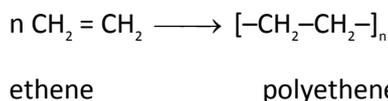


POLYMERS

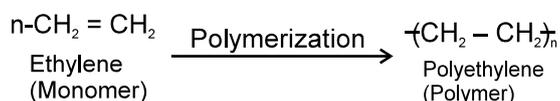
Polymers are very high molecular mass substances where each molecule is derived from very large number of simple molecules joined together in a regular way. This simple molecule is monomer and the process of formation of polymers from simple molecule is polymerization.



Polymers are two types :

(i) Homopolymers :

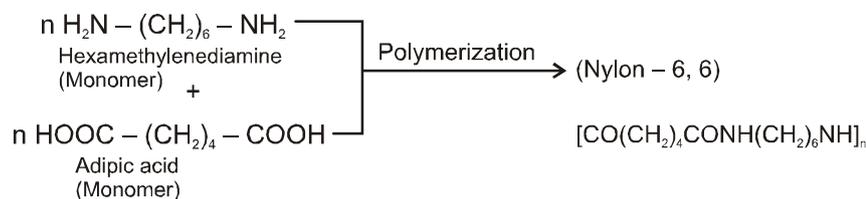
Polymers in which repeating structural units are derived from only one type of monomer units are called homopolymers.



Ex. Polypropylene, polyvinyl chloride (PVC), polyisoprene, neoprene (polychloroprene) polyacrylonitrile (PAN), nylon-6, polybutadiene, teflon (polytetrafluoroethylene), cellulose, starch etc.

(ii) Copolymers :

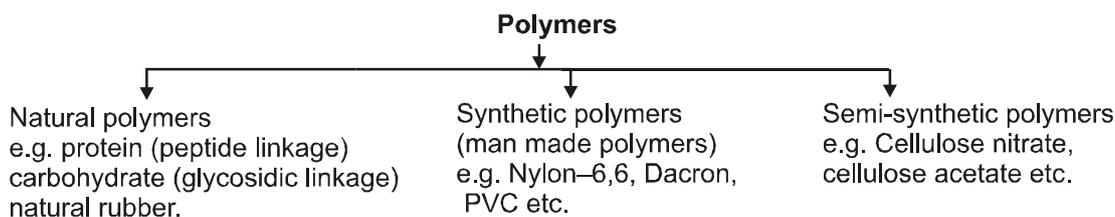
Polymers in which repeating structural units are derived from two or more types of monomer units are called copolymers.



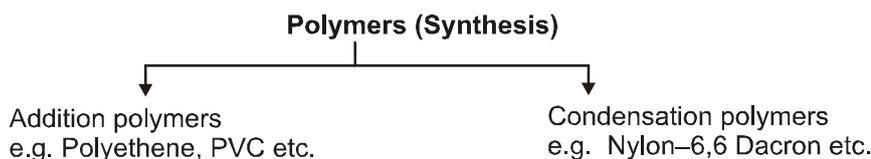
Note : In Homo polymer empirical formula of monomer and polymers are same

1.1 Polymers can be classified by following ways :

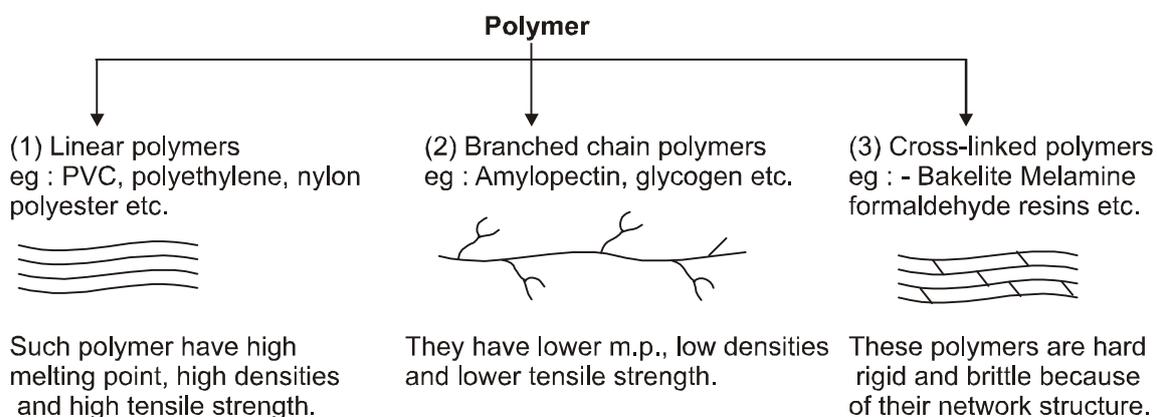
(A) Classification based on origin or source :



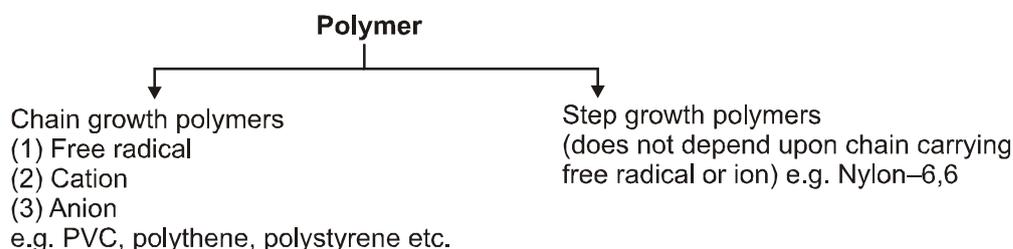
(B) Classification based on synthesis :



(C) Classification based on Structure:

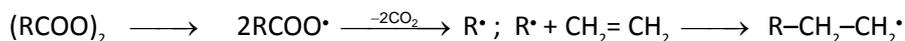
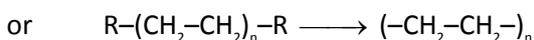
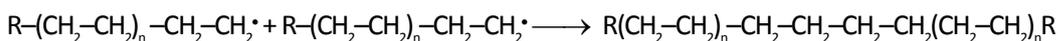


(D) Classification based on Mechanism :

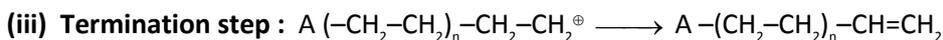
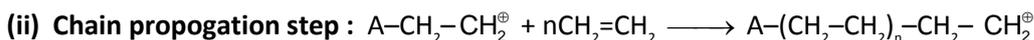
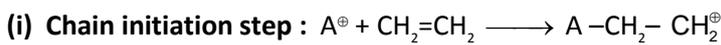
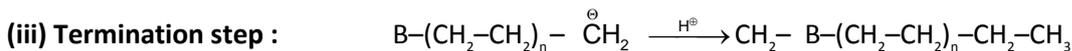
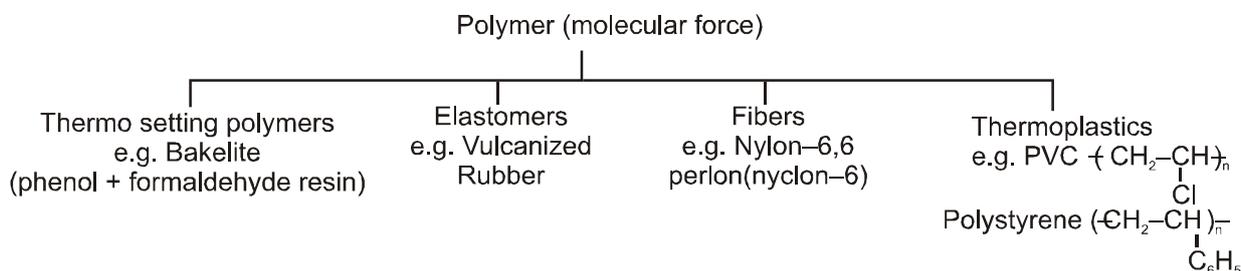


(1) Free radical :

This mechanism involve catalyst which generate free radical. Steps involved are :

(i) Chain initiation step :**(ii) Chain propagation step :****(iii) Termination step :****(2) Cationic addition polymerisation.**

This polymerisation is initiated by acid. Steps involved are :

**(3) Anionic addition polymerization :****(E) Classification based upon molecular force :**

(i) Elastomers : Polymers in which the intermolecular forces of attraction between the polymer chains are the weakest are called **elastomers**.

e.g. Buna rubber, Natural rubber etc.

(ii) Fibres : Polymers in which the intermolecular forces of attraction are the strongest are called fibers. These forces are either due to H-bonding or dipole-dipole interactions. In case of nylon (polyamides), the intermolecular forces are due to H-bonding while in polyesters (terylene, dacron) and polyacrylonitrile (orlon, acrylin) Dipole-dipole interactions between the polar carbonyl (C = O) groups and, between carbonyl and cyano ($-C \equiv N$) groups respectively.

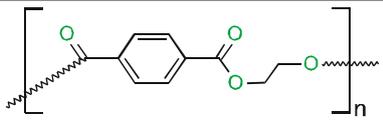
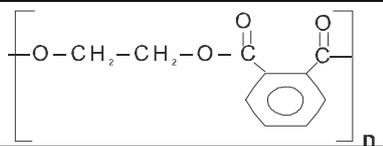
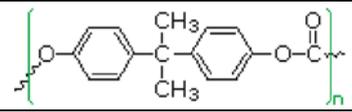
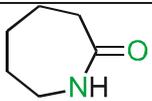
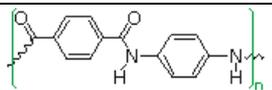
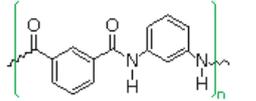
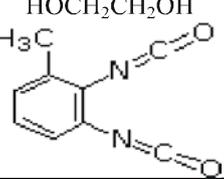
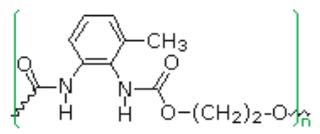
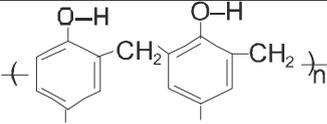
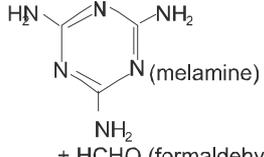
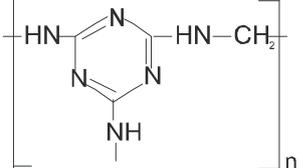
(iii) Thermoplastics : Polymers in which the intermolecular forces of attraction are in between those of elastomers and fibres are called thermoplastics. The process of heat softening and cooling can be repeated as many times as desired without any change in chemical composition and mechanical properties of the plastic.

e.g. Polyethylene, polypropylene, polystyrene, PVC, teflon etc.

(iv) Thermosetting polymers : These are semifluid substances with low molecular weights which when heated in a mould, undergo change in chemical composition to give a hard, infusible and insoluble mass. This hardening on heating is due to extensive cross-linking between different polymer chains to give a three-dimensional network solid. Examples : Phenol-formaldehyde (bakelite), urea-formaldehyde, etc.

e.g. Bakelite urea-formaldehyde resin, terylene etc.

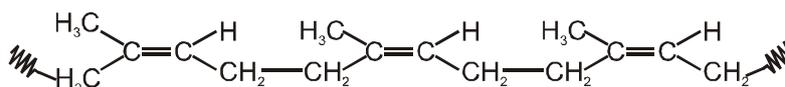
Some Common Addition Polymers/ Chain Growth Polymer (Homopolymers)				
No.	Monomer	Formula	Name(s)	Uses
1.	CH ₂ =CH ₂ (ethylene)	-(CH ₂ -CH ₂) _n -	Polyethylene (low density (LDPE))	film wrap, plastic bags
2.	CH ₂ =CH ₂ (ethylene)	-(CH ₂ -CH ₂) _n -	Polyethylene (high density (HDPE))	electrical insulation bottles, toys
3.	CH ₂ =CHCH ₃ (propylene)	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}-\text{CH}_2 \end{array} \right]_n$	Polypropylene (PP) different grades	similar to LDPE carpet, upholstery
4.	CH ₂ =CHCl (vinyl chloride)	$\left[\begin{array}{c} \text{Cl} \\ \\ \text{CH}-\text{CH}_2 \end{array} \right]_n$	Poly vinyl chloride (PVC)	pipes, siding, flooring
5.	CH ₂ =CCl ₂ (vinylidene chloride)	$\left[\begin{array}{c} \text{Cl} \\ \\ \text{C}-\text{CH}_2 \\ \\ \text{Cl} \end{array} \right]_n$	Poly(vinylidene chloride) (Saran A)	seat covers, films
6.	CH ₂ =CHC ₆ H ₅ (styrene)	$\left[\begin{array}{c} \text{CH}_2-\text{CH} \\ \\ \text{C}_6\text{H}_5 \end{array} \right]_n$	Polystyrene (PS) (Styron)	toys, cabinets packaging (foamed)
7.	CH ₂ =CHCN (acrylonitrile)	$\left[\begin{array}{c} \text{N} \\ \\ \text{C} \\ \\ \text{CH}-\text{CH}_2 \end{array} \right]_n$	Polyacrylonitrile (PAN, Orlon, Acrilan)	rugs, blankets clothing
8.	CF ₂ =CF ₂ (tetrafluoroethylene)	-(CF ₂ -CF ₂) _n -	Polytetrafluoroethylene (PTFE, Teflon)	non-stick surfaces electrical insulation
9.	F ₂ C=CFCl Chlorotrifluoro ethylene	-(CF ₂ -CFCl) _n -	Polychlorotrifluoro ethylene (PCTFP)	For making non-stick utensils coating making etc.
10.	CH ₂ =C(CH ₃)CO ₂ CH ₃ (methyl methacrylate)	- [CH ₂ C(CH ₃)CO ₂ CH ₃] _n -	Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas, perspex)	lighting covers, signs skylights
11.	CH ₂ =CHOCOCH ₃ (vinyl acetate)	-(CH ₂ -CHOCOCH ₃) _n -	Poly(vinyl acetate) (PVAc)	latex paints, adhesives
12.	CH ₂ =CH-C(CH ₃)=CH ₂ (isoprene)	-[CH ₂ -CH=C(CH ₃)- CH ₂] _n -	<p>Polyisoprene</p> <p>(zigler-natta)</p> <p>Cis-form (natural rubber) (1, 4-addition)</p> <p>Trans-form Gutta-purca</p> $\left(\begin{array}{c} \text{H}_2\text{C} \quad \text{CH}_2 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H} \quad \text{H} \end{array} \right)_n$ $\left(\begin{array}{c} \text{H} \quad \text{CH}_2 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{H}_2\text{C} \quad \text{H} \end{array} \right)_n$	requires vulcanization for practical use
13.	CH ₂ =CH-CCl=CH ₂ (chloroprene)	-[CH ₂ -CH=CCl-CH ₂] _n -	Polychloroprene (cis + trans) (Neoprene)	synthetic rubber oil resistant

Some Condensation Polymers (step Growth Polymers)				
S.No.	Type	Components	Formula	Classified as
1.	Polyester /Dacron/ Terylene/Mylar	HO ₂ C C ₆ H ₄ CO ₂ H (Terephthalic acid) HO-CH ₂ CH ₂ -OH Ethylene glycol		Copolymer Step growth, Linear Polymer
2.	Glyptal or Alkyds resin	HO ₂ C-C ₆ H ₄ -CO ₂ H (Phthalic acid) HO-CH ₂ CH ₂ -OH Ethylene glycol		Copolymer Step growth, Linear Polymer
3.	Polycarbonate Lexan	(HO-C ₆ H ₄ -)C(CH ₃) ₂ (Bisphenol A) X ₂ C=O (X = OCH ₃ or Cl)		Copolymer Step growth, Linear Polymer
4.	Polyamide (Nylon 6,6)	HO ₂ C-(CH ₂) ₄ -CO ₂ H H ₂ N-(CH ₂) ₆ -NH ₂	~[CO(CH ₂) ₄ CO-NH(CH ₂) ₆ NH] _n ~	Copolymer Step growth, Linear Polymer
5.	Nylon 6,10	HOOC-(CH ₂) ₈ -COOH H ₂ N-(CH ₂) ₆ -NH ₂	~[C(=O)-(CH ₂) ₈ -C(=O)-NH-(CH ₂) ₆ -NH] _n ~	Copolymer Step growth, Linear Polymer
6.	Polyamide Nylon 6, Perlon- L		~[CO(CH ₂) ₅ NH] _n ~	Homopolymer, Step growth, Linear Polymer
7.	Polyamide Kevlar	para HO ₂ C-C ₆ H ₄ -CO ₂ H para H ₂ N-C ₆ H ₄ -NH ₂		Copolymer Step growth Linear polymer
8.	Polyamide Nomex	meta HO ₂ C-C ₆ H ₄ -CO ₂ H meta H ₂ N-C ₆ H ₄ -NH ₂		Copolymer Step growth Linear polymer
9.	Polyurethane Spandex	HOCH ₂ CH ₂ OH 		Copolymer Step growth Linear polymer
10.	Bakelite	PhOH + HCHO in (excess)		Copolymer Cross- linked polymer Step growth
11.	Urea- formaldehyde Resin	H ₂ N-CO-NH ₂ (Urea) HCHO (Formaldehyde)	~[NH-CO-NH-CH ₂] _n ~	Copolymer Step growth Cross- linked polymer
12.	Melamine formaldehyde resin	 + HCHO (formaldehyde)		Cross-linked polymer

Some Useful Copolymers			
Monomer A	Monomer B	Copolymer	Uses
$\text{H}_2\text{C}=\text{CHCl}$	$\text{H}_2\text{C}=\text{CCl}_2$	Saran	films & fibers
$\text{H}_2=\text{CH}-\text{CH}=\text{CH}_2$ 1, 3-Butadiene		Buna Rubber (Homo-polymer)	In manufacture of tyres, hoses, etc.
$\text{H}_2\text{C}=\text{CHC}_6\text{H}_5$	$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$	SBR styrene butadiene rubber (Buna-S)	Tires
$\text{H}_2\text{C}=\text{CHCN}$	$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$	Nitrile Rubber (Buna-N)	Adhesives hoses
$\text{H}_2\text{C}=\text{CHCN}$	$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$ + $\text{H}_2\text{C}=\text{CHC}_6\text{H}_5$	ABS rubber	Fuel tanks
$\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2$	$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$	Butyl Rubber	Inner tubes
$\text{F}_2\text{C}=\text{CF}(\text{CF}_3)$	$\text{H}_2\text{C}=\text{CHF}$	Viton	Gaskets

Natural rubber :

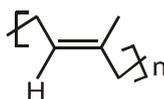
Natural rubber is a polymer of isoprene, and obtained from natural source-latex tree. In natural rubber, isoprene units are joined together in head-to-tail fashion and all double bonds in the polymer chain have cis configurations as shown in the given figure.



Cis-1,4-polyisoprene

(Natural rubber)

The polymer contains cis repeating units and has a molecular weight ranging from 100,000 upto 1,000,000. A related polymer, called *gutta percha* which has a structure with trans double bonds and a much lower molecular weight. A typical sample of gutta percha has a molecular weight of about 7,000.



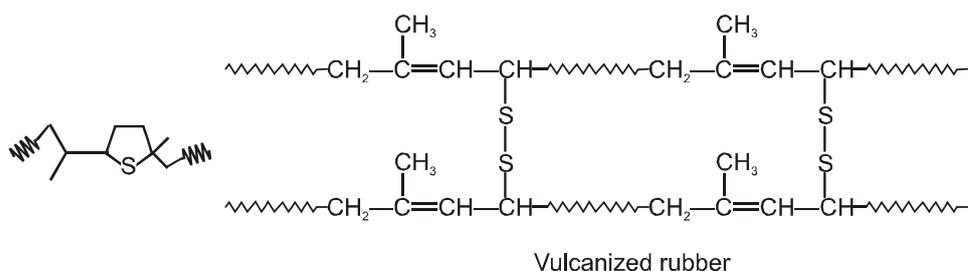
Gutta percha

The cis arrangement of the double bonds in natural rubber prevents the rubber molecules from fitting into an ordered structure. Thus, rubber is an amorphous polymer. Because of the random coiling of its polymer chains, rubber stretches easily. When stretched, the rubber molecules are forced into a higher energy state. when the tension is released, rubber snaps back to its original random coiled state.

Vulcanization of Natural Rubber

Raw rubber is soft and tacky, they have very low mechanical strength, affected by environmental factors such as light, temperature, and oxygen and are of no use for any commercial purpose. These factors make rubber unsuitable for a number of applications. To enhance the mechanical properties and stiffness of natural rubber in 1839, Charles Goodyear devised a method of reacting rubber with sulphur to form a more durable material.

Vulcanization is a process in which natural rubber is heated with sulphur, where it undergoes crosslinking and connects the isolated rubber chains through a network, making them strong and stiff. Vulcanization forms both the cyclic structure shown on the left and the more desirable cross-linked structure shown on the right in the following figure.



Increasing the amount of sulphur makes the vulcanized polymer harder and more durable. Adding 3-5% sulphur makes a product good for rubber bands and inner tubes. Adding 20-30% sulphur makes a hard rubber that was once widely used in ways that a hard synthetic plastic is used today. The vulcanization process made early automobile tires possible.

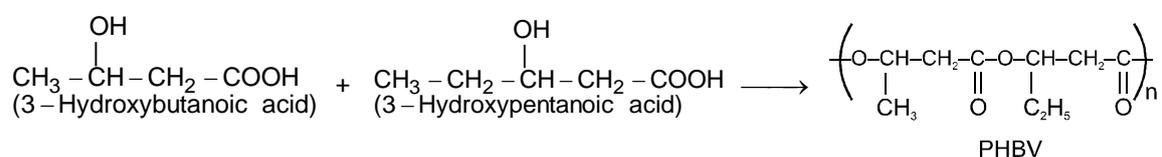
1.2 Biodegradable Polymers :

A large number of polymers are quite resistant to the environmental degradation processes and are thus responsible for the accumulation of polymeric solid waste materials. These solid wastes cause acute environmental problems and remain undegraded for quite a long time. In view of the general awareness and concern for the problems created by the polymeric solid wastes, certain new biodegradable synthetic polymers have been designed and developed. These polymers contain functional groups similar to the functional groups present in biopolymers.

Aliphatic polyesters are one of the important classes of biodegradable polymers. Some examples are given below :

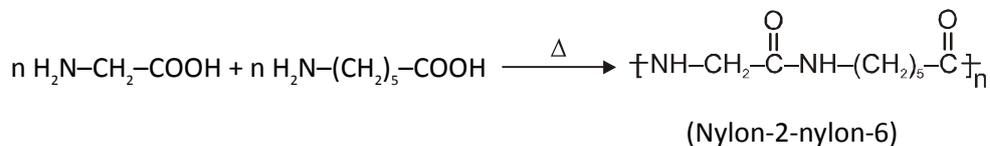
(A) Poly β -hydroxybutyrate – co- β -hydroxy valerate (PHBV) :

It is obtained by the copolymerisation of 3-hydroxybutanoic acid. PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.



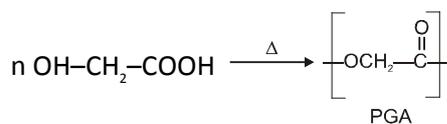
(B) Nylon-2-nylon-6 :

It is an alternating polyamide copolymer of glycine ($\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$) and amino caproic acid [$\text{H}_2\text{N}(\text{CH}_2)_5\text{COOH}$].



It is step-growth copolymer.

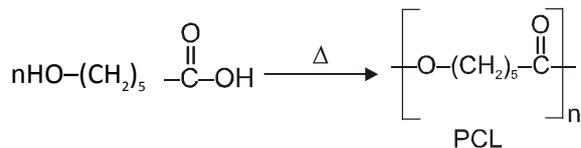
(C) Poly glycolic acid (PGA) and poly lactic acid (PLA) :- This copolymer is commercially called dextron.



Glycolic acid

A copolymer of PGA and PLA (90 : 10) was the first biodegradable polyester used for stitching of wounds after operation.

(D) Poly- Σ -caprolactone lactone (PCL) :- It is obtained by chain polymerization of the lactone of 5(or Σ) hydroxy hexanoic acid.



5(or Σ) hydroxy hexanoic acid

