CHEMICAL PROCESS INDUSTRIES

UNIVERSITY OF DIYALA
CHEMICAL ENGINEERING
DEPARTMENT

LECTURE(4)

End Products:

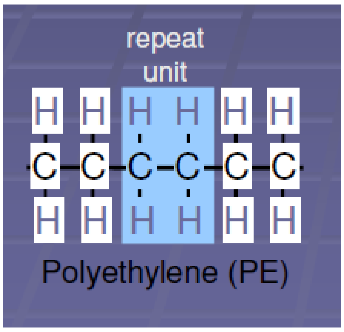
a. Polymers:

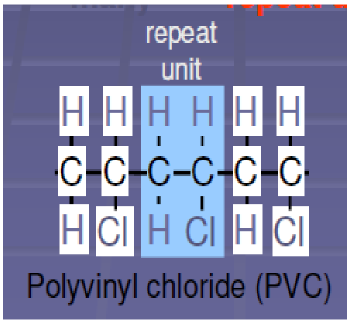
Macromolecule which contains large number of building blocks or molecule joined together.

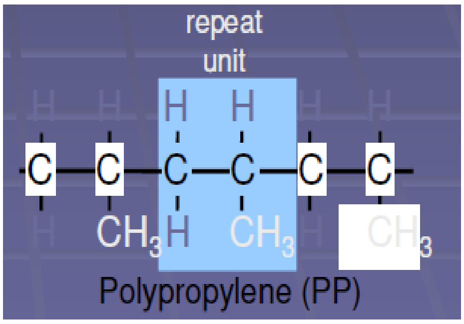
Building units: monomers =or repeating unit.

Homopolymer: polymer formed from same monomer. ex: polyamide, polyester.

Copolymer: polymer formed from more than one monomer. ex :Styrene-BD copolymer.







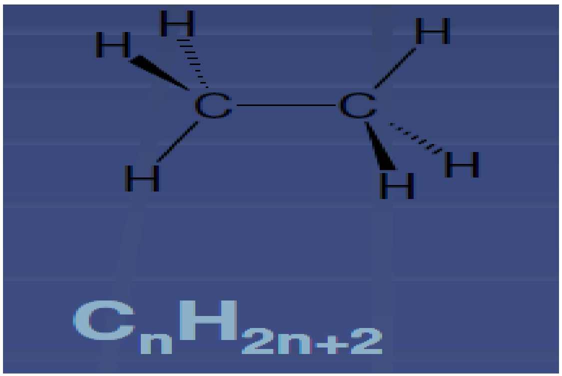
Polymer Composition:

Most polymers are hydrocarbons

– i.e. made up of H and C

_ Saturated hydrocarbons

_ Each carbon bonded to four other atoms

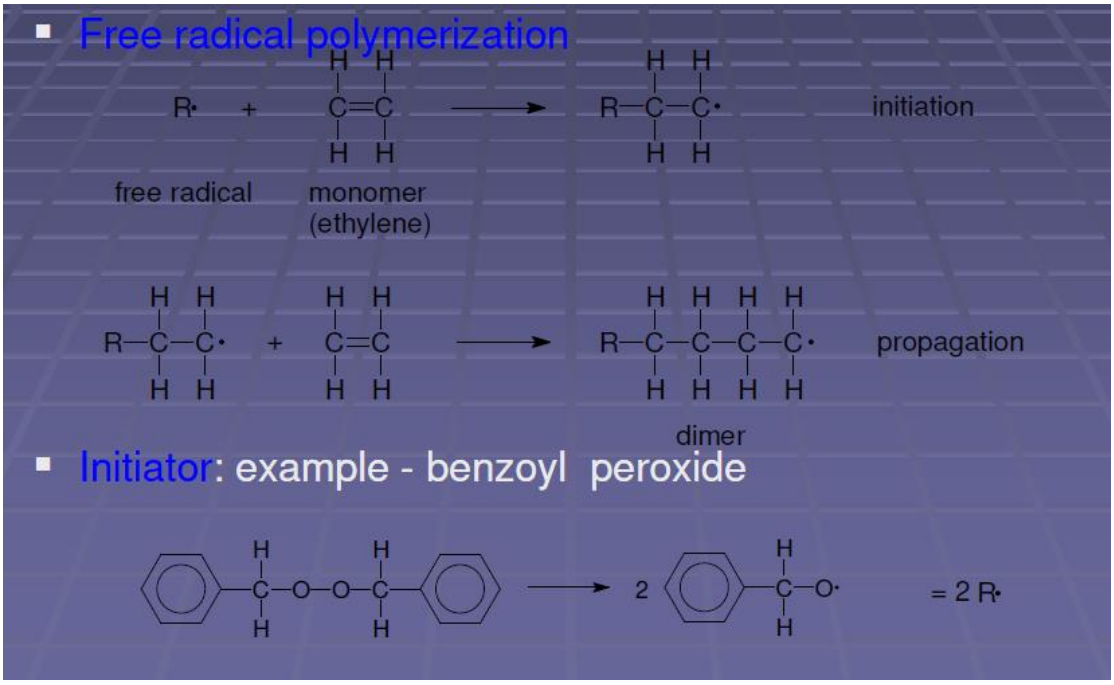


Polymer chemistry

_ In polyethylene (PE) synthesis, the monomer is ethylene

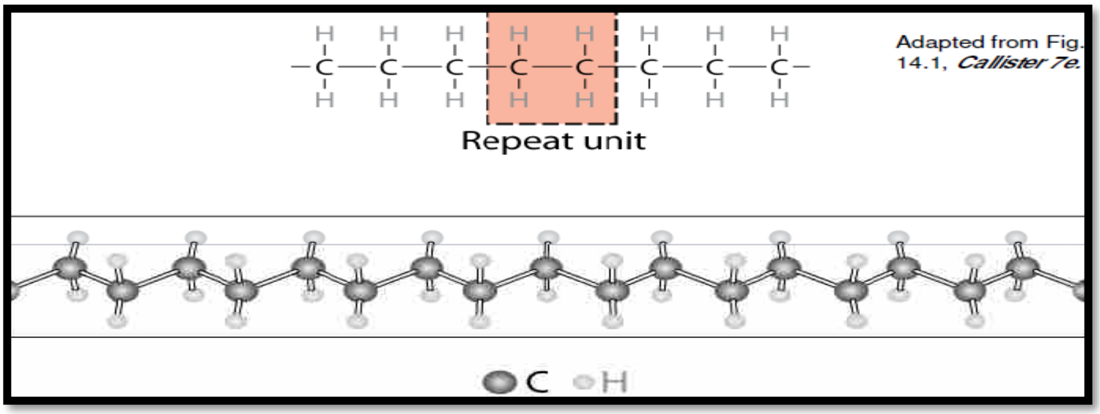
_ Turns out one can use many different monomers

_ Different functional groups/chemical composition – polymers have very different properties



- Free radical polymerization

- Initiator: example - benzoyl peroxide



Adapted from Fig. 14.1, *Callister 7e.*

Note: polyethylene is just a long HC

- paraffin is short polyethylene

Classification of polymer according to type of utilization:

1-Thermoplastic . 2- Thermoset.

3-Elastomer. 4-Fibers 5-Adhesive.

Classification of polymer according to end use:

1-Plastic.

1-Tough substance with H.Mwt.

2-Softening when heated –moulded plastic.

a-Thermoplastic:PE,PP. b-Thermoset:PF,Polyester.

2-Fibers.

1-Low elongation

2- Lighter weight

3-High tensile strength.

4-High resistance to deformation.

5-Low moisture absorption.

6-Highly crystalline due to secondary forces.

3-Elastomers:

1-H.Mwt unsat. HCS.

2-Has long flexible chains.

3-Weak intermolecular forces.

4- Amorphous with certain degree of cross linking
To prevent them from slipping over each other.

Polymer classification according to reaction:

1-Addition polymerization

2-Condensation polymerization

Addition

1-used in preparation of PE,PP,PS.

2-initiated by a-free radical b-cationic ,anionic, cationic .coordination catalyst.

3-reaction occurs by self addition of unsat. molecule .

4-H.Mwt polymer formed at once even at low conversion.

Condensation

1-Produced by reaction between two molecule with elimination of small molecule such as water .

$M+M \rightarrow M\text{-}M$

$M\text{-}OH+M\text{-}COOH \rightarrow M\text{-}M+H_2O$

2-H.Mwt is not observed until the end of polymerization.

3-Long reaction times are needed for high conversion .

4- PF,UF.

5- Insulator (electrical and thermal)

1-Polyethylene:

PE :The most commodity polymers ,and PCs final products(widely used) Why PE is widely used?

1-Easly in producing monomer (E) from NG or petroleum fractions or Naphtha.

2-Low cost 3- PE posses especial properties such as resistance to corrosion and plastering.

Classification of PE;

1-Low density PE **:LDPE**

Density:0.915-0.935 gm/cm3**.**
Mwt=30000-50000.
Branched chain polymer .
Degree of crystallization is low.
Low ability to absorb water.
High resistance to chemicals(acids and bases)
Resistances to impact and electricity thus it is used in insulating.

2-High density PE **:HDPE**

a-Density=0.95-0.96gm/cm$_3$.
b- Linear polymer(no branches).
c-Highly crystalline.
d-Highly packed molecule, less permeable to gases.

3-Linear low density :**LLDPE**

It posses good physical and mechanical properties

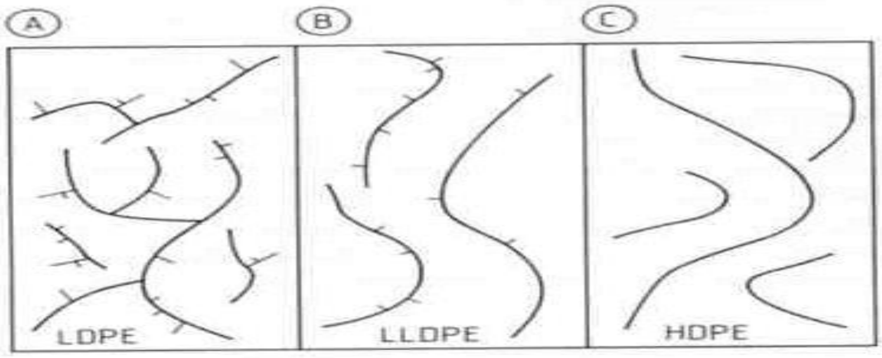
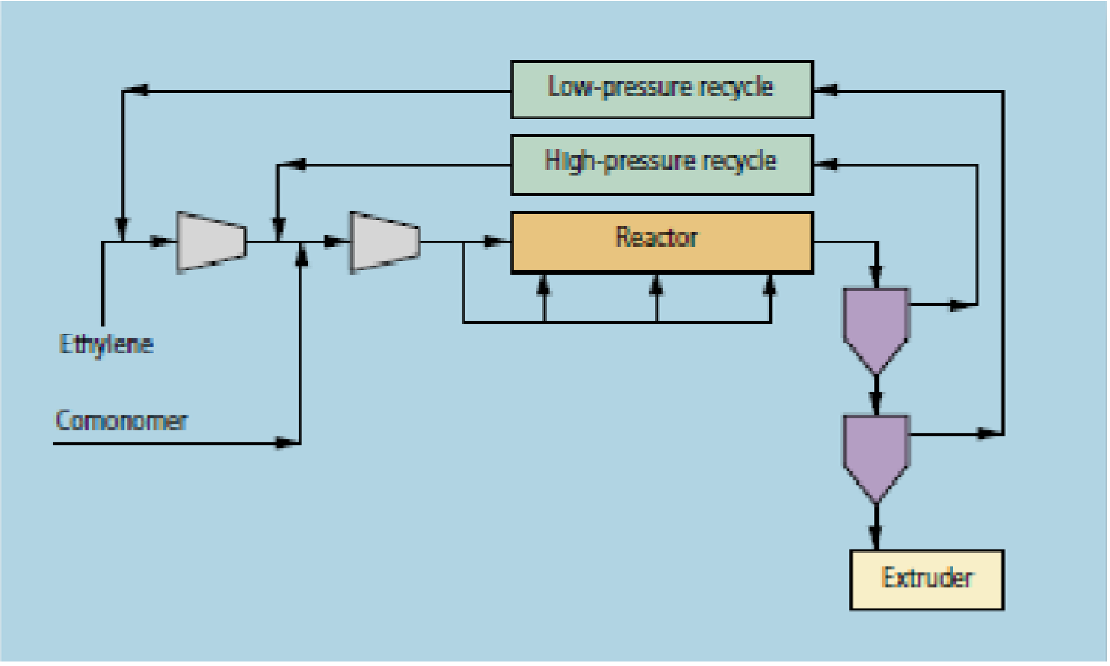


Figure 1.1. Schematic molecular structure A) Low-density polyethylene; B) Linear low-density polyethylene; C) High-density polyethylene

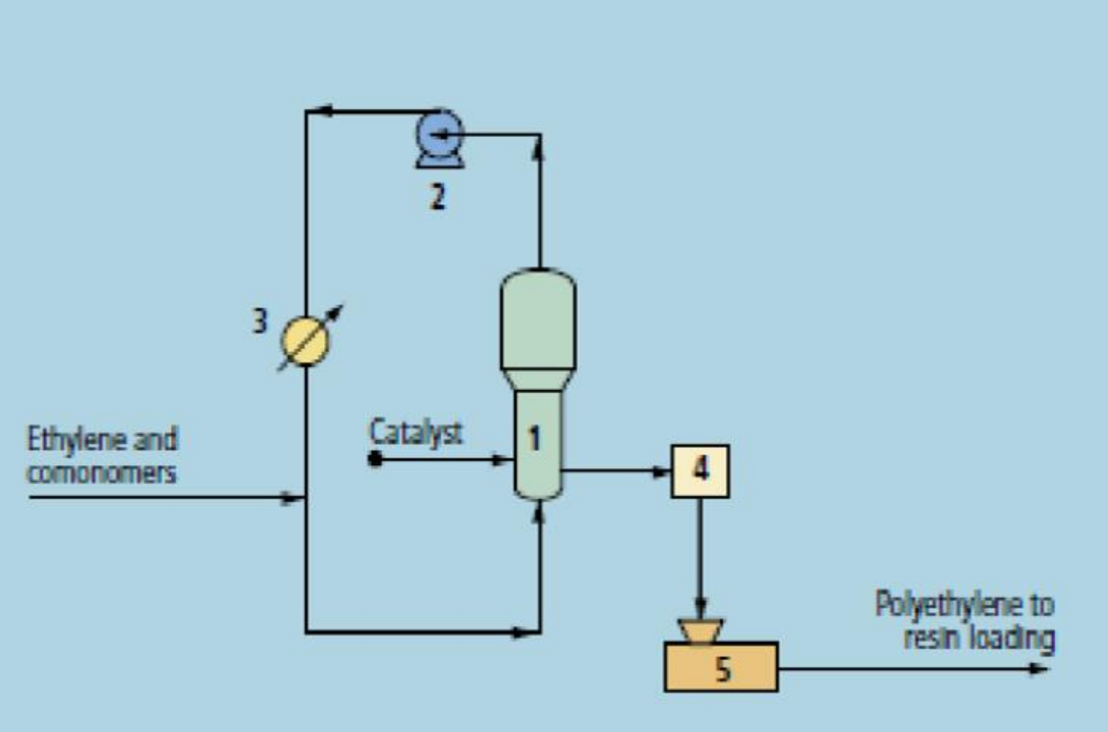
1-LDPE: low density poly ethylene:-



Description: Ethylene, initiator and, if applicable comonomers are fed to the process and compressed to pressure up to 3100 bar before entering the tubular reactor. In the TS mode, the complete feed enters the reactor at the inlet after the preheater; in the TM mode, part of the gas is cooled and quenches the reactor content at various points of injection. The polymer properties are controlled by the initiator, pressure, temperature profile and comonomer content. After the reactor, excess ethylene is recovered and recycled to the reactor feed stream. The polymer melt is mixed with additives in an extruder to yield the final product A range of products can be obtained using the *Lupotech* T process, ranging from standard LDPE grades to EVA copolymers or N-butyl-acrylate modified copolymer. The products can be applied in (shrink) film extrusion, injection molding, extrusion blow molding, pipe extrusion, pipe coating, tapes and monofilaments. There is no limit to the number of reactor grades that can be produced. The product mix can be adjusted to match market demand and economical product ranges. Advantages for the tubular reactor design with low residence time are easy and quick transitions, startup and shutdown.

Note: When **tubular reactor** is used LDPE produced is used for production of films while when **Autoclaves reactor** used LDPE produced is used for coatings.

2-HDPE:High density polyethylene:

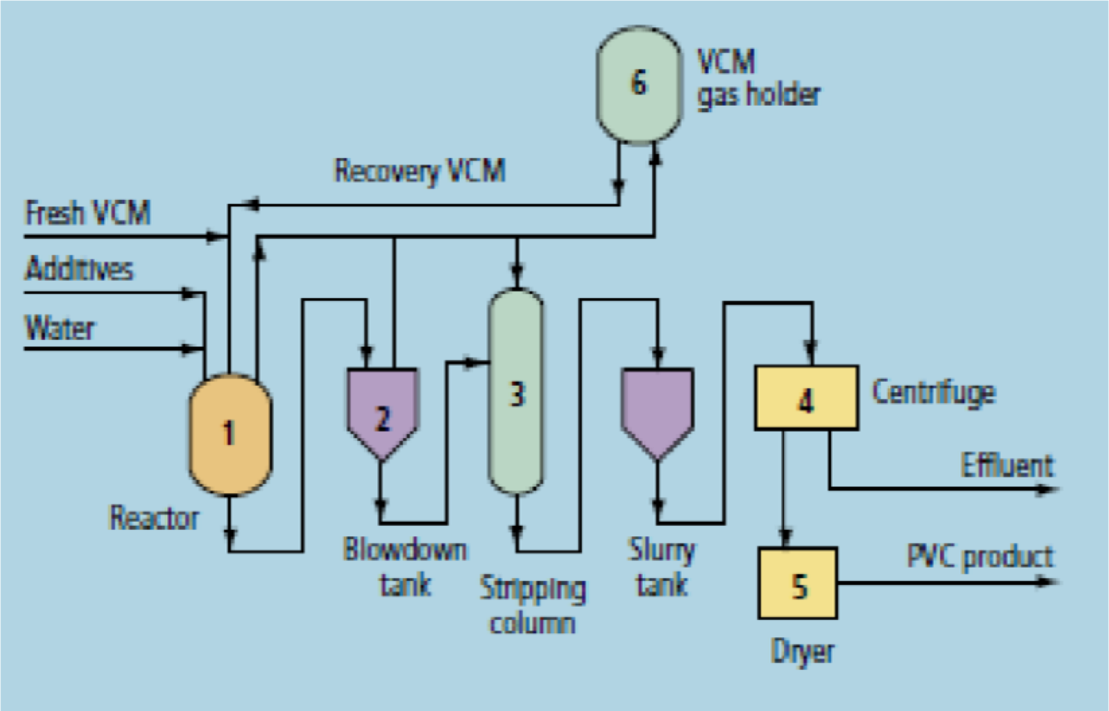


Description: A wide range of polyethylene is made in a gas-phase fluidized bed reactor using proprietary solid and slurry catalysts. The product is in a dry, free-flowing granular form substantially free of fines as it leaves the reactor and is converted to pellet form for sale. Melt index and molecular weight distribution are controlled by selecting the proper catalyst type and adjusting operating conditions. Polymer density is controlled by adjusting comonomer content of the product. High productivity of conventional and metallocene catalysts eliminates the need for catalyst removal The simple and direct nature of this process results in low investment and operating costs, low levels of environmental pollution, minimal potential fire and explosion hazards, and easy operation and maintenance. Gaseous ethylene, comonomer and catalyst are fed to a reactor (1) containing a fluidized bed of growing polymer particles and operating near 25 kg / cm^2 and approximately 100°C. A conventional, single-stage, centrifugal compressor (2) circulates reaction gas, which fluidizes the reaction bed, provides raw material for the polymerization reaction, and removes the heat of reaction from the bed. Circulating gas is cooled in a conventional heat exchanger (3). The granular product flows intermittently into product discharge tanks (4) where un reacted gas is separated from the product and returned to the reactor. Hydrocarbons remaining with the product are removed by purging with nitrogen. The granular product is subsequently pelletized in a low-energy system (5) with the appropriate additives for each application.

Products: Polymer density is easily controlled from 0.915 to 0.970 g/cm.

Depending on catalyst type, molecular weight distribution is either narrow or broad. Melt index may be varied from less than 0.1 to greater than 200. Grades suitable for film, blow-molding, pipe, roto-molding and extrusion applications are produced.

PVC Poly(vinylchloride) (suspension):

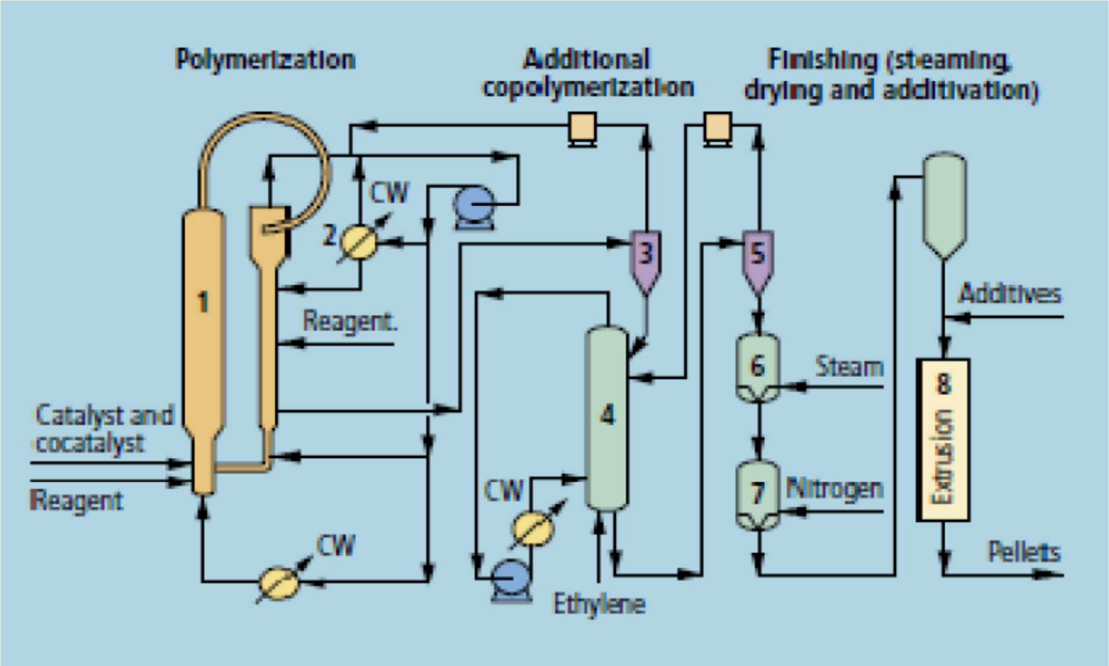


Application: A process to produce polyvinyl chloride (PVC) from vinylchloride monomer (VCM) using suspension polymerization. Many types of PVC grades are produced including: commodity, high K-value, low K-value, matted type and co-polymer PVC. The PVC possesses excellent product qualities such as easy processability and good heat stability.

Description: PVC is produced by batch polymerization of VCM dispersed in water. Standard reactor sizes are 60, 80, 100 or 130 m^3. The stirred reactor (1) is charged with water, additives and VCM. During polymerization reaction, the temperature is controlled at a defined temperature depending on the grade by cooling water or chilled water. At the end of the reaction, the contents are discharged into a blowdown tank

(2) where most of the un reacted VCM is flashed off. The reactor is rinsed and sprayed with an anti-fouling agent, and is ready for the following batch. The PVC slurry containing VCM is continuously fed to the stripping column(3). The column has a proprietary design and effectively recovers VCM from the PVC slurry without any deterioration of PVC quality. After stripping, the slurry is de-watered (4), and dried effectively by the proprietary dryer (5). It is then passed to storage silos for tanker loading or bagging. Recovered VCM is held in a gas holder (6), then compressed, cooled and condensed to be reused for the following polymerization batch.

Polypropylene:PP:-

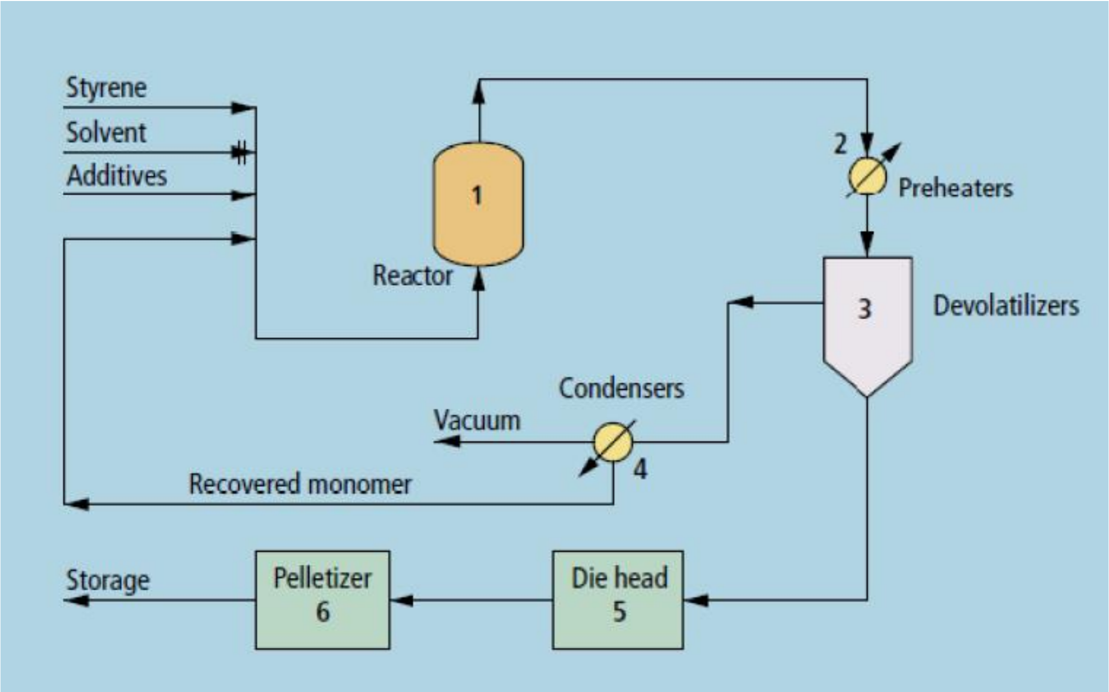


Description: In the process homopolymer and random copolymer polymerization takes place in liquid propylene within a tubular loop reactor (1). Heterophasic impact copolymerization can be achieved by adding a gas-phase reactor (3) in series. Removal of catalyst residue and amorphous polymer is not required. Unreacted monomer is flashed in a two-stage pressure system (2, 4) and recycled back to the reactors. This improves yield and minimizes energy consumption. Dissolved monomer is removed from the polymer by a steam sparge (5). The process can use lower-assay chemical-grade propylene (94%) or the typical polymerization-grade (99.5%).

Yields: Polymer yields of 40,000 – 60,000 kg / kg of supported catalyst are obtained. The polymer has a controlled particle size distribution.

Products: The process can produce a broad range of propylene-based polymers, including homopolymer PP, various families of random copolymers and terpolymers, hetero phasic impact and speciality impact copolymers(up to 25% bonded ethylene), as well as high-stiffness, high clarity copolymers.

Polystyrene,PS: general purpose (GPPS):



Description: Styrene monomer, a small amount of solvent and additives are fed to the specially designed reactor (1) where the polymerization is carried out. The polymerization temperature of the reactor is carefully controlled at a constant level to keep the desired conversion rate. The heat of polymerization is easily removed by a specially designed heat transfer system. At the exit of the reactor, the polymerization is essentially complete. The mixture is then preheated (2) and transferred to the devolatilizers (3) where volatile components are separated from the polymer solution by evaporation under vacuum. The residuals are condensed (4) and recycled back to the process. The molten polymer is pumped through a die (5) and cut into pellets by a pelletizer (6)

Synthetic fibers:

Fibers":Length/diameter>100:

(1)Textiles are main use.

1-Must have high tensile strength.

2-Usually highly crystalline and highly polar.

(2)Formed by spinning: ex. extrude polymer through a spinneret:

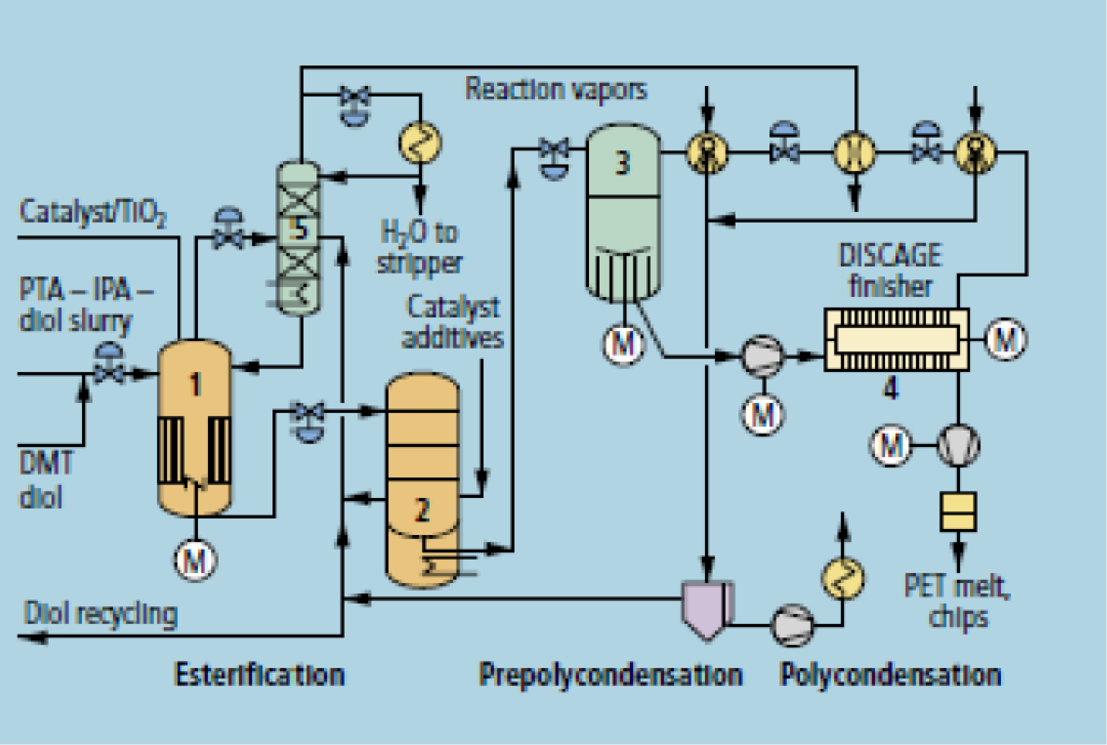
Pt plate with 1000"s of holes for nylon. Melt spinning

Ex. Rayon-dissolved in solvent then pumped through die head to make fibers.Solution spinning

(3) The fibers are drawn .

(4) Lead to a highly aligned chains-febrile

1-Polyesters (polyethylene terephthalate)



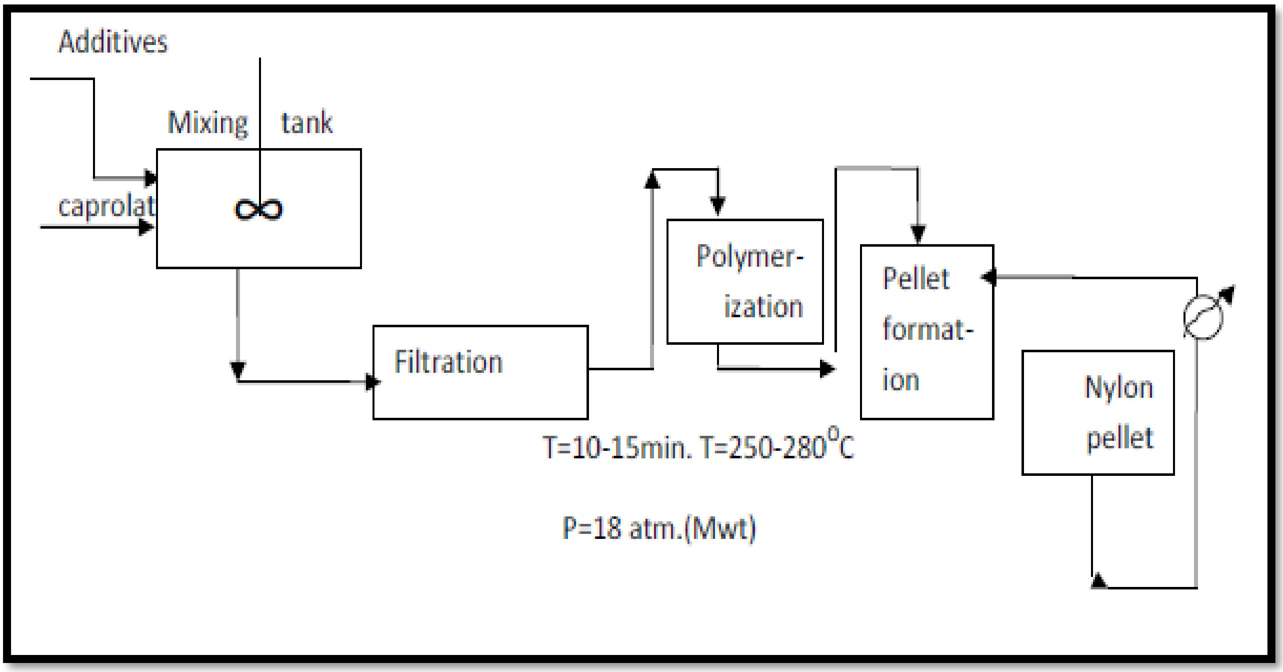
Application: To produce polyesters for resin and textile applications from terephthalic acid (PTA) or dimethyl terephthalate (DMT) and diols [ethylene glycol (EG) or others], using the UIF-proprietary four-reactor(4R)- process including DISCAGE-finisher.

Description: A slurry composed of PTA and EG, or molten DMT and EG is fed to the first esterification/ester-interchange reactor (1) in which main reaction occurs at elevated pressure and temperatures (200°C–270°C). Reaction vapors—water or methanol— are sent to a low/high boiler separation column. High boilers are reused as feedstock. The oligomer is sent to a second cascaded, stirred reactor (2) operating at a lower pressure and a higher temperature. The reaction conversion continues to more than 97%. Catalyst and additives may be added. Reaction vapors are sent to the process column (5). The oligomer is then prepolymerized by a third cascaded reactor (3) under sub atmospheric pressure and increased temperature to obtain a degree of polycondensation >20. Final polycondensation up to intrinsic viscosities of i. V. = 0.9 is done in the DISCAGE-finisher (4). Pelletizing or direct melt conversion usage is optional. EG is recovered by condensing process vapors at vacuum conditions. Vacuum generation may be done either by water vapor as a motive stream or by the diol (EG). The average product yield exceeds 99%.

2-Nylon 6 :

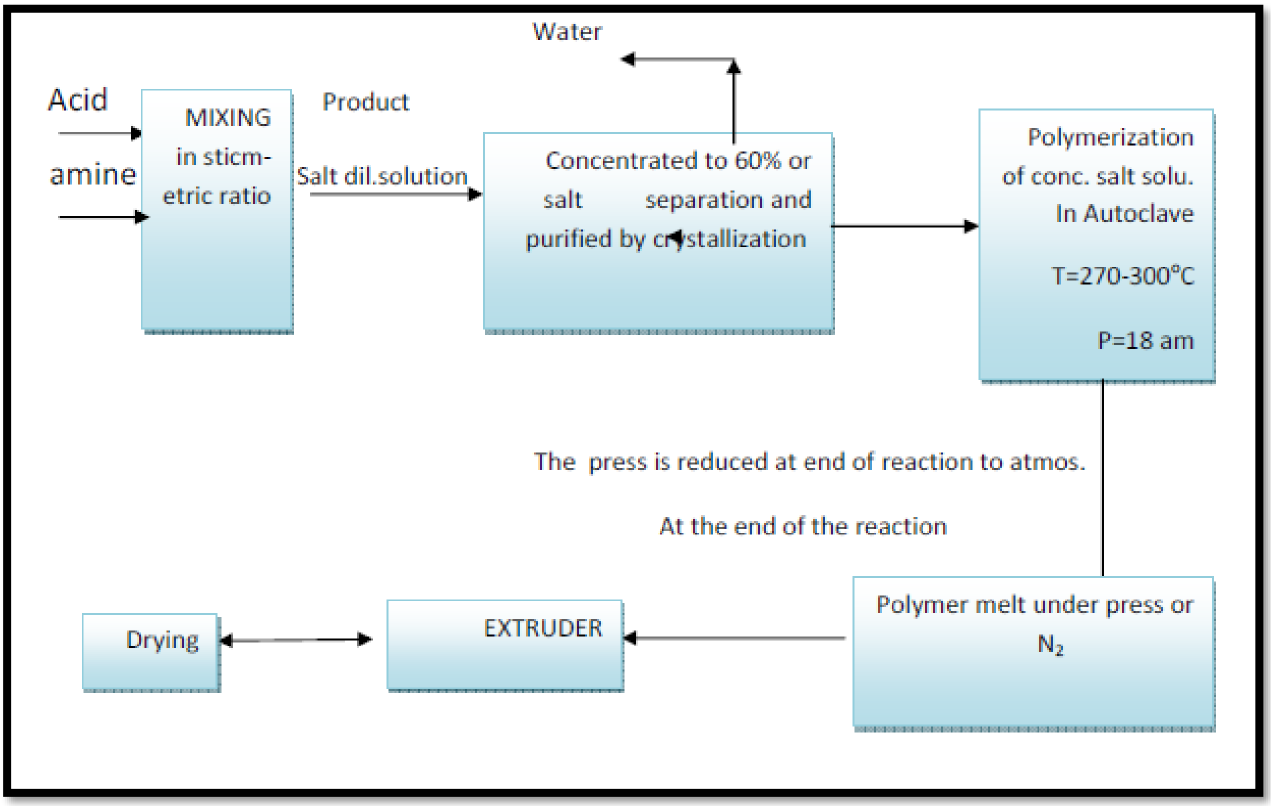
Is a polyamide contain –CONH

Raw material: Caprolactum.



3-Nylon 66:

Polymer is produced from hexamethylene adipamide which produced from condensation polymerization of adipic acid and hexamethylenediamine.



4-Acrylic :

Uses: Wool replacement

Production: Copolymerization of acrylonitrile with comonomer in presence of reaction initiators either free radicals or anionic at low temperature.

Polymerization on industrial scale:

1-Suspnsion polymerization: in presence of water.

2-Solution polymerization: in presence of suitable solvent : DMF or DMSO.