3 Jan 2022

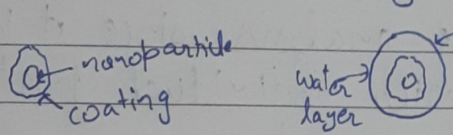
Page No. / Date / /

Material Chemistry

Nanomaterial

This is a top-down approach in which you chop down the material and convert one of the dimension <100nm. This material is called nanomaterial.

Cohesive forces, some droplets, Sur. area, sur. energy, how ~~television~~ led screen works, quantum dots screen, microscopic image of tooth, HRTEM, dispersity (Đ) acceptable (Đ) Đ<1.5, why sugar is soluble?.



3 diameters → nano-particle
→ coating (shell)
→ water layer
hydrodynamic dia. D_H.

Concept of dispersity, concept of D_H, diff. b/w nano-material sized measured by microsclopy & DLS, (why it is always higher that microscopy ones?), concept of light scattering.

Dispersity

It is a measure of heterogeneity of sizes of molecules or particles in a mixture.
A set of objects is said to be uniform if they have same size, shape or mass.
Non-uniform if the sizes, masses are varying.
$Đ_M = M_w / M_n$
M_w is the mass-mass (or molecular weight) and M_n is the number-average molar mass (or mol. weight).

Page No.
Date

Hydrodynamic diameter (D_H) of a molecule is defined as the diameter of a perfect solid sphere that would exhibit the same hydrodynamic friction as the molecule of interest. Thus, it reflects primarily the same ~~for~~ D_H friction ~~as the~~ ~~be~~ but is usually also a good estimation of the absolute size of the molecule. Generally, the more globular the shape of a molecule is, the better D_H value reflects the actual diameter.

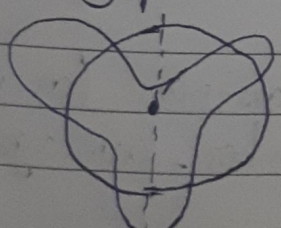
Microscopy can be used as an absolute method of particle size analysis, since it is the only method in which individual particles are ~~also~~ observed & measured.

~~Microscopy~~ - The image of a particle seen in a microscope is 2D and from this image an estimate of particle size can be made.

Optical microscope range - 0.5 - 150 micron
Can be used for finding molecules sizes in suspensions, dry powders, emulsions & aerosols.

Electron microscope - range - 0.001 - 10 micron
→ suitable for colloidal dispersion.

~~Principle~~
Dia is measured along any arbitary line, made across the center of particle.

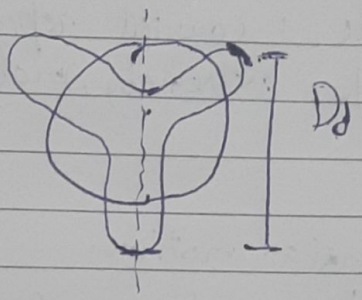


Page No. / Date / /

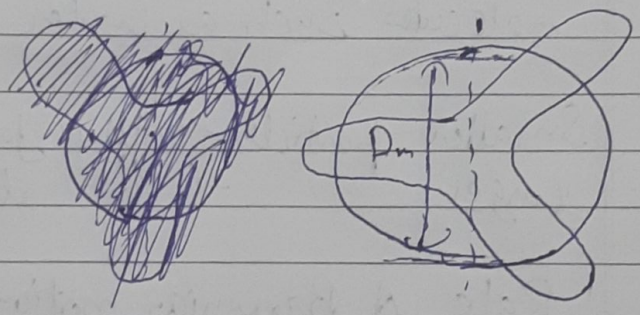
Popular measurements are

a. Feret diameter
b. Martin diameter
c. projected area dia.

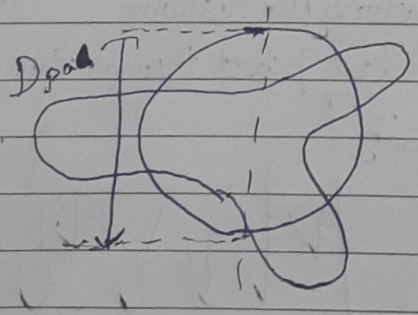
a. It is the distance b/w two diameters on opposite sides of the particle parallel to some fixed direction.



b. It's the line that bisects the particle image.



c. It's the dia. of circle with the same area as that of the particle observed ⊥ to the surface on which the particle rests.



Page No.
Date

Advan:
1. Accurate & simple
2. Particles easily observed.
3. Agglomeration & contamination can be detected.

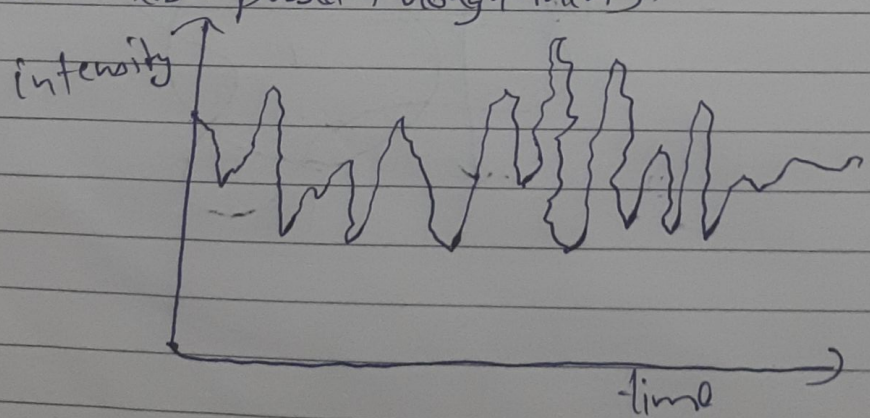
Disadv.
1. Time consuming
2. Same particle → counted repeatedly
3. Not suitable for extremely small size particles.

DLS
- measures brownaian-motion.
- Brownian motion - random movement of particles that results to collision with solvent & solute molecules such as water.

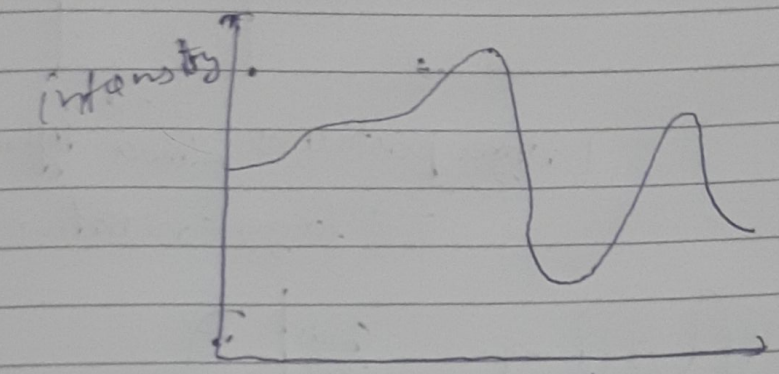
Smaller particles → diffuse faster
Larger " → " slowly

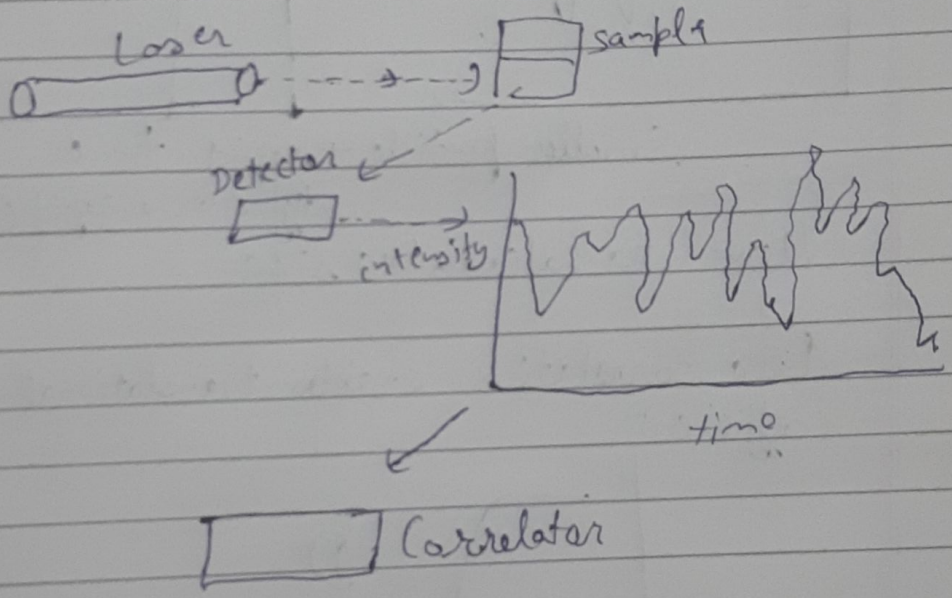
Rate of Brownian motion
→ Translational diffusion coefficient (D)

Smaller particles
rapid ~~fluctions~~ fluctuations
(when laser passed through them).

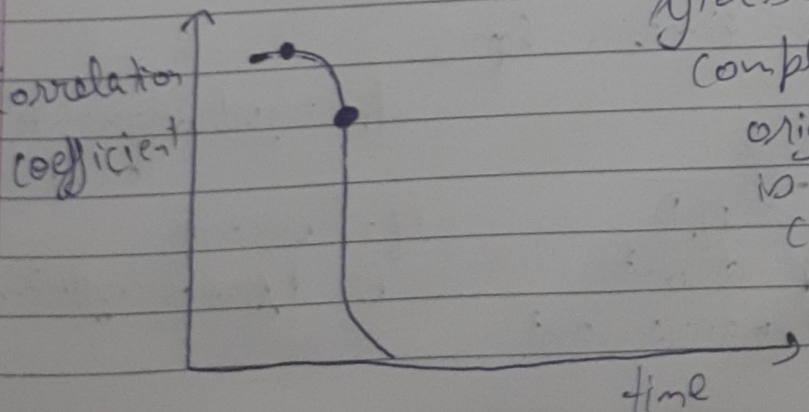


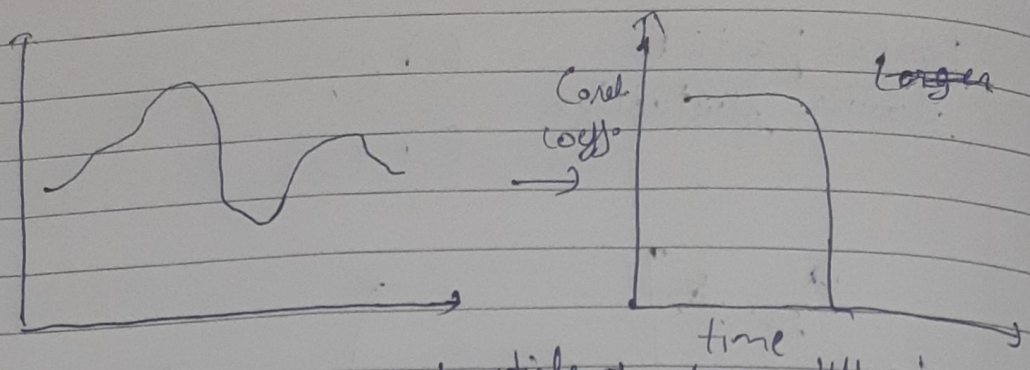
Larger particles
slower fluctuations



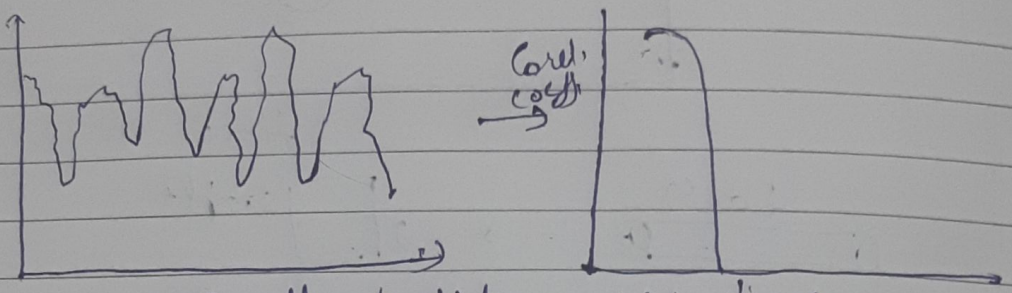


- Rapid snapshots
- Compared to original → after some time completely diff. from original → process is called auto-correlation.





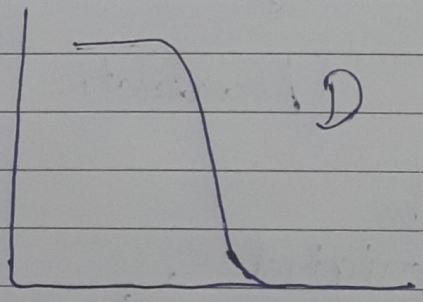
Larger particle → slower diffusion
→ longer correlation



Smaller particle → rapid diffusion → rapid correlation.

How to calculate size

Auto correlation enables translational diffusion coefficient



Stokes - Einstein Eqn

$$d_H = \frac{kT}{3\pi\eta D}$$

d_H = hydrodynamic dia.

T = Temp absolute

k = Boltzmann's Const.

η = viscocity

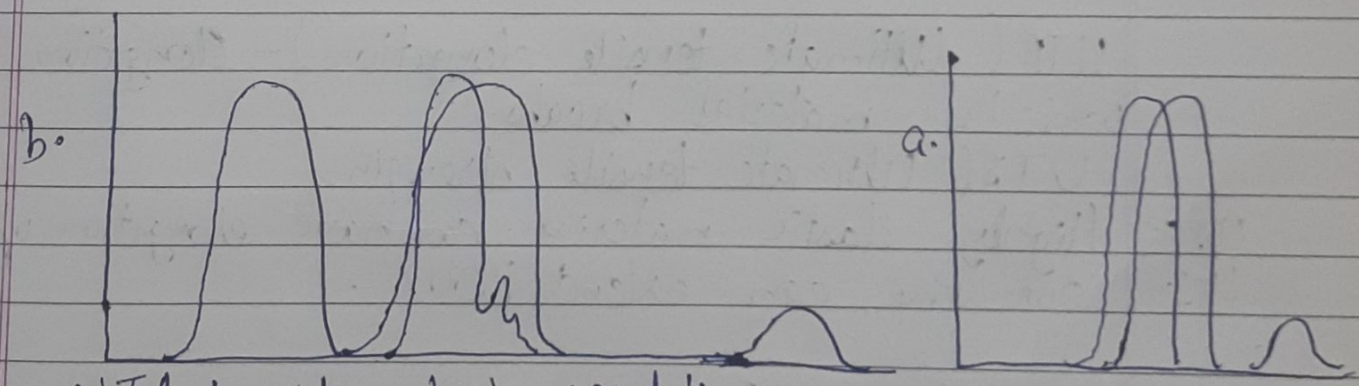
D = diffusion coefficient

DLS

- measure size of all particles

Diff. b/w DLS and NTA

	DLS	NTA (Nanoparticle light scattering)
Dist^n based:	Intensity-based	Number-based
Measurement:	Ensemble	Particle-by particle
Method:	Scattering intensity	Light scattering & digital camera.
Data type:	Diffusion coefficients & particle size dist^n.	Visualisation of individual particles in sol.
Data out:	Faster assesment of the mean size & polydispersity	Higher resolution particle size dist^n
When to use:	• ~~Polydisperse~~ <1um/ want to cover a broad range. • A broad conc^n range is desired • Can't be diluted for NTA. • Fluorescent with same laser wavelength.	• Polydisperse & you want higher resolution. • Flourescent with need to change wavelength of layer used. • Too diluted for DLS.



a. NTA provides high-resolution measurement of the primary peak

- DLS offers a broader dist^n intensity-weighted towards larger particles, as well as the presence of a very

low conc^{n} of large particles.

- NTA has more info about the vesicles, while DLS provides added info about a wider range of constituents.
- DLS picks up the micron-scale aggregates & free lipid < 10 nm.
- NTA has a resolution to give a highly resolved measurement of the primary peak which represents the vesicles themselves.

Material prop req for credit/debit cards
→ availability
→ low cost
→ high durability
→ elasticity
→ light weight
→ hydrophobic

UTM: (Ultimate tensile machine) - It's used to measure strength of a material.

UTE (Ultimate tensile elongation) - Elongation until which material breaks.
UTS (Ultimate tensile strength)
UTS → Highly elastic material can have elongation upto 900%.
UTS → Our veins can extend 800%.

What is BPA?

Page No. / Date / /

Water Contact Angle

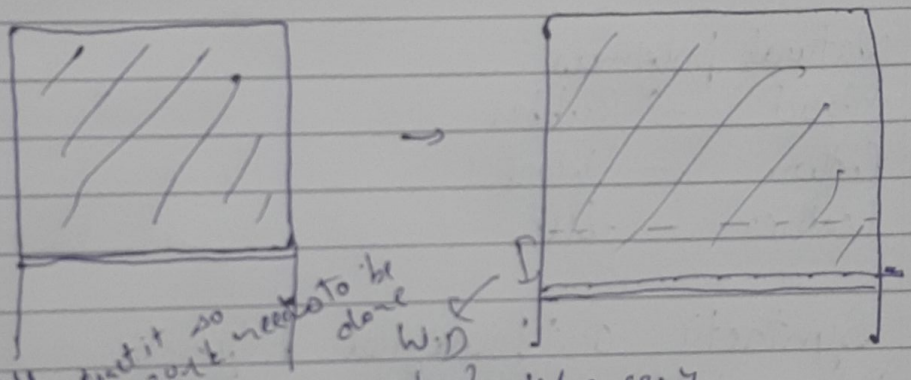
To read: Forever chemicals/materials

SS - Soft segment] → structure of spandex clothing fiber
HS - Hard "
BDO - Butane diol

SS provides elasticity or mechanical flexibility
HS " structural rigidity.

NIPU - Non Isocynaide Poly urethanes

Surface Energy



because fillm will try to contract it so work need to be done

W.D = potential energy

$$S.E. = \frac{W.D}{\Delta A} = \frac{\Delta P.E.}{\Delta A} = \frac{P.E.}{A}$$

What is BPA?
BPA → BPA is a type of plastic. It is safe ~~if not excess~~ at a very low levels that occurs in some foods.

How much BPA does a normal ~~pers~~ person takes in?
Very low only visible at micro levels

What we know?

BPA → Biphenyl A which is plastic additive
BPA inc. qualities of plastic products like strength, shininess etc.
B.P.A. looks similar to other hormones in the body.

Monomer
A chemical compd. that is made of small molecules that are arranged in a simple repeating struc. to form a large molecule.

Polymer
Very large molecular struc. chain-like in nature.

Natural polymers:
- Wood - Rubber
- Cotton - Wool
- Leather - Silk

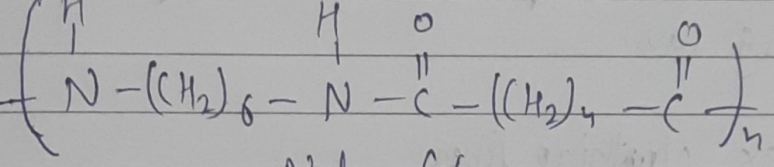
Synthetic and Biological Polymers
Polymers: Macromolecules formed by the covalent attachment of a set of small molecules termed monomers.
Synthetic poly: nylon, poly-ethylene, poly-styrene
Biological " : DNA, proteins, carbohydrates

Pipes/Credit cards $\left[-\underset{H}{\overset{H}{C}} - \underset{Cl}{\overset{H}{C}} - \right]_n$
- PVC is used to make these.
- PVC sheets are thin, so to make credit card 2-3 layers are glued together.

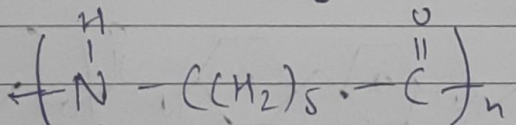
- This includes a layer with the printed information on it plus 1-2 clear ones.

Parachutes

- Polyamide, trade name nylon.
- It is strong - durable as well as moisture resistant.
- It also have ample temp. resistance, making it ideal for use in engineering components



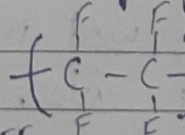
Nylon-6,6



Nylon 6

Spectacles

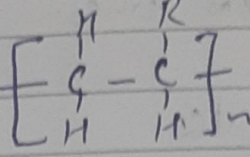
- Polycarbonate is most versatile polymers.
- It's used to make high quality eye-lenses. These lenses offer advan. over glass bec. they are lighter & thinner, and they offer UV protection.
- They are also impact resistant, scratch/cracking resistant.
- It is so strong, it is used in bullet proof glass.



Cookwares

- Polytetrafluoroethylene, ~~is~~ PTFE is used in making Teflon® and other nonstick cookwares.
- It is a waxy, thermally stable, tough, corrosion resistant & non-flammable.
- Can resist temp. upto 380°C

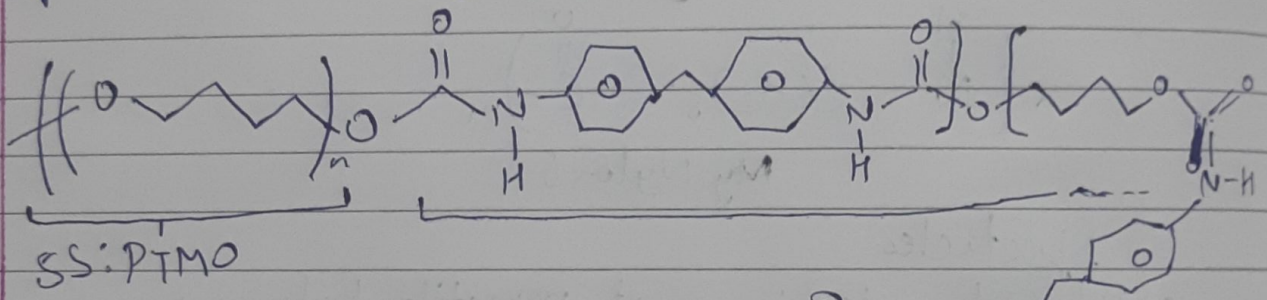
- PTFE generates no smokes when exposed to high temp.



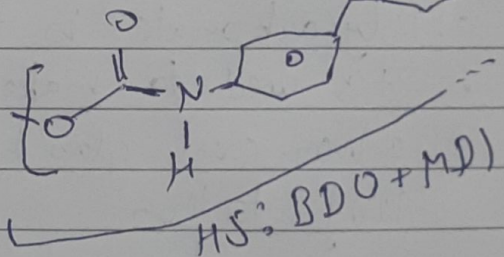
Car interiors

- Polyolefin (polyalkene) is widely used in the const- industry.
- It's often used in car to make it lighter.
- It's more malleable than metal, designers can use plastic to come up with more aerodynamic & better- looking cars.

Spandex clothing fiber



- Polyurethane, PU is a quick drying, highly elastic polymer, used to make apparel that are stretches.



- Spandex clothing fiber, like Lycra®, is made of PU & is used in no of clothing items, including bathing suits, exercise clothing, leggins, skinny jeans, socks & wet suits.
- Disposable diapers are made using spandex polymers.

9 Jan, 22

Page No. /
Date / /

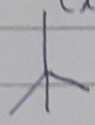
Smart Materials

Materials that changes their physical features ~~with~~ by external field like pressure ~~etc~~, pH, light, temp. etc

* Chemical Na^+ & K^+ in blood,

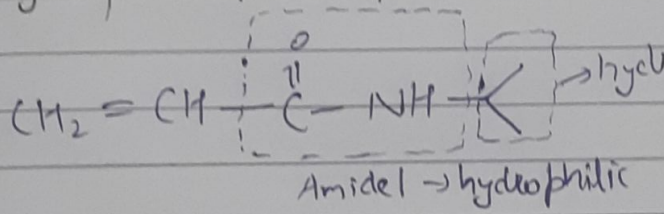
Nanorobots

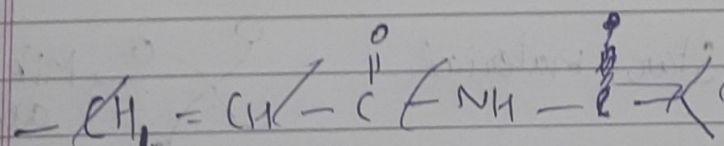
Click - Grab Actuator

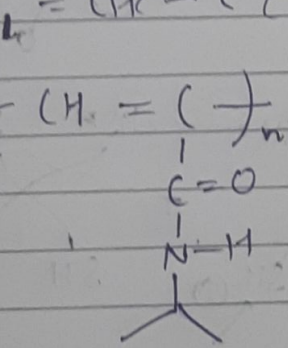


any nanorobot has this type of arms.

Hydrophilic / hydrophobic

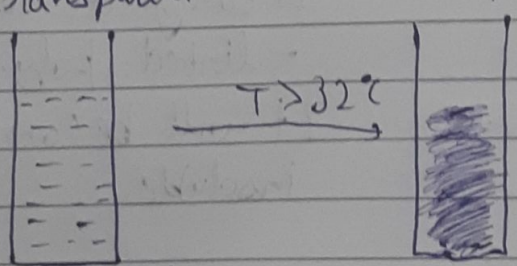






transparent

Hazy



PNIPAM in H_2O

linear

Globule

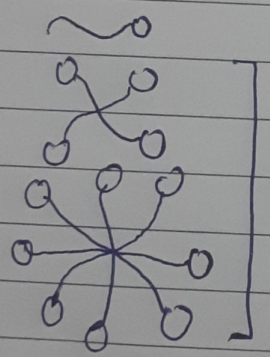
Lower Critical Sol^{n} temp. - The temp at which sol^{n} becomes completely insoluble. Approx. 32°C

PNIPAM is temp- responsive material.

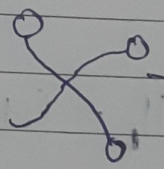
Redox-responsive

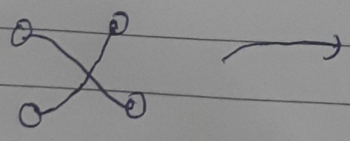
Cysteine $\rightleftharpoons$ Cystine
-SH dynamic exchange S-S

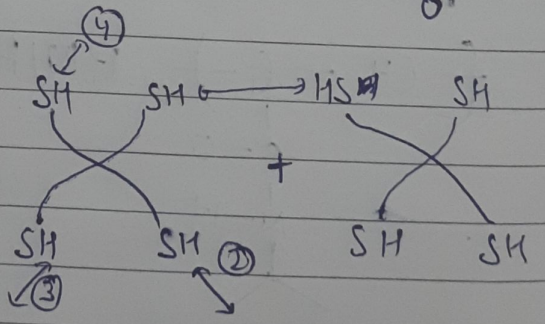
Octopus



Star-material

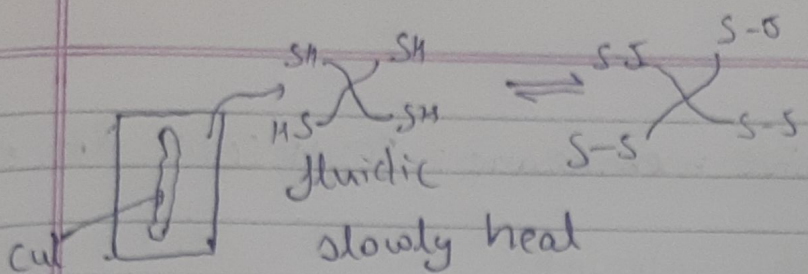


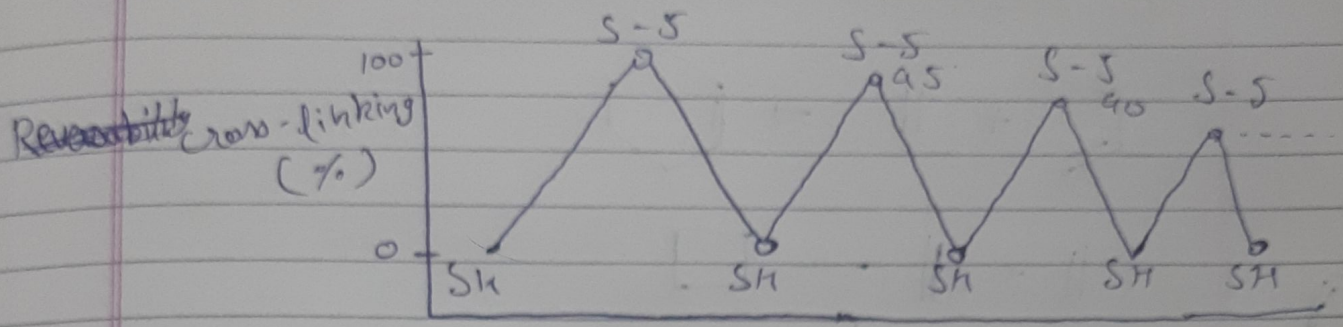




It can form a cross-linked polymer.

It will become rigid, insoluble.



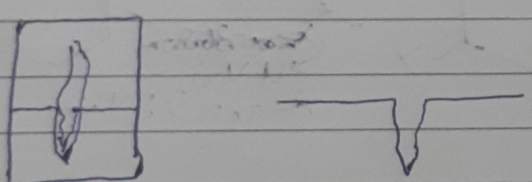


After some time won't cross link

↗

Reversibility

* Atomic force microscopy (AFM)

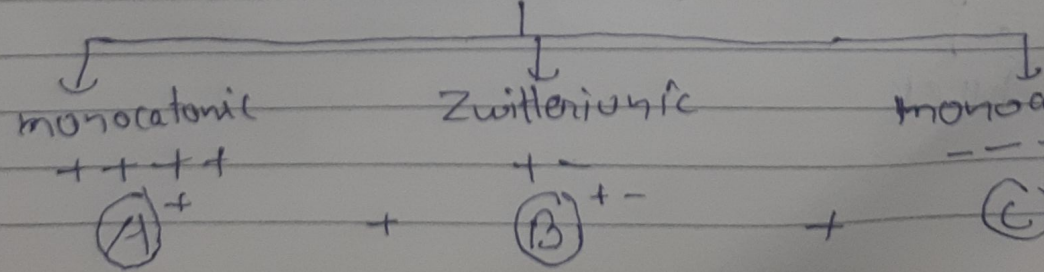


Genome Sequencing (March 2020)

→ Shell of microbe made of proteins

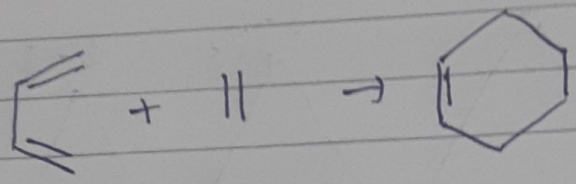
Genome → Seperation of [illegible] similarly sized proteins

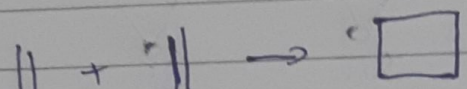
Amino Acid (AA)

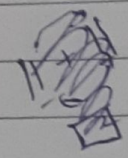


In pH responsive membrane :- SO_3H, COOH, NH_2 etc.

Light responsive material



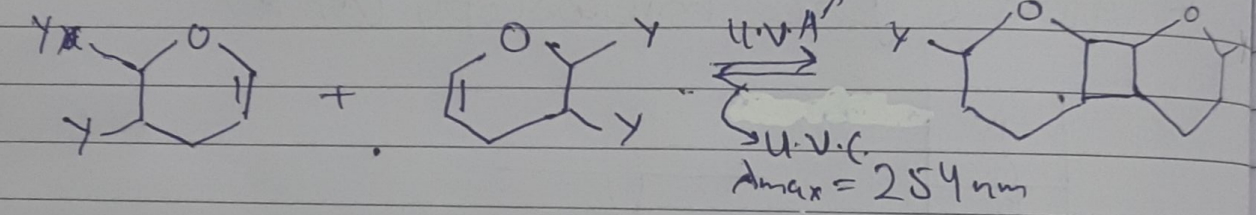




Chromophore - Molecule that can absorb light and emit it.

Coumarin -

Y is something



outgoing

Smart Materials

Also known as - intelligent material, responsive material.

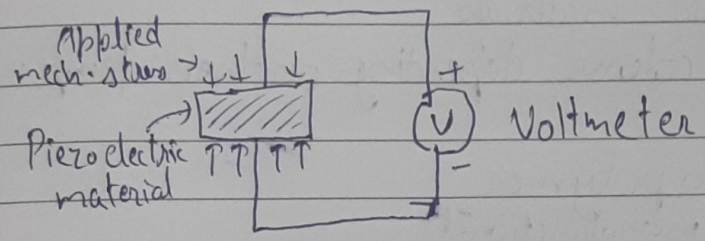
→ These are the materials that change behaviour in systematic manner in a response of stimulus. Eg

- moisture
- E.F or M.F.
- Light
- Temp
- pH etc.

Page No. /
Date / /

Applications
- Sensors
- Actuators
- Artificial muscles
- polymers etc.

Types
a. Piezoelectric materials
- Converts electrical energy to mech. energy & vice versa



b. Magnetostrictive material
- Materials exhibit a change in shape under the influence of M.F.

c. Thermostrictive material
- Converts temp. diff. into elec. and vice-versa.

d. Photomechanical materials
- Change shape under exposure to light.

e. Photovoltaic materials
- Converts light to electrical current.

f. pH sensitive polymers
- Change in vol. when the pH of the surrounding med. changes.

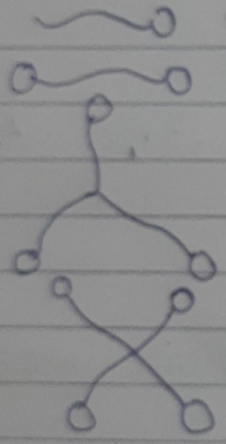
g. Electrochromic materials
- Change their colour or opacity on the application of a voltage.

h. Photochromic materials
- Change colour in response to light.
Eg- Light-sensitive sunglasses that darken when exposed to bright sunlight.

i. Thermochromic materials
- Change in colour depending on their temp.

10 January, 23

Homopolymer



Copolymer

AAA Monoblock copolymer

AAA BBB Diblock copolymer
'A' block 'B' block

ABC Triblock copolymer

ABA → $H_2N-(Lys)_n-NH_2$

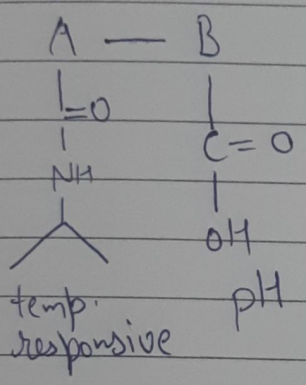
$H_2N-(Lys)_n-NH_2$

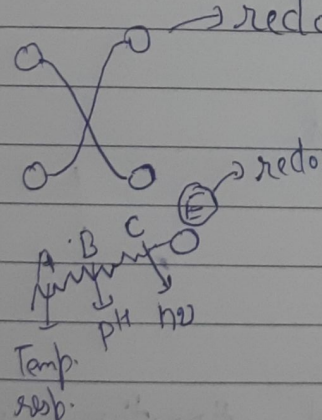
↓ Hystedine

$(H_2S)_m-(Lys)_n-(H_2S)_m$

$(Lys)_n-NH_2 \xrightarrow{his} (Lys)_n-(His)_m-NH_2$

$AB \xrightarrow{alter} ABC$

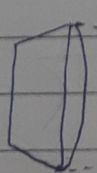




→ Multi-stimuli responsive material

Cylodextrin

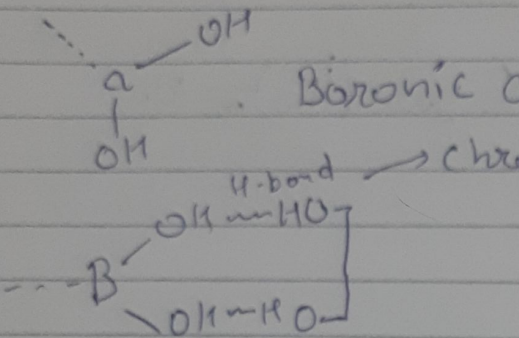
It is a bucket type molecule also called nano-box container.



Page No.
Date

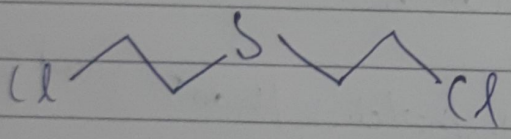
* Crown ether

Chemo-responsive



Chemical Warfare

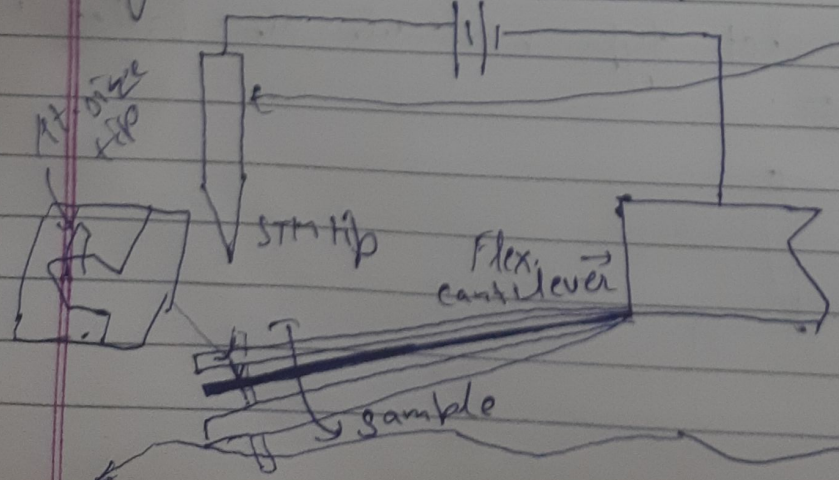
Mustard Gas



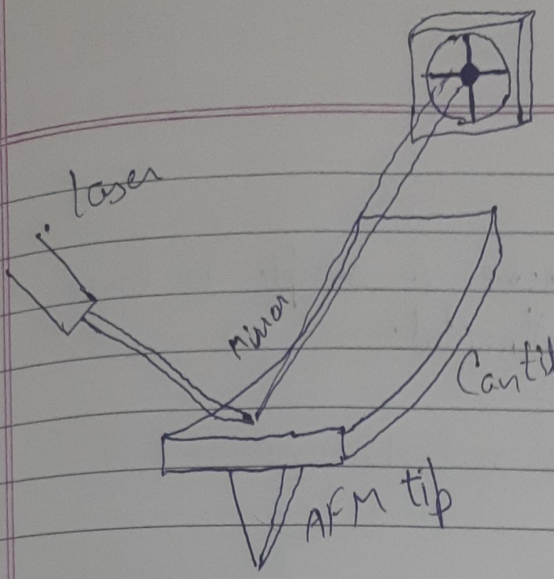
17 Jan, 23

Atomic Force Microscope

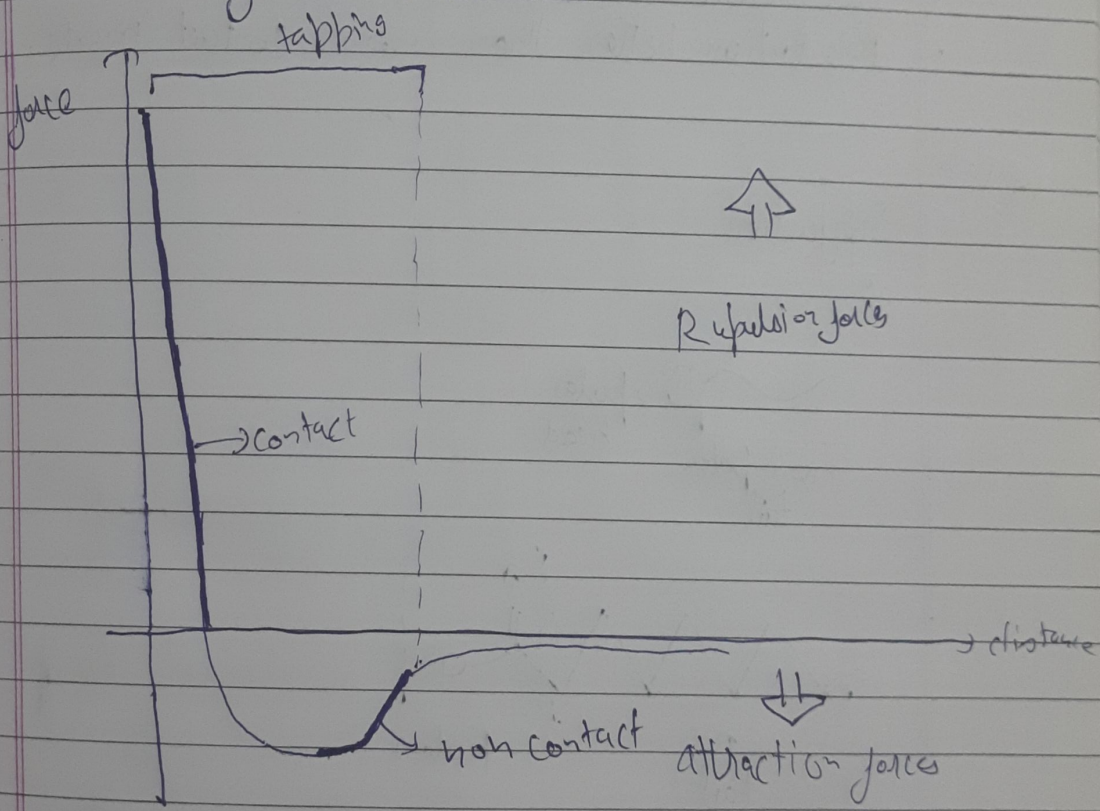
- Was made in 1986.
- Works on the principle of attractive & repulsive forces at atomic level.



Old version of AFM used STM tip (Scanning Tunneling Microscope) which recorded the oscillation of cantilever based on the tunneling current obtained



Movement of cantilever is detected by laser & detector.



Contact mode:

- Distance b/w probe & sample is very short.
- Cantilever is repelled.
- Resolution - High
- Bec. of short distance - probe may collide with sample.
- Sample & probe may get damaged.

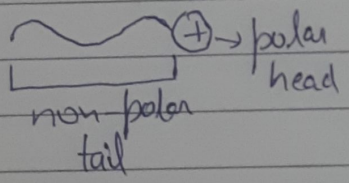
Page No.
Date

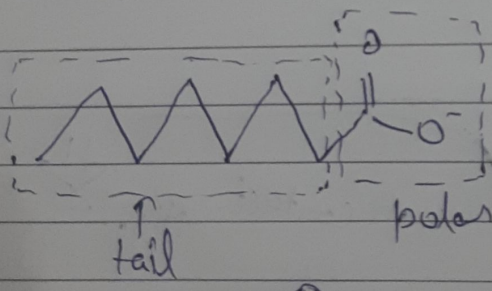
Non-contact mode
- Distance b/w probe & sample is large.
- Cantilever is attracted.
- Resolution - low
- Sample & probe not damaged.

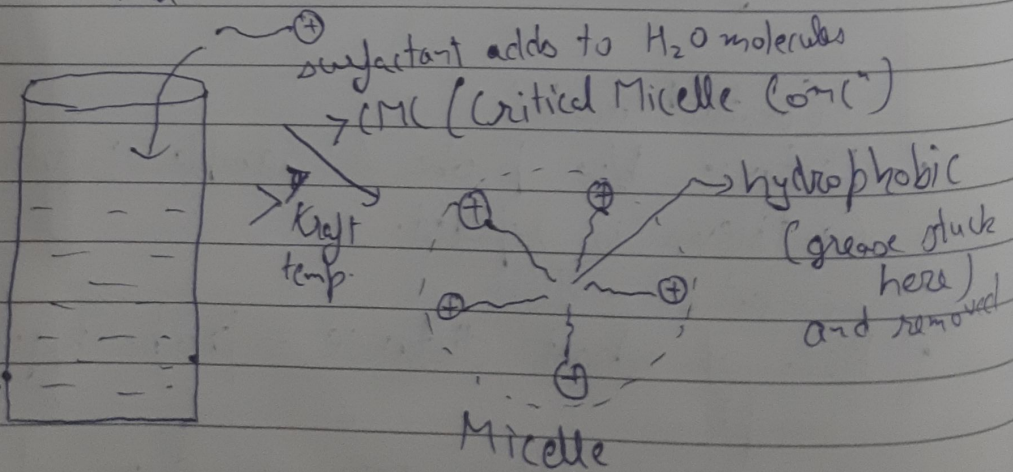
Tapping Mode
- Distance b/w probe & sample is intermediate.
- Cantilever - oscillates.
- Resolution better than non-contact mode.

18 Jan, 23

Surfactant







Page No. / Date / /

* Reverse Micelle (When we takes organic solvent)

* Blood Brain Barrier

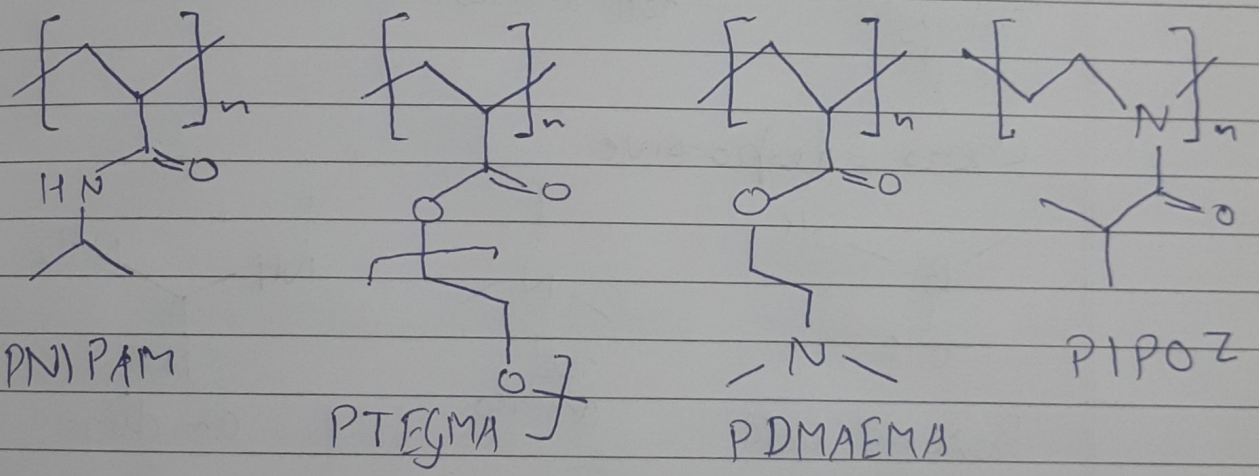
Amphiphilic Block Copolymer

AAA BBB

hydrophilic

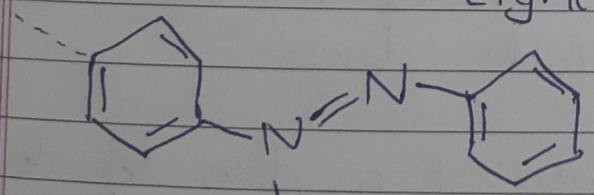
hydrophobic

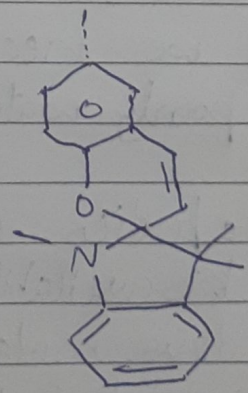
19 Jan, 23 Temp. Responsive Polymers

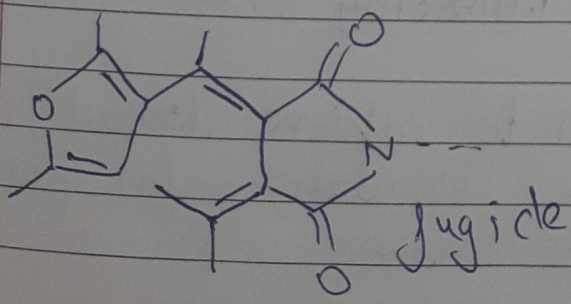


Light Responsive Polymers

Light







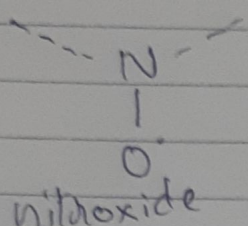
Light Responsive

UV sensitive

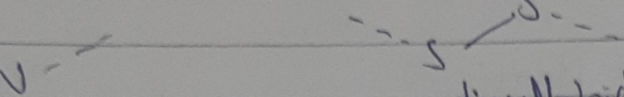
Visible sensitive

Page No.
Date

Redox Responsive

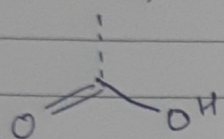


nitroxide

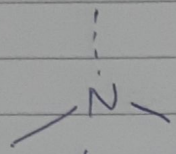


disulphide ← main

pH responsive

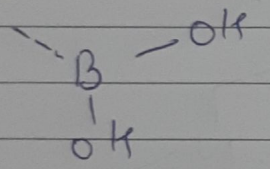


Carboxylic acid

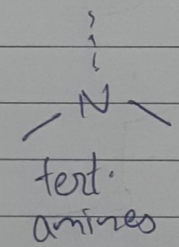


tert. amines

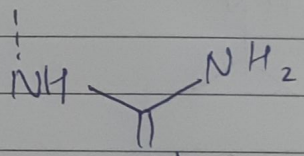
Chemo-responsive



Boronic acid



tert. amines



amidine

Cyclodextrin

Why we need it? ⇒ To inc. the water solubility of poorly water-soluble drugs.

Therapeutics effectiveness of a drug depends upon the bioavailability and ultimately on the solubility of drug molecule.

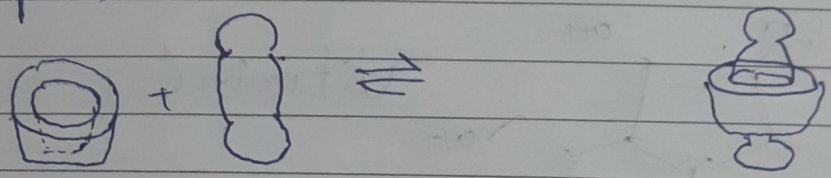
It's important parameter to achieve desired conc^{n} of drug in systemic circulation for pharmacological response to be shown

→ Complexation

Complexation is a reversible association b/w 2 or more mole. to form a non-bonded entity with a well defined stoichiometry.

Monomolecular Inclusion Complex

Inclusion complex is a type of complex in which one of the components is trapped in the open lattice or cage like crystal struc. of the other (also called occlusion compd.)



Most commonly used host molecular are cyclodextrin.

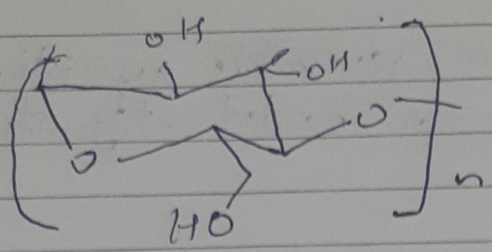
Inclusion complex are formed by the insertion of the non-polar molecule or the non-polar region of one molecule into the cavity of another molecule or gp. of molecules.

Cyclodextrins are non-reducing, crystalline, water soluble cyclic, oligosaccharides.

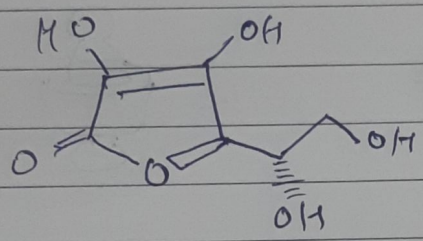
Struc.

These are a gp. of structurally related natural products formed during bacterial digestion of cellulose.

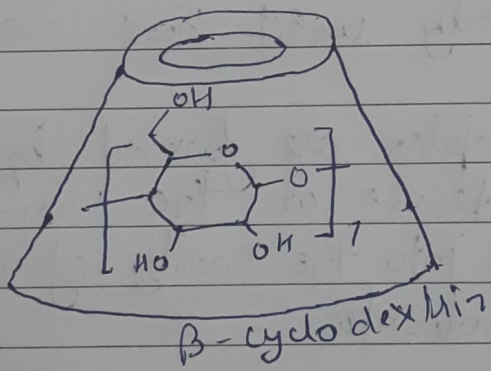
These cyclic oligosaccharides consists of (α-1, 4)-linked α-D-glucopyranose units.



Mech.
The surface of cyclodextrins molecules makes the H_2O soluble, but the hydrophobic cavity provides a microenvironment for appropriately sized non-polar molecules. (poorly water soluble drug molecules).



Vitamin C



β-cyclodextrin

~~Synthesis~~

β-CD , α-CD , γ-CD
↑ ↑ ↑
has 7 members ring, 6 members, 8 members (highest H_2O solubility)

Synthesis
Mainly done by (CGTase enzyme)
cyclodextrin glucosyltransferase

Starch $\xrightarrow[\text{liquified}]{\text{Heat + alpha amylase}}$ liq. starch $\xrightarrow[\text{org. solvent}]{\text{CGTase}}$ Noncyclic starch

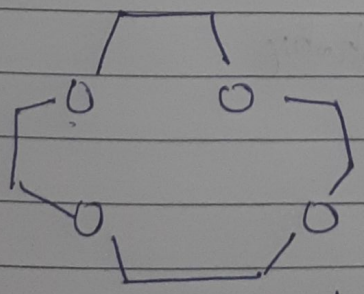
α-CD
β-CD — Purified — Cyclodextrin (All available)
δ-CD

(crystallisation)

Applications
1. Oral drug delivery
2. Parenteral " "
3. Ophthalmic " "
4. Nasal " "
5. Topical " "
6. Novel Delivery Systems

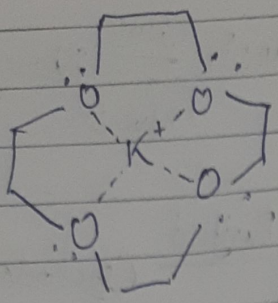
It should be stored in a tightly sealed container in a dry & cool place.

Crown ethers
→ Macrocyclic polyethers
Cyclic ether of ethylene glycol $+O-CH_2-CH_2+_n$
Eg



[12] Crown 4

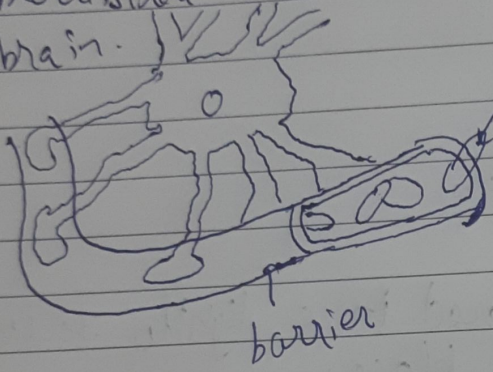
It forms complexes with +ive ions (metallic ion). The bonding in these complexes results from ion-dipole attraction b/w the hetero atoms & the +ive ions. In most cases +ive ions are held tightly in the centers (cavity) of cyclic ethers.



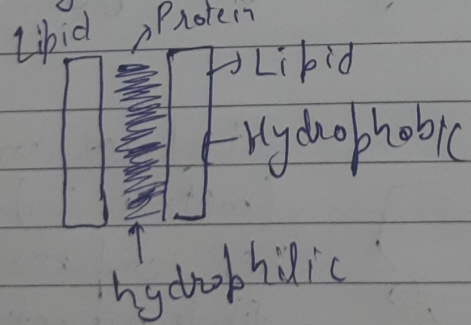
Crown ether complex

Blood Brain Barrier

It is a complex that surrounds most of the blood vessels in the brain. It acts as a barrier b/w the bloodstream and the extracellular space of the brain.



It allows only certain substances like O_2, water & small lipid-soluble substances. This prevents toxics, pategors etc. to pass through the circulatory sys into the brain.



23 Jan 23

Page No.
Date

* Lubricant
Encapsulate the unwanted nanoparticle formed inside the engine.
Due to ~~nanoparticles~~ friction, nanoparticles (unwanted) are formed inside the engine which dec. its efficiency.
* concept of dispersity.
* Why chain-end ... ?
* Why dis. is imp. for biopolymers?
* What is the significance of functionality & topology of biopolymer? → When we need to make network structure. Max. func^n, min. vol.
Why dis. imp. → we need to know chain length.
If $D < 1.5$ → biopolymer → useful.
$D = 1.0$ → probably most useful.

24 Jan, 23

* Atom Transfer Radical Polymerization

Transition Metal / variable oxid^n state

Ag – 0, +1

Homogenous catalysis – Can't seperate catalyst after reac^n.

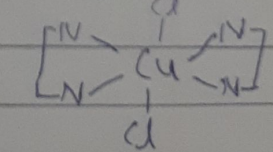
Mt^{m} → CuII

$$P_n - X + M^m/L_n \underset{K_d}{\overset{K_a}{\rightleftharpoons}} X - Mt^{m+1}L_n$$

↳ Ligand

→ $CuBr_2$/AgCl

P_n = transition metal with 2 oxid^n state only

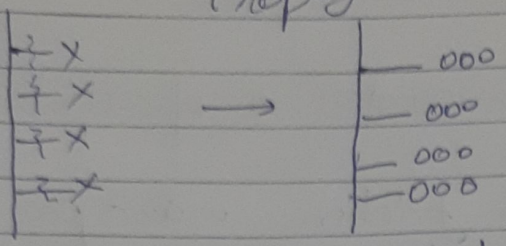


C – X
C$^\cdot$ – X$^\cdot$

Page No. / Date / /

t = 1 ms

Propagation



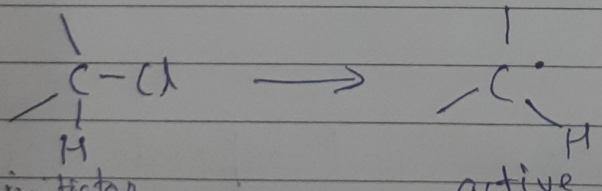
we can make polymers that are super hydrophobic

Initiation state is fast & propagation state is slow, then we can generate super hydrophobic material.

Initiation state → at which C-X bond ~~breaks~~ undergoes homoletic cleavage.

Role of trans. metal to undergo oxid^n & capture X & reduced. Ligand used to stabilize metal at higher oxid^n state. Deactivator to conc^n the active radical is very low. (C· radical).

What will happen to C·?

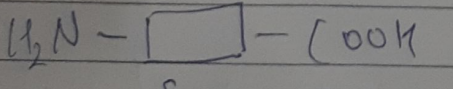


initiator

active

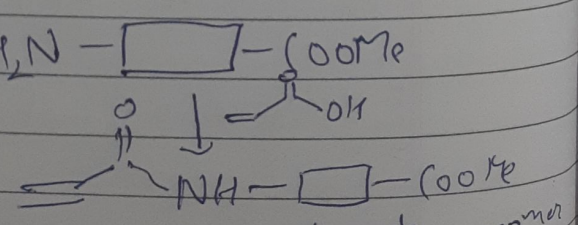
[low energy state] dormant 10^5

10^1 (low conc^n req.)

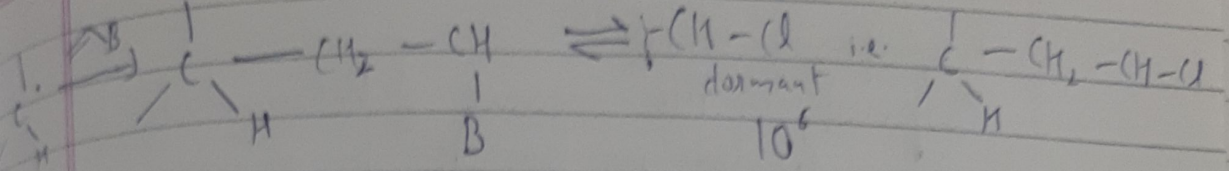


Some amino acid

C-protection



AA derived acrylamide monomer



$P_n (n=1)$

propagating radical 10^{-}

Grafting

* Grafting density -

Block Copolers

1st reac^n → Esterification → generate bi-functional initiator

ABA type polymer formed

now added styrene

still ABA type

Click reac^n now

converted Br to azide

again click reac^n

polystyrene is used for making hydrophobic material.

triazo gp. is antifungal gp. (in last struc. with 3N in cyclic struc.)

also has antimicrobial properties.

Page No. /
Date / /

Polydispersity Index

Dispersity is the measure of heterogeneity of sizes of molecules or particles in a mix.

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

ratio of weight avg. molecular mass to number avg. molecular mass is called PDI.

For monodisperse $\bar{M}_w = \bar{M}_n$

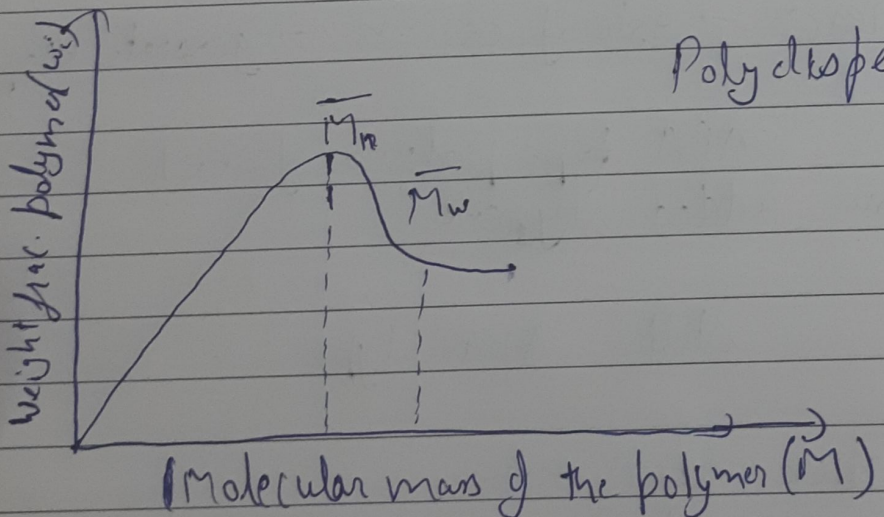
$PDI = 1$

Eg = Natural polymers

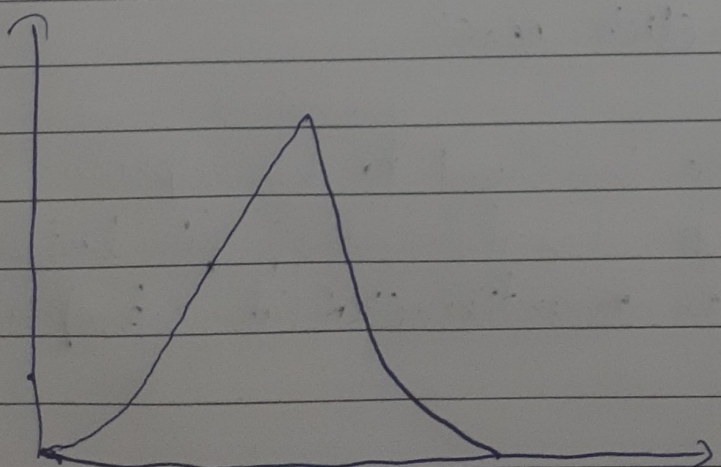
For Polydisperse $\bar{M}_w > \bar{M}_n$

$PDI > 1$

Eg : synthetic polymers



Polydispers



Mono dispers

Why dispersity is imp. for bio polymers?

→ Don't know

What is the ~~functionality~~ significance of functionality & topology of biopolymer?

Topological polymers is referred to as a polymeric molecule that poses unique spatial features, such as linear, branched or cyclic architecture. It could also refer to polymer networks that exhibit topologies owing to special crosslinkers.

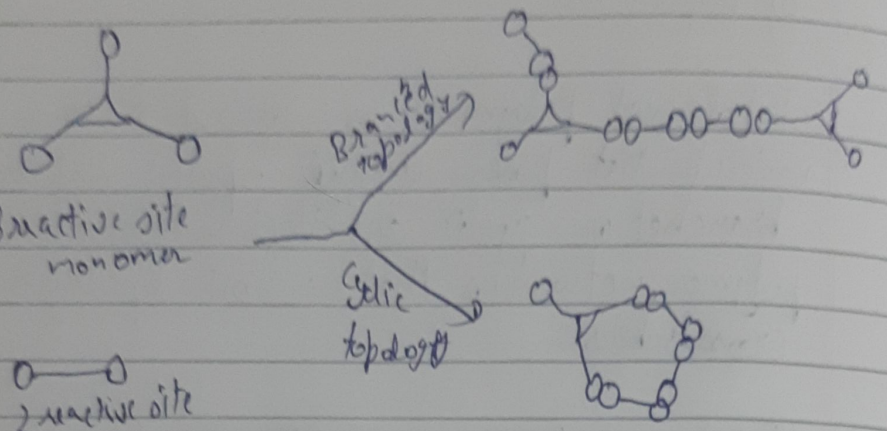
Topological polymers could refer to a single polymeric chain with topological information or a polymer network with special junctions or connections. In investigating it, the way of junctions or connections attached to it are more considered.

topology of a bio-polymer can determine it's physical properties due to the crosslinking arrangement of the monomeric unit in different ways like branched crosslinking or cyclic crosslinking.

Branched crosslinking

Branched crosslinkers are entities that don't form cyclic topologies. The 'degree' (no. of edges linked to each node), of branched demonstrates the theoretical no. of polymer strands at the junc^ns of a cross linker, also known as branch functionality.

Combining monomers with diff. degree of branch functionality could generate various topological network with distinct elastic properties.



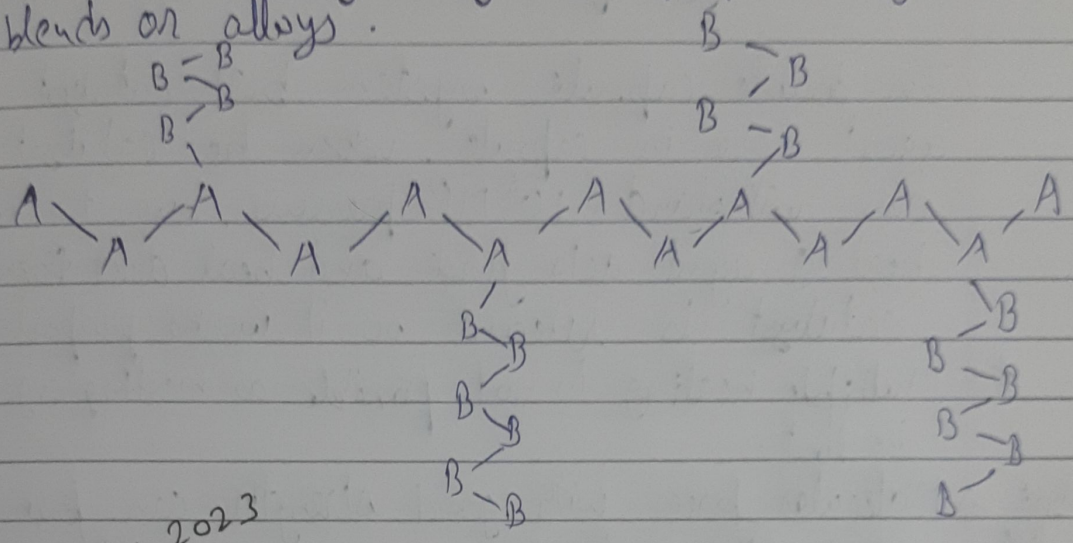
Cyclic crosslinking

These are more sophisticated and show multiple possibilities. Loops or cycles could form in a smaller scale b/w 2 polymer chains or in a larger scale among multiple polymer strands. The characterization of cyclic topologies within a polymer network, compared to branched, is relatively harder to perform.

Graft Polymer

In polymer chem., graft polymers are segmented copolymers with a linear backbone of one composite and randomly distributed branches of another composite. The structure below shows how grafted chains of species B are covalently bonded to polymer Species A. Although the side chains are structually distinct from the main chain, the individual grafted chains may be homopolymers or

copolymers. These are synthesised for many decades and are especially used as impact resistant materials, thermoplastic elastomers, emulsifiers for the preparation of stable blends or alloys.



25 January, 2023

Self-healing

Automatic
* without any external intervention

Non-automatic
* external intervention req.

Role of catalyst is that it solidifies quickly.

We can't have anything that is too brittle.

Multiple healing is not possible.
Due to crack, there is transmission of energy due to which it bursts.

Dual Capsule System

In single capsule system, if catalyst is always present in the matrix and the healing agent can solidify before even reaching the crack.

In double capsule system both catalyst & healing agent are in capsule, ~~when~~ the catalyst capsule can withstand 10^5 MPa pressure, due to which healing agent acts first and heal and then the catalyst is released so it works properly.

Multiple healing is not possible as healing agent will be lost.

Catalyst free slide → Molecular forces with good strength can form self-healing molecules.

Photovoltaic Devices

→ Why self-healing req?
To give protection from scratch, moisture, temp etc. and to provide better stability.

Substrate →

adhesive → to paste if sealant.
inorganic coating → can fold but can't roll
display media → like quantum dot