CHEM3020: POLYMER CHEMISTRY

Unit-5: Preparation, structure, properties and application of polymers

Polyethylene, polystyrene and styrene copolymers

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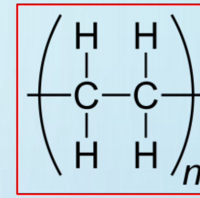
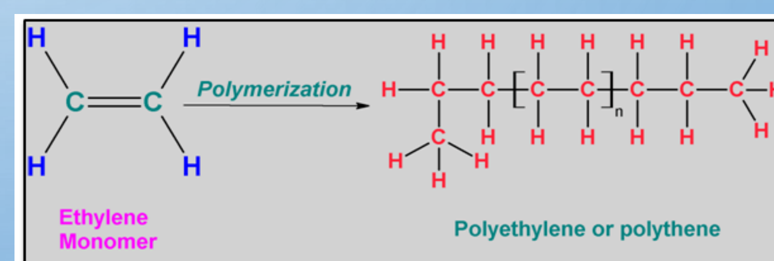


Polyethylene: The first commercial ethylene polymer was branched polyethylene commonly designated as Low density polyethylene.

Polyethylene was first prepared using ethylene under 1400 atm pressure at 170^0 C. Ethylene is made from the thermal and catalytic cracking of different hydrocarbons ranging from ethane obtained from natural gas to fuel oil. Presence of traces of oxygen initiate the polymerization process of ethylene readily. Rapid exothermic reaction can occur, and violent explosion have take place. Impurities present in the monomer, such as hydrogen and acetylene, may act as chain transfer agents and yield low molecular weight polyethylene. To obtained high molecular weight polymeric product, the imputiies must be carefully removed. Besides oxygen, peroxides, hydroperoxides and azo compounds can also be used as initiators for the polymerization process.

Manufacturing: The manufacture of polyethylene follows addition polymerization kinetics involving catalysis of purified ethylene. Its melting point is 85–110^{o}C. Under high pressure process, the density of polyethylene is 0.91-0.93 , whereas under low pressure the density is 0.96.



There are three ways by which polyethylene is manufactured –

a. **High Pressure Process** : In this process, peroxide is used as a catalyst at 100-300^oC and produces low density randomly oriented polymer of low melting point. The process is carried out at pressure of 1000–2500 atms. In this process Low Density Polyethylene (LDPE) is obtained.

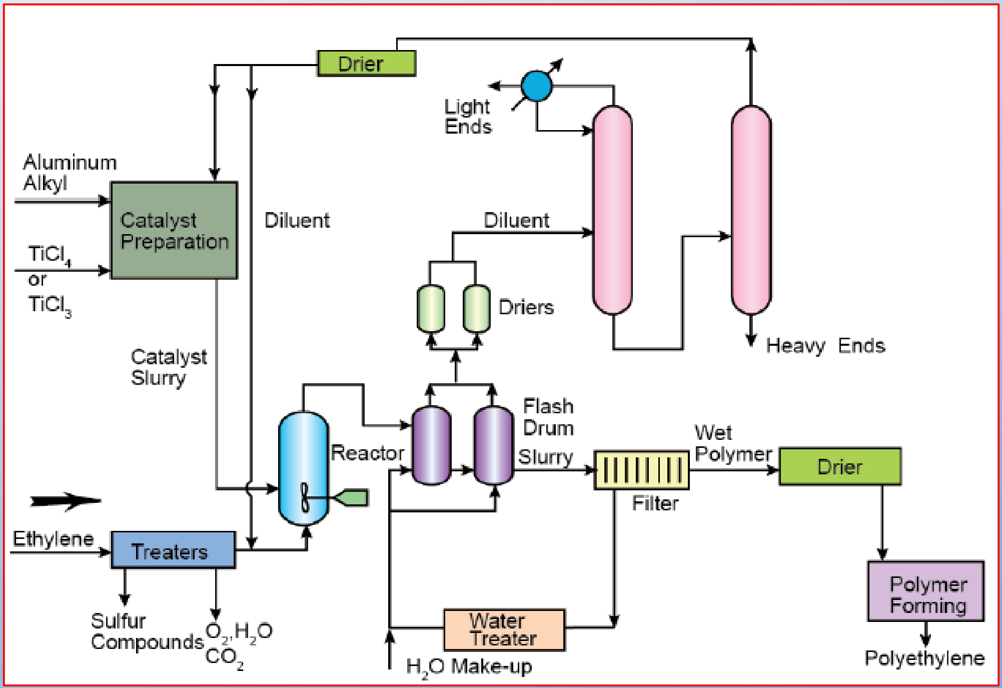
b. **Intermediate Pressure Process:** This process was developed for preparing high density polymer with increased rigidity, crystallinity, tensile strength and softening point. The process uses MoO_3 and Cr_2O_3 on alumina as catalyst and is operated at 30–100 atms.

c. **Low Pressure Process:** This process was also used for preparing high density polyethylene (HDPE). The catalyst used in this process consists of aluminum triethyl activated with heavy metal derivatives such as $TiCl_4$.

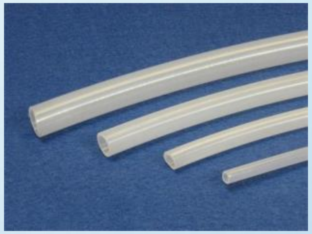
Manufacture of Polyethylene using low pressure technique: In the process flow sheet (Figure in the next slide), is the description of Low Pressure Ziegler Process to produce polyethylene.

Initially, through the process of desulphurization and removal of light impurities were done to high purity ethylene. The ethylene is further treated to remove traces of oxygen and its compounds which can possibly deactivate the catalyst. The ethylene is first pumped into a reactor where it is mixed with catalyst diluents stream. The optimum temperature and pressure maintained should be 70^{o}C and 7 atms gage.

The effluent stream then follows across a series of flash drums in order to remove the solvent from the catalyst. The residual catalyst at this point is removed by adding water. The flashed solvent is thereafter recycled to the catalyst make–up unit after appropriate drying and redistillation. The slurry which results is then centrifuged to remove the water, The final products of polyethylene solids are then dried, extruded and given the required final forms.



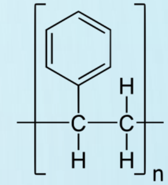
Applications of polyethylene


Low density polythene is chemically inert and tough but flexible and a poor conductor of electricity. Hence, it is used in the insulation of electricity carrying wires and manufacture of squeeze bottles, toys and flexible pipes.

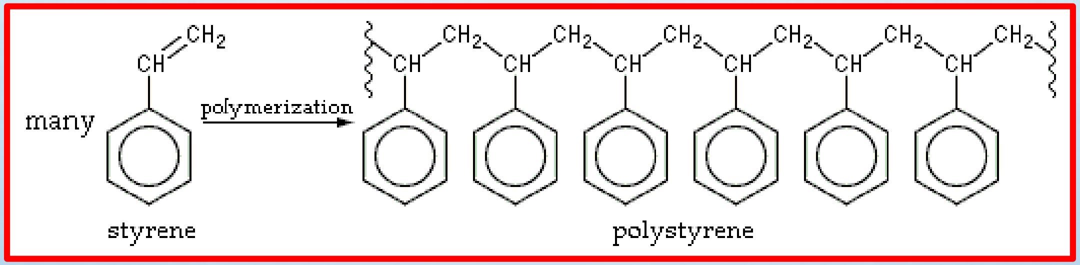

High density polythene (HDP) thus produced, consists of linear molecules and has a high density due to close packing. It is also chemically inert and more tough and hard. It is used for manufacturing buckets, dustbins, bottles, pipes etc.

VLDPEs are used for hose and tubing, ice and frozen food bags, food packaging and stretch wrap as well as impact modifiers when blended with other polymers.



Polystyrene

Polystyrene (**PS**) is a synthetic aromatic hydrocarbon polymer made from the monomer styrene. Polystyrene is a thermoplastic having many desirable properties and it can be solid or foamed. General-purpose polystyrene is transparent, hard, and slightly brittle.



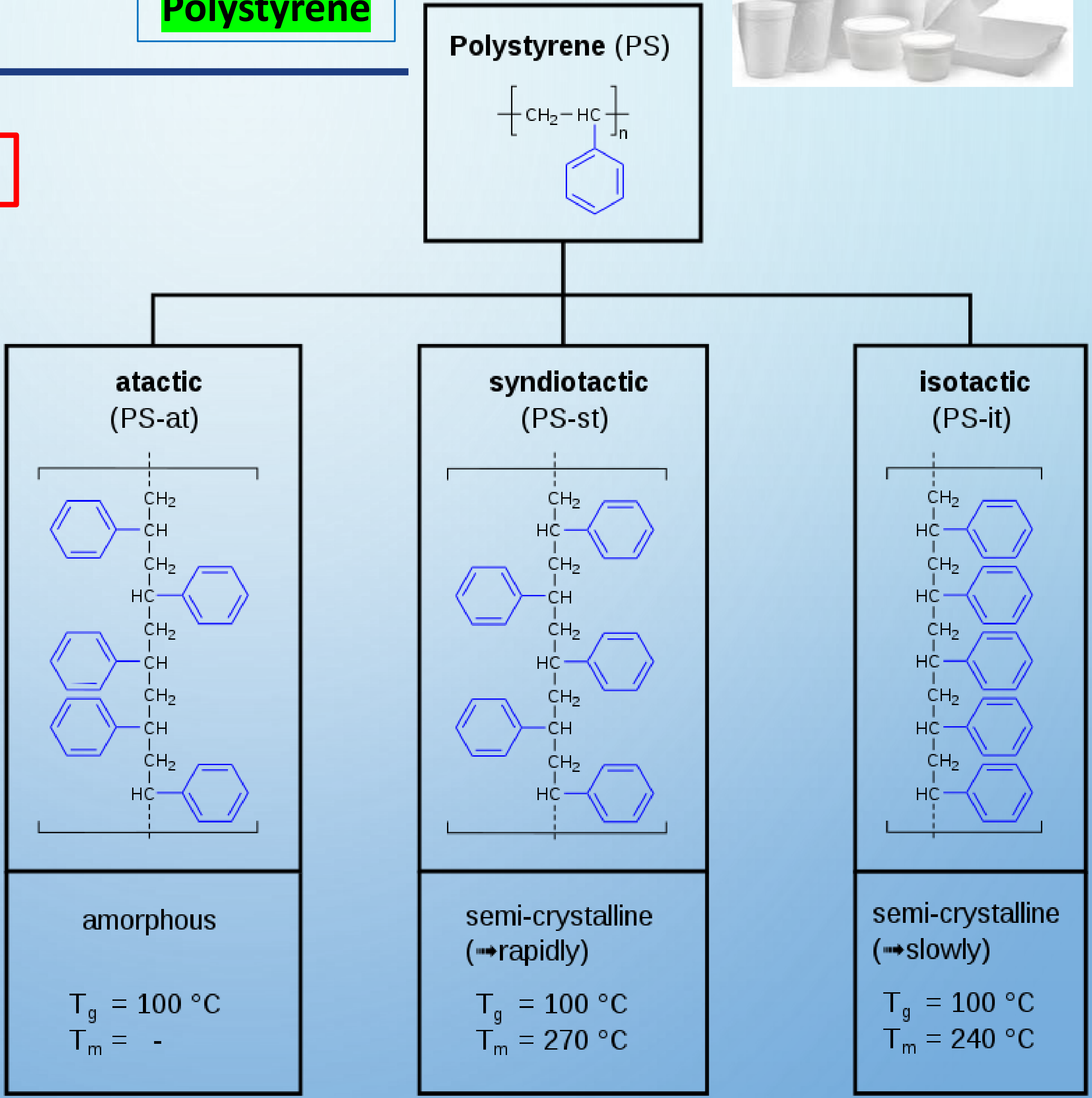
Most polystyrene is prepared either suspension polymerization or by bulk polymerization.

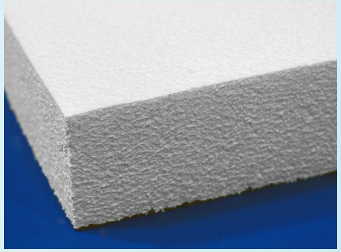
Tacticity(Configuration): Tacticity of polystyrene describes the extent to which the phenyl group is uniformly aligned (arranged at one side) in the polymer chain. Tacticity has a strong effect on the properties of the plastic. Standard polystyrene is atactic. The diastereomer where all of the phenyl groups are on the same side is called *isotactic* polystyrene, which is not produced commercially.

Polystyrene

Configuration of polystyrene:

Depending on the position of the phenyl groups in the hydrocarbon backbone of the polymer, the above three types of configuration is possible in polystyrene.





Polystyrene

Atactic polystyrene: Polystyrene is a linear polymer and **t**he commercially important form of polystyrene is *atactic*, in which the phenyl groups are randomly distributed on both sides of the polymer chain. This random positioning prevents the chains from aligning with sufficient regularity to achieve any crystallinity. The plastic has a glass transition temperature (T_g)of ~90°C. This type of polymerization is initiated with free radicals.

Syndiotactic polystyrene: Ziegler–Natta polymerization can produce an ordered *syndiotactic* polystyrene with the phenyl groups positioned on alternating sides of the hydrocarbon backbone. This form is highly crystalline with a T_m of 270°C (518°F). Syndiotactic polystyrene resin is currently produced using a metallocene catalyst for the polymerization reaction.

Applications: Polystyrene (PS) is used for producing disposable plastic cutlery and dinnerware, CD "jewel" cases, smoke detector housings, license plate frames, plastic model assembly kits, and many other objects where a rigid, economical plastic is desired

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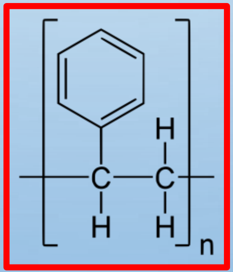
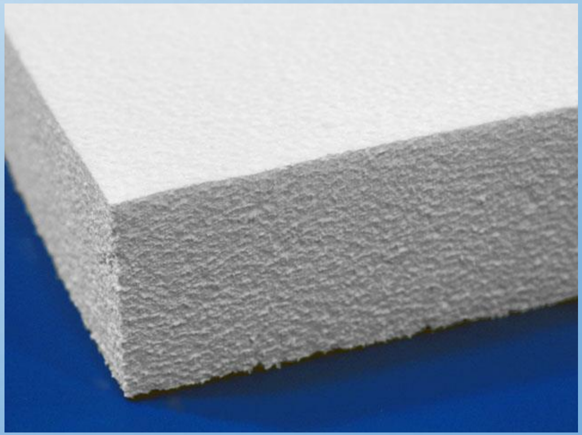
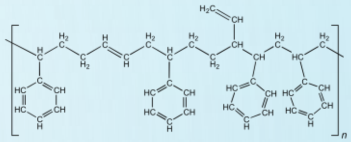


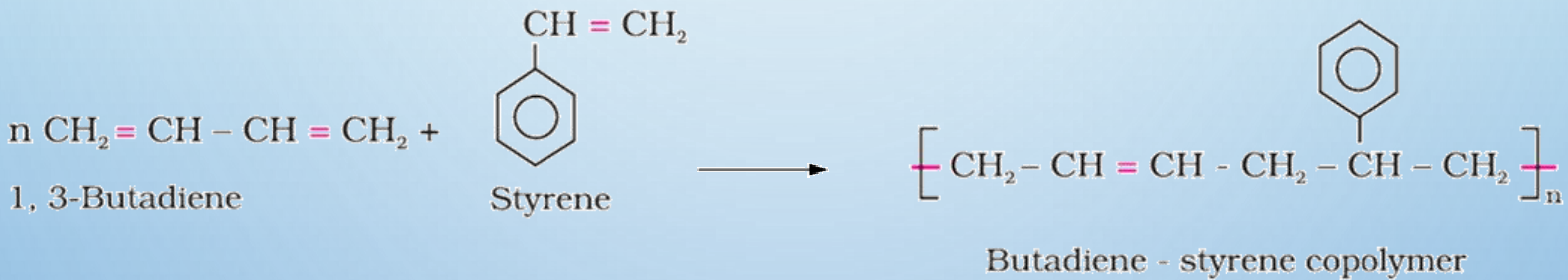




STYRNE BUTADIENE RUBBER

STYRNE BUTADIENE RUBBER (SBR): The styrene-butadiene rubber is prepared by addition polymerization from monomer of butadiene and styrene in presence of an initiator.

SBR is a thermoplastic elastomer which behaves like elastomeric rubbers at room temperature, but when heated, can be processed like plastics.



The material was initially marketed with the brand name **Buna S**.

STYRNE BUTADIENE RUBBER

SBR is derived from two monomers, styrene and butadiene. The mixture of these two monomers is polymerized by two processes: from solution polymerization or as an emulsion polymerization and the latter one is more widely used.

Emulsion polymerization: E-SBR produced by emulsion polymerization is initiated by free radicals. The polymerization is carried out with the two monomers, a free radical initiator potassium persulfate and hydroperoxides, and a chain transfer agent (an alkyl mercaptan) along with emulsifying agents (soaps and detergents). The chain transfer agent is used to control the molecular weight of the copolymer, and hence the viscosity, of the copolymer.

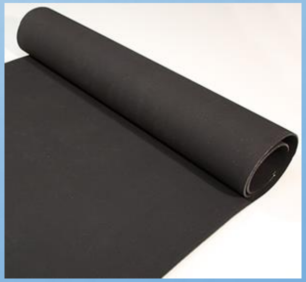
Solution polymerization: Solution-SBR is produced by an anionic polymerization process and is initiated by using alkyl lithium compounds. All the materials are in same phase and homogenous, hence it provides a better control over the process, allowing tailoring of the polymer. The organolithium compound adds to one of the monomers, generating a carbanion that then adds to another monomer, and so on.

STYRNE BUTADIENE RUBBER

SBR prepared by solution polymerization is favored in tire manufacture, due to its improved wet grip and reduced rolling resistance and also in terms of safety and fuel economy.

Applications: E-SBR uses include shoe heels and soles, gaskets, Latex (emulsion). SBR is extensively used in coated papers, being one of the cheapest resins to bind pigmented coatings.

Poly(styrene-butadiene-styrene), or SBS, is a hard **rubber** that's used for things like the soles of shoes, tire treads, and other places where durability is important.



References and suggestions for further reading:

1. Textbook of Polymer Science by Fred W. Billmeyer, Wiley

2. Polymer Chemistry by Charles E Carraher, Jr., Marcel Dekker, Inc.

3. Principle of Polymerization by George Odian, Wiley

THANK YOU