INTRODUCTION

The fundamental process by which low molecular weight compounds are converted into higher molecular weight compounds is called polymerization. The polymers contain repeating units called monomers.

BASIS OF CLASSIFICATION

The basic way of classification of polymers is on the basis of their origin. Other ways are:

1) Origin
   a) Natural – Nucleic acids, proteins, cellulose,
   b) Synthetic— Plastics, Nylon etc.

2) Line Structure
   a) Linear – polyvinyl chloride
   b) Branched – resins
   c) Crosslinked – epoxy resins

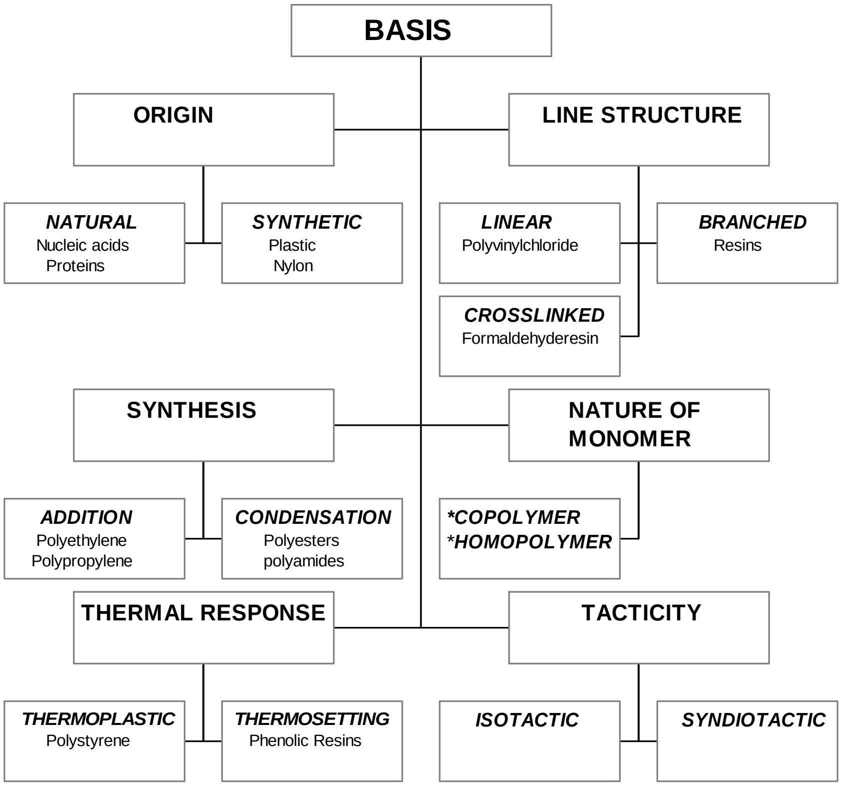
3) Synthesis
   a) Addition polymers – polyethylene, polypropylene
   b) Condensation polymers – polyamides, polyesters

4) Nature of monomers
   a) Copolymers

5) Thermal Response
   a) Thermoplastic – polyolefins, polystyrene, nylon.
   b) Thermosetting – phenolic resins

6) Tacticity
   a) Isotactic
   b) Syndiotactic

CLASSIFICATION OF POLYMERS



ELASTOMERS

These are a group of polymers that can undergo very large reversible elongations at comparative low stress. The requirements for a polymer to be an elastomer are:

a) It should be a high polymer
b) It must be cross-linked and amorphous
c) It should have flexibility of chains

fibers

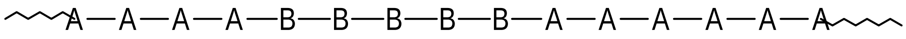
The properties of fibers include high tensile strength. This property results when there is high molecular symmetry and high cohesive energy between the chains. Both require a high degree of crystallinity and the required polymers are normally linear. Polyesters and nylon, which are condensation polymers, exhibit these properties.

plastics

Plastic materials comprise of a wide range of polymers, both rigid and flexible. Their mechanical properties are intermediate between those of elastomers and fibers. The rigid plastics are characterized by high rigidity and resistance to deformation, e.g. Phenol-formaldehyde resin, melamine-formaldehyde resin and polystyrene. Flexible plastics have moderate to high crystallinity. They have low tensile strength and high elongation. E.g. polyethylene

COPOLYMERS

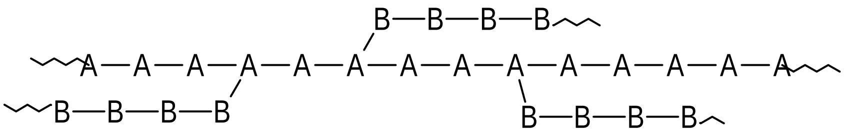
BLOCK COPOLYMER

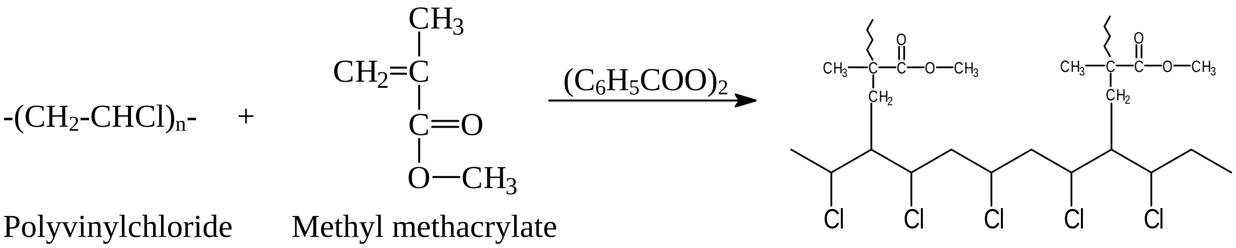


Polyamides

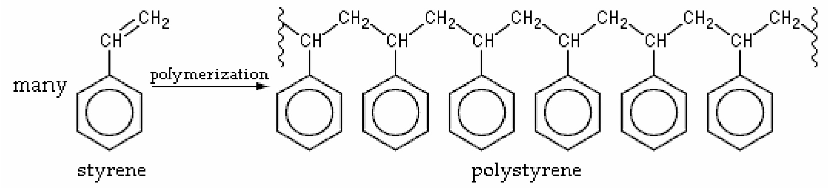
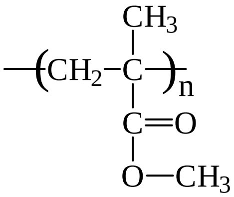
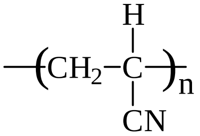
$nH_2N\text{-}R\text{-}NH_2 + nHOOC\text{-}(CH_2)_Y\text{-}COOH \rightarrow H[NH\text{-}R\text{-}NH.CO\text{-}(CH_2)_Y\text{-}CO]_nOH$

GRAFT COPOLYMER





Polyvinylchloride Methyl methacrylate

POLYETHYLENE	$-(CH_2-CH_2)_n-$
POLYSTYRENE	
POLY TETRAFLUOROETHYLENE (PTFE, TEFLON)	$R-(CF_2-CF_2)_n-$
POLY VINYL CHLORIDE	$R-(CH_2-CHCl)_n-$
POLYMETHYL METHACRYLATE (Plexi glass)	 $-\left(CH_2-\underset{\substack{\vert\\C=O\\\vert\\O-CH_3}}{\overset{\substack{CH_3\\\vert}}{C}}-\right)_n$
POLY ACRYLO NITRILE (Acrilan) Used as synthetic fiber	 $-\left(CH_2-\underset{\substack{\vert\\CN}}{\overset{\substack{H\\\vert}}{C}}-\right)_n$
POLY ESTER	$HO-(CH_2)_X-O.OC-(CH_2)_Y-CO.O-(CH_2)_X-OH$
POLYAMIDE (Nylon 6,6)	$-[-OC-(CH_2)_4-CO.NH-(CH_2)_6-NH-]_n-$
RUBBER	
Buna	$-[-CH_2-CH=CH-CH_2-]_n-$
Neoprine	$-[-CH_2-CCl=CH-CH_2-]_n-$

CONDENSATION POLYMERIZATION

This is a process of formation of polymers from polyfunctional monomers of organic molecules with the elimination of some small molecule such as water, hydrochloric acid, ammonia etc. This type of polymerization is also known as step-growth polymerization, the molecular weight of the polymer chain builds up slowly and there is only one reaction mechanism for the formation of the polymer. When a bifunctional molecule is used, a linear condensation product is formed.

Types of condensation polymers

i) Polyester: this is formed either by the self-condensation of a hydroxy carboxylic acid or by the reaction of a dicarboxylic acid with a glycol.

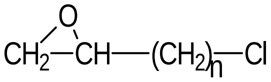
HO-(CH2)X-OH + HOOC-(CH2)Y-COOH (HO-(CH2)X-O.OC-(CH2)Y-COOH (HO-(CH2)X-O.OC-(CH2)Y-CO.O-(CH2)X-OH (

HO-(CH2)X-O.OC-(CH2)Y-CO.O-(CH2)X-O.OC-(CH2)Y-COOH

ii) Polyamides: these are obtained by the condensation of a diamine with a dicarboxylic acid

nH2N-R-NH2 + nHOOC-(CH2)Y-COOH (H[NH-R-NH.CO-(CH2)Y-CO]nOH

iii) Polyethers: When a compound containing an epoxide group reacts with a glycol, a poly ether results



+ HO-R-OH (-O-CH2-CH-(CH2)n-O-R-O-

iv) Polyurethanes: A polyurethane is obtained by the condensation of a by the condensation of a glycol with a diisocyanate

HO-R-OH + OCN-R’-NCO (-(O-R-O-CO-NH-R’-NH-CO)-

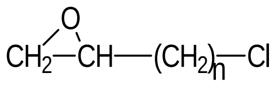
POLYESTER

$$\mathrm{HO\text{-}(CH_2)_X\text{-}OH + HOOC\text{-}(CH_2)_Y\text{-}COOH \rightarrow HO\text{-}(CH_2)_X\text{-}O.OC\text{-}(CH_2)_Y\text{-}COOH \rightarrow}$$
$$\mathrm{HO\text{-}(CH_2)_X\text{-}O.OC\text{-}(CH_2)_Y\text{-}CO.O\text{-}(CH_2)_X\text{-}OH \rightarrow}$$
$$\mathrm{HO\text{-}(CH_2)_X\text{-}O.OC\text{-}(CH_2)_Y\text{-}CO.O\text{-}(CH_2)_X\text{-}O.OC\text{-}(CH_2)_Y\text{-}COOH}$$

POLYAMIDES

$$\mathrm{nH_2N\text{-}R\text{-}NH_2 + nHOOC\text{-}(CH_2)_Y\text{-}COOH \rightarrow H[NH\text{-}R\text{-}NH.CO\text{-}(CH_2)_Y\text{-}CO]_nOH}$$

POLYETHERS



$$\mathrm{+\ HO\text{-}R\text{-}OH \rightarrow \text{-}O\text{-}CH_2\text{-}CH\text{-}(CH_2)_n\text{-}O\text{-}R\text{-}O\text{-}}$$

POLYURETHANES

$$\mathrm{nHO\text{-}R\text{-}OH + nOCN\text{-}R'\text{-}NCO \rightarrow \text{-}(O\text{-}R\text{-}O\text{-}CO\text{-}NH\text{-}R'\text{-}NH\text{-}CO)_n\text{-}}$$

CHAIN POLYMERIZATION (Addition Polymerization)

These polymers are formed by chain reactions. The reactive center may be formed by reaction with a free radical, a cation or an anion. Polymerization occurs through the propagation of the active species by the successive additions of a large number of monomer molecules in a chain reaction occurring in a matter of second or so at the most. The reaction generally occurs between molecules containing double or triple bonds. There is no liberation of small molecules during addition polymerization. The arrangement of monomers could be in the following manners:

1. Head to head – $-CH_2-CHY-CH_2-CHY-$
2. Head to tail – $-CH_2-CHY-CHY-CH_2-$
3. Random – Combination of 1 and 2

The mechanism of addition polymerization involves the following three steps
1. Initiation or Activation
2. The growth or Propagation
3. Termination

E.g. Free radical polymerization of ethylene

$$R^{\cdot} + nCH_2=CH_2 \rightarrow R-CH_2-CH_2^{\cdot} \xrightarrow{CH_2=CH_2} R-CH_2-CH_2-CH_2-CH_2^{\cdot}$$

Ionic Mechanism

$H^+ + CH_2=CMe_2 \rightarrow Me_3C^+$

$Me_3C^+ + CH_2=CMe_2 + CH_2=CMe_2$ ----n $\rightarrow Me_3C-(CH_2-CMe_2)-CH_2-C^+Me_2$

$\rightarrow Me_3C-(CH_2-CMe_2)-CH=CMe_2$

Head to head – $-CH_2-CHY-CH_2-CHY-$
Head to tail – $-CH_2-CHY-CHY-CH_2-$
Random – Combination of 1 and 2

Free radical polymerization of ethylene

$$R^{\cdot} + nCH_2{=}CH_2 \longrightarrow R-CH_2-CH_2^{\cdot} \xrightarrow{CH_2=CH_2} R-CH_2-CH_2-CH_2-CH_2^{\cdot}$$

Ionic Mechanism

$$H^+ + CH_2{=}CMe_2 \longrightarrow Me_3C^+$$

$$Me_3C^+ + CH_2{=}CMe_2 + CH_2{=}CMe_2 \text{ ----n} \longrightarrow Me_3C-(CH_2-CMe_2)-CH_2-C^+Me_2$$

$$\longrightarrow Me_3C-(CH_2-CMe_2)-CH{=}CMe_2$$

TACTICITY

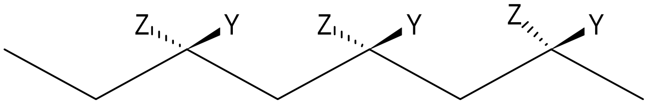
In the polymerization of the monomer of the type CH2-CYZ, there are two extreme stereoisomers possible

All the Y groups lie on one side of the chain and all the Z groups lie on the other side. This type of polymer is known as isotactic polymer.

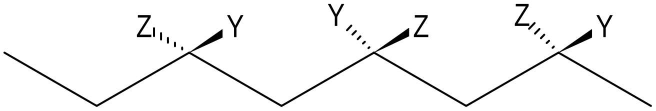
When all the Y and Z groups lie alternately on each side of the chain, this is known as syndiotactic polymer.

Between these two extremes, there are those polymers in which the two groups Y and Z are arranged in random order, these are known as atactic polymers.

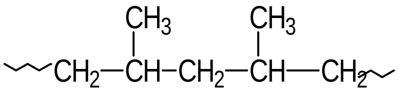
Isotactic



Syndiotactic



e.g. POLYPROPYLENE

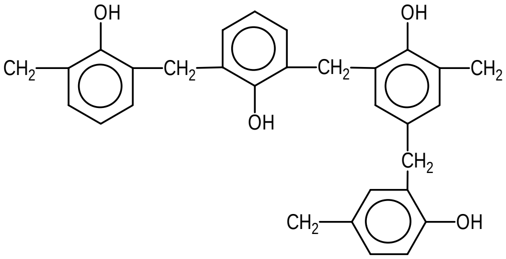


$$\sim CH_2-\underset{}{\overset{CH_3}{\overset{|}{C}}}H-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2\sim$$

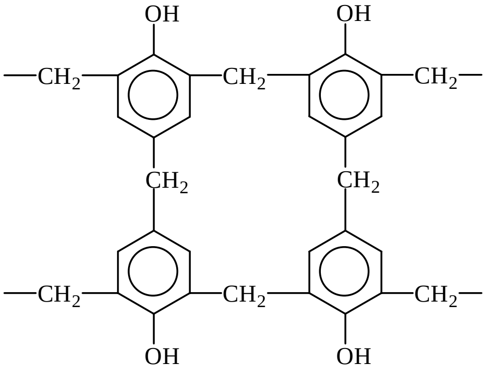
ISOTACTIC	High melting	Crystalline
ATACTIC	Rubbery	Amorphous

RESINS

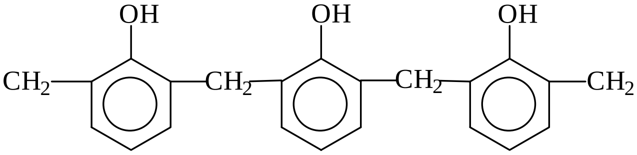
PHENOL FORMALDEHYDE RESINS
(Resoles)



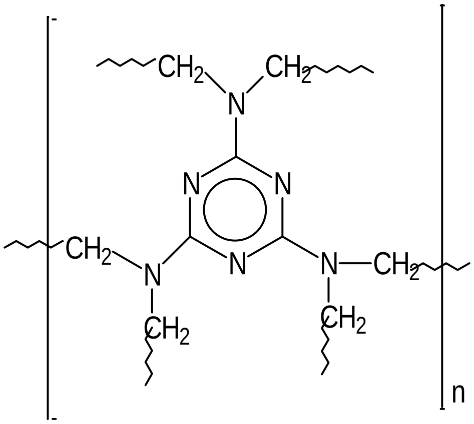
Resities



Bakelite



Melamine-Formaldehyde



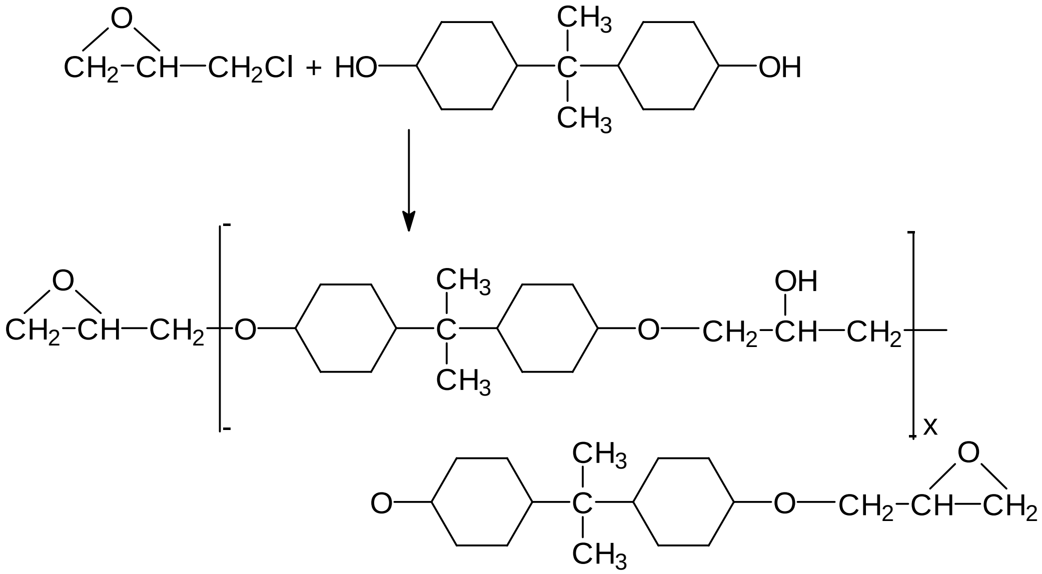
Thermal response

Thermoplastic resins are those which under the influence of heat and sometimes of pressure become plastic ie. They can flow, and can be molded into different shapes under this condition. They retain their shape on cooling. They can be remolded into different shapes on heating. They do not lose their chemical properties on heating. E.g. Polystyrene and cellulose acetate.

Thermosetting resins are those that under the influence of heat and pressure become soft and can be molded into different shapes. On further heating, they become hard and infusible on account of chemical change. They retain their shapes and cannot be remolded. E.g. Phenol-formaldehyde resins urea formaldehyde resin.

EPOXY RESINS

The epoxy resins are fundamentally polyethers, but retain their name on the basis of their starting material and the presence of epoxide group in the polymer before cross-linking. The epoxy resins are most widely prepared by condensing epichlorohydrin with bisphenolA, diphenylolpropane. An excess epichlorohydrin is used to leave epoxy groups on each end of the polymer. Depending on the molecular weight, the polymer is a viscous liquid or a brittle high melting solid.



The major use of epoxy resins is as surface coating material, which combine toughness, flexibility, adhesion and chemical resistance. They can be used in moulding and laminating techniques to make glass fiber reinforced articles with better mechanical strength. These are also used in industrial flooring, adhesives etc.

FLUORINE CONTAINING POLYMERS

Fluorine containing polymers represent in many respects the extremes in polymer properties. Within this family are found materials having the following properties:

1. High thermal stability and concurrent usefulness at high temperatures.
2. Extreme toughness and flexibility at very low temperatures
3. Many of the polymers are almost totally insoluble and chemically inert.
4. Some of them have extremely low dielectric loss and high dielectric strength.
5. Most of these polymers have unique non-adhesive and low friction properties.

POLY TETRA FLUORO ETHYLENE

Poly tetra fluoro ethylene is a highly crystalline, orientable polymer. These facts indicate a regular structure and absence of branching and cross-linking. It consists of linear $–CF_2$-CF_2- chains. It is extremely resistant to attack by corrosive reagents or solvents. It reacts to some extent with alkali metals presumably by removing the fluorine atoms from the chain.

Uses: the uses of polytetrafluoroethylene are largely those requiring excellent toughness, electrical properties, heat resistance, low friction coefficient, or a combination of these. Among the electrical applications of the polymer are wire and cable insulation, insulation for motors etc. These have a wide usage as valve packings, anti stick applications and other industrial functions.

Fluorocarbon Copolymers

A copolymer of hexafluoro propylene and tetrafluoroethylene has a crystalline melting point near 265^0C. It retains most of the properties of Poly tetra fluoro ethylene. This copolymer is tough at liquid air temperatures, yet retains adequate mechanical strength for service at temperatures upto 200^0C.

Polychloro tri fluoro ethylene

Polychloro tri fluoro ethylene is formed by the polymerization of chloro tri fluoro ethylene in aqueous systems using a redox initiator. Its chemical inertness and resistance to elevated temperatures are only surpassed by Poly tetra fluoro ethylene and hexafluoro propylene-tetrafluoroethylene copolymer. This polymer is soluble in a number of solvents above 100^0C and is swelled by several solvents at room temperature.

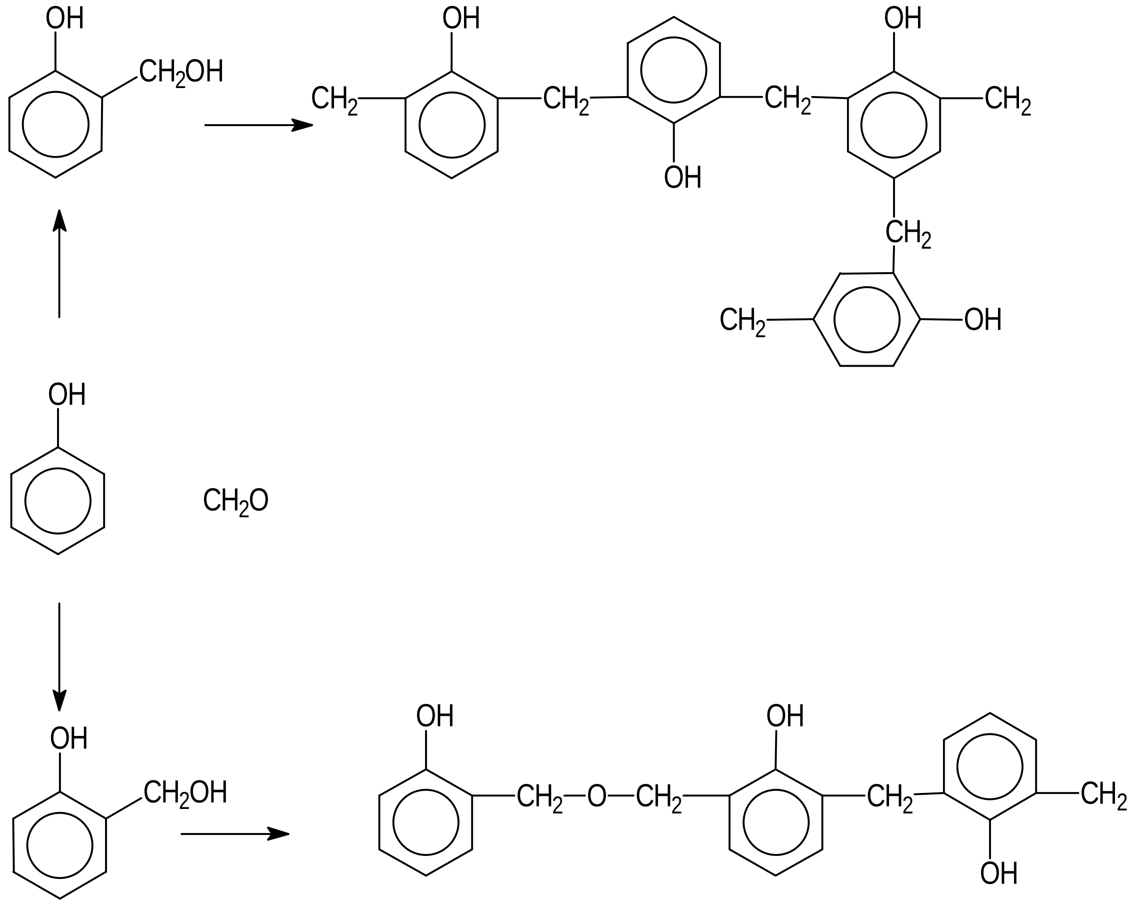
Poly vinyl fluoride

Poly vinyl fluoride is a highly crystalline plastic, which is commercially available in the form of a tough but flexible film. It has outstanding chemical resistance and is also resistant to thermal degradation. The film is used as a protective covering in the building industry.

Fluoroplastic Copolymers

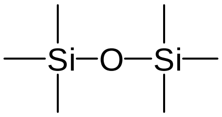
Copolymers of ethylene with tetrafluoroethylene and with chlorotrifluoroethylene have essentially 1:1 alternating structures. They have high melting points and retain much of the superior chemical resistance and good weatherability of the fully fluorinated materials.

Copolymers of chlorotrifluoroethylene and vinylidine fluoride range from tough, flexible thermoplastics to elastomers, depending on composition. Copolymers of hexafluoropropylene and vinylidine fluoride are elastomers combining high resistance to heat and to fluids and chemicals with good mechanical properties. These materials can be compounded to remain serviceable for short periods as high as 300^0C and retain useful properties indefinitely at 200^0C.


OH
CH2OH
OH
CH2
CH2
OH
CH2
OH
CH2
CH2
CH2
OH
OH
CH2O
OH
CH2OH
OH
CH2—O—CH2
OH
CH2
CH2
OH

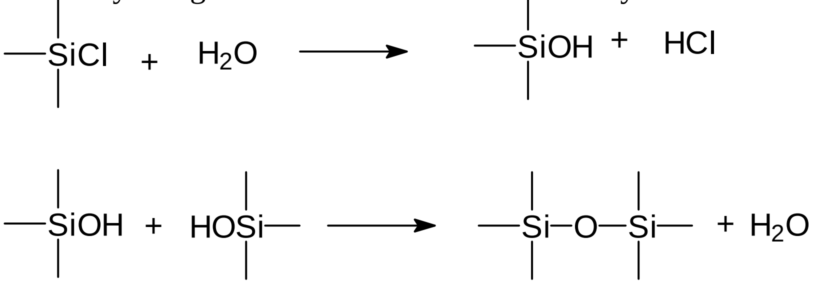
SILICONE POLYMERS

Like carbon, silicone has the capability of forming covalent bonds. Silicon hydrides (silanes) up to Si_6H_{14} are known. The Si-Si chain becomes thermally unstable at about this length. The siloxane link is more stable and is the one found in commercial silicone polymers. Unlike carbon, silicon does not form double or triple bonds. Thus silicone polymers are usually formed only by condensation type reactions.



$$-\mathrm{Si}-\mathrm{O}-\mathrm{Si}-$$

Silicon polymers are produced by intermolecular condensation of silanols which are formed from the halide or alkoxy intermediate by hydrolysis. The desired siloxane structure is obtained by using silanols of different functionality.



$$-\mathrm{SiCl} + H_2O \longrightarrow -\mathrm{SiOH} + HCl$$

$$-\mathrm{SiOH} + \mathrm{HOSi}- \longrightarrow -\mathrm{Si}-\mathrm{O}-\mathrm{Si}- + H_2O$$

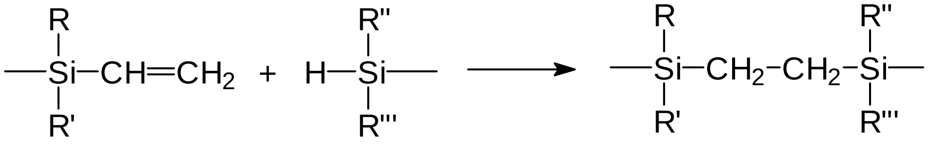
Silicone Fluids

The silicone fluids are low polymers produced by the hydrolysis of halide or alkoxy intermediate. In this reaction predetermined mixture of chlorosilanes is fed into water with agitation.

Silicone Elastomers

Silicone Elastomers are high molecular weight polymers usually polydimethyl siloxanes. They can be cured in several ways:

1. By free radical crosslinking with peroxides through the formation of ethylinic bridges between chains.
2. By cross-linking of vinyl or allyl groups attached to silicon through reaction with silylhydride groups.



$$-\underset{R'}{\overset{R}{\mathrm{Si}}}-CH=CH_2 + H-\underset{R'''}{\overset{R''}{\mathrm{Si}}}- \longrightarrow -\underset{R'}{\overset{R}{\mathrm{Si}}}-CH_2-CH_2-\underset{R'''}{\overset{R''}{\mathrm{Si}}}-$$

3. By cross-linking linear or slightly branched siloxane chain having reactive end groups such as silanols. In contrast to the above reactions, this yields Si – O – Si cross-links.

Silicone Resins

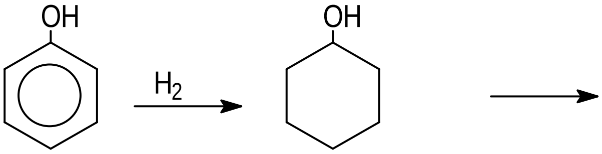
In contrast to the silicone fluids and elastomers, silicone resins contain Si atoms with no or only one organic substituent. They are therefore crosslinkable to harder and stiffer compounds than elastomers, but must be handled in solution to prevent premature cure. They are in fact, usually made by hydrolysis of the desired chlorosilane blend in the presence of a solvent such as mineral spirits, butyl acetate, toluene or xylene. These materials are usually cured with metal soaps or amines. The silicone resins are used primarily as insulating varnishes, impregnating and encapsulating agents and in industrial paints.

POLYURETHANES

Polyurethanes are polymers containing the NHCOO group. They are formed through the reaction of a diisocyanate and a glycol. The polymers formed in this way are useful in four major types of products: foams, fibers, elastomers and coatings. In the formation of urethane foams, excess isocyanate groups in the polymer react with water or carboxylic acids to produce carbon dioxide, blowing the foam, at the same time the cross linking is effected. The polyurethane foams can be made in either flexible or rigid forms depending on the nature of the polymer and type of cross-linking produced.

$$x\mathrm{OCN{-}R{-}NCO} + x\mathrm{HO{-}R'} \rightarrow \text{--}[\mathrm{OCONHRNHCOOR'}\text{---}]_X$$

The flexible foams are used for cushions and furnishings. Rigid urethane foams are resistant to compression and may be used to reinforce hollow structural units with minimum of weight. In addition, they consist of closed cells and so have low rates of heat transmission.



Phenol Cyclohexanol

$HOOC\text{-}(CH_2)_4\text{-}COOH$
Adipic Acid (I)

$$I \xrightarrow{NH_4OH} H_2NOC\text{-}(CH_2)_4\text{-}CONH_2 \xrightarrow{P_2O_5} NC\text{-}(CH_2)_4\text{-}CN$$

Adipamide Adiponitrile

$$\xrightarrow{Redn.} H_2N\text{-}(CH_2)_6\text{-}NH_2$$

Hexamethylene diamine(II)

$$I + II \longrightarrow HOOC\text{-}(CH_2)_4\text{-}COOH.H_2N\text{-}(CH_2)_6\text{-}NH_2 \xrightarrow{-H_2O}$$

Nylon salt

$$HOOC\text{-}(CH_2)_4\text{-}CO.NH\text{-}(CH_2)_6\text{-}NH_2 \longrightarrow \text{-}[\text{-}OC\text{-}(CH_2)_4\text{-}CO.NH\text{-}(CH_2)_6\text{-}NH\text{-}]_n\text{-}$$

Nylon 6,6

DEGRADATION OF POLYMERS

Degradation of a polymer can be defined as the undesirable change that occurs in a polymer affecting its physical and chemical properties. The degrading agencies may be heat, radiation, chemical and mechanical energy. To overcome the problem of degradation, the polymer is treated with heat stabilizers and antioxidants. The degradation process is divided into three types depending upon the degrading agent.

1. Thermal degradation
2. Oxidative degradation
3. Photo Degradation

THERMAL DEGRADATION

Thermal degradation of a polymer is the degradation due to it being exposed to heat. Many different kinds of degradation reactions are possible. The two main classes, namely, *depolymerization* and *substituent* reactions.

In depolymerization reaction the main polymer backbone is broken in such a way that the products of degradation are similar to the parent material in the sense that the monomer units are still distinguishable. E.g. Degradation reactions of poly methyl methacrylate and polyethylene.

In the substitution reactions, the substituents attached to the polymer backbone are involved. The chemical nature of the repeating units is changed although the chain structure of the backbone remains intact. E.g. dehydrohalogenation of polyvinylchloride.

OXIDATIVE DEGRADATION

This is the degradation of a polymer due to oxygen. Oxygen reacts with the polymer in a radical chain reaction involving the ground state oxygen diradical. E.g. in the oxidative degradation of polystyrene. Hydroperoxides are formed in the initial stages of the reaction. The decomposition of the hydroperoxide may then result in the rupture of the chain.

PHOTO DEGRADATION

The breakage of the polymeric bonds due to exposure to light is known as photo degradation. Presence of double bonds or oxygen results in the homolytic cleavage of the bonds. E.g. in polyethylene, both chain cleavage and cross-linking have been reported to occur. The fact that abnormalities such as carbonyl group may be present in polyethylene makes it most photolabile on exposure to UV radiation.

Natural and Synthetic Rubber

Natural rubber is a polymer found in the sap of the rubber tree, Hevea brasilensis, originally native to Brazil. The rubber tree grows throughout the tropics and is cultivated in plantations, primarily in Southeast Asia; Malaysia and Indonesia are the most significant sources. The sap is collected, and on exposure to air and mild heat gives natural rubber. Chemically, this is a polymer of 2-methyl-1,3-butadiene (isoprene),

$$CH2{=}C(CH_3)\text{-}CH{=}CH_2.$$

The polymerization reaction is:

$$nCH_2{=}C(CH_3)\text{-}CH{=}CH_2 \rightarrow \text{-}[CH_2\text{-}C(CH_3){=}CH\text{-}CH_2]_n\text{-}.$$

Natural rubber has long been known, but became valuable only with the development of vulcanizing (heating in the presence of sulfur) developed by Charles Goodyear, which gives a much more rubbery and coherent substance.

The development of synthetic rubber was a German program for many years. Germany produced some 2500 tonnes of methyl rubber (polymer of 2,3-dimethyl-1,3-butadiene) during World War I, but returned to natural rubber at the end of the War. Specialty rubbers were produced and research was carried out in Germany and elsewhere prior to World War II, but the synthetic rubber industry of the world arose during World War II. At the present time over 75% of the rubber used in the United States is synthetic, while on a world basis about 65% of the rubber used is synthetic.

The most significant forms of synthetic rubber used today are the Buna S, Buna N, and synthetic natural rubbers developed in Germany. Other types (Thiokol, Neoprene) have somewhat different properties and specialty uses. Buna-S, by far the most significant, has been made since 1933 in Germany. It is a copolymer of 1,3-butadiene and styrene. The polymerization reaction is:

$$nCH_2{=}CHCH{=}CH_2 + nC_6H_5CH{=}CH_2 \rightarrow \text{-}[CH_2CH{=}CHCH_2CH(C_6H_5)CH_2]_n\text{-}.$$

The Buna-N rubber, which is soil-resistant, is a copolymer of 1,3-butadiene and acrylonitrile. The polymerization reaction is:

$$nCH_2{=}CHCH{=}CH_2 + nCH_2{=}CHCN \rightarrow \text{-}[CH_2CH{=}CHCH_2CHC{=}N]_n\text{-}.$$

Like the Buna-S type, Buna-N rubber can be vulcanized.

True synthetic rubber, a polymer of isoprene, was achieved almost simultaneously in 1955 by several major rubber manufacturers using different catalysts. The process is a polymerization of isoprene itself and the product is virtually identical to the natural Hevea product. The feedstocks for the synthetic rubber industry are products of the petrochemical industry.

Rubber, either natural or synthetic, is normally vulcanized, most often with sulfur, although for some specialty uses other agents are used. The majority of rubber used is used for automobile tires. For this and similar applications a filler or reinforcing agent must be added, of which carbon black is by far the most common