Superior to natural rubber in some properties
- High tensile strength and abrasion resistance
- Priced economically

Butyl Rubber

- Monomers: isobutylene + 5-10% isoprene.

(a) Synthesis



Reasons for Reaction conditions

- -90°C : highly exothermic rxn

- $AlCl_3$: Lewis acid – cationic mechanism
- change mechanism to ionic to control
- Free radical would be uncontrollable

- CH_3Cl solvent to dilute system & control rxn (too much heat liberated)

- 5-10% isoprene used for synthesis of butyl rubber
- If no isoprene (polyisobutylene), final product low tensile strength (like polyethylene)
- Final product has small amount of unsaturation
- Useful : can vulcanise & make strong
- Too much isoprene, oxidative degradation.

(b) Properties

(i) Good insulating properties
(ii) Low gas permeability

(c) Applications

(i) Used in tyre tubes (low gas permeability)
(ii) Football bladder for air
(iii) Insulation of high voltage wires and cables
(iv) Used in chewing gum (banned in Singapore)

18.11.2019
Monday

3. Adhesives

- liquid
- only adhesive when it solidifies
- Substances used to bind together two materials by surface attachment due to IMF and penetration of the adhesive into the material and solidifying, thereby interlocking the two surfaces.

Natural

- gum, starch

Synthetic

- epoxy resin, U-F resin, P-F resin

- low molecular wt. polymers - soft and gummy
- two parts: polymer and hardener (curing agent)

  soluble form — triggers 3D cross-linking; solidifies

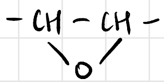
- curing is very important
- Fevicol - curing agent is air
- Novolac with excess formaldehyde — forms Bakelite

  Phenol + formaldehyde — curing agent

- Phenol-formaldehyde resin is used for rubber.
- Urea-formaldehyde resin is used for wood.
- Epoxy resin can bind metal, wood, glass, concrete, leather (extremely strong) – Araldite, Epon

Epoxy resin

- Araldite, Epon



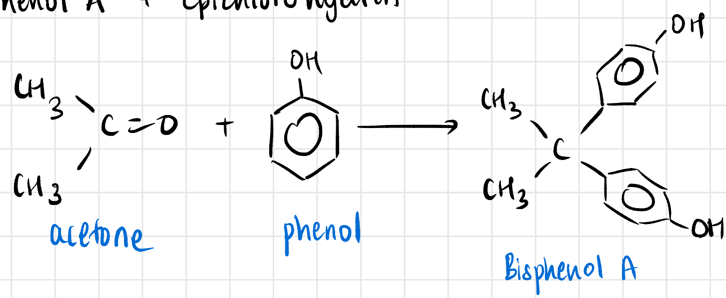
epoxy group

(a) Synthesis

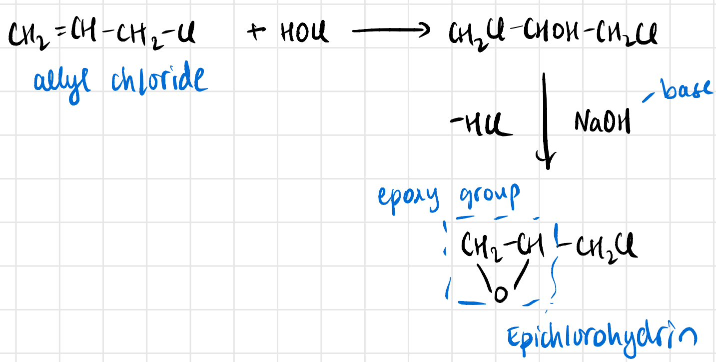
- Monomers: Bisphenol A + epichlorohydrin

  acetone

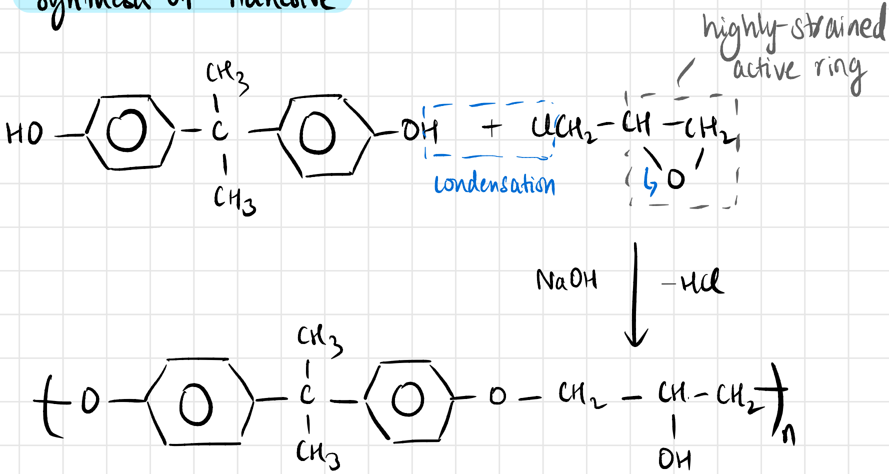
- **Synthesis of Bisphenol A:**



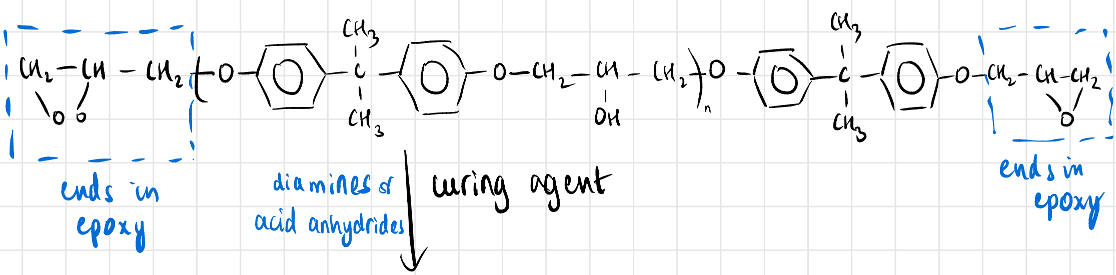
- **Synthesis of Epichlorohydrin:**



Synthesis of Adhesive



- Epichlorohydrin (epoxy) always taken in excess
- End of chain should be mostly epoxy groups



3D cross-linked structure
solidifies & binds to surface

- Epoxy groups are highly reactive
- When curing agents are added, form cross-links
- 4-5 monomers in a polymer chain (bulky, low molecular weight)
- Curing very important; otherwise just a polymer

(b) Properties

1. Excellent adhesion quality
2. Excellent resistance to water, acid, alkali and other corrosive chemicals
3. Good electrical insulating property

- Professor in RV college patented epoxy resin; used by BSNL

(c) Applications

1. Used as an adhesive
2. Used for laminating materials
3. To impart crease and shrinkage resistance to fabrics.

POLYMER COMPOSITES

- Composites are materials made of more than one component and their properties are not attainable by individual components acting alone.
- When these components are polymers, they are called polymer composites.

- Two components: fibre & matrix
- Fibre embedded into matrix
- Fibres have good tensile strength, bad impact strength
- Matrix absorbs impact; form material formed

- They are produced by suitably bonding fibre material with a polymeric resin matrix and curing the same under pressure and heat

Fibres

- carbon fibres
- glass fibres
- aramid fibres

Matrix

- epoxy resin
- polyesters
- polyamides

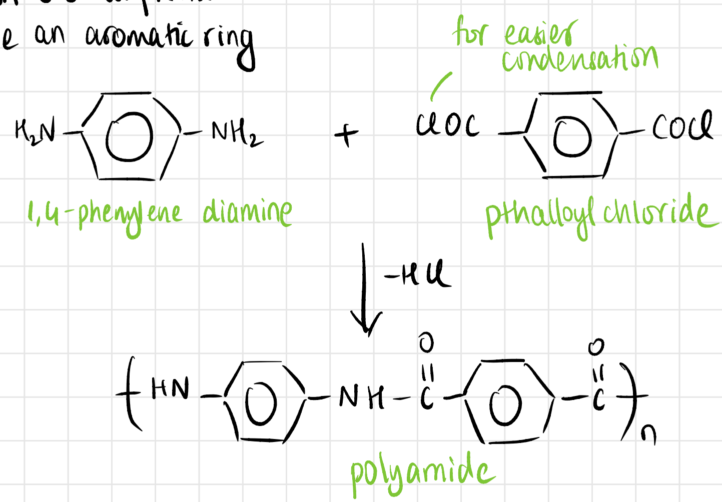
- Popular due to high strength-to-weight ratio

1. KEVLAR

- Five times stronger than steel
- Used for bulletproof vests
- Aramid fibre - aromatic amide
- Made by Dupont, 1965 (NAFION, Teflon)
- Long-chain polymeric fibres, spun together, ropes made, fabrics made

(i) Synthesis

- Nylon 6-6 aliphatic
- Made an aromatic ring



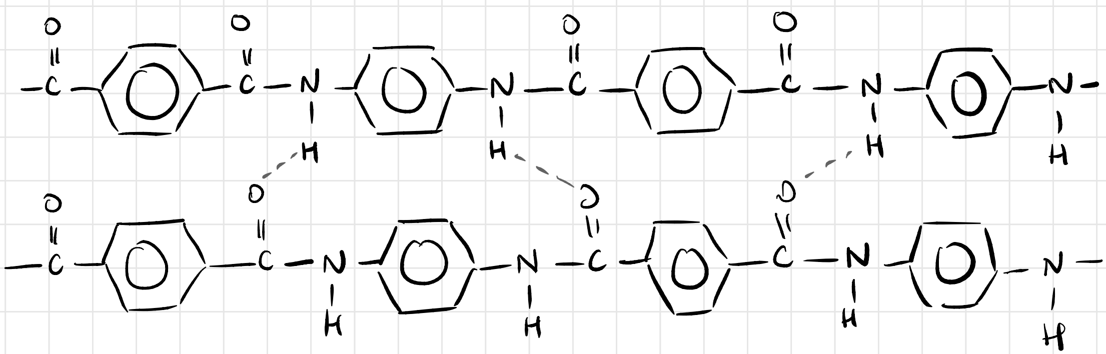
- Stronger than nylon
- In aliphatic chain, movement possible (more flexible)
- Aromatic chain is compact (no movement about single bond); more stiff

19.11.2019
Tuesday

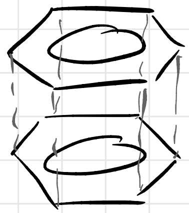
Q2: Why is kevlar 5 times stronger than steel on an equal weight basis?

A2:

1. Extensive H-bonding



2. Aromatic stacking
   - Between two aromatic rings, attraction exists
   - Not just for benzene



π-π attraction

- Much lower energy when stacked

ii) Properties

1. High tensile strength
2. Low weight
3. Very low co-efficient of thermal expansion
4. Flame resistance

iii) Applications

1. Personal armour like combat helmets, stab-proof vests and Bulletproof vests
2. For gloves, sleeves, jackets to protect from heat
3. Used in sails of high-performance racing boats
4. Woven into ropes and used in offshore drilling (metal undergoes corrosion)

KEVLAR COMPOSITE

- Fibre: Kevlar
- Matrix: Epoxy resin

Applications

1. Bodies of F1 racing cars (monocoque bodies - one person)
2. Helicoptor rotor blades
3. Kayaks
4. High-end tennis/squash raquets.

Disadvantages

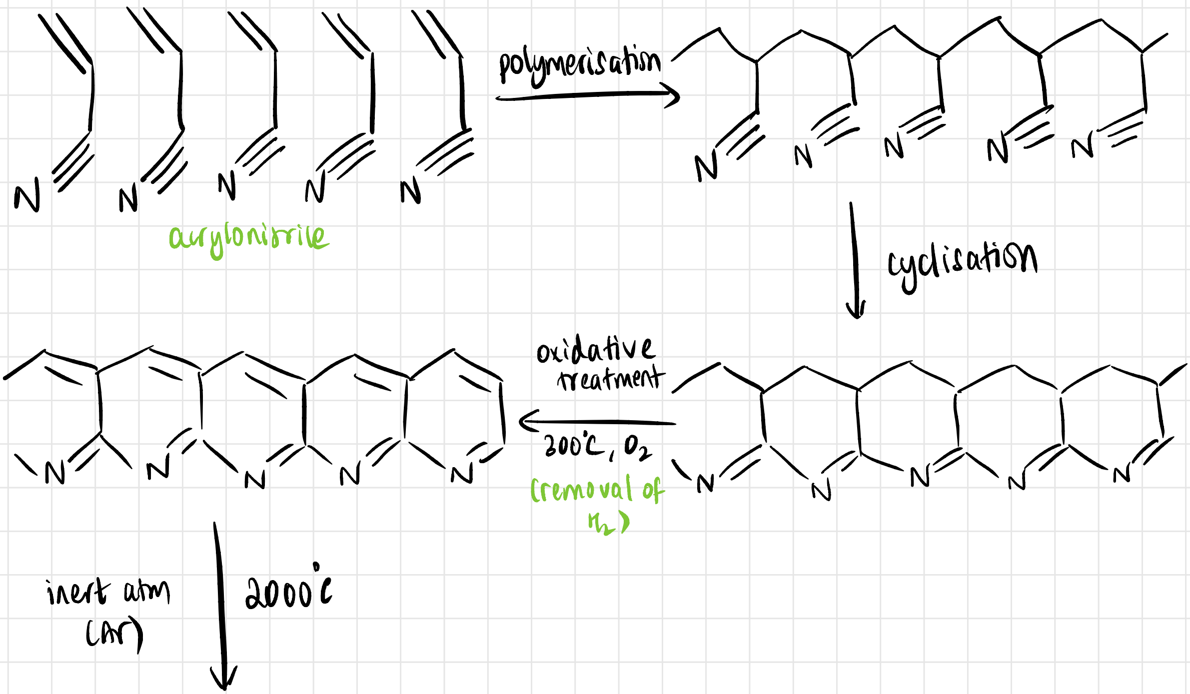
1. Too strong; need special equipment / cutting tools like scissors and drill bits for drilling cured laminates
2. Fibres themselves absorb moisture (hydroscopic) so they must be combined with moisture resistant materials.

2. CARBON FIBRE

- simple fibres made of ~90% carbon
- diameter ~ 5-10 μm (human hair: ~45 μm)
- Structure similar to graphite
- Material consisting of fibres about 5-10 μm in diameter and composed of carbon atoms

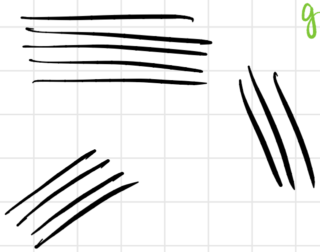
(i) Synthesis

- Precursor: polyacrylonitrile ($CH_2=CH-CN$ acrylonitrile)



graphite-like structures

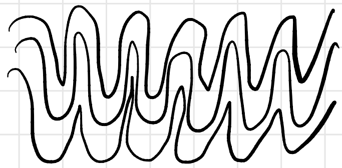
- Long, ribbon-like structures; not just sitting on top of one-another.



graphite is weak

graphite

ribbon-like structures



crumpled, folded structure
(turbostatic structure)

(ii) Properties

1. High tensile strength
2. Low weight
3. Low thermal expansion
4. Biocompatibility

(iii) Applications

1. Aerospace, military, motorsports
2. Medical treatment of severe burns and carbon fibre threads for skin grafts

CARBON-FIBRE REINFORCED POLYMER (CFRP)

- Fibre : C-fibre
- Matrix: Epoxy resin

(i) Properties

1. Lightweight
2. High strength-to weight ratio
3. Electrical conductivity

(ii) Applications

1. Aerospace and automotive fields
2. Used extensively in high-end automobile racing
3. Consumer goods like fishing rods
4. Racquet frames, golf clubs

(iii) Disadvantages

1. Process of production is expensive due to large energy expenditure
2. Volatile byproducts like HCN are formed, which are toxic

20.11.2019
Wednesday

CONDUCTING conducting POLYMERS

LiPo batteries

- Polyethylene oxide, NAFION — ionic conduction
- Here, electronic conduction studied

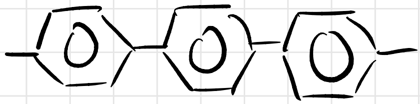
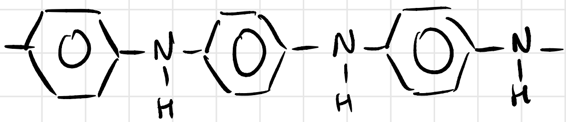
- Nobel Prize Chemistry - 2000: Heeger, MacDiarmid, Shivadawa
- Polyacetylene - like a metal
- Can be used as electrodes for light batteries (plastic batteries)

inorganic: Si-based

- Conducting polymer is an organic polymer with highly delocalised π-e^- system having electrical conductivity of the order of a conductor
- They are also referred to as synthetic metals.

- Cu: 10^8 Sm^{-1}, Teflon: 10^{-8} Sm^{-1}
- Doped polyaniline: 10^5 Sm^{-1}

CONDUCTING POLYMERS (AFTER DOPING)

- Polyacetylene - 
- Polyphenylene - 
- Polyaniline - 

Salient FEATURES

(1) Linear polymer
(2) Extensive conjugation in the polymeric backbone

- On its own, conductivity fairly low; need to be doped

DOPING OF POLYMERS

(1) OXIDATIVE DOPING / P-TYPE DOPING

- Use an oxidising agent to take π e^- from polymer
- Creates holes
- Holes conduct under the influence of applied potential
- Oxidising agent : I_2 in CCl_4 (check Shetty)

(2) REDUCTIVE DOPING / N-TYPE DOPING

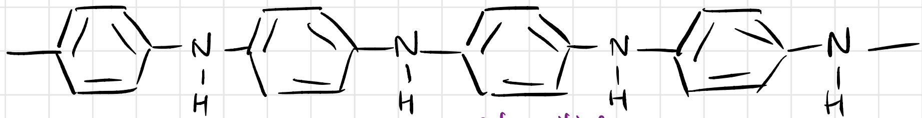
- Use a reducing agent to donate e^- to π cloud
- Reducing agent : Na Naphthalide

(3) PROTON DOPING

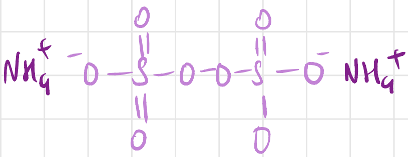
- H^+

Mechanism of doping in polyaniline

- Proton doping (H^+)

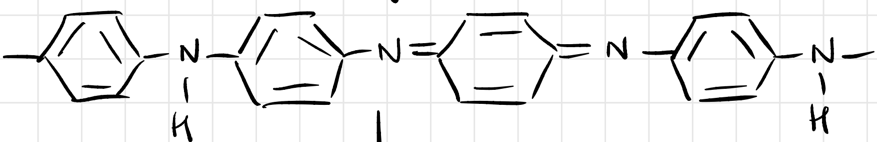


polyaniline

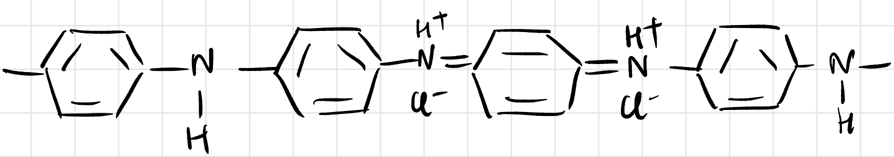


ammonium peroxydisulphate

(i) partial oxidation
(ii) $(NH_4)_2S_2O_8$



1 M HCl



emaraldine salt (conducting)
green colour

conducting polyaniline

(look up)*

Polyaniline colours (windows)

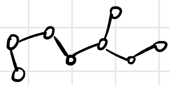
reduced form —— oxidised form —— partially oxidised conducting form

white/yellow — blue/ purple black (all alternate) — green

Applications

1. Electrodic material for commercial batteries (rechargible)
2. Conductive tracts on PCB (printed circuit boards)
3. Sensors
4. Electrochromic display windows
5. Information storage devices
6. Artificial nerves

MOLECULAR WEIGHT



- No fixed chain length
- Distribution of molecular weight
- Always refer to average molecular weight
- Represented as $\overline{M}$

(1) NUMBER AVERAGE MOLECULAR WEIGHT ($\overline{M}_n$)

$$\overline{M}_n = \sum f_i M_i$$

$$f_i = \frac{N_i}{N_{total}}$$

fraction of molecules having weight M_i

$$N_{total} = \sum N_i$$

$$\therefore \overline{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

Q3: 5 molecules with $M = 3000$, 3 molecules $M = 4000$, 2 molecules $M = 2000$. $\overline{M}_n = ?$

$$\overline{M}_n = \frac{\sum_i N_i M_i}{\sum N_i} = \frac{5 \times 3000 + 3 \times 4000 + 2 \times 2000}{10} = 3100$$

Determining $\overline{M}_n$ experimentally

- Properties that only depend on no. of molecules
- Need to use colligative properties
- Osmotic pressure — most common
- Relative lowering of V.P, ΔT_f, ΔT_b

(2) WEIGHT-AVERAGE MOLECULAR WEIGHT $(\overline{M}_w)$

$$\overline{M}_w = \sum_i w_i M_i$$

$$w_i = \frac{m_i}{m_{total}}$$ weight fraction

$$m_i = \text{no. of moles} \times M_i$$

$$= \frac{N_i}{N_A} \times M_i$$

$$m_{total} = \sum m_i$$

$$\overline{M}_w = \sum_i \frac{m_i}{m_{total}} \times M_i$$

$$= \frac{\sum_i \frac{N_i}{N_A} \times M_i \times M_i}{\sum_i \frac{N_i}{N_A} \times M_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

$$\therefore \overline{M}_w = \frac{\sum N_i M_i^2}{\sum_i N_i M_i}$$

Q4: Repeat Q3 for $\overline{M}_w$

$$\overline{M}_w = \frac{5\times(3000)^2 + 3\times(4000)^2 + 2\times(2000)^2}{31000} = 3258$$

- $\overline{M}_w >= \overline{M}_n$ (always)
- If only one kind of molecular weight, $\overline{M}_w = \overline{M}_n$
- Difference tells us how dispersed the weights are

- $\dfrac{\overline{M}_w}{\overline{M}_n}$ = Polydispersity index

Experimetal Methods to Determine $\overline{M}_w$

- light scattering
- sedimentation velocity

(3) VISCOSITY AVERAGE MOLECULAR MASS

$$\overline{M}_v = \left(\frac{\Sigma N_i M_i^{1+a}}{\Sigma N_i M_i}\right)^{1/a}$$

a = Mark-Howink constant
$0.5 < a < 0.9$

Q5. Same as Q_3 for $\overline{M}_v$ where $a = 0.75$

$$\overline{M}_v = \left(\frac{5 \times (3000)^{1.75} + 3 \times (4000)^{1.75} + 2 \times (2000)^{1.75}}{31000}\right)^{1/0.75}$$

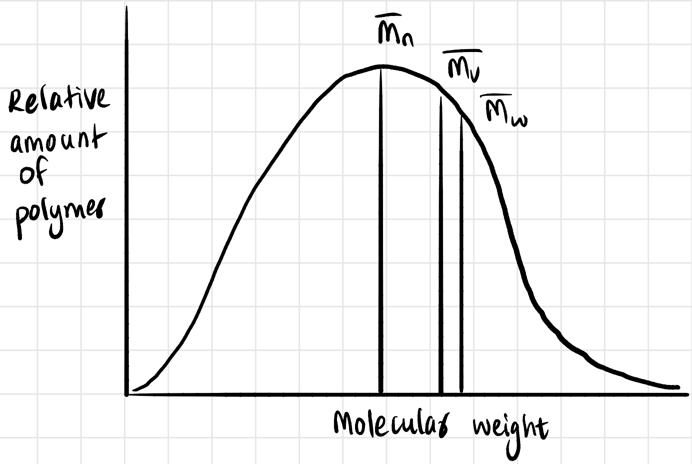
$= 3239.85$

- $\overline{M}_n < \overline{M}_v < \overline{M}_w$, but $\overline{M}_v$ is closer to $\overline{M}_w$ than $\overline{M}_n$

$$\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \qquad \overline{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i} \qquad \overline{M}_v = \left(\frac{\Sigma N_i M_i^{1+a}}{\Sigma N_i M_i}\right)^{1/a}$$

$0.5 < a < 0.9$

GRAPH



25.11.2019
Monday

nanomaterials

- Particles in the range of 10^{-9} m
- Applied to technology - nanotechnology
- Properties entirely different from bulk.

- Neither quantum nor bulk; in between but closer to quantum
- Some quantum effects observed.

- Very low MP for nanomaterials
- Composition same, properties different
- Melting point decreases wrt bulk.

- We say Al is passive in bulk
- In nano range, it is combustible (used as fuel for rocket propulsion).

- Nanocopper is transparent

- Gold is golden
- Nano-gold is red.
- 1857, Faraday made a colloidal suspension of gold nanoparticles

- Properties completely change.

NANOPARTICLES

- A material that has particles with at least one of its dimensions between 1 and 100 nm, we refer to it as a nanomaterial.

- 5 Si atoms arranged in a line: ~1 nm
  10 H atoms arranged in a line: ~1 nm

CLASSIFICATION OF NANOMATERIALS BASED ON DIMENSIONS

(i) Zero-D

- all of the dimensions under 100 nm
- none of the dimensions out of nanoscale
- nanoclusters, quantum dots

(ii) One-D

- one of the dimensions out of nanoscale
- nanowires, nanorods, nanowhiskers

(iii) Two-D

- Two of the dimensions are out of the nano-range
- nanofilms, nanocoatings

(iv) Three-D

- All three of the dimensions are out of the nanorange
- Individual components under nanoscale
- Multiple arrangement of nanosized crystals in a 3-D structure
- bundles of nanowires

Why Are Properties of Nanomaterials so Different From Bulk?

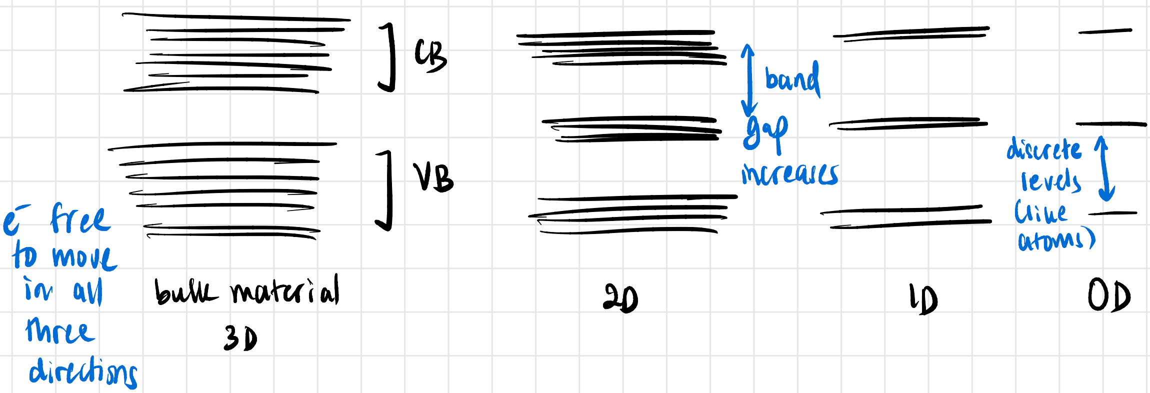
(1) LARGE FRACTION OF SURFACE ATOMS PER UNIT VOLUME

- Most properties of bulk dependent on forces of attraction in bulk.
- Atoms held less strongly at surface
- Surface atoms have different behaviour than bulk atoms
- Property of nanomaterial dictated by surface properties and not bulk properties.
- Surface atoms starts dominating.

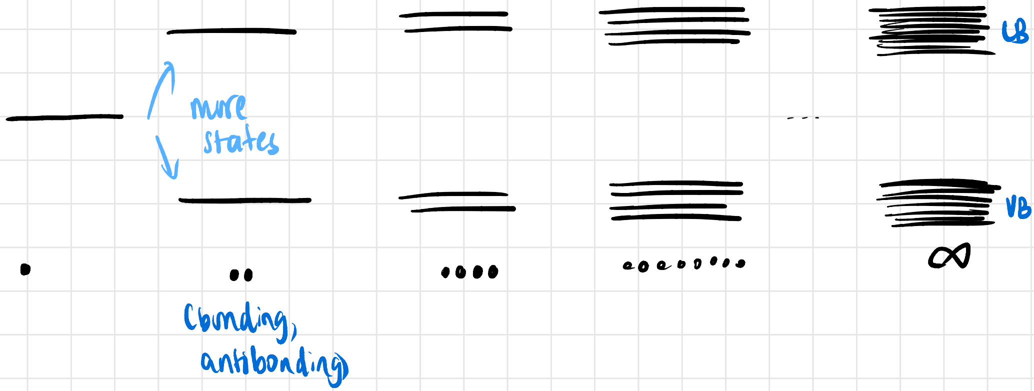
(2) LARGE SURFACE ENERGY

- Thermodynamically less stable
- Surface energy of nanoparticles high
- Al in bulk passive, combustible in nanorange - surface energy very high

(3) SPATIAL CONFINEMENT / QUANTUM CONFINEMENT



Building a Molecule



- e^- move from HOMO to LUMO
- In bulk, becomes CB and VB (metals)

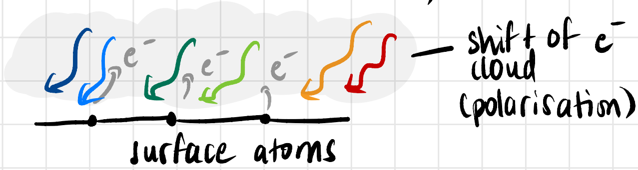
- This is called quantum confinement
- Restricting movement of e^- and h^+
- Outcome: discrete energy levels (approaching atoms)
- Band gap increases

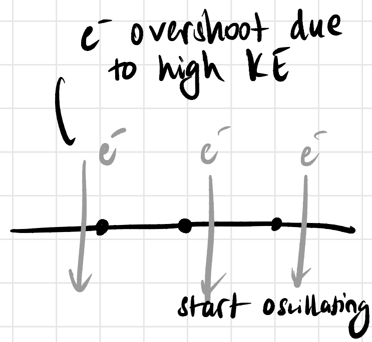
(4) REDUCED IMPERFECTIONS

- Bulk materials: defects, dislocations
- Nano-scale, imperfections in lattice reduced
- Due to small size

OPTICAL PROPERTIES

(i) Surface Plasmon Resonance (SPR)





- metals have +ve ions and free conduction e^-
- When radiation falls, e^- are moved away from the equilibrium position
- Polarisation of free e^- relative to cation lattice takes place
- If the density of e^- in one region increases, they repel each other and tend to return to eq. pos.
- They pick up KE and overshoot and thus oscillate back and forth with a frequency
- This collective oscillation (plasmon) gives rise to a strong absorption in the visible range due to resonance between collective oscillations of the conduction e^- and incident rad.
- As shape and size of particle changes, there is a shift in electrical field density on the surface. so, oscillation frequency of e^- changes.
- Hence, optical properties of nanoparticles depend on size.

(ii) Quantum Size Effect.

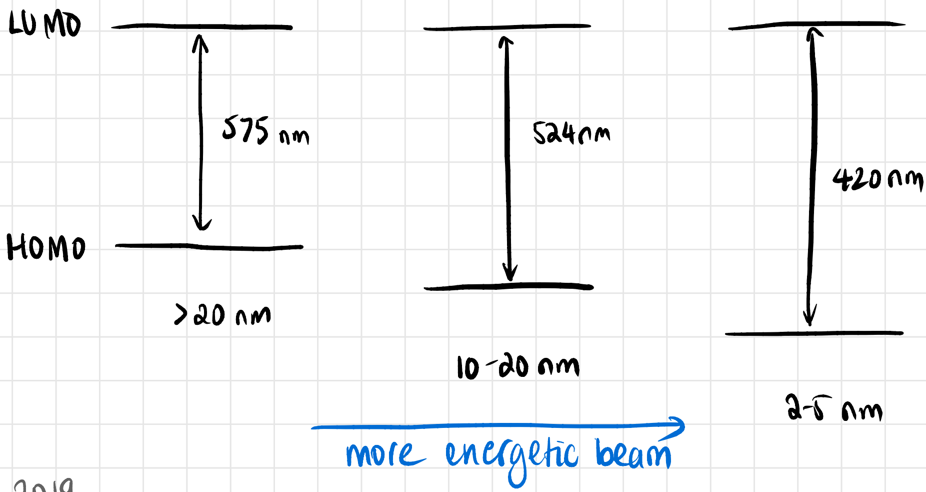
- as particle size decreases, blue shift occurs.
- gold colloidal suspension:

absorption

>20 nm	—	$\lambda = 575$ nm
10 - 20 nm	—	$\lambda = 524$ nm
2 - 5 nm	—	$\lambda = 420$ nm

↓ getting bluer (more energy)

- As size decreases colour gets more blue
- Absorption: shift from HOMO to LUMO



26. 11. 2019
Tuesday

THERMAL PROPERTIES

(i) Melting point is lower compared to bulk (and phase transition)
- Properties surface dominant (high surface-to-volume ratio)
- Less forces at surface
- Easier for surface molecules to leave
- Lesser bonds to break
- Phase transition temperature lower

(ii) Thermal conductivity decreases
- Due to spatial confinement
- Not enough space for lattice points to move
- Movement restricted due to small area
- Mean free path larger than size of particle
- Lattice vibrations: phonons
- Wavelength of phonon larger than particle size

electrical PROPERTIES

(i) Decrease in conductivity

- Nanowires: <u>some</u> metals act like semiconductors, some semiconductor nanowires become insulators
- Due to spatial confinement
- Band gap increases
- Almost like a molecule's discrete energy levels

- Defects less ⇒ defect scattering less ; expect an increase in conductivity
- Surface scattering dominant ; electrical conductivity decreases

SURFACE SCATTERING

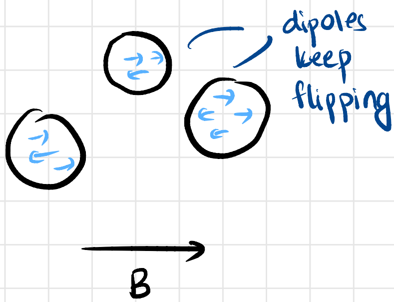
- The electron mean free path is terminated by impinging on the surface and random scattering happens.
- The scattered electron loses velocity and electrical conductivity decreases

MECHANICAL PROPERTIES

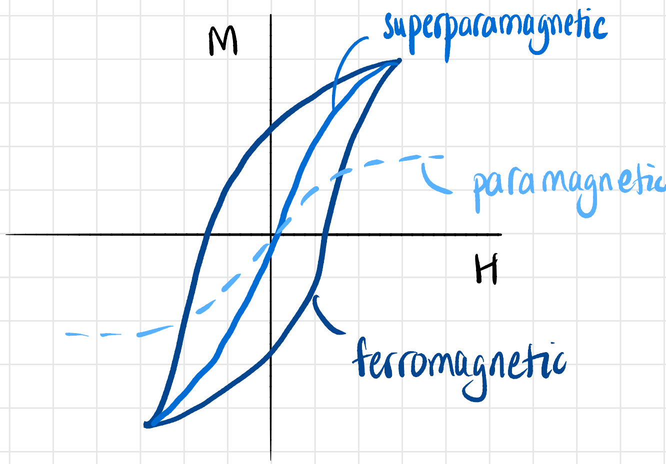
- In nanoparticles, the theoretical strength is 1-2 orders of magnitudes higher than the bulk
- Cu clusters > 50nm can be bent
- Less than 50 nm, Cu becomes super hard
- Does not exhibit the same malleability and ductility as bulk Cu
- Due to less probability of defects

MAGNETIC PROPERTIES

- Difference in the way they align in external magnetic field
- Ferromagnetic materials like Fe, Co become superparamagnetic
- Due to high surface energy, dipoles can flip easily
- Induces randomness



- Alignment in ferromagnetic materials due to lack of thermal energy at room temperature (exchange energy)
- At high temp, bulk ferro → para
- At nanoscale, ferromagnetic materials become superparamagnetic



$$\frac{M}{H} = \chi$$

- Paramagnetic behaviour switches to superparamagnetic behaviour due to high surface energy which provides sufficient energy to the domains to spontaneously switch polarisation directions

- Since they have high susceptibilities, they are called superparamagnetic
- Gold and Platinum (supposed to be non-magnetic), act as magnetic materials in nano-scale

APPLICATIONS

IN ELECTRONICS AND MEDICINE

- Targetted drugs
- Injectible nanobots - in future
- Injected into bloodstream, constantly repairs body

1) Injectible nanobots, where millions of blood cells-sized robots swarming through the body, repairing arteries, muscles

2) Nanomaterials as electrodes due to high surface area

3) Very good catalysts - high surface area

4) Elimination of pollutants

5) HD TVs, phosphors (pixels) glow - the size of pixels can be made very small.
Phosphors (which glow) are used for this
$ZnSe$, CdS

6) Nano ZnO and TiO_4 are used in sunblocks

7) Long-lasting tennis balls can be made using butyl rubber + nanoclay composites.

GREEN
Chemistry

- More about prevention, less about cure
- #1 is Mexico City, #2 Delhi
- Green economy, sustainability, green computing
- E-waste generated in excess, need long-lasting hardware, efficient algorithms
- Green chemistry is a concept
- There are 12 principles to follow

DEFINITION

- Green chemistry is the utilisation of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of products.

12 PRINCIPLES

1) Prevent waste

- Design products in the early stage to prevent waste

2) Atom economy

- earlier, we focused on yield improvement
- atom economy – rxns in such a way that all atoms used as reactants should be present in <u>products</u>, not by-products
- eg: addition rxn good economy
- in elimination, poor economy; substitution okay
- rearrangement: economy decent

$$\%\ \text{atom economy} = \frac{\text{mol. wt. of target compound}}{\text{mol. wt of all reactants used}} \times 100\%$$

- Addition rxn, % economy 100%
  Elimination rxn, % economy poor
  Substitution rxn, % economy average
  Rearrangement rxn, % economy 100%

3) Safer Synthesis

- use less hazardous compounds
- polyurathanes – cushions and mattress foam
- used to be made using phosgene; now uses primary amine and Chlorine

4) Designing Safer Chemicals

- cosmetics and pharmaceuticals
- no side effects, no loss in efficacy.

5) Safer Solvents and Auxiliaries

- benzene, chloroform, pyridine banned solvents
- extremely volatile organic compounds
- water, ethanol, methanol (sometimes)
- solvents to replace organic solvents – ionic solvents.

- $[Et\,NH_4]^+ NO_2^-$: ionic solvent – less volatile, greener
- Designer solvents: area of research

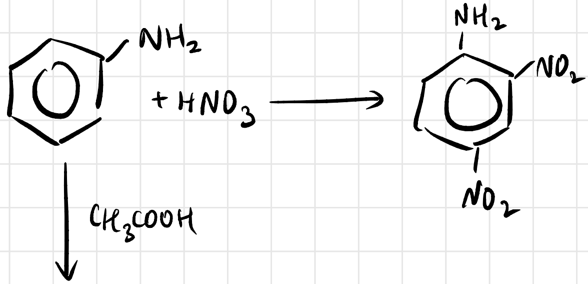
6) Design for Energy Efficiency

- Try to carry rxns out at ambient temperature, pressure
- Using microwave synthesis / ultrasound.
- Biodiesel: 1hour normally, 10 mins microwave

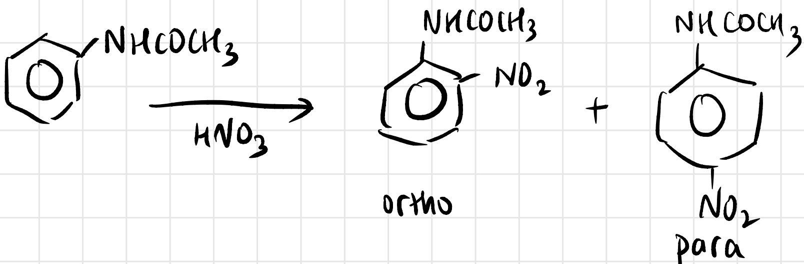
7) Use of Renewable Feedstocks

- Rely only on renewable feedstock
- Use biomass or agricultural wastes

8) Reduce Derivatives

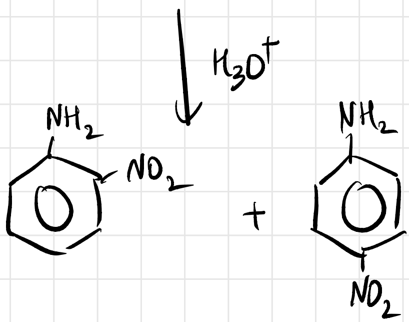


if you want only ortho or para



so many wasted products

(can be separated)



9) Catalysis

- mild conditions,
- faster
- pure products
- better yield
- less energy used
- selective catalyst

10) Design for Degradation

- Cauliflower – endosulphan
- Pesticides, fertilisers, insecticides need to be biodegradable

11) Real-Time Analysis for Pollution Prevention

- Monitor pollution in real-time and take measures
- Oxygen sensor (lambda sensor)

12) Inherently Safer Chemistry for Accident Prevention

- Methyl isocyanide released in Bhopal Gas Tragedy
- Union carbide India Limited - pesticide plant.