CHEMISTRY

89th & 90th Class, 12-01-2022

Dr. K. Ananthanarayanan
Associate Professor (Research)
Department of Chemistry
Room No 319, 3rd Floor, Raman Research Park

Email : ananthak@srmist.edu.in
Phone : 9840154665

Last class…

- ❑ Synthesis, properties and applications of

- ➢ Polyurethane

- ➢ Synthetic rubber

Last class…

❑ Synthesis, properties and applications of

➢ Conducting polymers

College of Engineering and Technology

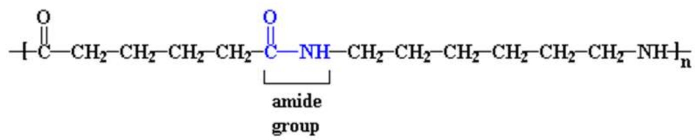
M.Tech (Integrated) - I Semester (All Programmes)

Schedule for Cycle Test-III - Revised

Day	Date	Session Batch 1	Course code	Name of the course
Wednesday	19.1.2022	8:00 AM to 9.40 AM	21CYB101J	Chemistry
Thursday	20.1.2022	8:00 AM to 9.40 AM	21MAB101T	Calculus and Linear Algebra
Friday	21.1.2022	8:00 AM to 9.40 AM	21LEH10XJ	Foreign Language
Saturday	22.1.2022	8:00 AM to 9.40 AM	21CSS101J	Programming for Problem Solving
Monday	24.1.2022	8:00 AM to 9.40 AM	21BTB101T	Applied Biology
Tuesday	25.1.2022	8:00 AM to 9.40 AM	21GNH101J	Philosophy of Engineering

Polyamides - Nylon

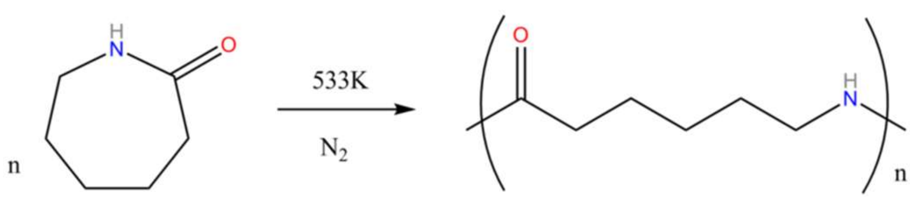
- Nylons are also called polyamides, because of the characteristic amide groups in the backbone chain
- These amide groups are very polar, and can hydrogen bond with each other.



- Due to this and also because the nylon backbone is so regular and symmetrical, nylons are often crystalline, and make very good fibers.

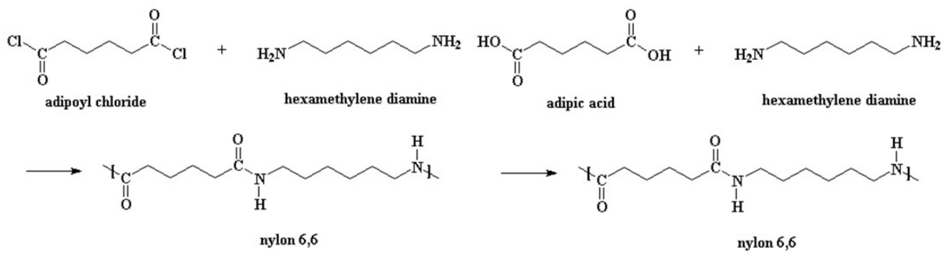
Nylon synthesis

- General nylon 6 has one kind of carbon chain, which is six atoms long.
- It's made by a ring opening polymerization from the monomer caprolactam



Nylon synthesis

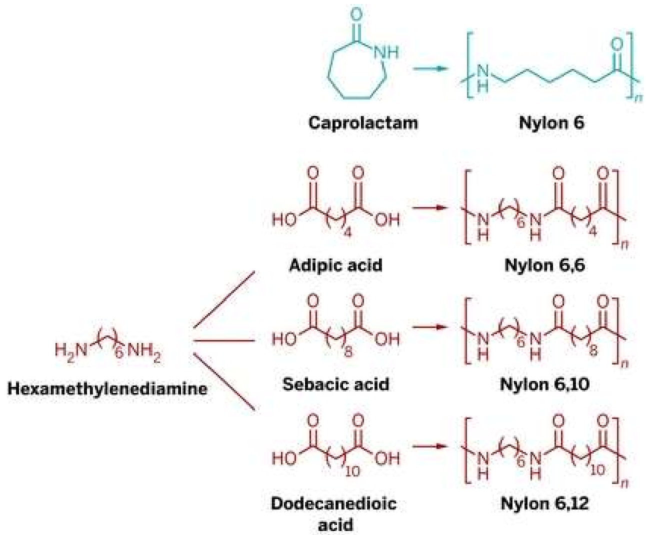
- Nylon 66 can be made from diacid chlorides and diamines. It is made from the monomers adipoyl chloride and hexamethylene diamine.
- In industrial plant, it's usually made by reacting adipic acid with hexamethylene diamine



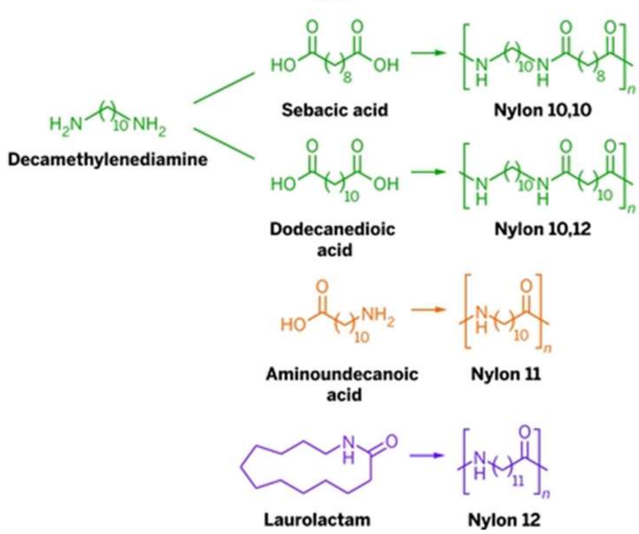
Nylon 66 synthesis

- Nylon 66 is synthesized by polycondensation of hexamethylenediamine and adipic acid.
- Equivalent amounts of hexamethylenediamine and adipic acid are combined with water in a reactor.
- This is crystallized to make nylon salt, an ammonium/carboxylate mixture.
- The nylon salt goes into a reaction vessel where polymerization process takes place either in batches or continuously.
- Removing water drives the reaction toward polymerization through the formation of amide bonds from the acid and amine functions.
- Thus molten nylon 66 is formed. It can either be extruded and granulated at this point or directly spun into fibers by extrusion.

Types of polyamide nylons



Types of polyamide nylons



Types of polyamide nylons

- **Nylon 6** was developed in an attempt to reproduce the properties of nylon 66. This grade of nylon is very tough and has high tensile strength.
- **Nylon 66** is similar to Nylon 6 but has a higher melting point and is more resistant to acids. It is made from two monomers, while Nylon 6 is made from only one.
- **Nylon 11** has increased resistance to dimensional changes due to moisture absorption. This is due in part to the lower concentration of amides. it has less mechanical properties that other nylons

Types of polyamide nylons

- **Nylon 12** has the lowest melting point of the main polyamides. It is typically used as a flexible film or sheet to cover food and pharmaceuticals & has relatively good resistance to water absorption.
- **Nylon 46** was primarily developed to have a higher operating temperature than other grades of nylon.

General properties of nylons

- **High Abrasion Resistance** – Higher levels of resistance to wear by mechanical action
- **Good Thermal Resistance** – Special grades of nylon can have a melting point of almost 300°C
- **Good Fatigue Resistance** – This makes it ideal for components in constant cyclic motion like gears
- **High Machineability** – can be machined into various components that would be too costly to cast into intricate shapes
- **Noise Dampening** – Nylon is a very effective noise dampener

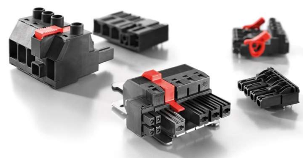
General properties of nylons

- The different types give a wide range of properties with **specific gravity, melting point and moisture content tending to reduce as the nylon number increases.**
- Nylons **tend to absorb moisture** from their surroundings.
- The extent of moisture content is dependent on temperature, crystallinity and part thickness.
- **Preconditioning can be adopted** to prevent negative effects of moisture absorption during service.
- Nylons tend to provide good resistance to most chemicals, however **can be attacked by strong acids, alcohol's and alkalis**.

Nylon applications

- **AUTOMOTIVE**
  - Door Handles & Radiator Grills
  - Engine covers and many parts

- **ELECTRICAL**
  - Low Voltage Switch Gears
  - miniature circuit breakers,
  - fuses, switches and relays,



- **GENERAL**
  - Nyon rope (high tough ship holders to dresses)
  - roller blade Ski Bindings & In-line Skates

15

Polyurethanes

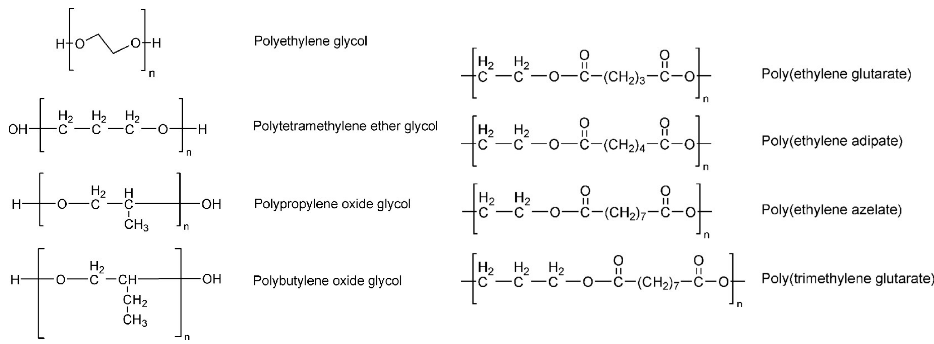
- The polymeric materials known as polyurethanes form a family of polymers which are essentially different from most other plastics in that there is no urethane monomer.

- Polyurethane is more commonly known for liquid coatings and paints, but applications can also vary from soft, flexible foams to rigid insulation.

16

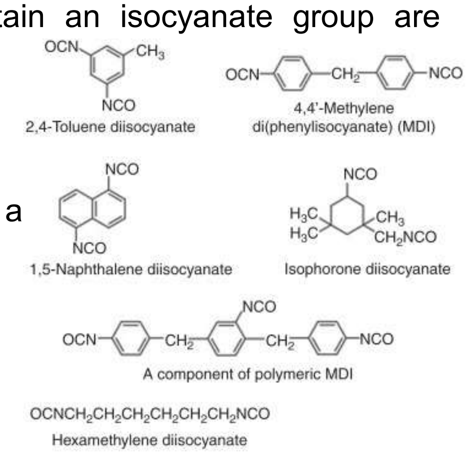
Polyols

- A polyol is an organic compound containing multiple hydroxyl (HO-) groups
- Major types : polyether polyols & polyester polyols



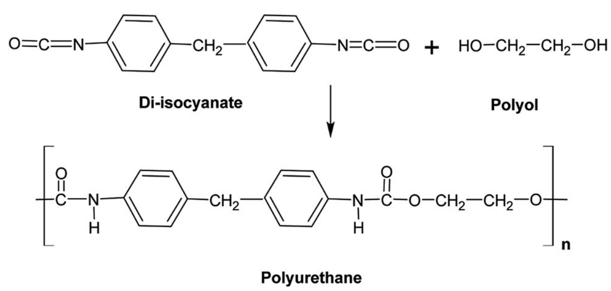
Isocyanates

- Isocyanate is the functional group with the formula R−N=C=O. Organic compounds that contain an isocyanate group are referred to as isocyanates.
- An organic compound with two isocyanate groups is known as a diisocyanate



Polyurethanes synthesis

- Polyurethanes are made by the exothermic reactions between alcohols with two or more reactive hydroxyl (-OH) groups per molecule (diols, triols, polyols) and isocyanates that have more than one reactive isocyanate group (-NCO) per molecule (diisocyanates, polyisocyanates).



19

Types of polyurethanes

POLYURETHANES

Thermoplastic PU	Flexible PU	Rigid PU	PUI	Water-borne PU
Examples: Keyboard protector for laptop, outer cases of mobile electronic devices, automotive instrument panels, caster wheels, power tools, sporting goods, medical devices, drive belts, footwear, inflatable rafts, and a variety of extruded film, sheet and profile applications.	Examples: Cushion materials, carpet underlays, furniture, bedding, automotive interior parts, packaging, biomedicine and nanocomposites	Examples: Thermal and sound insulators	Examples: Artificial hearts, connector tubing for heart pacemakers and haemodialysis tubes	Examples: Coatings, adhesives, sealants, binders

20

Properties of Polyurethanes

- **Wide Range of Hardness** - can be made from 20 shore A to 85 shore D
- **High Load Bearing Capacity** - has a high load capacity in both tension and compression. It may change in shape under a heavy load, but will return to its original shape once the load is removed
- **Flexibility** - Polyurethanes perform very well when used in high flex fatigue applications and has very good elongation and recovery properties.
- **Abrasion & Impact Resistance –** good resistance at low temperatures.
- **Tear Resistance** - possess high tear resistance along with high tensile properties.

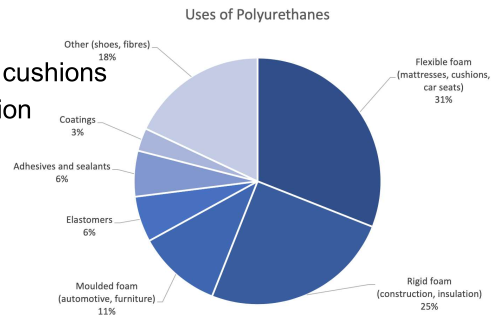
Properties of Polyurethanes

- **Resistance to Water, Oil & Grease** – properties will remain stable (with minimal swelling) in water, oil and grease.
- **Electrical Properties** - exhibit good electrical insulating properties.
- **Strong Bonding Properties** - bonds to a wide range of materials including other plastics, metals and wood.
- **Performance in Harsh Environments** - resistant to extreme temperature, meaning harsh environmental conditions and many chemicals rarely cause material degradation.
- **Economical Manufacturing Process**
- **Short Production Lead Times**

Polyurethanes applications

- **Foams**
  - Flexible – mattress, car seats , cushions
  - Rigid –construction and insulation
- **Moulded products**
  - Automotive

- **Elastomers**
  - Moulded casted rubber parts
- **Coatings**



23

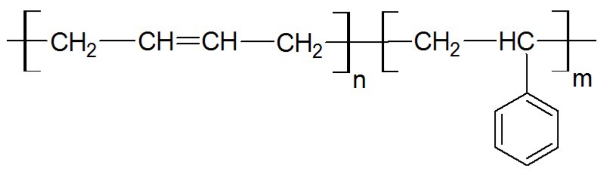
Synthetic rubber

- Rubber is a broad term used to refer to many types of different polymers, simply called the types of rubber that are all elastomers.
- Being elastomers mean they can be stretched out and will return to their original shape.
- Natural rubber is the first kind of rubber, it is still used in different forms.
- Other than natural rubber, all the other types of rubber are synthetic or man made.
- Examples of synthetic rubber types - Polychloroprene (generally sold by the trade name Neoprene); Polybutadiene; Poly(styrene-butadiene-styrene) rubber or SBS rubber; Polyisobutylene; Silicone among others.

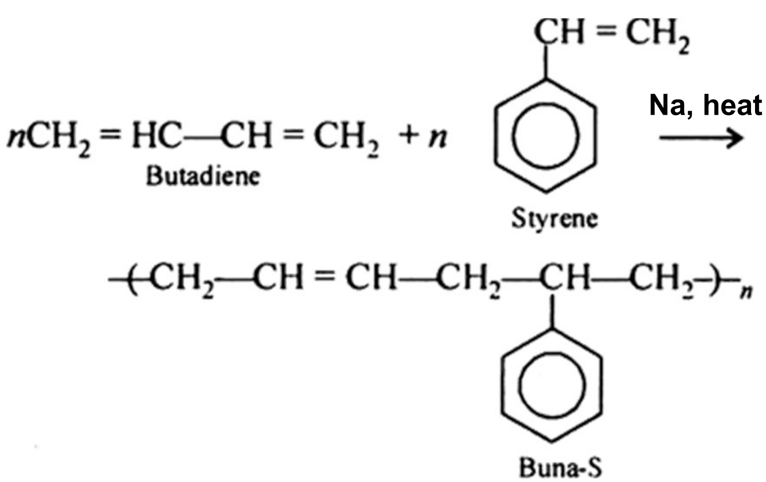
24

Types of Synthetic rubber

- **Styrene Butadiene Rubber (SBR) -** The outcome of synthetic rubber research under the impact of the shortage of natural rubber.
- The addition of styrene improves the strength and abrasion resistance, reduces the price

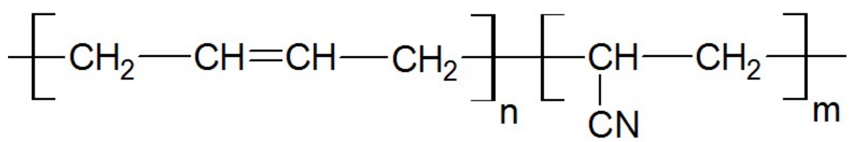


Synthesis, SBR



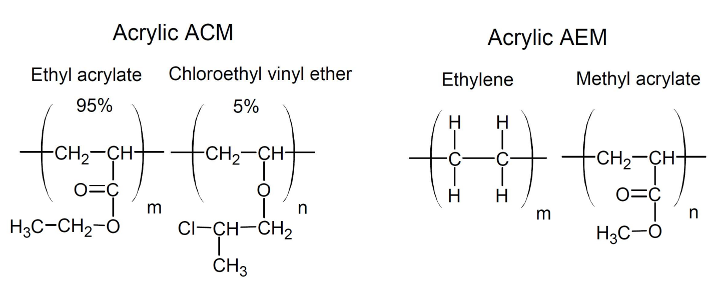
Types of Synthetic rubber

- **Nitrile Rubber (NBR) –** A synthetic rubber produced by polymerization of acrylonitrile with butadiene.
- This type of synthetic rubber is widely used as disposable non-latex gloves, automotive transmission belts, hoses, O-rings, gaskets, oil seals, V belts.



Types of Synthetic rubber

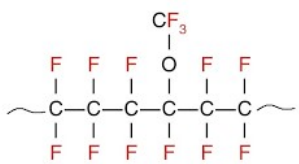
- **Acrylic rubber** - Synthetic rubber containing acrylonitrile, resistance to hot oil and to oxidation is good but poor resistance to water or moisture. Suitable for continuous use at temperatures up to 150 to 180^oC



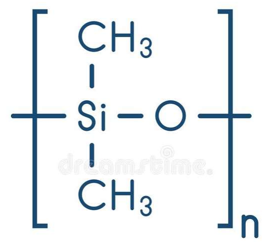
Types of Synthetic rubber

- **Perfluoroelastomer (FFKM)** - Perfluoroelastomers are a type of synthetic rubber having even greater heat and chemical resistance than the fluoroelastomers. It is widely used as seals on semiconductor wafer processing equipment.

FFKM



- **Silicone Rubber (SiR) -** is its higher heat resistance. The next good thing is chemical stability that helps it by providing better electrical insulation.



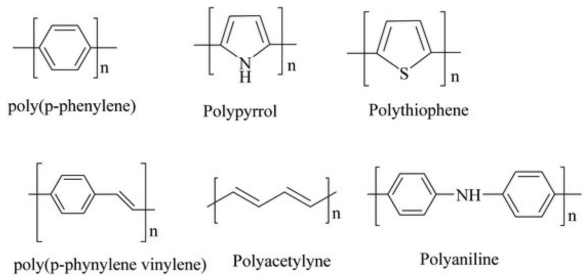
Synthetic rubber applications

- Acrylic Rubber (ACM) - Automotive transmissions and hoses
- Butadiene Rubber (BR) - Automobile tyres
- Butyl Rubber (IIR) - adhesives, fiber optic compounds, ball bladders, O-rings
- Ethylene Propylene Diene Monomer (EPDM) - window and door seals
- Isoprene Rubber (IR) – tires, adhesives and specialty elastomers.
- Nitrile Rubber (NBR) - fuel hoses, gaskets, rollers
- Perfluoroelastomer (FFKM) - Chemical processing, oil, Gas tubes & aerospace
- Polychloroprene (CR)/ Neoprene - gaskets, tubing, seals, tire-sidewalls
- Silicone Rubber (SiR) - insulating tape, medical tubing, adhesives, & defoamers.
- Styrene Butadiene Rubber (SBR) - car tyres, shoe soles and heels

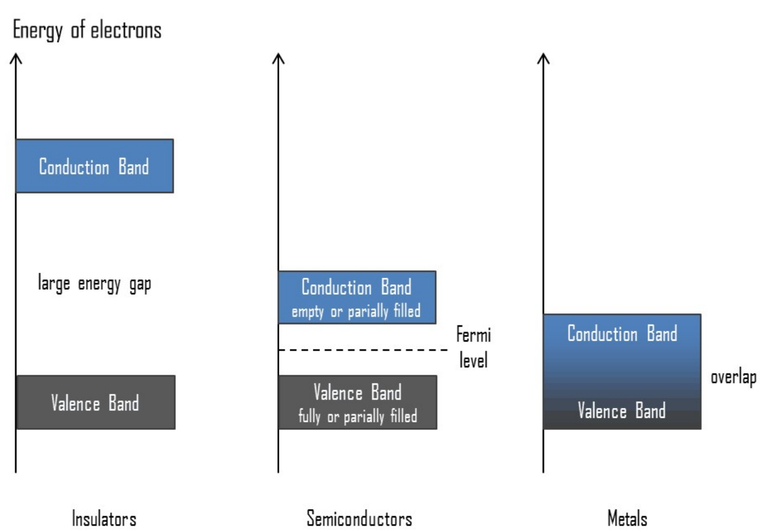
Conducting polymers

Typical conducting polymers

- ❑ polyacetylene (PA)
- ❑ polyaniline (PANI)
- ❑ polypyrrole (PPy)
- ❑ polythiophene (PTH)
- ❑ poly(para-phenylene) (PPP)
- ❑ poly(phenylenevinylene) (PPV)



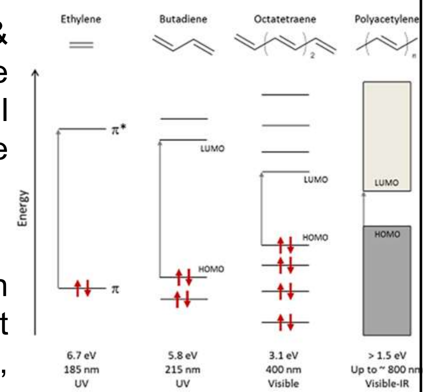
Band diagram



Frontier orbitals

- Filled orbitals ends with HOMO & the unfilled ones starts with the LUMO- critical role in the optical and electrical processes of the molecule.

- The large resonance interaction involved, σ and σ* orbitals are at fairly low and high energies, rendering charge injection from electrodes into molecular solids very difficult.



Frontier orbitals

- When the frontier orbitals are σ-orbitals, the σ→σ* transition is in the ultraviolet spectral range, while the lower splitting associated with π-orbitals implies π→π* transitions can take place in the visible spectral range.

- Weaker splitting of π and π*-orbitals compared to σ and σ* orbitals that results in favorable energy levels and that thus renders a molecule suitable for organic semiconductor applications.

- Absorption of light takes place by promoting an electron from the HOMO to the LUMO

Doping of conductive polymers

- ❑ As synthesized conductive polymers exhibit very low conductivities.
- ❑ It is not until an electron is removed from the valence band (p-doping) or added to the conduction band (n-doping, which is far less common) does a conducting polymer become highly conductive.
- ❑ Doping (p or n) generates charge carriers which move in an electric field. Positive charges (holes) and negative charges (electrons) move to opposite electrodes.
- ❑ This movement of charge is what is actually responsible for electrical conductivity. Doping is performed at much higher levels (20–40%) in conducting polymers than in semiconductors (<1%).

Doping of conductive polymers

Doping may be of two types:

- ❑ P-Doping for increasing positive charge(Holes)
- ❑ N-Doping for increasing negative charge(electrons)

❑ **p-Doping**

- It is done by oxidation process. In this process, the conducting polymer is treated with a Lewis acid.

$$\underset{\text{Polyacetylene}}{(CH)_x} + \underset{\text{Lewis acid}}{A} \rightleftharpoons \underset{p\text{-Doped polyacetylene}}{(CH)_x^+ A^-}$$

- p-type dopants are oxidizing agents capable of removing electrons from the valence band to create a positive charge on the polymer backbone.
- Oxidizing agents = I_2, Cl_2, AsF_5, BF_6, $LiClO_4$, $FeCl_3$ etc.

Doping of conductive polymers

- **n-Doping**
  - It is done by reduction process. In this process, the conducting polymer is treated with a Lewis base.
  - n-type dopants are reducing agents which donates electrons to the conduction band and make the polymer negatively charged.

$$\underset{\text{Polyacetylene}}{(CH)_x} + \underset{\text{Lewis base}}{B} \rightleftharpoons \underset{\text{n-Doped polyacetylene}}{(CH)^-_x B^+}$$

  - Reducing agents = Na, K, Li etc.

37

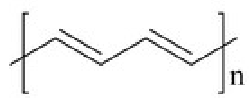
Doping of conductive polymers

- Advantages of doping in conducting polymers :
  - Conductivity improvement
  - Ability to store a charge.
  - Ability to undergo ion exchange.
  - They can absorb visible light to give colored products.
  - They are transparent to X-rays.

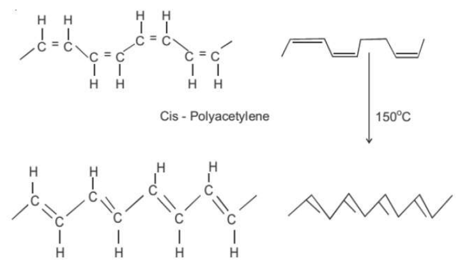
38

Polyacetylene (PA)

- Poly(acetylene) - first conducting polymer & a simple conjugated polymer.
- In its linear form it precipitates as a black, air sensitive, infusible and intractable powder out of solution
- It exists in two isomeric forms
  - cis-polyacetylene
  - trans-polyacetylene.



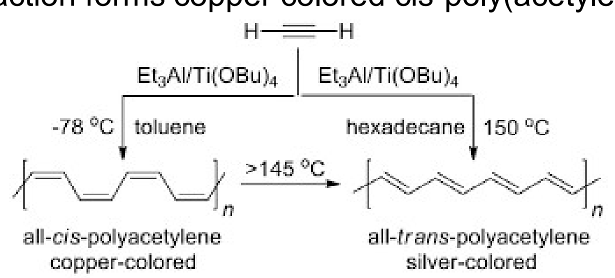
Polyacetylyne



Trans-polyacetylene

Polyacetylene (PA) synthesis

- Shirakawa, prepared poly(acetylene) by passing acetylene gas over the Zeigler-Natta catalyst.
- Z-N catalyst - coordination complex of tetra butoxy titanium, $[Ti(OBu)_4]$, an organo metallic compound and triethyl aluminium, $[Et_3Al]$.
- The reaction forms copper colored cis-poly(acetylene),



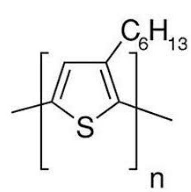
Polyacetylene (PA) properties

- PA having conductivity in the range 10^{-8}-10^{-7} S/cm, at low temperature (-78^oC).
- At higher temperatures (150^oC), more stable silver colored trans-poly(acetylene), having conductivity in the range 10^{-3}-10^{-2} S/cm is formed.
- Cis-poly(acetylene) can be converted to trans-poly(acetylene) by heating it at 150^oC for few minutes.
- Disubstituted polyacetylene has a strong thermal decomposition resistance and an efficient emission of blue light, making it a good candidate for a polymeric chemosensor.

41

Poly(3-hexylthiophene) (P3HT)

- Poly(3-hexylthiophene) (P3HT) belongs to this semiconductor family and is one of the most common hole conductors investigated for Organic solar cells
- Polythiophenes (P3HTs) exhibit a unique combination of high environmental/thermal stability, electrical conductivity, processability,
- It has the most synthetic versatility, which allows a wide range of properties to be accessed through facile ring modifications.

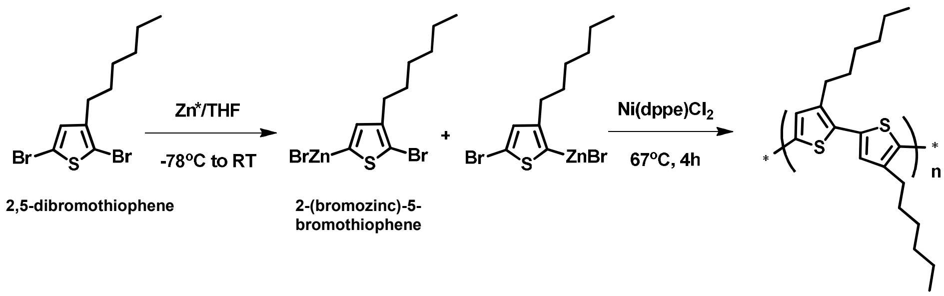


42

Synthesis scheme of organic semiconductors

❑ Synthesis of Poly(3-hexylthiophene) (P3HT)

Rieke Method



Applications of conducting polymers

Conducting polymers are widely used :

- ❑ In rechargeable batteries.
- ❑ In making analytical sensors for pH, O_2, SO_2, NH_3, glucose etc.
- ❑ In the preparation of ion exchangers.
- ❑ In controlled release of drugs.
- ❑ In optical filters.
- ❑ In photovoltaic devices.
- ❑ In telecommunication systems.
- ❑ In micro-electronic devices.
- ❑ In bio-medical applications.

Syllabus overview

Total FIVE chapters

- ❑ Inorganic chemistry
- ❑ Physical chemistry
- ❑ Organic chemistry
- ❑ Polymers
- ❑ Advanced engineering materials

Inorganic chemistry

- ❑ Coordination complexes, introduction
- ❑ Crystal field theory : different complexes, low and high spin, magnetism and optical properties
- ❑ Periodic properties : Slater's rule, electronic configurations
- ❑ Variation in periods and groups : Size, electronegativity, ionisation energy & electron affinity

Physical chemistry

- Thermodynamics : U, Q, W, T, H, S, ΔG, Gibbs-Helmholtz equation
- Electrochemistry : Nernst equation, Applications
- Corrosion : Types, Pourbaix diagram
- Chemical equilibrium and solubility product

Organic chemistry

- Isomerism : Structural, Configurational and Conformational
- Absolute configuration : CIP rules (naming enantiomers)
- Conformational analysis
- Reactions : Substitution, Elimination, Oxidation, Reduction, Addition, Cyclisation and C-C bond formation reactions
- Synthesis of pharmaceutical products, few examples

Advanced engineering materials

- ❑ Mechanical properties of solid – stress-strain relationship
- ❑ Tensile strength, Hardness, Fatigue, Impact strength, Creep
- ❑ Composite materials - introduction and types (FRC, MMC, CMC) – Applications
- ❑ Surface characterisation techniques - XRD and XPS

Polymers

- ❑ Introduction to concept of macromolecules - Classification of Polymers
- ❑ Types of Polymerization - Important addition and condensation polymers
- ❑ Synthesis and properties – Polypropylene, polystyrene, PVC, Teflon, Nylon, PET, Polyurethane and Synthetic rubber
- ❑ Conducting polymers – introduction, types

List of experiments

- Determination of the amount of sodium carbonate and sodium hydroxide in a mixture by titration.
- Estimation of amount of chloride content of a water sample.
- Determination of hardness (Ca^{2+}) of water using EDTA – complexometric method
- Determination of strength of an acid using pH meter.
- Determination of strength of an acid by conductometry.
- Determination of the strength of a mixture of acetic acid and hydrochloric acid by conductometry.
- Determination of ferrous ion using potassium dichromate by potentiometric titration.
- Determination of molecular weight of polymer by viscosity average method.

Thank you all for your attention

Information presented here were collected from various sources – textbooks, articles, manuscripts, internet and newsletters. All the researchers and authors of the above mentioned sources are greatly acknowledged.