

# Smart Materials

→ Materials which changes its dimensions due to some external stimulus  
 chemical/physical properties  
 called stimulus responsive material.  
 Smart materials

BP → Na/K ions (external stimuli)

Nanorobot

Click-Grat Actuator

arm,

pH → cancer cell  
 diff from  
 Normal  
 Cells.

change its shape due to change  
 in environment.

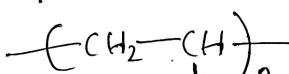


hydrophylic (amide)



hydrophobic. (Isopropyl)

PNIPAM



TRANSPARENT



PNIPAM  
 in water  
 (soluble)

linear.

$T > 32^\circ$

HAZY (opaque)



not, much  
 solubl.

(precipitate)

globul.

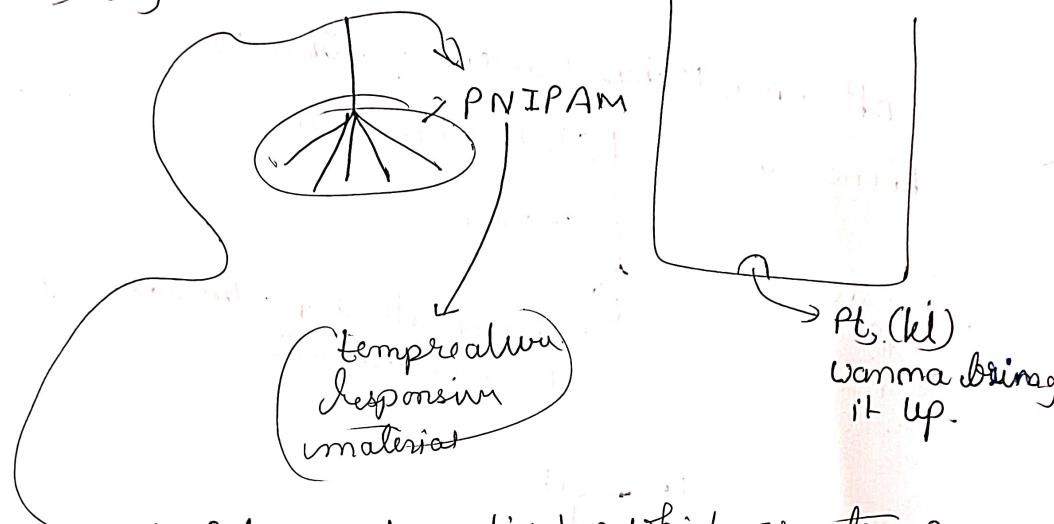
temp. at which it becomes precipitate

Lower critical solution temperature (LCST)

↓

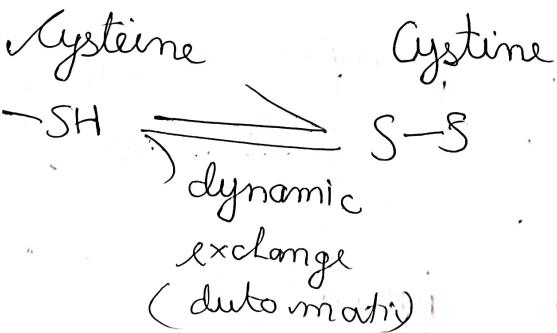
below LCST → soluble  
above LCST → insoluble

Lets, Nanorobot



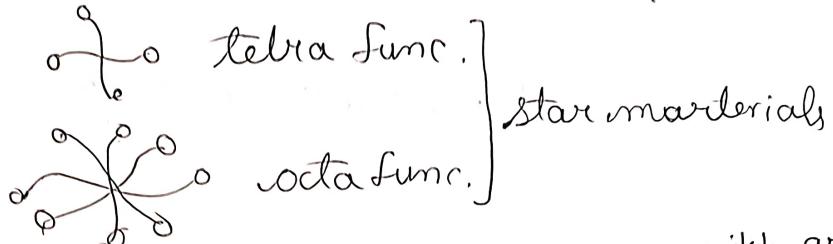
Used to make activator which are temp.-responsive.

→ Redox responsive



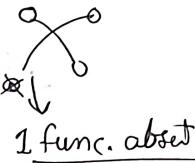
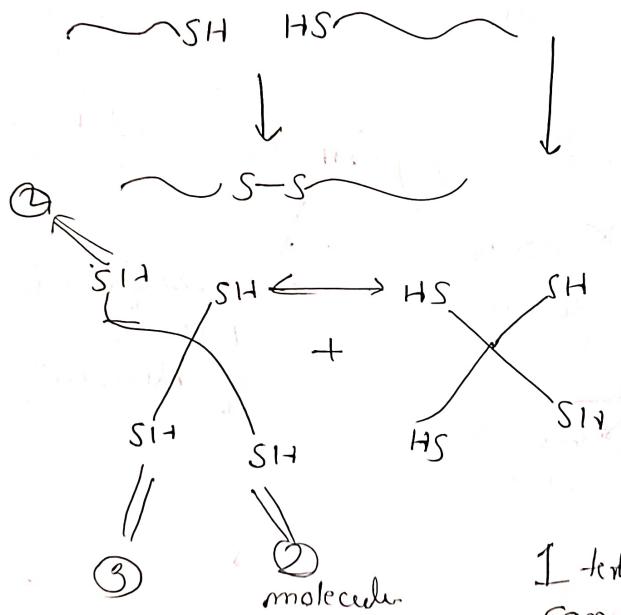
## Octopus

~ monofunctional.



mikto arm

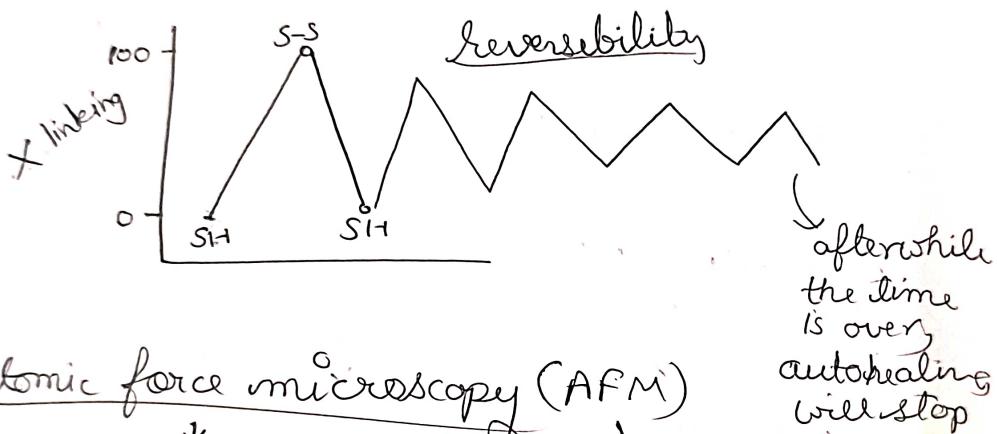
## Redox responsive



Can be used  
to make self  
healing material

I tetramolecule  
can form is truc.  
with 4 molecule  
makes it rigid/  
insoluble/

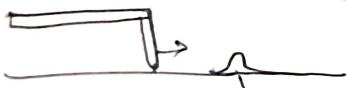

 made of HS SH fluidic,  
~~SH~~ ~~S-S~~ ~~S-S~~  
 Pile up of material  
 top then fill the crack  
 and cross link to  
 heal the scar.



## → Atomic force microscopy (AFM)

↓  
70,000 X zoom,

scratches the surface,



rod cell  
jump.

to see Self healing  
process  
of Nanocut



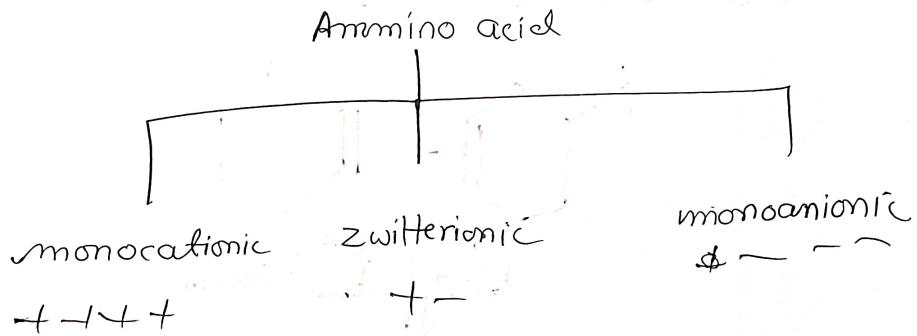
March, 2020

Genome Sequencing:

Seq. of amino acid → protein.

Genom sequencing  
 ↓  
 wanna study the constituent  
 separation of protein (similar sites)  
 Problem,

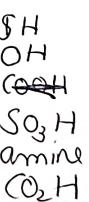
$A + B + C$



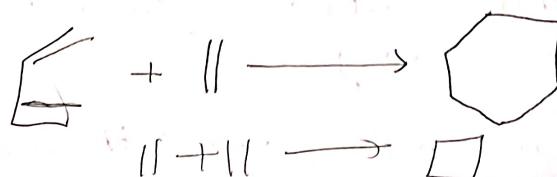
let  $A^+ + B^- + C^-$  mixture,

passed through, +ve membranes }  
-ve membranes }

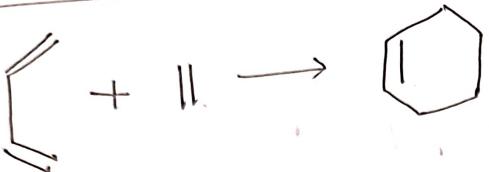
$B^-$  left only,



pH responsive membranes are used to separate  $A^+, B^-, C^-$

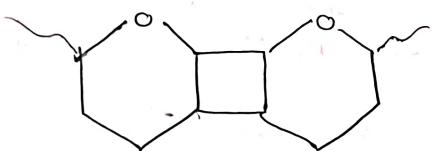
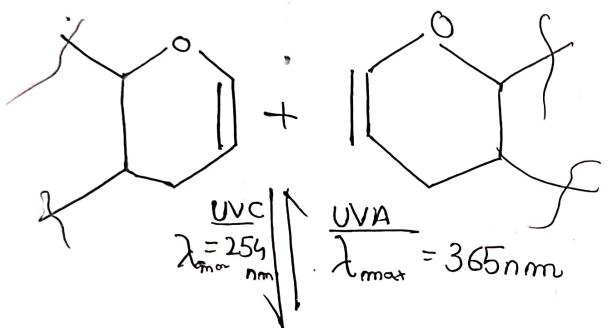


## Light responsive material



chromophore → material that absorbs light  
 (chlorophyll)

→ coumarin → chromophore.



dimerization (crosslinking)

Using UVC, UV, we can make crosslink, delink

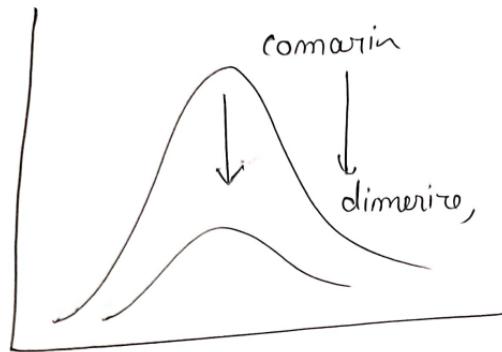
by the hole in ozone, UVA, NC are available for free, 5-10%.

due to this, material is going through dynamic exchange

•  $\text{SH-SH}$  cause rotten egg smell, this material is used

can also be used as self healing

1.



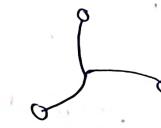
→ functionalities



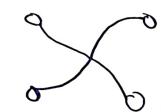
monofunctional



bifunctional

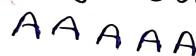


trifunctional



tetrafunctional

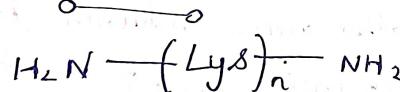
→ Copolymer:



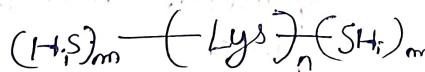
Diblock copolymer.

'A' Block      'B' Block.

ABC → triblock copolymer.



byfunc.  
polylysine

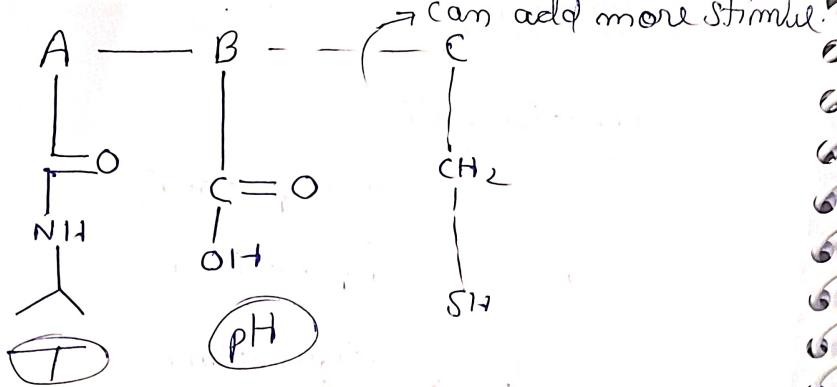


A

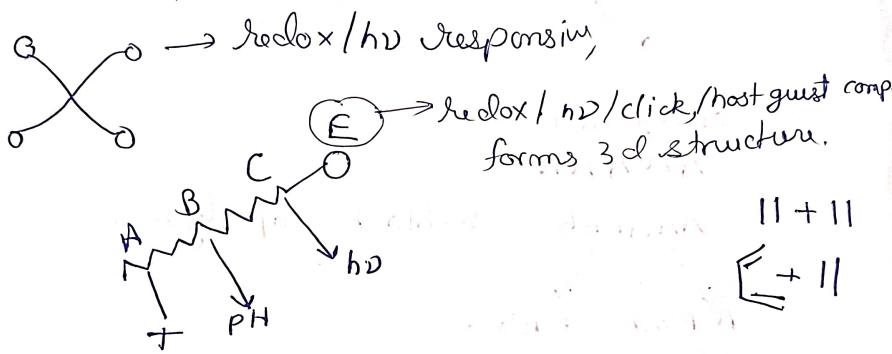
B

Bifunctional polylysine

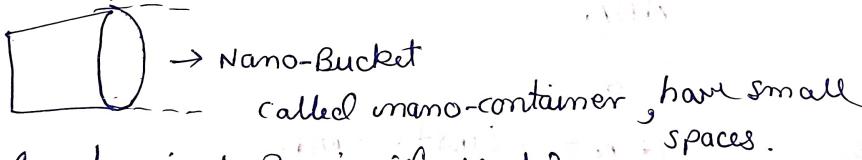
let A-B is Bifunc. compolymer



in a single material  $\rightarrow$  multiple stimulus response  
 star material



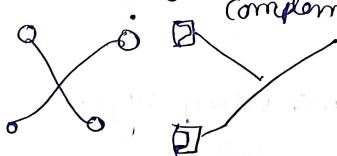
### Cyclodextrine



can we do chemical Rxn inside that?

$10^{-9}$  molar dilution  $\rightarrow$  can get single molecule separated, Rxn become faster.

host guest conformation.



form Complex  
 when size matches

how does self healing material join?

- H-Bonding interaction,  
non-isocyanate polyurethane  
with multi H-Bond site,

→ can't be separated by UTM also.

Biodegradable → degrade

Polylysine

Bioaccumulative → accumulate slowly

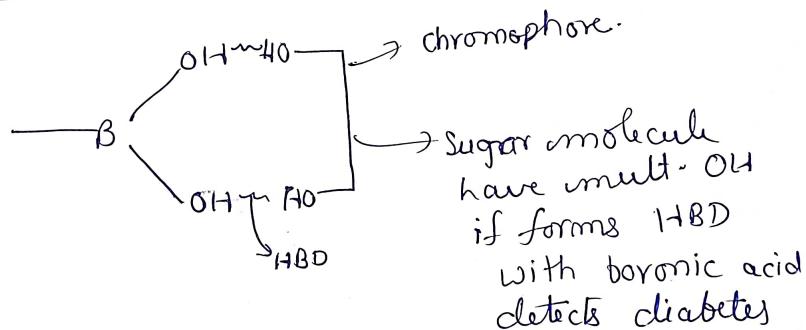
↑

Biocompatible → fool the body by some protein coating.

→ Chemoresponsive.

Boronic acid.

How to detect diabetes cost effectively.  
Fluorescent detection → by eyes, but costly



PDMAEMA

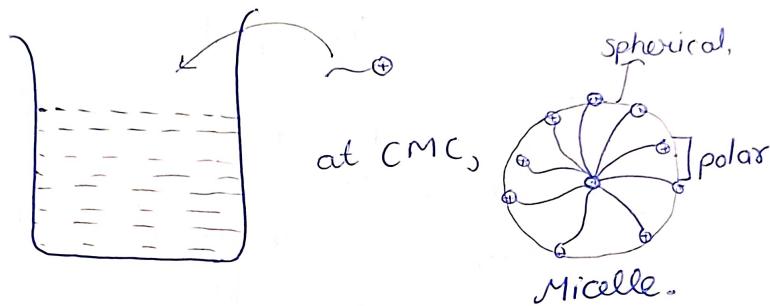
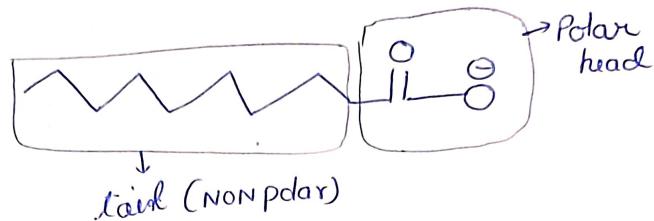
1



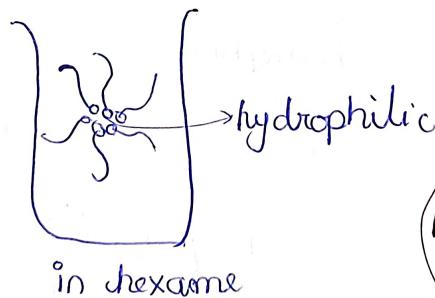
Thero + pH

## \* Double stimuli responsive smart polymer.

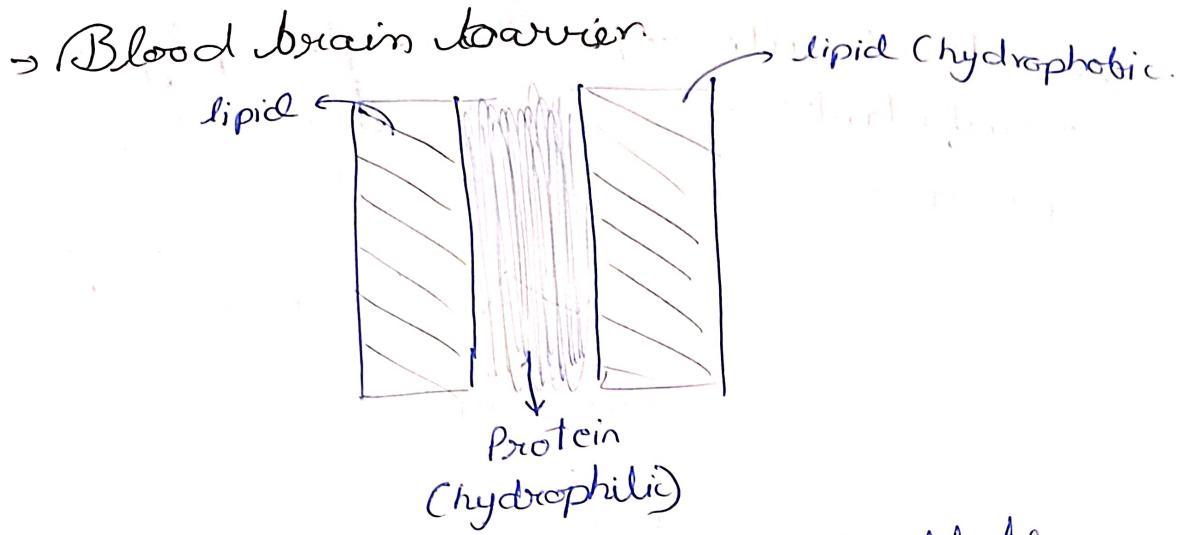
- Surfactants  $\downarrow$  contain polar head groups and non-polar tail  
(Shampoo)



- $\rightarrow$  above CMC dirt is attracted and encapsulated inside the micelle
- $\rightarrow$  Reverse micelle in organic solvent  
 $\rightarrow$  a hydrophilic core is formed,



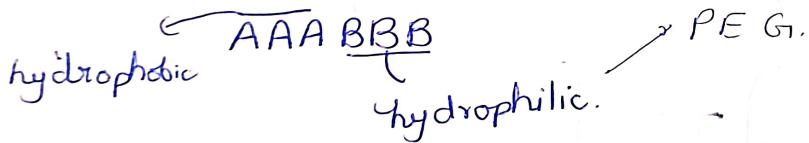
(polyglycolic acid  
Oxygen barrier  
moisture barrier)



to penetrate inside, drug should be  
all rounder,  
therefore it should be both hydrophilic  
and hydrophobic

→ SURFACTANT:

→ Block copolymer.



can be considered as surfactant.

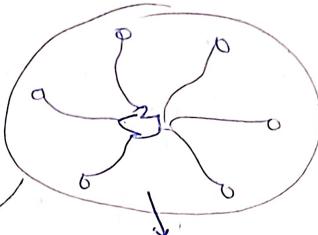
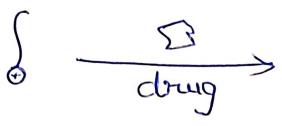
also called, Amphiphilic Block copolymer.

↓  
can be used  
to deliver  
drug.

→ Cancer cell

CHROMOPHOR are used to check whether vesicle is forming or not

pH lower than normal.



encapsulation,

taken to desired place.  
to release,

In case of cancer, a little dec. in pH, triggers to release the cargo (drug)

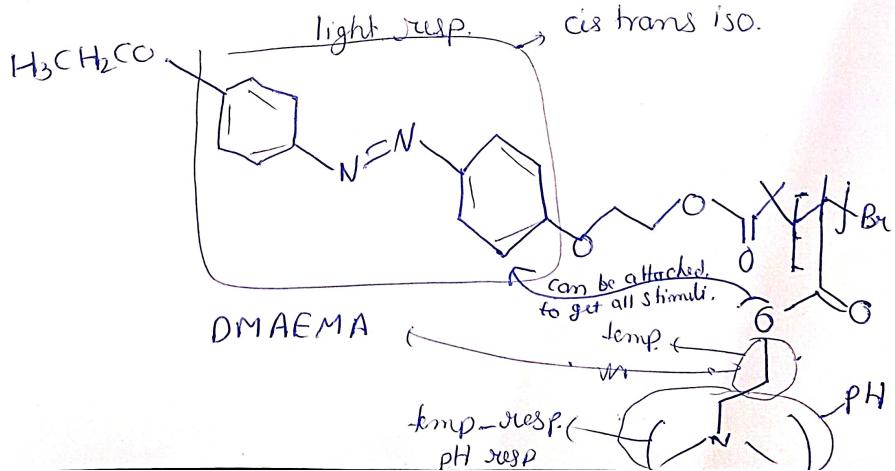
Release.

sustained release  
↓  
slow release acc. to need

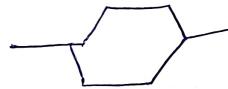
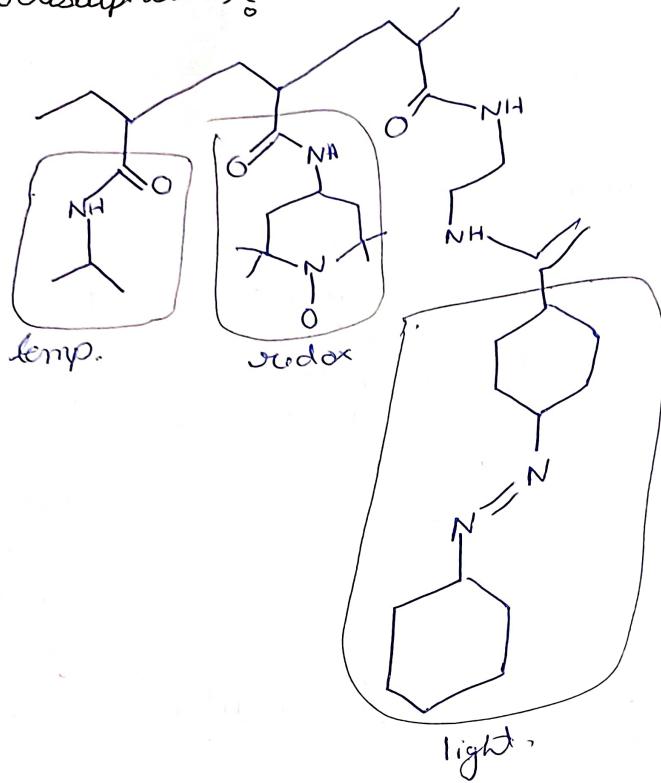
If burst happen,  
i.e. trigger is so fast it can be fatal

for insulin

sugar, salt conc. can also be trigger



thiodisulphite  $\rightarrow$  ?



29/01/2023

Doubt "Creating" session. 1 - Feb - 2023

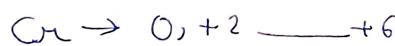
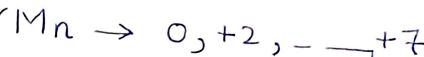
Tierce Exam → MCA only.

25 Ques × [2]

+2, -0.5.

→ Atom transfer Radical Polymerization

o Transition metal with variable oxid<sup>n</sup> state.



at zero O.S. react as good catalyst (nanop form)

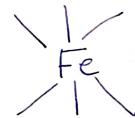
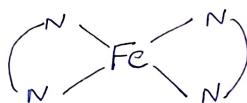


react as catalyst,

catalyst leaching

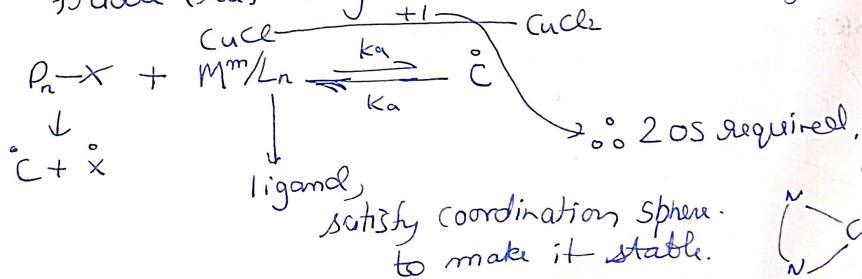
homogeneous catalyst: can't separate (due to same state)

heterogeneous catalyst: can be separated,  
tetra coordinated complex:

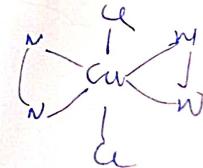


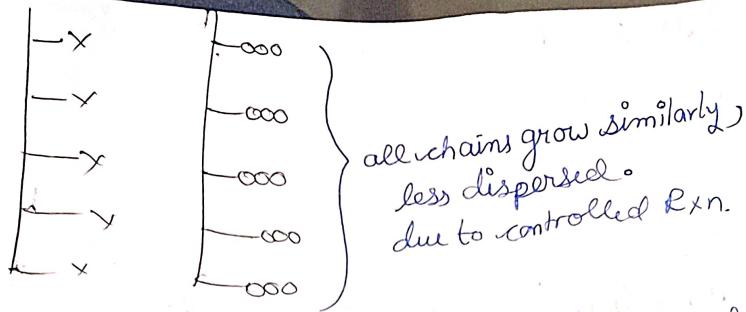
hexa coordinated

Friedel-Crafts alkylation → radical pathway.

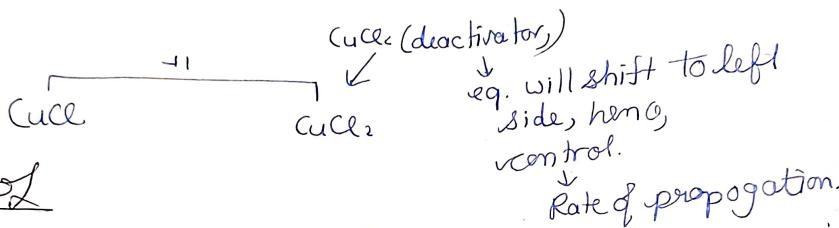


forward Rxn is made slow → controllable.





ensure, at  $t = -\infty$ , all alkyl halide bonds are broken,  $\rightarrow$  then propagation is same.  
 $\rightarrow$  (initial step is fast) ( $\downarrow$  slow) control-growth of polymer, less dispersed



### Role of

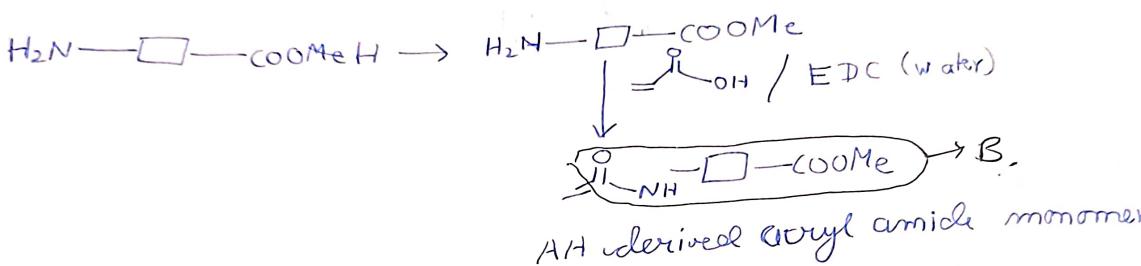
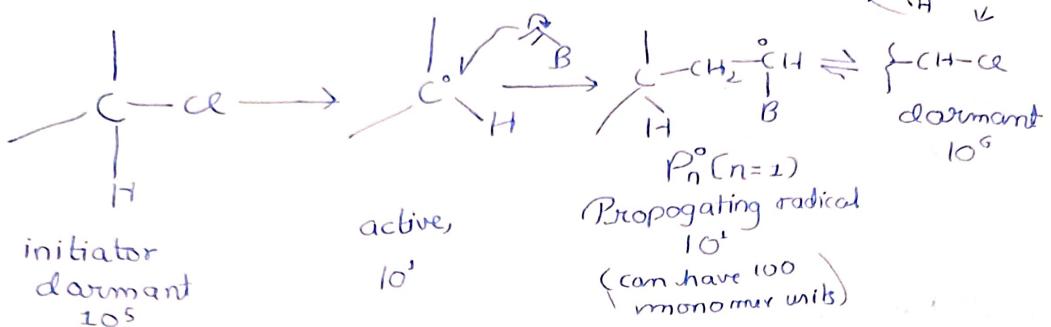
$\rightarrow$  Role of  $Tn \rightarrow$  undergoes OX.  
 trap halide

$\rightarrow$  deactivator  $\rightarrow$  conc. of active radical is very low.  
 eq. goes to left.

$\rightarrow$  ligand  $\rightarrow$  ensure  $TnX$  is stabilized, by stabilizing coordination number.

Notes: In homogeneous catalysis, polymer traps the metals in PPM make it useless for medical purpose.

# les us ess



the aim is to

reduce Bimolecular termination, Disproportionation  
 $\text{R}_x-\text{R}_y / \text{R}^\bullet \& \text{R}^\bullet$

(to make diblock co-polymer)

→ Technique of grafting polymers to a surface



(No. of molecule/  
 $\text{nm}^2$  of  
area.)

GRAFTING  
density.

$\therefore$  they repel, it is difficult to  
get high density of polymer  
by "Grafting to" start

$\therefore$  we use "Grafting from"

$\text{NH}_2$  COOH  
coupling  
esterification

# Cycloaddition, click Rxn:



silver sulphazide.

1. Esterification → by func. initia.

2. Polymeric " "

triazole → antifungal,

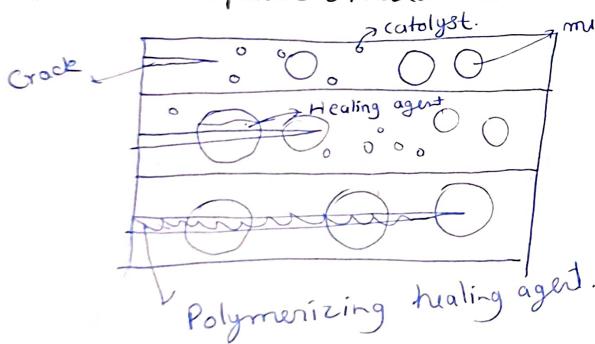
25/01/2023.

Self healing.

Automatic  
without any  
external  
intervention.  
(Gecko)

Non automatic  
external  
intervention  
required.

→ Via microsphere Embedment



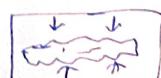
microcapsule.  $10^{-6}$  m.

nano  $\rightarrow$  micro  $\rightarrow$   
 $10^{-9} \rightarrow 10^{-6}$

trigger. (system should sense.)

healing material  
should not be  
too brittle.

will not stick to  
the surface,  
it should reach  
the surface deeply  
before solidifying



→ PROBLEM with this sys

- can heal only once, once microcapsule used (consumed)
- can't be used again
- mult-healing can't happen (no reversibility)

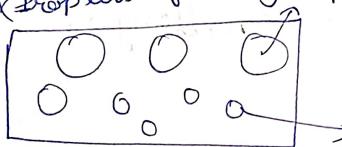
- Dual capsule system (can't heal multi. times) (Healing agent lost)  
 IPR (Intellectual property Rights)
- Wait a min... how does a capsule breaks ??



Wall made in such a way.  
 nano crack can rupture them.  
 (Pressure sensitive)

Now, back to topic.

(Propellers of healing agent) HOPDMS + PDES



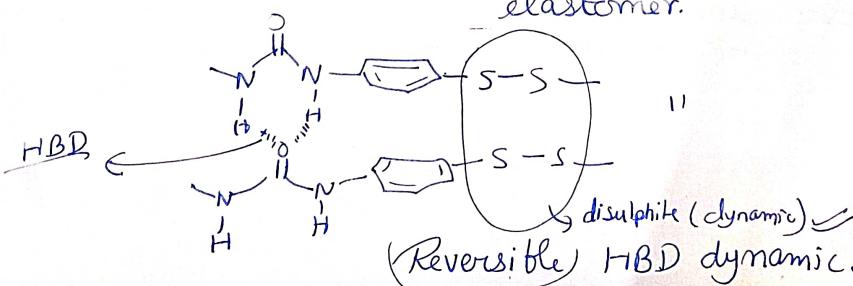
① catalyst di-n-butyltin dilaurate (DBTL) encapsulated in (polyurethane micro capsule) withstand 24 MPa pressure.

②

- In 1st case, catalyst already present, Healing agent already start solidifying before reaching everywhere,
- In 2nd case, catalyst (In PU) released late. Solidification starts late, ie after healing material reaches crack completely.

○ Catalyst free, room temp. self healing elastomer

Self healing poly(urea-urethane) elastomer.



~~✓~~ Multiple healing possible

→ Smart, self healing coating  
scratch resistance self healing coating.

New scratches

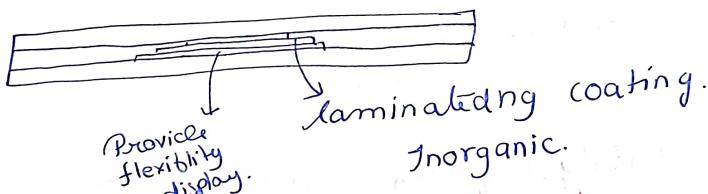
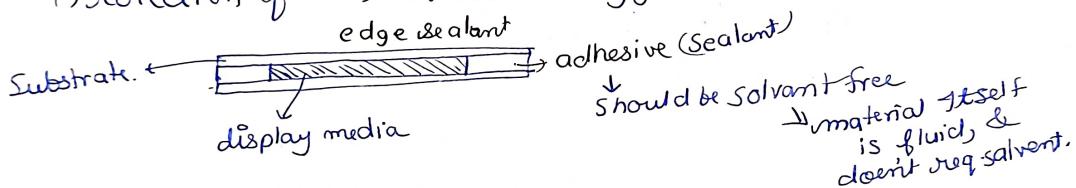


One week later

o Photovoltaic Devices & Challenges.



Protection from, moisture/oxygen is needed.



for screen { moisture oxy-  
external damage.  
mechanical damage

~~YF=I~~

## SUMMARY,

we discussed HOW?

this material works,

3 ex, 1 major application.

Mechanical response, pressure → TRIGGER.

2nd ex: catalyst has delay release; Healing material  
reach & heal efficiently.

Catalyst → req. multiple trigger

Healing agent → single trigger enough.

→ more no. of sites, faster healing, better healing  
amide bond → best HBD, healing.

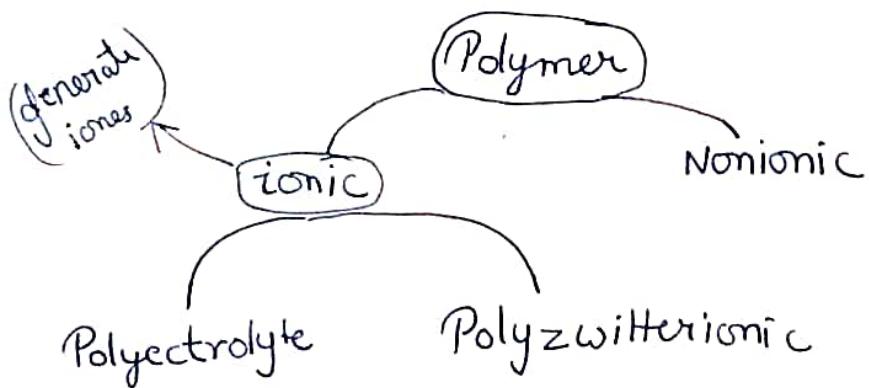
Why self healing adhesives without solvent are  
more imp. → req. high barrier properties  
protec. moisture

for non-hazardous sys. → req. Solvent free.  
Coating.

more imp.  $\rightarrow$  req. protec. moister,  
 for non-hazardous sys.  $\rightarrow$  req. Solvant free.  
 Coating.

31-01-2022

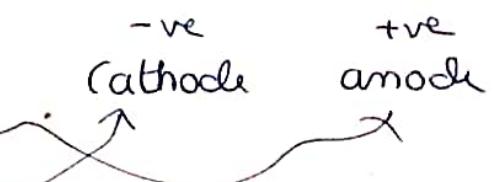
$\rightarrow$  Zwitterionic polymer.



$\rightarrow$  Electrolyte



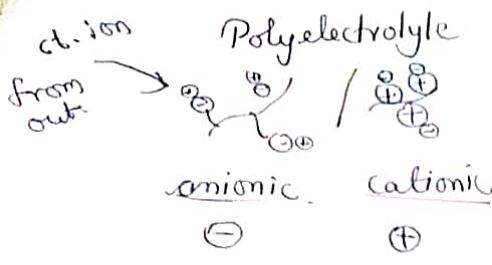
Solution conductivity vs



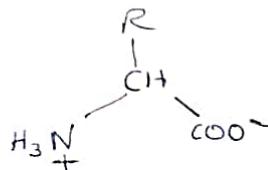
$\rightarrow$  zeta pt.  $\rightarrow$  no net mig. of ion

surface charge

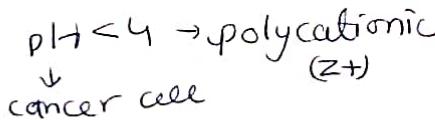




at iso-electronic point  
amino acid are  
zwitterionic.



have some NO. of  
 $\text{NH}_3^+$  &  $\text{COO}^-$   
 $\therefore$  O zeta potential.



- ∴ can use amino acid as cancer sensor

→ sensor amminoacid, monocat, mona anion,  
zwitter,  $\downarrow$  atacidic

sensor → measure zeta

for healthy  $\rightarrow$  0

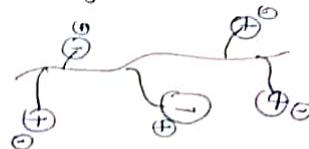
sharp jump  $\rightarrow$  (+)ve zeta.

cancerous cell

how<sup>2</sup> endoscopy.

## Polyzwitterion.

## Polyampholyte



ex:  $\text{SO}_3\text{Na}^+$        $\text{CO}_3\text{Na}^+$   
 $\hookrightarrow$  counterion  
 exist in soln

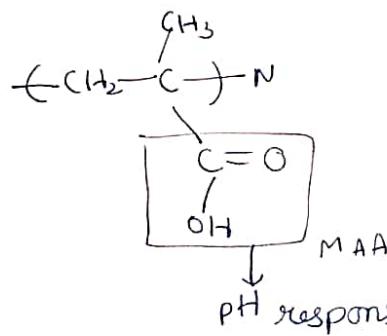
Biopolymer → ~~re~~ bioderived,

## pH responsive materials

- o acidic group.

→ Drug release system

- controlled release of insulin
  - hydrogel works as insulin containing reservoir within  $P(MMA-g-EA)$  graft polymer.  
→ Methacrylic acid.



## Graft copolymer

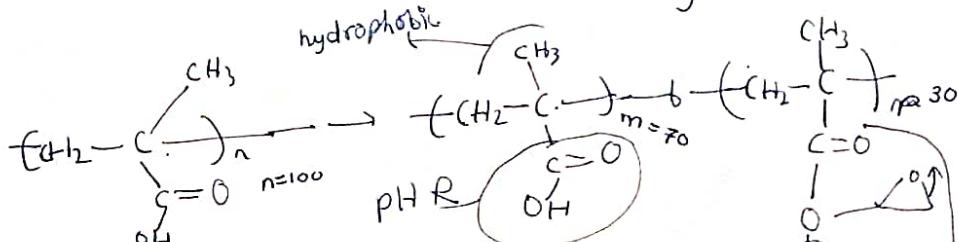
A hand-drawn diagram showing a horizontal line representing a "linear backbone". A curved arrow points from the text "linear backbone" to this line. Below the line, there are vertical tick marks. At the bottom center, there is a circled "1". To the right of the circled "1", there is a partial circle.

-N  
-O

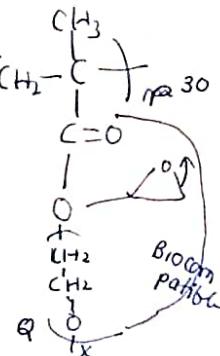
Normal  
ph, Glucose  
pH 7.4

Higher glucose  
pH 4.0

ester  $\rightarrow$  breakaffi



Polyethylene glycol - drug di)

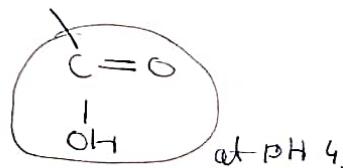


Increased glucose conc.  $\rightarrow$  pH ↓  
trigger the is pH.

Insulin in vesicle encapsulation,



∴ at pH 4

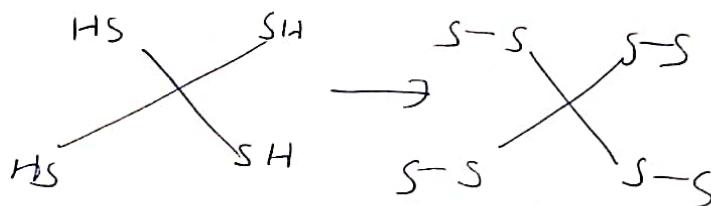


at pH > 4

$\text{COO}^-$ , vesicle formation,  
ambiphilic.

pH < 4 all  $\text{COO}^-$  protonated,  
NO vesicle,  
collapse release insulin.

→ Drug release system.



Reversibly crosslinked  
3D network

4D system?

Yes! the ability to transform its shape

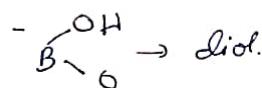
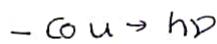
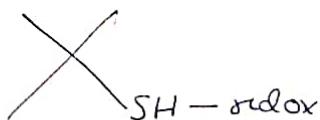
→ swell on water conc.

solvent, water, air, → swelling  
↓  
controllable  
due acc.  
to env.

o → can be tuned. → can't be used, → its temp. resp.

ex: P(NIPAAm), → crosslinked struct  
above LCST of homo polymer.

swell → encapsulate,  
shrink → release.



outer of body  
internal recognise.  
scaffold external.



(D)

used as tissue scaffold.

→ Cell Adhesion control.

→ Blood stop? → adhesive property.

o Platelets on Polyethylene glycol grafted tissue.  
culture of polymer polystyrene (TcPS)  
retain a rounded shape at 37°C