NEXTCT SYLLABUS: Complete Unit 1

Date 04/Nov/2024

POLYMERIC MATERIALS

The term 'Polymer' is derived from two greek words poly-many, mer-which means parts.
Polymers are macromolecules whose structure consist of large number of repeat units.

$$\underset{\text{(monomer)}}{n\,CH_2=CH_2} \xrightarrow{\text{Polymerization}} \underset{\text{(Polymer)}}{-\!\!(CH_2-CH_2)\!\!-_n}$$

Repeat unit : $-\!(CH_2-CH_2)\!-$

There is a difference between repeat unit and monomer.

Characterstics of Polymer

① Degree of Polymerization: n = degree of polymerization = number of monomer sites

② functionality: The number of active bonding site on monomer.

③ Molecular weight of Polymers: Polymers are polydispersed So we have to take average molecular weight.

Two types of Bonding

① Strong Covalent bonding between atoms within a polymeric chain about 1-1.5 Å.

② Weak Vander Wall forces of attraction between different polymeric chain of about 3-4 Å.

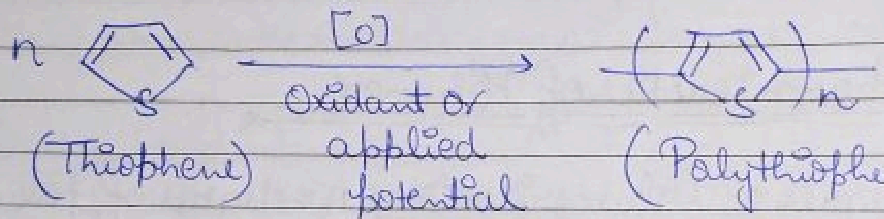
★ They have excellent corrosion resistance.

★ Act as thermal and electrical insulators.

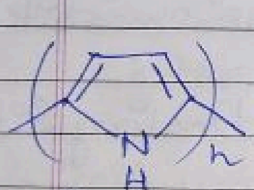
★ are semicrystalline materials.

Organic Conducting Polymers: They have long carbon based chains composed of simple repeat units derived from monomers and are capable of conducting current across the chain.

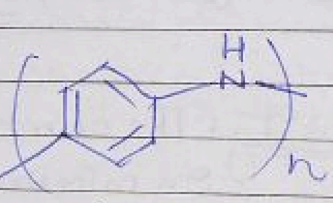
for ex:



(Thiophene) → (Polythiophene)



(Polypyrrole)
(PPy)



(polyaniline)
(PANI)

Classification

Conducting Polymers (CPs)

- Intrinsically Conducting Polymers
  - Conducting polymers having conjugation
  - doped conducting polymers
- Extrinsically Conducting Polymers
  - Conducting element filled polymers
  - Blended CP

Date
Page

Extrinsically Conducting Polymers

Their electrical conductivity is due to externally added ingredients

They are classified as:

★ **Conductive element filled Polymers**: here polymers act as a binder to hold the conducting element (carbon black, metal fibres).

The minimum concentration of conducting filler required to make the polymer Start conducting/ act as a conductor is known as Percolation threshold.

★ **Blended Conducting Polymers**: They are formed by blending a conventional polymer with conducting polymer. Such polymer possess better physical & chemical properties.

06/Nov/2024

Intrinsically Conducting Polymers

They have extensive conjugation in their backbone

(1) **Conducting polymers having π e-s**: Their π orbitals over the entire backbone overlap to form valence band & conduction band which are separated by significant energy gap. Electrical conductivity can occur only after thermal or photolytic activation of e-s.

eg: polyacetylene

$n\,\overset{*}{C}H \equiv \overset{*}{C}H \longrightarrow$ 

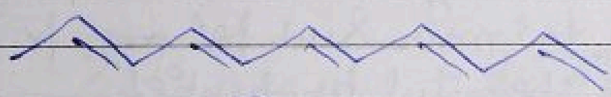
(Acetylene) (polyacetylene)

$-(CH=CH)_n-$

② **Doped Conducting Polymers**: Polymers having conjugation can easily be oxidized & reduced. They have low ionisation potential & high electron affinity.

Doping is done in two ways:

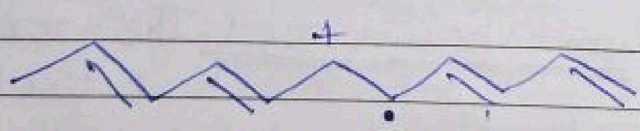
① **P-Doping**: It is done by oxidation process and treatment with lewis acids (e⁻ acceptor).



Polyacetylene

$*(CH)_x + LA \longrightarrow (CH)_x^+ LA^-$

$-e^-$ (oxidation) $\Big\downarrow$ I_2/CCl_4



Polaron (Radical cation)

$-e^-$ (oxidation) $\Big\downarrow$ I_2/CCl_4

Bipolaron (dication)

Bipolaron

$\downarrow$ (Segregation of cation)

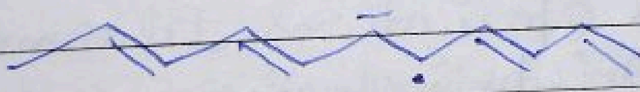
(Soliton pair)

② <u>N-Doping</u>: Reduction process & it is done by treatment with Lewis base.

(Polyacetylene)

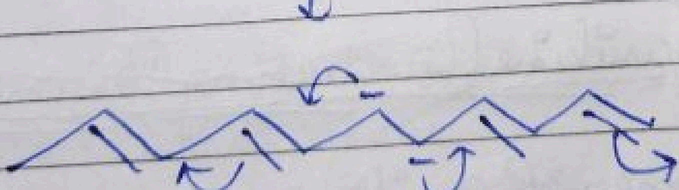
★ $(CH)_x + LB \longrightarrow (CH)_x^- LB^+$

$+e^-$ (Reduction) $\downarrow$ $Na^+(C_{10}H_8)^-$ (Sodium Napthalide)



~~Polaron (Radical Anion)~~

$+e^-$ $\downarrow$ $Na^+(C_{10}H_8)^-$



(Bipolaron)

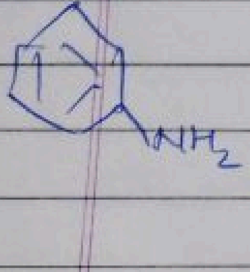
Applications of Conducting Polymers

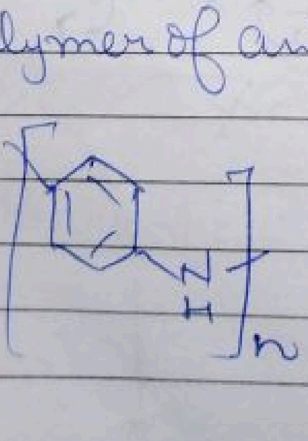
- In rechargeable batteries due to small size, long ecologically good
- Sensors for PH, O_2, SO_2, Glucose, etc
- used as electro chromic materials change colour which during electrochemical process of charge and discharge.
- Preparation of ion exchangers, Conductive paints.
- In photovoltaic devices in Al / Polymer / Au device.
- In biomedical applications, telecommunication system, microelectronic devices
- used in smart windows which can change their colours

PANI

Polyaniline (Conducting Polymer) (PANI)

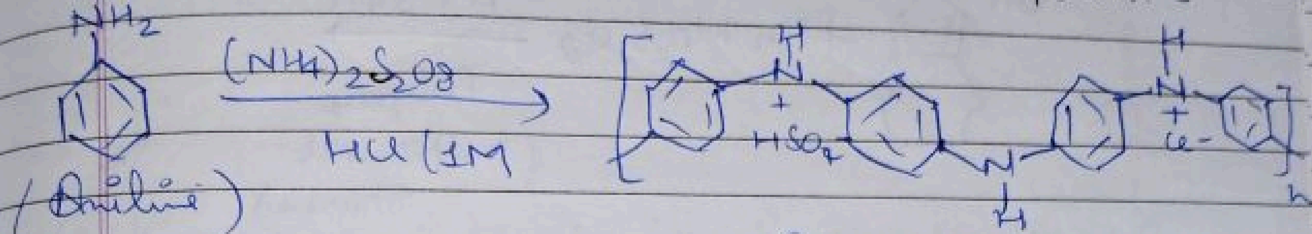
It is a polymer of aniline





Preparation:

★ addition is occuring at para positions



(Aniline)

(Polyaniline)

★ PANI can be prepared by physical or chemical method. It can also be prepared by dissolving Aniline in HCl adding APS (ammonium per sulphate) and stirring for 1 hr.

Benefits:

★ It can be easily synthesized and doped, high environmental stability, biocompatibility and its electrical conductivity can be optimized.

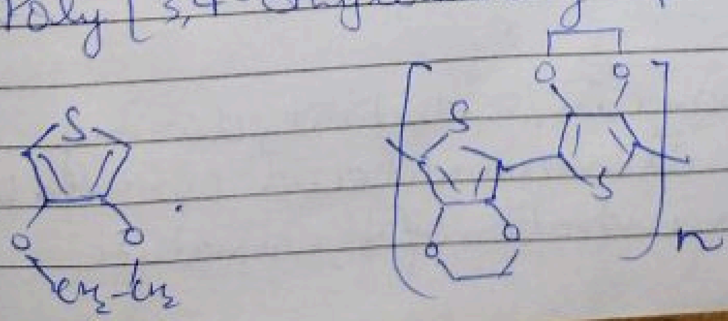
Applications:

★ Chemical vapor sensors due to electrical property.
★ electrochemical sensors with nanomaterials
★ Biological sensors for enzymes
★ Colorimetric sensors for study of bacteria in food, water
★ Ammonia sensors.

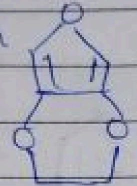
★ chemiresistive sensors
★ Transistor based sensors

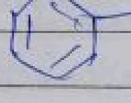
(PEDOT) PEDOT

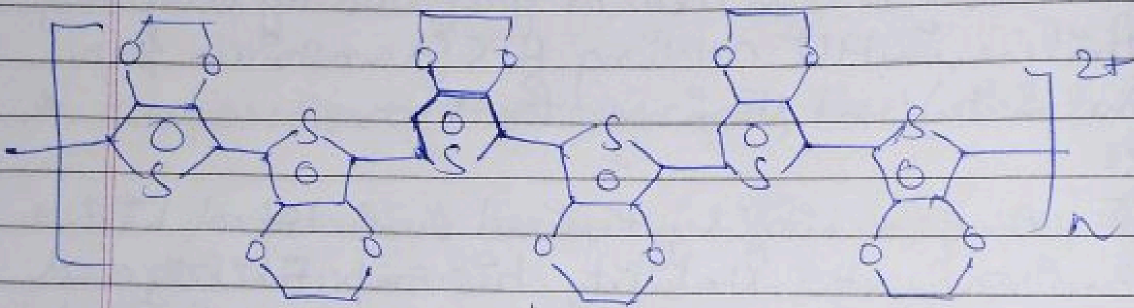
Poly (3,4-ethylenedioxythiophene) Conducting polymer



Preparation:

$6n$  $+ 14n\ Na_2S_2O_8 \xrightarrow{Fe_2(SO_4)_3}$ PSS poly (sulphonated styrene)

 $-CH=CH_2$ (Styrene)



$+ 14n\ SO_4^{2-} + 14n\ Na^+ + 2n\ H^+$

* The monomer EDOT are joined at 2,5-positions of each 5 membered thiophene ring to create linear polymer chains

USES: * Conductometric sensors
* Pressure and strain sensors
* Temperature sensors
* Optical sensors.

1) Chemical Sensors

Conductometric Sensors: change in conductivity during experiment is measured and correlated to the concentration of the analyte

Date ______ Page ______

Electrochemical Sensors: using Redox rxns presence of biomolecules or biopollutants is detected

2) Biosensors

(1) Biomolecule detection: by functionalization of PEDOT with specific biomolecules biosensors can be created.

3) Pressure & Strain Sensors

* Flexible Sensors

* ~~Vari~~ Wearable Sensors

4) Temperature Sensors: change in Temperature affects conductivity. In this way PEDOT can be used as a temperature sensor

Advantages of PEDOT

(1) High Conductivity:

(2) Stability:

(3) Flexibility:

(4) Ease of functionalization:

PMMA :

Date 11/Nov/2024

PMMA: Polymethyl methacrylate (PMMA)

also known as acrylic or plexiglass or lucite.

Preparation: It is synthesis by addition polymerization of methyl methaacrylate in presence of benzoyl peroxide as catalyst.

$$n\,CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-COOCH_3 \xrightarrow[\text{peroxide}]{\text{Benzoyl}} \left(CH_2-\underset{\underset{\displaystyle COOCH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}- \right)_n$$

(methyl methaacrylate) (393K) (Polymethylmethacrylate)

USES OF PMMA:
- ★ furniture
- ★ Scooter toy
- ★ Acrylic trophy
- ★ Display case
- ★ motor lamp
- ★ head lamp
- ★ acrylic roof
- ★ cosmetic box

① Display Technology

- **Transparent Substrates:** It is light weight & Shatter resistant so, alternative to glass in Screen & displays.

- **Optical Coatings:** Such as anti scratch treatments or anti reflective coatings.

② Light Guide Applications

· LED lightings: light transmission properties

③ It can be used as a protective layer for touch sensitive displays.

④ Sensor housing: to encapsulate sensors

⑤ 3D printing and prototyping

· Rapid prototyping: 3D printing for creating prototypes

⑥ Smart home applications

Appliances
· Smart Applications: housings and interfaces of smart appliances.

Advantages of PMMA in Smart devices

★ Lightnings
★ Shatter resistance
★ Chemical Resistance
★ Optical Clarity

Sustainable Polymers: are materials designed to minimi environmental impact throughout their lifecycle, from production to disposal.

Types:

1. **Biodegradable Polymers:** Polylactic acid (PLA)
   Polyhydroxyalkanoates (PHA)

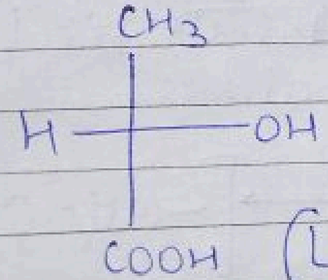
2. **Bio-based polymers:** Bio-polyethylene (bio-PE)
   Bio-polyethylene terephthalate (bio-PET)

3. **Recycled Polymers:** Recycled high density polyethylene (HDPE)

PLA

PLA: polylactic Acid (polymer of lactic acid)

- ☆ PLA is a biodegradable
- ☆ bio-based polymer primarily derived from renewable resources like cornstarch, sugarcane and other plant materials.



(Lactic Acid)

Synthesis of PLA: ① Via lactide

There are 2 main steps:

- ☆ production of lactic acid (or lactide)
- ☆ its polymerization into PLA

Date
Page

S-1: fermentation: production of lactic Acid: it occurs by microbial fermentation of carbohydrates like glucose using bacteria, Lactobacillus.

$$C_6H_{12}O_6 \longrightarrow 2CH_3CH(OH)COOH$$
(glucose) (lactic Acid)

S-2: Formation of Lactide: (Cyclic dimer of lactic Acid) dimer lactide is formed by condensation Rxn

$$2CH_3CH(OH)COOH \xrightarrow{\text{dehydration}} (CH_3CH(OO)_2 + 2H_2O$$
(lactide)

★ Lactide is easier to polymerize.

S-3: Ring opening polymerization: of dimer occurs in presence of catalysts tin (II) Octoate & an initiator like alcohol.

$$n(CH_3CH(OO)_2 \xrightarrow{\text{catalyst}} \left[-CH(CH_3)COO-\right]_n$$
(polylactic acid)

★ This rxn can be controlled to produce low molecular weight & high molecular weight PLA.

2nd Method: Direct Polycondensation: it gives low molecular weight PLA & sometimes incomplete polymerization may result into low quality PLA.

$$n\,CH_3CH(OH)COOH \xrightarrow{\text{dehydration}} [CH(CH_3)COO]_n + nH_2O$$

(Lactic Acid) (PLA)

Properties of PLA

1. Biodegradable (only under high temperature & humidity) (industrial composting conditions).
2. Renewability : it is desired from Renewable plant resource
3. Mechanical Properties : it has high tensile strength but it is brittle & prone to cracking under stress. that's why copolymers like (PCL-polycaprolactone) is mixed.
4. Thermal Properties : Glass transition temperature (55-60°C)
   melting point (150-180°C)
5. Transparent, clear, glass like material
6. Barrier properties : oxygen barrier properties useful in food packaging
7. Biocompatibility : used in biodegradable implants.

Applications :
1. Packaging
2. 3D Printing
3. Medical devices
4. Textiles

Applications of PLA

- **Packaging:** PLA is commonly used in food containers, bottles and packaging films.

- **3D printing:** PLA is one of the most popular filaments for 3D printing due to its ease of use and low toxicity.

- **Medical devices:** PLA is used in biodegradable sutures, stents and scaffolds for tissue engineering.

- **Textiles:** PLA can be used to make fibres for clothing and biodegradable bags.

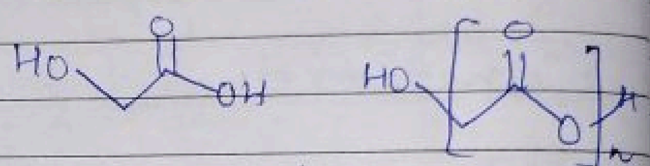
PGA

PGA (PolyGlycolic Acid)

- ★ a biodegradable polymer
- ★ part of polyesters family

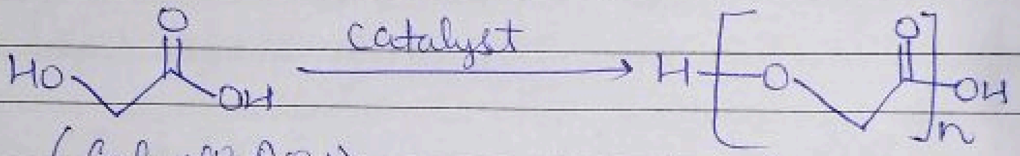
CH_2OH
|
$COOH$ $-H_2O$
(Glycolic Acid)

Glycolic Acid — Polyglycolic Acid



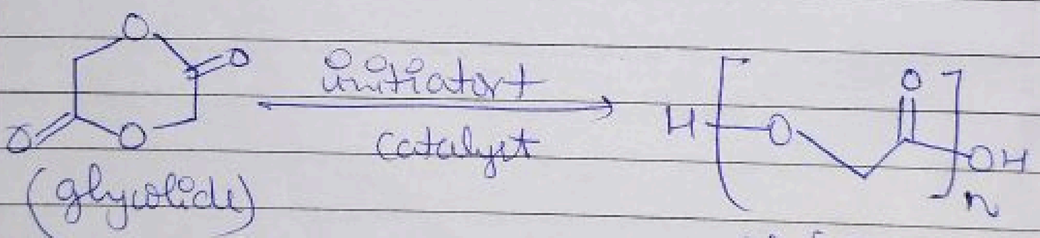
Synthesis: PGA is formed by ring opening polymerization of glycolic Acid (in its cyclic dimer form)

(a)



(Glycolic Acid) — poly(glycolic acid)

(b)



(glycolide) — poly(glycolic acid)

Properties:
- ★ Biodegradability – through hydrolysis
- ★ Mechanical properties – high tensile strength
- ★ Thermal properties – melting temp^r – 225°C

Applications: ① Medical Applications
- → Sutures (biodegradable & biocompatible)
- → Drug delivery Systems (as microspheres for controlled drug release)
- → Tissue engineering (as scaffolding material).

HW: # What do you know about microplastics?
Study about microplastics

(2) Environmental Applications

→ In Biodegradable packaging
→ Agricultural films

(3) Biomedical devices

→ Implants
→ Wound dressings

PHBV :-

(PHBV): Poly(3 hydroxybutyrate-co-3-hydroxyvalerate)

* is a biopolymer
* belonging to the family of polyhydroxyalkanoates
* it is a thermoplast

Synthesis: It is obtained by the copolymerization of 3 hydroxybutanoic acid and 3 hydroxy pentanoic acid

$$n\,(HO-\overset{\beta}{CH}(CH_3)-\overset{\alpha}{CH_2}-COOH) + n\,(HO-\overset{\beta}{CH}(CH_2-CH_3)-\overset{\alpha}{CH_2}-COOH)$$

$$\xrightarrow{-H_2O} \left[-O-CH(CH_3)-CH_2-\underset{O}{\underset{\|}{C}}-O-CH(CH_2-CH_3)-CH_2-\overset{O}{\overset{\|}{C}}-\right]_n$$

Properties: (1) Mechanical properties: high tensile strength and elasticity which depends upon the ratio of monomers

(2) Biodegradability: easy to biodegrade

T_g: 5°C and T_m: 170°C

(3) Thermal properties: Thermal Stability So it can be easily processing.

(4) Barrier properties: good gas barrier properties, used for packaging.

Applications:
1. Packaging
2. Sutures and Scaffolds
3. Drug delivery Systems
4. Agriculture
5. 3D printing
6. Textiles